Study of the oil interaction towards oil spill recovery skimmer material: Effect of the oil weathering and emulsification properties

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Abstract

The primary aim of this research was to identify the physicochemical properties of the oil and water-in-oil (W/O) emulsions used during a NOFO Oil-on-Water field trials that reduced the performance of the skimmers recovery efficacy during the trials. Extensive studies were performed at SINTEF laboratories with the residues of oil topped (i.e. evaporative loss of crude oil components by distillation process at large scale) for the field trial and compared it with different residues of oil topped by bench scale laboratory procedures. In order to obtain a sufficient stable W/O emulsion for the field trial, bunker fuel oil (IFO380) and various concentrations of an emulsifier (Paramul[®]) were also added to the residues of oil topped on large scale and investigated through interfacial tension, contact angle, droplet adhesion and "dip and withdraw" tests. The investigations revealed that the addition of an emulsifier lowered the interfacial tension of oil residues, which consequently reduced the adherence properties of the oil and emulsions to the surface of the skimmer material. Too high concentration of an emulsifier (> 0,5%) also had a negative effect on the stability of W/O emulsion.

Key words: Oil spill, Mechanical recovery, Oil adhesion, Interfacial tension, Oil weathering

1- Introduction

The goal of any response strategy during oil spill accidents is to select the effective and efficient countermeasures that minimize the overall impact of the oil spill on the environment. Net Environmental Benefit Analysis (NEBA) that was renamed as Spill Impact Mitigation Assessment (SIMA) is a structured approach that formalizes the evaluation and comparison of the expected response effectiveness versus the potential environmental impacts of the oil spill, as well as impacts from response options **(IPIECA-IOGP-API, 2017; Taylor et al., 2017, 2018; Camus and Smit, 2018)**. The output from the NEBA/SIMA process is the selection of response technique(s) that promote the most rapid recovery and restoration of the affected area, and consequently limit the overall impacts of a potential spill on the environment (IPIECA-IOGP-API, 2017). Mechanical recovery techniques (boom and skimmers) along with oil spill dispersants and in-situ burning are the main strategies that need to be assessed through a NEBA/SIMA process. Previous operational experiences for assessing the effectiveness of the use of multiple response techniques deployed during different oil spill situations (e.g. type of oil, release and environmental conditions) is an important part of such NEBA/SIMA process **(IPIECA-IOGP-API, 2017)**.

The efficacy and window of opportunity of mechanical oil spill cleanup operations in the marine environment will vary depending on many parameters such as: the selection of skimming principle, environmental conditions, response time, platforms, the boom confinement capacity, oil thickness in the boom, type and weathering degree of the oil. The effectiveness for use of different skimmers, related to the changes in oil properties is highly dependent on the interfacial tension between oil and water, oil stickiness/adhesiveness, rate of evaporation, photo-oxidation, W/O emulsification, water content and stability of emulsion, the subsequent increase in the

viscosity, and their effect on the various skimming principles **(Ornitz and Champ, 2002; Fingas, 2011)**. Depending on the physical mechanisms employed, skimmers can be categorized into the five main types: sorbent surface, weir, suction, elevating, and submersion. Comparatively, the skimmers using an oleophilic sorbent surface in the form of discs, drums, belts, brushes, or ropes are most suitable for rougher water that is characteristics of the open sea and coastlines **(Fingas, 2011)**.

Sorbent (oleophilic) skimmers are one of the most common types of mechanical recovery techniques. Recovery is based on the adhesion of the oil to a rotating oleophilic skimmer surface. The rotating surface lifts the oil out of the water to an oil removal device (e.g. scraper, roller, etc.) **(Fingas, 2011; Keller et al., 2007; Broje and Keller, 2006)**. The adhesion surface is the most critical element of the skimmer since it will have large influence on the effectiveness of the oil recovery. The materials used to manufacture the surface of adhesion skimmers are normally steel, aluminium and plastics. In general, material selection has not been based on the surface adhesive properties, but rather on historical practice, price and availability. Limited efforts are attempted to systematically study the surface properties of the skimmer materials and utilize this knowledge for improving the oil spill recovery processes **(Broje and Keller, 2005; Jokuty et al., 1996; Keller et al., 2007; Liukkonen et al., 1995; Sassi et al., 2017)**.

It is important to understand the oil chemistry as well as the physical processes associated with oil adhesion to the recovery surface. The adhesion between spilled oil and the recovery surface depends on the oil composition and its properties at the time of recovery; these characteristics change over time as the oils and emulsions weathered at sea. It was confirmed that certain oil properties, especially its viscosity, significantly influence on the oil adhesion to skimmer surface

and recovery efficiency **(Sassi et al., 2017; Broje and Keller, 2007a; Daling et al., 2003; Moldestad et al., 2006)**.

Over the past decades, intensive research on wettability and adhesion processes between solids and liquids has been conducted in the fields of petroleum reservoirs **(Buckley, 1997; Buckley et al., 1998; Drummond and Israelachvili, 2002; Jarrahian et al., 2012; Kathel and Mohanty, 2013)** and polymer sciences **(Jamadagni et al., 2009; Kobayashi et al., 2012; Mittal, 2009)**. Although polymeric materials have been tested for their affinity to various chemicals, their affinity to weathered oil and W/O emulsions has barely been studied. **Jokuty et al., (1996, 1995)** and **Liukkonen et al. (1995)** employed "dip-and-withdraw" technique to determine the adhesion between oil and test materials. Adhesion was determined as the weight of oil remaining after withdrawal, per unit area of a test surface.

Contact angles of liquids on solid surfaces are widely used to predict wetting and adhesion properties of materials **(Zhang et al., 2016; Dunderdale et al., 2015; Mittal, 2009)** . The research conducted at the University of California, Santa Barbara, showed that modern Dynamic Contact Angle Analyzer can be used for selection of materials that can be most efficiently employed during the oil spill cleanup operations **(Broje and Keller, 2007b, 2005)**. The study found that the contact angle formed between oil and test surface can be used to characterize the affinity of material to oil. It was recommended that to find the relationship between the oil properties and recovery materials, contact angle measurements can be performed along with "dip and withdraw" tests **(Broje and Keller, 2007b)**.

According to Norwegian regulations, the capabilities and functionalities of oil spill counter measuring methods should be documented through realistic field test conditions. Since 1978, Norwegian Clean Seas Association for Operating Companies (NOFO) has performed full scale, Oil-on-Water field verifications, almost on a yearly basis. In 2013, NOFO performed field trials in the North Sea where one of the main objectives was to verify newly developed oil spill response equipment under realistic conditions and documented its recovery capacity. For representing a crude oil weathered at sea for minimum 0.5 – 2 days under the breaking wave conditions with a viscosity of 2500 – 3000 cP, the W/O emulsion was prepared from the crude oil topped to 190 ^{o}C+ residue (i.e. evaporative loss of light hydrocarbon components of crude oil by distillation process below 190 ^{o}C) at large scale vacuum distillation facility. To increase the viscosity and stability of the W/O emulsion, NOFO decided to add (spiked) 5 wt.% of bunker fuel oil (IFO380) and 0.37 wt.% of the commercially available emulsifier (Paramul®) to the crude oil residue before preparing the W/O emulsion where 65 wt.% of seawater was mixed into the oil residues using centrifugal pumps. During the field verifications, it was found that the skimmer was not adequately effective and the W/O emulsion was not properly trapped and recovered by the discs of the skimmer **(NOFO, 2013)**.

After the field verification, SINTEF was contacted by the NOFO and requested to test the effectiveness and physicochemical properties of W/O emulsion that was used during the full-scale field trials. At SINTEF, there has been continuous R&D activities on oil spill weathering and behavior of oils and W/O emulsions at sea since the Ekofisk Bravo accident in the North Sea, Norway, in 1977 **(Daling et al., 1990, 1999, 2003, 2014)**. The purpose within this study was to identify the properties of the tested oil and W/O emulsion used during the 2013 field trial and to

determine if the results could clarify the reduced performance of the skimmers. Systematic laboratory studies with the residues of the oil topped at large scale (for the field trial) were performed and compared with different residues of the oil topped on smaller scale at the SINTEF laboratory. To mimic the oil residue used for preparing the W/O emulsion during the NOFO field trials, the residue from the large-scale topping of the oil (for the field trial) was tested with addition of bunker fuel oil (IFO380) and various concentrations of the emulsifier Paramul®. A disc from the skimmer (High Density Polyethylene, HDPE) used during the field trial was cut into different sizes and tested to study the adhesion properties of different oil residues and their emulsions.

2- Experimental

2.1. Evaporation of crude oil

For preparing the different oil residues, crude oil was evaporated (topped) by following two different approaches and scales.

2.1.1. Evaporation of crude oil at small laboratory scale

Crude oil was evaporated at small scale in the SINTEF laboratory by following a procedure described by **Stiver and Mackay (1984)**. Evaporation of the lighter compounds from the fresh crude oil was carried out in a simple one-step distillation to vapour temperatures of 190 ^{o}C+ and 225 ^{o}C+, which resulted in remaining topped residues with an evaporation loss (depending on environmental conditions) corresponding to approximately 1 - 3 hours to < 1 day of oil weathering on the sea surface, respectively. These residues are referred to as Oseberg oil small scale weathering (OB-SSW) 190 ^{o}C+ and OB-SSW 225 ^{o}C+ throughout the paper. It is important to mention that the described method have been accepted at several oil spills research laboratories to generate artificial residues that simulate evaporative loss of spilled oils at sea **(Daling et al., 2014)**.

2.1.2. Evaporation of crude oil at large scale

For preparation of the artificial weathered oil used in the NOFO field trials 2013, crude oil was evaporated on large scale by the vacuum distillation facilities at Indus AS, Arnatveit, Norway. This was done by vacuum distillation in a closed system, and the oil was evaporated equivalent to 190 ^{o}C+ steam temperature. The 190 ^{o}C+ weathered residue of crude oil that was evaporated based on the vacuum distillation large scale method, is referred as OB-LSW 190 ^{o}C+ in this

paper. This was the same topped oil residue which was provided to NOFO for preparing the W/O emulsion used during the Oil-on-Water field verification in 2013.

2.2. Adding of bunker fuel oil and emulsifier

For obtaining a stable W/O emulsion to be used during the field trial in 2013, NOFO had added (spiked) 5 wt.% bunker fuel oil (IFO380) and the emulsifier Paramul® to the weathered crude oil residue (OB-LSW 190 °C) received from the large-scale facilities at Indus AS. To study the potential effect of this addition, in the SINTEF laboratory different samples of the OB-LSW 190 ^{o}C+ residue was prepared with successive addition of IFO380 and the emulsifier Paramul®.

A sample of the large scale 190 ^{o}C+ weathered residue of crude oil (LSW-190°C+) that was received by SINTEF for testing, added with 5 wt.% IFO380. This spiked oil sample was further mixed with 0.37 wt.% and 0.75 wt.% of an emulsifier Paramul®. The addition was done by heating the topped oil sample and IFO380, and afterwards mixed the oils in specified proportion. After mixing, the blended oil was further heated at 50 ^{o}C for one hour and then put on shaking for one hour for homogenization of the sample.

2.3. Preparation of emulsions and stability test

The different oil residues were emulsified (W/O emulsification with 65 wt.% water content) by rotating cylinder method developed by **Mackay and Zagorski (1982)**, which is described in detail by **Hokstad et al. (1993)**. This method also includes the measuring of the viscosity and the stability of the W/O emulsions. All W/O emulsions were prepared and tested at 10 ^{o}C.

The principle of the rotating cylinders method is illustrated in Fig. 1. Oil (105 mL) and seawater (195 mL) were mixed and rotated with a rotation speed of 30 rpm in separating funnels (0.5 L).

For testing the stability of the prepared emulsions, the water content was determined twice, first after 24 hours of rotation and subsequently after another 24 hours of settling time.

2.4. Cutting the disc of skimmer

A disc of polyethylene from skimmer drum used during the 2013 Oil-on-Water field verification was received from NOFO. This disc was cut into small (2.4 x 1.8 cm) and bar (2.4 x 15 cm) shaped pieces. Small pieces (Fig. 2) were used for droplet adhesion tests while bar shaped pieces (Fig. 3) were used for "dip and withdraw" test with emulsions.

2.5. Overview of samples

The different topped oil residues and their corresponding densities are given in Table 1 while the different W/O emulsions prepared during this study and their viscosities measured after 24 hours of rotation are given in Table 2.

2.6. Chemical characterization by GC/FID

The GC/FID analyses were performed according to a modification of EPA Method 8015D (**US EPA, 2003**). The distribution of hydrocarbons was analysed by using a Gas Chromatograph coupled with a Flame Ionisation Detector (GC/FID). The GC/FID system comprised with an Agilent 6890N GC with a 30m DB1 column.

2.7. Physical characterization by various methods

Analytical methods used for measurement of physical properties of oils and emulsions are listed in Table 3 and are described below.

2.7.1 Interfacial tension measurements by Pendant drop method

A drop shape analysis system (DSA100, KRUSS GmbH) was used to measure the interfacial tension between different oil residues and seawater **(Buckley and Fan, 2005)**. The aqueous phase was kept in a standard cuvette and an oil drop was immersed into the solution by an inverted syringe connected to a needle (Fig. 4). The syringe was equipped with a valve to close off the sample volume in the needle from the syringe in order to ensure constant drop volume (8-10 µl). The measurements were initiated immediately after preparation of the drop, and the drop profiles were recorded with one image per second continuously for 5 minutes. The interfacial tension was calculated by fitting the drop profiles to the Young-Laplace equation, using the densities of the liquids as input parameters. All measurements were performed at room temperature with reproducibility within a range of ±0.1 mN/m.

2.7.2. Droplet adhesion test

A drop shape analysis system (DSA100, KRUSS GmbH) was used to analyse the adhesion between the droplet of oil residue and surface of disc skimmer in the presence of seawater. The droplet adhesion test is described in detail by **Buckley et al. (1989, 1997)**. A piece of disc skimmer was cut and cleaned with dichloromethane (DCM) and deionized water (Milli-Q™). The piece was immersed in seawater and kept in a standard cuvette. A single drop (15µl) of the oil was applied to the surface of the disc skimmer by using a Gilmont buret. The size of the drop was slightly increased causing the drop to expand over the surface. Contact time of 2 minutes was allowed for standard measurements (Fig. 5A). After 2 minutes, the drop was retracted (Fig. 5B), - and the volume and contact angle of the droplet attached to the skimmer surface was measured. All measurements were done at ambient temperature under the presence of seawater.

2.7.3. Contact angle measurements after Droplet adhesion test

The contact angle measurements were performed on the surface of the disc skimmer after finishing the adhesion experiments. The disc surface remained in seawater and the contact angles were determined at the water/solid/oil interface at room temperature. The three-phase contact angle was determined by using an Optical Contact Angle Meter with a high-speed camera (DSA100, KRUSS GmbH). The contact angles were determined by fitting the Young-Laplace equation to the drop profile, with the tangent line as the limiting factor for reproducibility. The reported contact angles were obtained at equilibrium conditions and the mean values of the left and right contact angles. Furthermore, the standard error was less than 5%.

2.7.4. "Dip and withdraw" test

To study the adhesion properties of different oil emulsions, bars of disc skimmer were used. This technique was developed by **Jokuty et al. (1996, 1995)** and **Liukkonen et al. (1995)**. Prior to start the measurements, bars of disc skimmer were cleaned with dichloromethane (DCM) and deionized water (Milli-Q™) and afterwards blown dried with nitrogen. The bars were immersed into seawater for 15 seconds before being immersed into a container of oil emulsion for 30 seconds and subsequently installed vertically with clamps for 30 minutes for run off excess oil. A "dip and withdraw" test is illustrated in Fig. 6. Excess oil was collected in an aluminium dish. To quantify the amount of the adhered emulsion after the runoff phase, the bars of disc skimmers and the aluminium dishes were weighed before and after exposure to an emulsion. All measurements were made at 10 $^{\circ}$C.

3. Results and discussion

The chemical composition of the fresh Oseberg (OB) crude oil characterized by gas chromatography (GC/FID) suggested that the oil is a paraffinic crude oil (Fig. 7). The gas chromatograms showed the n-alkanes as systematic narrow peaks. The initial peaks in the chromatograms represented the components with the lowest boiling points. Some of the more complex components, such as resins and naphthenes appeared as a broad and poorly defined bump below the sharp peaks, and often described as an "Unresolved Complex Mixture" (UCM) of hydrocarbons. However, heavier compounds such as asphaltenes ($>nC_{40}$) were not possible to analyse with this technique. The gas chromatographic characterization of the hydrocarbon distribution of the corresponding residues (190 °C+ and 225 °C+) verified the very similar evaporation (topping) of the oil through distillation on small (laboratory scale) and large scale.

Crude oil and its different topped residues were also characterized by interfacial tension (IFT) measurements (Fig. 8). The results indicated that the oil topped on large scale (OB-LSW 190 °C+) displayed slightly lower interfacial tension compared to the oil that is topped on the small laboratory scale (OB-SSW 190 °C+). Moreover, the addition of 5 wt.% IFO380 into the oil residue weathered at large scale (OB-LSW 190 ^{o}C+) had no influence on the IFT and both residues displayed the same IFT behavior. However, the addition of an emulsifier lowered the IFT significantly. The reduction was more profound by addition of 0.75 wt.% of emulsifier in the OB-LSW 190 ^{o}C+ + 5 wt.% IFO380 residue than by addition of 0.37 wt.% of the emulsifier, - and IFT was decreased by a factor of 10 (from typically 10-20 mN/m to < 1 mN/m). Such a low IFT is not representative for indigenous crude oils. Emulsifiers are amphiphilic in nature and have a hydrophobic part that has an affinity for oil and a hydrophilic part that has an affinity for aqueous phase. Because of their amphoteric structure they tend to concentrate at oil/water

interface and thereby reduces the IFT. Low IFT may enhance the natural dispersion and subsequently increase the risk for boom leakage and less adhesion of the oil to the recovery surface of the skimmer. Interfacial tension is an important factor in the initial adhesion of oil to the recovery surface **(Broje and Keller, 2007b)**. Under typical conditions, the skimmer's drum rotates first into the oil, and then lifts the oil towards the scraper. Interfacial tension plays an important role in wetting the recovery surface during the first rotation. However, oil viscosity and cohesive forces also become important as the oil is transported up to the scraper, since these factors control the thickness of the oil on the recovery surface and significantly influence the overall recovery rates.

In this study, some of the topped (evaporated) and spiked residues of crude oil with IFO380 and emulsifier were also tested by droplet adhesion test on the surface of the disc skimmer under the presence of seawater (Fig. 9). The results indicated that the more extensively topped residue (OB-SSW 225 °C+) was adhered more to the surface of the disc skimmer compared to the OB-LSW 190 °C+ residue. The addition of the 5 wt.% IFO380 into the OB-LSW 190 °C+ residue increased the volume of the oil droplet adhered to the disc surface. However, the presence of an emulsifier in OB-LSW 190 °C+ +5 wt.% IFO380 fraction drastically reduced the adherence properties of the oil droplet and within a few seconds, the oil droplet was released from the disc surface (Fig. 10). The reduction of interfacial tension reduced the size of the oil droplet, which eventually released the oil from the disc surface. It is important to mention that for the droplet adhesion tests, same volume of oil droplet (15 µL) was applied to the disc of the skimmer each time. Moreover, as shown in Table 1, densities of the residues of topped crude oils before and after spiking with different concentrations of an emulsifier was very much similar. This implies that during adhesion experiments, the effect of inertial forces (i.e. buoyancy or gravitational

forces) applies on the oil droplets are considered to have equal effect and does not influence the release of oil droplet from the disc surfaces.

The contact angle measurements performed after the adhesion test indicated that the OB-SSW-225 °C+ topped fraction of crude oil showed comparatively low contact angle ($\theta = 69°$) and high wettability on the disc surface compared to OB-LSW 190 °C+ topped residue spiked with 5 wt.% IFO380 ($\theta = 82°$), Fig. 11 (a, b). It is previously reported **(Broje and Keller, 2005)** that contact angle value is more influenced by the interaction at oil-test surface interface and lower contact angles enhances the recovered mass of the oil. The lower contact angle values of the OB-SSW-225 °C+ oil residue showed its more interaction towards the disc material as compared to OB-LSW 190 °C+ topped residue spiked with 5 wt.% IFO380. Furthermore, it was not possible to compare the contact angles of the OB-LSW 190 °C+ +5 wt.% IFO380 spiked with 0.37 wt.% and 0.75 wt.% emulsifier as most of the adhered oil was released from the surface of the disc just after few seconds of adherence, Fig. 11 (c, d).

As described previously, W/O emulsions were prepared from different topped and spiked residues and viscosities were determined after 24 hours of mixing of emulsions at 10 °C, Table 2. The results indicated that the viscosities of different prepared emulsions were in a wide range of 500-2800 cP (measured at shear 10 s^{-1}). Such viscosities are representative for Oseberg crude oil that has been between 3 hours to < 1 day at sea surface (under breaking wave conditions, see SINTEF oil weathering model predictions at 10 m/s wind speed, Fig. 12,). The SINTEF oil weathering model (SINTEF-OWM) (Daling and Strøm, 1999) is a tool that predicts the changes in the oil properties and its behaviour on the sea surface due to weathering under chosen set of conditions (oil/water-in-oil emulsion film thickness, sea state and temperature). The predictions

from the SINTEF OWM also showed that 190 °C+ weathered residue (representing only 1-3 hours of evaporative loss on the sea surface at 5-10 m/s wind conditions) of Oseberg oil is not sufficiently evaporated as compared to the 225 °C weathered residue (representing 0.5-2 days of evaporative loss), Fig. 13.

Emulsion stability tests were also performed by the rotating cylinder method on various emulsions after 24 hours of rotation and 24 hours of settling phase at 10 ^{o}C and results are shown in Table 4. All emulsions remained stable after 24 hours of settling phase except the emulsion that contained 0.75 wt.% of an emulsifier.

The overall results indicated that the viscosity of OB-SSW 225 ^{o}C+ emulsion is relatively high (2719 cP) compared to the less topped oil (190°C+) emulsions (ca. 1421 – 1650 cP), Table 2. Spiking of the OB-LSW 190 °C+ + 5 wt.% IFO380 with an emulsifier at a concentration of 0.37 wt.% relative to the oil, seemed to give a slightly higher viscosity (1773 cP). However, doubling in the concentration of an emulsifier (0.75 wt.%), showed a dramatic reduction in emulsion stability (settling out of water from 65% to a 24% W/O-emulsion, Table 4) and subsequently also resulted in a much lower emulsion viscosity. It is also important to mention that other than the emulsion that was prepared after spiking of the OB-LSW 190 °C+ + 5 wt.% IFO380 with an emulsifier at a concentration of 0.37 wt.%, - stabilities of all emulsions were very temperature sensitive. When raising the ambient temperature by 5 °C only (from 10 °C to 15 °C), the emulsions were destabilized and separated into oil and water phases (results not shown).

Determination of the adhesion of W/O emulsions to the disc of the skimmer was also performed by the "dip and withdraw" technique at 10 °C (Fig. 14), as previously described. The results of an

emulsifier (Paramul®) free emulsions of topped oil residues were highly influenced by their viscosities and degree of oil weathering. However, the results of emulsions containing different concentrations of emulsifier Paramul® were more dependent on its amount of addition. The results showed that the emulsion prepared from 225 °C+ residue of oil topped on small scale relatively showed the highest adhesion to the disc of the skimmer. The emulsion prepared from OB-LSW 190 °C+ residue observed significantly lower adhesion properties. Furthermore, the addition of IFO380 to the OB-LSW 190 °C+ residue showed some improvement in adhered amount of the emulsion due to increase in its viscosity, but still significantly less than the adhered amount of emulsion prepared from OB-SSW 225°C+ topped residue of oil. The presence of an emulsifier relatively decreased the adhesion properties of the emulsion to the disc surface. With increase of the concentration of an emulsifier Paramul® in OB-LSW 190 °C+ + 5 wt.% IFO380 residue, the adhered amount was even more decreased.

Comparison of the results obtained by droplet adhesion test with topped and spiked oils and by "dip and withdraw" test on W/O emulsions indicated the same trend. Both tests revealed that the presence of emulsifier in the oil residues and emulsions significantly reduced the adhesion properties. The amphiphilic components of the emulsifier are surface active which may reduce the adhesive forces between the oil and the polymeric surface of the disc.

4. Conclusions and recommendations

The overall results indicated that the crude oil topped on large scale vacuum distillation was not sufficiently evaporated to generate W/O emulsion with sufficient stability and viscosities at prevailing seawater temperatures (e.g. 10 °C). It is concluded from the results that crude oils should be topped to a minimum of 220-240 °C+ residue to give stable emulsions with viscosities

of minimum 2500 – 3000 cP. Furthermore, it is concluded that when oil or its residues were spiked with an emulsifier, it lowered the interfacial tension. Reduction in the interfacial tension significantly decreased the adherence properties of the W/O emulsion to the surface of the tested recovery material.

For the significant documentation on the feasibility and functionality of different countermeasure techniques deployed during the oil spills, it is important to consider the type and properties of the oils and emulsions used during such field trials. During the test with adhesion skimmers, it is significant to use oils/emulsions with viscosities that are within the range for which the skimmer is customized for. Controlled laboratory / basin test should be carried out prior to full-scale functionally testing in the field.

During this study, besides using standardized methodologies to characterize and predict the physical and emulsification properties of crude oils weathered at sea surface, methods for characterizing the oil-water interfacial tension and adhesion of the oil/emulsion to a relevant substrate (surface materials) of adhesion skimmers are also successfully performed. These methods have shown valuable quantitative parameters to characterize those properties of oil/emulsions that are relevant for evaluating the effectiveness of skimmers. Therefore, it is recommended to consider these test parameters for future functionality testing of oil spill response technologies and response strategies.

Table 1
Overview of the oils and their densities

Name of oils	Densities (g/m^3)
Oseberg oil (OB) Fresh	0.83
OB-SSW 190 ^{o}C+	0.88
OB-SSW 225 ^{o}C+	0.89
OB-LSW 190 ^{o}C+	0.88
OB-LSW 190 ^{o}C+ + 5 wt.% IFO380	0.88
OB-LSW 190 ^{o}C+ + 5 wt.% IFO380 + 0.37 wt.% emulsifier	0.88
OB-LSW 190 ^{o}C+ + 5 wt.% IFO380 + 0.75 wt.% emulsifier	0.88

Table 2
Overview of the oil emulsions and their viscosities measured by shear 10s^{-1} at 10 °C after 24 hours of rotation

Name of oil Emulsions	Water Content (%)	Viscosity (cP)
OB-SSW 225 ^{o}C+	65	2719
OB-LSW 190 ^{o}C+	65	1421
OB-LSW 190 ^{o}C+ + 5 wt.% IFO380	65	1650
OB-LSW 190 ^{o}C+ + 5 wt.% IFO380 + 0.37 wt.% emulsifier	65	1773
OB-LSW 190 ^{o}C+ + 5 wt.% IFO380 + 0.75 wt.% emulsifier	24	513

Table 3
Analytical methods for measurement of physical properties

Physical Analysis	Analytical Method	Instruments
Viscosity	McDonough et al., 1995	Physica MCR 300
Density	ASTM method D4052-81	Anton Paar, DMA 4500
Interfacial tension	Pendant drop method	Drop shape analysis system DSA100, KRUSS GmbH
Adhesion test of oil droplet with substrate	Oil droplet adhesion testing method by Buckley et al. (1989, 1997)	Drop shape analysis system, DSA100, KRUSS GmbH
Contact Angle	Sessile drop method	Drop shape analysis system, DSA100, KRUSS GmbH

Table 4
Stability of various emulsions after 24 hours of mixing + 24 hours of settling

Samples	Free water initial (ml)	Oil Initial (ml)	Free water 24 hrs mix. (ml)	Oil/Emulsion 24 hrs mix. (ml)	Free water 24 hrs mix. +24 hrs rest (ml)	Oil/Emulsion 24 hrs mix. +24 hrs rest (ml)	Free water 24 hrs mix. +24 hrs rest +10 rotations (ml)	Oil/Emulsion 24 hrs mix. +24 hrs rest +10 rotations (ml)
OB-SSW 225 °C+	195	105	0	300	0	300	0	300
OB-LSW 190 °C+	195	105	0	300	0	300	0	300
OB-LSW 190 °C+ + 5 wt.% IFO380	195	105	0	300	0	300	0	300
OB-LSW 190 °C+ + 5 wt.% IFO380 + 0.37 wt.% Emulsifier	195	105	0	300	0	300	0	300
OB-LSW 190 °C+ + 5 wt.% IFO380 + 0.75 wt.% Emulsifier	195	105	162	138	162	138	162	138
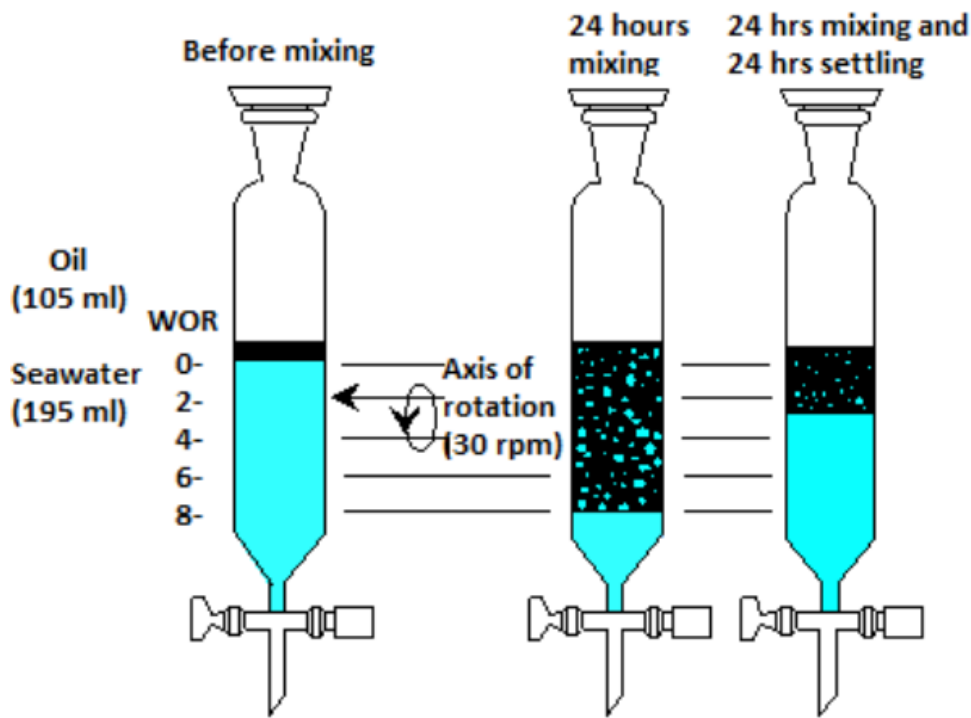
Fig. 1. Principle of the rotating cylinder method
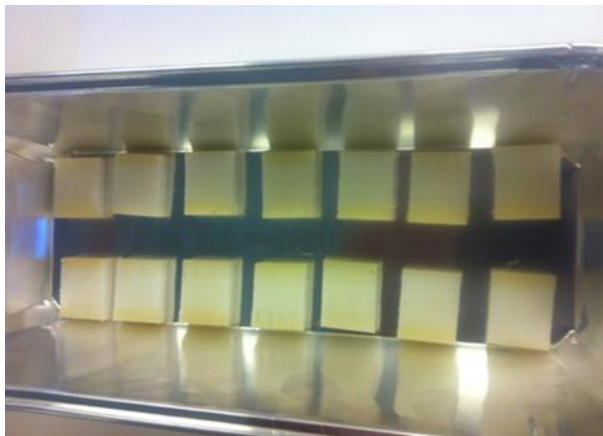
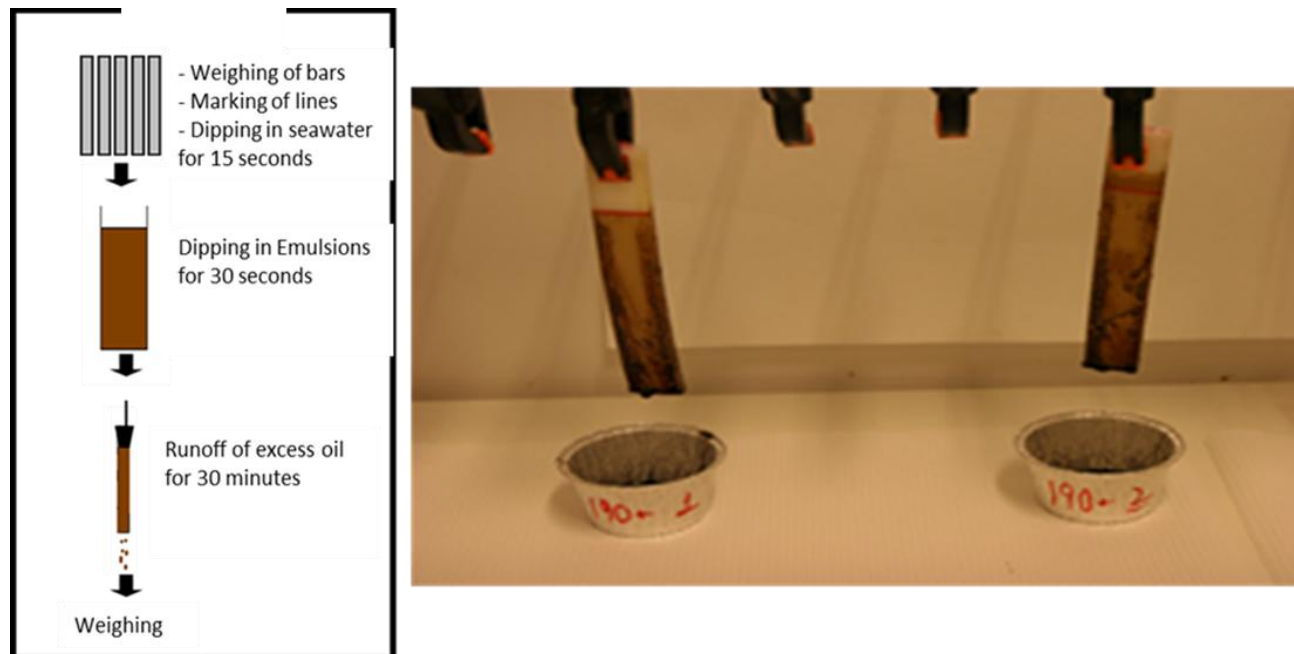**Fig. 2.** Small pieces of disc (2.4 x 1.8 cm) used for adhesion tests

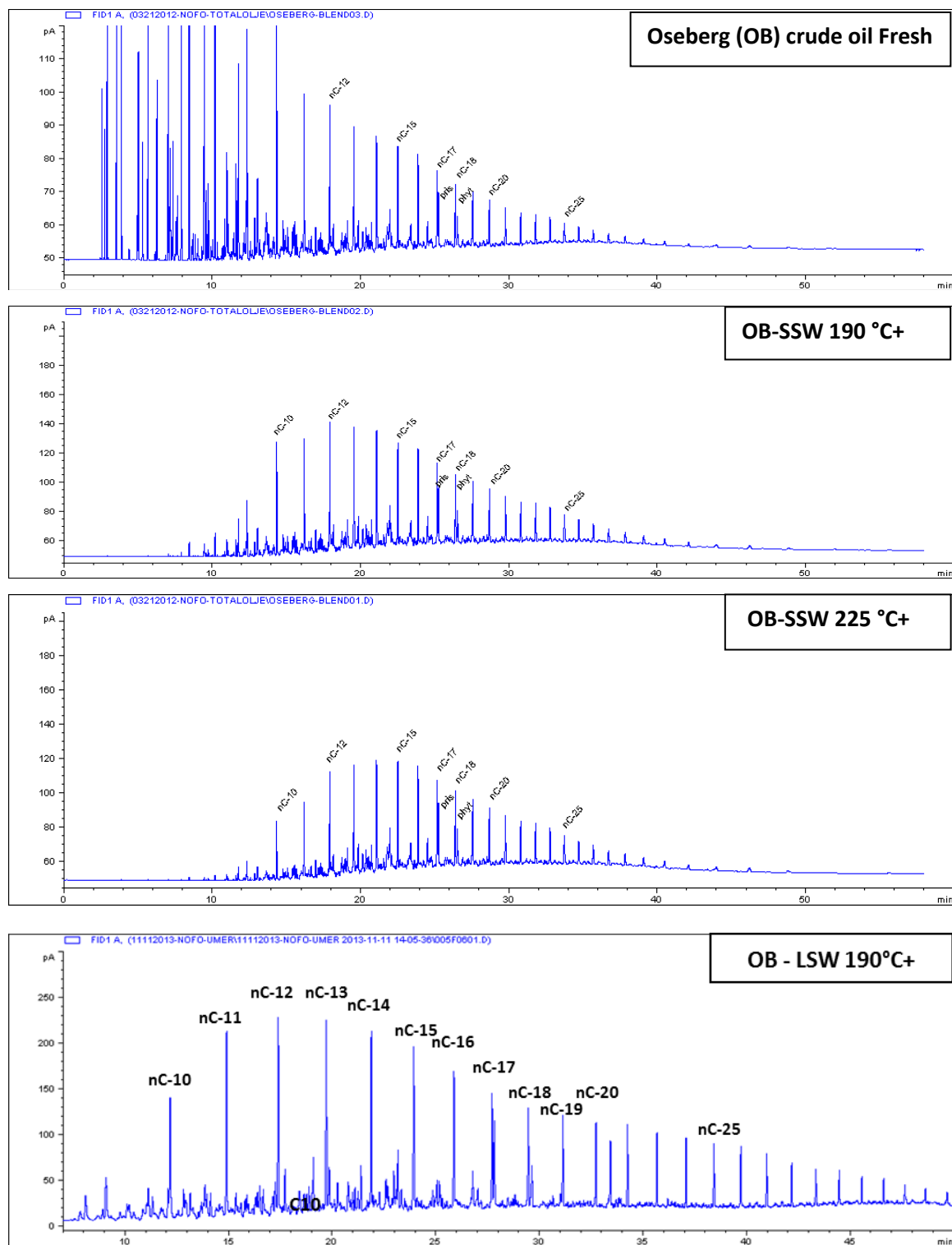**Fig. 3.** Bars of disc (2.4 x 15 cm) used for "Dip and withdraw" test
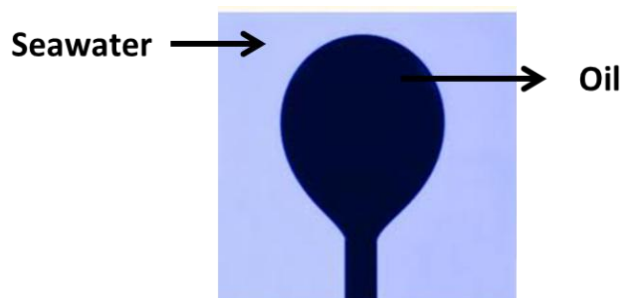
Fig. 4. Interfacial tension measurement by Pendant drop method
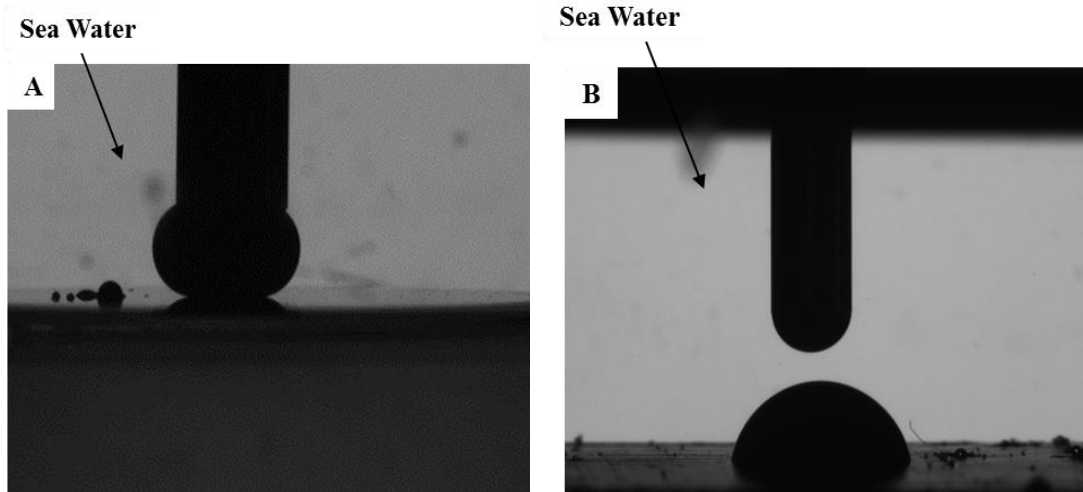
Fig. 5. Pictorial representation of the droplet adhesion test. A) Contact of oil droplet with disc surface for 2 minutes B) Oil droplet retracted, after 2 minutes

Fig. 6. Pictorial representation of the "Dip and withdraw" test

Fig. 7. GC/FID chromatograms of the various oil samples (NB! The GC analysis of OB-LSW 190 ^{0}C+ has shown a slightly different retention time as compared to the other upper GC-chromatograms)
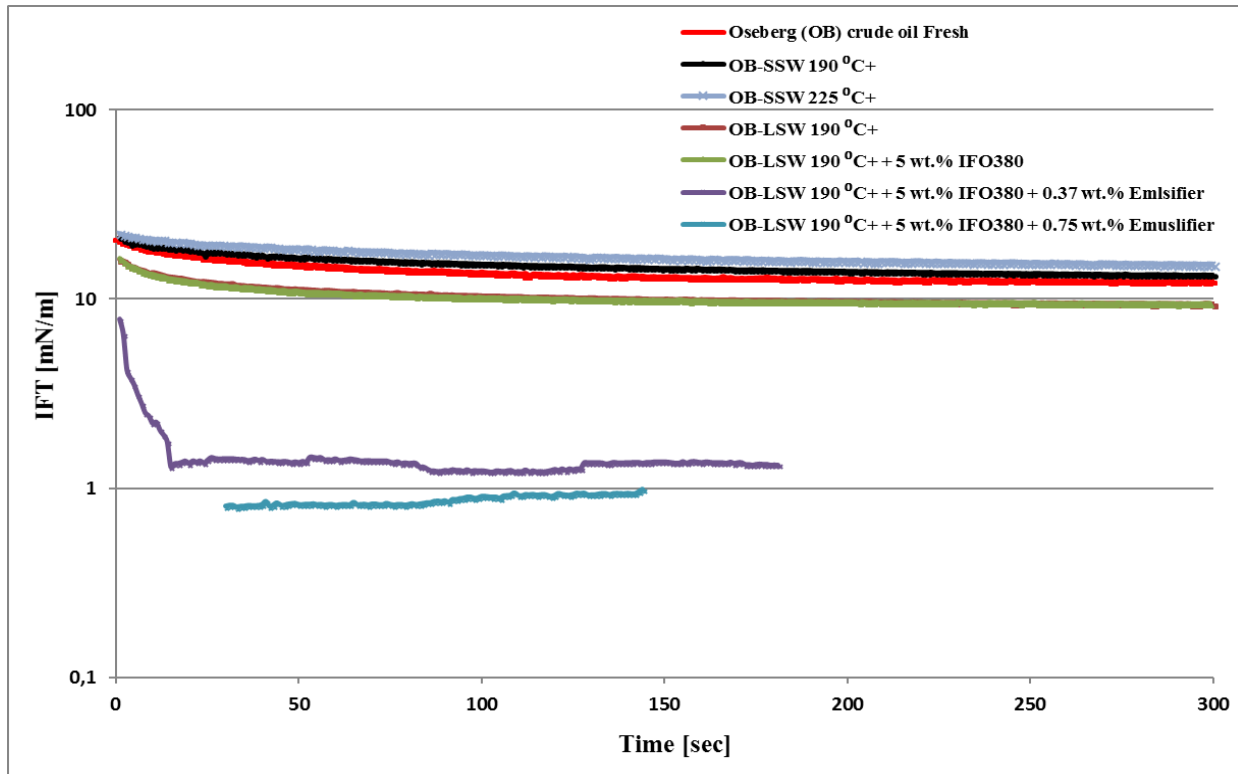
Fig. 8. Interfacial tension decay of various oil samples and residues with respect to time
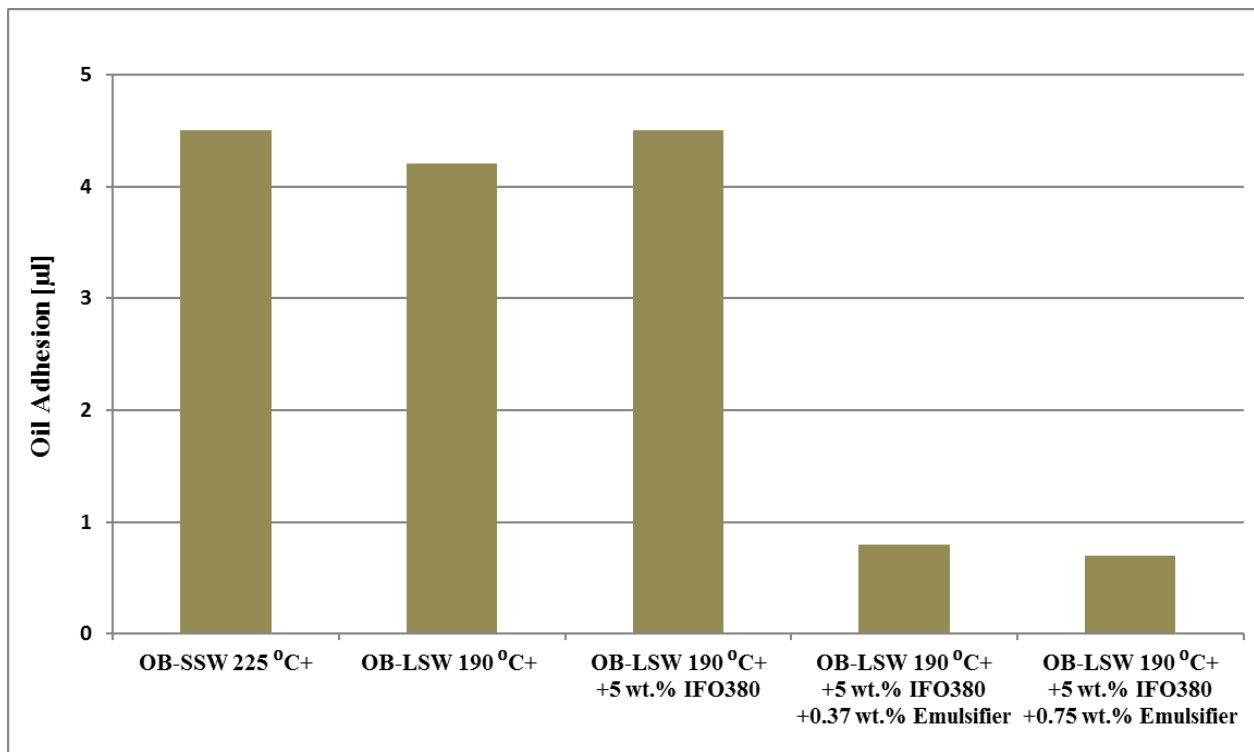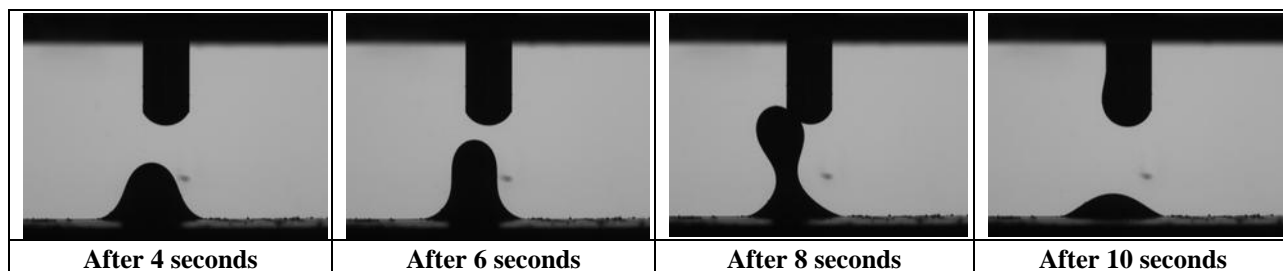

Fig. 9. Adhered volume of oil droplet (water free) with surface of the disc of skimmer at room temperature

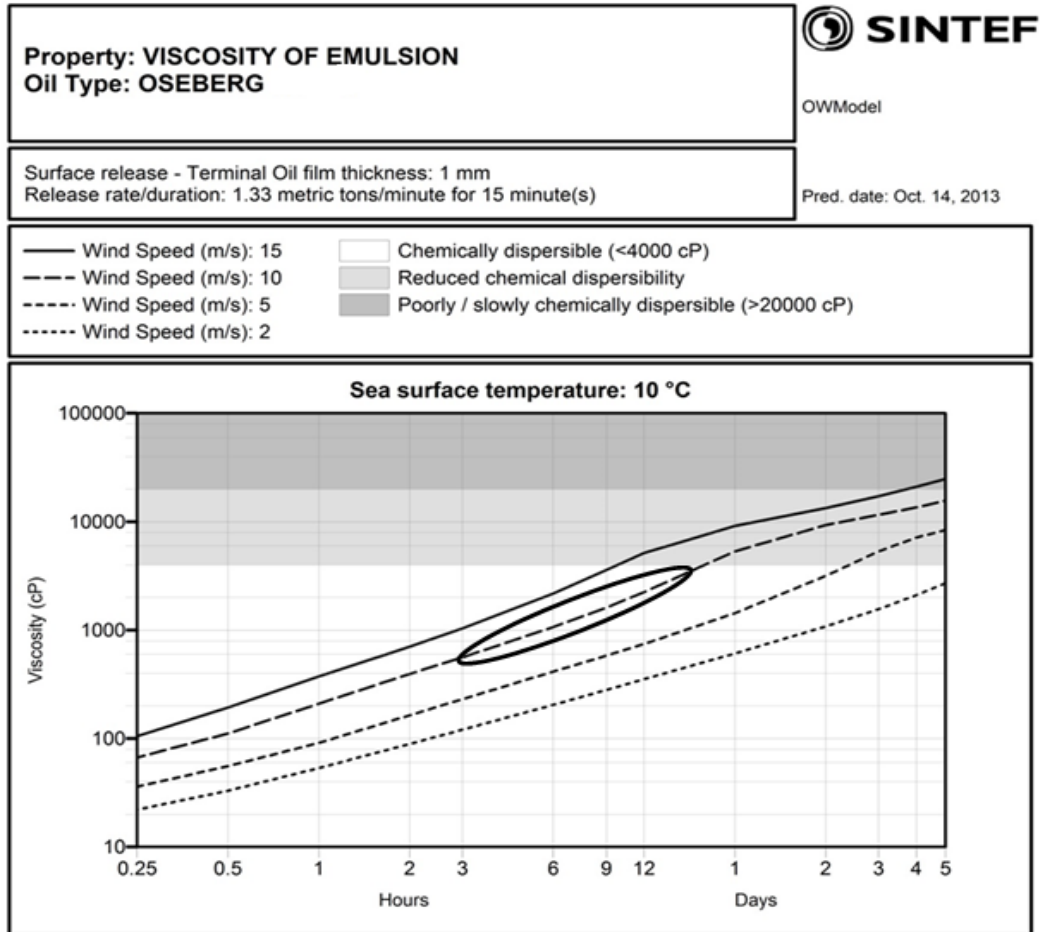| After 4 seconds | After 6 seconds | After 8 seconds | After 10 seconds |

Fig. 10. The sequences of photos showing the release of oil droplet (OB-LSW 190 °C+ +5 wt.% IFO380 + 0.37 wt.% emulsifier) after adhesion to the surface of disc.
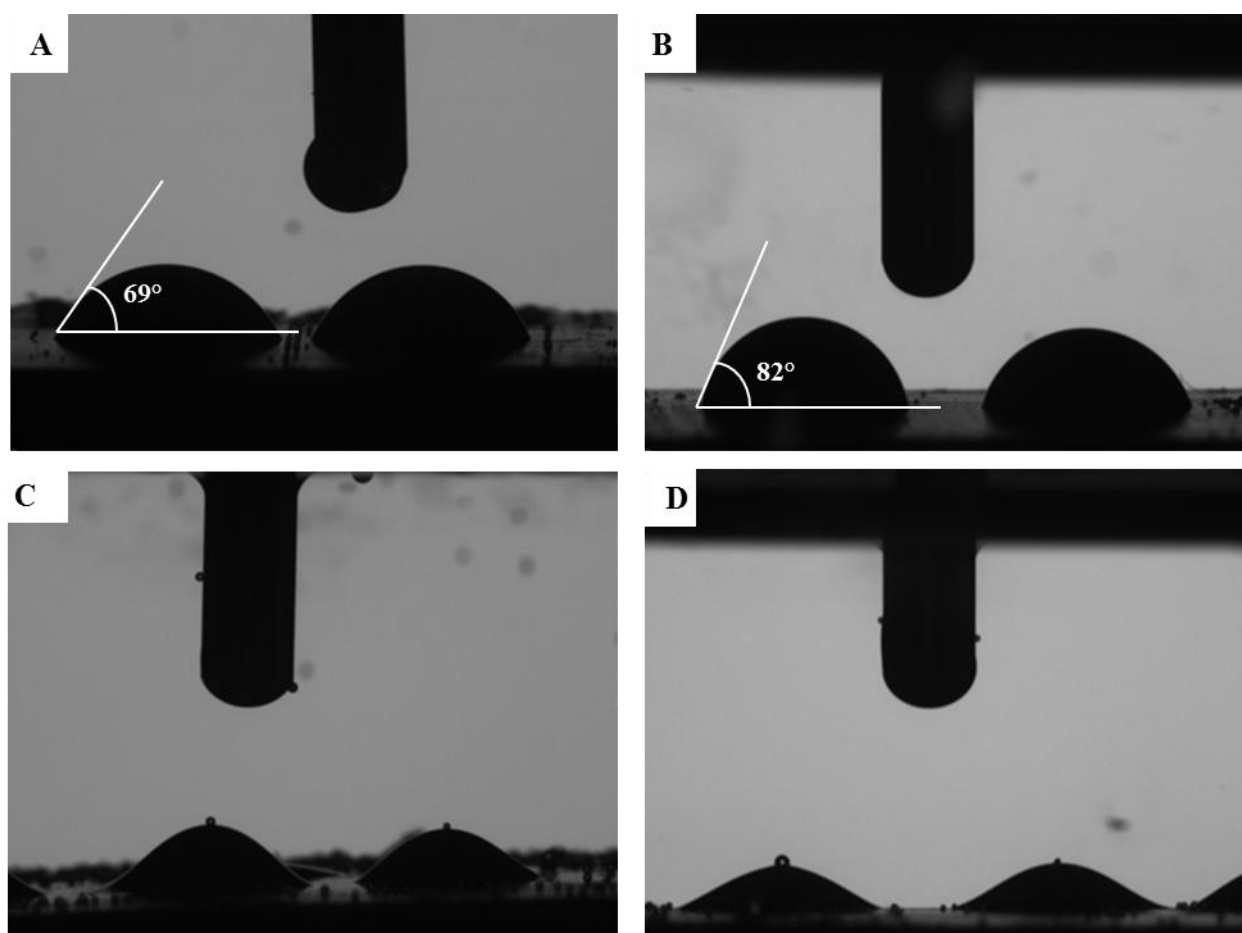
Fig. 11. Contact angle measurements on water free oil residues performed after adhesion test **A)** OB-SSW 225 °C+, θ= 68°±1, Vol= 4.5µL **B)** OB-LSW 190 °C+ +5 wt.% IFO380, θ=77°±5, Vol= 4,5µL **C)** OB-LSW 190 °C+ +5 wt.% IFO380 + 0.37 wt.% emulsifier, droplet released from surface **D)** OB-LSW 190 °C+ +5 wt.% IFO380 + 0.75 wt.% emulsifier, droplet released from surface (i.e. not possible to measure the contact angles)

Property: VISCOSITY OF EMULSION
Oil Type: OSEBERG

SINTEF

OWModel

Surface release - Terminal Oil film thickness: 1 mm
Release rate/duration: 1.33 metric tons/minute for 15 minute(s)

Pred. date: Oct. 14, 2013

Wind Speed (m/s): 15
Wind Speed (m/s): 10
Wind Speed (m/s): 5
Wind Speed (m/s): 2

Chemically dispersible (<4000 cP)
Reduced chemical dispersibility
Poorly / slowly chemically dispersible (>20000 cP)

Sea surface temperature: 10 °C

Viscosity (cP)

100000

10000

1000

100

10

0.25   0.5   1   2   3   6   9   12   1   2   3   4   5

Hours   Days

Fig. 12. Prediction of viscosity of Oseberg oil at 10 °C and at 4 different wind speeds (data not shown)
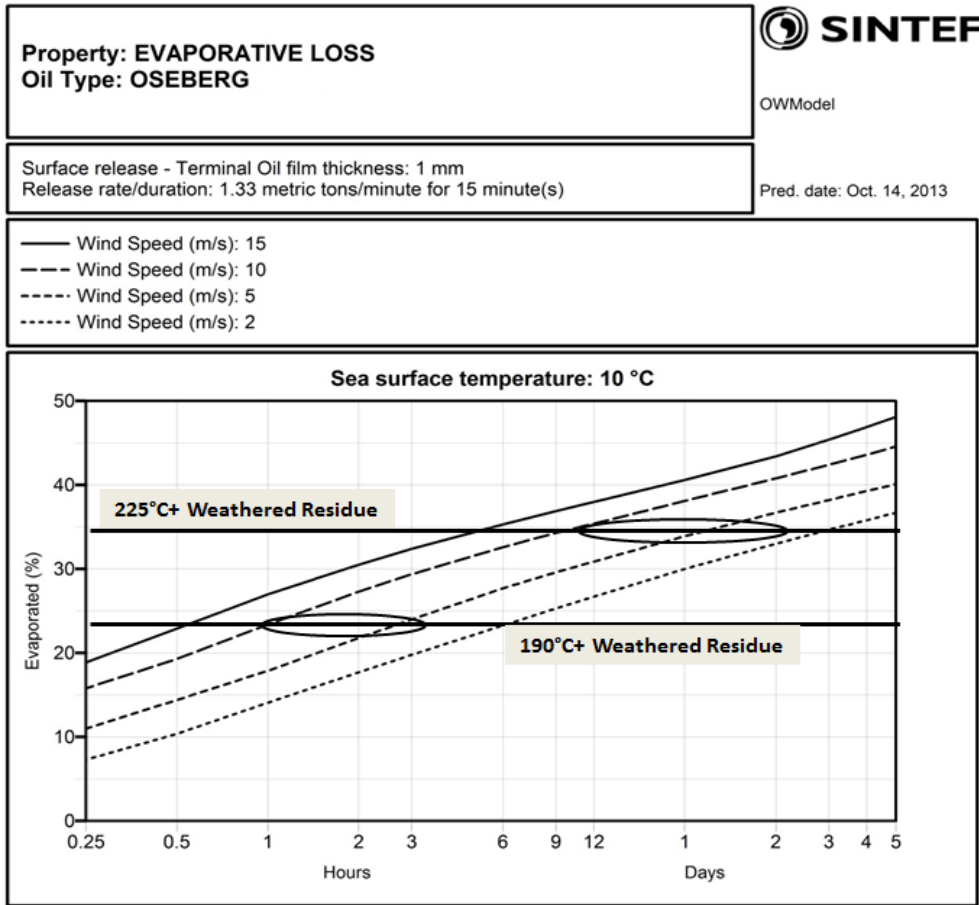
Fig. 13. Prediction of evaporation of Oseberg oil at 10 °C and at 4 different wind speeds (data not shown)
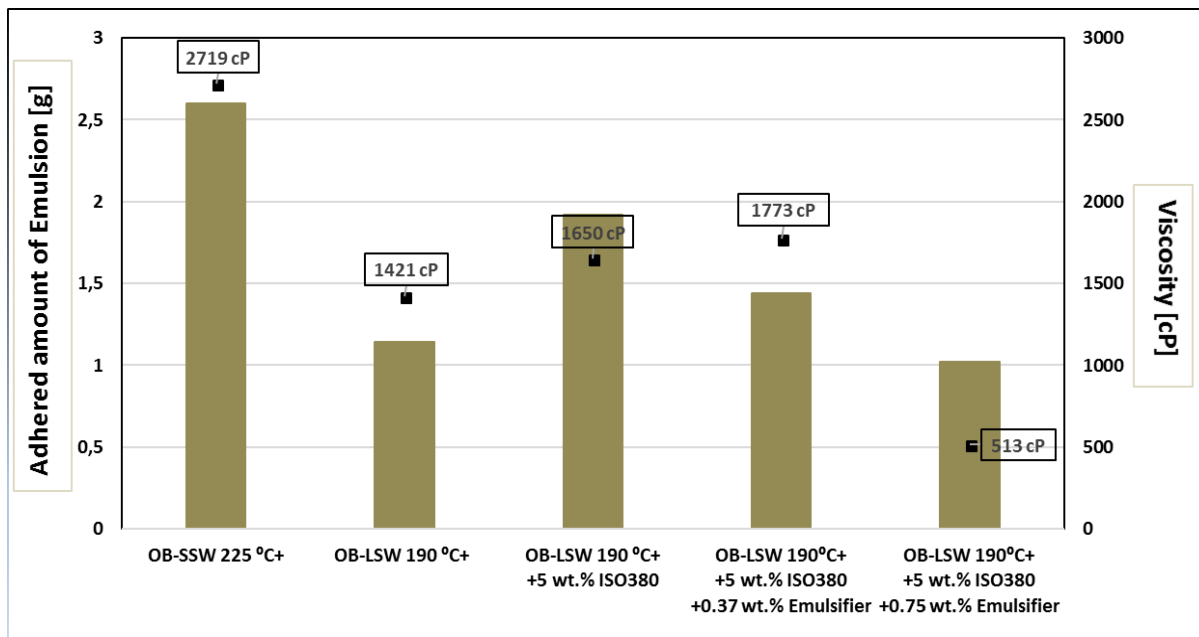

Fig. 14. Adhered amount of different oil emulsions with surface of the disc of skimmer at 10 °C

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