

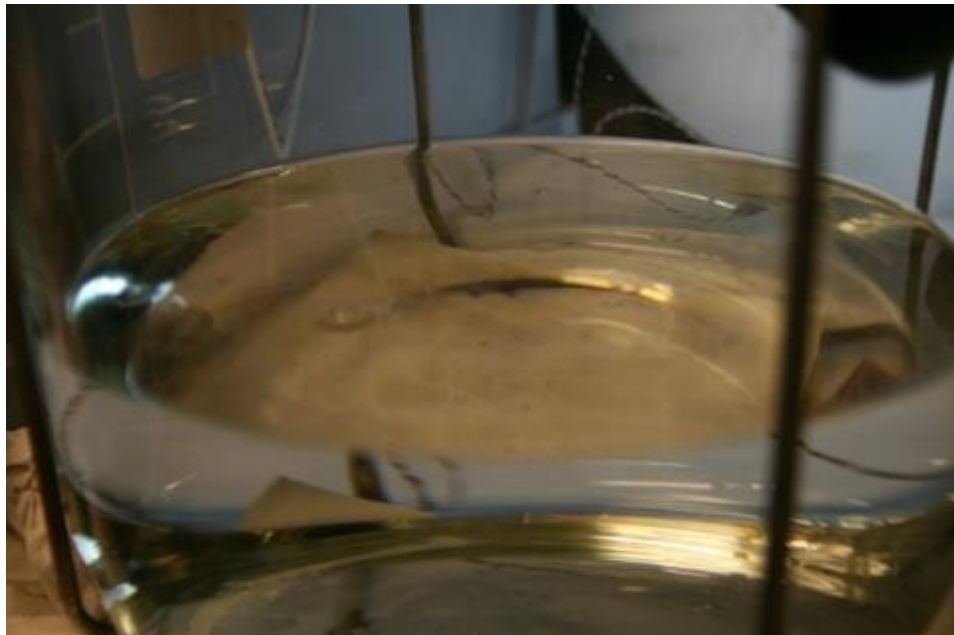
Report

Thin Oil Films – Properties and behaviour at sea

Laboratory studies and oil weathering predictions

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Report

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ABSTRACT

The Petromaks 2 project "Formation and behaviour of thin oil films and evaluation of response methods including HSE", in the following short "Thin oil films" has the objective to achieve new knowledge more efficient and safe oil spill response operations for releases of condensates and light crude oils that may lead to thin oil films on the sea surface.

Main objectives are:

1. Increased understanding of the formation and behaviour of thin oil films
2. Assessment of the potential human exposure to volatile compounds
3. Refined processes in oil trajectory models in order to give more reliable predictions of the lifetime and behaviour of thin oil films and to assess the efficacy of response options.

This report addresses objective 1 and summarizes the results from the laboratory experiments to study weathering properties and characteristic of surface residues from thin oil films formed under calm weather conditions (1-2 m/s wind). The SINTEF Oil Weathering Model (OWM) was used to predict oil weathering properties with a standard set of thin oil film scenario (<200 µm) at 2/13 °C under calm condition (2 and 5 m/s). Data and observations of thin oil films in the laboratory were compared and discussed with the OWM predictions of the condensates (Alve, Ormen Lange, Marulk, Atla and Skarv), the light crude oils (Gjøa and Vale), including a reference crude oil (Statfjord C Blend).

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1 Executive summary

Condensates and light crude oils are normally characterized by a high portion of light compounds. The light compounds will evaporate rapidly when the oil is spilled to the marine environment. These oils could generate thin oil films under calm conditions (non-breaking waves). The behaviour and weathering of such thin oil films have been studied and compared in laboratory experiments and predictions of weathering properties using the SINTEF Oil Weathering Model (OWM) for eight different and representative oils from the Norwegian petroleum sector.

The oils used in this project are in general light oils, which contain very large (40-80%) portion of semi-volatile/volatile compounds (boiling point < 200 °C). These light compounds will evaporate at a high rate in the initial phase after release (< 1 hour). The composition and the physical properties of the oil remaining on the sea surface (evaporated residue) varies over a wide range. The experimental studies and model predictions have shown that further fate and behaviour at the sea surface will depend on the chemical composition of the residues and thereby their physical properties.

For oil spill contingency planning, it has been assumed that oil slicks from these oils form thin oil films (typically less than 0.1-0.2 mm), which is below what is regarded as the minimum thickness for effective recovery using traditional mechanical and dispersant response strategies. It has also been assumed that they have a very short lifetime on the surface due to a rapid evaporation and a high degree of natural dispersion and dilution in the water under wave exposure. Therefore, aerial monitoring of surface oil and subsea monitoring of oil naturally dispersed into the water column has been regarded as the only option for oil spills creating thin oil films on the sea surface. However, the oil industry and the Norwegian Environmental Agency have realised that more knowledge about the fate and behaviour of thin oil films is required in order to modify, develop, or customize new response technology for condensates and light crude oils.

The main objective of this project is to achieve new knowledge to provide more efficient and safe oil spill response operations to combat condensates and light crude oils that generate thin oil films on the sea surface. The weathering processes and behaviour of the residues of thin oil films were studied systematically using open (modified MNS and Flume, 250 µm film thickness) and closed (Tilting table, 200 µm film thickness) experimental systems. These experiments were performed at two different temperatures (2 and 13 °C) under calm conditions not generating breaking wave conditions.



Figure 1-1 Visual presentation of the project oils.

Five condensates (Atla, Skarv, Alve, Marulk and Ormen Lange) and two light crude oils (GjØa and Vale), in addition to a paraffinic North Sea crude as reference oil (Statfjord C Blend) were used in this project. These oils give a representative and wide span of condensates and light crude oils produced in the Norwegian petroleum sector. The weathering, fate and behaviour of thin oil films and characteristic of surface residues from oil films were documented by physicochemical analysis in combination with visual observations.

The SINTEF Oil Weathering model (OWM) was used to generate predictions of weathering properties of oils generating initial thin oil films (< 200 µm) under calm conditions. The predictions were performed for 2 and 13°C with 2 and 5 m/s wind speed. The predictions showed, in accordance with the experimental studies, that there are very large differences in weathering, fate and behaviour for the different oils. This is exemplified in Figure 1-2 for surface oil thickness over a period of 5 days (13°C and 2 m/s wind). In general the OWM predictions and laboratory experiments gave similar results, but with some important exceptions.

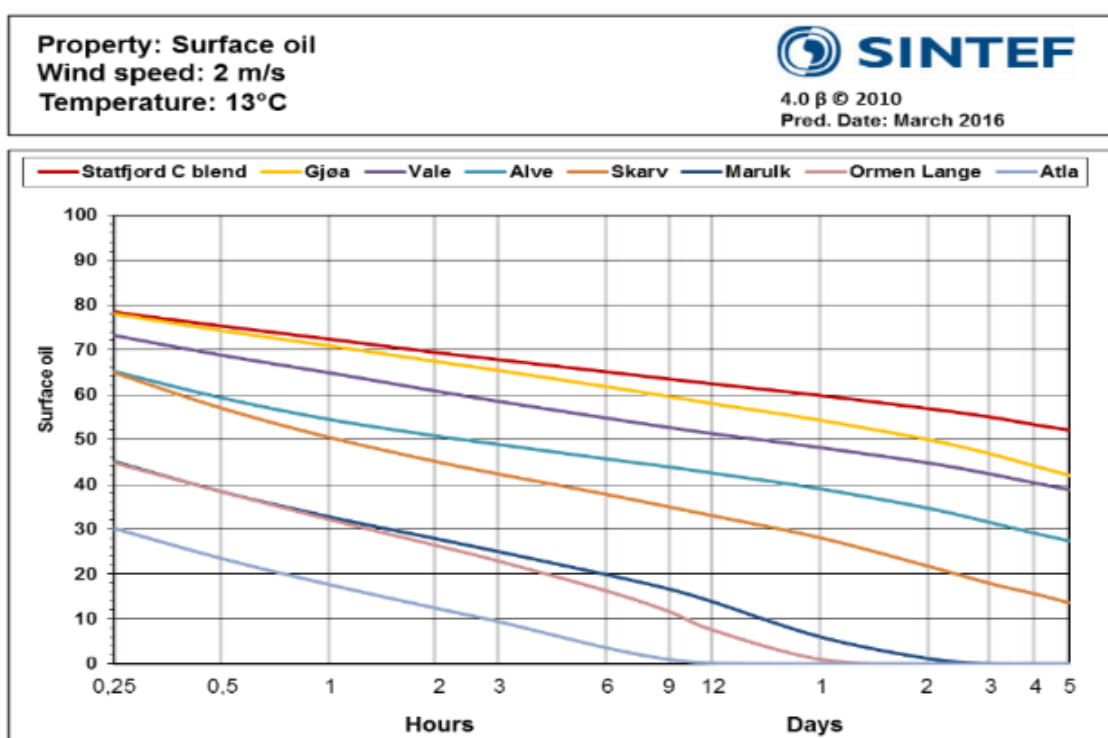


Figure 1-2 OWM predictions - Surface oil at 13 °C with 2 m/s wind speed

The evaporation of the lightest compounds from the condensates and light crude oils was predicted to be very high during the first 15-30 minutes (25-75%), and this was verified by the experimental studies by use of gas chromatographic (GC/FID) analysis of thin oil films, and by monitoring volatile hydrocarbons compound performed as part of the human exposure studies. However, for some of the oils (Alve, Skarv and Vale) the experimental evaporation loss was found to be reduced due to solidification (high pour point) of the oil film residue and thereby restriction in release of light compounds from the oil film.

The laboratory experiments did not give any observation of natural dispersion/entrainment into the water column by generating oil droplets under very calm conditions with 1-2 m/s wind speed. The OWM predictions for the 2 m/s wind speed scenario gave minor dispersion/entrainment, which was increased significantly with 5 m/s wind speed. In the closed experimental system, the thin oil film was exposed to increasing tilting frequency, and the energy required to generate oil droplets was strongly dependent on both pour point and viscosities of the oil residues.

At the end of the open experimental systems experiments, the residue surface oil was exposed to breaking wave conditions for 30 minutes, and the oil residues were found to behave very differently. The oil residues with low pour point (Atla, Ormen Lange and Marulk) in addition to Gjøa generated oil droplets, whereas residues with higher pour points solidified. The residue of Vale remained as one lump, whereas residues of Skarv and Alve solidified as flakes and droplets respectively. This difference in behaviour could be of importance for possible oil spill response strategies. These observations and details could not be extracted from the OWM predictions.

Atla, Ormen Lange and Marulk residues have a low density, low wax and asphaltene content, and will not generate water-in-oil (w/o) emulsions. They have a low pour point with no yield stress (the yield stress is defined as the stress that must be applied to an oil /emulsion to make it begin to flow), and can therefore undergo further spreading at the sea surface. These oils will have a rapid evaporation and the oil films of these residues will easily be dispersed/entrained into the water column by (increasing) wave exposure.

Alve and Skarv residues have high wax content. They have a yield stress, which will restrict spreading at the sea surface. The evaporated residues have a high pour point that may result in solidification. The residues do not take up water for emulsion formation. The fate of the solidified oil film is dependent on the environmental conditions. Under calm condition, the evaporation will probably be slowed down due to the solidification, and spreading of the oil may be restricted. The solidified film could be accumulated in *e.g.* windrows. Under increasing wave exposure, the solidified residues will be entrained into the water column as solidified lumps or large droplet/"flakes".

Gjøa and Vale are representatives for oils that have potential for water uptake and emulsion formation, as shown in the standard weathering studies. The water uptake is however dependent on the oil film thickness and wave energy exposure. The emulsion generated had a high water content with limited stability. In the laboratory studies performed in this project, with very calm condition, no water uptake with these residues was observed. Gjøa and Vale are, however, different with respect to chemical composition and physical properties. The properties of Vale residues are also similar to Alve and Skarv residues with high wax content and a high pour point and may be solidified under calm conditions.

Use of current operational oil spill response techniques and strategies (i.e. mechanical recovery and use of chemical dispersants) may have limitations for oil spills from condensates and light crude oils. This is due to the low oil film thicknesses that can be encountered dependent on the properties of the oils. Also discharge (e.g. sub-sea versus surface spills), oceanographic and weather conditions may play an important role. Observations from laboratory studies show that properties of the oil residues changes very rapidly due to the high evaporation rate. The efficacy for clean-up using mechanical and dispersion methods will also vary significantly due to the differences in the physical properties of the weathered residues of condensates and light crude oils.

The lifetime of an oil spill from condensates and light crude oils with low viscosity and low pour point, showing no or low yield stress when spilled to the sea surface, will in general be short. Under most scenarios, it may be difficult to perform any clean-up operations by use of mechanical recovery or dispersants. However, in case of a response operation quick response close to the source is expected to be important. From this study Ormen Lange, Atla and Marulk are examples of oils that may fall under this category.

Residues from condensates and light crude oils with high pour point may have a significant lifetime at sea surface under calm conditions, as solidified residues. These oil residues could be recovered by mechanical methods, although the efficacy will probably be low due to a scattered surface distribution. Chemical dispersants normally show low efficacy on solidified oils, and used on residues from such oils the operations should be performed in an early phase before the oil film is solidified. Alve and Skarv is an example of condensates with high pour point studied in this project.

Some light crude oils are able to generate water-in-oil (w/o) emulsions with varying stability. Water uptake will increase the film thickness and generate surface emulsion, which makes use of mechanical response strategies possible. Use of chemical dispersants could also have a wider time window for the emulsified oils. Gjøa and Vale may have a tendency to form w/o emulsion after an oil spill, especially at increased wind speed (> 5 m/s). However, at low wind speed forming low oil film thicknesses they may not form w/o-emulsions or form very unstable emulsion, which makes use of current operational oil spill response techniques more challenging.

The effectiveness of different response strategies for oils creating thin oil films in a spill situation, are not well documented. Based on further testing in this project we will evaluate the possibility to use seawater

flushing or low-dosage dispersant treatment as a response method for thin oil films. This will be further evaluated and discussed in "Project Recommendation for response to oil spills from condensates and light crude oils" (Singsaas *et al.*, 2017).

2 Introduction

There is an increasing number of condensates and light crude oils coming into production on the Norwegian Continental Shelf (NCS), particularly those expected in the Arctic area. In addition, there is an increasing transport of condensates, crude oils and refined oil products along the Norwegian coast.

For oil spill contingency planning it has been assumed that oil slicks from condensates and light crude oils form thin oil films, typically less than 0.1-0.2 mm thickness, which is below what is regarded as the minimum thickness for effective recovery using traditional mechanical and chemical response strategies. It has also been assumed that these oil types have very short life time on the surface due to a high degree of evaporative loss and natural dispersion in the water column by wave activity. Hence, it has been accepted that aerial monitoring of surface oil and subsea monitoring of oil naturally dispersed oil droplets into the water column was a sufficient "oil spill response option" for such oil spills scenarios.

However, the chemical composition and thereby their physical properties among the condensates and light crude oils varies over a very wide range. Due to the high content of lighter components, the properties of the evaporated residues change rapidly after release to the environment. Some condensates and light crude oils furthermore contain high content of waxes that may precipitate and contribute to high pour point, and the residues may solidify on the sea surface, especially under cold water conditions typically found in the northern and Arctic areas. The fate and behaviour of such solidified residues at sea is not well scientifically documented.

As a response to these shortcomings, the oil industry and the Norwegian Environmental Agency have realised that more knowledge about the fate and behaviour of thin oil films is required in order to modify, develop, or customize new response technology for condensates and light crude oils anticipating forming thin oil films. In the current project, the fate and behaviour of thin oil films from condensates and light crude oils have been studied in closed (200 and 250°C+ residue) and open (fresh oils) experimental systems under controlled and reproducible conditions. For this purpose standard operational procedures and well-known experimental designs have been modified and developed to simulate calm wind condition.

In this report, visually observations and physicochemical analysis from these experiments have been compared with predictions using the SINTEF Oil Weathering Model (OWM) for an initial thin oil film scenario under calm wind conditions. Data are presented to document the differences between various condensates and light crude oils under different environmental conditions as temperatures and wind speeds.

3 Selection of oil and condensate

A total of eight condensates and light crude oils, including a paraffinic North Sea crude as reference oil, were selected to study the behaviour and properties of thin oils films in the laboratory. The selection of the light crude oils and condensates was based on three main criteria:

- Previous laboratory weathering study of the light oils and condensates.
- A wide span in their physicochemical properties to represent most condensates and light oils under production in the Norwegian sector
- Important for oil companies to include and study one of their condensates/oils under production.

Previously weathering studies have shown that the oils are unique with respect to their weathering properties that influence on their fate and behaviour at sea, where the weathering properties influence on the film formation, natural dispersion, emulsification and solidification over time. The selected oils could fulfill the criteria listed above given as Atla, Alve, Marulk and Skarv (condensates), and GjØa and Vale (light crude oils). In addition, the Statfjord C Blend was chosen as a reference crude oil. Table 3-1 shows an overview of the selected oils that could full-fill the selection criteria. The oils were categorized as either a condensate or light (crude) oil, based on the oil composition and weathering properties from the previously weathering studies.

Table 3-1 Light crude oils and condensates used in the laboratory testing – in closed and open experimental systems- including the reference crude (Statfjord C blend).

Oil name	Oil type*	Oil company	References-Weathering study
Atla	Condensate	Total	Andreassen and Pettersen (2013)
Ormen Lange**	Condensate	Shell	Leirvik (2008)
Marulk	Condensate	Eni Norge	Hellstrøm and Pettersen (2014)
Skarv	Condensate	BP Norge	Øksenvåg (2014)
Alve	Condensate	Statoil	Sørheim <i>et al.</i> (2010)
GjØa	Light (crude) oil	Engie	Sørheim <i>et al.</i> (2011)
Vale	Light (crude) oil	Centrica	Hellstrøm and Andreassen (2014)
Statfjord C Blend**	Crude oil	Statoil	Moldestad <i>et al.</i> (2001)

* The classification of oil type is mainly based on the weathering properties from existing weathering studies

** Weathering studies were conducted on previously batches of Ormen Lange and Statfjord C Blend. SINTEF received new batches of both oils that were used in experiments from this project.

The visually color/appearance of the oils is shown in Figure 3-1, where the condensates had clear, yellow and/or orange appearance, whilst the crude oils were more light (Vale) or dark brown (GjØa and Statfjord C Blend). Figure 3-2 shows an overview of the oils based on their properties for categorizing into four different oil types (crude oils): Paraffinic, Waxy, Naphthenic, and Asphaltenic crudes. In addition, the same figure also presents the distribution of the condensates used in this project based on their increasing solidifying residue properties.



Figure 3-1 Visual presentation of the project oils. Condensates (A–E) were clear/yellow, light oils (F–G) were dark red/brown. A: Skarv, B: Atla C: Alve, D: Marulk E: Ormen Lange F: GjØa G: Vale H: Statfjord C

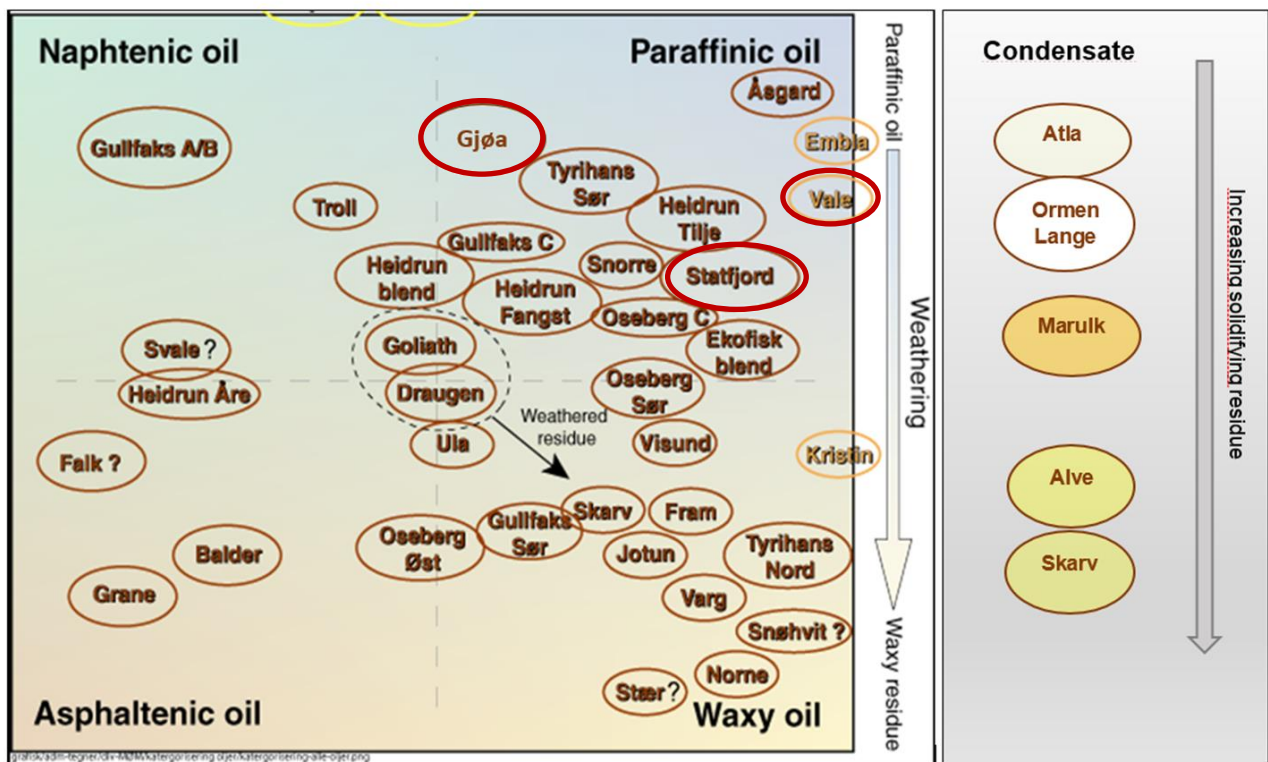


Figure 3-2 Selection of oils indicating the distribution of oil properties and their categorization into different crude oils: Naphthenic, Paraffinic, Asphaltenic, and Paraffinic, and Condensates. The categorization of the condensates from this project are based on their increasing solidifying residue. The selected oils are Atla, Ormen Lange, Marulk, Alve and Skarv (condensates), and GjØa and Vale (light crude oils), and the reference crude oil Statfjord C blend (red circles).

SINTEF normally categorizes crude oils with low emulsifying properties producing unstable/loose water-in-oil (w/o) emulsions as light (crude) oils, and these oil types also exhibit low densities as Vale and GjØa. Crude oils that form more stable water-in-oil (w/o) emulsions are categorized as emulsifying crude oil (e.g. Statfjord C Blend). However, if we have used the API (American Petroleum Institute) definitions, all the oils from this project would have been defined as light crude oil with respect to their densities. In this project, the definition of light (crude) oil has been mainly based on their weathering /emulsifying properties, and light (crude) oils together with condensates are in higher extent anticipated to form thin oil films when released on the sea surface compared to typically emulsifying crude oils.

Low emulsifying crude oils can be regarded as an intermediate between emulsifying crude oils and condensates, and are characterized with a relatively high content of the lightest components, where the 250°C+ residue typically evaporates in the range of 50 –70 vol. %. In contrast to condensates, these oils may also contain emulsion-stabilizing components as asphaltenes that cause light crudes to form water-in-oil emulsions. Condensates evaporates typically more than 70 vol. % for the 250°C+ residue, and have very low to insignificant amount of emulsion-stabilizing components that reduce the ability for emulsification.

The weathered residues from thin oil films were characterized with use of closed experimental system, and the behaviour and weathering properties of thin oil films were studied in open modified MNS-system, and in the meso-scale Flume basin. A summary of the most important physiochemical properties of the oils and their residues is given in Chapter 4, and tabulated in Appendix A. The experimental setup design are described in Chapter 5.

4 Physicochemical properties of oils

The variation in selected physicochemical properties of the oils are shown in figures below and are tabulated in Appendix A. The content of wax, asphaltenes, viscosity and pour point are presented for the 250°C+ residue, whilst the variation within the densities and viscosities are given for the fresh oils. In addition, the physicochemical properties of Åsgard Blend are also presented in figures below. Åsgard Blend was used in the TOF field experiments as part of the NOFO Oil-On-Water field trial in June 2016.

Previously weathering studies of oils have shown that the fresh oils exhibit low contents of asphaltenes (0.0–0.16 wt. %), low to medium wax content (0–5 wt. %), and low viscosities in the range of 1–37 mPa.s, measured at 13 °C. The densities of the oils were in the range of 0.75–0.84 g/mL, which are according to API (The American Petroleum Institute) categorized as light crude oils (< 0.87 g/mL).

4.1 True Boiling Point curve

The true boiling point curve (TBP) or distillation curve, which is obtained by measuring the vapour temperature as a function of the amount of oil distilled, shows the relative distribution of volatile and heavier components in the oil. The boiling point of a particular chemical component depends on its vapour pressure, which is a function of its molecular weight and chemical structure. Low molecular weight oil components have a higher vapour pressure, thus lower boiling points than higher molecular weight components of a similar type. Aromatic compounds boil at a higher temperature than paraffinic compounds of the same molecular weight, and *iso*-alkanes (branched alkanes) boil at a lower temperature than the equivalent *n*-alkanes (straight chain alkanes). Hence, the distillation curve is an indicator of the relative amount of different chemical components, principally as a function of molecular weight, but also as determined by the chemical composition. The distillation curves for the condensates and light crude oils, including reference oil are given in Figure 4-1. The lightest condensates (by density) Atla and Ormen Lange exhibit highest evaporative loss, whereas Statfjord C Blend (reference crude oil) has the lowest evaporative loss due to higher content of heavier components.

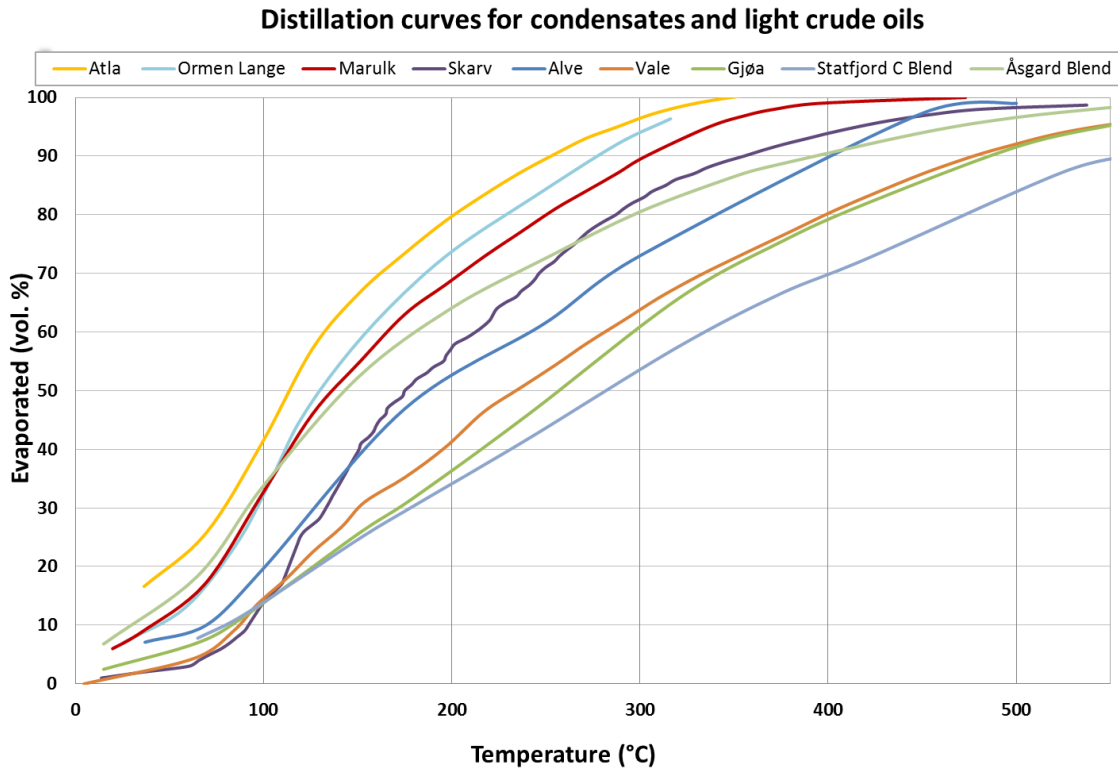


Figure 4-1 Distillation curves of the condensates and light crude oil, including reference oil.

4.2 Density

The density of an oil is the ratio between mass and volume expressed as *e.g.* g/mL or kg/m³, and is a combination of the density of all of its components. The density of the hydrocarbons increases with increasing molecular weight. Paraffinic oils have typically lower density than those containing large amounts of high molecular weight aromatics, naphthenes and asphaltenes. In American literature, the density of the oil is often expressed as API gravity, see Equation 1. The density of fresh oils normally lies in the range 0.78 to 0.95 g/mL that corresponds for 50 to 10 °API. The variation of densities of the project oils are shown in Figure 4-2. Gjøa and Statfjord C Blend exhibits the highest densities > 0.83 g/mL, whilst the condensates Alta, Ormen Lange and Marulk have the lowest densities (< 0.76 g/mL). The densities also reflects the evaporative loss/distillation curves given in Figure 4-1.

$$\text{Degree API gravity} = (141.5 / \text{Specific Gravity}) - 131.5 \quad (1)$$

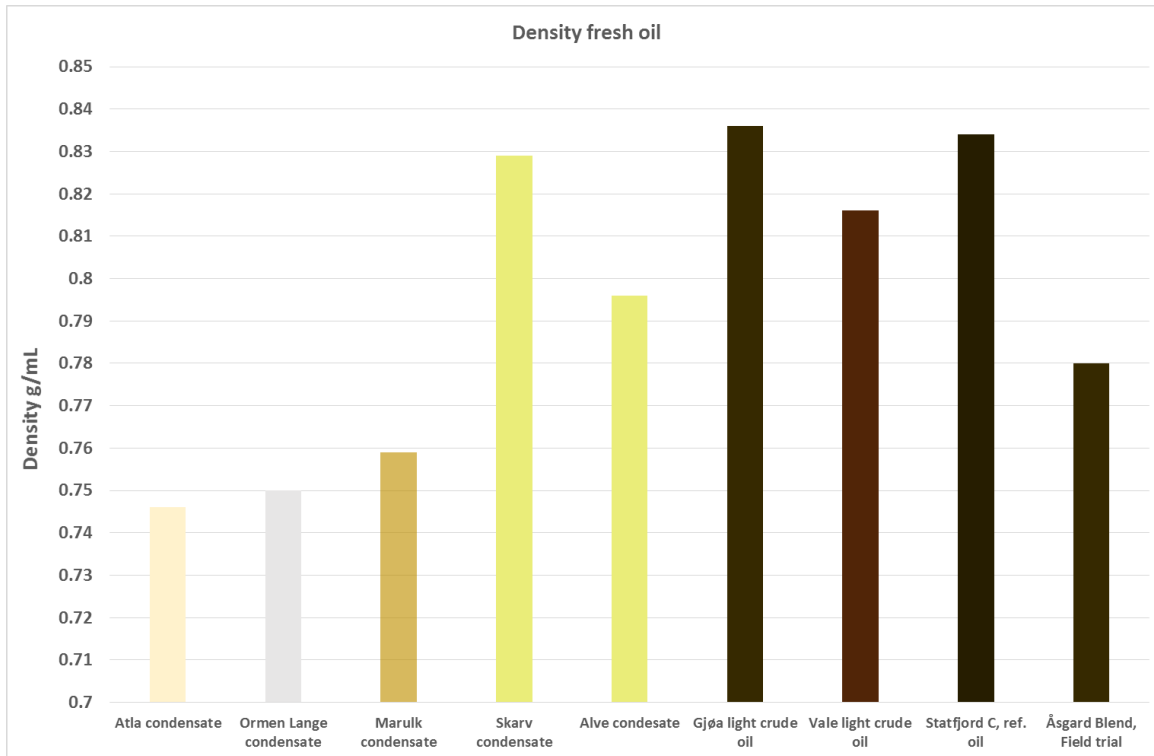


Figure 4-2 Variation of densities of the project oils (fresh oils) of condensates and light crude oil, including the reference crude oil.

4.3 Wax and asphaltenes

The content of wax (n -alkanes $> nC_{20}$) and surface-active components as asphaltenes and resins stabilize and promote formation of water-in-oil emulsions. Asphaltenes (and resins) have both hydrophobic and hydrophilic properties and will concentrate at the interface between the water and oil, and thereby form a layer that stabilizes the water droplets. The hydrophobic properties can also lead to the concentration of wax along the water droplets, which further stabilizes the interfacial "skin"-layer. The interfacial layer between the oil and water forms a physical barrier that hinders the coalescence of the water droplets and will stabilize the w/o emulsion.

The wax and asphaltene contents of the 250°C+ residue from the project oils are given in Figure 4-3. The amount of these components may be significantly higher in the residue compared with the fresh oil (see Appendix A) due to high evaporative loss of the lightest components. Condensates and the light crude oils exhibit low amount of asphaltenes. The reference crude oil has the highest content of asphaltenes and forms stable water-in-oil emulsions. Some of the residues with high amount of wax can lead to solidification on the sea surface particularly at low temperatures. The wax content also reflects the pour point as shown in Figure below; however, it is not a linear correlation between these two parameters.

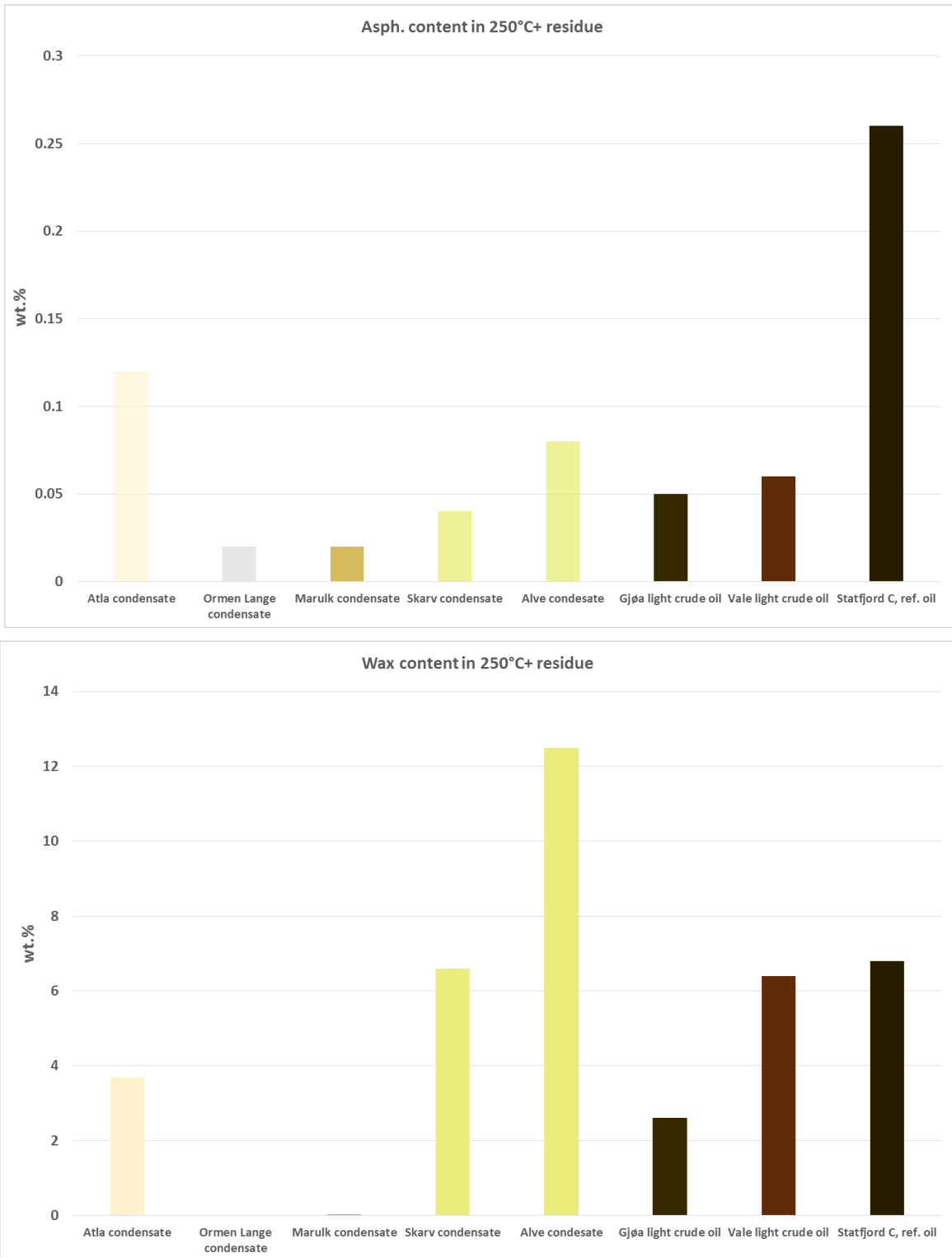


Figure 4-3 Wax content (lower) and asphaltene content (upper) in the 250°C+ residue of the project oils.

4.4 Pour point

The temperature at which oil ceases to flow when cooled without disturbance under standardized conditions in the laboratory is defined as the oil's pour point, and determines the temperature at which the oil become semi-solid. The pour point of oil with high wax content increases with evaporation as the lower weight compounds, which contribute to keeping the wax in solution, evaporate and hence promote solidification of the residue at the sea surface.

The pour points of the 250°C+ residue are given in Figure 4-4. Solidification may occur with pour points 10-15 °C above the sea temperature, and e.g. at 13 °C the residues for Skarv, Alve, Vale and Statfjord C Blend have potential for solidification.

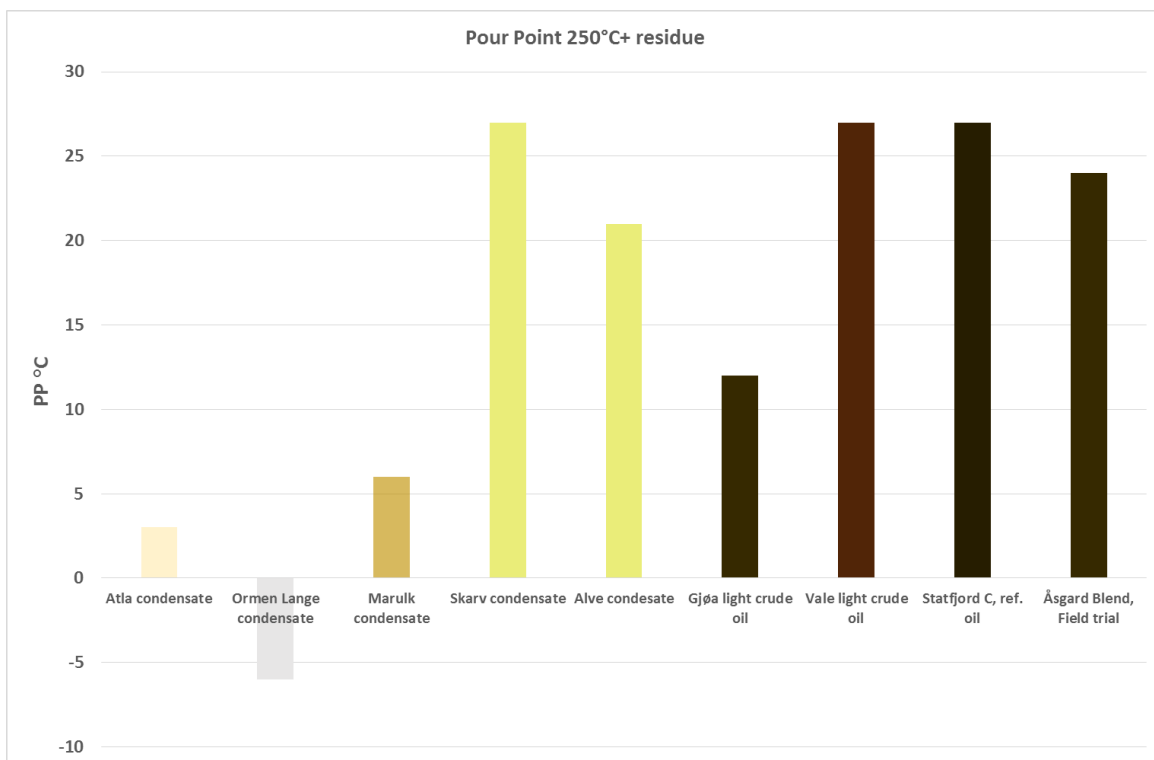


Figure 4-4 Pour point of the project oils (250°C+ residue) of CLOs and reference crude oil, and Åsgard Blend.

4.5 Rheology

Viscosity

The viscosity of oils expresses its resistance to flow. The viscosity is temperature dependent, and for liquids, the viscosity decreases with increasing temperatures. The viscosity of an oil increases with evaporation since the heavier, more viscous components remain in the residue (Mackay *et al.*, 1982). Viscous and waxy oils and water-in-oil emulsions exhibit non-Newtonian behaviour where the viscosity varies with shear rate (s^{-1}). The measurements of viscosities should therefore be carried out under controlled laboratory conditions with defined shear rates and preferably known thermal and mechanical history of the sample. The viscosities of oils can be expressed as:

- Absolute viscosity or dynamic (μ) is defined as the *Force distance/area speed*. The standard unit is $mPa.s = \text{centipoise (cP)}$.

- Kinematic viscosity (ν) is the absolute viscosity divided by density. The unit is centistoke (cSt) = cP / density

The viscosities (expressed as dynamic viscosity) measured at 13 °C with shear rate 10s^{-1} are shown in Figure 4-5, showing the viscosities of the fresh oil and its corresponding 250°C+ residue in the same figure. The figure illustrate that the viscosity increases with increased evaporative loss during the weathering process. Alta, Ormen Lange, Marulk and Åsgard Blend have very low viscosities, equally or less than 1 mPa.s.

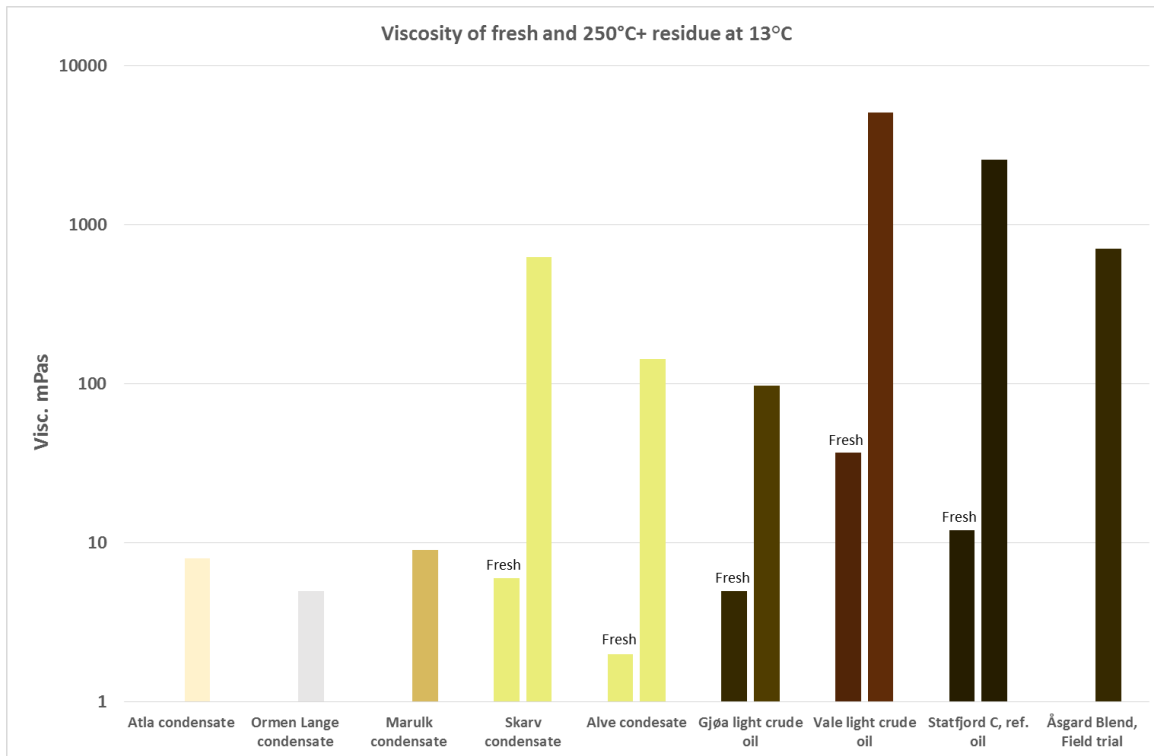


Figure 4-5 Viscosities of the fresh and 250°C+ residue of the condensates and light crude oils, including the reference crude oil (Statfjord C Blend) and Åsgard Blend (field trial). The viscosities are measured with shear rate 10s^{-1} at 13 °C. Oils without bars for the fresh oil means viscosities ≤ 1 mPa.s.

Yield stress

The yield stress is defined as the stress that must be applied to an oil /emulsion to make it begin to flow. Yield stress was found to be insignificant for Atla, Ormen Lange, Marulk and Gjøa measured on the fresh and the 250°C+ residue at 5 and 13 °C. These oils are also regarded as Newtonian, because their viscosities are independent of the shear rate, which are typically for low viscous oils with low wax content. However, Alve, Vale, Skarv, and Statfjord C Blend exhibit a yield stress particularly for the 250°C+ residue at lower temperature due to their wax content, and also typically exhibits non-Newtonian behaviour. Yield stress is assumed to be an important parameter for surface spreading, see SINTEF report Brønner *et al.*, (2017) for OSCAR modelling work.

Film strength related to rheology

The hypothesis that the strength of oil (thin) films could vary with film thicknesses and temperatures with a significant relation to interfacial rheology could not be proven with the method used (Pettersen, 2015). The film strength was found to be dominated by the bulk rheology parameters as viscosity and yield stress. Further, the relative film strength is related to both the shear rate and temperature, which is more pronounced for the weathered residues, and the film strengths were therefore found to increase as a function of weathering degree and increasing film thicknesses.

5 Experimental setup

SINTEF has for over more than three decades established and gained experience in the use of a large number of experimental systems to study the fate and behaviour, as well as characterisation of properties of crude oils and condensates. This project takes advantage of this knowledge and several of the established systems was used with some modifications and adaptations of operational parameters. The use of known and established experimental system (s) will make it possible to reproduce the experiments by other scientists working in this field of science.

The SINTEF experimental laboratory oil-in-water exposure systems are used for characterizing e.g. the weathering properties and determination of effectiveness of dispersants in connection to oil spill response planning for the specific oils according to Norwegian regulations. These experimental systems normally have specific operation of use, which is defined in Standard Operational Procedures documents (SOP, SINTEF internal documents as part of the QA system). However, the operation of these experimental systems can be modified to study other scenarios, including among others energy exposure, temperature, and oil quantity and weathering fraction, time intervals and application strategy.

The objective was to study weathering properties of thin oil film of the fresh oils, and to characterize surface residues from thin oils films in low exposure regimes (Beaufort scale 0-3, representing 0-4 m/s wind speeds) with respect to film formation, dispersion, emulsion formation and solidification in so-called open and closed laboratory experimental systems, as described in chapters below. This means that the criteria for choice of experimental system (s) and its operational parameters should include:

- Low energy, no droplet formation, *i.e.* dispersion/entrainment into the water column.
- Possibility to adjust/control the exposure over a wide range
- Allow generation of uniform thin oil films for highly evaporated fractions with high pour point
- Observation of surface oil film and the water column for video/photo documentation
- High surface area, giving larger oil quantities for analysis and characterisation of the weathered oil.
- Allow testing at constant temperature (2 and 13 °C)
- Limit possible wall effects

5.1 Closed experimental system

The "Tilting cylinder method" as shown in Figure 5-1 was decided as the test method for closed bench-scale testing in characterizing the properties of thin oil films from weathered oil residues.

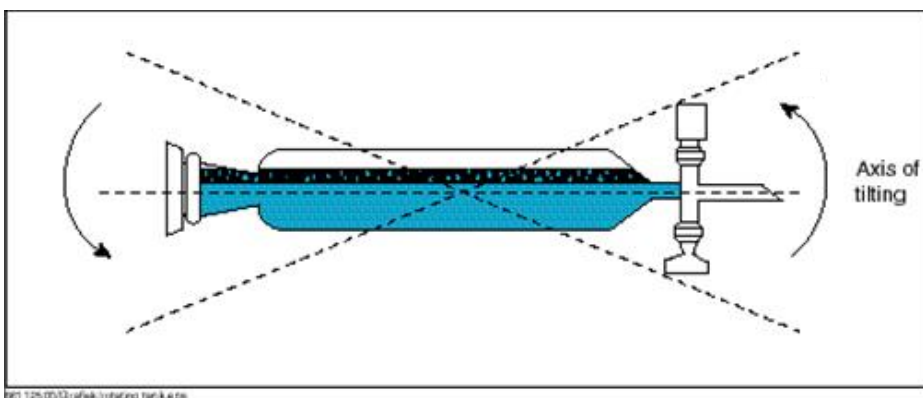


Figure 5-1 Principle of the tilting cylinder method.

This tilting cylinder method was modified using the rocking table from "Simulated Shoreline System" which was modified to an equal tilting of 16 degrees in both directions. The frequency can be controlled over

a large range simulating very calm condition to breaking wave conditions. The system uses closed system funnels of glass material which reduces the wall effects and allow observation of both the oil film and the water phase. An oil quantity of 2.76 mL was applied to give a film thickness of 200 μm that gave limitation for sampling and quantitative characterization of the oil residue. The results from these experiments were therefore mainly based on a qualitative observation by use of video and photo documentation to characterize the oil film.

The protocol for performing the closed system experiment is described in Andreassen (2014) (memo D2-3 Standard Operating Procedure for Rocking Table Test). The experimental design is described in Ramstad (2014) (memo D2-1 "Small-scale (closed) experimental system to study thin oil films from condensates and light crude oils - Evaluation and description").



Example from the "Tilting cylinder method" of different oils/residues with use of tilting energy.

5.2 Open system experiments

The study of the weathering processes of thin oil films from condensates and light oils requires use of fresh crudes in open experimental system (s) which simulates environmental parameters. To simulate calm conditions that is a prerequisite for generation and lifetime of thin oil film, a modification of the experimental design had to be done for the standard Flume and MNS systems.

5.2.1 Modified MNS

The MNS test (Mackay and Szeto, 1980) has been the approval method for dispersants effectiveness testing for Canada. The energy input in this system, applied by blowing air across the oil/water surface, is generating a circular wave motion. This energy has been estimated to correspond to a medium to high sea state condition, and had therefore to be reduced significantly. See Figure 5-1 for the principle of the MNS test apparatus. The operations of the MNS for thin oil film studies is described in the SOP D3-1 (Andreassen and Pettersen, 2015) "Standard Operational Procedure for weathering, fate and behaviour of thin oil films under calm conditions in modified MNS".

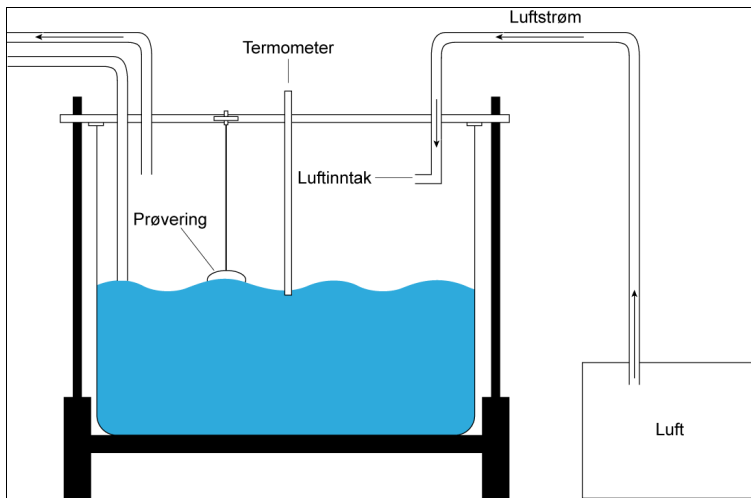


Figure 5-1 Standard MNS test apparatus.

5.2.2 Modified SINTEF Flume

SINTEF Flume was used for upgraded larger scale weathering studies of thin oil film, the. This allow use of 1 Litre of fresh oil and thereby potential for more frequent sampling and large quantities of oil at the end of the experimental period. A schematic drawing of the experimental meso-scale flume basin is presented in Figure 5-2. Approximately 5 m³ of seawater circulates in the 10 metres long flume. The flume basin is located in a temperature controlled room. Two fans are placed in a covered wind tunnel, controlling the wind speed and orientation.

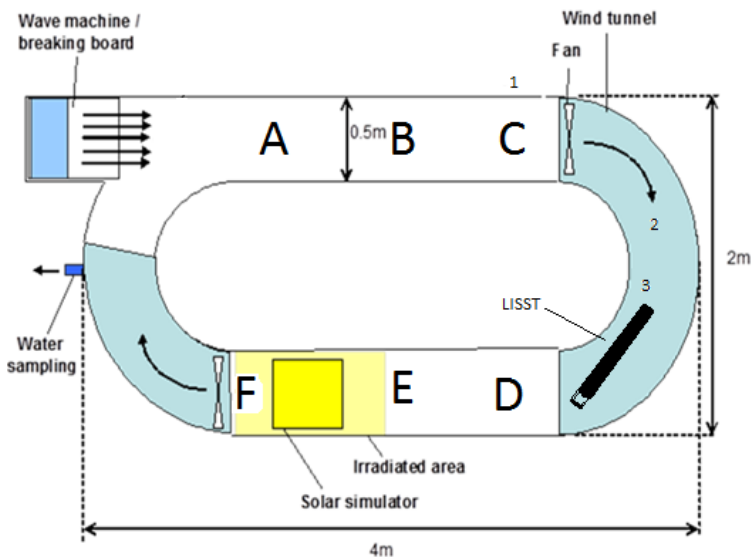


Figure 5-2 : Schematic drawing of the meso-scale flume basin.

Overview of experimental condition and design of open system experiments in Flume and modified MNS compared to a standard Flume study is given in Table 5-1. Modifications were established to simulate calm condition without any breaking wave, uniformness of the surface area and minimize attachment of oil residues at the equipment internal walls. Standard Operational Protocols (D3-2) was established for the modified flume experimental systems to study weathering of thin oil films (Pettersen and Sørheim, 2015), Meso-scale flume experiments with TOF – Technical specification.

Table 5-1 Parameters for weathering of thin oils films in the modified Flume and MNS, and the standard weathering parameters in the Flume.

Parameters	Weathering of Thin Oil Films in Modified Flume	Standard weathering in Flume	Weathering of Thin Oil Films in Modified MNS
Time period	18 h	3 days	18 h
Oil quantity (film thickness)	1.125 L (250 µm average)	9 L (2 mm average)	16 mL (250 µm average)
Oil application	Dispersed into water column (2 minutes)	Surface	Dispersed into water column
Wave exposure	Frequency:5 rpm Calm - No breaking waves	Frequency: 34 rpm Breaking waves	No
Wind speed	1-2 m/s	5-10 m/s	1 m/s
Fume /ventilation	0-8 h (no: avoid turbulence) 8-18 h (yes)	Yes	Air blow over the water surface
Lid	Partly, removed after 8 hours	No	Controlled air flow-through
Sampling	Surface 1-2-4-8-18 hours Water – during ramp up	Yes Yes	Surface 1-2-18 h No water samples
Observations	Visual Video/Photo Surface/subsurface	Visual Photo Surface/subsurface	Visual Video/Pictures – subsurface/surface
Termination	Ramp up – increasing frequency Droplet formation Sorbent adhesion Dispersant field effectiveness test (FET) Physical properties	Chemical dispersion	Ramp up Oil collection – physical properties, film thickness

6 OWM predictions and experimental laboratory results of oils properties and behaviour at sea

6.1 Standard OWM scenario

The SINTEF Oil Weathering Model (OWM) was used running one standard set scenario similar for all of the 8 condensates and light crudes oils from this project in order to simulate an initial thin film thickness lower than 250 μm . In this case, an underwater release was chosen to achieve such thin oil film thickness anticipated to be formed straight after a spill release. The objectives with such standard scenario predictions were:

- 1) to visualize the span in the weathering properties, and
- 2) a basis for discussion on the limitations in the current version of the model with respect to predicting the weathering properties of different oils that forms thin oil films based on this.

The OWM model relates the oils properties to a chosen set of release parameters and predicts the rate in change of oils properties and behaviour on the sea surface. The input parameters are given in Table 6-1, and an overview of the OWM predictions given as physical properties is shown in Table 6-2.

Table 6-1 Release parameters for OWM predictions.

OWM - Release input parameters	Figures and units
Release rate	250 m ³ /hours
Gas-to-oil ratio	50
Water depth	300 m
Temperature	2 and 13°C
Wind speed	2 and 5 m/s

Table 6-2 Overview of output from the OWM predictions.

OWM - Physical properties	Units
Surface oil	%
Evaporation	Vol. %
Water uptake	Vol. %
Surface emulsion	%
Pour point	°C
Viscosity oil/emulsion	mPa.s
Oil/emulsion film thickness	mm

6.2 Comparison of oils and condensates

A comparison between the predicted physical properties of eight condensates and light crude oils including the reference crude is illustrated in the figures below. Each physical property of the oils are shown in the same figure for one temperature (13°C) and for wind speeds of 2 m/s and 5 m/s. Data from similar predictions for 2°C is given in Appendix B. The following notes should kept in mind in evaluation the OWM predictions:

- In cases where the mass balances showed no surface oil due to high evaporation loss and entrainment into the water column, the data were removed and marked with a "dot" in the graphs.
- Water uptake is independent on the film thickness.
- Solidification shown as lumps or patchiness is not included in the OWM.
- Water uptake (emulsification) is independent of film thickness in the OWM.
- The input data for the OWM predictions are from standard laboratory weathering experiments (*i.e.* not using thin oil film).

- Predictions for 2 and 13 °C were done with available input data from the previously standard weathering studies at 5 and 13 °C. Alve weathering study included only experiments at 5 °C.
- The chemical composition for Ormen Lange condensate used in the current laboratory study had a higher concentration of the lighter compounds compared to the condensate that was used in the standard weathering study in 2008. A new batch of the reference crude oil Statfjord C Blend was also used in the present study similar properties to the previously weathering study.
- The energy exposure used in the experiments are difficult to quantify and relate to environmental wind speeds. The experimental parameters were chosen to simulate non-breaking wave conditions (< 5 m/s wind speed).
- The non-breaking wave will not favor generation of water droplets in the oil film, and the possibility to generate water-in-oil emulsions will be low.
- Because much of the laboratory testing in this project was performed in small scale, the "wall effects" should be considered. This could affect the behaviour of film residue and *e.g.* influence the evaporation from the oil film, adhesion to the walls and restrict further spreading of the oil residues without yield stress.
- The behaviour of the surface oil film behaved different during the experimental period from uniform liquid film to patchiness and differences in film thickness. Representative sampling of not uniform oil distribution and data evaluation more difficult.

6.2.1 Surface oil

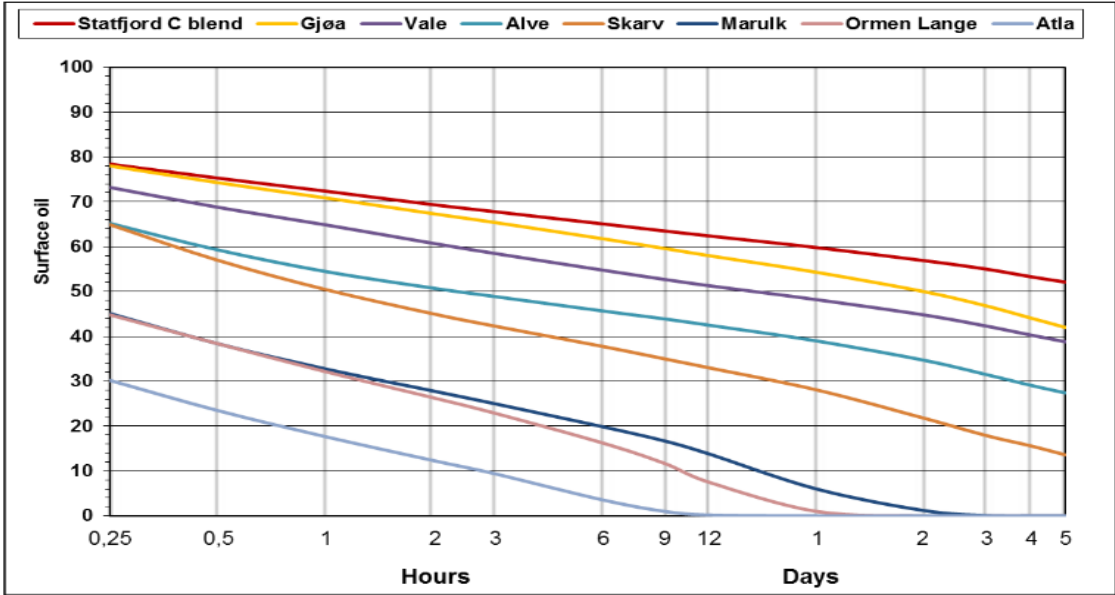
After release of oils to the sea surface, light components are removed by evaporation from the oil film. For condensates and light crude oil, under calm conditions, this is mainly caused by evaporation (Chapter 6.2.2), while natural dispersion/entrainment will be more importance with increasing wind speeds (Chapter 6.2.7). Emulsification (*i.e.* water uptake) described in Chapter 6.2.3 increases the film thickness and hence the surface emulsion quantity. These weathering processes are dependent on thickness of the oil film, and the pour point and viscosity seem also to play an important role for these oils.

Predictions for surface oil for the 13 °C scenario with 2 and 5 m/s wind speeds are given in Figure 6-1. The predictions show a very high initial reduction in surface oil quantity (20-70 %) over the first 15 minutes with 2 m/s wind speed. Highest removal rate of oil from the surface is with the lightest condensates (Atla, Marulk and Ormen Lange), which are quantitatively removed from the surface within 1-3 hours. The other condensates are removed from the surface after 1-5 days, while the oils classified as light crude oils (Vale and Gjøa) and the reference crude oil (Statfjord C Blend) may persist on the surface more than 5 days. The removal rate is slower with lower wind speed (2 m/s), due to lower evaporation, liquid/gas equilibrium constant and reduced natural dispersion/entrainment.

At low temperature (2 °C) the oil remain at the surface for a longer time period as shown in Appendix B. This is due to lower evaporation rate. This would be even more pronounced if the effect of solidification, which affects internal diffusion/transport, was included, resulting in more oil at the surface for a longer period.

Property: Surface oil
 Wind speed: 2 m/s
 Temperature: 13°C

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Property: Surface oil
 Wind speed: 5 m/s
 Temperature: 13°C

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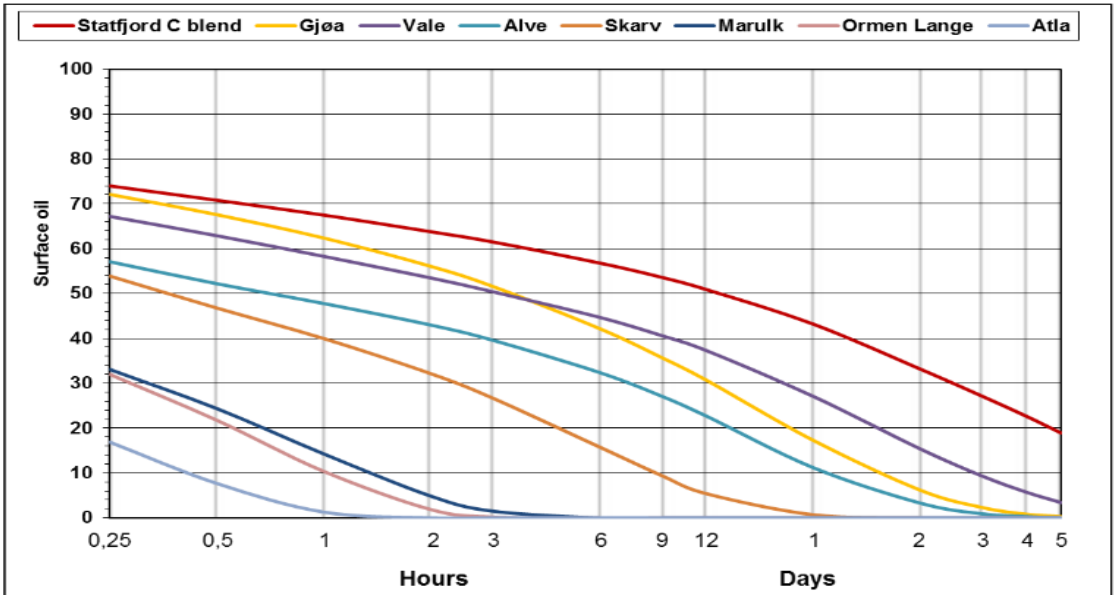


Figure 6-1 OWM predictions - Surface oil at 13 °C with 2 and 5 m/s wind speeds.

6.2.2 Evaporation

Condensates and light crude oils contains large fraction of components with a low boiling point that will be evaporated in the initial phase after a release to the environment. Results from OWM predictions with an initial thin oil film (< 200 μm) are shown for 13 °C at both 2 and 5 m/s wind speeds in Figure 6-2.. These show a rapid initial evaporation, of 55-70% for the lightest condensates Atla, Ormen Lange and Marulk, and 20-30% for the emulsifying light oils Vale and Gjøa as well as the reference crude Statfjord C Blend during the first 15 minutes after a release. These predicted data are in accordance with measurements of the volatile oil compounds performed as part of the human exposure studies. Benzene and toluene evaporated quantitatively within few minutes, and xylene was evaporated during the first 30 minutes. After application of the fresh oils in the Flume and MNS experimental systems, the evaporation process could be observed visually as "boiling" in the initial phase.

The first sampling for gas chromatographic (GC/FID) analysis was conducted after 1 hour from the MNS and Flume experiments. The GC-chromatograms for Gjøa and Skarv from the MNS experiment at 2 and 13°C sampled after 1 hour are shown in Figure . The amount of the alkane $n\text{C}_9$ compound (boiling point of 151 °C) was estimated to be reduced less than 50 % at 13 °C. The true boiling point curves (see Figure 4-1) indicate that this would account for approximately 25 % for Gjøa and 40 % for Skarv, which is in accordance with the OWM predictions (30 and 50 %, respectively). The chromatograms of each oil are given in Appendix B. The evaporation of the $n\text{C}_9$ compound varies to a very high degree among the oils, which is dependent on the chemical composition and the physical properties.

Figure 6-2 also shows the effect of temperature on the evaporation for Gjøa and Skarv. The differences between 2 and 13 °C are relative small for Gjøa, whilst for Skarv the differences is larger due to solidification of the surface residue. This phenomenon will be discussed further in Chapter 6.2.4 (Pour point).

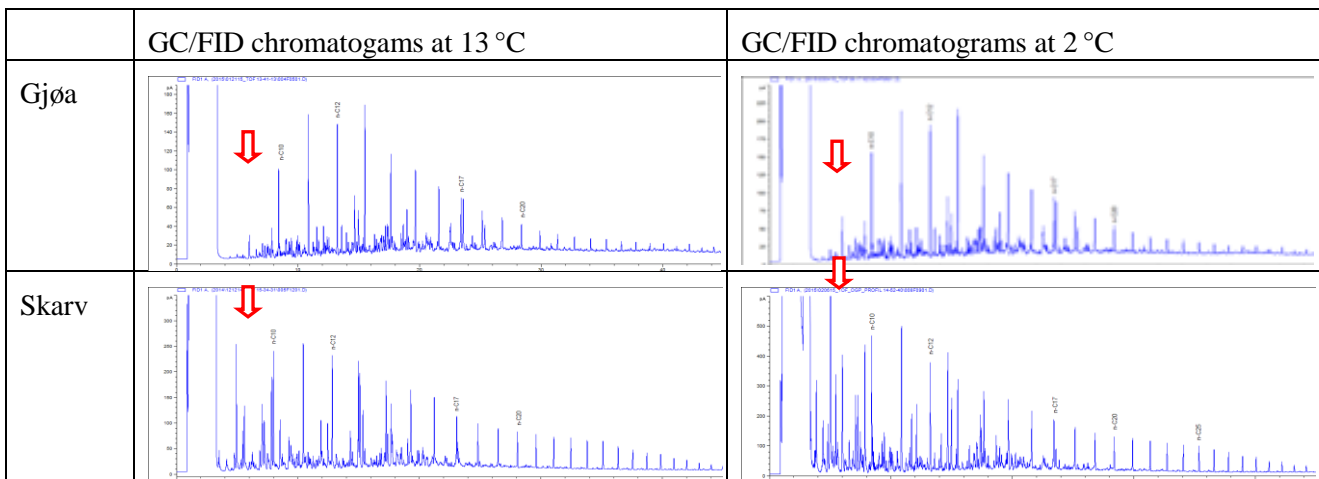
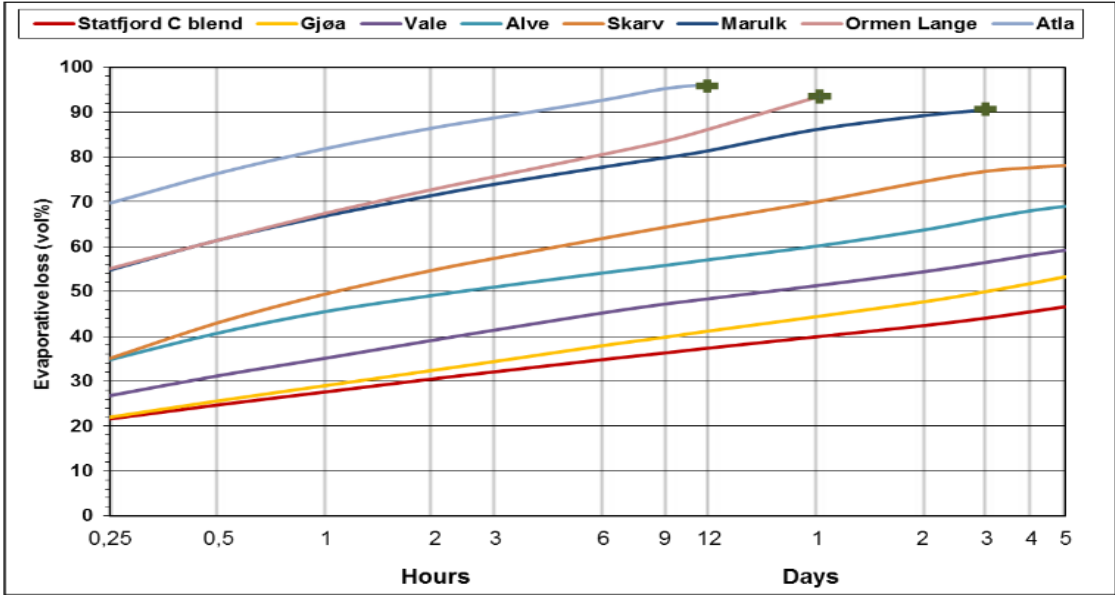


Figure 6-2 GC/FID chromatograms for Gjøa and Skarv samples after 1 hour in the modified MNS (red arrow indicate the $n\text{C}_9$ component).

Property: Evaporative loss
 Wind speed: 2 m/s
 Temperature: 13°C

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Property: Evaporative loss
 Wind speed: 5 m/s
 Temperature: 13°C

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 Pred. Date: March 2016

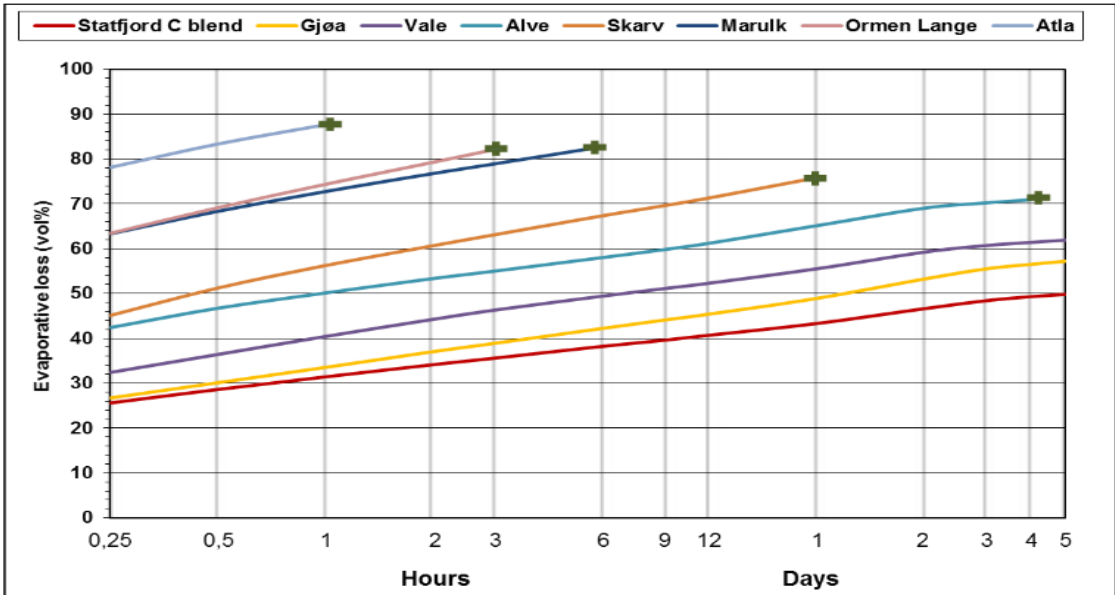


Figure 6-3 OWM simulations - Evaporative loss for test oils at 13 °C with 2 and 5 m/s wind speeds. The dots in the figure represent when no oil are predicted on the surface.

Figure 6-3 shows that the evaporative loss increases with increasing wind speed for more rapid spreading of the oil creating a thinner oil film and hence increases the evaporation. The evaporation after 1 hour of the oils classified as condensates is predicted to be 70-90 % at 5 m/s wind speed and 50-60 % for the light crude oils and the reference oil. The experiments in the open systems gave in general lower evaporation at the end of the experimental period after 18 hours, with a typical residue which could be characterized as 230-250 °C+ at 13 °C and 190-230°C+ at 2 °C. These differences are mainly due to the effect of solidification (*i.e.* Alve, Skarv, Vale and Statfjord C Blend) of surface residues. The reduction in film thickness due to natural dispersion/entrainment was not observed in the laboratory studies with 1-2 m/s wind speed.

Similar predictions of evaporative loss at 2 °C are given in Appendix B. The predictions follow more or less the same trends as for 13 °C, but the evaporation loss is significant slower resulting oil on the surface for a longer time period. The potential effect of solidification are also more pronounced for the 2 °C scenario.

6.2.3 Water uptake – emulsion formation

Previously standard weathering studies showed significant water uptake for Vale and Gjøa in addition to the reference crude oil Statfjord C Blend, and no significant water uptake and stable emulsions was observed with any of the condensates. The standard emulsifying studies were done with a thicker oil film (~2 mm) in rotating flasks, which may favour water uptake compared to thinner oil films.

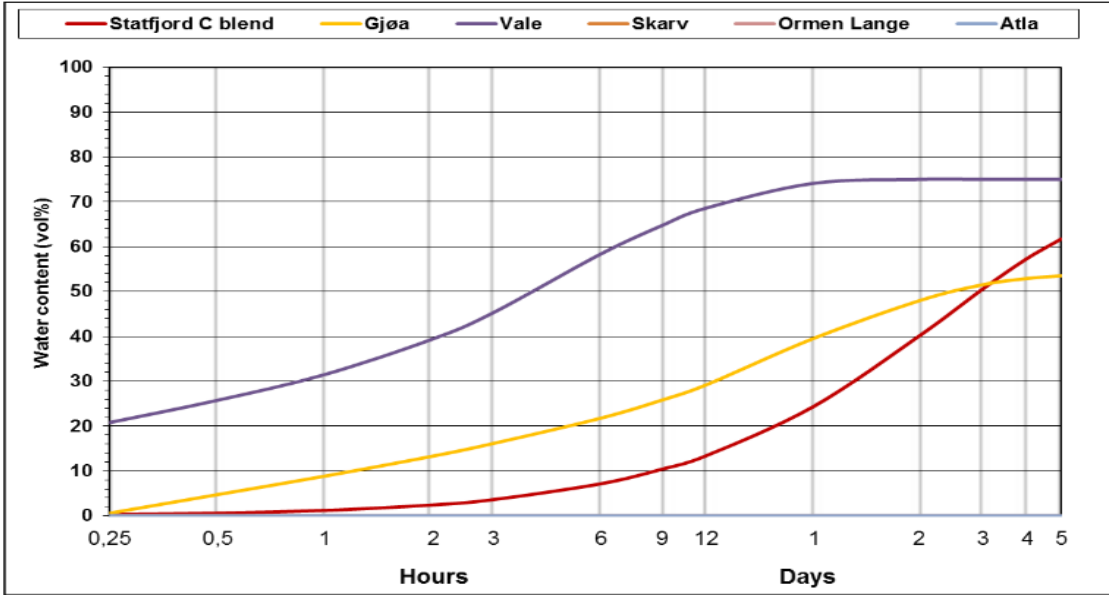
In the present study using thin oil films, no significant water uptake was found for none of the oils at 1-2 m/s wind speed, and reflects the OWM prediction of water uptake, as shown in Figure 6-4. The water uptake of Statfjord C Blend, Vale, and Gjøa is given at 13 °C at 2 and 5 m/s wind speeds. The predictions show an initial high water uptake for Vale with 30 and 45 vol. % at 2 and 5 m/s wind speed after 1 hour respectively, and reaches a maximum water uptake of 75 vol. % after 24 and 6 hours. For Gjøa and Statfjord C Blend, the water initial uptake was lower and slower compared with Vale. The maximum water uptake of the oils was reached after 1-3 days.

The findings from the MNS and Flume experiments showed low or no significant water uptake by visual observations for any of the oils with thin oil films under calm conditions (approx. 1-2 m/s wind speed), with initial uniform oil film thickness less than 250 µm. It is anticipated that thin oil films could accumulate e.g. with higher wind speeds and form more patchy thicker film, and hence increase the potential for emulsification of oils with emulsifying properties such as Vale, Gjøa and Statfjord C Blend. However, the MNS and Flume experiments showed only reduced water uptake, (*i.e.* 35 vol.% for Vale in MNS, and 23 % vol. % for Skarv in Flume), but the emulsions were highly unstable and released water after short time with breaking wave energy (higher wind speed) after 18 hours weathering at the end of the experimental period. The water contents of the oils after breaking wave conditions are given with the respective viscosities as shown in Table 6-3, Chapter 6.2.5. Visual observations also indicated that the water incorporation consisted of large water droplets with limited stability. It should be emphasized that the increased energy was applied for 30 minutes, and the emulsions could possibly be stabilised with even higher energy exposure for longer period.

In closed system experiments, using 200 µm film thickness with 200 and 250°C+ residues showed some limited water uptake of Marulk and Vale, only with breaking wave conditions after 18 hours, but also these emulsions were very unstable with larger water droplets. The only main exception was the photooxidized residue of Gjøa, which generated stable water-in oil (w/o) emulsion with a high water content of 80 vol. %. Photooxidized residues (under influence of sunlight) contain higher amounts of surface-active components (resins and asphaltenes), which stabilize the water droplets and hence the emulsification. Only limited data were available for the reference oil Statfjord C Blend, as the residue became very sticky and easily adhered to the internal wall of the test funnel, which restricted the potential emulsion formation.

Property: Water content
 Wind speed: 2 m/s
 Temperature: 13°C

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Property: Water content
 Wind speed: 5 m/s
 Temperature: 13°C

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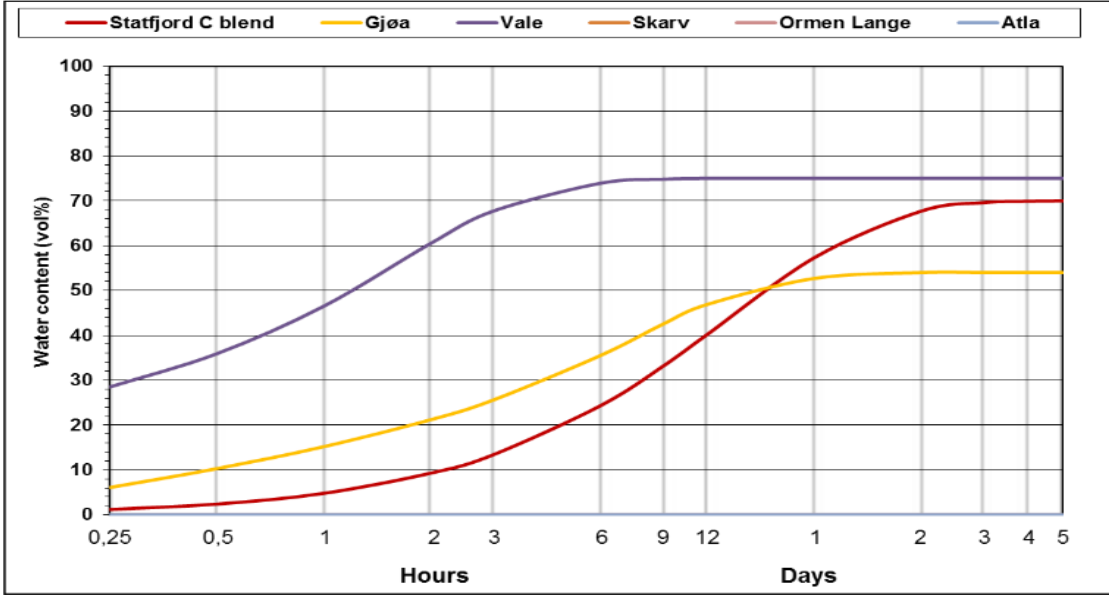


Figure 6-4 OWM predictions - Water content for test oils at 13°C with 2 and 5 m/s wind speeds. The figure includes only the oils with significant water uptake.

It was not observed any significant water uptake with the Vale residues in experimental studies under calm condition. This is likely due to the high pour point of Vale residues, which will result in solidification in an

early phase of the weathering processes. It is therefore unclear if the evaporated Vale film residue can take up water and form emulsion at calm conditions as predicted in the current OWM scenarios.

6.2.4 Pour point

The pour point of an oil is lowest temperature (°C) at which the fluid ceases to pour and become semi-solid and loses its flow characteristic. An oil may solidify 10 - 15 °C above the sea temperature due movement as wind and waves at the sea surface. In calmer conditions (2 m/s wind speed), the difference is assumed to decrease due to lower wave exposure. The OWM predictions show the pour point as a function of time in Figure for 2 and 13 °C at 2 and 5 m/s wind speeds. As shown in Chapter 6.2.2 the condensates and light crude oils contain high quantities of the lighter compounds, which evaporate in the initial phase after a spill. Due to this evaporation of the light components, and thereby "accumulation" of the heavier compounds, the pour point of the residue increases rapidly.

Atla, Ormen Lange, Marulk and Gjøa have a low pour point (fresh oil < -30°C). For the 13 °C scenario, the pour point of these oils will not be sufficient high to solidify on the sea surface. On the other hand, Alve, Vale, Skarv and Statfjord C Blend have much higher pour points for the fresh oils in the range from -9 to + 6 °C. Evaporated residues from these oils will within few hours have pour points higher than the sea temperature. These residues may also have a tendency for solidification on the sea surface, but are dependent on the wave energy.

In the open experimental studies (MNS), solidification of weathered residues were observed for Alve, Vale, Skarv and Statfjord C Blend. This was also observed in the modified flume experiments using Skarv and Statfjord C Blend.

In addition, an expression of solidification were calculated as the percentage-evaporated fraction of the nC_{12} compound from the hydrocarbon distribution of Skarv, Ormen Lange and Gjøa and Statfjord C Blend as a function of time (Figure 6-5). The percentage-evaporated fractions were based on the Flume experiments at 13 °C. Figure 6-5 shows that the evaporation rate of nC_{12} for Skarv is reduced very early (tentatively 2-3 hours). On the other side, the evaporation of nC_{12} in Ormen Lange is completed after approximately 9 hours, whereas Gjøa has a potential for solidification after longer time weathering. This difference is most probably due to reduced evaporation because of solidification of the oil film, which reduces transport processes in the oil.

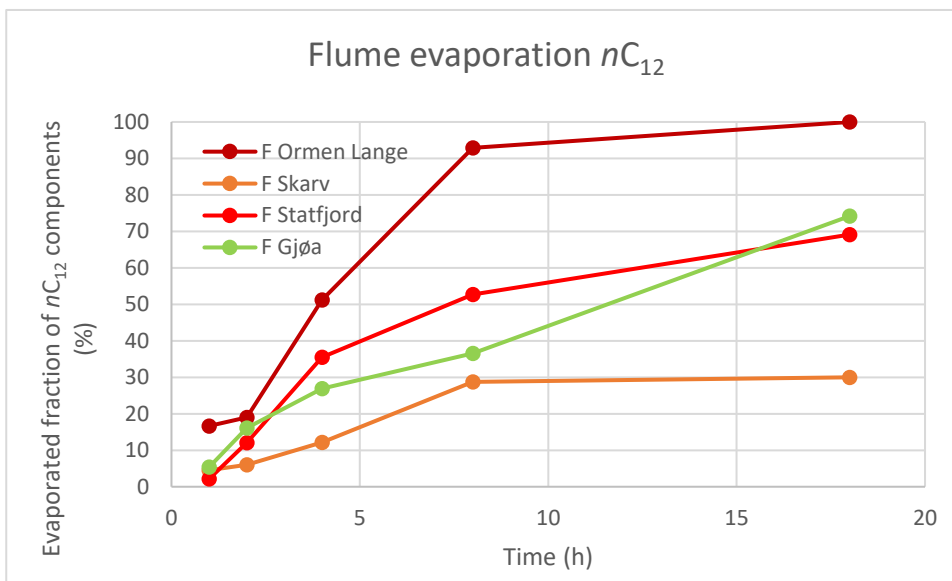
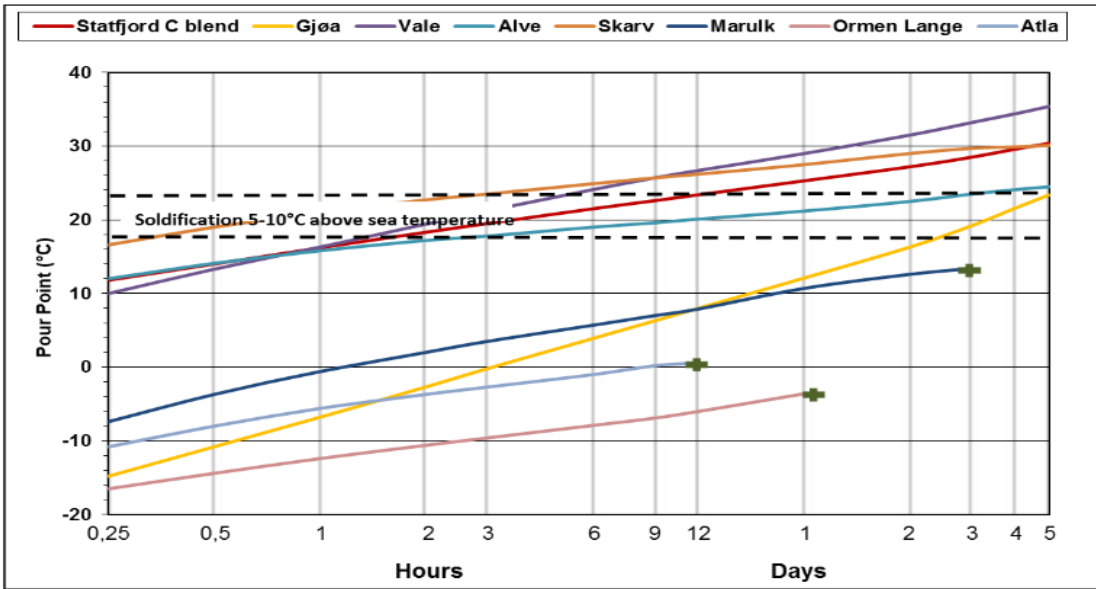


Figure 6-5 Evaporated fraction of the nC_{12} compound in thin oil film from Flume experiment as a function of time for the test oils.

Property: Pour point
 Wind speed: 2 m/s
 Temperature: 13°C

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Property: Pour point
 Wind speed: 5 m/s
 Temperature: 13°C

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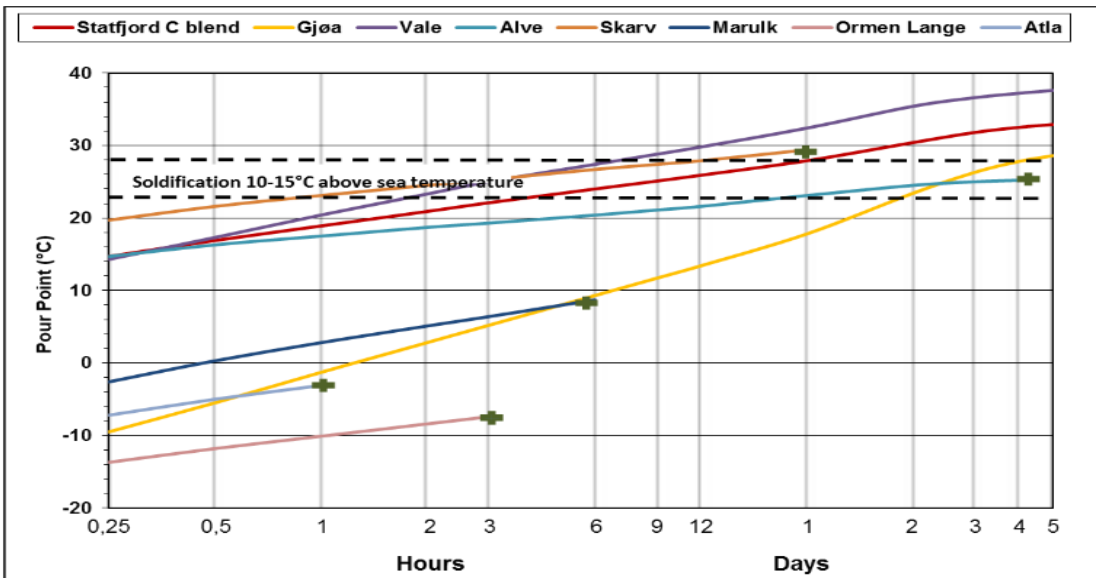


Figure 6-6 OWM predictions - pour point for test oils at 13°C with 2 and 5 m/s wind speeds. The dots in the figure illustrate when no oil are predicted on the surface.

A phenomenon with two phases of the surface oil film including solidified oil and liquefied oil film was observed in the laboratory studies as most pronounced in the closed system with generation of lumps, *i.e.* a solidified phase as lumps surrounded by a liquid film. This is illustrated in Figure 6-7 with GC/FID chromatograms for the two fractions from the flume experiments (13 °C) with the Skarv condensate. The

upper sample was taken from the flume wall as solidified lump, and the lower sample from film from the surface. The solidified sample has a significant higher concentration of the wax components $> nC_{20}$. Similar phenomenon with two phases as described above was also observed after the Staffjord A incident in 2007 some days after the release with breaking wave conditions. The phenomenon is probably due to generation of solidified lumps that after resurfacing allow "release/transport" of liquid components from the waxy lattice structure.

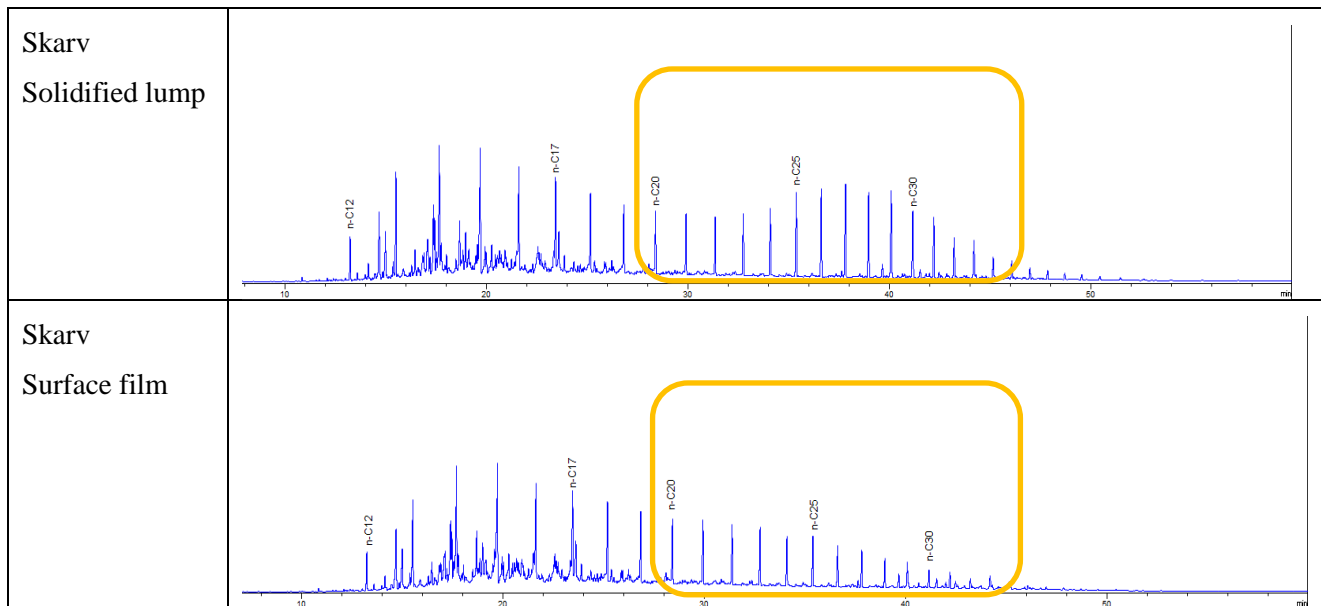


Figure 6-7 "Two-phase oil" with Skarv condensate in Flume experiment. Yellow frame – "wax fraction"

6.2.5 Emulsion/oil viscosity

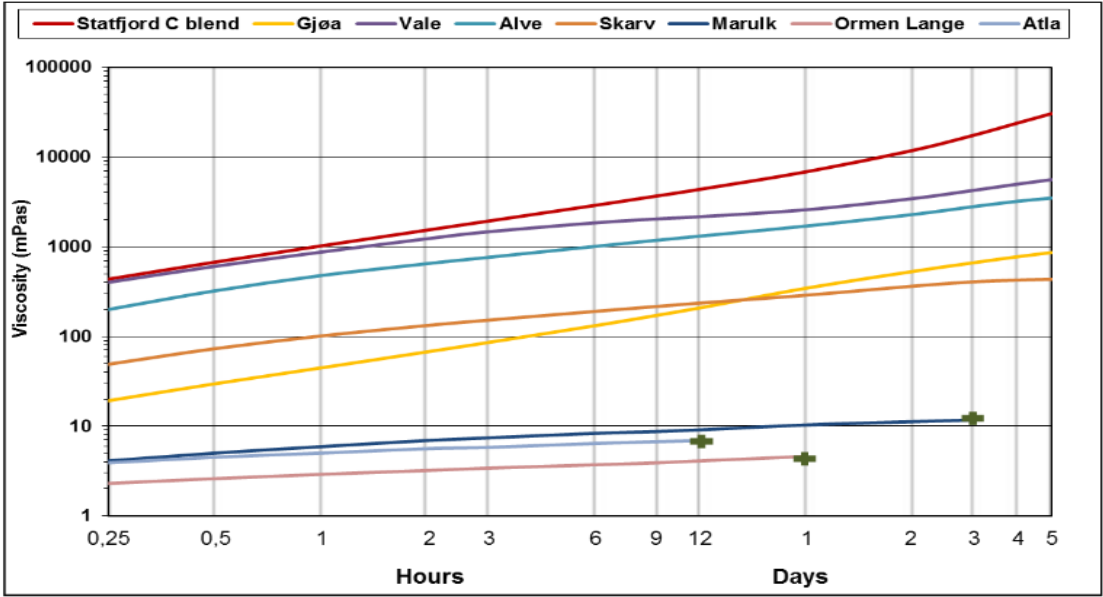
The OWM predictions of the viscosity of the surface oil/emulsion for the 13 °C scenario at 2 and 5 m/s wind speeds are given in Figure 6-8. The increase in viscosity varies over a very wide range and is dependent on the evaporation and the formation of w/o-emulsions, in addition to the chemical composition of the residue.

The predictions show that the viscosities of the light condensates Atla, Ormen Lange and Marulk are low and do not increase significantly during 5 days weathering. These condensates do not form w/o- emulsions and the increase of viscosity is only due to evaporation. The other non-emulsifying condensates Alve and Skarv have much higher wax content (6.6 and 12.5 wt. % for the 250°C+ residue) which contributes to increasing pour points and viscosities. For the emulsifying light oil Gjøa and the reference Staffjord C Blend, the viscosities increased due to emulsion formation. However, this increase of viscosity was less pronounced for Vale, because the waxy lattice structure break during the emulsifying process.

At the end of the experimental period in the open systems (MNS and Flume) an increasing wave exposure was applied for 30 minutes simulating breaking waves. After 30 min. the oil was collected and the viscosity and water content was analysed from some of the experiments. The results are given in Table 6-3 for residues from the 13 °C experiments, together with the viscosities of the 200 and 250°C+ water-free residues. In general, the measured viscosities from the experiences were in the range between the water-free 200°C+ and 250°C+ residues. This shows that the water uptake does not affect the viscosity, which indicates unstable emulsions.

Property: Viscosity emulsion
 Wind speed: 2 m/s
 Temperature: 13°C

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 Pred. Date: March 2016



Property: Viscosity emulsion
 Wind speed: 5 m/s
 Temperature: 13°C

SINTEF
 4.0 β © 2010
 Pred. Date: March 2016

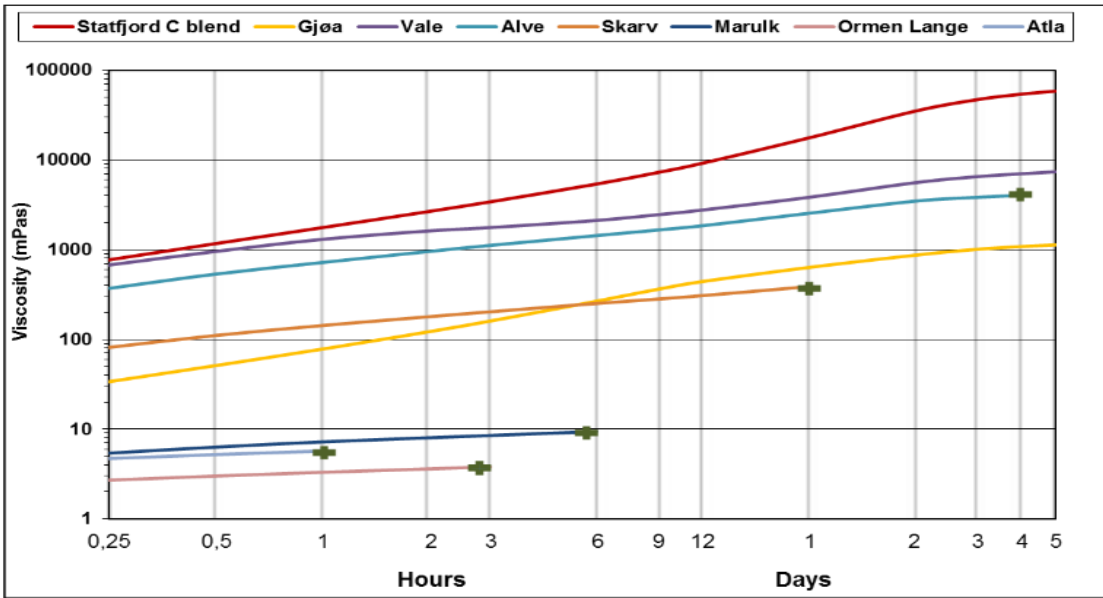


Figure 6-8 OWM predictions –emulsion/oil viscosity for test oils at 2 and 13°C with 2 and 5 m/s wind speed. The dots in the figure illustrate when no oil are predicted on the surface.

Table 6-3 Viscosity and water content (in brackets) of oil residues at the end of the test period at 13 °C.

Viscosity (mPa.s, 10 s ⁻¹ , 13 °C)				
	Modified MNS	Modified Flume	200°C+ water-free residue	250°C+ water-free residue
Ormen Lange	n.a.	-	n.a.	5
Marulk	10 (n.a.)	-	5	9
Atla	8 (0 % w)	-	4	8
Gjøa	130 (n.a.)	90 (7 % w)	34	98
Vale	4000 (35 % w)	-	1100	5100
Alve	89 (0 % w)	-	78	140
Skarv	340 (0 % w)	240 (23 % w)	630	4400
Statfjord C Blend	1300 (50 % w)	1800 (25 % w)	680	2500

n.a. = not analyzed

6.2.6 Oil/emulsion film thickness

For the OWM prediction, the oil/emulsion thickness profiles are very similar to the oil surface quantities for the non-emulsifying condensates (Atla, Marulk and Ormen Lange, and Alve and Skarv). The oil film thickness decreases as long as oil is predicted on the sea surface. On the oil hand, the oil film thickness increases for the light crude oils that allows uptake of water to form emulsions. The results from the OWM predictions for the 13 °C scenarios with 2 and 5 m/s wind are given in Figure 6-9.

In the laboratory studies using open experimental systems (MNS and Flume), oil remained at the surface for the completely experimental period (18 hours) with all combinations of test parameters (i.e. oil types, temperature, film thickness, wind speed). The "terminal" film thickness was therefore higher than the results from OWM predictions, and were in the range of 50-150 µm based on quantitative analysis of oil residues. This difference is probably mainly due to laboratory studies under very calm conditions, which did not generate any natural dispersion/entrainment of oil droplets/lumps into the water column, wall effects that does not allow spreading of the oils without yield stress, and that the OWM predictions does not include solidification.

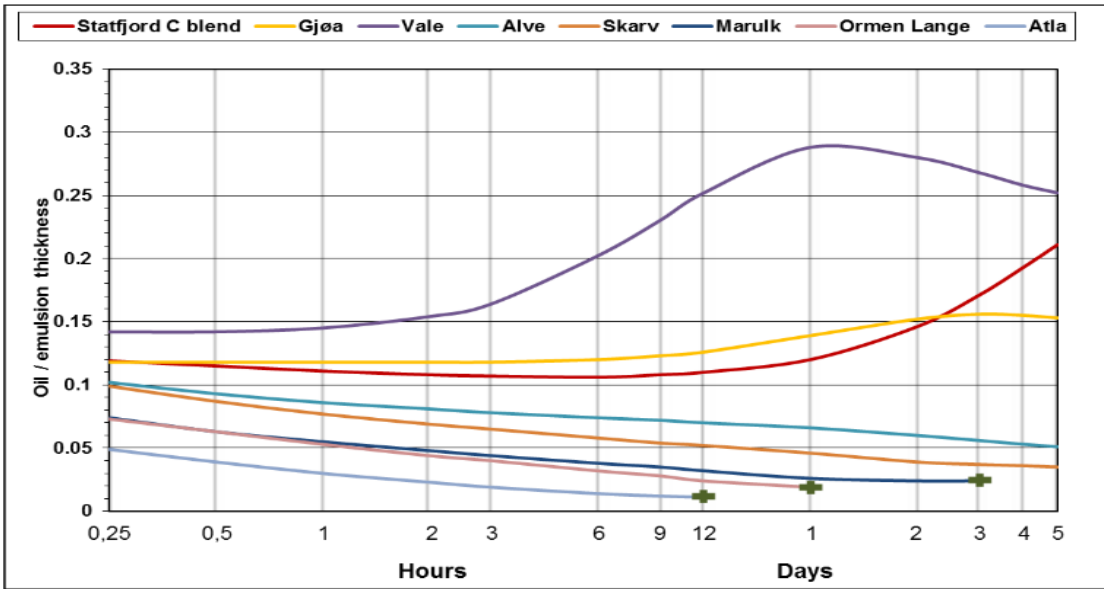
As discussed with surface oil, the residue quantity increases with lower temperatures. This is also seen with the increasing oil /emulsion film thicknesses with 2 °C scenarios (see Appendix B).

The chemical composition of the residues affects the evaporation and thereby the surface film thickness. The oils with highest content of the light components will achieve the 200 and 250°C+ residue characteristics at a significant earlier time as compared to the oils with lower portions of the lighter compounds. This is illustrated in Figure 6-10 (A and B) for the 13 °C scenario with 2 and 5 m/s wind speed. This figure shows that the 200 and 250°C+ residue are achieved at an earlier time and at lower oil film thicknesses. This is probably due to more rapid evaporation with thinner oil film.

The water uptake prediction for Vale indicated an initial high uptake rate of water, followed by a reduced water uptake rate for 6-12 hours. These were, however, very unstable giving oil water separation easily by physical exposure. The absence of emulsion formation with thin oil films is most probably due to its high pour point in combination with low physical exposure, which generates a solidified wax lattice, which does not allow encapsulation of water droplets.

Property: Oil / emulsion thickness
Wind speed: 2 m/s
Temperature: 13°C

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 Pred. Date: March 2016



Property: Oil / emulsion thickness
Wind speed: 5 m/s
Temperature: 13°C

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 Pred. Date: March 2016

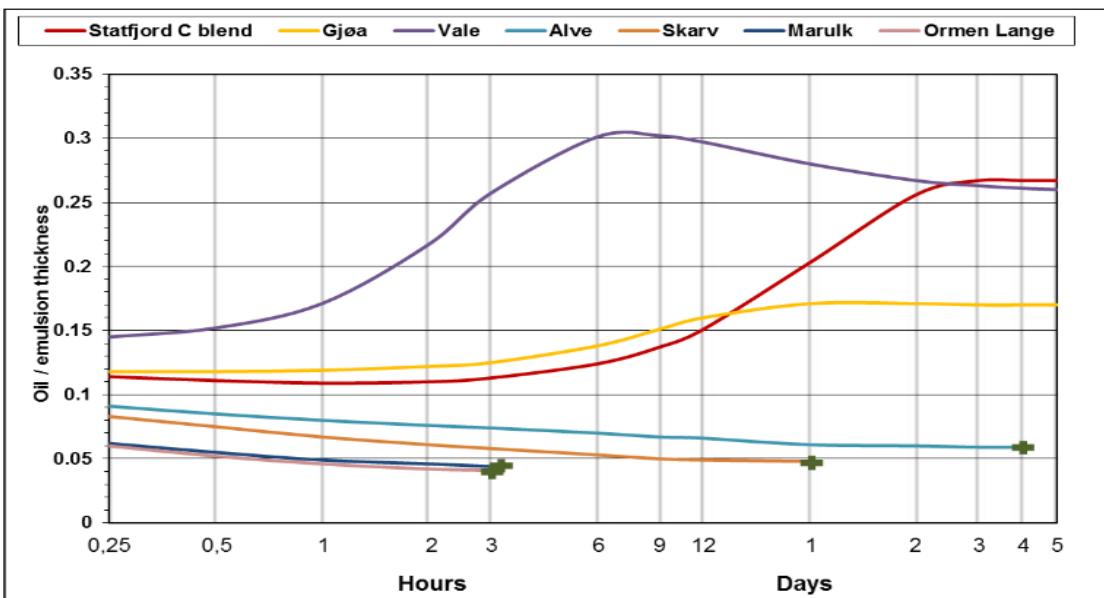


Figure 6-9 OWM predictions –oil/emulsion film thickness for test oils at 13 °C with 2 and 5 m/s wind speed. The dots in the figure illustrate when no oil are predicted on the surface.

The effect of film thickness on the relative evaporation rate was evaluated in an experiment using a stagnant open system (no physical exposure by wind or waves) with different oil film thicknesses within the range of 25-1000 μm (Gjøa) for 18 hours. Gas chromatographic (GC/FID) analysis at the end of the experimental period was used (combined with true boiling point curves) to calculate the time required to reach the 250 °C+

characteristics of the residues (i.e. time required to achieve the half height of the nC_{13} compound in the GC/FID chromatogram). The result is shown in Figure 6-11. This figure shows clearly that the initial film thickness is very important for the evaporation process to reach a specific evaporation degree. This will be of importance for condensates and light crude oils with high pour points, and when the residues solidifies, which will affect the potential for treatment of the residues.

The rheological characteristics of the oils varied over a wide range with type and weathering degree. The laboratory experiments were performed within defined area, which do not allow spreading of the oil residues after release. The spreading is dependent on if the oil residues having a yield stress or not, giving Newtonian or non-Newtonian behaviour, in addition to the gravity/friction forces (Leirvik, 2016). The lighter condensates (Atla, Ormen Lange and Marulk) as well as the light crude oil Gjøa (water-free) have no (or very low) yield stress for the standard evaporation degrees (150/200/250 °C), and could therefore be spread by gravity forces to form even thinner oil film thicknesses. For Gjøa, this process will however be affected by potential emulsion formation. For the other oils in this study, the possible spreading will be restricted by yield stress, which appears in an early phase after release to the sea surface by forming solidified oil films.

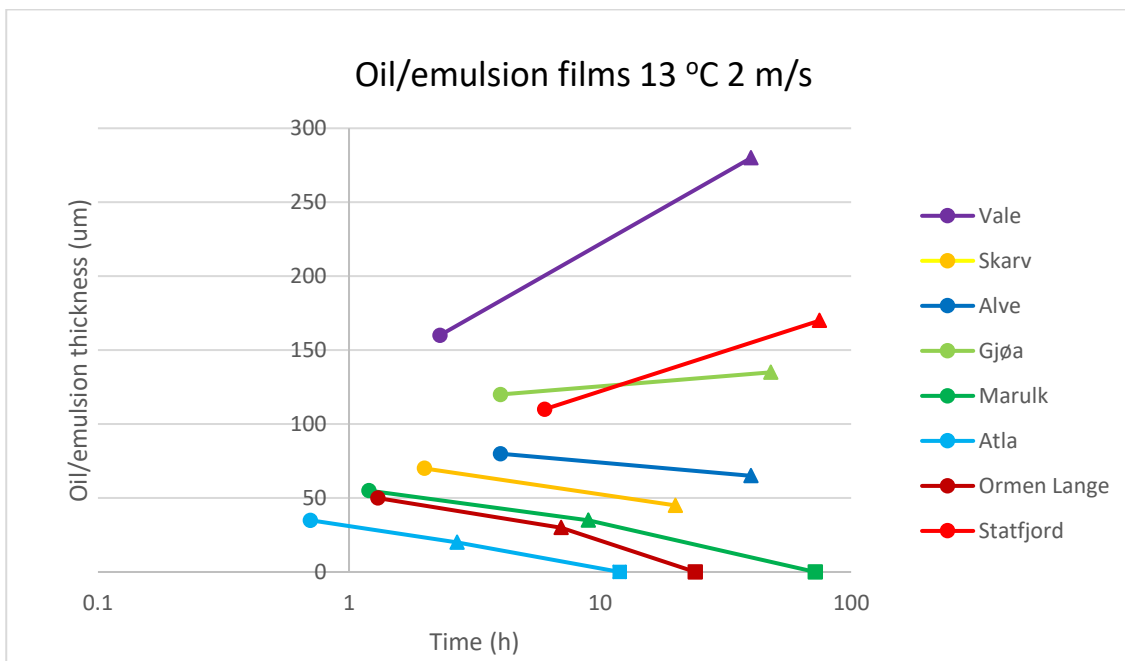


Figure 6-10A Oil film thickness for the 200°C+ (circles), 250°C+ (triangles) residue and time with no surface oil (squares) calculated from OWM (13 °C, 2 m/s wind)

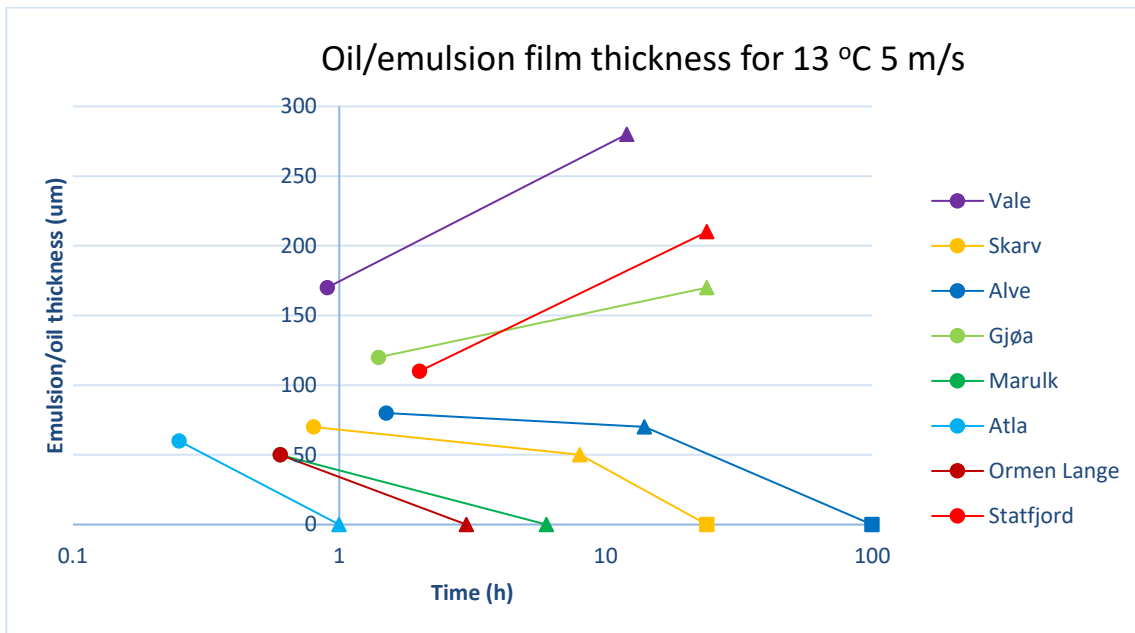


Figure 6-10B Oil film thickness for the 200°C+ (circles), 250°C+ (triangles) residue and time with no surface oil (squares) calculated from OWM (13 °C, 5 m/s wind)

However, the differences in residue film thickness affects the evaporation significantly. The time period required to obtain the 200°C+ and 250°C+ and its oil film thickness are calculated from the OWM predictions. These parameters are shown in Figure 6-10 for 2 (A) and 13 °C (B) at 5 m/s wind speed. These shows that the oils with high content of the lightest compounds (*i.e.* highest initial evaporation Atla, Ormen Lange and Marulk) reaches the 200 and 250 °C+ characteristics much earlier due to the reduction in residue thickness.

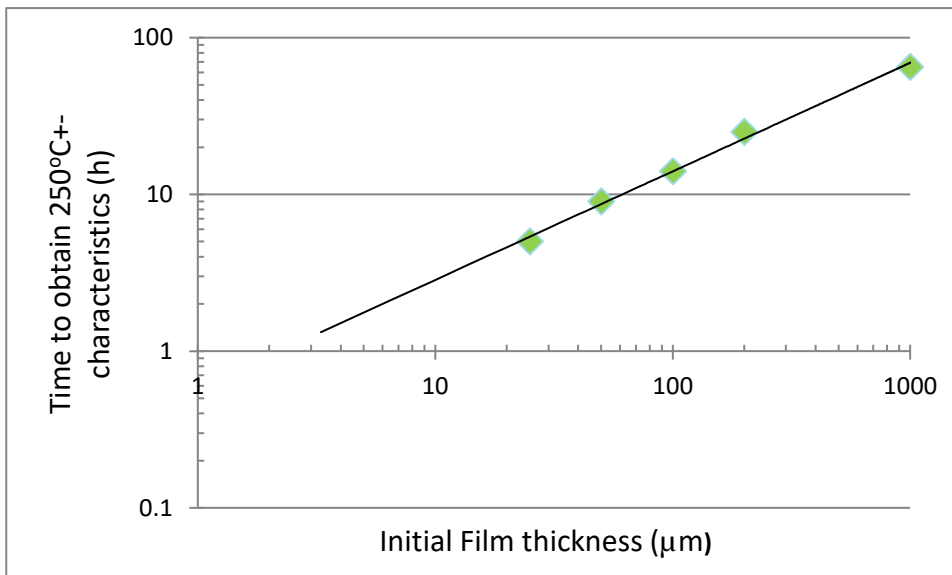


Figure 6-11 Estimated time for evaporation of Gjøa required to achieve a corresponding 250°C+ residue (*i.e.* half nC₁₃) in a stagnant (no wind and wave exposure) open system with no physical exposure and different initial oil film thickness.

6.2.7 Natural dispersion/entrainment

Evaporation and natural dispersion/entrainment are the most important processes for the removal of oil/emulsion from the sea surface. The natural dispersion/entrainment process is very dependent on the wave energy. The effect of waves is very dependent on the physical properties of the oil film residue, both for formation and stability of the droplets. This is also crucial for the droplet size formation that is very important for the buoyancy of the droplets and potential time for resurfacing.

The results from the OWM predictions are given in Figure for the 13 °C scenario with 2 and 5 m/s wind speeds. Under very calm conditions (2 m/s) the degree of entrainment is very low (< 10 %) even for the lightest condensates Atla, Ormen Lange and Marulk with during the first day of prediction. Under the laboratory experiments, the wind speed was estimated to be about 1-2 m/s, and confirms the prediction as no entrainment was observed during the experimental period in the MNS and Flume.

At higher wind speed (5 m/s) this process will be quantitative more important as the OWM predictions shows in (Figure). Some entrainment will occur for the lightest condensates (Atla, Ormen Lange and Marulk) from the beginning of the prediction and reaches a maximum of 25 vol. % when no more oil is present on sea surface after 3-6 hours. For the other oils the initial entrainment are slower but reaches 10 % within 6-15 hours, and reach a maximum of 30-50 % after 1-4 days.

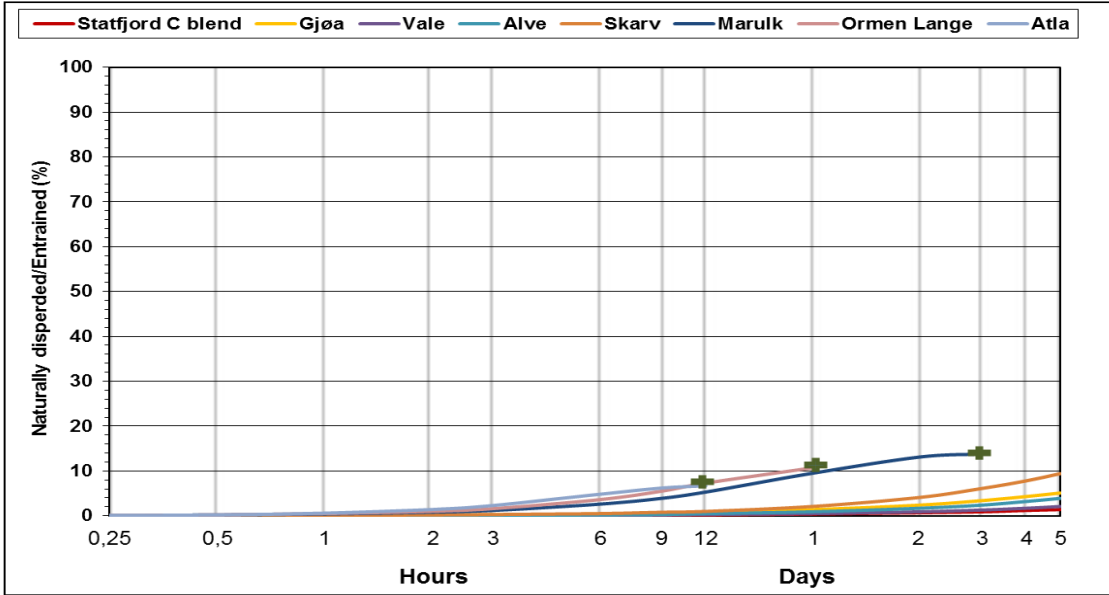
At the lower test temperature (2 °C, in Appendix B) the results from the simulation follow the same trend as with 13 °C for both wind speeds, but the time window for entrainment is further delayed.

In the closed system experiments, a series of experiments was performed to document the observation of droplet formation from 200 µm films of the 200 and 250 °C+ residues with use of increased tilting frequency (experimental settings). The tilting frequency was subsequently increased for every 30 minutes and the droplet formation was documented visually and with used of photo/video observations from the side of the glass wall. Droplets was formed at varying tilting frequencies for the different oil types and residues (200 and 250°C+), and test temperatures (2 and 13 °C). The first observed droplet formation is presented as the tilting frequency as a function of pour points and viscosities showed in Figure 6- and Figure 6-, respectively. It should be emphasised that the experimental settings from this study cannot directly be related to specific sea state conditions. Residues with high pour points and viscosities (Vale Skarv, Alve and Staffjord C Blend) require higher degree of energy to form oil droplets, compared with residues of oils with low pour points and viscosities (Gjøa, Atla and Marulk). In general, residues with pour points that is 10-15 degrees higher than the sea temperature expect to form a solidified lattice wax structure.

At the end of the experimental period in the open systems (MNS and Flume), the energy input was increased stepwise to breaking wave conditions for a period of 30 minute to simulate the fate of the residue oil film with increased exposure. This was observed visually and documented with photos and videos. In general – the residues behaved very different as illustrated and summarized in Table 6-4 for the MNS experiments. The condensates with low pour points (Atla, Ormen Lange and Marulk, as well as the light oil Gjøa) was easily dispersed into the water phase as small oil droplets, and would be diluted as such in the water column during this process. The other oils (Alve, Vale, Skarv, and reference crude Staffjord C Blend) have high pour points that easily solidifies on the water surface. Initially they formed larger oil lumps, but applied breaking wave gave very different behaviour. Vale remained as one solidified lump, Staffjord C Blend was broken into a number of larger lumps, whereas Skarv was broken into smaller flake particles, and Alve as smaller solidified droplets/particles. The reason for these observations is not possible to explain with the current available data, but could be due to differences in chemical composition of the waxy fractions and its physical properties of the wax fraction.

Property: Entrained /naturally dispersed oil
 Wind speed: 2 m/s
 Temperature: 13°C

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 Pred. Date: March 2016



Property: Entrained /naturally dispersed oil
 Wind speed: 5 m/s
 Temperature: 13°C

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 Pred. Date: March 2016

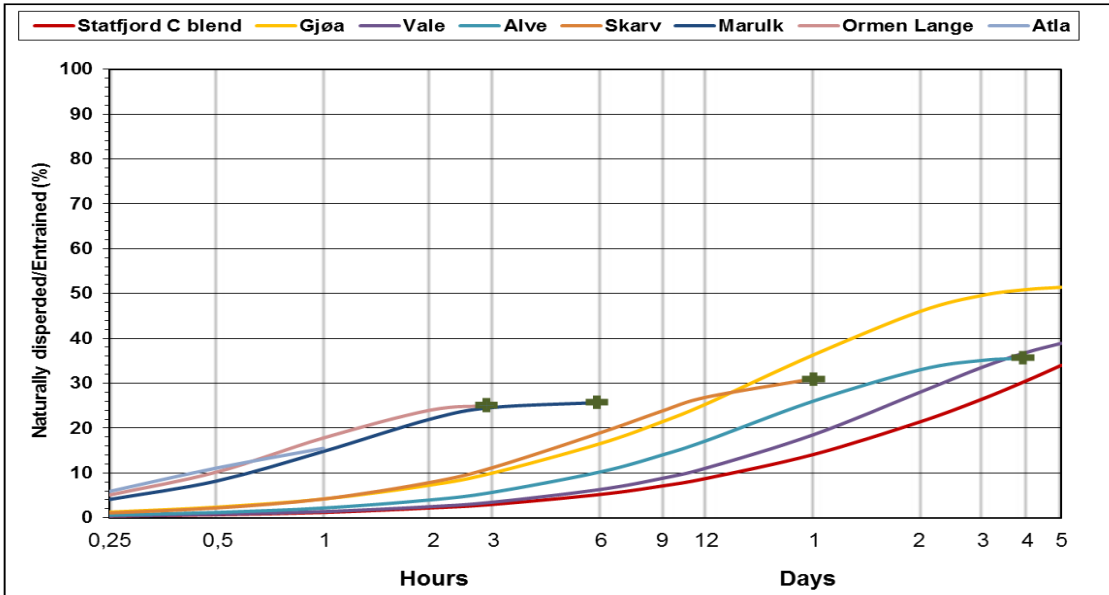


Figure 6-12 OWM predictions– Natural entrainment/dispersion for test oils at 13 °C and 2 and 5 m/s wind.

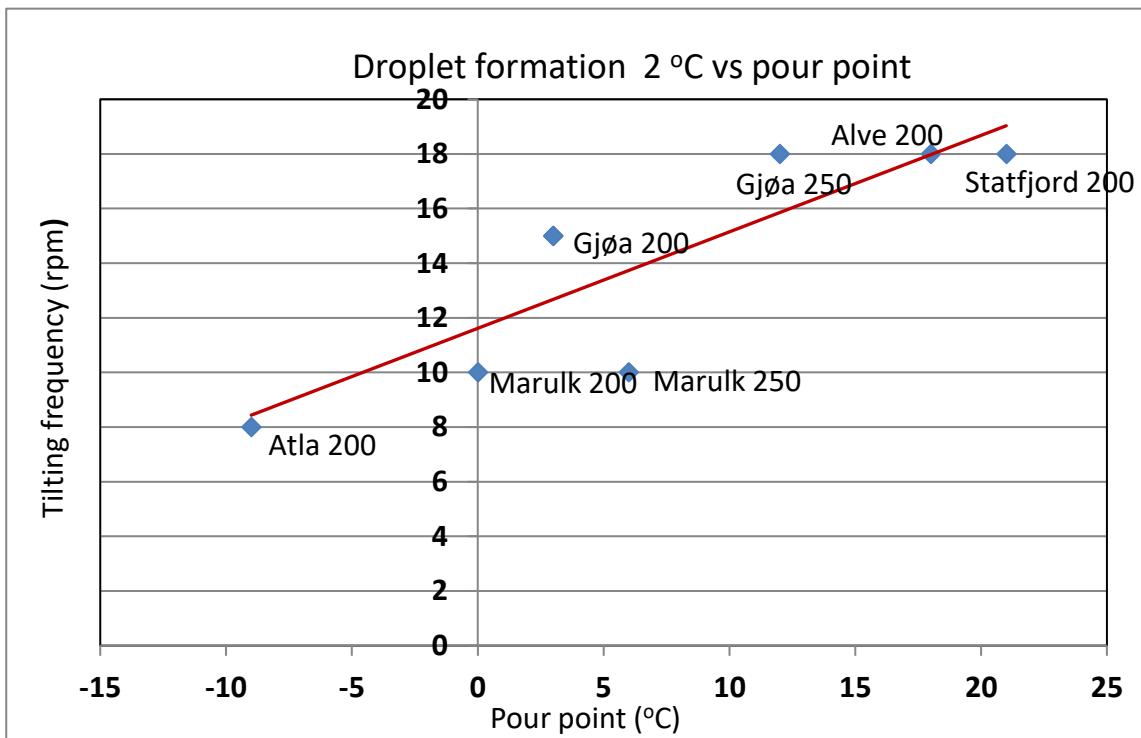
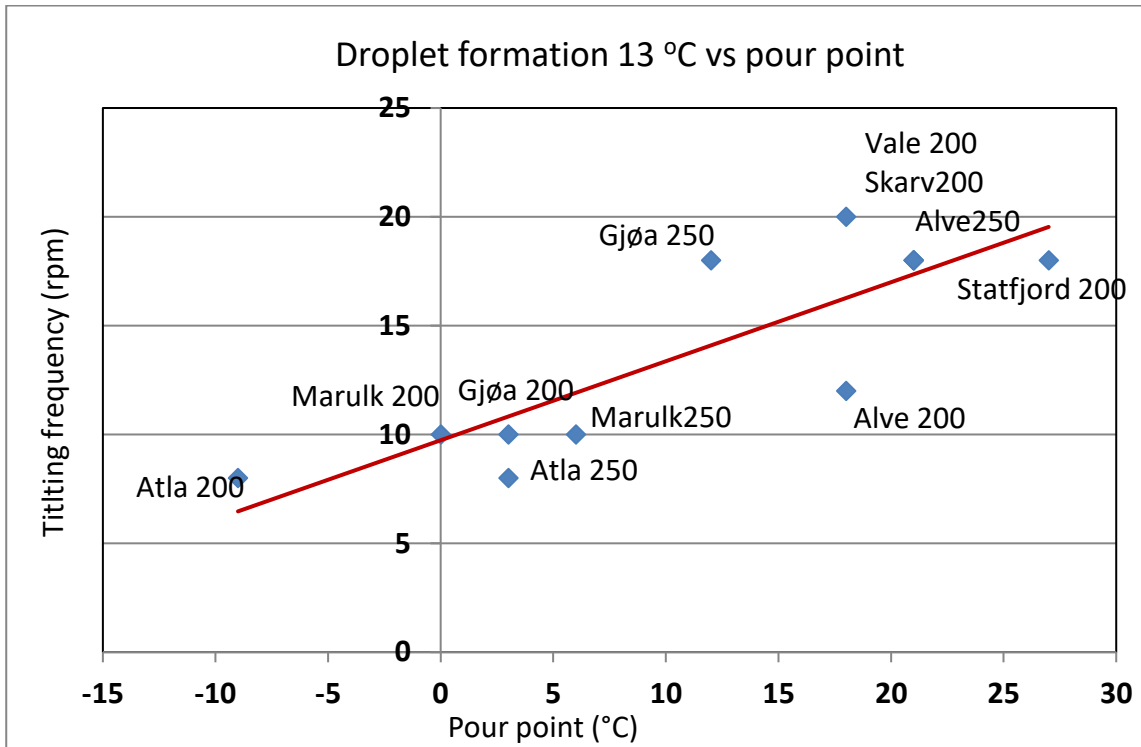


Figure 6-13 Tilting frequency (energy) required for the observation of first droplets in the closed experimental system for 200 and 250°C+ residues versus pour point at 2 and 13 °C.

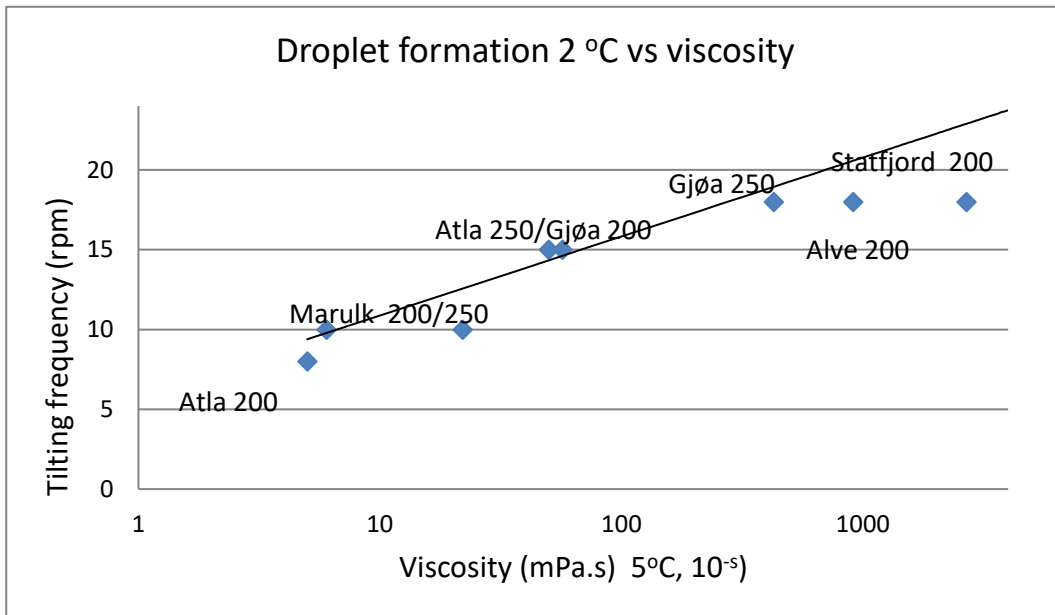
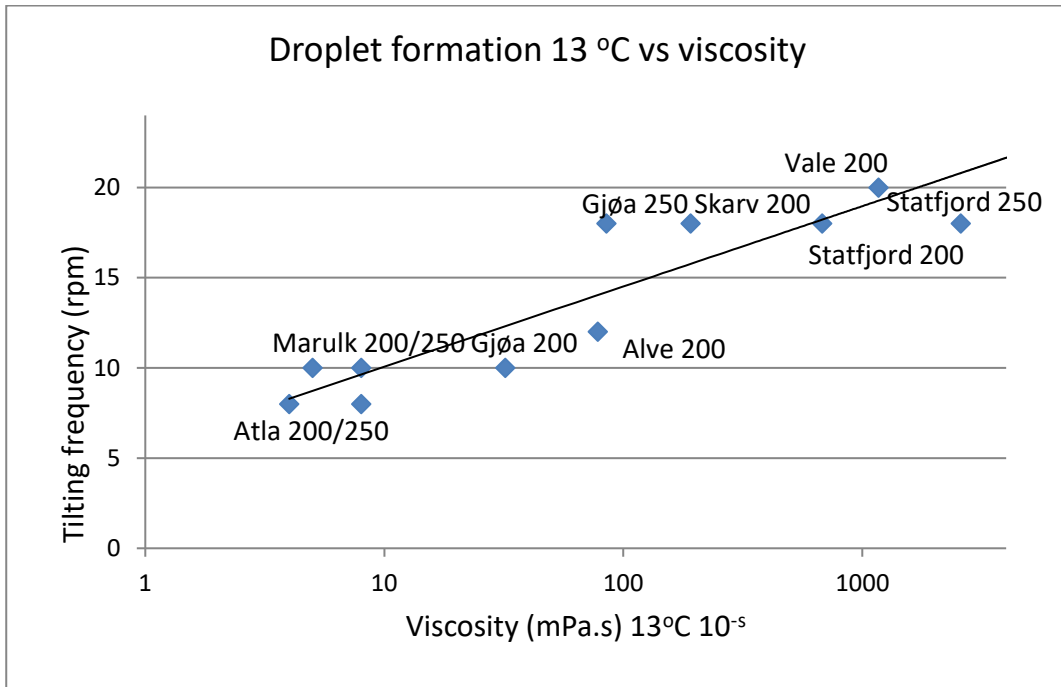





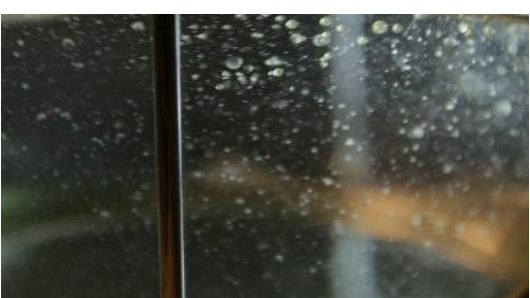


Figure 6-14 Tilting frequency (energy) required for the observation of first droplets in closed experimental system for 200 and 250°C+ residues versus viscosity.

Table 6-4 Behaviour of oil film residue with breaking wave conditions in the MNS system, after 18 hours weathering at calm condition

	<p>Gjøa – droplet generation</p>
	<p>Marulk, Atla and Ormen Lange – small oil droplets</p>
	<p>Vale – generation of one large lump</p>
	<p>Alve – solidified (apparent) film broke up and formed solidified droplets</p>
	<p>Statfjord C Blend (reference crude oil) – Initial generation of one large lump , which was broken up into smaller but still relative large droplets</p>
	<p>Skarv – solidified surface film was broken up into "flakes" (not droplets) of solidified oil</p>

6.3 Summary

Condensates and light crude oils are normally characterized by a high portion of light compounds. The light compounds will evaporate rapidly when spilled to the marine environment. These oils could generate thin oil films under calm conditions (non-breaking waves). The behaviour and weathering of such thin oil films and characterization of surface residue have been studied and compared in laboratory experiments and prediction using the SINTEF Oil Weathering Model (OWM) for eight different and representative oils from the Norwegian petroleum sector.

The condensates and light crude oils contain very large (40-80%) portion of semi-volatile/volatile compounds (boiling point < 200 °C). These light compounds will evaporate at a high rate in the initial phase after release less than a 1 hour. The composition and the physical properties of the evaporated residue varies over a wide range. The experimental studies and OWM predictions have shown that further fate and behaviour at sea surface will depend on the chemical composition of the weathered residues and thereby their physical properties.

The results and observations from the laboratory studies and the OWM predictions could divide the oils used in this project into three main groups, as followed:

Atla, Ormen Lange and Marulk residues have a low density, low wax and asphaltene content, and will not generate water-in-oil (w/o) emulsions. They have a low pour point with no yield stress, and can therefore undergo further spreading at the sea surface. These oils will have a rapid evaporation and the oil films of these residues will easily be dispersed/entrained into the water column by (increasing) wave exposure.

Alve and Skarv residues have high wax content. They have a yield stress, which will restrict spreading at the sea surface. The evaporated residues have a high pour point that may result in solidification. The residues do not take up water for emulsion formation. The fate of the solidified oil film is dependent on the environmental conditions. Under calm condition, the evaporation will probably be slowed down due to the solidification, and spreading of the oil may be restricted. The solidified film could be accumulated in *e.g.* windrows. Under increasing wave exposure, the solidified residues will be entrained into the water column as solidified lumps or large droplet/"flakes".

Gjøa and Vale are representatives for oils that have potential for water uptake and emulsion formation, as shown in the standard weathering studies. The water uptake is however dependent on the oil film thickness and wave energy exposure. The emulsion generated had a high water content with limited stability. In the laboratory studies performed in this project, with very calm condition, no water uptake with these residues was observed. Gjøa and Vale are, however, different with respect to chemical composition and physical properties. The properties of Vale residues are also similar to Alve and Skarv residues with high wax content and a high pour point and may be solidified under calm conditions.

Use of current operational oil spill response techniques and strategies (*i.e.* mechanical recovery and use of chemical dispersants) may have limitations for oil spills from condensates and light crude oils. This is due to the low oil film thicknesses that can be encountered dependent on the properties of the oils. Also discharge (*e.g.* sub-sea versus surface spills), oceanographic and weather conditions may play an important role. Observations from laboratory studies show that properties of the oil residues changes very rapidly due to the high evaporation rate. The efficacy for clean-up using mechanical and dispersion methods will also vary significantly due to the differences in the physical properties of the weathered residues of condensates and light crude oils.

The lifetime of an oil spill from condensates and light crude oils with low viscosity and low pour point, showing no or low yield stress when spilled to the sea surface, will in general be short. The yield stress is defined as the stress that must be applied to an oil /emulsion to make it begin to flow. Under most scenarios, it may be difficult to perform any clean-up operations by use of mechanical recovery or dispersants. However, in case of a response operation quick response close to the source is expected to be important. From this study Ormen Lange, Atla and Marulk are examples of oils that may fall under this category.

Residues from condensates and light crude oils with high pour point may have a significant lifetime at sea surface under calm conditions, as solidified residues. These oil residues could be recovered by mechanical methods, although the efficacy will probably be low due to a scattered surface distribution. Chemical dispersants normally show low efficacy on solidified oils, and used on residues from such oils the operations should be performed in an early phase before the oil film is solidified. Alve and Skarv is an example of condensates with high pour point studied in this project.

Some light crude oils are able to generate water-in-oil (w/o) emulsions with varying stability. Water uptake will increase the film thickness and generate surface emulsion, which makes use of mechanical response strategies possible. Use of chemical dispersants could also have a wider time window for the emulsified oils. GjØa and Vale may have a tendency to form w/o emulsion after an oil spill, especially at increased wind speed (> 5 m/s). However, at low wind speed forming low oil film thicknesses they may not form w/o-emulsions or form very unstable emulsion, which makes use of current operational oil spill response more challenging.

The effectiveness of different response strategies for oils creating thin oil films in a spill situation are not well documented. Based on further testing in this project we will evaluate the possibility to use seawater flushing or low-dosage dispersant treatment as a response method for thin oil films. This will be further evaluated and discussed in "Project Recommendation for response to oil spills from condensates and light crude oils" (Singsaas *et al.*, 2017).

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8 Appendices

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A Physicochemical properties of oils


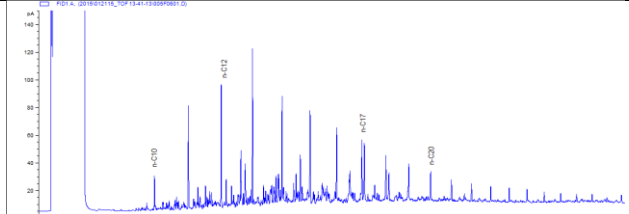

Physical properties of condensates and light oils used in the project from standard weathering studies


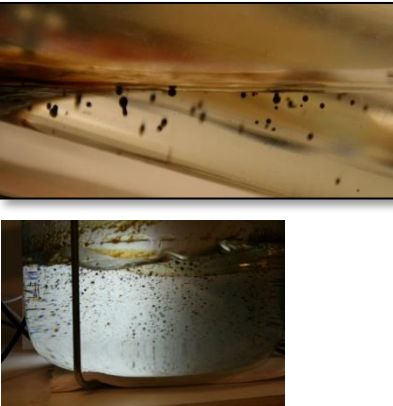
Oil type	Residue	Evap. (vol.%)	Residue (wt.%)	Density (g/mL)	Pour point (°C)	Viscosity, 10 s ⁻¹ (mPa.s)		Asphaltenes (hard) (wt.%)	Wax (wt.%)	Yield stress (Pa)	
						13°C	5°C			13°C	5°C
Vale	Fresh	0	100	0.816	-9	37	170	0.03	3.3	1.2	0.4
	150°C+	27	77	0.851	6	190	1200	0.04	4.3	0.5	2.9
	200°C+	40	64	0.866	18	1200	4100	0.05	5.1	3.1	6.6
	250°C+	53	51	0.879	27	5100	15000	0.06	6.4	22	40
Skarv	Fresh	0	100	0.829	6	6	98	0.01	2.2	N.D	1.8
	150°C+	31	71	0.857	15	47	200	0.02	3.1	1.8	2.8
	200°C+	55	48	0.882	21	190	600	0.03	4.5	2.8	1.8
	250°C+	69	33	0.897	27	630	4400	0.04	6.6	1.8	13
Alve	Fresh	0	100	0.796	0		12	0.03	5.0	N.D	N.D
	150°C+	37	62	0.837	12	9	770	0.05	7.8	N.D	1.8
	200°C+	51	51	0.849	18	78	910	0.06	9.8	0.8	1.8
	250°C+	61	40	0.859	21		2100	0.08	12.5	0.3	0.9
Gjøa	Fresh	0	100	0.836	<-36	5	4	0.03	1.5	N.D	N.D
	150°C+	25	78	0.866	-24	14	25	0.03	1.9	N.D	N.D
	200°C+	37	66	0.880	3	34	57	0.04	2.2	N.D	N.D
	250°C+	48	56	0.892	12	98	430	0.05	2.6	N.D	0.1
Marulk	Fresh	0	100	0.759	<-36	1	1	0.00	0.00	N.D	N.D
	150°C+	53	50	0.811	-12	3	4	0.01	0.01	N.D	N.D
	200°C+	69	34	0.829	0	5	6	0.01	0.01	N.D	0.3
	250°C+	80	22	0.842	6	9	22	0.02	0.02	N.D	0.3
Atla	Fresh	0	100	0.746	-36	1	-	0.02	0.51	N.D	N.D
	150°C+	62	41	0.809	-24	2	2	0.04	1.24	N.D	N.D
	200°C+	78	25	0.826	-9	4	5	0.07	2.05	N.D	N.D
	250°C+	88	14	0.842	3	8	50	0.12	3.71	N.D	N.D
Ormen	Fresh	0	100	0.750	-33	1	NA	<0.01	<0.01	N.A	N.A
	150°C+	53.5	49.5	0.795	-12	2	NA	0.01	<0.01	N.A	N.A
	200°C+	69.5	32.8	0.809	-12	3	NA	0.01	<0.01	N.A	N.A
	250°C+	81.5	18.4	0.820	-6	5	NA	0.02	<0.01	N.A	N.A
Statfjord C Blend	Fresh	0	100	0.834	-9	12	60	0.16	4.06	-	-
	150°C+	23	80	0.869	12	150	390	0.20	5.08	0.5	0.8
	200°C+	34	70	0.883	21	680	2700	0.23	5.80	1.2	3.0
	250°C+	44	60	0.897	27	2600	9600	0.27	6.80	5.4	26
Åsgaard	Fresh	0	100	0.780	-	1	-	-	-	0.2	-
	150°C+	50	55	0.845	6	16	-	-	-	0.3	-
	200°C+	63	41	0.866	15	132	-	-	-	14	-
	250°C+	72	32	0.883	24	707	-	-	-	3	-

B Observations and findings from closed and open experimental systems and OWM predictions using thin film from condensates and light oils

B.1Gjøa

B.1.1 TOF findings and observations in laboratory experiments

Distribution	
	<p>The Gjøa oil spread to form a relative uniform oil film on the water surface (upper picture from MNS). The film remained uniform during the experimental period, but less pronounced in the Flume, due to larger variation in the energy exposure around the wave generator (lower picture).</p>
Evaporation	
	<p>The evaporation was quantified by GC/FID analysis of the surface film, and as quantitative measurements of oil residue and oil film thickness measurements.</p> <p>The evaporation after 18h was estimated to be 40% at 2 °C and 45% at 13 °C.</p>
Solidification	
	<p>No solidification was observed of the thin oil film in any of the experiments. This is in accordance with laboratory analysis. No yield stress at 5 and 13 °C for the 200°C+ and 250°C+ residues, and a pour point of 12°C for the 250°C+ residue.</p>
Emulsification	
	<p>In closed system experiments, there was a tendency to generate oil droplets in the oil phase. However, these droplets were relatively large and did not facilitate formation of stable oil-in-water emulsions. The water content in these loose emulsions could be very high.</p> <p>In open system experiments there were observed some water uptake after high exposure at the end of the experimental period, and more pronounced at 2 °C (59%) than at 13 °C (7%), but these emulsions were also unstable (relative short exposure time). The measured viscosities of these emulsions were in the same range as the water-free laboratory residues, which also indicating the unstable emulsions.</p>

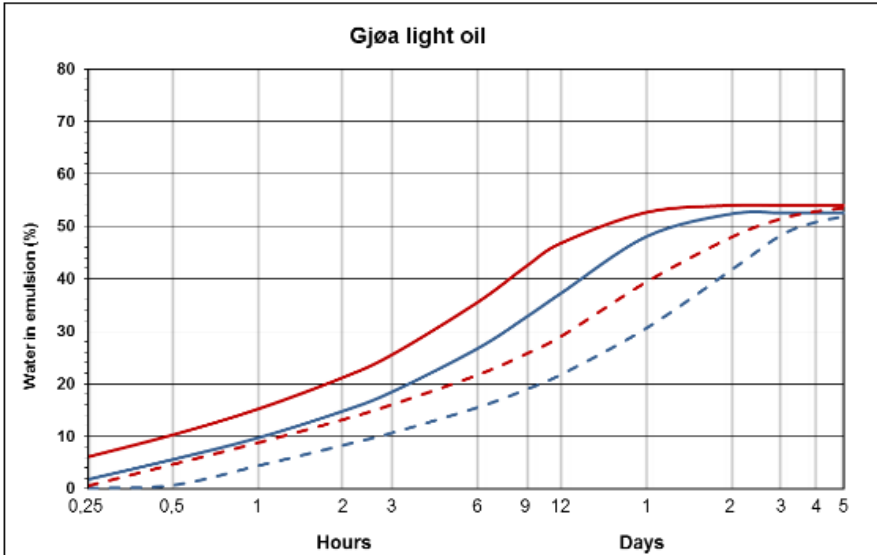
	<p>Stable emulsions were generated with the photooxidized oil residue from the closed systems with water content of 80% (13 °C) and 54% (2 °C) during 18 h exposure.</p>
<p>Dispersion</p>	
	<p>Gjøa generated oil droplets at both 2 °C and 13 °C in the closed systems for the 200°C+ and 250°C+ residues</p> <p>At the end of the experimental period in open systems, the energy exposure was increased to simulate breaking wave conditions. Oil droplets were generated at both temperatures. After termination of thigh exposure conditions, most oil resurfaced rapidly and formed a homogenous liquid film.</p>
<p>Response options</p>	
	<p>Dispersibility (FET): Good for 13 °C (Flume) Good/reduced for 2 °C (MNS)</p>
	<p>Absorption: Good at both 2 °C and 13 °C</p>

Property: Water content



-- 2°C, 2m/s
 — 2°C, 5m/s
 -- 13°C, 2m/s
 — 13°C, 5m/s

4.0 β © 2010
Pred. Date: March. 2016

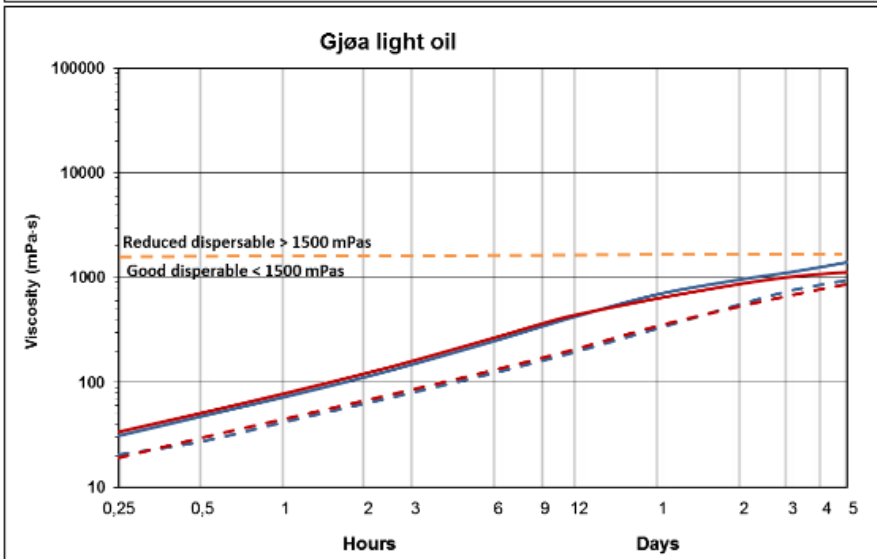


Property: Emulsion viscosity



-- 2°C, 2m/s
 — 2°C, 5m/s
 -- 13°C, 2m/s
 — 13°C, 5m/s

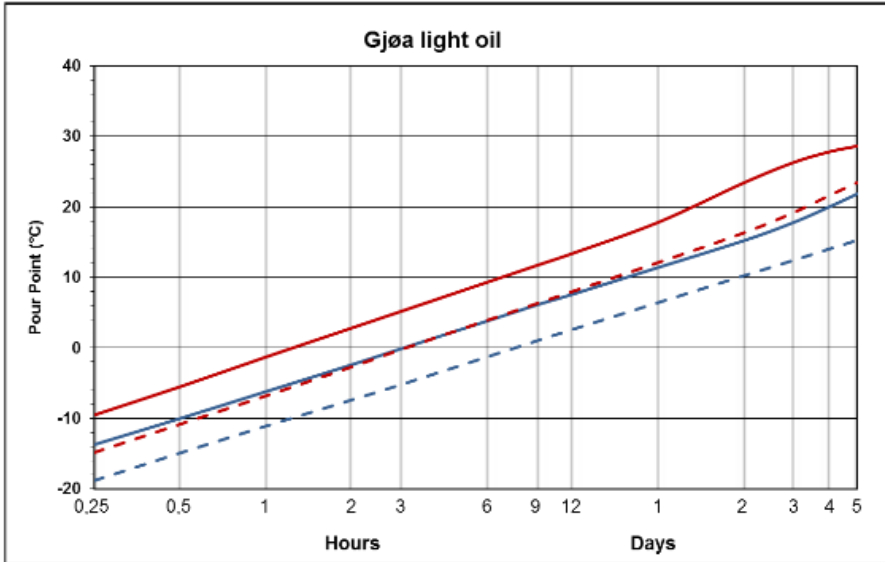
4.0 β © 2010
Pred. Date: March. 2016



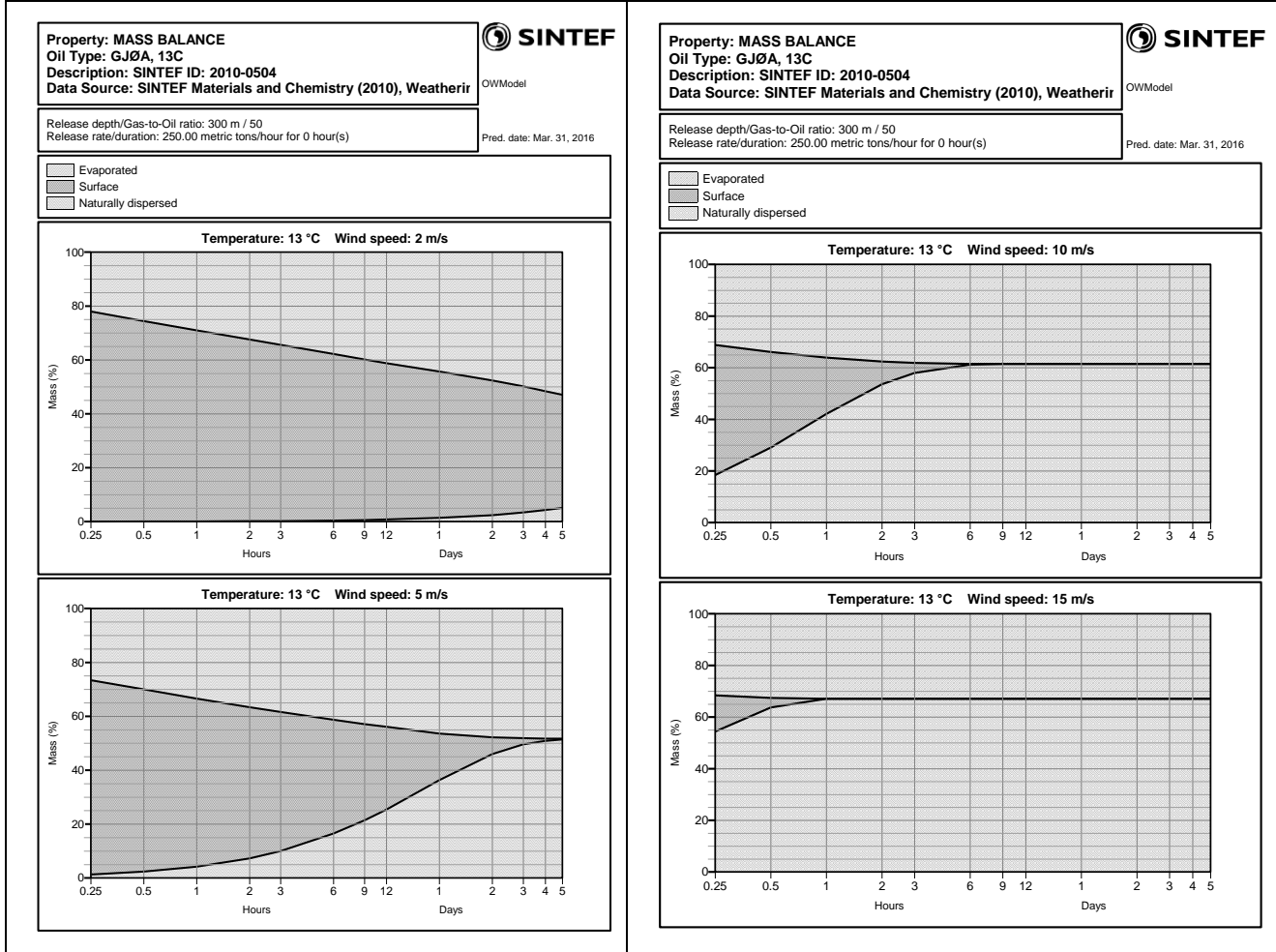
Property: Pour point

--- 2°C, 2m/s — 2°C, 5m/s - - - 13°C, 2m/s — 13°C, 5m/s

4.0 β © 2010
Pred. Date: March. 2016



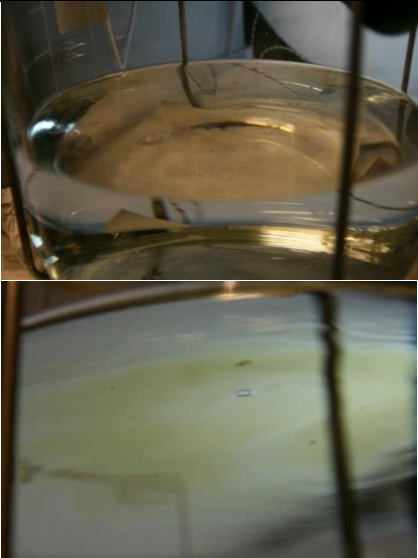
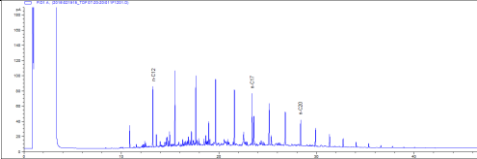
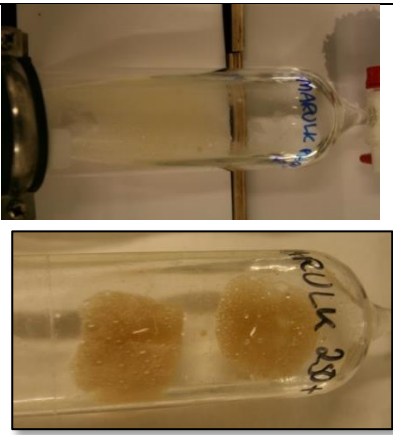
B.1.3 Predictions of mass balance for different wind speeds (2-5-10-15 m/s) at 13 °C

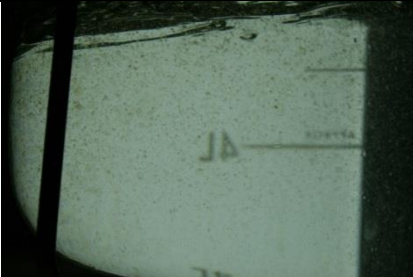


Predicted mass balance of Gjøa light oil at sea temperature of 13 °C.

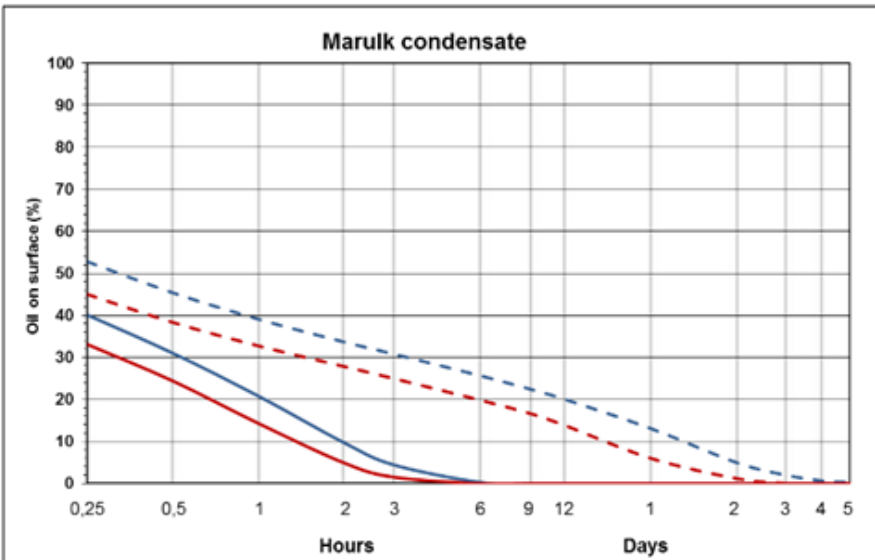
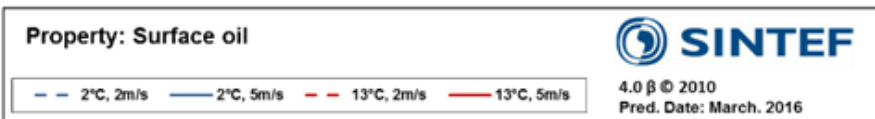
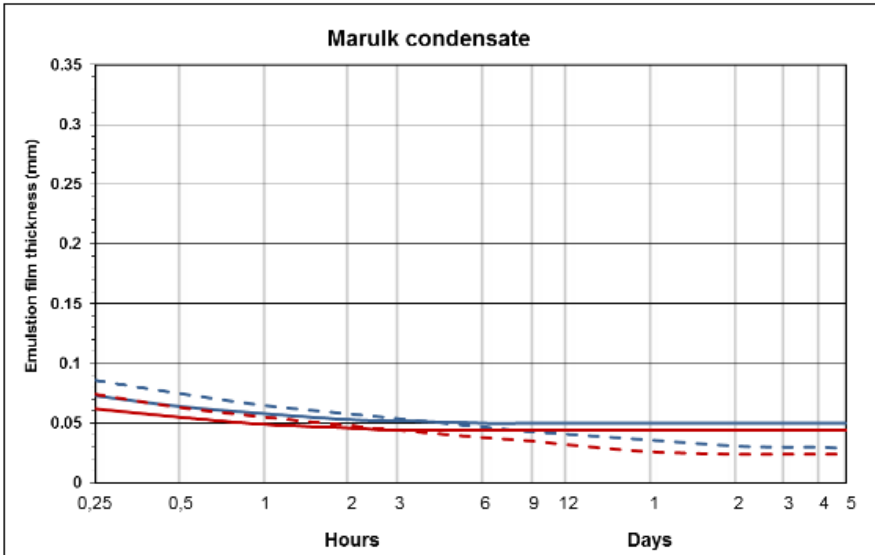
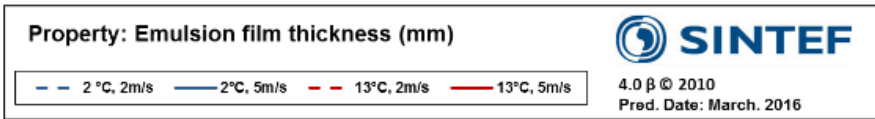
B.2 Marulk

B.2.1 TOF findings and observations in laboratory experiments

Distribution	
	<p>The Marulk condensate spread rapidly and formed a uniform film. This remained more or less unchanged during the experimental period in the MNS system at both temperatures. The 200°C+ and 250°C+ residues have a low yield stress at low temperature that could affect the spreading behaviour.</p> <p>At the end of the experiment the pictures indicate a minor variation in oil film thickness</p>
Evaporation	
	<p>The evaporation of the Marulk 200 µm iol film was in the order of 70% at 2 °C and 75% at 13 °C in the MNS over a period of 18 h.</p>
Solidification	
	<p>No solidification observed in MNS experiments. However, the distribution after 18h at 2 °C in MNS was not uniform indicating change in behaviour of the residue (pour point of 6 °C for the 250°C+ residue)</p>
Emulsification	
	<p>No water uptake or emulsification was observed with any of the experimental conditions, including the photooxidation residue and high energy input. This is in accordance with no/very low yield stress due to very low content of wax and asphaltenes.</p> <p>Foam" generation with Marulk 250°C+ at breaking wave condition (2 °C)</p>
Dispersion	

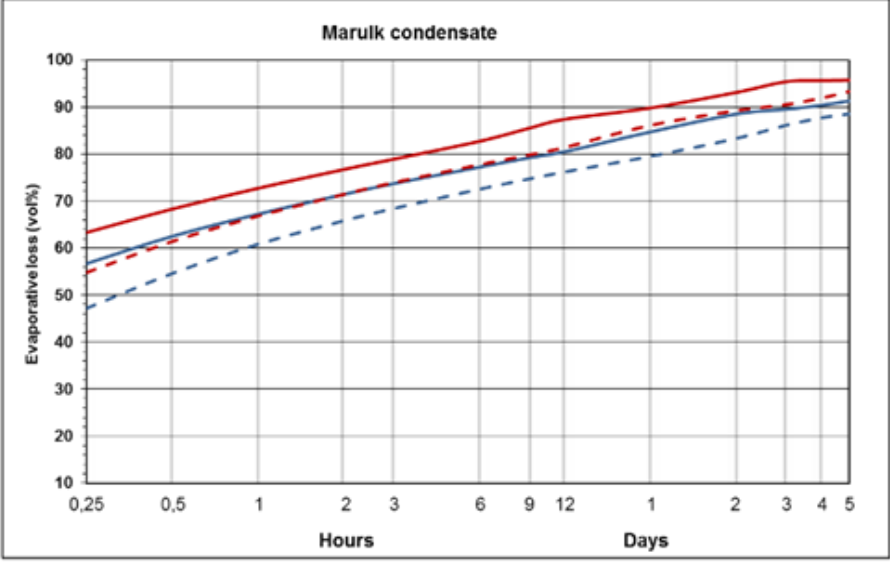
	<p>Droplets were easily generated in the closed system at low energy exposure for all combination of temperature and oil residues including the photooxidized residue. High-energy input at the end of the MNS experiments generated easily oil droplets, which resurfaced and generated a uniform surface oil film.</p>
Response options	
	Absorption: Good at both 2 °C and 13 °C
	Dispersibility; not tested

B.2.2 OWM Predictions (2 and 5 m/s and 2 and 13 °C)



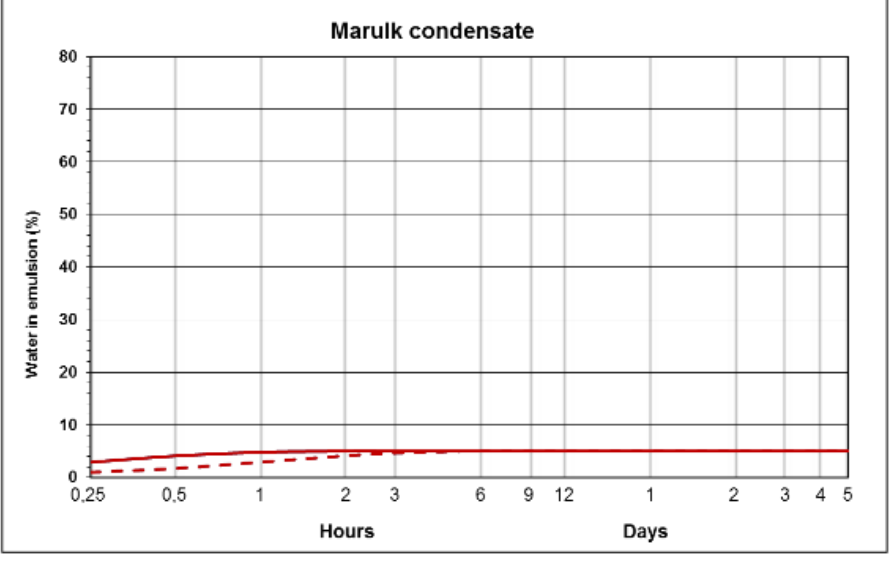
Property: Evaporative loss **SINTEF**

-- 2°C, 2m/s
 — 2°C, 5m/s
 -- 13°C, 2m/s
 — 13°C, 5m/s
 4.0 β © 2010
 Pred. Date: March 2016



Property: Water content **SINTEF**

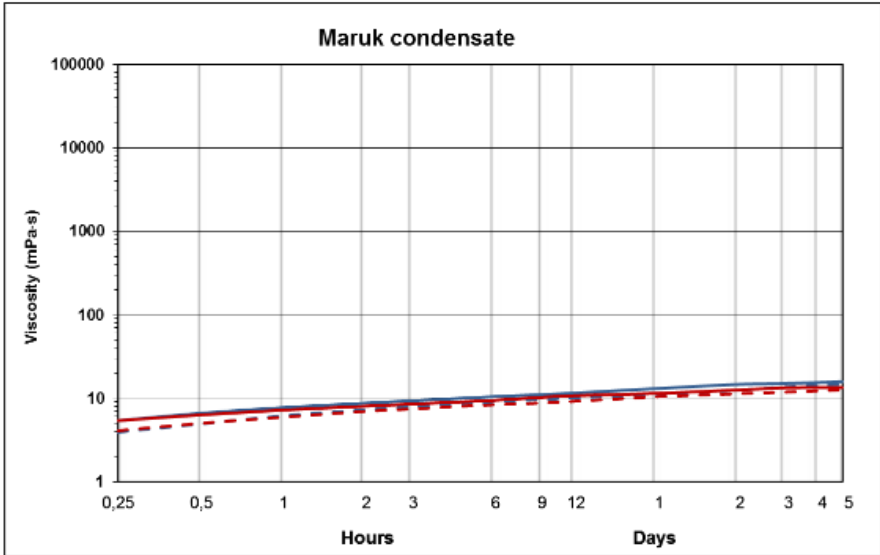
-- 2°C, 2m/s
 — 2°C, 5m/s
 -- 13°C, 2m/s
 — 13°C, 5m/s
 4.0 β © 2010
 Pred. Date: March. 2016



Property: Emulsion viscosity

--- 2°C, 2m/s
 — 2°C, 5m/s
 --- 13°C, 2m/s
 — 13°C, 5m/s

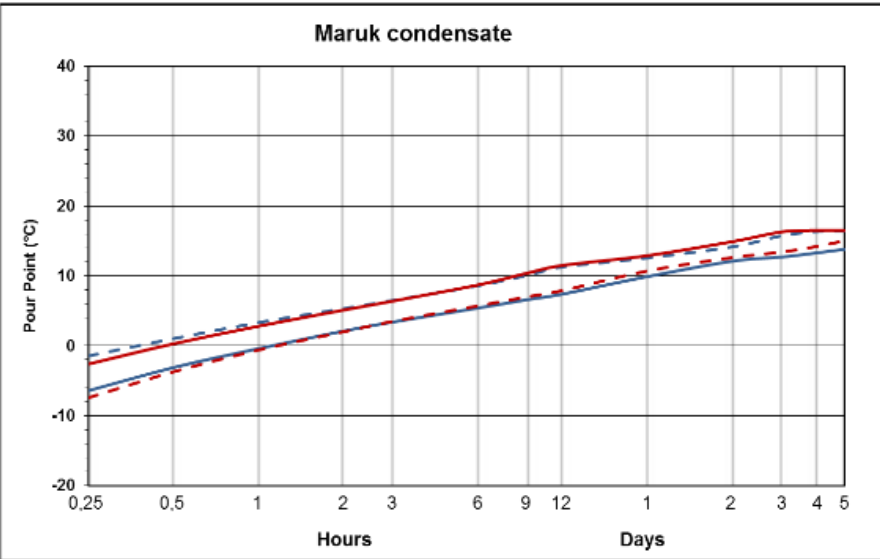
4.0 β © 2010
 Pred. Date: March. 2016



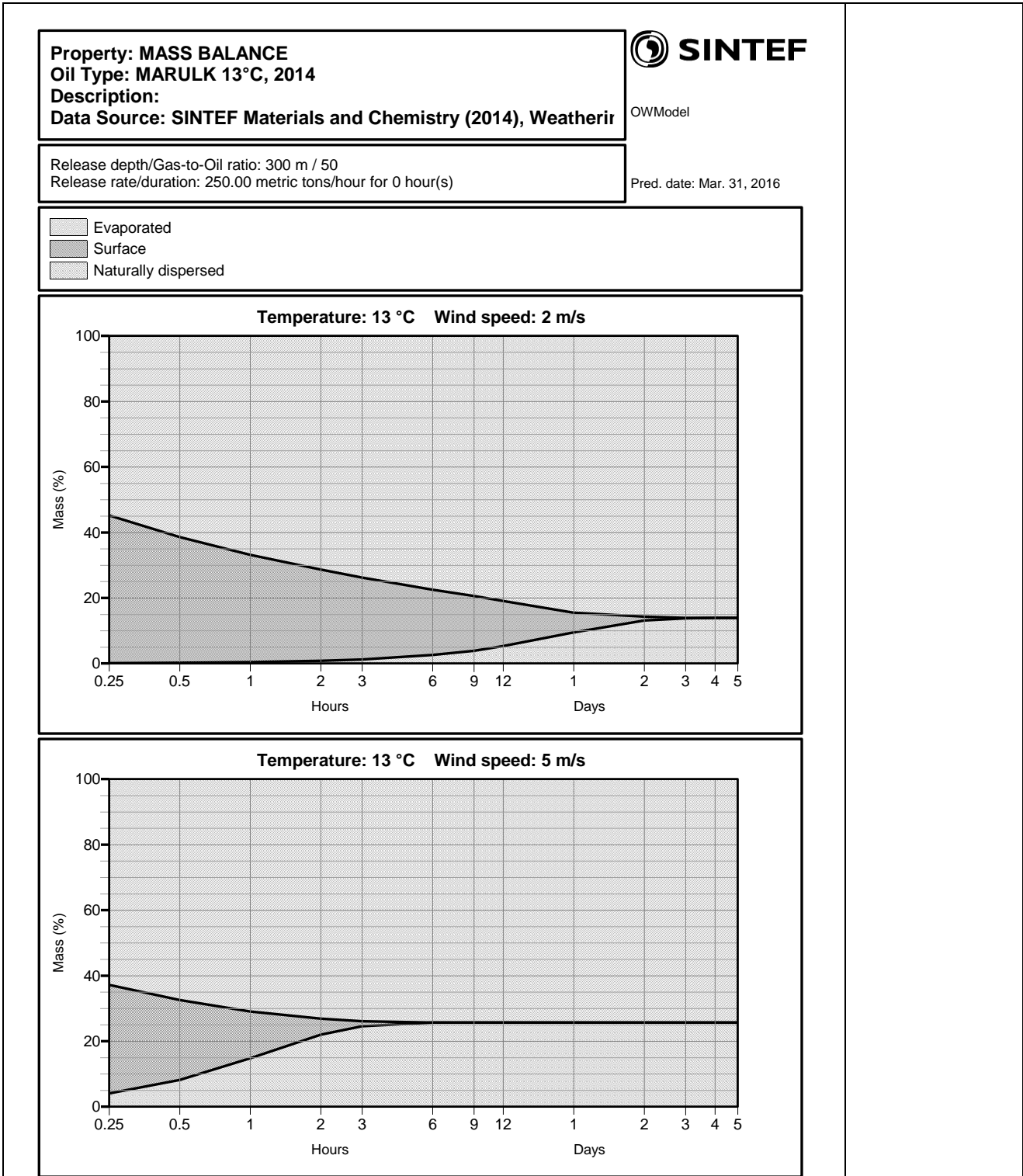
Property: Pour point

--- 2°C, 2m/s
 — 2°C, 5m/s
 --- 13°C, 2m/s
 — 13°C, 5m/s


4.0 β © 2010
 Pred. Date: March. 2016



B.2.3 Predictions of mass balance for different wind speeds at 13 °C



Predicted mass balance of Marulk condensate at sea temperature of 13°C.

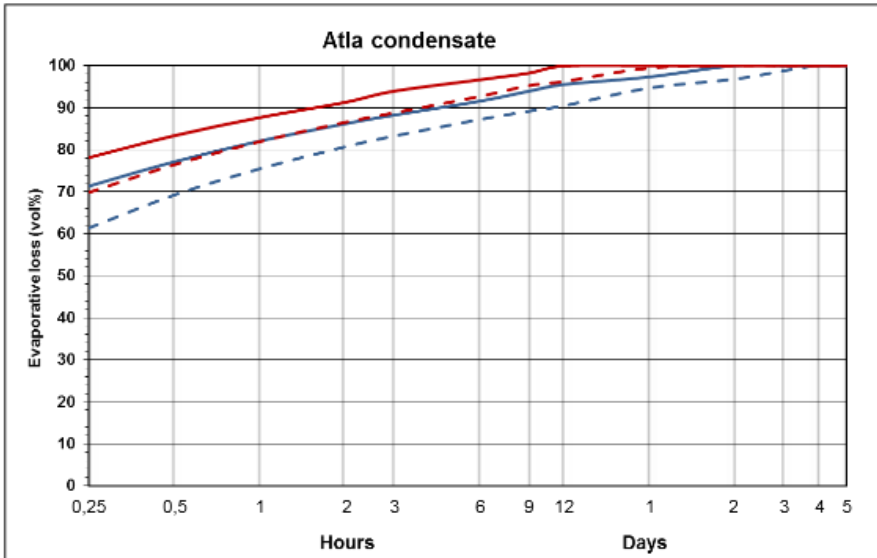
	<p>The Alta residues generated easily droplet during increasing exposure in MNS (pictures 13 °C and 2 °C respectively)</p>
<p>Response options</p>	
	<p>Adsorption: good</p>

Property: Evaporative loss



-- 2°C, 2m/s
 — 2°C, 5m/s
 -- 13°C, 2m/s
 — 13°C, 5m/s

4.0 β © 2010
Pred. Date: March 2016

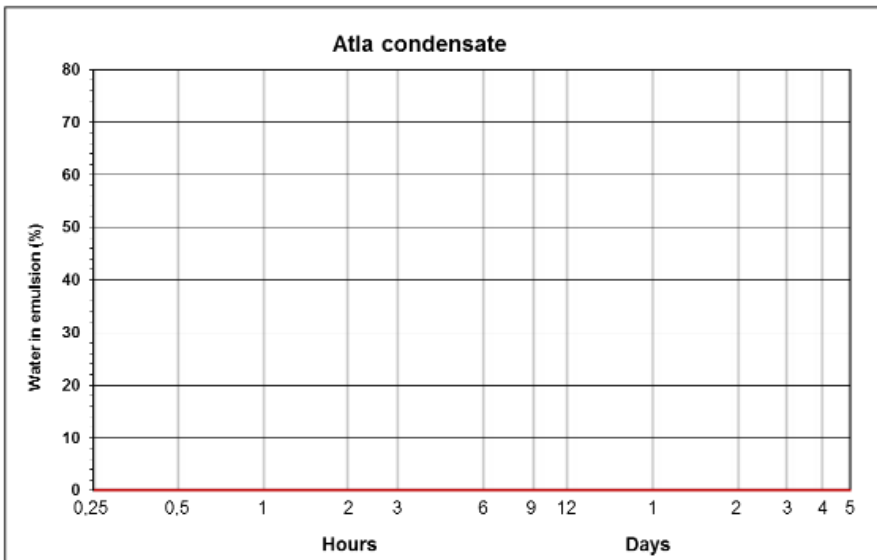



Property: Water content



-- 2°C, 2m/s
 — 2°C, 5m/s
 -- 13°C, 2m/s
 — 13°C, 5m/s

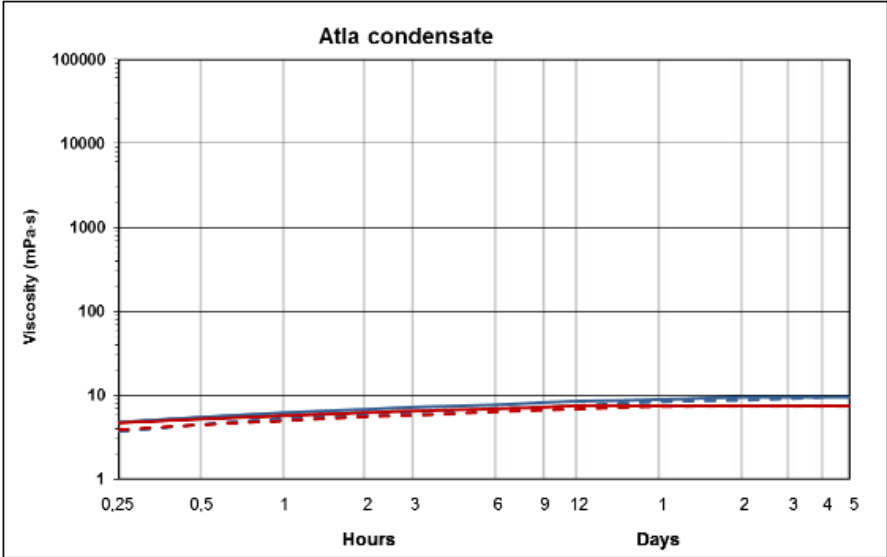
4.0 β © 2010
Pred. Date: March. 2016




Property: Emulsion viscosity  **SINTEF**

--- 2 m/s, 2°C
 — 5m/s, 2°C
 --- 2 m/s, 13°C
 — 5 m/s, 13°C

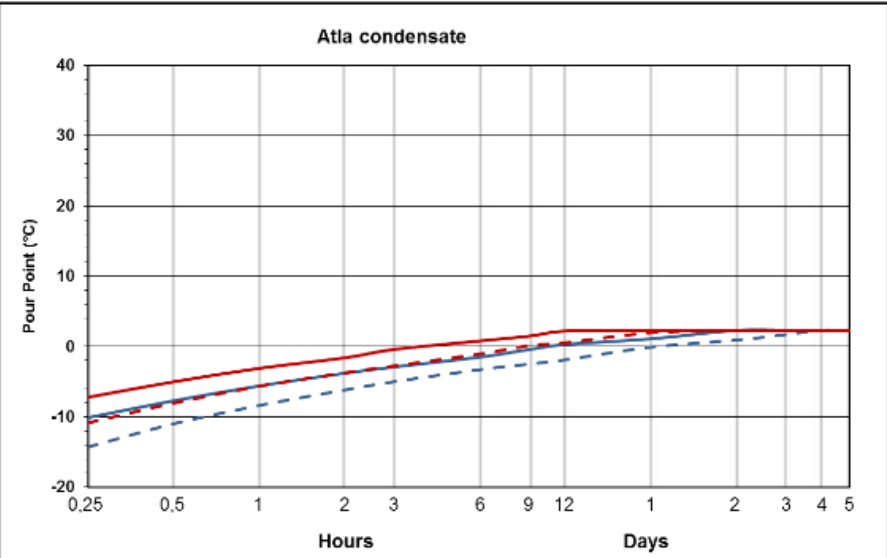
4.0 β © 2010
Pred. Date: March. 2016



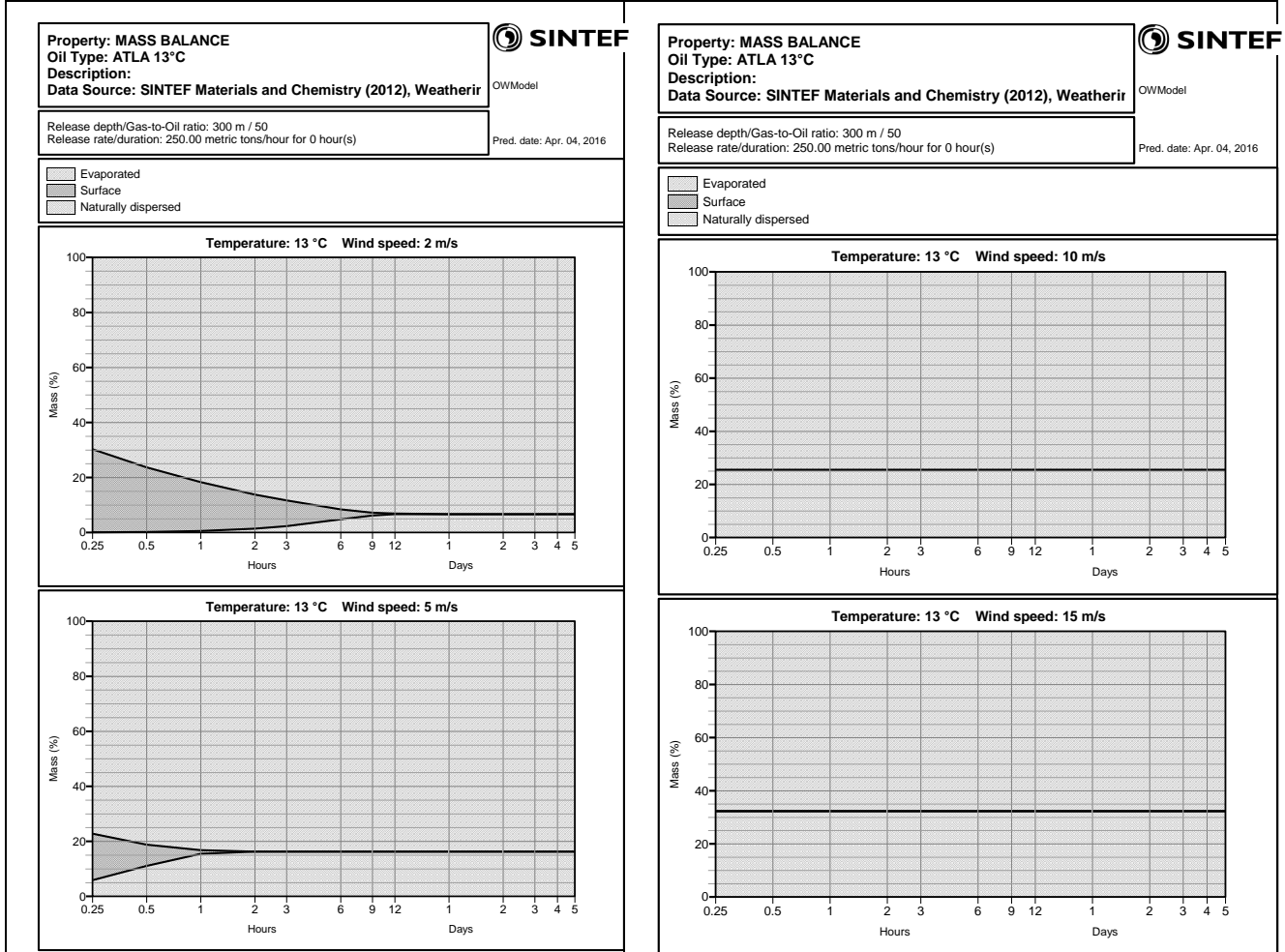
Property: Pour point  **SINTEF**

--- 2°C, 2m/s
 — 2°C, 5m/s
 --- 13°C, 2m/s
 — 13°C, 5m/s

4.0 β © 2010
Pred. Date: March. 2016



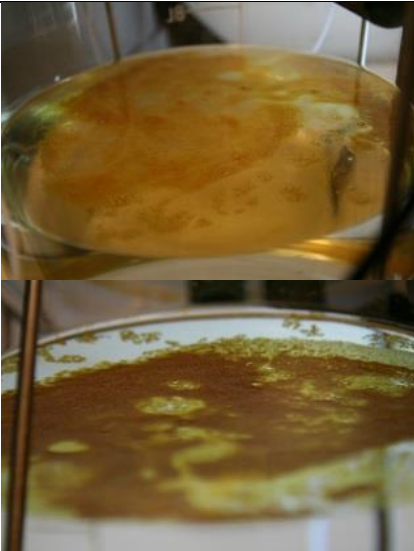
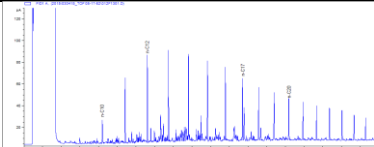
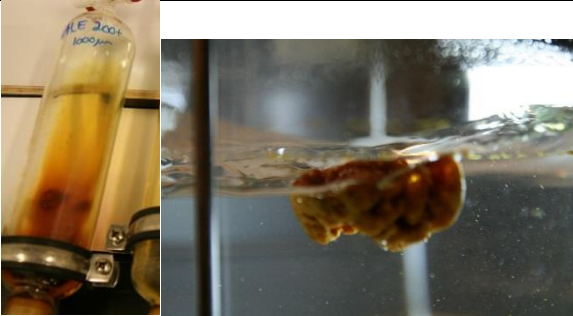
B.3.3 Predictions of mass balance for different wind speeds at 13 °C

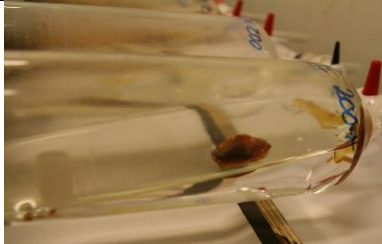


Predicted mass balance of Atla condensate at sea temperature of 13°C.

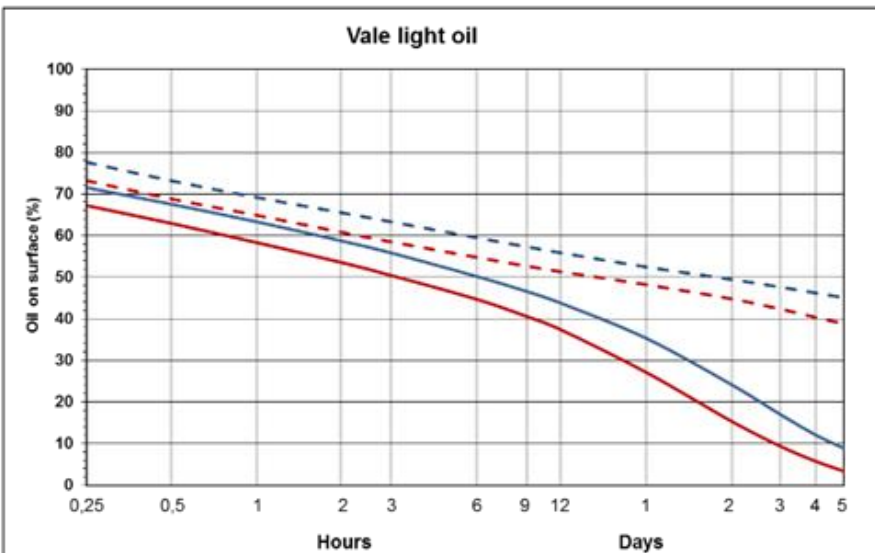
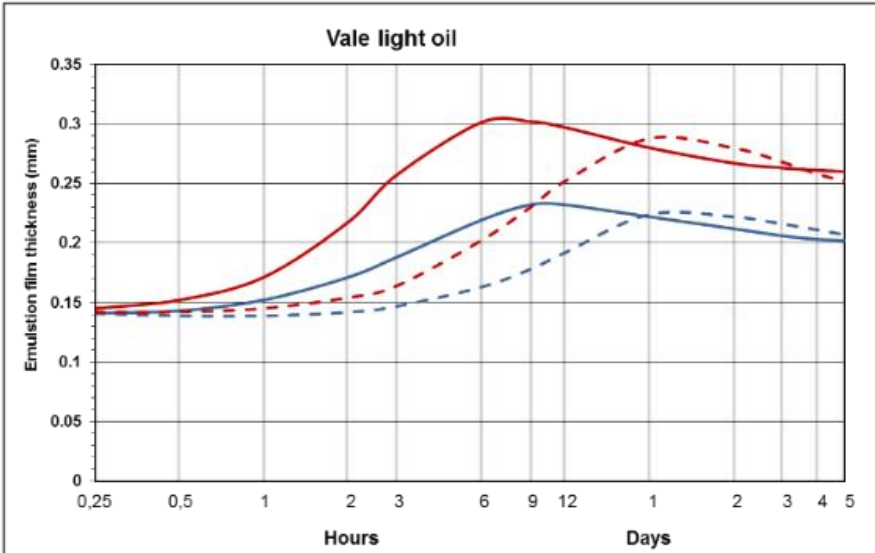
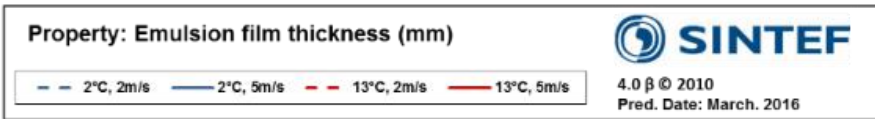
B.4Vale

B.4.1 TOF findings and observations in laboratory experiments

Distribution	
	<p>Vale light oil solidified rapidly after application to the MNS experimental system, and did not form a film with uniform thicknesses.</p> <p>The film stopped rotation after a few hours in the MNS experiments</p> <p>These observations is in accordance with the yield stress and pour point analysis of the various fractions of Vale light oil</p>
Evaporation	
	<p>Based on GC/FID analysis the evaporation of Vale was in the order of less than 40% after 18 h. The evaporation rate was significantly reduced during the experimental period of 18h, due to solidification of the film.</p>
Solidification	
	<p>Solidification in Closed system experiments after low/moderate exposure for 18 h; "two phase", with formation of oil lumps and surrounded by a continuous liquid film</p> <p>Solidified lump in MNS after high exposure. (generation of liquid film surrounding the lumps due to leakage from the lump is expected after a some hours under calm conditions)</p>

Emulsification	
	<p>Water uptake of the Vale residues was very limited. Water uptake from in experiment with 200°C+ residue at 15 rpm in closed system. The "emulsion" was unstable.</p>
Dispersion	
	<p>No dispersion as droplets by increasing exposure in Closed system; droplet formation only observed for 200°C+ residue at 13 °C at "breaking wave" conditions (20 rpm)</p>
Response options	
	<p>Adsorption; Good</p>

B.4.2 OWM Predictions (2 and 5 m/s and 2 and 13 °C)

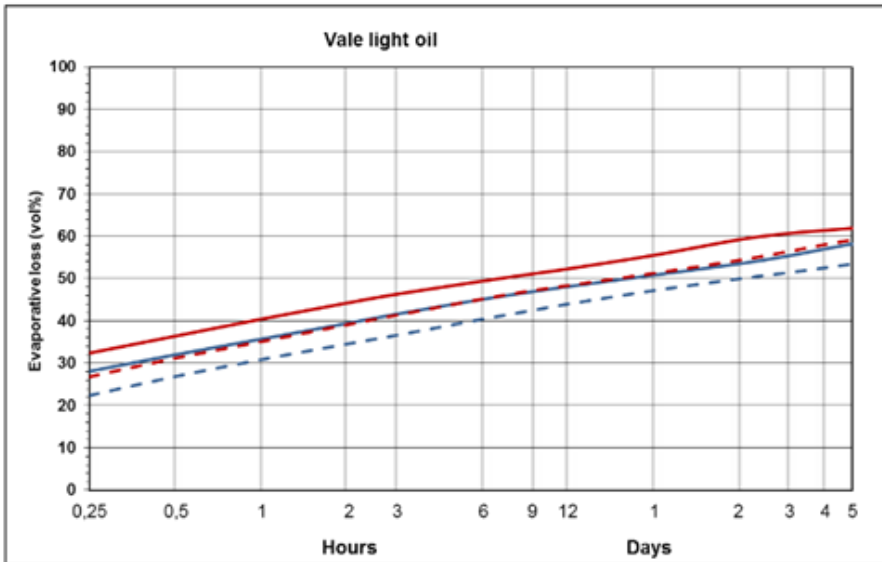


Property: Evaporative loss



--- 2°C, 2m/s — 2°C, 5m/s - - 13°C, 2m/s — 13°C, 5m/s

4.0 β © 2010
Pred. Date: March 2016

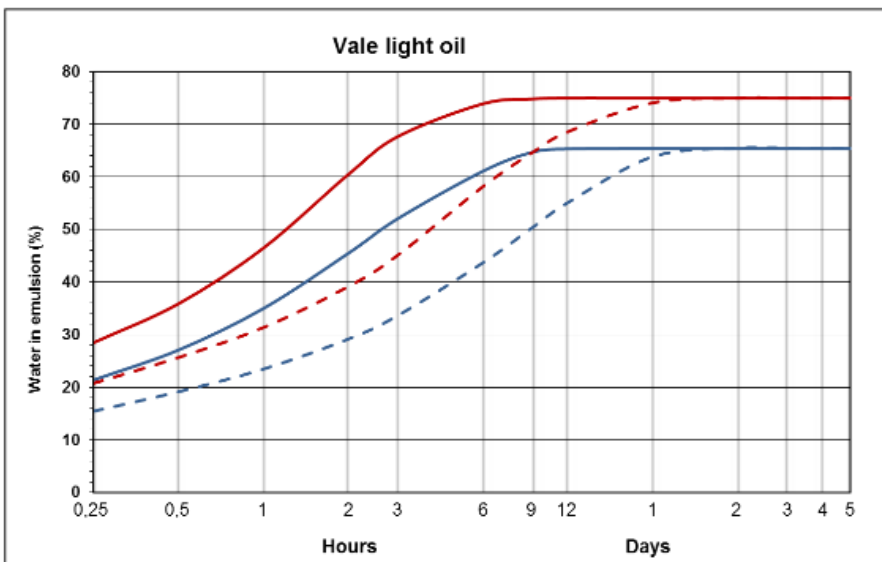



Property: Water content



--- 2°C, 2m/s — 2°C, 5m/s - - 13°C, 2m/s — 13°C, 5m/s

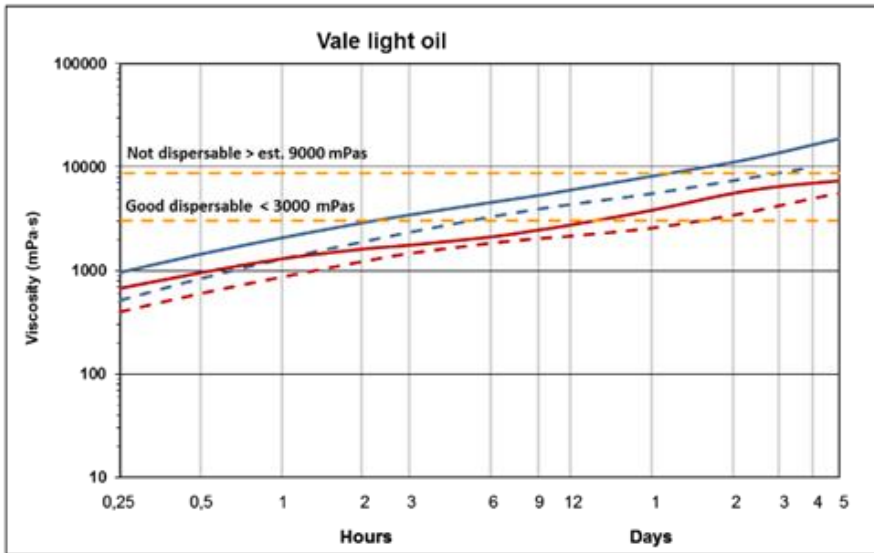
4.0 β © 2010
Pred. Date: March 2016



Property: Emulsion viscosity  **SINTEF**

-- 2 m/s, 2°C
 — 5m/s, 2°C
 -- 2 m/s, 13°C
 — 5 m/s, 13°C

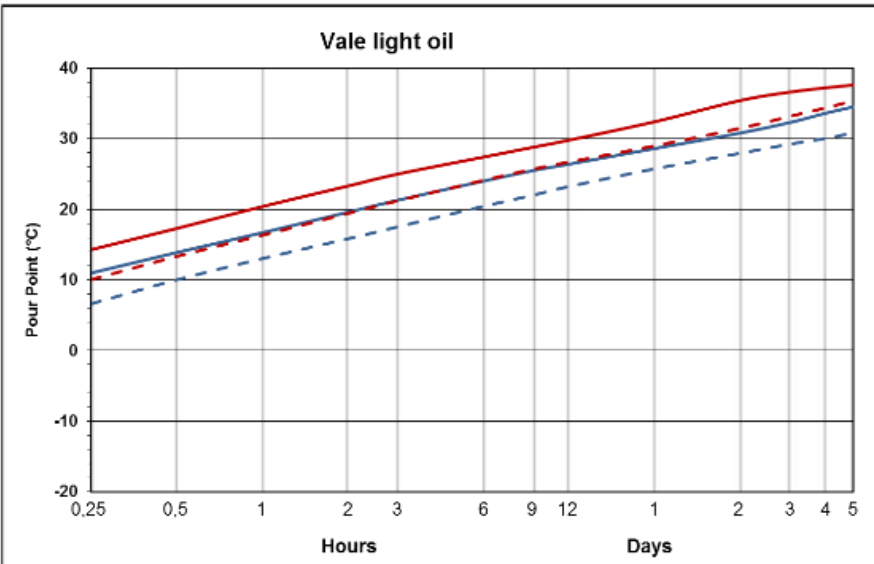
4.0 β © 2010
Pred. Date: March, 2016



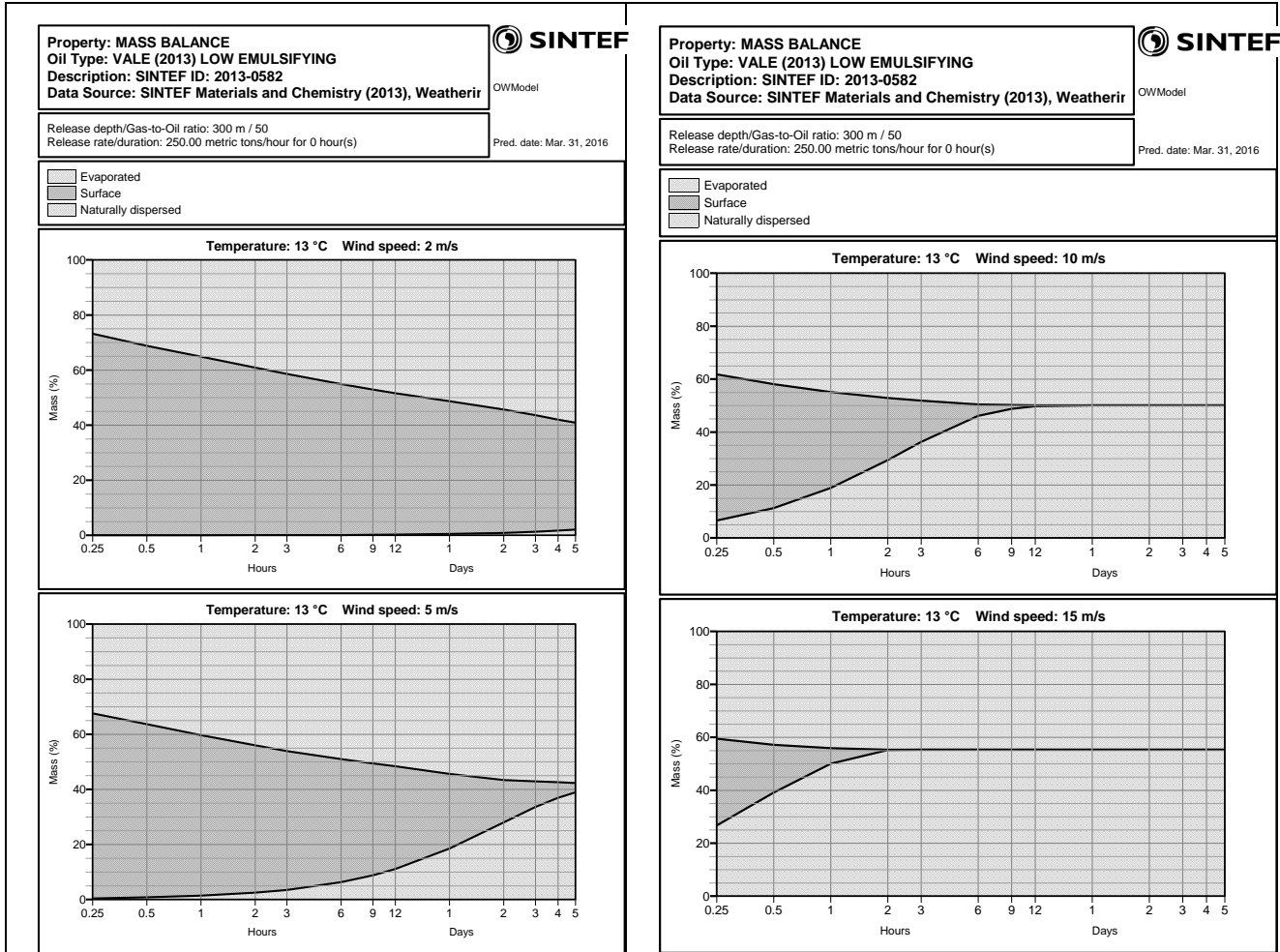
Property: Pour point  **SINTEF**

-- 2°C, 2m/s
 — 2°C, 5m/s
 -- 13°C, 2m/s
 — 13°C, 5m/s

4.0 β © 2010
Pred. Date: March, 2016




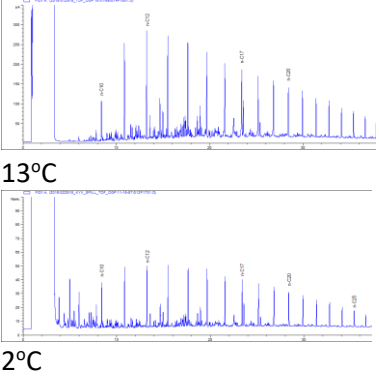

B.4.3 Predictions of mass balance for different wind speeds at 13 °C

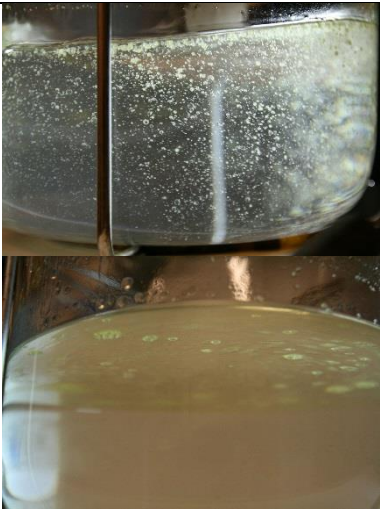


Predicted mass balance of Vale light oil at sea temperature of 13°C.

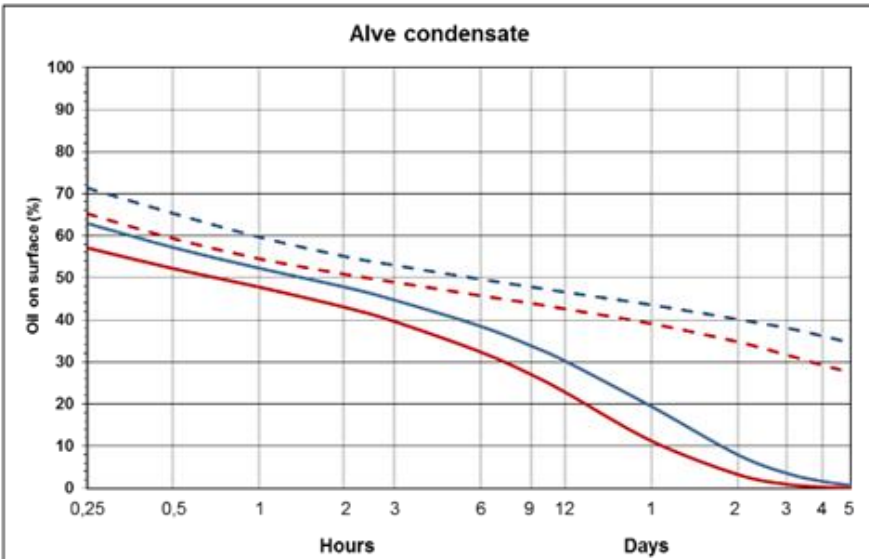
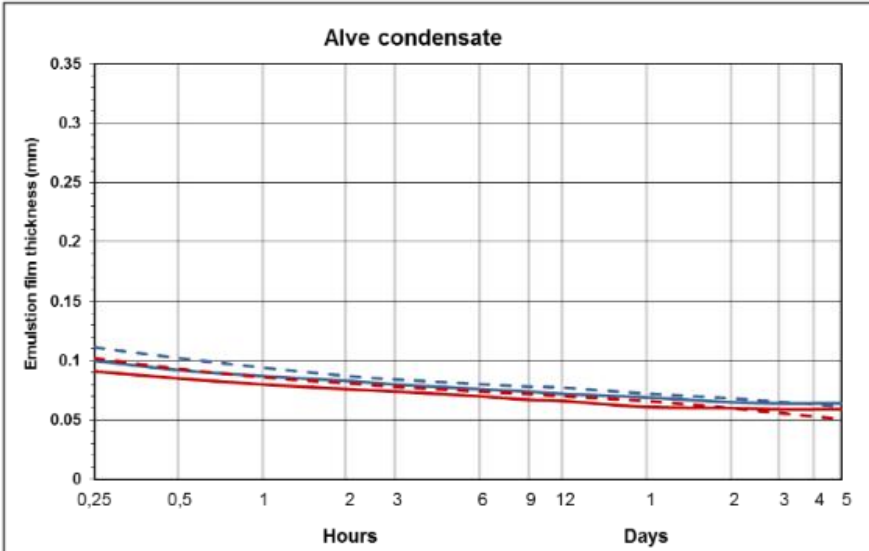
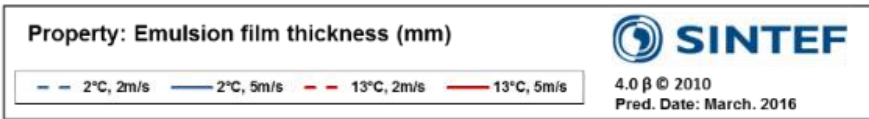
B.5Alve


B.5.1 TOF findings and observations in laboratory experiments

Distribution	
	<p>The Alve condensate was initially distributed to a uniform film thickness. However, the film solidified within a few hours. During the experimental period the oil film distribution was modified as a patchy oil film (lower picture)</p>
Evaporation	
 <p>13°C</p> <p>2°C</p>	<p>The Alve condensate evaporates rapidly as a thin oil film on the sea surface; typically 60% at 13 °C and 55% at 2 °C in the MNS. However, the evaporation rate was reduced by generation of the solidified film.</p>
Solidification	
	<p>The surface oil film appears to solidify more or less immediately at 2 °C, and within a few hours at 13 °C. During high exposure in MNS at the end of the experimental period larger droplets was generated, but no large lumps (se "Dispersion" below).</p> <p>In the closed system experiment the solidified surface film was accumulated (picture), but a "thick" lump like <i>e.g.</i> Vale was not formed</p>
Emulsification	
	<p>No water uptake was observed in open or closed system experiments using Alve condensate</p>
Dispersion/entrainment	

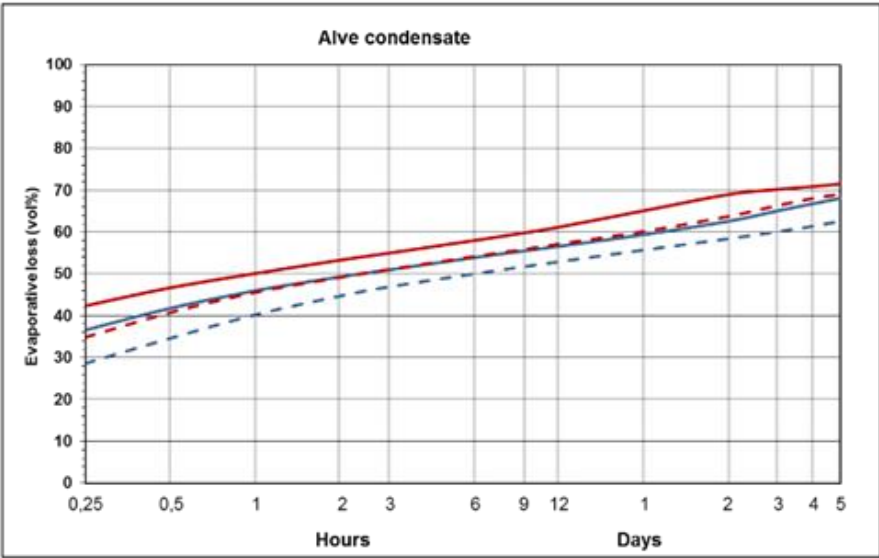
	<p>The apparent solidified surface film was broken down and generated patches/droplets of oil (no lumping) at high exposure in the MNS.</p> <p>After termination of high-energy exposure, the droplets/lumps resurfaced and formed a (solidified) surface film.</p> <p>In closed system experiments, droplet formation was observed for the 200°C+ residue at both temperatures, but only at 13 °C for the 250°C+ residue.</p>
<p>Response options</p>	
<p>Adsorption: Good at both 2 and 13 °C in MNS experiments</p>	


B.5.2 OWM Predictions (2 and 5 m/s and 2 and 13 °C)



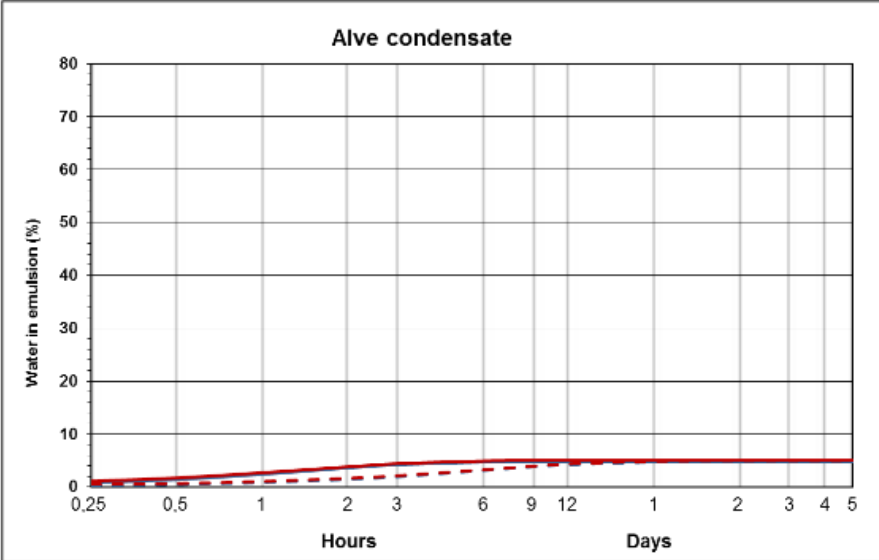
Property: Evaporative loss  SINTEF
 4.0 β © 2010
 Pred. Date: March 2016

--- 2°C, 2m/s — 2°C, 5m/s --- 13°C, 2m/s — 13°C, 5m/s



Property: Water content  SINTEF
 4.0 β © 2010
 Pred. Date: March. 2016

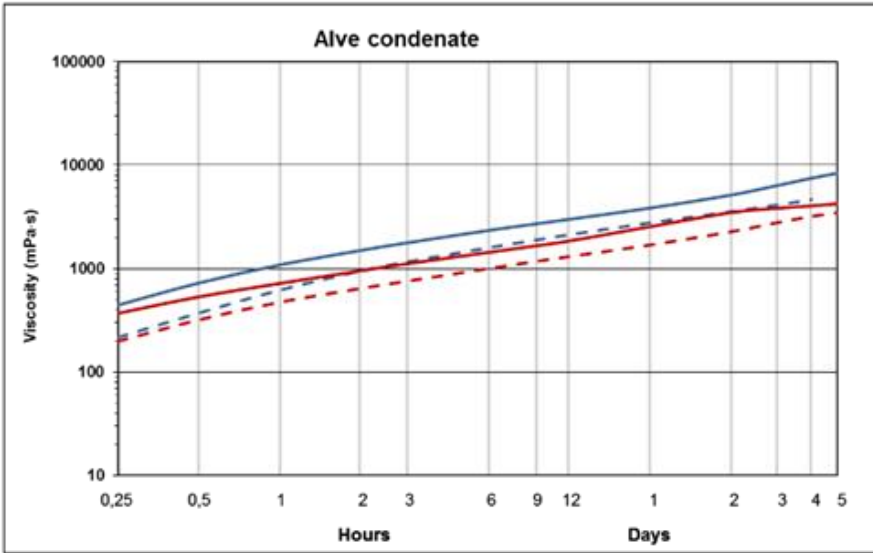
--- 2°C, 2m/s — 2°C, 5m/s --- 13°C, 2m/s — 13°C, 5m/s



Property: Emulsion viscosity  **SINTEF**

-- 2 m/s, 2°C
 — 5m/s, 2°C
 -- 2 m/s, 13°C
 — 5 m/s, 13°C

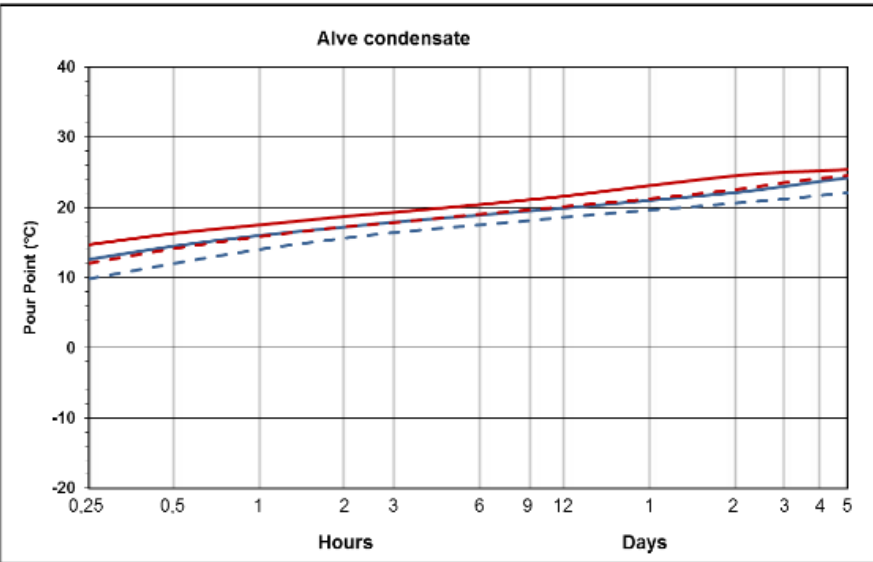
4.0 β © 2010
Pred. Date: March, 2016



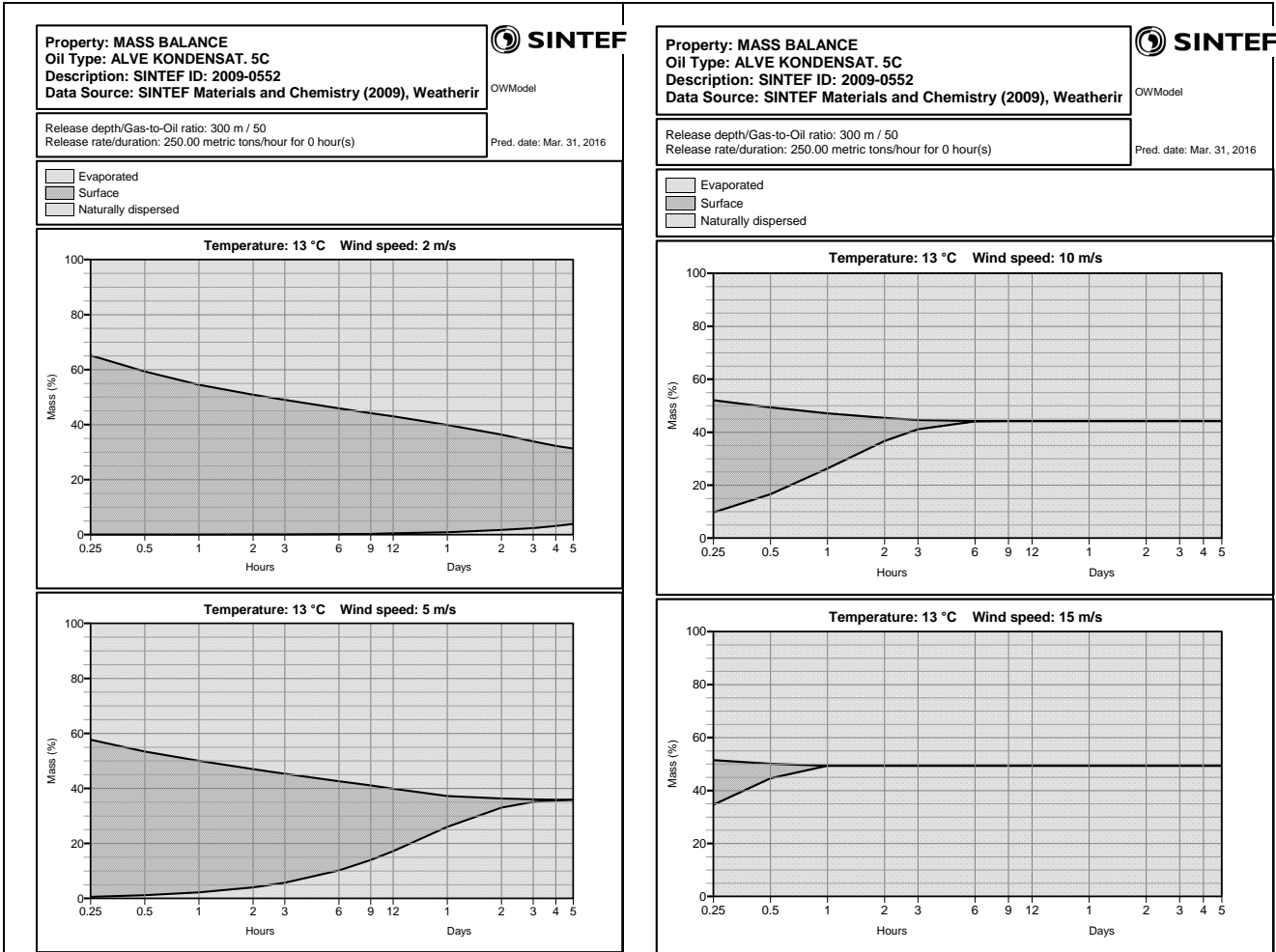
Property: Pour point  **SINTEF**

-- 2°C, 2m/s
 — 2°C, 5m/s
 -- 13°C, 2m/s
 — 13°C, 5m/s

4.0 β © 2010
Pred. Date: March, 2016



B.5.3 Predictions of mass balance for different wind speeds at 13 °C

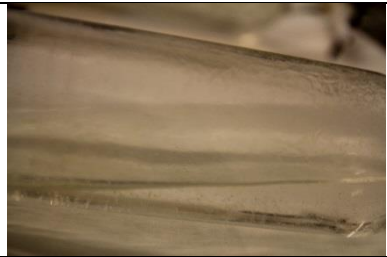



Predicted mass balance of Alve condensate at sea temperature of 13°C.

B.6Skarv

B.6.1 TOF findings and observations in laboratory experiments

Distribution	
	<p>MNS 13 °C: The oil film appears homogeneous from top side, but appears patchier from underneath. 18 h - Rigid film, thicker near centre</p> <p>2 °C MNS: Rigid, inhomogeneous film. Bubbles forming under film. Film stopped rotating in the MNS chamber</p> <p>Flume 13 °C: Rigid, flaky film. Breaks into smaller flakes.</p>
Evaporation	
	<p>The evaporation of Skarv was slower than most other condensates as can be illustrated by the GC/FID.</p> <p>During the 18 h experimental period the evaporation was in the range of 45% (2 °C) and 50% (13 °C)</p>
Solidification	
	<p>The 200 and 250°C+ residues solidified immediately in the closed system experiments at both temperatures. By increasing exposure in closed systems, the solidified thin film became a lump. When increasing the wave exposure the lump became fractionated and "flakes" was generated in the water phase.</p>

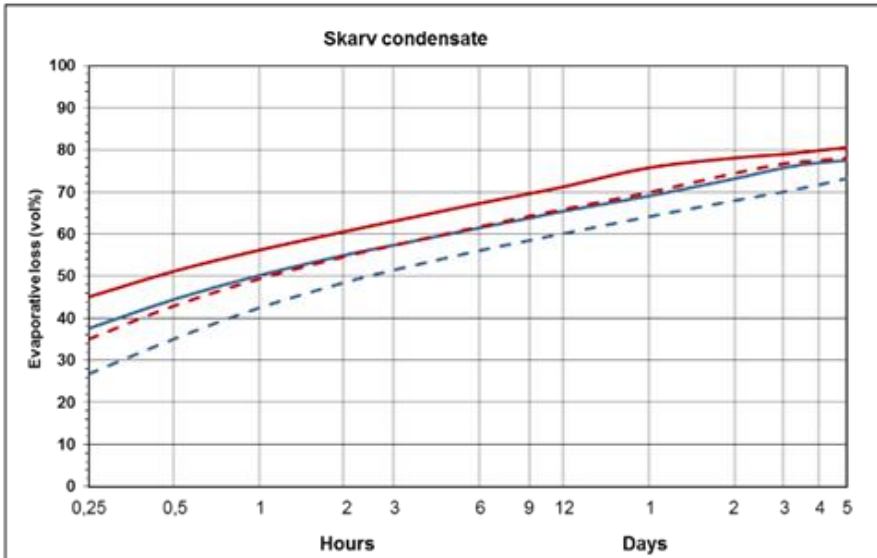
	<p>The oil residues solidified within a short period at both 2 and 13 °C in MNS/Flume experiments. During high exposure, similar observation was also made in the MNS and Flume experiment with generation of flakes. After termination of high exposure the solidified particle resurfaced and formed a thin (uniform) film</p>
Emulsification	
	<p>No water uptake in the oil residue phase was found</p>
Dispersion	
	<p>MNS 2 °C: The solidified oil film broke into smaller parts. Starts rotating. Solidified oil particles pushed into water . Most of oil resurfaces rapidly at end. Some droplets suspended in water</p> <p>MNS 13 °C: Patch starts breaking up. Oil forms lumps that congregate near outer edge. Oil droplets and larger lumps pushed into water. Many droplets in the water phase. Oil resurfaces rapidly at end and reforms a film.</p> <p>Flume 13 °C: The oil was "accumulated" in some areas, creating thicker film on the flume interior walls. Thin oil film (rainbow) was observed near wave generator, indicating formation of the two-phase film. The oil resurfaced rapidly after termination of high exposure and forming a thin solidified "film". Average diameter of droplets/particles in the water column after termination of high exposure was 200 µm.</p>
Response options	
	<p>Dispersibility; the residue from Flume experiment at 13 °C was found to have good/reduced dispersibility</p>
	<p>Good Sorption properties of the residue at the end of the open system experiments.</p>

Property: Evaporative loss



-- 2°C, 2m/s — 2°C, 5m/s - - 13°C, 2m/s — 13°C, 5m/s

4.0 β © 2010
Pred. Date: March 2016

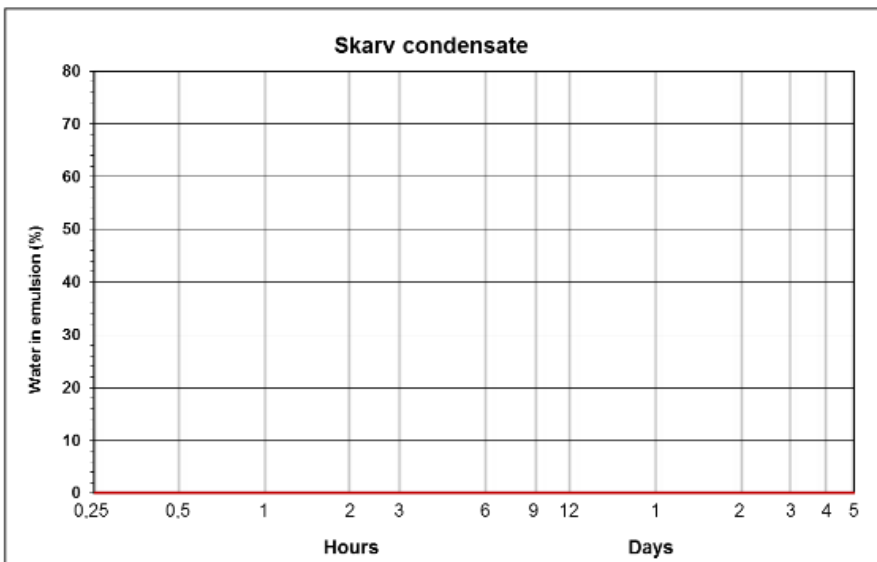


Property: Water content



-- 2°C, 2m/s — 2°C, 5m/s - - 13°C, 2m/s — 13°C, 5m/s

4.0 β © 2010
Pred. Date: March 2016

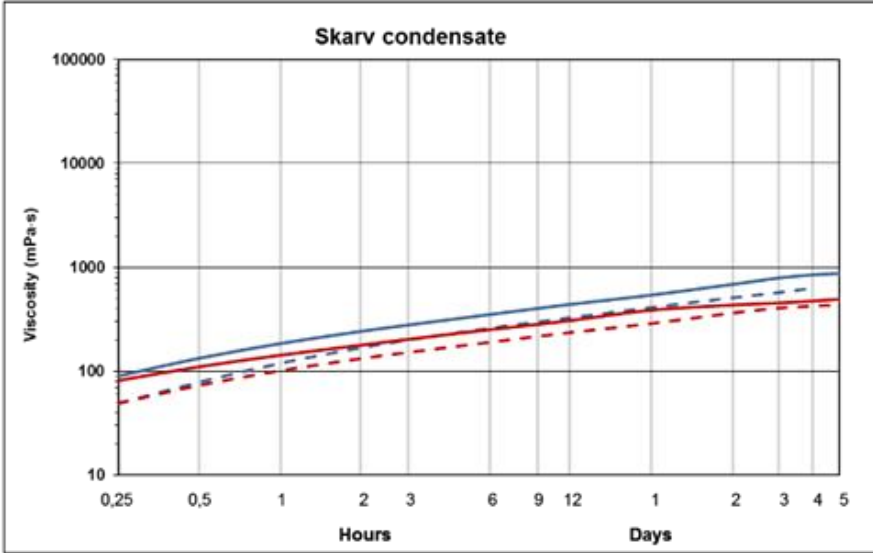


Property: Emulsion viscosity

SINTEF

4.0 β © 2010
Pred. Date: March. 2016

-- 2 m/s, 2°C
 — 5m/s, 2°C
 -- 2 m/s, 13°C
 — 5 m/s, 13°C

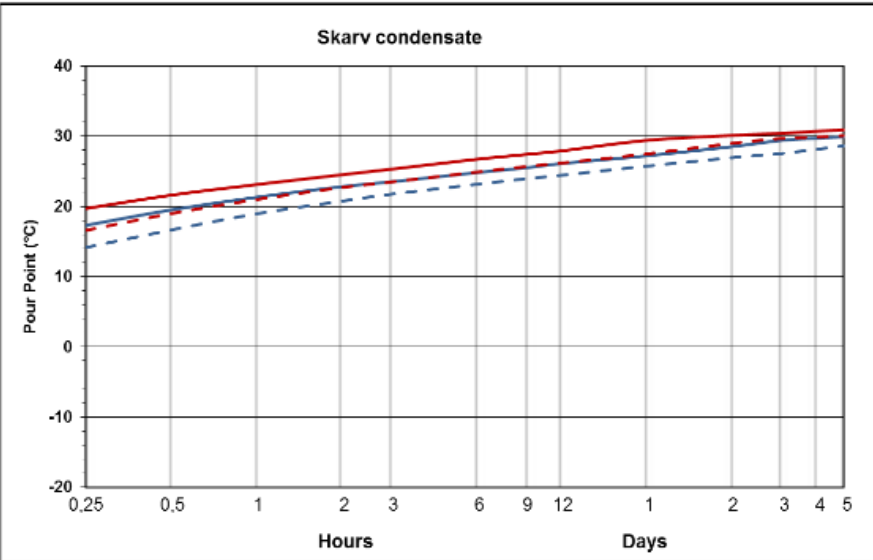


Property: Pour point

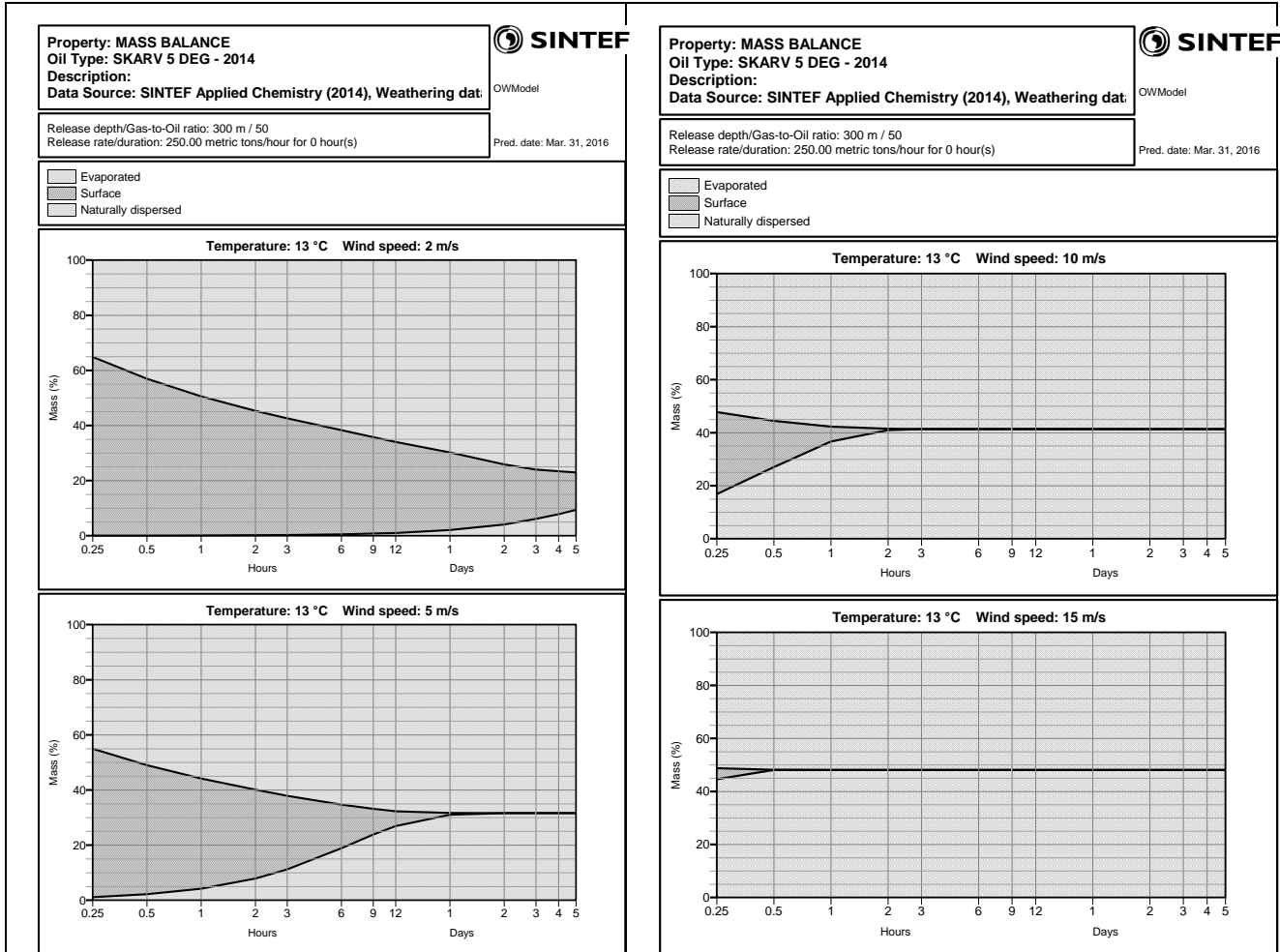
SINTEF

4.0 β © 2010
Pred. Date: March. 2016

-- 2°C, 2m/s
 — 2°C, 5m/s
 -- 13°C, 2m/s
 — 13°C, 5m/s




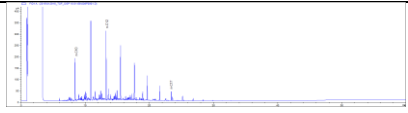
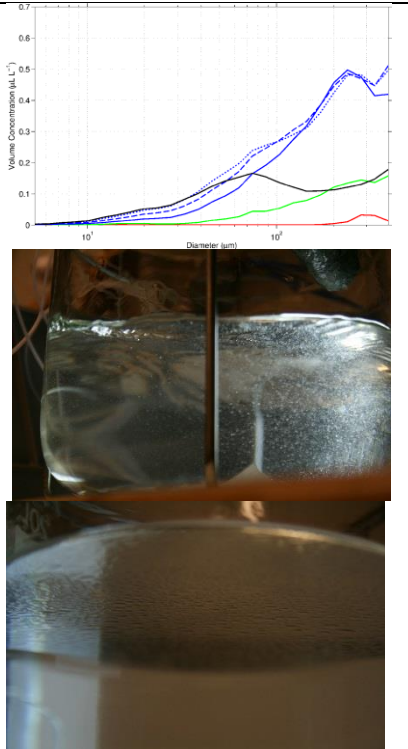
B.6.3 Predictions of mass balance for different wind speeds at 13 °C



Predicted mass balance of Skarv condensate at sea temperature of 13 °C.

B.7 Ormen Lange

B.7.1 TOF findings and observations in laboratory experiments

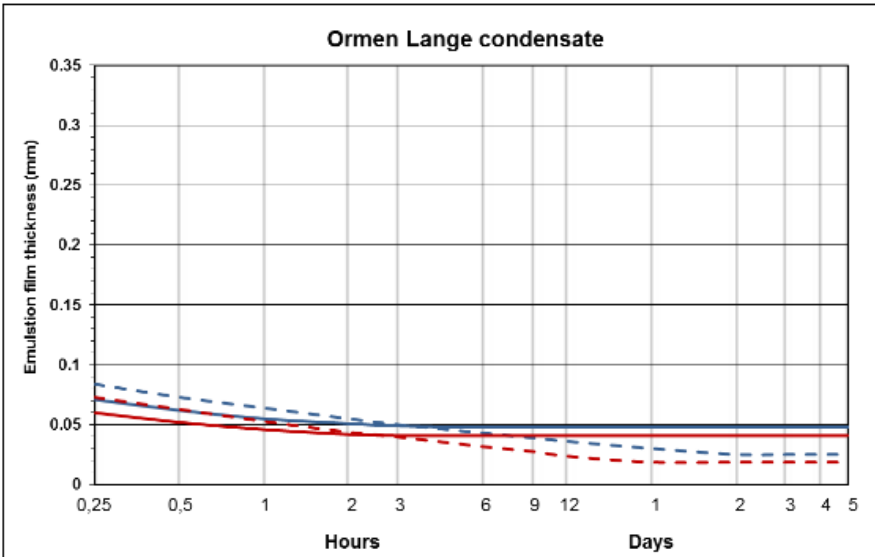
Distribution	
	<p>The condensate spread to form a uniform oil film thickness. This uniform film remained unchanged during the experimental period with calm condition</p> <p>In the flume experiment (13 °C) there was some inhomogeneity of oil distribution at the end of the experimental period, with areas with thicker residues (picture left)</p>
Evaporation	
	<p>Very high evaporation – more than 95% evaporated after 18h</p>
Solidification	
	<p>Little residue after 18h – less than 5%. No solidification was observed in any experimental combination in open system experiments</p>
Emulsification	
	<p>No water uptake was observed or measured</p>
Dispersion	
	<p>During high-energy exposure, the remaining surface oil was easily dispersed into the water column with a typical average droplet size of 200 µm. After termination of high-energy exposure most of the droplets resurfaced, and the remaining droplets was in the size of less than 70 µm.</p> <p>The resurfaced oil spread over the completely surface area in the MNS (2 °C), with some irregularity (lower picture).</p>
Response options	
	<p>Dispersibility; not tested</p>
	<p>Sorption; good</p>

B.7.2 OWM Predictions (2 and 5 m/s and 2 and 13 °C)

Property: Emulsion film thickness (mm)

-- 2°C, 2m/s
 — 2°C, 5m/s
 -- 13°C, 2m/s
 — 13°C, 5m/s

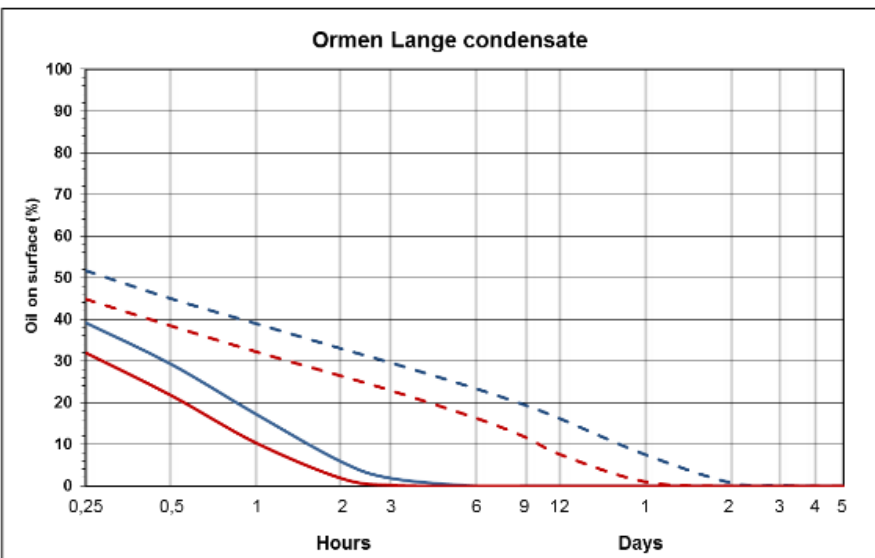
4.0 β © 2010
Pred. Date: March. 2016



Property: Surface oil

-- 2°C, 2m/s
 — 2°C, 5m/s
 -- 13°C, 2m/s
 — 13°C, 5m/s

4.0 β © 2010
Pred. Date: March. 2016

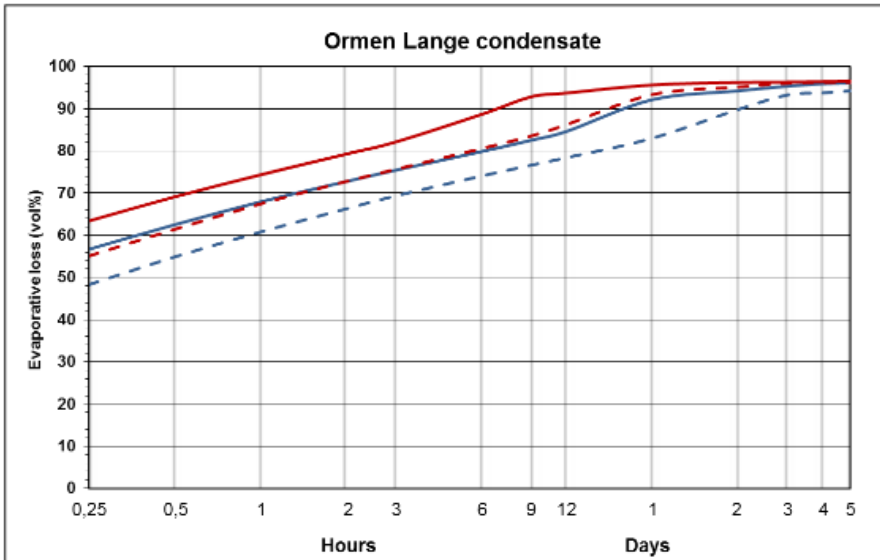


Property: Evaporative loss



--- 2°C, 2m/s — 2°C, 5m/s - - 13°C, 2m/s — 13°C, 5m/s

4.0 β © 2010
Pred. Date: March 2016

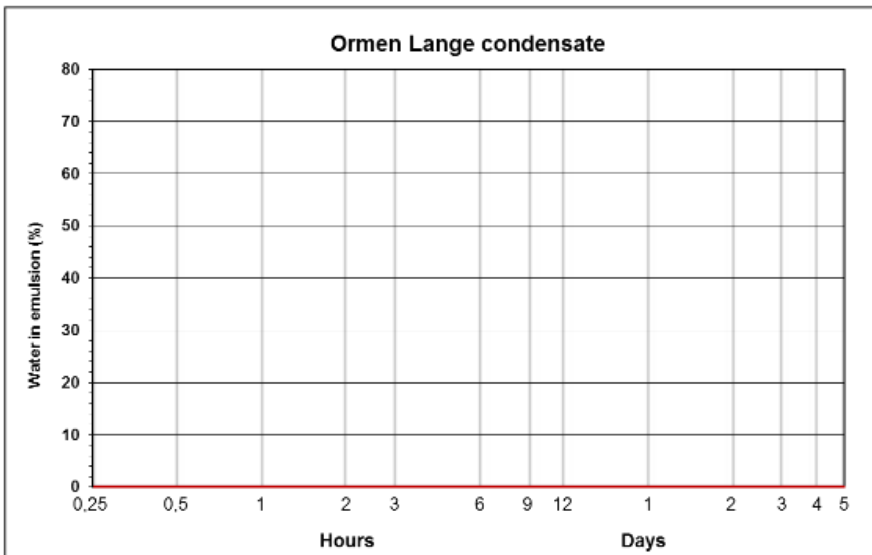


Property: Water content



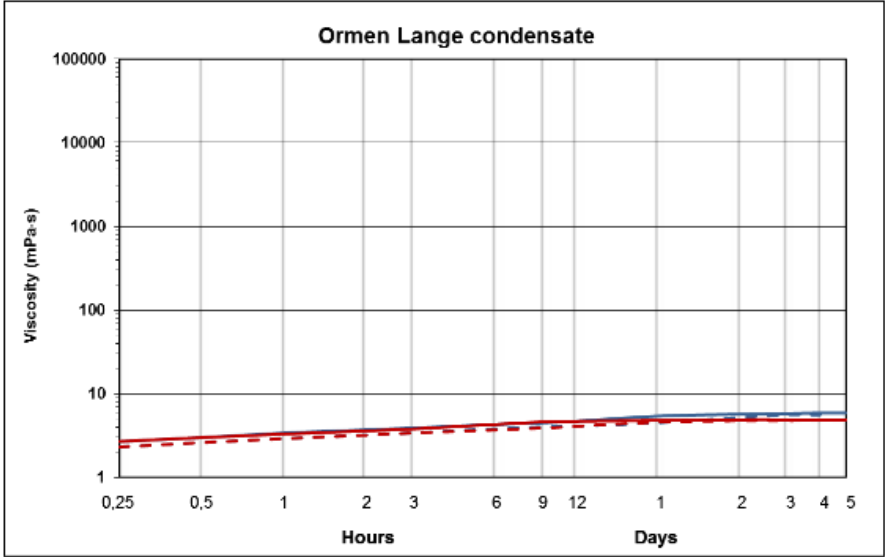
--- 2°C, 2m/s — 2°C, 5m/s - - 13°C, 2m/s — 13°C, 5m/s

4.0 β © 2010
Pred. Date: March 2016



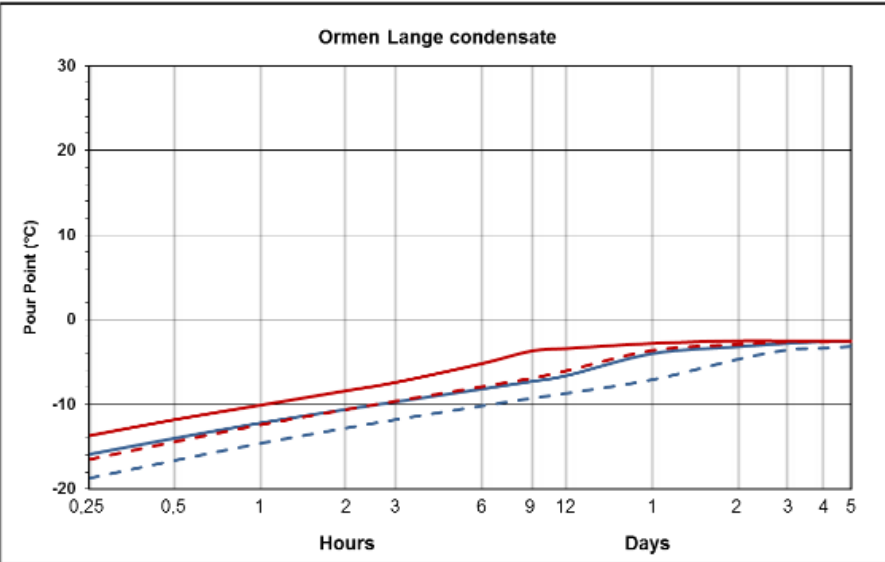
Property: Emulsion viscosity **SINTEF**
4.0 β © 2010
Pred. Date: March. 2016

-- 2 m/s, 2°C
 — 5m/s, 2°C
 -- 2 m/s, 13°C
 — 5 m/s, 13°C

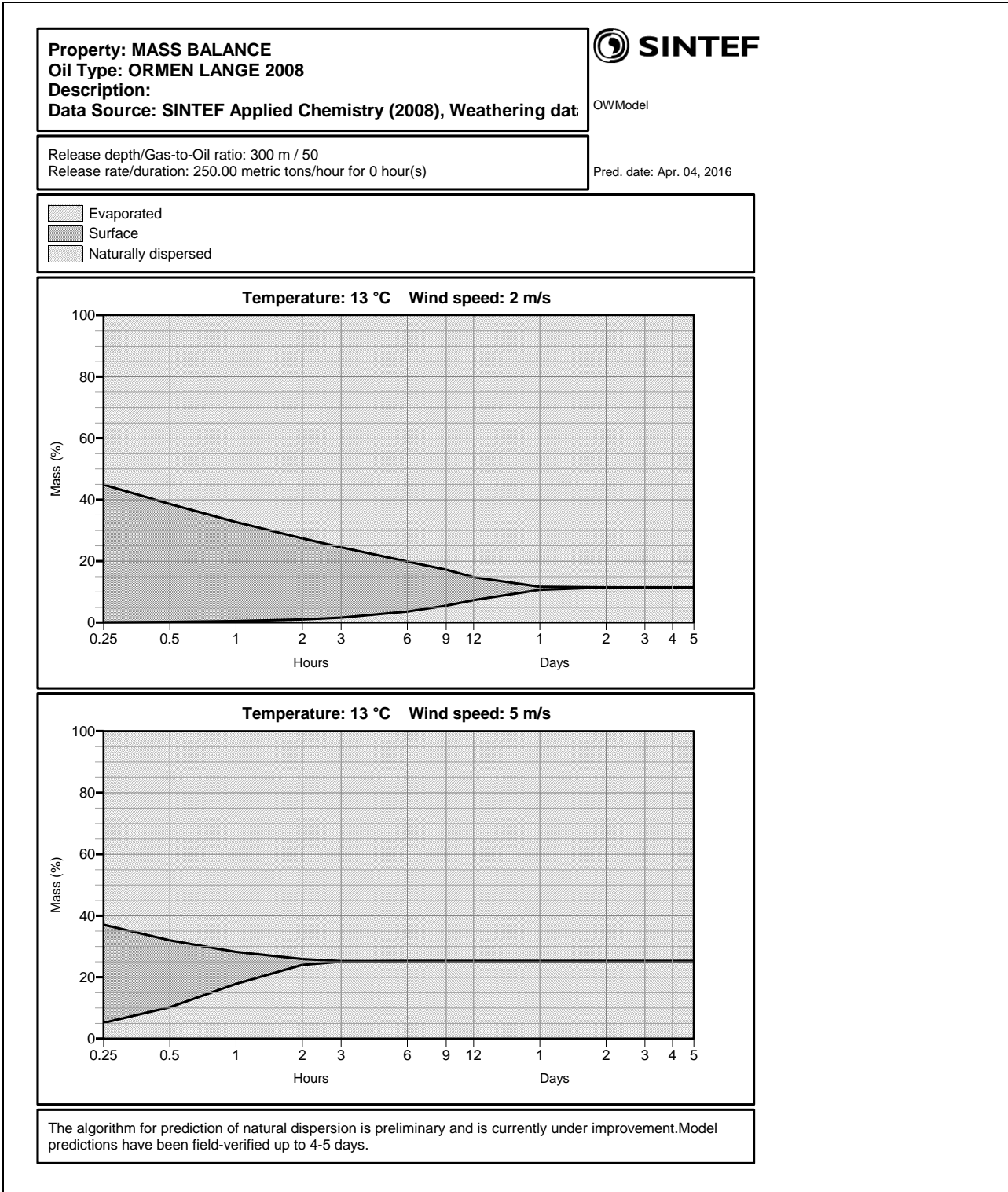


Property: Pour point **SINTEF**
4.0 β © 2010
Pred. Date: March. 2016

-- 2°C, 2m/s
 — 2°C, 5m/s
 -- 13°C, 2m/s
 — 13°C, 5m/s



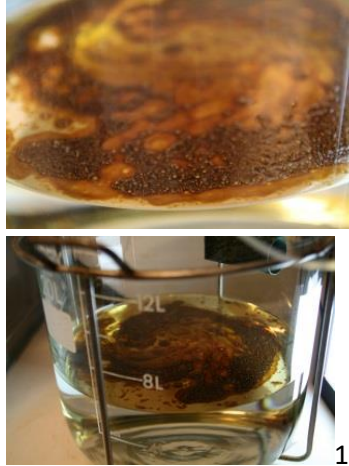
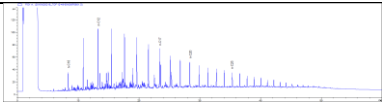
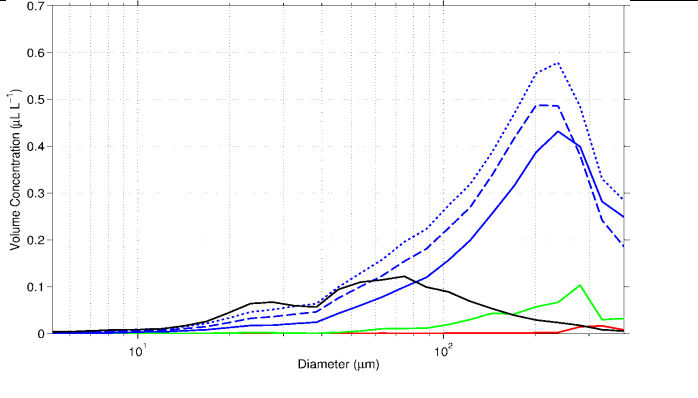
B.7.3 Predictions of mass balance for different wind speeds at 13 °C




Predicted mass balance of Ormen Lange condensate at sea temperature of 13 °C.


B.8 Statfjord

B.8.1 TOF findings and observations in laboratory experiments

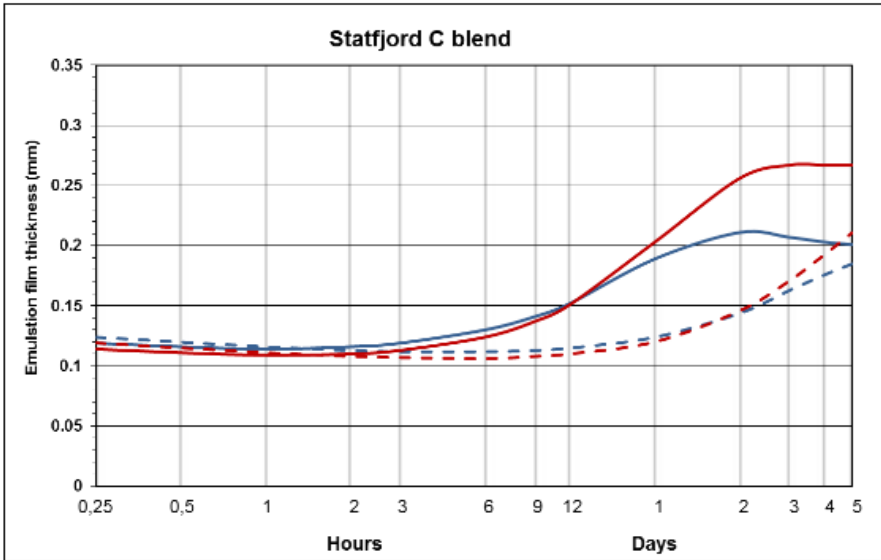
Distribution	
	<p>Statfjord C Blend with higher pour point, the distribution to generate a homogenous film was more difficult to obtain in the Flume than in the MNS. Initially the oil was spread over the entire surface area, but not as a uniform oil film. This lack of uniformity increases during the experimental period. At the end of the experimental period, there were several different characteristics areas of the surface oil.</p>
Evaporation	
	<p>Moderate evaporation – estimated 40-50 % evaporated after 18 h</p>
Solidification	
	<p>MNS 2 °C; No uniform film, but brown foamy patches. Solidification, and oil stops rotating over night MNS 13 °C; Inhomogeneous film and tendency of solidification. Flume 13 °C less pronounced solidification, and less thick oil patches in flume</p>
Emulsification	
	<p>Emulsification at the end of the experimental period with water content and viscosities given below. The emulsion stability was not quantified. MNS13 °C; 1300 mPa.s – 50% water Flume 13 °C; 1800 mPa.s – 25% water MNS 2 °C; 2700 mPa.s – 67% water</p>
Dispersion/entrainment	
	<p>Flume 13 °C: At the end of the experimental period, lot of oil adhered to the walls. During increasing wave exposure oil droplets/lumps, were pushed into water. Large droplets resurface and spread out. Oil droplet distribution seen in plot at different exposures. In MNS the surface oil was entrained as larger droplets/lumps (picture left)</p>

	<p>MNS 2 °C; Solidified oil film. Oil starts moving around. Lumping as oil patches collide. Ends up with 2-4 large lumps. Some oil droplets are pushed into the water phase, these droplets reformed a film</p>
Response options	
	Dispersibility; not tested
	Sorption; good

B.8.2 OWM Predictions (2 and 5 m/s and 2 and 13 °C)

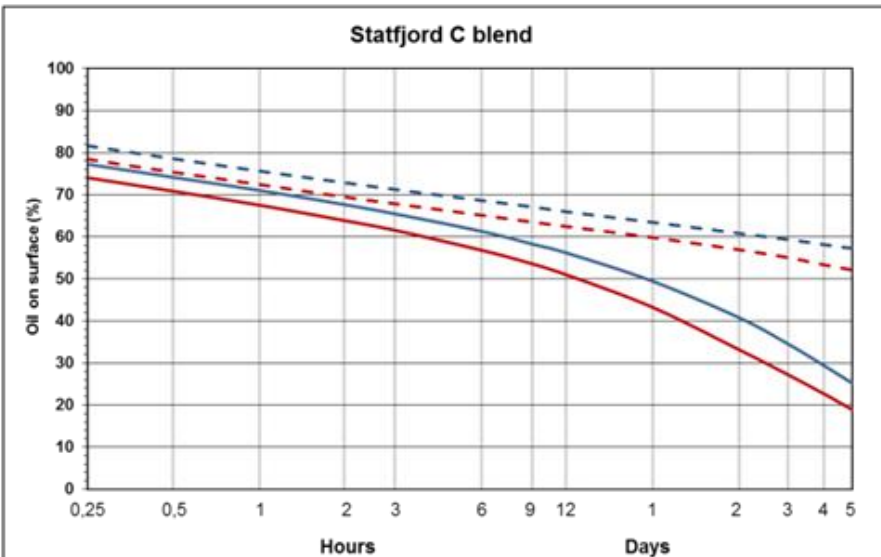
Property: Emulsion film thickness (mm)  **SINTEF**
 4.0 β © 2010
 Pred. Date: March, 2016

-- 2°C, 2m/s — 2°C, 5m/s -- 13°C, 2m/s — 13°C, 5m/s



Property: Surface oil  **SINTEF**
 4.0 β © 2010
 Pred. Date: March, 2016

-- 2°C, 2m/s — 2°C, 5m/s -- 13°C, 5m/s — 13°C, 5m/s

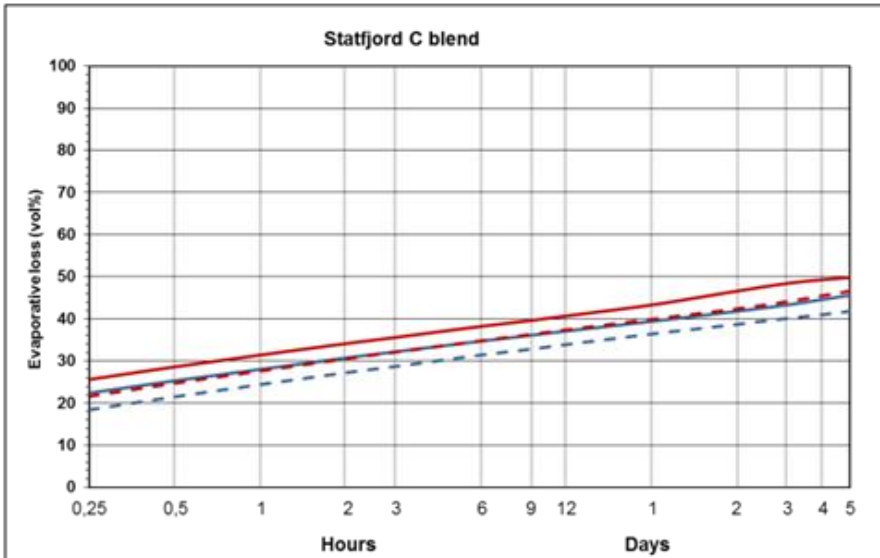


Property: Evaporative loss



--- 2°C, 2m/s — 2°C, 5m/s - - 13°C, 2m/s — 13°C, 5m/s

4.0 β © 2010
Pred. Date: March 2016

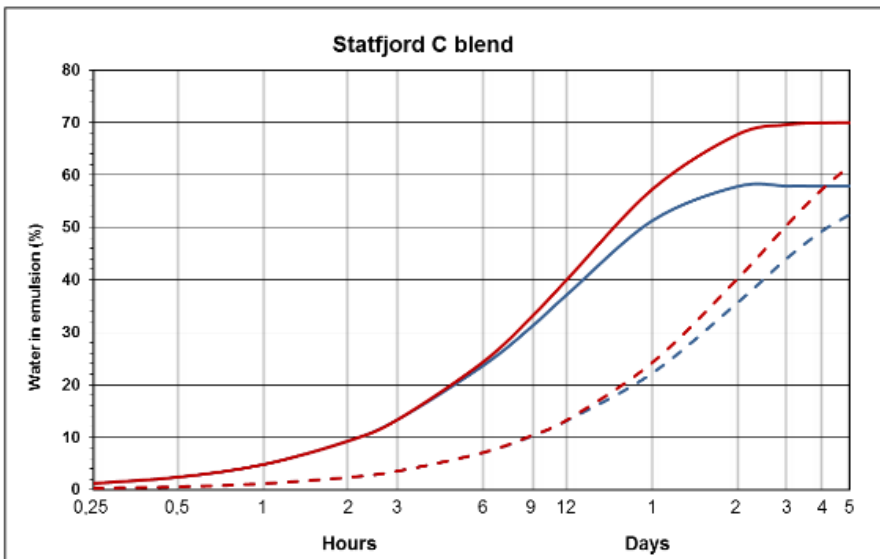


Property: Water content



--- 2°C, 2m/s — 2°C, 5m/s - - 13°C, 2m/s — 13°C, 5m/s

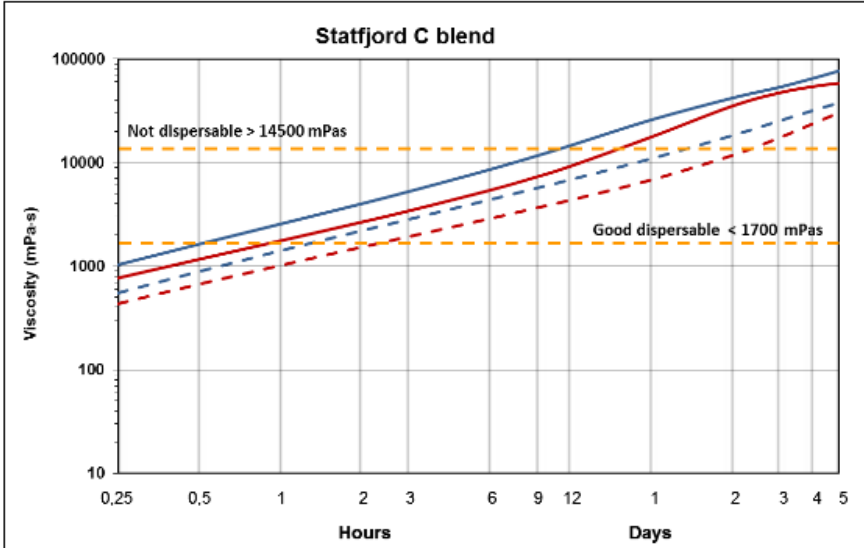
4.0 β © 2010
Pred. Date: March 2016



Property: Emulsion viscosity

-- 2 m/s, 2°C
 — 5m/s, 2°C
 -- 2 m/s, 13°C
 — 5 m/s, 13°C

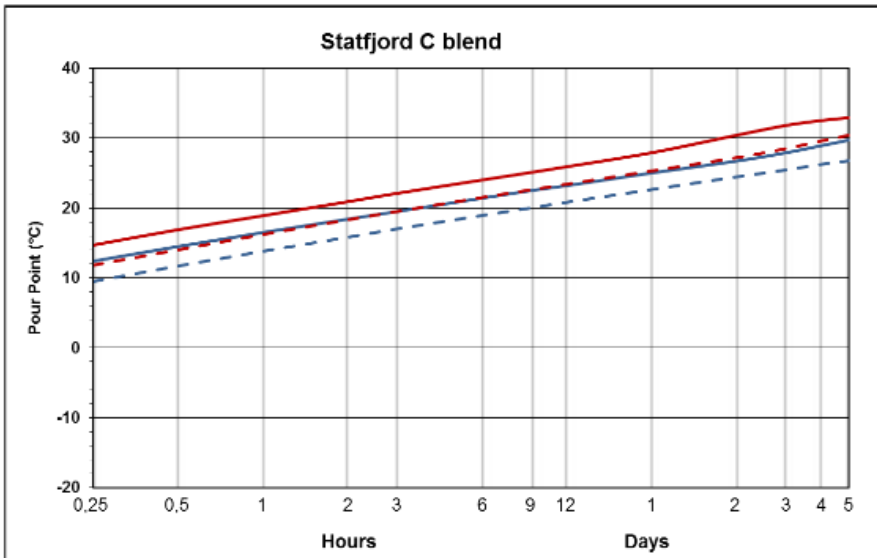
4.0 β © 2010
Pred. Date: March, 2016



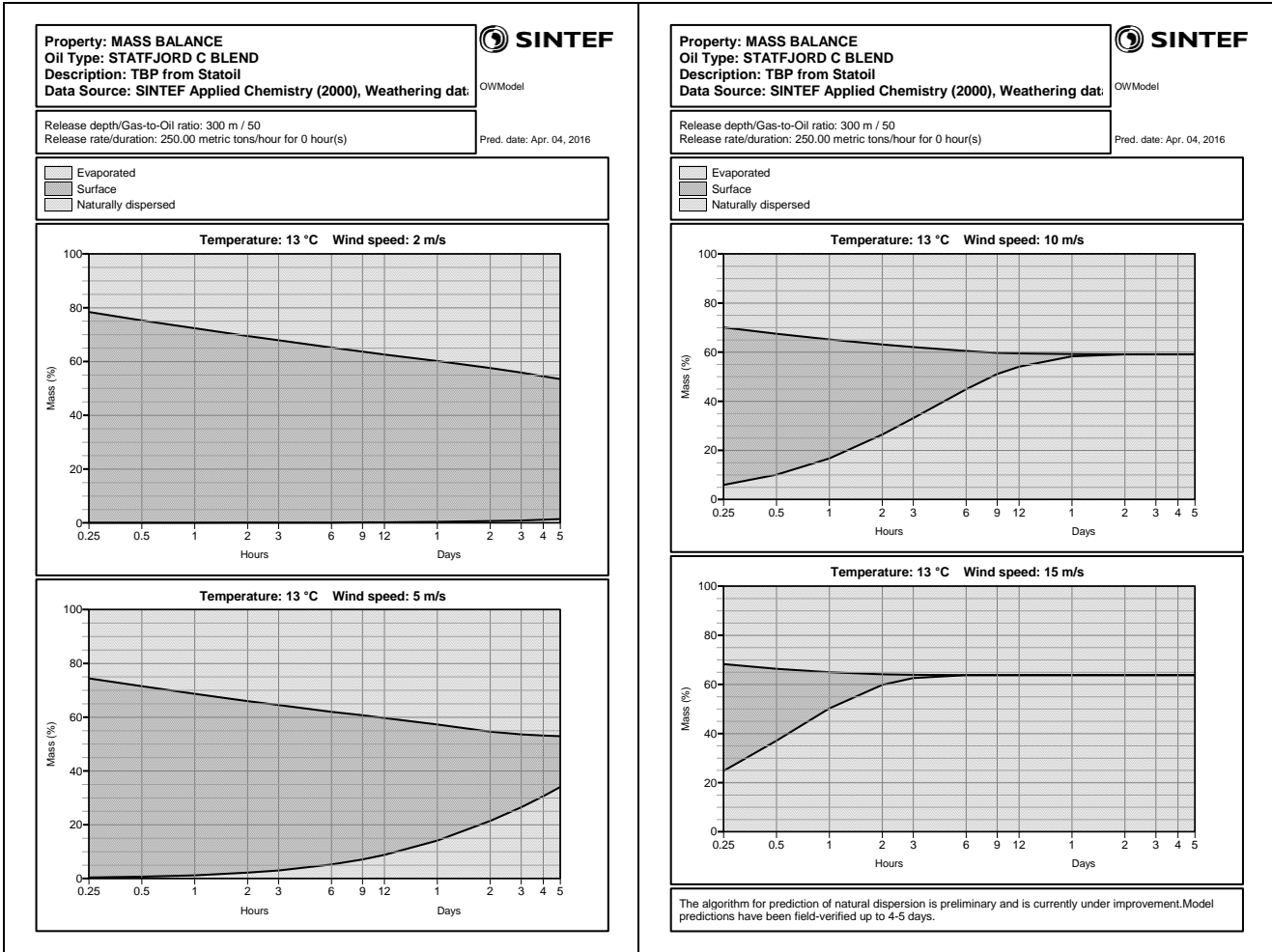
Property: Pour point

-- 2°C, 2m/s
 — 2°C, 5m/s
 -- 13°C, 2m/s
 — 13°C, 5m/s

4.0 β © 2010
Pred. Date: March, 2016



B.8.3 Predictions of mass balance for different wind speeds at 13 °C

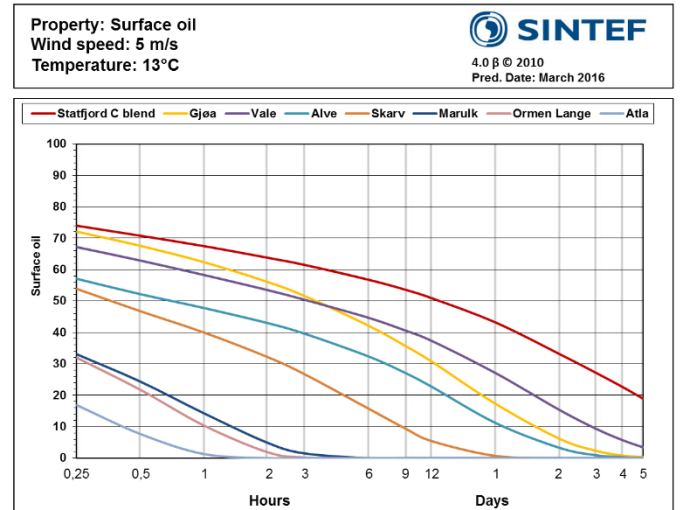
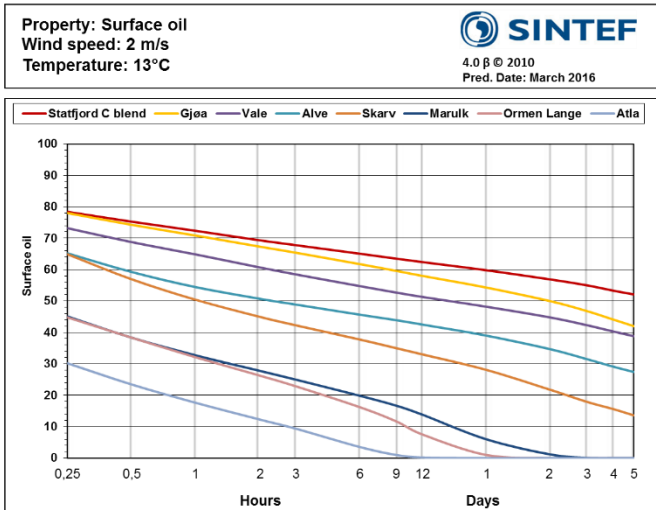
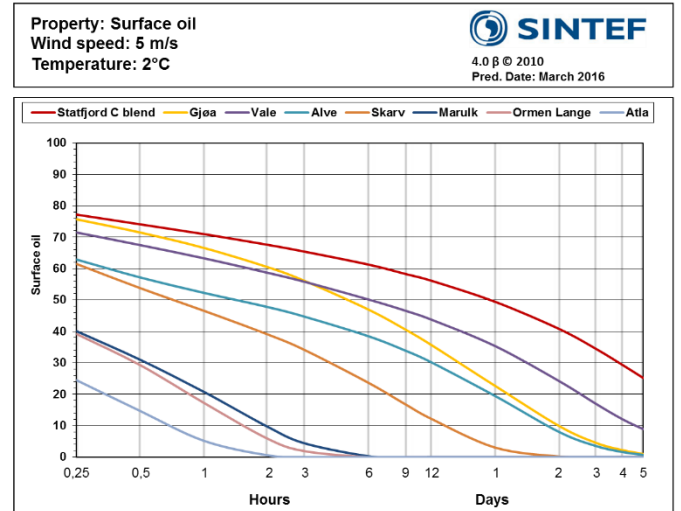
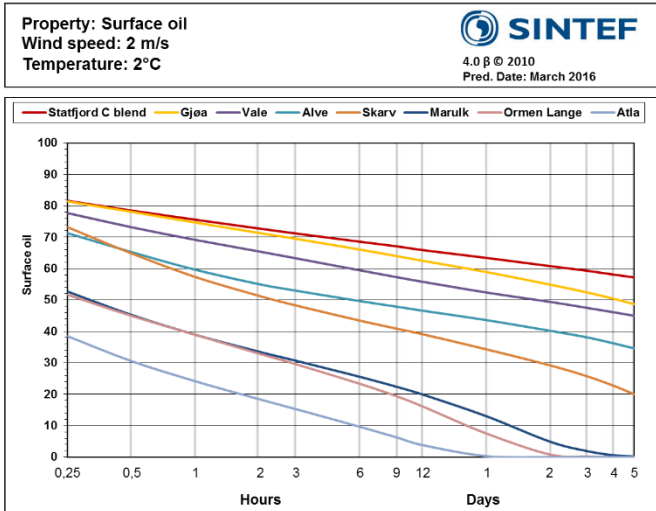


Predicted mass balance of Statfjord C blend ref. at sea temperature of 13 °C.

C OWM predictions for weathering processes and properties at 2 °C in comparison with 13°C

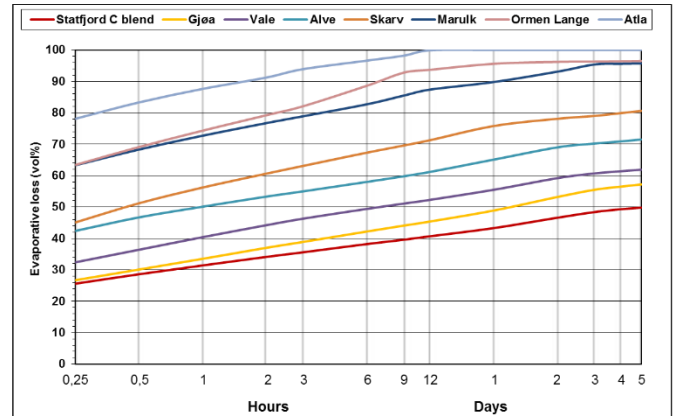
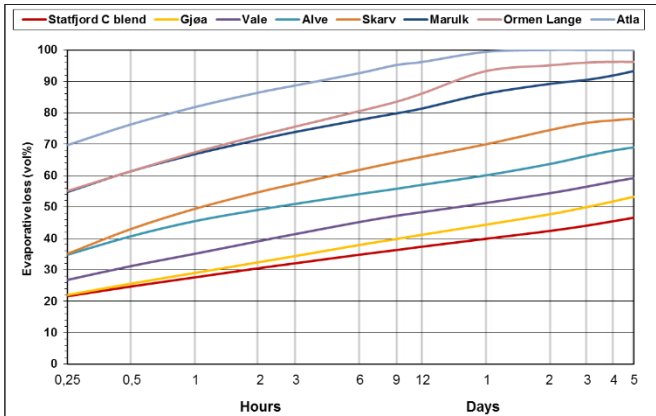
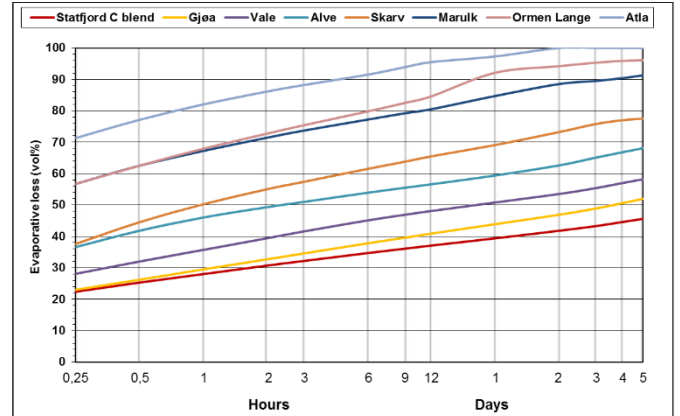
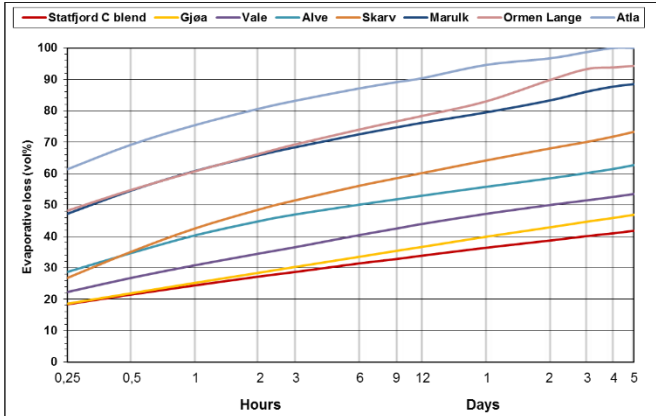
OWM Predictions for TOF project light oils and condensates at 2 °C with 2 and 5 m/s wind speeds. Data presented together with 13 °C predictions shown and discussed in main the report. Prediction not terminated when not surface oil present.

C.1 Surface oil



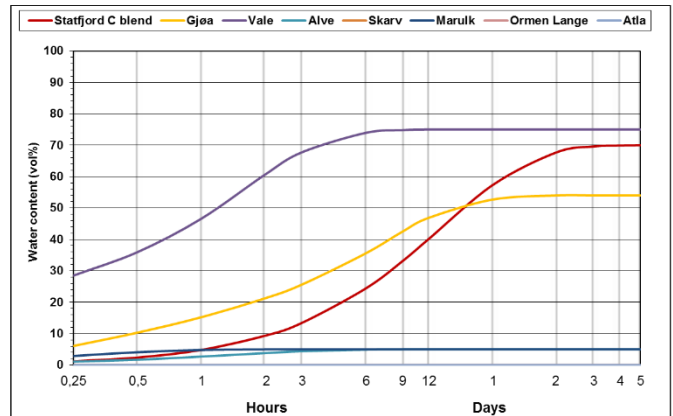
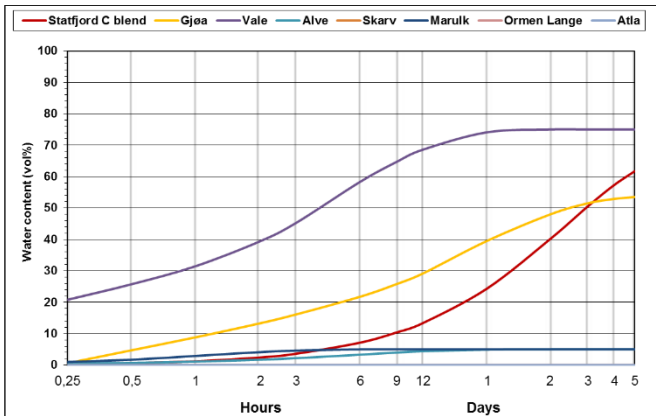
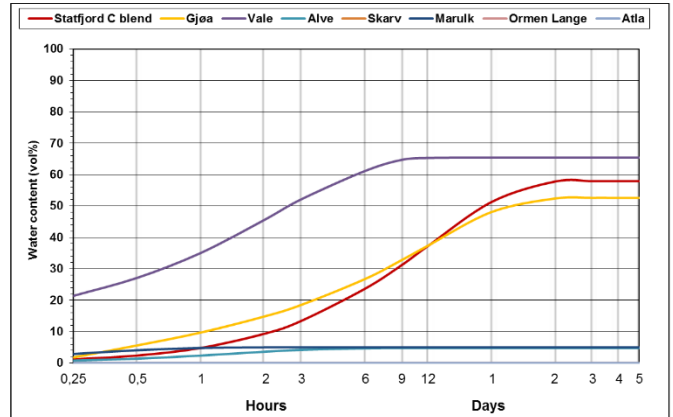
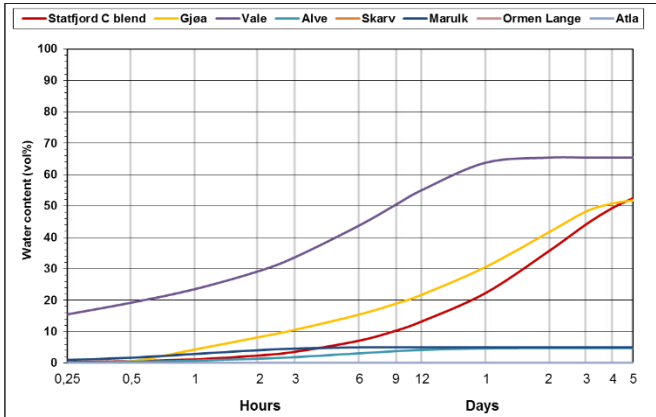
Comparison of surface oil for Statfjord C blend (ref. oil), Gjøa and Vale (light oils), and the condensates Alve, Skarv, Marulk, Ormen Lange and Atla at 2 and 13 °C with 2 and 5 m/s wind speeds.

C.2 Evaporative loss



Comparison of evaporative loss for Statford C blend (ref. oil), Gjøa and Vale (light oils), and the condensates Alve, Skarv, Marulk, Ormen Lange and Atla at 2 and 13 °C with 2 and 5 m/s wind speeds.

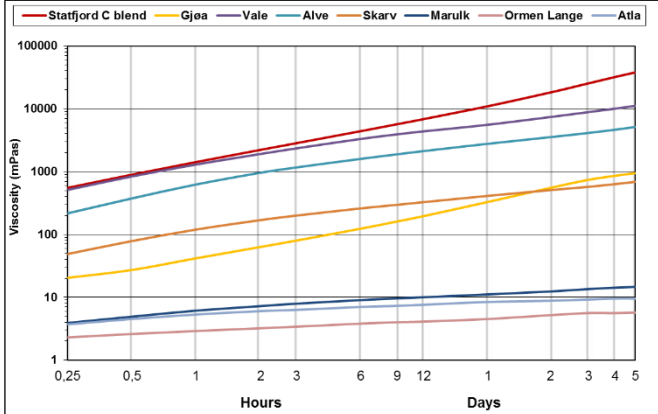
C.3 Water content



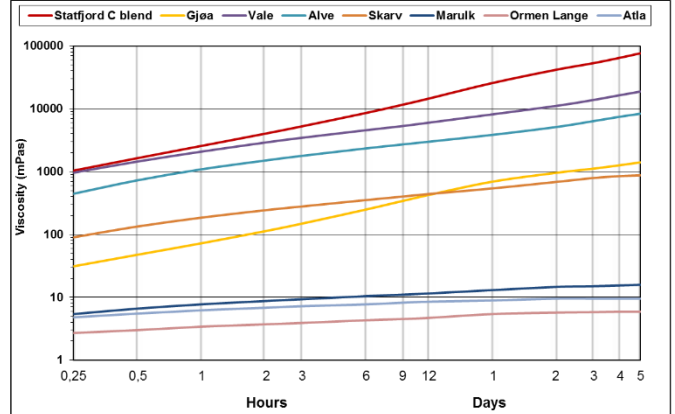
Comparison of water content for Statfjord C blend (ref. oil), Gjøa and Vale (light oils), and the condensates Alve, Skarv, Marulk, Ormen Lange and Atla at 2 and 13 °C with 2 and 5 m/s wind speeds.

C.4 Emulsion viscosity

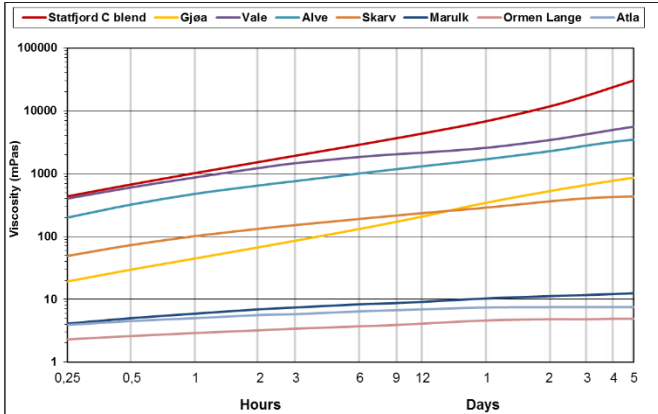
Property: Viscosity emulsion
 Wind speed: 2 m/s
 Temperature: 2°C



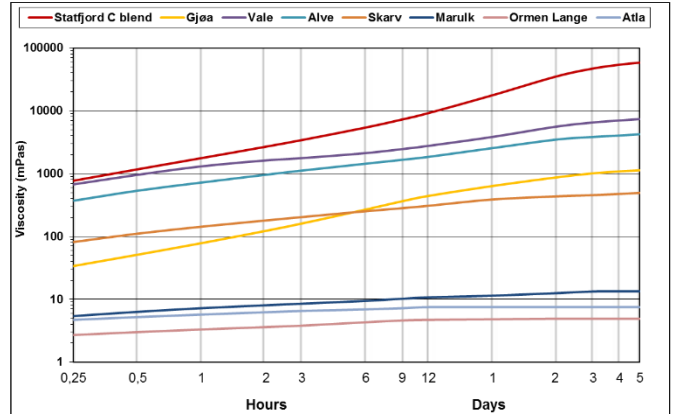
Property: Viscosity emulsion
 Wind speed: 5 m/s
 Temperature: 2°C



Property: Viscosity emulsion
 Wind speed: 2 m/s
 Temperature: 13°C



Property: Viscosity emulsion
 Wind speed: 5 m/s
 Temperature: 13°C

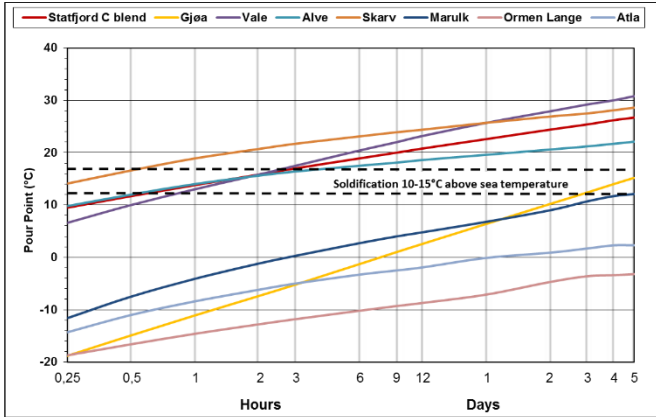


Comparison of emulsion viscosity for Statfjord C blend (ref. oil), Gjøa and Vale (light oils), and the condensates Alve, Skarv, Marulk, Ormen Lange and Atla at 2 and 13 °C with 2 and 5 m/s wind speeds.

C.5 Pour point

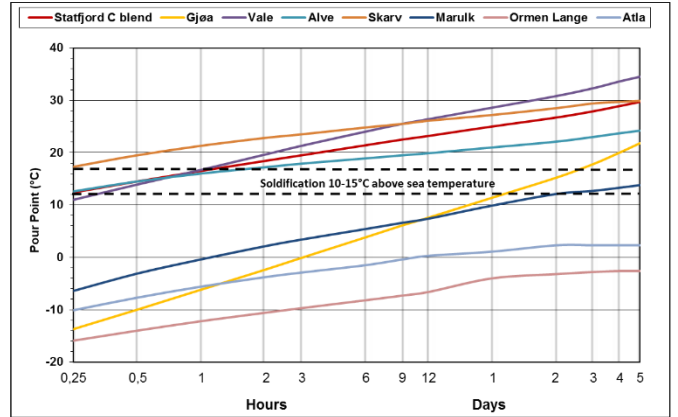
Property: Pour point
Wind speed: 2 m/s
Temperature: 2°C

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4.0 β © 2010
Pred. Date: March 2016



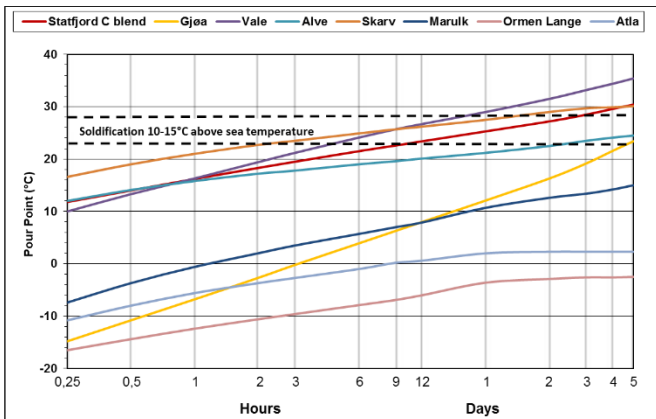
Property: Pour point
Wind speed: 5 m/s
Temperature: 2°C

SINTEF
4.0 β © 2010
Pred. Date: March 2016



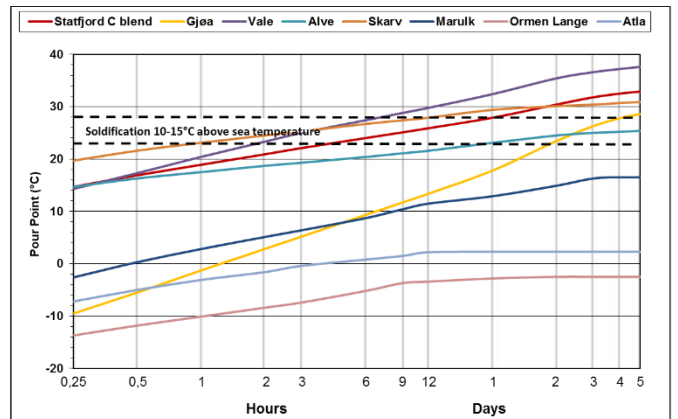
Property: Pour point
Wind speed: 2 m/s
Temperature: 13°C

SINTEF
4.0 β © 2010
Pred. Date: March 2016



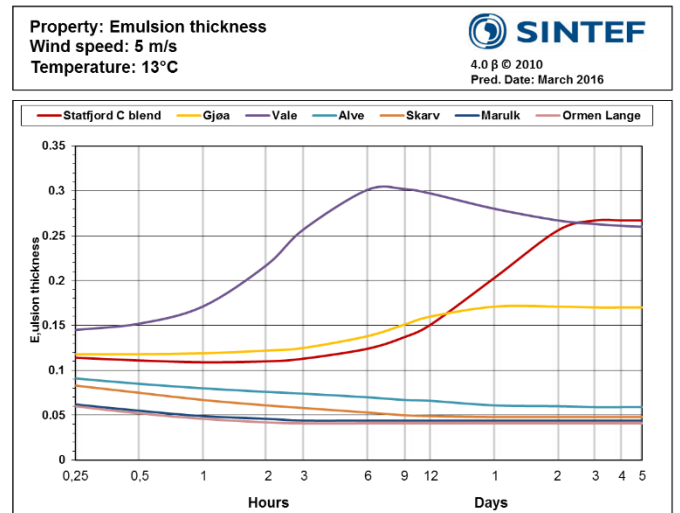
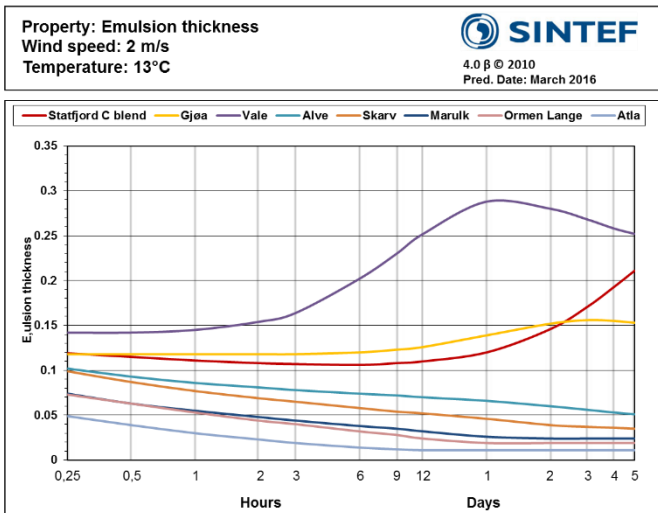
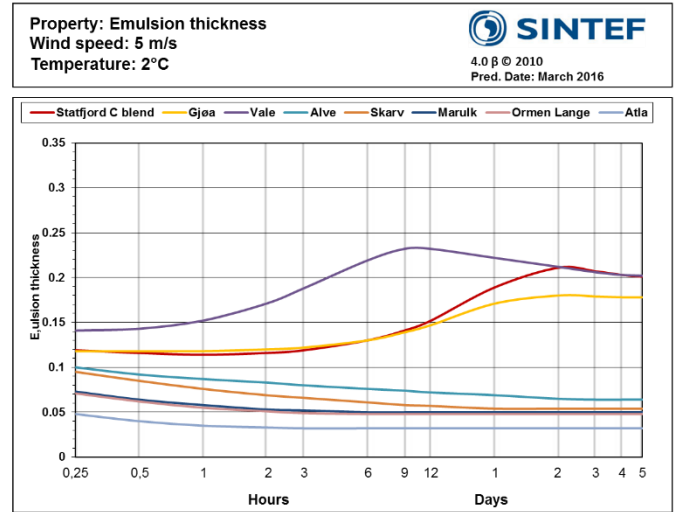
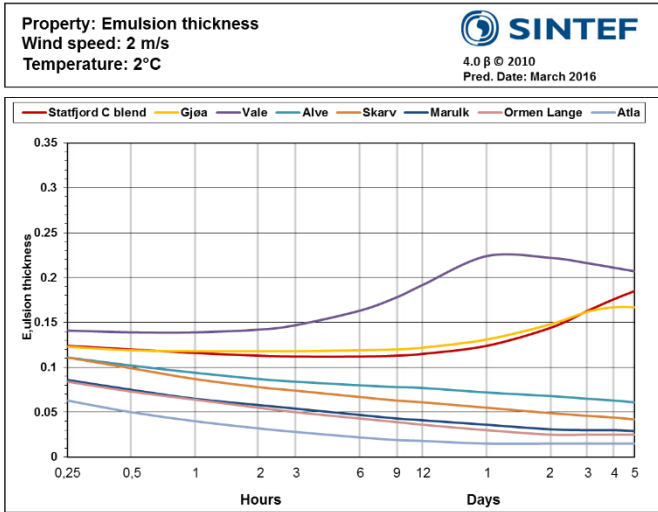
Property: Pour point
Wind speed: 5 m/s
Temperature: 13°C

SINTEF
4.0 β © 2010
Pred. Date: March 2016



Comparison of pour point for Statfjord C blend (ref. oil), Gjøa and Vale (light oils), and the condensates Alve, Skarv, Marulk, Ormen Lange and Atla at 2 and 13 °C with 2 and 5 m/s wind speeds.

C.6 Emulsion film thickness



Comparison of emulsion film thickness for Stafford C blend (ref. oil), Gjøa and Vale (light oils), and the condensates Alve, Skarv, Marulk, Ormen Lange and Atla at 2 and 13 °C with 2 and 5 m/s wind speeds.



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