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## **Revision of the OCS Oil-Weathering Model: Phases II and III**

MMS contract number : No. 1435-01-96-CT-30986

**U.S. Bepartment of the Interior** Minerals Management Service Alaska Outer Continental Shelf Region

### **MMS Report Number:**

### OCS Study MMS 2005-020

#### **Revision of the OCS-Weathering Model: Phases II and III"**

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ABSTRACT This project wa	is composed of the	e following tasks:			
A teleconf	erence with potent	tial users of the SINTEF O	il Weather	ing Model (OWM)within	
MMS;		and the CDITER OUD (			
Delivery a	nd training in the t	use of the SINTEF OWM;	in the OW		
Developm	g studies of selection	f Version 3.0 of the OWM	in the Ow.	M library;	
Preparation	n of test data sets f	for calibration and validation	, on of oil w	eathering models:	
Preparation	n of this final repo	rt a publication and sum	narv slides	describing the project	
This final report the publication accompanying	rt summarizes the , which is in prepa CD-ROM.	results of these tasks. Writ ration, and the model softw	ten deliver ware, are ir	ables, with the exception of a cluded in appendices on an	
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**Appendix A: Overheads Summarizing the Project** 

Appendix B: Weathering Properties of Endicott, Milne Point Unit, High Island Composite, the Alpine Composite, the Neptune Field Composite, and North Star Oil Samples

Appendix C: Development of Data Sets from Experimental Oil Spills for OWM Algorithm and Model Testing and Validation

**Appendix D: Users Manual for SINTEF OWM Version 3.0** 

Appendix E: Manuscript submitted to Journal of Environmental Software and Modelling: "The MMS/SINTEF Oil Weathering Model, Further Development and Applications" by R. Prentki, C. Smith, Ø. Johansen, P. Daling, M. Moldestad, K. Skognes, and M. Reed



#### **1** Introduction

The purpose of this study has been to provide and augment information needed to support development of environmental risk assessments, Environmental Impact Statements, review of contingency plans, and oil-spill response for offshore gas and oil leasing.

The MMS OCS Oil-Weathering Model (OWM) is a heavily used tool in the environmental assessment process for MMS. In the Alaska OCS Region, numerous estimates of oil-spill fate and behavior are derived from the OWM. The model provides analysts with a common, quantitative set of spill scenarios. The OWM is used to estimate whether State and Federal water quality standards and criteria would be exceeded by a spill, over what area, and for how long. The model calculates the area covered by a slick through time and the persistence of a slick. The model calculates how long the lighter, but most toxic components remain in the oil slick. The model is used to distinguish the effects of larger and smaller spills, for example between the effects of an average tanker spill versus an average pipeline spill. The *in situ* viscosity and degree of emulsification provided by the model are used in assessing the mitigation by and effectiveness of oil spill countermeasures such as mechanical recovery, dispersants, and *in situ* burning.

In the Gulf of Mexico Region, the OWM is more frequently used in environmental assessments to evaluate oil-spill contingency plans and the reliability of associated oil-spill models. The OWM is critical to the latter evaluation because, unlike most oil-spill models, the OWM incorporates specific chemistry of individual crude oils and petroleum products.

SINTEF Applied Chemistry completed the Phase I review "Revision of MMS Offshore Continental Shelf Oil-Weathering Model: Evaluation," OCS Study MMS 98-0031 for MMS.

The primary objectives of Phases II and III of this study have been:

- 1) to adapt the SINTEF Oil Weathering Model (OWM) to MMS needs,
- 2) to expand the OWM oil library to include oils of interest to MMS, and
- 3) to develop and collate data sets identified in Phase I from experimental oil spills for validation testing of algorithms and weathering models.

#### 2 Teleconference

The teleconference to kick off the project took place in October, 1999. Participants were:

MMS Alaska: Dick Prentki, Caryn Smith MMS Gulf of Mexico: Gail Rainey, George Guillen, and Darice Breeding MMS Herndon: Betty Estey SINTEF: Mark Reed, Per Daling, Janne Resby

The meeting started with a brief overview of the project, and a discussion of the trade-offs between performing more detailed weathering analyses for fewer oils or less detailed analyses for a layer variety of oils.

There were 4,731 producing oil wells in the GOMR as of Dec 1998 from multiple reservoirs, and over 26,000 miles of offshore pipeline, carrying oil mixed from production at approximately 4,000



platforms. The question of how to select one or two oils to study was raised. SINTEF suggested that one could either choose oils that are typical of a large number of others, or select those which are or will be shipped in largest quantities. In general, MMS does not have crude assay data on oils, so that comparison of oil types is difficult. It was decided to carry out limited weathering studies (no mesoscale runs) for 2 GOM oils. The GOMR may work with industry in developing a final determination.

It was asked whether SINTEF can use weathering data developed by others (e.g. Environment Canada) in the OWM. The answer was a reserved yes, given knowledge about what methods are used, how the results from those methods compare with those from SINTEF's, and given the possible necessity of additional information to fill any gaps. For example, the methodology for emulsification testing is very sensitive to energy input, and the kinetics of this process are key in determining both spill lifetime and the window of opportunity for dispersant application.

Minimum inputs to the SINTEF OWM are True Boiling Point curve, density, viscosity at some reference temperature, and pour point of the fresh crude. Beyond that, the actual weathering data becomes important for reliable predictions.

The Alaskan oils are much more limited in number. Priority oils are Liberty and North Star, but they were not available at the start of the project in the quantity needed (20 liters for bench scale, 10 liters for dispersant testing, 20 liters for meso-scale testing). One Cook Inlet oil was also to be selected.

After some discussion, it was agreed that 10°C would be a reasonable test temperature for the North Slope oils. The representative temperature for the Gulf of Mexico oils was eventually set at 25 C.

Each of the project tasks was then discussed in some detail, resulting in a set of action items at the conclusion of the teleconference.

#### 3 Delivery and Training in the Use of the SINTEF Oil Weathering Model

The SINTEF Oil Weathering Model Version 1.6 was delivered to MMS at project start in 1999, and served as the basis for the training course in February 2000. The OWM Version 1.8 was delivered in April 2000, followed by Version 2.0 in April 2001.

The training workshop took place on February 8-9, 2000, at MMS facilities in Denver, Colorado. A number of desired changes and improvements were noted during the workshop, and subsequently incorporated into Versions 1.8 and 2.0 of the OWM.



#### 4 Weathering Studies

#### **4.1 Introduction**

In Environmental Impact Assessment (EIA) studies and when planning the most effective response, it is important to have reliable predictions of how specific oil properties will change during an oil spill event. The efficiency of various oil spill combat methods (e. g. mechanical, dispersion and/or burning) depends greatly on the physical-chemical properties of the oil at the time of action.

The weathering behaviours of Alaskan and Gulf of Mexico crude oils were investigated at SINTEF. The results of the weathering studies were incorporated into the SINTEF OWM weathering library, and supplied to MMS with the OWM and Oil Database Editor.

#### 4.2 Oils investigated

The following six crude oils were received and investigated in the laboratory at SINTEF :

- Alpine Composite
- Endicott
- Milne Point Unit
- North Star
- High Island Composite
- Neptune Field Composite

The Neptune Field and High Island oils are Gulf of Mexico oils, the rest are Alaskan oils. Gulf of Mexico oils were tested at 23°C and Alaskan oils at 10°C.

Endicott, Alpine Composite, Neptune Field Composite and North Star were analysed following the SINTEF standardised weathering methodology. Due to too high water contents, Milne Point Unit and High Island Composite were not analysed using standard procedures. Meso-scale flume test were performed of the High Island Composite in order to establish a dataset for the OWM. The water content of Milne Point Unit was too high for performance of weathering analysis.

#### 4.3 Brief summary of the oils weathering properties

A brief summary of the oil and weathering properties of the crude oils is given below. For further details about oil properties see Table 4-1 and for discussion of weathering behaviour related to oil spill response see Leirvik *et al.*, 2002.

#### <u>Alaskan crude oils :</u>

Alpine Composite is a paraffinic crude oil, with a density of 0,834 g/mL. The Alpine Composite contains a relatively large amount of lower molecular weight compounds and approximately 25% of its original volume will be evaporated 24 hours after the spill at both summer and winter temperatures. Alpine Composite will form w/o-emulsions with a maximum water content of 80 % at both winter and summer temperatures, yielding approximately five times the original spill volume. The w/o-emulsion formed after one day of weathering at sea is stable.



**Endicott** is an asphaltenic crude oil, with a density of 0,913 g/ml with a relatively low evaporative fraction. Endicott will form w/o-emulsions with a maximum water content of approximately 60 % at winter temperatures and 65 % at summer temperatures, more than doubling the original spill volume. The w/o-emulsions formed are very stable.

**Milne Point Unit** oil is a heavy naphthenic, biodegraded crude oil with an approximate density of 0.95 g/ml. The oil seems to be highly biodegraded (i.e. no paraffinic components are present in the Gas Chromatogram). The emulsion is extremely stable and can only be dehydrated at high temperatures and with the addition of a high dosage of demulsifier (approximately 10%).

North Star oil is a light paraffinic crude oil, with a density of 0.816 g/mL. The North Star oil contains a relatively large amount of lower molecular weight compounds and approximately 30 % of its original volume will evaporate 24 hours after the spill at both summer and winter temperatures. North Star also forms stable emulsions.

#### Gulf of Mexico crude oils :

**High Island** is a naphthenic, biodegraded crude oil, with a density of approximately 0.85 g/mL. The High Island oil contains a medium amount of lower molecular weight compounds; over 20 % of its original volume will evaporate 24 hours after the spill at both summer and winter temperatures. Results from the meso scale flume study show that High Island oil forms unstable emulsions with low viscosity. Maximum water content is high at 70%, but observations from the meso scale flume show that emulsions dehydrate almost completely within an hour when left at rest (e.g. in a recovery storage tank).

**Neptune Field Composite** is a paraffinic crude oil, with a density of 0,869 g/mL. The Neptune Field Composite contains a relatively large amount of lower molecular weight compounds and over 30 % of its original volume will be evaporated 24 hours after the spill at both summer and winter temperatures. The experimental results showed that the Neptune Field Composite did not form stable w/o-emulsions. One normally would expect that a crude oil with a wax and asphalthene content similar to the Neptune Field Composite will form stable w/o-emulsions. SINTEF suspects that production/process chemicals are present in the oil sample thereby reducing the w/o-emulsion process. This suspicion is supported by the un-normal low interfacial tension value measured for the fresh crude (6 mN/m).

A comparison of the evaporation and emulsion viscosity of the Alaska and Gulf of Mexico oils is shown in Figure 4-1, Figure 4-2 and Figure 4-3, Figure 4-4 respectively. The evaporation of the Alaska oils is very different, from approximately 20 to 50% after 5 days at 10°C and 10 m/s wind. The emulsion viscosities of these oils vary from approximately 8000 to 40000 cP under the same conditions. The two Gulf of Mexico oils has evaporation and emulsion viscosity in the same range at 20°C and 10 m/s wind, however, the development is some different.

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Table 4-1: A summary of the physical and chemical variables for Endicott, the Alpine Composite and the Neptune Field Composite, The High Island Composite and the North Star. The viscosities for Endicott, the Alpine Composite, the North Star, the Neptune Field Composite and the High Island Composite and the were measured at  $10 \,\%$ ,  $10 \,\%$ ,  $23 \,\%$  and  $23 \,\%$  respectively.

		WHERE AN AND AND AND AND AND AND AND AND AND		Bearing "	Density	Pour	Viscosity at	Flash	Interfacia	Wax	Asphaltenes
	Oil type		Evaporated	Friendle	at 15,5°C	point	10 s <sup>-1</sup>	point	l tension	content	"hard"
ist Automatic	i	****.t. i		[wt 26]	[g/mL], []	[°C]	[cP] 1.	[°C]	[mN/m]	[wt%]	[wt%]
		Fresh	0	100	0,913	6	510	<20	24	5,5	1,6
	Endicott	150°C+	6	95	0,923	9	840	56	24	5,7	1,7
မ္	Endicou	200°C+	12	89	0,931	15	1630	85	25	6,1	1,8
lop		250°C+	19	84	0,940	18	5150	121	25	6,5	1,9
ЧS		Fresh	0	100	0,834	-18	103	<20	18	3,2	0,06
-To	Alpine	150°C+	22	81	0,867	-3	118	38	20	3,9	0,07
Z	Composite	200°C+	34	69	0,885	9	839	82	27	4,6	0,09
kar		250°C+	_44	60	0,898	18	1160	123	16	5,3	0,1
las		Fresh	0	100	0.816	-39	10	<20	20	5,8	0,016
×	North Stor	150°C+	24.7	78.5	0.850	-9	45	37	21	7,3	0,021
	North Star	200°C+	38.5	65.3	0.866	3	380	77	23	8,8	0,025
	_	250°C+	50.2	53.8	0.881	18	2272	119	24	10,7	0,030
		Fresh	0	100	0,869	-9	10	<20	6	3,7	0,3
<u>.</u>	Neptune Field	150°C+	11	90	0,887	0	50	46	6	4,1	0,4
xic	Composite	200°C+	22	81	0,900	3	110	93	7	4,6	0,4
Me		250°C+	30	73	0,911	9	300	128	8	5,0	0,4
of		Fresh	0	100	0,847	-15	23	-	14	1,6	0,03
ulf	High Island	150°C+	-	-	-	-	-	-	-	-	-
5	Composite	200°C+	-	-	-	-	-	-	-	-	-
		250°C+	33	70	0,879	0	83		16	2,3	0,04





Figure 4-1 : Evaporation of the Alaska oils.



Figure 4-2 : Viscosity of emulsion of the Alaska oils.





Figure 4-3 :Evaporation of the Gulf of Mexico oils.



Figure 4-4 : Emulsion viscosity of the Gulf of Mexico oils.

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#### 5 Oil Weathering Model Version 3.0

Version 3.0 of the OWM was delivered at the end of June, 2004. In addition to numerous improvements in the user interface, this version includes the following improvements over 2.0:

- possibility for surface and subsurface releases;
- internal computation of initial film thickness, based on release rate and duration;
- New spreading algorithm supporting both surface and underwater releases, with improved stability and better detection of erroneous input values;
- New oil type query filters in both OWM and the Oil Database Editor, allowing filtering on ranges of values for API gravity, specific density, and pour point;
- Capability to add/delete Data Source, Geographical Area, and Product in the Editor as documented in the User Manual how to achieve this during editing of oil information;
- New \*.TX2 data results file for easy EXCEL import;
- Enabled multi-selection capability in temperature and wind lists, and made Add and Delete buttons more dynamic to facilitate clearing the entire list at once;
- Revised User's Manual for Version 3.0.

The spreading mechanisms for instantaneous releases and continuous releases are different. Instantaneous releases will spread radially, while oil released continuously will spread laterally (i.e. cross-current). This difference in spreading behaviour will affect other weathering properties e.g. evaporation and natural dispersion. Version 2.0 of the model only accounts for lateral spreading (i.e. all releases are treated as continuous), but in Version 3.0, the spreading of instantaneous and continuous spills is treated differently. Also, a calculation of the surface spreading for sub surface releases in shallow to moderate water depths (depth less than e.g. 300 m) is included. This calculation requires input of gas-to-oil ratio (GOR) and depth in addition to release rate.

The spreading algorithms are documented in detail in Appendix D.



Helease amount		Release properties
Amount unit: metric tons	▼ Time unit: minute ▼	- <u>D</u> epth (m): 0
☞ <u>R</u> elease rate: 1.33 ○ Total amount:	20 metric tons/minute	<u>G</u> as-to-Oil ratio: 0 GOR uni <u>t</u> : cu.tl/bbl <u>▼</u>
D <u>u</u> ration:	15 minute(s)	Terminal film thickness (mm): 1
Ambient		
Density of water (gm/l):	1025	Water dept <u>h</u> (m): 50
Fetch (km)		
<u>N</u>	✓ Natural dispersion ✓ Evaporation	Ice type: No Ice 💌
<u>₩</u> 100 100 <u>E</u>	Emulsification	Ice coverage (%):
100	Weathering data prediction if	no la <u>b</u> data
100	The second se	CONTRACTORY AND

Figure 5-1. New Model Parameter dialog in Version 3.0, allowing for underwater releases, and with initial thickness computed internally depending on release type, rate, and duration.

Select data source	☐ Select	geographical <u>a</u> rea	☐ Select g	product
II Battelle Ocean Sciences Crude Assay HPI Crude Oil Database IKU Petroleum Research SINTEF Applied Chemistry	ABU DHA ALASKA, ALGERIA ANGOLA ATLANTIO BENIN BRAZIL	BI, U.A.E. USA C FRONTIER	CONDENS CRUDE HEAVY BL LOW EMU REFINED	GATE JNKER ILSIFYING DIST.
	Min	Мах		
I  ✓ Pour point range:	-10	10	°C	OK
API gravity range:	A Barry			Cancel
Specific density range:	0.9	1		
	the second second second	Statistics and statistics of the second statis	THE TOTAL OF	

Figure 5-2. New Oil Database Filter query options include selected oil properties.



MMS has an unlimited internal use license for the model.

#### 6 Test Data Preparation

#### 6.1 Background and objectives

In 1998 SINTEF Applied Chemistry completed the Phase I review "Revision of MMS Offshore Continental Shelf Oil-Weathering Model: Evaluation," OCS Study MMS 98-0031 for MMS. This review recommended the compilation of oil spill data sets that would be suitable for model testing and validation.

A framework for this task was described in the MMS OWM Phase I Technical Meeting held in Anchorage, in March, 1998 with two alternative approaches:

One approach at that time was that SINTEF, in collaboration with organizations like Alun Lewis Oil Spill Consultant in UK, CEDRE in France, and NOOA in US should try to develop a joint industry program to address model sensitivity testing, preparation and archival of specified data sets, and testing of model algorithms.

Many data sets of potential interest were identified in the Phase I Report (OCS Study MMS 98-0058). SINTEF investigated the possibility of developing a joint industry program developed to facilitate the data collation, but without success. We therefore agreed with MMS to proceed alone in this task with the limited budget from MMS allocated to address the two last scopes/goals: i.e. preparation of available oil spill data sets, and testing / validating these ground-truth data with the new version of the SINTEF OWM only. The data sets presented in this report can however, be used by any organizations /model operators in model algorithm testing / validation.

#### 6.2 Conclusions and recommendations from the Phase 1 report

In the Phase I Report (OCS Study MMS 98-0058, chap. 5.1.), criteria for an "ideal data set" from experimental oil releases at sea was specified with respect to:

- Environmental background data
- Oil characterization (original oil properties and changes as function of weathering)
- Documentation Standardized methods for sampling and analysis
- Sampling frequency
- Replicate samples

An overview of experimental oil releases was identified and preliminary evaluation of data sets was performed. None of the field trials satisfied the strict criteria for an "ideal data set", with respect to both methodology and data-documentation. We therefore selected best available data sets for calibration/validation of oil weathering models. Many of the older data sets from experimental trials had a limited potential for model calibration-/validation, because of varying quality of data due to lack of consistent procedures for sampling and analytical methodology.



Some recent field trials had better documented and suitable procedures for field sampling and analysis. The preliminary conclusion from this review was that data from recent field trials in the UK and Norway (see below) had a potential for calibration/verification of oil weathering models, and an effort in collecting relevant data from these series was given priority.

<u>UK: Field trials in the North Sea from the period 1992-97:</u> These experiments were conducted on a yearly basis with different objectives. The more recent experiments have well documented and suitable procedures for sampling and further analysis. These field trials cover several crude oil (Forties, Alaska North slope) and different bunker fuels. The weathering time ranges from only hours to several days and the weathering parameters include (emulsification, evaporation, natural dispersion, water soluble components, emulsion viscosity, emulsion stability, water droplets distribution in emulsion and others). Some of these UK sea trials also include extensive monitoring of dispersed oil concentrations versus time and also measurements of droplet sizes of the dispersed oil droplets. Some relevant data seemed to be available from AMOP publications by AEA Technology, but more extensive environmental data from the field test is needed to use them in model tests.

<u>Norway: Field trials in the North Sea and in the marginal ice zone of the Barents Sea from the period</u> (1989-96): In Norway, field experiments have been conducted on an almost yearly basis since the late 70's, but only some of the trials were considered to be relevant for our purpose. The SINTEF-89 and MIZ-93 trials produced data sets which can be used to compare weathering of the same crude oil type at a North Sea and an Arctic environment. These trials and the later NOFO trials (1994/95/96) have used well-documented procedures for sampling and analysis. The weathering time ranges from one day up to seven days, and the weathering parameters include emulsification, evaporation, natural dispersion, water-soluble components, emulsion viscosity, and emulsion stability, among others. Data are available from SINTEF as reports and publications.

#### **6.3 Datasets collected**

In the period from December 2002 to July 2003, an effort was made to collect all relevant data from the recommended series of field trials. As a result, data-set from the following trials are presented in this report:

- Haltenbanken 1989
- MIZ-experiment (in ice) 1993
- NOFO-trial 1994
- NOFO-trial 1995
- NOFO-trial 1996 (limited data)
- UK trials 1997 (AEA-trials)
- Surface oil data from the Deep spill 2000 experiment

The data-sets from the earlier field tests in the UK are not included in this report. This is due to lack of available documentation of environmental data during the field tests. Lewis Oil Spill Consultant in UK did an extensive search to obtain data reports from field various field trials in UK at the library at MCA (Maritime and Coastal Agency in Southampton) without any success.

Weathering data, wind speed, temperature and film thickness are presented from the trials. For the trials including dispersant treatment, only the weathering data before dispersant treatment is



presented in this report.

The film thickness parameters used as input to the model for the predictions of the different trials, are based on the film thickness data measured in the individual trials.

The full report is included as Appendix B: Development of Data Sets from Experimental Oil Spills for OWM Algorithm and Model Testing and Validation.

#### 7 Final Report, Publication, and Summary Slides

The Final Report is a self-reference to this document.

A publication with the working title "The MMS Oil Weathering Model: Further Developments and Applications" is in preparation. It is intended that the paper will be presented at the International Marine Environmental Modelling Seminar (IMEMS) to be held in Washington DC in October, 2004.

A set of summary overheads has been prepared in PowerPoint format, and is include on the CD-ROM as an Appendix to this report.

Separate documents on CD-ROM:

**Appendix A: Overheads Summarizing the Project** 

Appendix B: Weathering Properties of Endicott, Milne Point Unit, High Island Composite, the Alpine Composite, the Neptune Field Composite, and North Star Oil Samples

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**Appendix D: Users Manual for SINTEF OWM Version 3.0** 

Appendix E: Manuscript submitted to <u>Journal of Environmental Software and</u> <u>Modelling</u>: "The MMS/SINTEF Oil Weathering Model, Further Development and Applications" by R. Prentki, C. Smith, Ø. Johansen, P. Daling, M. Moldestad, K. Skognes, and M. Reed.



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Appendix A: Overheads Summarizing the Project

## Revision of the Offshore Continental Shelf Oil Weathering Model: Phases II and III

for

U.S. Department of the Interior Minerals Management Service Anchorage, Alaska

by

#### SINTEF

Division of Marine Environmental Technology Trondheim, Norway

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## **Presentation Overview**

- Project Summary
- Oil weathering studies
- Data sets for model testing and validation

# **Project Summary**

## **Primary Objectives**

- 1. Deliver and adapt the SINTEF Oil Weathering Model (OWM) to MMS needs;
- Expand the OWM oil library to include oils of interest to MMS;
- 3. Develop and collate data sets identified in Phase I from experimental oil spills for validation testing of algorithms and OWM's.

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## **Delivery and Adaptation the SINTEF Oil Weathering Model**

- Delivered the SINTEF OWM Windows 95/NT Version 1+, manuals (1999)
- Training session, and license for Department of Interior-wide internal use
- Provided scheduled updates
  - Version 2.0 (2001)
  - Version 3.0 (2004)

## **Delivery and Adaptation the SINTEF Oil Weathering Model**

Model improvements:

- Windows of opportunity for dispersant spill response
- Updating of the oil database
- Improved spreading algorithms for surface and sub-surface releases
- Simplified export to spreadsheets
- Arctic conditions (sea ice)
- Undersea blowouts and pipeline spills
- Import tool for external wind files
- Additional query options to filter oils from the database
- Revised user's manual

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# Expansion of OWM database to include oils of interest to MMS

Weathering studies performed for crudes from Alaska and the Gulf of Mexico:

- Alaskan North Slope: 4 crude oils
- Gulf of Mexico: 2 crude oils

## Development of Data Sets from Experimental Oil Spills for Model Testing and Validation

- Haltenbanken 1989
- Barents Sea Marginal Ice Zone (MIZ-experiment in ice) 1993
- NOFO-trial 1994
- NOFO-trial 1995
- NOFO-trial 1996 (limited data)
- UK trials 1997 (AEA-trials)
- Surface oil data from the Deep spill 2000 experiment

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## Final Report, Technical Summary, and Journal Article

Individual reports combined behind an Executive Summary in the Final Report.

- Final Report and Technical Summary submitted in Draft and Final versions
- Bibliographic references supplied in Prociteimportable format.

## Summary Weathering Properties Alaskan North Slope and Gulf of Mexico Oils

- Alaskan North Slope
  - Alpine Composite
  - Endicott
  - Milne Point Unit (not tested, water content in the crude oil too high)
  - North Star
- Gulf of Mexico
  - High Island Composite
  - Neptune Field Composite

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# Knowledge about oil properties, fate and weathering behaviour is important for :

- Environmental Risk Analysis
- Contingency analysis and planning
- NEBA-analysis (Net Environmental Benefit Analysis)
  - Weighing of advantages and disadvantages of alternative oil spill responses for all aspects of environmental effects, <u>compared with "no response"</u>
- Oil spill response operations
  - $\Rightarrow$  rapid and right decision-making during combat operations

# **Objectives**

Alaskan and Gulf of Mexico crude oils tested in order to :

- investigated the weathering behaviour of the oils and discuss the properties related to respone
- expand the SINTEF OWM oil library to include the oils of interest to MMS

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# **Crude oils**

- Mixture of thousands of components
- Relative composition vary
- Physical properties of various crude oils are very different due to differences in chemical composition
- Crude oils may be accidentally spilt during production or transportation



## Oils at sea – weathering processes



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# Bench-scale step-wise weathering study of an oil



16 different weathering samples from a fresh crude oil Representing various weathering times at sea

## **Temperature conditions**

## Alaskan North Slope crude oils

- Tested at 10°C
- Weathering predictions made at 0 and 10°C

## Gulf of Mexico crude oils

- Tested at 23°C
- Weathering predictions made at 20 and 29°C

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## **Crude oil properties**

Oil type	Category of crude oil	Density (g/mL)	
Alaska	n North Slope cr	ude oils	
Alpine Composite	Paraffinic	0,834	
Endicott	dicott Asphaltenic		
Milne Point Unit	Naphthenic, biodegraded	approx. 0,95	
North Star	Paraffinic	0,816	
Gul	f of Mexico crude	e oils	
High Island Composite	Naphthenic, biodegraded	0,85	
Neptune Field Paraffinic Composite		0,869	

## **North Star - emulsification studies**



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# High Island in the meso scale flume



After 6 hours weathering

After 72 hours weathering

# **SINTEF Oil Weathering Model**



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## **Alaskan North Slope oils - evaporation**



## **Alaskan North Slope oils – emulsion** viscosity



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# **Gulf of Mexico oils - evaporation**



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## **Gulf of Mexico oils - emulsion viscosity**



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## Data sets for model testing and validation

- Haltenbanken 1989
- Barents Sea Marginal Ice Zone (MIZ-experiment in ice) 1993
- NOFO-trial 1994
- NOFO-trial 1995
- NOFO-trial 1996 (limited data)
- UK trials 1997 (AEA-trials)
- Surface oil data from the Deep spill 2000 experiment

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# Haltenbanken 1989

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- Full-scale experimental oil spill carried out to study several objectives:
- Evaluation of different types of oil spill drifters (Argos positioned buoys) versus oil drift
- Inter-calibration of different aerial surveillance systems
- Study of weathering processes of the Sture Blend crude (also here called Oseberg Blend)

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 Study interactions between a drifting oil slick and sea birds



## **Barents Sea Marginal Ice Zone 1993**

## Objectives

The intention of the experimental oil spill in the marginal ice zone was to contribute further to existing knowledge about the behaviour of oil under Arctic conditions and to acquire knowledge about the specific conditions (wind, waves, ice conditions, drift and spreading) in the marginal ice zone.



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# **NOFO Field Exercise 1994**

The main objectives of the field trials were:

- To verify laboratory studies on rate of weathering (evaporation, natural dispersion and emulsification) of Sture Blend crude oil and determine the extent of changes in these processes caused by the application of dispersant.
- To assess quantitatively the effectiveness of aerially applied dispersant by following the fate and weathering properties of two slicks of partially weathered North Sea crude oil (one treated and one control slick).
- To define the operational parameters required for practical dispersant treatment strategies.
- To provide a realistic training scenario for oil spill combat personnel.



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## **NOFO Exercise 1995**

Objectives (dispersant application and underwater releases)

- Study the behavior, rate of spreading and weathering (evaporation, emulsification, natural dispersion etc.) of crude oil slicks released both from surface and sub-surface (107 meters depth simulating sub-sea pipeline leakage).
- Provide input data to the SINTEF OWM, as the basis for further refinements of algorithms in the model.
- Assess the effectiveness of different methods of applying dispersant concentrates on oil slicks (from boat and helicopter).
- Study the capability of satellite-tracked drifting buoys to simulate the drift of surface and dispersed oil under various environmental conditions.
- Calibrate aerial remote sensing sensors (in aircraft, helicopter, and satellites) with ground truth data of the surface oil slicks.

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NOFO Exercise 1995 Property: Emulsion viscosity Property: Evaporation SINTEF **SINTEF** rature ("C) : 15 2.0-6 2002 Pret, Data April 30, 2003 70 Trol Charlie 1995 Trol Sierra 1995 A Field data Charlie Field data Sierra (cP) (Vol%) 50 40 . . 0,5 6 9 12 0.5 0,25 3 4 2 3 6 9 12 2 3 4 Property: Water content **SINTEF** A modern dispersant, correctly 2.0 © 2002 Pred. Dato: April 30, 2003 applied with a helicopter bucket or with spray arms from a ship, within the "window of opportunity" for dispersant use, is capable of 10 Trot Charle 1995
 Trol Siena 1995
 Feit data Charle
 Feit data Siena dispersing thick oil completely, 7 ontent (%) within 10-30 minutes. 5 No significant emulsification of the Vater oil in the underwater plume was observed. 12 Days

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## **NOFO Exercise 1996**

Objectives

- To determine how the weathering processes (evaporation, water-in-oil emulsification and natural dispersion) of Troll crude oil proceeded in the control (Charlie) and the treated slick (Hotel, treated by helicopter with the new "Response 3000" bucket) after dispersant application.
- To determine how the surface slick resulting from the underwater release (designated Uniform) of Troll crude oil combined with gas (GOR of 1:67), behaved.
- The field trials in both 1995 and 1996 were performed in order to form basis for building up an operational and cost-effective dispersant response in Norway (for terminals, refineries, offshore oil fields etc.).

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FO Exercise 1996 Property: Emulsion viscosity Property: Evaporation SINTEF **SINTEF** Temperature (\*C) : 10 Wind Speed : Wind Nes Initial film thickness (me Temperature (\*C) : 10 Wind Speed ; Wind Re 2.0 @ 2002 Proof Date: April 30, 2003 2.0 @ 2002 Prest, Dato: April 30, 2003 Trol Hotel 1996 5 100 70 (Mulon) 80 50 40 Evan Emul 30 20 10 0.25 0.5 2 3 9 12 6 9 12 1 6 2 Property: Water uptake Troll crude oil emulsified slowly and SINTEF Temperature (°C) 10 Wind Speed - Wind Bes Inhai Rm thickness (mm reached a maximum water content of 2.6 @ 2002 Prest Data April 30, 2003 approximately 60 vol.% and a viscosity of 2000 cP (shear rate 10 s-1) after 10 hours weathering at the sea surface. These measured values were lower than the predicted values due to unstable 70 emulsions. The weather conditions were content (%) 80 rather calm, with an average wind speed of 50 about 4 to 5 m/s, and too low to cause breaking waves. The same situation 40 Water occurred during the August 1995 trials when the Sierra slick was monitored on Day 2 (5 to 6 m/s wind). 3 4.5 0,25 Da

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## **AEA field experiments UK 1997**

### Purpose

- to measure changes in oil properties during weathering at sea, and
- to determine the period of time during which Corexit 9500 can be considered as a viable response option for these oils:
  - 50 m<sup>3</sup> Forties oil weathered for 2 days at sea prior to treatment with 2.5m<sup>3</sup> Corexit 9500
  - 20 m<sup>3</sup> IFO-180 Heavy bunker fuel weathered for 4.5 hours at sea prior to treatment of 0.9 m<sup>3</sup> Corexit 9500 followed by a 2<sup>nd</sup> treatment 23-25 hours at sea (2.0 m<sup>3</sup> Corexit 9500)
  - 31 m<sup>3</sup> Alaska North Slope (ANS) crude (designated "Alpha") weathered for 2.5 days at sea prior to treatment of 1.0 m<sup>3</sup> Corexit 9500

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## **AEA field experiments UK 1997**



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# Deep Spill JIP 2000

**Primary objectives** 

- to obtain data for verification and testing of numerical models for simulating accidental releases in deep waters;
- to test equipment for monitoring and surveillance of accidental releases in deep waters;
- to evaluate the safety aspect of accidental releases of gas and oil in deep waters.



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## Deep Spill JIP 2000







Experiments were conducted at 844 m depth in the Helland Hansen region in the Norwegian Sea.

60 m3 marine diesel and 60 m3 Sture blend together with 18 m3 liquefied natural gas (LNG) equivalent to 10 000 m3 of gas at atmospheric pressure released from a discharge platform lowered to the seabed
# Data sets for model testing and validation: summary

Input data and field measurements are supplied in the report for each field trial

- Wind data
- Distillation curves for oils
- Crude assay data
- Oil weathering data
- Field measurements
  - Emulsion
    - Density
    - Water content
    - Viscosity
    - Stability
  - Surface film thickness

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Appendix B: Weathering Properties of Endicott, Milne Point Unit, High Island Composite, the Alpine Composite, the Neptune Field Composite, and North Star Oil Samples .

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		Weathering properties of Endicott, Milne Point Unit, High Island Composite, the Alpine Composite, the Neptune Field Composite, and North Star oll samples			
Enterprise No.: NO 9	48 007 D29 MVA	AUTHOR(S)			
		Frode Leirvik, Tina J. Sch	urader ar	d Merete 2	verli Moldestad
		CLIENT(S)			
		U.S. Department of the In (MMS)	terior M	inerals Ma	nagement Service
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Based on the find Weathering Mode continued with PJ of Phase II and II to adapt the SI to expand the f to develop and of algorithms and During Phase II a MMS. The result in Environmental	lings from the Pha b): Evaluation," O hase 11 and 111; the 1 are: NTEF Oil Weathe OWM oil library to 1 collate data sets i 1 OWM's. and 111 SINTEF ha s from these weath Impact Assessme	se I review "Revision of M CS Study MMS 98-0031 fo "Revision of the OCS Oil- sring Model (OWM) to MM o include oils of interest to dentified in Phase I from ex ve performed weathering st tering studies have been ad int studies and presented in	MS Offs r MMS, Weather IS needs MMS, a sperimen udies of ded to th this final	hore Contir SINTEF A ing Model" nd tal oil spill: total six crn e OWM lib i report.	nental Shelf Oil- pplied Chemistry has . The main objectives s for validation testing ude oils supplied by rary for use by MMS
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GROUP 2	Environmental		Miliø		

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SELECTED BY AUTHOR Weathering



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# 1 Background

SINTEF Applied Chemistry completed the Phase I review "Revision of MMS Offshore Continental Shelf Oil-Weathering Model: Evaluation," OCS Study MMS 98-0031 for MMS in 1998. This review recommended:

- upgrading to an existing state-of-the-art Oil Weathering Model (OWM)
- · additional improvements needed to maintain state-of-the-art and to meet needs of MMS users
- spill data sets that would be suitable for algorithm and model testing and validation.

Based on these findings, MMS initiated the ongoing Phase II and III "Revision of the OCS Oil-Weathering Model". The main objectives of Phase II and III are:

- to obtain and adapt the SINTEF OWM to MMS needs,
- to expand the SINTEF OWM oil library to include oils of interest to MMS

In Environmental Impact Assessment (EIA) studies and when planning the most effective response it is important to have reliable predictions of how specific oils properties will change during a spill. The efficiency of various oil spill combat methods (e. g. mechanical, dispersion and/or burning) depends greatly on the physico-chemical properties of the oil at the time of action.

In the literature, several approaches on how to predict oil properties have been established. SINTEF has chosen a direct empirical approach and in addition to crude oil data (Crude Oil Assay), the SINTEF OWM uses experimental weathering data obtained from both bench and meso-scale laboratory weathering testing of the actual crude oil as input data. Experience and data generated from full-scale field studies during the past 25 years has provided the basis for a continuous evolution of the algorithms used in the model. In recent years comparisons of the predictions obtained from the SINTEF OWM with field data have shown the strength in the prediction quality (Fiocce *et al.*, 1999 and Daling and Strøm, 1999).

SINTEF has performed weathering studies on the following six crude oils supplied by MMS: Endicott, Neptune Oilfield, Alpine Oilfield, High Island Oilfield, Milne Point Unit, and North Star. The Neptune Field and High Island oils are Gulf of Mexico oils, the rest are Alaskan oils. The results of these weathering studies will be added to the OWM library for use by MMS in Environmental Impact Assessment studies and are presented in this final report. SINTEP

# 2 The weathering predictions obtained from the SINTEF OWM

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 of an oils properties and behavior on the sea surface. The SINTEF OWM is schematically shown in Figure 2.1.





Figure 2.1: Schematic diagram of the input data to the SINTEF OWM and the predicted output oil properties.

The predictions obtained from the SINTEF OWM are a useful tool in Environmental Impact Assessment studies and for determining the most effective response. In this report the predictions are presented over a time period of 15 minutes to 5 days after the oil spill has occurred. This covers potential spill situations where the response time is short (e. g. close to terminals) to offshore spills where the response time can be several days.

#### 2.1 Fixed and variable parameters used in the SINTEF OWM

#### 2.1.1 Spill scenario

The spill scenario (e. g. sub-sea or surface blowouts, tanker spills, pipeline leakage etc.) and release rate chosen when using the SINTEF OWM is of importance. In this project a surface release at a rate of 1,33 metric tons per minute (i.e. 80 tons over one hour) was chosen as the spill scenario.

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# 2.1.2 Oil film thickness

In the SINTEF OWM the oils are categorised into condensates, low emulsifying crudes, emulsifying crudes, heavy bunker fuels or refined distillates based on experimental results obtained in the bench-scale testing. A default for the initial oil and terminal w/o-emulsion film thickness is given for each category of oil in the model.

From the experimental results of the bench-scale testing (see Appendix C) Endicott, High Island Composite, Alpine Composite and North Star are described as emulsifying crude oils whereas, the Neptune Field Composite, which did not form stable w/o-emulsions, is described as a low emulsifying crude oil.

The spill conditions, oil categories and initial and terminal film thickness' are summarized in Table 2.1.

#### Table 2.1: The spill criteria chosen for Endicott, the Alpine Composite and the Neptune Field Composite crude oils in this project.

Oil	Oil Category	Initial film thickness [mm]	Terminal film thickness [mm]
Endicott	Emulsifying crude oil	20	1,0
Neptune Field Composite	Low emulsifying crude oil	20	0,5
Alpine Composite	Emulsifying crude oil	20	1,0
High Island Composite	Emulsifying crude oil	20	1,0
Milne Point Unit	Emulsifying crude oil	20	1,0
North Star	Emulsifying crude oil	20	1.0

## 2.1.3 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 at the average summer temperature the other at the average winter temperature for the area of interest. The temperatures are chosen on background of climate statistics for the two regions and are given in table 2.2.

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Table 2.2:	The average summer and winter sea temperatures used for Endicott, the Alpine	
	Composite, the Neptune Field Composite, the High Island composite, the Miln	e
	Point Unit and the North Star crude oils in the SINTEF OWM.	

Oil type	Region	Summer temperature [°C]	Winter temperature [°C]	
Endicott	Alaska			
Alpine Composite	10		0	
Milne Point Unit		10	0	
North Star				
Neptune Field Composite	Gulf of	Gulf of		
High Island Composite	Mexico	29	20	

"Information provided from the Live Access to Climate Data server at the NOAA/ Pacific Environmental Laboratory.

#### 2.1.4 Wind speed

The relationship between the wind speed and the significant wave heights used in the prediction charts obtained from the SINTEF OWM are shown in Table 2.3.

Table 2.3:	The relationship be	etween the	wind speed	and the	significant	wave	heights	used	in the
	SINTEF OWM.		100 mar. 1 <b>8</b> mar. 19				0773542040		

Wind speed [m/s]	Beaufort wind	Wind type	Wave height [m]	Wave height [ft]
2	2	Light breeze	0,1-0,3	0.2-0.60
5	3	Gentle to moderate breeze	0,5-0,8	1-1.5
10	5	Fresh breeze	1,5-2,5	3-5
15	6-7	Strong breeze	3-4	6-8

#### 2.2 Input data for the SINTEF OWM

In the bench scale 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 an oil is spilled on the sea surface. The experimental design for the bench scale studies is described in Appendix B and the results are presented in Appendix C. The input data to the SINTEF OWM is given in Appendix D.

The experimental weathering data obtained in the bench-scale testing are processed and used as input for the SINTEF OWM. The following oil/emulsion properties obtained in the bench-scale testing are used in the model:

- specific gravity
- pour point
- · flash point
- viscosities of fresh and 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 half-life-time)

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The SINTEF OWM is described in more detail in Johansen, 1991 and in the users guide for the model.

#### 2.3 Weathering properties related to response

The efficiency of various oil spill combat methods (e. g. mechanical recovery, dispersion and/or burning) depends greatly on the physical and chemical properties of the oil at the time of action. When planning the most effective response the predictions charts provide important information.

#### 2.3.1 Mechanical response

Past experiences from Norwegian field trials have shown that the effectiveness of many mechanical clean up operations is reduced due to a high degree of leakage of the confined oil or w/o-emulsion from the oil spill boom (especially in high current). This leakage is especially pronounced if the viscosity of the oil or the w/o-emulsion is lower than 1000 cP at a shear rate of  $10s^{-1}$  (Nordvik *et al.*, 1992). The **lower viscosity limit** for an optimal mechanical clean up operation has therefore been set to 1000 cP.

The upper viscosity limit for an optimal mechanical clean up operation depends on the type of skimmer used. For some disk-skimmers the collection capacity is reduced significantly at w/oemulsion viscosities exceeding 10 000 cP (ITOPF, 1986), however ITOPF, 1986 does not state the shear rate.

Recent tests performed by SINTEF using a weir skimmer show that the efficiency may be reduced for semi-solidified oils, i. e. oils with a large wax content and high pour point values, and for oils with viscosities between 15000 and 20000 cP (Leirvik et.al.,2001).

#### 2.3.2 Chemical dispersion

A dispersibility methodology, based on the viscosity increase due to weathering, was developed at SINTEF (Daling and Strøm, 1999) in order to determine the window of opportunity for the effective use of dispersants for different oils. Chemical dispersibility testing was not included in this study. General limits for dispersibility based on pour point values are given in table 2.4. These values are not valid for all oils and situations, and should only be regarded as guidelines.

Table 2.4: The chemical dispersibility used in the SINTEF OWM based on pour points.

Pour point [°C]	Chemical dispersibility
< 5°C above the sea temperature	Dispersible
5-15°C above the sea temperature	Reduced dispersibility
>15°C above the sea temperature	Not dispersible



#### 2.4 How to use the prediction charts, an example

If e.g. Endicott has drifted for a period of time on the sea surface the prediction charts can be used to determine the remaining oil's chemical, physical and emulsifying properties. Table 2.5 shows examples for the following scenario:

- Drift time: 24 hours
- Temperature: 0°C/10°C
- Wind speed: 10 m/s

Table 2.5: Weathering properties for Endicott obtained from the prediction charts.

Property	Winter temperature [0°C]	Summer temperature [10°C]
Evaporation	13 vol%	15 vol%
Pour point	15 °C	17°C
Viscosity of the water free oil	5 000 cP	3 000 cP
Water content	50 %	58 %
Viscosity of the emulsion	12 000 cP	9 000 cP



2.5 Prediction charts for Alaskan oils

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2.5.1 Prediction charts and summary of the Endicott crude oil's weathering properties at sea

# Detailed information of the Endicott crude oil sample

 Area/block:
 Alaskan North Slope

 Common field name:
 Endicott

 Well number:
 133 G-12-00

# Summary of the Endicott crude oil's weathering properties at sea

Endicott is a heavy crude oil, with a density of 0,9131 g/mL. Endicott has a relative low content of lighter molecular weight compounds, and at 10 m/s wind speed only 10 % of its original volume will be evaporated 24 hours after the spill at summer temperatures.

Endicott will form w/o-emulsions with a maximum water content of approximately 60 % at winter temperatures and 65 % at summer temperatures doubling the original spill volume. The w/o-emulsions formed are very stable and in order to effectively dehydrate the w/o-emulsions when using an emulsion breaker (e. g. Alcopol O 60 %) a minimum dosage of 2000 ppm should be applied.

After approximately three hours at winter temperatures and half an hour at summer temperatures the Endicott w/o-emulsion will have a viscosity of over 1000 cP which is the recommended lower viscosity limit for an effective mechanical response. Viscosity of the Endicott emulsion will exceed 20 000 cP within 1-3 days at high wind speed. This might cause lowered efficiencies in a mechanical recovery operation using e.g. a weir or disk skimmer. At lower wind speeds this should not be a problem.

Given the high viscosity of the Endicott emulsions, a limited time window for the use of dispersants could be expected. A dispersibility study should be performed on the Endicott oil in order to establish the time-frame in which the use of dispersants are feasible, and to determine the optimal dosage of dispersants for an effective chemical treatment operation.

Due to the high viscosity of the Endicott emulsions a high "lifetime" should be expected for the slick on the sea surface. At low wind speeds natural dispersion is almost neglectable, and even at higher wind speeds the slick will endure for several days on the sea surface.

The prediction charts for the weathering of the Endicott crude oil at sea are given in Figure 2.2 to Figure 2.7. The mass balance for Endicott at the mean summer and winter temperatures in the Alaskan North Slope region at different wind speeds (2, 5, 10 and 15 m/s) are given in Figure 2.8 to Figure 2.11. These figures illustrate the degree of natural dispersion at varying sea conditions.

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Figure 2.2: The predicted evaporative loss for Endicott at summer (10°C) and winter (0°C) mean temperatures in Alaskan North Slope region.

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Figure 2.3: The Flash point for water-free Endicott at the mean summer (10°C) and winter (0°C) temperatures for the Alaska North Slope region.

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Figure 2.4: The predicted pour point for water-free Endicott at different wind speeds at the summer (10 °C) and winter (0 °C) mean temperatures in the Alaskan North Slope region.

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Figure 2.5: The predicted viscosity for water-free Endicott for different wind speeds at the summer (10°C) and winter (0°C) mean temperatures in the Alaskan North Slope region.

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Figure 2.6: The predicted water content in the Endicott w/o-emulsions for different wind speeds at the summer (10°C) and winter (0°C) mean temperatures in the Alaskan North Slope region.

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Figure 2.7: The predicted viscosity of the Endicott w/o-emulsions for different wind speeds at the summer (10 °C) and winter (0 °C) mean temperatures in the Alaskan North Slope region.

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Figure 2.8: The mass balance for Endicott at the mean winter temperature (0  $^{\circ}$ C) in the Alaskan North Slope region at wind speeds of 2 and 5 m/s.

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Figure 2.9: The mass balance for Endicott at the mean winter temperature (0  $^{\circ}$ C) in the Alaskan North Slope region at wind speeds of 10 and 15 m/s.

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Figure 2.10: The mass balance for Endicott at the mean summer temperature (10°C) in the Alaskan North Slope region at wind speeds of 2 and 5 m/s.

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Figure 2.11: The mass balance for Endicott at the mean summer temperature (10 °C) in the Alaskan North Slope region at wind speeds of 10 and 15 m/s.

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# 2.5.2 Prediction charts and summary of the Alpine Composite oil's weathering properties at sea

# Detailed information of the Alpine Composite

Area/block:	Alpine Central Production Facility
Sample date:	07-23-2001
Company name:	Phillips

Composite sample from all of the producing wells at Alpine.

## Summary of the Alpine Composite's weathering properties at sea

The Alpine Composite is a paraffinic crude oil, with a density of 0,834 g/mL. The Alpine Composite contains a relatively large amount of lower molecular weight compounds and approximately 25% of its original volume will be evaporated 24 hours after the spill at both summer and winter temperatures.

The Alpine Composite contains approximately 4 wt% wax and less than 0,1 wt% asphaltenes. The fresh oil has a pour point of -18°C and increases rapidly with weathering to approximately  $10^{\circ}$ C and 15°C at the mean winter and summer mean temperatures at a wind speed of 10 m/s.

Alpine Composite will form w/o-emulsions with a maximum water content of 80 % at both winter and summer temperatures, yielding approximately five times the original spill volume. The w/oemulsion formed after one day of weathering at sea is stable and in order to effectively dehydrate the w/o-emulsions when using the emulsion breaker Alcopol O 60 % a minimum dosage of 2000 ppm should be applied.

After one day of weathering the Alpine Composite w/o-emulsions at winter and summer temperatures will have a viscosity of over 1000 cP and the viscosity will only exceed 10 000 cP after several days of weathering on the sea surface. High viscosity should not compromise the success off a mechanical recovery operation, for at least a week after the time of the release.

The Alpine Composite will have a high degree of natural dispersion at high wind speeds. E.g. at 15 m/s wind speed the slick will be almost removed from the sea surface within a day.

The prediction charts for the weathering of the Alpine Composite oil at sea are given in Figure 2.12 to Figure 2.17.

The mass balance for the Alpine Composite at the mean summer and winter temperatures in the Alaska North Slope region at different wind speeds (2, 5, 10 and 15 m/s) are given in Figure 2.18 to Figure 2.21. These figures illustrate the degree of natural dispersion at varying sea conditions.





Figure 2.12: The predicted evaporative loss for the Alpine Composite oil at summer (10  $^{\circ}$ ) and winter (0  $^{\circ}$ ) mean temperatures.

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Figure 2.13: The Flash point for water-free Alpine Composite at the mean summer (10℃) and winter (0℃) temperatures for the Alaska North Slope region.

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Figure 2.14: The predicted pour point for water-free Alpine Composite at different wind speeds at the summer  $(10^{\circ}C)$  and winter  $(0^{\circ}C)$  mean temperatures.

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Figure 2.15: The predicted viscosity for water-free Alpine Composite for different wind speeds at the summer  $(10 \, \text{C})$  and winter  $(0 \, \text{C})$  mean temperatures.

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Figure 2.16: The predicted water content in the Alpine Composite w/o-emulsions for different wind speeds at the summer  $(10 \, \text{C})$  and winter  $(0 \, \text{C})$  mean temperatures.

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Figure 2.17: The predicted viscosity of the Alpine Composite w/o-emulsions for different wind speeds at the summer (10 °C) and winter (0 °C) mean temperatures.

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Hours

Based on viaccality measurements carried out at a shear rate of 10 reciproce) seconds.



Figure 2.18: The mass balance for Alpine Composite at the mean winter temperature  $(0^{\circ}C)$  in the Alaskan North Slope region at wind speeds of 2 and 5 m/s.

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Figure 2.19: The mass balance for Alpine Composite at the mean winter temperature  $(0^{\circ}C)$  in the Alaskan North Slope region at wind speeds of 10 and 15 m/s.

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Figure 2.20: The mass balance for Alpine Composite at the mean summer temperature  $(10^{\circ}C)$  in the Alaskan North Slope region at wind speeds of 2 and 5 m/s.

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Figure 2.21: The mass balance for Alpine Composite at the mean summer temperature (10 °C) in the Alaskan North Slope region at wind speeds of 10 and 15 m/s.



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#### 2.5.3 Summary of the Milne Point Unit Oil's weathering properties at sea

#### Detailed information of the Milne Point Unit oil sample

Area/block: Jerry cans marked: Alaskan North Slope MPJ-01 CRUDE OIL

# Summary of the Milne Point Unit oil's weathering properties at sea

The Milne Point Unit oil sample were emulsified at arrival. The emulsion were extremely stable and could not be broken without the addition of an excess of emulsion breaker and heating. The laboratory evaporation of the oil, that forms the fundament of the weathering studies, could not be performed on the emulsified oil. Predictions could therefore not be made for the Milne Point Unit oil.

The Milne Point Unit oil is a heavy naphthenic oil with an approximate density of 0.95 g/ml. The oil seems to be highly biodegraded (i.e. no paraffinic components are present in the Gas Chromatogram seen in fig C5) The emulsion is extremely stable and can only be dehydrated at high temperatures and with the addition of a high dosage of demulsifier (approximately 10%). Dehydration of the emulsion in a mechanical recovery operation could therefore prove difficult. The water content of the arrived oil was 30-40%.

From previous studies at SINTEF, testing with a weir skimmer has showed poor recovery efficiency at viscosities above 20.000. A 30% emulsion of the "fresh" Milne Point Unit oil has a viscosity of approximately 8000 cP at 10°C. A high degree of evaporation is not expected for the Milne Point Unit oil, but the viscosity will increase with weathering on the sea surface (both evaporation and further emulsification), and high viscosities could cause problems in a mechanical recovery operation for the Milne Point Unit oil, particularly at winter conditions.

SINTEF recommend a non emulsified Milne Point oil is supplied if possible, and the weathering properties are further investigated.

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## 2.5.4 Prediction charts and summary of the North Star Oil's weathering properties at sea

# Detailed information of the North Star oil sample

Sample no :	1.08
Client:	BP Alaska
Installation:	North Star
Date:	5.6-02
Bottle no.:	n/a
Well:	NS-08
Test:	testl
Time:	21:25
Sample	Nature: Atmospheric oil
Sampling point:	Separator Oil Line
Sample bottle:	5gallon can
Job no.:	NAM 1076

#### Summary of the North Star oil's weathering properties at sea

The North Star oil is a light paraffinic crude oil, with a density of 0.8155 g/mL. The North Star oil contains a relatively large amount of lower molecular weight compounds and approximately 30 % of its original volume will evaporate 24 hours after the spill at both summer and winter temperatures. The wax content of the North Star oil is 5.9 wt%. The pour point for the North Star oil is very low for a paraffinic crude at  $-39^{\circ}$ C for the fresh crude.

A viscosity of 1000 cP is considered to be a lower limit for efficient mechanical oil recovery. This is due to leakage under the oil booms at lower viscosities (Norvik *et.al.* 1992). The North Star oil will have viscosities below this limit initially and in a span of time highly dependent on wind and temperature (e.g. 2 hours for 0°C and 15m/s wind speed, and 2 days for 10°C and 2 m/s wind speed). During mechanical combat operations loss of oil could be expected within this time-frame.

No laboratory study is performed to assess the window of opportunity for the use of chemical dispersants. The natural dispersion, however, will be of significance at high wind speeds. At both summer and winter temperatures and 15 m/s wind speed the oil slick is expected to vanish from the sea surface within a day due to natural dispersion. At lower wind speeds the oil could be persistent on the sea surface for several days.

The prediction charts for the weathering of the North Star oil at sea are given in Figure 2.22 to Figure 2.27. The mass balance for the North Star oil at the mean summer and winter temperatures in the Alaska North Slope region at different wind speeds (2, 5, 10 and 15 m/s) are given in Figure 2.28 to Figure 2.31.





Figure 2.22: The predicted evaporative loss for the North Star oll at the mean summer  $(10^{\circ})$  and winter  $(0^{\circ})$  temperatures for the Alaska North Slope region.

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Figure 2.23: The predicted viscosity for water-free North Star oil at the mean summer (10°C) and winter (0°C) temperatures for the Alaska North Slope region.

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Figure 2.24: The Flash point for water-free North Star oil at the mean summer (10°C) and winter (0°C) temperatures for the Alaska North Slope region.

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Figure 2.25: The predicted pour point for water-free North Star oil at the mean summer (10°C) and winter (0°C) temperatures for the Alaska North Slope region.

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Figure 2.26: The predicted water uptake for North Star oil at the mean summer (10 °C) and winter (0 °C) temperatures for the Alaska North Slope region.

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Figure 2.27: The predicted emulsion viscosity for North Star oil at the mean summer (10°C) and winter (0°C) temperatures for the Alaska North Slope region.

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Figure 2.28: The mass balance for the North Star oil at the mean winter temperature (0 °C) for the Alaska North Slope region at wind speeds of 2 and 5 m/s.

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Figure 2.29: The mass balance for the North Star oil at the mean winter temperature  $(0^{\circ}C)$  for the Alaska North Slope region at wind speeds of 10 and 15 m/s.

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Figure 2.30: The mass balance for the North Star oll at the mean summer temperature (10 °C) for the Alaska North Slope region at wind speeds of 2 and 5 m/s.

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Figure 2.31: The mass balance for the North Star oil at the mean summer temperature (10°C) for the Alaska North Slope region at wind speeds of 10 and 15 m/s.

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2.6 Prediction charts for Gulf of Mexico oils

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# 2.6.1 Prediction charts and summary of the Neptune Field Composite's weathering properties at sea

## Detailed information of the Neptune Field Composite sample

Area/block: VK 826 MMS Structure name: А Sample date: 14. November 2000 Sample number: DGM 5870 Common field name: Neptune VK 825 Field/unit: Kerr-McGee Company name: MMS Platform ID: VK 826A

Composite sample from the following API well numbers: Well A-1 through A-10, A-12st, 825-4, 825-5 and 826-12.

#### Summary of the Neptune Field Composite's weathering properties at sea

The Neptune Field Composite is a paraffinic crude oil, with a density of 0,869 g/mL. The Neptune Field Composite contains a relatively large amount of lower molecular weight compounds and over 30 % of its original volume will be evaporated 24 hours after the spill at both summer and winter temperatures. The wax content of the Neptune Field Composite is medium (-4 wt%). The fresh oil has a pour point of -9°C and increases with weathering to approximately 15°C at a wind speed of 10 m/s.

The experimental results showed that the Neptune Field Composite did not form stable w/oemulsions. One normally would expect that a crude oil with a wax and asphaltene content similar to the Neptune Field Composite will form stable w/o-emulsions. SINTEF suspects that production/process chemicals are present in the oil sample thereby reducing the w/o-emulsion process. This suspicion is supported by the un-normal low interfacial tension value measured for the fresh crude (6 mN/m). SINTEF proposes that MMS inquire if offshore chemicals are present in this crude oil sample, and that a follow up study of an untreated oil should be discussed based on the findings.

The viscosity of the Neptune Field Composite only exceeds the lower viscosity limit for an effective mechanical response  $(1000 \text{ cP} \text{ at shear rate } 108^{-1})$  after 5 days. The viscosity will not increase drastically with weathering since the Neptune Field Composite does not form stable w/o-emulsions on the sea surface. The initial spill volume will not increase significantly and the Neptune Field Composite will most likely spread quickly on the sea surface. In a mechanical clean up operation the Neptune Field Composite may have a significant degree of leakage from the oil spill boom due to the oils low viscosity (< 1000 cP) (Nordvik *et.al.* 1992), even after several days of weathering on the sea surface. Chemical dispersion may be a possible response operation since the viscosity and pour point of the Neptune Field Composite are low, however, this was not investigated in this study.

The prediction charts for the weathering of the Neptune Field Composite at sea are given in Figures 2.32 to 2.35. The mass balance for the Neptune Field Composite at the mean summer and winter temperatures in the GOM region at different wind speeds (2, 5, 10 and 15 m/s) are given in Figures 2.36 to 2.40. These figures illustrate that the natural dispersion process of the Neptune Field Composite is high (at wind speeds above 10 m/s) due to the low viscosity and that the oil does not form stable w/o-emulsions (i. e. the Neptune Field Composite will have a short lifetime on the sea surface).

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Figure 2.32: The predicted evaporative loss for the Neptune Field Composite at the mean summer (29°C) and winter (20°C) temperatures for the GOM region.

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Figure 2.34: The predicted pour point for the Neptune Field Composite at the mean summer (29 °C) and winter (20 °C) temperatures for the GOM region.

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Figure 2.35: The predicted viscosity for water-free Neptune Field Composite at the mean summer (29°C) and winter (20°C) temperatures for the GOM region.

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Figure 2.36: The mass balance for the Neptune Field Composite at the mean winter temperature  $(20 \, \text{C})$  for the GOM region at wind speeds of 2 and 5 m/s.

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Figure 2.37: The mass balance for the Neptune Field Composite at the mean winter temperature  $(20 \, \text{C})$  for the GOM region at wind speeds of 10 and 15 m/s.

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Figure 2.38: The mass balance for the Neptune Field Composite at the mean summer temperature (29°C) for the GOM region at wind speeds of 2 and 5 m/s.

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Figure 2.39: The mass balance for the Neptune Field Composite at the mean summer temperature  $(29 \, ^{\circ} C)$  for the GOM region at wind speeds of 10 and 15 m/s.

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# 2.6.2 Prediction charts and summary of the High Island Composite's weathering properties at sea

Detailed information of the High Island oil sample Area/block: High Island Block A573

Area/DIOCK:	High Island Block AS
MMS structure name:	Α
Sample date:	December 8, 2000
Sample number:	DGM 6013
Common field name:	none
Field name:	HIA573A
Company name:	UNOCAL
Well number:	A006
API well number:	427094016200

Composite sample from the following API well numbers: Well A-1 through A-10, A-12st, 825-4, 825-5 and 826-12.

#### Summary of the High Island oil's weathering properties at sea

The High Island oil were emulsified at arrival (~15%). Water was removed by leaving the emulsion at rest for approximately a month in a 10 litre flask. At this time the oil/emulsion had formed a gradient with no water in the top layers of the flask increasing to an emulsion of 80% water in the bottom of the flask. The water free upper layer of the flask was used in the further weathering study. The meso-scale flume experiment, however, was performed on the emulsion as delivered, and yield supplementary data as input to the OWM.

The High Island oil is a naphthenic crude oil, with a density of approximately 0.85 g/mL. The High Island oil contains medium amount of lower molecular weight compounds and over 20 % of its original volume will evaporate 24 hours after the spill at both summer and winter temperatures. The wax content of the High Island oil is low (1.6 wt%), and the pour point for the High Island oil is also low  $(-16^{\circ}\text{C}$  for the fresh crude).

Results from the meso scale flume shows that High Island oil form unstable emulsions with low viscosity. Maximum water content is high at 70%, but observations from the meso scale flume shows that emulsions dehydrate almost completely within an hour when left at rest (e.g. in a tank).

A viscosity of 1000 cP is considered to be lower limit for efficient mechanical oil recovery. This is due to leakage under the oil booms at lower viscosities (Nordvik *et.al.* 1992). The High Island oil will have viscosities below this limit for at least four days of weathering at the sea surface, and problems with leakage under the boom could be expected during recovery.

No laboratory study is performed to assess the window of opportunity for the use of chemical dispersants. However, dispersibility testing in the meso scale flume shows fairly good dispersibility after 3 days of weathering in the flume basin. Natural dispersion is high at high wind speeds and the slick will have an estimated lifetime of 12 hours and 3 days respectively for 15 m/s and 10 m/s wind speed. For lower win speeds the slick will be persistent on the sea surface, and the lifetime will exceed 5 days.

The prediction charts for the weathering of the High Island oil at sea are given in Figures 2.40 to 2.44. The mass balance for the High Island oil at the mean summer and winter temperatures in the GOM region at different wind speeds (2, 5, 10 and 15 m/s) are given in Figures 2.45 to 2.48.

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Figure 2.40: The predicted evaporative loss for the High Island oil at the mean summer (29°C) and winter (20°C) temperatures for the GOM region.





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Figure 2.41: The predicted viscosity for water-free High Island oil at the mean summer (29°C) and winter (20°C) temperatures for the GOM region.

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Figure 2.42: The predicted pour point for water-free High Island oil at the mean summer (29 °C) and winter (20 °C) temperatures for the GOM region.

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Figure 2.43: The predicted water uptake for High Island oil at the mean summer (29°C) and winter (20°C) temperatures for the GOM region.

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Figure 2.44: The predicted emulsion viscosity for High Island oil at the mean summer (29°C) and winter (20°C) temperatures for the GOM region.





Figure 2.45: The mass balance for the High Island oil at the mean winter temperature (20°C) for the GOM region at wind speeds of 2 and 5 m/s.

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Figure 2.46: The mass balance for the High Island oil at the mean winter temperature (20°C) for the GOM region at wind speeds of 10 and 15 m/s.







Figure 2.47: The mass balance for the High Island oil at the mean summer temperature (29 °C) for the GOM region at wind speeds of 2 and 5 m/s.

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Figure 2.48: The mass balance for the High Island oil at the mean summer temperature (29°C) for the GOM region at wind speeds of 10 and 15 m/s.

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Appendix A: The behavior of crude oils on the sea surface

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#### A1 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, these are hydrocarbons and heteroatomic organics, see Figure A1.



Figure A1: The chemical composition of crude oil.

#### A1.1 Hydrocarbons

The majority of compounds in crude oil are hydrocarbons. Hydrocarbons are compounds that contain carbon (C) and hydrogen (H) and include both saturated and unsaturated molecules in linear, branched and cyclic configurations. Volatile gases, such as methane (CH<sub>4</sub>) as well as complex molecules containing more than one hundred carbon atoms ( $C_{>100}$ ) are included in this group.

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

#### Paraffins

Paraffins include *n*-alkanes and *iso*-alkanes aliphatic compounds. The common term for paraffinic molecules, which consist of more than twenty carbon atoms ( $C_{>20}$ ), is wax. At elevated temperatures the wax will be present in solution, however, at lower temperatures the wax can precipitate. The wax content of crude oils can vary from 0,5 to 50 wt%, however the majority have a wax content of 2 to 15 wt%.

#### Naphthenes

Naphthenes are saturated cyclic hydrocarbons with one or more rings. Each ring can have one or more paraffinic side chains.



#### Aromatics

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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 polynuclear aromatic hydrocarbons (PAH) contain three or more aromatic rings.

#### A1.2 Hetroatomic organics

Hetroatomic organics can, in addition to carbon and hydrogen, contain small amounts of sulphur (S), nitrogen (N), oxygen (O) and trace amounts of vanadium (V) and nickel (Ni). Resins and asphaltenes are important subgroups of organic non-hydrocarbons.

Carboxylic acids, sulphoxides and phenol compounds are relatively polar compounds classified as resins. Asphaltenes consist of high molecular weight polycyclic aromatic compounds.

#### A2 Physical properties of crude oils

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

A2.1 Density

The density of crude oil normally lies between 0,78 to 0,95 g/mL at 15,5°C. Paraffinic oils have lower density values, while oils that contain large amounts of high molecular weight aromatic, naphthenes and asphalthenic compounds usually have higher density values.

A2.2 Viscosity

The viscosity of crude oil expresses its resistance to flow and is of special interest when pumping mechanically collected oil. The viscosity of crude oils can vary from 3 to 2000 cP at 13°C. In comparison water has a viscosity of 1 cP and syrup a viscosity of 120 000 cP at 20°C.

The viscosity is temperature dependent. For liquids the viscosity decreases with increasing temperatures. Figure A2 shows the variations in viscosity as a function of temperature for various crude oils and oil products. Viscous crude oils or crude oils that contain wax can exhibit non-Newtonian behaviour (viscosity varies with shear rate), especially close to or below their pour point.

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Figure A2: The variation in viscosity as a function of temperature for several crude oils and oil products. The figure is not valid below the oil's pour points.

The viscosity of an oil increases with evaporation since the heavier, more viscous components remain. The difference in viscosity for crude oils is approximately 3 to 2000 cP for fresh crude oils and several hundred/thousand cP for their residues.

Water-in-oil (w/o) emulsions are generally more viscous than the parent crude oil, this is illustrated in Figure A3.

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Due to the shear thinning rheological properties, the viscosity of w/o-emulsions will decrease with increasing shear rate. A w/o-emulsion can therefore flow under turbulent conditions on the sea surface, but can become more viscous under calmer sea conditions or if washed on shore. Viscosity measurements must therefore be made under controlled conditions in the laboratory.

A2.3 Pour point

The temperature when an oil ceases to flow when cooled without disturbance under standardised conditions in the laboratory (ASTM-D97) is defined as the oils pour point. In oil spill clean up situations the pour point provides important information when determining the efficiency of various skimmers, pumping rates and the use of dispersion agents.

The pour point is related to the chemical composition of the parent crude oil, particularly its wax content. The ASTM Pour Point test is performed under static conditions. Field experience shows that under dynamic conditions on the sea surface, effects of oil solidification will occur 10-15°C below the laboratory generated pour points.

The pour point of an oil with a high wax content will increase dramatically with weathering as the lower weight molecules that contribute in keeping the wax in solution are lost. The pour point of oils with high wax contents can reach  $30^{\circ}$ C, while low viscous naphthenic (highly biodegraded) oils can have pour points as low as  $-40^{\circ}$ C.

#### A2.4 Distillation curve

Distillation curves for crude oils give important information about the relative amount of lighter compounds in the oil and is therefore fundamental for determining the degree of evaporative loss after it is spilled on the sea surface. The curve is obtained by plotting the vapour temperature as a function of the amount of distillate. Figure A4 shows segments of the distillation curves for selected crude oils.

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Figure A4: Distillation curves for the crude oils tested during the project.

#### A2.5 Flash point

The flash point is the lowest temperature at which the gas or vapour generated by heating an oil can be ignited by a flame. 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 of most significance 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 an oil.

A rule of thumb says that moving in an oil spill where the flash point of the oil is close to or lower than the sea temperature implies a fire and explosion hazard. Natural weathering processes like evaporation and emulsification formation contribute in reducing the potential hazard by increasing the flash point. There is therefore a relatively short fire and/or explosion danger in the initial stages of an oil spill.

In the laboratory, the flash point is measured in a closed system where there is equilibrium between the components in the oil and gas. In the field, however, the weather situation will influence the flammability of the air above the slick. For instance 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.



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#### A3 The behavior of crude oil spilt at sea

When a crude oil is spilt at sea a number of natural processes take place, which change the volume and the chemical properties of the oil. These natural processes are evaporation, water-in-oil (w/o) emulsification, oil-in-water (o/w) dispersion, release of oil components into the water column, spreading, sedimentation, oxidation and biodegradation. A common term for all of these natural processes is weathering. The relative contribution of each process varies during the duration of the spill. Figure A5 illustrates the various weathering processes and Figure A6 shows their relative importance with time.



Figure A5: The weathering processes that take place when an oil is spilt on the sea surface.

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Figure A6: Weathering processes' relative importance with time.

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, bacteria flora etc.).

#### A3.1 Evaporation

Evaporation is one of the natural processes that helps in removing spilt 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 amount evaporated depends on the chemical composition of the oil in addition to the prevailing weather conditions, sea temperature and the oil film thickness.

The rate of evaporation will vary 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 loose 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 increases the relative amounts of higher molecular weight compounds. The chemical and physical properties of the remaining oil change, for example the density, viscosity, pour point and the relative wax and asphaltene contents will increase with increase devaporation.



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#### A3.2 Spreading

Oil spilt at sea will spread on the sea surface. Spreading is often the dominating process in the initial stages of an oil spill, however see Figure A6, its importance 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 current) will affect the spreading process. The oil slick will be broken into windrows aligned in the wind direction, see Figure A7. The oil film thickness of the oil slick will vary, often differing with a factor of several thousand. Past experience has shown that 90 vol% of the oil spilt will consist of patches of w/o-emulsion with a film thickness of 1 to 5 mm that often constitute for less than 10 % of the total oil slick area. The remaining 10 vol% will cover 90 % of the spill area in the form of a sheen (<1 µm oil thickness).



Figure A7: The spreading of oil spilt on the sea surface and the distribution within the oil slick.

#### A3.3 Drift of an oil slick

Prevailing surface currents cause the oil slick to drift, see Figure A8. Surface currents are controlled by currents in the water column but will also be influenced by wind speed and direction. This influence will be about 3% off the wind speed and direction compared to the drift contribution from currents.

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Figure A8: An illustration showing how wind and current can influence the drift of an oil slick.

#### A3.4 Water-in-oil (w/o) emulsion

The formation of w/o-emulsions is one of the major weathering processes that contributes in keeping oil on the sea surface. A w/o-emulsion has a higher viscosity than the parent crude oil and the emulsification process will therefore retard/delay the evaporation and the natural dispersion process.

The minimum criteria for the formation of w/o-emulsions is the presence of breaking waves (i. e. a wind speed of 5 m/s), however, a slow water uptake can also take place during calmer weather.

Surface active components present in crude oil will promote the formation of w/o-emulsions and contribute in stabilising 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 shown 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, however, the rate of emulsification depends highly on the weather conditions. Previous tests of asphalthenic oils performed at SINTEF show that the water uptake is in inverse ratio with the viscosity.

The rate of formation of the w/o-emulsion varies for different oil types since it is dependent on the chemical composition if the oil. A large amount of wax will for instance increase the rate of formation. Another important factor that influences the rate of formation is the prevailing weather conditions. Figure A9 shows an example of how the wind speed influences the rate of formation.





Figure A9: An example of how the prevailing weather conditions influence the rate of the w/oemulsion formation for a typical crude oil.

The stability of the w/o-emulsion depends on the water droplet size in the emulsion. Not all of the water droplets in the emulsion are stabile. The largest droplets may coalesce and settle out of the w/o-emulsion. Larger water droplets may be reduced in size by the flexing, stretching and compressing motion of a slick due to wave action. After a period of time the emulsion may only contain small water droplets with a diameter of 1 to 10  $\mu$ m. Figure A10 illustrates the effect of rotation time on the water droplet size in a w/o-emulsion formed in the laboratory.



Figure A10: A picture taken with a microscope of the water droplet size in a w/o-emulsion after (A) I hour and (B) 24 hours in a rotating cylinder.

Another factor that influences the w/o-emulsion's stability is the amount of surface-active components present in the parent oil. Resins and asphaltenes have hydropholic and hydrophilic properties and will concentrate at the interface between the water and oil thereby forming a layer that stabilises the water droplets. The hydrophobic properties can lead to the concentration of wax along the water droplets, which further stabilises the interfacial "skin" layer. The interfacial layer between the oil and water forms a physical barrier hindering coalescence and will stabilise the w/o-emulsion by hindering the fusion of water droplets. The stabilisation of the water droplets by asphaltenes and by asphaltenes and wax are shown in Figure A11.

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Figure A11: Stabilization of the interfacial layer between the water and oll in a w/o-emulsion by wax and asphaltenes.

Oils that contain a large amount of wax and little asphaltenes can form w/o-emulsions that may appear to be stabile. These w/o-emulsions appear to be stabled by the continuos phase's rheological strength (viscosity and elasticity). This strength is due to the wax structure formed by precipitated wax. Wax stabilised emulsions are characterised by large water droplets and are fairly stabile when stored, however, they may break when stress is applied and/or when the emulsion is heated to e.g. 40-50°C.

#### A3.5 Oil-in-water (o/w) dispersion

Natural 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 typically with a diameter between 1 to 1000  $\mu$ m which are mixed into the water masses. The largest oil droplets will resurface forming a sheen (see 0) behind the oil slick.

In addition to weather conditions the 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. The natural o/w dispersion will gradually decrease since evaporation of the lighter components will increase the viscosity of the remaining oil.

The purpose of applying chemical dispersion agents is to increase the natural o/w dispersion rate. When effective chemical dispersion is achieved small oil droplets are formed with a diameter of 5 to 50  $\mu$ m. The dispersion agent reduces the interfacial tension between the water and oil and promotes dispersion.



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#### A3.6 Water solubility

The water solubility of saturated hydrocarbons ( $<C_4$ ) is very low, while lower molecular weight aromatic compounds are water-soluble. Within the various types of hydrocarbons the water solubility decreases from aromatics to naphthenes and from *iso*-paraffins to *n*-paraffins. In each series the water solubility decreases with increasing molecular weight.

Evaporation and the release of oil components in to the water masses 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 dissolution into the water column. The concentration of soluble oil components in the water column during an oil spill is quite low (<1 mg/L). The dissolution of oil components into the water column does not contribute in removing the oil from the sea surface. However the water-soluble fraction (WSF) is of great interest since it has a high bioavailability and therefore the potential to cause acute toxic effects on marine organisms.

#### A3.7 Photo-oxidation

Under the influence of sunlight some of the oil components will slowly be oxidised to resins and eventually asphaltenes. This contributes to the stability of w/o-emulsions and therefore has a large influence on the oils persistence on the sea surface. The photo-oxidised components will stabilise the w/o-emulsions. After a long period of weathering at sea, tar-balls can be formed. Tar-balls are broken down very slowly both at sea and on beaches.

#### A3.8 Biodegradation

Theoretically, seawater contains micro-organisms that can break down all types of oil components. The various micro-organisms prefer specific oil components as an energy source.

Several factors influence the biodegradation rate, among these are temperature, the supply of nutritive substances that contain nitrogen and phosphor, the oxygen supply, oil type and the degree of weathering. Bacteria can only degrade oil that is in contact with seawater and is dependent of the water/oil interface area. The interface area increases as the oil is spread over the sea surface as a thin layer or by chemical or natural dispersion of oil in the water masses. An area increase due to chemical and/or natural dispersion will increase the degradation rate in the water mass to 10 to 100 times the rate at the water/oil interface.

#### A3.9 Sedimentation

Crude oil and oil residues rarely sink into the water masses since there are few oils that have a density higher than water, even after extreme weathering. Oil can, however, sink if sticking to particular material present in the water masses. The increased density will make oil-soiled particles sink more readily.





#### A3.10 Submersion

Highly weathered oils can temporarily submerge from the sea surface. This can greatly influence the effectiveness of combating oil pollution in the marine environment. The oil density and viscosity in addition to the weather conditions influence submersion. W/o-emulsions have a higher density value than the parent oil and can therefore submerge more easily.

Appendix B: Experimental Design of the Bench-Scale and Meso-scale Laboratory Testing

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#### B1 Oil Samples received for the study

SINTEF received two fresh oil samples from the Alaskan North Slope (Endicott and Milne Point Unit) on the 14<sup>th</sup> of November 2000, two fresh oil samples from the Gulf of Mexico (Neptune Field Composite and High Island Composite) on the 30<sup>th</sup> of January 2001 and an oil sample from the North Slope (Alpine Central Production Facility) on the 15<sup>th</sup> of August 2001. At 11<sup>th</sup> of June 2002, the last Alaskan North Slope oil arrived (North Star Oil). These oil samples were supplied by MMS.

#### Alaskan North Slope samples

#### B1.1 Detailed information of the Endicott crude oil sample

Area/block:Alaskan North SlopeCommon field name:EndicottWell number:133 G-12-00

#### B1.2 Detailed information of the Milne Point Unit oil sample

Area/block: Alaskan North Slope Jerry cans marked: MPJ-01 CRUDE OIL

#### B1.3 Detailed information of the Alpine Central Production Facility oil sample (Alpine

Composite) Area/block: Alpine Oilfield Sample date: July 23, 2001 Composite sample of all of the producing wells at Alpine.

#### B1.4 Detailed information of the North Star oil sample

spheric oi
Line



#### **Gulf of Mexico Oils**

B1.5 Detailed information of the Neptune Field Composite sample Area/block: VK 826 MMS Structure name: Α Sample date: November 14, 2000 Common field name: Neptune Field/unit: VK 825 Kerr-McGee Company name: VK 826A MMS Platform ID: Composite sample from the following API well numbers: Well A-1 through A-10, A-12st, 825-4, 825-5 and 826-12

#### B1.6 Detailed information of the High Island Composite

Area/block: High Island Block A573 MMS structure name: Α Sample date: December 8, 2000 Common field name: none Field name: HIA573A UNOCAL Company name: Well number: A006 API well number: 427094016200

#### **B2** Test temperatures

The temperatures chosen for the bench-scale laboratory testing are:

Endicott:	10°C
Milne Point Unit:	10°C
Alpine Composite:	10°C
North Star	10°C
The Neptune Field Composite:	23°C
High Island Composite:	23°C

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#### B3 Bench-scale laboratory testing

In order to isolate and map the various weathering processes that take place when an oil is spilled on the sea surface, the weathering of the oils is carried out using a systematic, stepwise procedure developed at SINTEF (Daling *et al.*, 1990). The weathering process is illustrated in Figure B1.



Figure B1: Flow chart for the bench-scale laboratory weathering of a crude oil.

#### **B3.1 Evaporation**

Evaporation of the lighter components from the fresh crude oil is carried out according to a modified ASTM-D86/82 distillation procedure (Stiver and Mackay, 1984). The fresh crude oil is distilled, in a simple one step distillation, to a vapor temperature of 150, 200 and 250°C. This will give oil residues with an evaporation loss typically corresponding to 0,5-1 hour, 0,5-1 day and 2-5 days of weathering of an oil slick on the sea surface. These residues are referred to as 150°C+, 200°C+ and 250°C+ respectively.

#### B3.2 Water-in-oil (w/o) emulsification

The procedures used in the w/o-emulsification studies are described in detail by Hokstad et al., 1993.

The w/o-emulsification of the fresh crude oil is carried out based on the rotating cylinder method developed by Mackay and Zagorski, 1982. Oil (30 mL) and seawater (300 mL) are rotated (30 rpm) in a separating funnel (0,5 L), see Figure B2. The emulsification kinetics are mapped by measuring the water content at fixed rotation times. The maximum water content is determined after 24 hours of rotation.

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Figure B2: Principle of the rotating cylinder method.

To test the effectiveness of the emulsion breaker Alcopol O 60 %, two dosages (500 ppm and 2000 ppm relative to the oil volume) were added drop wise to the w/o-emulsion. After a contact period of 5 minutes and a rotation time of 5 minutes (30 rpm), the treated emulsion stood for 24 hours before the amount of water drained from the emulsion was determined.

The distilled residues were emulsified with 50 vol% and 75 vol% water in addition to the maximum water content w/o-emulsion. Four parallel runs were performed to map the w/oemulsion kinetics and two of the parallel runs were performed with the addition of Alcopol O 60%. Several physical and chemical properties of the twelve weathered samples (see Figure B1) were determined. A detailed description of the various analyses is given in B3.3.

#### B3.3 Physical and chemical analysis

The viscosity, density, pour point, flash point and interfacial tension of the water free residues and w/o emulsions were determined. The analytical procedures used are given in Table B1.

Properties		
Physical property	Analytical method	Instrument
Viscosity	McDonagh et al., 1995	Physica MCR 300
Density	ASTM method D4052-81	Anton Paar, DMA 4500
Pour Point	ASTM method D97	-
Interfacial tension	De Nouy Ring method	Kruss tensiometer
Flash point	ASTM D 56-82	Pensky-Martens, PMP1, SUR

Table B1: Summary of the analytical methods used in the determination of the physical properties.

The wax content and "hard" asphaltene content will be determined using the analytical procedures given in Table B2.

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Table B2: Summary of the analytical methods used in the determination of the chemical properties.

Chemical property	Analytical method
Wax content	Bridiè et al., 1980
"hard" asphaltene	IP 234/84

#### B4 Meso-scale laboratory testing

In the bench scale testing the oils are distilled and emulsified in separate processes. In an oil spill situation at sea these processes will occur simultaneously and affect each other. It is therefore important that the oils are weathered under realistic conditions when studying how the oils behaviour when spilled on the sea surface.

A meso-scale flume basin (Singsaas et al., 1993) located at SINTEF is routinely used to study the weathering processes simultaneously under controlled conditions. The experimental data obtained from the meso-scale testing provides a link between the bench scale testing and field trials and is important input in the OWM. In this study a meso-scale flume basin experiment is therefore performed as a supplement to the limited bench scale study to be conducted on the heavily emulsified High Island oil sample.

#### B4.1 Description of the meso-scale flume

Approximately 1,7 m<sup>3</sup> seawater circulates in the 10 meter long flume. The flume is located in a conditioning room ( $20^{\circ}C - 50^{\circ}C$ ). To fans (3) placed in a covered wind-tunnel allow various wind speeds. The evaporation- and emulsification rate is calibrated to simulate a wind speed of 5-10 m/s. A schematic drawing of the flume is given in Figure B3.



Figure B3: A schematic drawing of the meso-scale flume.



B4.2 Oil weathering in the meso-scale flume

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The emulsified oil sample (10 L) is carefully released on the water surface. The oil is weathered for a total of 72 hours. Surface oil residue, w/o-emulsion and subsurface water samples are taken after 0 min., 15 min., 30 min., 1 hour, 2 hours, 3 hours, 4 hours, 5 hours, 6 hours 12 hours, 1 day, 2 days and 3 days of weathering. The following physical properties are determined:

- water content
- viscosity
- density
- evaporation loss

#### **B4.3 In-situ chemical dispersion**

After 72 hours of weathering in the flume the dispersion agent Corexit9500 is sprayed onto the w/o-emulsion, see Table B3, where

DOR is the dispersion agent to oil ratio DER is the dispersion to w/o-emulsion ratio

Table B3: The application time and amount of the dispersion agent Corexit 9500.

Weathering	Amount of Dasic NS	Cumulative DOR	Cumulative DER
[h]	applied [mL]	[%]	[%]
72	56	0.9	0.3

Water samples are taken 3 min., 10 min., 30 min. and 2 hours after the dispersion agent is applied in order to determine the effect of the dispersion agent in addition to observations of the surface film and w/o-emulsion.

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# Appendix C: Experimental results from the bench-scale and meso-scale laboratory testing



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#### C1 Bench-scale laboratory testing

In this chapter the experimental results obtained for Endicott, the Neptune Field Composite, Alpine Composite and the North Star oils in the bench-scale laboratory testing are presented and compared.

The Milne Point Unit and the High Island oil samples were emulsified on arrival. A standard bench scale weathering study of these two oil samples could therefore not be performed. Both samples have water contents well above the safety limit for the laboratory distillation of crude oils enabling the artificial weathering of the oil samples.

The High Island Oil was emulsified on arrival at SINTEF. Three phases were formed after allowing the w/o-emulsion to settle for several weeks. A dark brown oil phase (water content less than 1%), a light brown phase (water content approximately 10%) and a water phase. The upper water free layer were "artificially" evaporated (described in B3.1), and used for obtaining data on the physical and chemical properties of the water free residues of the oil upon weathering. A meso scale experiment were performed to obtain data on the properties of the emulsions formed in a weathering situation.

The Milne Point Unit sample was an extremely stable emulsion and water could only be separated from the sample after an excess of emulsion breaker (approximately 10% of Alcopol O 60 %) was added to the sample, and the mixture were heated. The water content of the sample did not increase using the rotating cylinder method. A meso-scale laboratory study was not regarded appropriate for obtaining more information about this sample.

#### **C1.1** Chemical composition

#### C1.1.1 Gas chromatographic analysis

Fresh samples of Endicott, the Alpine Composite, the Neptune Field Composite, the North Star and their evaporated residues ( $150^{\circ}C+$ ,  $200^{\circ}C+$  and  $250^{\circ}C+$ ) were analysed by a gas chromatograph with a flame ionisation detector (GC-FID). The gas chromatograms are given in Figure Cl-C6.

The components with the lowest boiling points are seen first in the chromatogram. Some of the more complex components, e.g. resins, NSO-components and naphthenes are difficult to separate using this analysis technique and are seen as a broad, poorly defined envelope. This is described as Unresolved Complex Material (UCM). The *n*-alkanes are seen as systematic, narrow peaks protruding the UCM envelope. Heavier compounds (>C<sub>40</sub>) cannot be analysed by this technique.

From the gas chromatograms given in Figures C1-C6 it can be seen that Endicott, the Alpine Composite, the Neptune Field Composite and the North Star have paraffinic peaks protruding the UCM envelope. Endicott contains fewer lower molecular weight components and has a larger UCM envelope than both the Alpine Composite and the Neptune Field Composite that is therefore the heaviest of the three oils.

The Milne Point Unit's chromatogram (Figure C5) differs from the others in the total lack of n-alkane peaks. This indicates a high degree of biodegradation.

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Gas chromatography is an important tool in identifying oil spills due to the diversity of the  $n-C_{17}$ and pristane and  $n-C_{18}$  and phytane ratios for different oil types. The ratios for Endicott, the Alpine Composite, the Neptune Field Composite and the North Star oil are given in Table C1.

Table C1: nC<sub>12</sub>/Pristane and nC<sub>18</sub>/Phytane ratios, calculated from peak height, for Endicott, the Alpine Composite, the Neptune Field Composite and the North Star.

Crude oil	n-C17/pristane	n-C18/phytane
Endicott	2.0	2.8
Neptune Field Composite	2.3	3.4
Alpine Composite	1.7	3.1
North Star	2.4	3.3
High Island Composite	1.4	1.7





Figure C1: Gas chromatogram for fresh Endicott and it's evaporated residues.

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Figure C2: Gas chromatograms for the fresh Alpine Composite and its evaporated residues.



Figure C3: Gas chromatogram for the fresh Neptune Field Composite and it's evaporated residues.



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Figure C6: Gas chromatogram for the fresh North Star oil and it's evaporated residues.



#### C1.1.2 Asphaltene and wax content

Wax and asphaltenes are important parameters for water uptake ability and w/o-emulsion stability. The ("hard") asphaltene and wax content of Endicott, the Alpine Composite and the Neptune Field Composite and their evaporated residues are given in Table C3.

#### C1.1.3 Classification of the oil samples

From the experimental results all the crude oil sample, but the Milne Point Unit and the High Island Composite are classified as paraffinic crude oils. Endicott is the heaviest of the paraffinic oils with an asphaltene content of 1.6 wt% and a wax content of 5.5 wt%. The Alpine Composite has the lowest asphaltene and wax content of the three oils. The Neptune Field Composite contains a large amount of lighter weight compounds and has a relatively low asphaltene content (0,3 wt%).

Milne Point Unit is a heavily biodegraded heavy crude oil. Information obtained from the chromatogram indicates a low wax content. The extreme stability of the emulsion could indicate a high amount of asphaltenes.

The High Island oil is also biodegraded but not to the same degree as the Milne Point Unit oil.

#### C1.2 Physical properties

#### C1.2.1 Evaporative loss

Endicott, Alpine Composite, Neptune Field Composite and North Star were distilled to a vapour temperature of 150, 200 and 250°C. The volume percent evaporated during the distillation is given in Figure C7



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Figure C7: Evaporative loss of Endicott, the Alpine Composite , the Neptune field composite and the North Star crude oils.

Endicott contains a larger amount of higher weight compounds and the volume spilled on the sea surface will decrease slowly. The Alpine and North Star oils have a high amount of lighter components, and evaporative loss will yield great changes in physical properties for the oil.

#### C1.2.2 Density

The density of Endicott, the Alpine Composite the Neptune Field Composite, the North Star and their evaporated residues are given in Figure C8.



Figure C8: Density of Endicott, the Alpine Composite and the Neptune Field Composite and their evaporated residues at 15.5 °C.

The densities of the water free oil residue increase with evaporation, see Figure C8. Fresh Endicott has the highest density of the three crude oils indicating that it contains fewer lower weight molecules and a larger amount of heavier compounds than the others do. The North Star crude oil is the lightest of the four crude oils. This is in agreement with the results obtained from the GC analysis and the evaporation data (see chapters C.1.1 and C1.2).



#### C1.2.3 Pour Point

The pour points of fresh Endicott, the fresh Neptune Field Composite, the North Star and their evaporated residues are given in Figure C9.





The Alpine Composite and the North Star oil have the lowest initial pour points at -18°C and -39°C respectively. The low pour points are due to high amounts of light components in the oils, keeping heavier components as wax in solution. Upon evaporative loss the chemical composition changes, and as e.g. wax is allowed to precipitate the pour point is getting higher. As the Alpine and North Star oils have the greatest evaporative loss of the four, they also display the greatest change in pour point with evaporation.

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#### C1.2.4 Viscosity

The viscosity of the fresh crude oils and their evaporated residues measured at shear rate 10  $\rm s^{-1}$  is given in Table C2.

Table C2:	Measured viscosity for fresh Endicott, the Alpine Composite, the North Star, the
	Neptune field Composite and The High Island Composite.

Oil ty	pe		Viscosity at 10s" [cP]	Pour point [°C]
		Fresh	510	6
	Endicott	150°C+	840	9
	10°C	200°C+	1 630	15
		250°C+	5 150	18
		Fresh	100	-18
Alaskan North	Alpine	150°C+	120	-3
Slope	10°C	200°C+	840	9
		250°C+	1 160	18
	North Star 10°C	Fresh	10	-39
		150°C+	45	-9
		200°C+	380	3
		250°C+	2272	18
	Neptune	Fresh	10	-9
	Field	150°C+	50	0
Gulf of Mexico	Composite	200°C+	110	3
	23°C	250°C+	300	9
	High	Fresh	23	-36
	Island		-	-
	Composite		•	
	23°C	250°C+	83	-15

As the more volatile components are lost by evaporation, the viscosity of the remaining residue will increase. This is seen in Table C2 for all five crude oils.

The viscosities of Endicott 150°C+, 200°C+, 250°C+, Alpine Composite 250°C+ and North Star 250°C+ were measured close or below their pour points and the values obtained are therefore quite high.



C1.2.5 Flash point

The flashpoint of the fresh crude oils and their evaporated residues were determined and are given in Table C3.

#### C1.2.6 Interfacial tension

The interfacial tension of the fresh crude oils and their evaporated residues were determined and are given in Table C3.

The experimental results showed that the Neptune Field Composite did not form stable w/oemulsions. One normally would expect that a crude oil with a wax and asphaltene content similar to the Neptune Field Composite will form stable w/o-emulsions. SINTEF suspects that production chemicals are present in the oil sample thereby reducing the w/o-emulsion process. This suspicion is supported by the low interfacial tension value measured for the fresh crude (6 mN/m). SINTEF proposes that MMS inquire if offshore chemicals are present in this crude oil sample and that a follow up study be discussed based on the findings.

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Composite and the North Star. The viscosities for Endicott, the Alpine Composite, the North Star, the Neptune Field Composite and the	
A summary of the physical and chemical variables for Endicort, the Alpine Composite and the Neptune Field Composite, The High Islam	Table C3:

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valtenes and" «t%]	1,6 1.7	1,8	1,9	0,06	0,07	60'0	0,1	016	120	025	030	0,3	0,4	0,4	0,4	0,03	,	•	0,04
dsh d <sup>1</sup> ''			_	-	_	_		-	_	-	0								_
Wax content [wt%]	2,2 7,2	(')	6,5	3,2	3,9	4,6	5,3	5,8	7,3	8° 8'8	10,7	3,7	4,1	4,6	5,0	1,6	•	,	2,3
Interfacial tension [mN/m]	24	ន	25	18	2	27	16	20	21	23	24	9	9	7	×	14	'		16
Flash point [°C]	8 %	3	121	20 20	38	82	123	<20	37	11	119	\$	46	93	128		1	•	•
Viscosity at 10 s <sup>1</sup> [cP]	510 840	1630	5150	103	118	839	1160	10	45	380	2272	10	50	110	300	23	1	,	83
Pour point [°C]	9	15	18	-18	ų	6	18	-39	6-	<del>ر</del>	18	6-	•	ñ	6	-15	ı	•	0
Density at 15,5°C [g/mL]	0,913	0,931	0,940	0,834	0,867	0,885	0,898	0.816	0.850	0.866	0.881	0,869	0,887	006'0	0,911	0,847	1	•	0,879
Residue [wt%]	<u>8</u> %	8	2	100	81	69	8	100	78.5	65.3	53.8	8	8	81	73	90	•	ı	20
Evaporated [vol%]	0 9	12	61	0	22	¥	44	0	24.7	38.5	50.2	•	Π	22	œ	•	'		33
	Fresh 150°C+	200°C+	250°C+	Fresh	150°C+	200°C+	250°C+	Fresh	150°C+	200°C+	250°C+	Fresh	150°C+	200°C+	250°C+	Fresh	150°C+	200°C+	250°C+
Oil type		Endicott			Alpine Composite				i t t	North Star			Nepune	Field	composite	16.4		OHIETST C	Composite
4	eqol2 droV nadeslA									0	oix	٩W	30	Jlu	Ð				

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#### C1.3 W/o emulsion properties

The formation of w/o-emulsions on the sea surface delay the evaporation and the natural dispersion weathering processes increasing the lifetime for the oil on the sea surface. When determining the most effective plan of action after an oil spill it is important to know the emulsifying properties (e.g. the rate of formation and stability) of the oil that has been spilled.

#### C1.3.1 W/o-emulsion rate of formation

The rates of formation of the Endicott, the Alpine Composite, the Neptune Field Composite and the North Star w'o-emulsions were mapped using the rotating cylinder method (Mackay, 1982) at  $10^{\circ}$ C,  $23^{\circ}$ C and  $10^{\circ}$ C respectively. The kinetics of formation are expressed by the  $t_{1/2}$ -values, which is the time (in hours) it takes for the emulsions to reach half of their maximum water content. The calculated  $t_{1/2}$ -values for Endicott, Alpine Composite, the Neptune Field Composite and the North Star are given in Table C4.

The maximum water content of the Endicott w/o-emulsions is quite high (all are above 50%). The rate of formation is relatively slow, after approximately 10 hours the Endicott emulsions have reached their maximum water content. A slow rate of formation is typical for crude oils with a high asphaltene content.

The maximum water content of the Alpine Composite w/o-emulsions is high (all are above 80%). The rate of formation is relatively fast, after approximately 30 minutes the Alpine Composite w/oemulsions have reached a water content above 50 vol%.

The Neptune Field Composite w/o-emulsions contain little water (all water contents are below 10 vol%). The rate of formation is fast, after approximately  $\frac{1}{2}$  hour the emulsions have reached their maximum water content. These w/o-emulsion were not stable, see C1.3.2.

The North Star oil has a fast initial water-uptake and reaches 45% within 10 minutes. The water content gradually increases to a maximum water content of 70-80%.

The fast emulsification rates are typical for the Alpine Composite and the North Star oil is typical for paraffinic crude oils

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Table C4: The calculated t<sub>1/2</sub>-values and the maximum water content for Endicott, the Alpine Composite, the North Star and the Neptune Field Composite w/o-emulsions at 10 °C, 10 °C, 10 °C and 23 °C respectively.

	Oil type	tonia a'	t <sub>1/2</sub> [h]	max. water content [vol%]
	Endicott	150°C+	0,6	82
		200°C+	1,2	79
		250°C+	2,8	64
Alaskan	Alpine	150°C+	0,1	80
North	Composite	200°C+	0,2	80
Slope		250°C+	0,5	80
	North Star	150°C+	0.11	68
		200°C+	0.14	69
		250°C+	0.09	83
	Neptune	150°C+	0,1	6
GOM	Field	200°C+	0,2	8
	Composite	250°C+	0,1	7

#### C1.3.2 Stability of the w/o-emulsions and the effect of an emulsion breaker

Unstable w/o-emulsions may dehydrate at storage or upon mechanical influence (e. g. stirring or pumping). Stable w/o-emulsions, on the other hand, increase the volume that has to be collected considerably. This can give storage problems. Responding boats are therefore recommended to have an emulsion breaker available and it is important to know its effectiveness. A reduction of the water content in a w/o-emulsion from 80 to 20% will decrease the volume of the emulsion 4 times. One of the most common emulsion breakers is Alcopol O 60% (Ross, 1986).

From the experimental results the fractional dehydration factor, D, is calculated using equation C-1.

$$D_{s} = \frac{WOR_{ref} - WOR_{s}}{WOR_{ref}}$$
(C-1)

where:

- WOR<sub>ref</sub> = Volumetric water-to-oil ratio in the emulsion after 24 hours rotation
- WOR<sub>x</sub> = Maximum volumetric water-to-oil ratio in the emulsion after 24 hours rotation and x hours settling

The fractional dehydration value lies between 0 and 1. An emulsion is defined as totally stable if no water is separated from the emulsion during a 24 hour settling period (D = 0) and an increasing D means reduced stability after the application of an emulsion breaker.

The calculated fractional dehydration factor for the Endicott, the Alpine Composite and the North Star w/o-emulsions with and without application of Alcopol O 60% are given in table C6.

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Table C5	The calculated fractional dehydration of the Endicott, the Alpine Composite, and the
	North Star w/o-emulsions with and without the application of Alcopol O 60% (500 ppm
	and 2000 ppm) after 10 min settling and 24 hours settling with and without rotation at
	10°C

Oil res	idue	Alcopol O 60% [ppm]	D <sub>24 hours</sub>	D <sub>24 hours + rot</sub>
	150°C+		0	0
	200°C+	0	0,1	0,1
	250°C+		0	0
P. P	150°C+		0,2	0,2
Endicott	200°C+	500	0,2	0,4
	250°C+		0,3	0,3
	150°C+		1,0	1,0
	200°C+	2000	1,0	1.0
	250°C+		0,7	0,9
	150°C+		1,0	1,0
	200°C+	0	0	0
	250°C+		0,2	0,2
Alpine	150°C+		1,0	1,0
Composite	200°C+	500	0,93	0,93
	250°C+		0,93	0,93
	150°C+		1.0	1,0
	200°C+	2000	1.0	1,0
	250°C+		1,0	1,0
	150°C+		0	0
	200°C+	0	0	0
	250°C+		0	0
	150°C+		0,82	0,82
North Star	200°C+	500	0,89	0,89
	250°C+		0,90	0,90
	150°C+		0,92	0,92
	200°C+	2000	0,92	0,92
	250°C+		0,97	0,97

The asphaltene and wax content in Endicott stabilise the w/o-emulsion by preventing the fusion of water droplets. In order to effectively dehydrate the Endicott w/o-emulsions when using Alcopol O 60%, a minimum dosage of 2000 ppm should be applied in an oil spill situation. This will enable an effective dehydration of all of the Endicott w/o-emulsions.

The wax content and asphaltene content in the Alpine Composite oil sample is quite low, however, the relative amount of these stabilising components increase with weathering. This will increase the stability of the w/o-emulsions formed. In addition the increase in viscosity of the continuous phase (especially the 200°C+ and 250°C+ residues) decreasing the diffusion of water droplets will lead to a more stable w/o-emulsion. A dosage of 500 ppm Alcopol O 60% will dehydrate emulsions of the Alpine Composite oil to a water content of 6%, which should be sufficient for most practical purposes. A total dehydration demands a higher ratio of demulsifier.

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The experimental results showed that the Neptune Field Composite obtained a water content below 10 %, however, these w/o-emulsions were completely dehydrated after a settling period of 24 hours. The initial spill volume of the Neptune Field Composite will not increase significantly. One normally would expect that a crude oil with a wax and asphaltene content similar to the Neptune Field Composite will form stable w/o-emulsions. SINTEF suspects that production-/process-chemicals are present in the oil sample thereby reducing the w/o-emulsion process. This is supported by the low interfacial tension value measured for the fresh crude (6 mN/m), and as mentioned earlier, a follow up study is recommended.

The North Star crude has a low asphaltene content, but will form emulsions stabilised by the high wax content of the oil. Emulsions of the North Star oil is dehydrated to a water content of approximately 7% at an emulsion/demulsifier rate of 500ppm. For further dehydration of the emulsion a higher dosage (e.g. 2000ppm) will be needed.

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#### C1.3.3 Viscosity of the w/o-emulsions

The viscosities of the Endicott and the Alpine Composite w/o-emulsions with different water contents were measured at 10°C, the results are given in Table C6. The viscosities measured are used as input to the SINTEF Oil Weathering Model. Emulsification of Endicott will cause a dramatic increase in viscosity. The viscosity of the Alpine Composite w/o-emulsion could not be determined due to the emulsion's unstability.

#### Table C6: Viscosities of the Endicott and Alpine Composite w/o-emulsions (0 vol%, 50 vol%, 75 vol% and maximum water content) measured at 10°C.

Oil residue		Water content [vol%]	Viscosity at shear 10s <sup>-1</sup> [cP]
	150°C+		840
	200°C+	0	1 630
	250°C+		5 150
	150°C+		1 530
	200°C+	50	3 330
Provide state	250°C+		7 910
Endicolt	150°C+		6 240
	200°C+	75	12 200
	250°C+		*/
	150°C+	82 (max)	15 300
	200°C+	79 (max)	21 400
	250°C+	64 (max)	21 700
	150°C+		120
	200°C+	0	840
	250°C+		1 160
	150°C+	50	120
	200°C+		920
Alpine	250°C+	10-61371	2 940
Composite	150°C+		780
	200°C+	75	2 970
	250°C+	-	7 130
	150°C+	80 (max)	*:
	200°C+		5 960
	250°C+	1.0000	11 700
	150°C+		45
	200°C+	0	380
	250°C+		2272
	150°C+		305
	200°C+	50	405
www.www.co	250°C+		882
North Star	150°C+		624
	200°C+	75	1034
	250°C+		1967
	150°C+	68	421
	200°C+	69	850
	250°C+	83	752

- measurement not possible

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#### C2 Meso-scale laboratory testing of the High Island Composite

In this chapter the experimental results obtained for High Island oil in the meso-scale laboratory testing are presented. The High Island oil were emulsified at arrival SINTEF. The emulsion was difficult to break, and thus the untreated emulsion were used in the meso-scale laboratory test. The experimental test temperature was 23°C. Results from the meso scale experiment are given in table C8.

#### **C2.1** Visual observations

The High Island Composite oil sample spread quickly after its application to the water surface in the flume (Figure C14), an estimated 80-90% of the water surface was covered with oil within one hour. The formation of a w/o-emulsion could be observed during the first hour after application of High Island Composite.

An increase in the viscosity of the w/o-emulsion was observed throughout the experiment. The surface w/o-emulsion samples taken 5 hours after application of High Island Composite were dehydrated after a one-hour settling period, indicating the instability of the w/o-emulsion formed after 6 hours weathering is seen in Figure C15

Figure 16 shows the w/o-emulsion formed after 3 days of weathering in the flume. The w/oemulsion formed after 3 days of weathering has a darker colour and has become more viscous. Immediately after the first application of dispersant the w/o-emulsion was dehydrated (Figure C17) and after 10 minutes most of the surface oil had dispersed (Figure C18). A second dispersant application was therefore not necessary.

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#### **C2.2** Evaporation

The evaporation results obtained in the meso-scale laboratory testing of High Island oil are presented and compared with the predicted evaporation results from the SINTEF OWM in Figure C10.



Figure C10: The evaporation results obtained for High Island Composite in the meso-scale laboratory testing and the predicted results from the SINTEF OWM,

Predicted evaporative loss is in good accordance with results form the meso scale flume.

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#### C2.3 W/o-emulsification

The w/o-emulsification results obtained in the meso-scale laboratory testing are plotted with the predicted results from the SINTEF OWM in Figure C11 to Figure C12.

#### C2.2.1 Water uptake



Figure C11: Predicted water uptake for High Island Composite and the results obtained from the meso-scale laboratory testing.

The water uptake observed in the meso scale flume experiment is used as input to the OWM. As shown in figure C11, the predicted emulsification rate correlates with the results from the flume experiment.

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#### C2.3.2 Stability of the w/o-emulsions

The surface w/o-emulsion samples taken 5 hours after application of High Island Composite were debydrated after a one-hour settling period, indicating an unstable emulsion. An increase in the stability of the w/o-emulsions, however, was observed throughout the experiment.

#### C2.3.3 Viscosity of the w/o-emulsion

Viscosities of the emulsion formed in the meso scale flume is compared to predicted viscosities in figure C14. As results form the meso scale flume experiment are used as input to the OWM, good correlation is expected between predicted and measured values. Evaporation- and emulsification rates in the meso scale flume is calibrated to simulate weathering conditions at 5-10m/s wind speed. Measured viscosities are in good accordance with predicted values in this wind speed interval.



Figure C12: Predicted viscosity of the High Island Composite w/o-emulsions and the results obtained from the meso-scale laboratory testing.

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#### C2.4 In-situ chemical dispersion

In situ chemical dispersion of the surface emulsion was performed on the High Island oil after 3 days of weathering in the meso scale flume. The efficiency of the dispersant on the emulsion was tested by analysing the concentration of dispersed oil in sub surface water.

At the application of the dispersant the emulsion were quickly dehydrated from approximately 70% to a water content of 10%. As the water content decreased a decrease in viscosity were visually observed (to little surface oil for measurements). Analysis of the sub surface water in the meso scale flume shows a high dispersibility compared to other oils tested in the flume, and emulsions of the high Island oil is probably dispersable for at least 3 days in an oil spill situation. Re-emulsification of the surface oil were slow and a second dispersant application were not thought to be necessary.

#### C2.5 Mass balance

The main elements in a mass balance for a crude oil spilt at sea are:

- Evaporative loss
- Surface oil
- Dispersed oil

However, the initial sample and water volume in the flume is reduced throughout the test, therefore the following parameters must taken into consideration:

- Amount of oil sampled
- Amount of water sampled
- Amount of oil adsorbed to the flume walls

The amount of oil evaporated, dispersed and sampled was calculated, and the oil adsorbed to the flume walls was estimated. Table C7 shows the mass balance for High Island oil during weathering in the meso-scale flume at 23°C.

Table C7: Mass balance for High Island Composite during the meso-scale laboratory test at 23 ℃.

	After 72 hours of weathering (%)	After the application of dispersant (%)
Evaporated	35.2	35.2
Oil on water surface	53.1	30.7
Dispersed	4.1	26.3
Sampled amount of oil	2.6	2.8
Adsorbed to the flume walls	5.0	5.0

The mass balance for High Island Composite during the meso-scale laboratory testing was predicted by the SINTEF OWM at  $23^{\circ}$ C and is given in Figure C13



Figure C13: Mass balance for High Island Composite in the meso-scale laboratory test at 23°C.



Figure C14: High Island Composite 30 minutes after application in the meso-scale flume.

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Figure C15: High Island Composite 6 hours after application in the meso-scale flume.



Figure C16: High Island Composite 3 days after application in the meso-scale flume.

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Figure C17: High Island Composite immediately after application of dispersant in the meso-scale flume.



Figure C18: High Island Composite 10 minutes after application of dispersant in the meso-scale flume.

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 Table C8 Results from the meso-scale flume testing of the High Island Composite at 23°C

 Emulsion
 Waterfree residue

	Landision			thaternee realiance	
Sample	Time (hours)	Water content (vol%)	Viscosity (cP)	Evaporative loss (wt%)	Dispersed oil (wt%)
0	0.0	0	23	0	0
1	0.25	13	43	13	3.3
2	0.50	31	230	15	3.0
3	1.00	19	185	17	3.0
4	2.00	38	220	19	3.0
5	3.00	38	345	21	3.0
6	4.00	66	370	21	3.0
7	5.00	69	450	22	3.0
8	6.00	75	510	23	3.0
9	12.0	75	345	26	3.0
10	24.0	68	675	33	3.0
11	48.0	67		33	3.0
12	72.0	67	490	34	4.1
11-2-1		Application of	of 56 ml of Co	rexit 9500	
13	72.05	12		34	26,3
14	72.2	12		34	30,9
15	72.5	20		34	35,6

Appendix D: Input data for the SINTEF Oil Weathering Model

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#### D1 Endicott

Geographical area:	Alaskan North Slope
Initial oil film thickness:	20 mm
Terminal oil film thickness:	2 mm
Release rate:	1,33 metric tons/minute
Sea temperature:	0°C and 10°C

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

The data used as input to the SINTEF OWM for Endicott are given in Table D.1 to Table D.3.

Table D.1: Physical and chemical data for Endicott

Chemical/physical property	
Specific Gravity (60°F/15.56°C)	0,913
Pour Point	6°C
Reference temperature #1	10°C
Viscosity at reference temperature #1	510cP
Wax (wt%)	5.5
Asphaltenes (wt%)	1.6

Table D.2: The true boiling point values used for Endicott (obtained from Crude Assay at http://www.etcentre.org/main/e/db/db.html).

Temperature [°C]	Evaporated [vol%]
66	0
93	1
121	3
149	6
204	11
232	16
260	21
287	27
315	34
343	40
371	46
427	57
482	66
537	74
565	77

Table D.3: Experimental results from the bench-scale laboratory testing (see chapter C1) at 10 °C:

Chemical/physical property	Fresh	150°C+	200°C+	250°C+
Boiling point [°C]		190	185	275
Evaporation [vol%]	0	6	12	19
Residue [wt%]	100	95	89	84
Specific gravity [g/L]	0.913	0.923	0.931	0.9340
Pour point [°C]	6	9	15	18
Viscosity at shear 10s <sup>-1</sup> [cP]	510	840	1630	5150
Viscosity of 50% emulsion at shear 10s <sup>-1</sup> [cP]	-	1540	3330	7910
Viscosity of 75% emulsion at shear 10s <sup>-1</sup> [cP]		6240	12200	
Viscosity of max water emulsion at shear 10s <sup>-1</sup> [cP]	-	15300	21400	21700
Maximum water content in emulsion [vol%]	-	82	79	65
Halftime for water uptake [h]	*	0.6	1.2	2.8
Stability ratio	-	0.96	0.98	1.0

-: not determined

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#### **D2** Alpine Composite

Geographical area:	Alaskan North Slope
Initial oil film thickness:	20 mm
Terminal oil film thickness:	2 mm
Release rate:	1.33 metric tons/minute

The data used as input to the SINTEF OWM for the Alpine Composite are given in Table D4 to Table D6,

Table D.4: Physical and chemical data for the Alpine Composite

Chemical/physical property	
Specific Gravity (60°F/15.56°C)	0.834
Pour Point	-18
Reference temperature #1 (°C)	10
Viscosity at reference temperature #1 (cP)	103
Wax (wt%)	3.2
Asphaltenes (wt%)	0.06

Table D.5: The true boiling point values used for the Alpine Composite sample.

Temperature [°C]	Evaporated [vol%]
85	8
105	13
135	19
175	27
205	33
235	38
265	45
310	54
350	62
420	72
525	89

Table D.6: Experimental results from the bench-scale laboratory testing (see chapter C1) at 10 ℃:

Chemical/physical property	Fresh	150°C+	200°C+	250°C+
Boiling point [°C]		167	246	296
Evaporation [vol%]	0	22	34	44
Residue [wt%]	100	81	69	60
Specific gravity [g/L]	0.8340	0.8668	0.8845	0.8981
Pour point [°C]	-18	-3	9	18
Viscosity at shear 10s <sup>-1</sup> [cP]	103	118	839	1160
Viscosity of 50% emulsion at shear 10s1 [cP]		120	920	2940
Viscosity of 75% emulsion at shear 10s1 [cP]	-	780	2970	7130
Viscosity of max water emulsion at shear 10s <sup>-1</sup> [cP]	-	:40	5960	11700
Maximum water content in emulsion [vol%]	-	80	80	80
Halftime for water uptake [h]	-	0.1	0.2	0.5
Stability ratio	4	0	1	0.8

-: not determined

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#### D3 North Star oil

Geographical area:	Alaska North slope
Initial oil film thickness:	20 mm
Terminal oil film thickness:	1 mm
Release rate:	1.33 metric tons/minute
Sea temperature:	0°C and 10°C

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

The data used as input to the SINTEF OWM for High Island Composite are given in Table D7 to Table D9.

Table D.7: Physical and chemical data for North Star

Chemical/physical property	0.11
Specific Gravity (60°F/15.56°C)	0.816
Pour Point (°C)	-39
Reference temperature #1 (°C)	10
Viscosity at reference temperature #1 (cP)	20
Wax (wt%)	5.8
Asphaltenes (wt%)	0.016

Table D.8: The true boiling point values used for the North Star.

Temperature [°C]	Evaporated [vol%]
60	1.3
100	6.9
120	11.9
140	18.3
160	25.5
180	31.3
200	36.4
220	41.3
240	46.0
250	48.6
310	61.1
360	69.2
420	75.2
525	86.2

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Table D.9: Experimental results from the bench-scale laboratory testing (see chapter C1) at 23 ℃.

Chemical/physical property	Fresh	150°C+	200°C+	250°C+
Boiling point [°C]		160	231	280
Evaporation [vol%]	0	24.7	38.5	50.2
Residue [wt%]	100	78.5	65.3	53.8
Specific gravity [g/L]	0.816	0.850	0.866	0.881
Pour point [°C]	-39	-9	3	18
Viscosity at shear 10s <sup>-1</sup> [cP]	10	45	380	2272
Viscosity of 50% emulsion at shear 10s <sup>-1</sup> [cP]		305	405	882
Viscosity of 75% emulsion at shear 10s <sup>-1</sup> [cP]		624	1034	1967
Maximum water content in emulsion [vol%]		68	68	83
Viscosity of max water emulsion at shear 10s <sup>-1</sup> [cP]		421	850	752
Halftime for water uptake [h]		0.11	0.15	0.09
Stability ratio		1	0.99	1

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#### D4 The Neptune Field Composite

Geographical area:	Gulf of Mexico
Initial oil film thickness:	20 mm
Terminal oil film thickness:	0.5 mm
Release rate:	1.33 metric tons/minute
Sea temperature:	20°C and 29°C

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

The data used as input to the SINTEF OWM for the Neptune Field Composite are given in Table D10 to Table D12.

Table D.10: Physical and chemical data for Neptune Field Composite

Chemical/physical property	
Specific Gravity (60°F/15.56°C)	0.869
Pour Point (C°)	-9
Reference temperature #1 (C°)	23
Viscosity at reference temperature #1 (cP)	10
Wax (wt%)	3.7
Asphaltenes (wt%)	0.3

Table D.11: The true boiling point values used for the Neptune Field Composite.

Temperature [°C]	Evaporated [vol%]
53	1
93	4
125	9
150	13
173	17
195	20
213	23
240	28
267	33
288	36
321	42
370	50
450	62

Table D.12: Experimental results from the bench-scale laboratory testing (see chapter C1) at 23 °C.

Chemical/physical property	Fresh	150°C+	200°C+	250°C+
Boiling point [°C]		200	256	305
Evaporation [vol%]	0	11	22	30
Residue [wt%]	100	90	81	73
Specific gravity [g/L]	0.869	0.887	0.900	0.911
Pour point [°C]	-9	0	3	9
Viscosity at shear 10s <sup>-1</sup> [cP]	10	50	110	300
Maximum water content in emulsion [vol%]		0	0	0
Halftime for water uptake [h]	-	0	0	0
Stability ratio		0	0	0

-: not determined

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#### **D5 High Island Composite**

Geographical area:	Gulf of Mexico
Initial oil film thickness:	20 mm
Terminal oil film thickness:	0,5 mm
Release rate:	1.33 metric tons/minute

 Sea temperature:
 20°C and 29°C

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

The data used as input to the SINTEF OWM for High Island Composite are given in Table D13 to Table D15.

#### Table D.13: Physical and chemical data for High Island Composite

Chemical/physical property	
Specific Gravity (60°F/15.56°C)	0.846
Pour Point (C°)	-15
Reference temperature #1 (C°)	23
Viscosity at reference temperature #1 (cP)	23
Wax (wt%)	1.6
Asphaltenes (wt%)	0.03

#### Table D.14: The true boiling point values used for the High Island Composite.

Temperature [°C]	Evaporated [vol%]
120	3.0
140	5.7
150	7.0
160	8.6
170	10.7
180	12.8
190	15.3
200	18.2
210	20.3
220	23.0
230	25.5
240	26.8
250	31.9
280	40.0
300	45.0
350	56.0
380	61.0
400	64.0
425	68.0
450	72.0

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Table D.15: Experimental results from the bench-scale laboratory testing (see chapter C1) at 23 °C.

Chemical/physical property	Fresh	150°C+	200°C+	250°C+
Boiling point [°C]	-	-	-	285
Evaporation [vol%]	0	7.0b	18.2b	32.7
Residue [wt%]	100	93.9c	83.5c	70
Specific gravity [g/L]	0.847	0.853c	0.864c	0.879
Pour point [°C]	-36	-20*	-10*	0
Viscosity at shear 10s <sup>-1</sup> [cP]	23	40*	60*	83
Maximum water content in emulsion [vol%]	-	70f	70f	70f
Viscosity of max water emulsion at shear 10s <sup>-1</sup> [cP]	-	200f	400f	500f
Halftime for water uptake [h]	-	0.25f	0.25f	0.25f
Stability ratio		Of	Of	Of

b: From boiling point curve

c: Calculated from boiling point curve

\*constructed data

The High Island Composite sample received for the weathering study were in fact an emulsion. This disabled a proper weathering study, and a lot of the weathering data had to be extracted from data obtained in the meso scale flume, calculated, or constructed with background in experience from studies of similar oils. The results from the meso scale flume is, however, regarded realistic compared to a real weathering situation, and should provide relevant input data to the OWM.

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Term	Abbreviation, symbol or acronym
Benzene, toluene, etylbensen, o-, m- and p-xylenes	BTEX
Carbon	C
Centi Poise	cP
Cubic meters	m <sup>3</sup>
American Petroleum Index	API
Degrees Celsius	°C
Dehydrating	D
Flame Ionization Detector	FID
Gas Chromatograph/Gas Chromatography	GC
Gram	g
Hours	h
Hydrogen	н
Kilo Pascal	kPa
Liter	L
Meter	m
Microliter	μΙ.
Micrometer	μm
Milligram	mg
Milliliter	mĹ
Millimeter	mm
Millimeters	mm
Minute	min
Nickel	Ni
Nitrogen	N
Nitrogen, Sulfur and Oxygen	NSO
Oil Weathering Model	OWM
Oil-in-water	o/w
Oxygen	0
Parts per million	ppm
Percent	14
Polynuclear Aromatic Compounds	PAH
Reciprocal second	5-1
Rotations per minute	rpm
Second	5
Sulfur	S
The American Society for Testing and Materials	ASTM
The fractional dehydration factor after 24 hours rotation and x hour	D,
settling	
The fractional dehydration factor after 24 hours rotation and x hours	D <sub>34</sub>
settling	
The fractional dehydration factor after 24 hours rotation, 24 hours settling and 10 rotations	D <sub>24</sub> + tot
The time it takes in hours before the oil has emulsified half of its	tor
maximum water content	100
Unresolved Chromatographic Material	UCM
Vanadium	v
Volume percent	vol%
Volumetric water-to-oil ratio in the emulsion after 24 hours rotation	WOR,
and x hours settling	
Dispersant to Emulsion ratio	DER
Dispersant to Oil Ratio	DOR
Volumetric water-to-oil ratio in the emulsion after 24 hours rotation	WORef
Water Soluble Fraction	WSF
Water-in-oil	w/o
Water-to-oil ratio	WOR
Weight percent	wt%

Appendix E: List of abbreviations, symbols and acronyms

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**Appendix F: Literature list** 

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Appendix C: Development of Data Sets from Experimental Oil Spills for OWM Algorithm and Model Testing and Validation

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		U.S. Minerals Management Service,	Alaska Region
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ABSTRACT

Field data and weathering data from the following field trials are presented in this report:

Haltenbanken 1989

• MIZ-experiment (in ice) 1993

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- NOFO-trial 1994
- NOFO-trial 1995
- NOFO-trial 1996 (limited data)
- UK trials 1997 (AEA-trials)

Additionally, the surface oil data from the Deep Spill 2000 experiment is presented.

A short overview over each field trial is given together with the data sets, and weathering predictions made by the SINTEF Oil Weathering Model. The data sets has been developed and collated as a basis for validation testing of various oil weathering models, and we hope that these data will be valuable for other institutes/organisations for this purpose.

KEYWORDS	ENGLISH	NORWEGIAN
GROUP 1	Chemistry	Kjemi
GROUP 2	Environment	Miljø
BELECTED BY AUTHOR	Field data	Feltdata
	Weathering data	Forvitringsdata
	Oil spills	Olje utslipp

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#### **1** Introduction

#### 1.1 Background and objectives

In 1998 SINTEF Applied Chemistry completed the Phase I review "Revision of MMS Offshore Continental Shelf Oil-Weathering Model: Evaluation," OCS Study MMS 98-0031 for MMS. This review recommended:

- upgrading to an existing state-of-the-art OWM
- additional improvements needed to maintain state-of-the-art and to meet needs of MMS users
- spill data sets that would be suitable for model testing and validation.

The recommendations described in the Phase I report, lead to a follow-up study " Revision of the OCS Oil-Weathering Model: Phases II and III". The objectives of this study are:

- 1) to obtain and adapt the SINTEF Oil Westhering Model (OWM) to MMS needs,
- 2) to expand the OWM oil library to include oils of interest to MMS, and
- to develop and collate data sets identified in Phase I from experimental oil spills for validation testing of various OWModels.

This report is connected to the last objective in this study: Task 7: "Development of Data Sets from Experimental Oil Spills for OWM Algorithm and Model Testing and Validation"

A framework for this task 7 was described in the MMS OWM Phase I Technical Meeting held in Anchorage, in March, 1998 with two alternative approaches:

One approach at that time was that SINTEF, in collaboration with organizations like Alun Lewis Oil Spill Consultant in UK, CEDRE in France, and NOOA in US should try to develop a JIC program to address:

- model sensitivity testing
- preparation and archival of specified data sets
- testing of model algorithms.

Many data sets of potential interest were identified in the Phase I Report (OCS Study MMS 98-0058), and MMS would like to see an eventual such JIC program developed in a manner which could facilitate use of the data in OWM testing, for use with models, such as the NOAA ADIOS model, in addition to with the SINTEF OWM. During the project period, it appeared, however, to be difficult to develop such an extended JIC program. We therefore agreed with MMS that SINTEF proceeded alone in this task with the limited budget from MMS allocated for task 7 to address the two last scopes/goals: i.e. preparation of available oil spill data sets, and in testing / validating these ground-truth data with the new version of the SINTEF OWM only. The data sets presented in this report can however, be used by any organizations /model operators in model algorithm testing / validation.

#### 1.2 Conclusions and recommendations from the Phase 1 report

In the Phase I Report (OCS Study MMS 98-0058, chap. 5.1.), criteria for an "ideal data set" from experimental oil releases at sea was specified with respect to:

- Environmental background data
- · Oil characterization (original oil properties and changes as function of weathering)
- Documentation Standardized methods for sampling and analysis

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- Sampling frequency
- Replicate samples

An overview of experimental oil releases were identified and preliminary evaluated. None of the field trials satisfied the strict criteria for an "ideal data set", both with respect to methodology and data-documentation. However, this lack of the "ideal data set" should not prevent us from using the best series of these data sets for calibration/validation of oil weathering models. However, it also became very obviously during this review that many of the older data sets from experimental trials had a very limited potential for model calibration-/validation. This caused by varying quality of the data due to lack of consistent procedures for sampling and analytical methodology.

Some recent field trials had, however, more well-documented and suitable procedures for field sampling and further analysis. The preliminary conclusion from this preliminary review was that data from recent field trials in UK and Norway (se below) had a potential for calibration/verification of oil weathering models, and an effort in collecting <u>all</u> relevant data from these series should be given priority in task 7:

<u>UK: Field trials in the North Sea from the period 1992-97</u>; These experiments have been conducted on a yearly basis with different objectives. The more recent experiments have well documented and suitable procedures for sampling and further analysis. These field trials cover several crude oil (Forties, Alaska North slope) and different bunker fuels. The weathering time ranges from only hours to several days and the weathering parameters include (emulsification, evaporation, natural dispersion, water soluble components, emulsion viscosity, emulsion stability, water droplets distribution in emulsion and others). Some of these UK sea trials iso include extensive monitoring of dispersed oil concentrations versus time and also measurements of droplet sizes of the dispersed oil droplets. Some relevant data seemed to be available from e.g. AMOP-publications by AEA Technology, however, e.g. More extensive environmental data from the field test is needed in order to make then appropriate as validation data-sets.

Norway: Field trials in the North Sea and in the marginal ice zone of the Barents Sea from the <u>period (1989-96)</u>. In Norway, field experiments have been conducted on an almost yearly basis since late 70°s, but only some of the trials were considered to be relevant for our purpose. The SINTEF-89 and MIZ-93 trials give data sets which can be used to compare weathering of the same crude oil type at a North Sea and an Arctic environment. These trials and the later NOFO trials (1994/95/96) have used well-documented and suitable procedures for sampling and further analysis. The weathering time ranges from one day up to seven days, and the weathering parameters include emulsification, evaporation, natural dispersion, water-soluble components, emulsion viscosity, and emulsion stability, among others. Data are available from SINTEF as reports and publications.

#### 1.3 Datasets collected presented in this report

In the period from December 2002 to July 2003, an effort was made to collect all relevant data from the recommended series of field trials. As a result, data-set from the following trials are presented in this report:

- Haltenbanken 1989
- MIZ-experiment (in ice) 1993
- NOFO-trial 1994
- NOFO-trial 1995
- NOFO-trial 1996 (limited data)

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### • UK trials 1997 (AEA-trials)

Surface oil data from the Deep spill 2000 experiment

The data-sets from the earlier field tests in UK are not included in this report. This is due to lack of available documentation of environmental data during the field tests. Lewis Oil Spill Consultant in UK did an extensively search for obtaining data reports from field various field trials in UK at the library at MCA (Maritime and Coastal Agency in Southampton) without any success.

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Weathering data, wind speed, temperature and film thickness are presented from the trials. For the trials including dispersant treatment, only the weathering data before dispersant treatment is presented in this report.

The film thicknesses parameters used as input to the model for the predictions of the different trials, are based on the film thickness data measured in the individual trials.

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### 2 The Haltenbanken experiment 1989

### 2.1 The field experiments

This experiment was organized by the oceanographic research company OCEANOR with SINTEF (IKU) and NINA as partners. The oil was released at Haltenbanken (65° 00 N, 08° 00 E) 10.05 am July 1<sup>st</sup>. The oil was released from a small tanker by a hose hanging above the sea surface. The release of total 30 tons took 16 minutes, forming a small and concentrated oil slick in the beginning.

The first samples were collected 5 minutes after the oil was released and a comprehensive sampling program was carried out during the next four days. The results of the physico-chemical properties of the surface samples are given in the following tables. The results are average values of 2-3 replicate samples.

### 2.2 Objectives

- This full-scale experimental oil spill was carried out to study several objectives:
- 1. Evaluation of different types of oil spill drifters (Argos positioned buoys) versus oil drift
- 2. Intercalibration of different aerial surveillance systems
- 3. Study of weathering processes of the Sture Blend crude (also here called Oseberg Blend)
- 4. Study interactions between a drifting oil slick and sea birds

### 2.3 Conclusions

Generally, the measured changes in the oil properties with time gave a good agreement with predicted data of Sture based on small-scale laboratory experiments and using the SINTEF Oil Weathering model.

Due to relatively rough weather conditions during the release, the oil was discharged vertically into the sea from a hose (1-3 meter above sea surface). This release arrangement resulted in a temporary mixing of the oil into the seawater, leading to a relative high starting film thickness. An initial filmthickness of 20 mm has therefore been used in the model predictions. Additionally, the tanker had to use its thrusters (side propellers) during the discharge to keep distance to the oil slick. It is therefore reason to believe that this could cause additional mixing of oil and water and lead to higher water uptake for the samples from the first 5 - 30 minutes.

Weathering data for Sture blend is included in the report. Sture blend is the present name of the Oseberg Blend used in 1989. Sture is the name of an Oil Terminal on the west coast of Norway. Crude oil from the various wells at the Oseberg field is the main contributor to this terminal. There may be some minor variation in the chemical composition to the Sture blend due to the daily variation in the daily production at the various field.

Predicted evaporation, water uptake and emulsion viscosity together with field data is shown in Figure 2.1, Figure 2.2 and Figure 2.3, respectively.

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Figure 2.1 : Predicted evaporation and field data Haltenbanken 1989.



Figure 2.2 : Predicted water uptake and field data Haltenbanken 1989.

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Figure 2.3 : Predicted emulsion viscosity and field data Haltenbanken 1989.

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### 2.4 Field data Haltenbanken 1989

- Table 2.1 :Physico-chemical properties on waterfree residues of Sture Blend (1989 crude) and their water-in-oil emulsions.
- Table 2.2 :Water content and stability of the w/o-emulsions.
- Table 2.3 : Wind conditions at Haltenbanken July 1989.

Table 2.4 : Input data for weathering predictions Sture blend.

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	Thickne (mm)
emulsions.	Chemical disp- disp-
vater-in-oil	Latf. tension (mN/m)
)and their )	Pour- point (°C)
1989 crude,	Flash- point (°C)
ure Blend (	Density all (kg/
sidues of St	Density cmutsion (kg/)
aterfree re	Viscosity <sup>1</sup> (10°C, cP)
perties on w	Water cont. (vol.%, total)
emical proj	Evan heas (wf.%)
:Physico-ch	Time (weathering at sea)
Table 2.1	Station

Γ

	(weathering	in a constant	Cont.	(10°C, cP)	enuision	7	point	point	tension	- deil)	Thickness <sup>1</sup>
	at sea)	(mt. %)			(FS)		2	<u></u>	( <b>W</b> N <b>H</b> )	a bility	(22)
0 (crude)	0	0	•	12.4	0.855	0.855		-11	21	Good	
-	5 min.	1	42	39.0	0.900-	,	S*C	,	,	Good	
2	10 min.	5	80		•		5.1	•		Good	32(13) <sup>2</sup>
۴	15 m <b>in.</b>	2	53	9	0.944	0.872	13	-13	,	Good	7.7 (4.3)
4	30 min.	7	58	100	0.955	0.867	20	1	1	Good	6.5 (-)
s	1 hour	Ŷ	2	120	179.0	0.882	33		,	Good	2.4 (1.7)
9	2 hours	15	Q	225	0.975	0.888	102	ę	1	Good	43 (2.1)
۲	4 hours	18	83	1000	1.003	0.892	~100	•	1	Reduced?	4.4 (-)
*	6 hours	21	99	1300	0.965	0.895	00i~	-2	12	Good	4.0 (-)
9	8 hours	23	<b>S</b> 6	1600	0.970	0.895	~100			Good	1.8 (0.1)
0	10 hours	18	69	2300	876.0	0.893	001~	•	•	Good	6.1 (2.8)
	12 hours	21	2	1800	0.974	0.902	001~	-11	10	Good	, , ,
12	l day	8	11	6100		0.910	001~	+14	6	Reduced	2.4 (0.5)
13	2 days	26	78	11500	,	0.917	>100	+18		Bad	-
14	3.5 days	39	71	17500	•	0.935	>100	+32		Bad	1
I)The visc	cosity measure	ements wer	e performen	l at shear ru	ites 100 s <sup>-1</sup>	for the sam	ples taken a	il stations (	10 6, and si	hear rate [	0 s <sup>-1</sup> for the s

1)The viscosity measurements were performed at shear rates 100 s<sup>-1</sup> for the samples taken at stations 0 to 6, and shear rate 10 s<sup>-1</sup> for the samples stations 7 to 14. 2) The number in brackets gives the standard deviation based on three parallel film thickness measurement samples.

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samples. in brackets gives the standard deviation based on three parallel film thickness

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Table 2.2 : Water content and stability of the w/o-emulsions.

		_	_													
Efficiency <sup>3</sup> of chemical		10	0	86	16	97	10	8	3	68	8	92	87	8	76	
Stability <sup>11</sup> of emulsion				85	78	8	8	6	8	8	8	001	8	100	100	
Water residue in emulsion				-	~	7	~	5	1	9	1	5	10	~	11	
Total expet water (Vol.%)		42	8	52	53	62	65	80	53	8	38	65	67	75	3	
Expelled water a fter by 24 h setting of chemically treated emulsions (VaL%)		42	8	ø	\$	17	8	74	8	8	99	59	67	73	7	
Expetited water after 24 h setting (Vol.%)	,			22	13	45	15	9	3	0	0	0	0	0	0	
T otal water content (vol. %)		42	8	53	58	64	Ø,	83	98	*	\$6	64	μ	78	71	
ag V	0	5 min.	10 min.	15 min.	30 min.	1 hour	2 hours	4 hours	6 hours	8 hours	10 hours	12 hours	1 dany	2 days	3.5 days	
0(3169	0 (cruđe)	_	2		4	~	9	-	~	•	0]	=	12	13	14	

Fraction of total water content left in wlo-emulsion after 24 h settling. (0 -> emulsion is totally broken, 1.0 -> emulsion not broken). Fraction of total water content expelled after chemical treatment with Alcopol 0 60% and 24 h settling (0 -> no water expelled, low efficiency, 1.0 -> all water expelled, high chemical efficiency). りつ

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Start date :		01.07.1989	
Cum. time	Sea temp.	Wind speed	Direction
<u>(b)</u>	(°C)	(m/s)	(°)
0	9.6	11.3	287
3	9.8	10.1	337
6	9.8	8.4	350
9	9.8	7.5	164
12	9.8	6.9	262
15	9.8	3.9	1
18	9.6	7.8	273
21	9.6	6.3	96
24	9.9	7.5	230
27	10.1	5.4	263
30	10.2	6.9	14
33	10.2	7.5	26
36	10.2	7.5	157
39	10.1	14.3	214
42	10.1	16.1	231
45	9.8	24.2	279
48	9.6	25.1	256
51	9.6	22.1	247
54	9.8	17.0	312
57	9.8	16.1	266
60	9.8	11.0	233
63	9.8	8.7	255
66	9.8	4.8	325
69	9.9	3.6	30
72	9.9	4.2	86

Table 2.3 : Wind conditions at Haltenbanken July 1989.

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### Table 2.4 : Input data for weathering predictions Sture blend.

Fresh oil properties	
Specific Gravity (60 F/60 F)	0.85
Pour Point (°C)	-9
Reference temperature #1 (°C)	13
Viscosity at ref. temp.#1 (cP)	11
Vanadium (ppm wt.)	
Nickel (ppm wt.)	
Asphaltenes (wt. %)	
n-Pentane Insolubles (wt. %)	
Flash Point (°C)	•
Wax Content (wt. %)	
Dispersable for vise. <	2000
Poorly dispersable for vise. >	7000
Maximum water uptake (%) at 5°C/13°C	80

-: Data missing

True boiling point curve					
Temperature (°C)	Cumulative volume (%)				
90	10.62				
120	16.74				
145	21.48				
160	24.23				
205	32.29				
250	40.62				
295	50.27				
350	61.09				
420	70.84				
565	89.12				

Initial	20
Terminal	2

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Weathering	g properties (la	boratory dat	a)	
	Fresh	150°C+	200°C+	250°C+
Boiling temperature (°C)	-	185	250	303
Volume topped (%)	0	16	28	39
Residue (wt %)	100	86	76	65
Specific gravity (g/l)	0.847	0.877	0.892	0.907
Pour point (°C)	-3	6	15	18
Flash point (°C)		38	80	119
Viscosity at 13°C (cP)*	10	25	65	350
Viscosity of 50% emulsion (cP)*		190	480	2800
Viscosity of 75% emulsion (cP)*		1400	2600	6300
Viscosity of max water (cP)*		950	10000	14000
Maximum water content (%)	-	80	80	78
Halftime for water uptake (hrs)		0.13	0.1	0.18
Stability ratio	~	0,79	0.705	1

.: Not measured

\*: Viscosity measured at shear rate 10s<sup>-1</sup>.

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### 3 MIZ-1993

### 3.1 The field experiments

An experimental oil spill in the Barents Sea marginal ice zone (MIZ) was performed in the last part of April 1993. 26 m<sup>3</sup> of Sture blend was released approximately 45 km inside the ice edge at an ice concentration of approximately 90%. During a 7 day period of sampling and analysis of the surface oil/emulsion, the slick drifted to a position approximately 6 km from the ice edge, and the ice concentration varied from 70-90%. The dominant wind direction was from the ice towards open water, and the wave energy conditions were relatively low most of the time. The wind speed was 6-10 m/s and the temperature -16-0°C.

### Objectives

The intention of the experimental oil spill in the marginal ice zone was to contribute further to existing knowledge about the behaviour of oil under Arctic conditions and to acquire knowledge about the specific conditions (wind, waves, ice conditions, drift and spreading) in the marginal ice zone.

### Conclusions

Measurements performed during the MIZ experimental oil spill showed that oil spilled in ice will have a relatively high oil film thickness (often in cm-range) compared to oil spills in open waters (maximum 1 to 4 mm). The measured film thickness in the MIZ experiment ranged from 5-120 mm of emulsion. This is caused by a reduced spreading due to the presence of ice. The ice acted as a barrier and prevented spreading, especially at high ice concentrations. As a result of the high oil film thickness combined with low temperatures, the evaporation of the light components in the oil was low compared to experimental oil spills in open waters. The emulsification was low.

Prediction of evaporation, water uptake and emulsion viscosity for oil in ice (90% ice coverage), oil in open waters and field data from the MIZ-experiment is shown in Figure 3.1, Figure 3.2 and Figure 3.3 respectively.



Figure 3.1 Predicted evaporation and field data Sture blend MIZ 1993. ECH661189 MMS OWM Phases II and IIFTask 7/Final report doc



Figure 3.2 : Predicted water uptake and field data Sture blend MIZ 1993.



Figure 3.3 : Predicted emulsion viscosity and field data Sture blend MIZ 1993.

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3.2 Field and input data MIZ 1993

The data from samples taken of the oil slick is given in the tables described here.

 Table 3.1
 : Field data Sture blend MIZ 1993.

 Table 3.2
 : Input data for weathering predictions of Sture blends behaviour at sea.

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: Field data Stare blend MIZ 1993. Table 3.1

		Water	(j) #						In terfacted		_
		content (%)		Density	Density	Evaporation (Val%)	Evaporation (Val%)	Four Dolar	tension (m//m)	Disnerschätzer	_
	-	2	) [	1		(based en	(based en			frances and and	_
			emulsion	emulsion	Oll/residue	density))	GC)				-
	0	0	32		0.847	0	0	÷	2,12	Good	_
L,	0	0	33		0,847	0	1			Good	_
H	0,17	ð	62		0,872		12	9	18,4	Good	_
	0,33	0	150		0,872	13	11	0	2'61	Good	_
	0,71	0	97	826,0	0,88	17	18			Good	
_	3	0	105		0,89	24	61	12	2'11	Good	
	4	7	3	<b>306'0</b>	0,882	61	14	12	6,7	Good	
	s	12	255	0,903	0,887	21	21	12	5,3	Good	
	5,2	1	240	0,895	0,885	20	77			Good	
	6	6	300	0,895	0,89	24	23			Good	
	7	ន	680	0.912	0.893	25	74	12	55	Good/reduced	

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Table 3.2 : Input data for weathering predictions of Sture blends behaviour at sea.

Fresh oil properties					
Specific Gravity (60 F/60 F)	0.847				
Pour Point (°C)	-3				
Reference temperature #1 (°C)	13				
Viscosity at ref. temp.#1 (cP)	10				
Vanadium (ppm wt.)	· ·				
Nickel (ppm wt.)	· ·				
Asphaltenes (wt, %)	1.				
n-Pentane Insolubles (wt. %)	•				
Flash Point (°C)	•				
Wax Content (wt. %)					
Dispersable for visc. <	2000				
Poorly dispersable for visc. >	9000				
Maximum water uptake (%) at 5°C/13°C	80				
Data missing					

Data missing

True boiling point curve			
Temperature (°C)	Cumulative volume (%)		
90	10.62		
120	16.74		
145	21.48		
160	24.23		
205	32.29		
250	40.62		
295	50.27		
350	61.09		
420	70.84		
565	89,12		

Film thickness (mm)	
Initial	8
Terminal	8

Weathering properties (laboratory data)							
	Fresh	150°C+	200°C+	250°C+			
Boiling temperature (°C)		185	250	303			
Volume topped (%)	0	16	28	39			
Residue (wt %)	100	86	76	65			
Specific gravity (g/l)	0.847	0.877	0.892	0.907			
Pour point (°C)	-3	6	15	18			
Flash point (°C)	•	38	80	119			
Viscosity at 13°C (cP)*	10	25	65	350			
Viscosity of 50% emulsion (cP)*	-	190	480	2800			
Viscosity of 75% emulsion (cP)*	-	1400	2600	6300			
Viscosity of max water (cP)*	1.	950	10000	14000			
Maximum water content (%)	· ·	80	80	78			
Halftime for water uptake (hrs)	-	0.13	0.1	0.18			
Stability ratio	•	0,79	0,705	1			

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Not measured Viscosity measured at shear rate 10s<sup>-1</sup>.

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### 4 NOFO exercise 1994

### 4.1 The field experiments

The NOFO oil-on-water exercise 1994 was Phase 1 of a series of 3 field trials. Phase 1 included two surface releases and treatment with dispersant. The experiments were performed at the Frigg field in June 1994.

### Objectives

The main objectives of the field trials were:

- To verify laboratory studies on the rate of weathering (evaporation, natural dispersion and emulsification) of Sture Blend crude oil and determine the extent of changes in these processes caused by the application of dispersant.
- To assess quantitatively the effectiveness of aerially applied dispersant by following the fate and weathering properties of two slicks of partially weathered North Sea crude oil (one treated and one control slick).
- 0 To define the operational parameters required for practical dispersant treatment strategies.
- O To provide a realistic training scenario for oil spill combat personnel.

### Releases

Two slicks, each of 20 m<sup>3</sup> fresh, stabilized Sture Blend crude were released about 1 nautic mile (nm) apart. The oil were pumped gently on the sea surface by using the Transree system (leading to a generally lower starting film thickness compared to the e.g. 1989-Haltenbanken experiment). One slick, called Tango, was treated with the dispersant Corexit 9500 from a S61-N helicopter with a Rotor tech TC-3 underslung bucket after 3 hours weathering of the oil at sea. A re-application of dispersant on the same slick was performed after totally 7 hours weathering of the oil. The Tango slick disappeared totally from the sea surface and dispersed into the water column within 12 hours at sea.

The other slick, Charlie, was used as control slick the first day. The second day, about 29 hours after the oil had been released, and after the Tango slick had disappeared, the Charlie slick was treated with Corexit 9500. Soon after this treatment, the slick dispersed into the water column.

### Conclusions

The main conclusions from the field experiments were:

- In Sture Blend lost about 45 vol.% of its volume due to evaporation and reached a viscosity of approximately 9000 cP (at shear rate 10 s<sup>-1</sup>) within 28 hours at sea. The water content in the emulsions was 75-80%.
- The weathering predictions (evaporation and emulsification) of the Sture Blend crude (from 1993) proceeded similarly to what was observed in the Haltenbanken trial in 1989 with the Sture Blend (from 1989).
- In dispersant applications resulted in decreased emulsion water content and decreased emulsion viscosity. The oil/emulsion disappeared totally into the water column.

The quality of the data are good and gave valuable input to the IKU Oil Weathering Model and formed basis for further refinements and verifications of the algorithms in the model.

Further details from the field experiments are described in Lewis et al., 1995 and Strom-Kristiansen and Daling, 1994.

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Data from the Charlie slick and from Tango slick before dispersant treatment is presented in this report. Predicted evaporation, water uptake and emulsion viscosity from SINTEF OWM is presented together with field data in Figure 4.1, Figure 4.2 and Figure 4.3, respectively.







Figure 4.2 : Predicted water uptake and field data, Sture blend 1994.

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Figure 4.3 : Predicted emulsion viscosity and field data Sture blend 1994.

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### 4.2 Field and input data 1994

The data from samples taken of the oil slick are given in the tables described here.

Table 4.1 : Physico-chemical properties on waterfree residues of Sture Blend and their water-inoil emulsions from the control slick (Charlie) in the North Sea field trial in June 1994 (-: not performed, GC: gas chromatography, WOR is water-to-oil ratio, IFT is interfacial tension, D is fractional dehydration of emulsion).

Table 4.2 : Physico-chemical properties on water-free residues of Sture Blend and their water-inoil emulsions from the treated slick (Tango) in the North Sea field trial in June 1994 (-: not performed, GC: gas chromatography, WOR is water-to-oil ratio, IFT is interfacial tension, D is fractional dehydration of emulsion).

Table 4.3 : Wind conditions at June 1994 Frigg field trial.

Table 4.4 : Input data for weathering predictions of Sture blends behaviour at sea.

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Table 4.1 : Physico-chemical properties on waterfree residues of Sture Blend and their water-in-oil emulsions from the control slick (Charlie) in the North Sea field trial in June 1994 (-: not performed, GC: gas chromatography, WOR is water-to-oil ratio, IFT is interfacial tension, D is fractional dehydration of emulsion).

Charlie 52 mpling station	Weathering time	Evaporation (w1.%)		Pour point water-free residue	point Flash point r-free water-free Idue residue	IFT water-free residue	Emulsion w	ater content	Emulsion dispersibility
	(Elours)	Density *	GC	<u></u>	<u></u>	(m.N/m.)	(vel%) (WOR)		
Fresh	- o	0	0	0	-	24	0		
CI	0.2	4.6	-	-	22	-	55	1.2	-
C2	0.7	14.7	-		36	-	71	2.5	-
C3	1.1	20.3	19.8	15	58	19	69	2.2	Good
CS	3.1	24.6	-	18	90	-	75	3.0	Good
	6.5	30.3	-	21	•		78	3.5	
C8	13.3	33.1	32.7	24		7	81	4.3	Reduced bad
CU	27.7	479	43.7			3 **	66	19	Bad

Charlie		Viscosity (cP)		Density (g/mL)			Effect of	Emulsion			
sampling	Haske Rot	ovisce RV20	Bohlin \$88V		<u> </u>	E	mub	ion sta	bility	Alcopel O60%	, Chem
station	Water-free	Emulsion	Emulsion	Emulsion	Water-free					on emulsion	thic kness
	residue (10 <del>0s-1</del> )	(10r <sup>-1</sup> )	(10s <sup>-1</sup> )		resid <b>ue</b>	DI	D	h D24	b Died	(D <sub>Ak</sub> .)	(mm) •
Fresh	10				0.846	T					
CI	21 ± 1	-	75	0.949	0.857	1.0	1.0	1.0	1.0	-	12.9
C2	82 ± 5	123	271 ± 162	0.981	0.875	0.9	1.0	1.0	1.0	1.0	3.5 ± 1.4
3	113	297±4	845	0.981	0.884	0.3	1.0	1.0	1.0	1.0	1.8 ± 0.2
CS	190	638 ± 171	1410 ± 85	0.991	0.892	0.0	0.3	0.3	-	1.0	1.9±0.7
C6	356 ± 27	3333 ± 197	4130	0.996	0.901	0.0	0.0	0.0	-	0.7	1.1 ± 0.2
C8	554 ± 78	4159 ± 199	5010 ± 255	1.002	0.906	0.0	0.0	0.0	0.5	0.8	-
C11	T	0072	12/00	0.003	0.011	0.0	0.0		0.0		01+002

 C11
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Table 4.2 : Physico-chemical properties on water-free residues of Sture Blend and their water-in-oil emulsions from the treated slick (Tango) in the North Sea field trial in June 1994 (-: not performed, GC: gas chromatography, WOR is water-to-oil ratio, IFT is interfacial tension, D is fractional dehydration of emulsion).

Tange samphag station	Weathering time	Evaporat	ion (wt.%)	Pour point water-free residue	Flash point water-free residue	LFT water-free residue	Emulsion wa	ter content	Emulsion dispersibility
	(Hours)	Density *	<u> </u>	<u></u>	<u></u>	(m:N/m)	(vel%)	(WOR)	
Fresh	0	0	0	<u> </u>		24	0		
T2	1.0	17.6	-		-	•	57	1.4	Good
T3	1.9	23.8	23.6	-	-	-	76	3.2	
T4	3.3	22.0	-	-	•	16	75	2.9	Good
T5 **	3.8	24.2	-	-	-	11	63	1.7	Good
17	5.3	25.4	-	-	-	-	71	2.5	· ·
18	7.5	28.6	-	-	-	4	73	2.7	Good/reduced
T9 ***	7.9	28.9	26.7		-	****	49	1.0	Good

Tange	<u>·</u>	Viscosity (cl?)		Densit	y (g/mL)		Effect of	Emulsion
as mp ling	Haake Rote	visce RV20	Bohlin 88BV		T	Emulsion stability	Alcopel O69%	film (
station	Water-free residue	Emuision	Emuision	Emulsion	Water-free residue	Dec Dec De u	en emuision (D <sub>Alc.</sub> )	(bickaess (min) ●
	(100s <sup>-1</sup> )	(14r <sup>-1</sup> )	(10 <sup>-1</sup> )			Din D360246		
Fresh	10				0.846			
T2	64±7	-	602 ± 187	0.963	0.880	1.01.0 1.0	•	1.4 ± 0.7
T3	142 ± 4	840 ± 57	1415±148	0.992	0.890	0.20.7 0.8	1.0	2.7 ± 1.4
T4	181±11	1207 ± 164	1960	0.989	0.887	0.00.0 0.1	1.0	1.9 ± 0.2
T5 **	273 ± 68	1177 ± 324	1975 ± 148	0.975	0.891	0.00.0 0.0	0.9	1.8 ± 0.9
17	277 ± 77	1838 ± 190	2500 ± 127	0.986	0.893	0.00.0 0.0	0.7	2.4
T8	342 ± 85	2813 ± 149	3595 ± 318	0.990	0.899	0.00.0 0.0	0.4	1.9
T9 ***	374 ± 64	892 ± 15	744 ± 119	0.961	0.899	0.01.0 1.0	0.8	-

Based on predictions of oil density assuming zero water uptake. \*\* : After 1st treatment\*\*\*: After 2nd treatment
 \*\*\*\*: Impossible to measure •: Based on pad extraction.

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### Table 4.3 : Wind conditions at June 1994 Frigg field trial.

Start date :	07.06,1994	
Cum. time	Wind speed	Direction
(b)	(m/s)	(*)
0	8,2	245
4	9,8	255
8	8	243
12	8,2	230
16	8,2	250
20	8	260
24	7,5	270
28	8	290
32	8	290
120	8	290

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Table 4.4 : Input data for weathering predictions of Sture blends behaviour at sea.

Fresh oil properties				
Specific Gravity (60 F/60 F)	0,847			
Pour Point (*C)	-3			
Reference temperature #1 (°C)	13			
Viscosity at ref. temp.#1 (cP)	10			
Vanadium (ppm wt.)	•			
Nickel (ppm wt.)	•			
Asphaltenes (wt. %)	•			
n-Pentane Insolubles (wt. %)	•			
Flash Point (°C)				
Wax Content (wt. %)	· ·			
Dispersable for visc. <	2000			
Poorly dispensable for visc. >	9000			
Maximum water uptake (%) at 5°C/13°C				
-: Data missing				

Data missing

True boiling point curve				
Temperature (°C)	Cumulative volume (%)			
90	10.62			
120	16.74			
145	21.48			
160	24.23			
205	32.29			
250	40.62			
295	50.27			
350	61.09			
420	70.84			
565	89.12			

Film thickness (mm)	
Initial	10
Terminal	1

Weathering	properties (is	boratory dat	a)	
	Fresh	150°C+	200°C+	250°C+
Boiling temperature (°C)	•	185	250	303
Volume topped (%)	0	16	28	39
Residue (wt %)	100	86	76	65
Specific gravity (g/l)	0.847	0.877	0.892	0.907
Pour point (°C)	0	9	18	21
Flash point (°C)		38	80	119
Viscosity at 13°C (cP)*	10	25	65	350
Viscosity of 50% emulsion (cP)*	-	190	480	2800
Viscosity of 75% emulsion (cP)*		1.	2600	6300
Viscosity of max water (cP)*	•			-
Maximum water content (%)	•	80	80	78
Halftime for water uptake (hrs)		0.13	0.1	0.18
Stability ratio		0.2	0.705	1

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Not measured Viscosity measured at shear rate 10s<sup>-1</sup>.

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### 5 NOFO exercise 1995

### 5.1 The field experiments

The NOFO oil-water exercise 1995 included totally four surface releases and one sub-surface releases of stabilized Troll crude oil. The experiments were performed at the Frigg field in August 1995. The slicks were followed for about 0.5 - 2 days.

### Objectives

The main objectives of the dispersant and underwater release activities at the Frigg field during the NOFO 1995 oil on water exercise were:

- To study the behavior, rate of spreading and weathering (evaporation, emulsification, natural dispersion etc.) of crude oil slicks released both from surface and sub-surface (107 meters depth simulating sub-sea pipeline leakage).
- To support valuable input data to the IKU Oil Weathering Model. These data will form basis for further refinements of the algorithms in the model.
- To assess the effectiveness of different methods of applying dispersant concentrates on oil slicks (from boat and helicopter).
- To study the capability of satellite-tracked drifting buoys to simulate the drift of surface and dispersed oil under various environmental conditions.
- To calibrate aerial remote sensing sensors (in aircraft, helicopter, and satellites) with ground truth data of the surface oil slicks.

### Surface releases (day 1)

Three surface release slicks, each of 15 m<sup>3</sup> (Release rate: 1m<sup>3</sup> / min) of stabilized Troll crude oil, were released about 1 nm apart:

- One slick (designated Hotel), was treated with Corexit 9500 from a S61-N helicopter using a SOKAF 3000 underslung bucket after 2 hours weathering of the oil at sea. The thick emulsion of the Hotel slick totally disappeared from the sea surface and was dispersed into the water column just after the dispersant application, and only sheen was left behind.
- The other slick, (designated Bravo), was treated with Corexit 9500 from the response vessel Gullbas using the Clearspray system, after 2 hours weathering. The treatment caused the Bravo emulsion initially to lose water before the thick part of it gradually dispersed into the water column.
- O The third slick, (Charlie), was used as a control slick.

Results from the Charlie slick are presented in this report.

### Sub-surface release (day 2)

Two slicks, each of 25 m3 of stabilized Troll crude oil, were released about 1 nm apart:

- One slick, designated Uniform, was released by pumping the oil from 106 m depth. The oil was released without any gas present and resulted in a 2 to 5 mm thick surface slick of emulsion. No data are reported from this experiment due to very limited sampling.
- O The other slick, Sierra, was a <u>surface</u> release and was used as a control for the Uniform slick.

### Conclusions

The main conclusions from the 1995 NOFO sea trial were:

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- A modern dispersant, correctly applied with a helicopter bucket or with spray arms from a ship, within the oils "window of opportunity" for dispersant use, is capable of dispersing the thick oil completely, within 10-30 minutes.
- No significant w/o-emulsification, of the oil in the underwater plume was observed, probably due to the low release pressure and that no gas was released with the oil (this was simulating a pipeline leakage).

The weather conditions were rougher during the Phase 1 trial with 8 to 10 m/s wind compared to Phase 2, where the wind speed varied between 7 and 4 m/s wind on Day 1 and 6 and 2 m/s on Day 2.

A more entire overview of the total field trial is given in The Operation Plan (Brandvik et al., 1995-a), the Cruise Report (Jensen et al., 1995) and the main technical report (Brandvik et al., 1995-b). The analyses data are presented in Strom-Kristiansen et al., 1995.

Predicted evaporation, water uptake and emulsion viscosity from SINTEF OWM is presented together with field data for the Charlie and Sierra slicks in Figure 5.1, Figure 5.2 and Figure 5.3, respectively. The observed water content and emulsion viscosity of the Sierra slick was lower than for the Charlie slick. The Sierra emulsions taken during the first hour were very unstable, and both the water content and viscosity was probably under-estimated. The weather conditions were calmer during the Sierra release (2-6 m/s wind). The deviation in the viscosity from the OWM may be explained by that the majority of offshore field experiments which the development of the empirical algorithms are based on, have been performed under moderate to rough weather conditions (typical 6-15 m/s wind). Another explanation may also be due to that the input to the model are based on emulsion prepared in the laboratory (using the rotating flasks) that are simulating a more higher energy level.



Figure 5.1 : Predicted evaporation and field data Troll crude oil, Charlie and Sierra 1995.

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Figure 5.2 : Predicted water content and field data Troll crude oil, Charlie and Sierra 1995.



Figure 5.3 : Predicted water content and field data Troll crude oil, Charlie and Sierra 1995.

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### 5.2 Field and input data 1995

The data from samples taken of the oil slick is given in the tables described here.

Table 5.1: Physico-chemical properties on waterfree residues of Troll crude and their water-inoil emulsions from the control slick Day 1 (Charlie) in the North Sea field trial in August 1995.

Table 5.2 : Physico-chemical properties on waterfree residues of Troll crude and their water-inoil emulsions from the control slick Day 2 (Sierra) in the North Sea field trial in August 1995.

Table 5.3 : Wind conditions at August 1995 Frigg field trial. Charlie slick.

Table 5.4 ; Wind conditions at August 1995 Frigg field trial. Sierra slick.

Table 5.5 : Input data for weathering predictions of Troll crude oil behaviour at sea.

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Table 5.1: Physico-chemical properties on waterfree residues of Troll crude and their water-in-oil emulsions from the control slick Day I (Charlie) in the North Sea field trial in August 1995.

					V/e emulsion p	roperties						
							Stat	ility	**Eau	brea. eff.	Film thickn	ess (mm)
Sampling station	Weath. time (hours)	Water cont. (vol.%)	Density (g/mL)	Viscosity (cP)	Shear rate (s <sup>-1</sup> )	Dispers- ibility	*D <sub>m</sub>	*D <sub>246</sub>	*D <sub>R</sub>	*D <sub>26</sub>	Pad	In-situ
C0	0	0	0.886	-	-	Good	-	-	-	-		-
CI	0.25	5	0.903	56 ± 14	20	-	<u> </u>	-	-	-		10.3 ± 4.2
B	0.5	29	0.935	+40±6	20		0.35	0.59	0.40	0.77	-	6.0 ± 1.4
C	1.0	66	0.983	405 ± 92	20		0.15	0.79	0.87	0.88	2.2 ± 0.2	3.5±0.7
C4	2.2	57	0.974	699±1	8	Good	0.24	0.51	1.00	1.00	++1.2 ± 0.1	5.0±1.7
് <u>ന</u>	3.8	59	0.977	805 ± 76	8	Good	0.01	0.14	0.89	0.96	•••1.0±1.3	8.5 ± 2.1
- C6	7.3	74	0.996	3435 ± 64	8	Red. disp.	0.01	0.16	0.73	0.93	-	10.0 ± 2.8
C7	11.6	78	1.000	3280 ± 127	8	Red. disp.	0.00	0.01	-	0.41	****2.1 ± 0.4	7.5 ± 2.4
0	25.0	73	0.995	5430 ± 339	8	Bad disp.	0.00	-	0.57	0.76	-	10,0
C10	33.5	17	1.001	5320	8	-	0.00	0.01	0.83	0.89	-	6.3 ± 3.1

			_	Waterfree	residue properties		
Sampfing station	Weath. time (hours)	Evap. loss (wt.%)	Density (g/mil)	Viscosity (cP, 100 s <sup>-1</sup> )	Pour point (°C)	Flash point (°C)	Interf. tension (mN/m)
C0	0	0	0.886	21	-39	-	10.4
CI	0.25	3.0	0.897	42	-	34	-
C2	0.5	3.7	0.898	40	-	42	-
C3	1.0	7.4	0.902	64	-21	64	-
C4	2.2	12.4	0.908	83	-14	116	0.8
CS	3.8	13.3	0.909	99		125	•
C6	73	17.2	0.914	168	-6		0.6
C7_	11.6	17.7	0.914	193	-	-	-
	25.0	19.4	0.916	217	-3	-	0.4
C10	33.5	24.7	0.923	200	-	- ·	0,3

Not performed. D is fractional dehydration of emulsion. D<sub>1k</sub> is effect after 1 hour, D<sub>2k</sub> is effect after 24 hours. D=0: no water settled. D=: 1 all water settled. Effect of 500 ppm concentration of the emulsion breaker Alcopol O60%, relative to the oil volume. Unstable emulsion that was braken during measurement. Pad sumple grow 38 µm emulsion film thickness (in IR Black<sup>+</sup> area, firish aircraft, Lewis, 1995). Pad sumple and cylinder measurement are not comparable values; taken in different parts of the slick. Pos. B 26 µm (IR "black<sup>+</sup> area, German aircraft, Lewis, 1995), pos. C 9 µm (UV area, German aircraft, Lewis, 1995).

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Not performed

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Table 5.2 : Physico-chemical properties on waterfree residues of Troll crude and their water-in-oil emulsions from the control slick Day 2 (Sierra) in the North Sea field trial in August 1995.

_				- v	V/e emulsion pr	operties						
							Stat	jility	**Emul	brea. eff.	Film thic	caess (mm)
Sampling station	Weath. fime (hours)	Water cost. (vol.%)	Density (g/mL)	Viscosity (cP)	Shear rate (s <sup>-1</sup> )	Dispers- ibility	*Dn	*D24	*D <sub>th</sub>	*D2@	Pad	In-situ
<b>S0</b>	0	0	0.886	-	- 1	Good	-	-	-	-	· 1	-
S1	0.4	0	0.898	+15±2	20	-	-	-	- ·	-	-	5.8 ± 1.8
S2	0.7	4	0.904	•21 ± 2	20	-	0.00	1.00	1.00	1.00	-	6.8 ± 2.8
S3	0.9	2	0.903	•29	20	-	0.00	0.63	•	-	-	4.8 ± 1.6
S4	3.1	26	0.938	123 ± 9	8	-	0.00	0.62	1.00	1.00	4.5 ± 1.4	6.3 ± 3.2
<b>S6</b>	7.2	37	0.951	126±4	8	-	0.00	1.00	0.91	1.00	1.9 ± 0.4	3.4 ± 1.7

	_		Wa	terfree residue pro	perties	_
Sampling station	Weath. time (hours)	Evap. loss (wt.%)	Density (g/ml)	Viscosity (cP, 100 s <sup>-1</sup> )	Pour point (°C)	Flash point (°C)
50	0	0	0.886	21	-39	-
SI	0.4	3.6	0.898	41	-	-
S2	0.7	4.1	0.899	42	-	38
\$3	0.9	6.0	0.901	55	-27	52
S4	3.1	11.9	0.908	80	-18	110
<b>S6</b>	7.2	12.5	0.908	105	-12	119

-: Not performed.

Unstable emulsion that was broken during measurement.

• D is fractional dehydration of emulsion.  $D_{1h}$  is effect after 1 hour,  $D_{2th}$  is effect after 24 hours. D=0: no water settled. D=:1 all water settled.

Effect of 500 ppm concentration of the emulsion breaker Alcopol O60%, relative to the oil volume.

Table 5.3 : Wind conditions at August 1995 Frigg field trial. Charlie slick.

Cum. time	Wind	Direction	Cum. time	Wind	Direction
(bours)	(10/1)	<u> </u>	(hours)	(m/s)	(*)
*0.0	6,5	274	22.0	6.1	222
0.5	5.9	281	22.5	6.1	248
1.0	6.4	267	23.0	7.0	248
1.5	6.5	314	23.5	7.0	267
2.0	7.0	268	24.0	7.0	290
2.5	6.8	274	24.5	6,6	259
3.0	6.2	263	25.0	7.5	267
3.5	7.2	270	25.5	7.0	281
4,0	7.0	270	26.0	7.5	284
4.5	7.5	253	26.5	7.5	321
5.0	7.5	143	27.0	5,6	276
5.5	7.0	262	27.5	5.6	281
6.0	7.5	278	28.0	5.2	278
6.5	6.6	276	28.5	5.6	270
7.0	6.6	253	29.0	6.1	284
7.5	16	287	29.5	56	267
80	5.2	250	30.0	5.6	202
85	47	262	30.5	5.6	278
90	61	250	31.0	\$2	276
95	5.6	284	315	47	270
10.0	5.0	259	37.0	47	290
10.5	5.0	275	12.0	4.7	270
11.0	5.0	243	22.5		2/0
11.0	<u>,,,,</u>	246	33.0	3.8	20/
12.0	<u> </u>	202	33.5	3.3	2/0
12.0		230	34.0	2.3	204
12.5		204	34.3	1.4	250
13.0	4.7	233	35,0	2.3	230
13.3	4,/	243	35.5	2.3	- 222
14.0	4./	253	36.0	2.8	236
14.5	4.2	231	36.3	2.8	219
15.0	4.7	233	37.0	3.3	203
15.5	5.2	233	37.5		200
16.0		208	38.0	3.3	208
16.5	6.1	208	38.5	3.8	228
17.0	6.1	222	39.0	2.8	208
17.5	6.6	233	39,5	3,3	222
18.0	7.0	200	40.0	2.8	203
18.5	7.5	208	40.5	3.3	191
19.0	8.0	312	41.0	3.3	197
19.5	7.5	214	41.5	2.8	214
20.0	7.0	236	42.0	2.3	217
20,5	7.5	225	42.5	1.9	219
21.0	7.0	270	43,0	2.3	211
21.5	6,1	239	43.5	2.3	200
			120.0	2.3	200

\*: Start time is 06<sup>30</sup> 15<sup>th</sup> August 1995.

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Table 5.4 : Wind conditions at August 1995 Frigg field trial. Sierra slick

Cum. time (hours)	Wind (m/s)	Direction (°)	Cum. time (hours)	Wind (m/s)	Direction (°)
*0.0	5.6	270	8.0	2.8	219
0.5	6.1	284	8.5	3.3	203
1.0	5.6	262	9.0	3.3	200
1,5	5.6	298	9.5	3.3	208
2.0	5.6	278	10.0	3.8	228
2.5	5.2	276	10,5	2.8	208
3.0	4.7	270	11.0	3.3	222
3.5	4,7	290	11.5	2.8	203
4.0	4.2	270	12.0	3.3	191
4.5	3.8	287	12.5	3.3	197
5.0	3,3	278	13.0	2.8	214
5.5	2.3	264	13.5	2.3	217
6.0	1,4	256	14.0	1.9	219
6.5	2.3	256	14.5	2.3	211
7.0	2.3	222	15.0	2.3	200
7.5	2.8	236	120.0	2.3	200

\*: Start time is 1100 16th August 1995.

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### Table 5.5 : Input data for weathering predictions of Troll crude oil behaviour at sea.

Film thickness (mm) Initial

Terminal

Fresh oil properties	
Specific Gravity (60 F/60 F)	0.893
Pour Point (°C)	-12
Reference temperature #1 (°C)	13
Viscosity at ref. temp.#1 (cP)	27
Vanadium (ppm wt.)	-
Nickel (ppm wt.)	
Asphaltenes (wt. %)	· ·
n-Pentane Insolubles (wt. %)	-
Flash Point (°C)	3
Wax Content (wt. %)	•
Dispersable for visc. <	3000
Poorly/not dispensable for visc. >	7000
Maximum water uptake (%) at 5°C/13°C	-

### Data missing

True bolling	point curve
Temperature (°C)	Cumulative volume (%)
65	1.43
90	3.04
150	9.57
180	13.83
240	24.49
320	45.71
375	57.21
420	63.49
525	83.78
565	87.99

Weatherin	g properties (la	boratory dat	A)	
	Fresh	150°C+	200°C+	250°C+
Boiling temperature (°C)	•	210	255	300
Volume topped (%)	0	8	15	24
Residue (wt %)	100	93	87	78
Specific gravity (g/l)	0.893	0.903	0.909	0.919
Pour point (°C)	-39	-15	-9	3
Flash point (°C)	3	50	80	119
Viscosity at 13°C (cP)*	27	49	83	200
Viscosity of 50% emulsion (cP)*	-	343	593	1300
Viscosity of 75% emulsion (cP)*	-	1815	2673	4790
Viscosity of max water (cP)*		-	-	•
Maximum water content (%)	· ·	75	75	75
Halftime for water uptake (hrs)		0.09	0.07	0.13
Stability ratio	· ·	0.78	1	1

: Not measured

Viscosity measured at shear rate 10s<sup>-1</sup>.

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### 6 NOFO exercise 1996

### 6.1 The field experiments

The NOFO oil-water exercise 1996 included two surface releases and one sub-surface release of stabilized Troll crude oil with gas present. The experiments were performed at the Frigg field in June 1996.

### Objectives

The objectives of the 1996 exercise were :

- To determine how the weathering processes (evaporation, water-in-oil emulsification and natural dispersion) of Troll crude oil proceeded in the control (Charlie) and the treated slick (Hotel, treated by helicopter with the new "Response 3000" bucket) after dispersant application.
- To determine how the surface slick resulting from the underwater release (designated Uniform) of Troll crude oil combined with gas (GOR of 1:67), behaved.

The field trials in both 1995 and 1996 were performed in order to form basis for building up an operational and cost-effective dispersant response in Norway (for terminals, refineries, offshore oil fields etc.).

### Surface releases

- Two surface released slicks of fresh, stabilized Troll crude oil were released about 1 nm apart:
- One slick, (designated Hotel), was treated with the dispersant Corexit 9500 from a S61-N helicopter using the newly developed underslung bucket "Response 3000" (described in Brandvik 1996b) after 4 hours weathering of the oil at sea. The treated part of the Hotel slick totally disappeared from the sea surface and dispersed into the water column just after the dispersant application.
- Ohe other slick, Charlie, was used as a control slick.

### Sub-surface releases

In 1995 field trial the oil was released without any gas present, in the 1996 field trials compressed air was used to simulate an oil-gas blow-out.

One release of fresh, stabilized Troll crude oil, together with compressed air simulating gas, was released from 106 m depth (not discussed in this report, due to too low film thickness for surface oil sampling).

### Conclusions

The main conclusions from the experiments were :

Troll crude oil emulsified slowly and reached a maximum water content of approximately 60 vol.% and a viscosity of 2000 cP (shear rate 10 s<sup>-1</sup>) after 10 hours weathering at the sea surface. These measured values were lower than the predicted values due to unstable emulsions. The weather conditions were rather calm, with an average wind speed of about 4 to 5 m/s, and too low to cause breaking waves. The same situation occurred during the August 1995 trials when the Sierra slick was monitored on Day 2 (5 to 6 m/s wind).

The physico-chemical properties of surface oil from the field experiment in 1996 are further described by Strøm-Kristiansen *et al.*, 1996.

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Weathering data from the Charlie slick and the Hotel slick before dispersant treatment is presented in this report. Predicted evaporation, water uptake and emulsion viscosity from SINTEF OWM is presented together with field data in Figure 6.1, Figure 6.2 and Figure 6.3 respectively.

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Figure 6.1 : Predicted evaporation and field data Troll crude oil Charlie and Hotel 1996.



Figure 6.2 Predicted water uptake and field data Troll crude oil Charlie and Hotel 1996.

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Figure 6.3 : Predicted emulsion viscosity and field data Troll crude oil Charlie and Hotel.

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### 6.2 Field and input data 1996

The data from samples taken of the oil slick are given in the tables described here.

Table 6.1 : Overview surface oil sampling in Charlie slick (control) 11 - 12 June 1996.

Table 6.2 : Physico-chemical properties on water-free residues of Troll crude and their water-inoil emulsions from the control slick Day 1 (Charlie) in the North Sea field trial in June 1996.

 
 Table 6.3
 Physico-chemical properties on water-free residues of Troll crude and their waterin-oil emulsions from the helicopter treated slick released on Day 1 (Hotel slick) in the North Sea field trial in June 1996.

Table 6.4 : Wind conditions at June 1996 Frigg field trial. Charlie slick.

Table 6.5 : Wind conditions at June 1996 Frigg field trial. Hotel slick.

Table 6.6 : Input data for predictions of Troll crude oil behaviour at sea.

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D	Date	Time (local)	Weathering time	Latitude / Longitude GPS (Global Pvs. System)	Film Thickness (cylinder, in-sits)	Pad sample	Comments
Charlie	11.06.	08.00 - 08.15	0=				Release of Chartie slick.
CI		08.23	0.13	60.00.255 / 002.24.888			Full set of samples collected in thick part of the slick). Slick front just before sampling (08.19): 60.00.305 / 002.24.857.
C2-A		08.45	0.5	60.00.322 / 002.25.032			Full set of samples collected in thick part of the slick.
C2-8	*	08.50	0.6	60.00.322 / 002.25.032	3 mm		
C3	-	09.15	1.0	60.00.392 / 002.25.268			Full set of samples collected in thick part of the slick (at buoy 9810). Slick front just before sampling: 60.00.413 / 002.25.269.
C4	-	09.33	1.3	60.00425 / 002.25.432			Full set of samples collected in thick part of the slick (at buoy 9810). Slick front just before sampling: 60.00.472 / 002.25.498.
C7-A	-	13.53	5.6	60.00.135 / 002.25.595 60.00.318 / 002.25.097	5 mm 10 mm 10 mm		GPS positions were logged during the 3 thickness measurements.
С7-В		13.55	5.7	60.00.135 / 002.25.595			Full set of samples collected in thick part of the slick (at buoy 9810).
C8-A	-	16.51	8.6	60.01.361 / 002.23.752			Full set of samples collected in thick part of the slick. Lots of thick emulsion.
C8-B	-	16.55	8.7	60.01.353 / 002.23.742	15 mm		
(3)	-	18.45	10.5				
C10-A	12.06	14.25	30.2	60.01.398 / 002.29.092		1	· · · · · · · · · · · · · · · · · · ·
C10-B	-	-	30.2	60.01.367 / 002.29.081		1	

Table 6.1 : Overview surface oil sampling in Charlie slick (control) 11 - 12 June 1996.

•: Time 0 is 08.15.

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Table 6.2 : Physico-chemical properties on water-free residues of Troll crude and their water-in-oil emulsions from the control slick Day 1 (Charlie) in the North Sea field trial in June 1996.

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				W/o em	ulsion properti	ies i		_				Water-free	e residne
						Stat	ility	**Emui	brea. eff.	Em. fil	m thickness	prope	rties
Sampling	Weath. time	Water coat.	Density	Viscosity	Shear rate	*D <sub>њ</sub>	*D24	*D <sub>1h</sub>	*D <sub>24</sub>	Pad	In-situ	Evap. loss	Density
station	(hours)	(vel%)	(g/mL)	(cP)	<u>(5<sup>-1</sup>)</u>			_		(mm)	<u>(mai)</u>	(wt%)	(g/mL)
C0	0.	0	0.887			-		-	-	-	-	0.0	0.887
Cl	0.1	0	0.891	44	01	0.0	0.0	0.0	0.0	-	-	-	0.892
C2-A	0.5	6	0.904	41	10	1.0	1.0	1.0	1.0	-	-	2.6	0.897
C2-B	0.6	-	•		-	•	-		•	-	3	-	-
C3	1.0	5	•	37	10	1.0	1.0	1.0	1.0	-	-	-	•
C4	1.3	7	0.912	67	10	0.7	0.7	0.7	0.7	-	-	8.9	0.904
C7-A	5.6		-							-	5	-	-
	ł										10		
											10		
С7-В	5.7	56	0.975	1080	10	0.0	0.0	0.9	0.9	•	-	16.2	0.913
C8-A	8.6	61	0.981	1930	10	0.0	0.0	0.0	1.0	-	-	17.7	0.914
C8-B	8.7		-	-	-	-	-	-	-	-	15	-	•
C9	10.5	64	0.983	1740	10	0.0	0.2	0.0	0.9	•	-	16.4	0.913
C10-A	30.2	-	-		-	-	-		-	0.002	-	-	-
C10-B	30.2	•	-	-	-	-	-	- 1	-	0.001	-	-	

Time 0 is 08.15, 11 June (oil release finished).

Note of our results of the content of the second parameter. Not performed. D is fractional dehydration of emulsion,  $D_{1k}$  is effect after 1 hour,  $D_{2k}$  is effect after 24 hours, D=0: no water settled. D=:1 all water settled. Effect of 500 ppm concentration of the emulsion breaker Alcopol O 60 %, relative to the emulsion volume.

				W/a emi	licion pronerti	3		ļ				Water-free	racidae
						Stab	TELY .	••Emal 2	nea ell	Em. (h	n thickness	Droper	
Sampling	Weath. time	Water cont.	Denity	Visconity	Shear rate	*D*	•D.•	*Du	*D,	Pad	In-site	Evan, tons	Density
statio	(hours)	(vel.%)	(E/mL)	( <b>.</b> )	( <sub>1</sub> ,					(20)	( <b>m</b> m)	(mt%)	(Tm/d)
9Đ	8	•	0.889									0.0	0.889
V-IH	1.03	36	0.948	188	10	0.1	1.0	6.0	6.0	,		10.1	0.906
H1-B	1.5									,	13	,	
											15		
HIC	971	,	,	•	,	•				•	2	•	
IQ-IH	1.67	,	,		,		,		,	1.70	4	ł	
H1-D2	1.67			,		'				0.75	~		
H1-E	1.7	,			1	,			,			,	
H2-A	1.9	22	0.938	157	2	0.8	0.8	1.0	1.0		,	12.5	906:0
H2-B	3.7	12	,	241	9	•	,				1		
Disp. appl.				,			,	,	,			,	
H3-A	4.00	25	0.940	96	01	0.2	9.6	63	0.8	0.13	1	14.8	116.0
8-EH	4.07		,	'	ı		,	,	•	0.05			
HBC	4.13	•		,	ŀ	,	,			0.04	,		
R300	63 1	99	0.981	2480	10	0.1	0.1	0.1	0.2	•	,	20.3	0.917
H5-A	26	1		•	•		,	,		•	4		
H5-B	5.6	,	,	,	,	,		•		,	15	,	•
HS-C	5.6	,	•		,	,			,	,	10 - 15	1	•
i v	Time 0 is 09	1.15 (oil release fi	nished).										
ï	Sample colli	ected in a minor c	wee of the He	otel slick not h	it by dispersant.								
Ÿ	Not perform	ed.											
÷	D is fraction	al dehydration o	femulsion D	In is effect after	τ I hour, D <sub>ie</sub> is	effect aft	er 24 hour	T. D=0: №	water settly	ed D=.1 al	I water settled		
•	Effect of 500	9 ppm concentrati	ion of the emu	vision breaker	Alcopol 060%	relative a	o the oil w	olume					

treated slick released on the helicopter emulsions from -oil .5 Table 6.3 Physico-chemical properties on water-free residues of Troll crude and their water Day 1 (Hotel slick) in the North Sea field trial in June 1996.

settled. D=: I all water settled Time 0 is 19.15 (oit release finished). Sumple collected in a minor area of the Hotel stick not his by dispersant. D is provinted. Effect of 500 ppm concentration of the emulsion breaker Alcopol OGD's relative to the oil volume.

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Cum. time	Wind	Direction	Cum. time	Wind	Direction	
(hours)	(m/1)	<u></u>	(hours)	(m/s)	ര	
*0.0	4.7	174.4	17.0	4 2	174.4	
0.0	47	149 1	17.5	4 7	143.4	
1.0	4.2	177.2	18.0	4.7	120.9	
1.5	47	160.3	18.5	23	154.7	
20	4.7	168.8	19.0	2.3	154.7	
2.5	4.7	180.0	19.5	3.3	208.1	
3.0	4.2	160.3	20.0	2.3	230.6	
1.1	3.8	157.5	20.5	2.8	278.4	
4.0	4.2	149.1	21.0	4.2	275.6	
4.5	5.2	137.8	21.5	6.1	298.1	
5.0	5.6	146.3	22.0	8.0	289.7	
5.5	5.6	168.8	22.5	10.3	309.4	
6.0	3.3	174.4	23.0	10.8	309.4	
6.5	6.1	157.5	23.5	11.3	292.5	
7.0	6.6	135.0	24.0	11.3	300.9	
7.5	7.0		24.5	10.3	295.3	
8.0	7.0	160.3	25.0	10.3	303.8	
8.5	7.5	174.4	25.5	8.9	295.3	
9.0	7.0	146.3	26.0	8.9	292.5	
9.5	6.6	157.5	26.5	8.9	281.3	
10.0	6.6	163.1	27.0	9,4	286.9	
10.5	7.0	188.4	27.5	9,4	331.9	
11.0	6.6	157.5	28.0	9.4	264.4	
11.5	6.1	180.0	28.5	8.4	289.7	
12.0	6.1	177.2	29.0	8.4	275.6	
12.5	6.1	163.1	29.5	8.9	292.5	
13.0	5.6	171.6	30.0	8.9	261.6	
13.5	6.1	154.7	30.5	8.4	222.2	
14.0	5.6	168.8	31.0	8.9	275.6	
14.5	5.6	168.8	31.5	8.4	264.4	
15.0	5.6	160.3	32.0	8.4	267.2	
15.5	5.6	168.8				
16.0	5.2	165.9				
16.5	5.2	168.8				

Table 6.4 : Wind conditions at June 1996 Frigg field trial. Charlie slick.

\*: Start time is 0800 11th June 1996 (start oil release).

Table 6.5 : Wind conditions at June 1996 Frigg field trial. Hotel slick.

Cum. time (hours)	Wind (m/s)	Direction (°)	Cum. time (hours)	Wind (m/s)	Direction (°)
	_				
*0.0	4.2	177.2	16.0	4.2	174.4
0.5	4.7	160.3	16.5	4.7	143.4
1.0	4.7	168.8	17.0	4.7	120.9
1.5	4.7	180.0	17.5	2.3	154,7
2.0	4.2	160.3	18.0	2.3	154.7
2.5	3.8	157.5	18.5	3.3	208.1
3.0	4.2	149.1	19.0	2.3	230.6
3.5	5.2	137.8	19.5	2.8	278.4
4.0	5.6	146.3	20.0	4.2	275.6
4.5	5.6	168.8	20.5	6.1	298.1
5.0	3.3	174.4	21.0	8.0	289.7
5.5	6.1	157.5	21.5	10.3	309.4
6.0	6.6	135.0	22.0	10.8	309.4
6,5	7.0	149.1	22.5	11.3	292.5
7.0	7.0	160.3	23.0	11.3	300.9
7.5	7.5	174.4	23.5	10.3	295.3
8.0	7.0	146.3	24.0	10.3	303.8
8.5	6.6	157.5	24.5	8.9	295.3
9.0	6.6	163.1	25.0	8.9	292.5
9.5	7.0	188.4	25.5	8.9	281.3
10.0	6,6	157.5	26.0	9.4	286.9
10.5	6.1	180.0	26.5	9,4	331.9
11.0	6.1	177.2	27.0	9.4	264.4
11.5	6.1	163.1	27.5	8.4	289.7
12.0	5.6	171.6	28.0	8.4	275.6
12.5	6.1	154.7	28.5	8.9	292.5
13.0	5.6	168.8	29.0	8.9	261.6
13.5	5.6	168.8	29.5	8.4	222.2
14.0	5.6	160.3	30.0	8.9	275.6
14.5	5.6	168.8	30.5	8.4	264.4
15.0	5.2	165.9	31.0	8.4	267.2
15.5	5.2	168.8			

\*: Start time is 09<sup>00</sup> 11<sup>th</sup>June 1996 (start oil release).

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### Table 6.6 : Input data for predictions of Troll crude oil behaviour at sea.

Fresh oil properties		
Specific Gravity (60 F/60 F)	0.893	
Pour Point (°C)	-12	
Reference temperature #1 (°C)	13	
Viscosity at ref. temp.#1 (cP)	27	
Vanadium (ppm wt.)	•	
Nickel (ppm wt.)	-	
Asphaltenes (wt. %)	•	
n-Pentane Insolubles (wt. %)	· ·	
Flash Point (°C)	3	
Wax Content (wt. %)	•	
Dispensable for visc. <	3000	
Poorly/not dispersable for visc. >	7000	
Maximum water uptake (%) at 5°C/13°C	-	
-: Data missing		

Data missing

True boiling	point curve
Temperature (°C)	Cumulative volume (%)
65	1,43
90	3,04
150	9,57
180	13,83
240	24,49
320	45,71
375	57,21
420	63,59
525	83,78
565	87,99

Film thickness (mm)	
Initial	10
Terminal	1

Weathering properties (laboratory data)							
	Fresh	150°C+	200°C+	250°C+			
Boiling temperature (°C)	-	210	255	300			
Volume topped (%)	0	8	156	24			
Residue (wt %)	100	93	87	78			
Specific gravity (g/l)	0.893	0.903	0.909	0.919			
Pour point (°C)	-39	-15	-9	3			
Flash point (°C)	3	50	80	119			
Viscosity at 13°C (cP)*	27	49	83	200			
Viscosity of 50% emulsion (cP)*	•	343	593	1300			
Viscosity of 75% emulsion (cP)*		1815	2673	4790			
Viscosity of max water (cP)*	-	-	•	-			
Maximum water content (%)	-	75	75	75			
Halftime for water uptake (hrs)	-	0.09	0.07	0,13			
Stability ratio		0.78	1	1			

Not measured 

Viscosity measured at shear rate 10s<sup>-1</sup>.

7 AEA field experiments UK 1997

### 7.1 The field experiments

During the AEA'97 Experimental Sea Trial outside UK, September  $17^{th} - 24^{th}$ , the target was therefore to let the oils weather at sea to a stage where the weathered and emulsified oils were considered to be more difficult to disperse. During these experimental field trials the following three oils were released and weathered at sea prior dispersant application with Corexit 9500:

- 50m<sup>3</sup> Forties weathered for 2 days at sea prior to treatment of 2.5m<sup>3</sup> Corexit 9500
- 20m<sup>3</sup> IFO-180 Heavy bunker fuel weathered for 4.5 hours at sea prior to treatment of 0.9m<sup>3</sup> Corexit 9500 followed by a 2<sup>nd</sup> treatment 23-25 hours at sea (2.0 m<sup>3</sup> Corexit 9500)
- 31m<sup>3</sup> Alaska North Slope (ANS) crude (designated "Alpha") weathered for 2.5 days at sea prior to treatment of
- 1.0 m<sup>3</sup> Corexit 9500

Due to lack of ground truth sampling of oil weathering data of the Forties and the HFO slicks, only weathering data and predictions of the Alpha slick is presented in this report.

The primary purpose of the experiments was to measure the changes in oil properties during weathering at sea, and to determine the period of time during which Corexit 9500 can be considered as a viable response option for these oils.

In order to have a better understanding and documentation of the likely weathering properties and chemical dispersibility with Corexit 9500 on the oils planned to be used in the field, it was decided to perform some laboratory experiments prior the field trial.

### Summary

During a laboratory study prior the field trials, the weathering properties and the "dispersibility properties" for weathered ANS crude and IFO-180 heavy fuel oil were defined. The experimental data from this laboratory study were used as input to the SINTEF. Oil Weathering Model to improve the validity of the predictions of the weathering properties and in estimating the "time window" for effective use of Corexit 9500 on the oils to be used in the field trial.

Compared to earlier studies carried out with Corexit 9527 at SINTEF, Corexit 9500 shows an improvement in the dispersibility up to a viscosity of 20.000 cP on the ANS emulsions. This gives a significant increase in the "time window" for effective use of dispersant on the ANS crude.

In addition to the ANS testing, some limited chemical dispersibility testing with Corexit 9500 on two different batches of IFO-180 HFOs was carried out in SINTEFs laboratories. Also for the bunker fuels, the dispersant dosage seem to be very critical to the effectiveness results (dosages up to 1:10 is required). More systematic investigation is also needed in order to better establish the "viscosity areas" for dispersibility for different bunker oil qualities and their w/o-emulsions.

The viscosity data obtained in the laboratory and by the model predictions generated prior the trials corresponded well with the weathering and dispersant performance that took place in the field. These field trials therefore confirmed laboratory studies carried out at SINTEF indicating

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that it is possible to disperse ANS crude oil emulsions up to a viscosity of 20,000cP and IFO-180 emulsions to viscosities of 20,000 to 30,000 cP. Emulsions weathered to viscosities above these values seem to disperse slowly / poorly when treated with dispersant. Such available data of the 'viscosity area'' the dispersibility are crucial information for the OSC during spraying operations.

The ground truth data of the water content in the surface emulsion gave fairly good correlations to the model predictions for the first half day after release. However, over the next days, a <u>reduction</u> in the water content was obtained in the field. This may be explained by an evaporation of the emulsified water in the surface emulsion probably took place, due to high sea-temperature and extremely sunny conditions during the experiment period. Temperature in the oil was measured up to 5°C higher than sea temperature. This needs further investigation because this process in not reflected in present weathering models. Algorithms for evaporation of water in surface emulsions should therefore be developed. This is particularly relevant when predicting more long-term weathering (several days at sea) and under more temperate / tropical conditions.

The results from the field experiment in 1997 are further described by Daling, 1998 and also discussed by Daling and Strøm, 1999 and Lewis et al., 1998.

Predicted water uptake and emulsion viscosity from SINTEF OWM is presented together with field data in Figure 7.1 and Figure 7.1, respectively.



Figure 7.1 Predicted water uptake and field data Alaska North Slope 1997.



Figure 7.2 : Predicted emulsion viscosity and field data Alaska North Slope 1997

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### 7.2 Field and input data 1997

The data from samples taken of the oil slick is given in the tables described here.

 Table 7.1
 Physico-chemical properties and "field check" of dispersant and demulsifier

 effectiveness of Alaska North Slope crude ("Alpha slick") at sea. UK Trials, 20. - 23. September,

 1997."

 Table 7.2
 Wind conditions (average wind in m/s) during the AEA '97 field trial used as input to the SINTEF Oil Weathering Model.

Table 7.3 : Input data for predictions of Alaska North Slope crude oil behaviour at sea.

Sample / Time at Sea	Date / Time	AEA ID-no	Water (vol.%)	Viscosity (cP, at 15°C, at AEA)	Dispersibility (DER = 1 : 25)	Emulsion Demulsifie (fraction deh	stabilit r effect ydrated	ty and ivenes at 15	s °C)
			(Alcopol- method)	(at shear rate = 10s <sup>-1</sup> )	Field test (Concawe, 1988)	Dosage: DER = 500 ppm	Dzmin	Dih	D <sub>24h</sub>
Saturday, 20	). Sept.								
Release	0837-0900	3	1 Tons of Al	aska North Slope relea	sed		-	-	-
A0 / (fresh crude, an	alyzed at SINT	EF (0.883 kg/L)		20 (100 s <sup>-1</sup> ) !!					
A1 / 20 min.	0920	AA00167	<1	135 (100 s <sup>-1</sup> ) AEA	Good		-	-	-
A2 / 40 min.	0920	AA00171	<5	$157 (100 \text{ s}^{-1})$	Good				-
A3 Pos A / 1 h.	1000	AA00175	<5	165 (100 s <sup>-1</sup> )	Good		-		-
A3 Pos B / 1.5 h.	1030	AA00185	18	266 (100 s <sup>-1</sup> )	Good	Stability Alcopol O 60 Corexit 9500	0 0 0	0.2 0.4 0.3	0.8 1.0 1.0
A4 Pos A / 2 h.	1100	AA00189	<5	266 (100 s <sup>-1</sup> )	Good		+	-	
A4 Pos B / 2 h.	1100	AA00193	<5	182 (100 s <sup>-1</sup> )	Good		+		-
A5 / 2.5 h.	1230	AA00197	20	469 (10 s <sup>-1</sup> )	Good	Stability Alcopol O 60 Corexit 9500	0 0 0	0.3 0.7 0.5	0.8 0.8 1.0
A6 Pos A / 5 h.	1350	AA00206	33	1010	Good	Stability Alcopol O 60 Corexit 9500	0.1 0.3 0.2	0.2 0.6 0.3	0,4 0.6 0.6
A6 Pos B / 6 h.	1500	AA00212	25	818	Good	Stability Alcopol O 60 Corexit 9500	0 0 0	0.2 0.6 0.6	0.5 0.6 0.8
A7 Pos A / 8.5 h.	1720	AA00214	48	2491	Good	Stability Alcopol O 60 Corexit 9500	0 0 0	0 0.2 0.1	0.1 0.5 0.4

Table 7.1 Physico-chemical properties and "field check" of dispersant and demulsifier effectiveness of Alaska North Slope crude ("Alpha slick") at sea. UK Trials, 20. - 23. September, 1997."

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Sample / Time at Sea	Date / Time	AEA ID-no	Water (vol.%)	Viscosity (cP, at 15°C, at AEA)	Dispersibility (DER = 1 : 25)	Emulsion Demulsifie (fraction deh	stabilit r effecti ydrated	y and ivenes at 15	т °С)
			(Alcopol- method)	(at shear rate = 10s <sup>-1</sup> )	Field test (Concawe, 1988)	Dosage: DER = 500 ppm	D <sub>2min</sub>	D <sub>1h</sub>	D <sub>24h</sub>
A7 Pos B / 9.5 h.	1820	AA00220	45	1849	Good	Stability Alcopol O 60 Corexit 9500	0 0 0	0 0.1 0.1	0.4 0.8 0.7
Sunday, 21.	Sept.								
A8 Pos A / 22.5 h.	0730	AA00225	45	2703	Good	Stability Alcopol O 60 Corexit 9500	0 0 0	0 0.2 0.2	0.2 0.5 0.4
A8 Pos B / 22.5 h.	0739	AA00231	43	2812	Good	Stability Alcopol O 60 Corexit 9500	0 0 0	0 0.1 0.1	0.2 0.3 0.4
A9 / 32.5 h.	1720	AA00320	35 (36% KF)	4948 (AEA) 5300 (SINTEF)	Good / Reduced	Stability Alcopol O 60 Corexit 9500	0 0 0	0 0 0	0 0.1 0.1
Monday, 22.	Sept.								
A10/54.5 h.	1525	AA00363	30	15076	Reduced	Stability	0	0	0
A11 / 54.8 h.	1540	AA00367	30 (35% KF)	19700 (AEA) 22000 (SINTEF)	Slowly / Reduced	Stability Alcopol O 60 Corexit 9500	0 0 0	0 0 0	0 0.1 0.2
Treatment	1552-1600		CONTRACTOR OF	400 liters of Corexi	1 9500, spray runs	1-3			
A12 / 55 h. Non-treated area (?)	1555	AA00371	25	14200	Reduced	Stability	0	0	0
A13 / 55 h. Treated area	1610	AA00375	25 (22% KF)	10839 (AEA) 11800 (SINTEF)	Reduced / Good	Stability Alcopol O 60 Corexit 9500	0 0 0	0.1 0.1 0.1	0.22 0.7 0.4
A14 / 55 h. Non-treated area (?)	1625	AA00379	35 (37% KF)	8863 ?? (AEA) 15000 (SINTEF)	Reduced	Stability Alcopol O 60 Corexit 9500	0 0 0	0 0 0	0 0.2 0.1

Sample / Time at Sea	Date / Time	AEA ID-no	Water (vol.%)	Viscosity (cP, at 15°C, at AEA)	Dispersibility (DER = 1 : 25)	Emulsion Demulsifie (fraction deh	stabilit r effecti ydrated	y and ivenes at 15	s°C)
			(Alcopol- method)	(at shear rate = 10s <sup>-1</sup> )	Field test (Concawe, 1988)	Dosage: DER = 500 ppm	D <sub>2min</sub>	D <sub>1h</sub>	D <sub>24h</sub>
Treatment	1628-1638	and the state	600 liter, spri	ay runs 4-9. →Total 10	000 liters of Corexi	t 9500, now appli	ed.		200
A15 / 55.5 h. Non-treated area (?)	1645	AA00383	25	15027	Reduced	Stability	0	0	0

48 72

6 6

D is fractional dehydration of emulsion. After 2 min, Ihour and 24 hours settling after demulsifier addition in the vials

Time after release	Wind speed (m/s) ANS-slick
(hours)	Release: Sept. 20. 0840 - 0900
0	4
2	4
4	5
6	6
8	6
10	9
12	9
16	S
20	3
24	4
28	S
32	6
36	S
40	4

Table 7.2 Wind conditions (average wind in m/s) during the AEA'97 field trial used as input to the SINTEF Oil Weathering Model

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Table 7.3	;	Input data for predictions of Alaska North Slope crude oil behaviour at sea.
		Fresh all proporties

Specific Gravity (60 F/60 F)	0.908
Pour Point (°C)	-31.666
Reference temperature #1 (°C)	13
Viscosity at ref. temp.#1 (cP)	76
Vanadium (ppm wt.)	•
Nickel (ppm wt.)	-
Asphaltenes (wt. %)	-
n-Pentane Insolubles (wt. %)	-
Flash Point (°C)	
Wax Content (wt. %)	•
Dispersable for visc. <	4000
Poorly/not dispensable for visc. >	>20000
Maximum water uptake (%) at 5°C/13°C	75
Wax Content (wt. %) Dispersable for visc. < Poorly/not dispersable for visc. > Maximum water uptake (%) at 5°C/13°C	4000 >2000 75

-: Data missing

True beiling	point curve
Temperature (°C)	Cumulative volume (%)
30	3
82	7
166	19
193	23
288	38
343	49
510	74

Film thickness (mm)	
Initial	20
Terminal	1

Weatherin	g properties (la	boratory dat	1)	
	Fresh	150°C+	200°C+	250°C+
Boiling temperature (*C)		197	255	320
Valume topped (%)	0	20	26	32
Residue (wt %)	100	84	78	67
Specific gravity (g/l)	0.908	0.919	0.93	0.947
Pour point (°C)	-30	0	3	9
Flash point (°C)	· ·	43	78	127
Viscosity at 13°C (cP)*	76	109	287	853
Viscosity of 50% emulsion (cP)*		676	1776	4991
Viscosity of 75% emulsion (cP)*		1819	10000	22000
Viscosity of max water (cP)*	· ·	3059	10000	22000
Maximum water content (%)	· · ·	75	75	75
Halftime for water uptake (hrs)	•	0.28	0.22	0,43
Stability ratio	•	1	1	1

Not measured

Viscosity measured at shear rate 10s<sup>-1</sup>.

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### 8 Deep Spill JIP 2000

In order to increase the understanding of how oil and gas from subsea leaks or blowouts will behave in deep water. The DeepSpill Joint Industry Project was established with the aim of determining the fate of oil and gas released in deepwater by performing full-scale field experimental releases.

### Objectives

The main purposes of these experiments were:

- to obtain data for verification and testing of numerical models for simulating accidental releases in deep waters;
- to test equipment for monitoring and surveillance of accidental releases in deep waters;
- to evaluate the safety aspect of accidental releases of gas and oil in deep waters.
   Verified numerical models combined with improved surveillance of the releases should then

provide a better basis for oil spill contingency planning and environmental impact assessments in conjunction with future deep water exploration, development and production.

### Releases

The experiments were conducted at 844 m depth in the Helland Hansen region in the Norwegian Sea. 60 m<sup>3</sup> marine diesel and 60 m<sup>3</sup> Sture blend together with 18 m<sup>3</sup> liquefied natural gas (LNG) equivalent to 10 000 m<sup>3</sup> of gas at atmospheric pressure were released from a discharge platform lowered down to the seabed.

The results from the DeepSpill JIP 2000 are presented in Johansen et al., 2000.

Figure 8.1- Figure 8.3 predictions of evaporation, water content and viscosity of emulsion of Sture Blend compared to sample data from the deep spill experiment. The data from the deep spill experiment is in good accordance to the predictions made by the SINTEF OWM (Johansen *et al.*, 2001).



Figure 8.1 Evaporative loss of crude oil after resurfacing. Measured values compared with predictions based on laboratory data obtained from Sture Blend (2000). Note that this is essentially the same blend of crude oils as the Sture blend used in the experiment, but previously marketed with another name.



Figure 8.2 Water uptake of Sture Blend crude oil after resurfacing. Predicted and measured values.



Figure 8.3 : Viscosity of emulsion, Sture Blend crude oil after resurfacing. Predicted and measured values

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8.1 Field data 2000

The data from samples taken of the oil slick are given in the tables described here.

Table 8.1 : Emulsion film thickness (µm) - Sture Blend crude oil

Table 8.2 : W/o emulsion properties

Table 8.3 : Wind data 2000

Table 8.4 : Model input - weathering data Sture blend

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### Table 8.1 : Emulsion film thickness (µm) - Sture Blend crude oil

Sampling time	Water	Emulsion Film thickness	Positi	on <sup>1</sup> )	Comments (sampling technique / Visual
(local time)	content,1)	(µ, m)	Lat	Long	observations)
0902	29	19	65 00.037	4 50,775	PP-Pad, spot sampling / metallic
0904	29	171	65 00.034	4 50.775	PP-Pad, spot sampling / Thick oil
0908	29	38	65 00.009	4 50.772	(Discontinuous) (Discontinuous) PP-Pad, spot sampling / thick oil (Discontinuous)
0909	29	7	65 00.001	4 50.719	PP-Pad, spot sampling / metallic
1035	29	15	65 00.150	4 51.517	PP-Pad, spot sampling / 4 samples
1036	29	101	65 00.146	4 51.500	in thick (discontinuous) oil and
1037	29	27	65 00,139	4 51,496	metallic. In an area with relatively
1038	29	36	65 00.130	4 51.487	fresh oil
1100	66	676	64 59.635	4 51.091	PP-pad, spot sampling from emulsified patches
1105	66	1983	64 59.588	4 51.156	PP-pad, spot sampling from thick emulsion
1110	63	1187	64 59.433	4 50.971	Thick emulaion, estimated > 1-3
1116	63	1008	64 59.398	4 50.989	PP-Pad, spot sampling from thick emulsion
1116	63	1902	64 59,398	4 50.989	PP-pad, spot sampling from thick emulsion
1617	69	1264	3		PP-pad in thick emulsion, 3
1617	69	1204			parallel samples
1617	60	777			• •

Position given in geographical degrees followed by decimal minutes
 Samples taken in the southern front of the slick (Position not recorded)

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Table 8.2 : W/o emulsion properties

Water free residue properties <sup>39</sup>

					effici.	ency		Î		
Sampling station	Tentative Weath time	Density (ofmD	Viscosity at 10(s <sup>-1</sup> ) (mPas)	Water cont (vol%)	2		ů d		Density (s/m)	Evep loss (wetk) <sup>9</sup>
906	2.0	0.9259	4	29.2	¢,	F.	¢,	4	0.8852	28.2
026	0.75	0.9550	706	51.5	00.1	1.00	0.50	0.78	0.8306	31.7
1010	-	0.9810	1935	65.8	0.53	0.53	0.16	19:0	0.8962	32.3
1055	1.5	0.9841	3400	67.6	0.82	0.82	0.00	0.27	0.8987	33.5
1116	2	0.9822	3100	66.7	0.83	0.83	0.08	0.41	0.8967	36.2
1427	s	0.9910	7600	75.1	0.61	0.61	0.00	0.00	0.8885	35.6
1506	9	8266.0	5000	72.1	69.0	0.69	0.00	0.24	960610	5.95
1620	-	0.9840	6700	68.5	0.73	0.73	00.0	0.00	0:6950	39.3
Fords Crude		0 8423	84				,		0 8423	
200°C+	ı	0.8903	477	,	,	,		,	0.8903	

٠

D is fractional dehydration of emulsion. D<sub>u</sub> is effect after 4 hours. D<sub>uu</sub> is the effect after 24 hours. D=0: no water settled. D = 1: all water settled.
 Effect of 500 ppm concentration of the emulsion breaker Alcopol 060%, relative to the oil volume
 Properties of the oil residue after the water hours diared off by 0.5% emulsion breaker Alcopol a 60<sup>°</sup>C
 Pre sample volume was no small to perform the analysis.
 Evaporative loss quantified by GC - SINTEF Evap-program.



Figure 8.4 Plot of wind speed and direction at the Helland Hansen site during the DeepSpill sea trial. Based on smoothed data as shown in Figure 6.1.

Table 8.3 : Wind data 2000

Start date :	25.06.2000	00 UTC
Time from start	Wind speed	Direction
(n)	(m/s)	0
0	10,4	15
6	9,3	10
12	4,9	6
18	2,8	337
24	2,9	316
30	2,1	331
36	2,1	0
42	3,2	0
48	6,3	347
54	9,3	336
60	11,7	335
66	13,5	334
72	14,2	336
78	14,0	339
84	12,8	341
90	10,7	346
96	9,1	356
102	8,2	8
108	8,8	19
114	10,7	26
120	13,6	30

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Table 8.4 : Model input - weathering data Sture blend (2000)

Fresh oil properties	
Specific Gravity (60 F/60 F)	0.847
Pour Point (°C)	-3
Reference temperature #1 (°C)	13
Viscosity at ref. temp.#1 (cP)	10
Vanadium (ppm wt.)	247
Nickel (ppm wt.)	
Asphaltenes (wt. %)	
n-Pentane Insolubles (wt. %)	-
Flash Point (°C)	125
Wax Content (wt. %)	÷.
Dispersable for visc. <	2000
Poorly dispersable for visc. >	9000
Maximum water uptake (%) at 5°C/13°C	75
	_

Data missing

True boiling	point curve
Temperature (°C)	Cumulative volume (%)
90	10.62
120	16.74
145	21.48
160	24.23
205	32.29
250	40.62
295	50.27
350	61.09
420	70.84
565	89.12

Film thickness (mm)	
Initial	0,5
Terminal	0,5

weathering	properties (in	Looratory unit		
	Fresh	150°C+	200°C+	250°C+
Boiling temperature (°C)		185	250	303
Volume topped (%)	0	16	28	39
Residue (wt %)	100	86	76	65
Specific gravity (g/l)	0.847	0.877	0.892	0.907
Pour point (°C)	0	9	18	21
Flash point (°C)	-	38	80	119
Viscosity at 13°C (cP)*	10	25	65	350
Viscosity of 50% emulsion (cP)*	-	190	480	2800
Viscosity of 75% emulsion (cP)*		1.00	2600	6300
Viscosity of max water (cP)*				
Maximum water content (%)		80	80	78
Halftime for water uptake (hrs)	-	0.130	0.100	0.180
Stability ratio	+	0.200	0.705	1

.

Not measured Viscosity measured at shear rate 10s<sup>-1</sup>.

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# **Appendix D: Users Manual for SINTEF OWM Version 3.0**



# SINTEF Oil Weathering Model User's Manual

Version 3.0



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### 1. Installation

The **SINTEF Oil Weathering Model (OWM)** is delivered on a single CD-ROM, containing the model computation engine, user interface and oil type database. It requires Microsoft Windows NT. Install the **OWM** from Setup.exe from the CD-ROM, and follow the installation instructions.

### 2. Running the SINTEF OWM under Microsoft Windows

The SINTEF Oil Weathering Model may be started from Microsoft Windows by double clicking either the icon installed on the desktop by the setup program, or the executable file C:\OWModel\OWModel.exe.

### 3. Getting started: a simple scenario

When the model is started using the procedure described above, the main window appears (Figure 3.1). The main window contains a menu bar at the top, and dialog controls for a short description of the scenario, oil type and weather conditions.



Figure 3.1. The main window of the SINTEF Oil Weathering Model.

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To run a scenario, first select an oil from the list in the *Oil Type dropdown-list*. If there is a description available for this oil in the database, it will appear in the *Description field* in the top of the dialog. If no description appears, or you want to change the description, you can type a description yourself (for example "Test case").

The model gives some default weather conditions, but one has also the opportunity to use the Add and Remove buttons to alter the sea surface temperatures and winds speeds that are required in a specific case. For example, a sea surface temperature may be added by typing the value in the blank field, and clicking the Add button. The specified temperature will appear in the list to the left. To remove items in either the sea surface temperature or wind speed list, highlight items by clicking, or multi-select by <crl> click, and then click on the Delete button. Notice that a rerun of the model computations will be necessary to see the effect of a change made in one of the lists.

In the example above, we have selected to run the model for one sea surface temperature (10 °C) and three (constant) wind speeds (5, 10 and 15 m/s). By clicking the Go button on the menu, we thus run 3 scenarios: 1 sea surface temperature, and 3 wind speeds for this sea temperature. To save your current scenario settings, choose File/Save As from the main menu.

### 3.1 Graphical output

Graphics displays are obtained by choosing *Output* and *Graphics* from the main menu. This brings up a menu containing the various properties calculated by the model (Figure 3.2). Click on one of them, for instance the evaporative loss, to display an x-y plot of the property as a function of time. Then go back to the main window by using the *Window menu* on top, choose one of the other properties and you can study the graphics by turn in the Window menu. Evaporative loss, water uptake, viscosity of emulsion, and mass balance are also available using buttons on the tool bar.



Figure 3.2 Graphical output menu.

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Examples of the graphical output are shown in Figure 3.3 and Figure 3.4.



Figure 3.3 Evaporative loss, 10°C sea surface temperature and 3 wind speeds.



Figure 3.4 Mass balance 10°C sea surface temperature and 10 m/s wind speed.

3.2 Output textfiles (.TXT, .TX2)

The model produces a text file with a summary of input parameters, and a table with prediction results. To view this file, choose *Output* and *Text* from the main menu. As the output file shows, the model calculates several properties. These are listed in table form for the time cuts specified in the *Time Cuts form* (Section 6). You can print hardcopy of the output file by clicking the Print button. When you are finished studying the output file, click on the menu *File/Exit* to close the output window.

An example of an output text file is shown in Figure 3.5.

UWMode1.TXT - Not	epad	-			and the second	العلم
He Edit Format Help				-	and the second sec	
···· Input Paramet	ers for W	eathering	Scenario 0	WHodel *****		
SINTEF Oil Meather	ing Model		: v	9.0		
011 type			: 3	KOFISK BLEND	2000	
Wind speed			: 0	onstant speed	(=)	
Terminal film this	kness (an	) ( ) ( ) ( ) ( ) ( ) ( ) ( ) ( ) ( ) (	1	1.000		
Amount oil spilled	i (tonnes)		÷.	9600.0000		
Release Duration	(min)		=	2880.0		
Release Depth (net	ers)		:	0.0		
Gas-oil-ratio (GO)	23		I	0.00 /	0.00 cubic feet/bbl	
Factor for lab to	field enu	Isificatio	n rate :	6.000		
Density of sea wat	er (kg/m^:	3)		1025.000		
Water depth (m)			· · · · · · · · · · · · · · · · · · ·	50.000		
Fetch (m) N: 100	0.000 S: .	100.000 E:	100.000	W: 100.000		
Duration of wind a	trength ()	hrs)	2	1440.000		
Ice type				0		
Ice Coverage (1)			÷	0.000		
Mass transfer			: 7	riction		
Viscosity ratio			: L	ab		
Calculate entrain	inent		: 3	0		
Calculate evaporat	ion		: Y			
Calculate emulsifi	cation		: 7	05		
Maximum water cont	ent (1)		: U	se weathering	data below	
Laboratory weather	ing data:					
PROPERTY	FRESH	150+	200+	250+		
BOTL-TEND C		192	249	250		
UOLA TOPPYD	0.0	17.8	28.0	37 3		
WTA SECTION	100.0	84.2	26.0	66 0		
SD CONV borli	0.851	0.876	0 688	0.899		
BOILD DOTET C	0.001	12.0	15.0	21.0		
PLASHDOTHY C	0.0	0.0	0.0	0.0		
VISC at 13.C.cP	93.	374	1390	3800		

Figure 3.5 Output text file.

For the purpose of giving the user the possibility of making his/her own graphs of prediction results, a <scenario name>.TX2 file is generated in the same directory as the scenario file (.OWM-file); e.g. in the C:/OWModel3.0/SCENARIO directory. This file may be directly imported into Microsoft EXCEL, simply by opening it from EXCEL, and clicking *Finish* (without having to do any further specifications). By this procedure, the data table(s) "slides" directly into the actual worksheet, and the user is free to graph the fields in the preferred way.

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### 4. Variable wind speed

In the example above, constant wind speed was used in the predictions. In an actual spill situation, however, the wind varies with time in a way that may be specified from measurements or weather forecasts. Click on the radio-button labeled "Read Wind Data from Disk" to enable the dropdown wind speed file list. This list works in a way similar to the scenario list. The user may either specify a new wind file in the edit box, or he may click on the Browse button to select an existing wind file.

A simple wind speed editor is included to create and edit wind files. Click on menu *Model/Wind Editor* to bring up the editor. The wind file editor is shown in Figure 4.1. To create a new file, it is suggested to use an existing file as a template. The first five lines in the file are header information, not used in the present version of the OWM. Each subsequent line contains a time in hours from spill start, a wind speed in meters per second, and a direction in compass degrees from which the wind comes. The wind direction thus follows meteorological convention, with  $0^{0}$  being from the north towards the south and  $90^{0}$  being from the east towards west. When one has specified the wind data for the desired period, click on the *Save As or Save* button to save the wind file and close the editor. Select the new wind file in the *Read Wind Data from Disk edit box*, and the model is ready to run. If you wish to re-format existing wind files for use with the SINTEF OWM, either a tab or a blank space between time, speed, and direction in each row will suffice.

Note that the OWM checks the wind file for new values at each time cut, and uses the previous wind values until a new time cut is encountered. To assure that all wind values are accounted for in a simulation, the time cuts (under the menu item Model) should match with the wind time intervals.

ear 04		-	
onth: 06		New	
ay: 01 our: 0		Oper	n
me(hrs) Speed 15.0	d(ms) Dir 280 260 220	Sav	e
8.0 12.0		Save	As
4 13.0 5 12.0 8 10.0 0 18.0 2 15.0	190 270 270 190 280	Close	8
12.0 13.0	250 240		

Figure 4.1 Example format for input of time-variable wind.
# 11

### 5. The graphics output window

Examples of the graphical output window were shown in Figure 3.3 and Figure 3.4. The menu bar of this window has several extensions in addition to the standard system menu items. These give the user the opportunity to:

- · Edit the text in the graph, Edit/Select Caption Font and Select Label Font.
- manually scale the y-axis, View/Set Scaling,
- · put comments in the graph, View/Edit Comments,
- save the graph to disk, File/Save as,
- · get hardcopies of graphs File/Print,
- · and load an old graph from disk File/Open

Choosing Edit/Select Caption Font, brings up the window shown in Figure 5.1.



Figure 5.1 The text formatting window.

Choosing View /Set Scaling, brings up the window shown in Figure 5.2, where certain settings may be altered in order to customize the y-axis scale.



Figure 5.2 The scaling window.

Choosing View/Edit Comments... brings up the window shown in Figure 5.3.

Comments	11
The algorithm for prediction of natural dispersion is preliminary and is currently under improvement. Model predictions have been field verified up to 4.5 days	0000000
Cancel DK	-

Figure 5.3 The comments editor window.

This window lets you type comments that will be displayed beneath the graph. Text will automatically wrap to the next line when a line is too long. To force a line break, type Ctrl-Return.

#### 6. Changing the time window

By default, predictions are performed for the time window ranging from fifteen minutes to 5 days after the spill. The user may change this time window by selecting *Model* and *Time cuts*, in the main menu. This brings up the window shown in Figure 6.1.



#### Figure 6.1 The time cuts window.

In this window the user may add and delete time cuts in the same manner as with sea temperatures and wind speeds by using the edit box and Add and Delete buttons. A utility for quickly filling the time cuts list box is also included. Here, one types the number of time cuts to use, the start time, and the step (linear scale) or factor (logarithmic scale) between succeeding time cuts into the corresponding edit controls, and then clicks on the *Fill list button*. Clicking on the *Clear list button* empties the list of time cuts. Notice that the time scale may be logarithmic or linear. The default time scale is logarithmic in order to get a higher resolution in the early stages of a spill. The maximum time for which the model can perform predictions is currently set to 480 hours (20 days).

Care should be taken when specifying the time cuts in order to obtain smooth graphs. The time cuts specify for which times the weathering state of the oil will be stored under prediction, and for which times to put numbering on the x-axis in graphs. Thus, a sufficient number of time cuts should be used to obtain a satisfactory resolution, while at the same time not making the graph crowded with numbers along the x-axis. A number of 13-20 time cuts gives visually good results. For time cuts exceeding 24 hours, the numbering along the x-axis is divided by 24 to give the time elapsed in days. Thus, the time cuts exceeding 24 hours should be chosen at an even 6, 12 or 24 hours so that the numbering along the x-axis becomes easy to interpret (1.25 or 1.5 days instead of 1.208 days and the like).

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#### 7. Changing model parameters

In addition to oil type and weather conditions, the experienced user may change a number of model parameters. By choosing *Model* and *Model Parameters* from the main menu, the window in Figure 7.1 appears.

Release amount		Release properties
Amount unit Inetrictions	Time unit minute	Depth (m): 0
© Belease rate: 1.33	3333333 metric tons/minute 20 metric tons(s) 15 minute(s)	Gasto-Oil ratio 0 GOR unt cummer 2 Tergonal film thickness (mm) 1
the second s		
Ambient	1005	
Ambient Density of water (gm/l):	1025	Water depth (m)
Ambieni Density of water (gm/l):	1025	Water depth (m) 50
Ambienk Density of water (gmv <sup>1</sup> ): [ Fetch (km) <u>N</u>	1025 Processes	Water depth (m) 50 Arctic Conditions Lee troe: No ice
Ambient Density of water (gm/l) [ Fetch (km) <u>N</u> [100	1025 Processes Notucal dispersion F Eveneration	Water depth (m) 50 Arctic Conditions Ice type: No Ice
Ambiere Density of water (gm/1). [ Fetch (lum) 100 100 E	1025 Piocesses Natural dispersion Evoporation F Enultification	Water depth (m): 50 Arctic Conditions (ce type: No Ice  ice coverage (%)
Ambier# Density of water (gm/1) [ Fetch (km) 100 22 [100 100 E 100	1025 Piccesses Natural dispersion Exclosoration Enulsingation Weathering data prediction #	Water depth (m): 50 Arctic Conditions (ce type: No Ice loe coverage (3): 0 no lab data

Figure 7.1 The Model Parameters window.

#### Terminal film thickness (default from database)

Specifies the minimum oil film thickness that the oil film will approach in the case of an oil release on the sea surface. The default value depends on the oil product selected. The value specified refers to the terminal thickness of the thick oil, not the blue sheen that appears around the edges. In the case of some petroleum products such as gasoline, the terminal thickness may equal the sheen thickness. In the case of a seabed blowout (specified by *Depth* greater than zero), the physical processes governing the film thickness forming on the sea surface are not petroleum product specific. In the latter case, the terminal film thickness is set to zero, and the respective field in the screen window is disabled.

#### Depth (from where the oil release occurs)

The depth of the release, in the case of an underwater release, is specified in the *Depth* field in the *Release properties section* of the screen window. By choosing a value greater than zero, the model implicitly assumes an underwater release from this depth. This also activates the *Gas-to-Oil ratio field* described below. Note that *Depth* should not be set greater than *Water depth* described below.

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#### Gas-to-Oil ratio (GOR)

In the case of an underwater release (when the *Depth* field is set to a value greater than zero), the *Gas-to-Oil ratio* (*GOR*) field in the Release properties section of the screen window is activated. The GOR is a petroleum well specific value, and may vary greatly from field to field. The values may be given as a pure ratio (without denomination) or in cubic feet/bbl, specifying the volume ratio between gas and oil in an underwater leakage. The OWM 3.0 implementation assumes a regime where the dominating force regarding surfacing of the oil is gas driven (dominating the oil's inherent buoyancy). For this reason a lower limit is set for GOR; at least 10 or equivalent 56.15 cu. ft/bbl.

#### Release amount and duration

Amount spilled is specified in metric tons, barrels, cubic meters or liters. Duration is specified in minutes, hours, or days. The user may choose specifying either oil release *volume* and duration or oil release *rate* and duration. In the calculations, the program first calculates the rate of release in metric tons/minute, and uses this rate in all calculations.

#### Density of water

Specifies the density of the water in which the oil is spilled. The default value is 1025 gm/1, which is a typical value for seawater. Water density affects spreading of both fresh oil and emulsion.

#### Water depth

Specifies the depth of water at (and around) the spill location. The default value is 50m. This value is used by the model for calculating wave height, and needs to be changed to suit your area. Note that this value should be set greater or equal to the *Depth* of the oil release, described above.

#### Fetch

Specifies the distance to shore (or an ice edge) in four directions; north, south, east and west. The default value is 100 km in all directions, which corresponds to a spill in open sea. These values will influence the build-up of waves and thus the rate of natural dispersion. They need to be changed only if the spill site is very close to shore or an ice edge. Appendix D shows equations for shallow water significant wave prediction curves as functions of wind speed, fetch length, and wind duration, and depth (based on the U.S. Army Corps of Engineers <u>Shore Protection Manual</u>, 1984).

### Processes: natural dispersion, evaporation and emulsification

These are on/off buttons for the three processes calculated by the model. The *Evaporation button* is always turned on (cannot be turned off), but the other two may be turned on or off to study their individual effects on the oil spilled at sea. By default, all processes except natural dispersion are turned on.

#### Arctic conditions

Data from a full scale field trial in the Arctic ice south of Svalbard (Spitsbergen) in the Barents Sea have been used to calibrate spreading, natural dispersion, evaporation and emulsification in the presence of ice blocks, or thick (> 0.5 m) sheet ice. The presence of sea ice reduces the spreading rate of the oil, which in turn reduces the evaporation rate (and increases the thickness). The ice also damps wave activity, which reduces both natural dispersion and emulsification.

#### 7.1 Viewing oil database contents

The oil type database is designed to contain fresh oil properties, boiling point curve, laboratory weathering data and properties of cuts for an arbitrary number of oil types. To load and view information on a specific oil type follow these steps:

Select the oil type from the oil type drop down list in the main window. Select *Oil types* and *Oil Properties* from the main menu (Figure 7.2). Select the type of information you want.

File Edit Vie	ering Model - OWM av Model Output	ode1.0WM Oftypes Window Help		
		Of Database Query	It-Ited real @1 Presh OI Properties	-
== 0WMode	1.0WM	Of Type List	Eoling Point Curve	Text
Description: 2000 - TBP crude as		say	Cut Properties	U decision
OJ Type	EKOFISK BLEND 20	00 (Weathering Data	Al	9
10	2 Add Edd	C Equators Specific Contract S	ada Tom Disk	

Figure 7.2 Oil properties window.

The selected information is displayed in a dedicated text editor shown in Figure 7.3, and may be altered, copied or printed. Alterations to the text are made possible so that the user may prepare printouts, for example a subset of the information. These alterations will not be stored in the database. The boiling point curve may be viewed in graphics as well by choosing the button labeled *Graphics*, in the editor window.

Laboratory weathering data presently exists for about 50 crudes and 15 refined products. However, predictions may be performed based merely on the standard crude assay for an oil type. This allows predictions to be performed for all the oil types in the oil database, but with results being less accurate for the oil types for which no laboratory weathering data exist. S TMP.TX1 Notepad file Edit Format Help Product Name: EKOFISK BLEND 2000 Product Type: CRUDE NORTH SEA Location: Data Source: SINTEF Applied Chemistry Tear 2000 Bolling point curve: Temp. ("C) Volume(%) Weight (%) 65.0 D.82 80.0 3.70 8.87 100.0 120.0 12.23 155.0 18.83 170.0 21.73 190.0 25.19 210.0 20.57 230.0 32.13 275.0 40.86 335.0 52.32 57.97 400.0 61.70 65.43 425.0 450.0 

Figure 7.3 Example of information from the text editor.

#### 7.2Setting filters on the oil database

The oil type database contains about 200 crude oils and refined products, mostly taken from the HPI Crude Oil Assay Handbook (1987). Although these are ordered alphabetically, the list is sometimes difficult to navigate. For this reason, a database filter utility has been included. Choosing Oil types and Oil database query, from the main menu, brings up the window shown in Figure 7.4:

Select glata source	T Select (	peographical grea	Select	product:
II Bottelle Doean Sciences Crude Assay HPI Crude Di Database IKU Petroleum Research SINTEE Applied Chemistry	ABU DHAU ALASKA, U ALGERIA ANGOLA ATLANTIO BENIN BRAZIL	BI, U.A.E. JSA : FRONTIER	CONDENS CRUDE HEAVY BI LOW EMU REFINED	SATE UNKER JLSIPYING DIST
	Min	Max		
Pour point range		Call In 18	°C	OK
Pgur point range. API gravity range.			-C	OK Cancel
<ul> <li>Pgur point range.</li> <li>API gravity range.</li> <li>✓ Specific density range.</li> </ul>	0.65	0.88	чС	OK Cancel

Figure 7.4 The oil database query window.

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Filters may be set on seven different properties (and combinations of them):

- Data source
- · Geographical area
- Product type
- · Existence of weathering data (laboratory analysis results)
- · Pour point range
- · API gravity range
- · Specific gravity range

A filtering by data source, geographical area and product type is set by clicking on a line of text in one of the list boxes. For example, if you click on Alaska, USA in the geographical area list box, only oil types from this location will be visible in the oil type dropdown list in the main window. If you also click on HPI Crude Oil Database in the data source list box, and CRUDE in the Product list box, only crude oils from Alaska and provided by the HPI Crude Oil Database will be visible in the oil type dropdown list.

The filter also gives the possibility of selecting oils within a specific pour point range and/or gravity range (either API or specific gravity). This is done, simply by putting a tick-mark in the box to the left of the according range box(es), and specifying the desired range(s) in the *Min* and *Max* fields. If the user furthermore wants to restrict the selection of oils to those with lab weathering data, this may be done by putting a tick-mark in the box to the left of the text "Oiltypes with lab weathering data only".

If the user wants to The contents of the oil type dropdown list may be sent to a printer device by selecting *Oil type* and *Oil type list* from the main menu.

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### 8. Making graphics for standard SINTEF manuals

A special tool for making graphics for the standard SINTEF Oil Weathering Manuals is designed to quickly get printouts of all the properties predicted by the model. The window for defining characteristics of manual graphics is brought up by selecting *Output* and *Manual*. from the main menu. This window is shown in Figure 8.1

roperty: EVAPORA il Type: EKOFISK E escription: TBP cru ata Source: SINTE	TIVE LOSS BLEND 200 Ide assay F Applied C	0 Tvernistry (2000),	Weatherin	besu alab gr	
	8888	anios:	333	191213	
Minimum volum	0	MajorUnit	10	Automati	e scalno
Maximum value:	50	Minor Unit,	5	C Logarithe	nic scale
Comments	-				Const
					Paste
				00000	
				8	

Figure 8.1 The manual window.

The Manual window lets the user edit the header, customize the y-axis, and add comments to the various oil properties calculated by the model.

The dropdown list at the top of the window lets the user select one of the available properties. The graph header, y-axis scaling and comments for this property will then be loaded and displayed, and the user may alter these as he pleases.

The utilities for customizing the y-axis and typing comments work as described in Section 5, but some extra facilities have been added to the comments editor. These are represented by the buttons along the right and lower edge of the comments edit box. The two upper buttons let the user copy or paste text to and from the Windows clipboard. The two lower buttons let the user save the text in the comments edit box to a text file, or load a text file into the comments edit box.

The edit box for the graph's header is similar to the comments editor, except that words don't wrap to the next line when the line is to long. Instead the text automatically scrolls to the left. However, if the lines are too long, they will be clipped when sent to the printer for hardcopies.

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Although this tool is intended for creating standard SINTEF Manual graphics, which use four constant wind speeds and two sea surface temperatures, it may just as well be used for other

configurations, including variable wind speed.

To print graphics, select *File* and *Print*. Then select the specific properties one wants to print. To create a graphics file (Windows Metafile format) for use in reports or other documents, select *File* and *Export to Metafile*.

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#### 9. Coupling the SINTEF oil weathering model to oil drift models

It is possible to link the SINTEF Oil Weathering Model to oil drift models through a common block that allows the programs to share information characterizing oil patches or spillets. This capability, described further in Aamo et al. (1993; Appendix E), requires some cooperative effort with the developers. Contact SINTEF Materials and Chemistry, Marine Environmental Technology, for further information.

### 10. Editing oil database

By using the oil database edit utility, OILDBED, the user may add, delete and change data on existing oil types as well as entering new oil types. The oil data base editor is started from Microsoft Windows by double clicking either the icon installed on the desktop by the setup program, or the executable file C:\OWModel\OILDBED.exe. The Main window is shown in Figure 10.1.

🗐 Oil Data	abase Editor							
Elle Data	Help	1	The second states	-	-	1.		
EKOFISK Source Location Product Year Descriptio	BLEND 2000 SINTEF Appled Che NORTH SEA CRUDE 2000 orr de assay	emietry	Fresh Properties Gravity (BAP) Specific Gravity (50 F7601 Density correction Factor Total Sultur (wt. %) Mercepten Sultur (ppm wt. Total Nitrogen (wt. %)	n 1				
Boiling I Ac. Deac. H1 H2 H3 H4 H5	Port Curve           Tp. ICI         Vol. ISI           65         0.82           80         3.78           100         8.57           120         12.23           155         18.83	WL [X]	Lab Weathening Data Balling Point Temp (JC) Vol. Topped (Vol. %) Weight Residue (Wl. %) Specific Gravky (Kg/f) Pour Point (JC)	Fresh [0 [100 [0.8507 [0 [0 [0 [0 [0 [0 [0 [0 [0 [0 [0 [0 [0	150C+ 192 17.8 84.2 0.876 12	2000+ [248 [28 [75.1 [0.888 [15]	250C+ 250 37.3 66.9 0.855 21	

Figure 10.1 Main window of oil database editor.

### 10.1 Editing data on existing oils and create new oils in the database

To edit data on existing oils in the database, select *File/Open* and choose an oil from the list. The data for the selected oil type will appear in the main window and editing can be done. The editing is done in accordance with the description of how to add oils to the database (chapter 10.2) below. Choose *File/Save* before closing (and saving changes) of existing oils and *File/Save As* and give new oil type name before closing (and saving) the new oil type. If the user wants to filter out a selection of oils just press the *Filter* button in the *File/Open* screen window. This will bring up the filtering menu for which the use is described in chapter 7.2 above.

#### 10.2 Add oil types to database

To add oil types to the database select File/New and type the new oil type name. This name will appear in the oil type selection list. The main window (fig. 10.1) will appear on the screen (with

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blank data fields). The Main window includes fields for entering oil type descriptions, true boiling point curves, fresh oil properties and data from weathering analysis. Use *Tab* or *left-click* with the cursor to move from one field to another. Use **period** as decimal point.

### 10.2.1 Fields for entering oil type description and source

Fields for entering oil type description and sources are listed below:

#### Source:

Select (laboratory) source from the *Source scroll menu*. If the relevant source does not appear in the list select *Data/Source* on the menu bar, add the source name and eventual extra description in the Description field, and close the source window. Fig 10.2 shows the screen window for adding new source data.



Figure 10.2 Adding new source data.

#### Location (region):

Select the region location from the scroll menu. If the region location does not appear in the list, select *Data/Location* on the menu bar, and add the new location similar to the procedure described for adding new source data above.

#### Product:

Select product (type) from the scroll menu. Selection of a product (type) will initialize the default terminal film thickness for OWM predictions using this product. If the relevant product does not appear in the list, select *Data/Product* on the menu bar, and add the new product similar to the procedure described for adding new source data above.

#### Year:

Enter the year the analysis has been prepared or added to the oil database.

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### Description:

Describe the history of the data like e.g. "data from XXX 1999 have been updated with TBP data from 2002". Descriptions, that do not fit inside the Description field, may be added using the *Info File button*, which opens a description text file for entering free textual information (e.g. oil company, date of sampling etc), to be saved together with the actual oil type.

El Oil Database Editor Ele Data Help		<u>ao x</u>
EKORISK BLEND 2000 Source SINTEF Applied Chemistry × Location NORTH SEA × Product CRUDE × Yes 2000 Description Into File TBP crude assay Boling Point Curve Ac. Desc. Tb ICI Vol (NJ WI, (N) H1 55 0.82 * H2 80 3.78 H3 100 8.57 H4 120 12.23 *	Presh Picperties Gravity (JAPI) Specific Gravity (SDF/SDF) Density concellent factor Total Suffur (vit. %) Total Suffur (vit. %) Total Suffur (vit. %)	

Figure 10.3 Adding extra information for the actual oil type.

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# 13. Glossary

### Blue sheen

The part of an oil slick that is very thin (just a few microns).



The properties predicted by the model are those of the thick part of the slick.

#### Emulsification

The process of mixing water-droplets into the oil, forming an emulsion.

# Emulsion

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Refers to a water-in-oil emulsion, where water droplets of varying sizes are mixed into the oil. This water/oil mixture has properties that are quite different from the water-free oil.

### Evaporation

The process of releasing lighter fractions of the oil to the atmosphere as vapor.

### Natural dispersion

The process of oil going into the water column as droplets of varying sizes. Induced primarily by breaking wave activity.

### Viscosity ratio

A number giving the ratio between the viscosity of the emulsion and the viscosity of the corresponding water-free oil:

# $r = \frac{\mu}{\mu_o}$

where  $\mu$  = viscosity of emulsion

μ<sub>0</sub> = viscosity of water-free oil

### Stability

An emulsion is considered completely stable if no water separates out after 24 hours of setting. The dehydration D of an emulsion is simply

D = (WOR<sub>ref</sub>-WOR<sub>24</sub>)/WOR<sub>ref</sub>

where WOR is the water-to-oil ratio in the emulsion, and the subscripts ref and 24 refer to the reference emulsion and the emulsion after 24 hours of settling, respectively. The stability S is then 1 - D, so that a stability of 1 corresponds to a completely stable emulsion (D = 0).

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Appendix A: Table of the Beaufort Wind Scale

Beaufort Scale	Description	Wind speed		
number		m/s	kte	_
0	Calm	0-0.2	1.0	
1	Light air	0.3-1.5	1-3	
2	Light breeze	1.6-3.3	4-6	
3	Gentle breeze	3.43.4	7-10	
4	Moderate breeze	53-7.9	11-16	
5	Fresh breeze	8-10.7	17-21	
6	Strong breeze	10.8-13.8	22-27	
7	Near gale	13.9-17.1	28-33	
8	Gale	17.2-20.7	34-40	
9	Strong gale	20.8-24.4	41-47	
10	Storm	24.5-28.4	48-55	
11	Violent storm	28.5-32.6	56-63	
12	Hurricane	≥32.7	≥64	

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# Appendix B: Step-wise instructions for running the SINTEF Oil Weathering Model

- 1. Double-click on the SINTEF Oil Weathering Model icon, or on the executable file OWModel.exe. The main window of the model now appears.
- Type a description into the description edit field. Choose an oil type by clicking on the arrow at the right of the oiltype box, and then selecting from the list that appears. Type a sea surface temperature into the temperature edit box and click on the Add button (or select and delete one or more default values) Type a wind speed into the wind speed edit box, and press the Add button (or select and delete existing values).
- 3. Choose "Run" from the Model menu to perform predictions.
- 4. Choose "Graphics" and 'Evaporative loss" from the Output menu to view resulting graphics.
- 5. Double-click on the icon in the upper-right-hand corner of the graphics window to close it.
- 6. Repeat 6 and 7 for other graphs of interest.
- 7. Double-click the icon in the upper-left-hand corner of the main window to close the SINTEF Oil Weathering Model.

# Appendix C: Technical documentation

The model calculates four physical processes; spreading, evaporation, oil-in-water dispersion and water-in-oil emulsion formation.

# C.1 Spreading of surface spills

#### Force balance

The force balance equations may be derived for an oil slick in a channel with a counter flow in the underlying water, i.e. corresponding to an oil slick confined by a boom (Figure C1). On this basis, a relationship is obtained between the density and volume of oil confined by the boom, and the strength of the counter current.



Figure C1. Idealised view of oil spreading against a counter flow in a channel.

The pressure force  $F_p$  is due to the density difference between oil and water:

$$F_p = \frac{1}{2}Bh^2\rho g'$$

where B (m) is the width of the channel, h (m) is the oil film thickness,  $\rho$  (kg/m<sup>3</sup>) is the oil density, and g' (m/s<sup>2</sup>) is the reduced gravity:  $g' = g(\rho_w - \rho) / \rho_w$ .

(1)

The shear force  $F_s$  is due to the friction between the oil and water in motion:

$$F_s = B X \mu_* \frac{U}{\delta}$$
(2)

where X(m) is the length of the oil layer,  $\mu_w$  (Ns/m<sup>2</sup>) is the dynamic viscosity of water, U(m/s) is the water velocity, and  $\delta$  (m) is the thickness of the boundary layer in the water.

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The latter may be expressed by the Blaussius formula for flow around a flat plate:

$$\delta = 3v_{*}^{1/2}\sqrt{\frac{X}{U}}$$
(3)

where  $v_w$  (m<sup>2</sup>/s) is the kinematical viscosity of water.  $v_w = \mu_w / \rho_w$ .

### Spreading equation

By taking into account that the confined oil volume is V = B X h, substituting for the boundary layer thickness, and equating the two forces, the following expression is derived for the equilibrium length of the oil layer:

$$K = \left[\frac{3}{2} \frac{V^2 \rho g'}{B^2}\right]^{\frac{1}{5}} (\rho_* \mu_*)^{\frac{1}{5}} U^{-\frac{1}{5}}$$
(4)

If the oil is spreading on stagnant water, the velocity U may be presumed to represent the spreading velocity, i.e. U = dX/dt. Equation 4 will then be transformed into a separable differential equation in t with the solution:

$$X(t) = 1.3 \left(q^2 \rho g'\right)^{\frac{1}{4}} \left(\rho_{\mu} \mu_{\mu}\right)^{\frac{1}{8}} t^{\frac{2}{8}}$$
(5)

where q = V/B, i.e. volume of oil per unit width of the channel.

By use of the mass conservation equation q = X h, equation 5 may alternatively be expressed in terms of the film thickness h, and be transformed into a suitable differential form which may account for changes in the oil properties with time:

$$\frac{d}{dt}X^{4/3} = 1.75 \left(h^2 \rho \, g'\right)^{\frac{2}{3}} \left(\rho_w \mu_w\right)^{-\frac{1}{3}} \tag{6}$$

This differential equation may be combined with any oil mass conservation equation relating h and X to the oil volume, i.e. any equation of the type V = f(t, h, X). It should be noted that a conservation equation may also account for changes in the oil volume with time due to evaporation or emulsion formation. Excluding this for the moment, we may illustrate the concept by a few examples:

- For lateral spreading of a slick formed from a continuous surface leak with a discharge rate  $m (m^3/s)$  in a steady surface current of velocity u (m/s), the oil conservation equation may be written as q = m/u = 2hX, where X represents the half width of the slick.
- For an instantaneous spill, the conservation equation may be written as V = π X<sup>2</sup>h, where V (m<sup>3</sup>) is the spilled oil volume and X represents the radius of the circular slick.
- For a continuous leak on calm water, the same equation applies, but V will be increasing with time; V = m t, where m (m<sup>3</sup>/s) is the release rate.

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For a continuous leak from a point source in a steady current, the oil volume will also increase in proportion with time. In this case, gravity spreading will take place along two axis (cross-stream and downstream), but the cross-stream (lateral) component is conventionally presumed to dominate as the slick is extended downstream due to advection with the current. This assumption may be valid in cases with relatively strong currents and moderate spill rates. For weak currents and large spill rates, gravity spreading may have to be considered along both axis to get a realistic picture (see Figure C2).



Figure C2. Spreading of an oil slick from a continuous oil leak in a steady current. The slick may be defined in terms of  $X_1$  and  $X_2$ , representing half axis of an elliptical slick, with  $X_1$  aligned in the downstream direction. The oil conservation equation may then be expressed as  $V = mt = h \pi X_1 X_2$ , where  $m (m^3/s)$  is the spill rate. The progression of  $X_1$  and  $X_2$  may be computed by equation 6, while including an extra downstream elongation due to the current ( $dX_1 = 0.5$  u dt) in the period of time when the oil is leaking.

The approach sketched in Figure C2 is in fact unifying all the "classical" Fay spreading problems, from instantaneous spills, via continuous spills on calm water to continuous spills in a steady current (Fay 1969, Fannelop and Waldman, 1972). Figure C3 illustrates this concept for two cases. The same amounts of oil are released in both spills (2400 m<sup>3</sup>), but the duration of the release is 2 hours in the first case (a), and 24 hours in the second case (b). The oil density is 850 kg/m<sup>3</sup> in both cases, and the surface current is presumed to be moderate (10 cm/s). The results show that the calculations for the first case approaches Fay's equation for radial spreading on calm water, while the second case approaches Fay's equation for lateral spreading of a continuous spill in a steady current.

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Figure C3. Gravity spreading computed with equation 6 for two cases: 2400 m<sup>3</sup> of oil released in 2 hours (top), and 2400 m<sup>3</sup> released in 24 hours (bottom). The calculations are made with an oil density of 850 kg/m<sup>3</sup>. The coloured lines depict the corresponding results of spreading equations for instantaneous releases ("Radial Fay"), and lateral spreading for continuous releases in a steady current ("Lateral Fay").

# C.2 Surface spreading of subsea blowouts

The surface spreading of oil from a subsea blowout is governed by the generation of a rising gas bubble plume that entrains ambient water. Surfacing of the entrained water produces a radial outflow at the sea surface. The oil will be carried to the surface as fine oil droplets dispersed in the entrained water. A surface slick will form as the dispersed oil droplets settle out of the radial outflow of entrained water.

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According to Fanneløp and Sjøen (1980), the surface velocity distribution in the radial outflow can be approximated by a source flow equation:

$$U(r) = \frac{S}{2\pi r}$$

where  $S(m^2/s)$  is the source strength.

Under such conditions – provided that all the oil comes to the surface, the oil film thickness h(m) may be estimated from the source strength and the oil spill rate  $m(m^3/s)$ :

$$h = m/S \tag{8}$$

Fanneløp and Sjøen (op cit) also show that the source strength S depends on the characteristic radius b (m) and velocity w (m/s) of the surfacing plume:

$$S = k \pi b w$$

where k = 4.86 is a constant.

The same authors also presented a basis for establishing the characteristic plume radius b and velocity w in terms of a non-dimensional solution to the plume equations (Figure C4).



Figure C4. Non-dimensional plume radius and plume velocity computed for subsea gas blowouts (Fanneløp and Sjøen 1980). See text for definitions of the non-dimensional variables.

The non-dimensional variables are defined as follows:

 $X = z/H, B = b/2\alpha H, W = w/M,$ 

w

here 
$$\mathbf{M} = \left[\frac{\varphi_0(\lambda^2 + 1)}{2\alpha^2 H}\right]^{1/3}$$
 (10)

In these equations, H(m) is the pressure height,  $H = H_0 + H_a$ , where  $H_0$  is the water depth and  $H_a$  is the pressure height corresponding to 1 atmosphere (10 m),  $\varphi_0 = g \dot{V}_0 / \pi (m^4/s^3)$  is the buoyancy flux at the exit, where  $\dot{V}_0 (m^3/s)$  is the exit gas volume flow rate, while  $\alpha = 0.1$  and  $\lambda = 0.65$  are parameters related to plume dynamics.

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The basic blowout specific variables in these equations are water depth  $H_0$  and the exit gas volume flow rate  $\dot{V}_0$ . The latter may usually be derived from the oil discharge rate m (m<sup>3</sup>/s) and the Gas-to-Oil Ratio, GOR, representing the ratio between the released gas volume and oil volume at normal conditions (1 atmosphere and 15°C). Neglecting the minor correction due to the temperature difference, the ideal gas law gives:

$$\dot{V}_0 = m GOR H_o / H \tag{11}$$

The non-dimensional variable X at the sea surface is defined from the actual water depth, i.e.  $X = H_0/H$ . The corresponding non-dimensional values B and W may then be found from the graphs shown on figure C4, or from curve-fitted functions based on the original data. The actual plume variables (b and w) may then be determined by rescaling B and W with known X and M, the latter calculated from the exit volume flux (see equation 10).

It should be noted that this approach is valid under certain conditions that in general imply that effects of cross flow and stratification can be neglected. In practice, the concept should be limited to cases with significant gas volume fluxes (GOR > 50) from moderate water depths (< 300 m).

#### C.3 Evaporation

The evaporative loss is computed based on a pseudo-component approach, where the composition of the fresh oil is given by it's distillation curve (Reinhart and Rose, 1982). The rate of evaporation for component *i* is given by:

$$\frac{dQ_i(t)}{dt} = -\frac{\alpha(t)Q_i(t)M(t)p_i(t)}{\rho(t)h(t)RT}$$
(12)

where

- $Q_i(t)$  is the mass per unit area remaining of fraction *i* (kg/m<sup>2</sup>)
- $\alpha(t)$  is a wind dependent mass transfer coefficient (m/s)
- M(t) is molar weight of liquid mixture (kg/kmol)
- $p_i(t)$  is vapor pressure of fraction *i* (N/m<sup>2</sup>)
- $\rho(t)$  is density of liquid mixture (kg/m<sup>3</sup>)
- h(t) is oil film thickness (m)
- R is universal gas constant (J/kmol K)
- T is absolute temperature (K)

The wind dependent mass transfer coefficient  $\alpha(t)$  is calculated according to Amorocho and DeVries (1980):

 $\alpha(t) = C_d U(t)$ 

(13)

where

Cd is an air/sea drag coefficient

U(t) is wind speed (m/s)

The air/sea drag coefficient Cd is itself dependent on the wind speed:

$$C_{d} = \left(\frac{U^{*}}{U(t)}\right)^{2} \tag{14}$$

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with

$$U^{*} = \begin{cases} CU(t) & \text{for } U(t) < u_{1} \\ Cu_{1} + (Du_{1} - Cu_{1}) \frac{U(t) - u_{1}}{u_{2} - u_{1}} & \text{for } u_{1} \le U(t) \le u_{2} \\ DU(t) & \text{for } U(t) > u_{2} \end{cases}$$
(15)

where

C, D, u<sub>1</sub> and u<sub>2</sub> are constants (0.0323, 0.0474, 7 and 20 respectively).

# C.4 Oil-in-water dispersion

The model used for prediction of entrainment of oil from the sea surface is described in Reed et al. (1992), and is based on the empirical formulation of Delvigne and Sweeney (1988):

$$Q_{dt} = C^* D^{0.57} S F_{bu} d_1^{0.7} \Delta d \tag{16}$$

where

- Q<sub>di</sub> is the entrainment rate per unit surface area of oil droplets with diameters in the range  $d_i - \Delta d$  to  $d_i + \Delta d$  (kg/m<sup>2</sup>s)
- C\* is an empirically derived entrainment coefficient
- is dissipated wave energy per unit surface area (kg/s<sup>2</sup>) D
- S is fraction of sea surface covered by oil
- Fbw is fraction of sea surface covered by breaking waves per unit time (1/s)
- is mean diameter of particles in size class i (m) di
- Δd is particle diameter interval (m)

The empirical coefficient C\* is a function of the viscosity of the oil:

 $C^* = 4450v^{-0.4}$ 

where

v is the kinematic viscosity  $(m^2/s)$ 

The dissipated wave energy D is approximated as:

 $D = 0.0034 \rho_{-g} H_{h}^{2}$ 

where

is density of seawater (kg/m<sup>3</sup>) ρw

is gravitational acceleration (m/s<sup>2</sup>) g HL

is breaking wave height (m)

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The fraction F of sea surface covered by breaking waves is approximated as (Monahan and O'Muircheartaigh, 1980):

F = 3	$3 \cdot 10^{-6} U(t)^{1.5}$	(19)
where U(t)	s is wind speed (m/s)	

The fraction covered by breaking waves per unit time  $F_{bw}(s^{-1})$  is found by dividing F by the mean wave period:

$$F_{bu} = F/T_{m} \tag{20}$$

where

is the mean wave period (s) computed from wind speed, water depth and fetch (Appendix D) Tm

Currently, no rise times are calculated in the model. Resurfacing of oil is assumed to happen instantaneously for oil droplets with a diameter of more than a limiting value d<sub>lim</sub> = 370 µm, while smaller droplets are assumed to be permanently entrained, or to resurface behind the slick, forming a blue-sheen. Droplets are divided into 10 groups between 0 and the limiting droplet size.

# C.5 Water uptake and surface oil properties

The algorithms for water uptake and changes in oil properties are calibrated to laboratory weathering data. Laboratory weathering data relates the different oil properties to fraction evaporated. The following table shows an example of a lab data table for a North Sea crude.

Property	Fresh oli	150°C+ (≈ 1 hour)	200°C+ (≈ 1 day)	250°C+ (~ 1 week)
Boiling temp. (°C)	-	197	254	305
Volume topped (%)	0	14.6	27.8	36.9
Residue (wt. %)	100	88.1	76.9	67.2
Specific gravity (kg/l)	0.853	0,883	0.895	0.913
Pour point (°C)	-6	9	12	21
Flash point (°C)	-	51.2	93.9	126
Viscosity at 13°C (cP)	15	33	67	254
Viscosity of 50% emulsion (cP)		880	1420	2700
Viscosity of 75% emulsion (cP)	-	5300	8600	16000
Viscosity of max water (cP)	-	-	-	•
Max. water content (%)	-	90	85	72
Halftime for water uptake (hrs)	-	0.22	0.27	0.56
Stability ratio	-	0.85	0.86	1.0

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C.6 Water uptake

Water uptake W(t) is calculated as a step-wise exponential:

 $\mathcal{W}(t+\Delta t) = \mathcal{W}_{\mu}(t) - \left[\mathcal{W}_{\mu}(t) - \mathcal{W}(t)\right] 0.5^{\frac{\omega}{1/t}}$ (21)

where

W<sub>m</sub>(t) is maximum water content (%)

 $\Delta(t)$  is the time-step (s)

 $t_{1/2}$  is a wind dependent half time for water uptake (s)

The  $t_{1/2}$ -value and  $W_m(t)$ -function are derived from laboratory data which relates rate of water uptake and maximum water content to fraction evaporated. From this data, a reference half time  $t_{ref}$  for a reference wind speed of 10 m/s (in the field) is found as:

$$t_{ref} = C t_{iab} \tag{22}$$

where

 $t_{iab}$  is an average of half time values found in the laboratory for artificially weathered oil samples (s)

C is an empirical constant (4-6)

This reference half time is used to adjust  $t_{1/2}$  to other wind speeds based on data reported by Cormack (1983):

$$I_{1/2} = \left[\frac{1+U_{nq'}}{1+U_{(r)}}\right]^2 I_{nq'}$$
(23)

where

 $t_{ref}$  is found from equation (22) (s)

U<sub>ref</sub> is 10 (m/s)

U(t) is wind speed (m/s)

 $W_m$  as a function of fraction evaporated is found from lab data by assuming that maximum water content is linearly dependent on the fraction evaporated and fitting a straight line to the available data. By applying the evaporative loss found from integrating equation (12) to this line,  $W_m(t)$  is found.

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# C.7 Surface oil properties

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Four oil properties are predicted in the model. These are pour point, flash point, density and viscosity of water-free oil. These properties vary as curve fits with laboratory measured values and fraction evaporated as shown below (Johansen, 1991). Pour point (°C):  $P = e^{(a_p + b_p f)} - 273$ (24)Flash point (°C):  $F = e^{(a_F + b_F f)} - 273$ (25) Density (g/l):  $\rho_a = a_a + b_a f$ (26) Viscosity (cP):  $\mu_{a}=e^{(a_{\mu}+b_{\mu}f)}$ (27) where f is fraction evaporated (-)

 $a_p$ ,  $b_p$ ,  $a_F$ ,  $b_F$ ,  $a_\rho$ ,  $b_\rho$ ,  $a_\mu$ ,  $b_\mu$  are regression factors

By applying the evaporative loss found by integration of equation (12) to equations (24)-(27), the corresponding functions of time are found.

The density of emulsion  $\rho(t)$  is calculated as:

$$\rho(t) = \frac{W(t)\rho_w + [100 - W(t)]\rho_v(t)}{100}$$
(28)

where

W(t) is water content (%)

ρw is density of seawater (g/l)

 $\rho_o(t)$  is density of water-free oil (g/l)

The Mooney (1951) equation is used to calculate the emulsion viscosity  $\mu(t)$ :

$$\mu(t) = \mu_*(t) e^{\frac{aW(t)}{100 + bW(t)}}$$

(29)

where

W(t) is water content (%) a, b are empirical constants C\modelling projects\Documentation\User Guides\SINTEP OWM\SINTEF Oil Weathering Model 3.0\_for pdf.doc

The empirical constants, a and b, are according to Mackay (1980) a = 2.5 and b = 0.654. These are however in the model found by fitting equation (29) to lab data, with the optimal a between -10 and 5 and b between -2 and 0.9, found based on a least squares criterion.

### C.8 Arctic conditions

The weathering of oil changes significantly in the presence of sea ice. The present version of the SINTEF OWM contains field-derived algorithms adjusting spreading, natural dispersion, and water uptake (emulsification) as functions of fractional sheet- or block-ice cover (Singsaas et al, 1994). Two new variables are introduced:

I(t) is the percentage of ice cover [0, 100]

 $G_1(t)$  is the ice modification factor for spreading.

These variables are related as follows:

$$G_{1}(t) = \begin{cases} 1 - \left(\frac{I(t)}{100}\right)^{2} & 0 \le I(t) \le 95 \\ 0.1 & 95 < I(t) \end{cases}$$
(30)

 $G_1$  is applied as a reduction factor to the spreading length computed by the spreading algorithm (6), and was chosen to obtain a reasonable fit to the Marginal Ice Zone (MIZ) evaporation data (Sørstrøm, 1993; Singsaas et al, 1994).

One major impact of ice in water is the damping of wave energy. This entails a reduction in both oil-in-water dispersion and water-in-oil emulsion rates. A proper arctic model should account for this effect directly by incorporating ice terms in the wave equation. However, no such models are currently available; an indirect empirical approach is required. Thus, in accordance with the MIZ data, we have introduced an ice parameter,  $G_Z(t)$ , into the dispersion and emulsion formulae. This cubic factor severely reduces dispersion in ice-infested waters.

$$G_{2}(t) = \begin{cases} \left(1 - \frac{I(t)}{100}\right)^{3} & 0 \le I(t) \le 95 \\ 0 & 95 < I(t) \end{cases}$$
(31)

The expression for  $G_2$ , chosen to fit the MIZ water content (in the oil) data, serves as a multiplier in both the natural dispersion and emulsification equations (16) and (21) respectively.

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Appendix D: US Army Corps of Engineers Shallow Water Wave Equations

Following are the governing equations used in the SINTEF Oil Weathering Model to compute wave height (H) and period (T) as functions of wind speed (U<sub>A</sub>), depth (d), fetch (F), and gravitational acceleration (g). These equations are taken from the U.S. Army Corps of Engineers Shore Protection Manual (1984), Volume 1.



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Appendix E:Manuscript submitted to Journal of Environmental<br/>Software and Modelling: "The MMS/SINTEF Oil<br/>Weathering Model, Further Development and<br/>Applications" by R. Prentki, C. Smith, Ø. Johansen, P.<br/>Daling, M. Moldestad, K. Skognes, and M. Reed.

#### **Review version of paper presented at IMEMS 2004**

# The MMS/SINTEF Oil Weathering Model, Further Development and Applications

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### Abstract

The U.S. Minerals Management Service (MMS) is responsible for the development of environmental risk assessments, impact statements, review of contingency plans, and oil-spill response for offshore gas and oil leasing. An Oil-Weathering Model (OWM) is heavily used to support fulfillment of these responsibilities.

In the Alaska OCS Region, numerous estimates of oil-spill fate and behavior are derived from the OWM. The model provides analysts with a common, quantitative set of spill scenarios. The OWM is used to estimate whether State and Federal water quality standards and criteria would be exceeded by a spill, over what area, and for how long. The model calculates the thickness and persistence of a slick through time, and how long the lighter, but most toxic components remain in the oil slick. The model is used to distinguish the effects of larger and smaller spills, for example between the effects of an average tanker spill versus an average pipeline spill. The *in situ* viscosity and degree of emulsification provided by the model are used in assessing the mitigation by and effectiveness of oil spill countermeasures such as mechanical recovery, dispersants, and *in situ* burning.

In the Gulf of Mexico Region, the OWM is more frequently used in environmental assessments to evaluate oil-spill contingency plans and the reliability of associated oil-spill models. The OWM is critical to the latter evaluation because, unlike most oil-spill models, the OWM incorporates specific chemistry of individual crude oils and petroleum products.

This paper describes experience with several applications in both sub-arctic and subtropical regions of U.S. coastal waters. Software availability The SINTEF Oil Weathering Model is available from

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#### 1. Introduction

The U.S. Minerals Management Service (MMS) is responsible for the development of environmental risk assessments, Environmental Impact Statements, review of contingency plans, and oil-spill response for offshore gas and oil leasing. The MMS/SINTEF Oil-Weathering Model (OWM) is a heavily used to support fulfillment of these responsibilities.

In the Alaska OCS Region, numerous estimates of oil-spill fate and behavior are derived from the OWM. The model provides analysts with a common, quantitative set of spill scenarios. The OWM is used to estimate whether State and Federal water quality standards and criteria would be exceeded by a spill, over what area, and for how long. The model calculates the thickness and persistence of a slick through time. How long the lighter, but most toxic components remain in the oil slick is estimated from the evaporation rate.

The model is used to distinguish the effects of larger and smaller spills, for example between the effects of an average tanker spill versus an average pipeline spill. The *in situ* viscosity and degree of emulsification provided by the model are used in assessing the mitigation by and effectiveness of oil spill countermeasures such as mechanical recovery, dispersants, and *in situ* burning.

In the Gulf of Mexico Region, the OWM is more frequently used in environmental assessments to evaluate oil-spill contingency plans and the reliability of associated oil-spill models. The OWM is critical to the latter evaluation because, unlike most oil-spill models, the OWM incorporates specific chemistry of individual crude oils and petroleum products.

The SINTEF OWM is used by Norwegian authorities and by Norwegian and international oil companies to predict the weathering behavior of crude oils and fuel oils at prevailing conditions. The weathering predictions are an useful tool in contingency analysis and planning for determining the most effective response and for Environmental Impact Assessment studies. In case of an oil spill, the weathering predictions form the basis for rapid and right decision-making during the combat operation.

# 2. Overview of the model

When a crude oil is spilled at sea it is subjected to several processes which rapidly alter its composition and therefore physical properties and behavior. The most important processes governing the overall characteristics of oil spilled at sea are:

- spreading.
- · evaporation of the more volatile components,
- · water-in-oil emulsion formation, and
- natural dispersion.

These processes occur simultaneously and the rate and extent to which they proceed depend on the chemical composition of the oil and prevailing conditions such as temperature and sea state. All these processes are inter-related. Other processes such as photo-oxidation, dissolution, bio-degradation and sedimentation also influence the fate and behavior of spilled oil in the longer term.

The chemical data generated through a SINTEF oil weathering and dispersibility study are used as input to the OWM, for predictions of the oil's behavior at sea under different weather conditions.

The weathering study will supply basic information useful for

- modeling the range of drift and spreading of potential oil spills during different seasons;
- evaluating the time window for and effectiveness of chemical dispersant application;
- planning and carrying out mechanical oil spill response actions;
- quantifying the environmental benefit of alternative response activities.

Examples of addition information coming out of the weathering studies, and useful in oil spill contingency planning, are:

- offectiveness of emulsion breakers, to assist in on-board separation of water from oil;
- establishment of exclusion zones based on the ignition point of the oil as a function of weathering time;
- changes in the viscosity of the emulsion over time, to achieve most effective oil recovery.

Oil weathering in the laboratory consists of the following sub-activities:

- Artificial evaporation (topping) and photo-oxidation of the fresh crude oil to give 4 different residues.
- Water-in-oil emulsification of the 4 residues to give a total of up to 12 different emulsified residues (Figure 1).
- Physical-chemical analyses of the artificially produced samples (oil residues and emulsions)

To isolate the influence of the different weathering processes (i.e. evaporative loss, photolysis and water-in-oil emulsification), the weathering of the oils are carried out using a systematic, step-wise procedure established at SINTEF (Daling et al., 1990, 1997). The weathering process is illustrated in Figure 1.



Figure 1 Flow chart for weathering of a crude oil

The OWM relates oil properties to a chosen set of conditions (oil/emulsion film thickness, sea state and sea temperature) and predicts the changes in these properties and behavior on the sea surface. The structure of the OWM is schematically shown in Figure 2.



Figure 2 Schematic diagram of the input data to the SINTEF OWM and the predicted output oil properties

#### User-defined Input to the SINTEF OWM

#### Spill scenario

A spill scenario (e.g. sub-sea or surface blowout, tanker spill, pipeline leakage etc.) is specified by entering the release rate (or total amount) and duration into the Graphical User Interface. For underwater releases the gas-oil ratio (GOR) is also required together with the discharge depth.

# Terminal oil film thickness

In the SINTEF OWM the oils are categorized into condensates, low emulsifying crudes, emulsifying crudes, heavy bunker fuels or refined distillates based on experimental results obtained in the bench-scale testing. A default for the terminal w/o-emulsion film thickness is given for each category of oil in the model.

#### 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 at the average summer temperature the other at the average winter temperature for the area of interest.

# Wind speed

Wind speed can be entered either as a set of constant values, for comparing situations, or as a variable time series. Wind is used in both the evaporation and natural dispersion computations, the latter being dependent on the computed wave field. The user can enter wind fetch in the four primary compass directions, such that the model computations for significant wave height and period account for the presence of land or ice fields. The relationship between the wind speed and the significant wave height is based on the US Army Corps of Engineers (1984) calculation procedures. Example values of wave heights for fully developed seas shown in Table 1.

# Table 1. The relationship between the wind speed and the significant wave heights (for fully developed sea) used in the SINTEF OWM

Wind speed [m/s]	Beaufort wind	Wind type	Wave height [m]	Wave height [ft]
2	2	Light breeze	0.1-0.3	0.2-0.60
5	3	Gentle to moderate breeze	0.5-0.8	1-1.5
10	5	Fresh breeze	1.5-2.5	3-5
15	6-7	Strong breeze	3-4	6-8

### Input data for the SINTEF OWM

In the bench scale 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 weathering data obtained in the bench-scale testing are processed and used as input for the SINTEF OWM. The following oil/emulsion properties obtained in the bench-scale testing are used in the model:

- specific gravity
- pour point
- flash point
- viscosities of fresh and 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 half-life-time)

### Weathering properties related to response

The efficiency of various oil spill combat methods (e. g. mechanical recovery, dispersion and/or burning) depends greatly on the physical and chemical properties of the oil at the time of action. When planning the most effective response the predictions charts provide important information.

#### Mechanical response

Past experiences from Norwegian field trials have shown that the effectiveness of many mechanical clean up operations is reduced due to a high degree of leakage of the confined oil or w/o-emulsion from the oil spill boom (especially in high current). This leakage is especially pronounced if the viscosity of the oil or the w/o-emulsion is lower than 1000 cP at a shear rate of  $10s^{-1}$  (Nordvik *et al.*, 1992). The **lower viscosity limit** for an optimal mechanical clean up operation has therefore been set to 1000 cP.

The upper viscosity limit for an optimal mechanical clean up operation depends on the type of skimmer used. For some disk-skimmers the collection capacity is reduced significantly at w/o-emulsion viscosities exceeding 10 000 cP (ITOPF, 1986), however ITOPF, 1986 does not state the shear rate.

Recent tests performed by SINTEF using a weir skimmer show that the efficiency may be reduced for semi-solidified oils, i. e. oils with a large wax content and high pour point values, and for oils with viscosities between 15000 and 20000 cP (Leirvik et.al.,2001).

#### **Chemical dispersion**

A dispersibility methodology, based on the viscosity increase due to weathering, was developed at SINTEF (Daling and Strom, 1999) in order to determine the window of opportunity for the effective use of dispersants for different oils. Chemical dispersibility testing was not included in this study. General limits for dispersibility based on pour point values are given in

Table 2. These values are not valid for all oils and situations, and should only be regarded as guidelines.

### Table 2 The chemical dispersibility criteria used in the SINTEF OWM based on pour points

Pour point [°C]	Chemical dispersibility				
< 5°C above the sea temperature	Dispersible				
5-15°C above the sea temperature	Reduced dispersibility				
> 15°C above the sea temperature	Not dispersible				

### 3. Recent model developments

Version 3.0 of the OWM was completed at the end of June, 2004. In addition to numerous improvements in the user interface, this version includes the following improvements over 2.0:

- possibility for subsurface as well as surface releases;
- internal computation of initial film thickness, based on release rate and duration;
- New spreading algorithm supporting both surface and underwater releases, with improved stability and better detection of erroneous input values;
- New oil type query filters in both OWM and the Oil Database Editor, allowing filtering on ranges of values for API gravity, specific density, and pour point;
- Capability to add/delete Data Source, Geographical Area, and Product in the Editor as documented in the User Manual how to achieve this during editing of oil information;
- New \*.TX2 data results file for easy EXCEL import;
- Enabled multi-selection capability in temperature and wind lists, and made Add and Delete buttons more dynamic to facilitate clearing the entire list at once:
- · Revised User's Manual for Version 3.0.

The spreading mechanisms for instantaneous releases and continuous releases are different. Instantaneous releases will spread radially, while oil released continuously will spread laterally (i.e. cross-current). This difference in spreading behaviour will affect other weathering properties e.g. evaporation and natural dispersion. Version 2.0 of the model only accounts for lateral spreading (i.e. all releases are treated as continuous), but in Version 3.0, the spreading of instantaneous and continuous spills is treated differently. Also, a calculation of the surface spreading for sub surface releases in shallow to moderate water depths (depth less than e.g. 300 m) is included. This calculation requires input of gas-to-oil ratio (GOR) and depth in addition to release rate

The user may specify a surface or underwater release, the latter presumed to be a subsea blowout, where gas is released together with oil. In the former case, the spreading of the surface slick will be governed by gravity forces, while in the latter case the spreading will be governed by the radial surface flow induced by the surfacing gas bubble plume.

Formulas for gravity spreading were established in the 1980's by Fay and Fannelop, but these formulas distinguish between instantaneous releases and continuous releases. Since in practice it is difficult top make a clear distinction between such cases, a unified algorithm has been derived that works in the general case. The user simply specifies the spill in terms of duration and released amounts of oil (or release rate), and the model sorts out the dominating spreading case. This is done by introducing spreading along two axes; the major axis oriented in the wind direction and the minor in the cross-wind direction. Gravity spreading is supposed to act along both axes; while wind induced drift will cause an additional elongation along the major axis. The spreading of strongly elongated slicks will approach the spreading rates determined by Fay's formula for lateral spreading, while the spreading of a circular slick will approach the spreading rates determined by Fay's formula for instantaneous releases, while more or less elongated slicks will spread at intermediate rate, eliminating the need for a default or user specified initial thickness in the former version of the OWM.

In case of underwater releases, the user must provide water depth and Gas-to-Oil Ratio (GOR) in addition to oil release rate. This is used to calculate the velocity and radius of the surfacing gas bubble plume, and on that basis the source strength of the radial outflow of water in the surface layer. The plume parameters are computed from a non-dimensional solution of the plume equations (Fanneløp and Sjøen 1980), while the source strength is found by an equation derived by the same authors. The film thickness is determined as the ratio between the oil release rate and the source strength. This method is justified for blowouts with significant gas releases (GOR  $\geq$  50) from shallow to moderate water depths (< 300 m), where the mass flow rate of gas may be assumed to be unchanged during the rise to the surface. However, blowouts with small gas flow rates or blowouts from large water depths will be more sensitive to cross currents and stratification in the water masses. Gas bubbles may consequently leak out of the deflected plume and/or dissolve in the ambient water, causing a significant reduction in the gas related buoyancy flux.

The model calculates four physical processes; spreading, evaporation, oil-in-water dispersion and water-in-oil emulsion formation.

#### Spreading of surface spills

#### Force balance

The force balance equations may be derived for an oil slick in a channel with a counter flow in the underlying water, i.e. corresponding to an oil slick confined by a boom (Figure 3). On this basis, a relationship is obtained between the density and volume of oil confined by the boom, and the strength of the counter current.



#### Figure 3. Idealised view of oil spreading against a counter flow in a channel

The pressure force  $F_p$  is due to the density difference between oil and water:

$$F_{\mu} = \frac{1}{2}Bh^2\rho g^{\prime}$$
(1)

where B (m) is the width of the channel, h (m) is the oil film thickness,  $\rho$  (kg/m<sup>3</sup>) is the oil density, and g' (m/s<sup>2</sup>) is the reduced gravity:  $g' = g(\rho_* - \rho)/\rho_*$ .

The shear force  $F_x$  is due to the friction between the oil and water in motion:

$$F_{s} = B X \mu_{u} \frac{U}{\delta}$$
(2)

where X (m) is the length of the oil layer,  $\mu_{u}$  (Ns/m<sup>2</sup>) is the dynamic viscosity of water, U (m/s) is the water velocity, and  $\delta$  (m) is the thickness of the boundary layer in the water. The latter may be expressed by the Blaussius formula for flow around a flat plate:

$$\delta = 3v_w^{1/2}\sqrt{\frac{X}{U}}$$
(3)

where  $v_{\perp}$  (m<sup>2</sup>/s) is the kinematical viscosity of water.  $v_{\perp} = \mu_{\perp} / \rho_{\perp}$ .

### Spreading equation

By taking into account that the confined oil volume is V = B X h, substituting for the boundary layer thickness, and equating the two forces, the following expression is derived for the equilibrium length of the oil layer:

$$X = \left[\frac{3}{2}\frac{V^{2}\rho g^{*}}{B^{2}}\right]^{\frac{2}{5}} (\rho_{w}\mu_{w})^{-\frac{1}{5}}U^{-\frac{3}{5}}$$

If the oil is spreading on stagnant water, the velocity U may be presumed to represent the spreading velocity, i.e. U = dX/dt. Equation 4 will then be transformed into a separable differential equation in t with the solution:

$$X(t) = 1.3 \left( q^2 \rho g' \right)^{\frac{1}{4}} \left( \rho_x \mu_y \right)^{\frac{1}{3}} t^{\frac{3}{8}}$$
(5)

(4)

where q = V/B, i.e. volume of oil per unit width of the channel.

By use of the mass conservation equation q = Xh, equation 5 may alternatively be expressed in terms of the film thickness h, and be transformed into a suitable differential form which may account for changes in the oil properties with time:

$$\frac{d}{dt}X^{4/3} = 1.75 \left(h^2 \rho g'\right)^{\frac{2}{3}} \left(\rho_w \mu_w\right)^{\frac{1}{3}}$$
(6)

This differential equation may be combined with any oil mass conservation equation relating *h* and *X* to the oil volume, i.e. any equation of the type V = f(x, h, X). It should be noted that a conservation equation may also account for changes in the oil volume with time due to evaporation or emulsion formation. Excluding this for the moment, we may illustrate the concept by a few examples:

- For lateral spreading of a slick formed from a continuous surface leak with a discharge rate m (m<sup>3</sup>/s) in a steady surface current of velocity u (m/s), the oil conservation equation may be written as q = m/u = 2hX, where X represents the half width of the slick.
- For an instantaneous spill, the conservation equation may be written as  $V = \pi X^2 h$ , where  $V (m^3)$  is the spilled oil volume and X represents the radius of the circular slick.
- For a continuous leak on calm water, the same equation applies, but V will be increasing with time; V = m t, where m (m<sup>3</sup>/s) is the release rate.

For a continuous leak from a point source in a steady current, the oil volume will also increase in proportion with time. In this case, gravity spreading will take place along two axis (cross-stream and downstream), but the cross-stream (lateral) component is conventionally presumed to dominate as the slick is extended downstream due to advection with the current. This assumption may be valid in cases with relatively strong currents and moderate spill rates. For weak currents and large spill rates, gravity spreading may have to be considered along both axis to get a realistic picture (see Figure 4).



Figure 4. Spreading of an oil slick from a continuous oil leak in a steady current. The slick may be defined in terms of  $X_1$  and  $X_2$ , representing the half-axes of an elliptical slick, with  $X_1$  aligned in the downstream direction. The oil conservation equation may then be expressed as  $V = mt = h\pi X_1 X_2$ , where m ( $m^3/s$ ) is the spill rate. The progression of  $X_1$  and  $X_2$  may be computed by equation 7, while including an extra downstream elongation due to the current ( $dX_1 = 0.5 \ u \ dt$ ) in the period of time when the oil is leaking.

The approach sketched in Figure 4 is in fact unifying all the "classical" Fay spreading problems, from instantaneous spills, via continuous spills on calm water to continuous spills in a steady current. Figure 5 illustrates this concept for two cases. The same amounts of oil are released in both spills (2400 m<sup>3</sup>), but the duration of the release is 2 hours in the first case (a), and 24 hours in the second case (b). The oil density is 850 kg/m3 in both cases, and the surface current is presumed to be moderate (10 cm/s). The results show that the calculations fro the first case approaches Fay's equation for radial spreading on calm water, while the second case approaches Fay's equation for lateral spreading of a continuous spill in a steady current.



Figure 5. Gravity spreading computed with equation 7 for two cases: 2400 m<sup>3</sup> of oil released in 2 hours (top), and 2400 m<sup>3</sup> released in 24 hours (bottom). The calculations are made with an oil density of 850 kg/m<sup>3</sup>. The coloured lines depict the corresponding results of spreading equations for instantaneous releases ("Radial Fay"), and lateral spreading for continuous releases in a steady current ("Lateral Fay").

### Surface spreading of subsea blowouts

The surface spreading of oil from a subsea blowout is governed by the generation of a rising gas bubble plume that entrains ambient water. Surfacing of the entrained water produces a radial outflow at the sea surface. The oil will be carried to the surface as fine oil droplets dispersed in the entrained water. A surface slick will form as the dispersed oil droplets settle out of the radial outflow of entrained water.

According to Fanneløp and Sjøen (1980), the surface velocity distribution in the radial outflow can be approximated by a source flow equation:

$$U(r) = \frac{S}{2\pi r}$$
(7)

where  $S(m^2/s)$  is the source strength.

Under such conditions – provided that all the oil comes to the surface, the oil film thickness h (m) may be estimated from the source strength and the oil spill rate m (m<sup>3</sup>/s):

Fanneløp and Sjøen (op cit) also show that the source strength S depends on the characteristic radius b (m) and velocity w (m/s) of the surfacing plume:

 $S = k \pi b w$ where k = 4.86 is a constant.

h = m/S



Figure 6. Non-dimensional plume radius and plume velocity computed for subsea gas blowouts (Fanneløp and Sjøen 1980). See text for definitions of the non-dimensional variables.

The same authors also presented a basis for establishing the characteristic plume radius b and velocity w in terms of a non-dimensional solution to the plume equations (Figure 6). The non-dimensional variables are defined as follows:

X = z/H, B = b/2
$$\alpha$$
H, W = w/M,  
where M =  $\left[\frac{\varphi_0(\lambda^2 + 1)}{2\alpha^2 H}\right]^{1/3}$ 

In these equations, H(m) is the pressure height,  $H = H_0 + H_a$ , where  $H_0$  is the water depth and  $H_a$  is the pressure height corresponding to 1 atmosphere (10 m),  $\varphi_0 = g \dot{V}_0 / \pi$  (m<sup>4</sup>/s<sup>3</sup>) is the buoyancy flux at the exit, where  $\dot{V}_0$  (m<sup>3</sup>/s) is the exit gas volume flow rate, while  $\alpha = 0.1$  and  $\lambda = 0.65$  are parameters related to plume dynamics.

(10)

The basic blowout specific variables in these equations are water depth  $H_D$  and the exit gas volume flow rate  $\dot{V}_0$ . The latter may usually be derived from the oil discharge rate m ( $m^3/s$ ) and the Gas-to-Oil Ratio, GOR, representing the ratio between the released gas volume and oil volume at normal conditions (1 atmosphere and 15°C). Neglecting the minor correction due to the temperature difference, the ideal gas law gives:

$$\dot{V}_{n} = m GOR H_{n} / H \tag{11}$$

The non-dimensional variable X is defined from the actual water depth. The corresponding non-dimensional values B and W may then be found from the graphs shown on Figure 6, or from curve-fitted functions based on the original data. The actual plume variables (*b* and *w*) may then be determined by rescaling B and W with known X and M, the latter calculated from the exit volume flux (see equation 10).

It should be noted that this approach is valid under certain conditions that in general implies that effects of cross flow and stratification can be neglected. In practice, the concept should be applied to cases with significant gas volume fluxes (GOR > 50) from moderate water depths (< 300 m).

# 4. Example applications within MMS

The Alaska OCS Region uses the oil weathering model to set up generalized weathering scenarios in environmental impact statements to guide the impact assessment. To judge the effect of an oil spill, the model is used to estimate information regarding how much oil evaporates, how much oil is dispersed, and how much oil remains after a certain time period. Weathering estimates are derived from modeling results from the SINTEF Oil Weathering Model (OWM) for time periods up to 30 days. Below are presented the assumptions used to set up the weathering scenario, the uncertainties and the results from an oil spill scenario for the Cook Inlet Planning Area Oil and Gas Lease Sales 191 and 202 Environmental Impact Statement (USDOI, MMS 2003; ).

The following assumptions are made regarding oil weathering in a Cook Inlet crudeoil spill:

- The crude oil properties will be similar to Cook Inlet crude.
- The size of the spill is 1,500 or 4,600 barrels.
- The wind, wave, and temperature conditions are as described.

Melt-out spills occur into 50% ice cover.

- · The properties predicted by the model are those of the thick part of the slick.
- The spill occurs over a short period of time.

Actual conditions in a real spill event will of course be different from those assumed, but these scenarios provide our best estimate of the behavior and fate of potential releases.



Figure 7 Map of Cook Inlet in the Gulf of Alaska

Table 3 through Table 6 show the results for Cook Inlet crude-oil spills using the SINTEF model. The SINTEF OWM changes both oil properties and physical properties of the oil. The oil properties include density, viscosity, pour point, flash point, and water content. The physical processes include spreading, evaporation, oil-in-water dispersion, and water uptake. The SINTEF OWM Version 2.0 performs a 30-day time horizon on the model-weathering calculations but with a warning that the model is not verified against experimental field data for more than 4-5 days. The SINTEF OWM has been tested extensively with results from three full-scale field trials of experimental oil spills (Daling and Strom, 1999).

The SINTEF OWM does not incorporate the effects of the following:

- beaching,
- containment,
- photo-oxidation,
- microbiological degradation,
- adsorption to particles, and
- encapsulation by ice.

We simulated three general scenarios: two in which the oil spills into open water during summer or winter and one in which the oil spills into 50% ice cover during winter. We assume open water can occur year-round depending on the area of lower Cook Inlet, and we also assume that winter occurs October to April. For open water and ice, we model the weathering of the 1,500- or 4,600-barrel spill as if they are instantaneous spills. We report the results at the end of 1, 3, 10, and 30 days. Table 3 through Table 6 summarize the results we assume for the fate and behavior of Cook Inlet crude oil in our analysis of the effects of oil on environmental, economic and socio-cultural resources. In our analysis, we assume the following fate of the crude oil without cleanup. After 30 days in open water or ice: 33-36% evaporates, 13-62% disperses, and 5-52% remains.

#### Table 3 Fate and Behavior of a Hypothetical Open-Water Oil Spill, 1,500 Barrels in Size, from a Platform in Lower Cook Inlet

Description	Summer Spill <sup>1</sup> (Time after spill in days)				Winter Spill <sup>2</sup> (Time after spill in days)			
	1	3	10	30	1	3	10	30
Oil Remaining (%)	76.9	69.3	53.4	29.2	73.1	59.5	29.8	5.4
Oil Dispersed (%)	1.4	4.0	15.1	35.7	4.0	13	38.8	61.5
Oil Evaporated (%)	21.7	26.7	31.5	35.1	22.9	27.5	31.4	33.1
Thickness (mm)	2.3	1.3	1.0	1.0	1.8	1.1	1	1
Discontinuous Area (km <sup>2</sup> ) <sup>3</sup>	8	32	150	621	8	31	77	618
Estimated Coastline Oiled (km)4	23					17		

Notes:

Calculated with the SINTEF oil-weathering model Version 2.0 of Reed et al. (2000) and assuming a Cook Inlet Crude (S.L. Ross, 2001).

<sup>1</sup>Summer (April-September), 11.5 knot wind speed, 8.8 °C, 1-meter-wave height. Average Weather Marine Area A, Brower et al. (1988).

<sup>2</sup>Winter (October-March), 16-knot wind speed, 4.76 °C, 1.8-meter-wave height. Average Weather Marine Area A, Brower et al. (1988).

<sup>3</sup> Calculated from Equation 6 of Table 2 in Ford (1985) and is the discontinuous area of a continuing spiil or the area swept by an instantaneous spiil of a given volume.
Calculated from Equation 17 of Table 4 in Ford (1985) and is the result of stepwise multiple

<sup>4</sup> Calculated from Equation 17 of Table 4 in Ford (1985) and is the result of stepwise multiple regression for length of historical coastline affected.

#### Table 4 Fate and Behavior of a Hypothetical Broken-Ice Oil Spill, 1,500 Barrels in Size, from a Platform in Lower Cook Inlet

	Winter Spill <sup>1</sup> (Broken Ice) (Time after spill in days)						
Description	1	3	10	30			
Oil Remaining (%)	77.4	71.1	61.6	48			
Oil Dispersed (%)	0.9	2.6	6.7	15.8			
Oil Evaporated (%)	217	26.3	31.7	36.2			
Thickness (mm)	3.2	1.9	1	1			
Discontinuous Area (km <sup>2</sup> ) <sup>2</sup>	8	31	77	618			
Estimated Coastline Oiled (km)3			17				

Notes:

Calculated with the SINTEF oil-weathering model Version 2.0 of Reed et al. (2000) and assuming a Cook Inlet Crude (S.L. Ross, 2001).

1Winter (October-March), 16-knot wind speed, 4.76 oC, 1.8-meter-wave height. Average Weather Marine Area A, Brower et al. (1988).

2 Calculated from Equation 6 of Table 2 in Ford (1985) and is the discontinuous area of a continuing spill or the area swept by an instantaneous spill of a given volume.

3Calculated from Equation 17 of Table 4 in Ford (1985) and is the result of stepwise multiple regression for length of historical coastline affected. Table 5 Fate and Behavior of a Hypothetical Open-Water Oil Spill, 4,600 Barrels in Size, from a Offshore Pipeline in Cook Inlet

The state is a state	(Tim	Summe after s	er Spill spill in d	iays)	Winter Spill <sup>2</sup> (Time after spill in days)			
Description	1	3	10	30	1	3	10	30
Oil Remaining (%)	77.8	70.6	55.4	30.2	74.3	62.2	32.2	5.8
Oil Dispersed (%)	1.1	3.3	13.4	34.7	3.3	10.8	36.6	61
Oil Evaporated (%)	21.1	26.1	31.2	35.1	22.4	27	31.2	33.2
Thickness (mm)	2.9	1.6	1	1	3.4	1.6	1	1
Discontinuous Area (km <sup>2</sup> ) <sup>3</sup>	13	56	265	1100	13	55	263	1094
Estimated Coastline Oiled (km)4	38						28	

Notes:

Calculated with the SINTEF oil-weathering model Version 2.0 of Reed et al. (2000) and assuming a Cook Inlet Crude (S.L. Ross, 2001).

1Summer (April-September), 11.5 knot wind speed, 8.8 oC, 1-meter-wave height. Average Weather Marine Area A, Brower et al. (1988).

2Winter (October-March), 16-knot wind speed, 4.76 oC, 1.8-meter-wave height. Average Weather Marine Area A, Brower et al. (1988).

3 Calculated from Equation 6 of Table 2 in Ford (1985) and is the discontinuous area of a continuing spill or the area swept by an instantaneous spill of a given volume.

4 Calculated from Equation 17 of Table 4 in Ford (1985) and is the result of stepwise multiple

regression for length of historical coastline affected.

Table 6 Fate and Behavior of a Hypothetical Broken-Ice Oil Spill, 4,600 Barrels in Size, from a Offshore Pipeline in Cook Inlet

	Winter Spill' (Broken Ice) (Time after spill in days)							
Description	1	3	10	30				
Oil Remaining (%)	79.3	73.6	65.9	52				
Oil Dispersed (%)	0.6	1.6	4	12.5				
Oil Evaporated (%)	20.1	24.8	30.1	35.5				
Thickness (mm)	5.6	3.3	1.1	1				
Discontinuous Area (km <sup>2</sup> ) <sup>2</sup>	13	33	263	1,094				
Estimated Coastline Oiled (km)3	28							

Notes:

Calculated with the SINTEF oil-weathering model Version 2.0 of Reed et al. (2000) and assuming a Cook Inlet Crude (S.L. Ross, 2001).

1Winter (October-March), 16-knot wind speed, 4.76 oC, 1.8-meter-wave height. Average Weather Marine Area A, Brower et al. (1988).

2 Calculated from Equation 6 of Table 2 in Ford (1985) and is the discontinuous area of a continuing spill or the area swept by an instantaneous spill of a given volume.

3Calculated from Equation 17 of Table 4 in Ford (1985) and is the result of stepwise multiple regression for length of historical coastline affected.

# 5. Conclusions and possible future extensions

In general, the MMS has a relatively long timeframe of interest regarding oil weathering, through at least 30 days or as long as a slick persists. Furthermore, there is surprisingly little empirical data for how long a spill persists as an identifiable slick. We would like to see this end point better tracked and reported in real spill events. MMS is working to improve data and algorithms for cold climate weathering. Using a range of Alaska oil types, looking at:

- · Evaporation rates down to very cold temperatures (-40).
- · Evaporation rates in snow cover
- · Spreading of oil under and above ice and equilibrium thicknesses
- · Brine channel migration
- · Water-in-Oil emulsification in broken ice wave field

These and other improvements are anticipated in future versions of the oil weathering model described here.

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