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# Report

## Compilation report for shoreline activities in Phase I

Coastal Oil Spills - JIP - report no. 19 – C2/C3/C4

**Author(s)**
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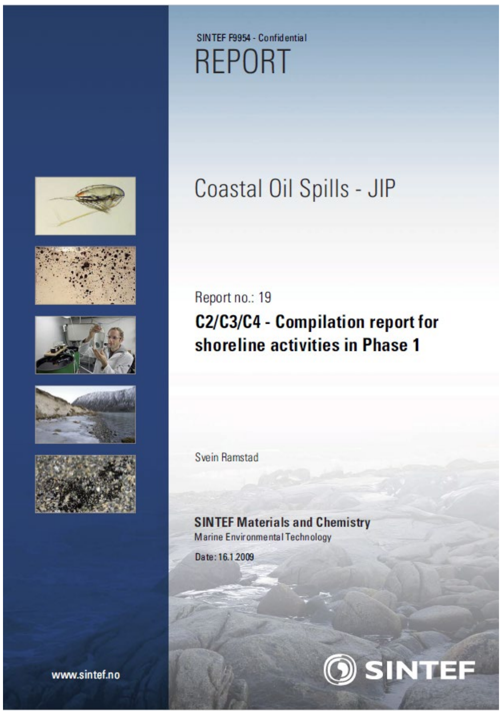


**SINTEF Ocean AS**

2019-03-04

SINTEF

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# Report

# Compilation report for shoreline activities in Phase I

Coastal Oil Spills - JIP - report no. 19 – C2/C3/C4

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**ABSTRACT**

Downgrading of SINTEF report STF F9954 originally issued on 2009-01-16 in accordance with the 5 year exclusive rights agreement in the JIP Project Contract.

The report was downgraded by SINTEF Ocean AS, department of Environment and New Resources.

The original report is enclosed.



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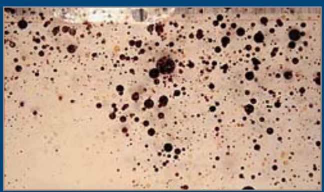
# REPORT



## Coastal Oil Spills - JIP

Report no.: 19

# C2/C3/C4 - Compilation report for shoreline activities in Phase 1

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Date: 16.1.2009

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# SINTEF REPORT

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TITLE

**Compilation report for shoreline activities in Phase I Coastal Oil Spill JIP. Report No. 19**

AUTHOR(S)

Svein Ramstad

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Eni Norge AS, A/S Norske Shell and StatoilHydro ASA

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ABSTRACT

In the Coastal Oil Spill JIP a large number of activities related to natural processes in the acute and restoration phase on shorelines have been studied. Each of these activities are reported in separate technical reports. In the present report, these reports are merged together, however, without the appendences.

| KEYWORDS | ENGLISH | NORWEGIAN |
|---|---|---|
| GROUP 1 | Oil | Olje |
| GROUP 2 | Environment | Miljø |
| SELECTED BY AUTHOR | Shoreline | Strand |
| | Natural processes | Naturlige prosesser |
| | Laboratory and meso-scale studies | Lab og meso-skala studier |

# TABLE OF CONTENTS

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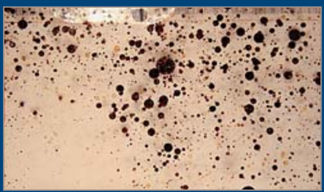
# REPORT



## Coastal Oil Spills - JIP

Report no.: 14

# C2.2 - Meso-scale weathering and characterisation of crude oils

Svein Ramstad, Jane H. C. Øksenvåg, Tor Arne Oltedal, Bror Johansen and Frode Leirvik

**SINTEF Materials and Chemistry**
Marine Environmental Technology

Date: 2008-12-19

SINTEF

# SINTEF REPORT

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TITLE

**C2.2 - Meso-scale weathering and characterisation of crude oils**

**Coastal Oil Spill JIP Report no 14**

AUTHOR(S)

Svein Ramstad, Jane H. C. Øksenvåg, Tor Arne Oltedal, Bror Johansen and Frode Leirvik

CLIENT(S)

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ABSTRACT

After an accidental release of crude oils from offshore installation, the oil will undergo a number of weathering processes before reaching coastal zone, including evaporation, emulsification and photo-oxidation. A typical drifting time will be ½-1 week for the oil fields along the Norwegian coast. After this period the crude oil will be similar to a 250°C+ residue and have a maximum water uptake. This was decided to be the standard weathering degree for the selected crude oils in the Coastal Oil Spill JIP. For more easy comparison of results from the different experimental studies in the program the oil properties should be the same for all experiments. The standard laboratory scale weathering processes were scaled up;

- Evaporation; Two barrels of the crude oils were evaporated to a 250°C+ residue in a meso-scale system (95°C, circulation/spraying).
- Emulsification; Meso-scale emulsification of the oil was performed for each study in a standard concrete-mixer system (maximum of 25L emulsion).
- Photo-oxidation; 2L batches of oil was exposed to simulated day-light irradiation.

The processes were documented by chemical analysis and physical properties.



| KEYWORDS | ENGLISH | NORWEGIAN |
|---|---|---|
| GROUP 1 | Environment | Miljø |
| GROUP 2 | Oil | Olje |
| SELECTED BY AUTHOR | Weathering | Forvitring |
| | Meso-scale | Meso-skala |
| | | |

# TABLE OF CONTENTS

# 1 Summary

After an accidental release of crude oils from offshore installation, the oil will undergo a number of weathering processes before reaching coastal zone, including evaporation, emulsification and photo-oxidation. A typical drifting time will be ½-1 week for the oil fields along the Norwegian coast.

After this period the crude oil will be similar to a 250°C+ residue and have a maximum water uptake. This was decided to be the standard weathering degree for the selected crude oils in the Coastal Oil Spill JIP.

For more easy comparison of results from the different experimental studies in the program the oil properties should be the same for all experiments. The standard laboratory scale weathering processes were scaled up;

- Evaporation; Two barrels of the crude oils were evaporated to a 250°C+ residue in a meso-scale system (95°C, circulation/spraying), These oil residues are the basis for the present and possible future studies.
- Emulsification; Meso-scale emulsification of the oil was performed for each study in a standard concrete-mixer system (maximum of 25L emulsion).
- Photo-oxidation; 2L batches of oil was exposed to simulated day-light irradiation.

The processes were documented by chemical analysis and physical properties.

The evaporated oil residues were used in all experimental studies. The oil has been stored in suitable size containers until use (typically 5L).

Preparation of emulsions in the concrete mixer system was done for meso-scale basin studies, and the rotary seperatory funnel was used for the laboratory scale experiments.

## 2 Introduction

This project has been a part of phase 1 in the Coastal Oil Spills JIP. The research projects in the JIP have been focused on the fate and behavior of oil spills in coastal areas and on shoreline. Laboratory studies have been performed in order to obtain data for further development of numerical models.

The first phase of JIP was performed in the period from 2006 to 2008, and was funded by Eni Norge, Shell Technology and StatoilHydro. The overall objectives of the JIP have been:

- to contribute to an adequate and sufficient basis of competence to document possible consequences in case of an oil spill close to the coast
- to provide documentation ensuring the countermeasures giving the optimal environmental gain

In laboratory- and meso-scale studies it is always important to have good documentation of the oil in use and, and that it will be possible to use the same oil quality both in experimental series as well as in future projects for more easily comparison of experimental data. Prior to stranding of oil after an accidental release to the marine environment, the oil will undergo a number of weathering processes which alter the chemical composition and the physical properties of the oil/emulsion. After release from Norwegian petroleum installation the oil will reach the coastal zone typically minimum after 2-5 days. The main processes will be

- Evaporation; similar to 250$^{o}$C+
- Emulsification; maximum water content
- Photo-oxidation; depending on weather situation.

For the experimental studies on shoreline in both acute and restoration phase in the Coastal Oil Spill JIP, the oil had to be weathered with respect to these processes prior to initiation of the experimental studies.

During the SINTEF Statoil project “Upgrading meso-scale and laboratory facilities at SINTEF SeaLab” (2005), a number of experimental systems was established at SINTEF SeaLab including the large scale evaporation unit. In addition the meso-scale flume with artificial solar light was used for photo-oxidation of the oil, however, this procedure allowed only smaller residues of oil to be produced (2L). Oil emulsions have to be produced for every experiment, but a method for preparation of larger quantity had to be established.

The objectives of the present task have been to:

- establish standardized protocols for preparation of weathered oil residues in meso-scale systems
- prepare weathered oil (evaporated, emulsified and photo-oxidized) in” large” quantities for use in both laboratory- and meso-scale experimental studies.

## 3 Test oils

The properties of crude oils and bunker oils vary over a very wide range. The properties of the oils change even further during weathering processes after a release to the marine environment. The selection of oils in the Coastal Oil Spills JIP was based on two main aspects:

- The oils should represent different oil properties
- The oils should be relevant for the oil companies..

Crude oils can be characterised in four categories: asphaltenic, naphtenic, paraffinic and waxy crude oils. The crude oils studied in the Coastal Oil Spills JIP were selected among the oil companies' crude oils. It was important to select crude oils representing different categories of oils. The selected crude oils represent the categories:

- Troll – naphtenic crude oil
- Norne – waxy crude oils
- Kobbe – light paraffinic crude oil

In addition to the crude oils, a heavy fuel oil (IFO380) was also tested. IFO 380 is representative heavy fuel oils for bunker oils used as fuel for ships going along the Norwegian coast. The content of light oil components in fuel oils is low, typically lower than 5 vol% for IFO 380 oils. The light oil components are generally in a boiling point area up to 250°C. The testing of the IFO 380 was therefore concentrated on the "fresh" fuel oil, not on an evaporated residue. The IFO 380 oil used in this project is a low sulphur fuel oil produced at the Esso refinery at Slagentangen.

Some physical and chemical properties of the oils studied are listed in Table 3.1.

*Table 3.1 Oils used in the Coastal Oil Spills JIP.*

| SINTEF Id | Oil type | Residue | Density (Kg/m$^3$) | Evaporative Loss (Vol%) | Pour point (°C) | Wax (wt%) | Asphaltenes (wt%) | Viscosity $10^{-s}$, 5°C (cP) |
|---|---|---|---|---|---|---|---|---|
| 07-0287 | Troll | Fresh | 0,900 | 0 | -36 | 0,9 | 0,04 | |
| | | 250°C | 0,930 | 25,5 | -27 | | | 770 |
| | | Ph.ox. | 0,931 | - | -21 | | | |
| 07-0260 | Norne | Fresh | 0,860 | 0 | 21 | 4,3 | 0,30 | |
| | | 250°C | 0,888 | 28,4 | 30 | | | 39100 |
| | | Ph.ox. | 0,885 | - | 30 | | | |
| 06-1061 | Kobbe | Fresh | 0,797 | 0 | -39 | 3,4 | 0,03 | |
| | | 250°C | 0,875 | 53,6 | 21 | | | 4630 |
| | | Ph.ox. | 0,877 | - | 15 | | | |
| 06-1125 | IFO 380 | Fresh | 0,932 | 0 | 15 | 5,0 | 3,4 | 87100 |

*-: not measured*

A memo presenting the properties of the oils was worked out when initiating the laboratory studies in the JIP, see Appendix 2

# 4 Large scale evaporation of crude oils

Laboratory-based artificial "weathering"/evaporation of oils can be accomplished by distilling ("topping") a crude oil to a desired temperature. Distillation provides a relative distribution between the volatile and non-volatile components at a given temperature. The destillation removes the light-end components of the oil, up to the temperature used. Typically, the oil is evaporated to 150°C, 200°C, and 250°C, to simulate, approximately, 1 hour, 1 day, and 1 week, respectively, of natural weathering/evaporation in a temperate ocean environment (e.g., north Atlantic).

## 4.1 Equipment

For larger scale evaporation SINTEF has established a meso-scale system that allows evaporation of a minimum of 2 barrels (400L) of oil. A principal sketch of this system is shown in Figure 4.1, and a picture of the upgraded system is shown in Figure 3.3. The oil is heated by steam injection in the bottom of the tank (3m height and 1,5 m in diameter), and pumped through a nozzle in the to of the tank. Another pump circulates the oil in the tank. Fresh air is introduced into the tank, and removed together with the volatile compound from the top of the tank and out of the building. Sample of the oil is taken through a valve in the loop in the circulation system.

The evaporation of the oil was controlled by density measurements, and verified by GC/FID analysis.

In addition to this large scale weathering of crude oils, laboratory scale weathering was performed to produce other evaporation residues in smaller quantities, as described in SINTEF procedure "Distilling of oil" (KS 66-21-L-134). Each weathering residue was documented and characterized using standard methods.

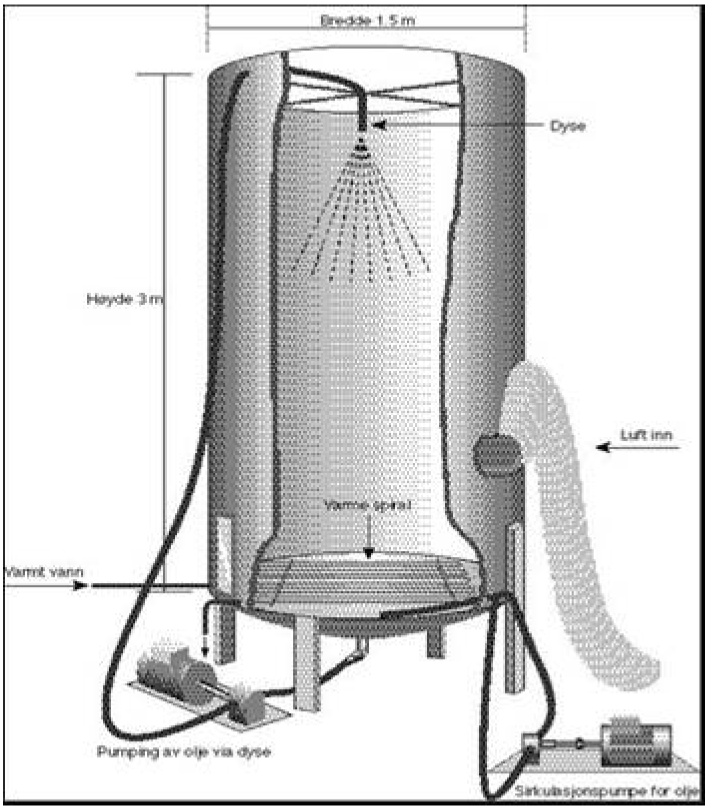



*Figure 4.1 Sketch of the upgraded evaporation system*

**4.2 Procedure for production of crude oil residues**

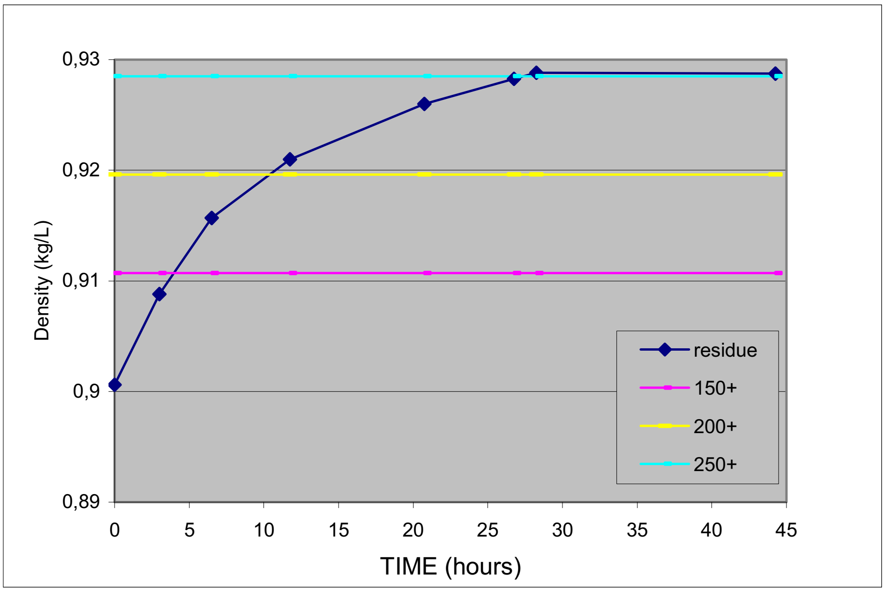
The large scale evaporation procedure was:

- Allow crude oil barrels to temperate to room temperature
- Mix the barrels thoroughly by e.g. shaking, tilling and rolling to homogenize oil content
- Start exhaust air fan and assure unhindered transport of exhaust gas over building.
- Pump the oil into the tank
- Start circulation pump
- Start steam injection and adjust temperature in the oil to be 60$^{o}$C.
- Start pumping the oil through the nozzle
- After 1 hour increase the temperature to 90-95$^{o}$C
- Take samples from the tank every 2-4 hour for documentation of the weathering process.
- Termination of evaporation is determined by density curves from laboratory data on distillation of the same oil.
- Stop pumping through the nozzle
- After the oil has reached the goal density the temperature is reduced to temperature above the pour point for the oil (30$^{o}$C).
- The evaporated oil is pumped from the tank into adequate storing containers (barrel, jerry can etc)

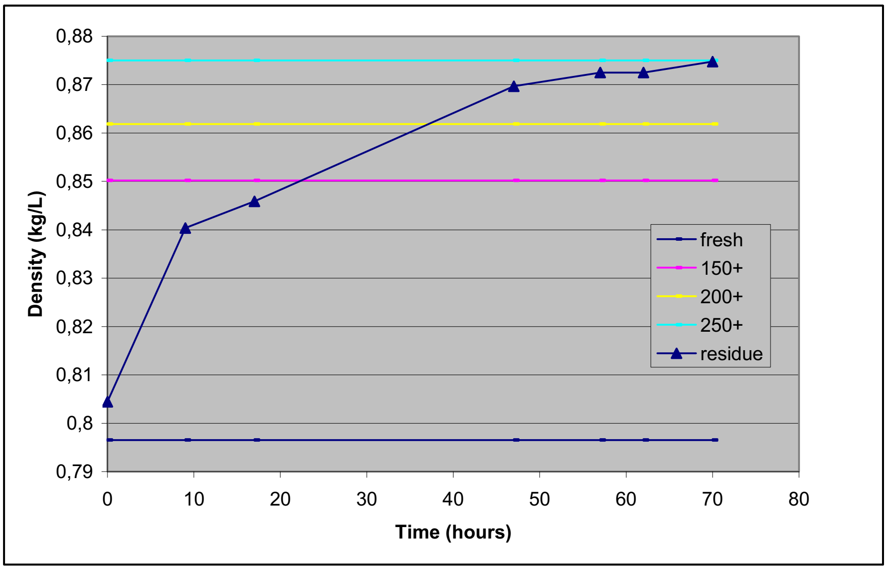
### 4.3 Evaporation of crude oils

Figure 4.2 gives the time course of density during the evaporation process in the meso-scale equipment for the three crude oils. Data given for the different residue is taken from the laboratory weathering studies.

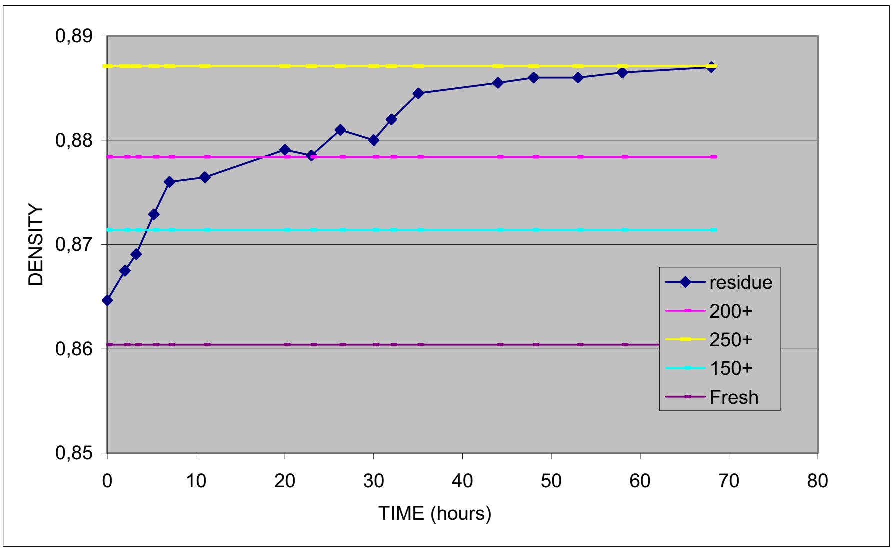
The time necessary to reach the 250°C+ residue varies to some extent for the different crude oils used. This was due to different factors including; content of light residues (% removed), temperature profiles used, clogging of exhaust air system and specific care related to water content in the crude oil.




Troll




Kobbe




Norne

*Figure 4.2 Density of oil residue during the evaporation process.*

### 4.4 Characterisation of evaporated crude oils

The evaporated oil residue was analyzed by GC/FID chromatography. Pour point measurements and rheological measurements were also performed.

#### 4.4.1 GC-FID chromatography

Figure 4.3 to 4.5 gives the GC chromatograms for the 250$^{o}$C+ residues of the crude oils. The chromatograms for different residues for each crude oil are given in Appendix 1 A-C. The chromatograms for the different weathering processes (laboratory vs. meso-scale) show a good agreement for all crude oils (please observe the different scales).

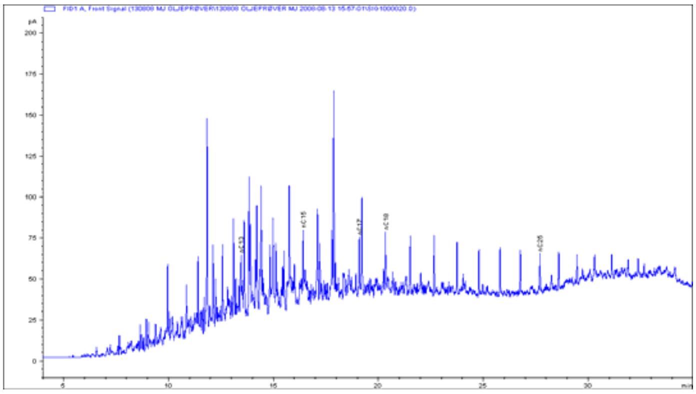
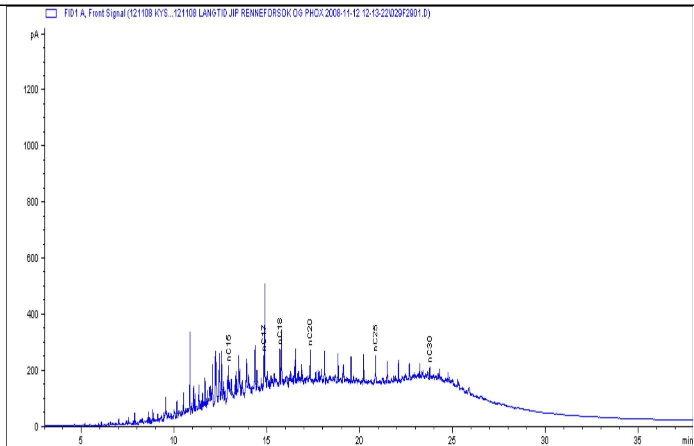
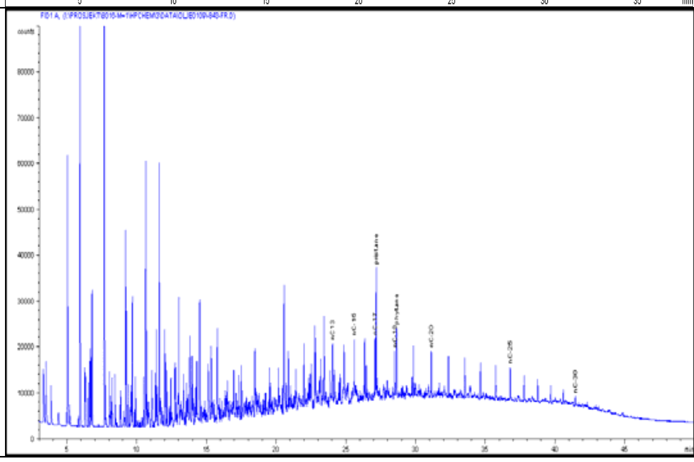
| | |
|---|---|
| Troll 250$^{o}$C+ residue<br>Meso-scale |  |
| Troll 250$^{o}$C+ residue<br>laboratory |  |
| Troll oil |  |





*Figure 4.3 GC analysis of fresh crude oil and 250$^{o}$C+ residues – Troll.*

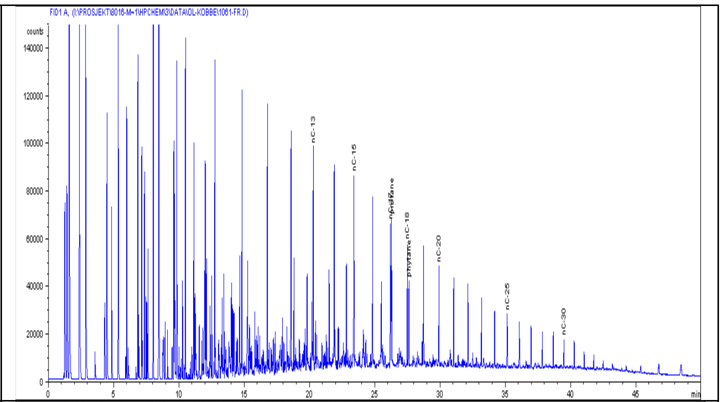
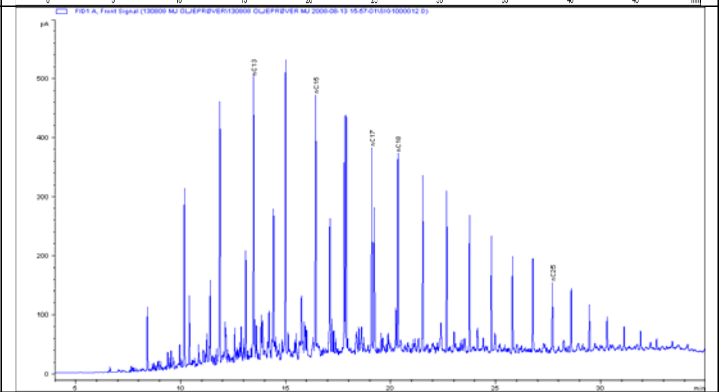
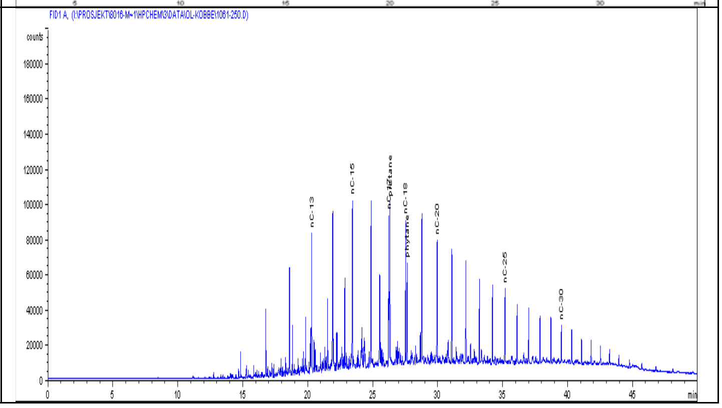
| | |
|---|---|
| Kobbe fresh |  |
| Kobbe 250°C+ residue meso-scale |  |
| Kobbe 250°C+ residuelaboratory |  |

*Figure 4.4 GC analysis of fresh crude oil and evaporated residue – Kobbe.*

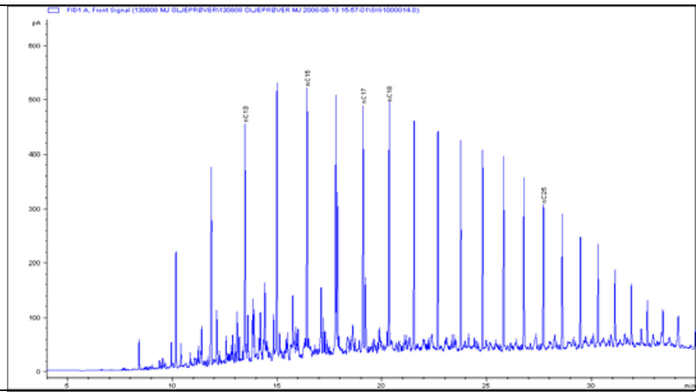
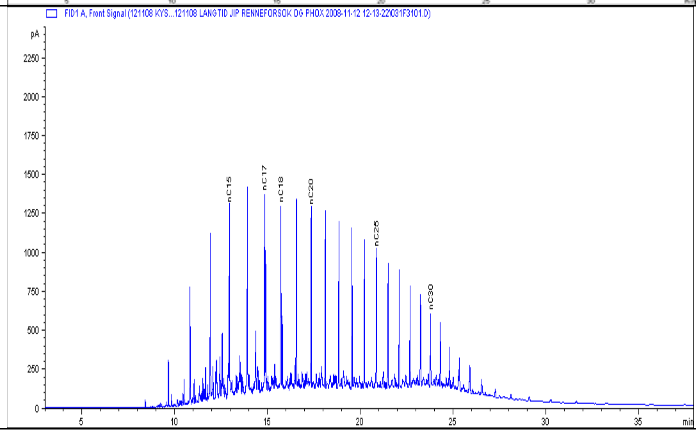
| | |
|---|---|
| Norne 250°C+ residue Meso-scale |  |
| Norne 250oC+ residuelaboratory |  |

*Figure 4.5 GC analysis of fresh crude oil and evaporated residue –Norne.*

### 4.4.2 Pour point

The pour point for the evaporated oil residues is given in Table 4.1. The Pour point was determined by ASTM D-97 by WestLab, and were measured both for 250°C+ and the photo-oxidized residues.

*Table 4.1 Pour point of the 250°C+ residue of the crude oils and IFO380.*

| Oil residue | Pour point (°C) |
|---|---|
| Troll 250°C+ | -27 |
| Troll photo oxidized | -21 |
| Norne 250°C+ | 30 |
| Norne photo oxidized | 30 |
| Kobbe 250 °C+ | 21 |
| Kobbe photo oxidized | 15 |
| IFO 380 | 15 |

The pour point for all oils, expect Troll, is above normal seawater temperature in cold climate environment.

# 5 Large scale emulsification of test oils

One of the weathering processes an oil is subjected when oil is spilt at sea, is water-oil emulsion formation. Water droplets are mixed with the oil as a result of the mixing energy (waves and currents) on the water surface, and emulsions are formed. In order to characterize the weathering properties of oil and their dispersility at different stages of weathering at sea can be prepared in the laboratory.

The basis of method for formation of a water-in-oil emulsion in the laboratory is using a rotating cylindrical seperatory funnels containing both water and oil. The rotation simulates mixing energy from wave and current activity at sea. For laboratory studies in small scale, oil emulsions are prepared according to a standard procedure (Preparation of water-oil emulsions for dispersability testing and viscosity determination using the rotating-flask apparatus KS 66-21-A-125), by the use of a rotating apparatus and cylindrical separation funnels (500mL). Each funnel allows production of a maximum of 300mL emulsion, which can be sufficient for some laboratory experiments. However, for meso-scale experiments a system allowing larger scale production of emulsion is necessary. Among different principle of mixing, use of a standard concrete mixed was chosen. The water and oil is treated similarly as in the standard rotating funnel procedure.

## 5.1 Procedure for emulsion preparation

The procedure for emulsion preparation was:

- Seawater temperate to appropriate temperature over night
- The oil is heated to 50°C
- The concrete mixer is washed thoroughly (high pressure and water)
- Water is weight and filled into the mixing system
- Oil is weight and filled on the water in the mixing system
- Cover the opening of the mixer using Al-folio
- Allow to conditioning for 1 hour
- Start mixing
- Allow to mix for at least 18 hours
- Prior to use the viscosity of the viscosity of the emulsion is measured

For preparation of Norne emulsion the mixing was initiated immediately after the oil was poured into the mixing equipment (no conditioning) due to the high pout point.

## 5.2 Emulsion

The maximum water uptake for the 250$^{o}$C+ residues was determined by standard methodology in rotation flask procedures. The maximum water uptake for the different oils is given in Table 5.1

*Table 5.1 Maximum water uptake in crude oil 250°C+ residues and IFO380.*

| Oil type/residue | Maximum water uptake (%) | Standard water content used (%) |
|---|---|---|
| Troll 250°C+ | 74 | 70 |
| Kobbe 250°C+ | 78 | 75 |
| Norne 250°C+ | 65 | 60 |
| IFO380 | 44 | 40 |

The emulsion to be used in experimental studies was decided to be below the maximum water because, because maximum water content emulsions may be instable. The water content used in the experimental studies is given in Table 5.1.

The same water content was used both for the 250°C+ residue and the photo-oxidized oil.

### 5.3 Characterisation of emulsions

Pictures during preparation of Troll $250^{o}$C+ emulsion is shown in Figure 5.1. The emulsification process was rapid and normally no free water was observed after one hour.

| | |
|---|---|
| T=0<br>Oil applied on water |  |
| T=4,5 h |  |
| T=14 h |  |

T= 18h

*Figure 5.1 Preparation of Troll emulsions in meso-scale concrete mixer.*

The preparation of emulsions by rotating flasks and in a concrete mixer is different. The viscosities of emulsions prepared in both systems were determined prior to initiation of each experiment. The results from these measurements are summarized in Table 5.2. The viscosities for both Troll and Kobbe are not significantly different using the two preparation methods. The viscosity for the IFO380 emulsion is significantly lower when produced in the concrete-mixer equipment. From earlier testing of Norne at SINTEF, we know that the reproducibility of emulsions are difficult due to the high pour point. Norne was solidified with at strong wax structure at the test temperature. The viscosity of every emulsion were determined before use, to avoid use of ”extreme” emulsion properties.

*Table 5.2 Viscosity of emulsions prepared in rotating seperatory funnels (lab. scale) and in concrete mixing equipment (meso scale). Viscosity measured in cP at 10 $s^{-1}$ and 5$^{o}$C before initiation of experiments.*

| | **Troll** | | **Kobbe** | | **Norne** | | **IFO380** | |
|---|---|---|---|---|---|---|---|---|
| | Lab | Meso | Lab | Meso | Lab | Meso | Lab | Meso |
| Number of measurements | 15 | 2 | 11 | 2 | 8 | 2 | 7 | 2 |
| Average (cP) | 17600 | 16800 | 7760 | 8870 | 30600 | 12100 | 135000 | 97400 |
| SD (cP) | 1170 | 2120 | 1020 | 682 | 1250 | 1370 | 11600 | 3600 |
| % SD | 7 | 13 | 13 | 8 | 4 | 11 | 9 | 4 |

Compared to the viscosities of the water free residues (cfr Table 3.1) emulsification affected the viscosity differently: from a drastic increase for Troll, through a moderate increase for Kobbe and IFO380 to a reduction in viscosity for Norne.

The properties of the emulsions prepared in the laboratory rotating funnels and the meso-scale concrete mixer are similar for Troll and Norne. For the high viscous IFO380 bunker oil and the waxy Norne with a high pour point the viscosities are lower for the emulsions prepared in meso-scale mixer. This is most probably due to the difference in mechanical exposure in the mixing systems. This was special clear with Norne with possible disturbance of the wax structure in the emulsion.

# 6 Photo-oxidation

Sun exposure will affect the chemical composition of oils, which can result in changes of the physical properties. SINTEF has a standard laboratory method which simulated this process ("Foto-oksidering av olje film", KS 66-21-L-104). This procedure was used as a basis for scale up of this process using the flume and a UV-lamp simulating natural sunlight.

## 6.1 Equipment

A solar simulator (Solarconstant 4000) from Gmbh Steuernagel is used for photo oxidation of crude oils. The solar simulator emits light with the same spectral distribution as natural sunlight (at high noon and without clouds). The setup of the photo oxidation rig is shown in Figure 6.1.

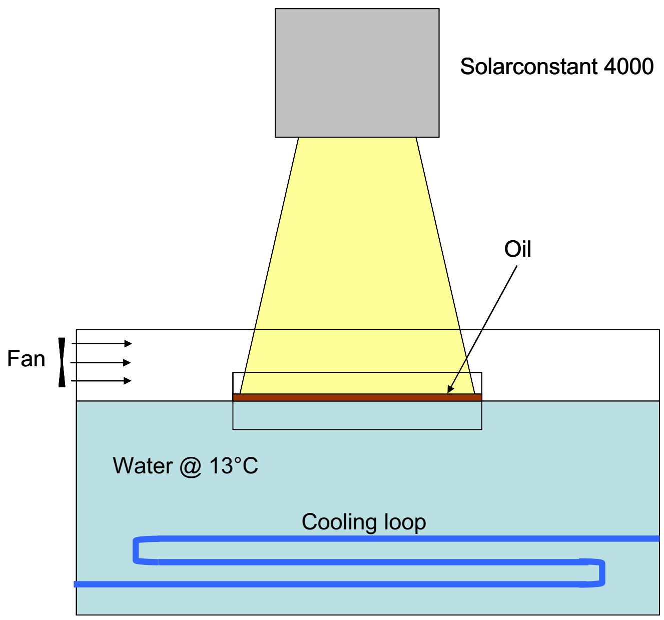



*Figure 6.1 Setup of the photo oxidation rig*

## 6.2 Procedure for photo-oxidation of oil

Two litres of crude oil is applied in a vessel floating in the larger cooling basin. The oil surface is 80x46 cm and the thickness of the oil is 0.5 cm. The crude oil is exposed to the artificial sunlight for 18 hours. A fan is blowing across the surface of the vessel. The wind is circulating the oil, and enhancing transport of heat from oil to both air and water. Simultaneous with the photo oxidation of the sample, evaporation occurs. The system is calibrated to give both evaporation and irradiation corresponding to approximately one week of weathering on the sea surface.

Irradiation due to sunlight is not the same around the year. Figure 6.2 shows the radiation dosage in the photo oxidation rig compared to weekly irradiation in 3 different Norwegian cities. The figure shows that the energy from irradiation with the artificial sunlight (18 hours) corresponds to a week of irradiation with natural sunlight at summertime in Norway

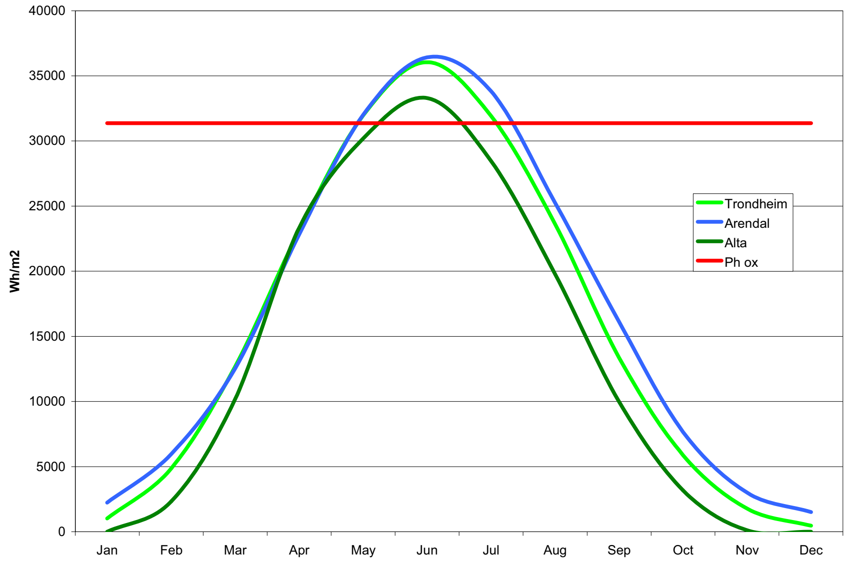



*Figure 6.2 Irradiation in one week for three Norwegian cities compared to the irradiation in 18 hours in the photo oxidation setup.*

### 6.3 Characterisation of photo-oxidized oils

The GC profiles of the photo-oxidized residues are given in Figure 6.3 to together with the 250°C+ residues (Troll, Norne and Kobbe respectively). For all three crude oils the GC-diagram shows great similarities between the two residues, indicating

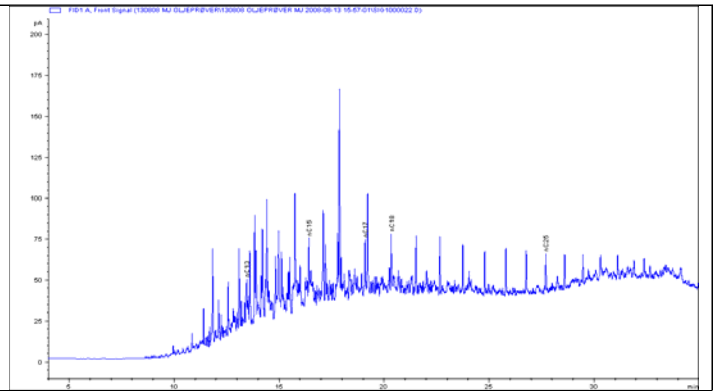
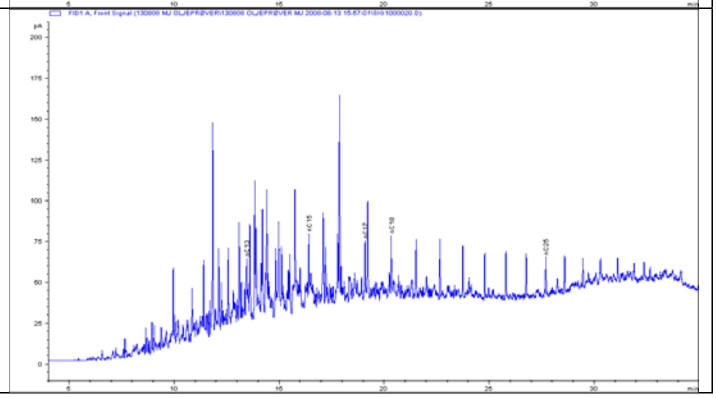
| | |
|---|---|
| Troll 250°C+ |  |
| *Troll photo-oxidized* |  |

*Figure 6.3 GC analysis of evaporated and photo oxidized residues - Troll*

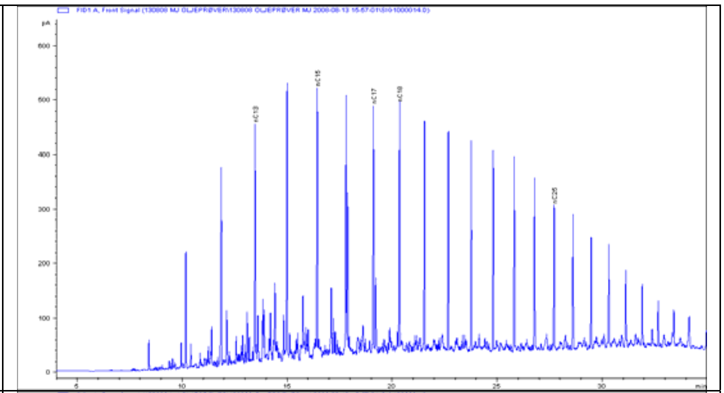
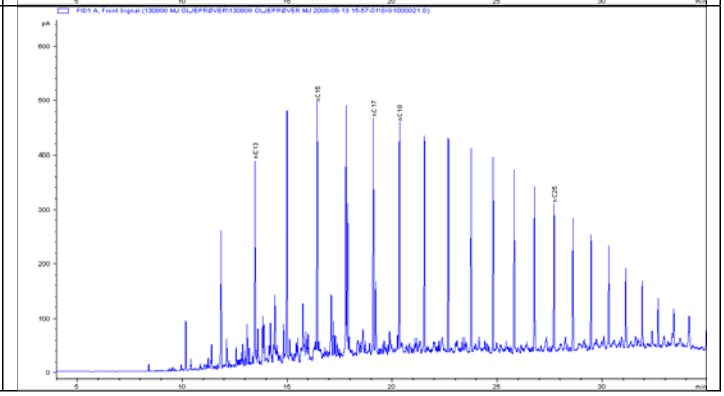
| | |
|---|---|
| *Norne 250°C+* |  |
| *Norne photo-oxidized* |  |

*Figure 6.4 GC analysis of evaporated and photo oxidized residues – Norne.*

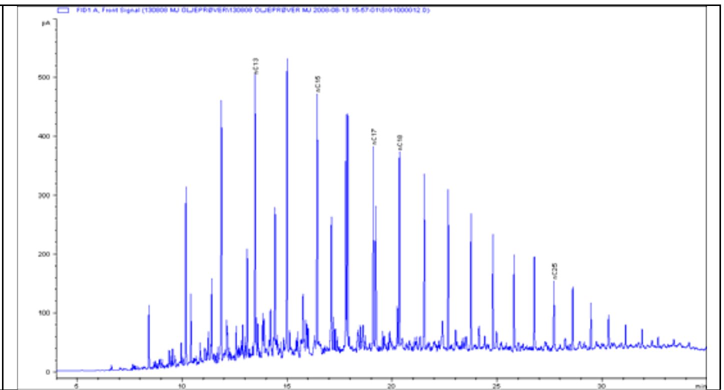
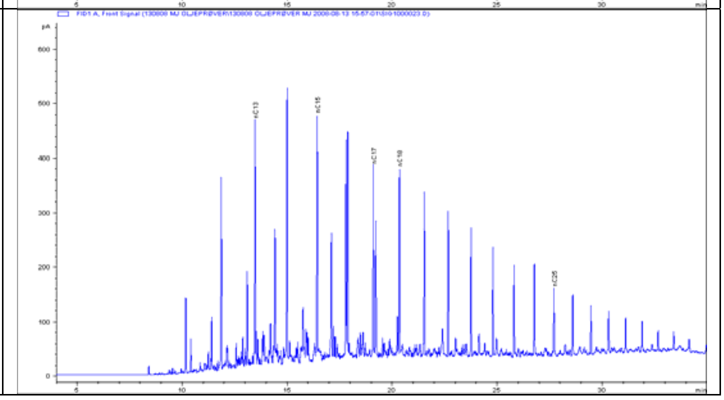
| | |
|---|---|
| *Kobbe 250°C+* |  |
| *Kobbe photo-oxidized* |  |

*Figure 6.5 GC analysis of evaporated and photo oxidized residues – Kobbe.*

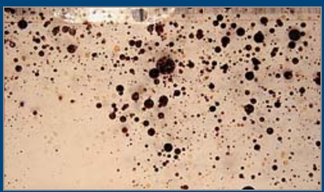
The viscosity of the emulsions was measured prior to initiation of each experiment. In general the viscosities of the photo-oxidized oil was significantly higher than the 250°C+ emulsions. This is in accordance with earlier studies at SINTEF. The viscosity data is summarized in Table 6.1. The stability of the emulsions was not measured, but it was expected that photo-oxidation products will stabilize the emulsions.

*Table 6.1 Viscosities (cP, at 5°C and $10^{-s}$) of laboratory scale emulsions of 250°C+ and photo-oxidized residue of the crude oils.*

| | Troll | | Kobbe | | Norne | |
|---|---|---|---|---|---|---|
| | 250°C+ | Ph.ox | 250°C+ | Ph.ox | 250°C+ | Ph.ox |
| Average (cP) | 17600 | 26500 | 7760 | 11200 | 30600 | 29200 |
| SD (cP) | 1170 | 5200 | 1020 | 71 | 1250 | 1740 |
| % SD | 7 | 20 | 13 | 1 | 4 | 6 |

STF - F8507

# REPORT



## Coastal Oil Spills - JIP

Report no.: 13

## Numerical simulation of waves on a porous beach

Bård Brørs

**SINTEF Materials and Chemistry**
Marine Environmental Technology

Date: 2008-12-17

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TITLE

**Numerical simulation of waves on a porous beach**

**Coastal Oil Spills JIP. Report No. 13**

AUTHOR(S)

Bård Brørs

CLIENT(S)

Eni Norge AS, A/S Norske Shell and StatoilHydro ASA

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| | 2008-11-07 | Tore Aunaas, Research Director | |

ABSTRACT

The wave action on beaches with different porosity was predicted with the CFD model Flow-3D. The code is based on the volume of fluid method (VOF) and can represent complex free surfaces like those of breaking waves. The simulations were set up in order to mimic a laboratory experiment. The wedge-shaped wavemaker of the experiment was represented by Flow-3D's general moving object (GMO) model. Both the external (wave) flow and the pore-water flow inside the porous beach substrate were predicted with an emphasis on the erosive power along the slope.

| KEYWORDS | ENGLISH | NORWEGIAN |
|---|---|---|
| GROUP 1 | Wave | Bølge |
| GROUP 2 | Beach | Strand |
| SELECTED BY AUTHOR | Numerical model | Numerisk model |
| | Flow in porous media | Strømning i porøse media |
| | | |

# TABLE OF CONTENTS

# 1 INTRODUCTION

This project has been a part of phase 1 in the Coastal Oil Spills JIP. The research projects in the JIP have been focused on the fate and behavior of oil spills in coastal areas and on shoreline. Laboratory studies have been performed in order to obtain data for further development of numerical models.

The first phase of JIP was performed in the period from 2006 to 2008, and was funded by Eni Norge, Shell Technology and StatoilHydro. The overall objectives of the JIP have been:

- to contribute to an adequate and sufficient basis of competence to document possible consequences in case of an oil spill close to the coast
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The wave action on beaches with different porosity was predicted with the CFD model Flow-3D. The code is based on the volume of fluid method (VOF) and can represent complex free surfaces like those of breaking waves. The simulations were set up in order to mimic a laboratory experiment. The wedge-shaped wavemaker of the experiment was represented by Flow-3D's general moving object (GMO) model. Both the external (wave) flow and the pore-water flow inside the porous beach substrate were predicted. The effect of an oil layer on the porous beach has not been studied.

# 2 Experiment

Wave action on a beach was simulated in a 4 m long and 2 m wide flume with water depth 0.54 m as shown in Figure 2.1. Waves were generated by a sinusoidal up and down motion of the wedge on the left hand side. A beach module (substrate inside a box) was held at an angle of $\alpha = -9°$ with the horizontal, and was moved slowly up and down with an amplitude of 0.28 m in order to account for the action of the tide. The 2.5 m long and 4 m wide beach module is divided into four 2.5 m long and 0.5 m wide sections, one of them forming an impermeable wall and the other three each containing a different substrate.

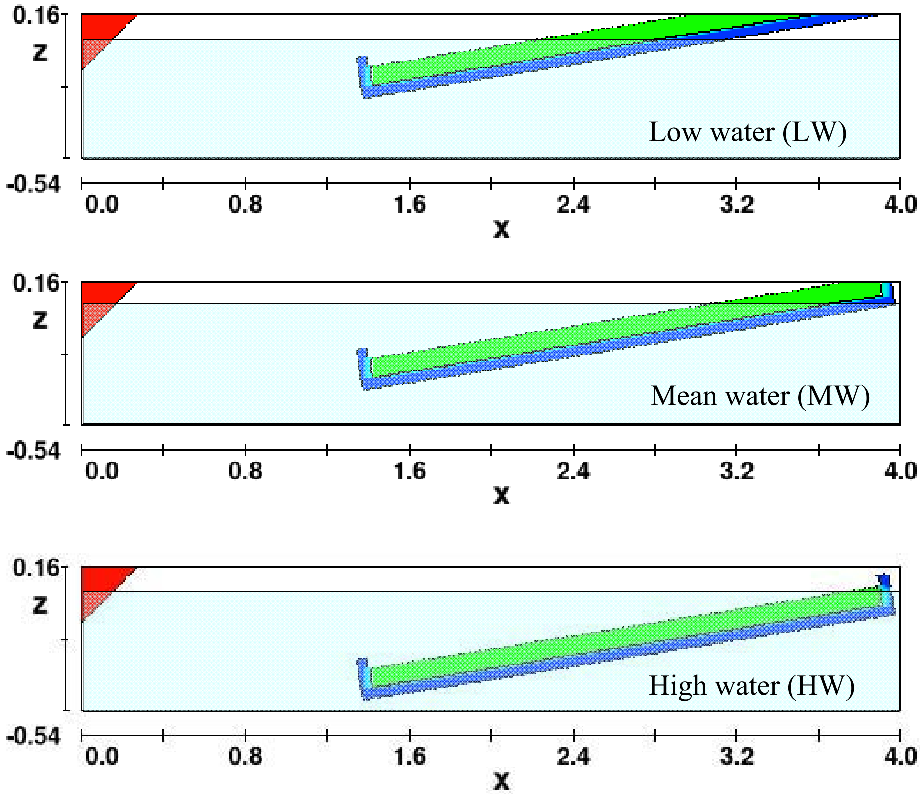


Figure 2.1 Setup of experiment and numerical model. 2D vertical slice through the flume showing the wave-maker (red) and beach (the permeable substrate is shown in green and the container in blue).

# 3 NUMERICAL MODEL

## 3.1 General approach

The flow induced by the slow up and down motion of the beach module is negligible compared to the wave-induced flow, and was not modeled. Instead, separate simulations were made for three different tidal levels low water (LW), mean water (MW) and high water (HW). Actually, all of these were made using the same water level, with the beach raised by 0.14 m from MW in order to simulate low water and lowered by 0.14 m from MW in order to simulate high water, cf. Figure 2.1. With plane incoming waves normal to the beach, the situation is two-dimensional, and is modeled in 2D as a vertical plane.

## 3.2 Model setup

Test runs showed that a detailed mesh was needed in order to resolve the relatively low waves and their impact on the slope. A mesh with cell size $\Delta x = 0.025$ m in the horizontal and $\Delta z = 0.004$ m in the vertical direction proved to be sufficient, producing a 160 by 175 mesh with 28 000 cells.

The motion of the wave-maker was specified so as to produce waves with a period of $T = 1.667$ s and a wave height (trough to top) of approximately $H = 0.026$ m in front of the beach module.

A renormalized group (RNG) model was devised as turbulence closure for the solution of the Reynolds-averaged Navier-Stokes equations. This is a two-equation model based on the widely used (k – ε) model. Inside the substrate, the equations of flow in porous media were solved, with values of linear drag (oadrg) and quadratic drag (obdrg) coefficients as presented in Table 3.1. These are recommended values from the literature based on the size of the substrate. The surface roughness (rough) was set to 0.001 m for the impermeable beach and to the mean grain diameter for the substrate covered beach. A total of 12 combinations of water level and substrate were run, with labels as indicated in Table 3.1.

Table 3.1 Overview of simulation runs and choice of porous media flow parameters.

| Section number | Substrate diameter *D* and model parameters | | | | Tide, simulation label | | |
|---|---|---|---|---|---|---|---|
| | *D* (cm) | oadrg | obdrg | rough | Low | Mean | High |
| 0 | Solid wall | 0 | 0 | 0.001 | C0-LW | C0-MW | C0-HW |
| 1 | 2 – 6 | 11 250 000 | 750 | 0.004 | C1-LW | C1-MW | C1-HW |
| 2 | 8 – 16 | 1 250 000 | 250 | 0.012 | C2-LW | C2-MW | C2-HW |
| 3 | 10 – 80 | 89 000 | 67 | 0.045 | C3-LW | C3-MW | C3-HW |

### 3.3 Results

The structure of the beach (impermeable or porous, and size of substrate) is found to have a significant influence on the water flow. Figure 3.1 shows snapshots at two different times of the flow field for an impermeable beach and a beach with the coarsest 10 – 80 mm substrate. It is evident that the wave is smoothened when the water is allowed to seep into the beach (upper plots) compared to when it is not (lower plots).

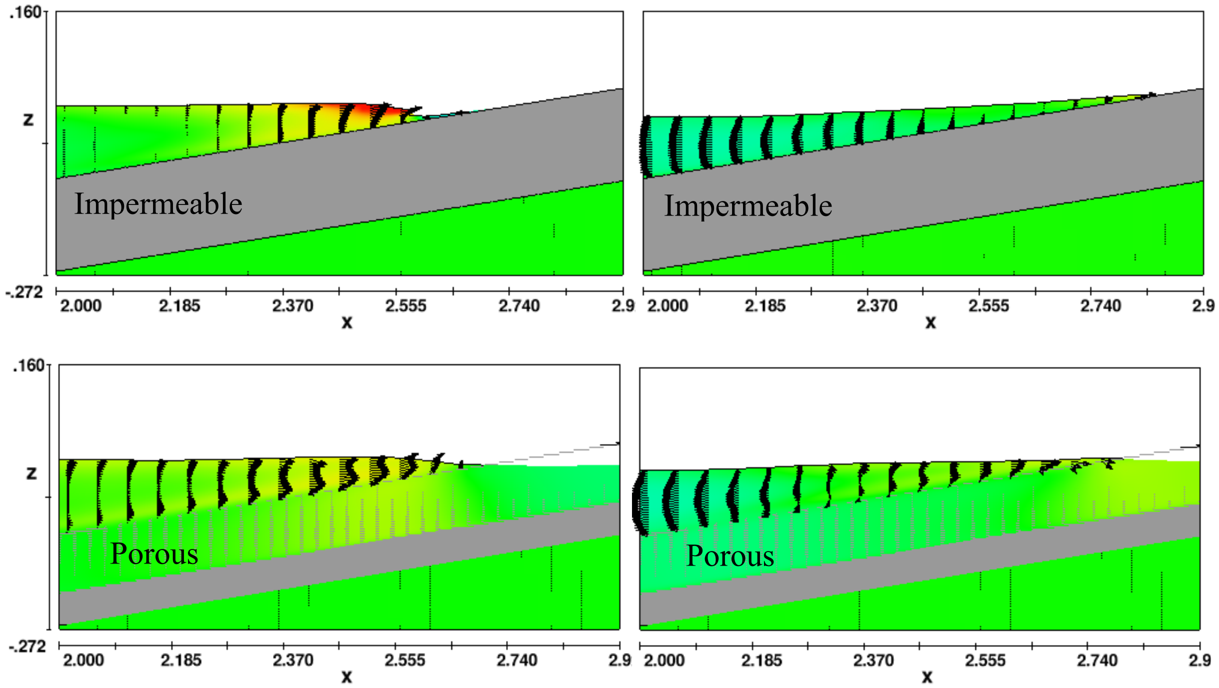


Figure 3.1 Predicted flow field at the time of early (left) and late (right) wave up-rush. Solid wall (top) and coarse substrate beach (lower plots).

In order to get an impression of the wave eroding power along the beach, flow velocities were extracted for every wet cell next to the solid (C1) or porous (C1 – C3) layer at 25 times during a wave period. The result is plotted in Figure 3.2 to Figure 3.5 as contours of *u* velocity as a function of distance *x* (along the horizontal axis) and time *t* (along the vertical axis). The dashed blue line in the upper plot of Figure 3.2 (low water situation) marks the motion of the waterline on the slope. At $t/T = 0$ the water is seen to be retracting from the beach with a velocity in the order of $u = -0.2$ m/s (blue colour). Soon after, at $t/T = 0.1$, the water has retracted maximally, and a breaking wave hits the slope with a maximum velocity of $u = 0.45$ m/s (red colour). The velocity then gradually decreases to zero at the time of maximum up-rush at $t/T = 0.5$. A maximum down-rush of $u = -0.35$ m/s occurs slightly offshore at $t/T \sim = 0.8$. At this time, the footprint of a new approaching wave is seen to form further out (in $x = 1.5$ m) and the sequence repeats itself.

The lowermost plot in Figure 3.2 to Figure 3.5 shows maxima and minima as well as mean values of *u* during a wave period. The mean water and high water cycles closely resemble the low water cycle, only with slightly higher values for higher water levels. The mean values are negative, except for the up-rush portion, as one would expect because the net shoreward flow in the upper layer due to Stokes drift has to be compensated by an outward directed flow near the bottom.

The predicted flow velocities over porous sea-beds are lower than over the solid bed, and velocities decrease with increasing roughness of the substrate (Figure 3.3 to Figure 3.5). The retracting wave is more reduced by substrate porosity and roughness than the up-rushing wave, and the duration of the peak in the up-rush decreases with increasing substrate roughness.

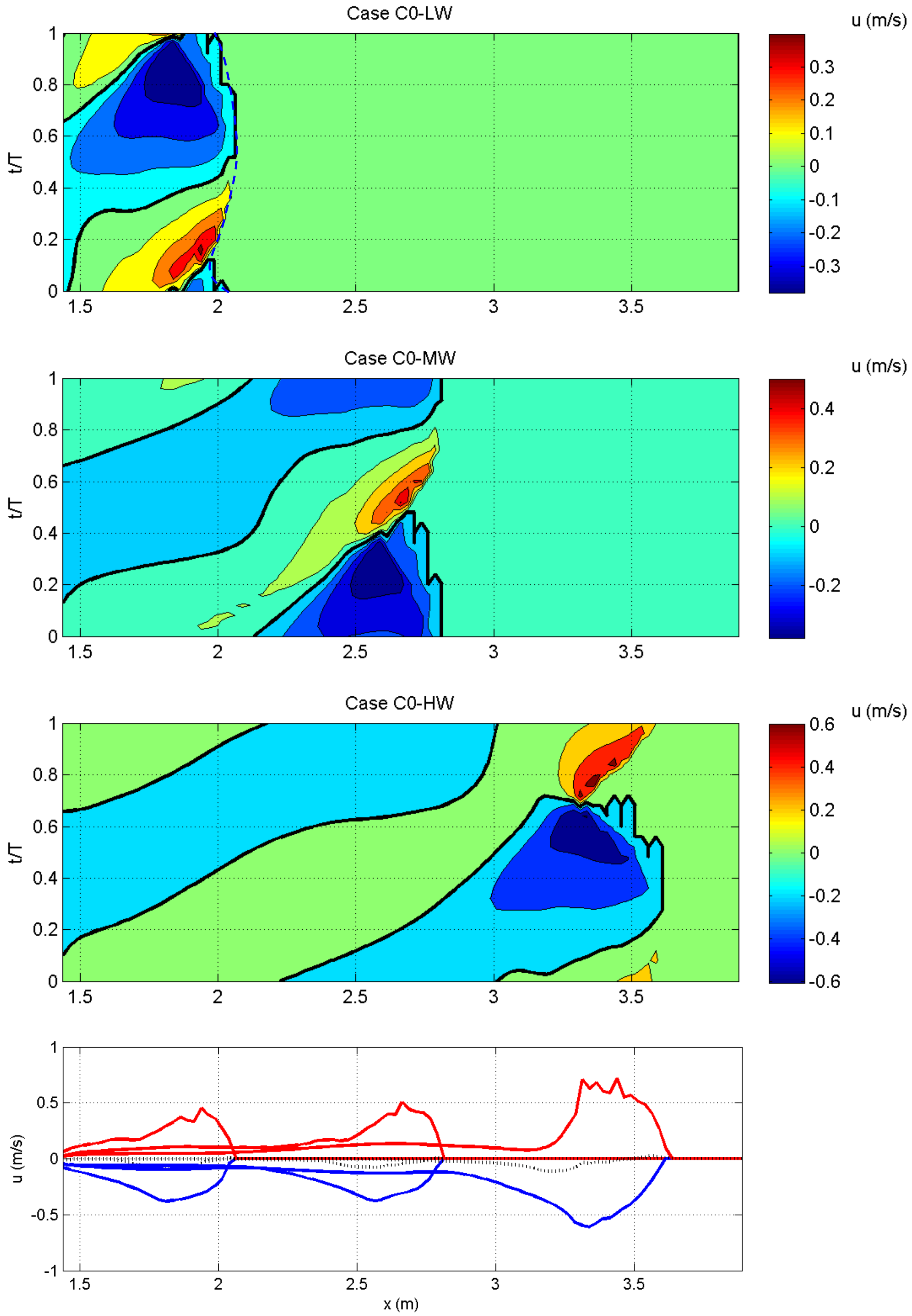


Figure 3.2 Flow velocity *u* component near the seabed during one wave period for Case C0: Smooth bottom. Upper three plots show contours of *u* vs. slope distance *x* and time for low, mean and high water situation, respectively. Lower plot shows max (red) min (blue) and mean (black) of *u* during one wave period.

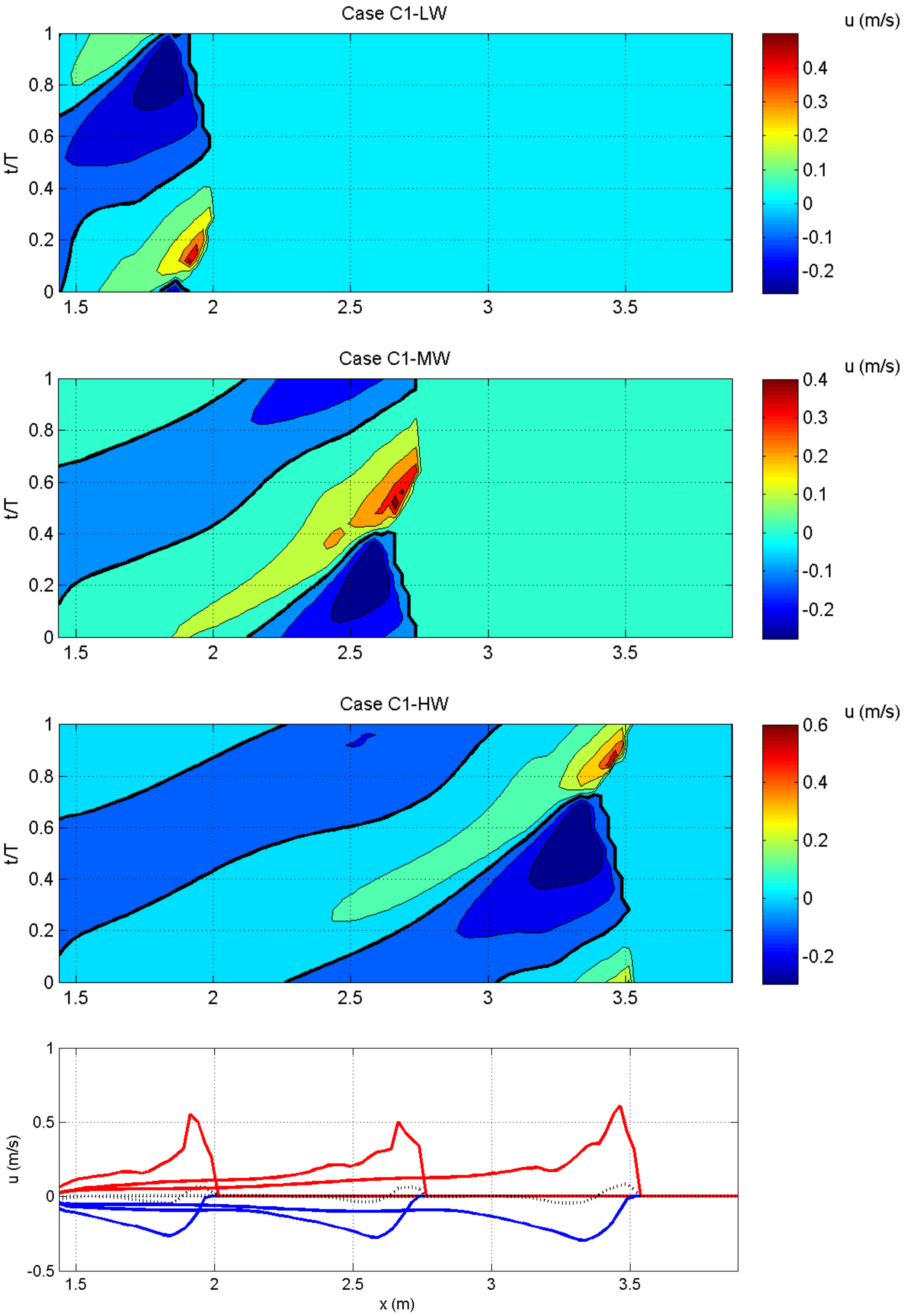


Figure 3.3 Flow velocity *u* component near the seabed during one wave period for Case C1: Substrate with $D = 2 - 6$ mm. Upper three plots show contours of *u* vs. slope distance *x* and time for low, mean and high water situation, respectively. Lower plot shows max (red) min (blue) and mean (black) of *u* during one wave period.

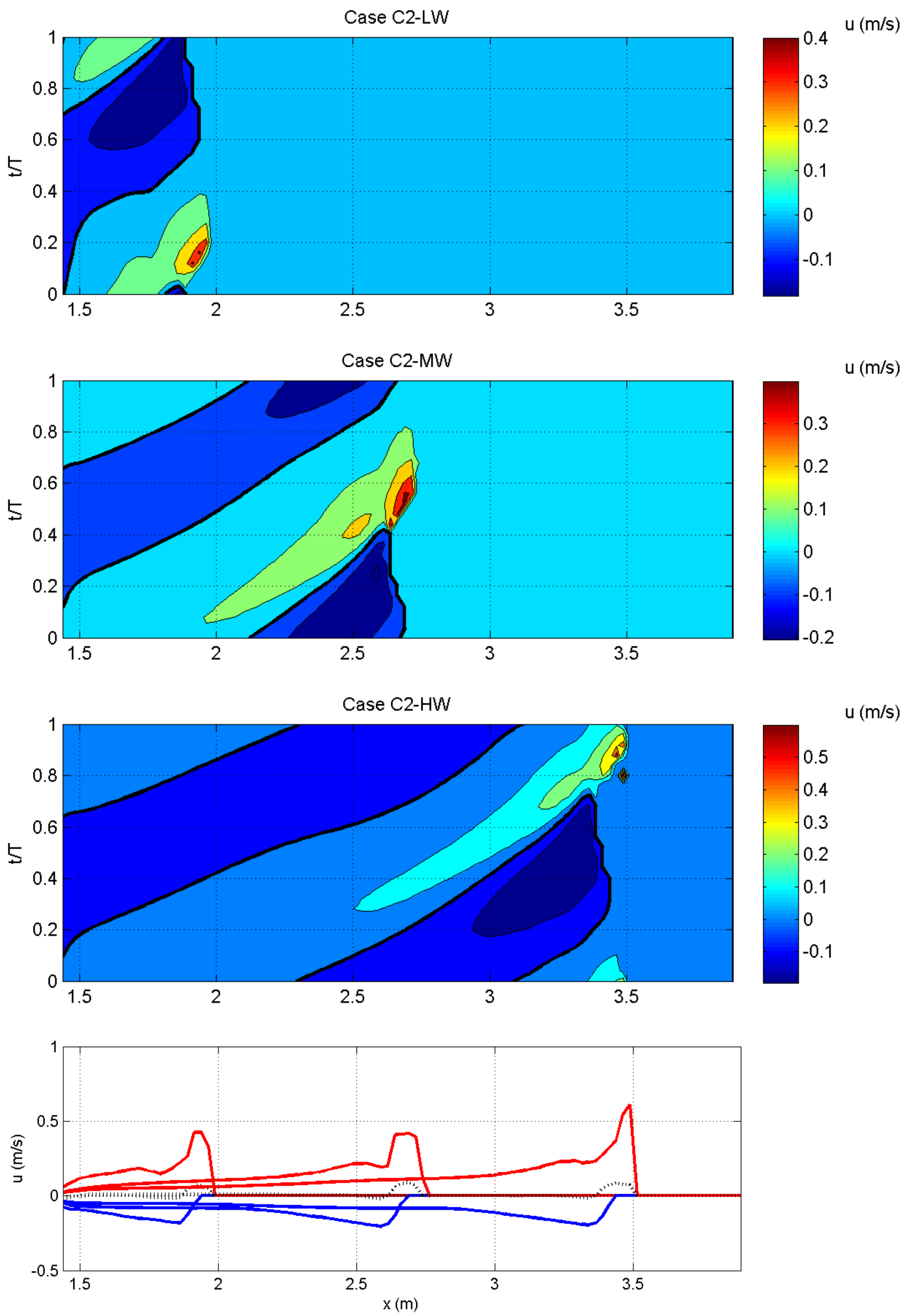


Figure 3.4 Flow velocity *u* component near the seabed during one wave period for Case C2: Substrate with $D = 8 - 16$ mm. Upper three plots show contours of *u* vs. slope distance *x* and time for low, mean and high water situation, respectively. Lower plot shows max (red) min (blue) and mean (black) of *u* during one wave period.

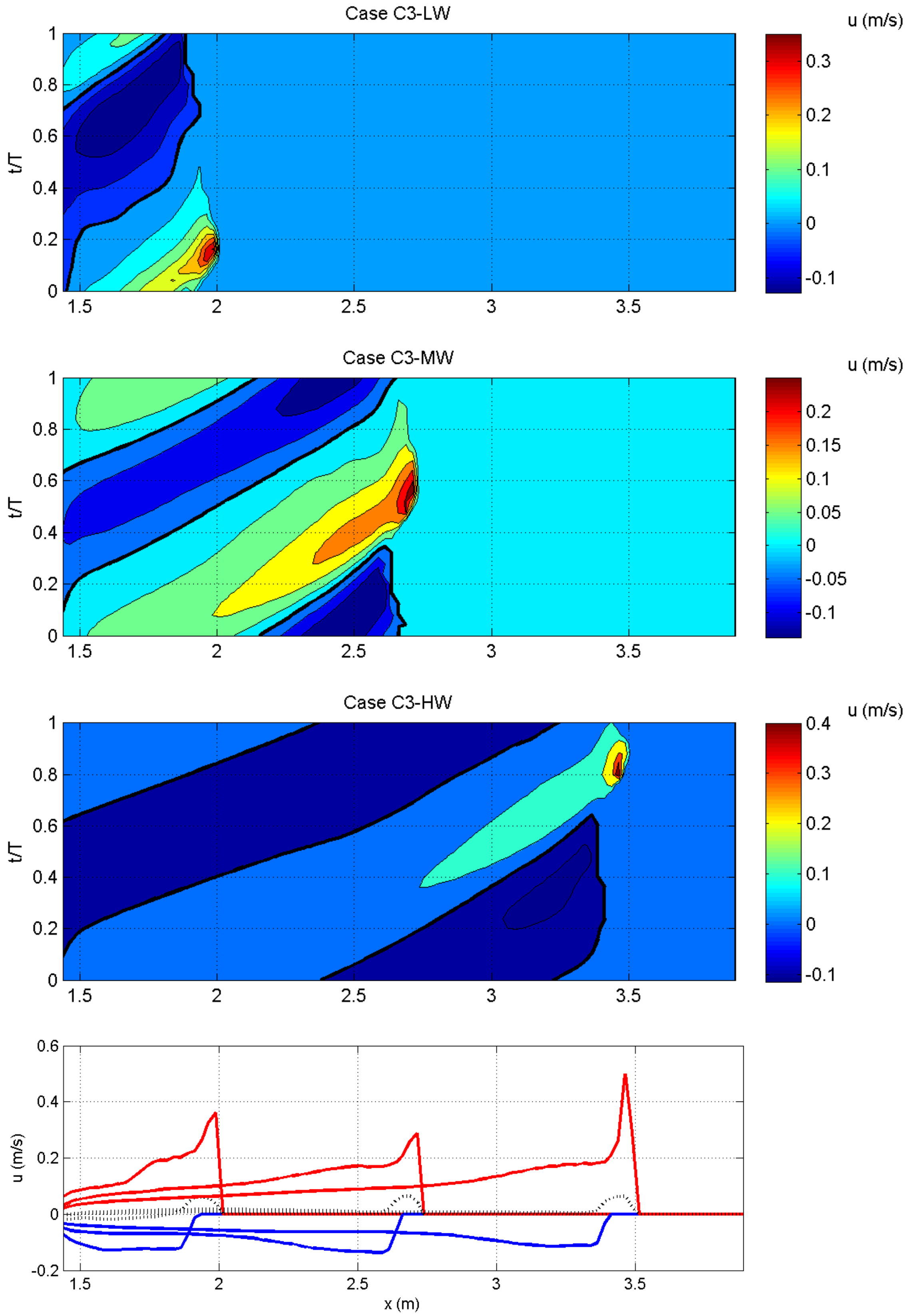


Figure 3.5 Flow velocity *u* component near the seabed during one wave period for Case C3: Substrate with $D = 10 - 80$ mm. Upper three plots show contours of *u* vs. slope distance *x* and time for low, mean and high water situation, respectively. Lower plot shows max (red) min (blue) and mean (black) of *u* during one wave period.

The power exerted on the seabed by the flow (stress times velocity) is probably a more appropriate parameter for the natural restoration of a contaminated beach than the flow velocity. With the shear stress expressed by a quadratic friction law involving a drag coefficient $C_D$ and the density $\rho$ as $\tau_b = C_D \rho u_b^2$, the power in W/m$^2$ can be estimated as $\tau_b u_b = C_D \rho u_b^3$.

In order to present the results in a more general form, they should be expressed in appropriate length and velocity scales. In the present case, the relations for shallow-water wavelength $L_0$ and celerity $u_0$ from linear (Airy) wave theory can be used:

$$L_0 = T\sqrt{gh}\,, \tag{1}$$

$$u_0 = \sqrt{gh}\,. \tag{2}$$

On a slope, waves are usually assumed to break at the point when the wave-height $H$ becomes larger than 0.8 times the local depth, $h$. In the present case, it is reasonable to evaluate (1) and (2) at the breaking point:

$$h = 1.25H\,. \tag{3}$$

With $H$ = 0.026 m and $T$ = 1.667 s, the breaking depth is $h$ = 0.0325 m, $u_0$ = 0.56 m/s and $L_0$ = 0.94 m.

Figure 3.6 shows plots of velocity and power using the shallow-water wave celerity $u_0$ defined by (2) as velocity scale. The cross-shore coordinate is scaled with the shallow-water wavelength $L_0$ defined by (1) and translated a distance $x_0$ = 3.425 in order to place the origin where the still water line meets the slope. For the smooth impermeable slope (C0-HW, upper left plot in Figure 3.6) both the maximum and minimum velocity during a wave cycle are predicted to be slightly higher than the shallow wave celerity $u_0$ and to occur about 0.15 $L_0$ outwards of the shoreline. The mean near-bed flow is sea-wards. With a porous slope (C0-HW – C3-HW) the maximum (up-rush) velocity maintains its value, but lasts shorter and moves upwards of the still water line. The strength of the minimum (down-rush) weakens significantly for coarser substrate. This, and the fact that the mean near-bed flow gets positive for coarser substrate, indicates that much of up-rushing water seeps into the substrate and returns seaward as pore-water. The wave power at the sea-bed (right side plots in Figure 3.6) is seen to be significant for both flow directions over a length of about $L_0$/3 for the smooth slope. For a porous slope, only the wave up-rush is predicted to be significant, and its extent decreases to $L_0$ /10 for the coarsest substrate (C3-HW).

In order to evaluate the effect of turbulence, the turbulent velocity was expressed as the square of the predicted turbulent kinetic energy at the seabed as $k_b^{1/2}/u_0$. Figure 3.7 indicate that turbulence is significant compared to the main flow for the smooth slope and the slope with a fine substrate, but less so for beaches with coarse substrate. This is explained by the fact that that the down-rush weakens or disappears and its impingement on the next wave is weaker or does not happen.

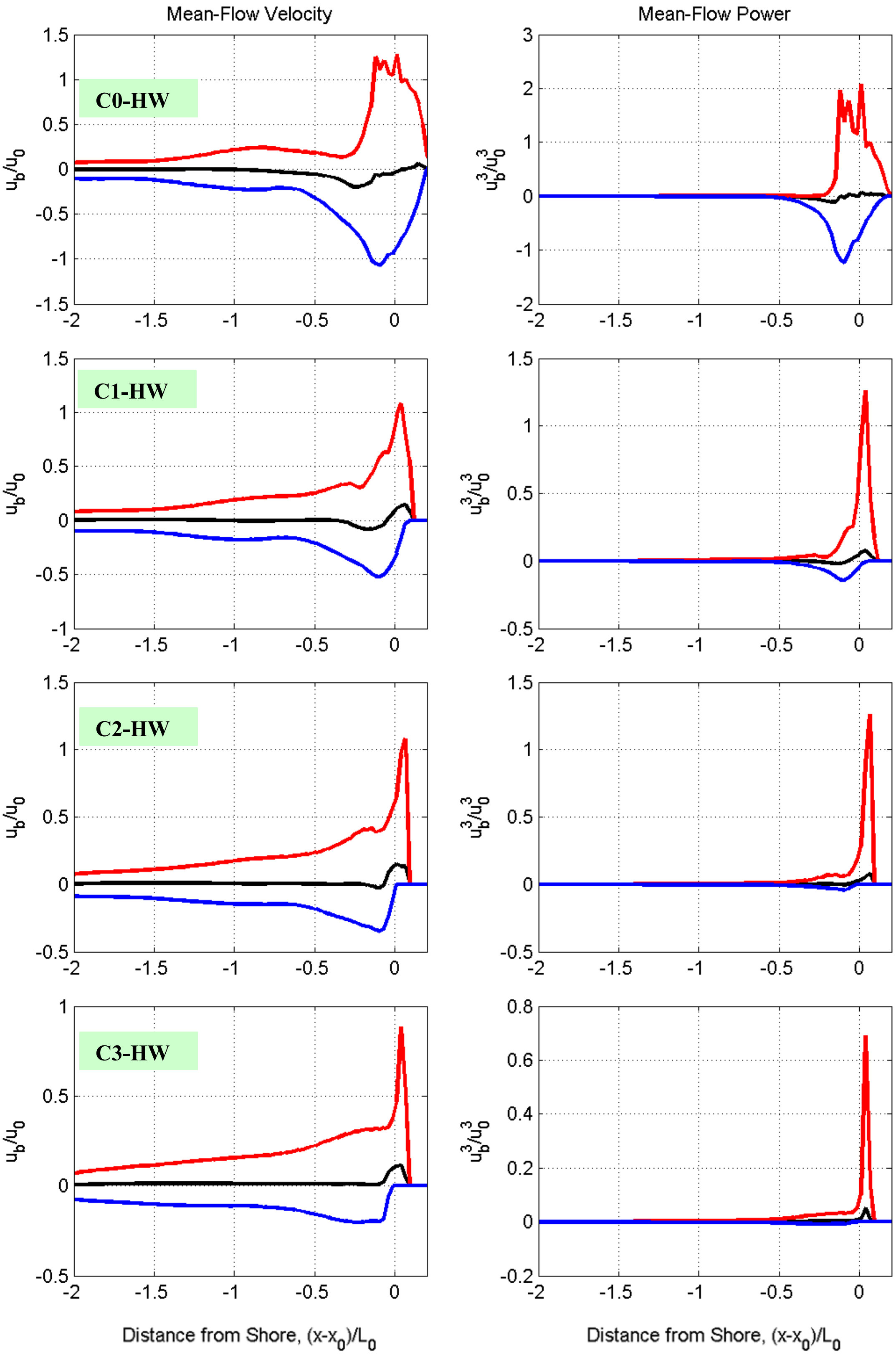


Figure 3.6 Flow velocity $u_b/u_0$ (left) and power $u_b^3/u_0^3$ (right) along the seabed. Maximum (red), minimum (blue) and mean value (black) during one wave period. Scaling with shallow water wave celerity $u_0$ and length $L_0$ at the breaking point ($h = 1.25 \cdot H$).

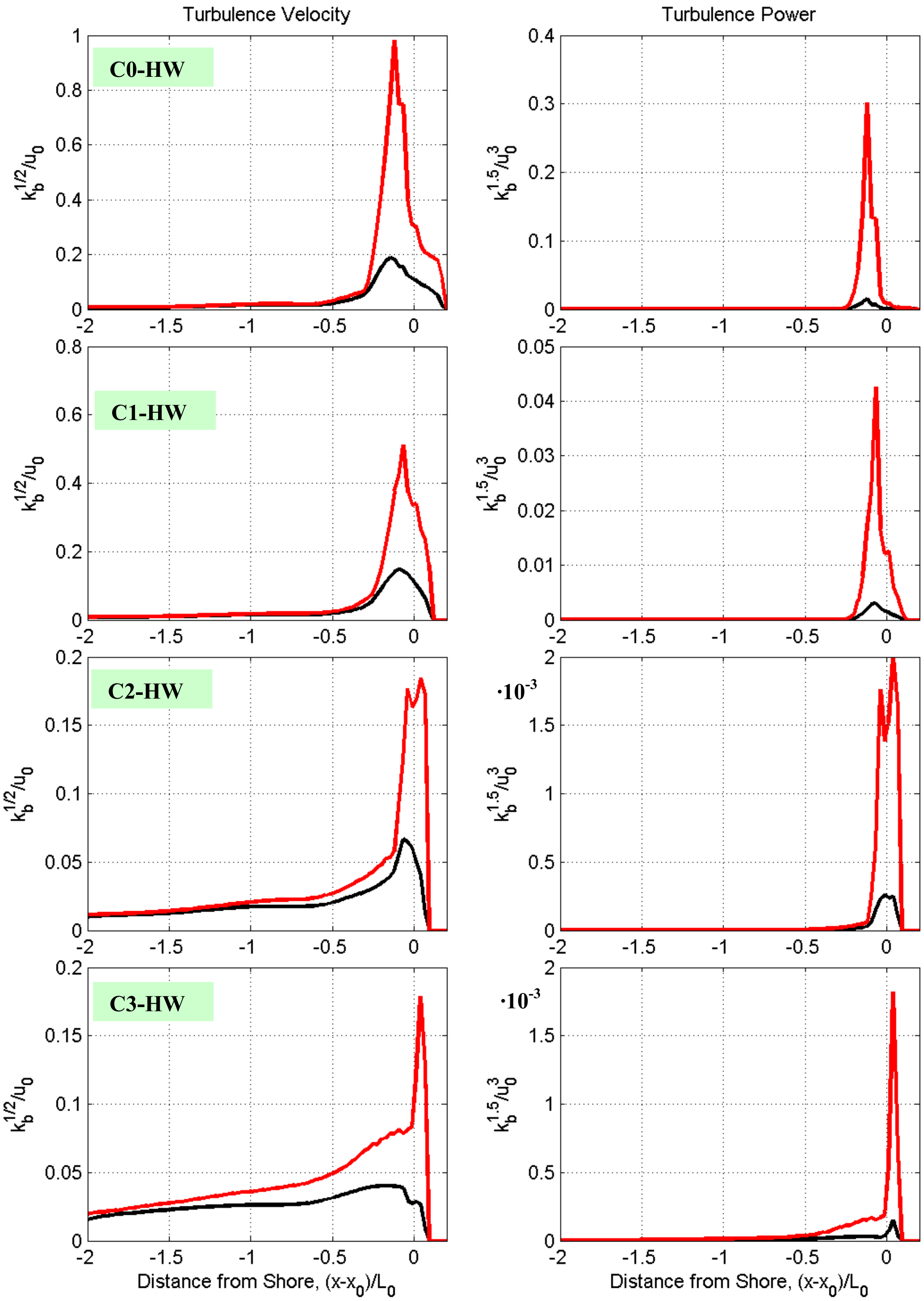


Figure 3.7 Turbulent velocity $k_b^{1/2}/u_0$ (left) and power $k_b^{3/2}/u_0^3$ (right) along the seabed. Maximum (red) and mean value (black) during one wave period. Scaling with shallow water wave celerity $u_0$ and length $L_0$.at the breaking point ($h = 1.25 \cdot H$).

# 4 CONCLUSIONS AND RECOMMENDATIONS

The wave up-rush and down-rush on an impermeable slope are both predicted to have a maximum velocity in the order of the shallow water wave celerity $u_0 = (gh)^{1/2}$ evaluated at the breaking point defined by the water depth $h$ and wave height $H$ as $h = 1.25\ H$. Both maxima are located ~ 0.15 $L_0$ (shallow water wavelengths, $L_0 = u_0\ T$) outwards of the mean water line. The mean near-bed flow on an impermeable is predicted to be directed sea-wards.

On porous slopes, the maximum velocity in the up-wash maintains its value, but lasts shorter and moves to the upward side of the still water line. The down-rush is predicted to weaken significantly the coarser the substrate. This, and the fact that the mean near-bed flow gets positive for coarser substrate, indicates that much of up-rushing water seeps into the substrate and returns seaward as pore-water.

The wave power at the sea-bed is predicted to be significant for both flow directions over a length of about $L_0/3$ for the smooth slope. For a porous slope, only the wave up-rush is predicted to be significant, and its extent decreases to $L_0\ /10$ for the coarsest substrate.

The turbulent velocity was estimated by the predicted turbulent kinetic energy at the seabed as $k_b^{1/2}/u_0$. Turbulent velocity is found to be significant compared to the main flow for the smooth slope and the slope with a fine substrate, but less so for beaches with coarse substrate. This is explained by the fact that the down-rush weakens or disappears on a coarse and permeable substrate, and therefore impingement on the next wave is weaker or does not happen.

An oil layer on the substrate could probably change the behaviour of the porous beach, by changing the roughness and acting as a membrane stopping or reducing the water exchange between wave and porous medium. Pore-pressure build-up underneath an oil layer is likely to be of importance for its break-up, and this topic would be suitable for a dedicated numerical model study.

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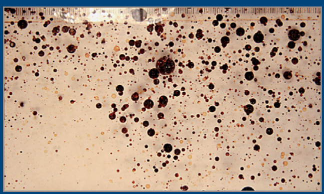
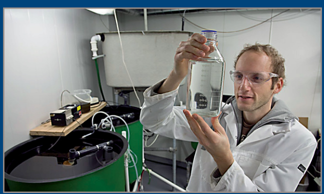
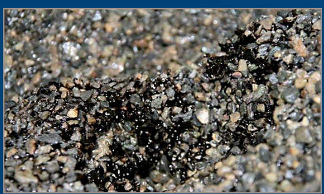
# REPORT







## Coastal Oil Spills - JIP

Report no.: 12

# Numerical simulation of flow inside a tilting box with an obstacle

Bård Brørs

**SINTEF Materials and Chemistry**
Marine Environmental Technology

Date: 2008-12-17

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TITLE

**C2.2 - Numerical simulation of flow inside a tilting box with an obstacle**

**Coastal Oil Spills JIP. Report No. 12**

AUTHOR(S)

Bård Brørs

CLIENT(S)

Eni Norge AS, A/S Norske Shell and StatoilHydro ASA

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| FILE CODE | DATE | APPROVED BY (NAME, POSITION, SIGN.) | |
| | 2008-11-07 | Tore Aunaas, Research Director | |

ABSTRACT

The flow of water in a tilting box with a surface-mounted obstacle (a tile for testing oil samples) was predicted with the CFD model Flow-3D. Two- and three-dimensional simulations were run with one, two and four liters of water in the box. The simulations were set up in order to mimic a laboratory experiment, using the same box size and motion.



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|---|---|---|
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| SELECTED BY AUTHOR | Numerical model | Numerisk modell |
| | Sloshing | Skvulping |
| | | |

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The flow of water in a tilting box with a surface-mounted obstacle inside was predicted with the CFD model Flow-3D. Two- and three-dimensional simulations were run with one, two and four liters of water in the box. The simulations were set up in order to mimic a laboratory experiment, using the same box size and pattern of motion.

# 2 EXPERIMENT

The effects of wave action on oil contaminated rock is simulated by placing a piece of oil-stained slate in a moving rectangular box with water (tilting box). A cluster of boxes were mounted on one common axle providing a pre-defined rotational motion. Figure 2.1 shows a cross-section through one of the 0.4 m long by 0.2 m wide boxes. The slate measures 0.14 m by 0.14 m and has a thickness of 0.02 m.

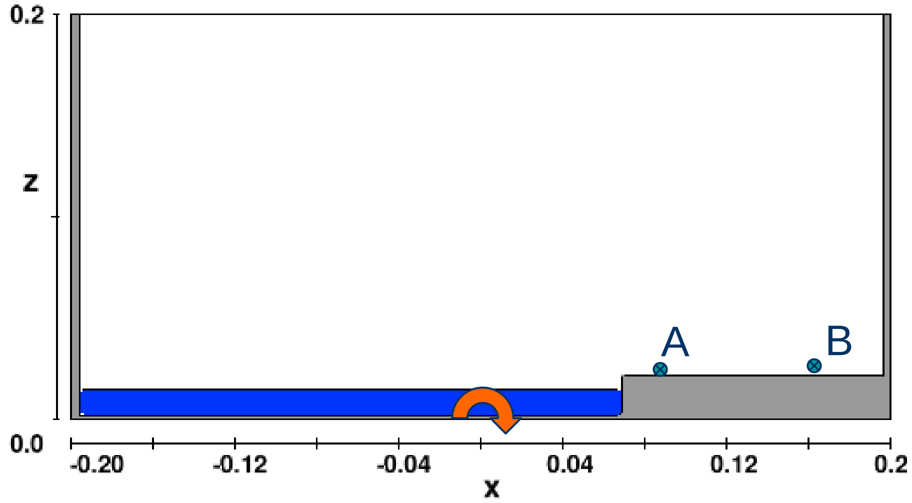



Figure 2.1 2D vertical slice through a tilting box. The situation pictured is with 1 liter of water. A and B indicate positions for output of *u* velocity time-series, 1 mm above the slate (shown with grey). The box is rotated with respect to the *y* axis (arrow).

The box is rotated quickly from an angle of $\alpha = -11.5°$ to an angle of $\alpha = 11.5°$ during a time of 0.8 seconds, and then slowly rotated back to $\alpha = -11.5°$ during a time of 4.8 s. This $T = 5.6$ seconds sequence is set in order to represent a wave hitting a slope and then retracting from the slope. It is repeated over and over in long-term simulations. Runs were made with three different water volumes: $V = 1$ L, 2 L and 4 L. The corresponding depth in front of the slate is 0.013 m, 0.025 m and 0.051 m, respectively.

# 3 NUMERICAL MODEL

## 3.1 General approach

For the numerical simulation, the tank was divided into a regular 102 by 101 mesh, giving a cell size of $\Delta x$ = 0.04 m in the horizontal and $\Delta z$ = 0.02 m in the vertical direction. Rather than letting the tank itself move, it was chosen to force the water by letting the direction of the acceleration of gravity vector $\boldsymbol{g}$ vary in a manner consistent with the prescribed motion. Each simulation was run for two $T$ = 5.6 s periods, after which the flow was found to be periodic, and then continued for one more period with output of flow results.

Both the 2D and 3D simulations were made with a renormalized group (RNG) turbulence model, a two-equation model based on the widely used ($k - \varepsilon$) model.

## 3.2 Simulations in 2D

Figure 3.1 – Figure 3.3 shows snapshots of the flow fields at different times during one ”wave” cycle with one, two and four liters of water in the tank, respectively.

The first frame shows the state when the tank is tilted to its maximum negative angle, at $\alpha = -11.5°$. At this time, the water has retracted maximally down the “beach”, and the flow velocity is very low.

The second frame shows a snapshot of the flow field 0.8 s later, when the box has completed the quick rotation to its maximum positive angle at $\alpha = 11.5°$. At this time, the water is rushing “up” the beach in the 1 litre case (Figure 3.1), but a significant part of it is deflected as it impinges on the toe of the slate. The wave in the 2 litre case (Figure 3.2) has been deflected to a lesser extent by the front of the slate. It has moved faster, and is seen to be running up the right wall. The wave in the four litre case (Figure 3.3) has moved faster still, and the top of the wave has started to retract to the left at the same time as the lower part is still moving up the beach (to the right) with good speed. Separation of the up-flow is occurring at the upper leading edge of the slate, forming a local re-circulation zone (whirl) with low flow velocity. The flow velocity is also low at the far end of the slate, possibly with a whirl forming inside the lower right corner of the flow domain.

The four last frames show the situation as the box slowly rotates back to the horizontal, and represents the retracting wave. Apparently, only the one liter case mimics this realistically, with the water flowing off the tile. In the two liter case, the wave is reflected from the left wall and is hitting the toe of the tile at $t = +4.8$ s. This, however, seems to have limited effect on the water flowing down the top of the tile. In the four liter case, this secondary reflected wave is seen to be on top of the tile (probably moving towards the left) at $t = +4.8$ s and is likely to have an effect of the local flow. At $t = +5.6$ it is still seen to be present, in front of the tile, going to the right. Its velocity of propagation is consistent with the velocity of a shallow water wave being the square root of $g$ times the water depth, being about 0.7 m/s in the present case.

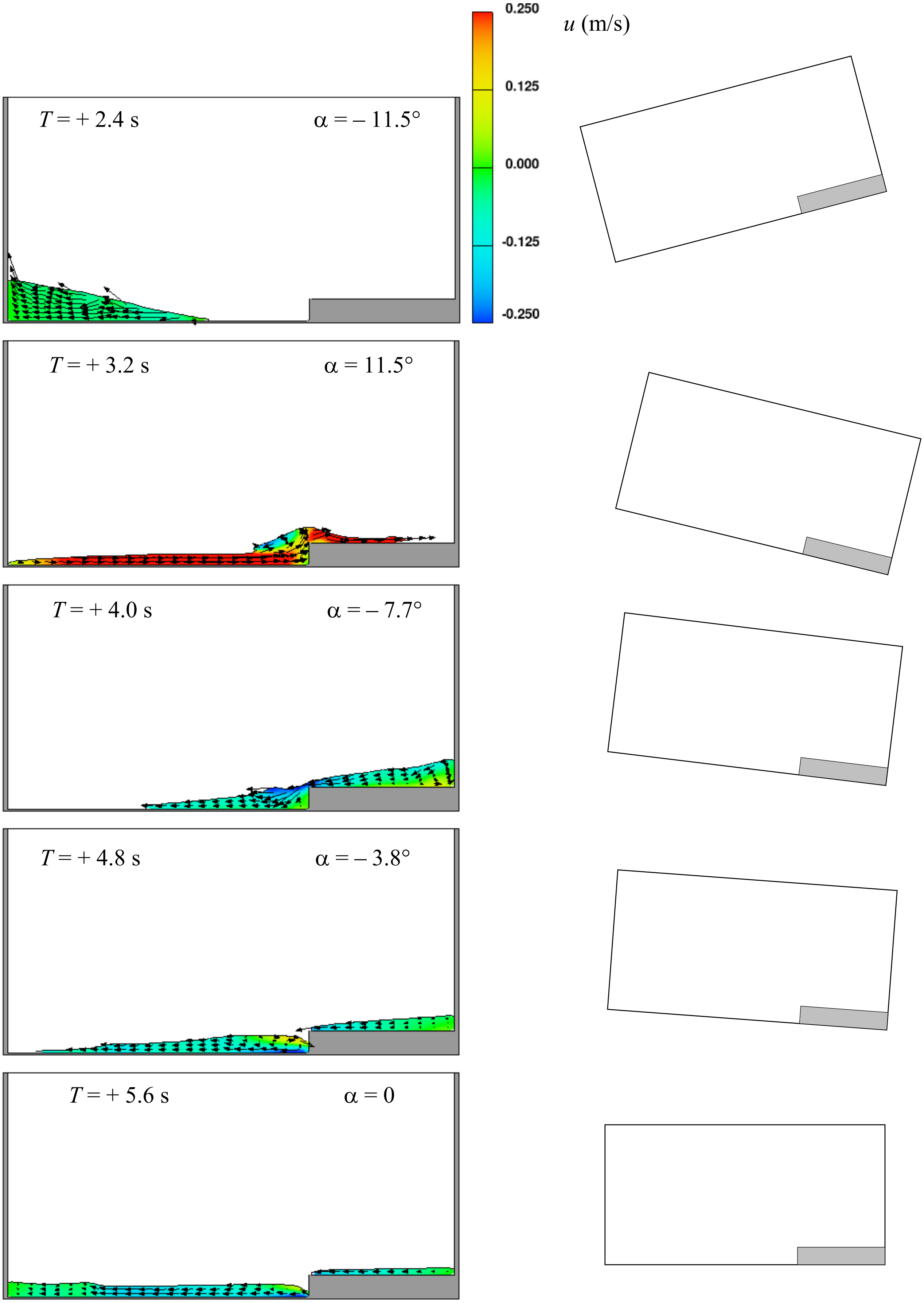



Figure 3.1 Predicted flow field at selected times for the $V = 1$ L case. The colour represents the horizontal velocity component, $u$. The position of the tank is shown to the right.

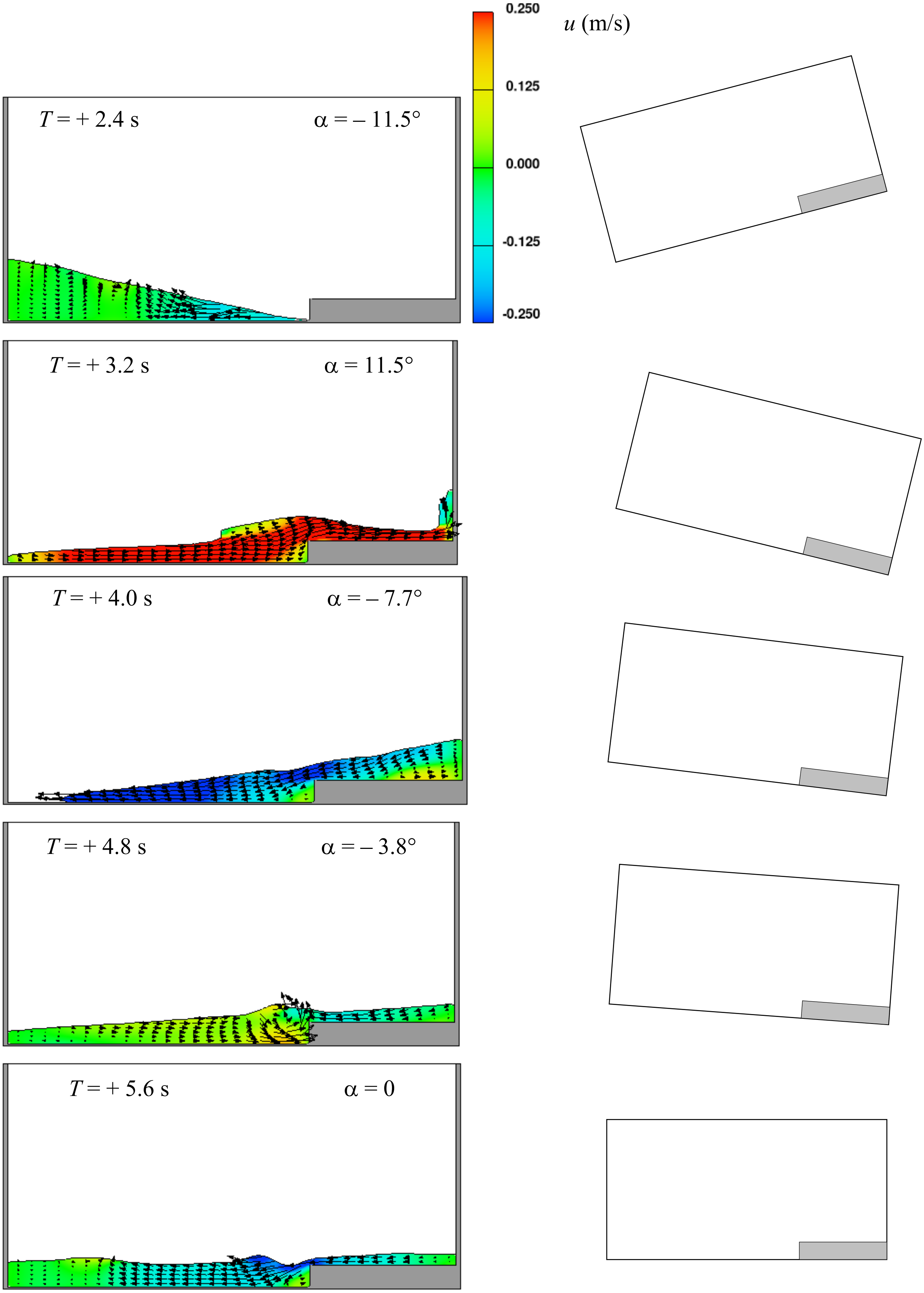



Figure 3.2 Predicted flow field at selected times for the $V = 2$ L case. The colour represents the horizontal velocity component, $u$. The position of the tank is shown to the right.

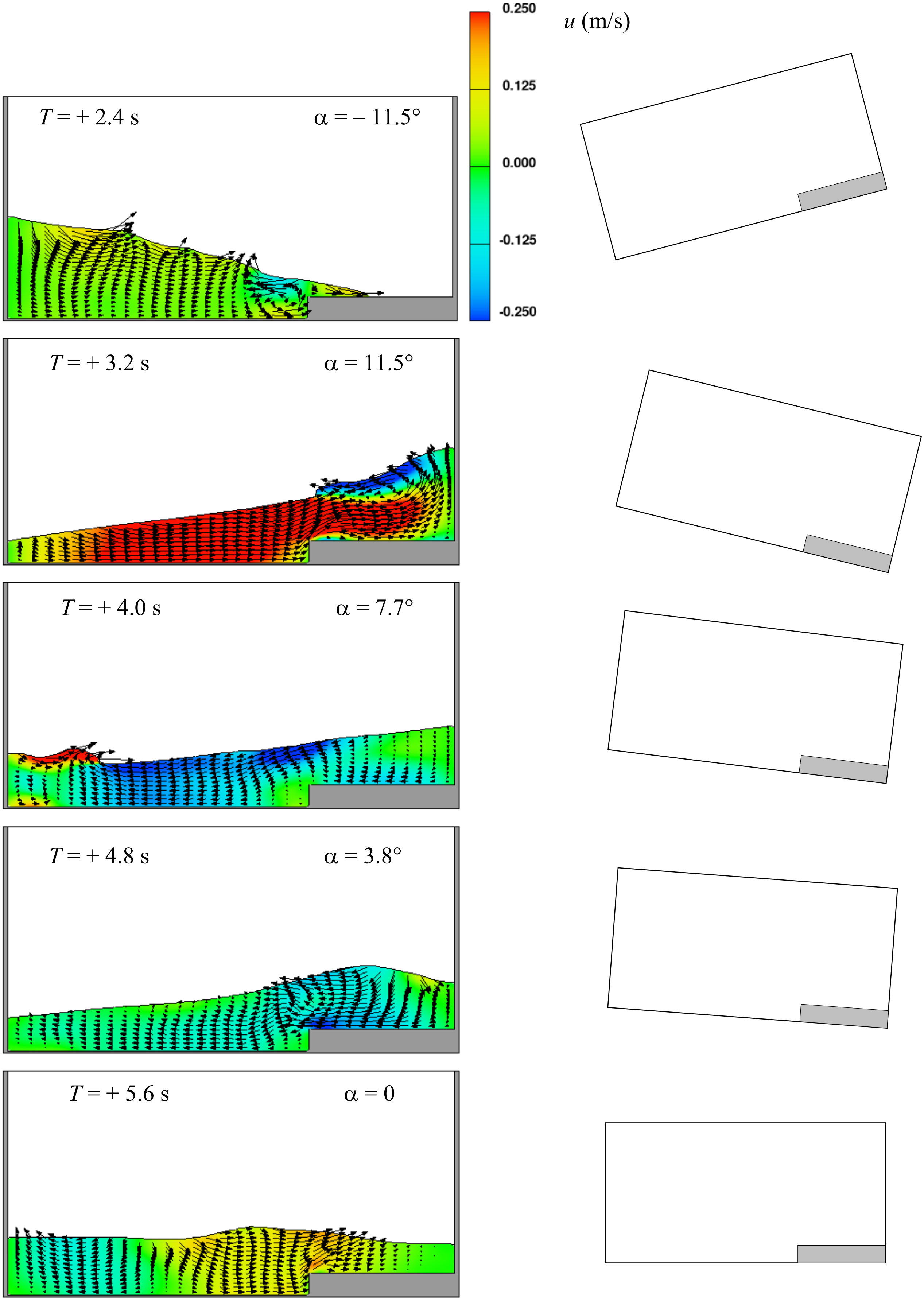



Figure 3.3 Predicted flow field at selected times for the $V = 4$ L case. The colour represents the horizontal velocity component, $u$. The position of the tank is shown to the right.

Figure 3.4 shows time-series of predicted velocity in two points located just above the slate, 0.02 m and 0.08 m from its left edge. Both qualitatively and quantitatively, the one and two liter cases are seen to be similar: A velocity pulse in the order of 0.2 – 0.3 m/s with a duration of about 0.7 – 0.8 s is seen to happen in point A near the leading edge of the tile at about *t* = 3 s, when the wave hits. With a short (~ 0.1 s) delay, the pulse hits point B with about 0.6 m/s with a very sharp rise and more gradual decay. The wave is seen to retract with a maximum velocity of about – 0.15 m/s in point B and – 0.2 m/s in point A.

The four liter case is seen to be entirely different. The wave hits the slate sooner (at *t* = 2.5 s in point A and t = 2.6 s in B) and the associated flow-speed is lower, with a maximum of less than 0.2 m/s in point A and 0.4 m/s in point B. The lower velocities can probably explained by the above mentioned separation of the flow, and that both points at times are situated inside the re-circulation zones. The many maxima and minima are caused by the wave going back and forth in the tank between the two end walls.

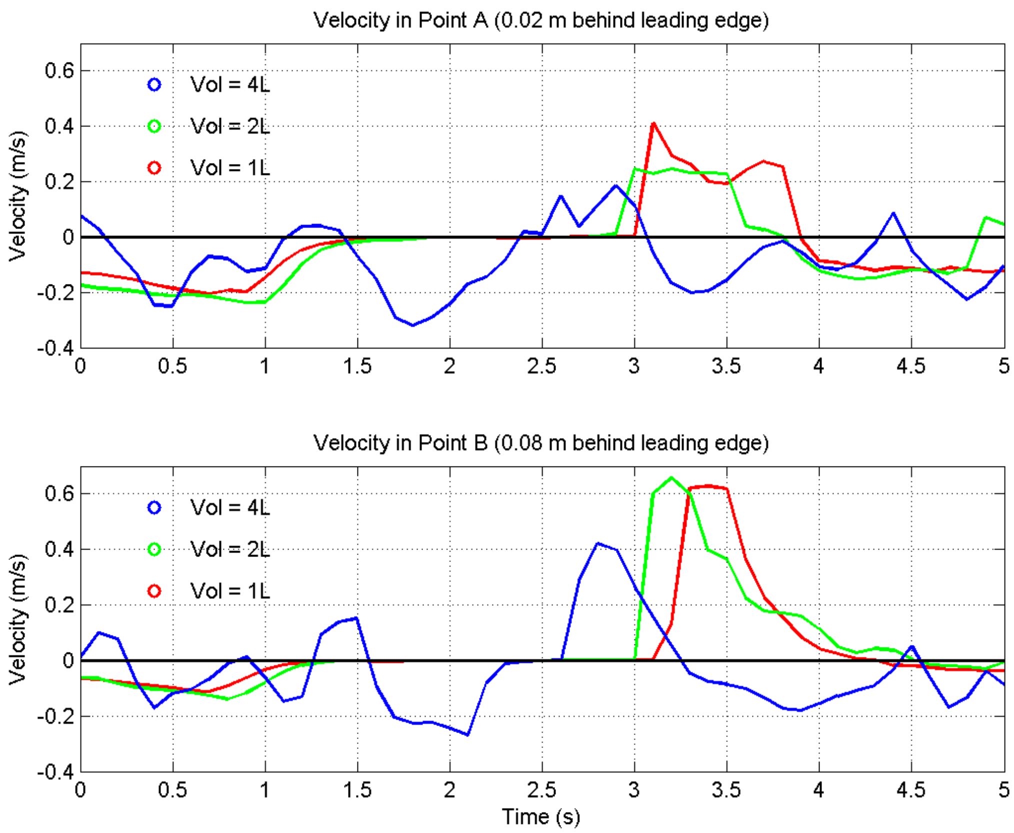
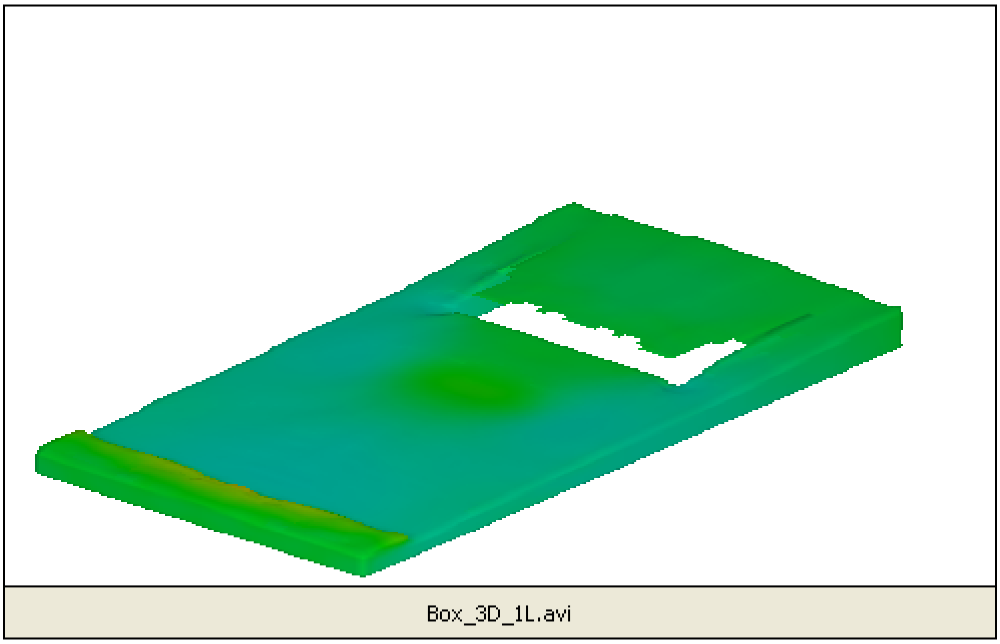



Figure 3.4 Time-series of flow velocity in point A and B, cf. Figure 2.1.

Base on these results, the 1 L and 2 L runs are considered to be more representative for wave action on a beach than the 4 L run.

### 3.3 Simulations in 3D

In order to check for possible three-dimensional effects caused by the 0.03 m wide gap on each side of the tile, three-dimensional (3D) simulations were run with the same setup as for the 2D simulations, except for a slightly different horizontal resolution of $\Delta x = \Delta y = 0.05$ m. The animations in Figure 3.5 show that there are 3D effects at the corners and side edges of the tile.



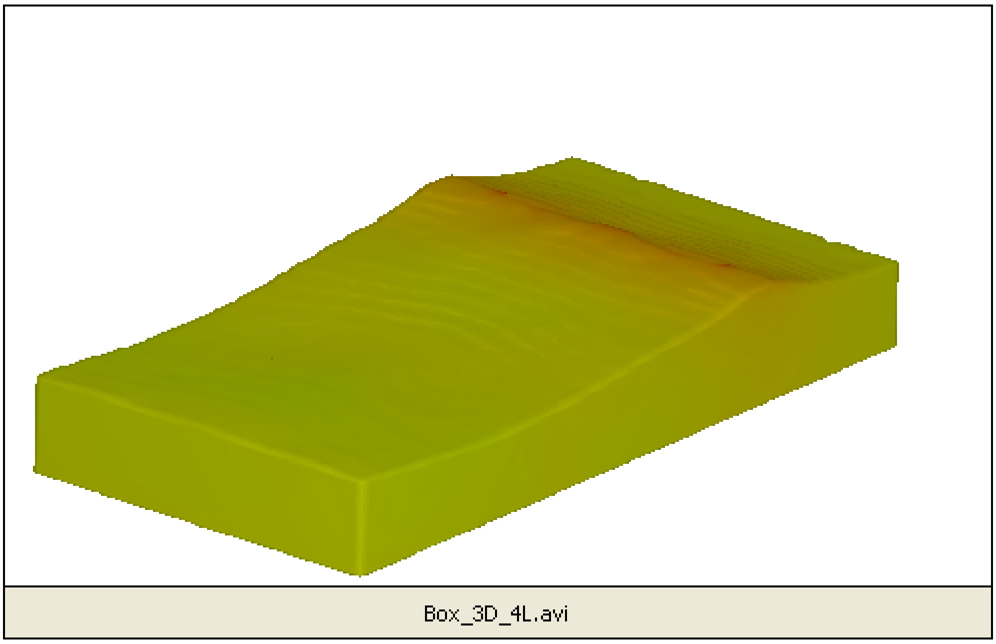




Figure 3.5 3D view of $V = 1$ L (upper image) and 4 L (lower image) simulation. The colour represents the $u$ velocity at the water surface. Double-click on image to run simulation (requires the files *Box_3D_1L.avi* and *Box_3D_1L.avi* to be stored on the same folder as this Word document).

This is also apparent on the horizontal plane (seen from above) flow field plots shown in Figure 3.6. Water is seen to flow off the sides of the tiles both when the wave hits and when it retracts. Apparently, more water drains to the sides than to the front of the tile as the wave retracts. Along the centre of the tile, however, the 2D and 3D solutions still agree quite well.

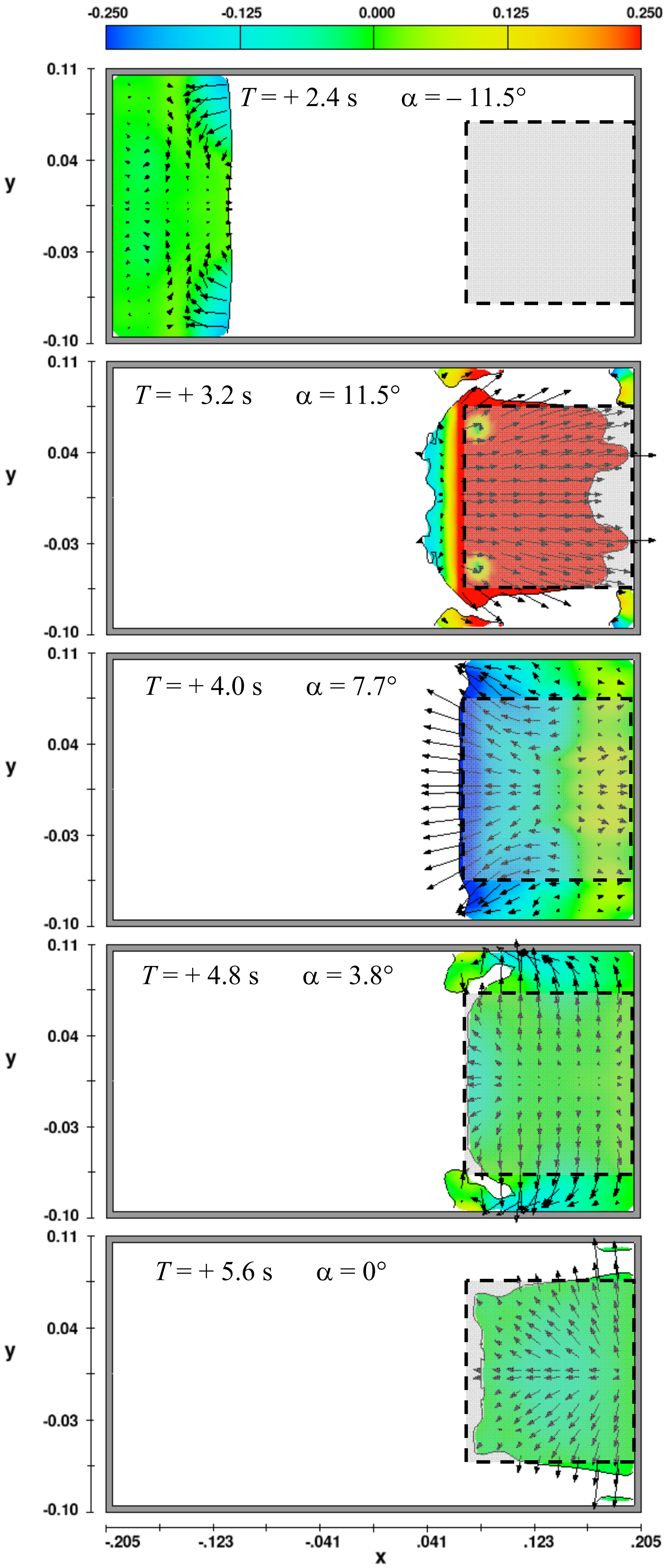



Figure 3.6 Predicted flow field in a slice just above the tile ($z$ = 0.061 m) for the $V$ = 1 L case.

# 4 CONCLUSIONS AND RECOMMENDATIONS

The cases with 1 L and 2 L of water in the box are predicted to behave similarly, with the water washing over the tile with a speed of 0.4 – 0.6 m/s for about one second, and then retracting with a speed of 0.1 – 0.2 m/s during the next two seconds. The tile is then dry for the last ~ 2 seconds of the “wave” period before the next wave hits. These runs are considered to be representative for the splash zone on a beach.

The simulated 4 L case behaves differently. With the tile and bottom of the box being immersed in water all of the time, water is sloshing back and forth between the end walls and generating multiple weaker velocity maxima on the tile during each “wave” period. This run is considered to be less representative for the situation on a beach than the 1 L and 2 L runs.

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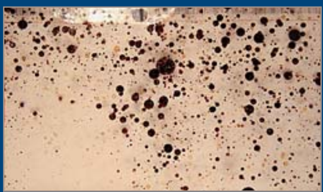
# REPORT



## Coastal Oil Spills - JIP

Report no.: 16

# C2.3 - Fate and behaviour of oil in acute phase – meso scale shoreline basin studies

Svein Ramstad, Jane HC Øksenvåg, Tor Arne Oltedal, Bror Johansen and Per S Daling

**SINTEF Materials and Chemistry**
Marine Environmental Technology

Date: 2008-12-19

# SINTEF REPORT

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TITLE

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**Coastal Oil pills Report No 16**

AUTHOR(S)

Svein Ramstad, Jane HC Øksenvåg, Tor Arne Oltedal, Bror Johansen and Per S Daling

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ABSTRACT

A total of eight experiments were performed to study the fate and behaviour of weathered oil emulsion during stranding and in the acute phase. The meso-scale shoreline basin which simulate environmental parameters, were used with four different shoreline substrate fraction ranging from coarse sand to solid substrate at constant temperature representing cold climate conditions (5°C) with continuous supply and exchange of fresh seawater. The experiments were performed with wave exposure and tidal variation for 24 hours (8 tidal periods). Three different weathered crude oil emulsions (Troll, Kobbe and Norne) and one bunker oil (IFO 380) were used as 250°C+ residues and emulsion with close to maximum water.

The main findings from the experimental studies were;

- A very large variation in fate and behaviour was observed with respect to both oil types and sediment characteristic during the acute phase (defined as 8 tidal periods).
- The IFO380 emulsion adhered very good to the sediment surface. The oil was remobilized by gradually reduction in oil film thickness during the experimental period.
- Presence of biofilm at the substrate surface reduced the adherence and allowed enhanced oil remobilisation during the experimental period.
- Penetration depth increased with increasing sediment size and physical properties (viscosity and pour point) of the emulsions.

The findings and observations from these studies and can contribute to an improved oil spill contingency and strategies during cleanup operations.

| KEYWORDS | ENGLISH | NORWEGIAN |
|---|---|---|
| GROUP 1 | Environment | Miljø |
| GROUP 2 | Oil | Olje |
| SELECTED BY AUTHOR | Meso-scale studies | Meso-skala studier |
| | Shoreline | Strand |
| | Natural processes | Naturlige prosesser |

# TABLE OF CONTENTS

# 1 Introduction

This project has been a part of phase 1 in the Coastal Oil Spills JIP. The research projects in the JIP have been focused on the fate and behavior of oil spills in coastal areas and on shoreline. Laboratory studies have been performed in order to obtain data for further development of numerical models.

The first phase of JIP was performed in the period from 2006 to 2008, and was funded by Eni Norge, Shell Technology and StatoilHydro. The overall objectives of the JIP have been:

- to contribute to an adequate and sufficient basis of competence to document possible consequences in case of an oil spill close to the coast
- to provide documentation ensuring the countermeasures giving the optimal environmental gain

SINTEF has for three decades been involved in studies on the fate and behaviour of oil on shoreline sediment. From the late seventies to the nineties, the focus was on field studies under cold climate conditions, first in Ny-Ålesund and later in Svea on Svalbard, as well as on several location along the Norwegian coast in connection to smaller accidental spills. After the Exxon Valdez incident in Alaska 1989, founding of larger research programs was possible. Through the ESCOST, BIOREN and ITOSS programs, SINTEF established and used meso-scale laboratory facilities (basins and columns) to study the fate and behaviour of oils and development of in-situ treatment techniques. These experimental systems allowed studies to be designed and performed under controlled and reproducible conditions under simulated realistic conditions including use of fresh seawater.

The experimental facility was upgraded in the Statoil project “Upgrading meso-scale and laboratory systems at SINTEF SeaLab” in 2005-6. The meso-scale basin system was modified and upgraded for more easy and reliable operation and less waste generation. The present experimental system is unique world-wide; a significant larger outdoor systems (COSS – Coastal Oilspill Simulation System, now; SERF Shoreline Environment Research Facilities) has been established by TGLO (Texas General Land Office, http://www.glo.state.tx.us/) in Texas USA. However, these facilities are not adopted for screening or research studies (e.g. large size, freshwater). Therefore, very little data on this topic is available from the literature. Most of the data comes therefore from observations and measurements of real spill situation.

During design and upgrading of the meso-scale basins, focus was on simulation and downscale of the most important environmental parameters, continuous supply and exchange of fresh seawater, temperature, wave exposure, tidal variation, shoreline substrates among others. The meso-scale basins therefore simulates well the environment, which allows studying of more processes that will affect the fate, behaviour and weathering of the oil on and in the shoreline substrate. The SINTEF SeaLab facilities has also established different other less complex laboratory systems to study specific processes taking place in the acute and restoration phase.

After an accidental release of petroleum products, the oil undergoes a number of weathering processes before stranding; evaporation, emulsification and photo-oxidation as the most important within the first day after the spill. However, most experimental data for laboratory studies has used waterfree and only slightly evaporated oils giving less realistic/relevant data to be used in e.g. oil spill contingency and response technique development. In the present study, SINTEF has focused on use of oil emulsion with realistic properties after 2-5 days on sea surface prior to strand; evaporation to a oil residue of 250$^{o}$C+ and a water content of close to maximum for four different petroleum products; three crude oils (Troll, Norne and Kobbe) and one heavy bunker fuel oil (IFO380).

# 2 Summary

The main objective of this task within the COS-JIP was to study and document fate and behaviour of oil on shoreline in the acute phase (defined as the period the oil is mobile, and chosen to be 8 tidal periods each 3 hours), as a function of oil type, weathering degree and environmental parameters. To reach these objectives, the meso-scale experimental basin systems were utilized in a total of eight experiments. The meso-scale basin (2m x 4m x 1m) simulates a number of environmental parameters allowing controlled and reproducible studies. This includes; continuous supply and exchange of fresh seawater (1vol/vol,day), wave exposure (approx 5cm), tidal variation (3h period) , constant temperature (5$^o$C), shoreline characteristics; including slope (12$^o$) and four sediment size (sand 2,8-6,3mm, coarse sand 8-16mm, gravel 10-80mm and solid substrate) and no light exposure. In each experiment the four substrate types were used separated by interior walls.

Three different crude oil were used representing different "groups" of oil; Troll crude (naphtenic), Kobbe (paraffinic) and Norne (waxy). In addition an IFO380 was included in the study. The crude oils were a 250$^o$C+ residue, and all oils were emulsified to a water content of just below maximum water content (Troll 70%, Kobbe 75%, Norne 60% and IFO380 40% water).

The experiments designed to study the fate and behaviour of emulsions (crude oil 250$^o$C+ residue with maximum water content) in the meso-scale basins include simulation of stranding of the oil followed by 8 tidal periods (3 hours) at 5$^o$C simulating cold climate conditions. The surface and subsurface oil in the intertidal zone was observed, measured and analysed at defined intervals to describe the fate and behaviour of the oil. Due to a relative small experimental area for each oil and sediment, it was not possible to take parallel samples at each sampling period which makes it more difficult to give clear conclusions. The information obtained through the studies gives, however, a good picture on the fate and behaviour of the oils in the acute phase and fulfils the objectives of study and document fate and behaviour of oil on shoreline in the acute phase.

The main findings from the experimental studies were;

- A very large variation in fate and behaviour was observed with respect to both oil types and sediment characteristic during the acute phase (defined as 8 tidal periods).
- The IFO380 emulsion adhered very good to the sediment surface. The oil was remobilized by gradually reduction in oil film thickness during the experimental period.
- Presence of biofilm at the substrate surface reduced the adherence and allowed enhanced oil remobilisation during the experimental period.
- Penetration depth increased with increasing sediment size and physical properties (viscosity and pour point) of the emulsions.

Other findings and observation from these studies includes:

- The crude oil emulsions with a high pour point (Kobbe and Norne) did not adhere well to the sediment surface, and was remobilized from the surface as lumps by wave exposure.
- Low viscous crude oil emulsion (Troll) adhered as a thin oil layer to the sediment surface and was also remobilized by wave exposure.
- Penetration of the oil emulsion was dependent on the viscosity and pour point of the emulsion. The low viscous Troll emulsion penetrated rapidly to a maximum depth, whereas the Kobbe and Troll emulsion (high pour point) remained mainly at the upper sediment layer. The penetration increased slightly during the experimental period. The penetration of the high viscous bunker emulsion increased during the experimental period.

- The subsurface sediment oil quantity (retention) increased with increasing viscosity and pour point.
- A very low retention on solid substrates with crude oil emulsion was observed. The IFO380 emulsion retained at the solid substrate surface, but he oil layer thickness decreased due to wave exposure.
- The low viscous oil (Troll) was removed from the subsurface sediment due to erosion and water flow exposure. Crude oil emulsions with high pour point that adhered to the sediment was retained. The high viscous bunker emulsion was remobilized from the subsurface sediment at a low rate.

The findings and observation from the meso-scale basin experiments will give important input to contingency plans and cleanup strategies for the different oil types characteristic.

- Troll (low viscosity, low pour point); the oil will penetrate into the sediment which are difficult to cleanup., and should avoid stranding at sediment shoreline. The stranded oil will be removed easy by sediment and water exposure. High self-cleaning properties.
- IFO380 (high viscosity); will adhere to shoreline sediment, and penetrate into the shoreline sediment. Difficult to cleanup and a low self-cleaning rate is predicted. If possible sediment shorelines should be protected and redirected towards e.g. bare-rock shorelines.
- Kobbe and Norne (high pour point ad moderate viscosity); the emulsion do not adhere well to substrate surface and are easily remobilized. Prevent spreading of remobilized oil by e.g. booming. High self cleaning rate at sediment surface in intertidal zone, accumulates in the supralitoral zone.

# 3 Materials and methods

## 3.1 Experimental system

The experiments were performed according to a SOP in the continuous flow and water exchange meso-scale basins. The experimental systems were upgraded during the Statoil project "Up-grade the meso-scale experimental facilities at SINTEF SeaLab (2006/7)"- The experimental system is shown in Figure 3.1. The basin of 4m x 2m x 1m has a constant water level (70cm) and a constant water throughput (exchange of approx. one volume every day, 5,6$m^3$), and the tidal variation is controlle by moving the shoreline section according to a sinus curve with a period of 3 hours and is controlled by two separate motors. The shoreline section was chosen to have a constant angle (12 degree), and is constructed of a perforated bottom covered by a geotextile allowing water transport. The shoreline section (3m x 2m) is divided into four separate sections divided by PE-plates.

The shoreline sections were filled with sediment in a depth of approximately 10-13cm of sediment fractions. For solid substrate shale tiles (15cm x 15cm) placed on a raised platform to give a equal height as the sediment sections. In the experiment four different sediment fraction/characteristic were used:

- Fraction I  2,8-6,3 mm  coarse sad
- Fraction II  8-16 mm  gravel
- Fraction III  10-80 mm  pebble
- Fraction IV  solid  Shale tiles (15x15 cm)

The sediment (I-III) was sorted fraction from natural sediment from Trondheim Mørtelverk and the shale tiles was from Altaskifer.

A wave generator in mounted in the lower end of the basin. The frequence and amplitude of the wave generator can be adjusted to give different wave exposure intensity.

The basin is located in an air temperature controlled room. The water comes directly from Trondheim fjord (water depth of approx. 80m) with a temperature of approximately 6-10°C (seasonal dependent), and the water temperature in the basins are controlled by the air.

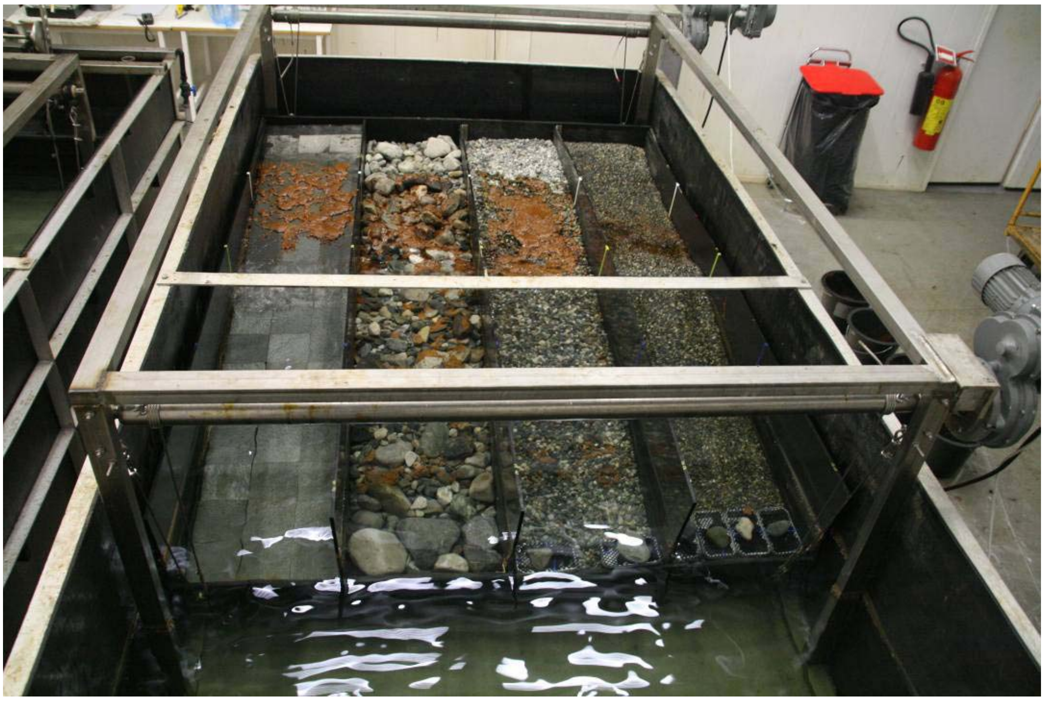


*Figure 3.1 Meso-scale shoreline basin*

### 3.2 Experimental protocol

The experiments in the meso-scale basin were performed according to a standard protocol, which include;

- The basin and interior parts were throughoutly washed prior to initiation of new experiment.
- The shoreline sections were filled with pre-washed sediments of defined sediment size in a thickness of 10-13 cm. The sediment was distributed evenly giving a smooth surface.
- The basins were filled with fresh seawater (70cm). A constant water flow rate equal to one volume pr day was started.
- The tidal variation and wave exposure was started, at least one day prior to initiation of the experiment.
- Oil emulsion (25L for each basin) was prepared using a standard concrete mixer, and allowed to mix for at least 18 hours. The viscosity of the emulsion was measured and compared to previous data before acceptance for use.
- The emulsion was split into four equal parts in buckets.
- The emulsion was applied to each section at high tide at the water surface within plastic frames.
- The experiments were started by "simultaneous" removal of the frames, and starting tidal variation and wave generator.
- During the first falling period the oil was kept within each individual section.
- Sampling, measurement and observations are described in Chapter 3.5.
- After termination of the experimental period, the wave generator, tidal movement and water flow were turned off. The contaminated sediment was collected and sent for destruction and oil residues on solid substrate tiles was removed by washing and DCM extraction.
- The residual oil in the basin and on interior parts were removed by high pressure warm water washing using.

Detailed description of the use of the meso-scale basin are described in the Standard operational protocol for studies on the fate and behaviour of oil in the acute phase.

The wave exposure generated by the wave-machine is described by numerical modelling using Flow-3D modelling (Brørs, B., 2008, "Numerical simulation of waves on a porous beach, SINTEF F8507).

## 3.3 Experimental

A total of eight experiments have been performed studying the fate and behaviour of oil in the acute phase. The experimental parameters are summarized in Table 3.1.

*Table 3.1; Experimental parameters in the meso-scale experiments for acute phase*

| ID | Oil type (emulsion) | Oil application method* | Sediment type (mm) | | | | Solid surface |
|---|---|---|---|---|---|---|---|
| | | | 2,8-6,3 | 8,16 | 10-80 | solid | Biofilm |
| 1A | Troll | A | X | X | X | X | - |
| 1B | Kobbe | A | X | X | X | X | - |
| 2A | Troll | B | X | X | X | X | - |
| 2B | Kobbe | B | X | X | X | X | - |
| 3A | Norne | B | X | X | X | X | - |
| 3B | IFO380 | B | X | X | X | X | - |
| 7A | Troll | B | | | | X | +/- |
| 7B | IFO380 | B | | | | X | +/- |

Oil application; A – oil applied together for all sections below each sediment section,
B – oil applied separately in each sediment section

## 3.4 Experimental oils

Crude oils can be characterised in four categories: asphaltenic, naphtenic, paraffinic and waxy crude oils. The crude oils studied in the Coastal Oil Spills JIP were selected among the oil companies' crude oils. It was important to select crude oils representing different categories of oils. The selected crude oils represent the categories:

- Troll – naphtenic crude oil
- Norne – waxy crude oils
- Kobbe – light paraffinic crude oil

In addition to the crude oils, a heavy fuel oil (IFO380) was also tested. IFO 380 is representative heavy fuel oils for bunker oils used as fuel for ships going along the Norwegian coast. The content of light oil components in fuel oils is low, typically lower than 5 vol% for IFO 380 oils. The testing of the IFO 380 was therefore concentrated on the "fresh" fuel oil, not on an evaporated residue. The IFO 380 oil used in this project is a low sulphur fuel oil produced at the Esso refinery at Slagentangen in Norway.

Some physical and chemical properties of the oils studied are listed in
Table ***3.2***.

*Table 3.2 Oils used in the Coastal Oil Spills JIP.*

| SINTEF Id | Oil type | Residue | Density (Kg/m$^3$) | Evaporative Loss (Vol%) | Pour point (°C) | Wax (wt%) | Asphaltenes (wt%) | Viscosity at 5°C/10$^{-s}$ (cP) |
|---|---|---|---|---|---|---|---|---|
| 07-0287 | Troll | Fresh | 0,900 | 0 | -36 | 0,9 | 0,04 | |
| | | 250°C | 0,930 | 25,5 | -27 | | | 770 |
| | | Ph.ox. | 0,931 | - | -21 | | | |
| 07-0260 | Norne | Fresh | 0,860 | 0 | 21 | 4,3 | 0,30 | |
| | | 250°C | 0,888 | 28,4 | 30 | | | 39100 |
| | | Ph.ox. | 0,885 | - | 30 | | | |
| 06-1061 | Kobbe | Fresh | 0,797 | 0 | -39 | 3,4 | 0,03 | |
| | | 250°C | 0,875 | 53,6 | 21 | | | 4630 |
| | | Ph.ox. | 0,877 | - | 15 | | | |
| 06-1125 | IFO 380 | Fresh | 0,932 | 0 | 15 | 5,0 | 3,4 | 87100 |

*-: not measured*

It was decided to weather the oils to represent the properties of the oils after ½-1 week at sea. Evaporation, emulsification and photo-oxidation were performed according to SINTEF laboratory procedures. An evaporated residue of 250˚C+ was used for the three crude oils. That means that compounds with a boiling point typically below 250˚C have evaporated, and the product used is therefore a residue. IFO 380 is a refined product, the bunker fuel oil was therefore used without further evaporation. To ensure reproducible production of emulsions, a water content just below the maximum water uptake for the respective oils was used. After some initial studies, the standard water content was decided to be 70% for Troll, 75% for Kobbe, 60% for Norne and 40% for IFO 380.

### 3.5 Analysis

The oil concentration of oil in the sediment was determined as described in the SOP which include extraction with dichloromethane (DCM), and analysis using a spectrophotometer (Hitachi U-2000 spectrophotometer).

Prior to initiation of each experiment the emulsion was characterised by rheological measurements (Physica MCR300 MC1+ rheometer with an US200 software).

### 3.6 Observations, documentation, sampling and measurements

During an experimental period, the observation, measurements, documentation and sampling were performed as described in Table 3.3.

*Table 3.3 Observation, measurements, documentation and sampling during an experimental period on studies during acute phase*

| Time | Activity |
|---|---|
| Prior to initiation | Temperature measurements; ambient and water |
| Oil application<br>Initiation of experiment | Photo documentation of oil behaviour |
| 1st falling tide | Control spreading of oil within each shoreline section<br>Quantify collected/released oil<br>(Photo documentation) |
| 1st low tide | Photo documentation<br>Visual observations - Surface oil layer/film; thickness and coverage measurement<br>Sediment sampling at e.g. 60, 90 and 120cm from to of shore<br>Observation of oil penetration |
| 1st rising tide | Collect released oil from sediment surface (manual or absorbent pad) – quantify collected oil (gravimetric)<br>Photo documentation |
| 2nd low tide | As 1st low tide |
| 3rd low tide | As 1st low tide |
| 8th low tide | As 1st low tide<br>Sediment sampling at different depth and various positions |
| | Documentation of sediment transport in relevant sediment sections |

Surface and subsurface oil was quantified as;

- Adhesion; product of average coverage and oil layer thickness in different sections.
- Refloating/washout; floating oil in each section during the first tidal period collected by sorbent pads or by manual collection and quantified gravimetrically.
- Penetration; Observation of visible oil in a vertical profile into the sediment prepared with a trowel

Photo documentation was done from same position and angle every time for more easy comparison of oil behaviour.

Sediment sampling was normally performed 60-90 cm below shore top position, approximately 10cm down the shore for each sampling time. The available sampling area did not allow sampling replicates.

In some experiment the fate and behaviour of the oil was documented by continuous video recording.

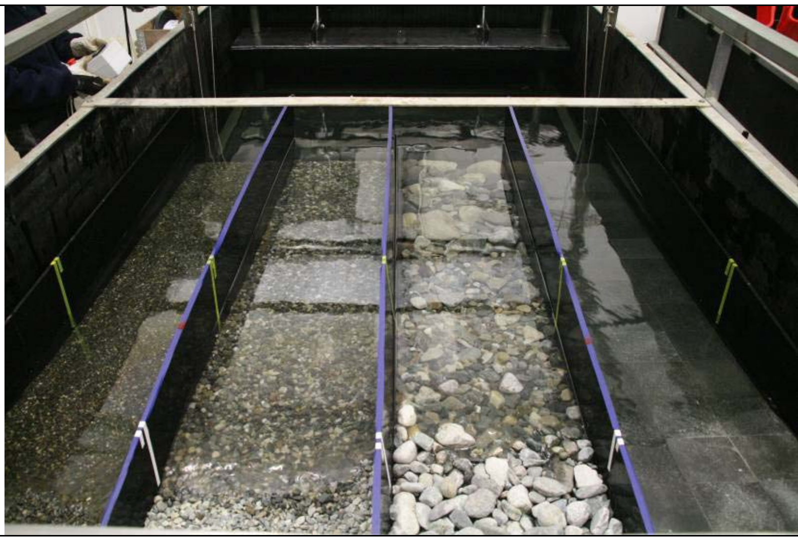
# 4 Results and discussions

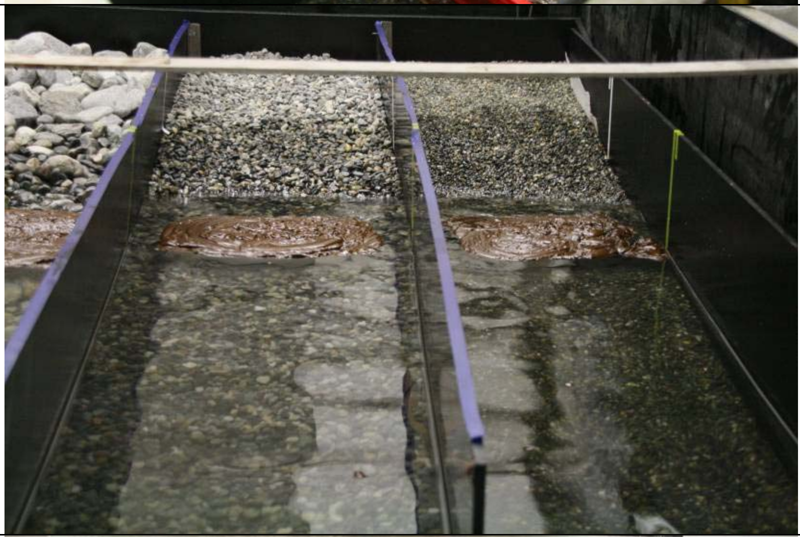
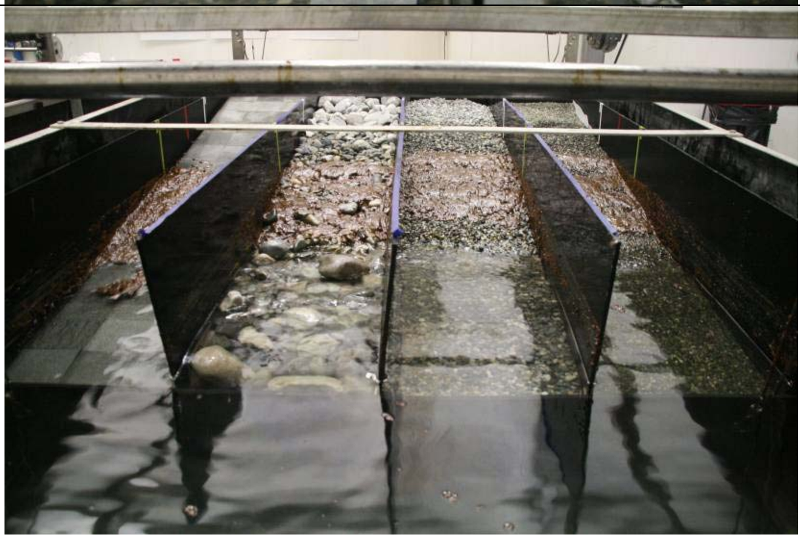
The meso-scale basin experimental systems was designed to study the fate, behaviour and weathering of oil under realistic, controlled and reproducible conditions including continuous supply and exchange of fresh seawater, tidal variation and wave exposure for different shoreline substrate characteristics. A total of eight experiments were performed during this study, each for 8 tidal periods in 24 hours. The use of different shoreline substrate sections reduced the experimental area for each shoreline type and did not allow parallel sampling and thereby statistical analysis of the results. The available sampling areas for the acute phase studies were therefore only approximately 60-80cm x 30cm (width). Samples were taken in the middle of the section from the top to the bottom of the section. The results are therefore more descriptive.

The main results from the studies are presented in this section, and all experimental observations, monitoring, documentation and analysis for each experiment is given in Appendix (1-8).

## 4.1 Experimental protocol

Pictures and comments on the experiments for studying the fate and behaviour of oil emulsion in the acute phase representing the first 8 tidal cycles, are given in Figure 4.1. A standard experimental protocol was established based on experience and finding during these experiments. The meso-scale basins had not been used for this purpose previously, and no relevant documentation in the literature could be used. The division of the shoreline into four separate sections with different sediment characteristics allowed more screening studies, but reduce the experimental area and loose the possibility to take parallel samples for statistical analysis of experimental data.

| | |
|---|---|
| Basin prior to oil application.<br>Shoreline sediment from left;<br>• Fraction I; 2,8-6,3mm<br>• Fraction II; 8-16mm<br>• Fraction III; 10-80mm<br>• Fraction IV; Solid<br>Water supply and exchange and tidal variation initiated at least 24 hour before oil application. |  |

| | |
|---|---|
| 25L oil emulsion was prepared in a standard concrete mixer at test temperature for minimum 18 hours before application. The emulsion were split into 4 equal parts. Emulsion were applied at high tide at water surface in plastic frame without bottom. |  |
| Initiation of experiment; plastic frame removed, and tidal variation and wave generator were started. Oil emulsion was not allowed to be transported outside each section. |  |
| First low tide (t=1,5h). No excess oil on water surface. Observation and photo-documentation, and sampling of each section – same procedure also at 2nd, 3rd and 8th low tide. |  |

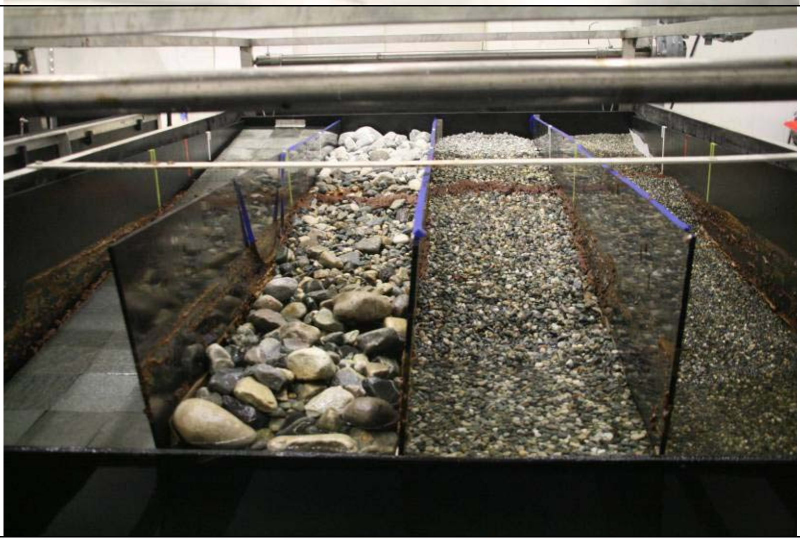
| | |
|---|---|
| First rising tide; surface oil was remobilized from the shoreline surface to water surface. Released oil collected manually or by sorbent pads. |  |
| Second low tide. Continuous oil layer on sediment in the top of the intertidal zone. Scattered oil in the intertidal zone. |  |
| 8th low tide. Oil removed from the shoreline sediment surface in the intertidal zone. Some surface oil in the top of the tidal zone and at the surface of the division plate. |  |

*Figure 4.1; Photo-documentation from one experimental period studying the fate and behaviour of emulsified oil in the acute phase.*

## 4.2 Adhesion/surface coverage

The experiments were designed to give a realistic interaction between the oil emulsion and the shoreline substrates. The oil was applied separately for each sediment section at the water surface at high tide. The plastic frames were removed simultaneously to initiation to wave exposure and tidal variation, expect experiment 1 and 2 (cfr. Table 3.1). The oil emulsion therefore came in contact with the shoreline substrate through natural mechanisms during the first falling tide. During the first falling tide, all the oil emulsion remained at the shoreline within the shoreline sections as surface and/or subsurface oil. In Figure 4.2 and Table 4.1 the coverage (degree of cover in initially oiled area) and thickness of the oil emulsion are given for the solid substrate section. The results show that Troll, Norne and IFO380 emulsions covered the surface totally (90-100%) whereas the Kobbe emulsion gave coverage of approximately 25%, which most probably is due to its high pour point. The oil layer thickness varied much from an initial thickness of Troll of 2mm to 10-20mm for both Kobbe and Norne. A significant part of the oil did not adhere to the shoreline substrate. This phenomenon was most pronounced with the low viscous Troll emulsion (run-off) and the Kobbe oil emulsion adhesion with high pour point. This phenomenon varied also to some extent with the different shoreline substrate characteristics, and will be discussed further in Chapter 4.3 and 4.4.

The most pronounced difference between the oil types, was the difference in behaviour for the bunker oil compared to the crude oil emulsions. The bunker oil covered the surface during the experimental period (90-100%), whereas adhesion between the crude oil emulsion and shoreline substrate were weaker giving a reduction in coverage to <10% at the end of the experimental period. The oil layer thickness was however gradually decreased for the Troll oil emulsion (pour point below experimental temperature), whereas the thickness of the other oils (Norne and Kobbe) remained the same. The thickness of the IFO380 bunker oil emulsion decreased also during the experimental period.

*Table 4.1 Oil layer/film thickness at Fraction IV (solid) substrate in upper intertidal zone*

| | Oil emulsion thickness (mm) | | | |
|---|---|---|---|---|
| Tidal period (#low tide) | Troll | Kobbe | Norne | IFO380 |
| 1 | 2 | 1-10 | 1-20 | 2-4 |
| 2 | 1 | 1-10 | 1-10 | 2 |
| 4 | <1 | 1-10 | 1-10 | 1-2 |
| 8 | <1 | <1 | 1-10 | 1 |

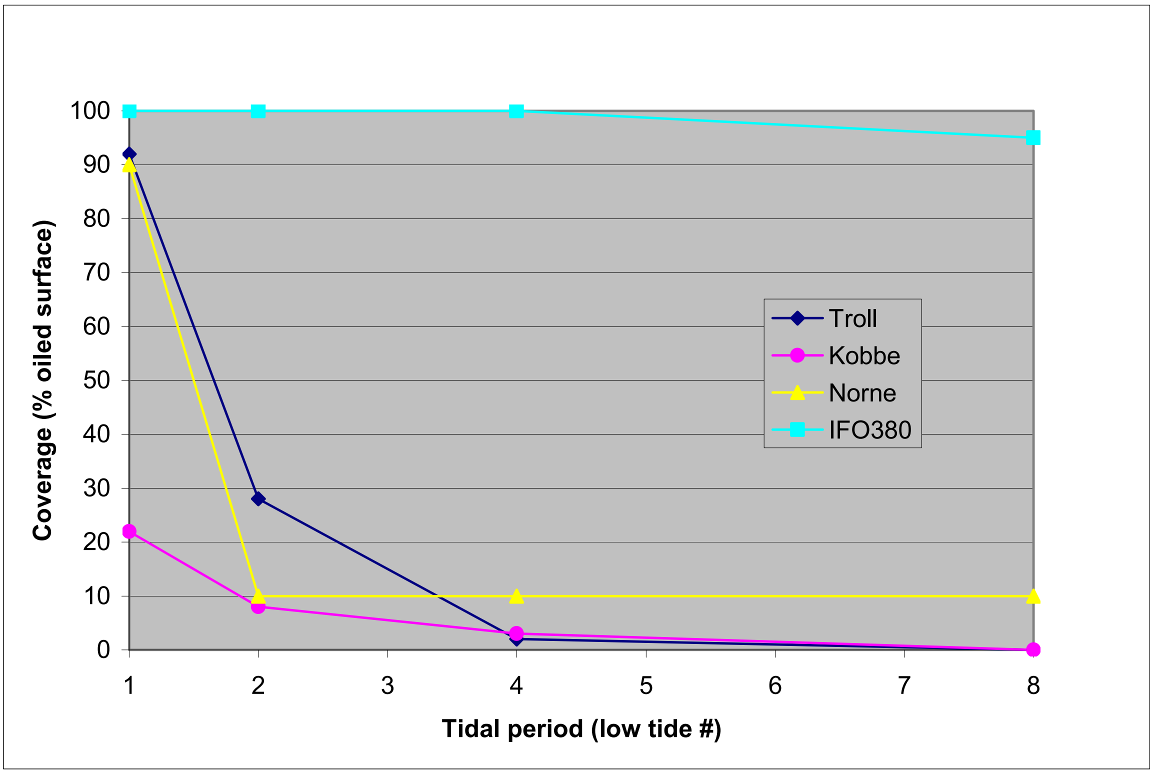



*Figure 4.2 Oil film/layer coverage of Fraction IV (solid) substrate in the upper intertidal zone*

### 4.3 Refloating and wash-out

After the initial falling tidal period with stranding of the oil, the oil at the sediment surface and in the upper subsurface zone is exposed to wave action and water transport. The oil will be transported from the surface by refloating and washout mechanisms. The quantities of the oil at the surface of the different substrates were estimated by coverage and thickness observations and measurements. The results for the different oil emulsions and shoreline substrates are given in Figure 4.3, Figure 4.4, Figure 4.5 and Figure 4.6. For the crude oil emulsion the oil was rapidly removed from the surface for all shoreline characteristics, and after typically 4 tidal periods only small quantities remained on the surface. This indicates that the contact area between the oil and the sediment surface was not important for adhesion of emulsions with high pour point (Kobbe and Norne). This difference could be due to the low stability of the Kobbe emulsion. The mobile Troll oil emulsion could be transported into the sediment or washed out. With the bunker oil emulsion no oil was observed at the surface of the finest sediment indicating transport of the mobile oil into the sediment or wash out. However, significant amounts of oil emulsion adhered to the sediment surface with both solid substrate and the pebble sediment fraction was observed for the bunker oil.

With the present observation and measurements it is not possible to distinguish between the mechanisms for oil removal from the surface; refloating and washout and possibly erosion. These processes are studied in more detail in the laboratory experiments in Task C3.

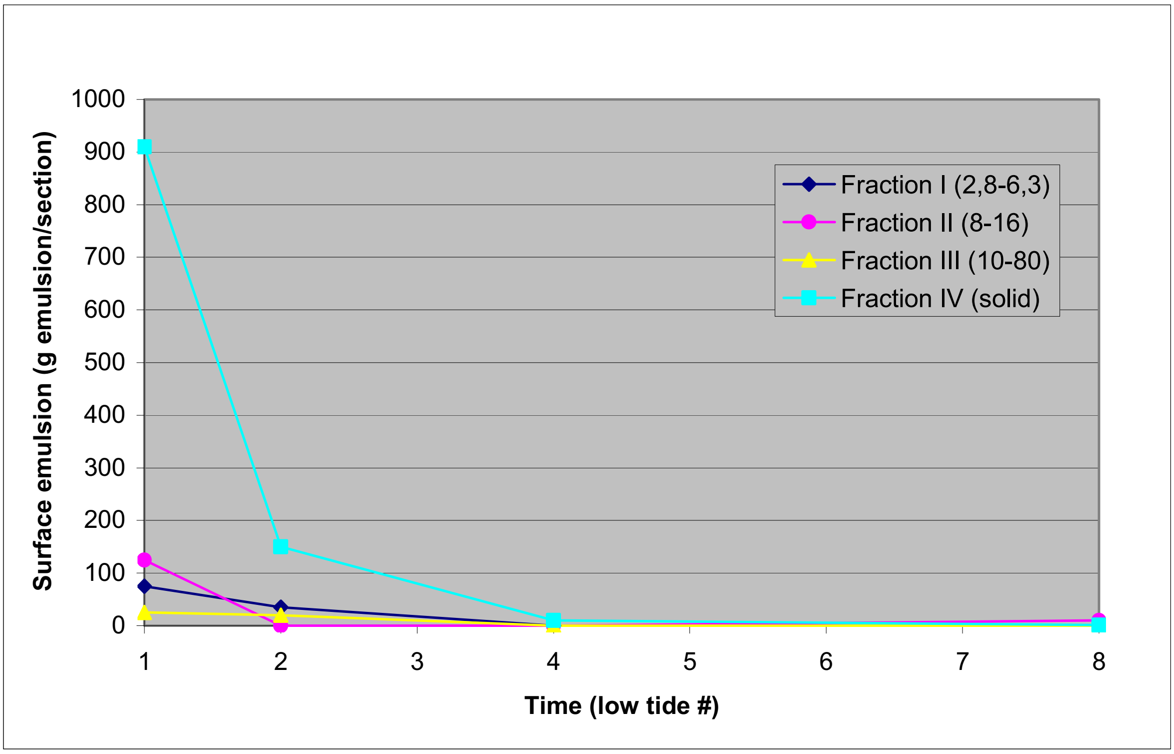



*Figure 4.3 Troll 250°C+ emulsion at surface of different sediment fraction*

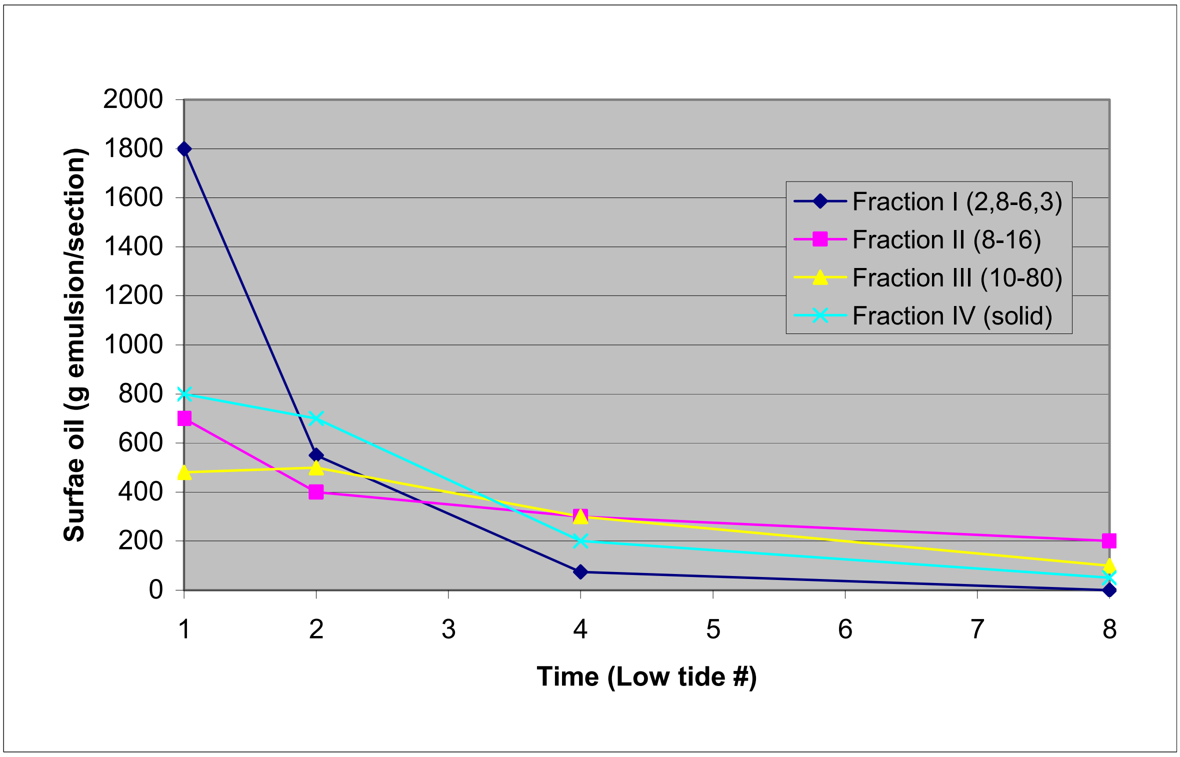



*Figure 4.4; Kobbe 250$^o$C+ emulsion at surface of different sediment fraction*

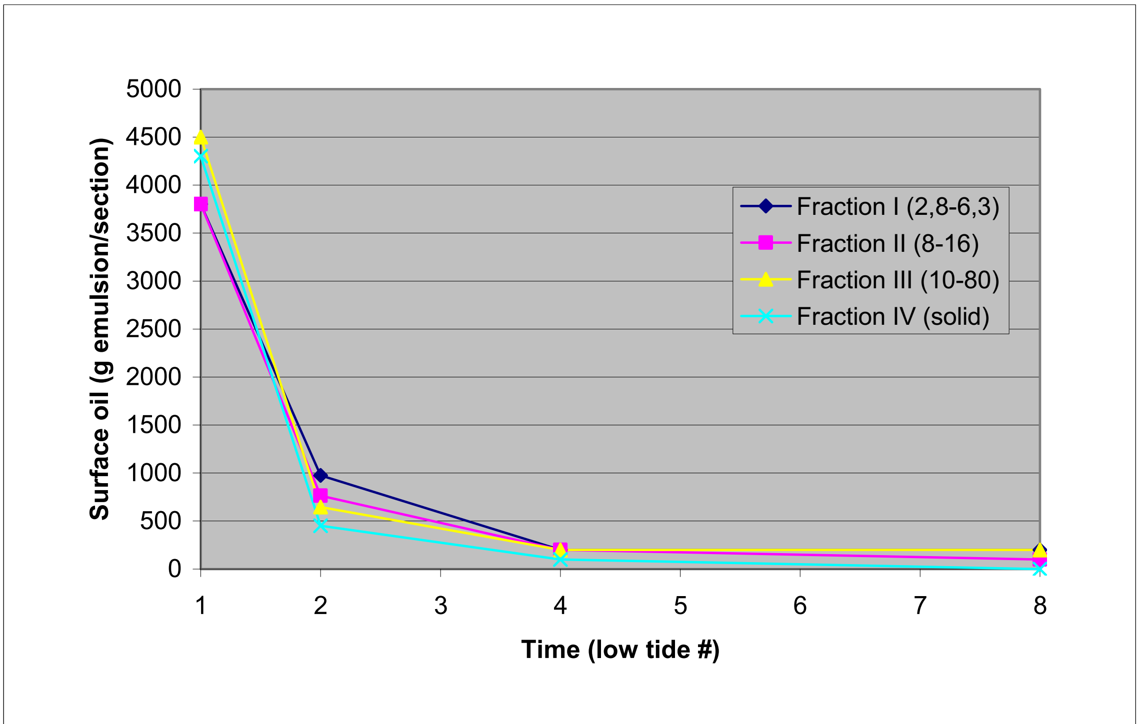



*Figure 4.5 Norne 250$^o$C+ emulsion at surface of different sediment fraction*

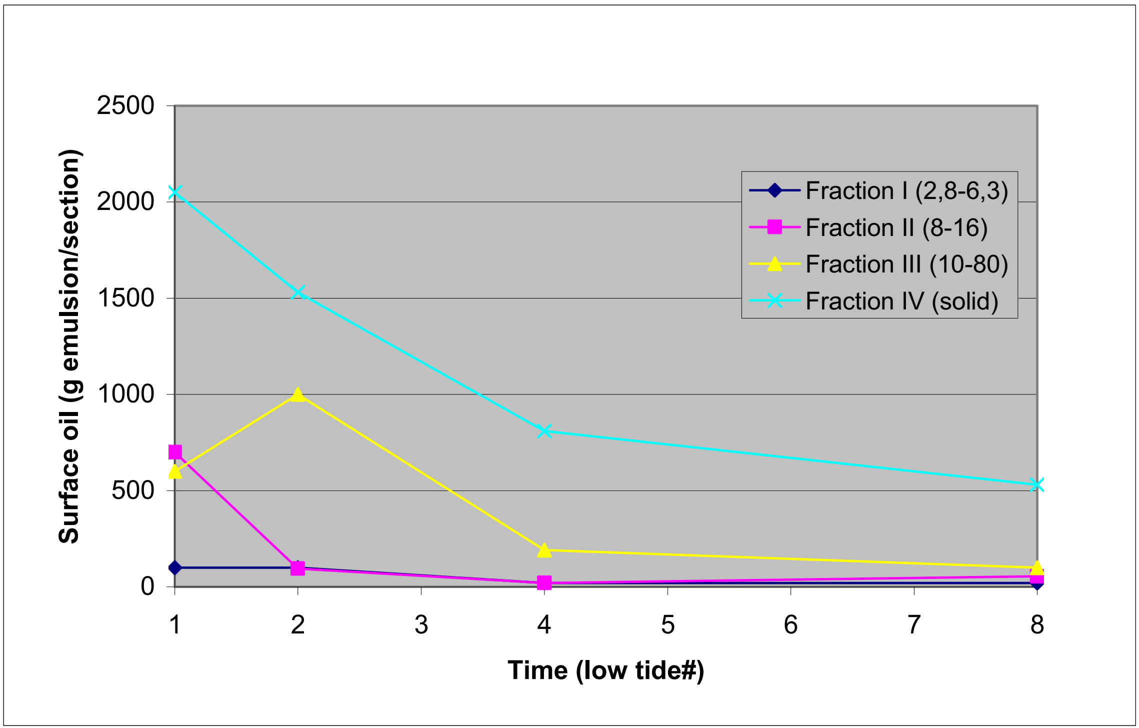



*Figure 4.6; IFO 380 emulsion at surface of different sediment fraction*

### 4.4 Penetration/retention

As discussed in Chapter 4.3 the oil emulsion adhered and remained at the sediment surface in different quantities and condition, initially and during the experimental period for the different oil emulsions and sediment fraction. The surface oil was partly removed from the surface to the water phase, and/or partly penetration into the sediment. In the basin studies the oil was distributed on the shoreline section naturally dependent on oil properties, wave exposure and sediment characteristics, and will therefore be unevenly distributed on the surface. At low tides cross-section of the sediment was prepared for sediment sampling and observation of oil penetration into the sediment. Figure 4.7 shows the observation data with the different oils and sediment fraction. For all oils the penetration depth increase with time and sediment particle size. It should be pointed out that the observation uncertainties increases with increasing sediment sizes and variations.

Norne oil emulsion penetrate very little into the sediment, with a small increase at the end of the experimental period. The concentration of oil in the sediment is, however, high as shown in Figure 4.10 for the upper sediment layer at the end of the experimental period. The Norne oil appeared in the sediment not as continuous oil layer but more as scattered lumps, which could give results with high variance with parallel sampling.

The Troll oil emulsion is rapidly transported to the maximum depth of the sediment layer for the two largest sediment types with highest porosity. For the smallest sediment fraction (2,8-6,3mm) the oil penetrates only to 7 cm which is most probably due to a larger sediment particle surface. This is in accordance with the sediment oil concentrations as a function of time and sediment type for the Troll oil in Figure 4.8. A higher oil loading would probably result in similar oil concentration, and a higher penetration depth as observed in the column experiments (cfr. C3.2 report).

For the Kobbe oil emulsion and the bunker oil emulsion, the oil was observed at larger depths during the experimental period. This was expected with the Bunker oil which is fluid at the experimental temperature. The Kobbe emulsion is, however, non-fluid and as the column studies showed the oil remains mainly at the sediment surface. These basin studies introduce water transport and possibly sediment movement, which could break up the unstable Kobbe emulsion. This was, however, not possible to confirm with available analytical methods and the oil quantities present in the sediment fraction.

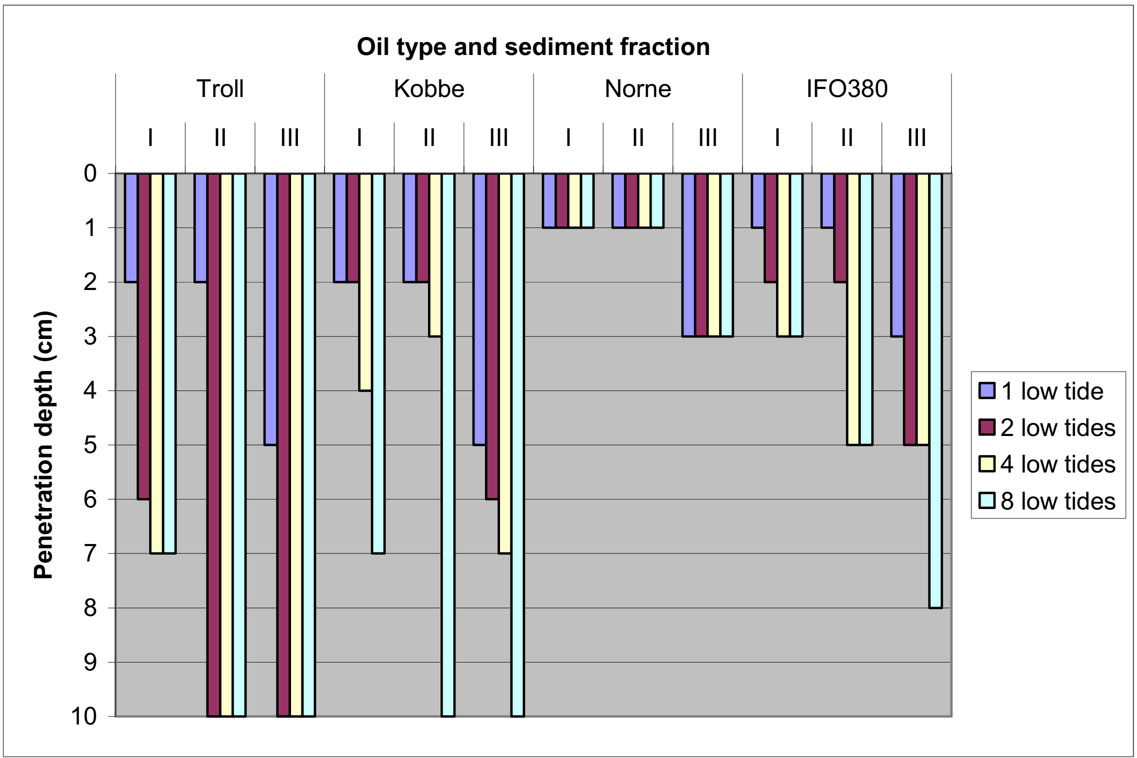



*Figure 4.7; Penetration depth in basin experiment for different oil types and sediment fractions as a function of time*

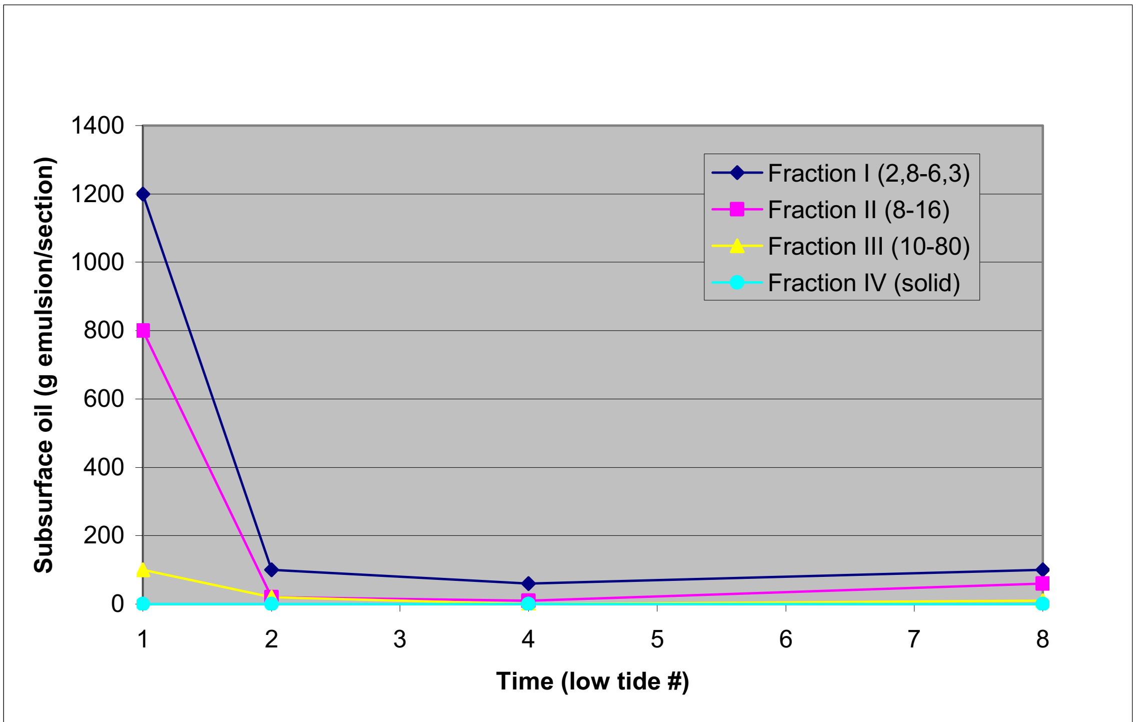



*Figure 4.8 Oil quantities in subsurface sediment for Troll emulsion as a function of time*

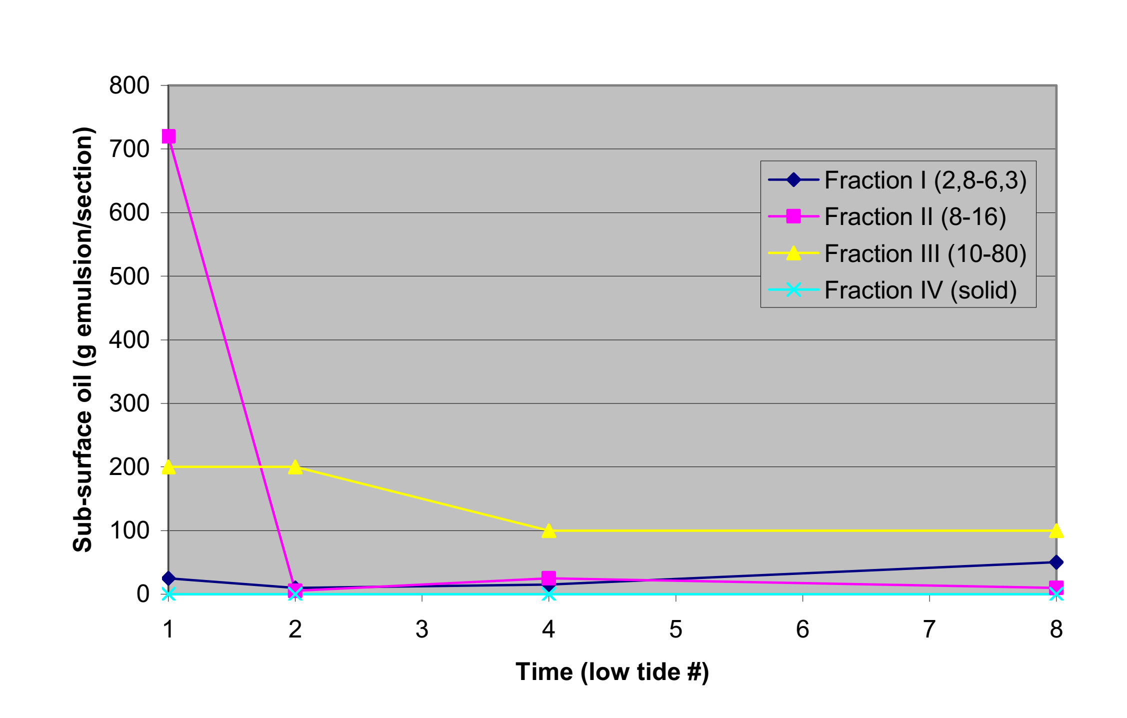



*Figure 4.9 Oil quantities in subsurface shoreline sediment for Kobbe as a function of time*

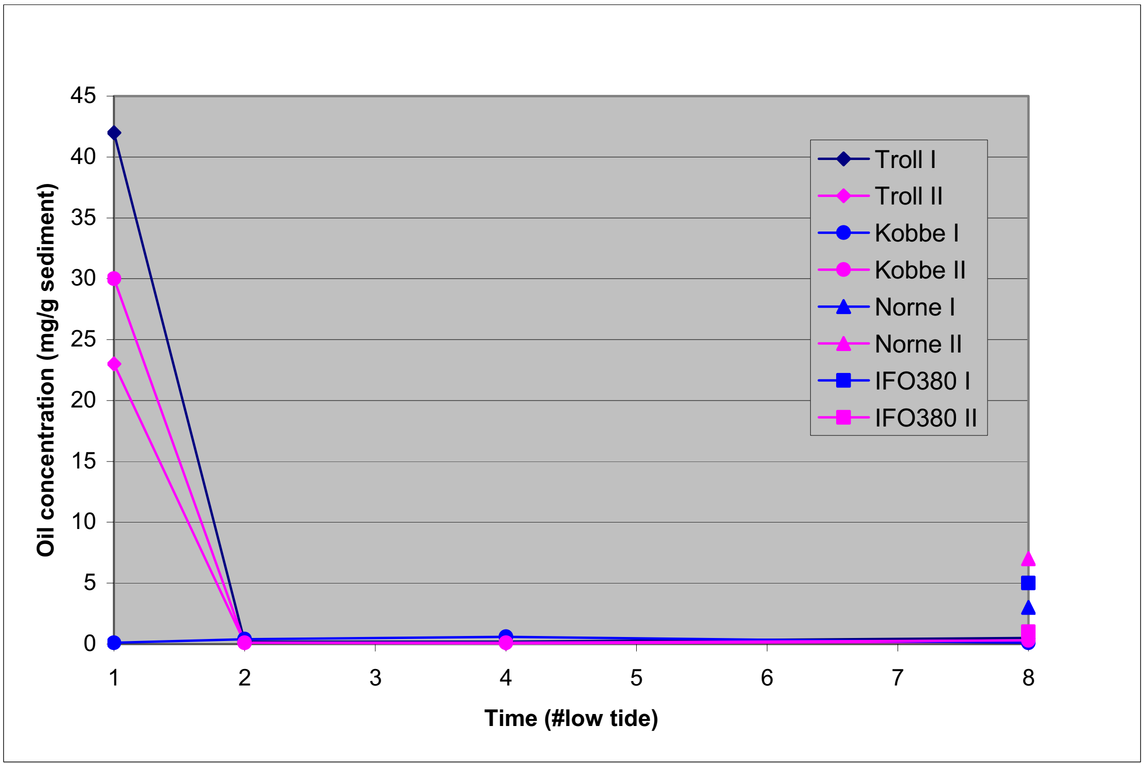



*Figure 4.10 Oil concentration in upper layer of shoreline sediment for different oils and the two smallest sediment fractions as a function of time*

### 4.5 Erosion

With the experimental design, including shoreline characteristics (slope, particle size and distribution) and wave exposure, some sediment transport was observed with the smallest sediment fraction. This is shown in Figure 4.11 with transport of sediment upward during rising tide and build-up of a pile in the upper intertidal zone. This pile could be as high as 5 cm, and resulted in different outcome for the subsurface oil. The oil on relocated sediment will most probably be removed by physical mechanism (abrasion). Whereas the oil in the upper part of the inertidal zone was buried by the transported sediment and become less available for removal processes (refloating, washout and erosion).

*Figure 4.11; Sediment transport in basin with smallest sediment fraction (to left)*

During sediment sampling in experiments with different oil emulsion, it was observed that the upper part of the sediment contained no detectable oil residues. The observation for the two smallest sediment fractions is summarized in Table 4.2. The observations shows that the Troll oil was removed in the upper 2-4 cm. Whereas for the other oil types oil residues was observed to remain in the top of the remaining sediment. The sediment that was transported upwards contained very low quantities of oil (observed, not analyzed).

The observed sediment transport will be higher in the present basin studies than in a real situation with same wave exposure. This is mainly due to the use of sorted sediment fractions. In a real situation the sediment size distribution will be varied over a much wider range, where the smaller sediments grains will stabilize the sediment and thereby reducing the sediment transport. The relatively high frequence of the wave generator giving short wave periods, will also result in higher sediment transport.

*Table 4.2; Removal of oil from subsurface sediment fraction, measured as sediment depth (cm) from the surface without detectable oil residues at the end of the experimental period.*

| | Troll | Kobbe | Norne | IFO380 |
|---|---|---|---|---|
| Fraction I | 2 cm | <1 cm | <1 cm | <1 cm |
| Fraction II | 3,5 cm | <1 cm | <1 cm | <1 cm |

### 4.6 Sediment surface characteristics

Laboratory studies has shown that the presence of biofilm at the sediment surface may affect the adhesion properties to a very large extent (Activity C3.2). To study this phenomenon in larger scale, the shale tiles used in the basin studies was allowed to stay in seawater for three weeks to allow biofilm establishment on the surface. Experimental studies were performed using tiles with and without biofilm for IFO380 and Troll emulsions. Pictures from the first two low tides from these experiments are given in Figure 4.12 and Figure 4.13. These pictures shows clearly that the surface characteristics will be of great importance for the fate and behaviour of oil during the acute phase. This is especially clear for the Troll emulsion which is completely washed away from the surface at the second low tide in the biofilm experiment.

The IFO380 emulsion was also less tightly adhered to the shoreline substrate covered with biofilm. At the second low tide oil coverage is reduced from 90% to 70% in the intertidal zone, and the situation at the end of the experimental period was a 50% coverage on tiles with biofilm. This confirms that the surface characteristics is of major importance, but also that the bunker emulsion will be far more challenging and labour-intensive in a real spill situation compared to the crude oil emulsions during clean-up operations.

*Figure 4.12; Effect of biofilm at shoreline surface on oil adhesion, 1$^{st}$ low tide; from left to right; IFO380 without biofilm, IFO380 with biofilm, Troll without biofilm, Troll with biofilm*

*Figure 4.13; Effect of biofilm at shoreline surface on oil adhesion, 2nd low tide; from left to right; IFO380 without biofilm, IFO380 with biofilm, Troll without biofilm, Troll with biofilm*

# 5 Conclusions and operational gains

The experiments designed to study the fate and behaviour of emulsions (crude oil 250$^o$C+ residue with maximum water content) in the meso-scale basins include simulation of stranding of the oil followed by 8 tidal periods (3 hours) at 5$^o$C simulating cold climate conditions. The surface and subsurface oil in the intertidal zone was observed, measured and analysed at defined intervals to describe the fate and behaviour of the oil. Due to a relative small experimental area for each oil and sediment, it was not possible to take parallel samples at each sampling period which makes it more difficult to give clear conclusions. The information obtained through the studies gives, however, a good picture on the fate and behaviour of the oils in the acute phase and fulfils the objectives of study and document fate and behaviour of oil on shoreline in the acute phase.

The main findings from the experimental studies were;

- A very large variation in fate and behaviour was observed with respect to both oil types and sediment characteristic during the acute phase (defined as 8 tidal periods).
- The IFO380 emulsion adhered very good to the sediment surface. The oil was remobilized by gradually reduction in oil film thickness during the experimental period.
- Presence of biofilm at the substrate surface reduced the adherence and allowed enhanced oil remobilisation during the experimental period.
- Penetration depth increased with increasing sediment size

Other findings and observation from these studies includes:

- The crude oil emulsions with a high pour point (Kobbe and Norne) did not adhere well to the sediment surface, and was remobilized from the surface as lumps by wave exposure.
- Low viscous crude oil emulsion (Troll) adhered as a thin oil layer to the sediment surface but was also remobilized by wave exposure.
- Penetration of the oil emulsion was dependent on the viscosity and pour point of the emulsion. The low viscous Troll emulsion penetrated rapidly to a maximum depth, whereas the Kobbe and Troll emulsion (high pour point) remained mainly at the upper sediment layer. The penetration increased slightly during the experimental period. The penetration of the high viscous bunker emulsion increased during the experimental period.
- The subsurface sediment oil quantity (retention) increased with increasing viscosity and pour point.
- A very low retention on solid substrates with crude oil emulsion was observed. The IFO380 emulsion retained at the solid substrate surface, but he oil layer thickness decreased due to wave exposure.
- The low viscous oil (Troll) was removed from the subsurface sediment due to erosion and water flow exposure. Crude oil emulsions with high pour point that adhered to the sediment was retained. The high viscous bunker emulsion was remobilized from the subsurface sediment at a low rate.

The findings and observation from the meso-scale basin experiments will give important input to contingency plans and cleanup strategies for the different oil types characteristic.

- Troll (low viscosity, low pour point); the oil will penetrate into the sediment which are difficult to cleanup., and should avoid stranding at sediment shoreline. The stranded oil will be removed easy by sediment and water exposure. High self-cleaning properties.
- IFO380 (high viscosity); will adhere to shoreline sediment, and penetrate into the shoreline sediment. It will be difficult to cleanup and a low self-cleaning rate is predicted.

If possible, sediment shorelines should be protected and redirected towards e.g. bare-rock shorelines.

- Kobbe and Norne (high pour point ad moderate viscosity); the emulsion do not adhere well to substrate surface and is easily remobilized. Spreading of remobilized oil by should be prevented by e.g. booming. High self cleaning rate at sediment surface in intertidal zone is predicted and the oil will accumulates in the supralitoral zone.

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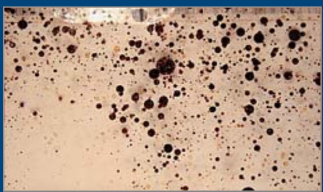
# REPORT



## Coastal Oil Spills - JIP

Report no.: 15

# C2.4 - Fate and behaviour of oil on shoreline in restoration phase – meso scale basin studies

Svein Ramstad, Jane Helen Carlsen Øksenvåg, Bror Johansen and Tor Arne Oltedal

**SINTEF Materials and Chemistry**
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TITLE

**Fate and behaviour of oil on shoreline in restoration phase – meso scale basin studies**

**Coastal Oil Spill Report No 15**

AUTHOR(S)

Svein Ramstad, Jane Helen Carlsen Bror Johansen and Tor Arne Oltedal

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| | 2009-01-07 | Tore Aunaas, Research Manager | |

ABSTRACT

The meso-scale shoreline basins were used to study the fate, behaviour and weathering of stranded oil emulsion during the restoration phase with immobilized oil. The meso-scale shoreline basin which simulate environmental parameters, were used with five different shoreline substrate fraction ranging from medium sand to solid substrate at constant temperature representing cold climate conditions (5°C) with continuous supply and exchange of fresh seawater. The experiments were performed with wave exposure and tidal variation for 14 days (112 tidal periods). Three different weathered crude oil emulsions (Troll, Kobbe and Norne) and one bunker oil (IFO 380) were used as 250°C+ residues and emulsion with close to maximum water. The main findings from the experimental studies were;

- A very large variation in fate and behaviour of the emulsion/oil was observed with respect to both oil types and sediment characteristic during the restoration phase
- Crude oil emulsions with high pour point (Kobbe and Norne) adhered poorly to sediment surface, had low penetration and were easily remobilized from shoreline surface
- Bunker oil emulsion with high viscosity adhered to the shoreline sediment, with increasing penetration during the experimental period, and were wash-out by reducing the oil film thickness.
- Crude oil emulsions with low viscosity and pour point penetrated into the shoreline sediment, but remobilized through washout an erosion. The emulsions were easily washed out from the sediment surface. re
- Increasing wave exposure increased remobilisation of oil emulsions.

The findings and observations from these studies and can contribute to an improved oil spill contingency



| KEYWORDS | ENGLISH | NORWEGIAN |
|---|---|---|
| GROUP 1 | Environment | Miljø |
| GROUP 2 | Oil | Olje |
| SELECTED BY AUTHOR | Meso-scale studies | Meso-skala studier |
| | Emulsion | Emulsjoner |
| | Shoreline | Strand |

# TABLE OF CONTENTS

# 1 Introduction/background

This project has been a part of phase 1 in the Coastal Oil Spills JIP. The research projects in the JIP have been focused on the fate and behavior of oil spills in coastal areas and on shoreline. Laboratory studies have been performed in order to obtain data for further development of numerical models.

The first phase of JIP was performed in the period from 2006 to 2008, and was funded by Eni Norge, Shell Technology and StatoilHydro. The overall objectives of the JIP have been:

- to contribute to an adequate and sufficient basis of competence to document possible consequences in case of an oil spill close to the coast
- to provide documentation ensuring the countermeasures giving the optimal environmental gain

SINTEF has for three decades been involved in studies on the fate and behaviour of oil on shoreline sediment. From the late seventies to the nineties, the focus was on field studies under cold climate conditions, first in Ny-Ålesund and later in Svea on Svalbard, as well as on several locations along the Norwegian coast in connection to smaller accidental spills. After the Exxon Valdez incident in Alaska 1989, founding of larger research programs was possible. Through the ESCOST, BIOREN and ITOSS programs, SINTEF established and used meso-scale laboratory facilities (basins and columns) to study the fate and behaviour of oils and development of in-situ treatment techniques. These experimental systems allowed studies to be designed and performed under controlled and reproducible conditions under simulated realistic conditions including use of fresh seawater.

The experimental facility was upgraded in the Statoil project "Upgrading meso-scale and laboratory systems at SINTEF SeaLab" in 2005-6. The meso-scale basin system was modified and upgraded for more easy and reliable operation and less waste generation. The present experimental system is unique world-wide; a significant larger outdoor systems (COSS – Coastal Oilspill Simulation System, now; SERF Shoreline Environment Research Facilities) has been established by TGLO (Texas General Land Office, http://www.glo.state.tx.us/) in Texas USA. However, these facilities are not adopted for screening or research studies (e.g. large size, freshwater). Therefore, very little data on this topic is available from the literature. Most of the data comes therefore from observations and measurements of real spill situation.

During design and upgrading of the meso-scale basins, focus was on simulation and downscale of the most important environmental parameters, continuous supply and exchange of fresh seawater, temperature, wave exposure, tidal variation, shoreline substrates among others. The meso-scale basins therefore simulates well the environment, which allows studying of more processes that will affect the fate, behaviour and weathering of the oil on and in the shoreline substrate. The SINTEF SeaLab facilities has also established different other less complex laboratory systems to study specific processes taking place in the acute and restoration phase.

After an accidental release of petroleum products, the oil undergoes a number of weathering processes before stranding; evaporation, emulsification and photo-oxidation as the most important within the first day after the spill. However, most experimental data for laboratory studies has used waterfree and only slightly evaporated oils giving less realistic/relevant data to be used in e.g. oil spill contingency and response technique development. In the present study, SINTEF has focused on use of oil emulsion with realistic properties after 2-5 days on sea surface prior to strand; evaporation to a oil residue of 250°C+ and a water content of close to maximum for four different petroleum products; three crude oils (Troll, Norne and Kobbe) and one heavy bunker fuel oil (IFO380).

Very limited literature data are available on studies on the fate, behaviour and weathering of stranded oil emulsion under controlled and reproducible conditions, with simulation of the main natural parameters. The main knowledge and data comes from real spill situation, which are well summarized in the MMS report " Review of the state-of-the-art on modelling interactions between spilled oil and shorelines for the development of algorithms for oil spill risk analysis" (OCS Report, MMS 2007-063). In this report a number of natural processes are quantified and reported from different spill scenarios. The data from this publication can be used together with data from the present studies for development of algorithms to be used in numerical models.

## 2 Summary

The main objective of this task within the COS-JIP was to "study and document weathering processes of immobile oil on shoreline in meso-scale experimental systems". To reach these objectives the meso-scale experimental basin systems was utilized in a total of six experiments. The meso-scale basin (2m x 4m x 1m) simulates a number of environmental parameters allowing controlled and reproducible studies. This includes; continuous supply and exchange of fresh seawater (1vol/vol,day), wave exposure (up to approx 10cm), tidal variation (3h period) , constant temperature (5°C), shoreline characteristics; including slope (12°) and sediment size (sand 2,8-6,3mm, coarse sand 8-16mm, gravel 10-80mm and solid substrate) and no light exposure. In each experiment the four substrate types were used separated by interior walls.

The different crude oil types were used representing different "groups" of oil; Troll crude (naphtenic), Kobbe (paraffinic), Norne (waxy). Additionally one bunker oil (IFO380) was included in the study. The crude oils were used as a 250°C+ residue, and all oils were emulsified to a water content of just below maximum water content (Troll 70%, Kobbe 75%, Norne 60%). The bunker oil had a water content of 40%. To simulate the restoration phase the emulsion was allowed to condition for 5 days prior to initiation of the experimental studies. The experiments were normally followed for 112 tidal periods (14 days, 3 hour tidal period). The surface and subsurface oil in the intertidal zone was observed, measured and analysed at defined time intervals to describe the fate and behaviour of the oil. Due to a limited experimental area for each oil and sediment, it was not possible to take multiple samples.

The different oil type emulsions behaved very different both at the sediment surface and subsurface, initially and during the experimental period.

- Penetration; The crude oil emulsions with high pour point (Kobbe and Norne) were not transported into the sediment initially. After initiation of tidal variation and wave exposure only low penetration was observed with the two smallest sediment fractions (size). Troll emulsion with low pour point and low viscosity penetrated completely into the sediment fraction. The penetration depth increased during initial tidal periods with exposure.
- Adherence. The crude oils with high pour point did not adhere well to the sediment surface. Adherence increase with increasing sediment size, due to larger contact area between oil and sediment. Troll oil emulsion at the solid surface was easily remobilized (washed out) during first tidal periods. The IFO380 bunker emulsion adhered well to the solid substrate surface, and coated most of the surface during the experimental period.
- Oil weathering. Analysis of the physical properties of test oil could only be performed for a limited number of sampling points. The viscosity of the IFO380 emulsion dropped slightly the first 3 days, but remained constant during the experimental periods at different shoreline tidal positions. The viscosity of the Troll emulsion was reduced significantly during acclimatisation and remained constant during the initial period of the exposure period. The change in viscosity is most probably due to change in the water structure (e.g. water coalescence) for the Troll emulsion, but could not be documented by water content analysis. The analysis or observation did not give any indication on the emulsion stability vs emulsion breaking.
- Surface oil remobilisation – solid substrate. For the solid substrate studies, the bunker oil emulsion was mainly removed by reduction in the oil film thickness. It was more difficult to study the behaviour of surface crude oil emulsion during the experimental period as only minor amounts remained at the surface, *i.e.* the crude oil emulsions were mainly removed from the sediment surface. For Troll oil emulsion the removal rate from the surface was increased by increasing wave exposure.

- Surface oil remobilisation – sediment substrate. For the Crude oil emulsions with high pour point (Kobbe and Norne), that were adhered to the surface, was mobilized to a low degree during the experimental period. The oil was instead mixed and partly stabilized with the upper sediment layers after wave exposure and sediment transport. For Troll emulsion, very little oil was found at the surface of sediment substrates. The IFO380 remained partly at the shoreline substrate surface. With the smallest sediment fraction, the oil remained at the surface with a low transport into the sediment due to a high viscosity and high adherence to sediment surface which stabilize the upper sediment layer and reduced remobilisation of oil.
- Subsurface remobilisation; The fate and behaviour of the subsurface oiled sediment was dependent on sediment characteristics. The smallest sediment fraction was exposed to wave energy sufficient to sediment transport resulting in a higher oil remobilisation, for the upper part of the sediment. A higher remobilisation rate was observed with Troll than with IFO380 emulsion. In larger sediment fraction the oil was also remobilized by water transport exposure from the upper part of the sediment layer. The results from the oil analysis have however relative large uncertainties due to lack of parallel analysis and uneven oil distribution.

The data from these studies show clearly a very different behaviour for the different oil types at different sediment characteristics both surface and sub-surface, which could be utilized for contingency planning and strategies in an oil spill cleanup operation:

- Natural remobilisation – self-cleaning, by different mechanisms (refloating, dispersion, erosion, wash-out)
- Bunker oil – adhere well and lower self-cleaning rate
- Crude oil emulsions with high pour point – low adherence, and high remobilisation from wave exposed intertidal zone.
- Self-cleaning (remobilisation) increase with increasing wave exposure
- Low viscous (and floating) oil penetrate into the sediment, whereas emulsion with high pour point did penetrate less.

The experimental studies were performed under simulated conditions. It is however, difficult to transfer these data to a real spill situation. This will require field studies under realistic condition for verification or adjustment of experimental data from the meso-scale experimental conditions using the same test oils.

The result from the present studies could also used for development of algorithms that describes the remobilisation/removal natural processes from shoreline substrate/sediment during the restoration phase, together with field data from real and experimental spills with the same oils.

# 3 Materials and methods

## 3.1 Experimental system

The experiments were performed according to a Standard Operational Procedure (SOP) for the continuous flow and water exchange meso-scale basins, on the fate, behaviour and weathering of oil on shoreline in the restoration phase. The experimental systems were upgraded during the Statoil project "Up-grade the meso-scale experimental facilities at SINTEF SeaLab"- The experimental system is shown in Figure 3.1. The basin of 4m x 2m x 1m has a constant water level (70cm) and a constant water throughput (exchange of one volume every day), and the tidal variation is control by moving the shoreline section according to a sinus curve with a period of 3 hours and is controlled by two separate motors. The shoreline section has a constant angle (12 degree), and is constructed of a perforated bottom covered by a geotextile. The shoreline section (3m x 2m) is divided into four sections divided by PE-plates.

The shoreline sections are filled with sediment in a depth of approximately 10-13cm of sediment fractions. The solid substrate shale tiles (15cm x 15cm) were placed on a raised platform to give an equal height as the sediment sections.

A wave generator in mounted in the lower end of the basin. The frequence and amplitude of the wave generator can be adjusted to give different wave exposure intensity.

The basin is located in a temperature controlled room with air temperature control. The water comes directly from Trondheim fjord (water depth of approx. 80m) with a temperature of approximately 6-10$^{o}$C (seasonal dependent), and the water temperature in the basins are controlled by the air temperature.

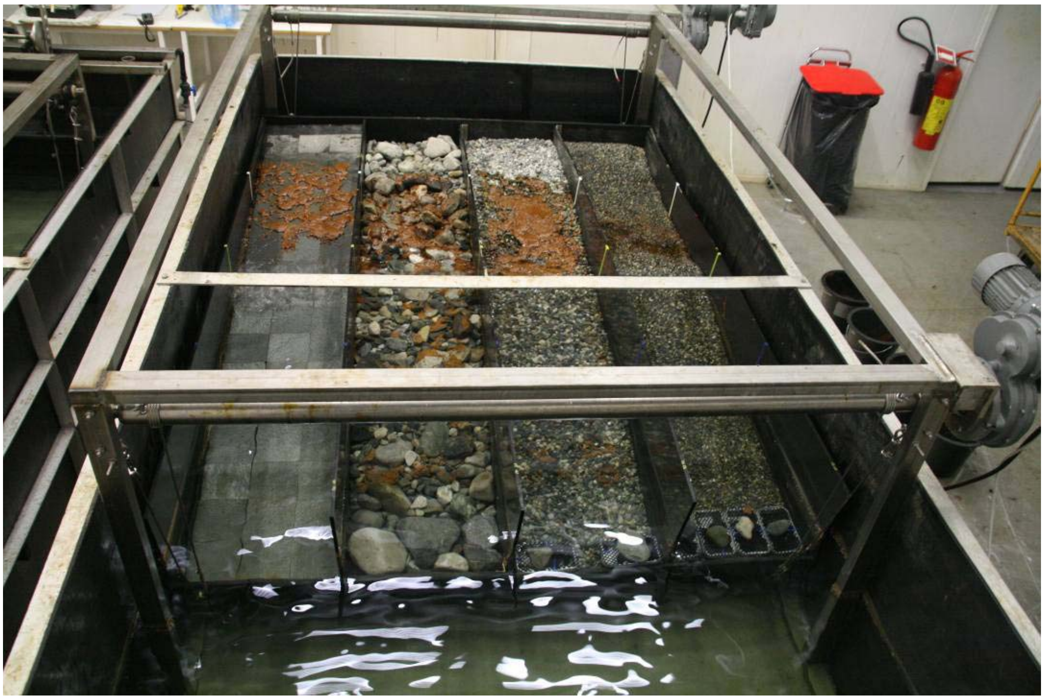


*Figure 3.1 Meso-scale shoreline basin*

### 3.2 Experimental protocol

The experiments in the meso-scale basin including fate, behaviour and weathering of oil on shoreline in the restoration phase, were performed according to a standard protocol, which include;

- The basin and interior parts were throughoutly washed prior to initiation of new experiment.
- The shoreline sections were filled with pre-washed sediments of defined sediment size in a thickness of 10-13 cm. The sediment was distributed evenly giving a smooth surface.
- The basins were filled with fresh seawater (70cm), giving a total water volume of 5,6m$^3$. A constant water flow rate was used, equal to one volume pr day.
- The tidal variation and wave exposure was started at least one day prior to initiation of the experiment.
- Oil emulsion (25L for each basin) was prepared using a standard concrete mixer, and allowed to mix for at least 18 hours. The viscosity of the emulsion was measured and compared to previous data before acceptance for use.
- The emulsion was spilt into four equal parts in buckets.
- The shoreline platform with the sediment section was lowered to a horizontal position at 5-7 cm below the water level.
- The emulsion was applied at the water surface to each shoreline section (0,5m x 2.4m). The oil was spread as evenly as possible within the whole section, and the method used was dependent on the flow properties of the oil emulsion.
- After 2 hours the water was drained out to a level below minimum sediment layer.
- The experimental system was allowed to “settle” for 3 days without water contact or exposure, simulating establishing of the restoration phase.
- The water level was raised to the initial situation 5-7cm above the sediment surface.
- Oil emulsions not adhered to the sediment surface refloated and was collected manually during one day.
- The shoreline platform angle was adjusted to the standard 12 degrees, and put at low tide position.
- Prior to initiation of the experimental period the sediment surface were characterized and sediment samples were taken for analysis.
- The sampling, measurement and observations are described in Chapter 3.5.
- The experiment was initiated by starting the tidal variation (3 hour periods) and wave generator (t=1,67s).
- After termination of the experimental period the wave generator, tidal movement and water flow were turned off. The contaminated sediment was collected and sent for destruction and oil residues on solid substrate tiles was removed by high pressure washing and extraction with Dichloromethane (DCM).
- The residual oil in the basin and on interior parts was removed by high pressure warm water washing.

…

### 3.3 Experimental

A total of six experiments have been performed studying the fate and behaviour of oil in the restoration phase. The experimental parameters are summarized in Table 3.1.

*Table 3.1; Experimental parameters in the meso-scale experiments for acute phase*

| ID | Oil type (emulsion) | Energy exposure* (frequence) | Sediment type/fraction (mm) | | | | |
|---|---|---|---|---|---|---|---|
| | | | Fraction V 1,4-2,8 | Fraction I 2,8-6,3 | Fraction II 8-16 | Fraction III 10-80 | Fraction IV solid |
| 4A | Troll | Medium – 1.67s | | x | x | x | x |
| 4B | IFO380 | Medium | | x | x | x | x |
| 5A | Kobbe | Medium | | x | x | x | x |
| 5B | Norne | Medium | | x | x | x | x |
| 6A | Troll | Low | x | x | x | x | |
| 6B | Troll | High | | x | x | x | x |

* The different exposure was adjusted by wave frequence
(Medium; 1.67s, High; 1s; Low; 5s)

### 3.4 Experimental oils

Crude oils can be characterised in four categories: asphaltenic, naphtenic, paraffinic and waxy crude oils. The crude oils studied in the Coastal Oil Spills JIP were selected among the oil companies' crude oils. It was important to select crude oils representing different categories of oils. The selected crude oils represent the categories:

- Troll – naphtenic crude oil
- Norne – waxy crude oils
- Kobbe – light paraffinic crude oil

In addition to the crude oils, a heavy fuel oil (IFO380) was also tested. IFO 380 is representative heavy fuel oils for bunker oils used as fuel for ships going along the Norwegian coast. The content of light oil components in fuel oils is low, typically lower than 5 vol% for IFO 380 oils. The light oil components are generally in a boiling point area from up to 250°C. The testing of the IFO 380 was therefore concentrated on the "fresh" fuel oil, not on an evaporated residue. The IFO 380 oil used in this project is a low sulphur fuel oil produced at the Esso refinery at Slagentangen.

Some physical and chemical properties of the oils studied are listed in Table 3.2.

*Table 3.2 Oils used in the Coastal Oil Spills JIP.*

| SINTEF Id | Oil type | Residue | Density (Kg/m$^3$) | Evaporative Loss (Vol%) | Pour point (°C) | Wax (wt%) | Asphaltenes (wt%) | Viscosity at 5°C/10$^{-s}$ (cP) |
|---|---|---|---|---|---|---|---|---|
| 07-0287 | Troll | Fresh | 0,900 | 0 | -36 | 0,9 | 0,04 | |
| | | 250°C | 0,930 | 25,5 | -27 | | | 770 |
| | | Ph.ox. | 0,931 | - | -21 | | | |
| 07-0260 | Norne | Fresh | 0,860 | 0 | 21 | 4,3 | 0,30 | |
| | | 250°C | 0,888 | 28,4 | 30 | | | 39100 |
| | | Ph.ox. | 0,885 | - | 30 | | | |
| 06-1061 | Kobbe | Fresh | 0,797 | 0 | -39 | 3,4 | 0,03 | |
| | | 250°C | 0,875 | 53,6 | 21 | | | 4630 |
| | | Ph.ox. | 0,877 | - | 15 | | | |
| 06-1125 | IFO 380 | Fresh | 0,932 | 0 | 15 | 5,0 | 3,4 | 87100 |

*-: not measured*

It was decided to weather the crude oils to represent the properties of the oils after ½-1 week at sea. Evaporation, emulsification and photo oxidation were performed according to SINTEF lab procedures. An evaporated residue of 250˚C+ was used for the three crude oils. That means that compounds with a boiling point below 250˚C have evaporated, and the product used is a residue. To ensure reproducible production of emulsions, a water content slightly below the maximum water uptake for the respective oils was used. After some initial studies, the standard water content was decided to be 70% for Troll, 75% for Kobbe, 60% for Norne and 40% for IFO 380.

### 3.5 Analysis

The oil concentration of oil in the sediment was determined as described in the SOP which include extraction with dichloromethane (DCM), and analysis using a spectrophotometer (Hitachi U-2000 spectrophotometer).

Prior to initiation of each experiment the emulsion was characterised by rheological measurements (Physica MCR300 MC1+ rheometer with an US200 software).

### 3.6 Observations, documentation, sampling and measurements

During an experimental period the observation, measurements, documentation and sampling were performed as described in Table 3.3.

*Table 3.3 Observation, measurements, documentation and sampling during the experimental period on studies during restoration phase*

| Time | Activity |
|---|---|
| Prior to initiation | Temperature measurements; ambient and water |
| "Continuously" | Photo documentation |
| Day -1 | Surface documentation, collection refloated oil |
| Day 0, prior to start | Surface/subsurface characterisation, sediment samples |

| | |
|---|---|
| Day 0 – first tidal period | Collection of remobilized oil |
| Day 3 | Surface/subsurface characterisation, sediment samples |
| Day 7 | As day 3 |
| Day 10 | As day 3 |
| Day 12-14 | As day 3 |
| | Oil sampling for rheological characterisation from sediment surface |

Photo documentation was performed as close to the same position and angle every time for more easy comparison.

Sediment sampling was normally performed in the upper intertidal section (60-90 cm below shore top position), approximately 10cm downwards the shore for each sampling time. The available sampling area did not allow replicate sampling.

In some experiments the fate and behaviour of the oil was documented by video recording.

# 4 Results and discussion

The experimental protocol for the basin experiment to study the fate, behaviour and weathering of oil emulsions in the restoration phase (no mobile oil) was based on experience from previous studies in the present project and other industrial programs. To simulate the oil properties in the restoration phase, in the present program defined as when the oil is not mobile – normally 4 days (96 hours), the oil was applied and allowed to equilibrate for that period of time before initiation of the experiments.

During the experimental period (normally 14 days with 3 hours tidal period, simulating tidal variation for approximately 2 months), a large number of observation, monitoring and sampling and analysis were performed. These data are systemized in one appendix for each experiment;

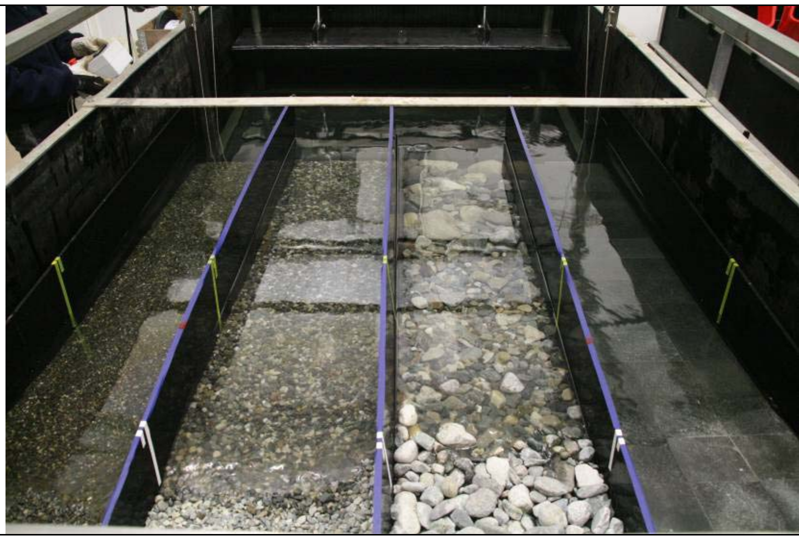
Appendix A; Troll 250$^{o}$C+ emulsion(70% water)
Appendix B; IFO emulsion (40% water)
Appendix C; Kobbe 250$^{o}$C+ emulsion (75% water)
Appendix D; Norne 250$^{o}$C+ emulsion (60% water)
Appendix E; Troll 250$^{o}$C+ emulsion (70% water) – "low" energy wave exposure
Appendix F; Troll 250$^{o}$C+ emulsion(70% water) – "high" energy wave exposure

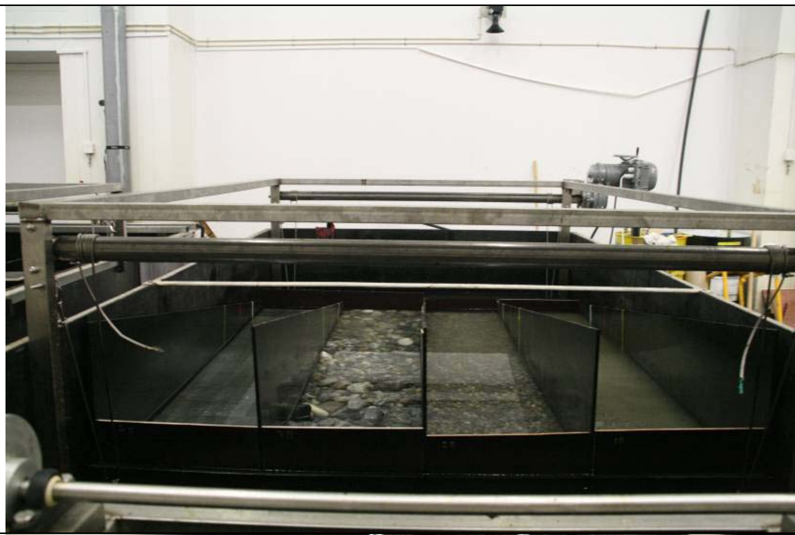
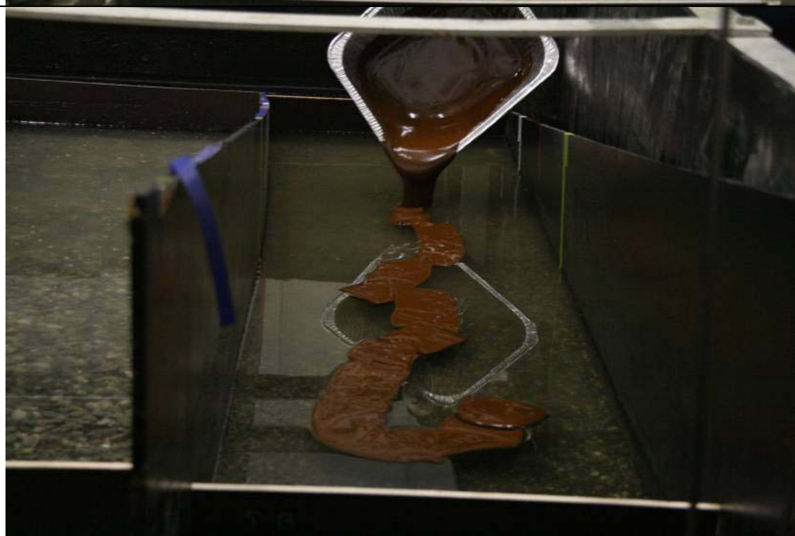
The shoreline platform was divided into four sections with different sediment characteristics. This reduced the effective sampling area for each shoreline type (approximately 90 x 30cm), which did not allow parallel sampling at different sampling days and thereby statistical analysis of the experimental data. The data series gives, however, a good description of the fat, behaviour and weathering of the oil emulsion on shoreline substrate.

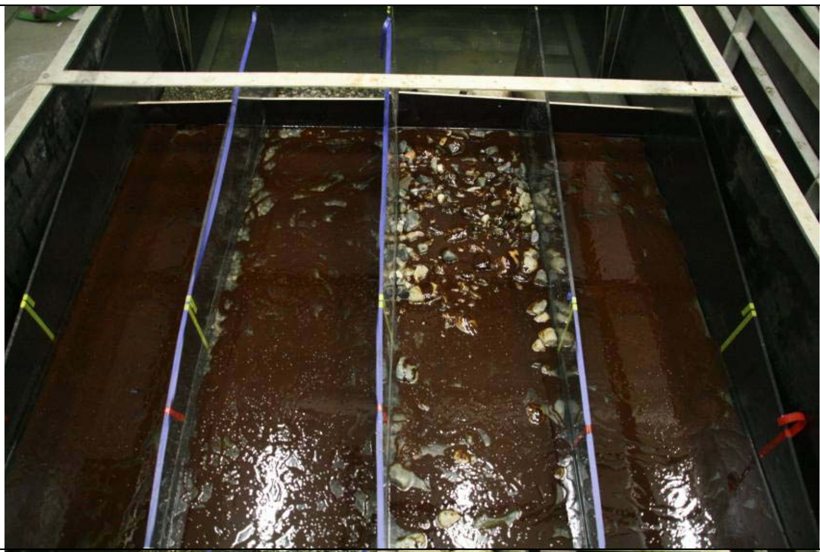
## 4.1 Experimental protocol

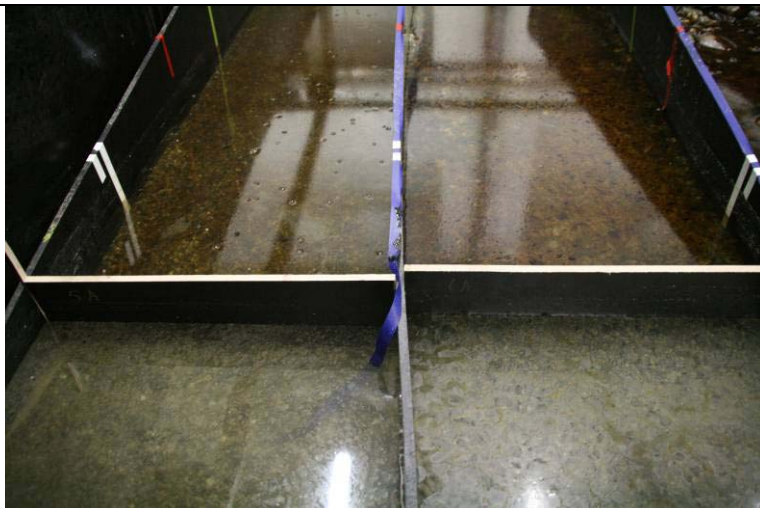
One of the experiment (Troll) is described by photos and observation in Table 4.1. The use of different oil types, shoreline characteristics and other parameters are described and discussed in the following chapters.

*Table 4.1; Photo-documentation and description from one experimental period studying the fate and behaviour of emulsified oil (Troll if nothing else stated) during the restoration phase.*

| | |
|---|---|
| Basin prior to oil application. Shoreline sediment from left;<br>• 2,8-6,3 mm<br>• 8-16 mm<br>• 10-80 mm<br>• Solid (Shale tiles 15x15cm)<br>Water supply and exchange and tidal variation were initiated at least 24 hour before oil application. |  |

| | |
|---|---|
| Prior to initiation of experiments. The shoreline platform is put into a horizontal position 5-7 cm below the water surface. The sediment section is closed in both ends with a "boom" to control the oil (30cm from the top and bottom of the section giving an total area of approximately 0,45m x 2,3m) |  |
| Oil application. The oil was applied carefully to the water surface. In each section approximately 4,5L of emulsion was used giving an average oil layer thickness of 3,75mm. |  |
| The oil was distributed as good as possible in the full section. None of the oil emulsions formed homogenous oil layer. Both Kobbe and Norne have a pour point above the ambient temperature, which did not allow spreading of the oil after application – an initial evenly distribution of the emulsion was therefore very important. |  |

| | |
|---|---|
| 2-8 hours after oil application (when no more spreading is expected) the water is carefully drained from the basin simulating falling tide, and the oil come in contact with the sediment and further penetrate into the sediment. |  |
| After water drainage. The oil spread evenly on the solid surface (right), whereas for the finest sediment (left) the oil penetrate more or less quantitatively into the sediment(left). For the other test oils a significant part of the oil remained at the sediment surface. |  |
| After four days of acclimatisation, the oil should be in "equilibrium" with the shoreline substrate, and a representative part of the oil should be immobilized.<br>No difference in surface appearance (for non of the oil emulsions) compared to day - 4. |  |

| | |
|---|---|
| Day -1; Initiation of oil/sediment and water contact. The water level was increased to a level 5-7cm above the sediment surface. Mobile oil/emulsion from the surface will refloat (Troll) as observed at water surface. For the other crude oils (Kobbe and Norne; pour point above water temperature) larger amounts of emulsion were refloated indicating a less stable contact with the sediment surface. Refloated emulsion was collected manually or by absorbent pads. |  |
| Day 0 Before start-up of tidal variation and wave exposure. The shoreline section was adjusted to a correct angle position (12 degrees). |  |
| Day 0; First rising tide. Kobbe emulsion was remobilized from the substrate surface, and collected in each sediment section. Picture; Kobbe emulsion - Oil patches was remobilized from the sediment surface. |  |

| | |
|---|---|
| Day 1: Troll oil was removed from the surface in the intertidal zone to approximately 60cm from the top. Oil remains a the sediment surface in the supralitoral zone. |  |
| Day 14; During the experimental period no difference was observed at the surface of the sediment. Some sediment transport was found with the smallest sediment fraction (see below) |  |
| Day 14 Upper intertidal zone. Indication of extent of sediment transport. A cut into the sediment shows subsurface oil as a brownish layer. |  |

Pictures from each sediment section in the different experiments are given in the Appendices for preparation and initiation and at every sampling time.

## 4.2 Oil weathering

The main weathering processes that takes place after an accidental release of oil on the water surface (evaporation, emulsification, photo-oxidation), proceeds also after standing on the shoreline sediment together with other weathering processes. The time constants could, however, be different, and other processes could be more dominant and important from an operational point of view.

In the meso-scale basin experiments most of the continuous crude oil emulsions layers in the intertidal zone was removed by different mechanisms for the crude oil emulsions, whereas the bunker fuel emulsion remained on the surface of the solid substrate. Oil samples which were exposed to waves and tidal variation could therefore only be taken from the IFO380 study for characterisation of the oil properties for the whole experimental period, in addition to the initial experimental period for the Troll emulsion.

Oil/emulsion samples were taken from different positions in the solid substrate section during the experimental period, and the data is given as viscosity (measured at 5$^{o}$C at shear 10 $s^{-1}$) in Figure 4.1. During the initial period prior to start of the experiment the viscosity increased from 100.000cP to 115.000cP. After initiation of wave exposure and tidal variation the viscosity are reduced in all tidal position and remains constant during the experimental period; approximately 100000cP in the superlitoral zone (mainly exposed to air), and in the range of 80-90.000cP in the water exposed zones. The increase in viscosity during the initial period is most probably due to evaporation of the lighter compounds. The decrease after initiation of tidal variation is uncertain, but could be due to reduction in water content and distribution of water in the emulsion

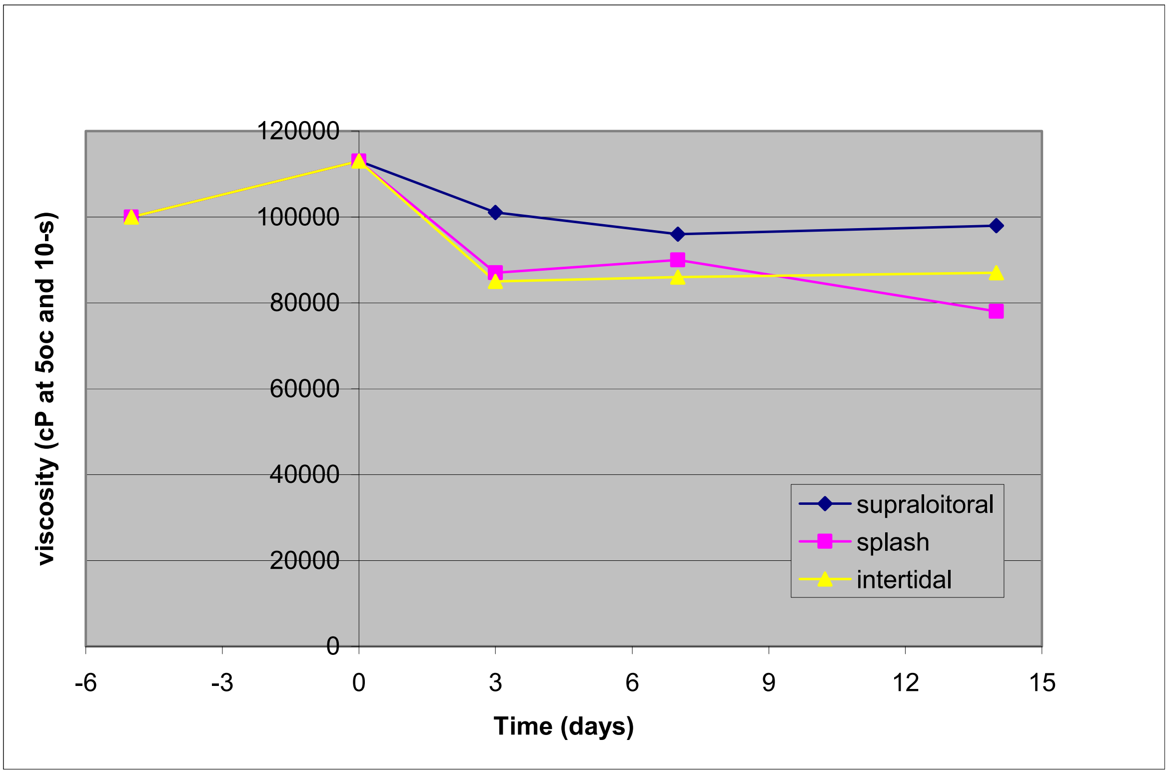



*Figure 4.1; Viscosity of IFO380from surface solid substrate as a function of time at different shoreline position in the meso-scale basin (solid substrate).*

The experiments using the crude oil emulsions gave only very limiting possibility to document changes in the properties of the oil after the initial period on solid substrate, mainly due to a high remobilisation of the oil. Troll emulsion samples were taken until the third day, and the viscosity data are given in Table 4.2. The viscosity decreased after production and application to the shoreline sediment (solid substrate). The samples taken at Day 3 was from the supralitoral position not exposed to wave action.

*Table 4.2; Viscosity of Troll emulsion from basin experiment*

| Time | Viscosity |
|---|---|
| (days) | cP (5°C and $10^{-s}$) |
| -5 | 15300 |
| -1 | 5240 |
| 0 | 6020 |
| 3 | 4080 |

The reason for changes in the viscosity of the emulsion could be changes in water composition and distribution due to e.g. wave exposure. However, no analysis was performed to document potential explanation for the viscosity observations. In general, the oil film thickness was to thin to allow sampling for water content analysis.

Physical characterisation of subsurface oil was not possible. After penetration into the sediment the oil/emulsion will be distributed on the surface of the sediment particles. An estimate of the oil film thickness using the sediment surface area and oil concentration gives a maximum oil film thickness, dependent on oil type, in the range of 0,01-0,1 mm. A major question for subsurface oil will be if the oil emulsion will be stable or broken up in contact with substrate for the different oil emulsions.

### 4.3 Adhesion

The experimental design of the meso-scale basin experiments allow for a realistic stranding of oil, by contact between the oil and the horizontal shoreline substrate. After an initial acclimatisation period of four days a part of the emulsion should be immobilized. Excess oil was removed from the sediment surface during rising tide followed by wave exposure and tidal variation. The adhesion of oil to the surface in the meso-scale basins can be quantified by measuring the area that is covered by oil. This is shown for the different oil types during the experimental period in Figure 4.2, and show a very great difference between the different oil types.

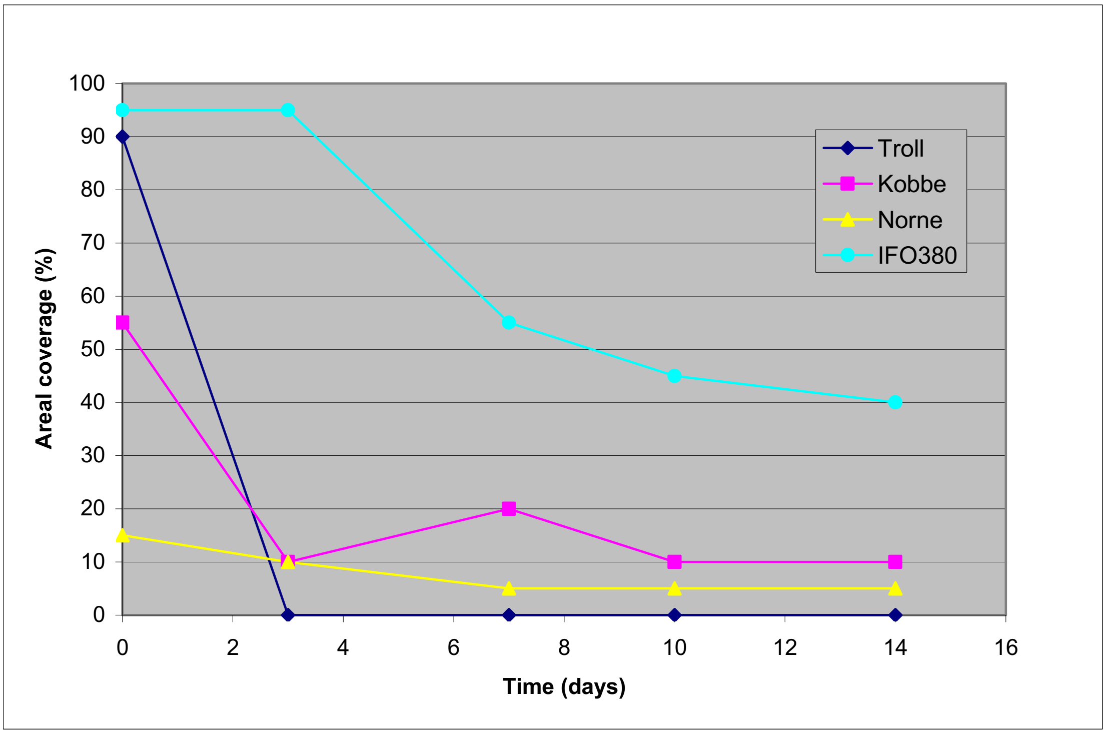



**Figure 4.2; Coverage of oil on the solid substrate section for the different oil during the experimental period.**

Both Troll and IFO380 emulsions covered the sediment surface until initiation of wave exposure and tidal variation. During the first tidal periods the Troll emulsion were quantitative removed from the exposed section. The interaction between the IFO380 emulsion and the sediment surface on the other hand, was much stronger and the oil remained on the surface for a much longer period of time. The coverage decreased gradually to approximately 40% at the end of the experimental period (14 days, 112 tidal periods).

The Kobbe and Norne emulsions, which both have a pour point above the ambient temperature, was partly easily removed from the sediment surface during the first rising water period without wave exposure, indicating a weak interaction between the oil and the sediment surface. For the Kobbe emulsion only 15% of the substrate surface area was covered with oil when the experimental period was initiated. For both Norne and Kobbe emulsion the major part of the remaining oil at surface was remobilized during the first tidal periods. The remaining oil (approx 5-10% coverage) is mainly due to edge effect at the division plates as shown in the photos in Appendix C and D. This data show clearly that the adhesion properties of the crude oil emulsions are low compared to the bunker oil emulsion.

In addition to the solid substrate, three sediment fractions were used in the basin experiments. With these sediment types the oil emulsion can be distributed both as surface and subsurface oil/emulsion. The transport into the sediment is dependent on the rheological properties of the oil emulsion. Surface oil will be adhered to the surface, as shown with the solid substrate, however the contact area between the oil emulsion and the sediment will vary and be dependent on sediment size and the elastic properties of the emulsion. The oil surface coverage is given for IFO380 and Kobbe emulsion with different substrate characteristics in Figure 4.3 and Figure 4.4 respectively. With IFO380 the oil is manly transported into the sediment for all sediment types, and little oil were at the surface after initiation of wave exposure and tidal variation due to the flow properties of the emulsion. For the Kobbe emulsion on the other hand, there were little difference in behaviour between the solid substrate and the two largest sediment fraction (8-16 and 10-80 mm), whereas very little oil was adhered to the surface for the smallest sediment fraction. His behaviour of the oil emulsion is mainly due to the high pour point and low elasticity of the emulsion.

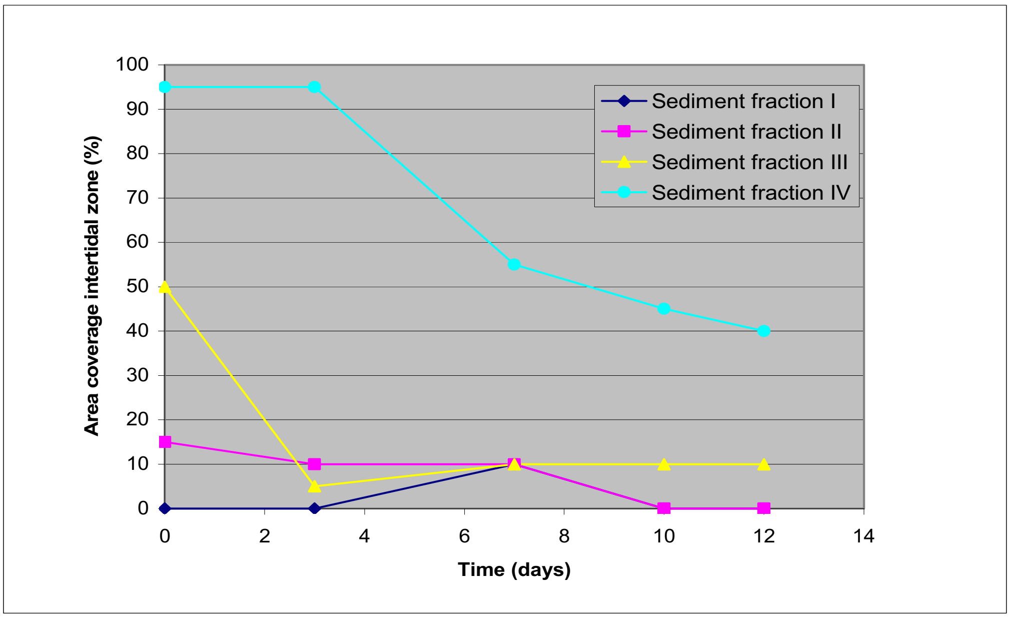



*Figure 4.3; Surface coverage in the intertidal zone with IFO380 emulsion for different sediment fractions as a function of time.*

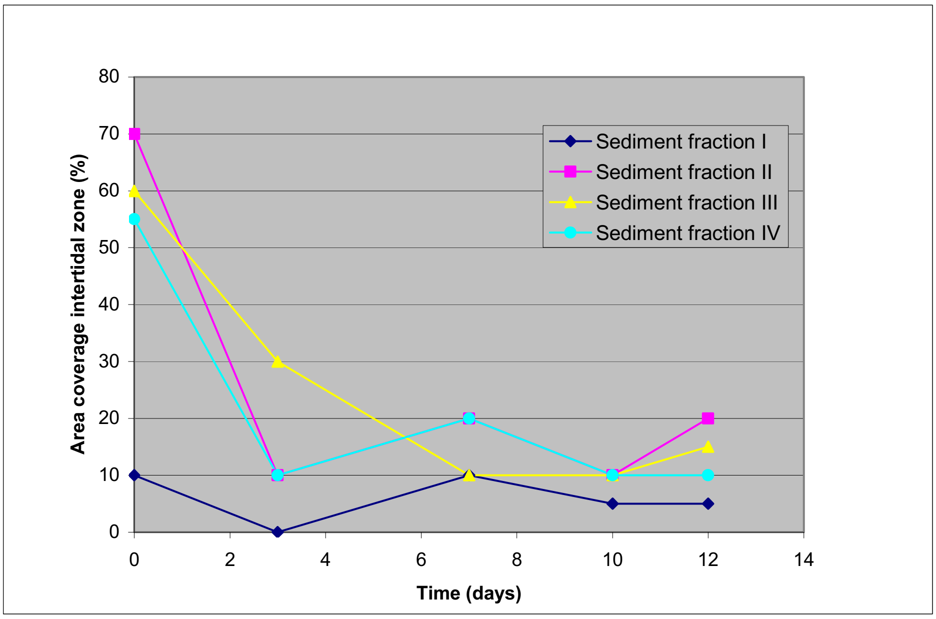



*Figure 4.4; Surface coverage in the intertidal zone with Kobbe emulsion for different sediment fractions as a function of time*

## 4.4 Wash-out of surface emulsion

After the initial adherence of oil to the substrate surface, the oil can be remobilized by different mechanisms, including refloating (buoyancy) and washout due to physical exposure by wave action. The latter process can take place by gradually reduction of the oil film thickness or by loosening of oil lumps from the sediment surface. These processes has been quantified by estimating the amount of oil on the sediment surface (coverage and average thickness). The results of these observation for the Troll and IFO380 emulsion for the different substrate fractions are given in Figure 4.5 and Figure 4.6, respectively.

For both oil types the oil quantity is reduced during the experimental period, however, with a different time constant. Initially a low amount of oil remained at the surface with Troll emulsion, and the main quantity was removed from the sediment surface during the first tidal cycles from all sediment fractions. After initiation of the experiment (as documented in Figures from Day 3) there was no practical difference between the sediment fractions.

With the IFO380 emulsion the situation was however different as indicated by the oil coverage fractions presented in Chapter 4.3. The oil quantities are reduced during the experimental period for all sediment fractions. The difference in oil quantities for the two oil emulsions can also be clearly observed from the photos taken during the experimental period in Appendix A and B. For the solid substrate experiment the decrease in total amount is more pronounced than the reduction in oil coverage indicating that the oil emulsion removal is mainly de to a gradually reduction in the average oil layer/film thickness. For the Kobbe experiment the oil coverage and oil quantity follows the same trend, which indicates that removal of the oil takes place by removal of the oil from the surface which is more likely with less strong adhesion between the oil and the sediment surface and larger oil lumps which are more receptive to water exposure.

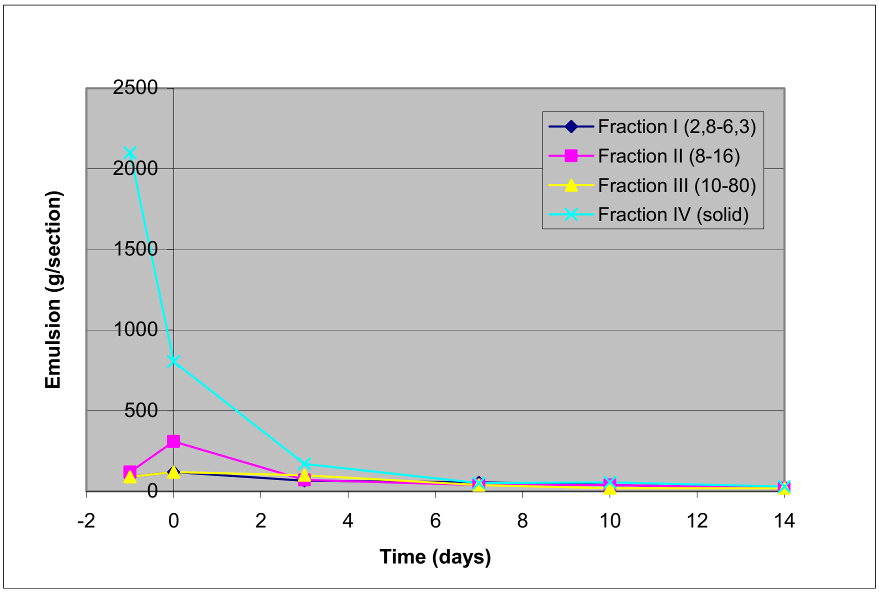



*Figure 4.5; Surface oil on different substrate fractions during the experimental period for Troll emulsion*

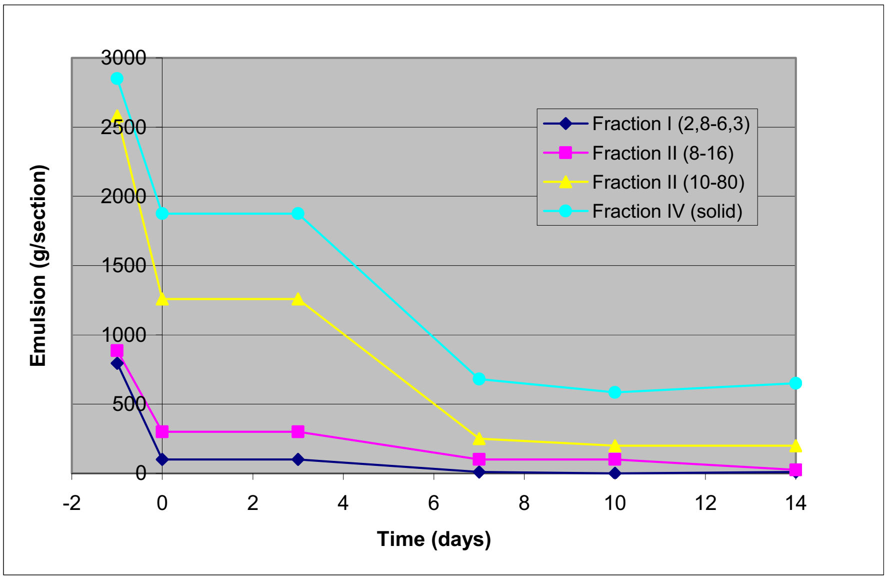



*Figure 4.6; Surface oil on different substrate fraction during the experimental period for IFO380 emulsion*

The removal of oil from the surface will also be dependent on the sediment surface "topography"/roughness. This roughness factor increases with increasing size of the sediment fraction allowing more oil to be protected at the sediment surface, reducing the oil removal due to water transport/exposure. This phenomenon was not documented clearly in the present study, but will be more clear with larger oil quantities which will give a high oil film thickness at the sediment surface.

### 4.5 Penetration

Observation and quantification of oil that has penetrated into the subsurface sediment can only be done through sampling and preparation of a cross-section of the substrate. This sampling will disturb the area and could not be used for further sampling and observation, which means that a limited number of observation/sampling can be performed and parallel sampling will not possible for the limited available area. Also the initial distribution of emulsion at the surface was not continuous, which most probably will affect the resulting in uneven penetration of oil emulsion into the sediment. The results from these observations and analysis will therefore be some uncertain but will give a clear indication on the fate and behaviour of the oil in the subsurface sediment. The result of penetration observations are only given of the two smallest fraction (I 2,8-6,3mm and II 8-16mm), because with the largest fraction (III 10-80mm) the size of the particle are in the same range as the sediment layer, and the penetration will vary over a wide range.

Figure 4.7 and Figure 4.8 shows the observed penetration depth of the different oils in sediment the during the experimental period for fraction I sediment (2,8-6,3 mm) and fraction II (8-16mm) respectively. The most important properties of the emulsion affecting the penetration were the pour point (if the oil emulsion are flow-able or not) and the viscosity of the emulsion. The highest penetration was found for the Troll emulsion, both with respect to the initial penetration rate and absolute penetration depth during the experimental period. This observation was expected due to the low pour point and relative low viscosity of the Troll emulsion. The IFO380 emulsion has also a pour point below the experimental temperature, but has a much higher viscosity compared to Troll. The penetration rate is much lower, however the penetration for both sediment fractions increases during the entire experimental period. It is expected that the penetration process continues until the oil layer/film at the sediment surface reaches an equilibrium based on oil viscosity, gravity and external forces by water transport. In a later phase the boarder will change and the penetration front will be less clear, due to weathering processes and changes in the physical properties of the oil fraction.

For both sediment fractions the Kobbe and Norne emulsions (with a pour point above study temperature) penetrate to a very low extent into the sediment. Initially both oil emulsions remained on the sediment surface, and the observed penetration into the upper 2-3 cm during the experimental period is most probably due to exposure by water transport and gravity in the sediment pore structure. The in general a slightly higher penetration was observed for Norne compared to Kobbe with a lower viscosity, may be due to differences in the stability of the emulsion structures.

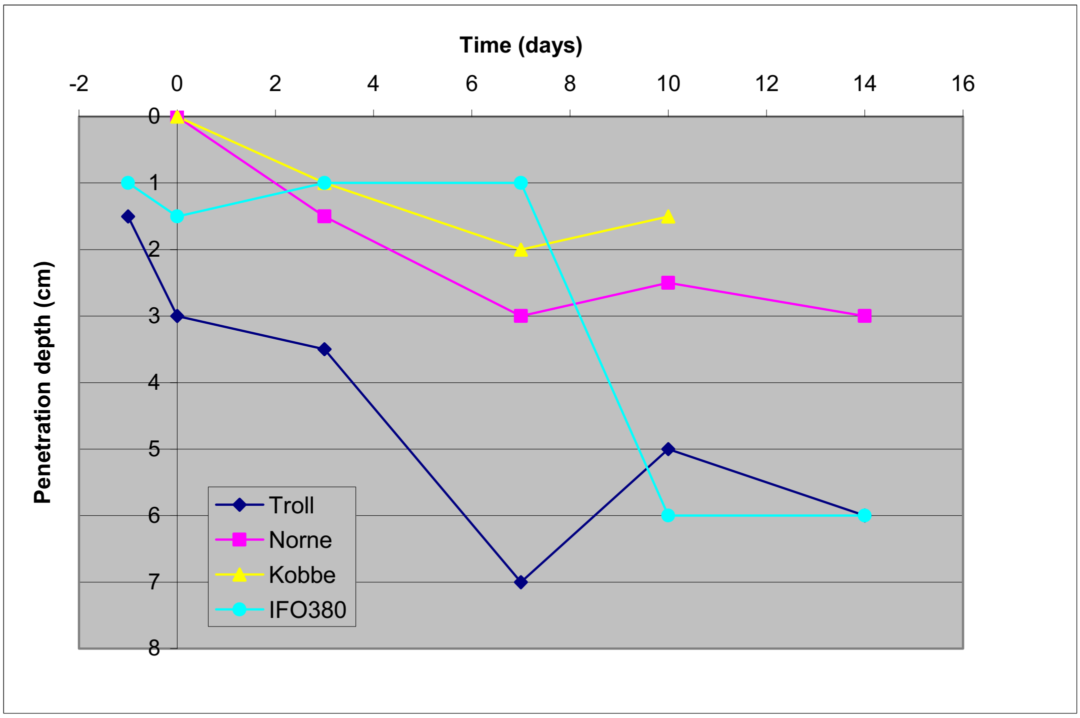



*Figure 4.7 Observed penetration depth of oil emulsions in sediment fraction I (2,8-6,3mm) in meso-scale basin experiments during the experimental period.*

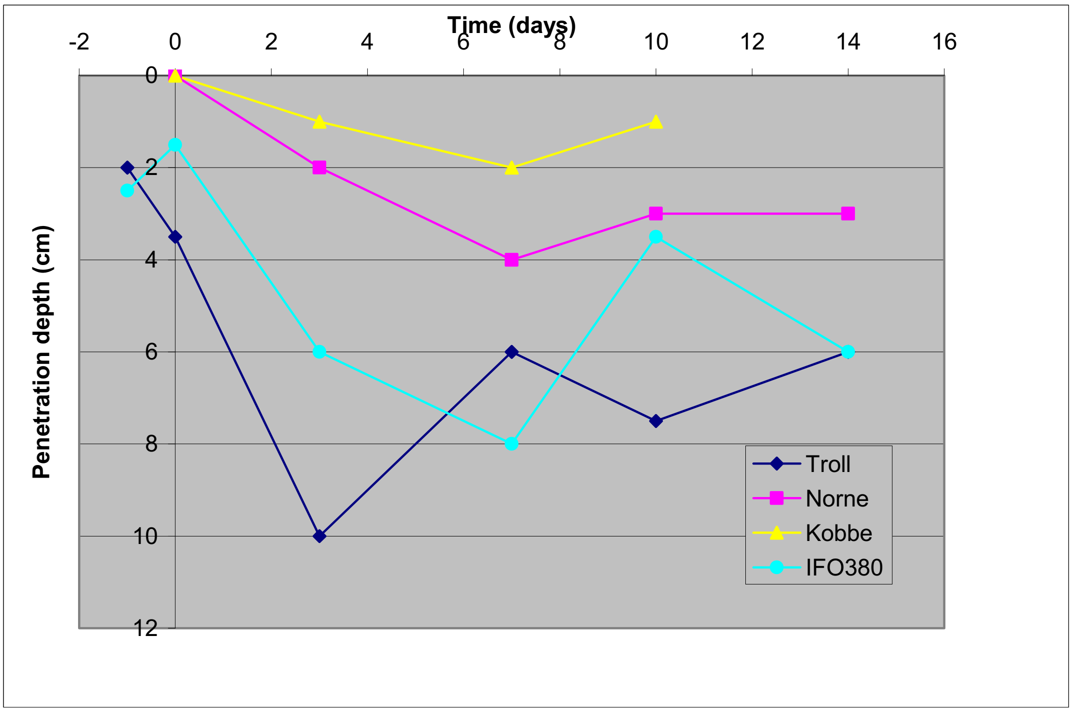



*Figure 4.8 Observed penetration depth of oil emulsions in sediment fraction II (8-16 mm) in meso-scale basin experiments during the experimental period*

## 4.6 Fate and behaviour of subsurface oil

The fate and behaviour of sub-surface oil in the restoration phase is dependent on several processes including retention (adhesion to solid surface), wash-out, erosion and refloating. These processes are dependent on environmental parameters like water exposure (wave and tidal), sediment transport and the properties of the different oil types as well as sediment characteristics. The present standard experimental design does not allow to separate between the different processes and mechanisms.

The quantity of the subsurface oil was estimated by oil concentration and oil distribution (thickness) within each sediment section. Figure 4.9 gives the total amount of oil (measured as emulsion) for the different sediment sections. In the Troll experiment the general trend is a decrease in oil quantity during the experimental period for all three sediment fractions. Most oil was found with the smallest sediment fraction (2,8-6,3mm), and a decreasing amount with increasing sediment particles. This gives a good correlation between sediment surface and oil quantity. After the initial period, the removal rate of oil are similar for the three different sediment fractions. This observation is most probably due to different mechanisms; sediment transport (erosion) will be more dominant for the smallest sediment fraction whereas larger pore structures with the larger sediment allows higher internal water transport.

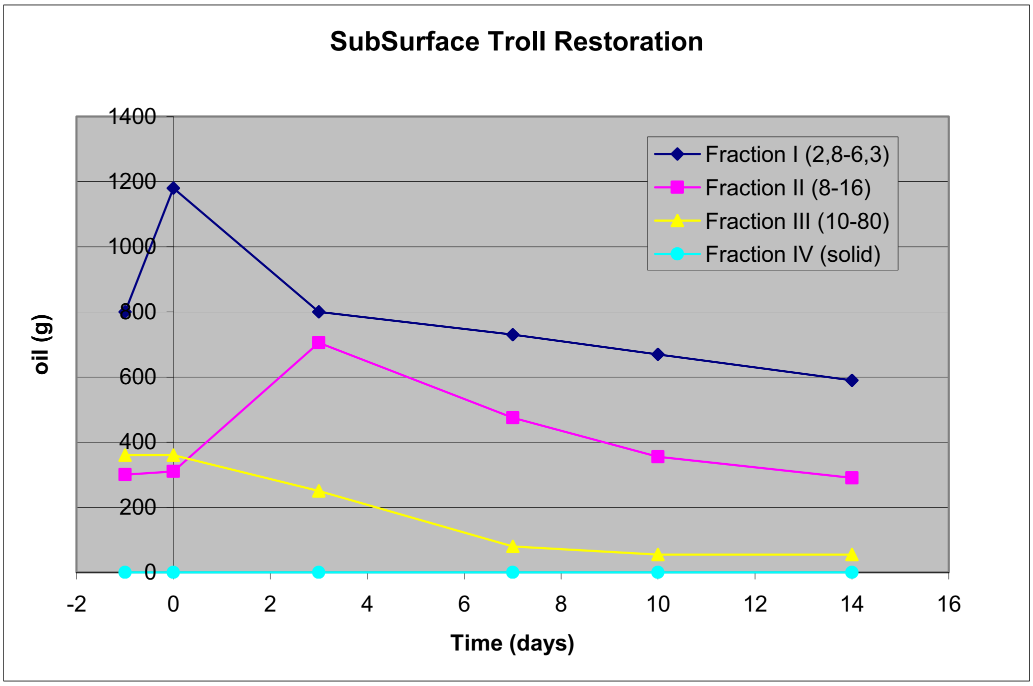



*Figure 4.9; Subsurface oil in different sediment sections with Troll during the experimental period*

For IFO380 the oil quantity was not altered significantly after the initial experimental period as shown in Figure 4.10. This is most probably due to the higher concentration of oil in the sediment, its higher viscosity and stronger adherence properties to sediment surface.

With both Norne and Kobbe oils, an initial low amount of oil was found in the subsurface sediment. But as shown previously in Figure 4.7 and Figure 4.8 the penetration increase as a function of time due to water transport and sediment movement, resulting in a slightly increasing quantity of oil into the subsurface sediment. This is shown in Figure 4.11 as emulsion quantities from the different oil types are summarized for the sediment fraction I (2,8-6,3mm) in the upper inter tidal zone. The oil quantities for both Norne (lowest) and Kobbe are lower compared to IFO380 and Troll.

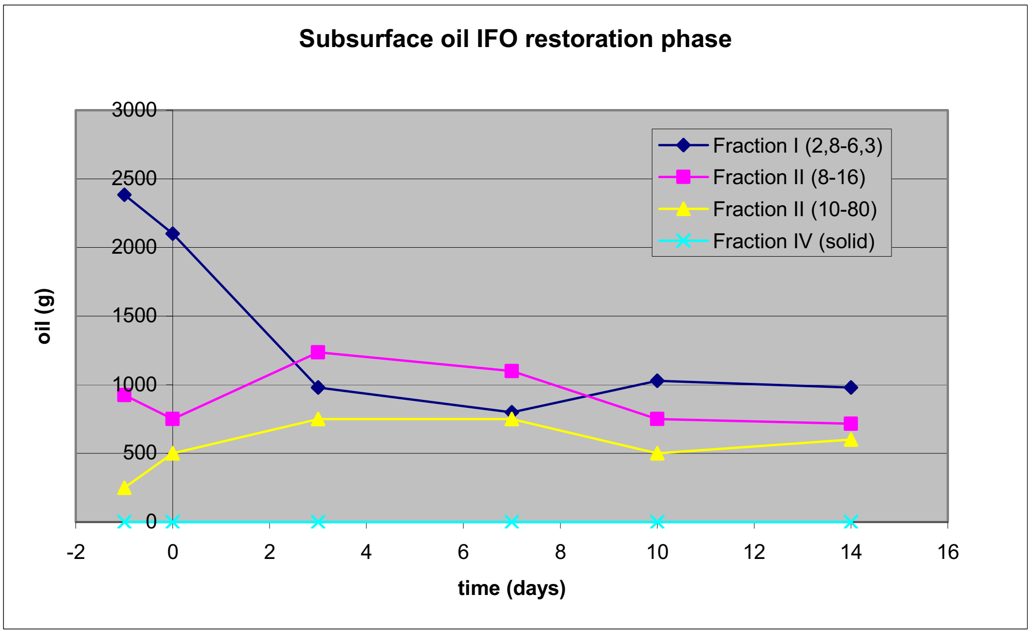



*Figure 4.10; Subsurface oil in different sediment sections with IFO380 during the experimental period*

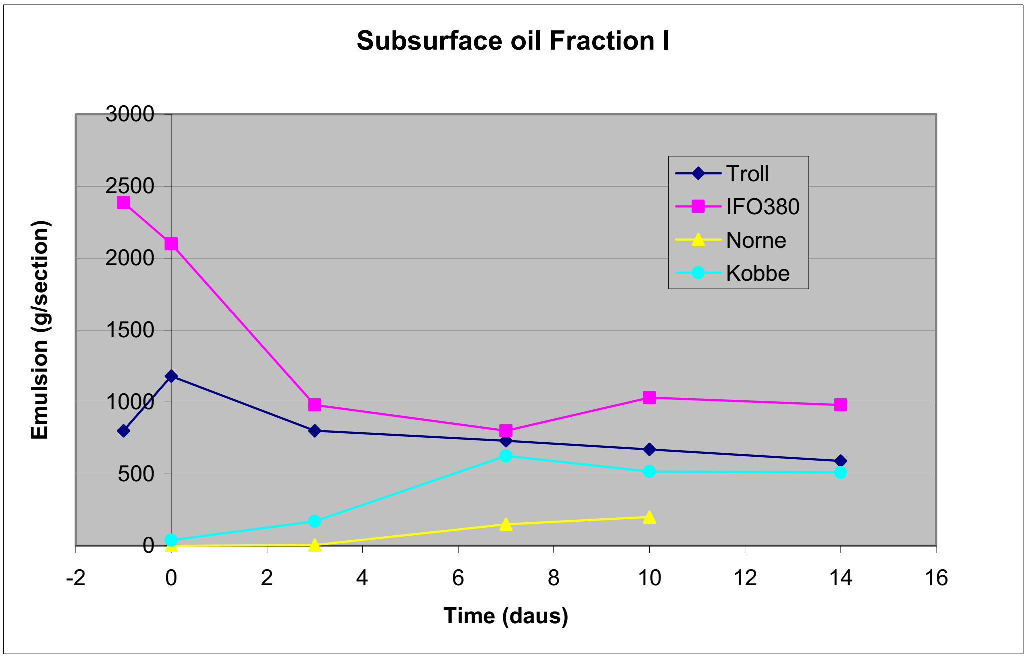



*Figure 4.11; Subsurface oil in Fraction I sediment (2,8-6,3mm) for the different oil types as a function of time*

The estimation of oil quantities above is based on oil penetration and oil concentration. The oil concentration for both the upper and lower intertidal zone for sediment fraction I (2,8-6,3mm) and fraction II (8-16mm) are given for Troll and IFO380 oil in Figure 4.12 and Figure 4.13, respectively. For Troll the oil concentration in the upper layer (0-2cm) decreases rapidly during the first tidal period in the lower intertidal zone and remains low during the experimental period. Oil concentration in the upper intertidal zone remain constant during the experimental period at approximately 7 and 13 mg oil/g sediment for the two sediment fractions respectively. This indicate that the wave exposure is low in the upper intertidal zone without braking waves, with a higher exposure in the lower intertidal zone. With IFO380 (Figure 4.13) the oil concentration decreases also in the upper intertidal zone during the experimental period and the oil is quantitative removed from the upper sediment layer at the end of the experimental period. The oil concentrations are in general much higher with the IFO380, due to stronger adhesion to the sediment surface and a higher viscosity of the oil emulsion.

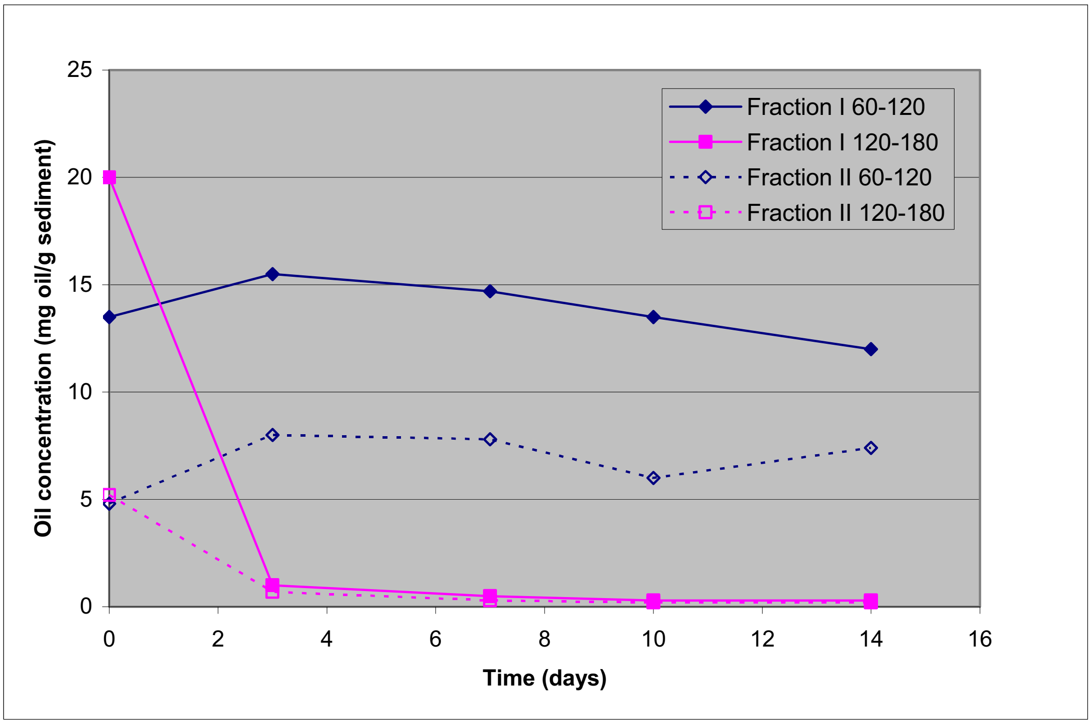



*Figure 4.12; Subsurface (0-2cm) oil concentration in upper (60-120cm) and lower (120-180cm) intertidal zone in meso-scale basin experiment with Troll emulsion*

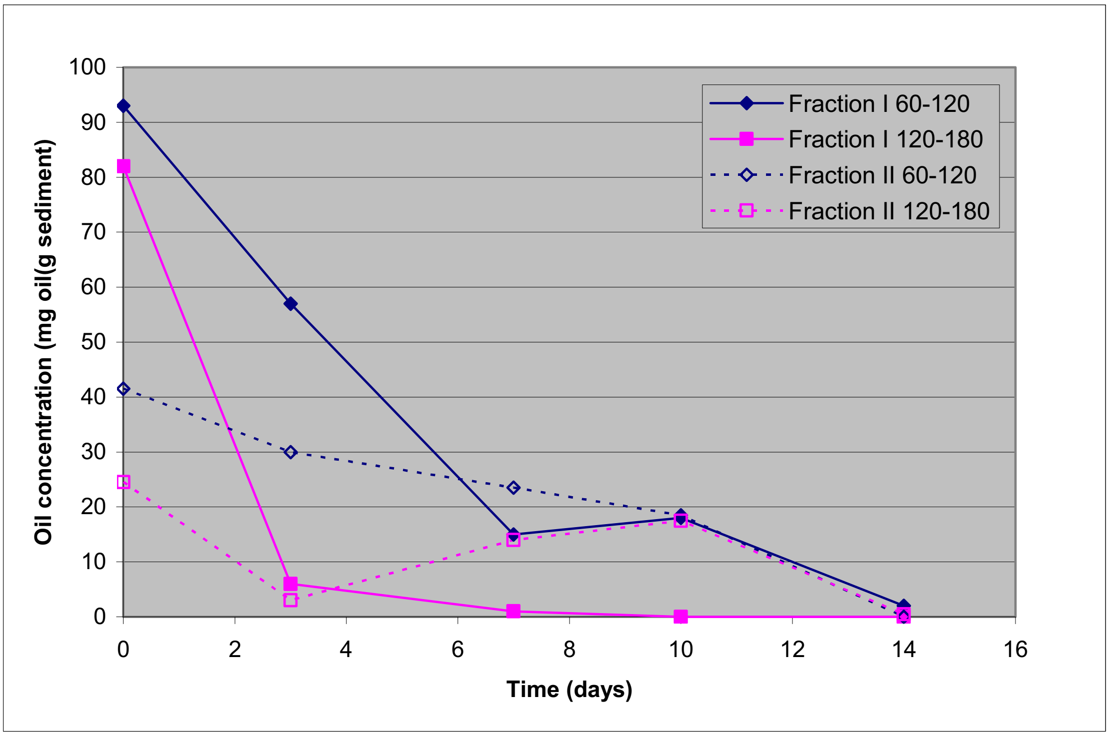



*Figure 4.13; Subsurface (0-2cm) oil concentration in upper (60-120cm) and lower (120-180cm) intertidal zone in meso-scale basin experiment with IFO380 emulsion*

At the end of the experimental period, sediment samples were taken as a function of sediment depth in 2cm layers in both upper and lower intertidal zone. The oil concentration as a function of sediment depth is given for sediment fraction I (2,8-6,3mm) and fraction II (8-16mm) and Troll and IFO380 are given in Figure 4.14 and Figure 4.15, respectively. The data varies over a wide concentration range. With Troll oil in upper intertidal zone with sediment fraction I and II, and IFO380 in lower intertidal zone and sediment fraction II the oil concentration increases at 2-4 cm indicating that the oil is remobilized from the upper section. With the limited data available it is very difficult to differentiate between the various removal processes, including water exposure by wave action and erosion by sediment transport.

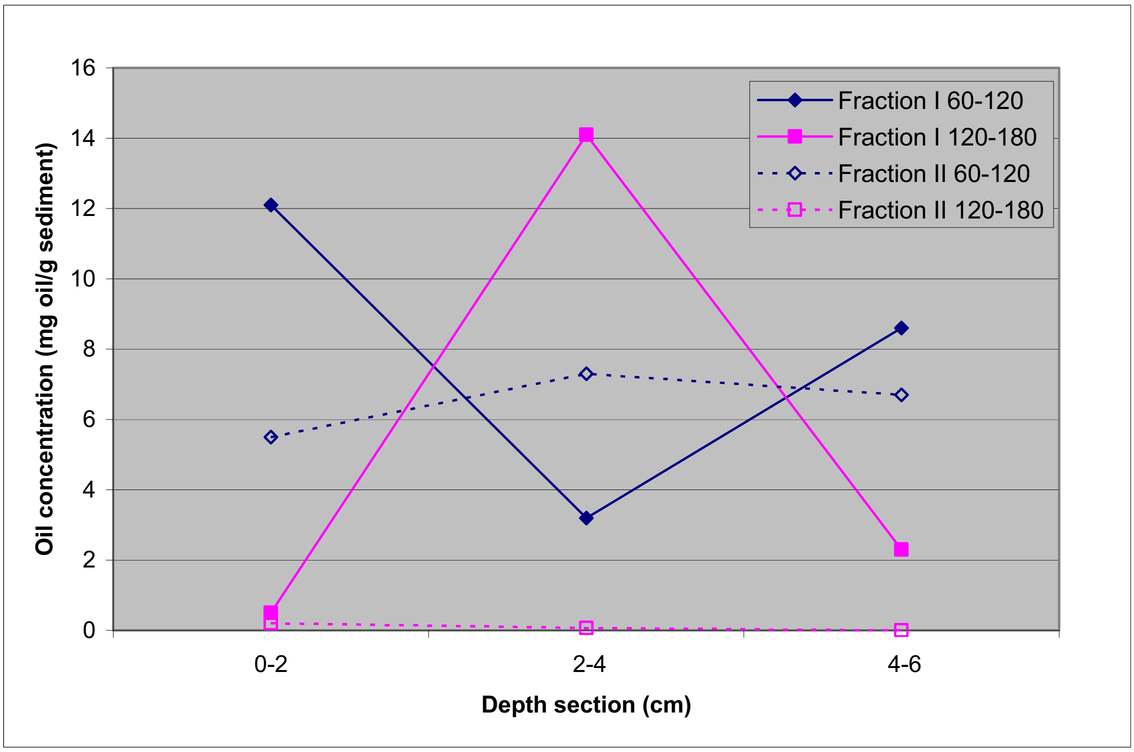



*Figure 4.14; Oil concentration at different sediment depths at the end of the experimental period with Troll oil emulsion*

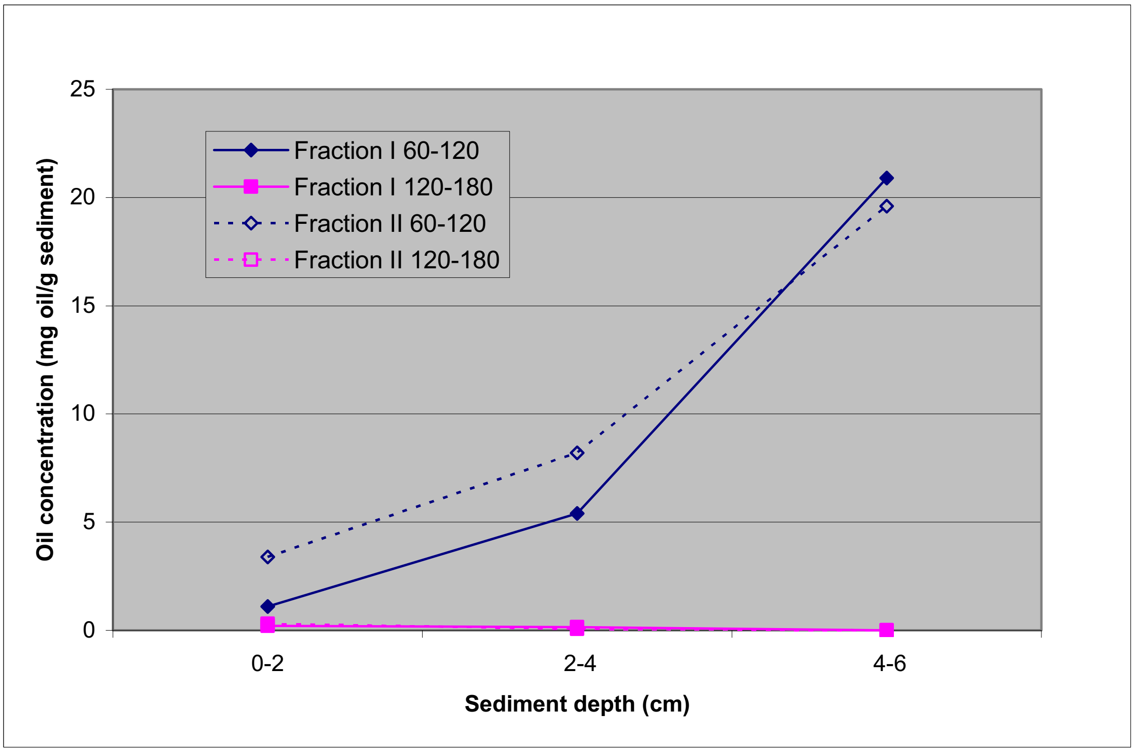



*Figure 4.15; Oil concentration at different sediment depths at the end of the experimental period with IFO 380 bunker oil emulsion*

## 4.7 Energy exposure

To study the fate and behaviour of the oil emulsions at different exposure, meso-scale basin experiments was performed with Troll oil emulsion at two additional wave frequencies; one with no (very low) wave expose and one high exposure giving approximately 10cm wave height, as compared to approximately 5 cm wave height in the standard experimental set-up presented previously. In the low energy system the largest sediment (Fraction III) was replaced with a smaller sediment of 1,4-2,8mm (Fraction V), because it as expected that this sediment fraction will not be transported by water movement.

With the highest wave exposure, the surface Troll oil was removed quantitatively during the first tidal periods with all sediment fraction. With low energy the oil penetrated at a higher extent into the sediment and only small quantities remained at the sediment surface (Figure 4.16) compared to the medium exposure experiment given in Figure 4.5. No good explanation for the low initial oil quantity at the surface can be given, as compared to *e.g.* Figure 4.5. For all sediment fractions the oil quantity decreased slowly at the surface during the experimental period, due to low wave exposure and sediment erosion.

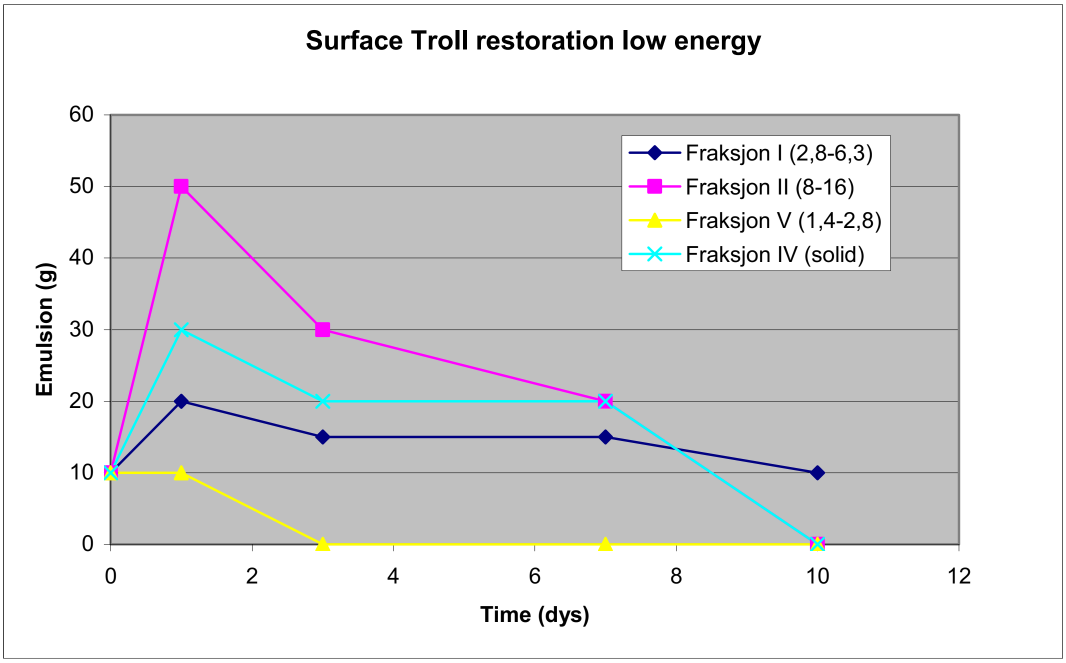



*Figure 4.16; Surface oil in meso-scale basin experiment with different sediment fractions and Troll oil emulsion with low energy exposure*

The estimated amount of subsurface emulsion in the upper intertidal zone and subsurface sediment (0-2cm) for sediment fraction I (2,8-6,3mm) and II(8-16mm) and exposure regimes are given in Figure 4.17 and Figure 4.18, respectively. For the finest sediment no significant difference was found between the different exposure regimes. The largest uncertainties is with the two highest wave exposures regimes giving sediment transport, which makes representative sampling difficult. However, the general trend for all exposure system is an decrease in oil concentration during the experimental period.

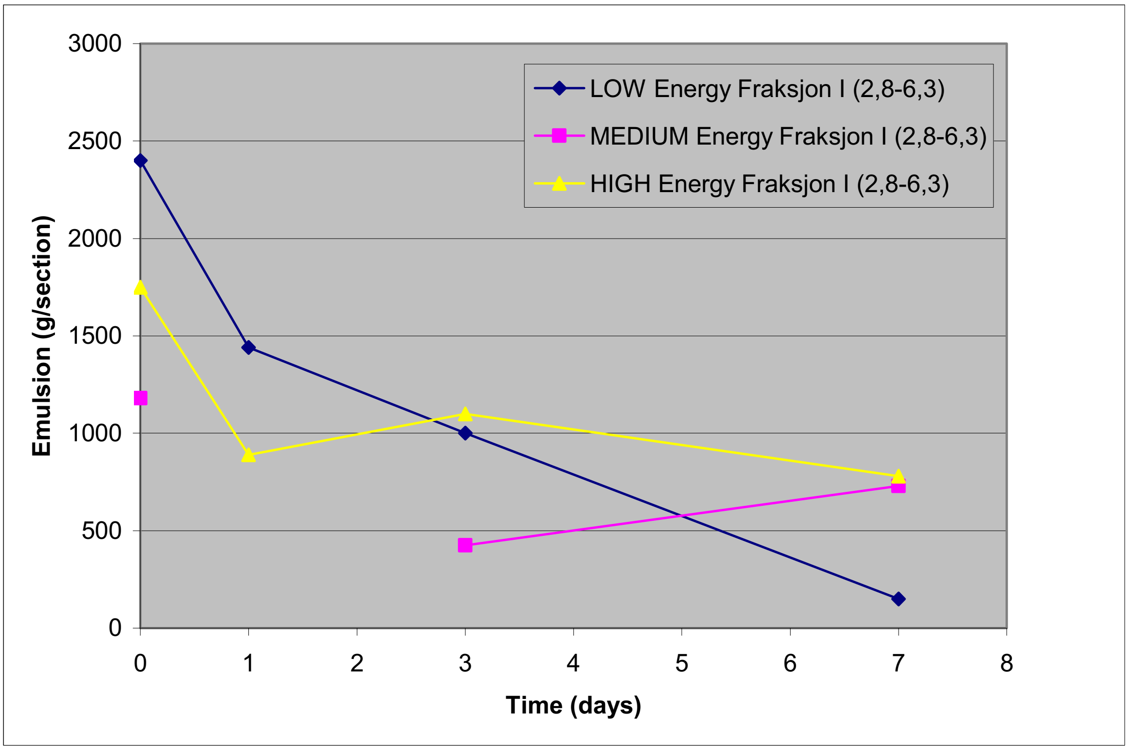



*Figure 4.17; Subsurface Troll oil in upper intertidal zone with sediment fraction I (2,8-6,3mm) with different wave exposure.*

The difference in remobilisation increases with increasing sediment size. In the experiments with sediment fraction II (8-16mm) the oil concentration decreases rapidly during the first tidal periods in the high exposure experiment. The sediment transport with the low exposure was low, indicating that water transport was the predominant effect observed for oil remobilisation. For both low and medium wave exposure the oil concentration decreased only slightly during the experimental period. These results show clearly that the wave exposure has a important effect on the retention of the oil both at the sediment surface and in subsurface sediment.

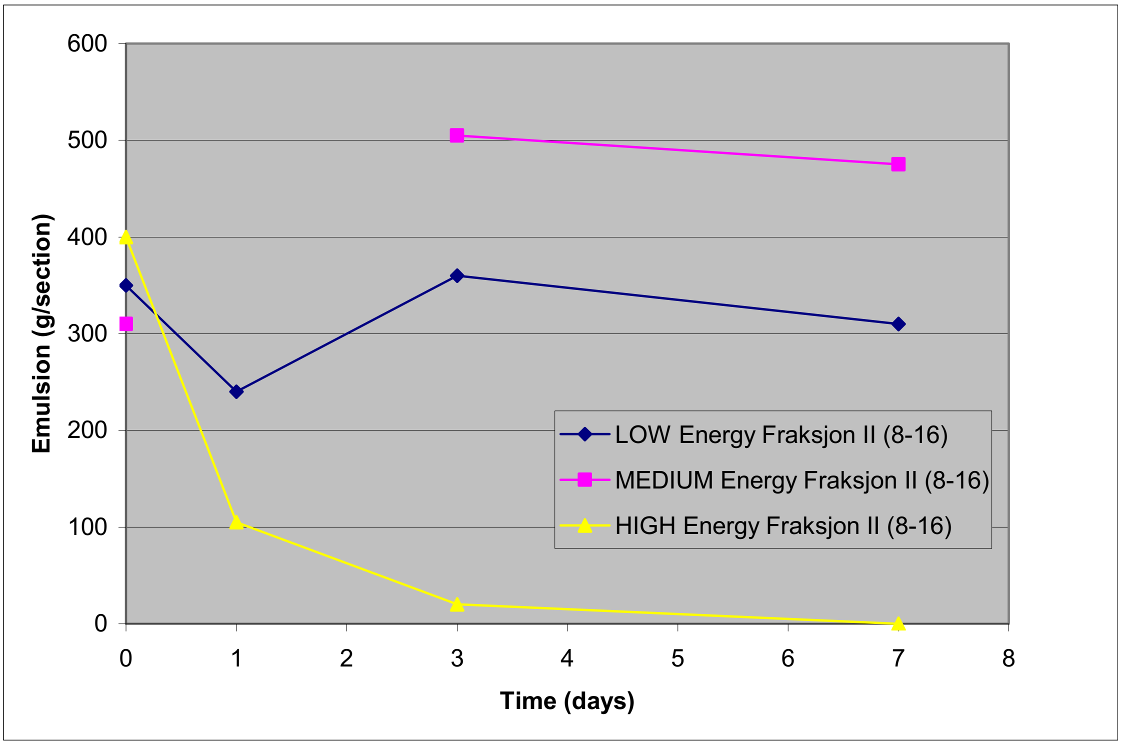



*Figure 4.18; Subsurface Troll oil in upper intertidal zone with sediment fraction II (8-16 mm) with different wave exposure*

**4.8 Mass balance**

The distribution of the oil emulsion in the meso-scale basin experiments are in general limited to sediment surface, subsurface sediment and remobilized. For a more easy comparison between the different oil types and sediment fractions a mass balance has been prepared. The mass balance is based on oil concentration in the sediment fraction and estimates on emulsion quantities on the surface. The remaining emulsion are considered to be remobilized through different processes, however this is not confirmed by any measurement or analysis and are therefore very uncertain. These graphical presentation will, however, give a good picture on the fate and behaviour of the different oil emulsion on sediment fraction.

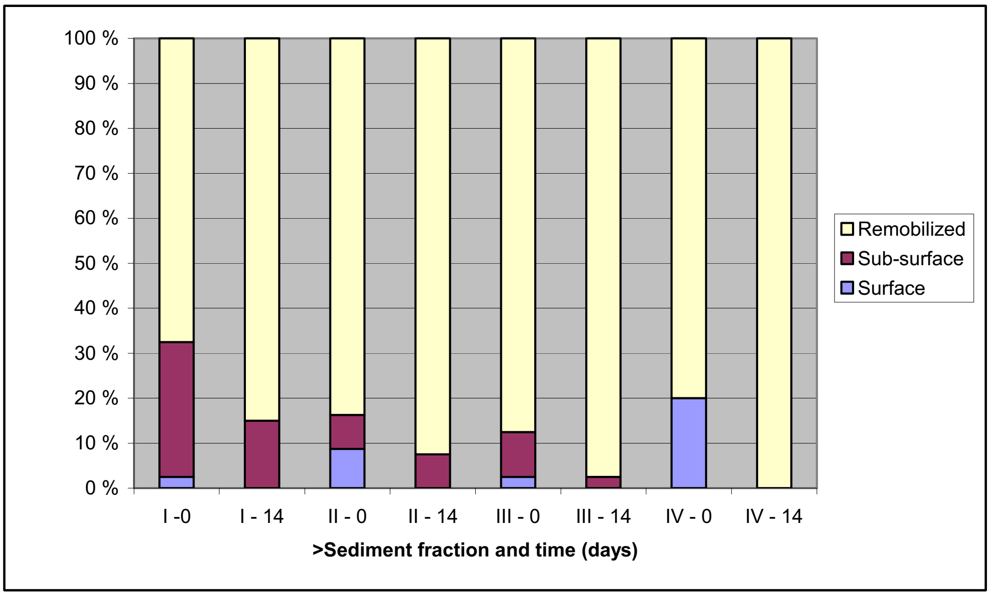



*Figure 4.19; Mass balance of Troll emulsion distribution at the beginning (0) and end (14) of the experimental period for the different sediment fractions*

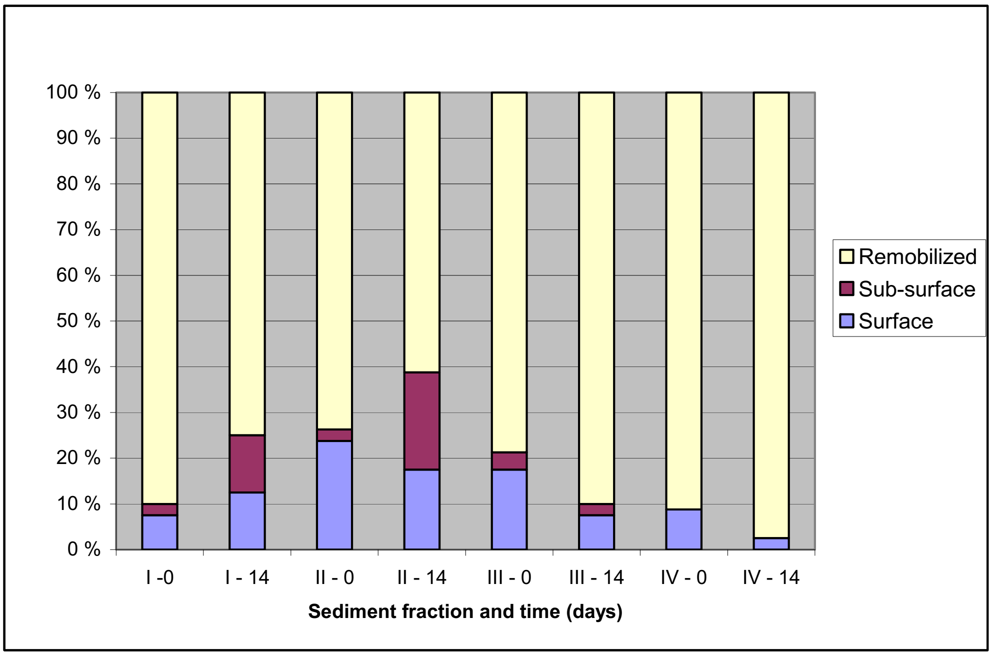



*Figure 4.20: Mass balance of Kobbe emulsion distribution at the beginning (0) and end (14) of the experimental period for the different sediment fractions*

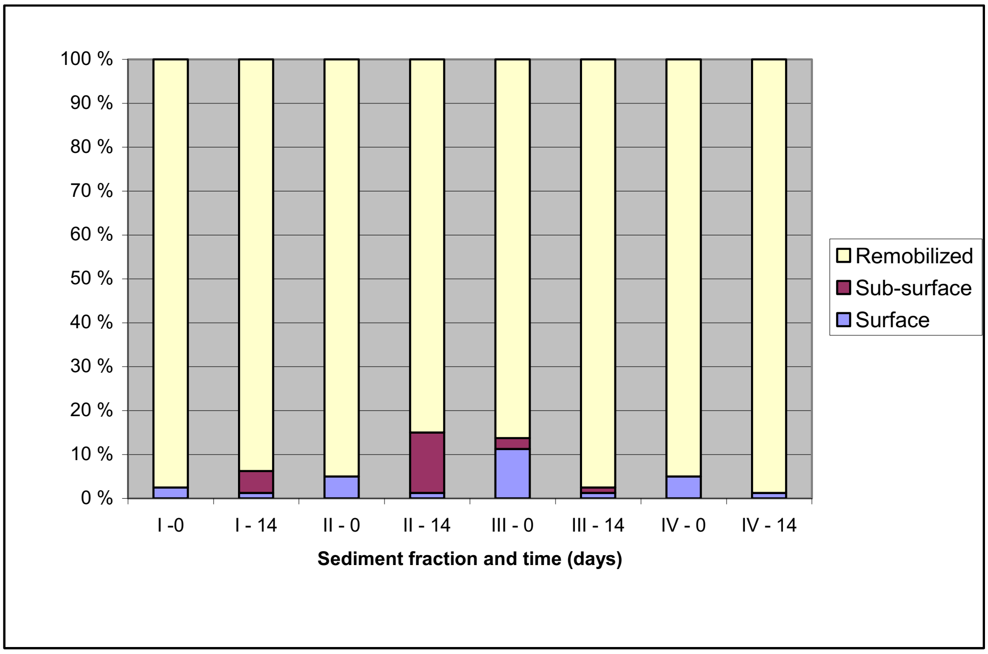



*Figure 4.21: Mass balance of Norne emulsion distribution at the beginning (0) and end (14) of the experimental period for the different sediment fractions*

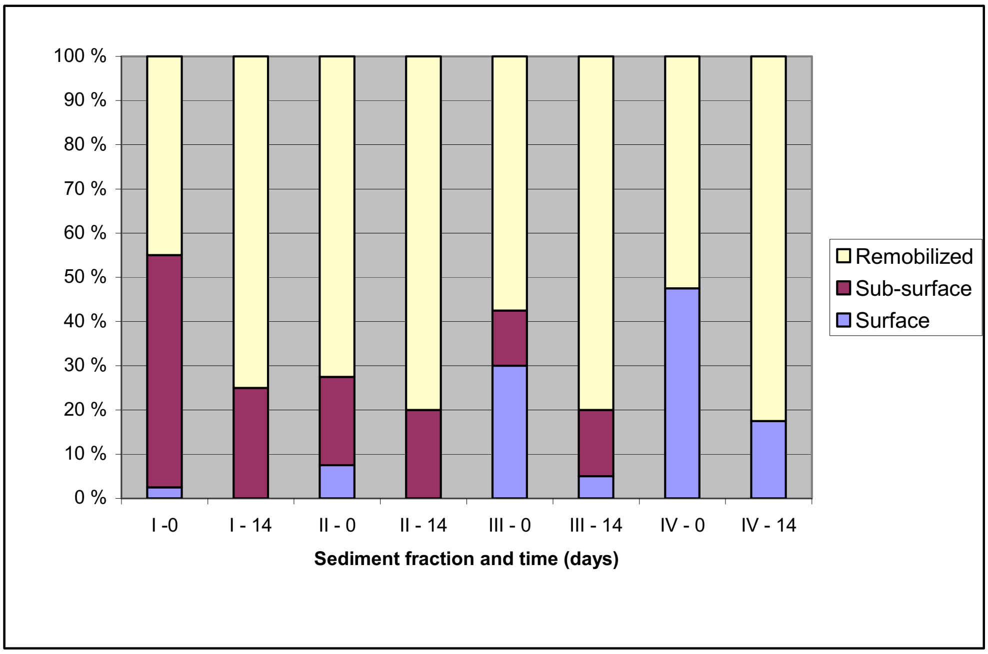



*Figure 4.22: Mass balance of IFO380 emulsion distribution at the beginning (0) and end (14) of the experimental period for the different sediment fractions*

# 5 Conclusions and operational gains

A total of six long-term experiments were performed to study the fate, behaviour and weathering of immobilized oil emulsions in the meso-scale shoreline basins under controlled and reproducible conditions simulating cold climatic conditions (5°C; water and ambient). Experimental parameters included oil types (three crude oil 250°C+ residue emulsion and one bunker oil emulsion), four sediment size fraction ranging from sand to solid substrate, three levels of energy exposure as wave energy, and different shoreline zones. The oil was observed, monitored and analysed as surface and subsurface oil, over an experimental period of 112 tidal periods (3 hours/tide). Prior to initiating of the experiments the oil emulsion was acclimated for five days on the shoreline.

The different oil type emulsions behaved very different both at the sediment surface and subsurface, initially and during the experimental period.

- Penetration; The crude oil emulsions with high pour point (Kobbe and Norne) were not transported into the sediment initially. After initiation of tidal variation and wave exposure only low penetration was observed with the two smallest sediment fractions (size). Troll emulsion with low pour point and low viscosity penetrated completely into the sediment fraction. The penetration depth increased during initial tidal periods with exposure.
- Adherence. The crude oils with high pour point did not adhere well to the sediment surface. Adherence increase with increasing sediment size, due to larger contact area between oil and sediment. Troll oil emulsion at the solid surface was easily remobilized (washed out) during first tidal periods. The IFO380 bunker emulsion adhered well to the solid substrate surface, and coated most of the surface during the experimental period.
- Oil weathering. Analysis of the physical properties of test oil could only be performed for a limited number of sampling points. The viscosity of the IFO380 emulsion dropped slightly the first 3 days, but remained constant during the experimental periods at different shoreline tidal positions. The viscosity of the Troll emulsion was reduced significantly during acclimatisation and remained constant during the initial period of the exposure period. The change in viscosity is most probably due to change in the water structure (e.g. water coalescence) for the Troll emulsion, but could not be documented by water content analysis. The analysis or observation did not give any indication on the emulsion stability vs emulsion breaking.
- Surface oil remobilisation – solid substrate. For the solid substrate studies, the bunker oil emulsion was mainly removed by reduction in the oil film thickness. It was more difficult to study the behaviour of surface crude oil emulsion during the experimental period as only minor amounts remained at the surface, *i.e.* the crude oil emulsions were mainly removed from the sediment surface. For Troll oil emulsion the removal rate from the surface was increased by increasing wave exposure.
- Surface oil remobilisation – sediment substrate. For the Crude oil emulsions with high pour point (Kobbe and Norne), that were adhered to the surface, was mobilized to a low degree during the experimental period. The oil was instead mixed and partly stabilized with the upper sediment layers after wave exposure and sediment transport. For Troll emulsion, very little oil was found at the surface of sediment substrates. The IFO380 remained partly at the shoreline substrate surface. With the smallest sediment fraction, the oil remained at the surface with a low transport into the sediment due to a high viscosity and high adherence to sediment surface which stabilize the upper sediment layer and reduced remobilisation of oil.
- Subsurface remobilisation; The fate and behaviour of the subsurface oiled sediment was dependent on sediment characteristics. The smallest sediment fraction was exposed to wave energy sufficient to sediment transport resulting in a higher oil remobilisation, for

the upper part of the sediment. A higher remobilisation rate was observed with Troll than with IFO380 emulsion. In larger sediment fraction the oil was also remobilized by water transport exposure from the upper part of the sediment layer. The results from the oil analysis have however relative large uncertainties due to lack of parallel analysis and uneven oil distribution.

The data from these studies show clearly a very different behaviour for the different oil types at different sediment characteristics both surface and sub-surface, which could be utilized for contingency planning and strategies in an oil spill cleanup operation:

- Natural remobilisation – self-cleaning, by different mechanisms (refloating, dispersion, erosion, wash-out)
- Bunker oil – adhere well and lower self-cleaning rate
- Crude oil emulsions with high pour point – low adherence, and high remobilisation from wave exposed intertidal zone.
- Self-cleaning (remobilisation) increase with increasing wave exposure
- Low viscous (and floating) oil penetrate into the sediment, whereas emulsion with high pour point did penetrate less.

The experimental studies were performed under simulated conditions. It is however, difficult to transfer these data to a real spill situation. This will require field studies under realistic condition for verification or adjustment of experimental data from the meso-scale experimental conditions using the same test oils.

The result from the present studies could also used for development of algorithms that describes the remobilisation/removal natural processes from shoreline substrate/sediment during the restoration phase, together with field data from real and experimental spills with the same oils.

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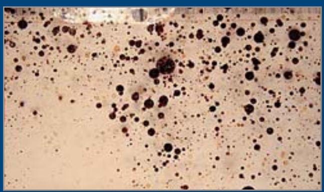
# REPORT



## Coastal Oil Spills - JIP

Report no.: 17

# C3.2 - Photo-oxidation and evaporation of immobilized oil emulsion on solid substrate

Tor Arne Oltedal and Svein Ramstad

**SINTEF Materials and Chemistry**
Marine Environmental Technology

Date: 2008-12-22



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TITLE

**C3.2 - Photo-oxidation and evaporation of immobilized oil emulsion on solid substrate**

**Coastal Oil Spill Report No 17**

AUTHOR(S)

Tor Arne Oltedal and Svein Ramstad

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| | 2008-11-13 | Tore Aunaas, Research Director | |

ABSTRACT

The effect of sun radiation and heat exposure on the fate, behaviour and weathering of the COS-Jip oil emulsions on solid substrate was studied on an experimental systems which simulated these processes with a light source simulating sun exposure during the summer season. The main findings were;

- Sun radiation affected the stability of the emulsion to the largest extent.
- Crude oil emulsions were generally unstable. Water content was not possible to quantify, but visual observation showed clearly a separation of water and oil.
- The Troll emulsion was unstable and broke up very rapidly
- The viscosities of the oil/emulsion increased significantly (3-10 x) due to sun radiation for Kobbe, Norne and IFO380 during the experimental period. The viscosity of Troll oil decreased during the experimental period.
- The chemical composition of the oils did not change during the experimental period as analyzed by GC/FID. The change in viscosity is not due to evaporation, but more likely to formation of photo-oxidized products.
- The IFO380 emulsion was the most stable emulsion under all experimental conditions.

The findings and observation from these studies will have an impact on the oil spill contingency plans and clean-up strategies

| KEYWORDS | ENGLISH | NORWEGIAN |
|---|---|---|
| GROUP 1 | Environment | Miljø |
| GROUP 2 | Oil | Olje |
| SELECTED BY AUTHOR | Shoreline | Strand |
| | Natural processes | Naturlige prosesser |
| | Photo-oxidation | Foto-oksidering |

# TABLE OF CONTENTS

# 1 Summary

The effect of sun radiation and heat exposure on the fate, behaviour and weathering of emulsions on solid substrate of an oil spill was studied for a period of one month simulating the restoration phase for the four Coastal Oil Spill JIP oils; Troll, Kobbe and Norne crude and IFO380 bunker oil. The crude oils were toppet to 250oC+ prior to use, and emulsified close to maximum water content. The different scenarios studied were;

- Sun exposure including UV-A/B radiation (6 hours per day)
- Heat exposure similar to sun exposure (up to 23°C in the oil phase)
- Reference without sun radiation or heat exposure

Experimental systems were designed to simulate these processes with a light source simulating sun exposure during the summer season. As a reference a similar heat exposure was established (UV A/B was filtered) and a system without sun and heat exposure. Oil was applied in 1mm thickness on standard shale tiles (15x15 cm) and the experiment was performed in a temperature controlled room with air temperature of 5°C. The oil emulsion was exposed for six hours every working day followed by water overflow to remove mobile oil and water soluble compounds, for a total of four weeks. One tile from each exposure scenarios and oil type was taken and analysed after 0, 3 and 7 days and 2, 3 and 4 weeks. The oil coverage ratio, oil viscosity and the chemical oil composition (GC/FID) were determined, together with visual observation on the behaviour of the oil.

During the experimental period, one sample tile was used for observation and analysis for each exposure scenario and oil type. The main findings were;

- Sun radiation affected the stability of the emulsion to the largest extent.
- Crude oil emulsions were generally unstable. Water content was not possible to quantify, but visual observation showed clearly a separation of water and oil.
- The Troll emulsion was unstable and broke up very rapidly
- The viscosities of the oil/emulsion increased significantly (3-10 x) due to sun radiation for Kobbe, Norne and IFO380 during the experimental period. The viscosity of Troll oil decreased during the experimental period.
- The chemical composition of the oils did not change during the experimental period as analyzed by GC/FID. The change in viscosity is not due to evaporation, but more likely to formation of photo-oxidized products.
- The IFO380 emulsion was the most stable emulsion under all experimental conditions.

The findings and observation from these studies will have an impact on the oil spill contingency plans and clean-up strategies:

- Sun exposure will affect the fate and behaviour to a large extent, different strategies should be used during winter and summer scenarios
- Crude oil emulsions are unstable under sun radiation. This will give a higher self-cleaning rate during summer season.
- The Troll emulsion is very unstable and will break-up rapidly by sun and heat exposure. The resulting oil has a lower viscosity which will allow higher penetration in sediment substrates.

- IFO380 emulsion will have a very high viscosity which makes clean-up and restoration more time consuming and laborious, and some cleanup techniques could only be utilized in the initial phase after stranding.

## 2 Introduction

This project has been a part of phase 1 in the Coastal Oil Spills JIP. The research projects in the JIP have been focused on the fate and behavior of oil spills in coastal areas and on shoreline. Laboratory studies have been performed in order to obtain data for further development of numerical models.

The first phase of JIP was performed in the period from 2006 to 2008, and was funded by Eni Norge, Shell Technology and StatoilHydro. The overall objectives of the JIP have been:

- to contribute to an adequate and sufficient basis of competence to document possible consequences in case of an oil spill close to the coast
- to provide documentation ensuring the countermeasures giving the optimal environmental gain

In the acute phase after stranding of oil, the oil normally accumulates and becomes immobile in the upper intertidal and supralitoral shoreline zone. During the acute and the restoration phase (immobilized oil), the weathering processes (e.g. evaporation, emulsification and photo-oxidation) that have taken place during drifting on the sea surface continues, but also other processes become more dominate. These processes will be important for the natural restoration (self-cleaning) of the oil contaminated shoreline and the strategies for shoreline clean-up and restoration.

The quantitatively most important processes will probably be evaporation, emulsification/de-emulsification and photo-oxidation which are affected by environmental parameters as sun radiation, temperature, wind and exposure by wave action. These phenomenons's have been studied and reported to a very little degree for highly weathered emulsions.

To study these phenomenons a new experimental system was established which allowed controlled and reproducible simulated sun radiation and heat exposure.

# 3 Materials and methods

## 3.1 Test oils

Crude oils can be characterised in four categories: asphaltenic, naphtenic, paraffinic and waxy crude oils. The crude oils studied in the Coastal Oil Spills JIP were selected among the oil companies' crude oils. It was important to select crude oils representing different categories of oils. The selected crude oils represent the categories:

- Troll – naphtenic crude oil
- Norne – waxy crude oils
- Kobbe – light paraffinic crude oil

In addition to the crude oils, a heavy fuel oil (IFO380) was also tested. IFO 380 is a representative heavy fuel oils for bunker oils used as fuel for ships going along the Norwegian coast. The content of light oil components in fuel oils is low, typically lower than 5 vol% for IFO 380 oils. The testing of the IFO 380 was therefore concentrated on the "fresh" fuel oil, not on an evaporated residue. The IFO 380 oil used in this project is a low sulphur fuel oil produced at the Esso refinery at Slagentangen in Norway.

Some physical and chemical properties of the oils studied are listed in
Table ***3.1***.

*Table 3.1 Characteristics of oils used in the Coastal Oil Spills JIP.*

| SINTEF Id | Oil type | Residue | Density (Kg/m$^3$) | Evaporative Loss (Vol%) | Pour point (°C) | Wax (wt%) | Asphaltenes (wt%) | Viscosity at 5°C/10$^{-s}$ (cP) |
|---|---|---|---|---|---|---|---|---|
| 07-0287 | Troll | Fresh | 0,900 | 0 | -36 | 0,9 | 0,04 | |
| | | 250°C | 0,930 | 25,5 | -27 | | | 770 |
| | | Ph.ox. | 0,931 | - | -21 | | | |
| 07-0260 | Norne | Fresh | 0,860 | 0 | 21 | 4,3 | 0,30 | |
| | | 250°C | 0,888 | 28,4 | 30 | | | 39100 |
| | | Ph.ox. | 0,885 | - | 30 | | | |
| 06-1061 | Kobbe | Fresh | 0,797 | 0 | -39 | 3,4 | 0,03 | |
| | | 250°C | 0,875 | 53,6 | 21 | | | 4630 |
| | | Ph.ox. | 0,877 | - | 15 | | | |
| 06-1125 | IFO 380 | Fresh | 0,963 | 0 | 15 | 5,0 | 3,4 | 87100 |

*-: not measured*

Oil spilled at sea will be subjected to several weathering processes as evaporation (lighter compound evaporates), emulsification (water droplets are incorporated in the oil phase) and photo-oxidation (changing the physical and chemical properties due to sun exposure). These weathering processes will change the physicochemical properties of the oil, being of great importance for the weathered oils fate and behaviour on the shoreline

For the crude oils, an evaporated residue of 250˚C+ was used. The 250°C+ residue corresponds to ½ - 1 week weathering of oil at sea, and will be representative for stranded crude oil along the Norwegian coast.

To ensure reproducible production of emulsions, a water content just below the maximum water uptake for the respective oils was used. After some initial studies, the standard water content was decided to be 70% for Troll, 75% for Kobbe, 60% for Norne and 40% for IFO 380.

To study the effect of photo-oxidation, the crude oils (Troll, Kobbe and Norne) were exposed for a solar simulator. The photo-oxidized oils represent oils exposed 5 days under ordinary sunlight exposure in the summertime. During this process, the oils were naturally evaporated to a 250˚C+ residue.

The oil were applied to the 15cm x 15 cm standard shale tiles. The tiles with oil were conditioned for one day at 5°C, before put into the experimental setup and started the experiment.

## 3.2 Experimental set-up

### 3.2.1 Experimental set-up

The experiment was conducted at SINTEF SeaLab, in a temperature controlled room. The test rig as shown in Figure 3.1 was constructed of aluminium profiles. The tiles were mounted on a wooden plate 20 cm beneath the specified filter. Due to wash-over the angle between surface and plates are fixed 5 degrees.

As shown in Figure 3.1, the four oils are represented with four different colours. From left: Troll then Norne, Kobbe and IFO-380. The double test rig was fitted with a polyethylene filter to the left and a borosilicate filter to the right. Polyethylene works as a UV- filter, and minimizes the UV-A and B radiation. Borosilicate is ordinary glass, and doesn't remove UV, and it was used only for keeping the temperature similar in both rigs. As reference, a test rig was placed at the without light or heat exposure.

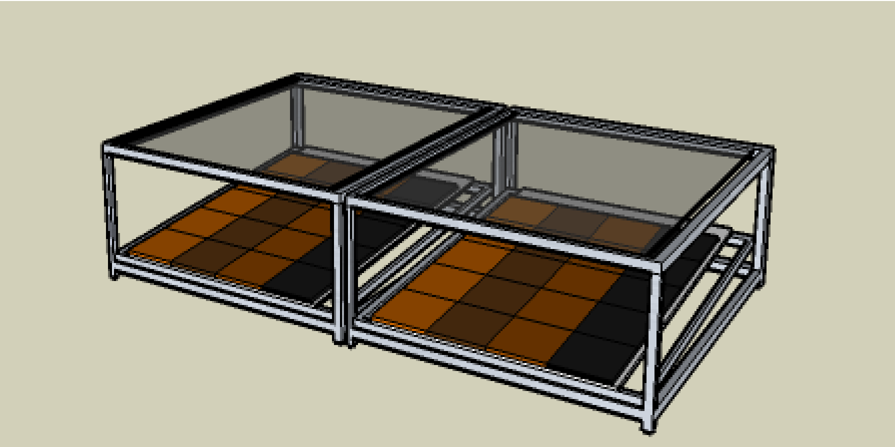


*Figure 3.1. Test rig to study effect of sun and heat exposure on oil fate behaviour and weathering*

### 3.2.2 Simulated sun-light exposure

The experimental setup was designed to be close to real sun radiation and temperature. The simulated sun exposure was calculated to be similar to a sunny day in the summer season.
The exposure was simulated by use of a Solar Constant 4000, which gives a spectrum similar to standard daylight. The sun was mounted under the roof, two meters above the tiles, giving similar exposure to both filters, and was verified by measurements of the intensity of the sun and radiation under the filters. The instrument used was a Gigahertz- Optik P9710 Optometer with sensors for UV-A and UV-B.

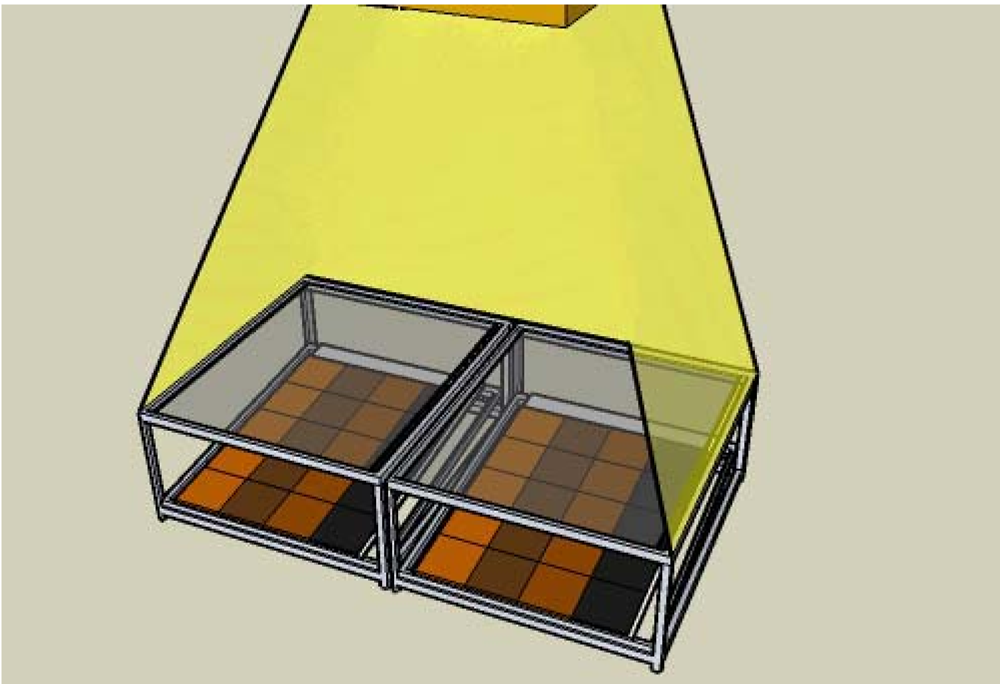


*Figure 3.2; The experimental test rig with simulated solar radiation*

The Solar Constant was operated manually (on/off). To simulate day-light the "sun" was running for six hours five days a week during the experiment.

Three different exposure scenarios was established to document effects, with one reference scenario;

- Light exposure through neutral Borosilicate glass filter, allow simulation of full spectre sun radiation
- Light exposure through Polyethylene filter - minimizes the UVA and B radiation which cause photo-oxidation of oil compounds. Heat exposure similar to full sun radiation.
- No light and heat exposure

### 3.3 Experimental procedure

- Day -2: Oil emulsion preparation initiation;  mixed for 18 hours.
- Day -1: Emulsion was applied to the shale tiles with a thickness of 1mm, and was allowed to condition at 5°C for 24 hours. Viscosity measurements were carried out on the emulsions directly from the emulsion tubes.
- Day 0 (Day of start): Viscosity measurements were performed for the different oil types..

- Day 1; simulated sun exposure for approximately six hours. After exposure, the tiles were flooded with water (2 minutes) to remove any water soluble components and removal of mobile oil/emulsion. The conditions of the tiles were documented by visual observations and by photo documentation.
- Day 2 and 3: Same as day 1. At day 3 one tile of each emulsion in each rig was sampled for further analysis.
- Each working day from day 6 until termination of the experimental period (day 28); as for Day 1. Samples at day 7, 14, 21 and 28 as day 3.

### 3.4 Analysis, monitoring and observations

The analysis plan in the experiment was:

- Day -1 and 0: Viscosity measurements of the emulsion after preparation and after conditioning of the shale tiles.
- Day 3, 7, 14, 21 and 28: Sampling of one tile for each oil and exposure; Viscosity, Gas chromatographic analysis (GC/FID), and water content and gravimetrical analysis.
- After the first sampling day the analysis plan was changed to only perform viscosity and some selected GC/FID- analysis, and the analysis plan was changed due to high loss of oil after exposure. The samples appearance and distribution changed over time and were not equally divided over the plate, which made representative sampling difficult.

**Viscosity**
To measure viscosity a Physica MC300 rheometer was set up with a PP25 measuring system 1 mm gap was used during the experiment. All values were noted for shear rate 10 (d(gamma)/dt = 10 1/s). Usually the viscosity measurements were carried out using a PP50- system, but PP25 give the same results requiring a smaller sample. All measurements were done at 5 °C.

**Photo documentation**
The state of the emulsion (emulsion appearance) were documented by photos each working day. Pictures are taken at start up, before wash-over and after sun exposure and wash-over. The pictures were taken in such a way that they easyly can be compared with each other.

**Observations**
All changes that were observed, was noted in a laboratory journal, and the observations were also documented with photos.

# 4 Results and discussion

## 4.1 Experimental set up

The effect of sun radiation and evaporation on the behaviour and weathering on stranded oil emulsions were studied for a period of four weeks. Three different exposure scenarios was established;

- Light exposure through neutral Borosilicate glass filter, allowing simulation of full spectre sun radiation
- Light exposure through Polyethylene filter, minimizing the UV A/B radiation which cause photo-oxidation of oil compounds. The heat exposure was similar to full sun radiation.
- No light and heat exposure

Each of the simulated exposure systems allowed use of five tiles (15x15 cm) for each oil type. One tile was sampled for each sampling day, therefore no statistical analysis of the result could be performed. The sampled tiles were observed for oil surface coverage, and viscosity measurements and GC/FID analysis was performed on recovered oil/emulsion .

The sun radiation generated heat (9kW), and the temperature was monitored in the oil phase of the three exposure systems and in the room. The temperature log for the entire experimental period is shown in Figure 4.1. With light exposure the temperature increased significantly in the oil phase compared to the room temperature. Highest temperature was measured in exposure system including UV radiation ("sun exposure"). The temperature in the exposure system without sun/heat exposure was similar to the room temperature. Towards the end of the experimental period, the effect of radiation was less pronounced, which indicate lower oil layer thickness making the measurement less accurate.

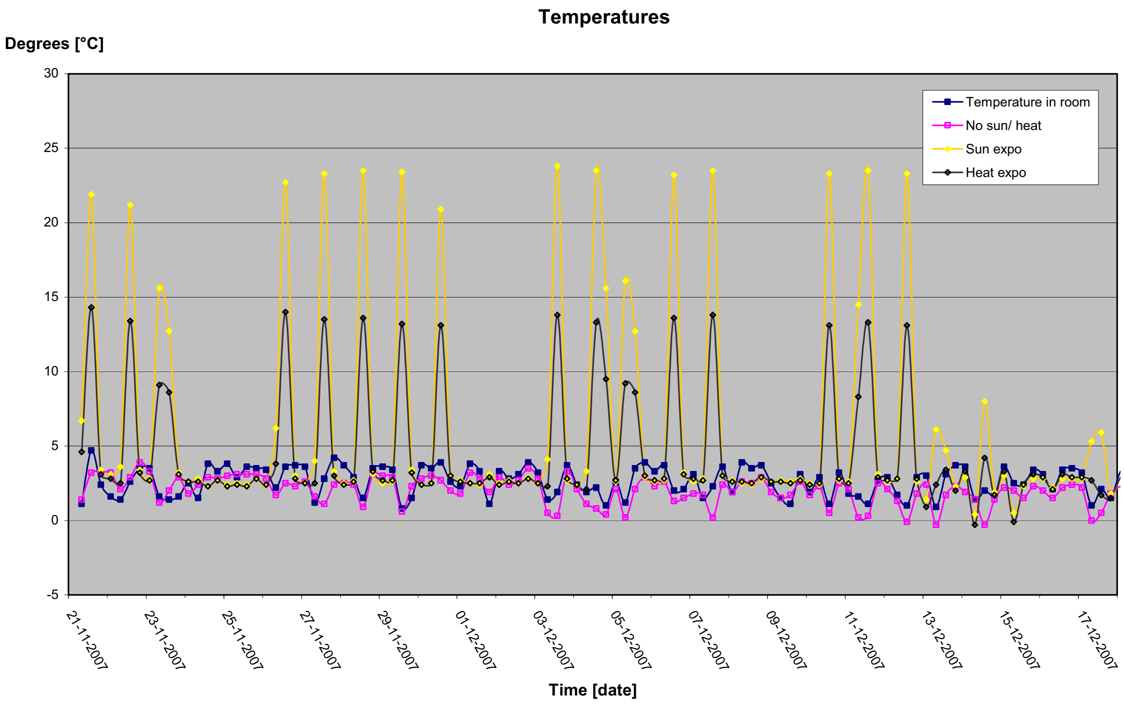



*Figure 4.1 Measured temperatures in the oil phase for the different exposure scenarios*

Based on experience during the experimental period, there are a few things that could have been done different. The following points are recommended for improvement of the experimental system:

- The tiles should be kept further apart from each other making it easier to take samples of the oil. The spillage from the wash-over can be collected and analysed for light components. Automatic control of sun-exposure time periods, and automatic water flooding. This will give the emulsions the exact same water doze and pressure every time.
- The room had one temperature controller which provided enough cooling for the system. The current controller is configured to reset every night, not influencing the cooling during the day.
- For a better temperature control both in the room and in the oil phase, a table fan was used to generate a wind in the experimental system. This helped to keep the temperature below the filters at a reasonable level and realistic with regards to wind conditions, but could be improved.

### 4.2 Visual observations

During the experimental period the tiles with oil emulsion was observed and photo documented each working day. Table 4.1 shows pictures and comments on the observations at start and after 1 day, 2 days, 2 weeks and 3.5 weeks in the experimental period. Each picture shows all four test oils used in the study. The pictures show a very different behaviour, both with respect to oil type and radiation type.

*Table 4.1 Observation of experimental system during the experimental period*

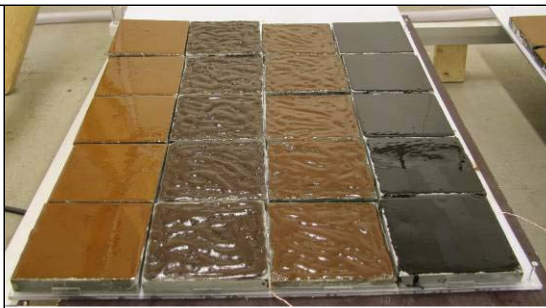
| | |
|---|---|
| Emulsion on the tiles at time = 0.<br>From left to right; Troll, Norne, Kobbe and IFO380.<br>All emulsions covered the tiles and had an average thickness of 1mm. |  |

*Table 4.1 A; Time = 0 day*

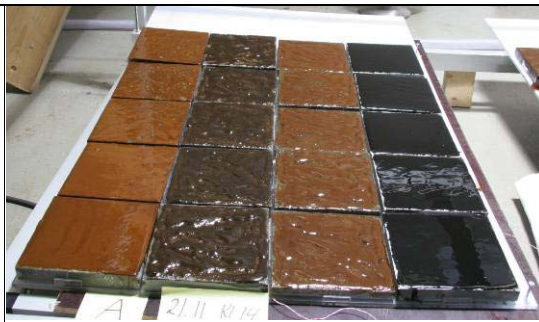
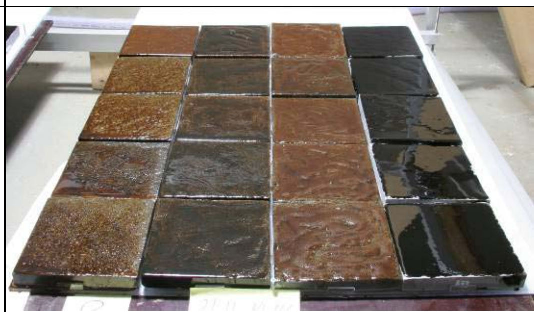
| | |
|---|---|
| Heat exposure; Emulsions after the first day under the polyethylene filter. A slight change in the Troll emulsion is visible, whereas Norne and Kobbe have the same appearance as for t=0. |  |
| Sun exposure; Emulsions after the first day with borosilicate filter. A significant change in colour and in amount of oil. Troll has lost a lot of the oil which was present at the beginning. Norne has become floating, and some spots are not fully covered with oil any more. Kobbe has minor colour change. |  |

*Table 4.1B; Time = 1 day*

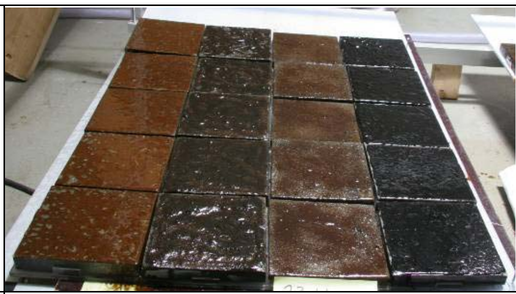
| | |
|---|---|
| Heat exposure; the Troll emulsion has big droplets of water inside and is about to break up. Kobbe is highly affected and was floating. IFO380 has lost water and is dried out. |  |
| Sun exposure; Crude oil emulsion were broken. The Troll and partly Kobbe emulsions have generally floated off the tiles. The Norne emulsion remained mainly on the tile surface. IFO380 covered the tile surface completely, but the emulsion had clearly lost water. |  |
| No exposure; The tiles which have not been exposed to the sunlight were almost visually unchanged. The flushing water remains on top of the oil, especially on the IFO380. |  |

*Table 4.1C; Time = 2 days*

| | |
|---|---|
| Heat exposure; A thin oil layer at the shale tile, and the. Norne appears to be unaffected, but little water remains in the emulsion. Kobbe and Troll have mostly been removed from the surface; only a thin surface layer is left on the tiles. The IFO380 appearance was still unaffected |  |
| Sun exposure; The tiles with Troll had dried out and are almost clean. Norne has spread out to a uniform oil phase. Kobbe has formed a thin layer on the tiles without water. IFO380 seems to be affected by sun exposure, but emulsion is broken up with water removal. |  |

*Table 4.1D; Time = 2 weeks*

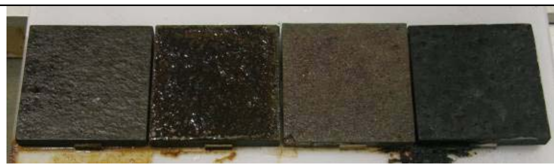
| | |
|---|---|
| Heat exposure; Troll has disappeared from tile surface, whereas Norne appearance was almost unaffected (but emulsion broken), Kobbe was a thin oil film, whereas the IFO-380 covered the surface completely (emulsion broken). |  |
| Sun exposure; The result of sunlight over several weeks. Troll was completely removed, and only small quantities of Kobbe remained at the surface. Both Norne and IFO380 covered the surface, but the emulsions were broken with no remaining water. |  |
| No exposure; Troll is removed, Norne is still there, but Kobbe has different appearance due to breakage of the emulsion than on the other exposure. IFO380 seems unaffected. |  |

*Table 4.1E; Time = 3.5 weeks*

The coverage of the tiles was determined by visual observation. The results for the different oil types and exposure scenarios are given in Figure 4.2. The coverage was in general less dependent on the different light exposure, but the oil types behaved very differently as described in Table 4.1. For the IFO380 the coverage did not change during the experimental period. For Troll and Kobbe the oil were completely removed from the substrate surface at the end of the experimental period.

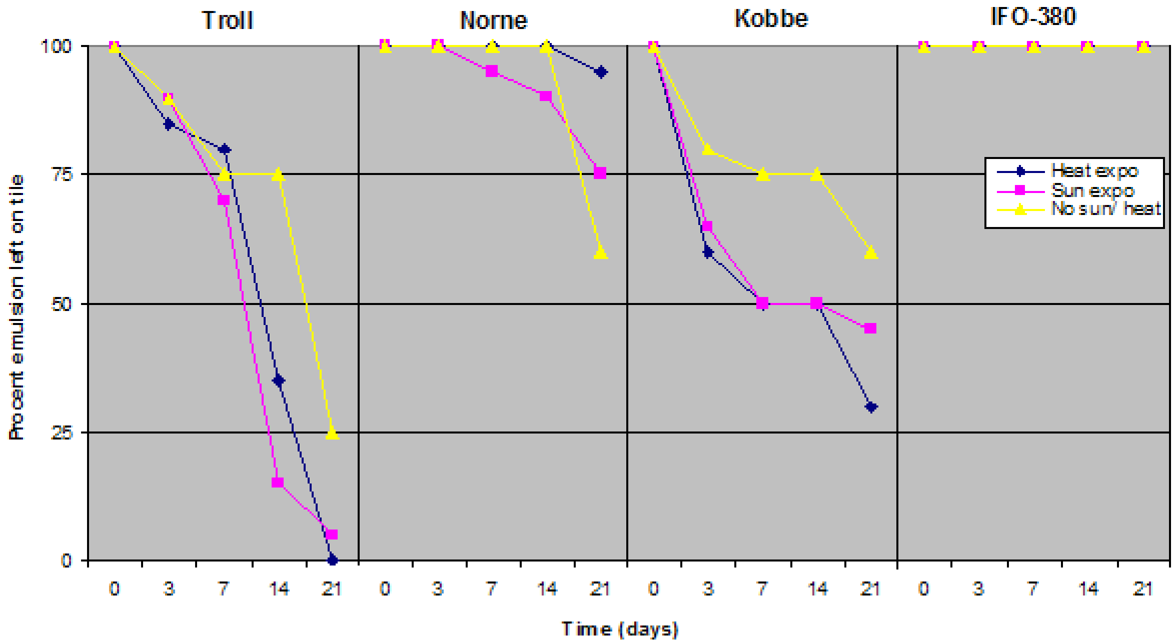



*Figure 4.2 Surface coverage of tiles with different exposure regimes*

The quantity of oil at the tile surface was reduced initially at a much higher rate due to loss of oil layer thickness (no quantified but observed visually). As shown in Table 4.1 the emulsions of the crude oil residues are unstable and water is released, especially for the Troll and Kobbe emulsions. This was specially clear in the scenarios with simulated sun exposure for all test oils, including the IFO380 emulsion that gave a ”water free film” at the tile surface.

### 4.3 Chemical properties and weathering

Oil emulsions were sensitive to temperature, radiation (photo-oxidation). Some were stable and not affected by the sun, but others are completely destroyed by the sun and wash-over. When oil is influenced by sunlight some of the oil components will be oxidised to surface active compounds. This contributes to an increased stability of w/o-emulsions, and therefore has a large influence on the oils persistence on the sea surface.

A significant change in the temperature was also observed during the experiment period whether the sun was on or off. The temperature in the room was stable, between 0 and 5°C even though the oil temperature reached up to 23°C during day-time as shown in Figure 4.1. The reference had stable temperatures, corresponding to the temperature in the room itself.

Oil samples were taken for viscosity measurement during the experimental period for the different oil types and sun/heat exposure. The viscosities as a function of time are given in Figure 4.2 to Figure 4.5 for Troll, Kobbe, Norne and IFO380 respectively.

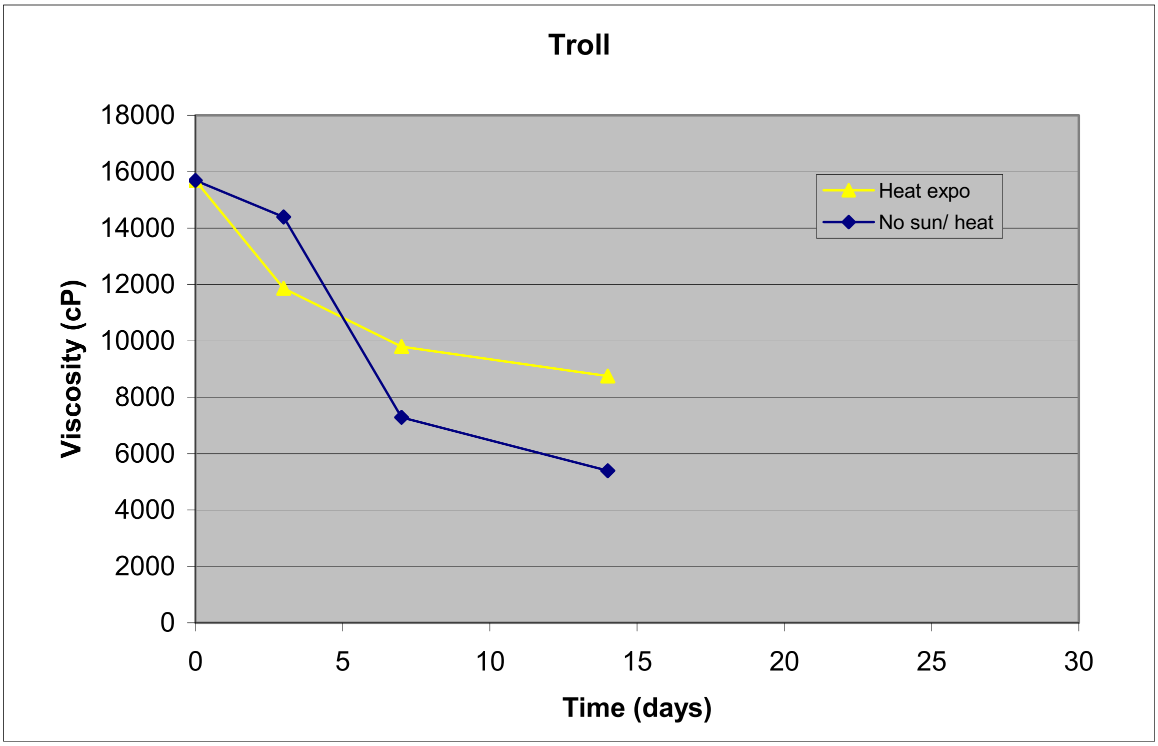



*Figure 4.2 Viscosity of the emulsion/oil at the substrate surface for the different exposure scenarios for Troll*

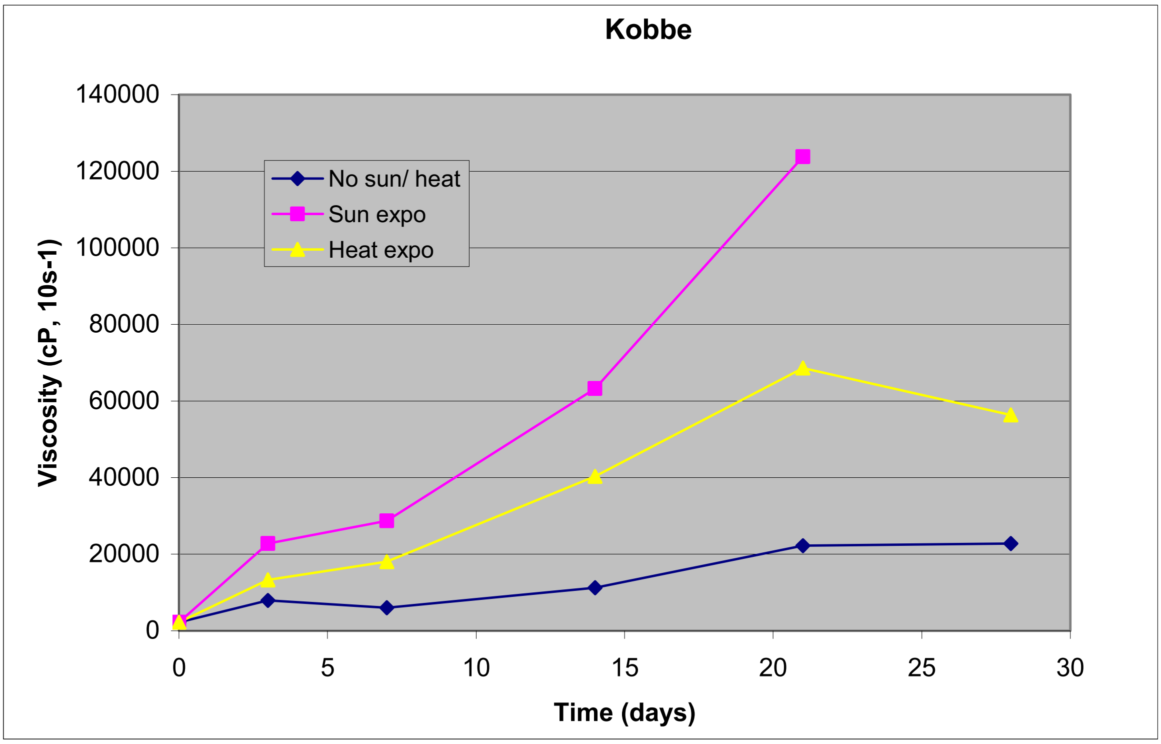



*Figure 4.3 Viscosity of the emulsion/oil at the substrate surface for the different exposure scenarios for Kobbe*

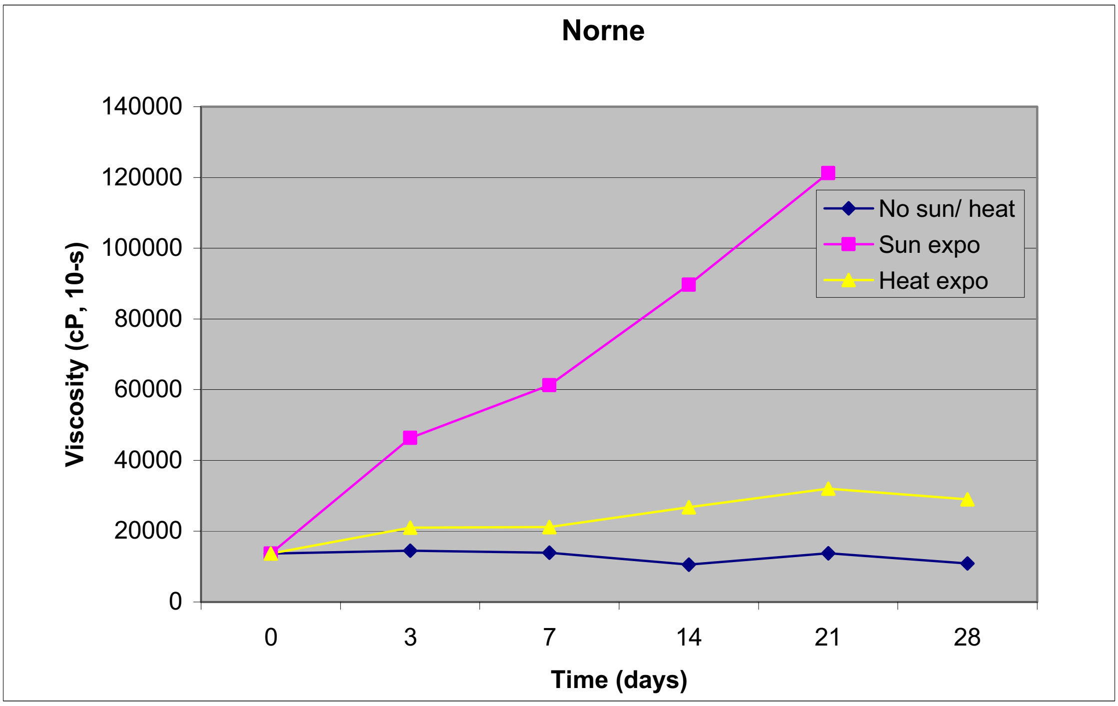



*Figure 4.4 Viscosity of the emulsion/oil at the substrate surface for the different exposure scenarios for Norne*

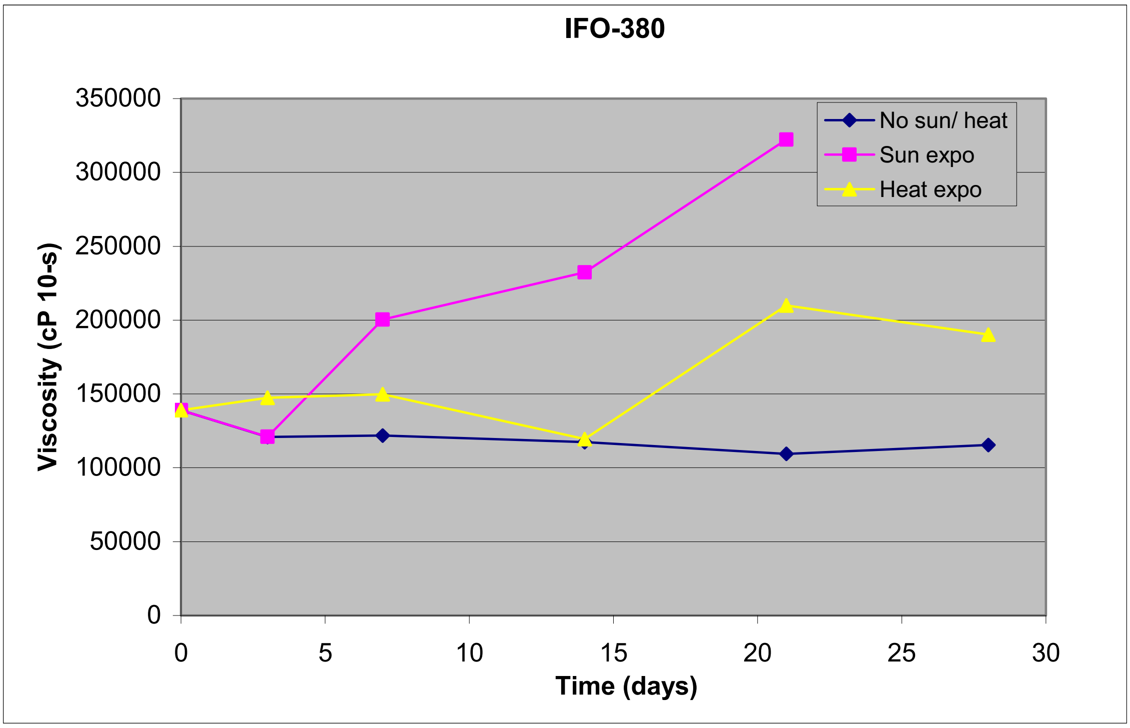



*Figure 4.5; Viscosity of the emulsion/oil at the substrate surface for the different exposure scenarios for IFO380*

The viscosity of the oil phase at the substrate varies significantly both with oil type in the radiation/heat exposure scenarios. In general the viscosities increases. Most pronounced increase was found for the simulated sun radiation scenarios, both for Kobbe, Norne and IFO380. The viscosity increases by a factor of approximately 3-10 as compared to the reference scenarios without heat and sun radiation exposure. This effect is mainly due to effect of UV radiation as the viscosity of in the "heat" scenarios increases, but at a significant lower rate.

The viscosity of the Troll has a different time coarse as compared to the other oils as shown in Figure 4.3, and decreases during the experimental period for both heat exposed and reference scenarios. There was not sufficient oil for viscosity analysis on the sun exposure scenarios.

The difference in time coarse of the viscosity was most probably be due to generation of photo-oxidized products as the chemical composition measured by GC/FID show a very little change in the oil during the experimental period. The GC/FID is shown in Figure 4.7 to 4.10.

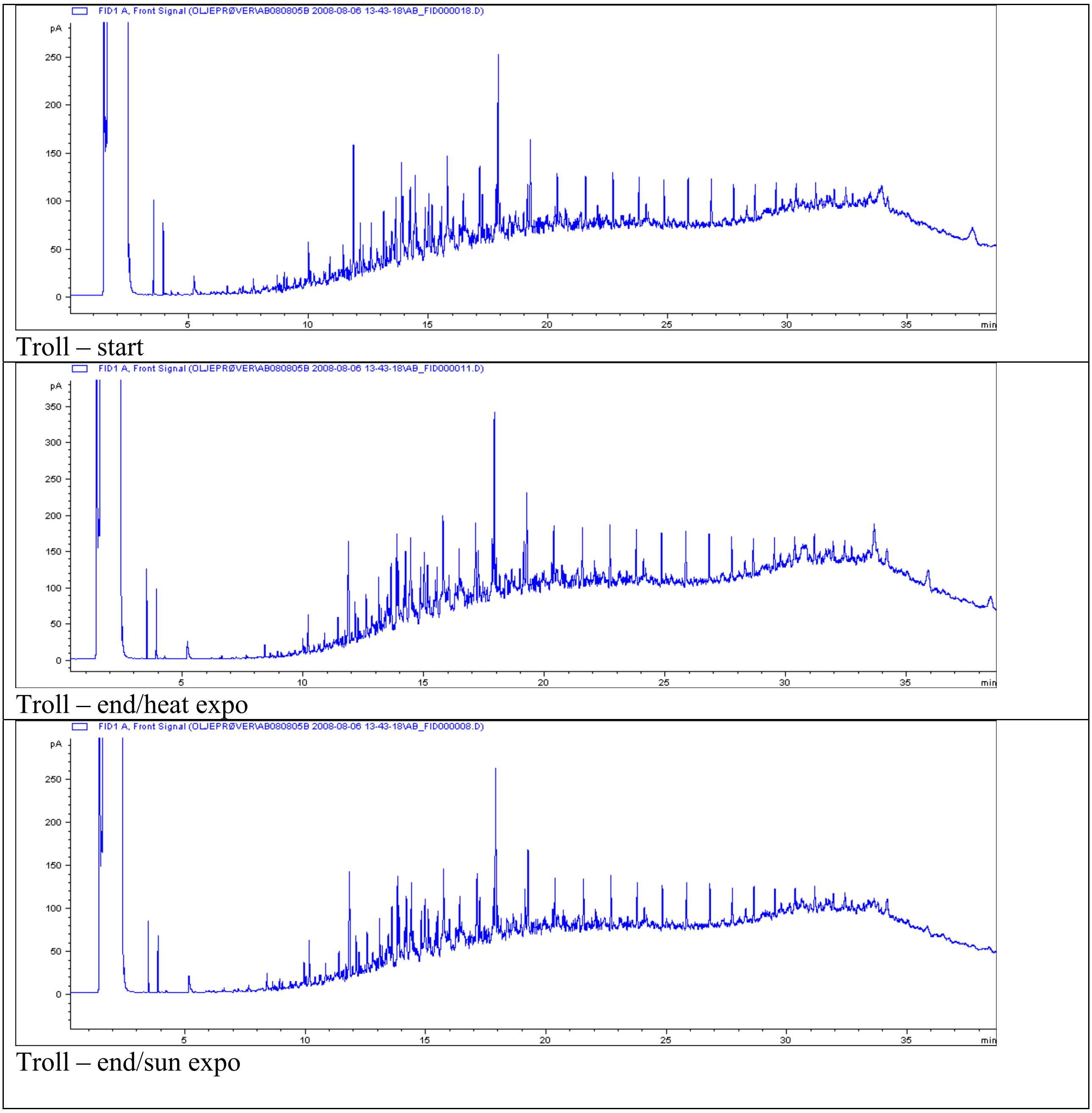
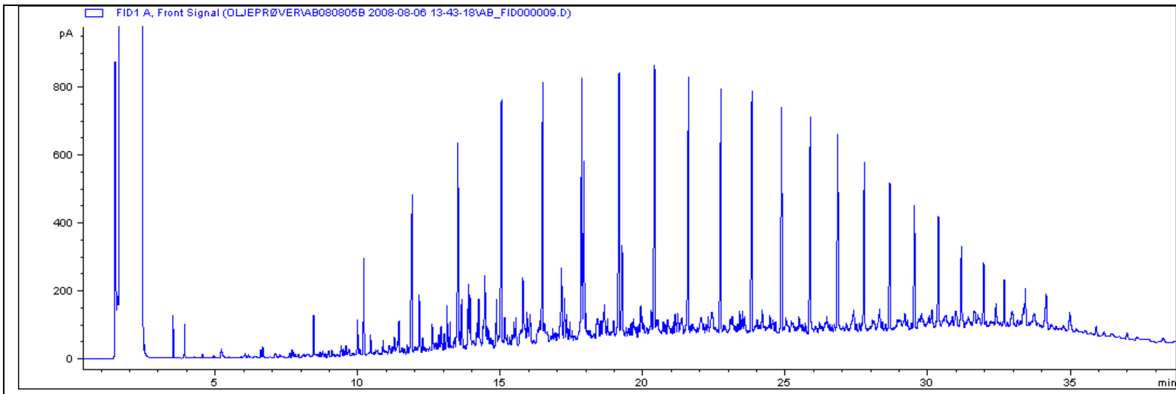
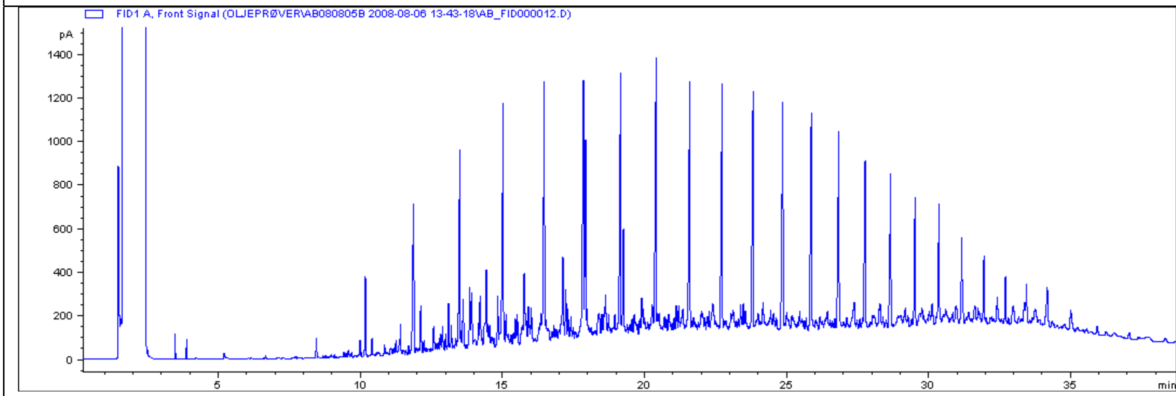


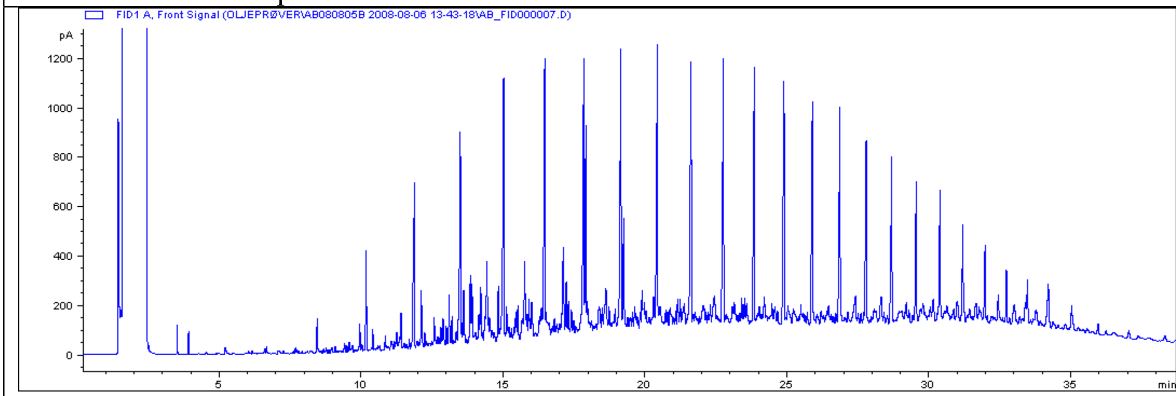

*Figure 4.6; GC/FID chromatograms of Troll oil*




Norne – start

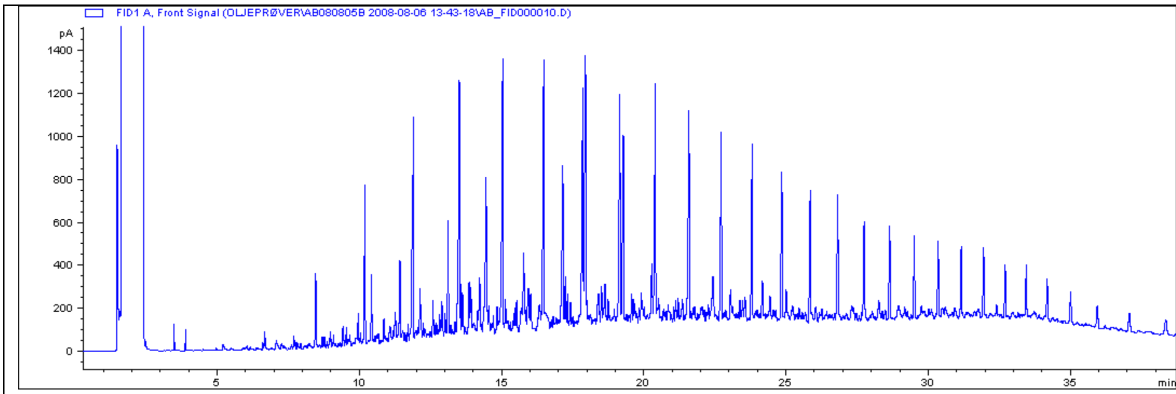



Norne – end/heat expo

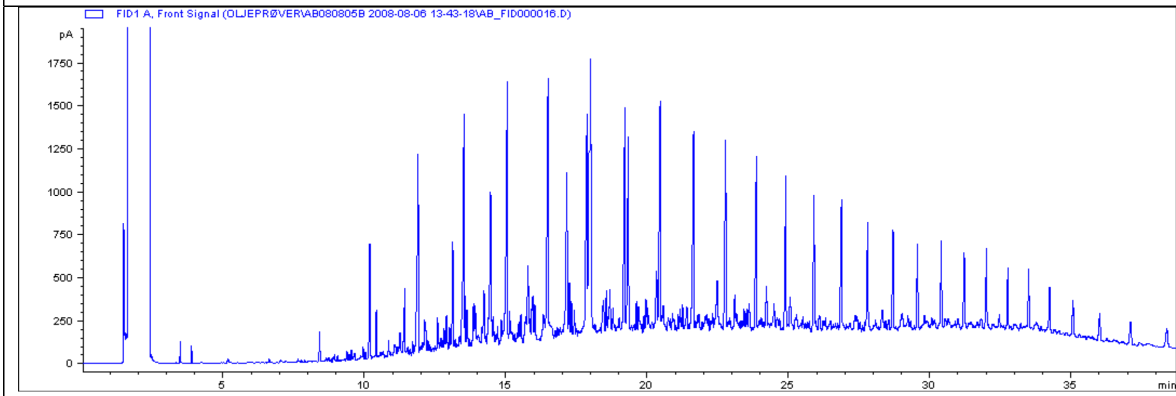



Norne – end/sun expo

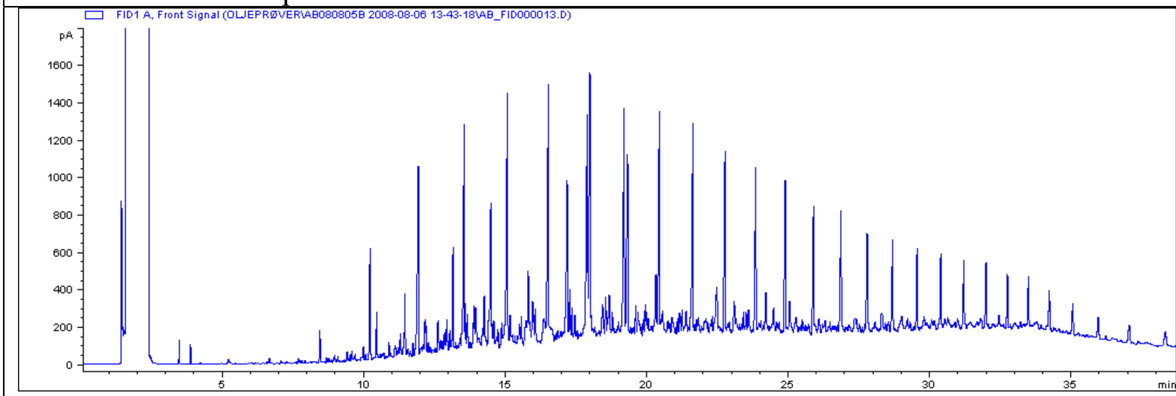
*Figure 4.7; GC/FID chromatograms of Norne*




Kobbe – start




Kobbe – end/heat expo




Kobbe – end/sun expo

*Figure 4.8; GC/FID chromatograms of Kobbe*

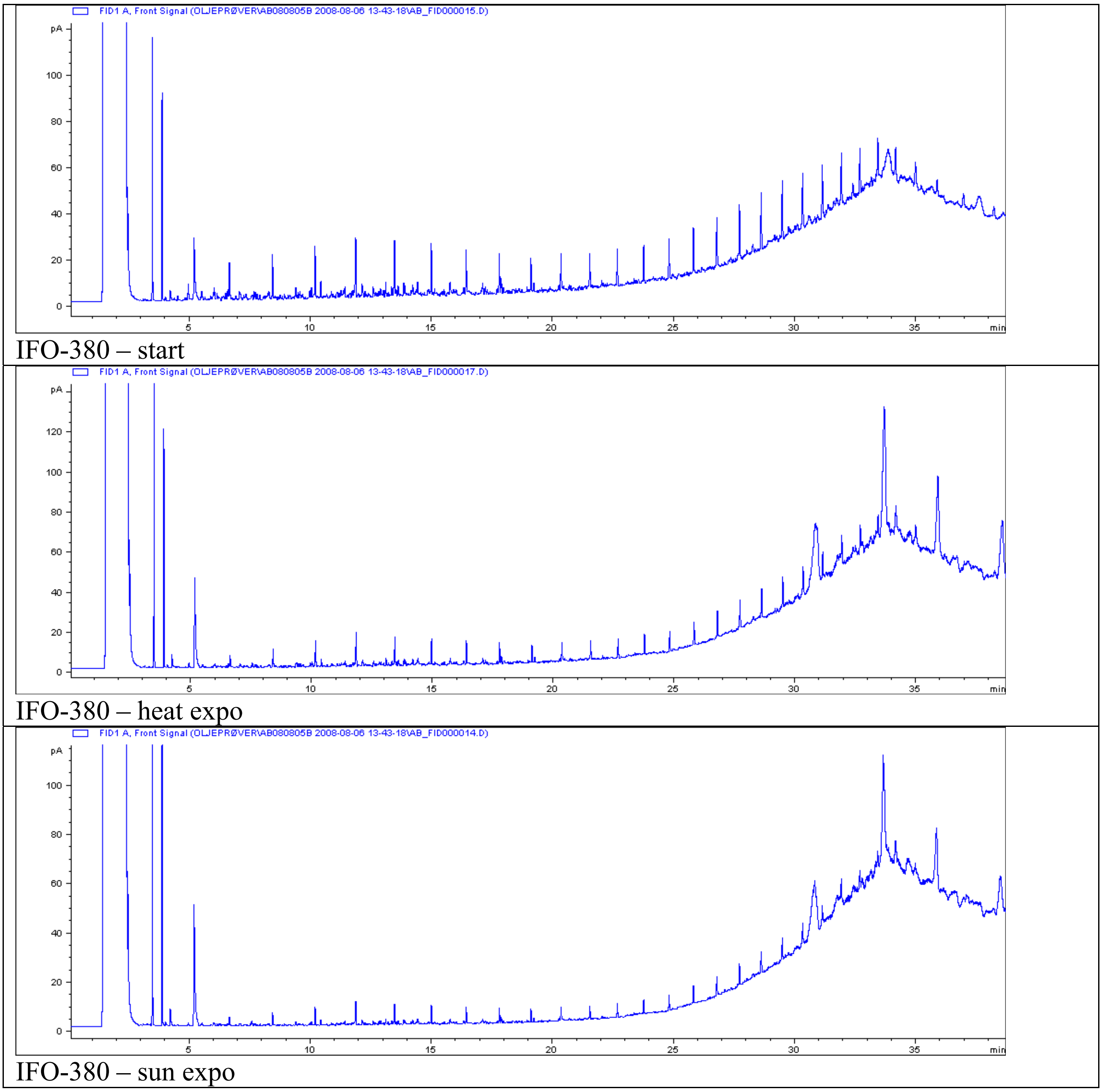



*Figure 4.9; GC/FID chromatograms of IFO380*

## 5 Conclusion and operational gains

The effect of sun radiation and heat exposure on the fate, behaviour and weathering of emulsions on solid substrate was studied for a period of one month simulating the restoration phase for the four Coastal Oil Spill JIP oils; Troll, Kobbe and Norne crude and IFO380 bunker oil. The crude oils were topped to 250°C+ prior to use and emulsified close to maximum water content. The different scenarios studied were;

- Sun exposure including UV-A/B radiation (6hour per day)
- Heat exposure similar to sun exposure (up to 23°C in the oil phase)
- Reference without sun radiation or heat exposure

During the experimental period, one sample tile was used for observation and analysis for each exposure scenario and oil type. The main findings were;

- Sun radiation affected the stability of the emulsion to the largest extent.
- Crude oil emulsions were generally unstable. Water content was not possible to quantify, but visual observation showed clearly a separation of water and oil.
- The Troll emulsion was unstable and broke up very rapidly
- The viscosities of the oil/emulsion increased significantly (3-10 x) due to sun radiation for Kobbe, Norne and IFO380 during the experimental period. The viscosity of Troll oil decreased during the experimental period.
- The chemical composition of the oils did not change during the experimental period as analyzed by GC/FID. The change in viscosity was not due to evaporation, but more likely to formation of photo-oxidized products.
- The IFO380 emulsion was the most stable emulsion under all experimental conditions.

The findings and observation from these studies will have an impact on the oil spill contingency plans and clean-up strategies;

- Sun exposure will affect the fate and behaviour to a large extent, different strategies should be used during winter and summer scenarios
- Crude oil emulsions are unstable under sun radiation. This will give higher self-cleaning rate during summer season.
- The Troll emulsion is very unstable and will break-up rapidly by sun and heat exposure. The resulting oil has a lower viscosity which will allow higher penetration in sediment substrates.
- IFO380 emulsion will have a very high viscosity which makes clean-up and restoration more time consuming and laborious, and some cleanup techniques could only be utilized in the initial phase after stranding.

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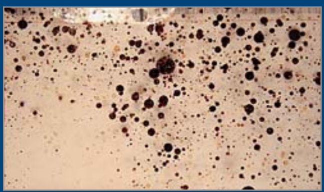
# REPORT



## Coastal Oil Spills - JIP

Report no.: 11

# C3.3 - Adhesion of weathered oil to solid shoreline substrate

Jane H.C. Øksenvåg, Svein Ramstad and Merete Ø. Moldestad

**SINTEF Materials and Chemistry**
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Date: 2008-12-17

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**C3.3 Adhesion of weathered oil to solid shoreline substrate**

**Coastal Oil Spills JIP. Report No. 11**

AUTHOR(S)

Jane H.C. Øksenvåg, Svein Ramstad and Merete Ø. Moldestad

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| | 2008-12-15 | Tore Aunaas, Research director | |

ABSTRACT

Experience from accidental releases and field studies have shown that oil acts from very sticky to repellent when spilled on a shoreline. Knowledge about the oil behaviour when spilled on shore is important for the choice of strategy for shoreline cleanup/protection in the initial phase of an oil spill.

The objective of this activity was to identify and quantify the main parameters affecting the adhesion of weathered oil to solid substrate. To study these parameters, standard laboratory procedures developed by SINTEF were used. Parameters studied were; oil type, photo-oxidation of crude oils, presence of biofilm on bedrock, surface properties (texture/mineralogy) and shoreline slope. The results show that oil type and photo-oxidation are important parameters for the adhesion of weathered oil to solid substrate and seem to over-rule the effect of bedrock texture and mineralogy. A simple correlation study showed that adhesion of weathered crude oil emulsions increases with an increase in oil structure (wax structure) and yield stress. Biofilm on bedrock seems to reduce the adhesion of weathered oil significantly with about 70%.

The knowledge gained from these results contributes to a better understanding of the oils fate and behaviour when stranded onshore. This might open possibilities for new and innovative development of countermeasures and preparedness for coastal oil spills. The data gained can be used for a further development of numerical models.



| KEYWORDS | ENGLISH | NORWEGIAN |
|---|---|---|
| GROUP 1 | Chemistry | Kjemi |
| GROUP 2 | Environment | Miljø |
| SELECTED BY AUTHOR | Coastal oil spill | Kystnær oljesøl |
| | Adhesion | Adhesjon |

# TABLE OF CONTENTS

# 1 Summery

The objective of this activity was to identify and quantify the main parameters affecting the adhesion of weathered oil to solid surface. To study these parameters, an adhesion test procedure, elaborated in a previous project for ENI Norge, *"Forvitring, klebrighet og adhesjonsegenskaper til Realgrunnen olje – TASK a-1*" (Nygaard *et al*., 2006), was used. As an initial study, adhesion of emulsion dependent on shoreline slope was tested. Other parameters studied were; oil type, photo-oxidation of crude oil, biofilm on bedrock and surface properties (texture/mineralogy). The studies were done under temperate controlled conditions at 5˚C, simulating northern and winter conditions.

The results show that oil type is of major importance for the adhesion of weathered oil emulsions to solid substrate. Oils with a high degree of structure, as for instance Norne (having high wax content), seems to have the highest adhesion properties. Sun exposure influences some of the rheological properties and resulted in an increased adhesion. This might indicate an increase emulsion adherence to solid shoreline during summertime. Biofilm on bedrock strongly reduced the adhesion of emulsion, leaving almost nothing of the crude oil emulsions and reduced amounts of IFO 380 on the bedrock. This, seen in an operational point of view, might contribute to a relocation of stranded weathered crude oil, in contrast to the bunker fuel emulsion, adhering to the solid shoreline regardless of the presence of biofilm.

Bedrock texture / mineralogy showed little effect for the adhesion of emulsion. Earlier studies have indicated that asphaltenes and quarts are adhesive to each other (Jokuty *et.al*, 1996). The results in this activity showed only a slight increase in adhesion of emulsion on shale bedrock (containing high amount of quarts) for the bunker fuel oil IFO 380 (having a high amount of asphaltenes). Over all, the results correlate well with results found in "*Forvitring, klebrighet og adhesjonsegenskaper til Realgrunnen olje – TASK a-1"* (Nygaard *et al*., 2006) and "*Adhesjon av olje på fast substrat*" (Carlsen, 2005).

The knowledge gained from these results contributes to a better understanding of the oils fate and behaviour when stranded onshore. This might open possibilities for new and innovative development of countermeasures and preparedness for oil spills drifting onshore. The data gained can be used for a further development of numerical models.

## 2 Introduction

This project has been a part of phase 1 in the Coastal Oil Spills JIP. The research projects in the JIP have been focused on the fate and behavior of oil spills in coastal areas and on shoreline. Laboratory studies have been performed in order to obtain data for further development of numerical models.

The first phase of the JIP was performed in the period from 2006 to 2008, and was funded by Eni Norge, Shell Technology and StatoilHydro. The overall objectives of the JIP have been:

- to contribute to an adequate and sufficient basis of competence to document possible consequences in case of an oil spill close to the coast
- to provide documentation ensuring the countermeasures giving the optimal environmental gain

Experience from several accidental releases and field studies have shown that the oil interacts very different, from very sticky to repellent when washed onshore. The oils adhesion properties are important knowledge to determine the strategy for shoreline cleanup/protection in the initial phase.

The objective of this activity was to identify and quantify the main parameters affecting the adhesion of weathered oil to solid surface.

Experience from accidental releases and field studies have shown that oil interacts from very sticky to repellent on shoreline substrate. Experiences from bunker fuel oil spills, as Rockness and Server, have shown bunker fuel oils to adhere well to the shoreline substrate. There have been no crude oil spills stranding on shore at the Norwegian coast so far, the knowledge of the fate and behaviour of weathered crude oil on shore are therefore limited. Knowledge about the oil behaviour is particularly important for the choice of strategy for shoreline cleanup/protection in the initial phase of an oil spill.

In a previous project for ENI Norge, "*Forvitring, klebrighet og adhesjonsegenskaper til Realgrunnen olje*" (Nygaard *et al*., 2006), SINTEF developed a standard operational procedure (SOP) to quantify the parameters of importance for the adhesion of weathered oil to shoreline substrate. The SOP elaborated for the adhesion test was used in this study. In 2006, a project work, studying "*Adhesjon av olje på fast substrat*" (Carlsen, 2005), were performed in cooperation with NTNU. Several other tests have been done to measure the adhesion properties of oil (Jokuty *et al*., 1995). The results from this study are discussed in regards in to results found in the mentioned studies.

# 3 Experimental

## 3.1 Materials

### 3.1.1 Oil types and weathering degree

Crude oils can be characterised in four categories: asphaltenic, napthenic, paraffinic and waxy crude oils. The crude oils studied in the Coastal Oil Spills JIP were selected among the oil companies' crude oils. It was important to select crude oils representing different categories of oils. The selected crude oils represent the categories:

- Troll – napthenic crude oils
- Norne – waxy crude oils
- Kobbe – light paraffinic crude oils

In addition to the crude oils, a heavy fuel oil (IFO 380) was tested. IFO 380 is representing bunker oils used as fuel for ships going along the Norwegian coast. The content of light oil components in fuel oils is low, typically lower than 5 vol% for IFO 380 oils. The light oil components are generally in a boiling point area from approximately 250°C and higher. The testing of the IFO 380 was therefore concentrated on the "fresh" fuel oil, not on an evaporated residue. The IFO 380 oil used in this project is a low sulphur fuel oil produced at the Esso refinery at Slagentangen. Some physical and chemical properties of the oils studied are listed in Table 3.1-1.

**Table 3.1 Oils used in the Coastal Oil Spills JIP.**

| SINTEF Id | Oil type | Residue | Density (Kg/m$^3$) | Evaporative Loss (Vol%) | Pour point (°C) | Wax (wt%) | Asphaltenes (wt%) |
|---|---|---|---|---|---|---|---|
| 07-0287 | Troll | Fresh | 0,900 | 0 | -36 | 0,9 | 0,04 |
| | | 250°C | 0,930 | 25,5 | -27 | | |
| | | Ph.ox. | 0,931 | - | -21 | | |
| 07-0260 | Norne | Fresh | 0,860 | 0 | 21 | - | 0,3 |
| | | 250°C | 0,888 | 28,4 | 30 | | |
| | | Ph.ox. | 0,885 | - | 30 | | |
| 06-1061 | Kobbe | Fresh | 0,797 | 0 | -39 | 3,4 | 0,03 |
| | | 250°C | 0,875 | 53,6 | 21 | | |
| | | Ph.ox. | 0,877 | - | 15 | | |
| 06-1125 | IFO 380 | Fresh | 0,963 | 0 | 15 | 5,0 | 3,4 |

-: *not measured*

Oil spilled at sea will be subjected for several weathering processes as evaporation (lighter compound evaporates), emulsification (water droplets are incorporated in the oil phase) and photo oxidation (changing the physical and chemical properties due to sun exposure). These weathering processes will change the physicochemical properties of the oil, being of great importance for the weathered oils fate and behaviour on the shoreline

For the crude oils, an evaporated residue of 250˚C+ was used. The 250°C+ residue corresponds to ½ - 1 week weathering of oil at sea, and will be representative for stranded crude oil along the Norwegian coast.

To ensure reproducible production of emulsions, a water content just below the maximum water uptake for the respective oils was used. After some initial studies, the standard water content was decided to be 70% for Troll, 75% for Kobbe, 60% for Norne and 40% for IFO 380.

To study the effect of photo-oxidation, the crude oils (Troll, Kobbe and Norne) were exposed for a solar simulator. The photo-oxidized oils represent oils exposed 5 days under ordinary sunlight exposure in the summertime. During this process, the oils were naturally evaporated to a 250˚C+ residue.

Evaporation, emulsification and photo-oxidation were performed according to established SINTEF lab procedures. For more information about the physical and chemical properties of the oils and weathering procedures, see *Technical report C2.2* (Ramstad et.al., 2008).

### 3.1.2 Bedrock bars and tiles

As a standard, bedrock of shale was used to test adhesion properties. The tile/bars origin from Alta in Norway and is characterised by its homogeneous and smooth surface. Shale bedrock is naturally accruing in wide areas of Norway.

Shoreline substrate varies in surface properties (mineralogy and texture) dependent on bedrock type and wave exposure grade. In addition to the shale bars, granite and marble bars was used to study the effect of texture and mineralogy on oil adhesion. All three bedrocks are relatively common along the Norwegian coast. A picture of the three bedrocks is shown in Figure 3.1-1.

**Figure 3.1-1 From left: Marble (fine structured), Shale (moderate structured), Granite (rough structured).**

Shale is a sedimentary bedrock and is known for its high content of quarts which make the rock resistant for exposure (http://www.alta-skiferbrudd.no). Granite is a magmatic bedrock made from harden magma. It contains quarts, feldspar and biotite, where feldspar is the most dominating mineral. Marble contains primary calcium carbonate ($CaCO_3$) (www.wikipedia.no).

## 3.2 Operational setup and procedures

To study the holding capacity of weathered oil, an operational procedure based on similar adhesion tests done at Cedre was used. For the adhesion test, an experimental procedure developed by SINTEF was used.

### 3.2.1 Holding capacity - screening study

To study the run off of emulsion for the selected oils, hence the amount of immobile oil left on bedrock, dependent on angle degree a screening study were performed. Shale tiles of 15*15 cm, washed with dichloromethane (DCM), were applied a 10-11 cm emulsion layer. After application, the tiles were left horizontally for 1 hour, in a temperate controlled room, to let the emulsion spread evenly on the tile surface. The tiles were then elevated to selected angles between 0 and 90 degrees. The quantities of emulsion on the tiles were measured initially and after 24 hour.

### 3.2.2 The adhesion test

To study the adhesion properties of weathered oils, shale bars of 2,8*15 cm were used. The shale bars were first masked with tape on the edges to only include emulsion adhered on the bar surface. The bars were immersed in to seawater for 15 seconds, for then to be immersed in to a container of oil emulsion for 30 seconds and installed on the experimental system for 30 minutes for run off of excess oil. A picture of the adhesion test is shown in Figure 3.2-1.

**Figure 3.2-1 The adhesion test – experimental setup.**

Excess oil was collected in aluminium forms. The shale bars and the aluminium forms were weighed before and after emulsion exposure to quantify the adhered emulsion in the initial phase and after runoff. The shale bars were photo documented right after exposure to emulsion and after runoff of excess emulsion.

### 3.2.3 Conditioning / growth of biological film

To study the effect of biological film on bedrock surface for the adhesion of weathered oil, shale tiles were placed in a container of seawater for a growth of biological film. To get circulation of seawater in the container, a flux of water, conditioned in a water reservoir, streamed through a perforated tube for then to drain out. In addition, rock tiles were placed outside in the harbour, in a natural environment, for a validation of the biological growing rate. Pictures of the biological film growth on shale bars in the lab and in the field are shown in Figure 3.2-2.


**Figure 3.2-2 Method for establishment of biological film on bedrock bars, in the laboratory (left) and in the natural environment (right).**

The shale bars were deployed in seawater for 2 weeks before quantification of biofilm on the shale surface, using a microscope. A shaking board was used over night, at rate 150 rpm, to release the majority of the biofilm. The bars were then placed in to an ultrasound container for 15 minutes to release the remaining biofilm. A sample was taken out and diluted in several ratios by using sterile seawater. The results showed about the same quantity of biological material for both setups, and the laboratory system for growth of biological material on bedrock was therefore used in the further studies. A procedure for establishment and quantification of biological film was elaborated during this process.

### 3.2.4 Oil properties

To study the oils rheology, a Physica MCR300 MC1+ rheometer with an US200 software was used. Parameters measured were; viscosity, storage modulus, loss modulus and yield stress. The parameters were measured before application on the tiles. Density and pour point for the different oils were measured initially, on un-emulsified oils.

### 3.3 Experimental parameters and design

Five different experimental parameters were tested in this study:

- **Shoreline slope**
  To study the adhesion of weathered oils as a function of oil type and slope angle, selected angles from 0 to 90 degrees were used.
- **Oil types**
  To study the adhesion of weathered oil, dependent on oil type, three crudes; Troll, Kobbe and Norne and one bunker fuel oil; IFO 380 were used. In addition, a Troll crude weathered in the flume (see Technical report C1) was studied, to look at how the Troll flume emulsion correlated to the other emulsions weathered of Troll oil.
- **Photo-oxidation of crude oil**
  To study the effect of sun exposure for the adhesion of weathered oil emulsions, photo-oxidized Troll, Kobbe and Norne were used and compared to the un photo-oxidized oils.
- **Biological film**
  To study the effect of presence of biofilm on bedrock surface for the adhesion of weathered oil emulsions, compared to rock bars without any biological material, a biological film was established on shale bars and tested for the photo- and un photo-oxidized oils.
- **Bedrock mineralogy and texture**
  To study the effect of bedrock mineralogy and texture for the adhesion of weathered oil, three different bedrock structures were tested; shale (medium texture), marble (fine texture) and granite (rough texture).

Weathered oil spilled on dry bedrock was considered as un realistic and was therefore not performed in this study. Results from earlier studies have shown an increase in adhesion to dry substrate in contrast to wet substrate (Carlsen, 2005).

Table 3.3-1 gives an overview of the experimental design including the experimental parameters for this activity.

**Table 3.3-1 Experimental design (WiO – Water in oil / emulsification)**

| SINTEF ID | Oil | WiO | Evaporated | Without biofilm | With biofilm | Bedrock texture |
|---|---|---|---|---|---|---|
| 2007-0287 | Troll | 70 % | 250˚C+ residue | x | x | x |
| | | | Photo oxidized | x | x | |
| 2006-1061 | Kobbe | 75 % | 250˚C+ residue | x | x | x |
| | | | Photo oxidized | x | x | |
| 2007-0260 | Norne | 60 % | 250˚C+ residue | x | x | x |
| | | | Photo oxidized | x | | |
| 2006-1125 | IF 380 | 40 % | | x | x | x |
| Troll flume | From flume | | | x | x | |

To validate the results, the experiments were done in triplicates. The standard deviation between the parallel samples was calculated to be less then 20%. This was considered to be an acceptable variance.

# 4 Results and discussions

Table 4-1 show the experimental parameters used in this activity.

**Table 4-1 Experimental parameters used in this activity.**

| Parameter | Variation |
|---|---|
| Oil type | • Troll crude<br>• Kobbe crude<br>• Norne crude<br>• Bunker fuel oil - IFO 380 |
| Evaporation | 250°C+ residue (crude oils) |
| Water content in emulsion | • 70% (Troll)<br>• 75% (Kobbe)<br>• 60% (Norne)<br>• 40% (IFO 380) |
| Temperature | 5°C |
| Bedrock surface properties | • Shale - medium texture (Standard)<br>• Marble – fine texture<br>• Granite - rough texture |

The experimental parameters used in the different studies are presented at the beginning of each chapter. The parameter of variance is marked with a bold text.

To get a better understanding of parameters effecting the different oils adhesion properties, several rheological parameters were measured A definition of the different properties is given in *Appendix 1*. The rheological parameters measured are given in *Appendix 2.* Due to Nornes high wax content, it was difficult to get reproducible rheological properties since wax has a tendency to crystallize when temperature falls below its pour point.

To study the correlation between emulsion adhesion and the rheological properties for the emulsified oils, the data was run through a simple correlation study in Excel. The results showed that storage modulus, loss modulus and yield stress were of relevance for the retention of emulsion. The results from the correlation study are given in *Appendix 3.*

Photo documentation for the studies is given in *Appendix 4.*

### 4.1 Holding capacity– screening study

**Table 4.1-1 Experimental parameters used in this study.**

| Parameter | Variation |
|---|---|
| Oil type | Troll, Kobbe, Norne and IFO 380 |
| Evaporation | 250°C+ residue (crude oils) and ph.ox (Troll and Norne) |
| Water content in emulsion | 70% (Troll), 75% (Kobbe), 60%(Norne), 40% (IFO 380) |
| Temperature | 5°C |
| Bedrock surface properties | Shale – moderate texture |
| **Shoreline slope** | **From 90 to 0 degrees** |

The emulsion film thickness, dependent on bedrock slope, for both un photo oxidized and photo oxidized oils are given in Figure 4.1-1

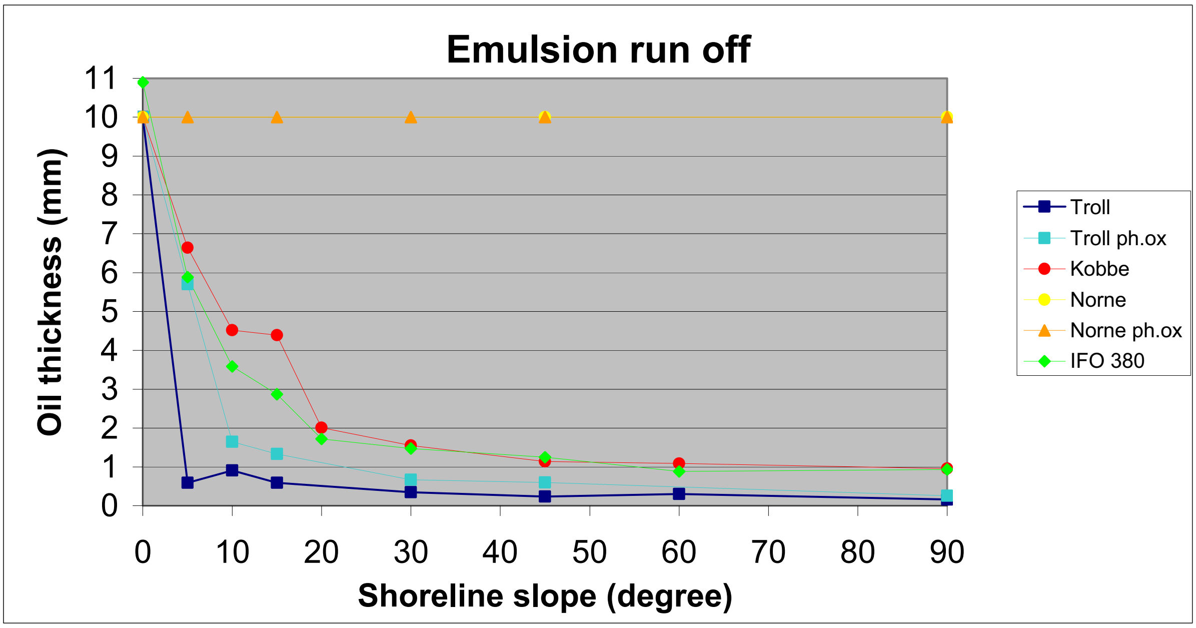


**Figure 4.1-1 Holding capacity for the selected oils as a function of the shoreline slope.**

As Figure 4.1-1 shows, retained emulsion varied with the slope of the tiles and oil type, indicating an increasing emulsion retention for photo-oxidized oils, as for the Troll oil. All the oils, except for Norne, started to run off the tiles at the lowest angle (5 degrees). For the Troll oil, being the only oil having a pour point below test temperature, most of the emulsion run off at the 5 degree angle. Kobbe and IFO 380 showed a slower run off trend than Troll, having a pour point higher than Troll, see Table 4-2. All the oils ended up at approximately the same emulsion thickness (between 0 and 1 mm), at the 90 degree angle, except for Norne, releasing no emulsion at any of the slope angles tested.

## 4.2 Oil type

**Table 4.2-1 Experimental parameters used in this study.**

| Parameter | Variation |
|---|---|
| **Oil type** | **Troll, Kobbe, Norne and IFO 380** |
| Evaporation | 250°C+ residue (crude oils) |
| Water content in emulsion | 70% (Troll), 75% (Kobbe), 60% (Norne), 40% (IFO 380) |
| Temperature | 5°C |
| Bedrock surface properties | Shale |

Four types of oils, each with different chemical and rheological properties, were used to study the adhesion properties for different oils. The results from the oil type study are given in Figure 4.2-1.

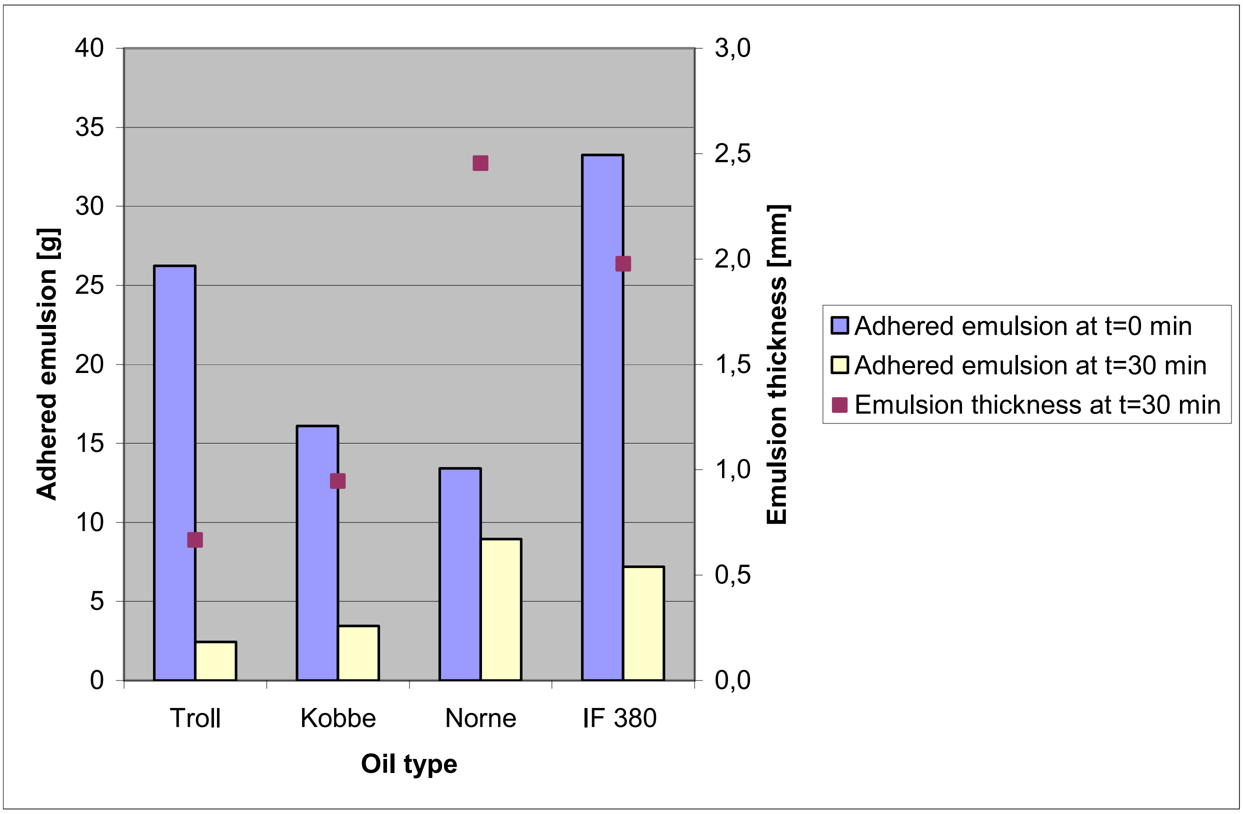


**Figure 4.2-1 Adhered emulsion, dependent on oil type, at t=0 min and after run off excess oil at t=30 min.**

Emulsions of Troll and IFO 380 adhered the most in the initial phase, but quickly released most of the adhered emulsion, see Figure 4.2-1. After run off of excess oil, emulsion of Norne showed the largest adhesion (approx. 70%). Nornes high adhesive properties might be due to its high yield stress, making the emulsion run off slower, in contrast to Troll and Kobbe having lower yield stress. Only about 10% of the Troll emulsion adhered in the initial phase (t=0 min) was left on the shale surface after run off (at t=30 min).

Converting the adhesion values to emulsion thickness, the results show a good correlation to the shoreline slope study in Chapter 4.1, except for Norne showing less oil adhered to the shale bars in the oil type study. All the oils showed a 100% emulsion coverage on the bars, both before and after run off of excess emulsion. It was observed a strong decrease in emulsion thickness after 30 min, see Chapter 1, *Appendix 4*. Earlier studies have indicated that wax content might be a ruling parameter for the adhesion of oil (Carlsen, 2006). This seems also to be valid for these results.

### 4.3 Photo-oxidation

**Table 4.3-1 Experimental parameters used in this study.**

| Parameter | Variation |
|---|---|
| Oil type | Troll, Kobbe, Norne + Troll renna |
| **Evaporation** | **250$^o$C+ residue, Ph.ox** |
| Water content in emulsion | 70% (Troll), 75% (Kobbe), 60%(Norne),<br>Troll renna (approx. 70%) |
| Temperature | 5$^o$C |
| Bedrock surface properties | Shale |

Emulsified photo-oxidized fractions of Troll, Kobbe and Norne oil were used to study the effect of photo-oxidation for the adhesion of emulsion on bedrock. For comparison, the results from Chapter 4.2 are included in this study. In addition, Troll oil weathered in the flume (named “Troll flume”) was tested to look at the correlation between the Troll oil being exposed to sun exposure and emulsification at the same time, in contrast to Troll oil weathered in the small scale laboratory in a stepwise process. The results from the adhesion study, dependent on photo-oxidation are given in Figure 4.3-1.

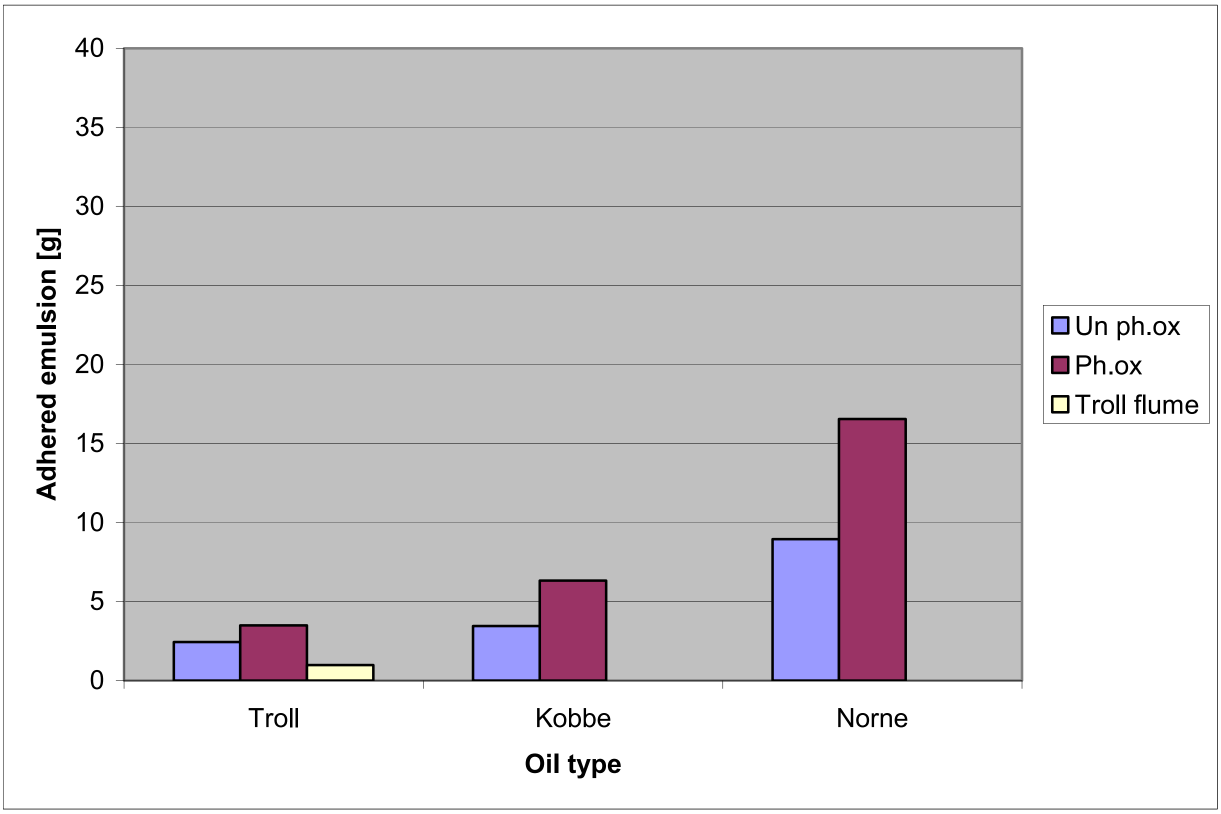


**Figure 4.3-1 Adhered emulsion on shale bars for un photo-oxidized and photo-oxidized oil.**

The results show an increase in adhered emulsion for the photo-oxidized oils compared to the un photo-oxidized oil. For Norne, the most adhesive oil, the adhesion of photo-oxidized emulsion increased with almost 50%. The increase in adhered emulsion to the shale bars, might be due to an increase in rheological properties as viscosity, see Table 4-2. A more detailed description of the adhesion properties is shown in Figure 4.3-2.

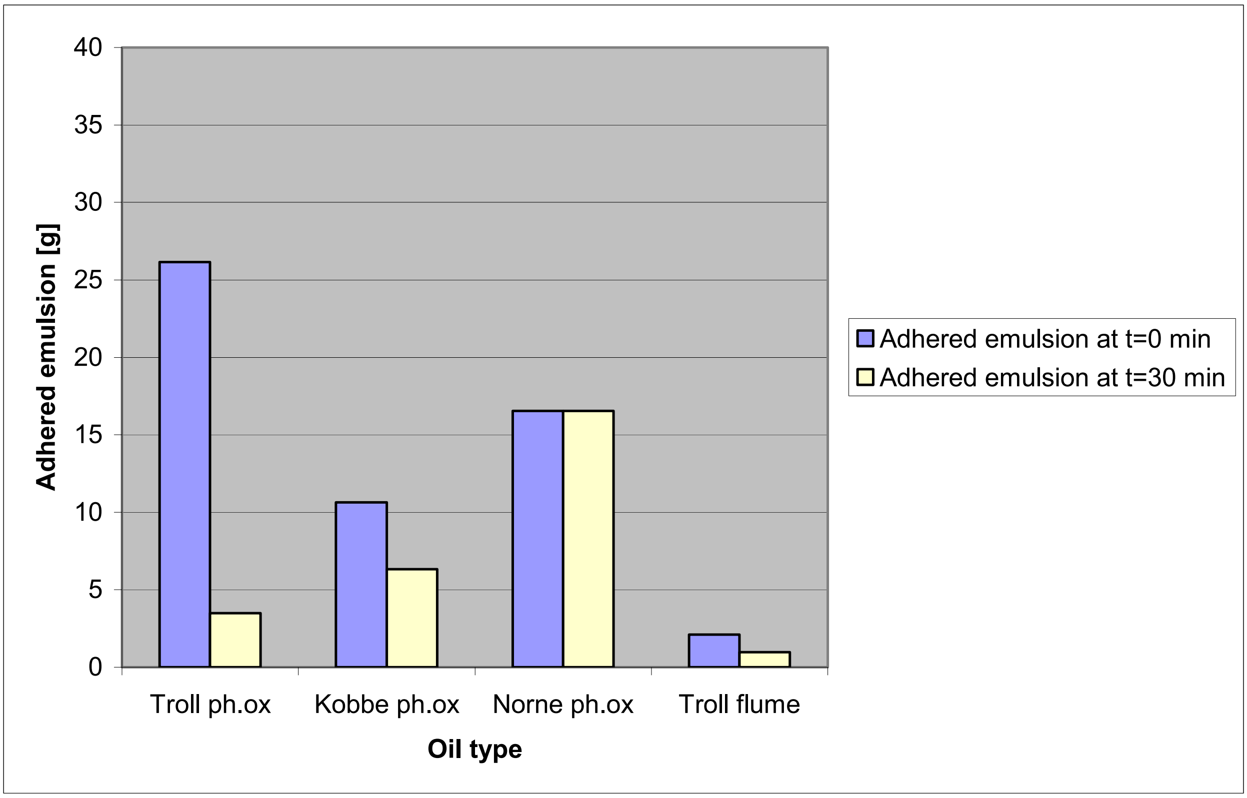


**Figure 4.3-2 Adhesion of photo-oxidized oils on shale bars, dependent on oil type, before and after run off of excess emulsion.**

Figure 4.3-2 show the same trend in emulsion retention for the photo-oxidized Troll oil as for the un photo-oxidized Troll, only with a slight increase in adhesive properties. Less Kobbe emulsion was released for the photo-oxidized oil. In contrast to the un photo-oxidized Norne emulsion, the photo-oxidized Norne did not release any emulsion at all. The "Troll flume" show less adhesion of emulsion at the initial phase (t=0 min) compared to the Troll photo- and un photo-oxidized Troll oils. The "Troll flume" emulsion was stored in a 5˚C climate room for some time before use. This is expected to change the weathered oils properties to some extent since water in emulsion start to fraction out with time.

The photo-oxidized oil was brighter in colour, in comparison to the un photo-oxidized oil, see Chapter 2, *Appendix 4*. The photo-oxidized Norne emulsion was also a bit rougher in texture compared to the Norne un photo-oxidized emulsion, see Table 2-3. For the Kobbe oil, pictures in Table 2-2 show a patchy structure of the emulsion covering the tiles, this was probably due to Kobbes low wax content (wax has emulsion stabilizing properties), resulting in a breaking of emulsion on the shale bar surface.

The major trends, found in these results, correlate well with conclusions found in "*Forvitring, klebrighet og adhesjonsegenskaper til Realgrunnen olje – TASK A-1*" (Nygaard. et.al. 2006).

### 4.4 Biological film

**Table 4.4-1 Experimental parameters used in this study.**

| Parameter | Variation |
|---|---|
| Oil type | Troll, Kobbe, Norne and IFO 380 |
| Evaporation | 250°C+ residue and Ph.ox (crude oils) |
| Water content in emulsion | 70% (Troll), 75% (Kobbe), 60%(Norne), 40% (IFO 380) |
| Temperature | 5°C |
| **Bedrock surface properties** | **Shale with biofilm** |

A thin biological film was established on the bedrock bars to study the effect of biofilm for the adhesion of weathered oil, for both photo and un photo-oxidized oils. Results from the adhesion study dependent on the presence of biofilm are given in Figure 4.4-1.

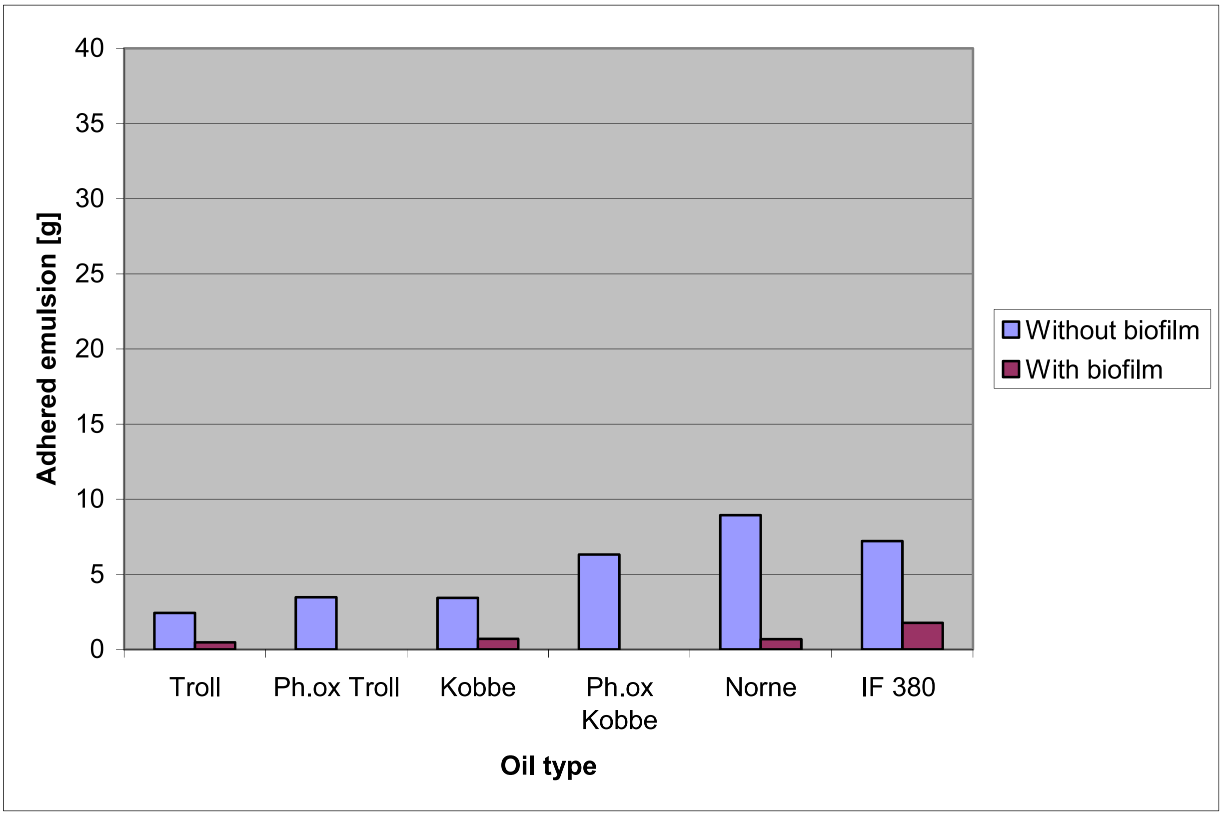


**Figure 4.4-1 Adhered emulsion on shale bars, with and without the presence of biofilm on the bar surface.**

Figure 4.4-1 show a drastic decrease in adhered emulsion for tiles covered with a biological film. Adhesion of emulsion decreased with about 75-100% for the oils tested. The IFO 380 showed the smallest response for the emulsion adherence on biofilm covered bars.

The effect of biofilm is visualised in the pictures shows in Chapter 3, *Appendix 4*. The emulsion coverage was less than 5% for the shale bars with biofilm, compared to about 100% for the ones without, except for IFO 380, showing an oil coverage of 50-80% for biofilm covered bars. A more detailed description of the adhesion properties is shown in Figure 4.4-2.

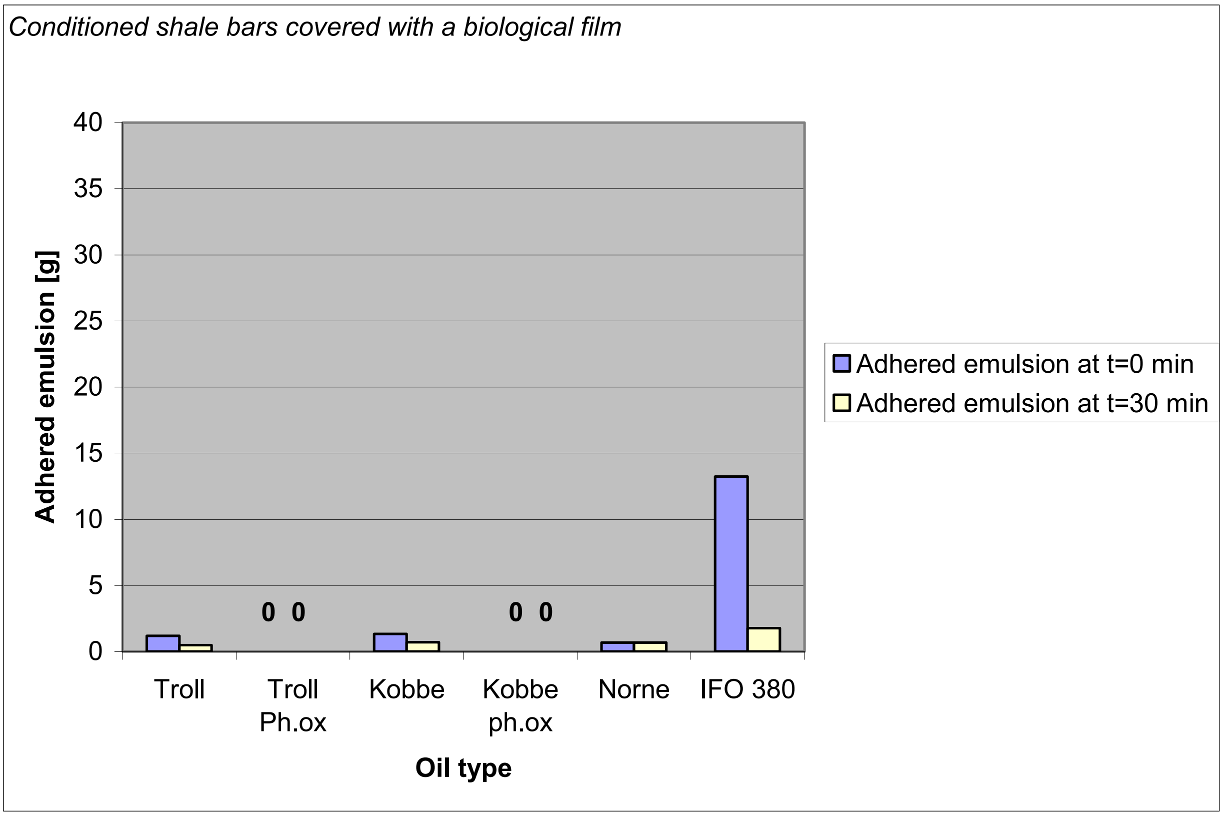


**Figure 4.4-2 Adhered emulsion for different oil types on shale bars with biological film, as a function of time,.**

Figure 4.4-2 show a low amount of emulsion adherence both in the initial phase and after run off, for all the crude oils. In contrast the bunker fuel oil (IFO 380) showed an adhesion of 14 grams in the initial phase.

The decrease in adhesion properties might be due to the biofilm surface properties. Biofilm being a hydrophilic film containing more than 95% water, will not adhere oil as good as bedrock.

### 4.5 Bedrock surface properties

**Table 4.5-1 Experimental parameters used in this study.**

| Parameter | Variation |
|---|---|
| Oil type | Troll, Kobbe, Norne and IFO 380 |
| Evaporation | 250°C+ residue (crude oils) |
| Water content in emulsion | 70% (Troll), 75% (Kobbe), 60%(Norne), 40% (IFO 380) |
| Temperature | 5°C |
| **Bedrock surface properties** | **Shale (moderate structure), Marble (fine structure), Granite (rough structure)** |

Three different bedrocks; shale, marble and granite, with different mineralogy and texture, were used to study the adhesion of oil dependent on bedrock surface properties. Results from the adhesion study dependent on bedrock surface properties are given in Figure 4.5-1.

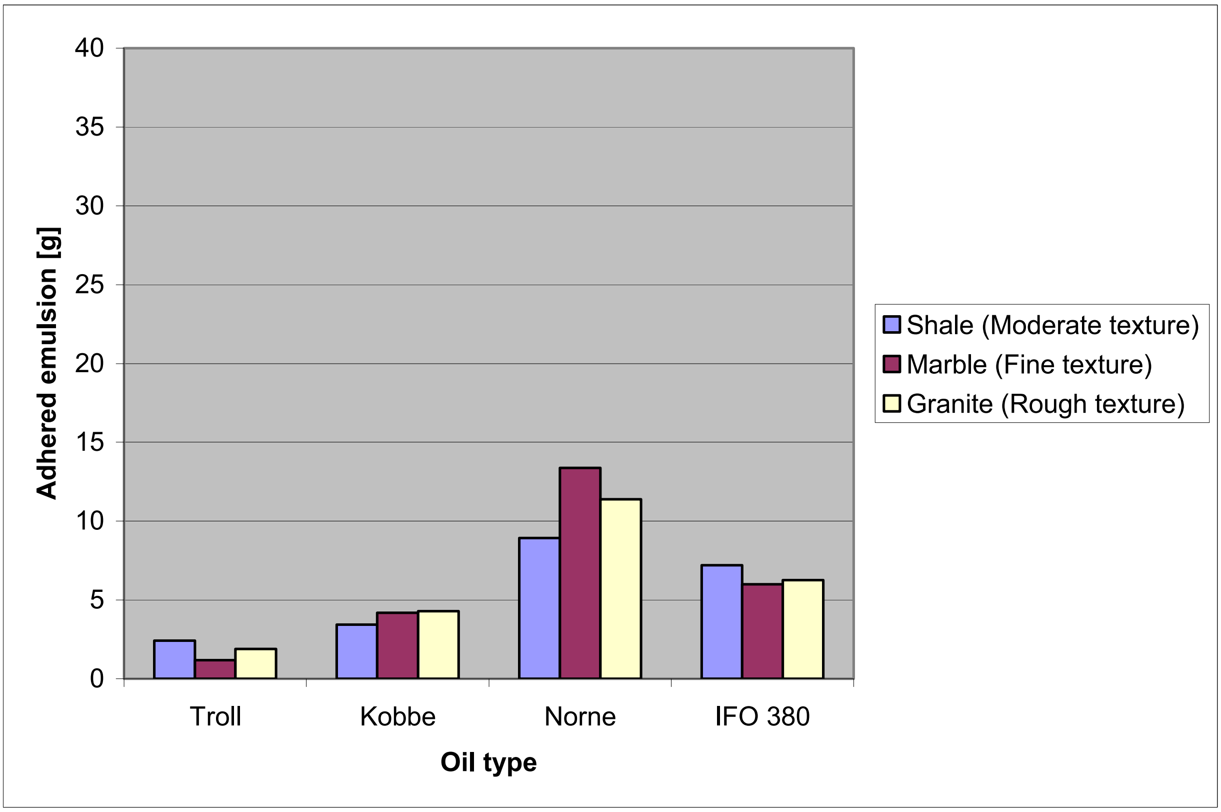


**Figure 4.5-1 Adhered emulsion for the selected oils, as a function of bedrock surface properties.**

Figure 4.5-1 show the same trend in adhesion properties for all the three bedrock structures, with highest adhesion properties for the Norne oil and lowest for the Troll oil. In contrast, there is no trend in which bedrock that adhere the most. Earlier studies have shown an increase in adhered emulsion to quarts minerals for oils with high asphaltenic contents (Jokuty *et al*, 1996). This might explain the slight increase in emulsion adherence of the IFO 380 oil for the shale bedrock, containing a high degree of quarts.

The pictures show a more patchy structure of adhered crude oil emulsion on the marble bars, compared to the other bars, see Chapter 4, *Appendix 4*.

A detailed study of the adhesion results for marble and granite are shown in Figure 4.5-2 and Figure 4.5-3. The detailed adhesion study for shale is given in Chapter 4.2.

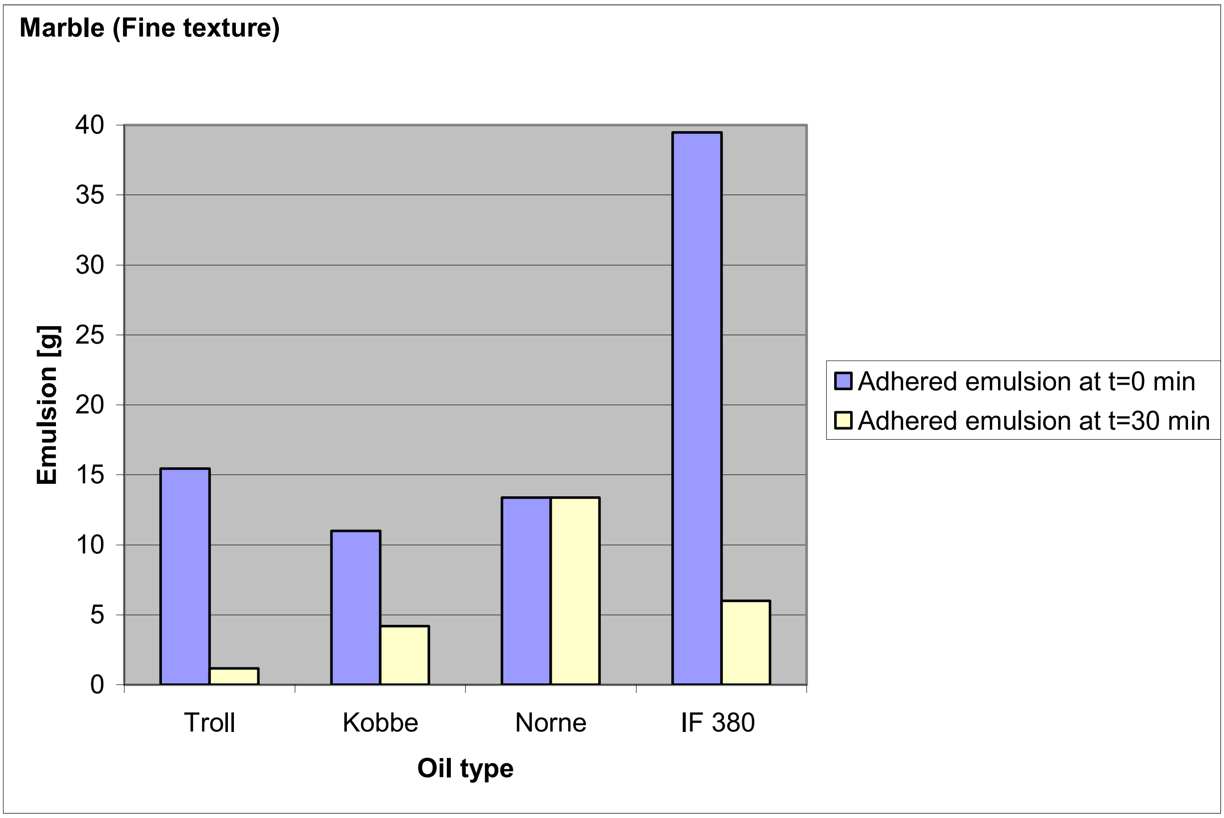


**Figure 4.5-2 Adhered emulsion on marble tiles, dependent on oil type, as a function of time.**

Just as for the shale bars, Figure 4.5-2 show that Troll and IFO 380 adhered the most emulsion in the initial phase, but quickly released most of the emulsion. For the Norne emulsion, 100% of the emulsion adhered in the initial phase, retained on the marble bar during the 30 min.

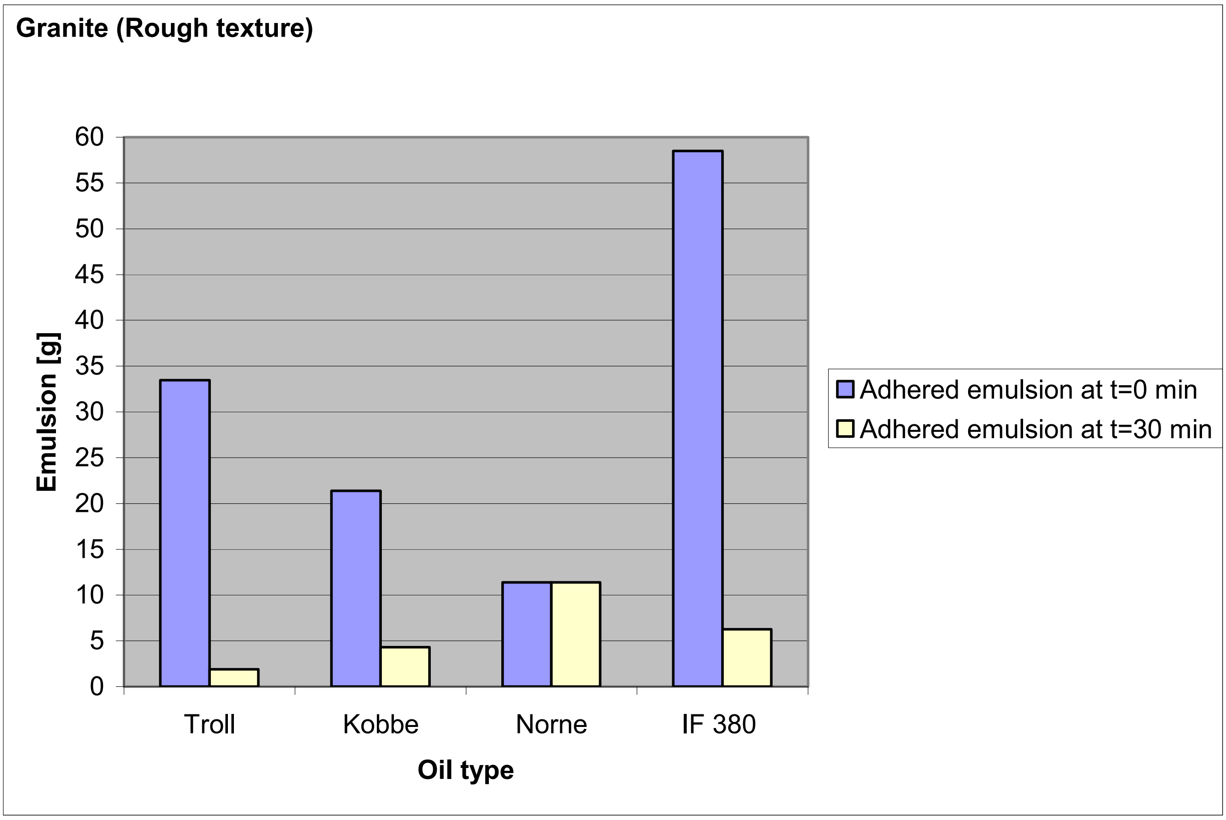


**Figure 4.5-3 Adhered emulsion on granite tiles, dependent on oil type, as a function of time.**

Just as for the shale and marble bars, Figure 4.5-3 show that Troll and IFO 380 adhered the most in the initial phase (at t=0 min), but quickly released most of the emulsion. As for marble, nothing of the Norne emulsion was released from the granite bars, compared to the shale bars as shown in Figure 4.2-1. This might be due to the low viscosity results measured for the Norne oil in the oil type study, see *Appendix 2*.

The results show that for all the oils, except for Norne, the Granite bars adhered most oil in the initial phase. The marble bedrock, containing no quarts and having a fine texture, adhered least emulsion for the crude oil in the initial phase.

# 5 Conclusions and operational gain

The adhesion test only gives an indication of the adhesion properties of the different oils and do not give information about the quantitative amount of emulsion that will adhere to exposed shorelines in case of an oil spill.

The adhesion of weathered oils showed to be strongly dependent on oil type. Results from a simple correlation study, showed the adhesion of oil to be correlated with the oils yield stress and degree of structure (being reflected in rheological parameters as storage modulus and loss modulus) which is dependent on the oils wax content. Oils with a high degree of structure, like Norne and IFO 380, might therefore have better adhesive properties then oils with a lower degree of structure when spilled on shore. Norne also showed a high retention time on the bedrock bars, this might be due to its high yield stress, making the emulsion run off slower, in contrast to Troll and Kobbe having lower yield stress.

Photo-oxidation changes the properties of the oils, mainly increasing the oils degree of structure. The changes in some of the rheological parameters seem to enhance the adhesive properties for all of the crude oils tested with about 40%. Oil spilled in the summertime might therefore adhere to the solid shoreline to a larger degree than oil spilled during the wintertime.

The presence of biofilm on the bedrock bars decreased the adhesion of emulsion with approximately 75-100%, both for photo- and un photo-oxidized oils. The bunker fuel oil (IFO 380) showed to be least affected by the presence of biofilm, covering about 50-80% of the bars with biofilm, compared to 100% for the bars without biofilm. This seen in an operational point of view might contribute to a relocation of stranded weathered crude oil, in contrast to the bunker fuel emulsion, adhering to the solid shoreline regardless of the presence of biofilm.

Rock texture and mineral contents seemed to be of minor importance for the adhesion of weathered oils. This, in combination with shale bedrocks presence along the Norwegian coast, make shale bars a good choice for studying the adhesion properties of oil emulsions. The physicochemical properties of the different oils seem to overrule the effect of structure and mineralogy. The granite bars adhered more emulsion than the other two bedrock types in the initial phase, which most likely is due to its rough texture rather than its mineralogy. There was also a slight increase in emulsion adherence of IFO 380 for the shale tiles, which might be explained by the good adherence between quarts and asphaltenes, as discussed in Chapter 4.5. Shale tiles

The knowledge gained from these results contributes to a better understanding of the oils fate and behaviour when stranded onshore. The data gained can be used for a refinement of algorithms implemented in numerical models, used as a tool in the countermeasure planning.

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www.wikipedia.no

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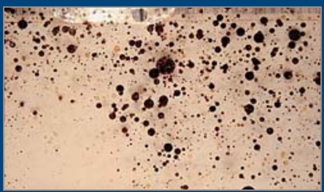
# REPORT



## Coastal Oil Spills - JIP

Report no.: 6

# C3.4 - Penetration and retention of weathered oil in shoreline sediment

Jane H.C. Øksenvåg, Svein Ramstad and Merete Ø. Moldestad

**SINTEF Materials and Chemistry**
Marine Environmental Technology

Date: 2008-12-17

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# SINTEF REPORT

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## C3.4 Penetration and retention of weathered oil in shoreline sediment

## Coastal Oil Spills JIP. Report No. 6

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ABSTRACT

To study the fate and behaviour of emulsified oil after stranding (acute phase) on shoreline sediment, an experimental column system with a continuous supply of seawater, simulating tidal variation, was used. Three crude and one bunker fuel - representing different chemical properties, were weathered and studied under simulated north and winter conditions at 5˚C. Other parameters tested were; sediment size, effect of sun exposure, emulsion loading and the effect of biofilm on the sediment surface.

Results from the studies show great variation for penetration (transport of emulsion in the sediment) dependent on oil type and weathering (photo-oxidation), sediment grain size and emulsion loading. The greatest penetration was observed for oils with generally low viscosities, at high loading, with large sediment grain size. It was observed a decrease in penetration with a decrease in sediment grain size and emulsion loading. Biofilm on the sediment surface showed little effect on the penetration and retention (immobilisation in the sediment) properties. In general, about 98% of the emulsified oil seemed to be retained into the sediment for all of the parameters tested.

Results from a simple correlation study showed that the viscoelastic properties of oils could be of importance for the retention of emulsion, giving a lower penetration and retention for oils with high viscoelastic properties.



| KEYWORDS | ENGLISH | NORWEGIAN |
|---|---|---|
| GROUP 1 | Chemistry | Kjemi |
| GROUP 2 | Environment | Miljø |
| SELECTED BY AUTHOR | Coastal oil spill | Kystnær oljesøl |
| | Penetration | Penetrasjon |
| | Retention | Retensjon |

# Table of contents

# 1 Summary

Penetration (transport of emulsion in the sediment) and retention (immobilisation in the sediment) of oil in the sediment are important parameters, forming a basis for understanding the effect on the shoreline habitat and for the choice of countermeasures to reduce the total impact on the habitat. The objective of this activity was to observe penetration and retention processes of oil in shoreline sediments and to identify and quantify the parameters affecting these processes.

To study the fate and behaviour of emulsified oil after stranding (acute phase) on a shoreline sediment, a column system with a continuous supply of seawater simulating tidal variation was used under temperate controlled conditions at 5˚C. For the use in this study, three crudes (Troll, Kobbe and Norne) and one bunker fuel oil (IFO 380) representing different chemical properties were weathered representing oils after ½ -1 week at sea. In addition, the following parameters were varied systematically; sediment grain size (ranging from medium sand to gravel), emulsion loading, photo-oxidation of oil and the effect of biofilm on the sediment surface studied.

The results from the studies show great variation for the penetration of emulsion, dependent on oil type and weathering (sun exposure), sediment grain size and emulsion loading. The greatest penetration was observed for a high loading of oils with low viscosities in sediments with large grain size. It was observed an increase in penetration with an increase in sediment fractions and emulsion loading. Biofilm on the sediment surface showed little effect on the penetration and retention properties. In general, about 98% of the emulsion was retained in the sediment for all the parameters studied, except for Norne, which due to its high viscosity only penetrated to a limited degree and resurfaced much easier compared to the other oils. Deep penetration and great retention of low viscous emulsion might complicate the restoration of contaminated shorelines, increasing the amount of polluted sediment. The effect of sun exposure has shown to reduce the penetration of emulsion, the weathered oils might be washed out and subjected for a secondary stranding on shoreline. Summer versus winter conditions must therefore be taken in to consideration for the countermeasure strategy.

Rheological properties seem to be of importance for the penetration and retention of emulsion. Earlier studies have showed that the viscosity of the oils is of major importance for the fate and behaviour of emulsified oil on a shoreline. These studies have shown the viscoelastic properties to be of importance, giving low retention for oils with high viscosities.

By studying these parameters, one might find better solutions for cleanup and disposal techniques in connection to an oil spill and with new technology predict the oils fate using this knowledge in numerical models, as a tool in the countermeasure planning.

## 2 Introduction

This project has been a part of phase 1 in the Coastal Oil Spills JIP. The research projects in the JIP have been focused on the fate and behavior of oil spills in coastal areas and on shoreline. Laboratory studies have been performed in order to obtain data for further development of numerical models.

The first phase of the JIP was performed in the period from 2006 to 2008, and was funded by Eni Norge, Shell Technology and StatoilHydro. The overall objectives of the JIP have been:

- to contribute to an adequate and sufficient basis of competence to document possible consequences in case of an oil spill close to the coast
- to provide documentation ensuring the countermeasures giving the optimal environmental gain

During the acute phase of an oil spill, a number of weathering processes take place which will affect the fate and behaviour of the oil on the shoreline. The further faith of the oil, if stranded on a sediment shoreline, will be dependent on a series of processes and mechanisms as; photo-oxidation, biodegradation and penetration in the shoreline sediment.

The objective of this activity was to observe penetration and retention processes of oil in shoreline sediments and to identify and quantify the parameters affecting these processes.

Experiences from earlier oil spills have shown great variance in shoreline impact. The Amaco Cadiz (1978) accident in France released 224 000 tons crude oil which covered a 200 km long coastline, penetrating half a meter into the sediment, this in contrast to the Braer (1993) accident at the Shetland islands where most of the 84 000 ton oil was weathered and dispersed after only some days at sea (Børresen, 1993). These accidents, among others, have laid the basis for experimental projects concerning the fate of the oil at shoreline oil spills, like the ITOSS experiment at Svalbard in 1997.

SINTEF have in over two decades been involved in laboratory and field studies, studying oils fate and behaviour on shoreline substrate. It has been, in cooperation with NTNU, performed laboratory studies on penetration and retention of oil in shoreline sediments using a modified test method developed by Environment Canada. The method was used in two experiments at Environmental Canada; “Subsurface Oil retention in Coarse Sediment beaches” (SOCS) and “Subsurface Oil in Coarse Sediment Experiments” (SOCSEX). The experiments in this study followed an operational procedure based on experience from the previous studies.

# 3 Experimental

## 3.1 Materials

### 3.1.1 Oil types and weathering degree

Crude oils can be characterised in four categories: asphaltenic, napthenic, paraffinic and waxy crude oils. The crude oils studied in the Coastal Oil Spills JIP were selected among the oil companies' crude oils. It was important to select crude oils representing different categories of oils. The selected crude oils represent the categories:

- Troll – napthenic crude oils
- Norne – waxy crude oils
- Kobbe – light paraffinic crude oils

In addition to the crude oils, a heavy fuel oil (IFO 380) was tested. IFO 380 is representing bunker oils used as fuel for ships going along the Norwegian coast. The content of light oil components in fuel oils is low, typically lower than 5 vol% for IFO 380 oils. The light oil components are generally in a boiling point area from approximately 250°C and higher. The testing of the IFO 380 was therefore concentrated on the "fresh" fuel oil, not on an evaporated residue. The IFO 380 oil used in this project is a low sulphur fuel oil produced at the Esso refinery at Slagentangen. Some physical and chemical properties of the oils studied are listed in Table 3.1-1.

**Table 3.1 Oils used in the Coastal Oil Spills JIP.**

| SINTEF Id | Oil type | Residue | Density (Kg/m$^3$) | Evaporative Loss (Vol%) | Pour point (°C) | Wax (wt%) | Asphaltenes (wt%) |
|---|---|---|---|---|---|---|---|
| 07-0287 | Troll | Fresh | 0,900 | 0 | -36 | 0,9 | 0,04 |
| | | 250°C | 0,930 | 25,5 | -27 | | |
| | | Ph.ox. | 0,931 | - | -21 | | |
| 07-0260 | Norne | Fresh | 0,860 | 0 | 21 | - | 0,3 |
| | | 250°C | 0,888 | 28,4 | 30 | | |
| | | Ph.ox. | 0,885 | - | 30 | | |
| 06-1061 | Kobbe | Fresh | 0,797 | 0 | -39 | 3,4 | 0,03 |
| | | 250°C | 0,875 | 53,6 | 21 | | |
| | | Ph.ox. | 0,877 | - | 15 | | |
| 06-1125 | IFO 380 | Fresh | 0,963 | 0 | 15 | 5,0 | 3,4 |

-: *not measured*

Oil spilled at sea will be subjected for several weathering processes as evaporation (lighter compound evaporates), emulsification (water droplets are incorporated in the oil phase) and photo-oxidation (changing the physical and chemical properties due to sun exposure). These weathering processes will change the physicochemical properties of the oil, being of great importance for the weathered oils fate and behaviour on the shoreline

For the crude oils, an evaporated residue of 250˚C+ was used. The 250°C+ residue corresponds to ½ - 1 week weathering of oil at sea, and will be representative for stranded crude oil along the Norwegian coast.

To ensure reproducible production of emulsions, a water content just below the maximum water uptake for the respective oils was used. After some initial studies, the standard water content was decided to be 70% for Troll, 75% for Kobbe, 60% for Norne and 40% for IFO 380.

To study the effect of photo-oxidation, the crude oils (Troll, Kobbe and Norne) were exposed for a solar simulator. The photo-oxidized oils represent oils exposed 5 days under ordinary sunlight exposure in the summertime. During this process, the oils were naturally evaporated to a 250˚C+ residue.

Evaporation, emulsification and photo-oxidation were performed according to established SINTEF lab procedures. For more information about the physical and chemical properties of the oils and weathering procedures, see *Technical report C2.2* (Ramstad *et al.*, 2008).

### 3.1.2 Sediment

The grain size distribution of the sediments in a shoreline system is assumed to be an important parameter for the fate of the emulsion during stranding. Shoreline sediments contain fractions classified over a broad spectre, mainly varying between sand and gravel. The sediment grains have a spherical form due to different weathering processes. It was preferred to use sediment with a limited variation in sediment grains size to get reproducible experimental conditions.

There are many classification scales for sediments and the boundaries between the fractions vary. The sediment used in this study was chosen on the basis of the Wentworth classification scale for sediments (www.wikipedia.no). The sediment grain size distribution used in this study is given in Table 3.1-1.

**Table 3.1-1 Sediment fractions and properties.**

| Size [mm] | Aggregate name | Porosity [Φ] (approx.) | Permeability [mD] (approx.) |
|---|---|---|---|
| 0,6-1,4 | Coarse sand | 1 to 0 | $10^5$ |
| 1,4-2,8 | Very coarse sand | 0 to -1 | $10^6$ |
| 2,8-6,3 | Very fine gravel | -1 to -2 | $10^7$ |
| 8-16 | Medium gravel | -3 to -4 | $10^8$ |

The porosity of a porous medium, such as sediment, describes the fraction of void space in a material. That means, if a medium have a large porosity, the medium will have a great amount of small void spaces for containment of liquids.

Permeability is a measure of the ability of a medium to transmit fluids. The permeability of sediments, are dependent on the size of the pores. Sand will generally have a high porosity due to several small void spaces per cubic meter, but low permeability because the voids are too small for fluid transportation. Gravel gives a high permeability due to fewer, but larger void spaces, the sediment will have a lower porosity (Brattli, 1999).

The sediment used in this study was supplied by Trondheim Mørtelverk AS and originates from glacial- and river deposits in Sør-Trøndelag. The sediment is therefore natural and rounded. In addition the sediment is fractioned and washed to remove unwanted dust, making the sediment representative as shoreline sediment.

## 3.2 Experimental setup

### 3.2.1 The column system

The sediment system consists of 16 columns, where a series of 4 columns are operated individually. A reservoir with temperate seawater is connected to the column system and the in- and output of seawater is placed at the bottom of the columns for tidal simulation. A computer program is used to simulate the tidal variation by controlling the number of tidal period and cycles. Figure 3.2-1 shows the set up of the column system with columns, pressure sensors for regulation of water level, valves, in- and outlets from the water reservoir and monitor.

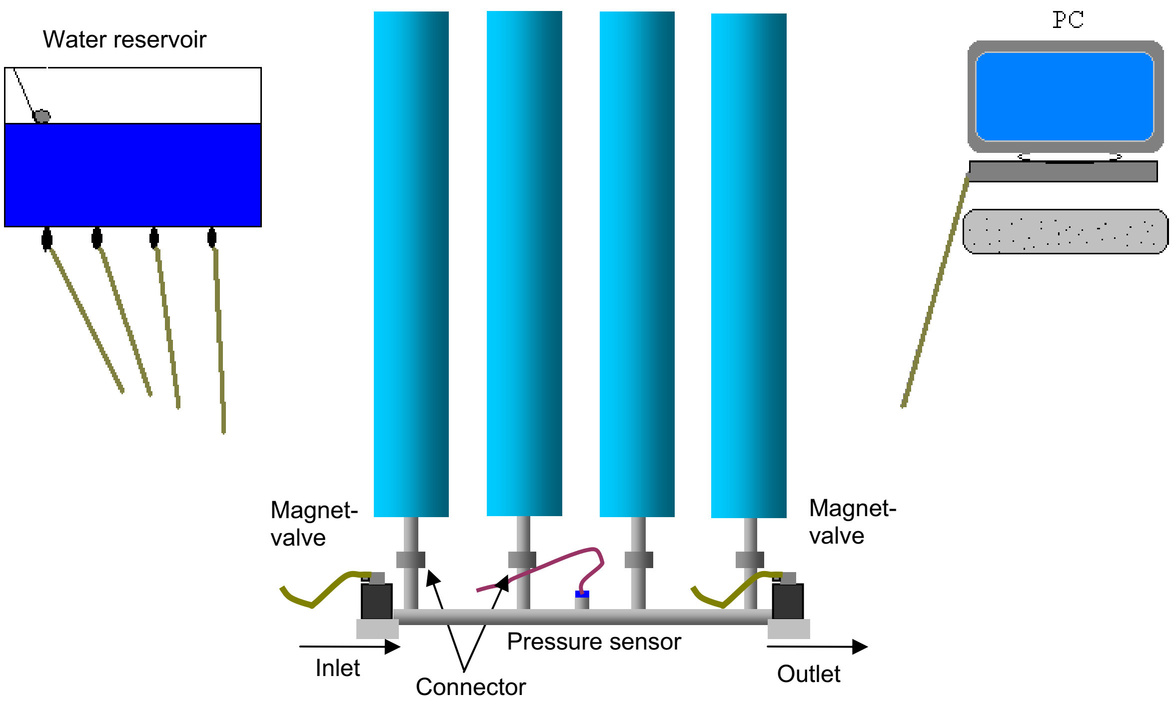



**Figure 3.2-1 Design of the column system.**

### 3.2.2 Column design

The columns have a length of 70 cm and an inner diameter of 10 cm. The columns are made of plexiglass for observation of oil behaviour. The columns are filled with sediments up to 50 cm above the bottom and a vertical flux of simulated tidal water varies between 10 and 60 cm. To prevent sediment infiltrating into the pipes, two filters with different mesh size are placed in the bottom of each column. Figure 3.2-2 shows the setup of one column.

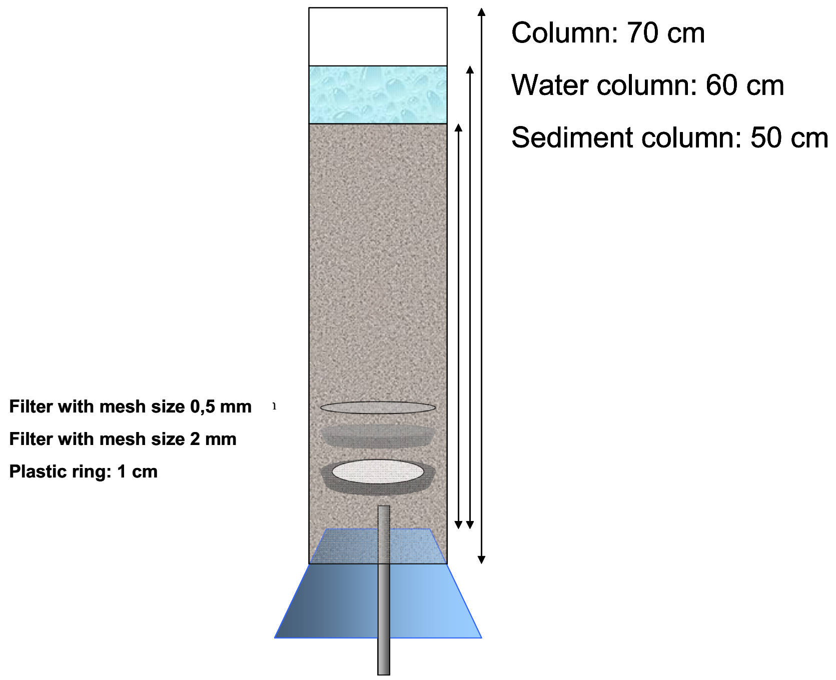



**Figure 3.2-2 Design of the sediment columns.**

### 3.2.3 Control and monitoring system – SimCol

With the use of the data system, SimCol, built up by modules from Labview, the flux of seawater could be operated automatically. The height of the sediment- and water column, tidal period and the number of tidal cycles were inserted into the data system. The water fluctuation takes form as a sinus curve, which is similar to natural tidal cycles. Figure 3.2-3 shows the graphical appearance of SimCol.

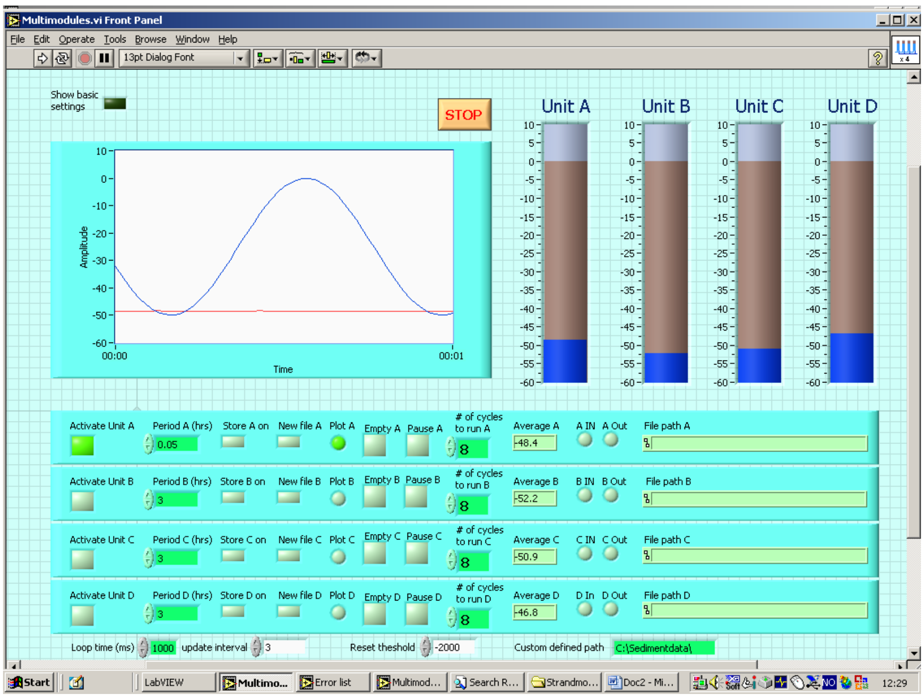



**Figure 3.2-3 Graphical appearance of SimCol.**

## 3.3 Experimental procedures

The columns were filled with sediments before starting the tidal variation program to remove the remaining fine particles from the sediment. When the sediment was clean, an emulsion layer of 10 mm (78,5 g) was applied to the water surface. 8 tidal cycles with a tide cycle of 3 hours was used, this based on initial studies (Carlsen, 2006). After finalisation, a hydraulic jack was used to do sediment sampling. To find the concentration of oil in the sediment samples, the samples were extracted in dichloromethane (DCM) and analysed using a Hitachi U-2000 spectrophotometer.

### 3.3.1 Observations and quantifications

Observation and photo documentation of the penetration of emulsion was mainly performed at the first three and the last low tide. The resurfing of emulsion was mainly documented during the 2nd and 3rd high tides, when the refloating of emulsion was at its greatest. The resurfaced emulsion was collected by pads and quantified gravitationally. The timing for application and documentation during the experimental period is given in Figure 3.3-1.

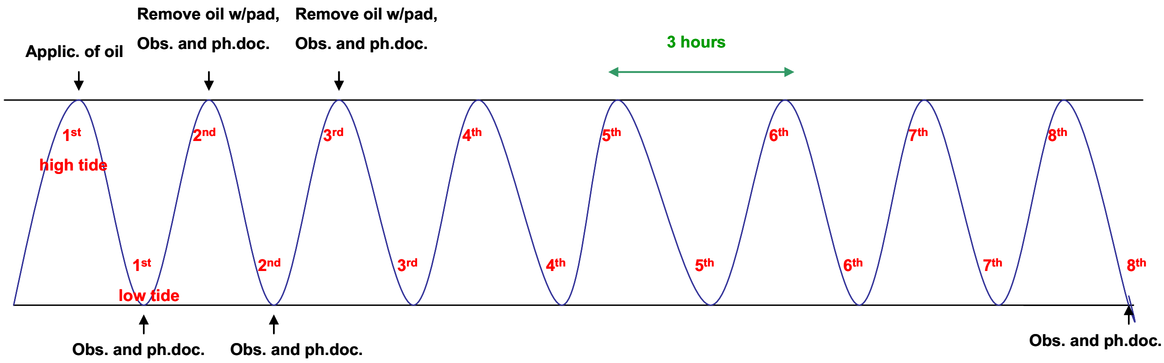



**Figure 3.3-1 Operational overview during one experiment.**

The retention of emulsion in the sediment was calculated by subtracting the resurfaced emulsion from the applied emulsion during the first high tides. By using these data, the relative retention could be calculated.

### 3.3.2 Sediment sampling and analyzing

To study the distribution of oil concentration in the sediment columns after ended study, a hydraulic jack was used, extracting sediment samples of 2 cm, see Figure 3.3-1. The sediment samples were extracted in DCM and analysed using a spectrophotometer.


**Figure 3.3-1 The hydraulic jack used for sediment sampling.**

### 3.3.3 Oil properties

To study the oils rheology, a Physica MCR300 MC1+ rheometer with an US200 software was used. Parameters measured were; viscosity, storage modulus, loss modulus and yield stress. The emulsion properties were measured before application to the column system. Density and pour point for the different oils were measured initially for un-emulsified oils.

## 3.4 Experimental parameters and design

Five different experimental parameters were tested in this study:

- **Sediment fraction / grain size distribution**
  To study the effect of sediment size, four different fractions was used; 0,6-1,4mm, 1,4-2,8mm, 2,8-6,3mm and 8-16 mm.
- **Oil type**
  To study the effect of oil type, three crude oils (Troll, Kobbe and Norne) and one bunker fuel oil (IFO 380) were tested.
- **Emulsion thickness / loading**
  To study the effect of emulsion loading, three different loadings were tested; 1, 2 and 4 times the standard loading (78,5g), representing 10, 20 and 40 mm emulsion thickness.
- **Photo-oxidation of crude oils**
  To study the effect of sun exposure, photo-oxidized crude oils (Troll, Kobbe and Norne) were tested.
- **Biological film in sediment - sediment surface properties**
  To study the effect of biological film in the sediments, a 2 week biofilm was grown in the 2,8-6,3 mm and 8-16 mm sediment fractions.

Table 3.4-1 gives an overview of the experimental parameters and design for this study.

**Table 3.4-1 Experimental parameters and design (WiO – Water in oil / emulsification).**

| SINTEF ID | Oil | WiO | Evaporated | Spesifikasjon | 0,6-1,4mm | 1,4-2,8mm | 2,8-6,3mm | 8-16mm |
|---|---|---|---|---|---|---|---|---|
| 2007-0287 | Troll | 70 % | 250˚C+ residue | Loading *1 | 3 | 3 | 5 | 3 |
| | | | | Loading *2 | | | 3 | |
| | | | | Loading *4 | | | 3 | |
| | | | | Ph.ox | | | 3 | 3 |
| | | | | Biofilm | | | 3 | 1 |
| 2006-1061 | Kobbe | 75 % | 250˚C+ residue | Loading*1 | | | 3 | 3 |
| | | | | Ph.ox | | | 1 | 3 |
| | | | | Biofilm | | | 1 | 3 |
| 2007-0260 | Norne | 60 % | 250˚C+ residue | Loading*1 | | | 3 | 3 |
| | | | | Ph.ox | | | 1 | 3 |
| 2006-1125 | IF 380 | 40 % | | Loading*1 | | | 3 | 3 |

To validate the results, most of the experiments were done in triplicates. The results from the triplicate samples showed an increase in the relatively standard deviation from approx 2% for the finest sediment (0,6-1,4mm), up to 30 for the largest sediment (8-16 mm), for the Troll oil. The deviation in results was considered as acceptable.

# 4 Results and discussions

Table 4-1 show the experimental parameters used in this activity:

**Table 4-1 Experimental parameters.**

| Parameter | Variation |
|---|---|
| Oil type | • Troll crude<br>• Kobbe crude<br>• Norne crude<br>• Bunker fuel oil - IFO 380 |
| Evaporation | 250°C+ residue (crude oils) |
| Water content in emulsion | • 70% - Troll<br>• 75% - Kobbe<br>• 60% - Norne<br>• 40% - IFO 380 |
| Temperature | 5°C |
| Emulsion thickness / loading | • 10 mm (78,5 g) (Standard)<br>• 20 mm (157 g)<br>• 40 mm (314 g) |
| Sediment fraction / grain size distribution | • 0,6-1,4mm – Coarse sand<br>• 1,4-2,8mm – Very coarse sand<br>• 2,8-6,3mm – Very fine gravel<br>• 8-16 mm – Medium gravel |

The experimental parameters used in the different studies are presented at the beginning of each chapter. The parameter of variance is marked with a bold text.

Several rheological parameters were measured in this study to get an understanding of how the rheological properties effect the penetration and retention of emulsion in sediments. A definition of the different properties is given in *Appendix 1*. The rheological parameters are given in *Appendix 2*. Due to Nornes high wax content, it was difficult to measure reproducible rheological properties since wax has a tendency to crystallize when temperature falls below its pour point.

Earlier studies have shown that viscosity is a controlling parameter for penetration and retention of oil in sediments, with less penetration and retention for emulsions with high viscosity values (Carlsen, 2006). To study the correlation between the penetration and retention data, and the rheological properties for the emulsified oils in this activity, the data was correlated using standard software routines in Excel. The results showed that storage- and loss modulus (the viscoelastic properties of the emulsions) and the yield stress were of importance the retention of oil. The results from the correlating study are given in *Appendix 3*.

Photo documentation, showing penetration and retention of emulsion in the sediment, for each of the studies are given in *Appendix 4*.

In the following sub chapters, only a selection of the measured data are presented, except for Chapter 4.1 – Sediment fraction / size, where all of the available data are presented. The additional data for rest of the study is given in *Appendix 5*.

## 4.1 Sediment fraction / size

**Table 4.1-1 Experimental parameters used in this study.**

| Parameter | Variation |
|---|---|
| Oil type | Troll |
| Evaporation | $250^oC$+ residue |
| Water content in emulsion | 70% (Troll) |
| Temperature | $5^oC$ |
| Emulsion thickness / loading | 10mm (78,5g) |
| **Sediment fraction** | • **0,6-1,4 mm (Coarse sand)**<br>• **1,4-2,8 mm (Very coarse sand)**<br>• **2,8-6,3 mm (Very fine gravel)**<br>• **8-16 mm (Medium gravel)** |

Four fractions of sediments, ranging from coarse sand to gravel, were used for Troll emulsion to study the effect of variance in sediment fractions. Penetration depth after 8 tidal cycles in regards to the different sediment fractions is shown in Figure 4.1-1.

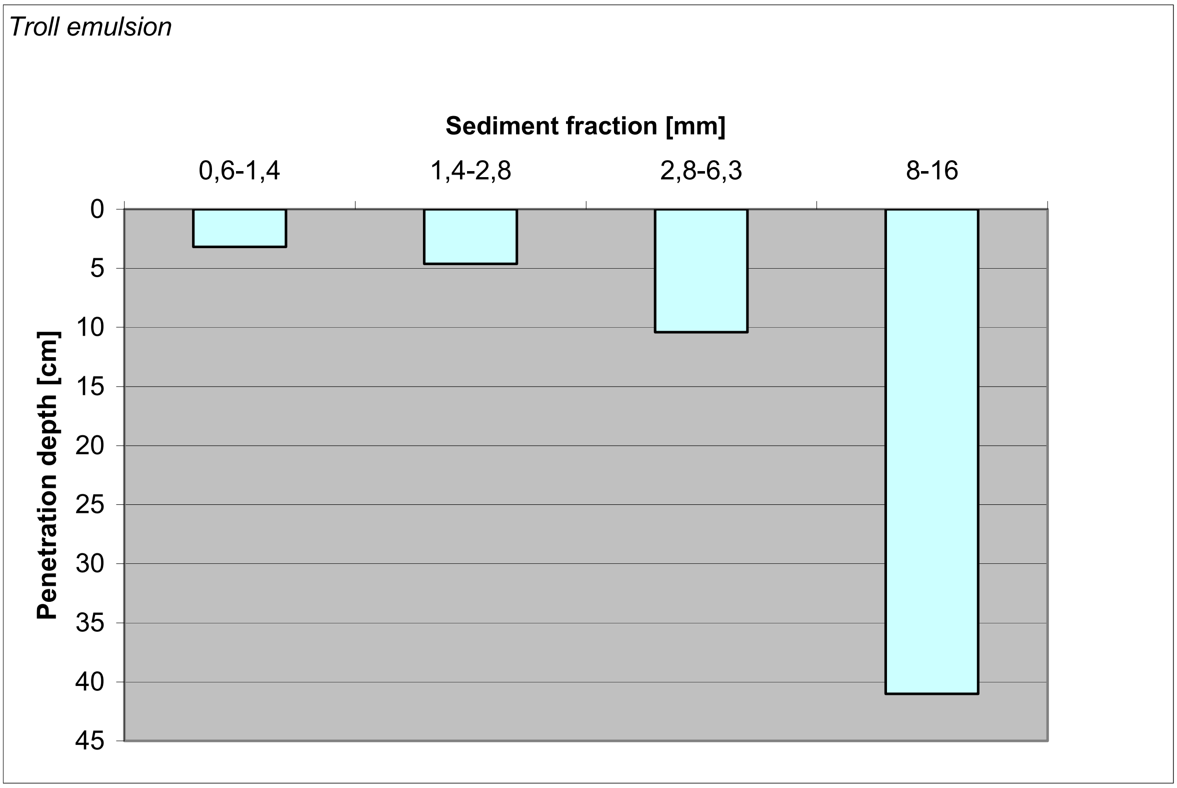



**Figure 4.1-1 Penetration depth as a function of sediment fraction after 8 tidal cycles.**

Figure 4.1-1 shows an increase in penetration with an increase in sediment fraction. The highest penetration was observed for the 8-16 mm fraction, which probably is due to the sediments high permeable properties. Photo documentation show a more definite boundary level of emulsion penetration for the smallest sediment fractions compared to the larger fractions, see *Appendix 4-* Table 1.The penetration results correlate well with conclusions found in SOCSEX (Harper et.al., 1995).

The tidal dependent penetration depth in regards to the different sediment fraction is shown in Figure 4.1-2.

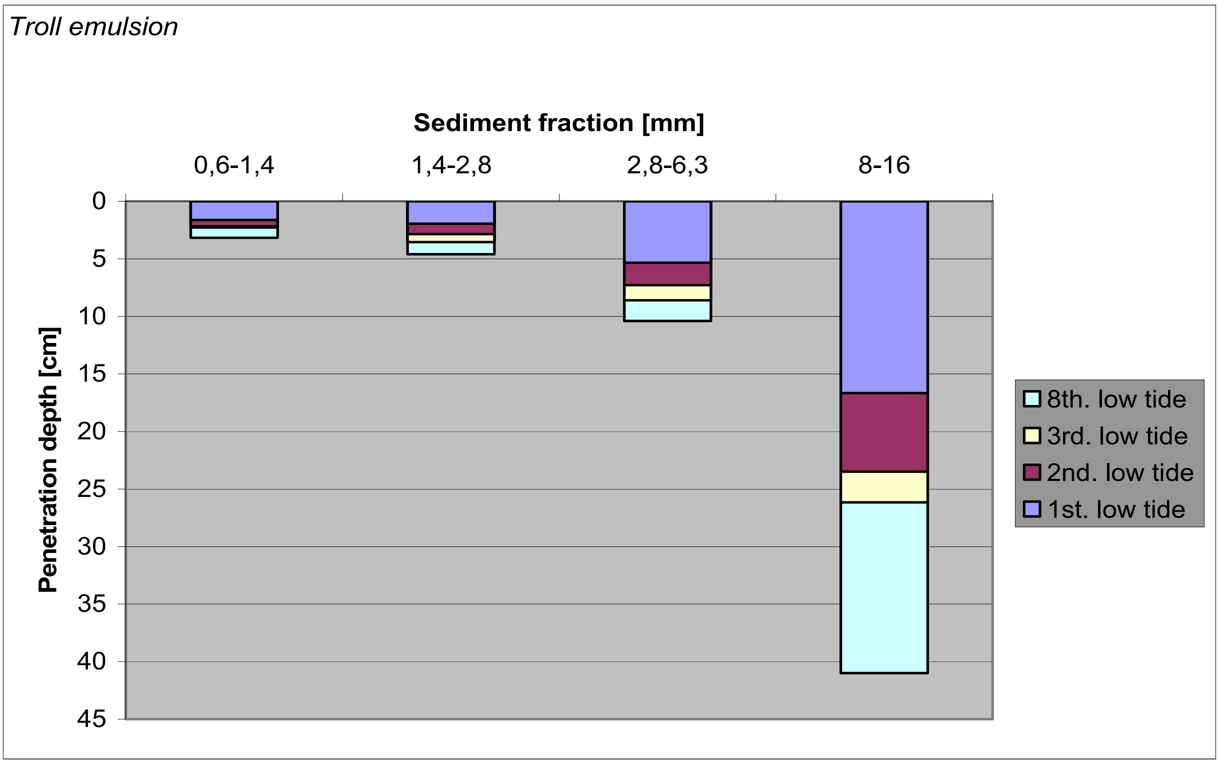



**Figure 4.1-2 Tidal dependent penetration depth as a function of sediment fraction.**

The largest rate of emulsion penetration was observed during the 1st low tide, for then to decrease with time, as shown in Figure 4.1-2. For the smallest fractions, the effect of number of tides was minor due to the sediments low permeable properties.

The retention of emulsion in the sediment is given in Figure 4.1-3.

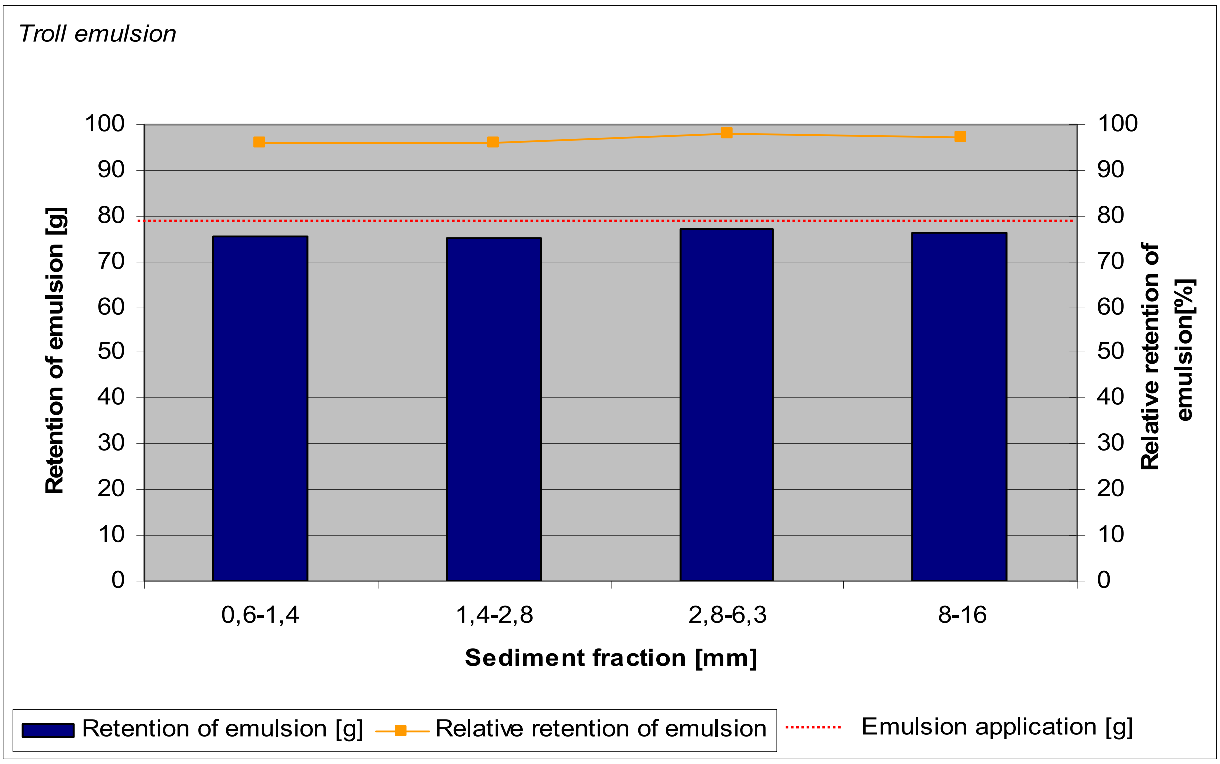



**Figure 4.1-3 Retention of emulsion given in grams and percent as a function of sediment fraction.**

Figure 4.1-3 shows the relative retention of emulsion to be approximately the same for the four fractions (about 95%). This might be due to a combination between the smallest sediment fractions good capacity to trap emulsion in small voids in the sediment (low permeability) and the largest fractions good capacity to store emulsion deeper down into the sediment, making it harder to resurface.

Photo documentation indicate a lower retention of emulsion from fraction 0,6-1,4 and 8-16 mm than for the other two fractions, see Appendix 4 - Table 2. This does however not seem to have a large impact on the quantity of retained emulsion according the retention calculations shown in Figure 4.1-3.

Earlier studies done at SINTEF show the same trend in penetration, but less retention of emulsion for the smallest sediment fraction (Carlsen, 2006).

Oil concentration dependent on penetration depth and sediment fraction is given in Figure 4.1-4 and Figure 4.1-5.

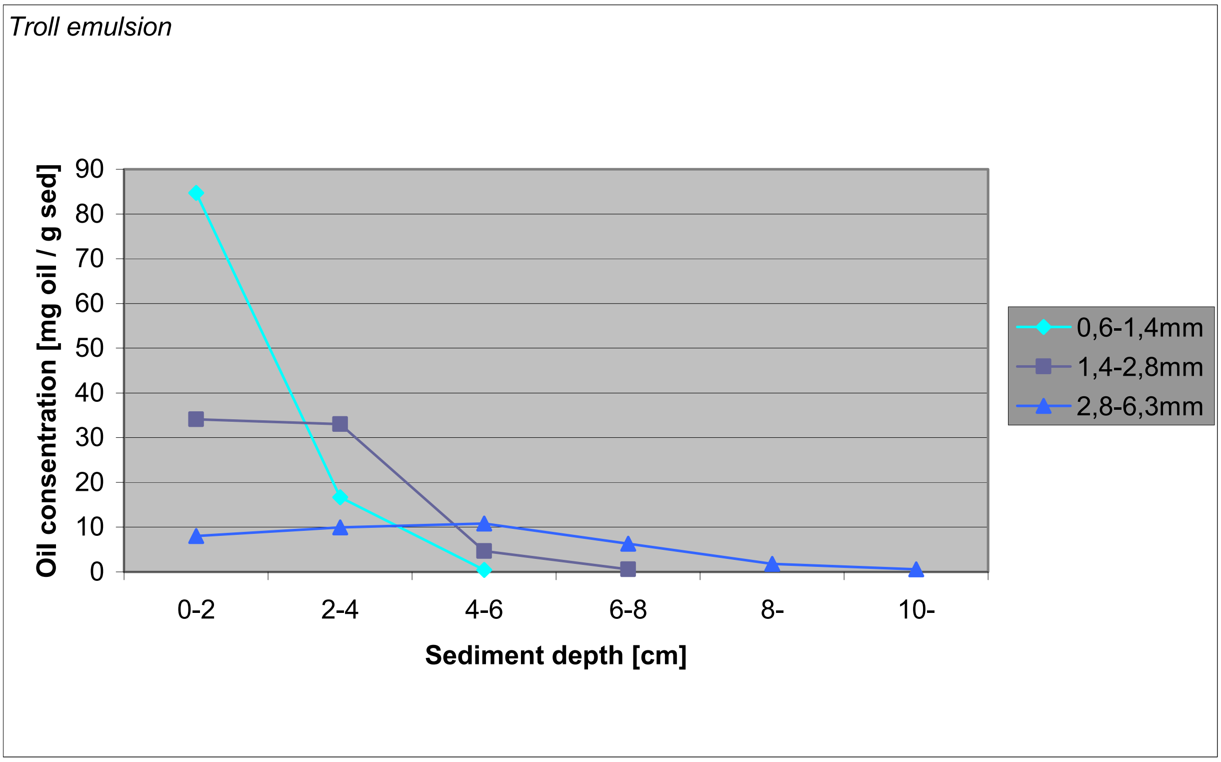



**Figure 4.1-4 Oil concentrations as a function of sediment fraction and depth.**

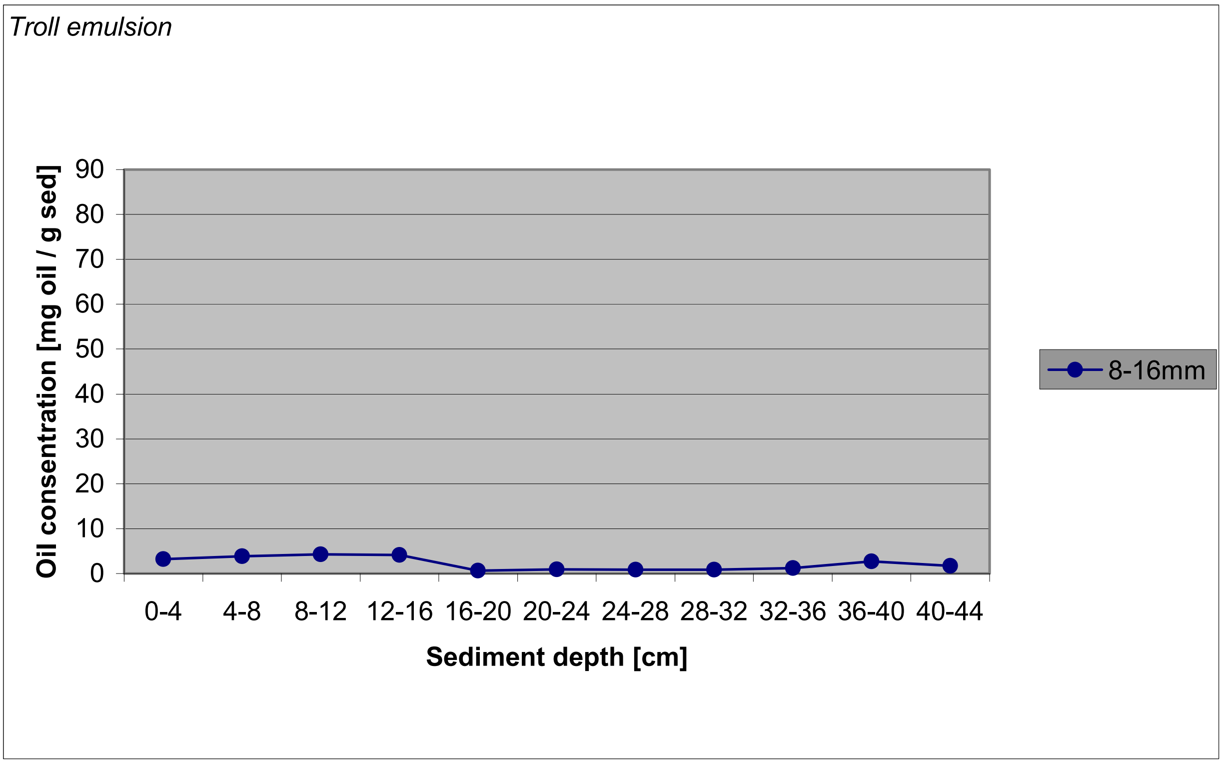



**Figure 4.1-5 Oil concentrations as a function of sediment depth.**

Figure 4.1-4 and Figure 4.1-5 show a relatively high oil concentration in the upper layers of the sediment columns for the two smallest sediment fractions. This high concentration decreases rapidly with sediment depth. For the two larger fractions, the oil seems to be more evenly distributed in the sediment columns without a definite interfacial boundary level between oil infested sediment and clean sediment. Literature state that the penetration are controlled by the number of contact point between sediment particles. Oil concentration correlated with the surface area of each sediment fraction is illustrated in Figure 4.1-6. The concentration values are given for the upper sediment layer (0-2 cm).

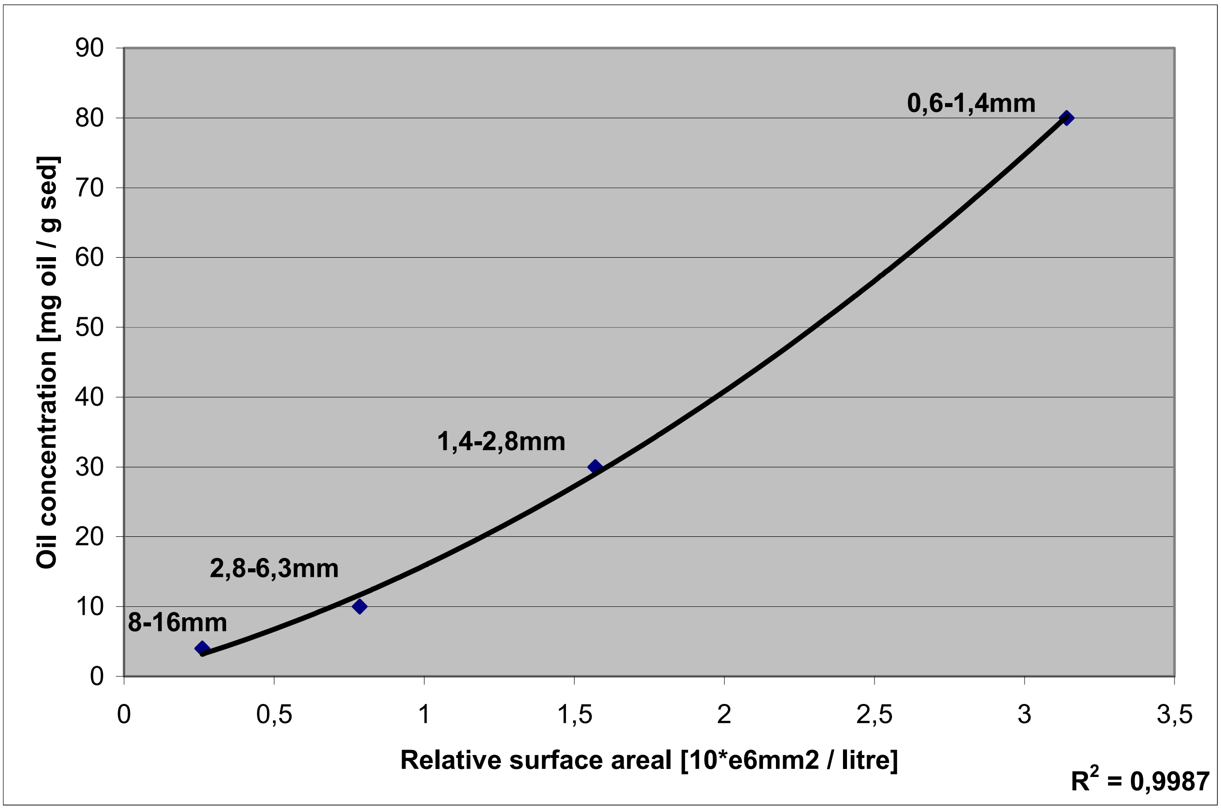



**Figure 4.1-6 Oil concentration related to relative surface area for the upper sediment layer (0-2 cm).**

Figure 4.1-6 show a very good correlation coefficient, 0,999, for the oil concentration and the number of contact points in the different sediment fractions

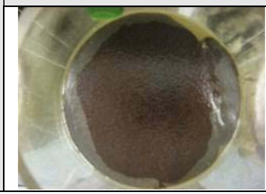
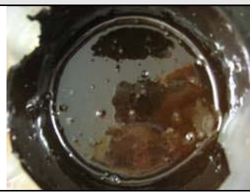
## 4.2 Oil type

**Table 4.2-1 Experimental parameters used in this study.**

| Parameter | Variation |
|---|---|
| **Oil type** | • **Troll**<br>• **Kobbe**<br>• **Norne**<br>• **IFO 380** |
| Evaporation | $250^oC$+ residue |
| Water content in emulsion | 70% (Troll), 75% (Kobbe), 60%(Norne) and 40% (IFO 380) |
| Temperature | $5^oC$ |
| Emulsion thickness / loading | 10mm (78,5g) |
| Sediment fraction | 2,8-6,3mm and 8-16 mm |

Four different oils were used to study the fate of oil in sediment dependent on oil type. Pictures of the emulsion appearance on the water surface at application are shown in Table 4.2-2.

**Table 4.2-2 Emulsion appearance on water surface after application (at the 1st high tide).**

| **Application 1st high tide** | **Troll** | **Kobbe** | **Norne** | **IFO 380** |
|---|---|---|---|---|
| |  |  |  |  |

Since the two smallest sediments fractions, studied in Chapter 5.1, had very low penetrable properties, it was decided to use only the two largest sediment fractions in further studies.

The penetration depth after 8 tidal cycles as a function of sediment fraction and oil type is shown in Figure 4.2-1.

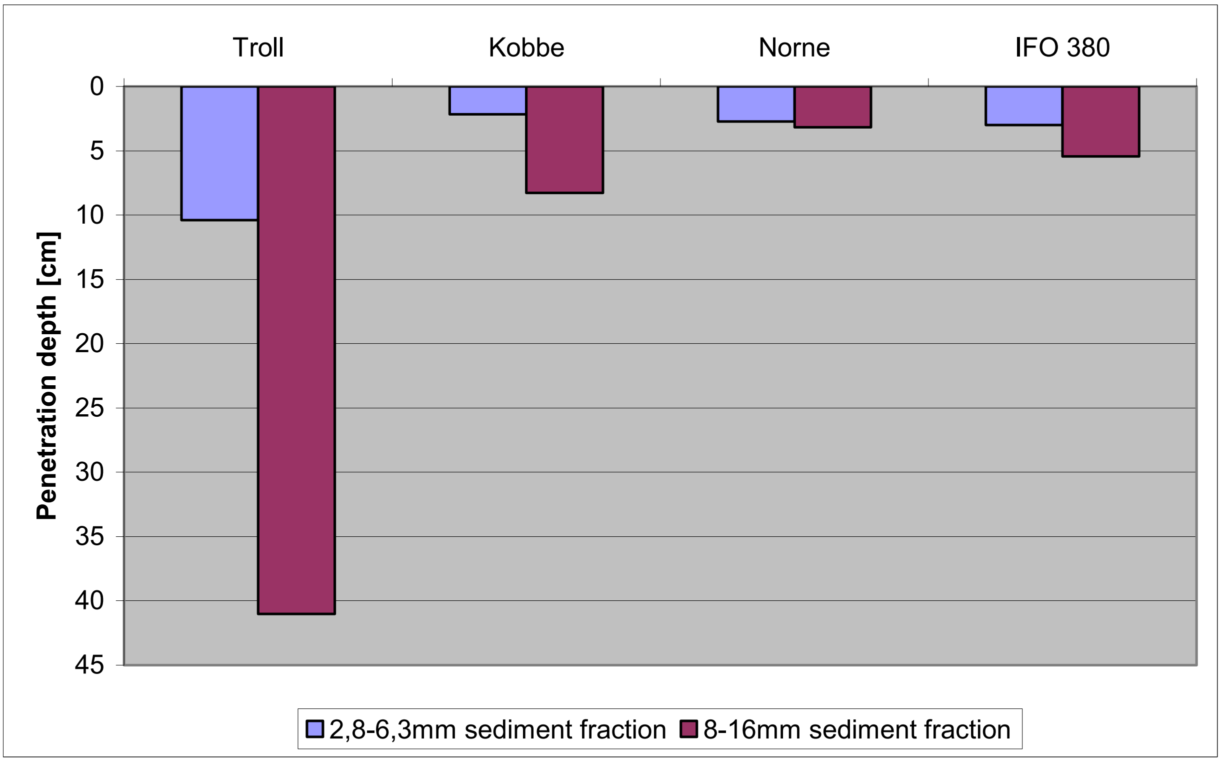



**Figure 4.2-1 Penetration depth as a function of oil type and sediment fraction after 8 tidal cycles.**

Figure 4.2-1 shows a large variance in penetration depth for the 4 oils, with the highest penetration of the Troll emulsion for both sediment fractions. The 8-16 mm sediment fraction show a greater penetration compared to the 2,8-6,3 mm sediment fraction, for all the 4 oils. Norne show almost no penetration for the any of the sediment fractions. A combination between Nornes high viscoelastic properties and the sediments relatively small grain size, makes the conditions in the columns almost impermeable. A more detailed study reflecting the effect of tide number is given in *Appendix 5*.

Photo documentation shows a relatively diffuse emulsion/sediment interface for the largest fraction, see Appendix 4- Table 4 and 5. Pictures in Table 8 and 9 show less and less emulsion on the sediment surface with an increase in number of tides. Nornes patchy like release of emulsion is shown in Table 9.

The retention of emulsion in the sediment during the experimental period is shown in Figure 4.2-2.

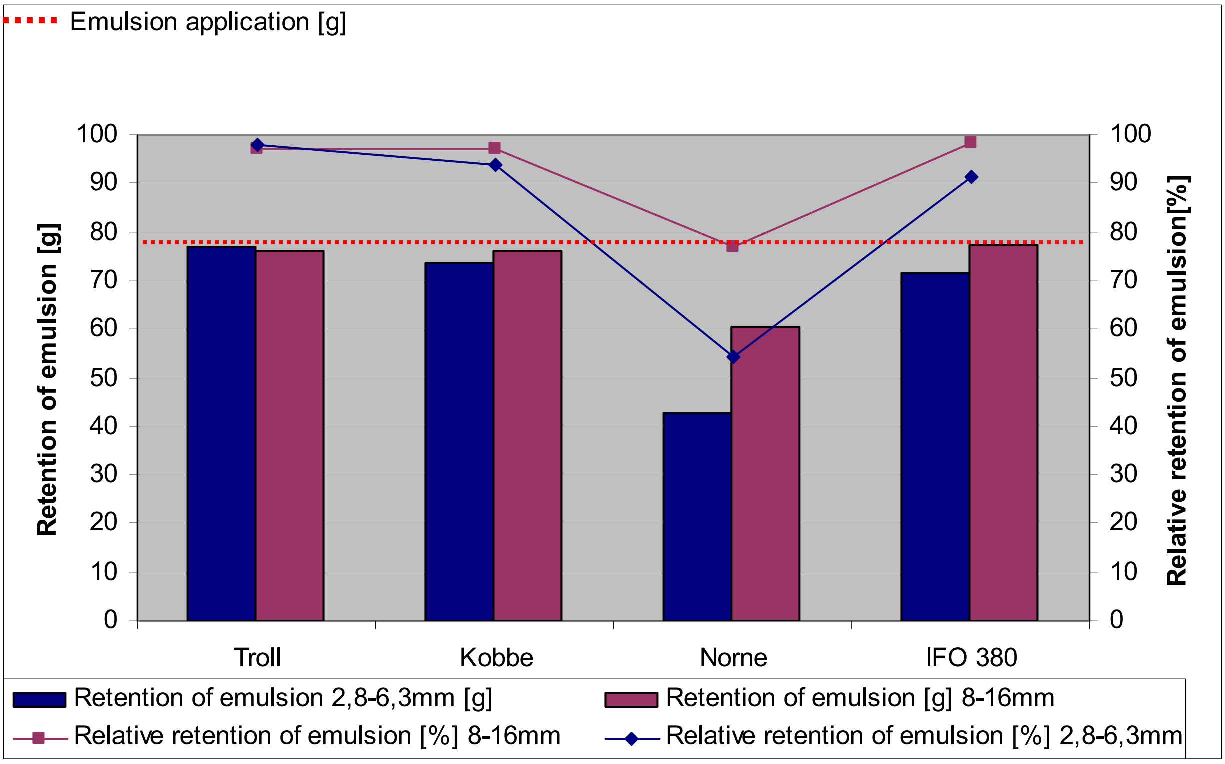



**Figure 4.2-2 Retention of emulsion given in grams and percent as a function of oil type and sediment fraction.**

Figure 4.2-2 show the retention of emulsion to be grater for the largest fraction (8-16mm) compared to the smallest fraction (2,8-6,3 mm) for all the oil except Troll, which show little change in retention dependent on sediment fraction. There is an exceptional low retention for Norne compared to the other oil types. Photo documentation show large quantities of resurfaced Norne emulsion for both fractions, see *Appendix 4*- Table 7. The low retention might be due to its high viscosity, see *Appendix 2*, the emulsion is then more accessible for refloating. These results seems to correlate good with findings in the SOCS report (Harper & Harvey-Kelly, 1994) stating that oil retention is likely to be highest under permeable conditions where the oils are viscous.

### 4.3 Emulsion thickness / loading

**Experimental parameters used in this study.**

| Parameter | Variation |
|---|---|
| Oil type | Troll |
| Evaporation | 250°C+ residue |
| Water content in emulsion | 70% (Troll) |
| Temperature | 5°C |
| **Emulsion thickness / loading** | **1 x Standard (10 mm)**<br>**2 x standard (20 mm)**<br>**4 x standard (40 mm)** |
| Sediment fraction | 2,8-6,3 mm |

To study the effect of emulsion thickness, three different amounts of Troll oil emulsion were applied to the water surface of the columns. Based on previous observations, the 2,8-6,3 mm sediment fraction was considered best to used for this study. The quantities used were 2x and 4x times the standard emulsion thickness (10mm oil layer). The penetration depth after 8 tidal cycles in regards to emulsion loading is shown in Figure 4.3-1.

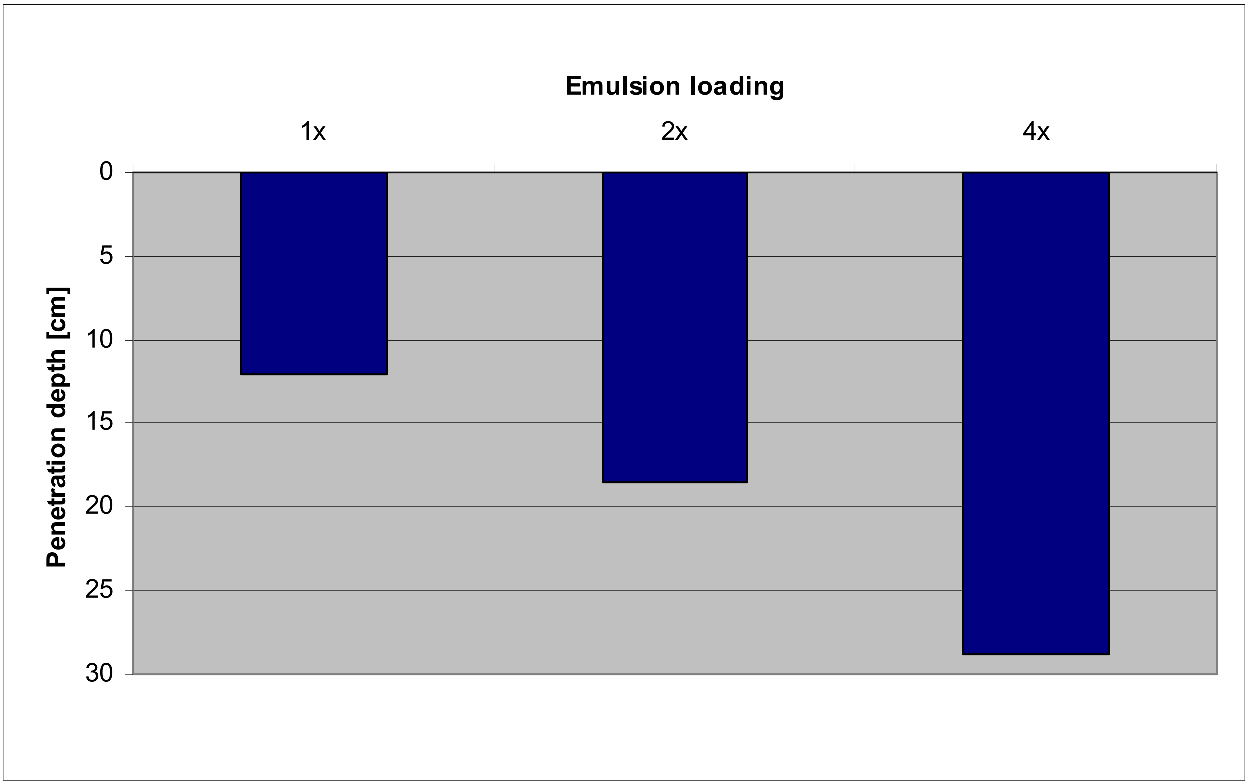



**Figure 4.3-1 Tidal dependent penetration depth as a function of loading after 8 tidal cycles.**

Figure 4.3-1 show an increase in penetration depth with an increase in emulsion loading. This is clearly shown in *Appendix 4,* Table 10.

The retention of emulsion in the sediment is shown in Figure 4.3-2.

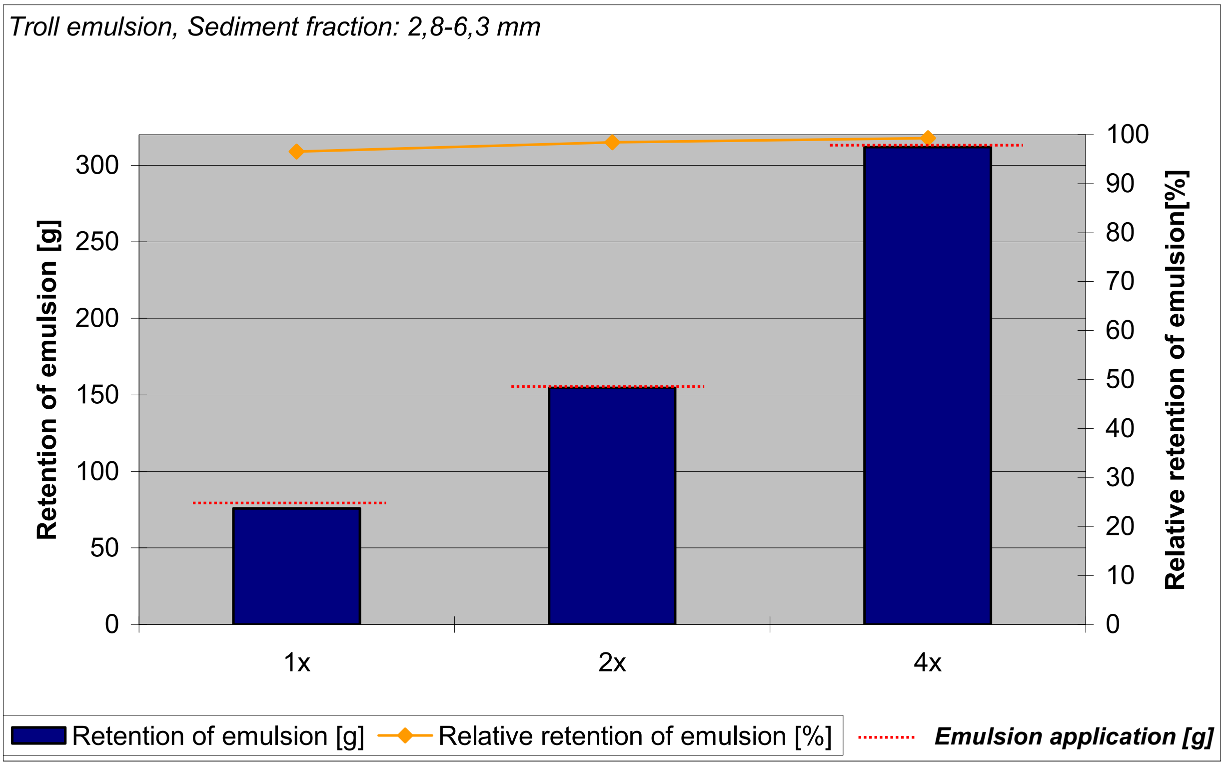



**Figure 4.3-2 Retention of emulsion given in grams and percent as a function of loading.**

Figure 4.3-2 shows a emulsion retention of 95-98%, regardless of the amount of emulsion loaded. Earlier studies done for water free IFO 180, show the same trend for the penetration of oil, but the retention of oil were more correlated to the penetration grade, increasing from 89-95% for the same sediment fraction, with an increase in loading (Carlsen, 2006).

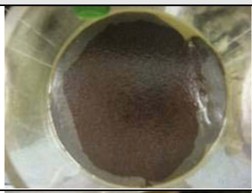
## 4.4 Photo-oxidation of crude oils

**Table 4.4-1 Experimental parameters used in this study.**

| **Parameter** | **Variation** |
|---|---|
| Oil type | Troll, Kobbe, Norne |
| **Evaporation** | **Ph.ox** |
| Water content in emulsion | 70% (Troll), 75% (Kobbe), 60%(Norne) |
| Temperature | 5°C |
| Emulsion thickness / loading | 10 mm |
| Sediment | 2,8-6,3 mm and 8-16 mm |

Troll, Kobbe and Norne crude oils were photo-oxidized to study the effect of sun exposure compared to oils that was un photo oxidized. The difference in emulsion appearance between photo-oxidized and un photo-oxidized emulsion is shown in Table 4.4-2.

**Table 4.4-2 Emulsion appearances on water surface as a function of photo-oxidized versus sun photo-oxidized oil at the 1st high tide**

| **Application 1st high tide** | **Troll** | **Kobbe** | **Norne** |
|---|---|---|---|
| **Un ph.ox** |  |  |  |
| **Ph.ox** |  |  |  |

The pictures in Table 4.4-2 show the photo-oxidized oil to be much brighter in colour and much more firm in its structure compared to the un photo-oxidized emulsion.

The penetration of photo-oxidized emulsion after 8 tidal cycles for the two sediment fractions, 2,8-6,3 mm and 8-16 mm are given in Figure 4.4-1 and Figure 4.4-2.

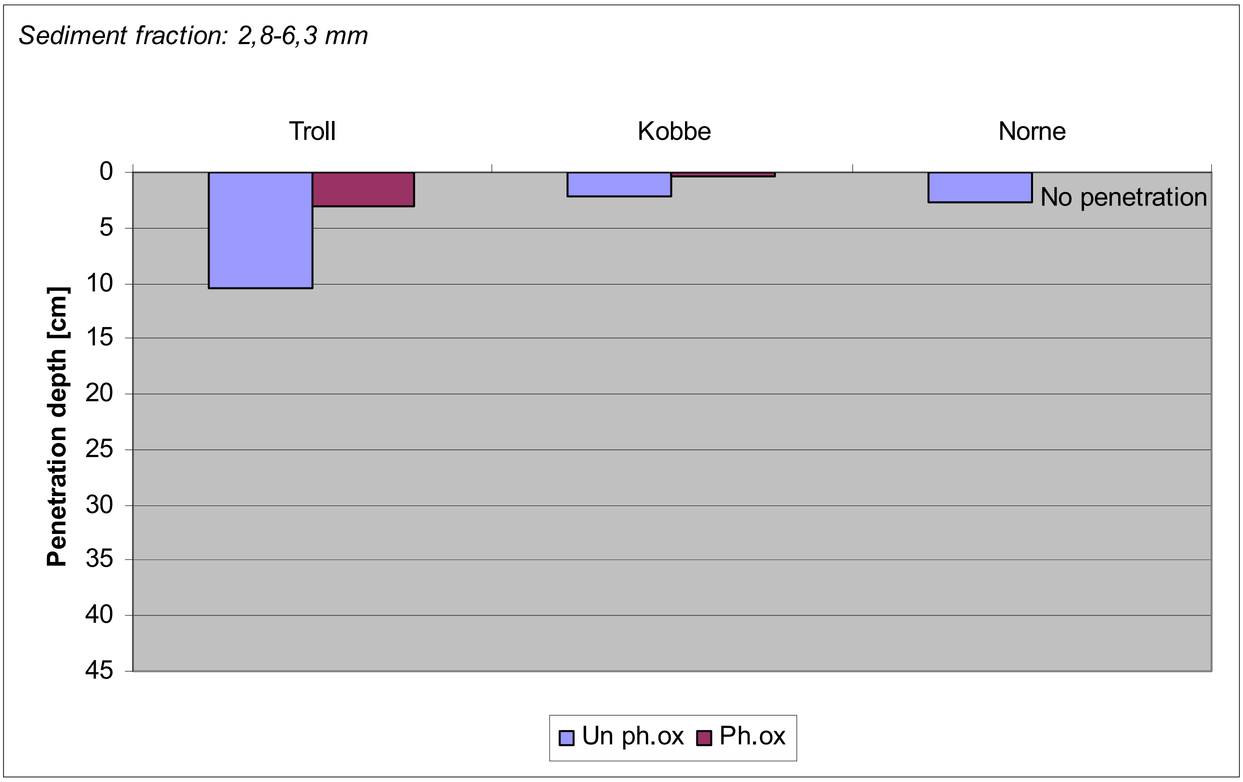



**Figure 4.4-1 Penetration depth as a function of un ph.ox. versus ph.ox. oil and oil type after 8 tidal cycles.**

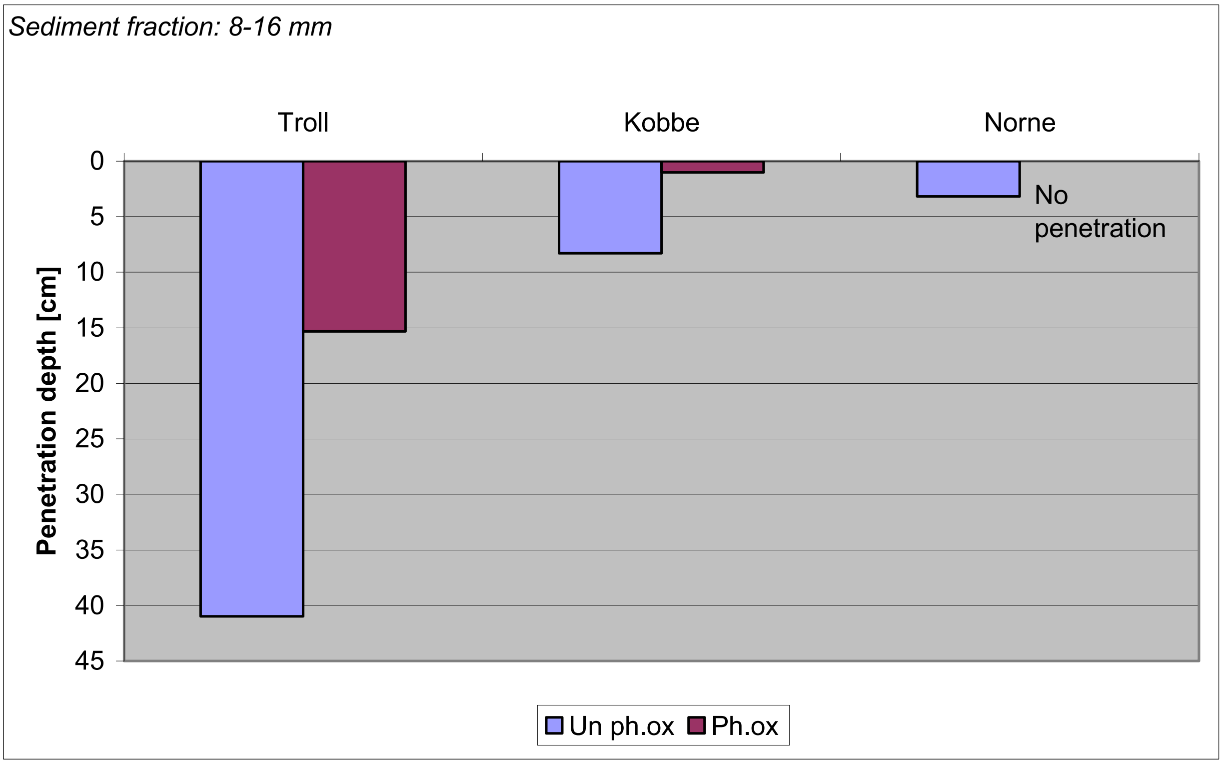



**Figure 4.4-2 Penetration depth as a function of un ph.ox versus ph.ox and oil type after 8 tidal cycles.**

Figure 4.4-1 and Figure 4.4-2 show a 3-4 times greater penetration for the un photo-oxidized oil compared to the photo-oxidized oil, regardless of the sediment fraction. Photo-oxidized Norne refloated at the 2nd high tide and did not penetrate at all for the two sediment fractions. Due to the photo-oxidation of the crude oils, the viscosity increased, this probably reduced the penetration properties for the oils. Photo documentation shows for the photo-oxidized emulsions a definite interface between emulsion and sediment, regardless of the sediment fraction, see *Appendix 4*, Table 13 and 14.

The retention of emulsion in the sediment is shown in Figure 4.4-3 and Figure 4.4-4.

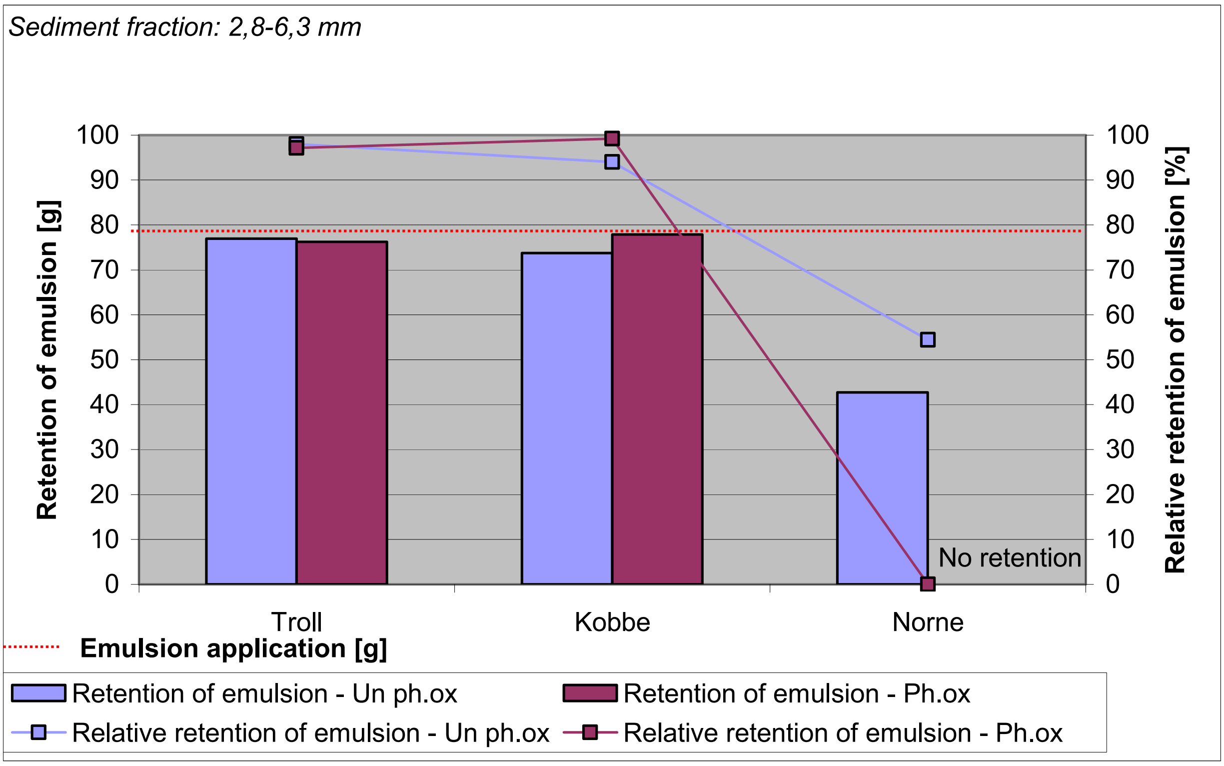



**Figure 4.4-3 Retention of emulsion given in grams and percent as a function of ph.ox oil versus un ph.ox. oil.**

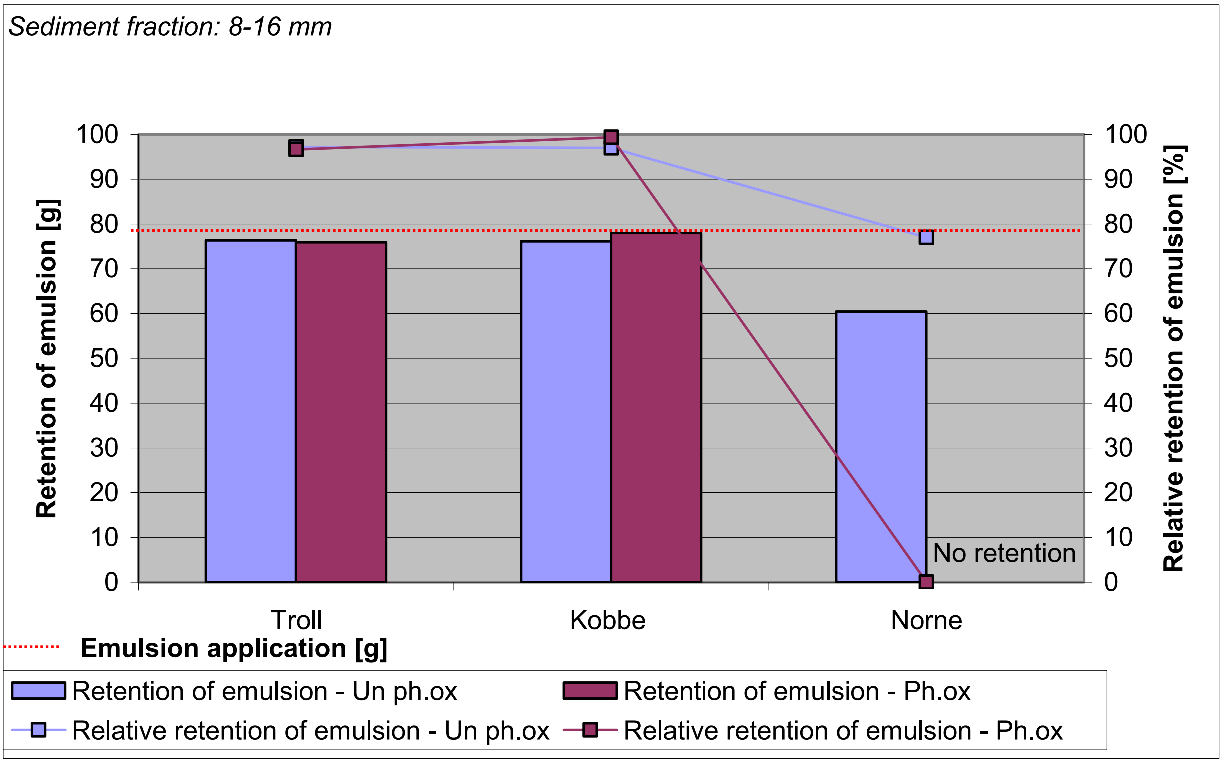



**Figure 4.4-4 Retention of emulsion given in grams and percent as a function of ph.ox oil versus un ph.ox oil.**

Figure 4.4-3 and 4.4-4 shows approximately no effect on emulsion retention for the Troll oil dependent on sun exposure for the two sediment fractions. There were no penetration of photo-oxidized emulsion for Kobbe and Norne. Kobbe adhered to the sediment surface without penetrating and was considered as retained. Norne refloated at high tide and resulted in zero retention. Photo documentation clearly shows the refloating of photo-oxidized Norne for both sediment fractions, see *Appendix 4*- Table 15 and 16.

## 4.5 Biological film in sediment - sediment surface properties

**Table 4.5-1 Experimental parameters used in this study**

| Parameter | Variation |
|---|---|
| Oil type | Troll and Kobbe |
| Evaporation | 250°C+ residue |
| Water content in emulsion | 70% (Troll) and 75% (Kobbe) |
| Temperature | 5°C |
| Emulsion thickness / loading | 10 mm |
| **Sediment** | **With biofilm - 2,8-6,3 mm and 8-16 mm** |

A biological film was grown at the sediment surface to study the significance of biofilm in a sediments shoreline system, simulated in the lab. The penetration depth after 8 tidal cycles for the two chosen sediment fractions as a function of biofilm in sediment is shown in Figure 4.5-1.

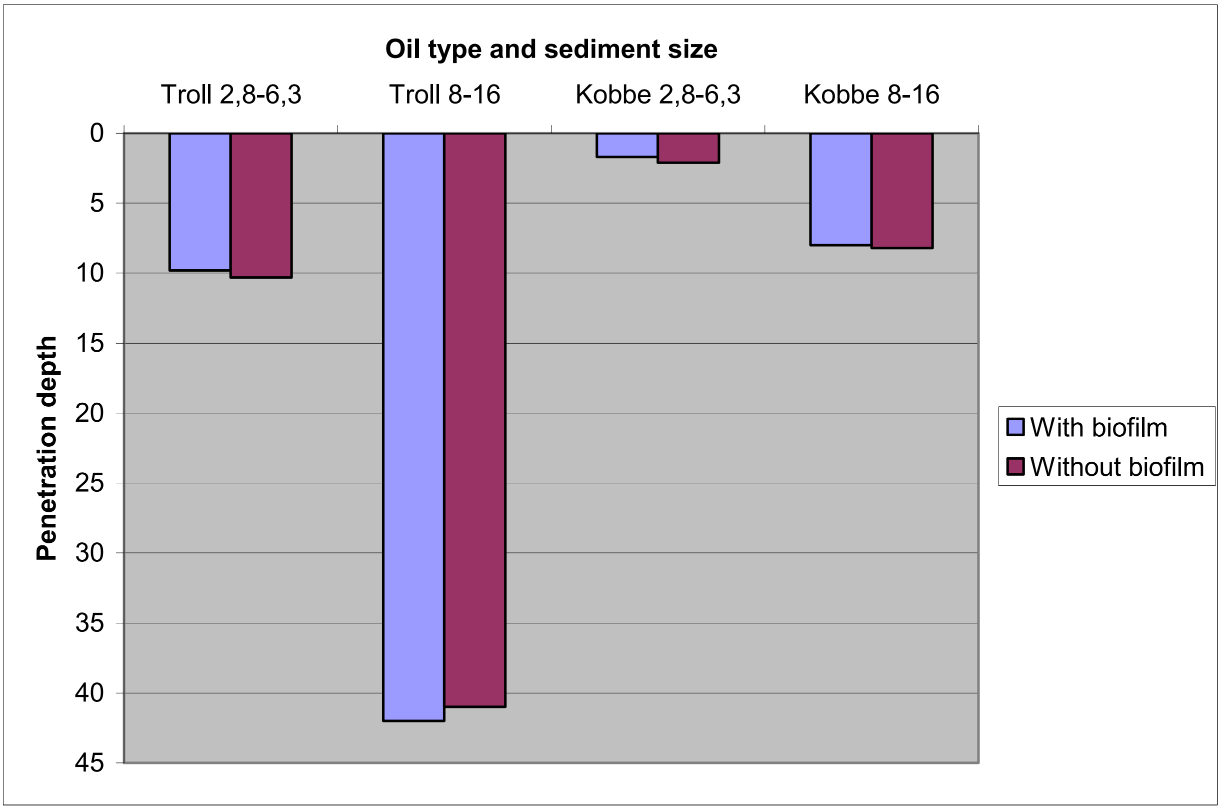



**Figure 4.5-1 Penetration depth as a function of biofilm, sediment fraction and oil type after 8 tidal cycles.**

Figure 4.5-1 shows approximately the same penetration rate regardless of the presence of biological film on the sediment surface and the sediment fraction. There are some few variations but no trend is observed. The photo documentation is a little misleading sense emulsions have a tendency to change in colour, see *Appendix 4*- Table 19 and 20.

The retention of emulsion in the sediment is shown in Figure 4.5-2.

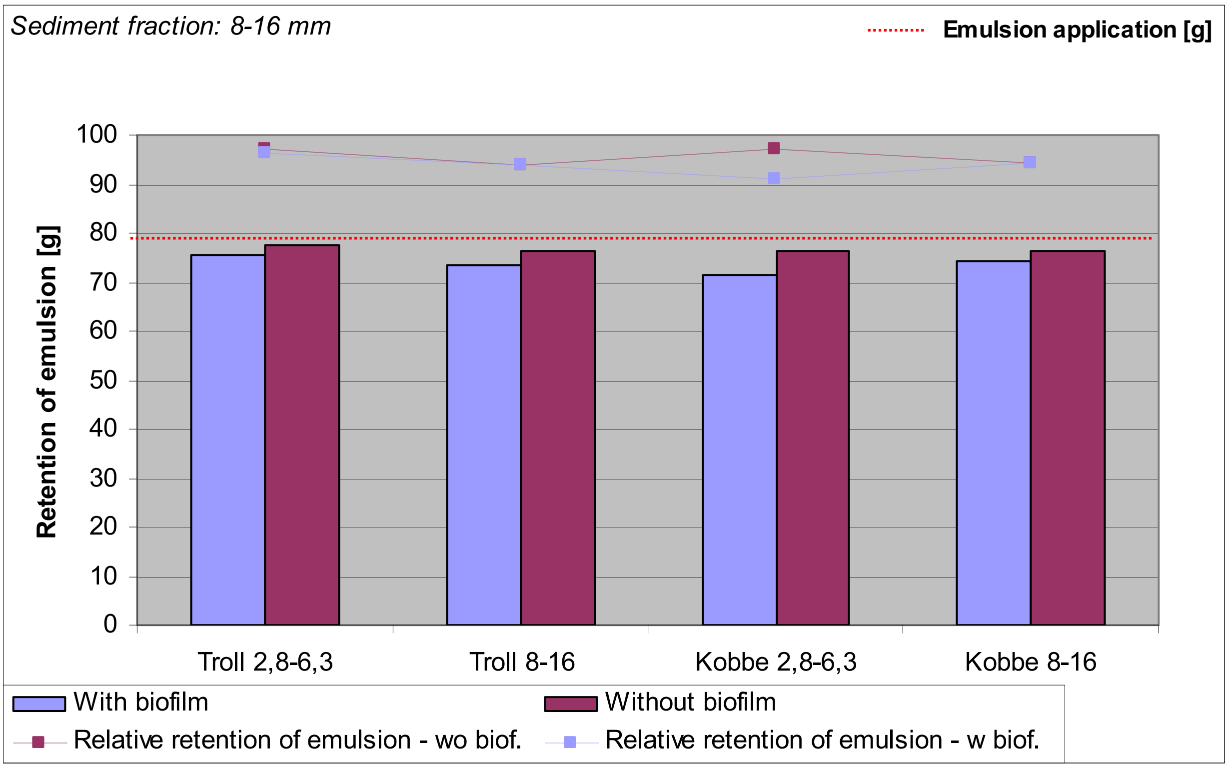



**Figure 4.5-2 Retention of emulsion as a function of sediment fraction and oil type.**

Figure 4.5-2 shows a slight decree in retention of the emulsion for the sediments with biofilm. This might be explained by a reduced adhesion between emulsion and the sediments surface with biofilm, making the emulsion more susceptible for refloating. Photo documentation shows an increased refloating of emulsion from the sediment surface for both of the sediment fractions by an increase in number of tides, see *Appendix 4*- Table 21 and 22.

# 5 Conclusions and operational gain

The results show that the penetration of emulsion in sediment is strongly dependent on oil type, weathering degree (photo-oxidation) and sediment grain size. A simple correlation study showed that the viscoelastic and yield stress properties of the emulsions were of importance the retention of oil.

Troll, the most penetrable oil, penetrated down to approximately 40 cm for the 8-16 mm sediment fraction. This might be due to a combination between the Troll oils low viscoelastic properties and pour point. Kobbe, Norne and IFO 380 only penetrated approximately one third of Troll, which might be due to their higher viscoelastic properties and pour point. Photo-oxidation changed the physicochemical properties of the crude oils, among other factors increasing the viscosity. The increase in viscosity reduced the penetration depth between 60% and 100%. Photo-oxidized Norne did not penetrate into the sediment and refloated at high tide. Due to low penetration of photo-oxidized oils, the emulsions might be washed out and subjected for a secondary stranding. Summer versus winter conditions must therefore be taken in to consideration for the countermeasure strategy, summer conditions changing the properties of the oils in a larger degree due to photo-oxidation.

Emulsion loading, tested on Troll oil, showed to be of great importance giving an initial increase in penetration, for then to decline with an increase in emulsion loading. This might be due to the increase in gravitation force. The increase in loading also affected the concentration curve, showing a concentration peak further down in the sediment. Emulsion loading is predicted also to have the same effect on the other test oils.

The results showed an increase in penetration depth for both photo and un photo-oxidized oils, with an increase in sediment fraction chosen after the Wentworth scale. Deep penetration of weathered oil will complicate the cleanup process on contaminated shorelines. Stranding of oils like Troll must therefore be prevented, especially if the oil is predicted to strand on coarse grained shorelines. The reduction in penetration depth reduces the volume for sediment treatment.

Oil concentration in the upper sediment layer (0-2 cm) is found to be correlated with the surface area of the sediment fraction, showing an increasing in oil concentration with a decrease in sediment grain size. For the finest sediment fraction (coarse sand), the concentration rapidly decreased with sediment depth. The greater sediment fractions showed a much lower concentration (distributed in the whole column) with an increase in sediment size. Due to the reduction in penetration for the photo-oxidized oils, the concentration distribution in the sediment changed, showing a higher concentration in the upper layers, compared to the un photo-oxidized oils. This is probably also due to an increase in emulsion film thickness on the sediment grains as an effect of the increase in viscosity.

Troll, Kobbe and IFO 380, showed little variation in retained emulsion in the sediment, being close to 95% for the parameters tested. The retention of Norne oil increased from 55% to 78% with an increase in sediment size and 43% to 100% with as an effect of sun exposure.

The studies showed that about 50% of the penetration happened within the first tidal cycle, the penetration rate was then reduced, except for the most viscoelastic oil, Norne.

Biofilm in the sediments did not effect the penetration and retention notably, using sediment uninfected with biofilm is therefore not of relevance for the data quality derived using the experimental system.

This study gives us a better knowledge of how weathered oil will interact with the shoreline sediment when drifted onshore, primarily for low exposed shorelines. Results have shown that factors as oil type and weathering, sediment size and emulsion loading must be taken into consideration in countermeasure planning to ensure an optimal shoreline restoration. The data gained can be used for a further development of numerical models. Field studies are important for a validation of the results and for a supplement to the data gained so far.

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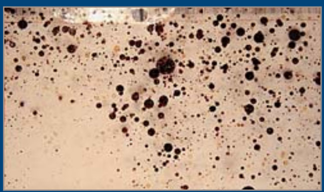
# REPORT



## Coastal Oil Spills - JIP

Report no.: 18

# C3.5 - Refloating and wash-out of stranded oil in the acute phase

Svein Ramstad

**SINTEF Materials and Chemistry**
Marine Environmental Technology

Date: 2009-01-15



SINTEF

# SINTEF REPORT

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**Refloating and wash-out of stranded oil in the acute phase**

**Coastal Oil pills JIP Report No 18**

AUTHOR(S)

Svein Ramstad

CLIENT(S)

Eni Norge AS, A/S Norske Shell and StatoilHydro ASA

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| | 2009-01-07 | Tore Aunaas, Research Director | |

ABSTRACT

The fate and behaviour of stranded oil emulsions have been studied under static and dynamic conditions using the simulated shoreline system. The experiments were designed to simulate the processes in the initial acute phase. The experimental design included studies with different oil types under static and dynamic condition, different oil layer thickness, and oil properties as photo-oxidized oil emulsions

The main conclusions from the present study are;

- Remobilisation of stranded oil emulsion are dependent on oil properties
- Crude oil emulsion are more easily remobilized compared to bunker oil emulsion.
- Remobilisation increases with increasing wave exposure
- Remobilisation increases with oil loading under dynamic condition
- Remobilisation decreases for photo-oxidized oil emulsion

The observations and findings from the present study clearly shows the difference between weathered crude oil emulsion and bunker oil emulsion which could affect the strategies for oil spill contingency plan and operation. The crude oil emulsion are more easily remobilized and requires booming of contaminated shoreline sections to avoid further spreading of the contaminants.

| KEYWORDS | ENGLISH | NORWEGIAN |
|---|---|---|
| GROUP 1 | Oil | Olje |
| GROUP 2 | Environment | Miljø |
| SELECTED BY AUTHOR | Refloating | Oppdrift |
| | Emulsion | Emulsjon |
| | Simulated shoreline experiment | Simulert strand system |

# TABLE OF CONTENTS

# 1 Introduction

This project has been a part of phase 1 in the Coastal Oil Spills JIP. The research projects in the JIP have been focused on the fate and behavior of oil spills in coastal areas and on shoreline. Laboratory studies have been performed in order to obtain data for further development of numerical models.

The first phase of JIP was performed in the period from 2006 to 2008, and was funded by Eni Norge, Shell Technology and StatoilHydro. The overall objectives of the JIP have been:

- to contribute to an adequate and sufficient basis of competence to document possible consequences in case of an oil spill close to the coast
- to provide documentation ensuring the countermeasures giving the optimal environmental gain

When large quantities of oil are stranded at the beach in the acute phase, the emulsion will in most cases remain mobile over a certain time period. The oil might then refloat and get washed out and contaminate new shoreline areas. This process is dependent on a number of parameters including, the physical properties of the oil, characteristics of the shoreline system and environmental parameters. The main processes affecting the fate of the mobile oil will be buoyancy, adhesion to solid substrate and physical exposure.

In the literature these processes has not been described or reported under controlled and reproducible conditions. But knowledge on these processes will be very important for the responders to establish the best possible contingency plan and strategy.

To study these processes, the simulated shoreline systems are used which allows both simulation of dynamic and static condition. The same experimental system has been used also in other activities within the Coastal Oil Spill JIP, including wash-out, erosion and oil fine interaction for immobilized oils (restoration phase), which makes comparison of the different processes easier. The wave exposure in this experimental system has also been described by numerical modelling (C2.2).

The main objective of this activity are to *study and quantify washout/refloating of mobile oil on solid substrate under controlled exposure conditions*

## 2 Summary

The fate and behaviour of stranded oil emulsions have been studied under static and dynamic conditions using the simulated shoreline system. The experiments were designed to simulate the processes in the initial acute phase. The freshly prepared emulsions were applied to the standard shale tiles (15x15cm) and allowed to acclimate for one hour before introduction to the exposure. In the experiments without wave exposure, the remobilisation of oil emulsions is due to refloating only, whereas the dynamic experiments with wave exposure is a combination of both refloating and wash-out. The remobilisation of emulsions were quantified at by measurement of residual emulsion on the test tiles. The experimental design included studies with different oil types under static and dynamic condition, different oil layer thickness, and oil properties as photo-oxidized oil emulsions

The main conclusions from the present study are;

- Remobilisation of stranded oil emulsion are dependent on oil properties
- Crude oil emulsion are more easily remobilized compared to bunker oil emulsion.
- Remobilisation increases with increasing wave exposure
- Remobilisation increases with oil loading under dynamic condition
- Remobilisation decreases with photo-oxidized oil emulsion

The observations and findings from the present study clearly shows the difference between weathered crude oil emulsion and bunker oil emulsion which could affect the strategies for oil spill contingency plan and operation. The crude oil emulsion are more easily remobilized and requires booming of contaminated shoreline sections to avoid further spreading of the contaminants.
The effect of photo-oxidation on remobilisation which represent winter and summer condition were minor and should not affect the contingency plan based on results for the present study.

# 3 Materials and methods

## 3.1 Experimental system

### 3.1.1 The shoreline simulation system

SINTEF have built up two identical shoreline simulation systems which each contains 12 reservoirs installed on an oscillating table. Single tiles are placed in each of the reservoirs, see Figure 3.1. The shoreline simulation system is placed in a temperature controlled room to ensure the required test temperature.

**Figure 3.1 The shoreline simulation system (to the left) and the water reservoirs (to the right).**

The simulation systems generate wave energy by tilting the oscillating table from one side to another with a standard angel and frequency, as shown in Figure 3.2-2. For this purpose a compressed air jack along with a control unit programmed for a uniform movement is used.

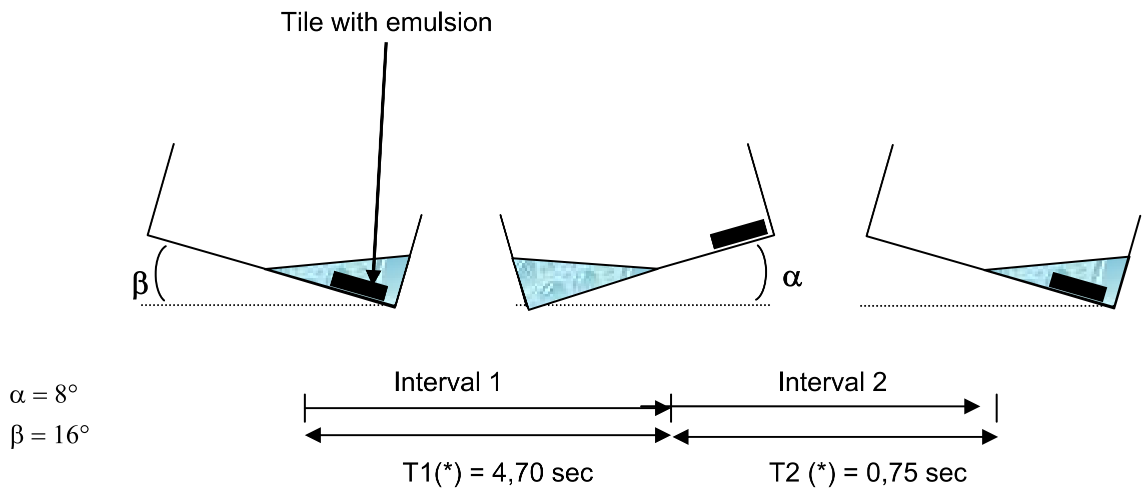


**Figure 3.1-2 The mechanism of the oscillating table – shoreline simulation system.**

### 3.2 Experimental oils

Crude oils can be characterised in four categories: asphaltenic, naphtenic, paraffinic and waxy crude oils. The crude oils studied in the Coastal Oil Spills JIP were selected among the oil companies' crude oils. It was important to select crude oils representing different categories of oils. The selected crude oils represent the categories:

- Troll – naphtenic crude oil
- Norne – waxy crude oils
- Kobbe – light paraffinic crude oil

In addition to the crude oils, a heavy fuel oil (IFO380) was also tested. IFO 380 is representative heavy fuel oils for bunker oils used as fuel for ships going along the Norwegian coast. The content of light oil components in fuel oils is low, typically lower than 5 vol% for IFO 380 oils. The testing of the IFO 380 was therefore concentrated on the "fresh" fuel oil, not on an evaporated residue. The IFO 380 oil used in this project is a low sulphur fuel oil produced at the Esso refinery at Slagentangen in Norway.

Some physical and chemical properties of the oils studied are listed in Table ***3.1***.

*Table 3.1 Oils used in the Coastal Oil Spills JIP.*

| SINTEF Id | Oil type | Residue | Density ($Kg/m^3$) | Evaporative Loss (Vol%) | Pour point (°C) | Wax (wt%) | Asphaltenes (wt%) | Viscosity at 5°C/10$^{-s}$ (cP) |
|---|---|---|---|---|---|---|---|---|
| 07-0287 | Troll | Fresh | 0,900 | 0 | -36 | 0,9 | 0,04 | |
| | | 250°C | 0,930 | 25,5 | -27 | | | 770 |
| | | Ph.ox. | 0,931 | - | -21 | | | |
| 07-0260 | Norne | Fresh | 0,860 | 0 | 21 | 4,3 | 0,30 | |
| | | 250°C | 0,888 | 28,4 | 30 | | | 39100 |
| | | Ph.ox. | 0,885 | - | 30 | | | |
| 06-1061 | Kobbe | Fresh | 0,797 | 0 | -39 | 3,4 | 0,03 | |
| | | 250°C | 0,875 | 53,6 | 21 | | | 4630 |
| | | Ph.ox. | 0,877 | - | 15 | | | |
| 06-1125 | IFO 380 | Fresh | 0,932 | 0 | 15 | 5,0 | 3,4 | 87100 |

*-: not measured*

It was decided to weather the oils to represent the properties of the oils after ½-1 week at sea. Evaporation, emulsification and photo-oxidation were performed according to SINTEF laboratory procedures. An evaporated residue of 250˚C+ was used for the three crude oils. That means that compounds with a boiling point typically below 250˚C have evaporated, and the product used is therefore a residue. IFO 380 is a refined product, the bunker fuel oil was therefore used without further evaporation. To ensure reproducible production of emulsions, a water content just below the maximum water uptake for the respective oils was used. After some initial studies, the standard water content was decided to be 70% for Troll, 75% for Kobbe, 60% for Norne and 40% for IFO 380.

### 3.3 Experimental procedures

Before introducing the tiles to the shoreline simulation system, the reservoirs were filled with seawater and placed on the oscillating table for water tempering.

#### 3.3.1 Tile preparation

Before emulsion application, the edges of the tiles were masked with tape to avoid quantification of emulsion covering the edges. The tiles were weighed before masking of the edges to document the initial weight. Emulsion (22,5 g +- 0,5) were applied evenly on the bedrock surface and placed horizontally for 1 day to let the emulsion cover the tile evenly. The tiles were then placed vertically for 4 days to let the excess emulsion run-off and to simulate secondary weathering of emulsion on the shoreline.

#### 3.3.2 Sampling, photo documentation and quantity analysis

Tile samples were retrieved from the shoreline simulation system during the wash-out process for quantification of washed out emulsion. The experimental period was 24 hours. Before start of the experiment the tiles were placed horizontally in a temperature controlled room at test temperature for 1 hour. The tiles were photo documented at application of emulsion, during and after the experimental period. After termination of the experiments excess water was removed and residual emulsion was quantified gravimetrically.

#### 3.3.3 Oil properties

To study the oils rheology, Physica MCR300 MC1+ rheometer with an US200 software was used.

### 3.4 Experimental parameters and design

Four different experimental parameters were varied in this study:

- Exposure degree
  Static condition (no wave exposure), and .dynamic conditions with 4 liters of water in the containers under standard conditions (angle and frequence)
- Oil types
  Three different crude oils; Troll, Kobbe, Norne (250$^o$C+ residue with close to maximum water content; 70, 75 and 60% respectively) and one bunker fuel oil; IFO 380 (fresh, close to maximum water content; 40%)was used to study the effect of oil type.
- Oil layer thickness
  Oil emulsion was applied in different thicknesses. For thickness above 1mm, a fence was established using a strong tape along the edges.
- Photo-oxidation of crude oil
  Photo-oxidized Troll oil emulsion were used to study the effect of sun exposure.

### 3.5 Analysis

The oil concentration of oil in the sediment was determined after extraction with dichloromethane (DCM), and analysis using a spectrophotometer (Hitachi U-2000 spectrophotometer).

Prior to initiation of each experiment the emulsion was characterised by rheological measurements (Physica MCR300 MC1+ rheometer with an US200 software).

# 4 Results and discussion

## 4.1 Mechanisms and experimental system

During stranding of oil emulsion on shoreline in the initial acute phase , the emulsion will be left behind in the superlitoral and intertidal shoreline zone. The fate of the oil during the next tidal periods will depend on the properties of the oil, shoreline characteristics and the actual environmental parameters. In many situations the oil emulsions will be remobilized as described in other activities in the ongoing project, including wash-out, refloating, adhesion, and erosion, both in the acute and restoration phase. In the initial phase before the oil emulsion has become immobilized and come into "equilibrium", the emulsion can be easily remobilised  by e.g. refloating, which reflects the adhesion versus the buoyancy forces. An illustration of this phenomenon is shown in Figure 4.1 during three time steps.


*Figure 4.1: Buoyancy of bunker oil emulsion in three time steps.*

In Figure 4.2 pictures of different crude oil emulsions and bunker oil emulsion in the initial phase after on solid substrates 1 hour after initiation of the buoyancy testing is shown. With both Norne and Kobbe (picture not shown) the oil was not remobilized, whereas for both the Troll and IFO380 the emulsions were released from the substrate and floated to the surface. In this type of study the only forces that affected the oil was buoyancy with no wave exposure.

Troll

Norne IFO380

*Figure 4.2; Refloating of oil emulsion from solid substrates for different crude oil emulsions and bunker oil emulsion.*

To study the remobilisation of oil emulsions from solid substrate (simulation the acute phase) the simulated shoreline system was used. This experimental system has also be used for other restoration phase activities in the present project on Oil fines interaction (C4.3) , Wash-out (C4.2) and Erosion (C4.5). The main difference between the present study and the restoration phase activities are use of emulsion layers with higher thickness and horizontal acclimatisation for only one hour prior to use. Picture from the wave exposure studies is given in Figure 4.3 with Troll oil emulsion. As can be seem in this picture much of the oil are removed from the shale surface and attached to the interior wall of the container. Quantification of remobilised oil (refloat and wash-out) could not be calculated directly, but as a difference of oil quantity after and before exposure.

*Figure 4.3: Shale tiles after exposure (24 hours) to waves action in the simulated shoreline system with mobile oil*

Tiles after "exposure" in both stagnant and with wave exposure are shown in Figure 4.4. The pictures show clearly that the oil removal by buoyancy and/or wash-out in the acute phase are patchwise and not a gradually reduction in oil layer thickness. The results from these studies are, for more easily comparison, presented as average oil layer thickness.

All experiments are performed in three parallels, and the average standard deviation are 36% and 28% for the acute and restoration phase, respectively. This is relatively high, but is mainly due to the patch wise removal mechanisms of the oil, and a relatively small experimental area (15x15cm) for each tile.



*Figure 4.4: Tiles after exposure (24h) for stagnant (above) and wave action (below) for the different oil emulsions (left to right; Troll, Kobbe, Norne and IFO380) and the two different oil film thicknesses (Front row; 2mm, Back row 10mm)*

**4.2 Oil types**

The behaviour of the four JIP-oil were studied under both static and dynamic condition at two different oil layer thicknesses, 2mm and 10mm. The data from these studies are presented in Figure 4.5 and Figure 4.6 respectively.

For the 2mm oil layer studies no oil refloating was observed during 24 hours for any oil emulsion, showing that the adhesion forces was stronger than the buoyancy. With wave exposure approximately half (41-58%) of the emulsion was remobilised for the crude oil emulsions, but all bunker oil emulsion remained at the sediment surface with the bunker oil emulsion.

For the 10mm layer emulsion studies, remobilisation was observed for both Troll crude oil emulsion (36%) and the bunker oil emulsion (18%) under static conditions, as shown by pictures previously in Figure 4.2. No refloating was observed with the Norne and Kobbe emulsion. Under dynamic condition (wave exposure) most of the crude oil emulsions were remobilized (84-86%). A significantly lower remobilisation was observed for the bunker oil emulsion (26%) than the crude oil emulsions. The wave exposure increased the remobilisation as compared to the static condition, 26% and 18% respectively.

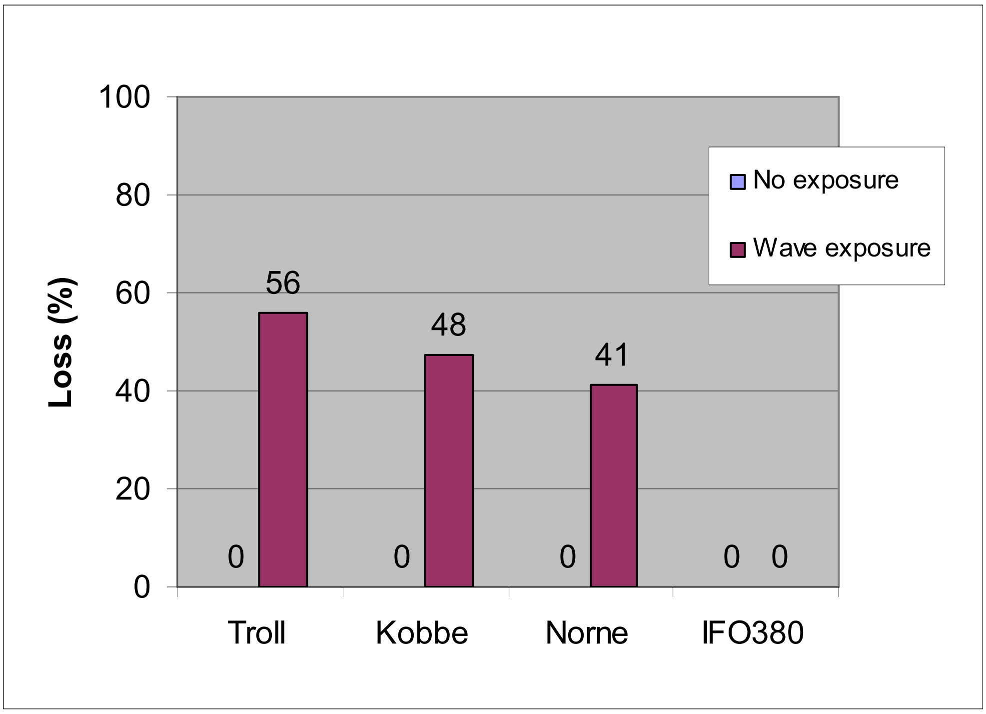


*Figure 4.5: Refloating of emulsion under static and dynamic condition for 2mm oil lay thickness*

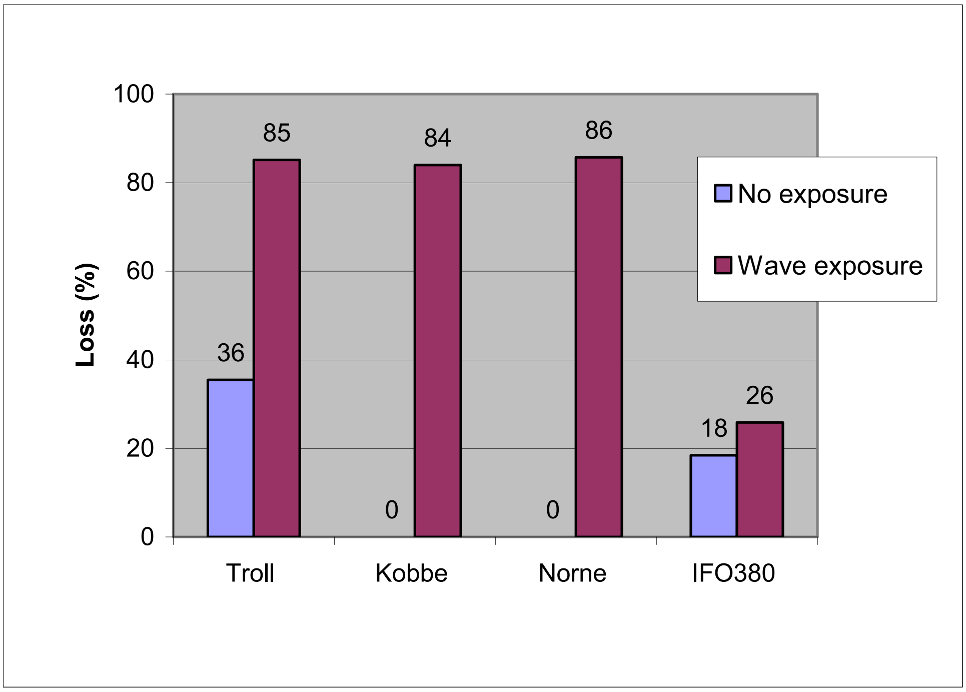


*Figure 4.6; Refloating of emulsion under static and dynamic condition for 10mm oil lay thickness*

**4.3 Oil properties and loading**

A number of parameters will affect the behaviour of oil emulsions during and after stranding in the acute phase. In this study the effect of oil loading (oil layer thickness) and oil properties (photo-oxidation) have been studied using Troll 250$^{o}$C+ emulsion (70% water) under dynamic conditions. Different oil layer thicknesses (4 and 3 thicknesses for 250$^{o}$C+ and photo-oxidized Troll respectively) in the range of 1 to 8 mm under dynamic conditions for 24 hours. The result from these studies are presented as % loss of emulsion from the sediment surface in Figure 4.7, and as the average film layer thicknesses in Figure 4.8. The results shows that oil remobilisation increases with increasing oil layer thickness down to approximately 2mm, and the resulting oil film thickness reaches an upper level with an initial layer thickness of 4mm.

With photo-oxidized Troll oil emulsion the remobilisation is lower as compared to the Troll crude oil residue emulsion. This was observed for all oil layer thicknesses that was tested in the present study, which is mainly due to an increased in adhesion properties generated by components generated through the photo-oxidation process. This phenomenon has also been observed in other studies in the present project.

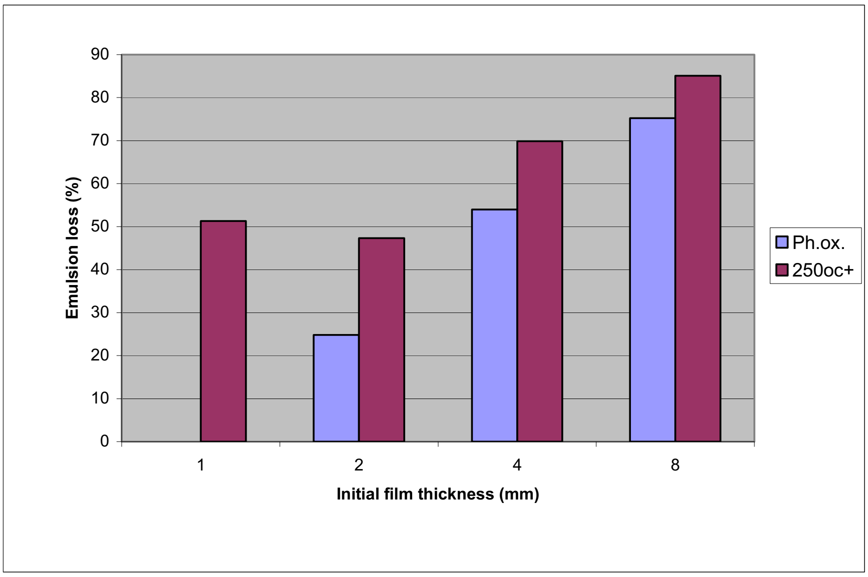


*Figure 4.7: Effect of oil layer thickness for Troll 250$^o$C+ and Troll photo-oxidized on remobilisation under dynamic condition*

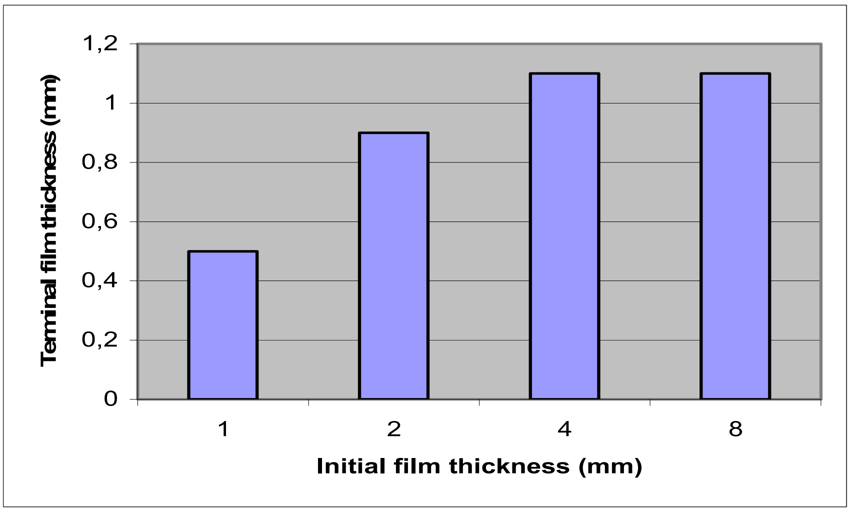


*Figure 4.8: Average terminal emulsion layer thickness of Troll 250$^o$C+ emulsion after remobilisation under dynamic conditions.*

# 5 Conclusions and operational gains

Remobilisation by refloating and wash-out of stranded oil (acute phase) were studied in the simulated shoreline system under dynamic and static conditions.
The main conclusions from the present study are;

- Remobilisation of stranded oil emulsion are dependent on oil properties
- Crude oil emulsion are more easily remobilized compared to bunker oil emulsion.
- Remobilisation increases with increasing wave exposure
- Remobilisation increases with oil loading under dynamic condition
- Remobilisation decreases with photo-oxidized oil emulsion

The observations and findings from the present study clearly shows the difference between weathered crude oil emulsion and bunker oil emulsion which could affect the strategies for oil spill contingency plan and operation. The crude oil emulsion are more easily remobilized and requires booming of contaminated shoreline sections to avoid further spreading of the contaminants.
The effect of photo-oxidation on remobilisation which represent winter and summer condition were minor and should not affect the contingency plan based on results for the present study.

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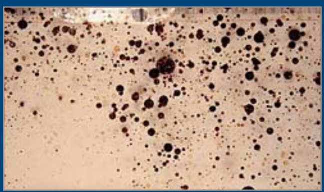
# REPORT



## Coastal Oil Spills - JIP

Report no.: 10

# C4.2 - Wash-out of weathered oil from solid shoreline substrate

Jane H.C. Øksenvåg, Svein Ramstad and Merete Ø. Moldestad

**SINTEF Materials and Chemistry**
Marine Environmental Technology

Date: 2008-12-17

# SINTEF REPORT

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TITLE

**C4.2 Wash-out of weathered oil from solid shoreline substrate**

**Coastal Oil Spills JIP. Report No. 10**

AUTHOR(S)

Jane H.C. Øksenvåg, Svein Ramstad and Merete Ø. Moldestad

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| | 2008-12-16 | Tore Aunaas, Research director | |

ABSTRACT

The objective of this project was to get a better understanding of the ruling parameters for the wash-out of weathered oil after an oil spill have stranded on shore. The effect of oil type, sun exposure, wave exposure degree and substrate texture have been tested using immobile emulsions adhered to solid substrate. For this study a shoreline simulation system was used. The studies were done under temperate controlled conditions at 5˚C, simulating north and winter conditions.

Three crude oils; Troll, Kobbe and Norne and one bunker fuel oil, IFO 380, were used as test oils. The oils were weathered before application on bedrock tiles to represent the properties of oils drifting at sea for approximately one week. The tiles were then introduced to the shoreline simulation system and subjected for wave exposure. The quantity and rheological properties of the emulsion retained on the tiles were measured before, during and after the wash-out process.

The results show that oil type and energy level are ruling parameters for the wash-out of emulsion on contaminated shorelines. The high energy regime more than doubled the wash-out effect for the crude oils, than for the low energy regime. For the oils receptive for wash-out, most of the emulsions were washed out during the first days. Fine textured bedrock increased the rate of wash-out for the Troll oil. Photo-oxidation retarded the wash-out process. The oils rheological properties, as viscosity and yield stress seem to be essential for the wash-out of emulsion.

| KEYWORDS | ENGLISH | NORWEGIAN |
|---|---|---|
| GROUP 1 | Chemistry | Kjemi |
| GROUP 2 | Environment | Miljø |
| SELECTED BY AUTHOR | Coastal oil spill | Kystnær oljesøl |
| | Wash-out | Utvasking |

# TABLE OF CONTENTS

# 1 Summary

The objective of this activity was to find the ruling parameters that influence the wash-out of immobile emulsions from solid shoreline substrate in the restitution phase of an oil spill stranded onshore.

Three crude oils; Troll, Kobbe and Norne and one bunker fuel oil (IFO 380) was used as test oils to get a better understanding of the fate of an emulsion after an oils spill stranded onshore. Parameters tested were oil type, exposure degree, substrate texture and the effect of sun exposure. The wash-out of emulsion was simulated under controlled conditions at 5˚C using a shoreline simulating system.

The results show that oil type and energy level are important factors for the wash-out of emulsion on contaminated shorelines. Troll and Kobbe, with low viscosities, were more easily subjected for wash-out compared to the Norne and IFO 380 emulsions, with high viscosities. Increasing the wave energy level, more than doubled the wash-out effect for the crude oils. For the Kobbe emulsion, photo-oxidation reduced the wash-out effect with about 30% for the high energy level. For the Troll oil, the fine textured bedrock increased the wash-out rate with about 60%, leaving little or no oil left one the bedrock. The bunker fuel oil (IFO 380) did not get washed out for any of the parameters tested.

This result indicate that shorelines polluted with oils like Troll and Kobbe might be naturally cleaned with time if the energy level in the area is sufficient (especially for fine textured bedrock), this compared to the Norne and IFO 380 emulsions, most likely having a need for artificial restorations techniques for a sufficient clean up. Oil spills during summertime might show a slower wash-out of emulsion, compared to oil spills during wintertime. This must be taken into consideration for countermeasure planning.

Data found in this study should be comparable with results found at Cedre, using the same experimental setup but at different test temperatures. SINTEF and Cedre are now in the process of coordinating experimental setups and standard operational procedures to get a better comperisment of results and knowledge about oil science. For further studies, a test matrix with an extended number of test parameters including; temperature representing summer conditions (13˚C) and weathering degree (water content and evaporation) would be recommended. The data gained can be used for a further development of numerical models. Well designed experiments at dedicated sites in the field, for both summer and winter conditions, are needed for a validation of the experimental results.

## 2 Introduction

This project has been a part of phase 1 in the Coastal Oil Spills JIP. The research projects in the JIP have been focused on the fate and behavior of oil spills in coastal areas and on shoreline. Laboratory studies have been performed in order to obtain data for further development of numerical models.

The first phase of the JIP was performed in the period from 2006 to 2008, and was funded by Eni Norge, Shell Technology and StatoilHydro. The overall objectives of the JIP have been:

- to contribute to an adequate and sufficient basis of competence to document possible consequences in case of an oil spill close to the coast
- to provide documentation ensuring the countermeasures giving the optimal environmental gain

Oil spills stranded on shore will be subjected for several natural physical and chemical processes as; biodegradation, photo-oxidation and wash-out. These processes will separately or together contribute to a degradation and removal of weathered oil from the shoreline. The significance of the different processes is dependent on the oil type spilled, environmental parameters and type of shoreline substrate.

The objective of this activity was to get a better understanding of the ruling parameters for the wash-out of immobile emulsion from solid shoreline substrate under controlled conditions using a standardised shoreline simulation system.

Depending on the circumstances, parts of an oil spill at sea might survive several days before stranding onshore. This depends on several factors including; spill distance from shore, weather conditions, oil type, release conditions etc. During the time at sea, the oil will be exposed to several weathering processes as evaporation, emulsification and photo-oxidation (particularly in the summer time). The oil will continue to weather also after stranding, the ruling weathering processes will change, and other chemical and biological processes will be important. Weathering of oil changes the oils physiochemical properties and further decides its fate on shore.

With time, oil stranded on shore may be released and removed from the substrate surface due to hydrodynamic and physical exposures as wave energy and tidal changes. Immobile oil may be resistant to the wave and tidal exposure and might need a great deal of time before degrading, if needed, response measures must be initiated.

In 2005, SINTEF adopted a shoreline simulating system from Cedre in Brest (France) to study the wash-out of oil from bedrock. The wash-out experimental system was established and standardised through the project *"Utvasking av Realgrunnen-olje fra fast substrat"* (Ramstad and Nygaard, 2006) carried out by SINTEF for ENI Norge (2005-2006). Based on the experimental work done in that project, a standard operating procedure (SOP) for quantification of washed out oil from bedrock in the restitution phase was elaborated. This was used as a background in this study.

# 3 Experimental

## 3.1 Materials

### 3.1.1 Oil types and weathering degree

Crude oils can be characterised in four categories: asphaltenic, napthenic, paraffinic and waxy crude oils. The crude oils studied in the Coastal Oil Spills JIP were selected among the oil companies' crude oils. It was important to select crude oils representing different categories of oils. The selected crude oils represent the categories:

- Troll – napthenic crude oils
- Norne – waxy crude oils
- Kobbe – light paraffinic crude oils

In addition to the crude oils, a heavy fuel oil (IFO 380) was tested. IFO 380 is representing bunker oils used as fuel for ships going along the Norwegian coast. The content of light oil components in fuel oils is low, typically lower than 5 vol% for IFO 380 oils. The light oil components are generally in a boiling point area up to 250°C. The testing of the IFO 380 was therefore concentrated on the "fresh" fuel oil, not on an evaporated residue. The IFO 380 oil used in this project is a low sulphur fuel oil produced at the Esso refinery at Slagentangen. Some physical and chemical properties of the oils studied are listed in Table 3.1-1.

**Table 3.1 Oils used in the Coastal Oil Spills JIP.**

| SINTEF Id | Oil type | Residue | Density (Kg/m$^3$) | Evaporative Loss (Vol%) | Pour point (°C) | Wax (wt%) | Asphaltenes (wt%) |
|---|---|---|---|---|---|---|---|
| 07-0287 | Troll | Fresh | 0,900 | 0 | -36 | 0,9 | 0,04 |
| | | 250°C | 0,930 | 25,5 | -27 | | |
| | | Ph.ox. | 0,931 | - | -21 | | |
| 07-0260 | Norne | Fresh | 0,860 | 0 | 21 | - | 0,3 |
| | | 250°C | 0,888 | 28,4 | 30 | | |
| | | Ph.ox. | 0,885 | - | 30 | | |
| 06-1061 | Kobbe | Fresh | 0,797 | 0 | -39 | 3,4 | 0,03 |
| | | 250°C | 0,875 | 53,6 | 21 | | |
| | | Ph.ox. | 0,877 | - | 15 | | |
| 06-1125 | IFO 380 | Fresh | 0,963 | 0 | 15 | 5,0 | 3,4 |

*-: not measured*

Oil spilled at sea will be subjected for several weathering processes as evaporation (lighter compound evaporates), emulsification (water droplets are incorporated in the oil phase) and photo-oxidation (changing the physical and chemical properties due to sun exposure). These weathering processes will change the physicochemical properties of the oil, being of great importance for the weathered oils fate and behaviour on the shoreline

For the crude oils, an evaporated residue of 250˚C+ was used. The 250°C+ residue corresponds to ½ - 1 week weathering of oil at sea, and will be representative for stranded crude oil along the Norwegian coast.

To ensure reproducible production of emulsions, a water content just below the maximum water uptake for the respective oils was used. After some initial studies, the standard water content was decided to be 70% for Troll, 75% for Kobbe, 60% for Norne and 40% for IFO 380.

To study the effect of photo-oxidation, the crude oils (Troll, Kobbe and Norne) were exposed for a solar simulator. The photo-oxidized oils represent oils exposed 5 days under ordinary sunlight exposure in the summertime. During this process, the oils were naturally evaporated to a 250˚C+ residue.

Evaporation, emulsification and photo-oxidation were performed according to established SINTEF lab procedures. For more information about the physical and chemical properties of the oils and weathering procedures, see *Technical report C2.2* (Ramstad *et.al.*, 2008).

### 3.1.2 Bedrock

Shale tiles of 15*15 cm were used as a standard in the experiments to represent bedrock with a medium texture. In addition, artificial cut shale tiles was used to represent a more fine textured bedrock and tiles of granite to represent a more rough textured bedrock. The different textures are shown in Figure 3.1-1.

**Figure 3.1-1 The tiles used in the experiments. From left: rough texture (granite), medium texture (shale) and fine texture (artificial cut shale)**

The shale tiles originate from Alta in Finnmark, Norway. The granite tiles are used at Cedre and are shipped from France. Shale is a sedimentary bedrock and is known for its high content of quarts which make the rock resistant for exposure (http://www.alta-skiferbrudd.no). Granite is a magmatic bedrock made from harden magma. It contains quarts, feldspar and biotite, where feldspar is the most dominating mineral. Both bedrocks are quite common along the Norwegian coast, shale in the north to the middle of Norway and granite in the southern parts of Norway.

## 3.2 Experimental setup

### 3.2.1 The shoreline simulation system

SINTEF have built up two identical shoreline simulation systems which each contains 12 reservoirs installed on an oscillating table. Single tiles are placed in each of the reservoirs, see Figure 3.2-1. The shoreline simulation system is placed in a temperature controlled room to ensure the required test temperature.

**Figure 3.2-1 The shoreline simulation system (to the left) and the water reservoirs (to the right).**

The simulation systems generate wave energy by tilting the oscillating table from one side to another with a standard angel and frequency, as shown in Figure 3.2-2. For this purpose a compressed air jack along with a control unit programmed for a uniform movement is used.

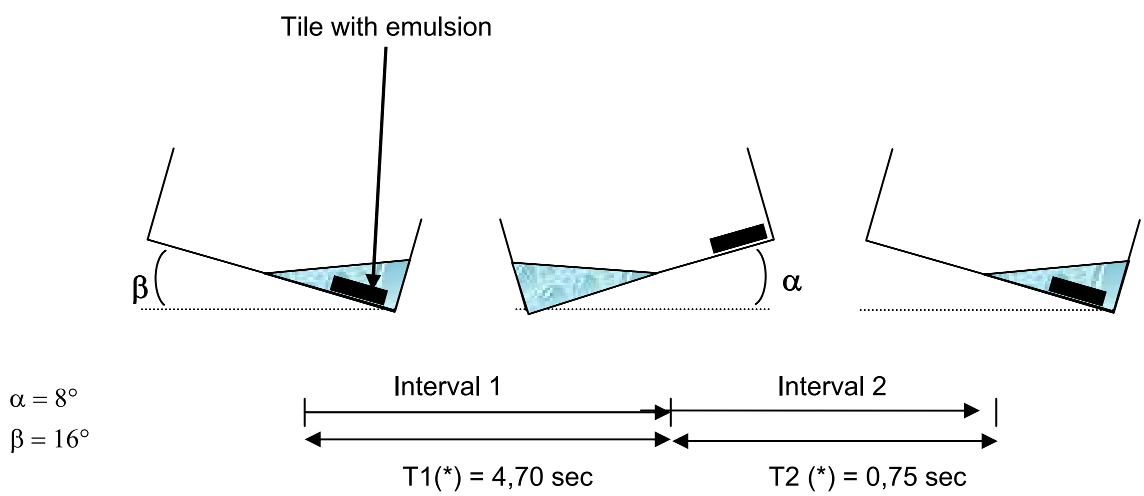


**Figure 3.2-2 The mechanism of the oscillating table – shoreline simulation system.**

### 3.2.2 Regulation of exposure degree

The exposure degree was regulated by adjusting the amount of water applied to the individual reservoirs. The reservoirs were applied 1 and 2 litres of seawater, representing high energy levels in the shoreline simulation system, and 4 litres representing a low energy level. To quantify and study the different energy levels more in detail, a numerical simulation of water flow in the reservoirs was performed. . The flow regime was simulated with a Computational Fluid Dynamics (CFD) model Flow-3D for point A and B, as shown in Figure 3.2-3 and Figure 3.2-4.

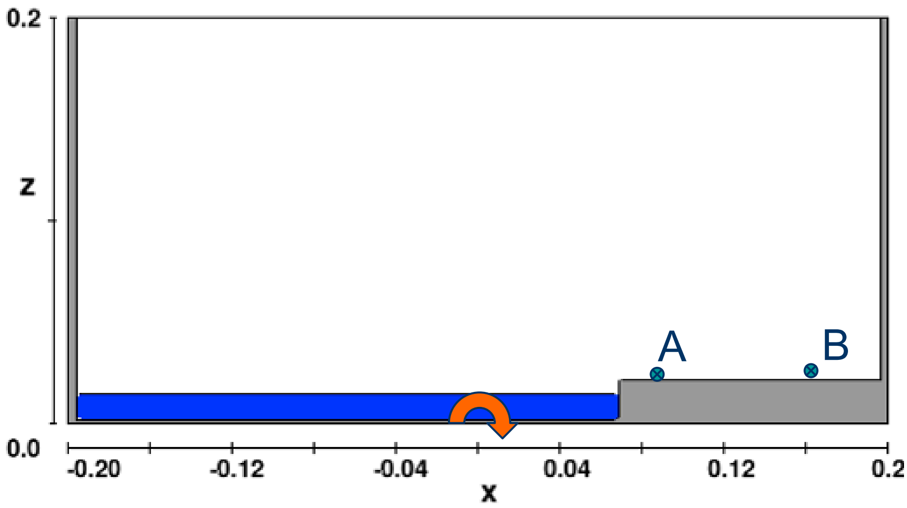


**Figure 3.2-3 Reservoir with tile, showing point A and B for velocity measurements.**

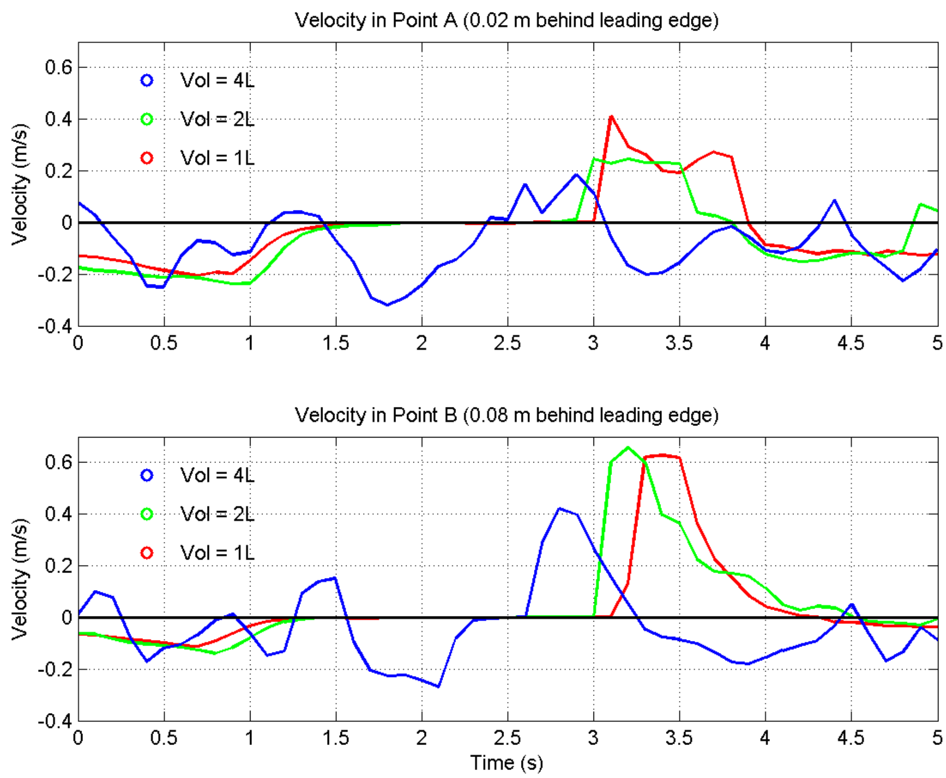


**Figure 3.2-4 Velocity profile simulation for point A and B on tiles in reservoirs containing 1, 2 and 4 litres of seawater, using a CFD model Flow-3D.**

The 1 litre (red line) and 2 litres (green line) cases showed approximately the same energy levels: During time t= 3 – 4 s a wave swept across the tiles with u ~ 0.3 – 0.6 m/s, it then retracted with u ~ - 0.15 m/s during the next couple of seconds, leaving the top of the tile dry for about 1.5 – 2 seconds until the next wave hit. The 2 l case had an additional weak secondary hit in point A at t = 4.8 s. The 4 l case was different, displaying three secondary hits by the reflected wave. The tile was constantly covered with seawater.

### 3.3 Experimental procedures

Before introducing the tiles to the shoreline simulation system, the reservoirs were filled with seawater and placed on the oscillating table for water tempering.

#### 3.3.1 Tile preparation

Before emulsion application, the edges of the tiles were masked with tape to avoid quantification of emulsion covering the edges. The tiles were weighed before masking of the edges to document the initial weight. Emulsion (22,5 g +- 0,5) were applied evenly on the bedrock surface and placed horizontally for 1 day to let the emulsion cover the tile evenly. The tiles were then placed vertically for 4 days to let the excess emulsion run-off and to simulate secondary weathering of emulsion on the shoreline.

#### 3.3.2 Sampling, photo documentation and quantity analysis

Tile samples were retrieved from the shoreline simulation system during the wash-out process for quantification of washed out emulsion. The experimental period extended between 0 and 28 days, depending on the parameters tested. Before emulsion quantification, the samples were placed vertically in a temperature controlled room at test temperature for 30 min to let the excess water run-off, the tape on the edges were then removed. The tiles were photo documented at application of emulsion, after run-off of excess emulsion, during and after experimental period. In some situations there were too little emulsion left on the tiles to ensure good quality of the quantitative weight measurements, the samples was then extracted in DCM and analysed in a Hitachi U-2000 spectrophotometer.

#### 3.3.3 Oil properties

To study the oils rheology, a Physica MCR300 MC1+ rheometer with an US200 software was used. Parameters measured were; viscosity, storage modulus, loss modulus and yield stress. To get an indication of how the restitution phase effected the emulsion properties, the parameters were measured before application on the tiles, after run-off of excess emulsion, during sampling and after test period. For some of the studies, too little emulsion was left on the tile surface to do all the measurements, the viscosity measurement was then prioritised. Density and pour point for the different oils were measured initially.

### 3.4 Experimental parameters and design

Four different experimental parameters were tested in this study:

- **Exposure degree**
  Three different seawater loadings, 1, 2 and 4 litres, were used to study the effect of different exposure degrees.
- **Oil types**
  Three different crude oils; Troll, Kobbe, Norne and one bunker fuel oil; IFO 380 was used to study the effect of oil type.
- **Bedrock texture**
  Two different bedrock textures were used to study the effect of bedrock texture. The three different tiles used were: medium texture (shale), fine texture (artificial cut tiles of shale) and rough texture (granite).
- **Photo-oxidation of crude oil**
  Photo-oxidized Kobbe were used to study the effect of sun exposure.

To validate the results, most of the experiments were done in triplicates. The standard deviation shows up to 10% deviation for the run-off of excess oil and up to 30% for the retained emulsion on the tiles after wash-out. This was considered as an acceptable variance. Some of the experiments were done as singles when screening test showed no wash-out of oil. Table 3.4-1 gives an overview of the experimental design, including the experimental parameters for this activity and the sampling frequency.

**Table 3.4-1 Experimental design (WiO – Water in oil / emulsification).**

| SINTEF ID | Oil | WiO | Evaporated | Spesification | Start | 1 | 2 | 3 | 5 | 7 | 8 | 9 | 14 | 15 | 16 | 28 days |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 2007-0287 | Troll | 70 % | 250°C+ residue | Standard (4 l, medium texture) | x | | x | | x | x | | x | x | | | x |
| | | | | Exposure degree - 1l | x | | x | | x | | | | | x | | |
| | | | | Exposure degree - 2l | x | | x | | x | | | | | x | | |
| | | | | No exposure | x | | | | x | | | | | x | | |
| | | | | Rock texture - Fine | x | | x | | x | | | x | | | | |
| | | | | Rock texture - Rough | x | | x | | x | | | x | | | | x |
| 2006-1061 | Kobbe | 75 % | 250°C+ residue | Standard (4 l, medium texture) | x | | | x | | x | | | x | | | x |
| | | | | Exposure degree - 2l | x | x | | x | | x | | | x | | | |
| | | | | No exposure | x | | | | x | | | | | x | | |
| 2007-0260 | Norne | 60 % | 250°C+ residue | Standard (4 l, medium texture) | x | | x | | x | x | | | x | | | x |
| | | | | Exposure degree - 2l | x | x | | x | | | x | | | | x | |
| | | | | No exposure | x | | | | x | | | | | x | | |
| | | | | Rock texture - Fine | x | x | | x | | | x | | | | x | |
| | | | | Rock texture - Rough | x | x | | x | x | | x | | | x | x | |
| 2006-1125 | IF 380 | 40 % | | Standard (4 l, medium texture) | x | | | | | x | | | x | | | x |
| | | | | Exposure degree - 2l | x | | | x | | x | | | x | | | |
| | | | | No exposure | x | x | | x | | | | | | | | |
| | | | | Rock texture - Fine (2 l) | x | | | x | | x | | | x | | | |

# 4 Results and discussions

Table 4-1 show the experimental parameters used in this activity:

**Table 4-1 Experimental parameters.**

| Parameter | Variation |
|---|---|
| Oil type | • Troll crude<br>• Kobbe crude<br>• Norne crude<br>• Bunker fuel oil - IFO 380 |
| Evaporation | 250°C+ residue (crude oils)<br>Photo-oxidation (crude oils) |
| Water content in emulsion | • 70% (Troll)<br>• 75% (Kobbe)<br>• 60% (Norne)<br>• 40% (IFO 380) |
| Temperature | 5°C |
| Emulsion thickness / loading | 1 standard film thickness – 1 mm (22,5 g) |
| Bedrock | • Medium texture - shale (Standard)<br>• Fine texture - artificial cut shale<br>• Rough texture - granite |
| Exposure degree | • 4 litres<br>• 2 litres<br>• 1 litre |

To get a better understanding of how the weathering of emulsion on bedrock affects the rheological properties of the oils, several rheological parameters were measured. A definition of the different properties is given in *Appendix 1*. The rheological parameters measured is given in *Appendix 2.*

To study the correlation between wash-out data and the rheological properties for the emulsified oils, the data was run through a simple correlation routine with commercial software (Excel). The results showed that yield stress and viscosity were of relevance for the retention of emulsion. The results from the correlating study are given in *Appendix 3.*

Photo documentation for the studies is given in *Appendix 4.*

## 4.1 Exposure degree

**Table 4.1-1 Experimental parameters used in this study.**

| **Parameter** | **Variation** |
|---|---|
| Oil type | Troll, Kobbe, Norne and IFO 380 |
| Evaporation | 250°C+ residue (Crude oils) |
| Water content in emulsion | 70% (Troll), 75% (Kobbe), 60% (Norne), 40% (IFO 380) |
| Temperature | 5 °C |
| Emulsion thickness / loading | 1 mm (22,5 g) |
| Bedrock | Shale – medium texture |
| **Exposure degree** | **1, 2 and 4 litres** |

Three different amounts of seawater were used in the shoreline simulating system for the selected oils to study the wash-out of emulsion dependent on exposure degree. The amount of emulsion remained on the bedrock surface, dependent on exposure degree, for the Troll oil is shown in Figure 4.1-1.

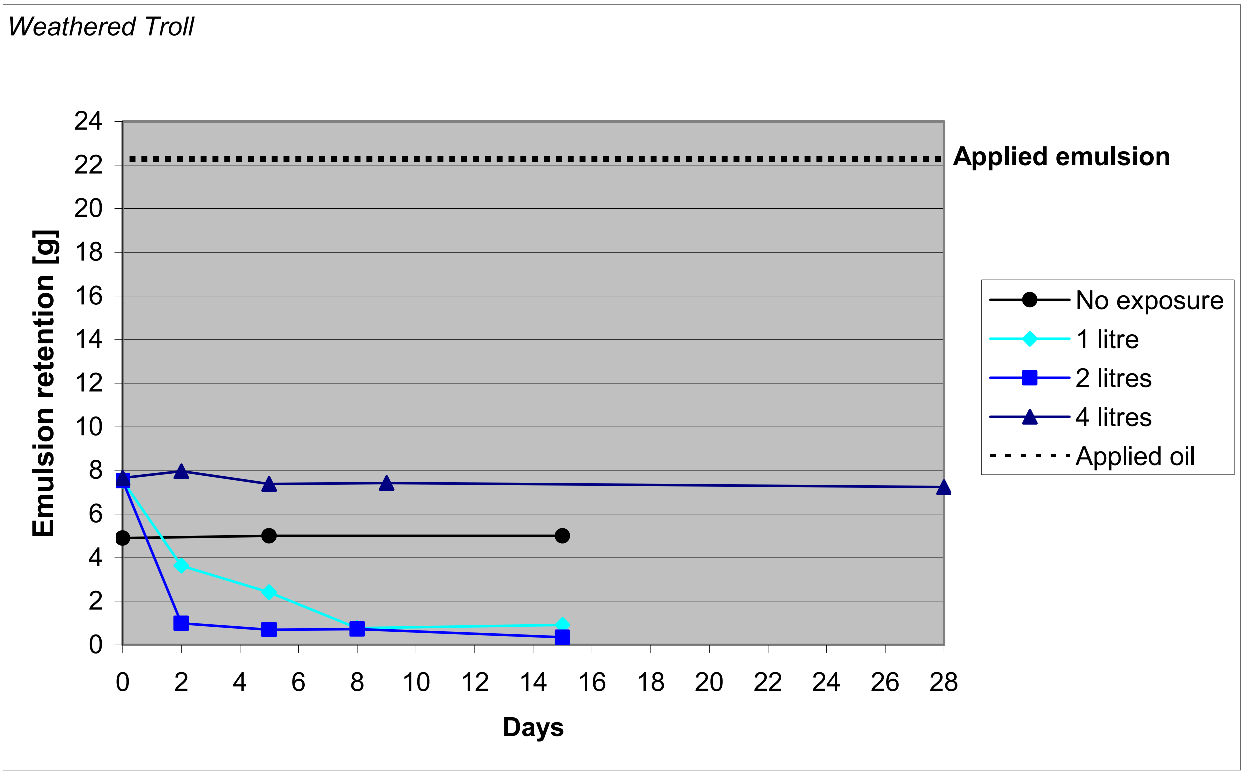


**Figure 4.1-1 Remaining emulsion for the Troll oil as a function of exposure degree.**

Figure 4.1-1 show a larger wash-out rate for the 1 and 2 litres energy levels, representing high exposure degrees, compared to the 4 litres energy level representing a low exposure degree (in the shoreline simulation system). The 1 litre exposure degree, showed a little slower wash-out response, than the 2 litres exposure degree, but resulted at approximately the same wash-out degree after 8 days. This might be due to the extra peak in energy exposure for the 2 litres velocity distribution screening, see Figure 3.2-4. Most of the Troll emulsion drained off the tiles when placed vertically. This was probably due to its combination between low yield stress at application on the tiles and low pour point.

Since the Troll oil showed little difference in wash-out degree, dependent on the energy levels representing 1 and 2 litres, it was decided to only proceed with the 4 and 2 litres energy levels for the other oils.

The amount of emulsion remained on the bedrock surface, dependent on exposure degree, for the Kobbe oil is shown in Figure 4.1-2.

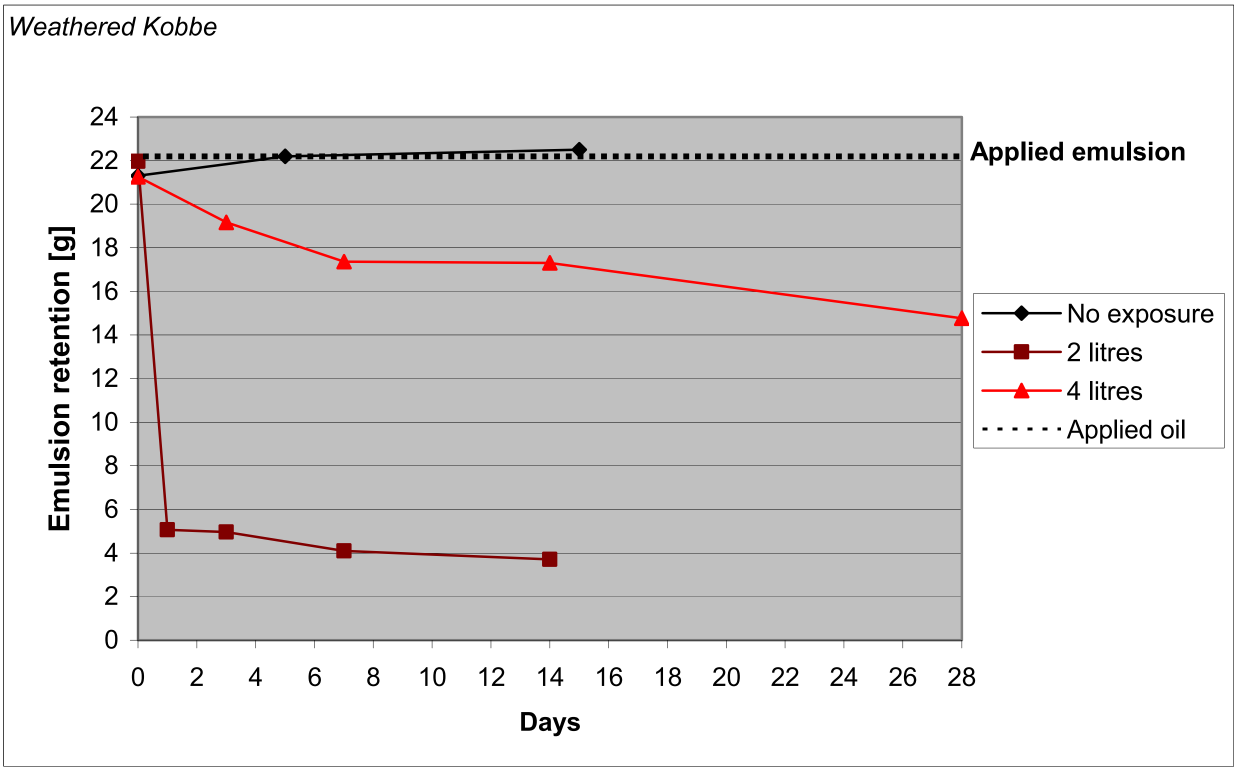


**Figure 4.1-2 Remaining emulsion for the Kobbe oil as a function of exposure degree.**

As observed for Troll and Kobbe the data showed a much higher wash-out of emulsion at the high energy level (2 litres), compared to the low energy level (4 litres), see Figure 4.1-2. For the high energy level, most of the emulsion was washed out during the first day.

The Kobbe emulsion had a tendency to break during the 5 days of weathering before introduction to the shoreline simulation system (seawater segregating from the water in oil emulsion). The emulsion might then have been more receptive for wash-out as the viscosity decreased. Nothing of the Kobbe oil drained off the tiles during the 5 days, leaving about 100% of the applied emulsion available for wash-out.

The amount of emulsion remained on the bedrock surface, dependent on exposure degree, for the Norne oil is shown in Figure 4.1-3.

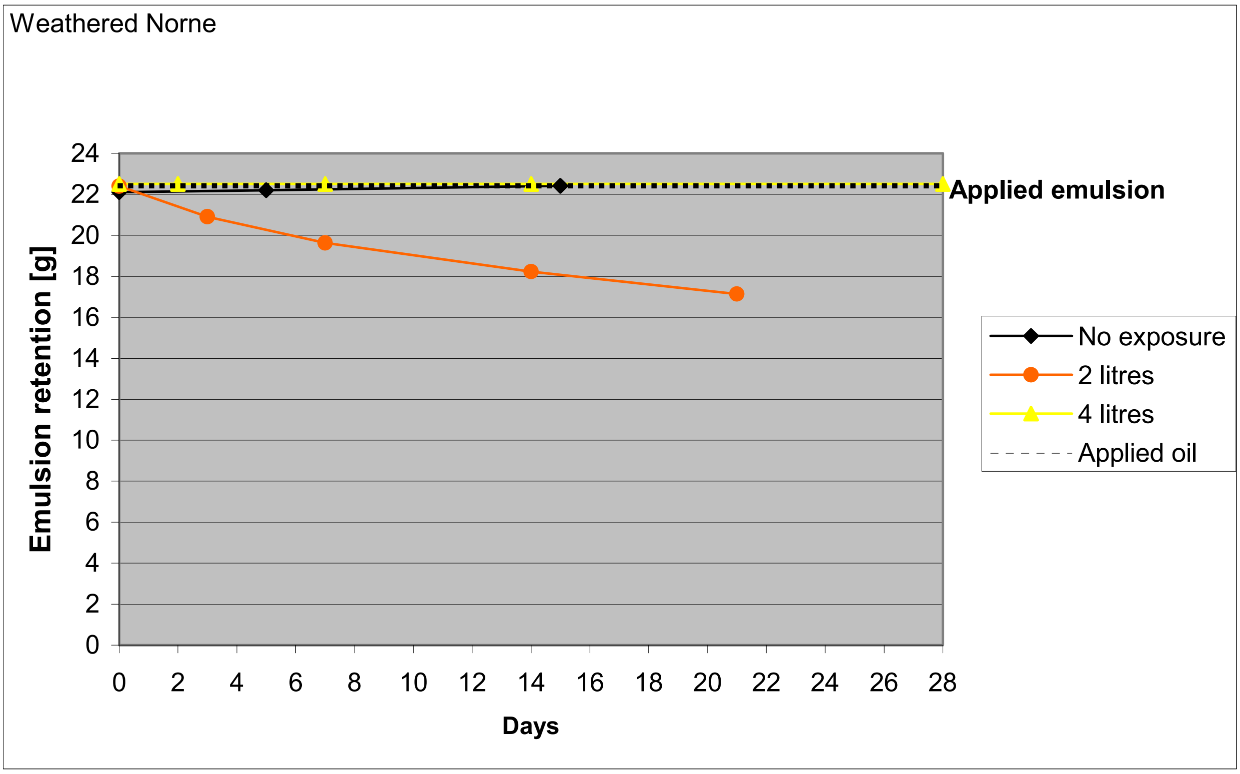


**Figure 4.1-3 Remaining emulsion  for the Norne oil as a function of exposure degree.**

For the Norne emulsion, no wash-out of emulsion was observed at the 4 litres exposure degree, as shown in Figure 4.1-3, a higher energy level (2 litres) was needed to observe a wash-out of emulsion. In contrast to Troll and Kobbe, the Norne emulsion was washed out after an almost linear rate. According the trend for the high energy study (2 litres), the wash-out of Norne emulsion might have continued with time.

The amount of emulsion remained on the bedrock surface, dependent on exposure degree, for the IFO 380 bunker fuel is shown in Figure 4.1-4.

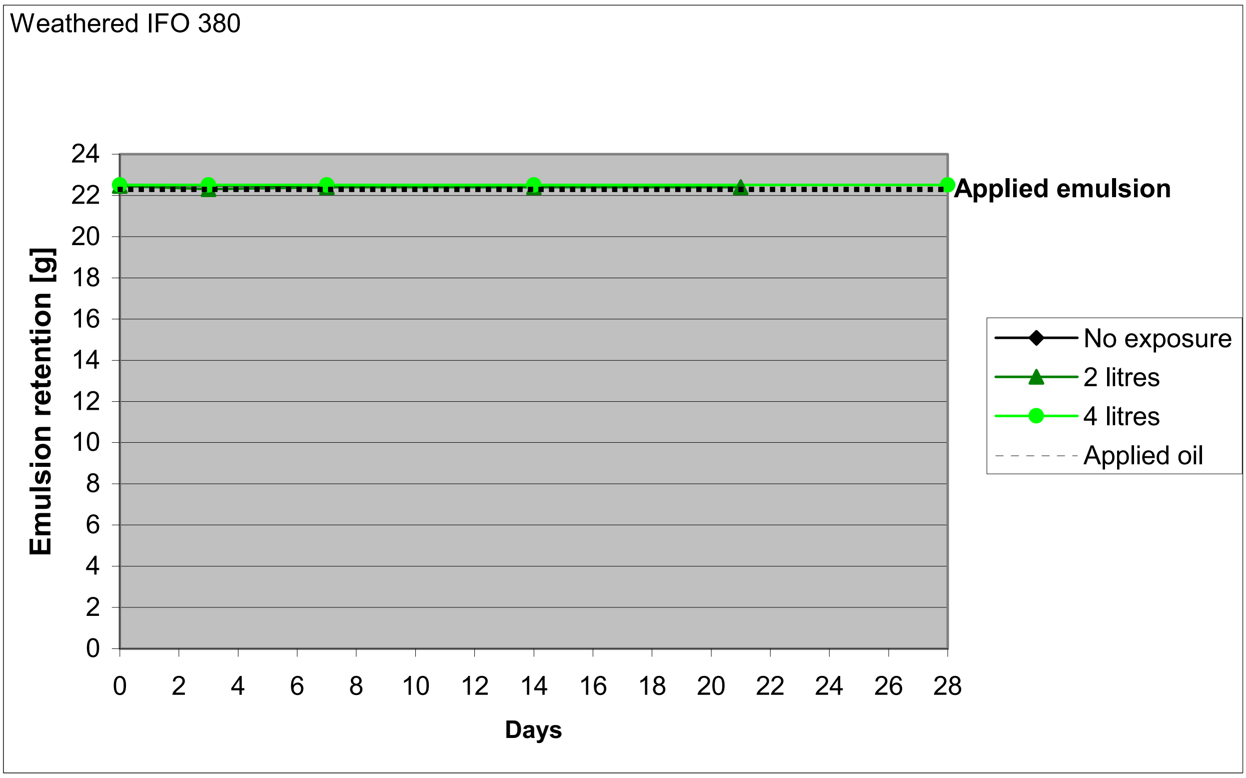


**Figure 4.1-4 Remaining emulsion for the IFO 380 oil as a function of exposure degree.**

As Figure 4.1-4 shows, there were no wash-out of IFO 380 for any of the exposure degrees tested. It was seen unlikely that the IFO 380 bunker fuel oil could be washed out at any other exposure degrees, possible simulated in the shoreline simulation system. No further exposure degree studies were therefore done.

Emulsion retention for the selected oils given in percent is shown in Chapter 4.2.

## 4.2 Oil types

**Table 4.2-1 Experimental parameters used in this study.**

| Parameter | Variation |
|---|---|
| **Oil type** | **Troll, Kobbe, Norne and IFO 380** |
| Evaporation | 250°C+ residue (Crude oils) |
| Water content in emulsion | 70% (Troll), 75% (Kobbe), 60% (Norne), 40% (IFO 380) |
| Temperature | 5 °C |
| Emulsion thickness / loading | 1 mm (22,5 g) |
| Bedrock | Shale – medium texture |
| Exposure degree | 4 and 2 litres |

Four selected oils were used in the shoreline simulating system to study the wash-out of oil dependent on oil type. Emulsion retention for the different oils, subjected for a low exposure degree (4 litres), is shown in Figure 4.2-1.

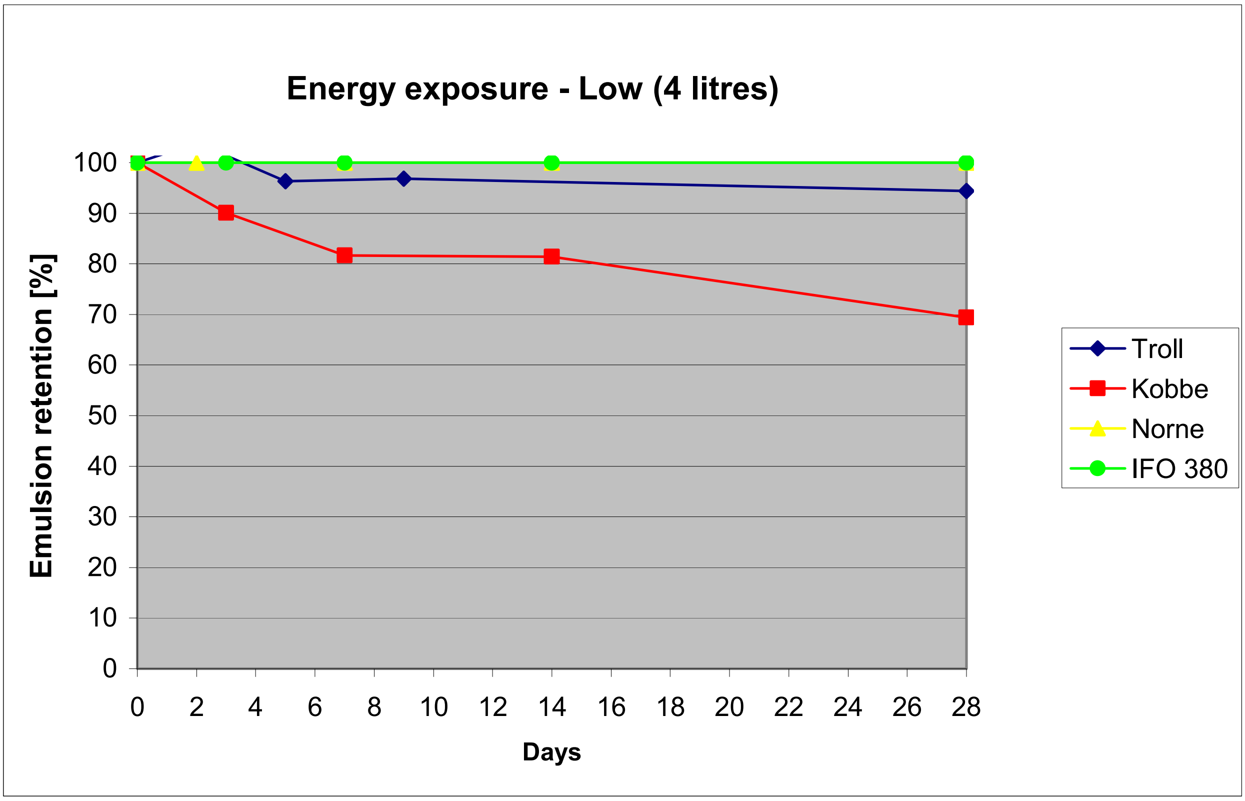


**Figure 4.2-1 Remaining emulsion as a function of oil type, subjected for a low energy exposure (4 litres).**

Figure 4.2-1 show a great wash-out of Kobbe oil compared to the other three oils; Troll, Norne and IFO 380. Much of the emulsion was washed out during the first 7 days, for then to decrease with time. After 28 days Norne and IFO 380 were not washed out at all, leaving 100 % of the applied emulsion on the tiles. Norne and IFO 380 contain relatively large amounts of wax which have a strong binding capacity (Børresen, 1993). This gives a great deal of structure in the emulsion, making it hard to drain and wash off. Most of the Troll emulsion run-off the tiles during the 4 initial days placed vertically, little were washed out in the low energy regime (4 litres).

Emulsion retention for the different oils, subjected for a high exposure degree (2 litres), is shown in Figure 4.2-2.

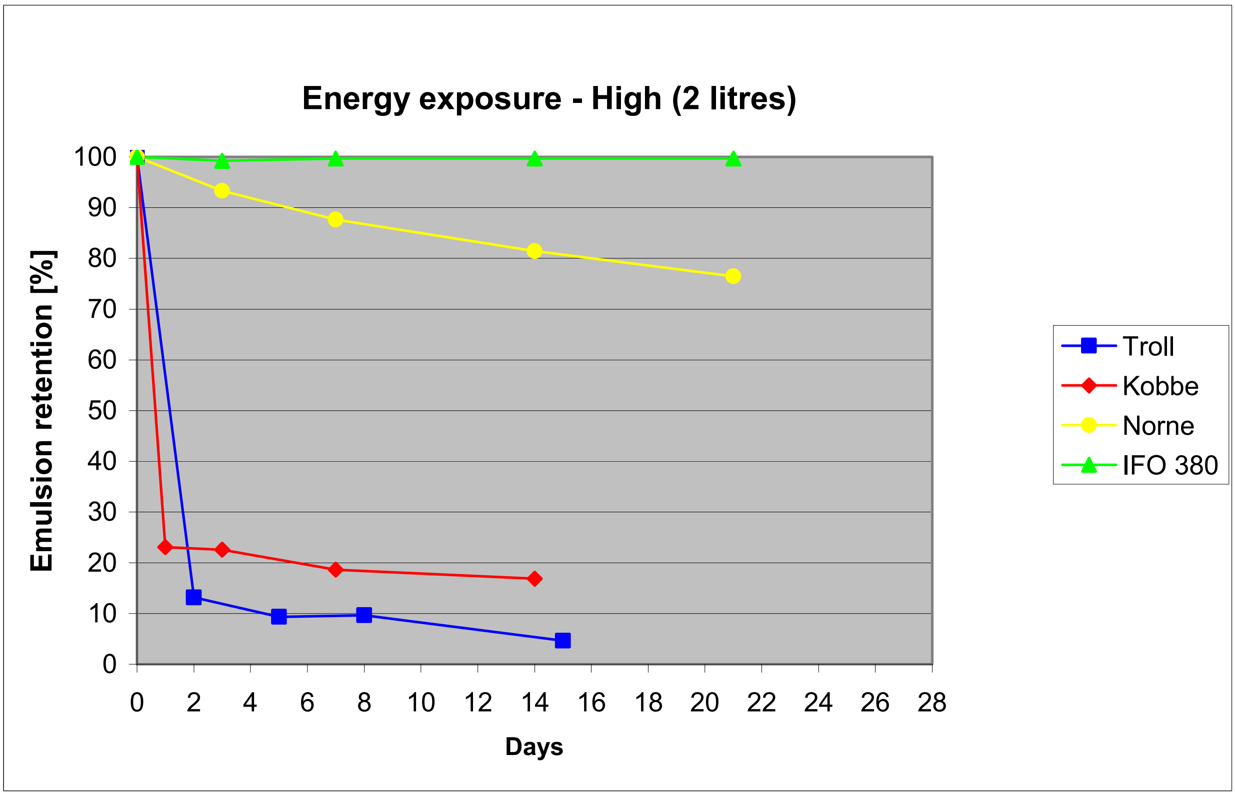


**Figure 4.2-1 Remaining emulsion  as a function of oil type, subjected for a high energy exposure (2 litres).**

Using a high exposure degree (2 litres), the results show a much higher wash-out rate for the three crude oils, compared to the low exposure degree (4 litres). Only 5% of the Troll emulsion was left on the tiles after 15 days.  Based on these studies, a high exposure degree (2 litres) would be preferred in future studies, giving a better distribution of data.

The rheological measurements showed a decrease in viscosity for Troll and Kobbe during the weathering phase on the tiles (1 day horizontally and 4 days vertically), making the emulsion more receptive for outwash, this in contrast to Norne and IFO 380 showing an increase in viscosity, see *Appendix 2*.

### 4.3 Bedrock texture

**Table 4.3-1 Experimental parameters used in this study.**

| Parameter | Variation |
|---|---|
| Oil type | Troll, Norne and IFO 380 |
| Evaporation | 250°C+ residue (Crude oils) |
| Water content in emulsion | 70% (Troll), 60% (Norne), 40% (IFO 380) |
| Temperature | 5°C |
| Loading thickness / loading | 1 mm (22,5 g) |
| **Bedrock** | **Shale – medium texture, Shale – fine texture, Granite – Rough texture** |
| Exposure degree | 4 litres and 2 litres (IFO 380) |

Two different bedrock types were used in the shoreline simulating system to study the wash-out of emulsion, dependent on bedrock texture. The amount of emulsion remained on the bedrock surface, in regards to the different bedrock textures, for the Troll oil is shown in Figure 4.3-1.

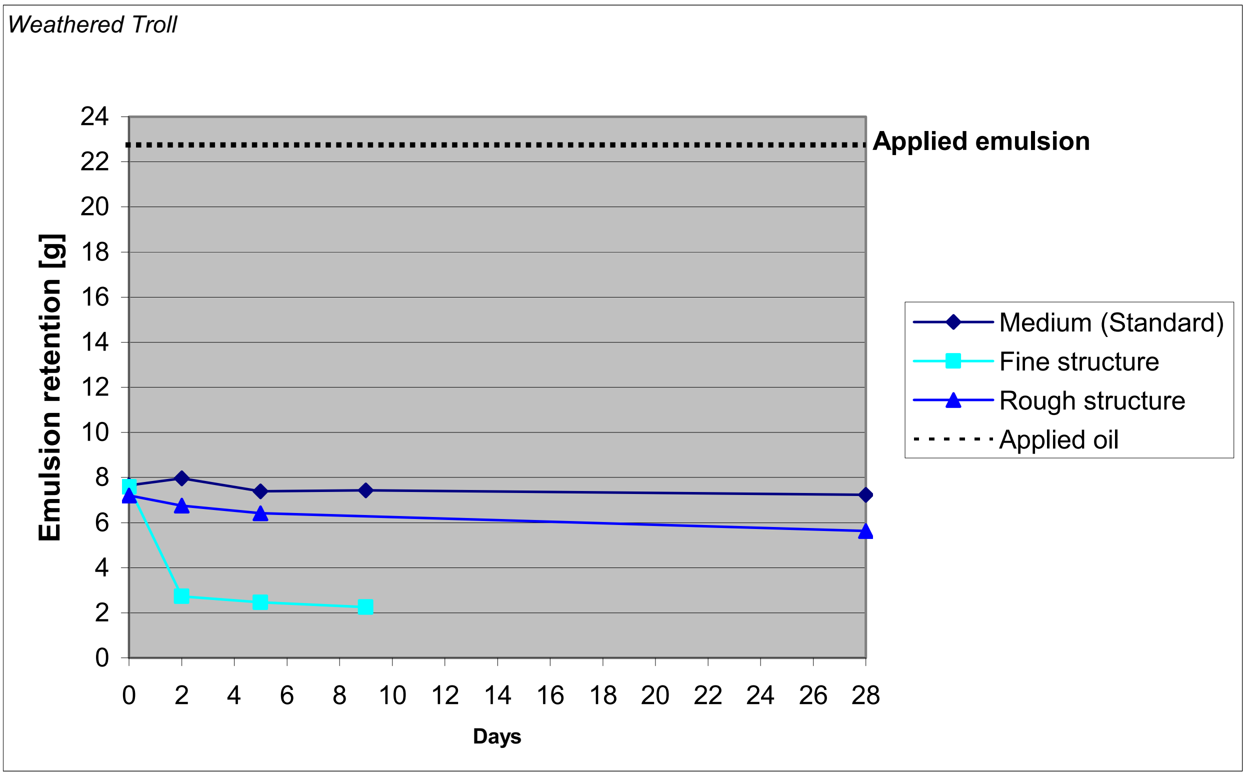


**Figure 4.3-1 Remaining emulsion for the Troll oil as a function of bedrock texture, subjected for a low exposure degree (4 litres).**

As shown in Figure 4.3-1, more emulsion was washed out for the fine and rough textured tiles compared to the medium texture. The greatest wash-out degree was found for the fine textured tiles. The rough textured tiles were showing approximately the same trend as the medium textured tiles, only with a little higher wash-out rate. Since the fine textured tiles are smoother in texture, less area is available for the emulsion to bind to the substrate surface, increasing the amount of emulsion washed out. For the rough texture tiles, the emulsion might be located in pounds, subjecting the emulsion for a greater wash-out.

The amount of emulsion remained on the bedrock surface, in regards to the different bedrock textures, for the Norne oil is shown in Figure 4.3-2.

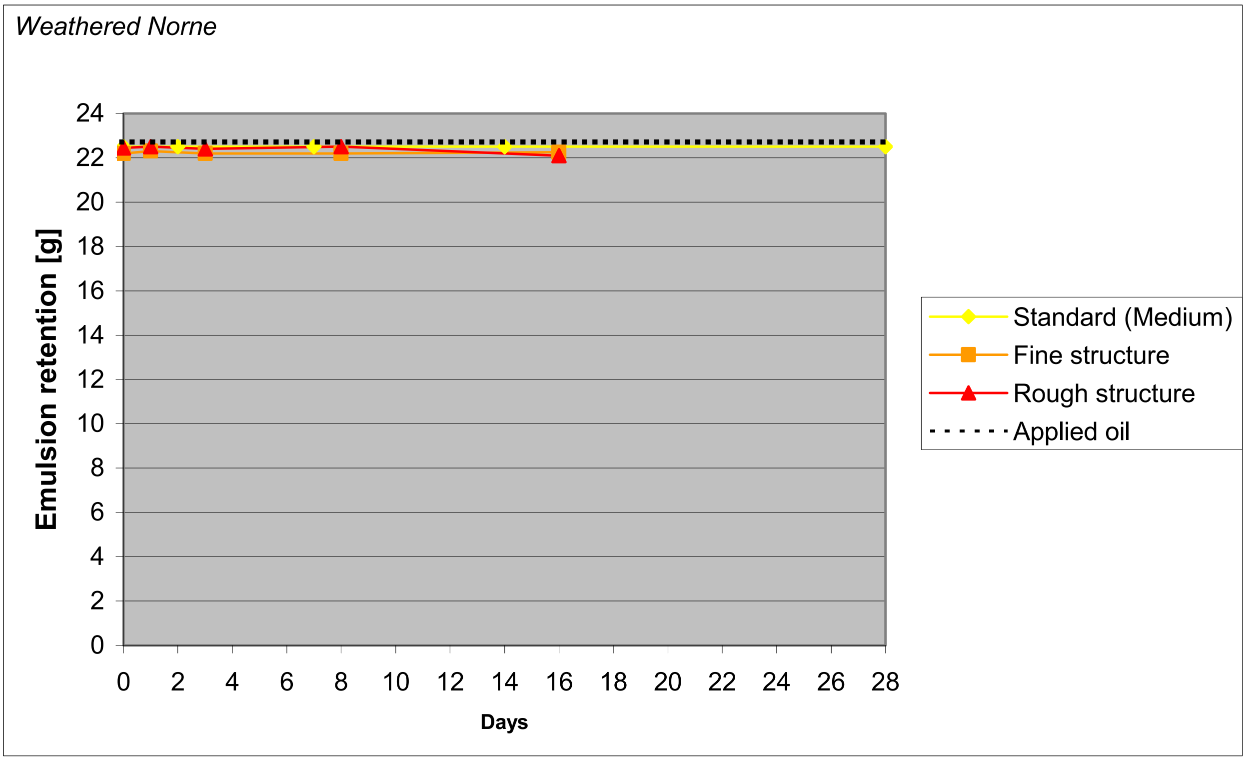


**Figure 4.3-2 Remaining emulsion for the Norne emulsion as a function of bedrock texture, subjected for a low exposure degree (4 litres).**

As shown in Figure 4.3-2, texture type showed little or no effect for the wash-out of emulsion for the Norne oil. Only a slight decrease in emulsion retention was registered for the fine and rough tiles after 16 days.

The amount of emulsion remained on the bedrock surface, in regards to the different bedrock textures, for the IFO 380 oil is shown in Figure 4.3-3. Based on results from the exposure degree study, a 2 litres energy regime was used in this study.

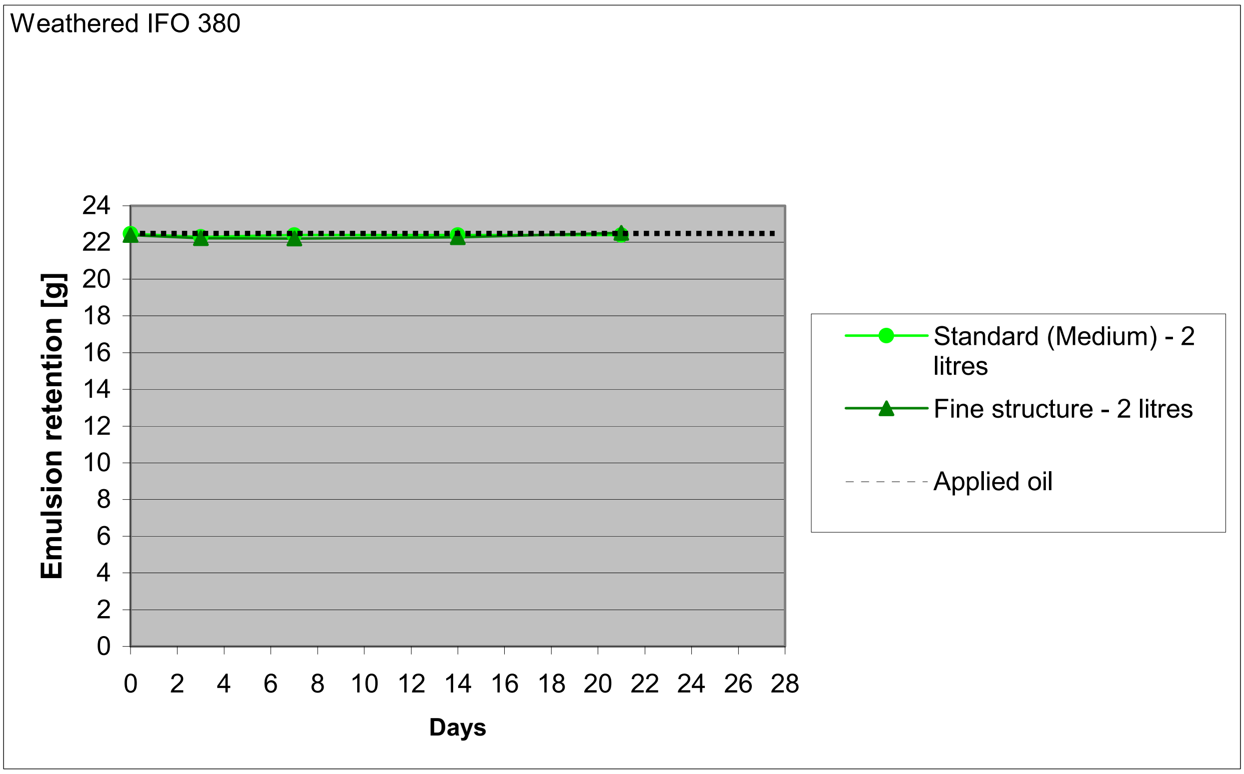


**Figure 4.3-3 Remaining emulsion for the IFO 380 oil as a function of bedrock texture, subjected for a high exposure degree (2 litres).**

Bedrock texture shows no effect on the wash-out of emulsion for the IFO 380 oil, see Figure 4.3-3.

### 4.4 Photo-oxidation

**Table 4.4-1 Experimental parameters used in this study.**

| Parameter | Variation |
|---|---|
| Oil type | Kobbe |
| **Evaporation** | **250°C+ residue and ph.ox** |
| Water content in emulsion | 75% (Kobbe) |
| Temperature | 5°C |
| Emulsion thickness / loading | 1 mm (22,5 g) |
| Bedrock | Shale – medium texture |
| Exposure degree | 2 litres |

Emulsion prepared from photo oxidized Kobbe were used in the shoreline simulating system to study the effect of photo-oxidation for the wash-out of emulsion. The amount of emulsion remained on the bedrock surface, in regards to the different weathering processes (un photo-oxidized versus photo-oxidized) is shown in Figure 4.4-1.

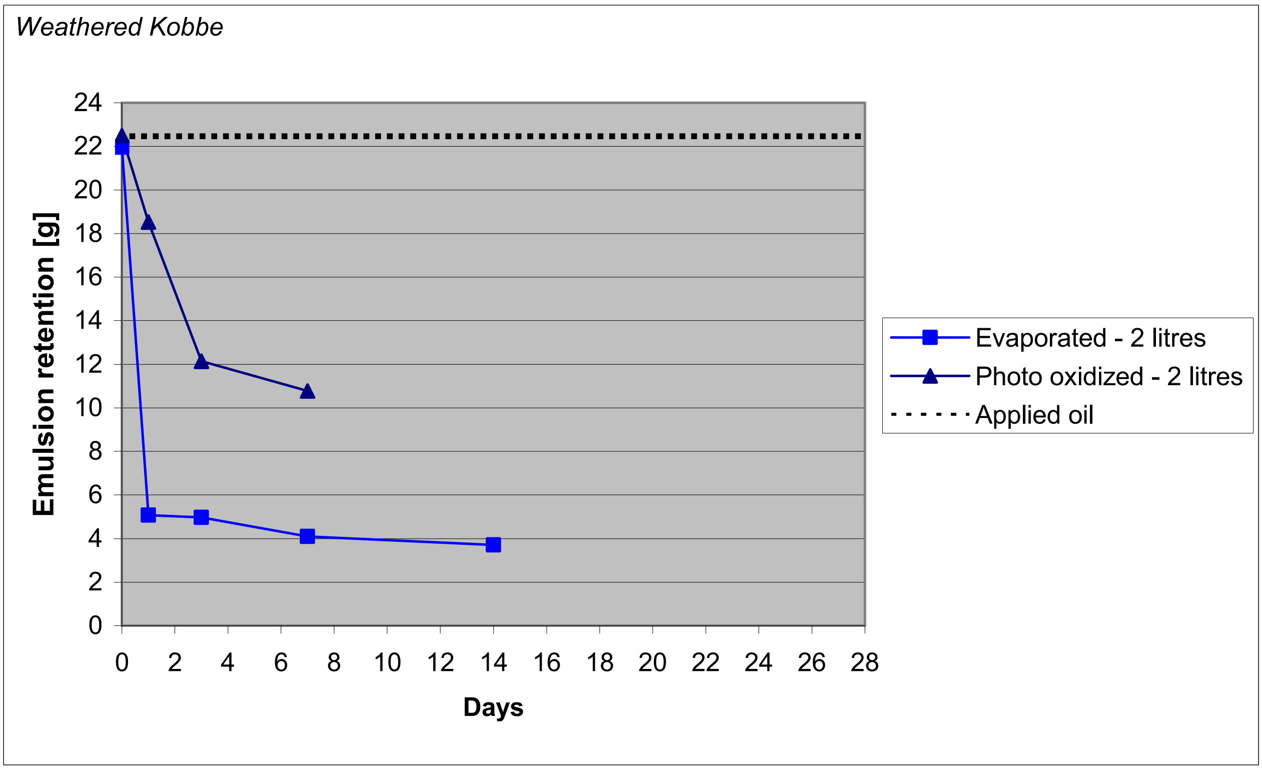


**Figure 4.4-1 Emulsion remains for the Kobbe oil as a function of photo-oxidation, subjected for a hig exposure degree (2 litres).**

Photo oxidized Kobbe show about 30% less wash-out of emulsion compared to un photo-oxidized Kobbe oil, see Figure 4.4-1. This might be due to the increase in viscosity for the photo-oxidized oil.

# 5 Conclusions and operational gain

The wash-out process studied in this activity does not represent a specific part of the shorelines segment vertically. Sense the polluted bedrock in this experimental system is subjected for a constant wash-out, the data can not directly be linked to a real life scenario. Well designed experiments at dedicated sites in the field, for both summer and winter conditions, are therefore needed for a validation of the experimental results and a better understanding of the wash-out processes in the tidal and splash zone.

Oil type and exposure degree seems to be ruling parameters for the wash-out of emulsion from contaminated shorelines. The results showed a wash-out degree of 30% for the Kobbe oil, for the lowest exposure degree (4 litres), after 28 days. The other oils showed little or no effect for the low exposure level. For the crude oils, an increase in exposure degree (2 litres), increased the wash-out effect significantly, leaving 5% remained emulsion for the Troll oil, about 15% for the Kobbe oil and 75% of the Norne emulsion on the shale tiles. IFO 380 was not washed out, for any of the exposure degrees. Oils like Troll and Kobbe might therefore be naturally washed out during time, compared to the Norne and IFO 380 emulsions, most likely having a need for artificial restorations techniques for a sufficient clean up.

Bedrock texture seems also to be of importance for the wash-out of low viscous oils like Troll. For the Troll emulsion, the wash-out degree increased from 7 to 70% for the fine textured tiles and about 7-25% for the rough textured tiles, subjected for low exposure. This might be due to the fines structured bedrock less surface area for the emulsion to bind. For the rough textured tiles, the emulsion seemed to collect in pockets between the textures, making it more easily subjected for wash-out. Bedrock texture showed no effect on Norne and IFO 380 emulsion. Photo-oxidation seemed to retard the wash-out process, reducing the wash-out degree from about 80% to 50% for the Kobbe oil. This might be due to the increase in viscosity and yield stress by photo-oxidation, masking the emulsion more resistant for wash-out. Sun exposure must therefore be taken in to consideration for countermeasure planning during the summer season, when the sun exposure is at its greatest.

A simple correlation study, showed that yield stress and viscosity were of relevance for the retention of emulsion. Troll and Kobbe emulsions might therefore easily be washed out from bedrock shorelines after an oil spill, if the energy level is sufficient, due to their low degree of structure giving low viscosities. This is in contrast to Norne and IFO 380, having a high degree of structure, giving high viscous emulsions.

This result indicate that shorelines polluted with oils like Troll and Kobbe might be naturally cleaned with time if the energy level in the area is sufficient (especially for fine textured bedrock), this compared to the Norne and IFO 380 emulsions, most likely having a need for artificial restorations techniques for a sufficient clean up. Oil spills during summertime might show a slower wash-out of emulsion, compared to oil spills during wintertime. This must be taken into consideration for countermeasure planning.

Due to little difference in wash-out results for the shale and granite bedrock, results derived at Cedre (France) could be used for comperisment. Based on these studies, a high exposure degree (2 litres) would be preferred in future studies, giving a better distribution of data. The data gained can be used for a further development of numerical models.

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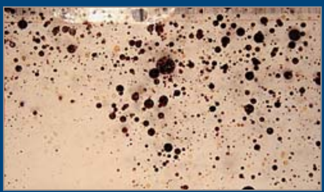
# REPORT



## Coastal Oil Spills - JIP

Report no.: 5

# C4.3 - Biodegradation; processes and techniques

Odd Gunnar Brakstad

**SINTEF Materials and Chemistry**
Marine Environmental Technology

Date: 2008-12-17

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**C4.5 – Biodegradation; processes and techniques**

**Coastal Oil Spills JIP. Report No. 5**

AUTHOR(S)

Odd Gunnar Brakstad

CLIENT(S)

Eni Norge AS, A/S Norske Shell and StatoilHydro ASA

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ABSTRACT

The objective of the experiment described here was to evaluate and study the possible influence of natural occurring micro-organisms in seawater on the degradation of the oil-water interphase. This included both the degradation of oil compounds and the release of oil compounds from the surfaces. Another objective was to determine the influence of the oil on the microbial communities in natural seawater.

In order to assess the influences of seawater microorganisms on biodegradation and dissolution of oil the oil was immobilized to a solid phase and submerged in natural seawater and biodegradation experiments conducted for 28 days at a seawater temperature of appr. 13°C. Degradation of hydrocarbons was then measured in the oil and water while changes microbial communities were analysed by molecular biology methods (PCR-amplification of the 16S rRNA gene)
The experiments and the data achieved have shown that a system with oil immobilised to hydrophobic adsorbents may be used to investigate microbial processes during biodegradation of oil. The conclusions of these experiments can be summarised as follows:

- By immobilisation the typical oil profile of an evaporated oil was retained
- The oil films may be generated up to a certain thickness which may correspond to the size of small oil droplets, and in this way the films may be also be used to study biotic processes related to oil droplets
- This system may be used for studies of both biotic and abiotic processes, including biodegradation, desorption and dissolution
- Biodegradation of oil and oil compounds could be determined separately in two phases, the oil phase and the surrounding water phase
- Water-soluble aromatic hydrocarbons were rapidly distributed between the oil film and the water, followed by detpeltion by biodegradation in the phases
- Microbial community analyses may be used to evaluate the bioavailability of compounds and estimate the status of the processes (further measures to characterise the members of the communities may also elucidate the oil compound groups



| KEYWORDS | ENGLISH | NORWEGIAN |
|---|---|---|
| GROUP 1 | Environment | Miljø |
| GROUP 2 | Oil | Olje |
| SELECTED BY AUTHOR | Biodegradation | Biodegradering |
| | Seawater | Sjøvann |
| | | |

# TABLE OF CONTENTS

# 1 Objective / purposes of the experiment

This project has been a part of phase 1 in the Coastal Oil Spills JIP. The research projects in the JIP have been focused on the fate and behavior of oil spills in coastal areas and on shoreline. Laboratory studies have been performed in order to obtain data for further development of numerical models.

The first phase of JIP was performed in the period from 2006 to 2008, and was funded by Eni Norge, Shell Technology and StatoilHydro. The overall objectives of the JIP have been:

- to contribute to an adequate and sufficient basis of competence to document possible consequences in case of an oil spill close to the coast
- to provide documentation ensuring the countermeasures giving the optimal environmental gain

The objective of the experiment described here was to evaluate and study the possible influence of natural occurring micro-organisms in seawater on the degradation of the oil-water interphase. This included both the degradation of oil compounds and the release of oil compounds from the surfaces. Another objective was to determine the influence of oil on the microbial communities in natural seawater.

# 2 Outline of experiments

In order to assess the influences of seawater microorganisms on biodegradation and dissolution of oil the oil was immobilized to a solid phase and submerged in natural seawater. Biodegradation experiments were then conducted for 28 days at seawater temperatures of appr. 13°C. Degradation of hydrocarbons was then measured in the oil and water phases by gas chromatographic methods, while polar compounds emerging in the water phase as results of oxidative processes (biodegradation) was analysed by liquid chromatography methods. Changes in microbial communities were analysed by PCR-amplification of the 16S rRNA gene by primers common for all bacteria and then analysing the community variations by denaturing gradient gel electrophoresis (DGGE).

# 3 Materials and Methods

## 3.1 Seawater and oils

The oil included in this study was evaporated Statfjord B 150°C+ (SINTEF ID 2000-0037).

Natural seawater was collected from 90 m depth in a non-polluted Norwegian Fjord (Trondheimsfjorden) and used as microbial inoculum. The water was filtered (50 µm exclusion limit) before tapping and stored for 7 days in containers at 0 or 5°C for acclimation to test conditions. Before test start seawater was aerated with sterile air, supplemented with inorganic nutrients (8.5 mg/l $KH_2PO_4$, 21.8 mg/l $K_2HPO_4$, 33.3 mg/l $Na_2HPO_4$ x $2H_2O$, 0.5 mg/l $NH_4Cl$, 27.5 mg/l $CaCl_2$, 22.5 mg/l $MgSO_4x7H_2O$, 0.25 mg/l $FeCl_3x6H_2O$) as recommended (OECD, 1992), and dispensed into 275 ml BOD bottles. Sterile seawater controls with Statfjord oil were prepared by adding 50 mg/l $HgCl_2$.

## 3.2 Experiments with immobilised oils

Statfjord 150°C+ was oil was applied to the surface of autoclaved seawater (121°C; 15 min) by introducing 100 µg of oil to a beaker containing 500 ml of water (temperature 20°C). The oil was immediately distributed across the water surface, generating an even surface film of approximate thickness 10 µm. Hydrophobic synthetic Fluortex fabrics (Sefar Inc., Thal, Switzerland) were pre-washed in dichloromethane (DCM), rinsed in sterile seawater, and air-dried. The fabrics were cut in pieces of 1 x 1 cm and carefully applied to the seawater surfaces approximately 2 minutes after the generation of the oil film. The fabrics were incubated for 60 minutes at room temperature (22°C) floating on the oil surfaces, then removed and carefully washed in two separated baths of sterile seawater. Thin fishing lines (thickness 0.30 mm according to information from the manufacturer) with knots in the ends (pre-washed in DCM, rinsed in sterile seawater and dried) were carefully forced through the fabric monofilaments, and used for submerging the fabrics in the seawater (nutrient-supplemented of sterilised) in 100-ml infusion bottles. The bottles were filled with seawater up to 100 ml, with some headspace, and incubated at 13°C for 0-28. Bottles with Fluortex fabrics in nutrient-supplemented seawater were withdrawn for chemical and microbiological analysis at days 0, 7, 14, 21 and 28 days of the biodegradation period. In addition, fabrics with immobilised oil were added to sterile seawater (see above), while fabrics without oil were added to normal seawater. In both cases, samples were retrieved at the start and the after 28 days of incubation. Dissolved oxygen was measured in all bottles with a sterilised BOD probe washed with 70 % ethanol and rinsed with sterile seawater (YSI, Yellow Springs, OH). Fabrics from sterile seawater controls (one parallel) were withdrawn for chemical analysis.

## 3.3 Gas chromatographic analyses

Fabrics were extracted with 50 ml dichlormethane (DCM). The solvent was dried ($Na_2SO_4$), filtered (glass wool), and concentrated to 0.5 – 1.0 ml in 2 ml GC vials in a TurboVap 500 closed cell concentrator (Zymark Co., Hopkinton, Ma). A surrogate recovery standard ($C_{20}$; 100 µl) was added to a final concentration of 20 µg/ml. Determination of total extractable organic compounds (TEOC; $C_{10}$–$C_{36}$) in DCM extracts was performed by GC-FID analysis (Hewlett Packard Model HP5890II gas chromatograph with a flame ionisation detector) using 0.05 – 15 µg/l Statfjord crude oil for generating external calibration curves. An internal standard ($C_{19}$; 100 µl) was added. Aromatic pseudo-compound groups were determined by GC-MS analysis (Hewlett Packard 6890 Gas Chromatograph with a 5973 MSD). These were grouped as Naph-1, Naph-2, PAH-1, and PAH-2; the compound composition within each group is described in Table 1.

Acidified water samples (WSFs) were analysed for TEOC and aromatic compounds, primarily as described for the analyses of immobilized oil (fabrics). Acidified WSFs were extracted with dichloromethane (DCM), and extracts evaporated to 0.5-1.0 ml before GC-FID analysis.

*Table 1. Naphthalenes and polyaromatic hydrocarbons (PAH) included in oil pseudo-groups.*

| Abbreviation | Compounds |
|---|---|
| Naph-1 | C0-to C1- naphthalenes |
| Naph-2 | C2- to C3- naphthalenes |

| | |
|---|---|
| PAH-1 | C4-naphthalenes, biphenyl, acenaphthylene, acenaphthene, dibezofurane, C0- to C1-fluorenes, C0- to C1- phenanthrenes/ anthracenes, C0- to C1- dibenzothiophenes |
| PAH-2 | C2- to C3-fluorenes, C2- to C4- phenanthrenes/ anthracenes, C2- to C4- dibenzothiophenes, Fluoranthrene, pyrene, C1- to C3-fluoranthrenes/pyrenes, benz(a)anthracene, C0- to C4-crysenes, benzo(b,k)fluoranthene, benzo(e,a)pyrene, perylene, dibenzo(a,h)anthracene, benzo(g,h,i)perylene, indeno(1,2,3-c,d)pyrene |

### 3.4 Liquid chromatography analyses

Liquid chromatography analyses of polar compounds of water-soluble samples are still under development. The work done so far to optimize this method is described in Appendix 1.

### 3.5 PCR-DGGE

Samples with adsorbents were placed in 2 ml lysis buffer (50 mM Tris-HCl, pH 8.0; 40 mM EDTA; 0.75 M sucrose) and frozen (-20°C).

Water samples from biodegradation vials were filtered through 0.2 µm Sterivex-GV filters (Millipore, Bedford, MA, USA). The filters were then filled with 1.5 to 2.0 ml of a lysis buffer and sent frozen. Each filter was thawed, and 2 µg lysozyme incubated at 37°C for 30 minutes, followed by incubation at 55°C with 1 µg Proteinase K and 1% (wt/vol) SDS.

Nucleic acids from fabrics and water samples were extracted by hot phenol-chloroform-isoamylalcohol according to standard procedures (Sambrook and Russel, 2001). Recovered nucleic acids were quantified by ethidium bromide (Sambrook and Russel, 2001) and stored at -20°C until analysis.

PCR amplification of bacterial 16S rDNA was performed with the domain-specific primers Bac341f (5'-CCT ACG GGA GGC AGC AG-3') and Bac907r (5'-CCC CGT CAA TTC CTT TGA GTT-3'). For DGGE a 40-mer GC-clamp (5'- CGC CCG CCG CGC GCG GCG GGC GGG GCG GGG GCA CGG GGG G-3') was added to the 5'-end of the Bac341f primer, yielding a PCR fragment of 590 bp (Muyzer *et al*., 1993). The amplification was conducted as a "touchdown" PCR to reduce formation of spurious by-products (Don *et al*., 1991), as previously described (Teske *et al*., 1996). Annealing temperature was initially set at 65°C, then decreased by 1°C every second cycle until 55°C, at which point 25 additional cycles were carried out.

DGGE was performed with a continuous gradient of 20-70 % of the denaturing agents urea and formamide (100 % denaturants corresponded to 7 M urea and 40 % deionised formamide), essentially as described by Teske *et al* 1996. Each well contained 0.5-1.0 µg DNA. DGGE was run at 60°C in a DCode Universal Mutation Detection System (Bio-Rad, Hercules, Ca) at 150 V constant voltage for 4.5 hours. Gels were stained for 20-30 minutes with SYBR Gold (Molecular Probes, Leiden, The Netherlands), and stained gels were scanned in a GelDoc system (Bio-Rad).

# 4 Results

## 4.1 Initial studies – immobilisation of Fluortex fabrics

In previous studies immobilised oil films were generated by generating films of 50 µg oil in 500 ml of water. However, initial studies showed that the generated films were more homogeneous by using 100 µg oil instead. The main reason for this was that we now used evaporated oil (150+) instead of fresh oil, which had been used in previous experiments (Brakstad *et al*., 2002; Brakstad and Bonaunet, 2006). This resulted in some excess of oil which was rapidly transferred to the oil phase. (Figure 1). The chromatograms of the immobilised oil also showed some peaks at low retention times (4, 5 and 7 minutes): These peaks did not originate from the oil, and were not included in the analyses.

A

B

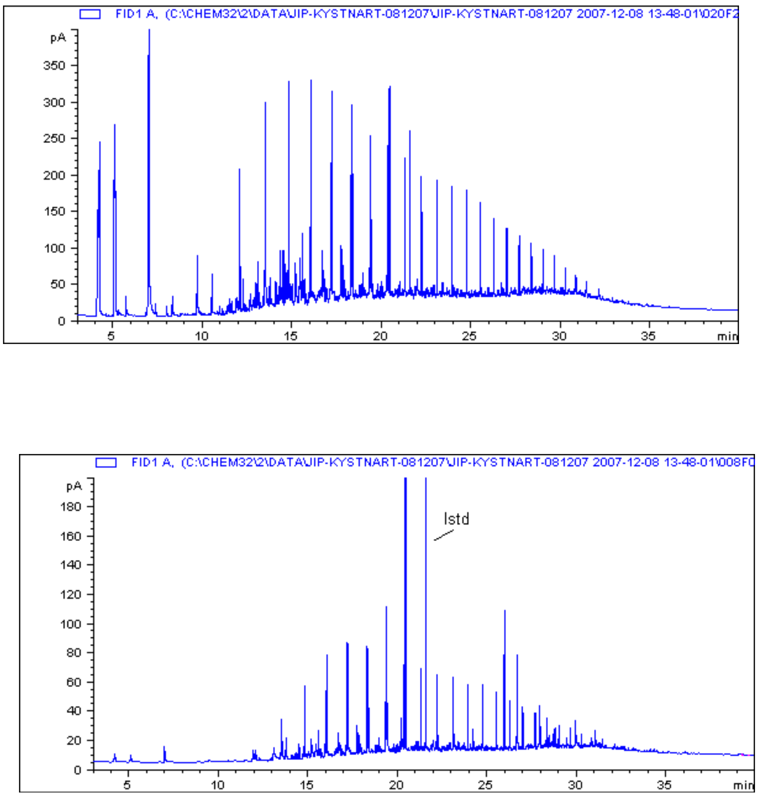



*Figure 1. GC-FID chromatograms of Statfjord B 150°C+ immobilised on Fluortex fabrics (A) and in seawater after fabrics with immobilised oil had been submerged in the water (B). An internal standard ($C_{20}$) is shown.*

## 4.2 Depletion of oil compounds on fabrics and in seawater

### 4.2.1 Total extractable organic carbon (TEOC)

GC chromatograms of the immobilised oil and oil in the seawater at the start and end of the biodegradation experiment were shown in Figure 2 and Figure 3, respectively. The amounts of TEOC in immobilised and the water phases are shown in Table 2.

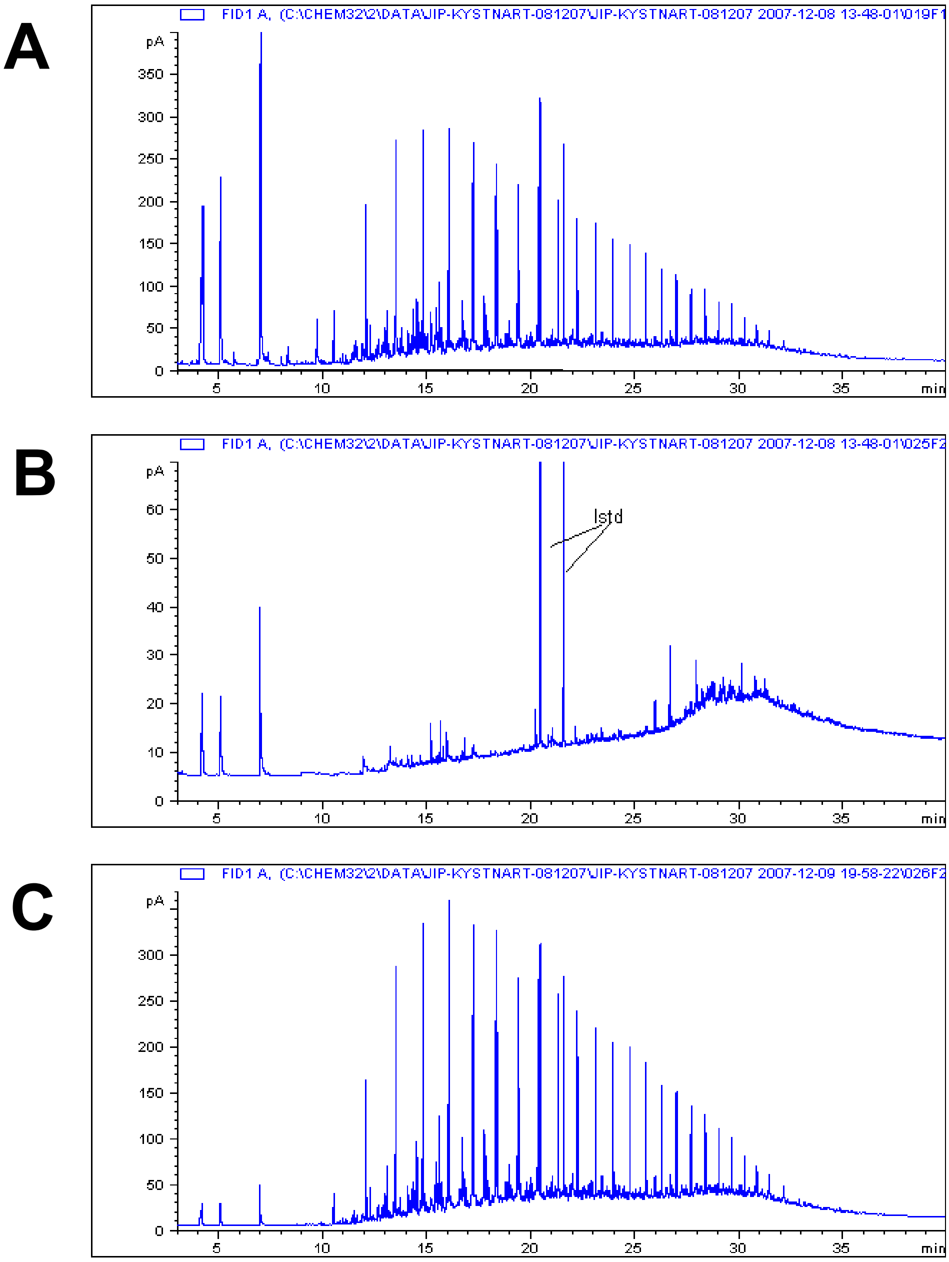



*Figure 2.* *GC chromatograms of immobilised Statfjord B 150°C+ at the start of the test (A) and at the end of the test (B, C) for fabrics submerged in normal seawater (B) and in sterile seawater (C). Internal standards ($C_{19}$ and $C_{20}$) are shown.*

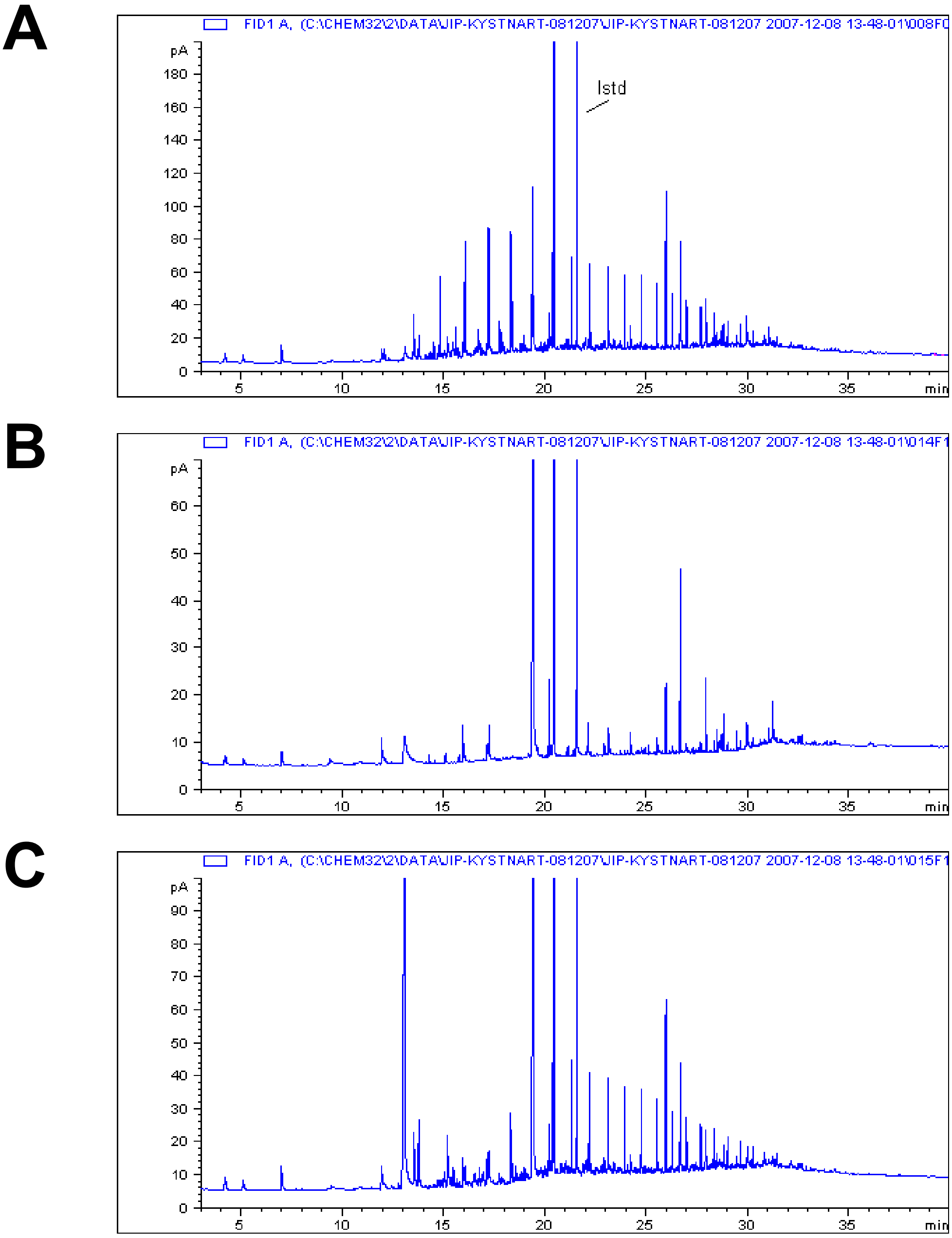



*Figure 3.* *GC chromatograms of Statfjord B 150°C+ in the seawater at the start of the test (A) and at the end of the test (B, C) for fabrics submerged in normal seawater (B) and in sterile seawater (C).*

The results from Table 2 and Figures 2 and 3 showed that hydrocarbons in oil and water phases could be measured separately. The amounts of TEOC in the water phase represented 10-11 % of the amounts in the immobilised phase both at the start of the test and in the sterile control at the end of the test. Thus, the dissolution of oil from the fabrics was the result of an immediate process, and further “leakages” did not appear. The results also showed that biodegradation was inhibited in sterile seawater, demonstrating that the depletion was caused by microbial processes, both on the immobilised oil and in seawater. In the seawater, one peak with a retention time of appr. 19.5 minutes persisted in the biodegraded samples (Figure 3, B). This peak were close to the $n$-$C_{18}$ and phytane peaks, but closer examinations and comparison with calibration standards showed that this peak did not fit exactly with any of these compounds. The data of Table 2 also showed that there was a background in the phases, ranging from 133-186

The amount of TEOC of immobilised oil and in the water is shown in Table 2.

*Table 2. Amounts of total extractable organic carbon (TEOC) in fabrics and in seawater with or without oil.*

| Sample | TEOC total amount per sample (µg) | |
|---|---|---|
| | **Fabrics** | **Water** |
| Day 0 – Oil Biotic | 630 | 72.4 |
| Dag 0 - Oil Sterile | 626 | 65.4 |
| Dag 0 : No oil | 133 | 17.6 |
| Day 7 – Oil Biotic | 511 | 61.6 |
| Day 14 – Oil Biotic | 187 | 26.3 |
| Day 21 – Oil Biotic | 201 | 28.3 |
| Day 28 – Oil Biotic | 199 | 26.9 |
| Dag 28 - Oil Sterile | 561 | 65.7 |
| Dag 28 : No oil | 186 | 24.5 |
| Blank | 630 | 14.8 |

The results of Table 2 showed TEOC backgrounds of 133-186 µg in the immobilised oil and 17-24 µg in the water phase. The biotic depletion of the oil as TEOC is demonstrated in Figure 4, in which the results were corrected for these backgrounds levels. The results showed that biotransformation of the immobilised oil appeared mainly during the first 14 days of the experiment. This was also the result in the water phase, substantiating that the oil in the water was the result of an immediate event at the start of the experiment. After 15 days the amounts of TEOC were reduced to 5 % in the oil and 10 % in the water of the amounts at the start of the test.

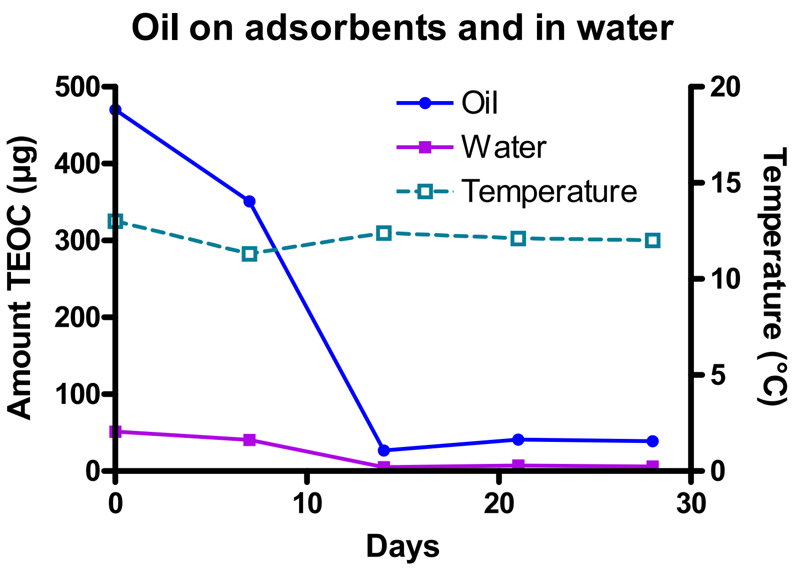



*Figure 4* *Depletion of TEOC in immobilised oil (Oil) and in seawater (Water) phases during the biodegradation experiment.*

### 4.2.2 Depletion of aromatic compounds

The depletion of aromatic compounds were analysed by GCMS. The results are shown in Figure 5. In the sterile systems depletion from the oil film was shown from start to the end of the experiment, corresponding to an increase in the water phase from the start to the termination. In the biotic system depletion was measured in the oil films. For the naphtalenes a rapid initial depletion corresponded to an temporary increase in the water, as a result of immediate dissolution. However, after 2 weeks of incubation naphthalenes had nearly completely disappeared from both oil film and water as a result of biodegradation. For phenanthrenes and dibenzothiothenes, which are not as soluble as the naphthalenes, lag phases were observed during the first week, and the dissolution of these compounds were not detectable. The initial amounts of these compounds could be the result of immediate transfer of compounds during test start (before the first analysis). After 2 weeks of incubation biodegradation of both phenanthernes and dibenzothiophenes were significant. At the end of the experiment 96 % of the phenanthrenes and 97 % of the dibenzothiophenes in the oil films had disappeared, while no compound was detected in the water.

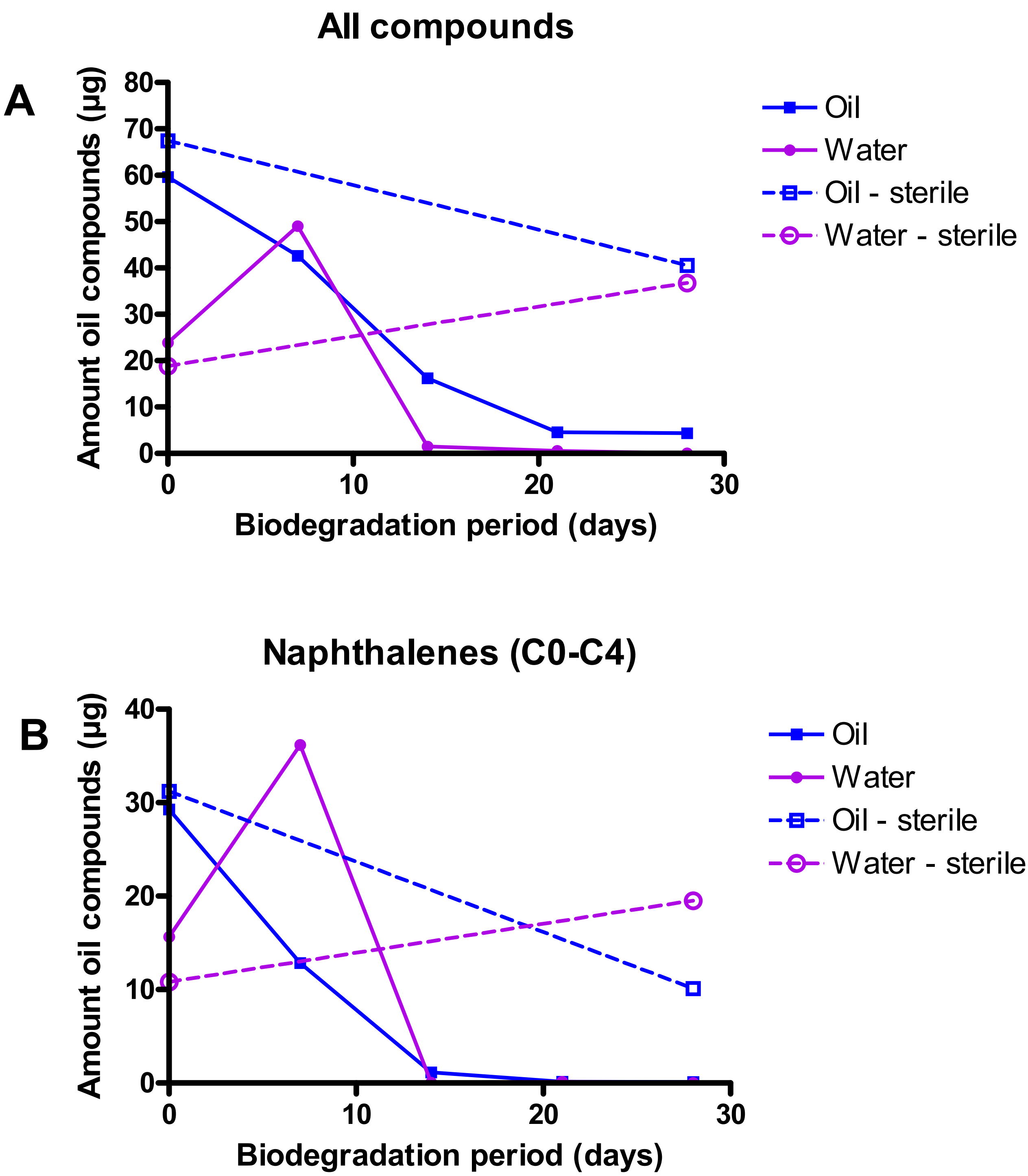
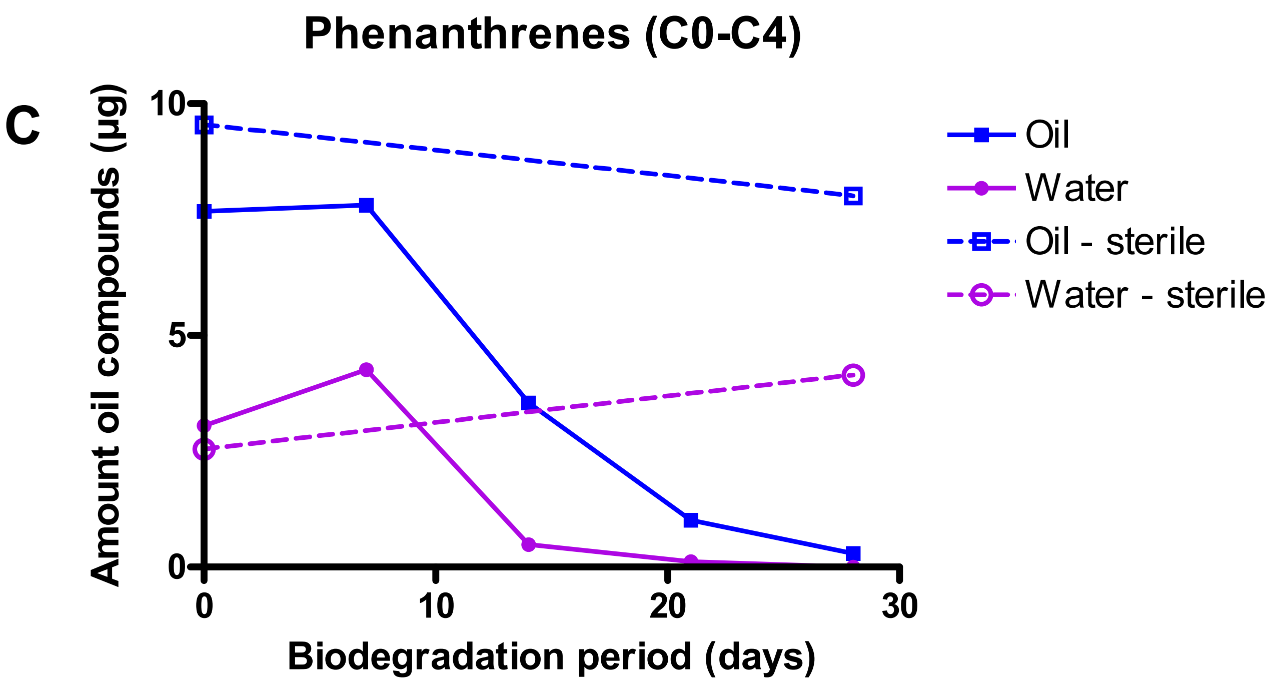



*Figure 5. Depletion of total amounts of oil compounds measured by GCMS (A), and C0-C4 naphthalenes (B) in oil or water phases of biotic or sterile systems.*



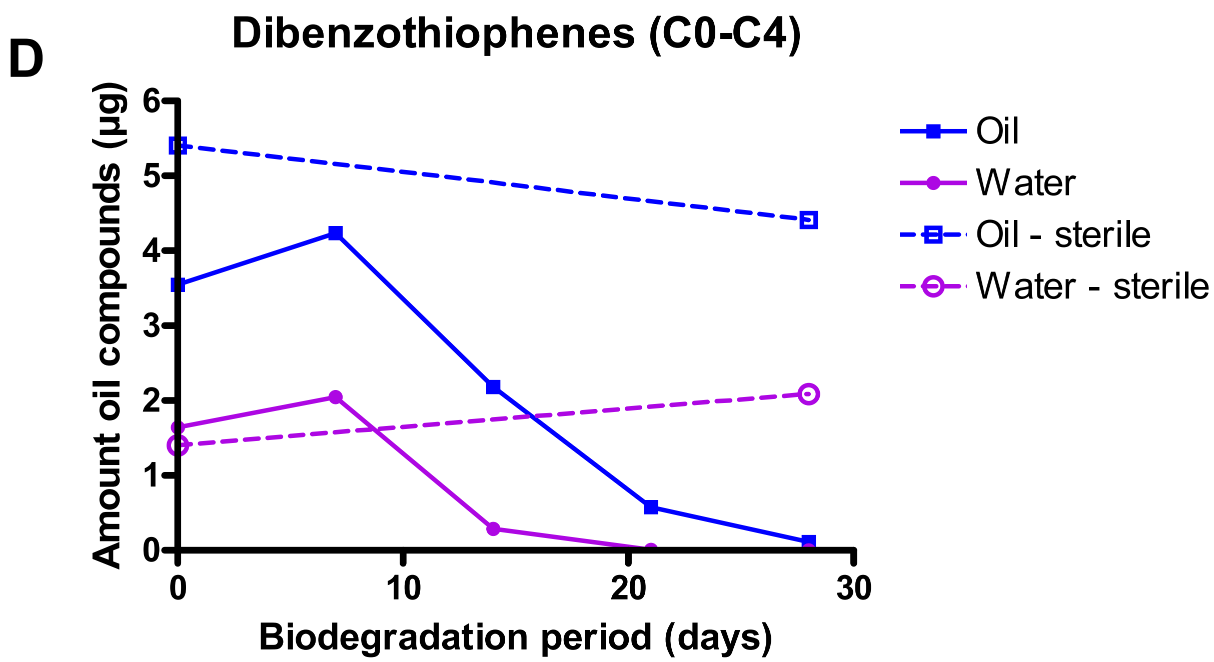



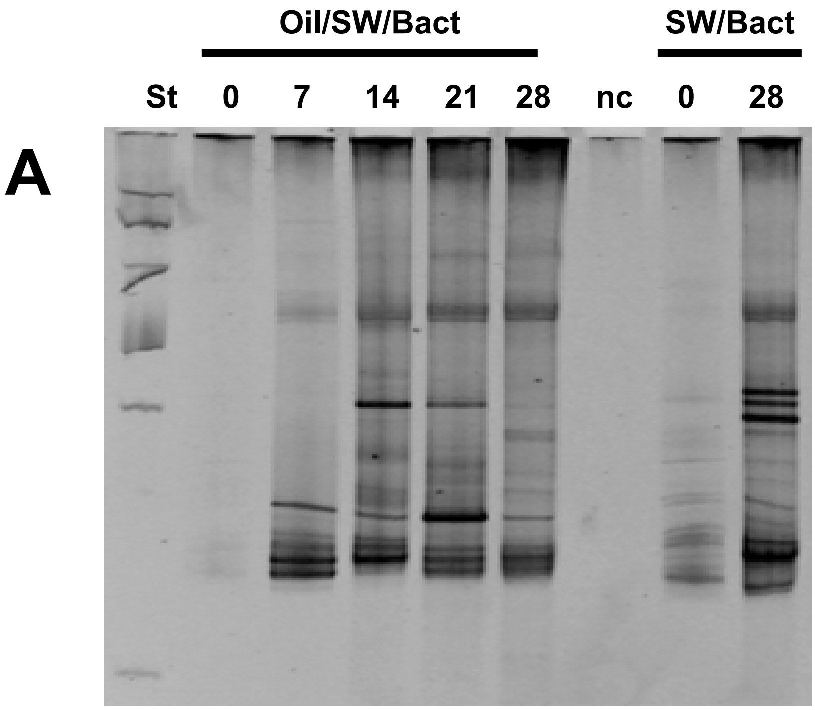

*Figure 5 cont. Depletion of total amounts of oil compounds measured by GCMS (A), and C0-C4 naphthalenes (B) in oil or water phases of biotic or sterile systems.*

### 4.2.3 Determination of polar compounds

Polar compounds in the water phase will be analysed by LCMS. This method is under development, using solid-phase extraction, and samples from the biodegradation experiments have been stored for these analyses. The development work is described in Appendix 1.

## 4.3 Changes in microbial communities

Microbial communities in the samples during the biodegradation experiment was determined by PCR-DGGE analyses, amplifying the bacterial 16S rRNA genes in the samples. The results for the communities associated with the oil and seawater phases are shown in Figure 6. The results of Figure 6A showed (Oil/SW/Bact) that at the start of the experiment the fabric surfaces only contained minor amounts of bacterial DNA. After 7 days a major band (see arrow) appeared in the DGGE and maintained during the degradation period. After 14 days a second band emerged (see arrow), but was absent after 28 days.  After 28 days the major bands became weaker, as a results of the fact that most easily degradable compounds had been already degraded. On the fabric without oil (SW/Bact) the communities were more complex with many DGGE bands after 28 days and contained bands at migration different from the samples with oil. In the water phase Figure 6B) different bands appeared during the degradation period, but in these samples the DGGE patterns in samples with and without oil did not differ to the same extent as for the fabrics. These results demonstrated 1) that only a few bacterial types are normally involved in biodegradation of oils, and 2) the communities may change during the degradation.



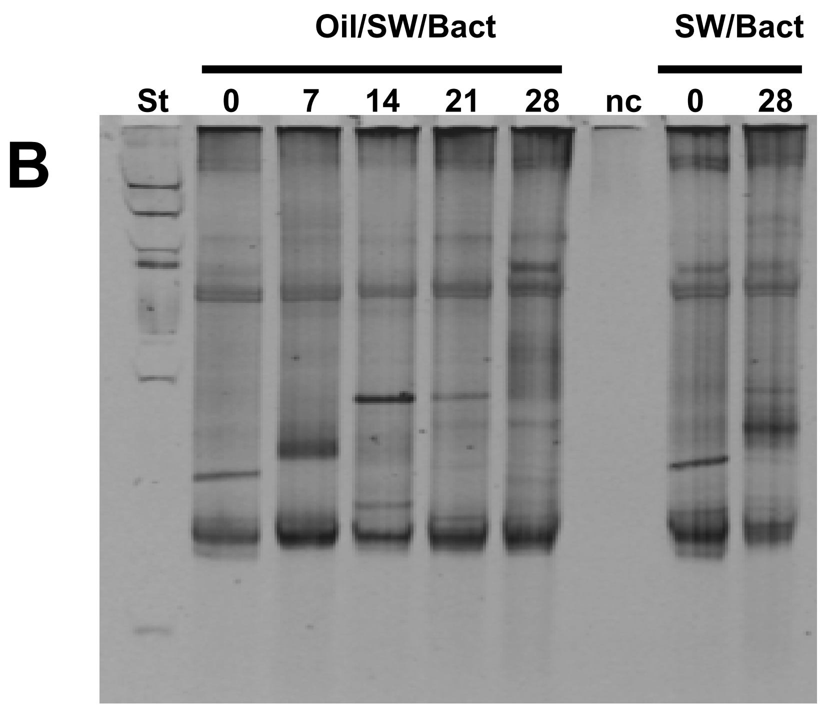




*Figure 6. DGGE analyses of bacterial 16S rRNA gene PCR products from oil (A) and seawater (B) phases during the biodegradation experiment. Results are shown for samples of oil in normal seawater (Oil/SW/Bact) and for samples with fabrics without oil (SW/Bact). Standard (St) and negative controls (nc) are included.*

## 5 Conclusions

The experiments and the data achieved so far have shown that a system with oil immobilised to hydrophobic adsorbents may be used to investigate microbial processes during biodegradation of oil. The conclusions of these experiments can be summarised as follows:

- By immobilisation the typical oil profile of an evaporated oil was retained
- The oil films may be generated up to a certain thickness which may correspond to the size of small oil droplets, and in this way the films may be also be used to study biotic processes related to oil droplets
- This system may be used for studies of both biotic and abiotic processes, including biodegradation, desorption and dissolution
- Biodegradation of oil and oil compounds could be determined separately in two phases, the oil phase and the surrounding water phase
- Microbial community analyses may be used to evaluate the bioavailability of compounds and estimate the status of the processes (further measures to characterise the members of the communities may also elucidate the oil compound groups being attacked by the bacteria)

The systems described here may therefore be used as a screening system to determine biodegradation processes and the effects of various factors and influencing the degradation processes, including use of fertilizers and different environmental factors.

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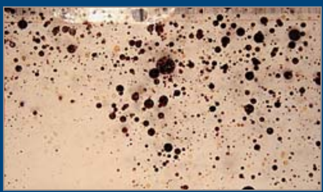
# REPORT



## Coastal Oil Spills - JIP

Report no.: 8

# C4.4 - Effect of mineral fines in seawater for the wash-out efficiency of weathered oil from solid shoreline substrate

Jane H.C. Øksenvåg, Svein Ramstad and Merete Ø. Moldestad

**SINTEF Materials and Chemistry**
Marine Environmental Technology

Date: 2008-12-17

# SINTEF REPORT

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TITLE

**C4.4 Effect of mineral fines in seawater for the wash-out efficiency of weathered oil from solid shoreline substrate**

**Coastal Oil Spills JIP. Report No. 8**

AUTHOR(S)

Jane H.C. Øksenvåg, Svein Ramstad and Merete Ø. Moldestad

CLIENT(S)

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ABSTRACT

The objective of this activity was to study and quantify the effectiveness of fine mineral particles in seawater for the removal of weathered immobile oil from solid substrate under controlled conditions at 5˚C, in a shoreline simulation system.

In this study, a laboratory shoreline simulation system adopted from Cedre in France was used. The effect of minerale fines was studied for three weathered crude oils (Troll, Kobbe and Norne) and one bunker fuel oil (IFO 380), with a variation in fines concentration and exposure grade. The physical effect of fines was also tested for a photo-oxidized Kobbe oil.

The presences of fines show only a slight increase of wash-out efficiency for weathered crude oils from bedrock, if a minimum energy level was present. The wash-out of emulsions was found to be dependent on oil type (physicochemical properties) and exposure degree. A simple correlation study showed the viscosity of the emulsion to be of significance for the wash-out effect, showing a decreasing in wash-out efficiency for the high viscous oils. For the crude oils, no clear trend in wash-out efficiency was observed for the different concentration levels. The presence of fines had no influence on the bunker fuel oil (IFO 380) for any of the parameters tested.



| KEYWORDS | ENGLISH | NORWEGIAN |
|---|---|---|
| GROUP 1 | Chemistry | Kjemi |
| GROUP 2 | Environment | Miljø |
| SELECTED BY AUTHOR | Coastal oil spill | Kystnær oljesøl |
| | Wash-out | Utvasking |
| | Fines | Småpartikler |

# TABLE OF CONTENTS

# 1 Summary

The objective of this activity was to study and quantify the effectiveness of fine mineral particles suspended in seawater, for the removal of weathered immobile oil from solid substrate under controlled north and winter conditions at 5˚C. For this purpose, a shoreline simulation system was used.

The effect of fines (ranging from < 2,3µm to 35µm) was studied for three weathered crude oils (Troll, Kobbe and Norne) and one bunker fuel emulsion (IFO 380), representing different chemical properties. Other parameters tested were fines concentration and exposure grade. The effect of fines was also tested for photo-oxidized Kobbe oil. Four fines concentration levels were used (10, 40, 100 and 400 mg/l). The different concentrations were tested for two energy levels, high and low, adjusted with a variance in water loading in the shoreline simulation system.

The wash-out of emulsions on bedrock with the presence of fines was found to be slightly dependent on oil type and exposure grade. A simple correlation study showed the viscosity of the emulsions to be of relevance for the retention of emulsion, increasing the retained emulsion on bedrock with an increase in viscosity. For the low energy level, the presence of fines showed an increased wash-out effect for the Troll and Kobbe oil. Norne showed no wash-out of emulsion for any of the concentration levels tested, the fines in the seawater seemed rather to adhere to the emulsion surface. For the high energy level, the energy were sufficient to start the wash-out process also for the, high elastic oil, Norne. The presence of fines showed a clear effect, enhancing the emulsion wash-out with approximately 10%. The presence of fines, also showed an effect on photo-oxidized Kobbe emulsion, decreasing the emulsion mass with approximately 17%. The presence of fines had no influence on the bunker fuel oil (IFO 380) for any of the parameters tested.

For the Troll oil, only the high and very high concentrations of fines seemed to have an effect on the wash-out of emulsion. For the other crude oils, there were observed no uniform trend in wash-out effect correlated to the concentration levels of fines. The results seem to correlate fairly well with a review and assessment written by Owens & Lee (2003).

## 2 Introduction

This project has been a part of phase 1 in the Coastal Oil Spills JIP. The research projects in the JIP have been focused on the fate and behavior of oil spills in coastal areas and on shoreline. Laboratory studies have been performed in order to obtain data for further development of numerical models.

The first phase of the JIP was performed in the period from 2006 to 2008, and was funded by Eni Norge, Shell Technology and StatoilHydro. The overall objectives of the JIP have been:

- to contribute to an adequate and sufficient basis of competence to document possible consequences in case of an oil spill close to the coast
- to provide documentation ensuring the countermeasures giving the optimal environmental gain

Oil spills stranded on shore will be subjected for several natural physical and chemical processes as; biodegradation, photo-oxidation, wash-out and interaction with particles. These processes will separately or together contribute to a degradation and removal of weathered oil from the shoreline. The significance of the different processes is dependent on the oil type spilled, environmental parameters and type of shoreline substrate.

Based on present literature publications, fines interactions with stranded oil have shown to be important for the natural cleaning process of oil contaminated shorelines. The interaction between fine mineral particles and oil form oil-fines aggregates (Braggs & Owens, 1995) and is found to be dependent on the movement of sediment particles created by wave exposure. The interaction between fine particles and stranded oil is found to reduce the adhesion of oil to solid surface, dispersing the micron size oil-fines aggregates in to the water column (Owens & Lee, 2003). Earlier studies have shown fines concentration and particle size to be of relevance for the wash-out effect of emulsion from bedrock (Ajijolaiya et. al., 2006). Removal of oil from shoreline sediment in the restoration phase by physical erosion has also been observed in field experiments (Sergy et.al, 2003).

The objective of this activity was to study and quantify the effectiveness of fine particles present in seawater, for the removal of immobile weathered oil from solid substrate under temperature controlled north and winter conditions at 5˚C. In 2005, SINTEF adopted a shoreline simulating system from Cedre in Brest (France) to study the wash-out of oil from bedrock. The same system is used in this experiment, to study the effect of fines in seawater. The wash-out experimental system was established and standardised through the project *"Utvasking av Realgrunnen-olje fra fast substrat"* carried out by SINTEF for ENI Norge (Rastad & Nygaard, 2006). Based on the experimental work done in that project, a SOP was established. The effect of mineral fines was studied for three weathered crude oils (Troll, Kobbe and Norne, plus photo-oxidized Kobbe) and one bunker fuel oil (IFO 380), to study the variance between crude oils with different physicochemical properties and their difference to a fuel oil used for ships going along the Norwegian coast. The effect of fines was also tested for four different fines concentration levels and two different exposure degrees.

# 3 Experimental

## 3.1 Materials

### 3.1.1 Oil types and weathering degree

Crude oils can be characterised in four categories: asphaltenic, napthenic, paraffinic and waxy crude oils. The crude oils studied in the Coastal Oil Spills JIP were selected among the oil companies' crude oils. It was important to select crude oils representing different categories of oils. The selected crude oils represent the categories:

- Troll – naphtenic crude oils
- Norne – waxy crude oils
- Kobbe – light paraffinic crude oils

In addition to the crude oils, a heavy fuel oil (IFO 380) was tested. IFO 380 is representing bunker oils used as fuel for ships going along the Norwegian coast. The content of light oil components in fuel oils is low, typically lower than 5 vol% for IFO 380 oils. The light oil components are generally in a boiling point area from approximately 250°C and higher. The testing of the IFO 380 was therefore concentrated on the "fresh" fuel oil, not on an evaporated residue. The IFO 380 oil used in this project is a low sulphur fuel oil produced at the Esso refinery at Slagentangen. Some physical and chemical properties of the oils studied are listed in Table 3.1-1.

**Table 3.1-1 Oils used in the Coastal Oil Spills JIP.**

| SINTEF Id | Oil type | Residue | Density (Kg/m$^3$) | Evaporative Loss (Vol%) | Pour point (°C) | Wax (wt%) | Asphaltenes (wt%) |
|---|---|---|---|---|---|---|---|
| 2007-0287 | Troll | Fresh | 0,900 | 0 | -36 | 0,9 | 0,04 |
| | | 250°C | 0,930 | 25,5 | -27 | | |
| | | Ph.ox. | 0,931 | - | -21 | | |
| 2006-1061 | Kobbe | Fresh | 0,797 | 0 | -39 | 3,4 | 0,03 |
| | | 250°C | 0,875 | 53,6 | 21 | | |
| | | Ph.ox. | 0,877 | - | 15 | | |
| 2007-0260 | Norne | Fresh | 0,860 | 0 | 21 | - | 0,3 |
| | | 250°C | 0,888 | 28,4 | 30 | | |
| | | Ph.ox. | 0,885 | - | 30 | | |
| 2006-1125 | IFO 380 | Fresh | 0,963 | 0 | 15 | 5,0 | 3,4 |

*-: not measured*

Oil spilled at sea will be subjected for several weathering processes as evaporation (lighter compound evaporates), emulsification (water droplets are incorporated in the oil phase) and photo-oxidation (changing the physical and chemical properties due to sun exposure). These weathering processes will change the physicochemical properties of the oil, being of great importance for the weathered oils fate and behaviour on the shoreline

For the crude oils, an evaporated residue of 250˚C+ was used. The 250°C+ residue corresponds to ½ - 1 week weathering of oil at sea, and will be representative for stranded crude oil along the Norwegian coast.

To ensure reproducible production of emulsions, a water content just below the maximum water uptake for the respective oils was used. After some initial studies, the standard water content was decided to be 70% for Troll, 75% for Kobbe, 60% for Norne and 40% for IFO 380.

To study the effect of photo-oxidation, the crude oils (Troll, Kobbe and Norne) were exposed for a solar simulator. The photo-oxidized oils represent oils exposed 5 days under ordinary sunlight exposure in the summertime. During this process, the oils were naturally evaporated to a 250˚C+ residue.

Evaporation, emulsification and photo-oxidation were performed according to established SINTEF lab procedures. For more information about the physical and chemical properties of the oils and weathering procedures, see *Technical report C2.2* (Ramstad et.a.l, 2008).

### 3.1.2 Sediment fines

Fines interactions with stranded oil have shown to be important for the natural cleaning process of oil contaminated shorelines. The interaction between fine particles and stranded oil is found to reduce the adhesion of oil to solid surface, dispersing the micron size oil-fines aggregates in to the water column (Owens & Lee, 2003). The principle for oil removal from pebbles is shown in Figure 3.1-1, which might also be valid for solid substrate as bedrock.

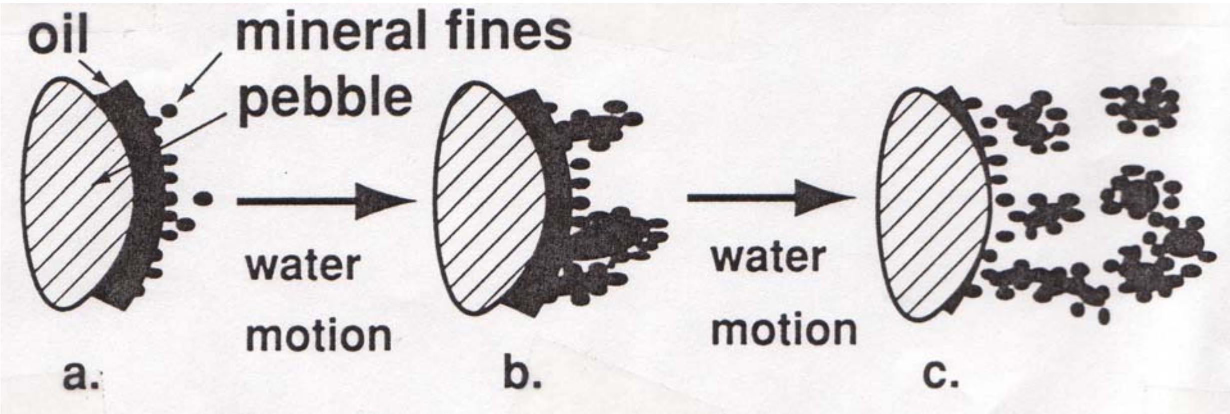


**Figure 3.1-1 Steps by which oil is removed from sediment and dispersed through flocculation with mineral fines: a) mineral fines are attracted to oil film by electrical charges, b) water energy ruptures oil film and creates droplets, c) floccules are washed away and dispersed (Bragg & Owens, 1995)**

To study the effect of fines in seawater, sediment fines from an area close to Trondheim, Buvika (Norway), was collected. A calculation of the slurry composition is given in *Appendix* 1. The results show the sediment to composite of particles varying from <2,3µm to 35µm, this represent sediments ranging from clay to silt according to the Wentworth classification scale for sediments (www.wikipedia.no). Due to the good size distribution in the sediment collected, it was considered unnecessary to test other sediments. Based on results from earlier studies (Ajijolaiya et. al., 2006), four fines concentration levels were used to study the effect of fines in seawater, see Table 3.1-2.

**Table 3.1-2 Fines concentrations used in this study, given for a suspension in 4 litres of seawater. For a 2 litres water loading, the concentration was twice as high.**

| Slurry quantity [ml] | Fines concentration [mg/l] | Definition |
|---|---|---|
| 0,1 | 10 | Low concentration |
| 0,4 | 40 | Moderate concentration |
| 1,0 | 100 | High concentration |
| 4,0 | 400 | Very high concentration |

### 3.1.3 Bedrock

As a standard, shale tiles of 15*15 cm were used in the experiments. The shale tiles originate from Alta in Finnmark (Norway). Shale is a sedimentary bedrock and is known for its high content of quarts which make the rock resistant for exposure (http://www.alta-skiferbrudd.no). Shale is a quite common bedrock along the Norwegian coast.

## 3.2 Experimental setup

### 3.2.1 The shoreline simulation system

SINTEF have built two identical shoreline simulation systems which each contains 12 reservoirs installed on an oscillating table. Single tiles are placed in each of the reservoirs, see Figure 3.2-1. The shoreline simulation system is placed in a temperature controlled room to ensure the required test temperature.

**Figure 3.2-1 The shoreline simulation system (to the left) and the water reservoirs (to the right).**

The simulation systems generate wave energy by tilting the oscillating table from one side to another with a standard angel and frequency. For this purpose a compressed air jack along with a control unit programmed for a uniform movement was used, see Figure 3.2-2.

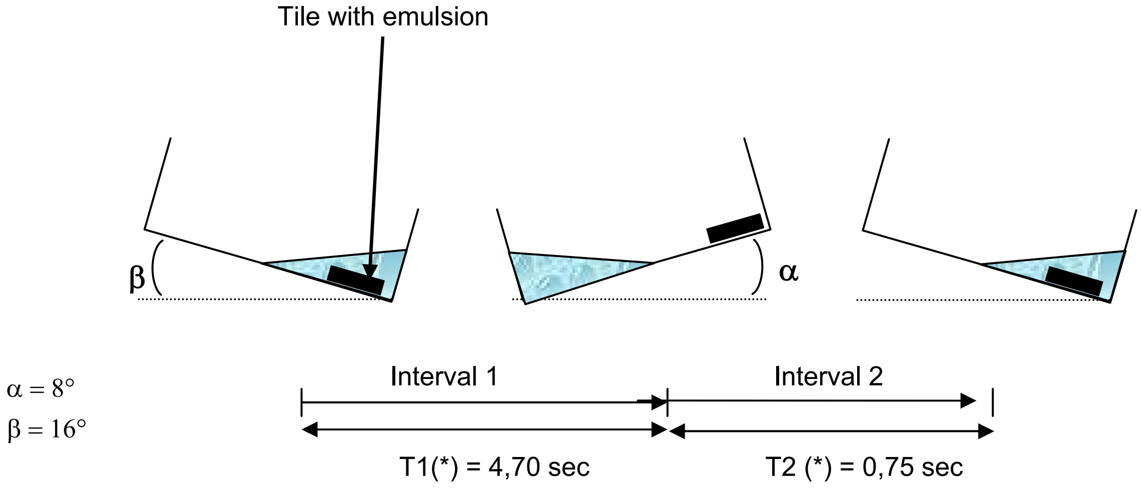


**Figure 3.2-2 The mechanism of the oscillating table – shoreline simulation system.**

### 3.2.2 Regulation of exposure degree

The exposure degree was regulated by adjusting the amount of water applied to the individual reservoirs. The reservoirs were applied 2 litres of seawater, representing a “high” energy level and 4 litres representing a “low” energy level, in the shoreline simulation system. To quantify and study the different energy levels more in detail, a numerical simulation of water flow in the reservoirs was performed. The flow regime was simulated with a Computational Fluid Dynamics (CFD) model Flow-3D for point A and B, as shown in Figure 3.2-3 and Figure 3.2-4.

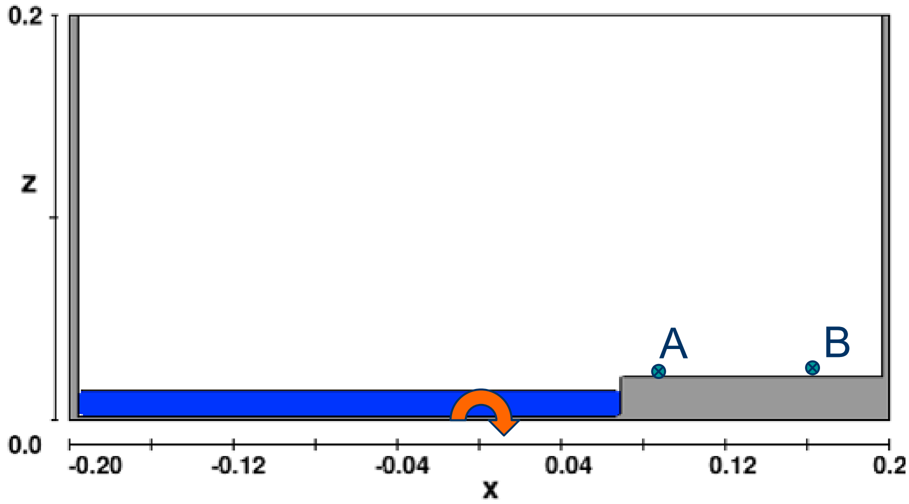


**Figure 3.2-3 Reservoir with tile, showing point A and B for velocity measurements.**

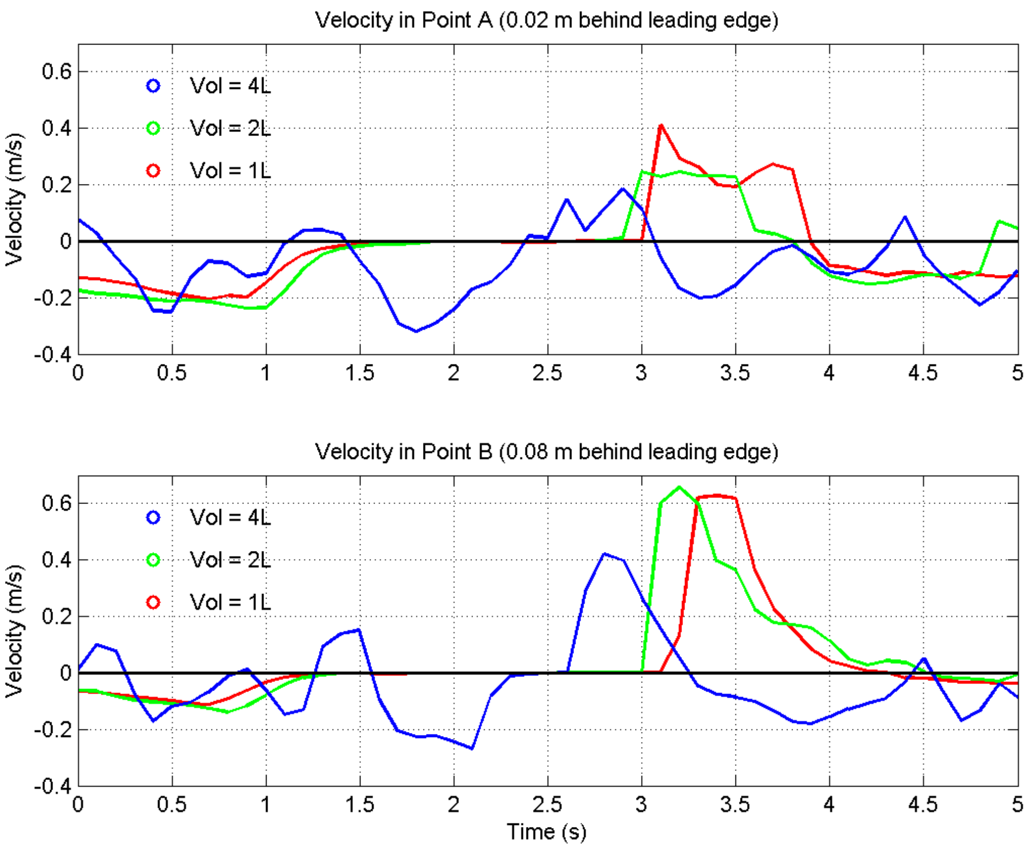


**Figure 3.2-4 Velocity profile simulation for point A and B on tiles in reservoirs containing 1, 2 and 4 litres of seawater, using a CFD model Flow-3D.**

The 1 litre (red line) and 2 litres (green line) cases showed approximately the same energy levels: During time t=3–4 seconds a wave swept across the tiles with u~0.3–0.6 m/s, it then retracted with u~-0.15 m/s during the next couple of seconds, leaving the top of the tile dry for about 1.5–2 seconds until the next wave hit. The 2 litres case had an additional weak secondary hit in point A at t=4.8 seconds. The 4 litres case was different, displaying three secondary hits by the reflected wave. The tile was constantly covered with seawater. Based on these studies, only the 2 and 4 litres energy regimes were used.

## 3.3 Experimental procedures

One day in advance of experimental start up, the reservoirs were filled with seawater containing suspended slurry of mineral fines and started for creating a sufficient mixing of the fines in the seawater, in addition to conditioning of seawater to test temperature. Shale tiles covered with emulsion were then introduced to the individual reservoirs in the shoreline simulation system for the wash-out process.

### 3.3.1 Tile preparation

Before emulsion application, the edges of the tiles were masked with tape to avoid quantification of emulsion covering the edges. The tiles were weight before masking of the edges to know the initial weight. Emulsion (22,5 g +- 0,5) were applied evenly on the bedrock surface and placed horizontally for 1 day to let the emulsion cover the tiles evenly. The tiles were then placed vertically for 4 days to let the excess emulsion run-off and to simulate weathering of emulsion on the shoreline with immobile oil.

### 3.3.2 Sampling, photo documentation and quantity analysis

Tile samples were retrieved from the shoreline simulation system during the wash-out process for quantification of removed emulsion. The exposure period extended between 0 and 28 days, depending on the parameters tested. Before emulsion quantification, the samples were placed vertically in a temperature controlled room at test temperature for 30 min to let the excess water run-off, the tape on the edges were then removed. The tiles were photo documented at application of emulsion, after run-off of excess emulsion and during and after exposure period. In some situations there were too little emulsion left on the tiles to ensure good quality of the quantitative weight measurements, the samples was then extracted in dichloromethane (DCM) and analysed in a Hitachi U-2000 spectrophotometer.

### 3.3.3 Oil properties

To study the oils rheology, a Physica MCR300 MC1+ rheometer with an US200 software was used. Parameters measured were; viscosity, storage modulus, loss modulus and yield stress. To get an indication of how the restitution phase effected the emulsion properties, the parameters were measured before application on the tiles, after run-off of excess emulsion, during sampling and after test period. For some of the studies, too little emulsion was left on the tile surface to do all the measurements, the viscosity measurement was then prioritised. Density and pour point for the different oils were measured initially, see Table 3.1-1.

## 3.4 Experimental parameters and design

Four different experimental parameters were tested in this study:

- **Exposure degree**
  To study the effect of different energy levels (high and low), two different seawater loadings were used, 2 litres representing high energy and 4 litres representing low energy.
- **Oil types**
  To study the effect of oil type, three different crude oils; Troll, Kobbe, Norne and one bunker fuel oil; IFO 380 was used.
- **Sediment fines concentration**
  To study the effect of suspended fines in the seawater, four different quantities of fines were used; 10 mg/l (low), 40 mg/l (moderate), 100 mg/l (high) and 400 mg/l (very high).
- **Photo-oxidation of crude oil**
  To study if the mineral fines had an effect on crude oil subjected for sun exposure, Kobbe crude oil was photo-oxidized.

To validate the results, most of the experiments were done in triplicates. The standard deviation shows up to 20% deviation for the run-off of excess oil and up to 30% for the retained emulsion on the tiles after exposure. This was considered as an acceptable variance. Table 3.4-1 gives an overview of the experimental design including the experimental parameters for this activity.

**Table 3.4-1 Experimental design (WiO – Water in oil / emulsification).**

| SINTEF ID | Oil | WiO | Evaporated | Spesification | Start | 1 | 2 | 3 | 5 | 6 | 7 | 8 | 12 | 14 | 15 | 16 | 26 | 28 days |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 2007-0287 | Troll | 70 % | 250°C+ residue | *Exposure degree - 4 litres:* | | | | | | | | | | | | | | |
| | | | | Low | x | | x | | | | x | | | | | | | |
| | | | | Moderate | x | x | | x | | x | | | x | | | | | |
| | | | | High | x | | | | | | | | | | | | | |
| | | | | Very high | x | | x | | x | | | | | | | | | |
| | | | | No fines (Ref.) | x | | x | | x | | x | | | x | | | | x |
| | | | | *Exposure degree - 2 litres:* | | | | | | | | | | | | | | |
| | | | | Low | x | x | | x | | x | | | | x | | | | |
| | | | | Moderate | x | x | | x | | x | | | | x | | | | |
| | | | | High | x | x | | x | | x | | | | x | | | | |
| | | | | No fines (Ref.) | x | | x | | x | | | | | | x | | | |
| 2006-1061 | Kobbe | 75 % | 250°C+ residue | *Exposure degree - 4 litres:* | | | | | | | | | | | | | | |
| | | | | Low | x | | x | | | | x | | | | | | | |
| | | | | Moderate | x | | x | | | | x | | | | | | | |
| | | | | High | x | | x | | | | x | | | | | | | |
| | | | | No fines (Ref.) | x | | | x | | | x | | | x | | | | x |
| | | | | *Exposure degree - 2 litres:* | | | | | | | | | | | | | | |
| | | | | No exposure | x | | | | | | x | | | | | | | |
| | | | Ph.ox | Photo oxidation | x | x | | x | | | x | | | | | | | |
| | | | | No fines (Ref.) | x | x | | x | | | x | | | | | | | |
| 2007-0260 | Norne | 60 % | 250°C+ residue | *Exposure degree - 4 litres:* | | | | | | | | | | | | | | |
| | | | | Low | x | | x | | | | x | | | | | | | |
| | | | | Moderate | x | | x | | | | x | | | | | | | |
| | | | | High | x | | x | | | | x | | | | | | | |
| | | | | No fines (Ref.) | x | | x | | x | | x | | | x | | | | x |
| | | | | *Exposure degree - 2 litres:* | | | | | | | | | | | | | | |
| | | | | Low | x | x | | x | | x | | | | x | | | | |
| | | | | Moderate | x | x | | x | | x | | | | x | | | | |
| | | | | High | x | x | | x | | x | | | | x | | | | |
| | | | | No fines (Ref.) | x | x | | x | | | | x | | | | x | | |
| 2006-1125 | IFO 380 | 40 % | | *Exposure degree - 4 litres:* | | | | | | | | | | | | | | |
| | | | | Low | x | | x | | | | x | | | | | | | |
| | | | | Moderate | x | | x | | | | x | | | | | | | |
| | | | | High | x | | | x | | | | x | | | | x | x | |
| | | | | No fines (Ref.) | x | | | | | | x | | | x | | | | x |
| | | | | *Exposure degree - 2 litres:* | | | | | | | | | | | | | | |
| | | | | Moderate | x | x | | x | | | x | | | | | | | |
| | | | | No exposure | x | | | | | | x | | | | | | | |
| | | | | No fines (Ref.) | x | | | x | | | x | | | x | | | | |

# 4 Results and discussions

Table 4-1 show the experimental parameters used in this activity. The parameters of variance was marked with bold text, the rest of the parameters is standard.

**Table 4-1 Experimental parameters.**

| Parameter | Variation |
|---|---|
| **Oil type** | • **Troll crude**<br>• **Kobbe crude**<br>• **Norne crude**<br>• **IFO 380 - bunker fuel oil** |
| **Evaporation** | **250°C+ residues (crude oils)**<br>**Photo-oxidation (crude oil)** |
| Water content in emulsion | • 70% (Troll)<br>• 75% (Kobbe)<br>• 60% (Norne)<br>• 40% (IFO 380) |
| Temperature | 5°C |
| Emulsion thickness / loading | 1 standard film thickness – 1 mm (22,5 g) |
| Bedrock | Shale tiles |
| **Exposure degree** | • **2 litres (High energy)**<br>• **4 litres (Low energy)** |
| **Fines concentration** | • **0 [mg/l] (No fines – reference)**<br>• **10 [mg/l] (Low)**<br>• **40 [mg/l] (Moderate)**<br>• **100 [mg/l] (High)**<br>• **400 [mg/l] (Very high)** |

The parameters of variance, used in the different studies, are presented at the beginning of each chapter. The experimental parameter tested is marked with a bold text.

To get a better understanding of how the weathering of emulsion on bedrock affects the rheological properties of the oils, several rheological parameters were measured. A definition of the different properties is given in *Appendix 2*. The rheological properties measured are given in *Appendix 3*. The rheological results showed a decrease in viscosity for the Troll oil during weathering on bedrock (likely due to emulsion instability - water segregating from the oil phase), in contrast to an increase in viscosity for the IFO 380 oil (stabile emulsion due to a high wax content). Troll, Norne and IFO 380 seems to increase in viscosity during exposure period in the shoreline simulation system.

To study the correlation between wash-out data and the rheological properties for the weathered oils, the data was correlated using standard software routines in Excel. The results showed the viscosity to be the main important parameter for the retention of emulsion. The results from the correlation study are given in *Appendix 4*.

Photo documentation for the studies is given in *Appendix 5*.

### 4.1 Effect of mineral fines concentration

**Table 4.1-1 Experimental parameters used in this study**

| Parameter | Variation |
|---|---|
| Oil type | Troll, Kobbe, Norne and IFO 380 |
| Evaporation | 250°C+ residues (crude oils) |
| Exposure degree | Low energy (4 litres) |
| **Fines concentration** | **Low, moderate, high and very high (Troll) concentration + no fines (reference)** |

Four different concentrations of fines were suspended in seawater and used for the selected oils to study the wash-out of emulsion dependent on the presence of fines.

The emulsion retention for the Troll oil, as a function of fines concentration and time is given in Figure 4.1-1 and Figure 4.1-2

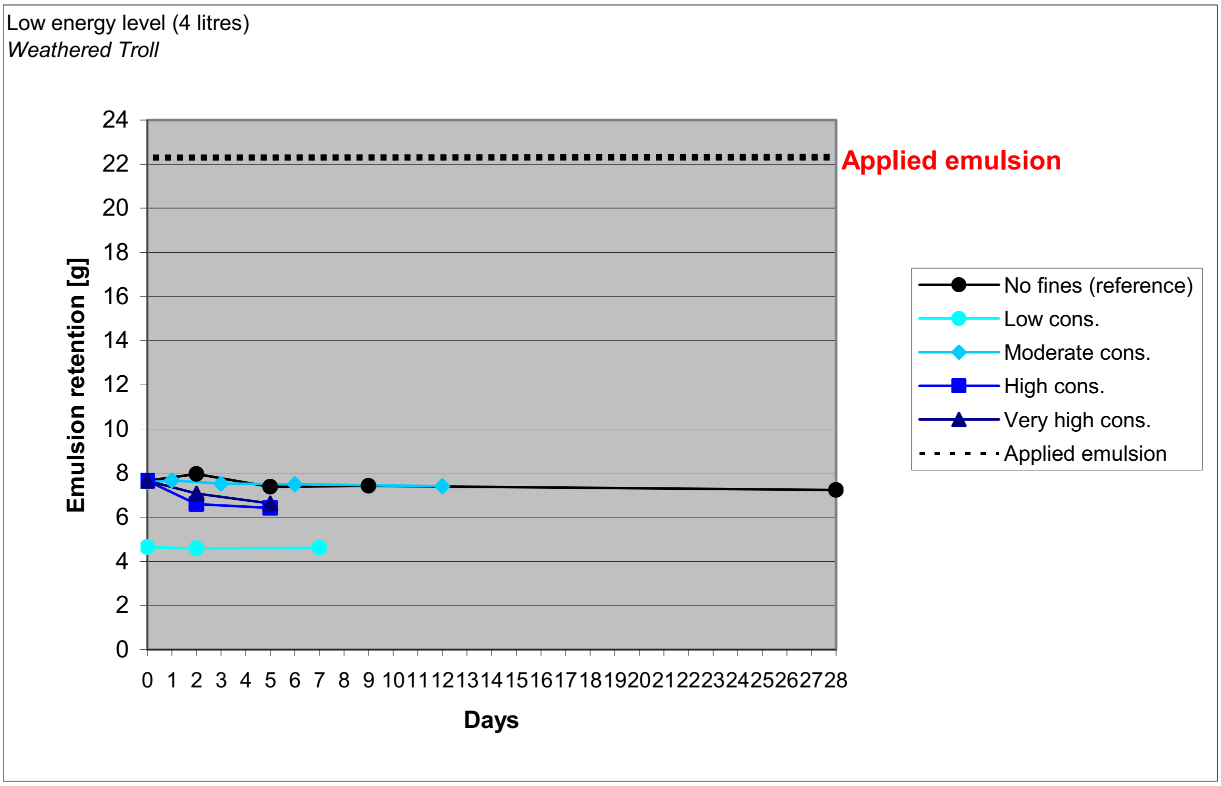


**Figure 4.1-1 Emulsion retention of Troll oil as a function of fines concentration and time, for the low energy level (4 litres).**

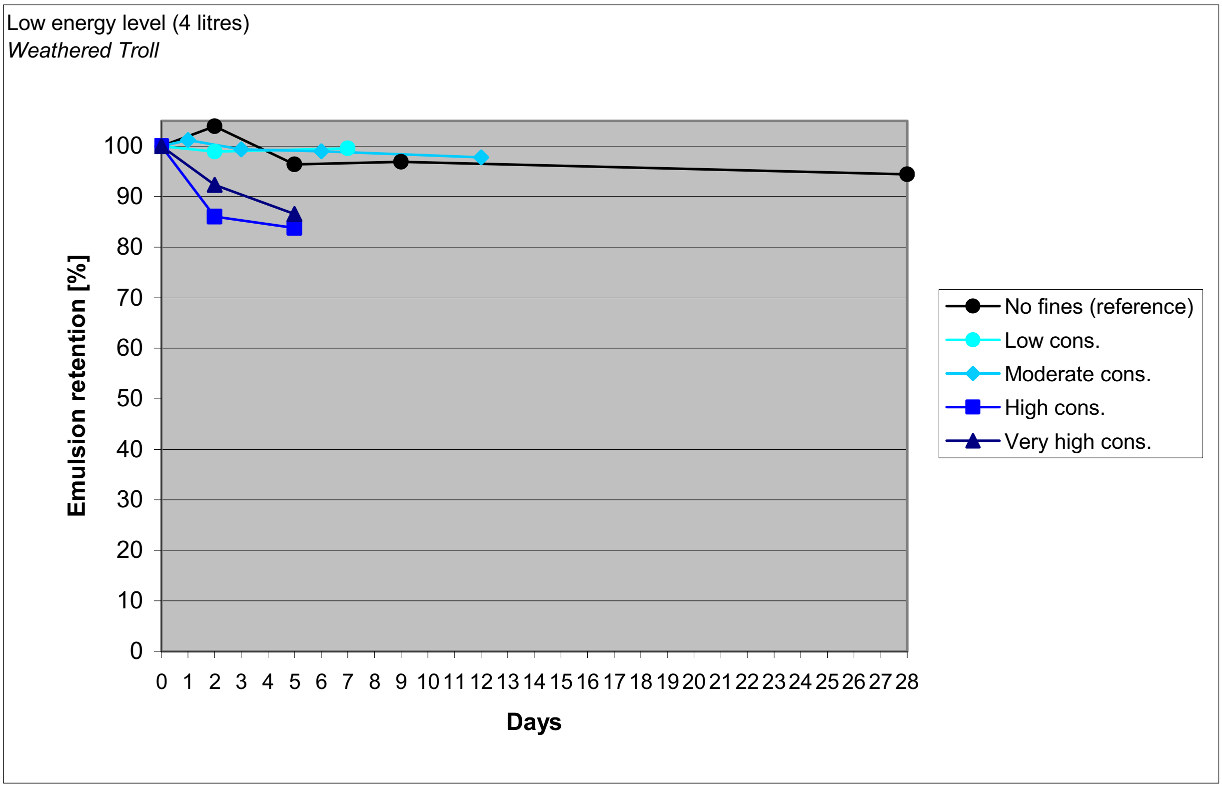


**Figure 4.1-2 Emulsion retention of Troll oil as a function of fines concentration and time, given in percent for the low energy level (4 litres).**

Due to the low yield stress and pour point of Troll oil, not much of the emulsion was left on the bedrock after drainage of excess emulsion, see Figure 4.1-1. The results show, however, an effect of fines in the seawater, decreasing the emulsion retention after 5 days. It was found less emulsion retention on the tiles subjected for high (100 mg/l) to very high (400 mg/l) concentration levels of fines in the seawater, compared to the other concentrations. Low to normal concentrations of fines do not seem to have any effect on the wash-out of emulsion for the Troll oil. Due to the small difference in efficiency for the high and very high concentration level, it was decided not to use the very high concentration level in the further studies.

Earlier studies have shown an increase in oil-fines aggregates with an increase in mineral fines concentration (Ajijolaiya et. al., 2006). The results elaborated in this study seem to correlate relatively well with that results, showing a greater wash-out of emulsion for the high concentration levels, compared to the low concentration levels.

Emulsion retention for the Kobbe oil, as a function of fine concentration and time is given in Figure 4.1-3 and Figure 4.1-4.

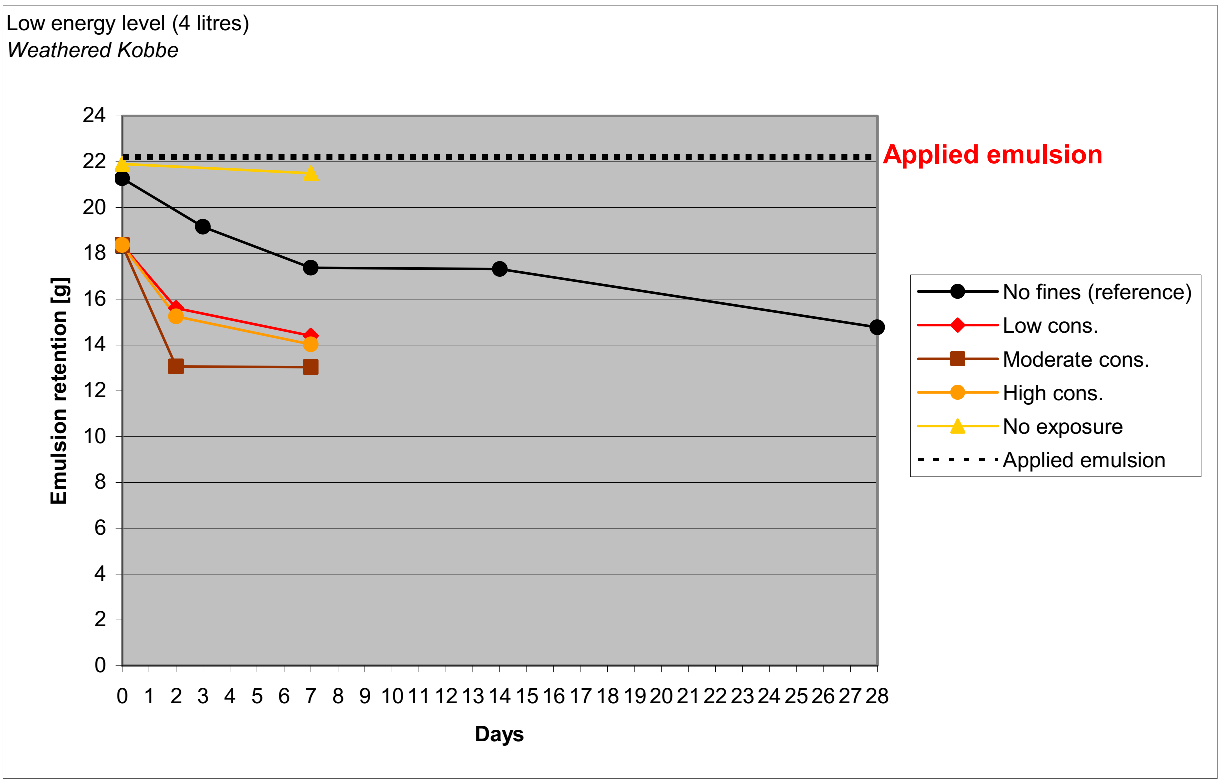


**Figure 4.1-3 Emulsion retention of Kobbe oil as a function of fines concentration and time, for the low energy level (4 litres).**

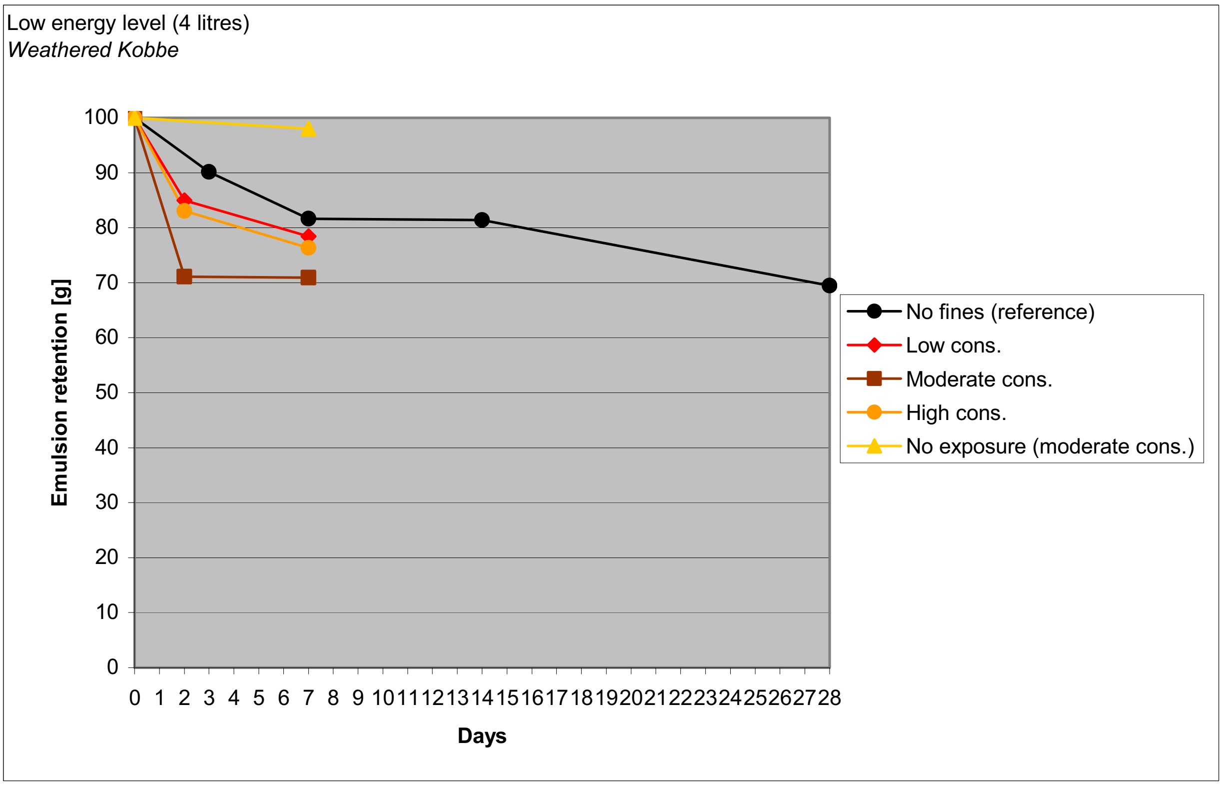


**Figure 4.1-4 Emulsion retention of Kobbe oil as a function of fines concentration and time, given in percent for the low energy level (4 litres).**

For the Kobbe oil, the presence of fine particles in the seawater also seemed to enhance the wash-out of emulsion. The results show no uniform increase in wash-out dependent on concentration level. As Figure 4.1-4 shows, energy is important to generate the effect of the fines. This correlate well with observations found in earlier studies (Owens & Lee, 2003).

Emulsion retention for the Norne and IFO 380 oil, as a function of fine concentration and time, are given in Figure 4.1-5, Figure 4.1-6.

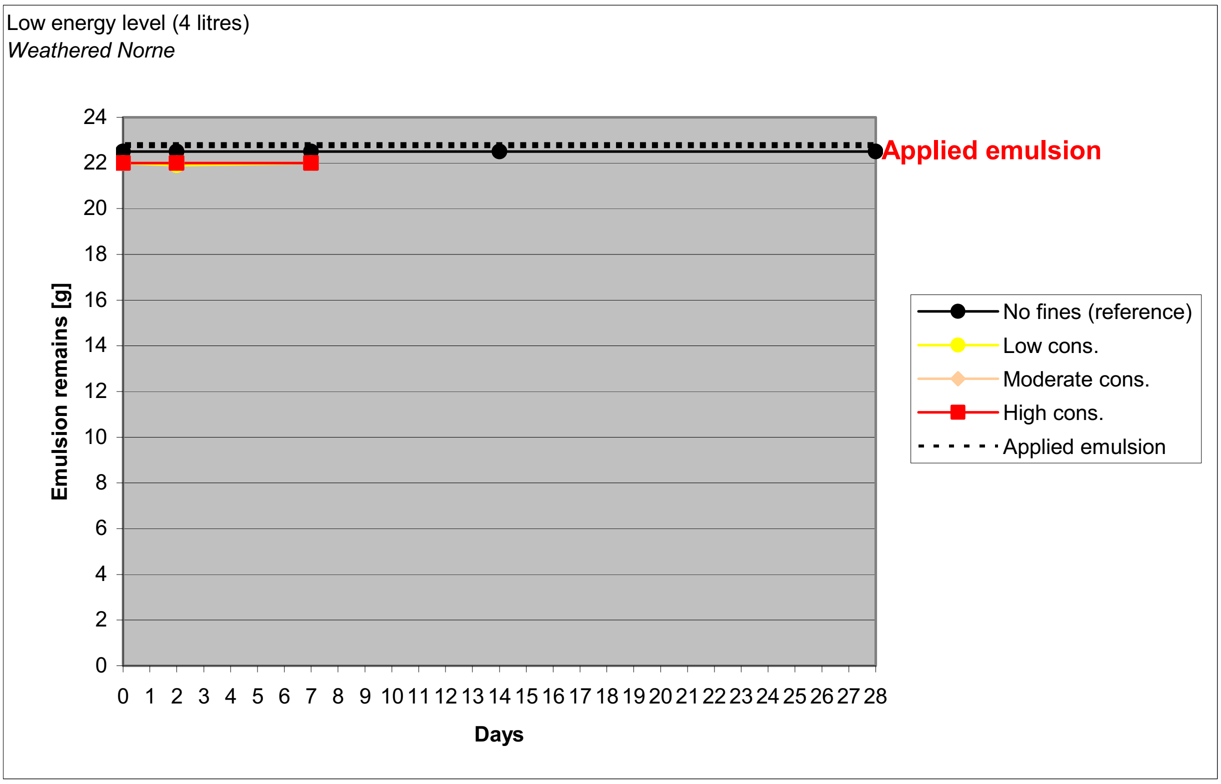


**Figure 4.1-5 Emulsion retention of Norne oil as a function of fines concentration and time, for the low energy level (4 litres).**

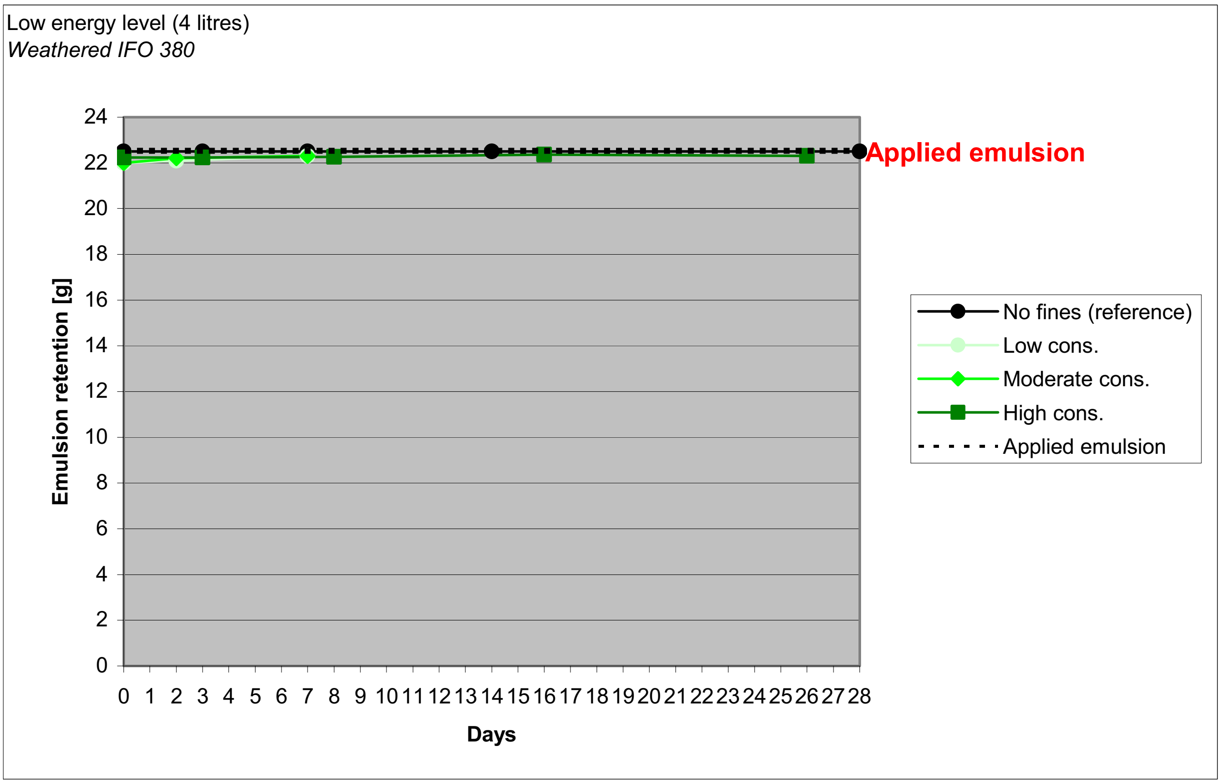


**Figure 4.1-6 Emulsion retention of IFO 380 as a function of fines concentration and time for the low energy level (4 litres).**

For the Norne and IFO 380 oil, the presence of fines in the seawater showed no effect. Due to little or no runoff of excess emulsion during the weathering process on the bedrock tiles, remaining emulsion were constant at approximately 21 grams. The small decrease in emulsion retention at start might be due to evaporation of oil or water in the emulsion.

### 4.2 Effect of exposure degree

**Table 4.2-1 Experimental parameters used in this study**

| Parameter | Variation |
|---|---|
| Oil type | Troll, Kobbe, Norne and IFO 380 |
| Evaporation | 250°C+ residues (Troll and Norne), ph.ox (Kobbe) |
| **Exposure degree** | **Low energy (2 litres), compared to 4 litres given in Chapter 4.1.** |
| Fines concentration | Low, moderate and high concentration + no fines (reference) |

To study the effect of exposure grade with the presence of fines, a high energy regime (2 litres) was used to correlate with the low energy regime (4 litres).

Emulsion retention for the high energy scenario as a function of fines concentration and time for the Troll oil is given in Figure 4.2-1 and Figure 4.2-2.

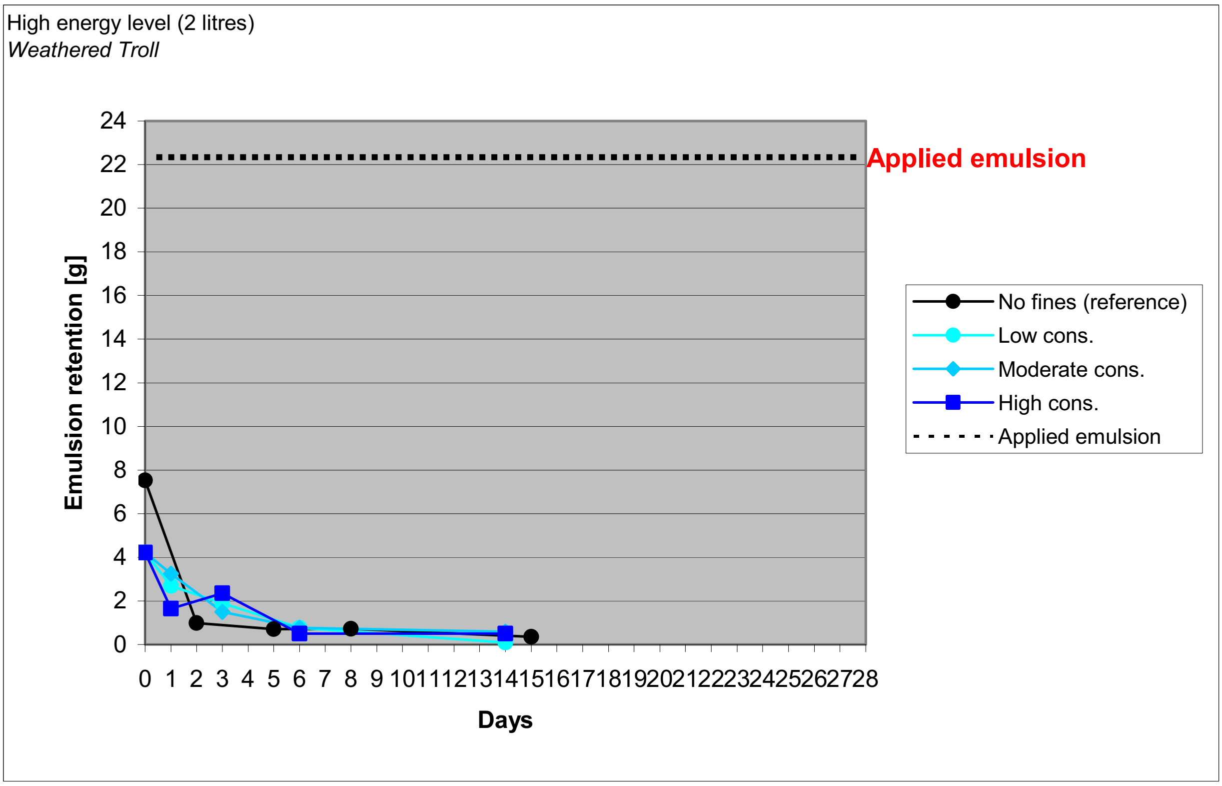


**Figure 4.2-1 Emulsion retention of Troll oil using a high energy level (2 litres) as a function of fines concentration and time.**

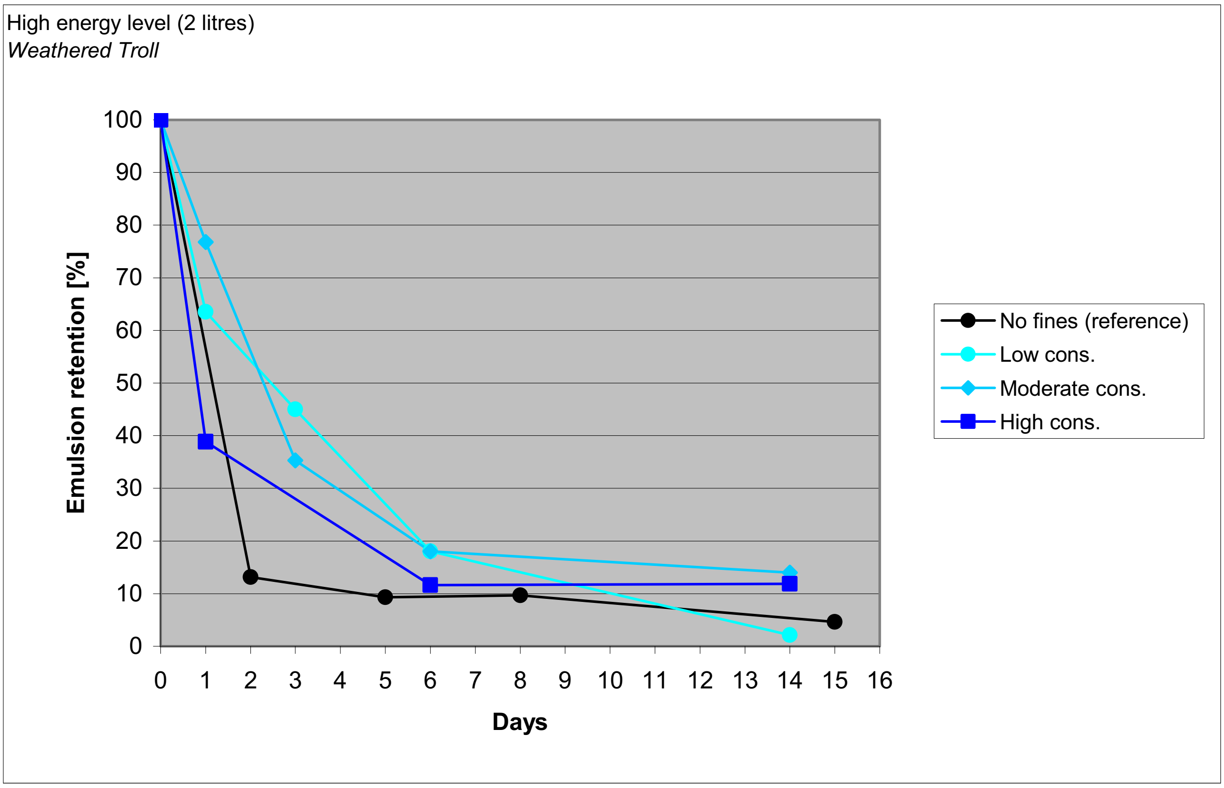


**Figure 4.2-2 Emulsion retention of Troll oil using a high energy level (2 litres) as a function of fines concentration and time, given in percent.**

The high energy scenario showed a great increase of washed out emulsion, compared to the low energy scenario. Due to the high energy regime, the effect of fines got over ruled, for the Troll oil. The presence of fines actually seems to reduce the wash-out effect the first days of the wash-out period.

To study if the presence of fines in seawater had an effect on oil subjected for sun exposure, a photo-oxidized Kobbe oil was tested for the high energy level, instead of testing an emulsified Kobbe 250˚C+ residue. Photo-oxidation changes the properties of the oil e.g. increasing the viscosity. Emulsion retention for photo-oxidized Kobbe oil as a function of fine concentration and time are given in Figure 4.2-3 and Figure 4.2-4.

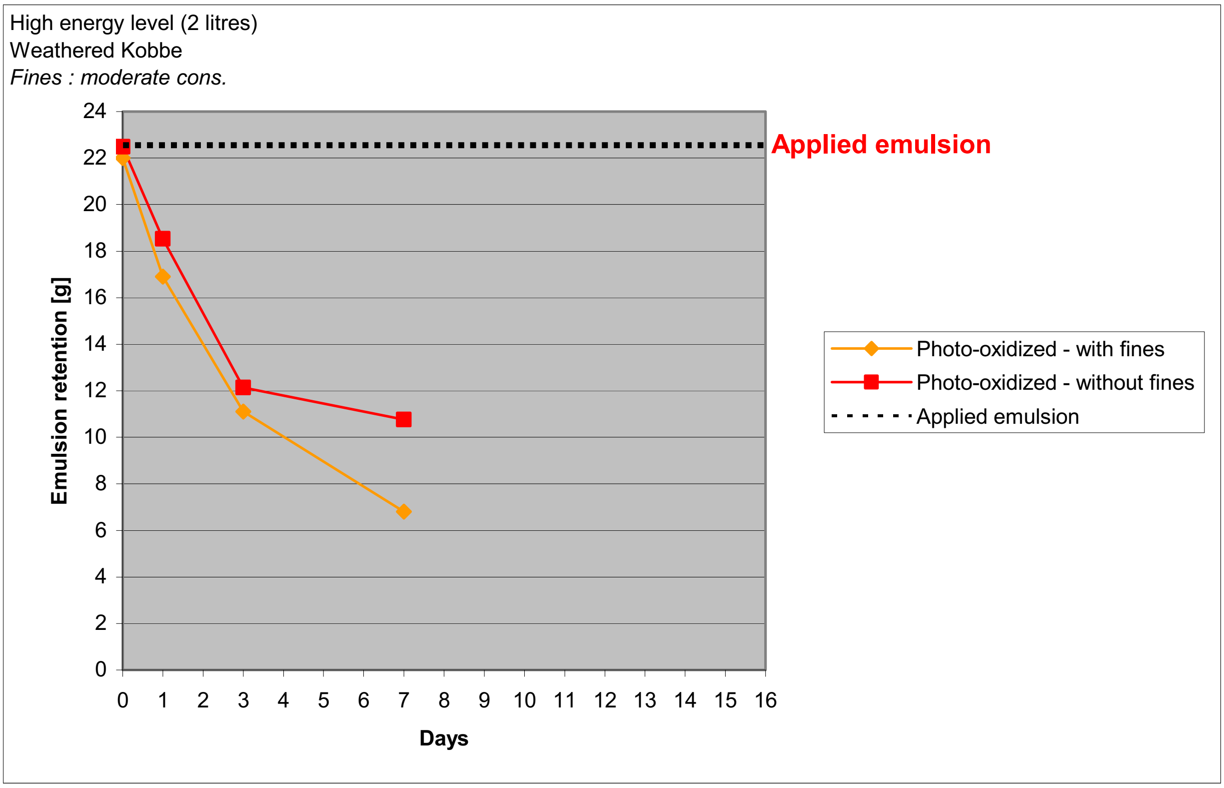


**Figure 4.2-3 Emulsion retention of photo-oxidized Kobbe oil using a high energy level (2 litres) as a function of the presence of fines and time.**

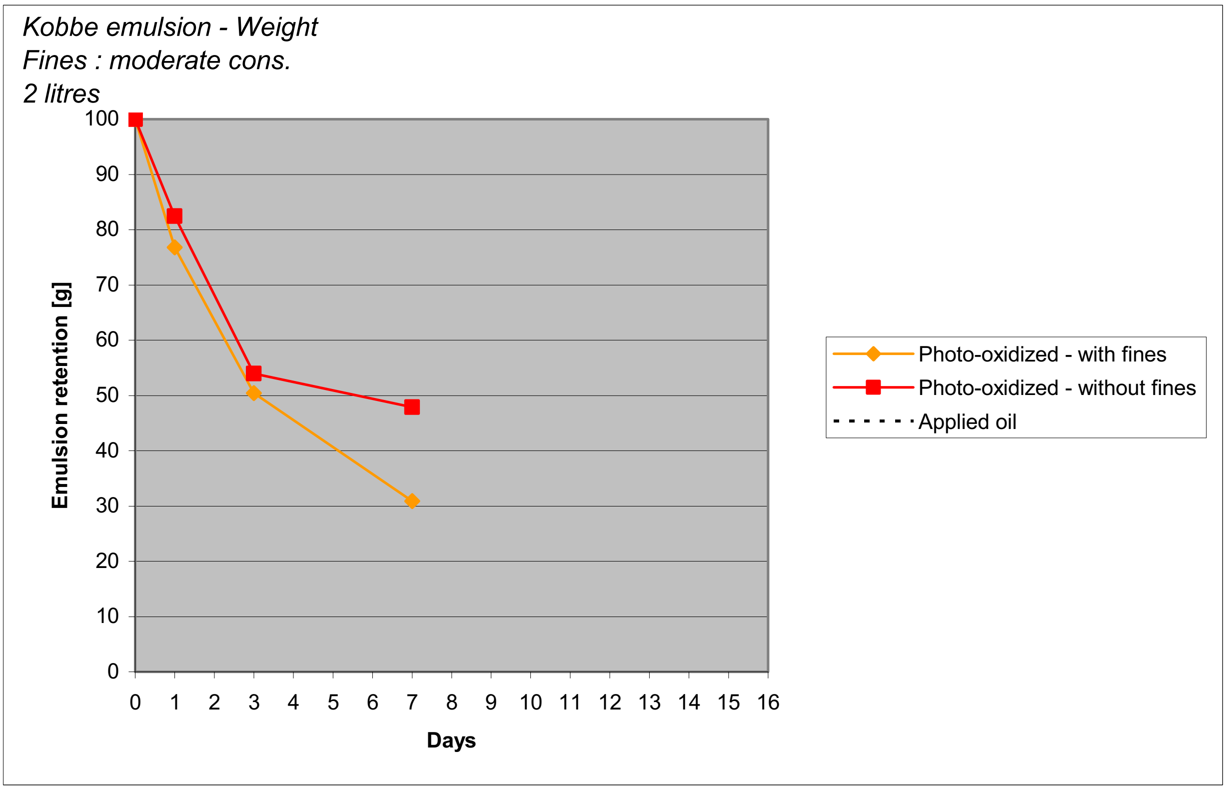


**Figure 4.2-4 Emulsion retention for photo-oxidized Kobbe oil using a high energy level (2 litres) as a function of the presence of fines and time, given in percent.**

The presence of fines, also seem to have an effect on photo-oxidized Kobbe oil, as for the un photo-oxidized oil in the low energy study, see Figure 4.1-4 and Figure 4.2-4. The wash-out rate seem to be approximately the same the first days, the presence of fines seems then to continue the emulsion wash-out, in contrast to the reservoirs without fines.

Emulsion retention for a high energy scenario as a function of fine concentration and time for the Norne oil are given in Figure 4.2-5 and Figure 4.2-6.

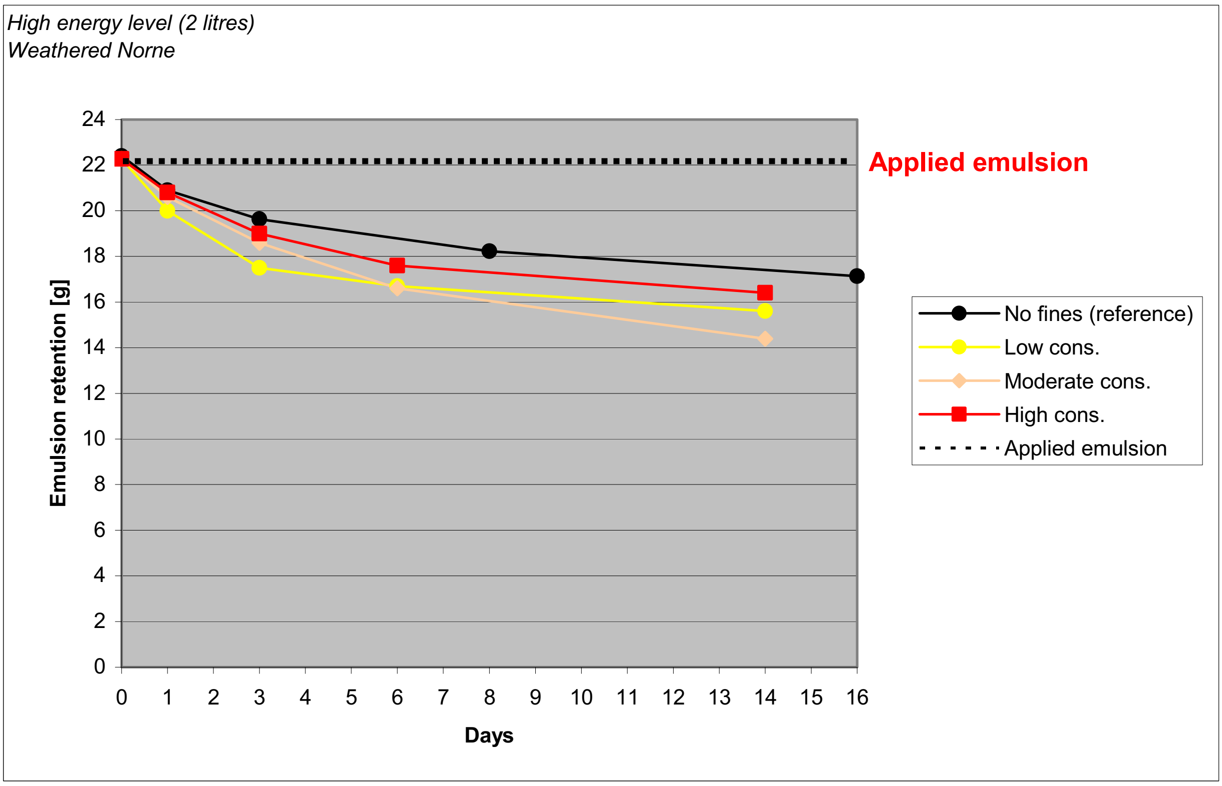


**Figure 4.2-5 Emulsion retention for Norne oil using a high energy level (2 litres) as a function of fines concentration and time.**

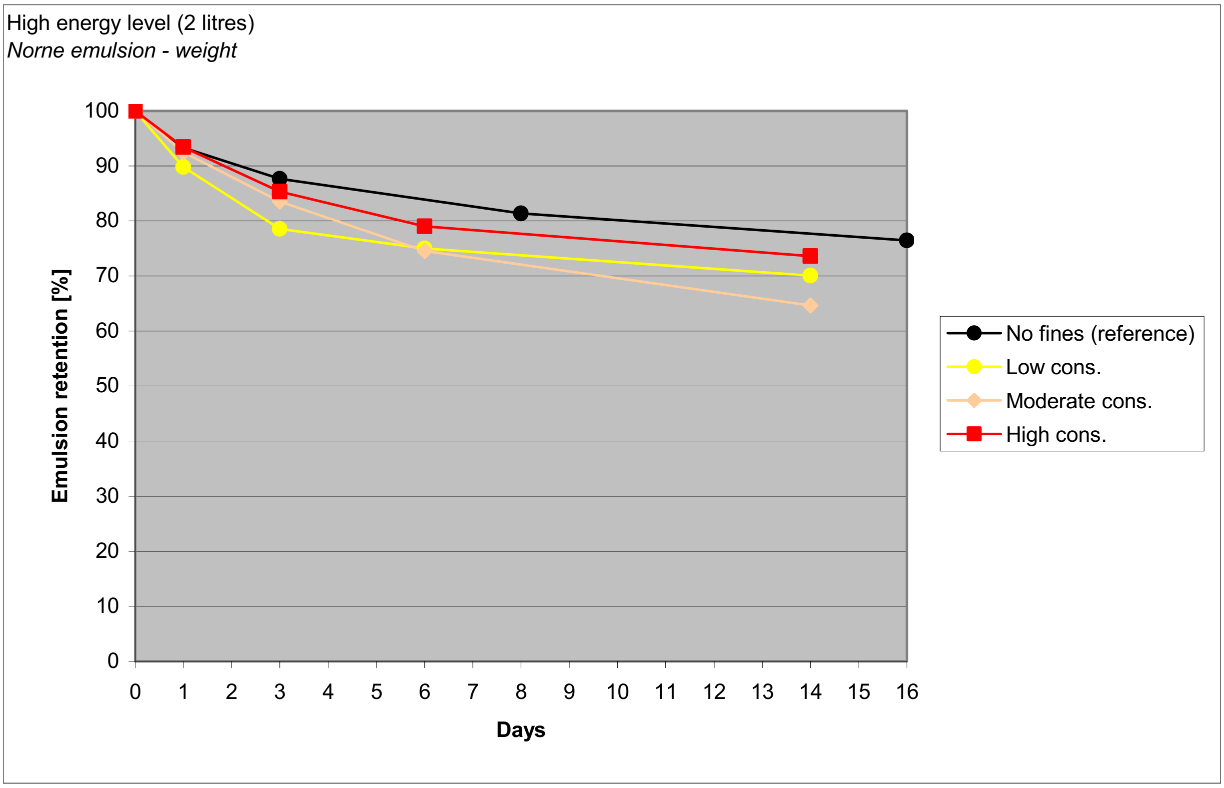


**Figure 4.2-6 Emulsion retention for Norne oil using a high energy level (2 litres) as a function of fines concentration and time, given in percent.**

In contrast to the Troll oil, the fines presence in seawater showed a clear effect for the Norne oil, decreasing the emulsion retention from 78% to 65% at the most. No trend in concentration effect could be observed in this study.

Emulsion retention for a high energy scenario as a function of fine concentration and time for the IFO 380 oil is given in Figure 4.2-7.

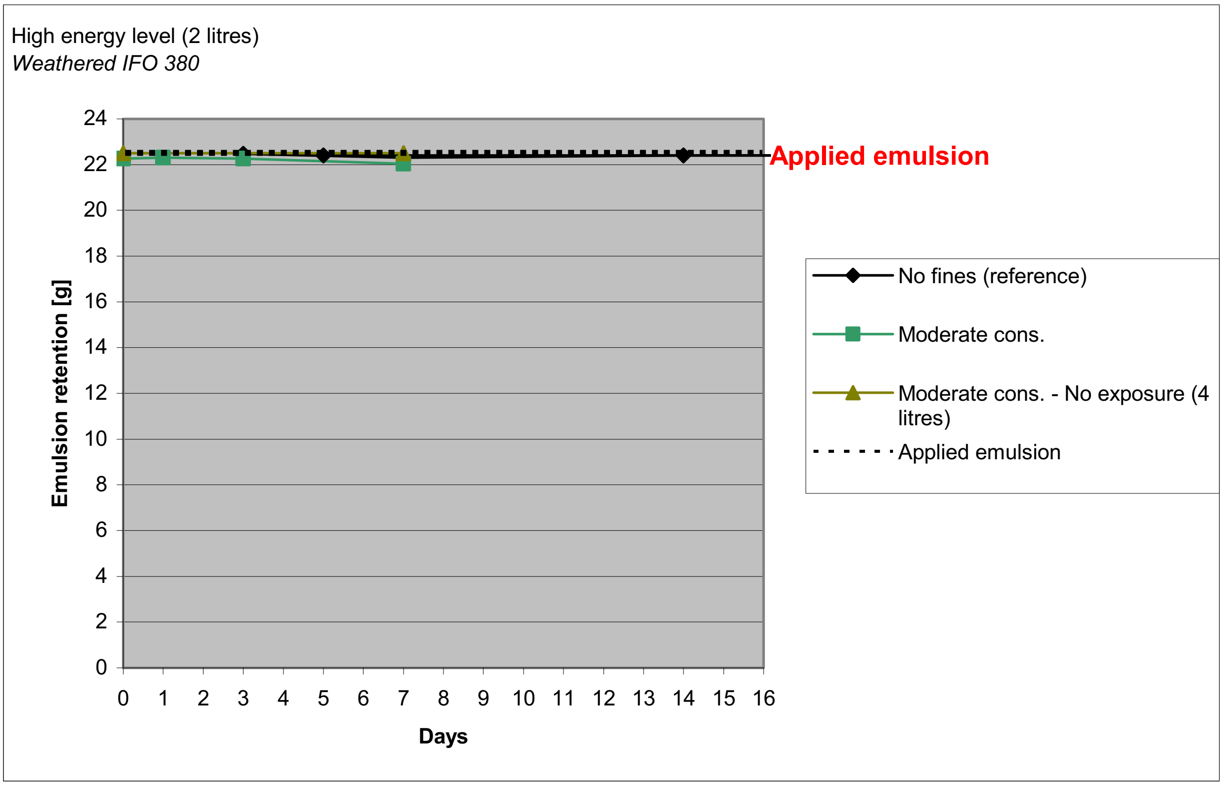


**Figure 4.2-7 Emulsion retention for IFO 380 using a high energy level (2 litres) as a function of fines concentration and time.**

The presence of fines for the IFO 380 bunker fuel oil did not seem to have any effect for either of the two energy regimes. As expected, a moderate concentration level for a no exposure regime showed no wash-out / refloating of emulsion.

It was considered as unlikely that the IFO 380 bunker fuel oil could be washed out at any other exposure degrees, possible simulated in the shoreline simulation system. No further exposure degree studies were therefore done.

The results given in an oil type perspective is shown in Chapter 4.3.

## 4.3 Effect of oil type

**Table 4.3-1 Experimental parameters used in this study**

| Parameter | Variation |
|---|---|
| **Oil type** | **Troll, Kobbe, Norne and IFO 380** |
| Evaporation | 250°C+ residues (crude oils) and photo-oxidized oil (Kobbe) |
| Exposure degree | Low energy (4 litres) and high energy (2 litres) |
| Fines concentration | Moderate concentration and no fines (reference) |

The amount of emulsion remained on the bedrock surface in regards to the different oils, at a low energy level (4 litres) for a moderate mineral fines concentration, is shown in Figure 4.3-1.

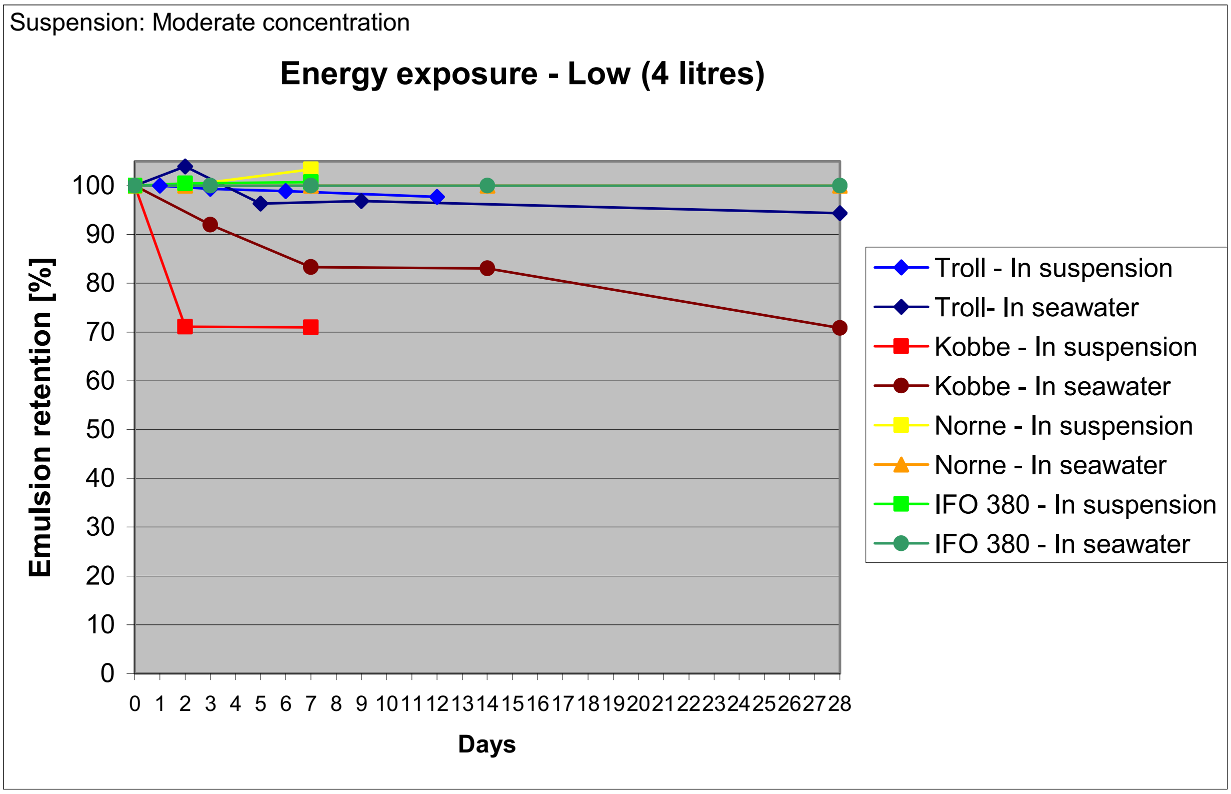


**Figure 4.3-1 Emulsion retention as a function of oil type for the low energy level (4 litres).**

The presence of fines in the seawater, for the low energy level, showed almost no wash-out of any of the oils, except for Kobbe, showing an increased wash-out of emulsion with the presence of fines. The greatest efficiency was found the first two days. Norne and IFO 380 seemed unaffected by the presence of the fine particles suspended in the seawater, the particles seemed actually to stick to the emulsion surface, resulting in an emulsion retention of over 100%, see Table 4 - *Appendix 5*.

The amount of emulsion remained on the bedrock surface in regards to the different oils at a high energy level (2 litres), is shown in Figure 4.3-2.

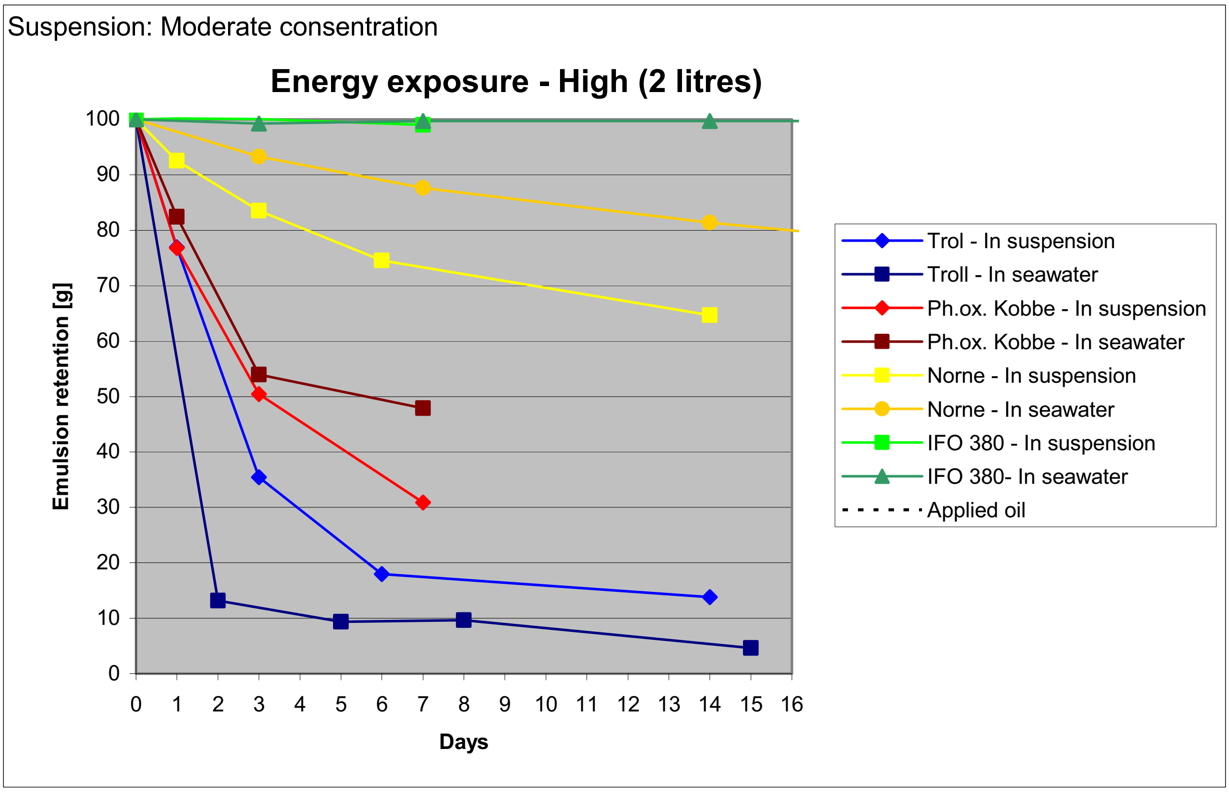


**Figure 4.3-2 Emulsion retention as a function of oil type for the high energy level (2 litres).**

The high energy study showed a strong increase in wash-out efficiency, compared to the low energy level. Emulsified Norne and photo-oxidized Kobbe oil were the only oils showing an increased wash-out effect with the presence of fines. As discussed in Chapter 4.1, the concentration study shows a wash-out effect for the high and very high concentrations for the Troll oil, compared to the moderate concentration level.

# 5 Conclusions

For the low energy scenario the presence of fines showed a slightly increased wash-out effect for the Troll and Kobbe oil. Norne showed no wash-out of oil for any of the concentrations tested. The fines in the seawater seemed to adhere to the emulsion surface, for the high viscoelastic emulsions like Norne and IFO 380, not subjected for wash-out.

For the high energy scenario, the exposure degree was sufficient to wash-out almost all of the Troll emulsion, leaving approximately 5% of emulsion left on the tiles. The effect of the presence of fines in the seawater was insignificantly compared to the natural processes. The presence of fines seemed to retard the wash-out process to some extent. For the Norne oil, the presence of fines showed a slight effect, increasing the emulsion wash-out with approximately 10% as an average for the three concentrations of fines tested. The studies indicate a need for some energy to generate the effect of the fines. The presence of fines, also showed an effect on photo-oxidized Kobbe oil, decreasing the retained emulsion with approximately 17%.

For the Troll oil, only higher concentration levels of fines seemed to have an effect on the wash-out of emulsion. There were observed no uniform trend in wash-out effect correlated to the concentration levels of fines for the Kobbe and Norne oil.

The presence of fines had no influence on the bunker fuel oil (IFO 380) for any of the parameters tested.

Results from a simple correlation study showed that viscosity was of relevance for the retention of emulsion, increasing in retained emulsion with an increase in viscosity.

The overall conclusion for this limited experimental study seems to indicate that the presence of fines in seawater close to shore is of minor importance for the wash-out kinetics of weathered oil for relevant Norwegian conditions.

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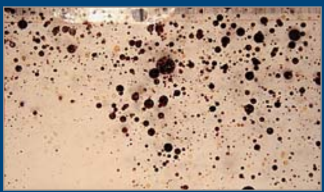

## Coastal Oil Spills - JIP

Report no.: 9

# C4.5 - Wash-out of weathered oil by erosion processes from shoreline sediment

Jane H.C. Øksenvåg, Svein Ramstad and Merete Ø. Moldestad

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**C4.5 - Wash-out of subsurface weathered oil by erosion processes from shoreline sediment**

**Coastal Oil Spills JIP. Report No. 9**

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ABSTRACT

Removal of oil from shoreline sediment by physical erosion is observed in field experiments to contribute significantly in the restoration process. The objective of this study was to study and quantify the physical removal of immobile subsurface weathered oil from sediment substrate with the influence of physical erosion under controlled conditions at 5˚C. For this purpose a shoreline simulation system was used. Parameters tested were oil type, sediment fractions, emulsion loading, exposure degree and the effect of restoration versus acute of emulsion in sediment.

The results indicated that oil type (reflecting viscosity) and oil loading are the most important parameters for the erosion process. Low viscous oils, like Troll and Kobbe, show a greater wash-out rate due to the erosion processes, than the high viscous oils Norne and IFO 380. The erosion process show a much higher wash-out rate from highly contaminated sediment compared to sediment with lower concentrations of oil. The wash-out rate of emulsion seems to decrease with time.

The experimental system was not optimal for studying erosion of oil infested sediment. The results show nevertheless an effect of the erosion process, giving a higher wash-out of emulsion during the exposure process.

| KEYWORDS | ENGLISH | NORWEGIAN |
|---|---|---|
| GROUP 1 | Chemistry | Kjemi |
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| SELECTED BY AUTHOR | Coastal oil spill | Kystnær oljesøl |
| | Sediment | Sediment |
| | Erosion | Erosjon |

# TABLE OF CONTENTS

## 1 Summary

The objective of this study was to study and quantify the physical removal of immobile oil from sediment substrate with the influence of physical erosion under controlled north and winter conditions at 5˚C.

To study the wash-out of weathered oil due to erosion processes, a shoreline simulation system was used. The shoreline simulation system contained 12 reservoirs installed on an oscillating table. Oil infested sediment, using two grain size fractions, was placed in each of the reservoirs. The reservoirs were then applied 4 litres of seawater, representing a "low" energy level in the shoreline simulation system. The wash-out of oil due to the erosion process was quantified by performing a concentration analysis in the sediment before and after exposure period (1 day). In addition, gravitational measurements were performed. Parameters tested were oil type, sediment fractions, emulsion loading, exposure degree and the effect of restoration of emulsion in sediment.

The results indicated that oil type and oil loading are the most important parameters for the erosion process. Low viscous oils, like Troll and Kobbe, show a greater wash-out due to the erosion processes, than the high viscous oils Norne and IFO 380. The wash-out of emulsion seems to decrease with time, having the highest wash-out rate in the initial phase. The erosion process show a much higher wash-out degree from highly contaminated sediment compared to sediment with lower concentrations of oil. Emulsified oils seem to be eroded out of the sediment more easily than the un-emulsified oil, for both fine and coarse grained sediment. The emulsified oils were dispersing in to the water column during the erosion process, this in contrast to water free Troll oil, forming an oil layer on the water surface without a large degree of dispersion. The results for the Troll oil indicate a similar wash-out rate for emulsion subjected for erosion in the acute and restoration phase.

The experimental system was not optimal for studying erosion of oil infested sediment. The results show nevertheless an effect of the erosion process, giving a higher wash-out of emulsion.

## 2 Introduction

This project has been a part of phase 1 in the Coastal Oil Spills JIP. The research projects in the JIP have been focused on the fate and behavior of oil spills in coastal areas and on shoreline. Laboratory studies have been performed in order to obtain data for further development of numerical models.

The first phase of the JIP was performed in the period from 2006 to 2008, and was funded by Eni Norge, Shell Technology and StatoilHydro. The overall objectives of the JIP have been:

- to contribute to an adequate and sufficient basis of competence to document possible consequences in case of an oil spill close to the coast
- to provide documentation ensuring the countermeasures giving the optimal environmental gain

Removal of oil from shoreline sediment by physical erosion is observed in field experiments to contribute significantly in the restoration process. The removal of oil is dependent on movement of sediment particles, created by wave exposure e.g. (Owens, 1998).

The objective of this study was to study and quantify the physical removal of immobile oil from sediment substrate with the influence of physical erosion under controlled north and winter conditions at 5˚C. For this purpose a shoreline simulation system was used.

# 3 Experimental

## 3.1 Materials

### 3.1.1 Oil types and weathering degree

Crude oils can be characterised in four categories: asphaltenic, napthenic, paraffinic and waxy crude oils. The crude oils studied in the Coastal Oil Spills JIP were selected among the oil companies' crude oils. It was important to select crude oils representing different categories of oils. The selected crude oils represent the categories:

- Troll – naphtenic crude oils
- Norne – waxy crude oils
- Kobbe – light paraffinic crude oils

In addition to the crude oils, a heavy fuel oil (IFO 380) was tested. IFO 380 is representing bunker oils used as fuel for ships going along the Norwegian coast. The content of light oil components in fuel oils is low, typically lower than 5 vol% for IFO 380 oils. The light oil components are generally in a boiling point area from approximately 250°C and higher. The testing of the IFO 380 was therefore concentrated on the "fresh" fuel oil, not on an evaporated residue. The IFO 380 oil used in this project is a low sulphur fuel oil produced at the Esso refinery at Slagentangen. Some physical and chemical properties of the oils studied are listed in Table 3.1-1.

**Table 3.1-1 Oils used in the Coastal Oil Spills JIP.**

| SINTEF Id | Oil type | Residue | Density (Kg/m$^3$) | Evaporative Loss (Vol%) | Pour point (°C) | Wax (wt%) | Asphaltenes (wt%) |
|---|---|---|---|---|---|---|---|
| 2007-0287 | Troll | Fresh | 0,900 | 0 | -36 | 0,9 | 0,04 |
| | | 250°C | 0,930 | 25,5 | -27 | | |
| | | Ph.ox. | 0,931 | - | -21 | | |
| 2006-1061 | Kobbe | Fresh | 0,797 | 0 | -39 | 3,4 | 0,03 |
| | | 250°C | 0,875 | 53,6 | 21 | | |
| | | Ph.ox. | 0,877 | - | 15 | | |
| 2007-0260 | Norne | Fresh | 0,860 | 0 | 21 | - | 0,3 |
| | | 250°C | 0,888 | 28,4 | 30 | | |
| | | Ph.ox. | 0,885 | - | 30 | | |
| 2006-1125 | IFO 380 | Fresh | 0,963 | 0 | 15 | 5,0 | 3,4 |

-: *not measured*

Oil spilled at sea will be exposed for several weathering processes as evaporation (lighter compound evaporates), emulsification (water droplets are incorporated in the oil phase) and photo-oxidation (changing the physical and chemical properties due to sun exposure). These weathering processes will change the physicochemical properties of the oil, being of great importance for the weathered oils fate and behaviour on the shoreline

For the crude oils, an evaporated residue of 250˚C+ was used. The 250°C+ residue corresponds to ½ - 1 week weathering of oil at sea, and will be representative for stranded crude oil along the Norwegian coast.

To ensure reproducible production of emulsions, a water content just below the maximum water uptake for the respective oils was used. After some initial studies, the standard water content was decided to be 70% for Troll, 75% for Kobbe, 60% for Norne and 40% for IFO 380.

Evaporation and emulsification were performed according to established SINTEF lab procedures. For more information about the physical and chemical properties of the oils and weathering procedures, see *Technical report C2.2* (Ramstad *et.al.*, 2008).

#### 3.1.2 Sediment

Shoreline sediments contain sediment fractions classified over a broad spectre, mainly varying between sand and gravel. It was preferred to use sediment with a limited variation in sediment grains size to get reproducible experimental conditions. There are many classification scales for sediments and the boundaries between the fractions vary. The sediment used in this study was chosen on the basis of the Wentworth classification scale for sediments (www.wikipedia.no). The sediment grain size distribution used in this study was:

- 0,6-1,4 – Coarse sand
- 2,8-6,3 – Very fine gravel

With time, the sediment grains have been exposed for several erosion processes giving the sediment particles a spherical form. The sediment used in this study was supplied by Trondheim Mørtelverk AS and originates from glacial- and river deposits in Sør-Trøndelag. The sediment is therefore natural and rounded. In addition the sediment is fractioned and washed to remove unwanted dust, making the sediment representative as shoreline sediment.

### 3.2 Experimental setup and procedures

#### 3.2.1 The shoreline simulation system

To study the wash-out of weathered oil due to erosion processes, a shoreline simulation system was used. The shoreline simulation system contains 12 reservoirs installed on an oscillating table. Based on results from initial studies, considering exposure grade which reflects water loading (2 litres - high energy and 4 litres - low energy), the reservoirs were applied 4 litres of seawater, representing a “low” energy level in the shoreline simulation system. The reservoirs were filled with seawater one day in advance of the wash-out process for a conditioning of seawater to test temperature. Oil infested sediment was placed in the reservoirs, see Figure 3.2-1. The shoreline simulation system was situated in a temperature controlled room to ensure the required test temperature at 5°C.

Figure 3.2-1 The shoreline simulation system (to the left) and a water reservoir with sediment (to the right).

The simulation systems generate wave energy by tilting the oscillating table from one side to another with a standard angel and frequency. For this purpose a compressed air jack along with a control unit programmed for a uniform movement was used. The principle for reservoirs with bedrock tiles is shown in Figure 3.2-2. As a reference, some sediment samples were studied using no exposure.

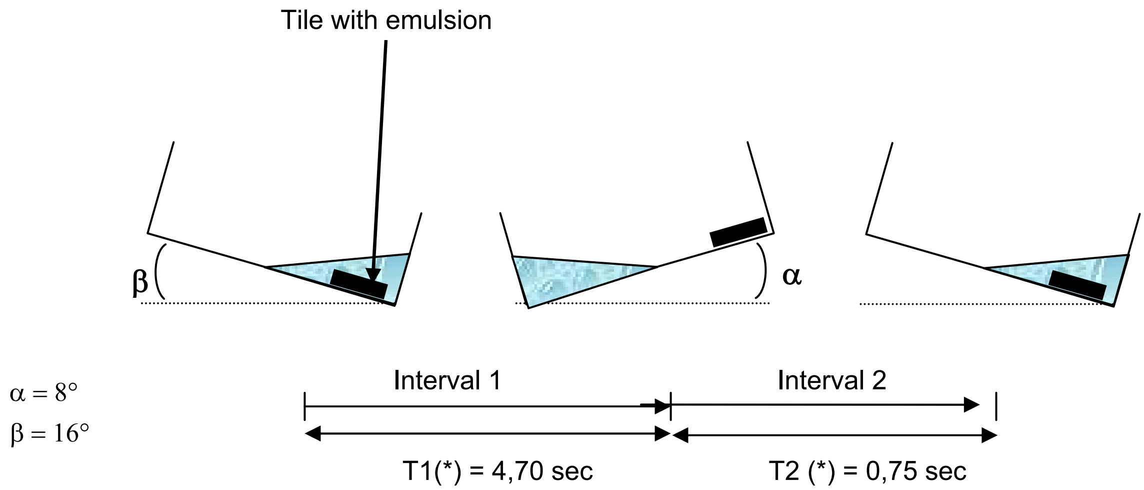



**Figure 3.2-2 The mechanism of the oscillating table – shoreline simulation system.**

### 3.2.2 Preparation of weathered oil infested sediment

Based on results from studies described in *Technical report C3.4* (Øksenvåg *et al.* 2008), oil concentrations of 10 and 50 mg oil/ g sediment were used. Weathered oils were applied to plastic containers filled with sediment and shaken manually for 1 minute to ensure a sufficient mixing of emulsion and sediment, see Figure 3.2-3.

**Figure 3.2-3 Sediment samples after mixing, containing different oil concentrations.**

Before introduction of the samples to the reservoirs in the shoreline simulation system, the samples were placed in a temperature controlled room at test temperature (5˚C) for 1 hour for condition of the samples to test temperature. To simulate the restoration phase of an oil spill stranded onshore, the containers were left in a temperature controlled room at test temperature for 5 days before introduction to the reservoirs.

### 3.2.3 Sampling, photo documentation and quantitatative analysis

For a quantitative analysis of emulsion wash-out due to the erosion process, fractions of the sediment samples were derived for concentration studies before and after the exposure period. The samples were extracted in dichloromethane (DCM) and analysed using a Hitachi U-2000 spectrophotometer. During the wash-out process, absorbent pads made of polypropylene were used to collect washed out emulsion, refloating to the water surface, to quantify the time related wash-out degree. The reservoirs, containing the sediment samples, were photo documented at introduction to the reservoirs, during and after the exposure period. The exposure period was 1 day.

### 3.2.4 Oil properties

To study the oils viscous properties, a Physica MCR300 MC1+ rheometer with an US200 software was used. The viscosities of the weathered oils were measured before application to the containers. Oil characteristic, as density and pour point, for the water free residues were measured before emulsification, see Table 3.1-1.

### 3.3 Experimental parameters and design

Six different experimental parameters were tested in this study:

- **Oil types**
  To study the difference in wash-out effect, due to the different physical and chemical properties of the oils, three crude oils; Troll, Kobbe, Norne and one bunker fuel oil; IFO 380 was used.
- **Sediment size / fractions**
  To study the effect of sediment size, two different fractions were used; 0,6-1,4 mm and 2,8-6,4 mm.
- **Oil loading**
  To study the effect of emulsion loading, two different oil concentrations were used; 10 and 50 mg oil / g sediment.
- **Emulsified versus un-emulsified oil**
  To study the effect of emulsified oil compared to un-emulsified oil, emulsified Troll oil and a Troll 250˚C+ residue were used.
- **Acute versus restitution phase**
  To study the effect of the time period the weathered oil retains in the sediment before wash-out, the sediment samples were exposed to water energy exposure after 1 hour (representing acute phase) and 5 days (representing restoration phase).
- **Exposure degree**
  To study the effect of exposure degree, two different exposure regimes were used; no exposure (having no wave energy) and with exposure (using 4 litres of seawater in the shoreline simulation system, simulating a low exposure).

Table 3.3-1 gives an overview of the experimental design including the experimental parameters for this activity.

**Table 3.3-1 Experimental design. (WiO – Water in oil / emulsification).**

| SINTEF ID | Oil | WiO | Evaporated | Spesification | Oil loading 10 mg oil / g sed | | Oil loading 50 mg oil / g sed | |
|---|---|---|---|---|---|---|---|---|
| | | | | | 0,6-1,4mm | 2,8-6,3mm | 0,6-1,4mm | 2,8-6,3mm |
| 2007-0287 | Troll | 70 % | 250˚C+ residue | Low energy (4 l) | 3 | 3 | 3 | 3 |
| | | | | No energy | 1 | 1 | 1 | 3 |
| | | | | Restitution | | | 3 | 3 |
| | | | | Restitution no energy | | | 1 | 3 |
| 2006-1061 | Kobbe | 75 % | 250˚C+ residue | Low energy (4 l) | | | | 3 |
| | | | | No energy | | | | 1 |
| 2007-0260 | Norne | 60 % | 250˚C+ residue | Low energy (4 l) | | | | 3 |
| | | | | No energy | | | | 1 |
| 2006-1125 | IF 380 | 40 % | | Low energy (4 l) | | | | 3 |
| | | | | No energy | | | | 1 |
| | | | | Restitution | | | | 3 |

## 4 Results and discussions

Table 4-1 show the experimental parameters used in this activity:

**Table 4-1 Experimental parameters used in this activity. The parameters marked with bold text were used as standard parameters.**

| Parameter | Variation |
|---|---|
| Oil type | • Troll crude<br>• Kobbe crude<br>• Norne crude<br>• Bunker fuel oil - IFO 380 |
| **Evaporation** | **250°C+ residue (crude oils)** |
| **Water content in emulsion** | • **70% (Troll)**<br>• **75% (Kobbe)**<br>• **60% (Norne)**<br>• **40% (IFO 380)** |
| **Temperature** | **5°C** |
| Emulsion loading | • 50 mg oil / g sediment<br>• 10 mg oil / g sediment |
| Sediment grain size | • Coarse sand (0,6-1,4 mm)<br>• Very fine gravel (2,8-6,3 mm) |
| **Exposure degree** | **Low exposure (4 litres)** |

The results from the rheological study are given in *Appendix A*.

Most of the experiments were done in triplicates. The standard deviation was less for the low viscous oil (Troll and Kobbe) than for the high viscous oils, showing a deviation of <10% before wash-out, increase to a value between (10-40%) after wash-out. The high viscous oils showed a deviation from 15-30% before wash-out and a deviation up to 50% after wash-out. This was considered as a high variance, the experimental system should therefore be modified before planning of any further studies on erosion processes.

### 4.1 Effect of oil type

Four selected oils were applied to the sediment to study the wash-out of oil due to the erosion process as a function of oil type. Oil retention, after one day of erosion exposure, for the different oils is shown in Figure 4.1-1.

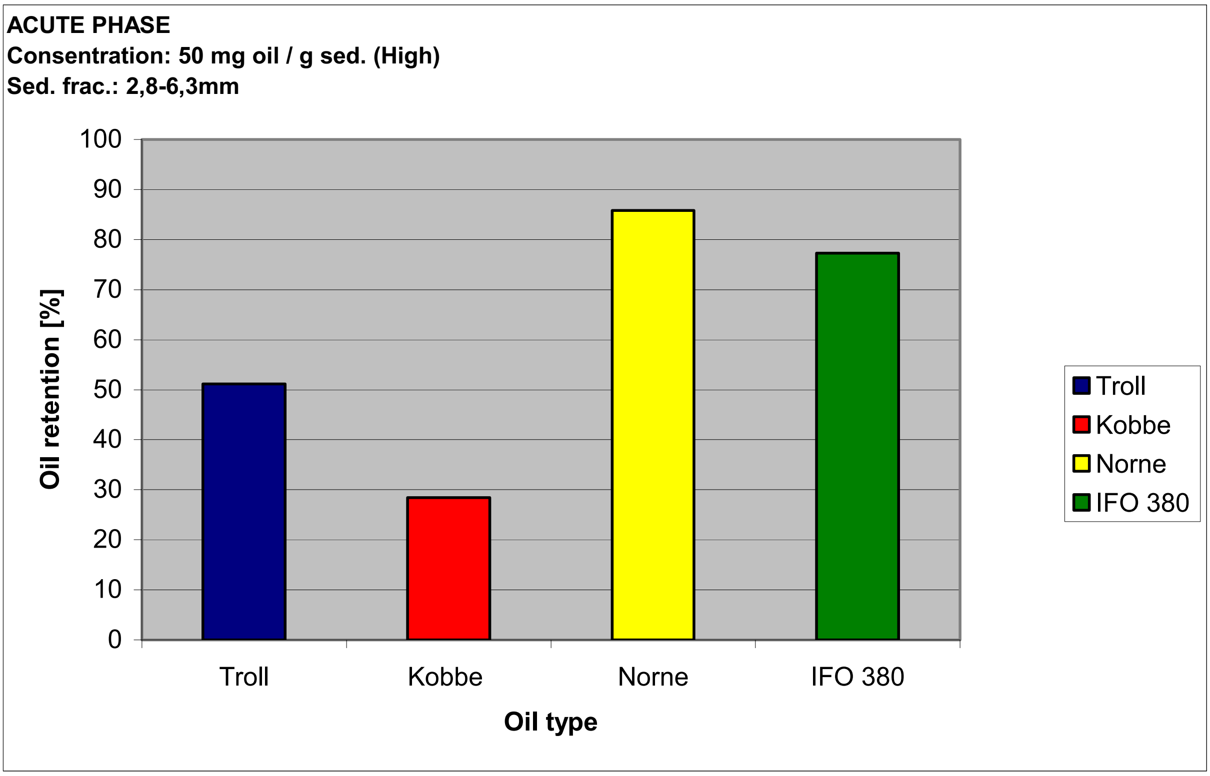
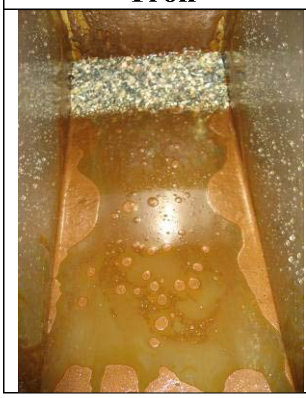
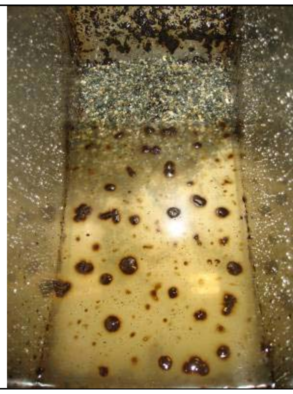



**Figure 4.1-1 Oil retention for the different test oils after 1 day of erosion exposure.**

Figure 4.1-1 shows that the washout of emulsion is dependent on oil type. A relatively great wash-out effect was observed for the Troll and Kobbe oil (having low viscosities), compared to the Norne oil (having a high viscosity). IFO 380 have a much higher viscosity than the crude oils, but still got washed out be the erosion effect. Table 4.1-1 show pictures of the washed out emulsion for the different oils due to the erosion process.

**Table 4.1-1 Emulsion wash-out due to erosion processes for the different oils. The pictures are given for very fine gravel (2,8-6,3mm) and high emulsion loading (50 mg oil / g sediment).**

| Troll | Kobbe | Norne | IFO 380 |
|---|---|---|---|
|  |  |  |  |

Some of the Troll emulsion refloated to the water surface, the rest of the washed out emulsion were dispersed in to the seawater, as same as Kobbe and Norne. Norne emulsion seemed to form lumps of emulsion on top of the sediment. The bunker fuel oil IFO 380 formed patches of washed out emulsion on the water surface, this was not observed for the crude oils.

A gravimetric analysis on emulsion wash-out, as a function of time, is given in Figure 4.1-2.

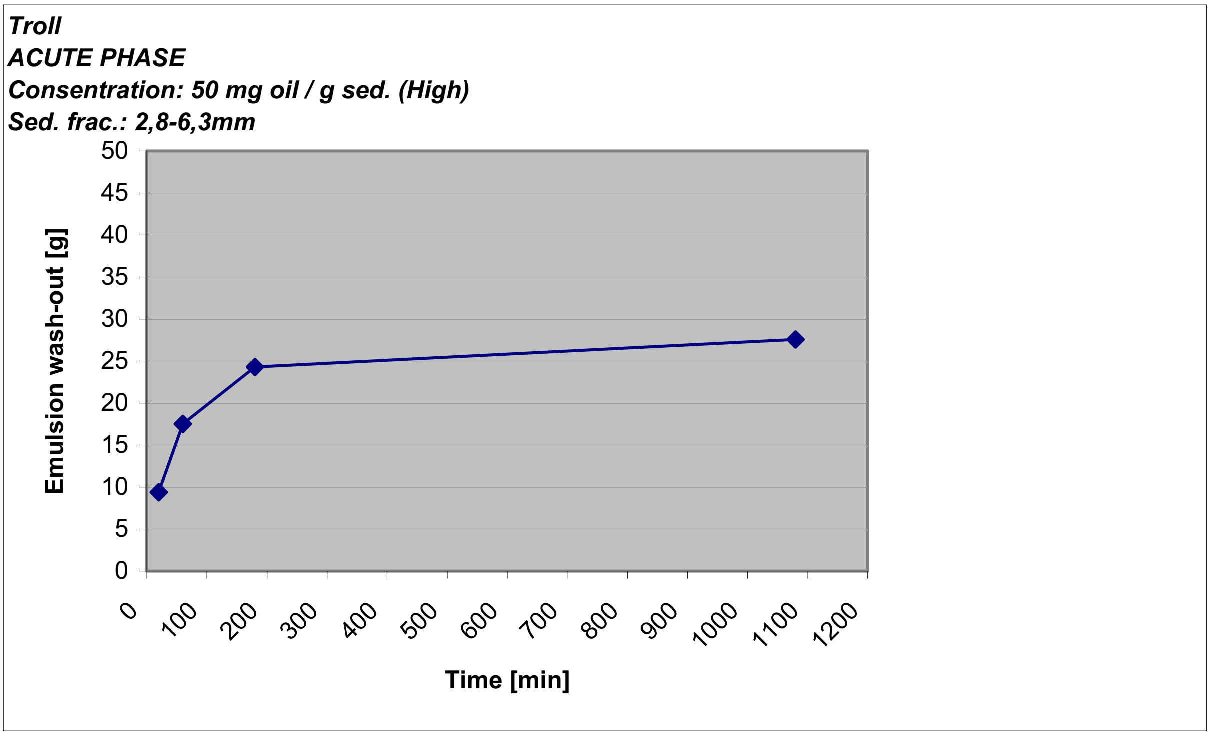



**Figure 4.1-2 Emulsion wash-out for Troll oil as a function of time.**

Figure 4.1-2 shows the erosion kinetics to have a great initial wash-out rate, decreasing with time. These results do not include emulsion adhered to the walls of the reservoirs, the emulsion wash-out is therefore predicted to be greater than measured. Emulsions made from oils like Troll, have a tendency to break (water segregating from the oil phase) with time. The water content of the emulsion after the exposure period is unknown. The quantitative analysis is based on emulsion wash-out, one could therefore assume that if the emulsion has broken, the wash-out results might be higher than measured.

### 4.2 Effect on emulsion loading

Two different oil loadings were applied to the sediment to study the wash-out of oil due to the erosion process as a function of oil concentration. The study was done with and without wave exposure. Oil retention, after one day of erosion exposure, for the different oil concentrations is shown in Figure 4.2-1.

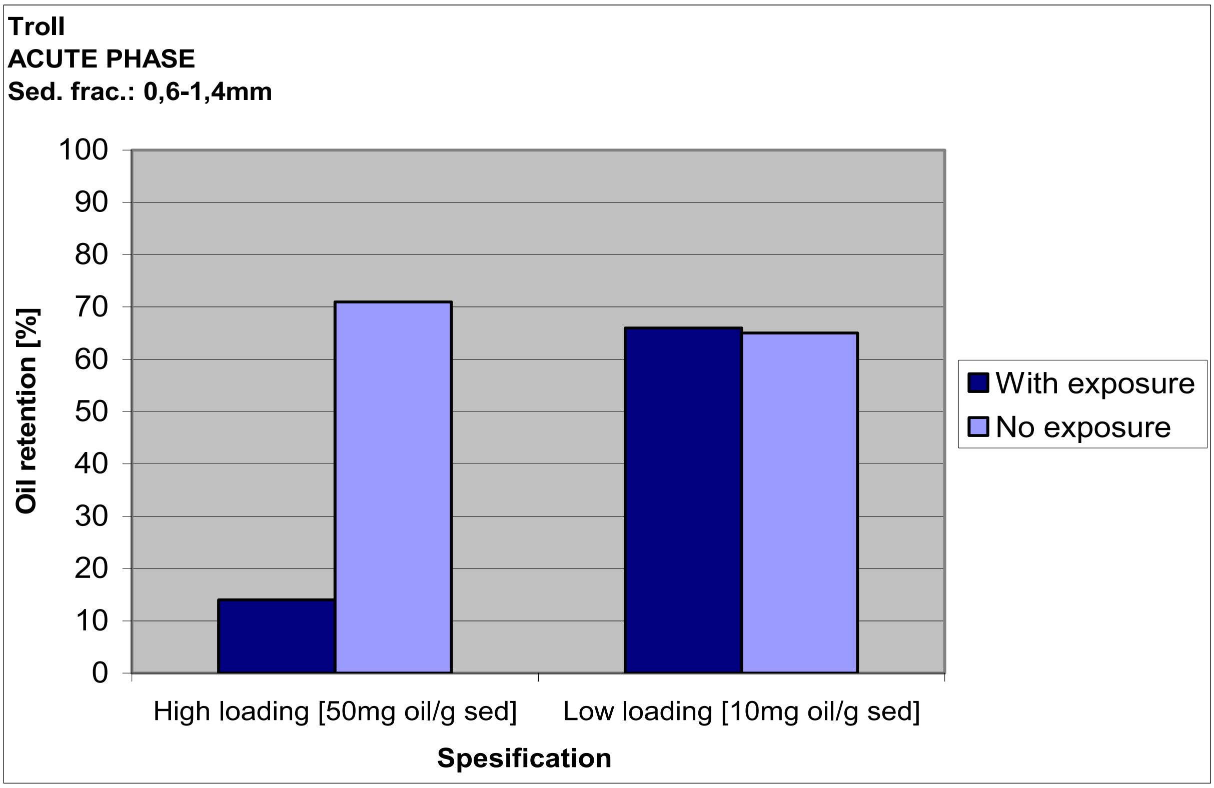



**Figure 4.2-1 Oil retention for two different emulsion loadings, with and without exposure.**

Figure 4.2-1 shows a greater wash-out degree for the highly contaminated sediment, than for the sediment with a lower concentration of oil, with the presence of wave exposure. This might be due to a thicker emulsion film thickness covering the sediment grains for the highly contaminated sediment, than for the less oil contaminated sediment, making the emulsion easier to mobilise. For the sediment containing a low oil concentration, wave exposure does not show any effect of the erosion mechanism. The no exposure oil retention values are predicted to be to higher, due to an unwanted disturbance of the sediment during experimental preparation.

### 4.3 Effect of sediment fraction and emulsified versus un-emulsified oil

Two different sediment fractions were used to study the wash-out of water free and emulsified oil due to the erosion process. Oil retention, after one day of erosion exposure, for the different sediment fractions is shown in Figure 4.3-1.

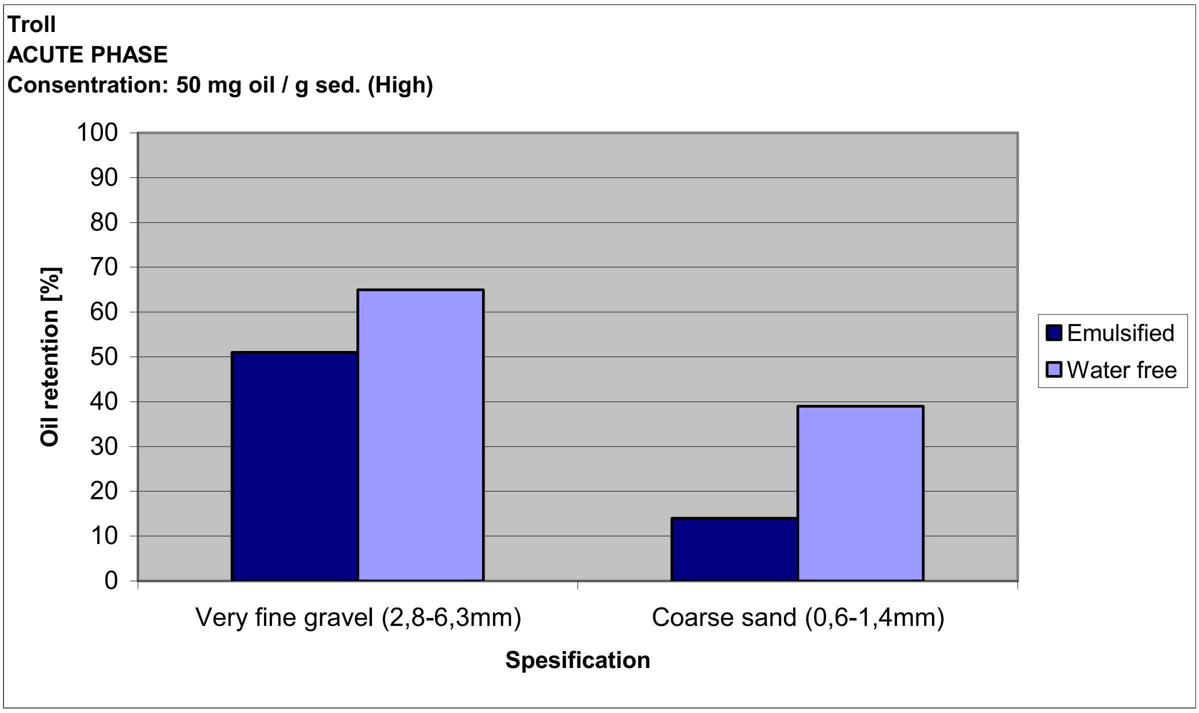



**Figure 4.3-1 Oil retention for emulsified versus water free oil using two different sediment fractions.**

Figure 4.3-1 show a greater erosion effect for the fine grained sediment (coarse sand), compared to the coarse grained sediment (very fine gravel). This might be due to the finest sediment fraction large number of grain to grain contacts, giving a high erosion effect. The finest sediment also has the largest surface area, contributing to a thinner oil film on the sediment grains, probably making the emulsion harder erode off. It was also found a greater wash-out of emulsified oil compared to water free oil. This might be due to a better binding capacity between bedrock and oil, compared to bedrock and water (emulsified Troll oil is containing 70% water). The emulsified oil was observed dispersed in to the water column in addition to partly refloating to the water surface during the exposure period. The water free oil was not dispersed and formed a thin oil layer on the water surface, see Table 4.3-1.

**Table 4.3-1 Emulsion wash-out due to erosion processes for emulsified versus water free oil, using two different sediment fractions. The pictures are given for a high emulsion loading (50 mg oil / g sediment).**

| Very fine gravel (2,8-6,3 mm) | | Coarse sand (0,6-1,4 mm) | |
|---|---|---|---|
| Emulsified oil (70% WiO) | Water free oil | Emulsified oil (70% WiO) | Water free oil |
|  |  |  |  |

## 4.4 Acute versus restitution phase

Two different oil types were used to study the wash-out of weathered oil due to the erosion process in the acute and restoration phase. Oil retention, after one day of erosion exposure, for the two oils as a function of retention time in the sediment is shown in Figure 4.4-1.

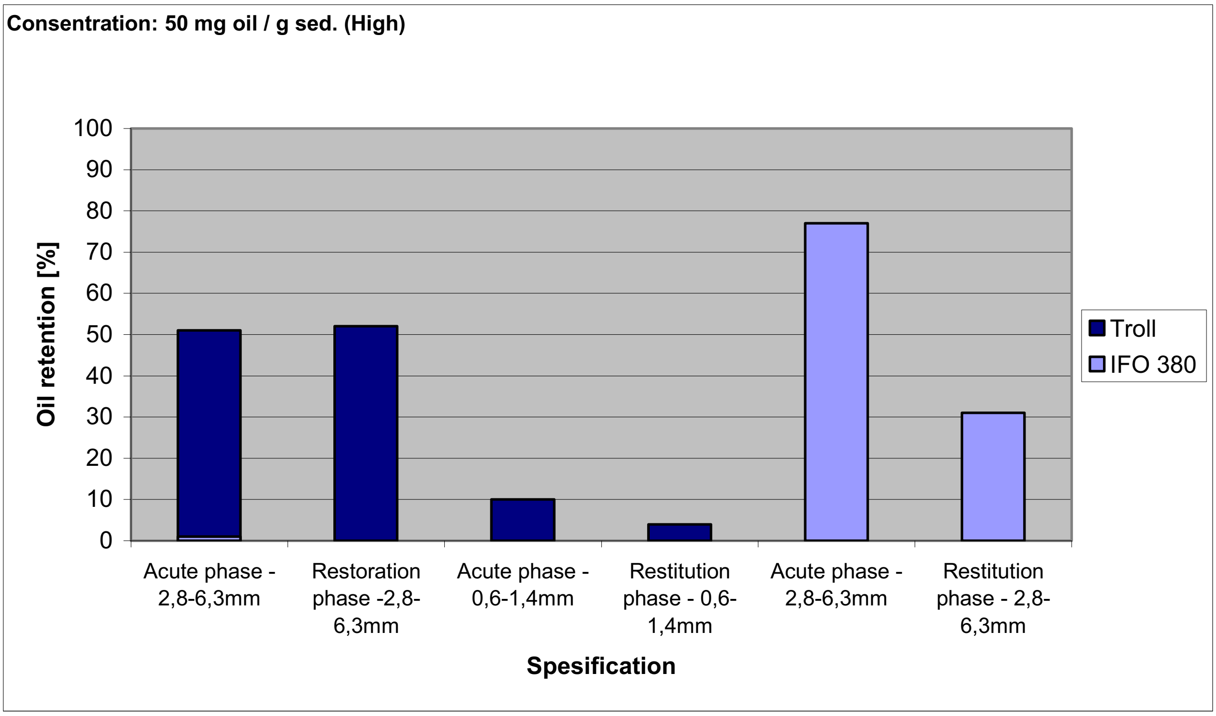



**Figure 4.4-1 Oil retention for Troll and IFO 380 as a function of acute versus restoration phase.**

Figure 4.4-1 shows no significant difference in wash-out, due to the erosion process, dependent on retention time of emulsion in sediment, for the Troll oil. For the bunker fuel oil IFO 380, a long retention time of emulsion in sediment showed a great effect, reducing the retained oil with approximately 50%. The standard deviation was much greater for the bunker fuel oil, than the Troll oil. This is probably due to its high viscosity, making it hard to cover the sediment grains evenly. The amount of emulsion retained in the sediment for the restitution phase results is therefore assumed to be higher.

# 5 Conclusions and operational gain

Oil type and emulsion loading seems to be significant factors for the wash-out of oil due to erosion kinetics. Low viscous oils, like Troll and Kobbe, show a greater wash-out than the high viscous oils, Norne and IFO 380. In a real oil spill scenario, low viscous crude oils are therefore predicted to be easier washed out than bunker fuel and crude oils with a high viscosity. The erosion process show a much higher wash-out from highly contaminated sediment compared to low contaminated sediment. This is probably due to an easier mobilisation of emulsion forming a thick emulsion film thickness on the sediment grains, compared to thinner emulsion film thicknesses. The wash-out of emulsion seems to decrease with time, having the highest wash-out rate in the initial phase.

Emulsified oils seem to be eroded out of the sediment more easily than the un-emulsified oil, for both fine and coarse grained sediment. Emulsified Troll oil, washed out from the sediment, seem to disperse in to the water column during the erosion process, this in contrast to water free Troll oil, forming an oil layer on the water surface without a large degree of dispersion. If the stranded oil is emulsified, one could predict a higher wash-out of emulsified oil, than un-emulsified oils trapped in sediment. The results for the Troll oil indicate a similar wash-out rate for emulsion subjected for erosion in the acute and restoration phase.

The experimental system was not optimal for studying erosion of oil infested sediment. An upgrading of the system is needed, e.g. applying a mechanical system for water circulation, ensuring a continuous change in seawater. This will avoid a secondary adhesion to the sediment. Also the no exposure experimental setup has to be modified to avoid wash-out of emulsion during experimental preparation. To ensure quantitative data with a lower deviation, an extraction of the whole sediment is needed, especially for the high viscous oils covering the sediment grains more unevenly. Since the emulsion for oils like Troll is expected to break with time (water segregation from the oil phase), a time related quantification of the water content is needed for a validation of the emulsion wash-out calculations. The results gave nevertheless some indications of the ruling parameters for the erosion process.