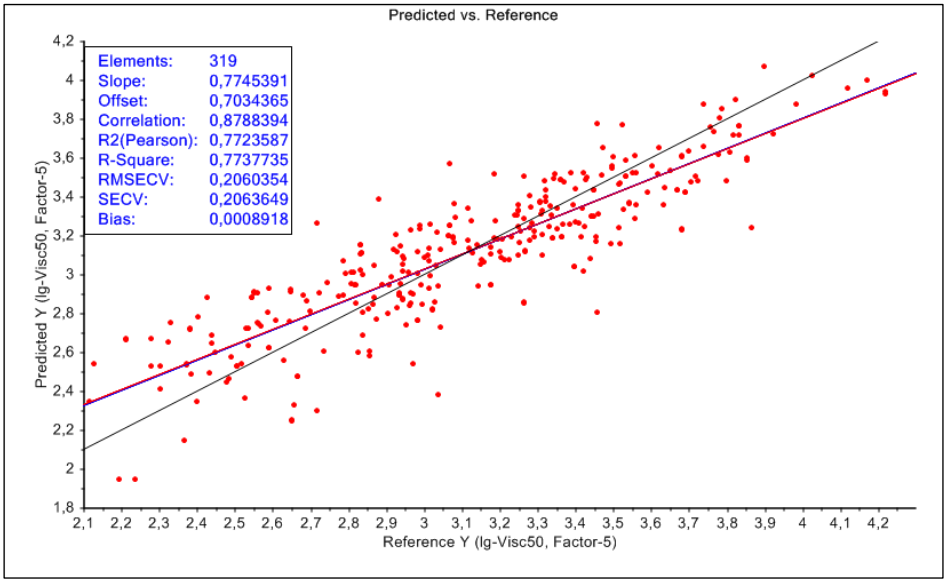
OC2018 A-040 - Unrestricted

Final Report

Modernisation and updating of SINTEF Oil Weathering Model (OWM)

Extending and recalibration of the Crude Assay (CA) module in SINTEF OWM

Authors
Per Johan Brandvik
Kaja Cecile Hellstrøm and Kristin Rist Sørheim



Multivariate prediction of maximum water uptake in emulsions (EM%), based on crude oil assay data. Predicted versus measured values (r = 0.88)

SINTEF Ocean AS
Environment and new resources
2018-05-15

SINTEF Ocean AS
Environment and new resources
2018-05-15

SINTEF Ocean AS
Address:
Postboks 4762 Torgarden
NO-7465 Trondheim
NORWAY
Switchboard: +47 46415000

Enterprise /VAT No:
NO 937 357 370 MVA

Final Report

Modernisation and updating of SINTEF Oil Weathering Model (OWM)

Extending and recalibration of the Crude Assay (CA) module in SINTEF OWM

REPORT NO.	PROJECT NO.	VERSION	DATE
OC2018 A-040	302003199	Final	2018-05-15

KEYWORDS:
Oil spill
Oil weathering
Modelling
Multivariate statistics
Crude Assay module

AUTHOR(S)
Per Johan Brandvik
Kaja Cecile Hellstrøm and Kristin Rist Sørheim

CLIENT(S)
Statoil and Norwegian Coastal Administration

CLIENT'S REF.
Cecilie Fjeld Nygaard and Kristin Øye, Statoil
Silje Berger, Norwegian Coastal Administration

NUMBER OF PAGES/APPENDICES:
52 incl. 1 Appendix

CLASSIFICATION	CLASSIFICATION THIS PAGE	ISBN
Unrestricted	Unrestricted	978-82-7174-333-8

ABSTRACT

SINTEF har siden åttitallet foretatt forvitringsstudier på en rekke oljetyper (både norske og utenlandske). Hovedmålsettingen med disse forvitringsstudiene har vært å predikere oljenes forvitringsegenskaper dvs. hvordan de oppfører seg på sjøen ved et eventuelt oljesøl (fordamping, emulgering, naturlig dispergering etc). Det ble i perioden 1997-99 utført et multivariabelt korrelasjonsstudie for Statoil av oljers sammensetting (Crude Assay (CA) data) og forvitringsegenskaper (data fra laboratoriestudier) som var generert hos SINTEF fram til 1997 (19 utvalgte oljetyper). En modell som beregner de input-data som SINTEFs Oil Weathering Model (OWM) trenger for å predikere oljens forvitringsegenskaper når forvitringsdata fra laboratoriet ikke er tilgjengelig, er etablert. Denne modellen ble også utvidet med et kalibreringssett bestående av 58 oljer gjennom et prosjekt finansiert av Statoil i 2005.

Prosjektet beskrevet i denne rapporten har styrket modellen og gjort den mere generell, dvs gjeldene for en større gruppe av oljer ved å utvide kalibreringssettet til 141 oljer inkludert rafineriprodukter. Dette gjør at forvitringsegenskaper også for bunkersoljer kan predikeres basert på enkle parametre (viskositet, voks/asfalten, tetthet, stivnepunkt og kokepunktsprofilen).

For å forbedre denne muligheten til å bruke SINTEF OWM direkte har dette prosjektet fokusert på:

1. Inkludere flere oljetyper/forvitringsstudier for å få flere oljer (totalt 141) i de enkelte klassene
2. Dele oljene inn i klasser (med/uten stivnepunktsproblemer, raffineriprodukter, meget voks/asfaltenrike) og predikere egenskapene innbyrdes i de enkelte klassene
3. Brukergrensesnitt med "warning messages" som gjør at modellen ikke kan brukes utenfor det området den er kalibrert for, samt angir forventet kvalitet på prediksjonene og "guiding messages" som hjelper brukeren å forstå hvordan CA-dataene kan brukes optimalt.
4. Det er ikke mulig å predikere forvitringsegenskaper basert på CA data fra lette raffeneriprodukter og kondensater.
5. Ny funksjonalitet "Find model oil" som rangerer oljer i oljedatabasen etter likhet med oppgitte CA data.

PREPARED BY	CHECKED BY	APPROVED BY
Per Johan Brandvik	Per S. Daling	Mimmi Throne-Holst

Document History

VERSION	DATE	VERSION DESCRIPTION
Draft	2017-12-05	First version to be discussed with the Clients
Final	2018-05-02	Final version after feedback on report, short user course and feedback on test version of software (OWM 9.2)

SINTEF

Table of Contents

1 Summary in Norwegian

SINTEF har siden åttitallet foretatt forvitringsstudier på en rekke oljetyper (både norske og utenlandske). Hovedmålsettingen med disse forvitringsstudiene har vært å predikere forvitringsegenskaper til ulike oljer typer dvs. hvordan de oppfører seg på sjøen ved et eventuelt oljesøl med hensyn på egenskaper som fordamping, emulgering, naturlig dispergering etc. Det ble i perioden 1997-99 utført et multivariabelt korrelasjonsstudie for Statoil av oljers sammensetting basert på Crude Assay (CA) data og forvitringsegenskaper (data fra laboratoriestudier) som var generert hos SINTEF fram til 1997 (19 utvalgte råoljer). En modell som beregner de input-data som SINTEFs Oil Weathering Model (OWM) trenger for å predikere oljens forvitringsegenskaper når forvitringsdata fra laboratoriet ikke er tilgjengelig, ble etablert via en CA modul. Denne modulen ble implementert i SINTEFs OWM og har vært brukt når forvitringsdata ikke eksisterer, og ble deretter utvidet med et kalibreringssett bestående av 58 oljer gjennom et prosjekt finansiert av Statoil i 2005. Statoil og Kystverket er begge brukere av SINTEF OWM for å være i stand til å predikere forvitringsegenskaper til relevante oljetyper, og begge parter har bidratt til å finansiere dette prosjektet med oppgradring av CA modulen med flere råoljer (Statoil) og raffinerte produketer (Kystverket).

Målsettingen med dette prosjektet har vært å styrke CA modulen og gjort modellen mer generell ved å utvide kaliberingssettet med flere nye råoljer og raffinerte produkter. Forvitringsegenskapene predikeres basert på 6 enkle CA parametere (produktdata /certificate of quality): viskositet, voks, asfalten, tetthet, stivnepunkt og kokepunktsprofilen. Det har vært viktig å inkludere nye oljer i kalibereringssettet som har et stort spenn i sine fysiskalsk-kjemiske egenskaper, samt at forvitringsdata for disse oljene var av god kvalitet og utført med sammenlignbare metoder og prosedyrer. Eldre forvitringsstudier ble derfor utelatt, samt at noen av de raffinerte produktene ble utelatt pga. mangel på asfalten - og voksinnhold. Totalt ble 141 oljer (råoljer og raffinerte produkter) valgt ut i det nye kaliberingssettet. Oljene i kalibreringssettet ble delt inn i klasser: med/uten stivnepunktsproblemer, raffineriprodukter, meget voks/asfaltenrike, slik at forvitringsegenskapene kunne predikeres innenfor i de enkelte klassene. Korrelasjoner mellom paramertre for fersk olje og parametre som beskriver forvitring av olje på sjø ble utført via en multivariat modelltilnærming. Basert på dette beregner CA modulen syntetiske datasett med forvitringsdata som brukes videre i SNTEF OWM for å predikere forvitringegenskaper til de aktuelle oljene.

CA modulen har sine begrensinger og noen typer oljer vil ikke kunne la seg predikere med denne tilnærmingen. Dette gjelder spesielt kondensater og lette raffinerte produkter med høyt fordampningstap, eller oljer med egenskaper som ligger utenfor kalibereringssettet. Brukergrensesnitt med ulike ”warning messages” angir forventet kvalitet på prediksjonene. Brukergrensesnitt med ”guiding messages” hjelper brukeren å forstå hvordan CA data kan brukes optimalt. Funksjonaliteten "Find Model Oil" kan for eksempel benyttes for å finne oljer med visse likheteter i forvitringsegenskaper for den aktuelle oljen. En såkalt "fit-faktor" beskriver grad av likhet inndelt i fargekodene grønn (høy grad av likhet), gul (middels grad av likhet), og rødt (liten grad av likhet).

Det nye utvidete kalibreringssettet har blitt validert med flere oljer ved å sammenligne CA prediksjoner med prediksjoner fra tidligere forvitringsstudier innenfor kategoriene naftenske, asfaltenske, parafinske og voksrike oljer, samt noen raffinerte produker. Imidlertidig bør Ca modulen brukes med noe forsiktighet, siden usikkerheten i disse prediksjonene kan være større sammenlignet med prediksjoner basert på forvitringsstudier. CA modulen kan gi større usikkerheter i prediksjoner som emulsjonsviskositeter, i tillegg til at tidsvinduet for bruk av dispergeringsmiddel ikke er kjent, som igjen kan ha betydning for operative beslutninger. Denne nye tilnærmingen vil derfor ikke erstatte behovet for forvitringsstudier relatert til beredskapsplaner og miljøriskoanalyser, men vil kunne være et viktig operasjonsverktøy i oljevernsaksjoner der det er behov for raske prediksjoner hvor forvitringsdata ikke er tilgjengelig.

2 Introduction and Background

The SINTEF Oil Weathering Model (OWM) relates oil properties to a chosen set of conditions (oil/emulsion film thickness, wind speeds and sea temperature) and predicts the change rate of the oil's properties on the sea surface with time. The SINTEF OWM is schematically shown in Figure 2.1. The predictions obtained from the SINTEF OWM are useful tools in oil spill contingency planning related to the expected behaviour of oil on the sea surface. It is also used to evaluate the time window for operational response strategies in a spill operation. The SINTEF OWM is e.g. described by Daling et al., 1989 and Daling et al. 1997, and in the user's guide for the model. Examples of weathering predictions of water content and emulsion viscosities for a Norwegian crude oil as a function of time, are shown in Figure 2.2.

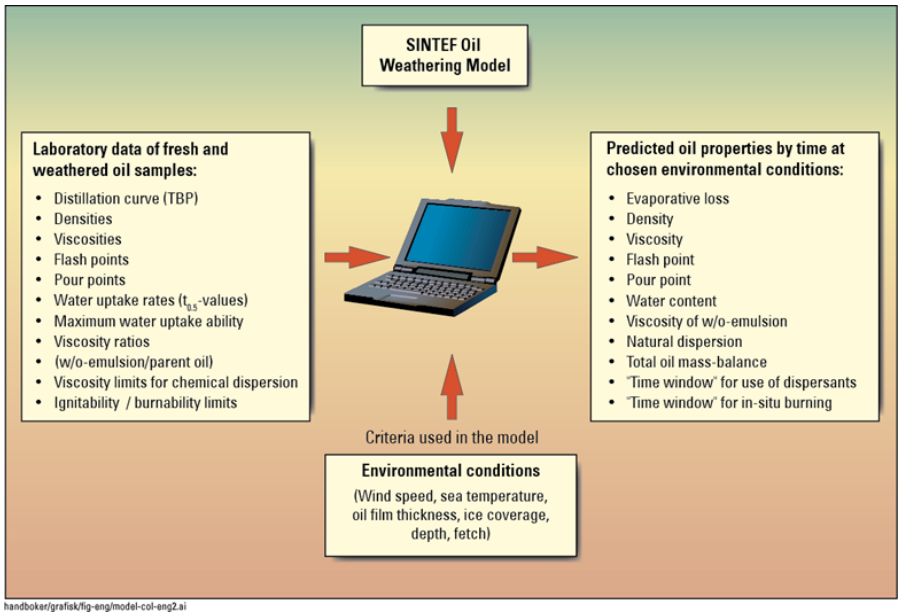


Figure 2.1: Schematic diagram of the input data to the OWM and the predicted output oil properties

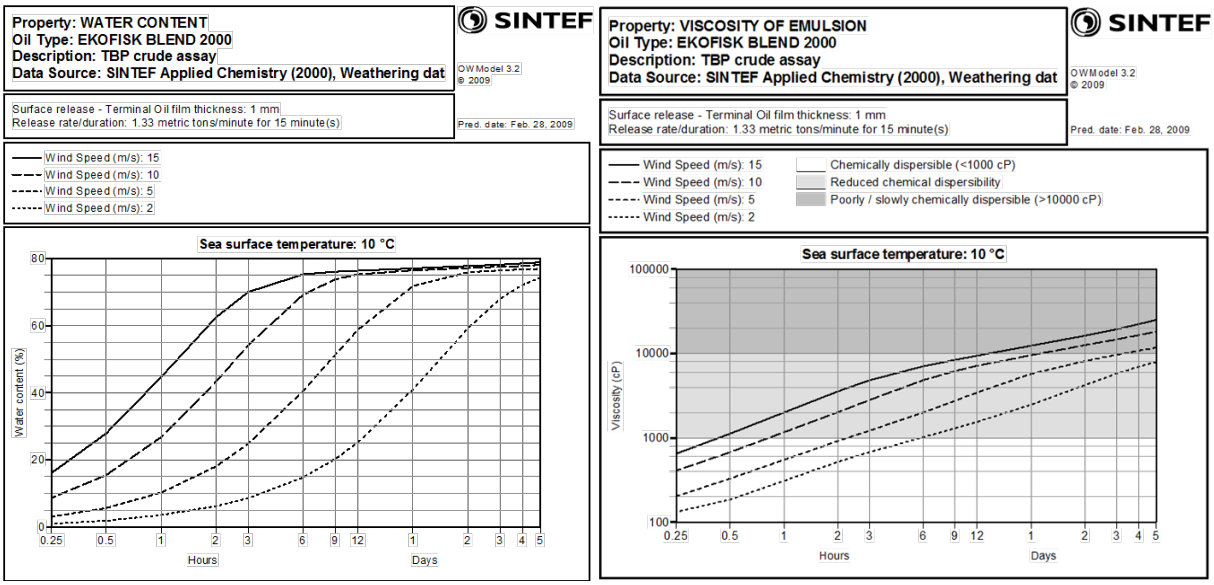


Figure 2.2: Prediction of water content (above) and emulsion viscosities (below) at different wind speeds

Most of the predictions made with the SINTEF OWM are based on laboratory weathering studies as described in Figure 2.1. However, there have always been an option to perform predictions from a minimum set of parameters describing the fresh oil (Crude Assay variables, see Table 4.1). Early versions of SINTEF

OWM was based on basic algorithms and not laboratory data (Daling and Johansen, 1986). Predictions based on only Crude Assay data (CA) were also possible after OWM was established, but the initial option was based on weathering data from only five North Sea crudes (Johansen & Brandvik 1988, unpublished data). However, predictions made by this approach resulted in many cases large deviations compared to predictions based on laboratory weathering data (Daling and Kristiansen, 1997).

Statoil co-funded a research study in 1999-2000 that used a broader range of data (more oils) from weathering studies as a fundament for calibration of a model to predict oil weathering at sea, based on CA data (Brandvik et al., 2000). This calibration dataset was expanded five years later including additional oil types (Brandvik et al., 2006). This study increased the accuracy in predictions using CA data, but important oil types like condensate and waxy oils were still poorly represented.

Two related projects, also funded by Statoil, have focused on OWM predictions of "dynamic blends". This option has proven useful in cases were compositions of blends in pipelines or offshore storage (FPSO) are changing over time. These projects were linked to weathering properties of variations in the export blends from the Gullfaks field (Brandvik et al., 2007) and the Norne field (Sørheim et al., 2010).

Table 1.1 below summarises earlier relevant projects for development of the SINTEF OWM with emphasis on the capability to make predictions based on CA-data.

Table 1.1: Overview of SINTEF OWM with focus on the development of the Crude Assay (CA) module.

1989	Initial study with 3 North Sea crudes	Johansen/Brandvik
2000	Calibration based on 40 crudes	Brandvik, Resby & Daling
2004	Extended calibration to 62 crudes	Brandvik & Resby
2003	EMSA Weathering study	Resby, Daling & Reed
2005	Prediction from CA-data for oil blends - Gullfaks C	Brandvik et al.
2009	Prediction from CA-data for oil blends – Tampen	Brandvik et al.
2010	Prediction from CA-data for oil blends – Norne	Brandvik & Sørheim
2015	BP Global oil mapping – Identifying surrogate oils	Brandvik & Sørheim

As described above, Statoil has participated in the development of the model tool and is now a frequent user of the SINTEF OWM. The Norwegian Coastal Administration (NCA) is also a user of the SINTEF OWM to be able to perform predictions of oil types that could be relevant for events related to actions along the Norwegian coast or in arctic areas, for example around Svalbard or Jan Mayen. NCA has also supported weathering studies of selected refined products.

It appeared to both SINTEF and Statoil that the OWM model was in a need for modernisation and updates. OWM was based on a software platform that were not supported anymore, so updating and further development was not possible without a major revision of the source code. Statoil and SINTEF had in 2016 several meetings to discuss modernisation of OWM and extending the CA module with additional oil types. A project was established, which included both a general modernisation of the OWM and addition of new functionalities (new graphics, find model oil function, extended CA module etc.).

The work described in this report was a part of this project, and aimed towards making the CA module more general by recalibrating it with 141 oil types also including refinery products. The implementation and re-calibration of refinery products into the CA module has been funded by NCA.

3 Objective

The overall objectives of this project have been to develop an operational tool for rapid prediction of weathering behaviour for oil slicks at sea (evaporation, water uptake, viscosity etc.) by use of CA data of the fresh oils in situations where laboratory weathering data not is available. Such situations could be:

- Re-check of oils. Determination of changes in oil properties of importance for weathering behaviour
- Spills of oil types which are only occasionally imported to Norway (laboratory weathering study not available)
- Spills of blends which rapidly and significantly changes composition (weathering study of limited significance)
- To widen and add robustness to the existing CA module improving the capability to predict weathering properties for a wider variety of oil types.

4 Experimental work

4.1 Oil properties - physicochemical variables

The fresh oil and weathering properties used to describe the difference between the different oils related to weathering properties are listed in Table 4.1.

Table 4.1 Variables used in this study

	Variables	Units	Method
Fresh oil properties	Wax content	weight %	2-butanon/DCM at –10ºC
	Asphaltene content	weight %	IP 234/84
	Viscosity of water free oil	cP shear rate 100 s^{-1}	Physica MCR 300
	Pour point	ºC	ASTM D97-77
	Density	g/mL	ASTM D4052-81
	Vol.% evaporated versus vapour temperature	True boiling point curve	Distillation
Weathering properties	Maximum water content in emulsified oil	Vol.%	Karl Fisher titration
	Water uptake rate	t½	Internal SINTEF method
	Viscosity of emulsion with 50%, 75% and max. water content	cP at shear rate 10 s^{-1}	Physica MCR 300

4.2 Selection of oil types

When selecting the oil types, it was important to cover as many different “categories” of crude oils and refined products as possible. This increased the ability of the model to predict oil weathering at sea for as broad variety of oil types as possible.

The criteria used for selecting the oils to be included in this study were:

- Obtaining a large variation in physical/chemical properties
- Good data quality (consistence in analytical methods and procedures)

Some of the older weathering studies (before 1991) have therefore been omitted due to changes in laboratory procedures. This has been done to ensure a good consistency in the data. Some of the refined products were also omitted from the database due to lack of wax and asphaltenes for these oils.

The oil types that are selected and included in this study are listed in
Table 4.2. These 141 oils are divided into the following groups:

1. **Crude oils**
    a. Asphaltenic: 10
    b. Naphtenic: 39
    c. Waxy: 25
    d. Paraffinic: 34
    e. Condensates: 14

2. **Refinery products**
    a. Light (distillates): 6
    b. Heavy (residual fuels): 13

Table 4.2 Oils used in this study including crude oils and refined products in alphabetic order

1. ADO
2. ALASKAN NORTH SLOPE
3. ALPINE
4. ALVHEIM BOA 2008
5. ALVHEIM KAMELEON 2008
6. ALVHEIM KNELER 2007
7. ALVHEIM_BLEND 2009
8. AQUILA
9. ATLA
10. BALDER (IKU)
11. BALDER 2001
12. BALDER BLEND, 2010
13. BITTERN
14. BLANE 2008
15. BOARDALE
16. BONNY LIGHT (IKU)
17. BRAGE (IKU)
18. BRAGE 2012
19. BREAM 2010
20. BRENT BLEND
21. BRENT BLEND (IKU)
22. BRYNHILD 2014
23. BØYLA 2015)
24. CLAIR (IKU)
25. DRAUGEN 2000 (UTEN PROD)
26. DRAUGEN 2007
27. EDVARD GRIEG 2010
28. EKOFISK BLEND 2000
29. ELDFISK
30. ELLI
31. ELLI SOUTH
32. EMBLA 2000
33. ENDICOTT 2001
34. ERICH GIESE
35. FOINAVEN (IKU)
36. FORSETI 2001
37. FRAM 2012
38. FRAM 1999
39. FRAM B
40. FRØY
41. GARANTIANA 2012
42. GAUPE 2010
43. GJØA
44. GLITNE 2001
45. MGO 10
46. GRANE (SINTEF)
47. GROSBEAK
48. GUDRUN
49. GULLFAKS A BLEND
50. GULLFAKS C
51. GULLFAKS C BLEND
52. GULLFAKS SØR (IKU)
53. GYDA 2000
54. HDME 50 2016
55. HEIDRUN EXPORT BLEND
56. HEIDRUN ÅRE
57. HULDRA COND.
58. IFO 180 NS
59. IFO 180LS FLUME KYV
60. IFO 380
61. IFO180 LS
62. IFO380
63. IFO-380 RUSSIAN BUNKER FUEL
64. IFO80LS
65. IVAR AASEN 2011
66. Johan Sverdrup
67. JORDBÆR 2010
68. KRISTIN 2006 FLUME
69. KRISTIN KONDENSAT
70. KVITEBJØRN
71. LINERLE
72. LUNO II 2014
73. MARIA
74. MARTIN LINGE CRUDE 2016
75. MARTIN LINGE KONDENSAT 2016
76. MARULK
77. MGO
78. MGO 500 PPM S 2016
79. MORVIN 13C
80. MURBAN ABU DHABI (IKU)
81. NJORD 2002
82. NORNE 1998
83. NORNE BLEND 2010
84. NORTH STAR
85. OSEBERG A (IKU)
86. OSEBERG A 2013
87. OSEBERG BLEND 2006
88. OSEBERG C (IKU)
89. OSEBERG SØR 2000
90. OSEBERG SØR 2000
91. OSEBERG SØR 2012
92. OSEBERG ØST 2001
93. OSEBERG ØST 2012
94. OSELVAR 2011
95. PIL 2014
96. REV 2009
97. RINGHORNE 2001
98. ROTTERDAM DIESEL 2016
99. RUSSIAN CRUDE 2006
100. SCHIEHALLION (IKU)
101. SIGYN 2017
102. SIRI-SOMMER
103. SKARFJELL
104. SKARV 2014
105. SKARV 2002
106. SLEIPNER (IKU)
107. SLEIPNER VEST
108. SMØRBUKK 2002
109. SMØRBUKK SØR 2002
110. SNORRE B
111. SNORRE TLP RESJEKK
112. SOUTH ARNE
113. STATFJORD A
114. STATFJORD B VIRGIN
115. STATFJORD C BLEND
116. STURE BLEND
117. TAMBAR
118. TAU
119. TORDIS
120. TRESTAKK
121. TROLL (IKU)
122. TRYM KONDENSAT 2011
123. ULA 1999
124. ULSFO 2017
125. URAL BALTIC 2003
126. VALE 2013
127. VALE 2001
128. VALHALL 2000
129. VARG
130. VESLEFRIKK (IKU)
131. VESLEFRIKK 2012
132. VIGDIS
133. VILJE 2009
134. VISUND
135. VISUND 2008
136. VOLUND
137. VOLVE
138. WIDE RANGE GAS OIL 2016
139. WRG (WIDE RANGE OIL)
140. YME (IKU)
141. ÅSGARD 2002

To span out a broad range of oil types as possible with respect to oil composition, a limited screening study was performed by the use of Principal Component Analysis (PCA). Oil types with the selected variables, as shown in Table 4.1, were plotted in a score plot. The score plot was further used as a selection tool to select the oil types and indicated that the oil types covered a broad range of oil properties with a reasonable number of oil samples. An introduction to the basic principles of PCA can be found elsewhere e.g. Martens et al., 1994, Esbensen et al., 1994, Brandvik, 1997 and Myrhaug, 1996 (Norwegian), and will not be further explained here.

5 Description of multivariate model

This chapter contains a brief introduction to the approach used in this study to model and predict "synthetic" laboratory weathering data from available fresh oil properties.

5.1 Data available from weathering studies

The basic idea behind this correlation and modelling study is to utilise the information available from the many weathering studies previously performed at SINTEF to predict oil behaviour based only on fresh oil properties. Weathering studies from 141 oil types were selected and used as input to this study. Readily available information (CA data and SINTEF weathering studies) was used to correlate the physical/chemical variables of the water free oil (oil composition) and the variables describing oil weathering at sea (evaporation, emulsification, increase in viscosity etc.). In other words, the knowledge from these previous weathering studies is combined with information on oil composition from crude assays to predict a "synthetic" laboratory weathering data set.

The relationship between laboratory study, fresh oil properties, multivariate model, SINTEF OWM and prediction are illustrated in Figure 5.1.

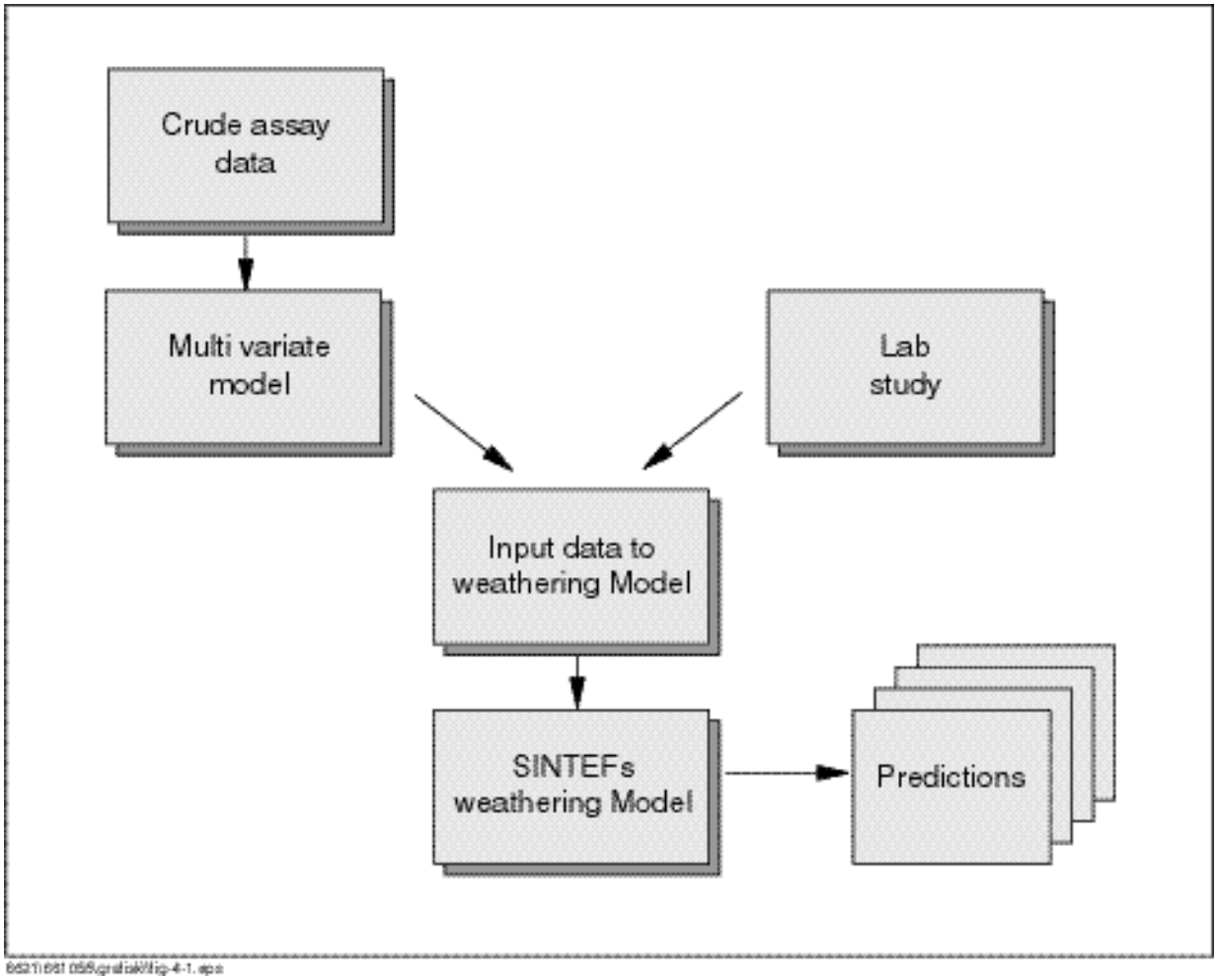


Figure 5.1: A "synthetic" laboratory weathering data set (input data), predicted from CA data (physical/chemical data), is used together SINTEF OWM) to predict oil weathering properties, instead of data from laboratory weathering studies.

The following data from a weathering study are necessary as a minimum input to the SINTEF OWM to be able to predict the weathering behaviour of an oil spill at sea. The basic input data are listed in Table 4.1. In addition, the true boiling point (TBP) curve or distillation curve is also needed for such predictions.

Table 5.1 Basic laboratory data used as input to the SINTEF OWM describing the fresh oil and the weathered fractions (150, 200 and 250ºC+ residues).

	Fresh	**150ºC+**	**200ºC+**	**250ºC+**
Vol. topped (vol.%)		*	*	*
Residue (wt.%)		*	*	*
Density (kg/l)	*	*	*	*
Asphaltene content (wt.%)	*			
Wax content (wt. %)	*			
Pour point (ºC)	*	*	*	*
Visc. (waterfree oil)	*	*	*	*
Visc (50% emulsion) [a)]		*	*	*
Visc (75% emulsion) [a)]		*	*	*
Visc (max.water emul.)		*	*	*
Max. wateruptake (%)		*	*	*
Uptake rate (t½, hrs)		*	*	*

a) Many of the refinery oil do not form 50 and 75% emulsions and predictions are performed without these data for them.

Based on the fresh oil variables, TBP and variables on the water free weathered residues, algorithms to predict synthetic lab weathering data are established.

5.2 Prediction of properties for water free weathered residues

Different approaches were selected to predict the different variables in the synthetic data set. The properties for the water free residues (150, 200 or 250ºC+) are predicted based on the fresh oil properties and the TBP curve, while the properties for the emulsified residues (water uptake and viscosities) are predicted by multivariate regression.

5.2.1 Prediction of volume topped and residue

The TBP curve contains information concerning the evaporative loss (vol. %) as a function of temperature (vapour temperature in a specific distillation set-up). The first variable in Table 5.1 (volume topped) showed only little deviation from 50 degrees above the vapour temperature (150, 200 or 250ºC), so vapour temperature + 50ºC was used as an estimator for the first variable. The two next variables (evaporative loss and residual weight) could both be calculated directly from the TBP curve as a function of vapour temperature (150, 200 or 250ºC).

Evaporative loss and residual weight are calculated directly from the TBP curve and there is generally an acceptable correlation with the experimental data from the weathering studies. The predicted density is used to calculate residual weight. The correlation coefficient (Pearson) between the predicted variables and the experimental data is generally above 0.9 for all three variables.

5.2.2 Prediction of density

A strategy using the value for the water free oil and the evaporative loss (from the TBP curve) was selected for prediction of density. This strategy is based on the observation that the density of the oil shows a systematic trend as a function of weathering (evaporative loss of the light components).

By using the slope of vapour temperature plotted against density (δdensity /δvapour temperature), the density for the weathered residues (150, 200 and 250ºC+) can be predicted. The "density slope" (δdensity /δvapour temperature) is dependent of oil composition and is specific for each oil type, see Figure 5.2. The "density slope" is correlated with the "evaporative loss slope" (δevaporative loss /δvapour temperature), since oils with high evaporative loss also have high changes in density, see Figure 5.3 . The "density slope" can then be predicted from the TBP curve via the "evaporative loss slope". A calibration curve including the 141 oils in the calibration set is used for this purpose, see Figure 5.3.

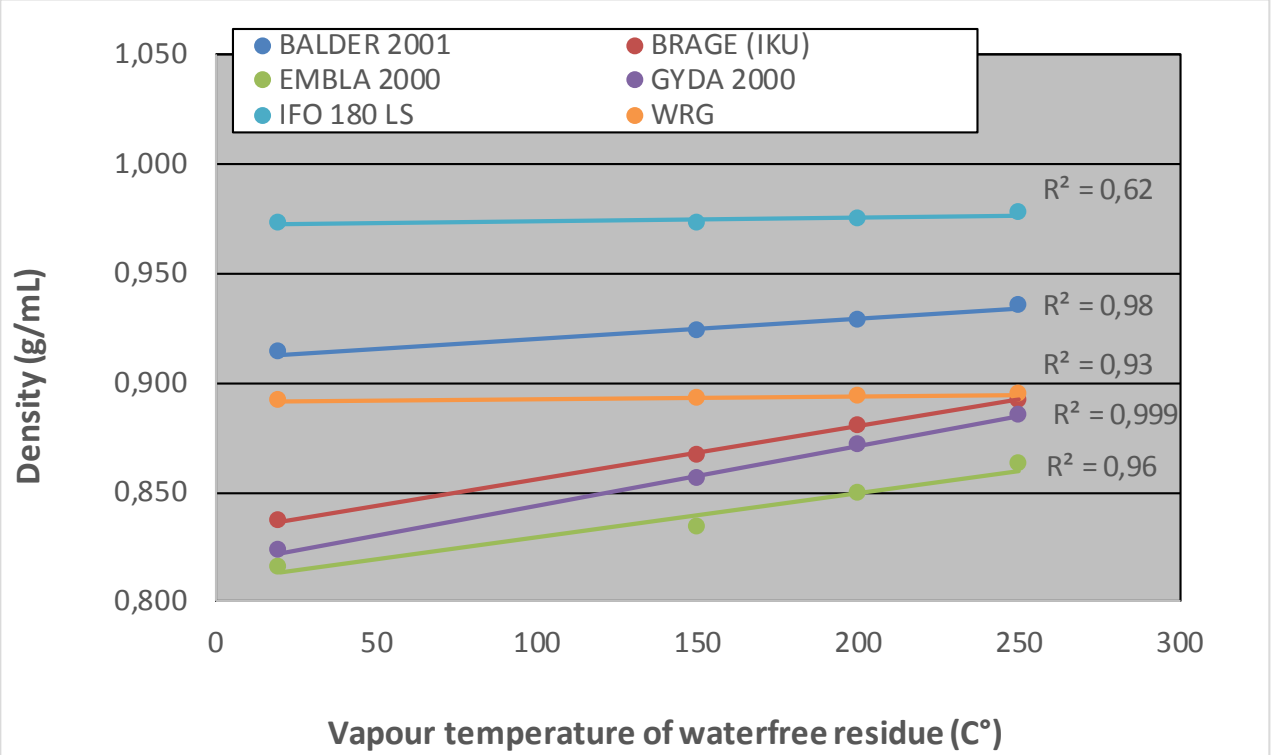


Figure 5.2 *Density for different oils as a function of vapour temperature of the residue. Only a limited number of oils, both crude and refinery products (IFO180 and wide range gasoil – WRG), are plotted to illustrate the main trends.*

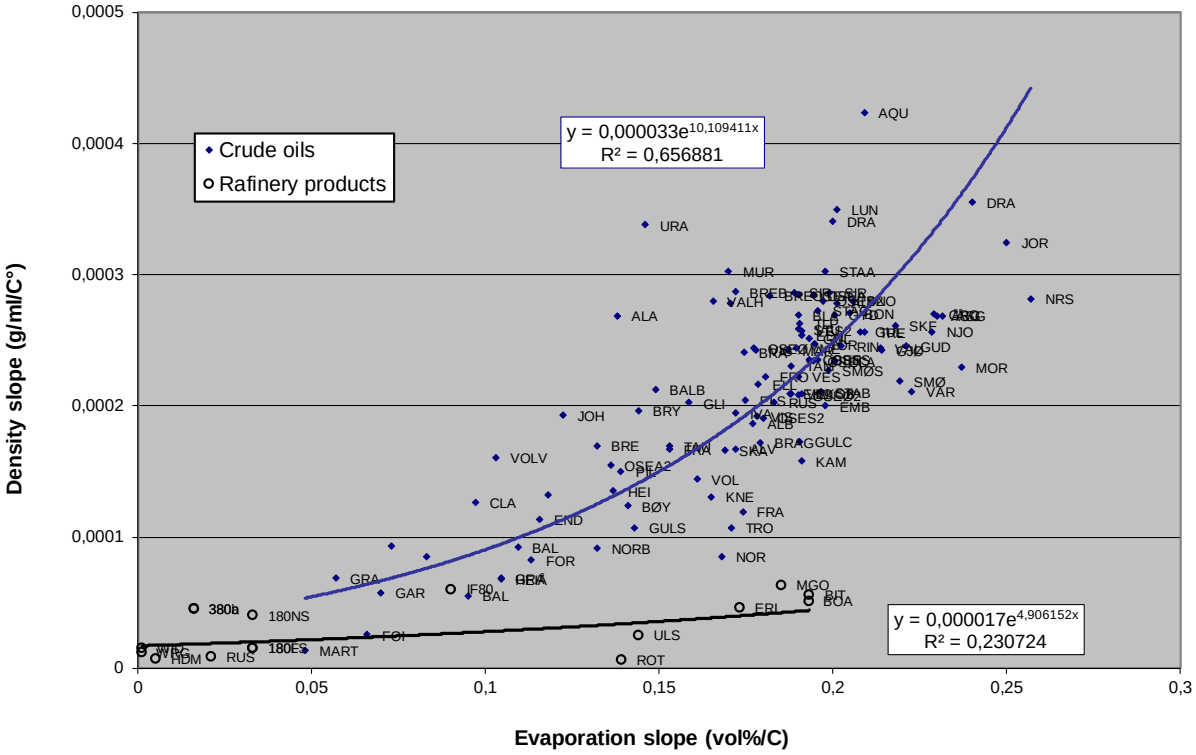


Figure 5.3 The exponential relationship between the "density slope" and the "evaporation slope" based on data from the 141 selected oil weathering studies (see Table 4.2). A separate class was identified for prediction of the refinery products.

This exponential relationship between evaporative loss/vapour temperature and density is used in the 50-250ºC region of the TBP curve to predict the density for the water free residues at 150, 200 and 250ºC+. The correlation between the exponential curve and the measured data for the 141 oils shows an acceptable fit between the modelled and the measured data.

Using a similar approach also slopes for pour point and viscosity for water free oil were predicted from the calibration set based on the correlation of these variables with evaporative loss.

5.2.3 Prediction of pour point

A similar approach (as for density) was used for predicting pour point. The exponential relationship in the calibration set between changes in pour point versus changes in evaporative loss (see Figure 5.4.) is used to predict pour points for the water free residues (150, 200 and 250ºC+).

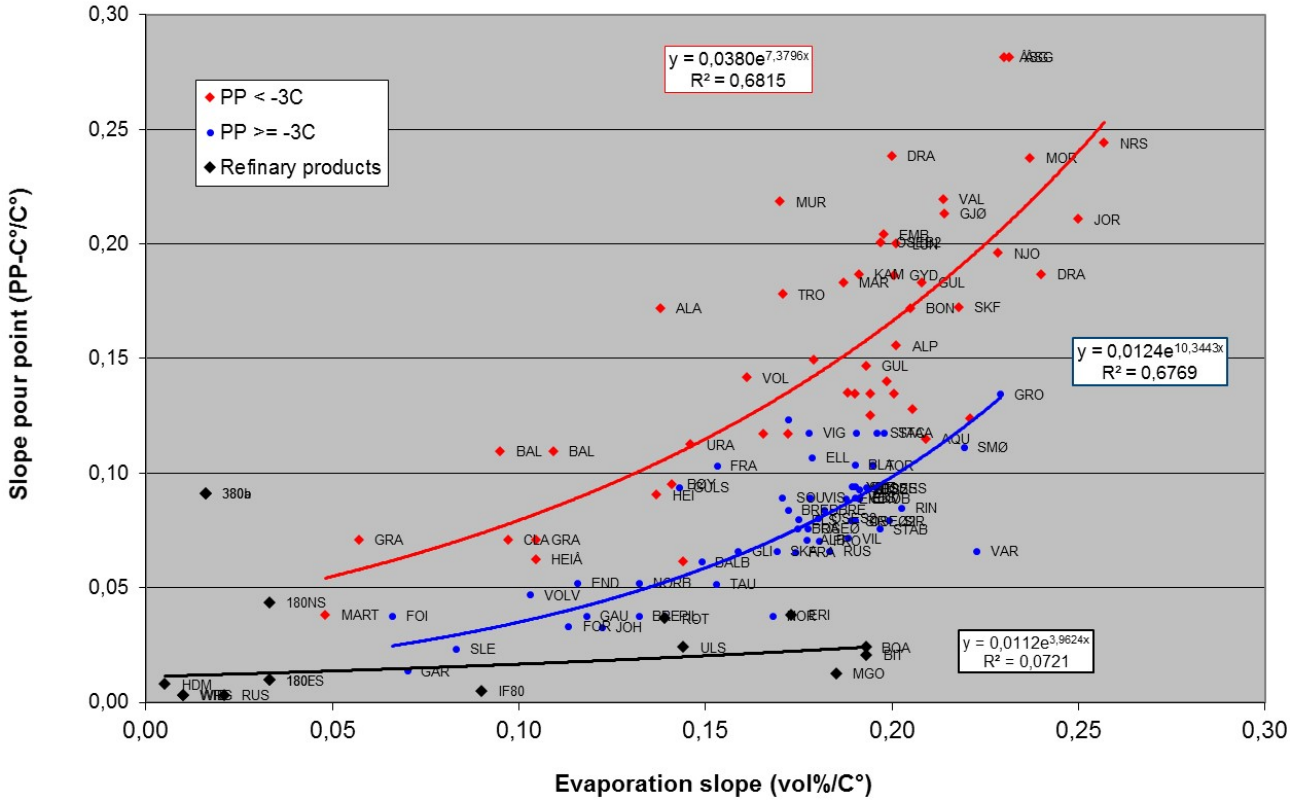


Figure 5.4: The exponential relationship between the "Pour point slope" and the "evaporative loss slope" based on data from the 141 selected oil weathering studies (see Table 4.2). Two different equations or classes are identified for the crude oils according to their initial pour point. In addition, a separate class was identified for the refinery products.

This exponential relationship in Figure 5.4 (see equations on chart) is used together with the "evaporative loss slope" in the 50-250ºC region from the TBP curve to predict the pour point for the water free residues (150, 200 and 250ºC+). Two different equations are established, the first equation is used for oils with initial low pour point (< -3ºC, red), the second for oils with medium initial pour point (≥ -3ºC, blue). The correlation between the exponential curve and the measured data for the oils shows an acceptable fit between the modelled and the measured data.

5.2.4 Prediction of viscosity

A similar approach was also used for predicting viscosity of the water free residues. The exponential relationship in the calibration set between changes in viscosity versus changes in evaporative loss (see Figure 5.5) is used to predict viscosity for the water free residues (150, 200 and 250ºC+).

It is assumed a linear relationship between density and pour point and evaporative loss. This linear relationship is not true for viscosity since the increase in viscosity as a function of evaporative loss usually shows an exponential behaviour. For this reason, it is not the "viscosity slope" which is predicted, but the constant in an exponential equation describing the viscosity ratio between weathered residue and fresh oil viscosity, see Equation 5.1. Variation of the constant in Equation 4.1 may give substantial changes in the predicted viscosity ratio. Figure 5.5 shows the span in viscosity ratios for exponential constants for some of the oils in the calibration set.

Equation 5.1: Visc ratio: $= e^{\text{Const} \cdot \text{Vapour temperature (°c)}}$

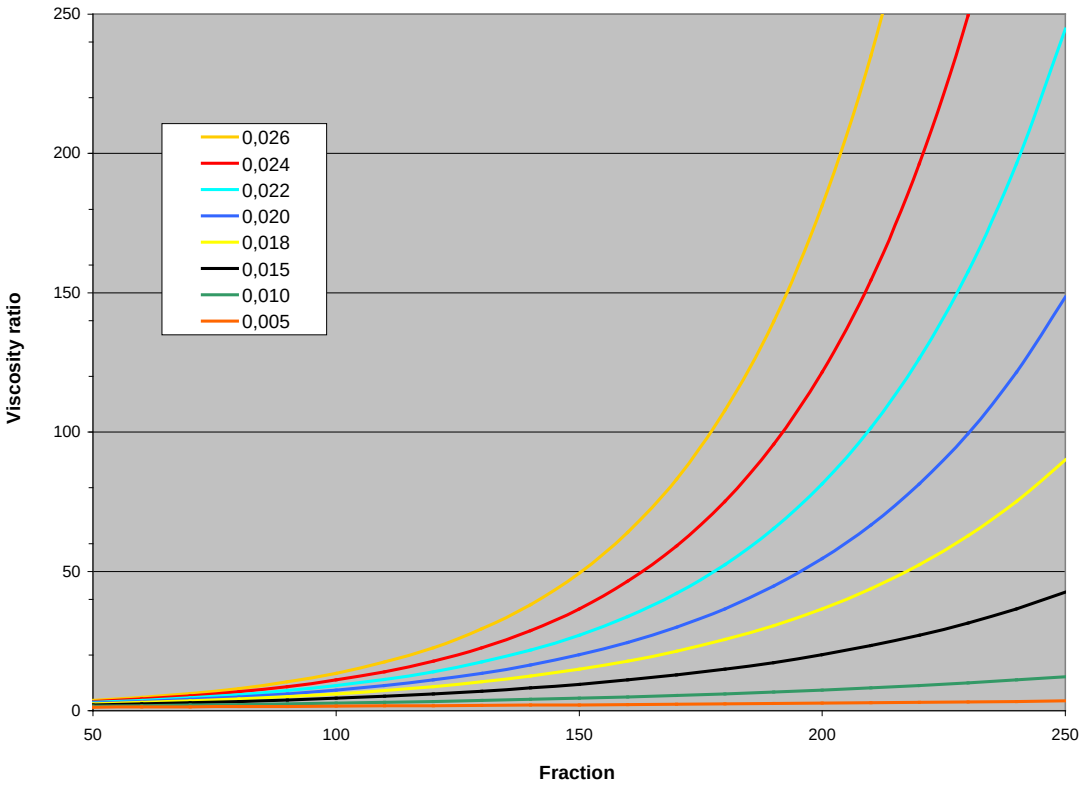


Figure 5.5: The exponential relationship between the viscosity ratio and the vapour temperature for weathered residue, see Equation 5.1. The constant is varied between 0.005 and 0.026 which is the range among the oils in the calibration set.

As illustrated in Figure 5.5 the span in the ratio between viscosity of weathered residue and fresh oil is wide. To better predict the rise in viscosity of the water free oils (the constant in Equation 5.1 describing viscosity ratios), the oils where divided into four different categories based on their fresh oil properties, as explained below:

1. **Category 1: Oil with high wax content (High Wax)**
   These oils have a high wax content and usually a high pour point. As the light component evaporate, wax particles precipitate and could make these oils semi solid and gives them high viscosity ratios. Three different combinations of the fresh oil properties define the “oil with High Wax” category:

   1a: Wax ≥ 5% AND Asp < 0.20%
   1b: Wax ≥ 4% AND Asp < 0.10% AND PP ≥ -3°C
   1c: Wax ≥ 5% AND Asp ≥ 0.20% AND PP ≥ 3°C

2. **Category 2: Oils with high evaporative loss that become “High Wax” oils when weathered (High Evap & Wax)**
   Some oils do not satisfy the conditions in Category 1, but have a very high evaporative loss and a high increase in relative wax concentration and pour point due to the large loss of light components. These oils will also show semi solid behaviour for the more weathered fractions and have high viscosity ratios, especially those with low initial viscosities. One combination of the fresh oil properties defines the "High Wax when weathered” category:

   2a: Evap ≥ 0.20 vol%/°C AND Wax ≥ 5% AND Visc < 5 cP (all viscosities at 13 °C)

3. **Category 3: High viscosity oils (High Visc)**
   Some oil types have initial high viscosities due to high wax and/or high asphaltene content. These oils have a low viscosity ratio and are defined by the following combination of fresh oil properties:

   3a: Visc ≥ 500 cP AND Wax ≥ 5%
   3b: Visc ≥ 500 cP AND Asph ≥ 1% (all viscosities at 13 °C)

4. **Category 4: Oils with low wax content (Low Wax)**
   Naphtenic-, asphaltenic- or crude oils with generally low wax content do usually not give precipitation of wax particles in the oil phase in the weathering range up to 250°C+ (approximate a week of weathering at sea). In this study, all oils which do not satisfy the conditions for Category 1-3 above, were defined as belonging to the “Oils with Low Wax” category.

The relationship between the viscosity ratio (constant from exp. equation) and the evaporative loss for the 141 oils in the calibration set is given in Figure 5.6 below.

As shown in Figure 5.6, the change in viscosity as a function of vapour temperature of weathered residue can be much more complex than the changes in density and pour point. A low-viscous oil with high wax content could therefore have a very steep exponential increase in viscosity as a function of vapour temperature if wax particles precipitate and make the oil semi solid. Other oil types have active components like asphaltenes which keep the waxes soluble in the oil and prevents high viscosities.

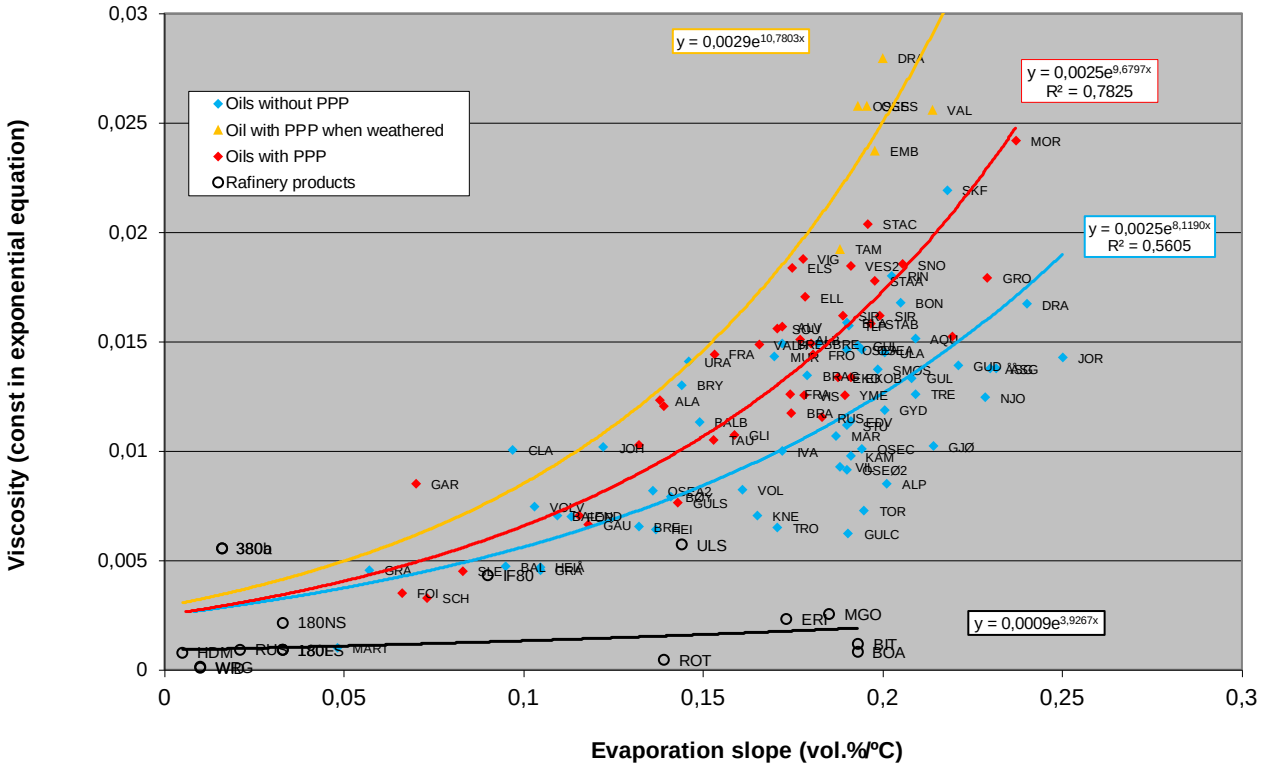


Figure 5.6: The exponential relationship between the "Viscosity ratio exp. constants) and the "evaporative loss slope" based on the data from the 141 selected oil weathering studies (see Table 4.2). Three different equations or categories are identified according to the crude oils initial viscosity, pour point and asphaltene/wax content and a separate class for prediction of refinery products.

Note! Annotations in the figure is different from the definition of the categories used earlier on page 16:
PPP = Pour Point Problems (Hi Wax)
"Oils with PPP" = "High wax oils"
"Oils with no PPP" = "Lo wax oils"
"Oils with PPP when weathered" = oils that become "High wax oils" when weathered

The exponential relationship in Figure 5.6 (see equations on chart) is used together with the evaporative loss slope in the 50-250ºC region from the TBP curve to predict the viscosity ratio for the water free residues. The correlations between the calculated exponential curve and the measured data shows a very good to acceptable fit between the modelled and the measured data.

5.3 Variables predicted based on multivariate models

The last variables needed to fulfil the "synthetic" laboratory weathering data set are the variables describing the emulsification of the oil slick at sea. These processes are more complicated to describe and several variables should be considered simultaneously. The predicted variables are the viscosity for emulsions consisting of 50 %, 75 % and maximum water content, and the uptake rate of water in emulsion (see Table 4.1).

These variables are predicted using a multivariate Partial Least Square (PLS) algorithm using the Unscrambler program (version 8.0). A description of the basic principles of this algorithm is given elsewhere e.g. Brandvik, 1997 or Martens *et al.*, 1994 and will not be further explained in any details here. Using PLS algorithm for multivariate calibration is similar to using ordinary linear regression for univariate calibration,

the only difference is that several variables (both X and Y matrices) are taken into account. The basic idea is to utilise the internal correlation between several x-variables to predict a limited number of y-variables. The x-variables used in this multivariate calibration are the original variables from the CA and the variables predicted from them are the variables on weathered residues listed previously in Table 4.1. Table 5.2 lists the X-variables used in the PLS regression.

Table 5.2: Data used as x- variables for the multivariate calibration of the emulsification properties.

Variable	Abbreviation	Units
Evaporative loss	*Evap*	*Vol.%*
Residue	*Res*	*Wt.%*
Density	*Dens*	*g/ml*
Pour point	*PP*	*℃*
Viscosity (water free oil)	*Visc*	*cP, shear 100 s^{-1}*
Wax	*Wax*	*Vol.%*
Asphaltene	*Asph*	*Vol.%*

A multivariate model was established based on the correlation of the x-variables and individual y-variables describing the emulsification properties e.g. the viscosity of the 50 % emulsions. The model used data on emulsions from the three residues of 150, 200 and 250ºC+, and the data set consisted of totally 162 objects (samples). Some objects were classified as outliers and omitted from the models, when it can be justified or explained by difference in composition or unusual behaviour in the laboratory.

To include interaction and second order effects, selected cross terms of the x-variables in Table 5.2 were also used. These cross terms are: Dens*PP, Dens*Visc, PP*Asph, PP*Wax, Visc*Asph, Visc*Wax, $Visc^2$ and Wax^2. Three of the original x-variables (Visc Asp and PP) were also transformed (logarithmic) to obtain a more normal distribution. All the 15 variables (7 first order + 8 interaction terms) were normalised (variance = 1) to avoid any unwanted scaling effects from different numerical ranges (viscosities in 1 – 30 000 cP and densities in 0.810 – 0.950 g/mL).

Four different “quality describing” parameters were used to describe the results from the multivariate calibrations and predictions in this section.

1. No of PCs: The number of principal components used in the model is determined by the complexity of the modelled variable and is used to maximise the correlation between measured and predicted values.
2. Expl. x var.: Explained variance among the x-variables. This is the variance explained by the used principal components compared to the total variance in the data material (x-variables).
3. Expl. y var.: Explained variance among the y-variables. As described above for the x-variables.
4. Correlation: The correlation between measured and predicted values for this specific variable.

Tables and graphs for predicting properties for both crude oils and refinery products are presented in the next chapters. The calibration coefficients for the multivariate linear equations are given in Appendix A.

The scatterplots illustrate predicted versus measured values (red dots) and the red lines is the best-fit line to the data, while the black lines are the ideal line giving a perfect match between measured and predicted values.

5.3.1 Viscosity of emulsified residues (50 %, 75 % and max. water)

Calibration models are built using the x-variables described above, giving totally 7 variables and 162 objects. Three separate PLS1 models were established for each of the three viscosities (50%, 75% and maximum water content). The PLS1 models were validated by cross validation (Martens et al., 1994) and refined by

omitting outliers to increase the predicting property of the models and the unexplained variance. The output from the Unscrambler program is a multivariate linear equation summarising the principal components used in the model. This equation is together with the x-variables used to predict values for the viscosity for the emulsified residues.

Variable: Viscosity of 50% emulsions
Crude oils:
no of PCs: 5
Expl. x var.: 92%
Expl. y var.: 78%
Correlation: 0.88

Note: The calibration laboratory data for the refinery products do generally not contain data for 50% emulsions. Most refinery products do not have a water uptake of 50%.

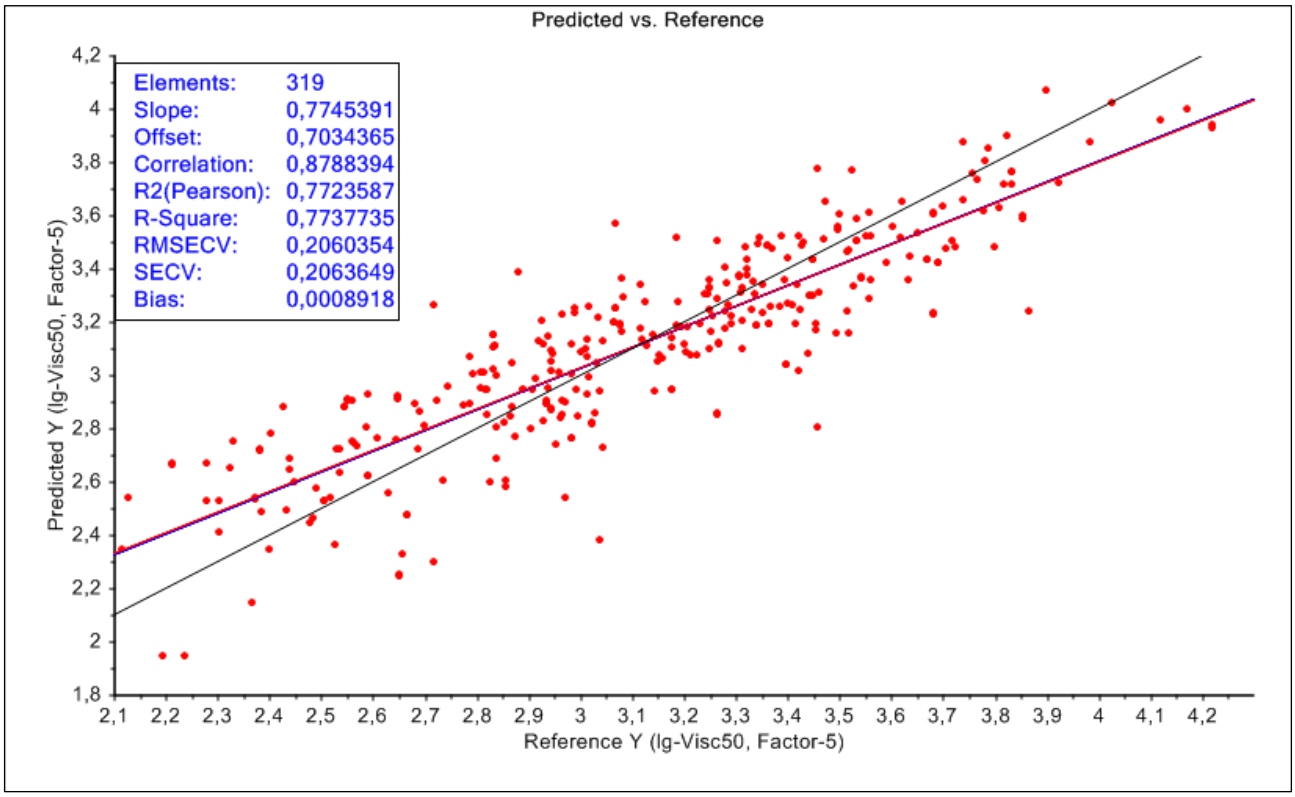


Figure 5.7 *Plot of measured versus predicted values for the 50% water emulsions for the weathered residues. The correlation is statistical significant with a correlation factor of 0.88. Only the validation samples with full cross validation are plotted and used in the calculation of the correlation factor.*

Variable: Viscosity of 75% emulsions
Crude oil:
no of PCs: 4
Expl. x var.: 84%
Expl. y var.: 61%
Correlation: 0.80

Note: The calibration laboratory data for the refinery products do generally not contain data for 50% emulsions. Most refinery products do not have a water uptake of 75%.

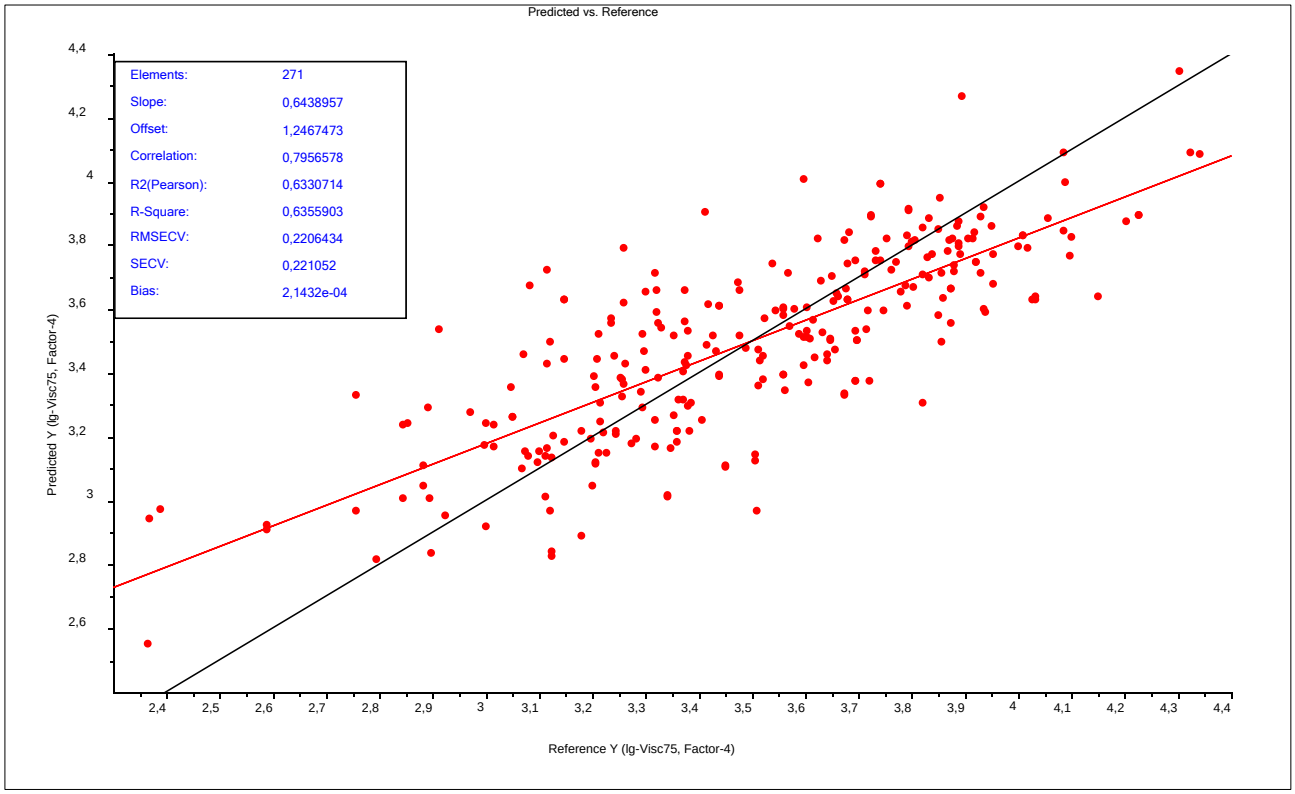


Figure 5.8 *Plot of measured versus predicted values for the 75% water emulsions for the weathered residues. The correlation is statistical significant with a correlation factor of 0.80. Only the validation samples with full cross validation are plotted and used in the calculation of the correlation factor.*

Variable: Viscosity of maximum water emulsions

Crude oils:

no of PCs:	6
Expl. x var.:	83%
Expl. y var.:	63%
Correlation:	0.78

Refinery products:

no of PCs:	4
Expl. x var.:	97%
Expl. y var.:	92%
Correlation:	0.93

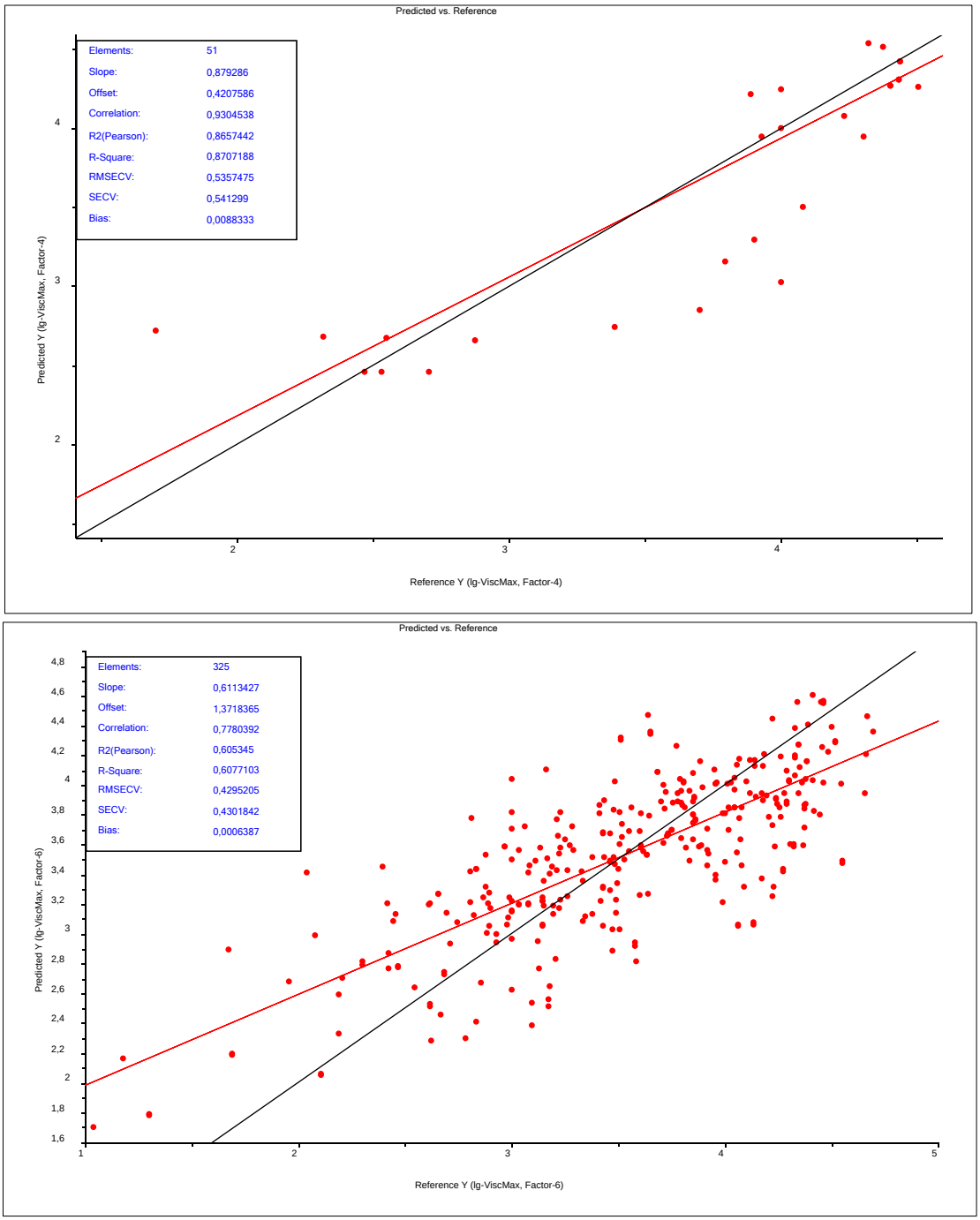


Figure 5.9 *Plot of measured versus predicted values for the max water emulsions for the weathered residues. The correlation is statistical significant with a correlation factor of 0.78. Only the validation samples with full cross validation are plotted and used in the calculation of the correlation factor.*

5.3.2 Water uptake (rate and maximum value)

A common calibration model is established for both the water uptake rate and the maximum water content in the emulsion. This approach gives a more robust model with better predicting properties because these two y-variables are strongly correlated. In general, high water uptake e.g. for paraffinic or waxy crudes will usually also give rapid uptake rate, while low water content e.g. for viscous asphaltenic crudes gives slow water uptake.

For some of the laboratory studies the data are adjusted based on observations from meso-scale weathering- or field studies. In most cases the maximum water uptake from the rotating flask apparatus has been adjusted to fit the weathering from meso-scale studies. The multivariate calibration in this study has been based on the original data from the small-scale laboratory tests. We have tried to use the adjusted values, but the correlation between the parameters describing the water free oil (especially viscosity and wax content) and the water uptake parameters (t½ and the maximum water uptake) became much weaker. A possible explanation for the reduced correlation may be that when the adjusted values are used, only one common value for maximum water uptake are used (for all residues) and the uptake rate is not changed. This means that in some cases, especially with waxy crudes, the maximum water uptake could be overestimated (see verifications in appendix A).

The output from the Unscrambler program is presented in the same manner as in the previous section.

Variable: Maximum water uptake (EM%)

Crude oil:

no of PCs:	7
Expl. x var.:	93%
Expl. y var.:	42%
Correlation:	0.61

Refinery products:

no of PCs:	7
Expl. x var.:	97%
Expl. y var.:	75%
Correlation:	0.83

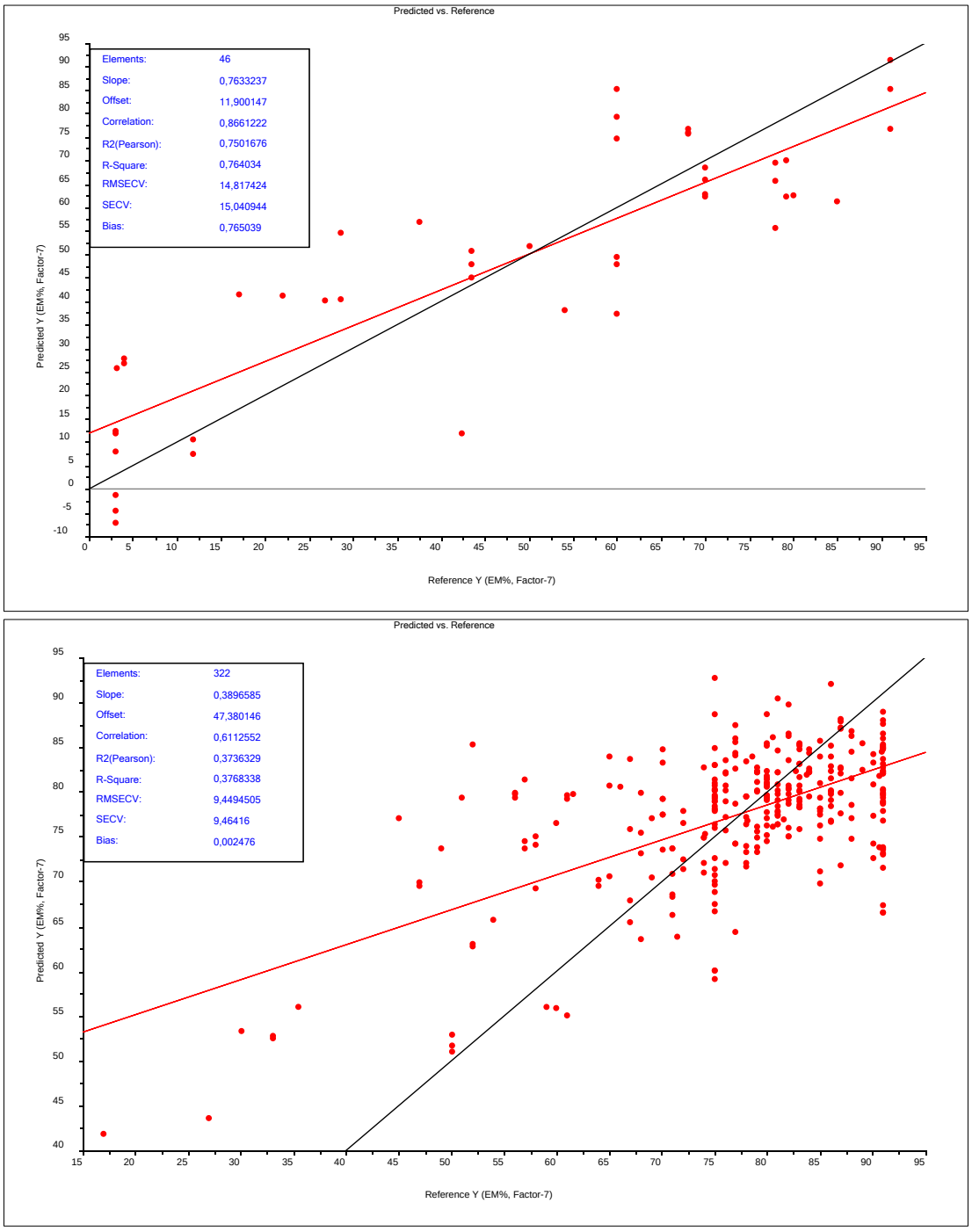


Figure 5.10 Plot of measured versus predicted values for the maximum water uptake for the weathered residues. The correlation is statistical significant with a correlation factor of 0.60. Only the validation samples with full cross validation are plotted and used in the calculation of the correlation factor.

Variable: Water uptake rate (t½)

Crude oil:

no of PCs:	6
Expl. x var.:	85%
Expl. y var.:	26%
Correlation:	0.47

Refinery products:

no of PCs:	5
Expl. x var.:	96%
Expl. y var.:	75%
Correlation:	0.85

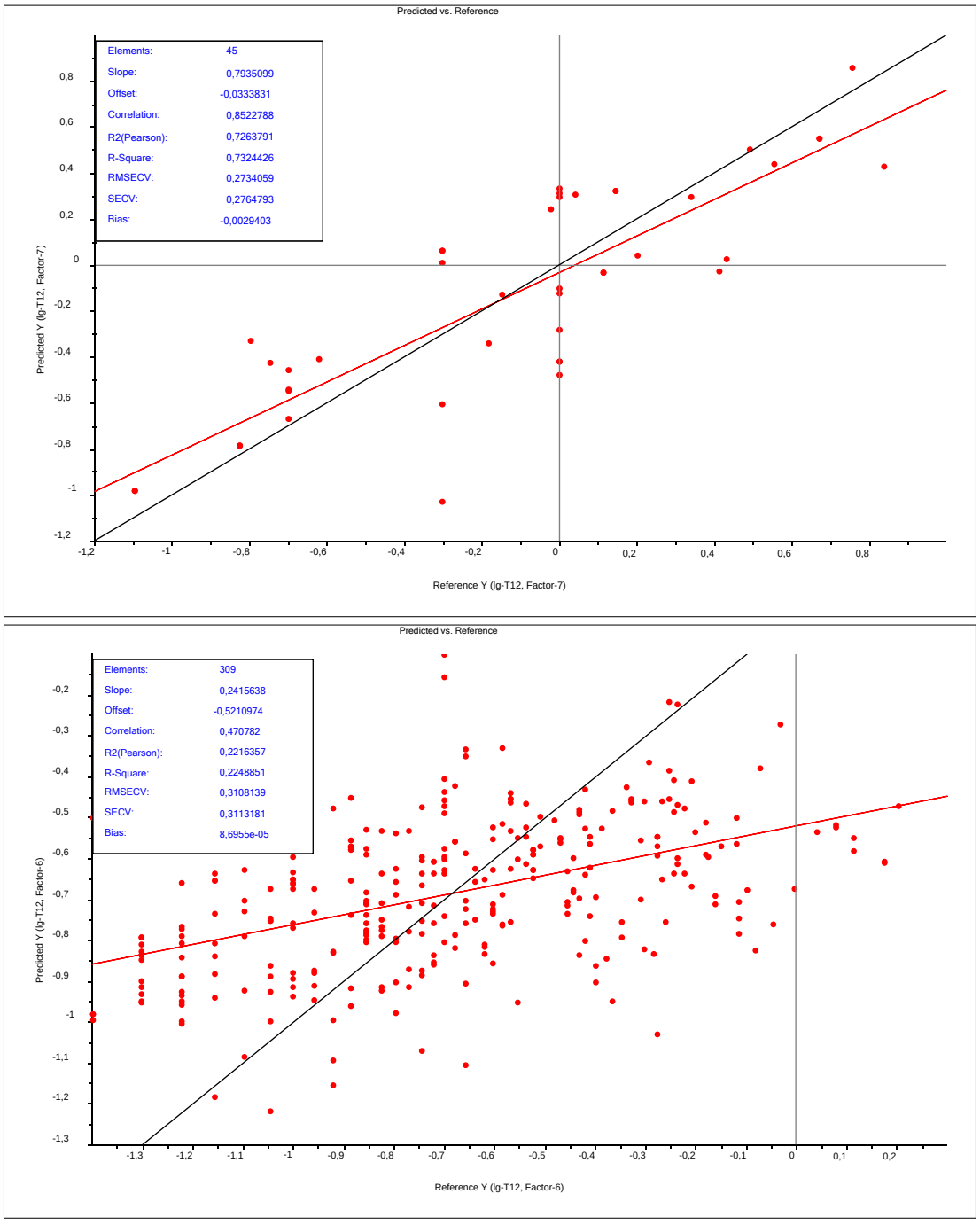


Figure 5.11 Plot of measured versus predicted values for the water uptake rate for the weathered residues. The correlation has a low statistical significance with a correlation factor of 0.47. Only the validation samples with full cross validation are plotted and used in the calculation of the correlation factor.

5.4 New functionality to identify "Find Model oil"

In some cases where only CA data is available it would be of interest to search the oil database for an oil type with similar CA data and a full laboratory dataset (weathering study). The new approach is based on calculating a parameter describing the correlation or fitness between the new oil and the characterised oil present in the SINTEF oil database. This approach is only based on the available CA variables. How this "fit factor" (r_i) is calculated is shown in Equation 5.2 below:

$$r_i = \frac{1}{n}\sum_{k=1}^{n} S_k \sqrt{\left(\frac{V_k - O_{ik}}{(V_k + O_{ik})/2}\right)^2} \qquad \textit{Equation 5.2}$$

for: k = 1..n and i = 1..p

Where:

V_k: Crude assay variables from Table 4.1 (and Appendix B)
O_i: Oils characterized in the SINTEF oil database (weathering studies)
S_k: Scaling factor specific for each CA variable
p: The number of characterized oil in SINTEF database
n: The number of crude assay variables

A similar approach has earlier been used by SINTEF e.g. in a project for EMSA in 2005 (Reed et al., 2005) and has (in a modified version) in this project shown to be a robust approach. Its simplicity is also appealing compared to the more complex alternative described in the previous section. New oils are assigned to the five different categories (paraffinic, waxy, naphtenic, asphaltenic and refinery products). Based on the "Fit factor" described in Equation 5.1 above, an approach as shown in Figure 5.12 could be followed. This enables the use of the CA data for new oils to calculate the "Fit factor" for all the oil in the openly available part of the SINTEF database of characterised oils (weathering properties). The ten best candidates are shown, and a colour code indicates their fit to the new oil (green, yellow and red).

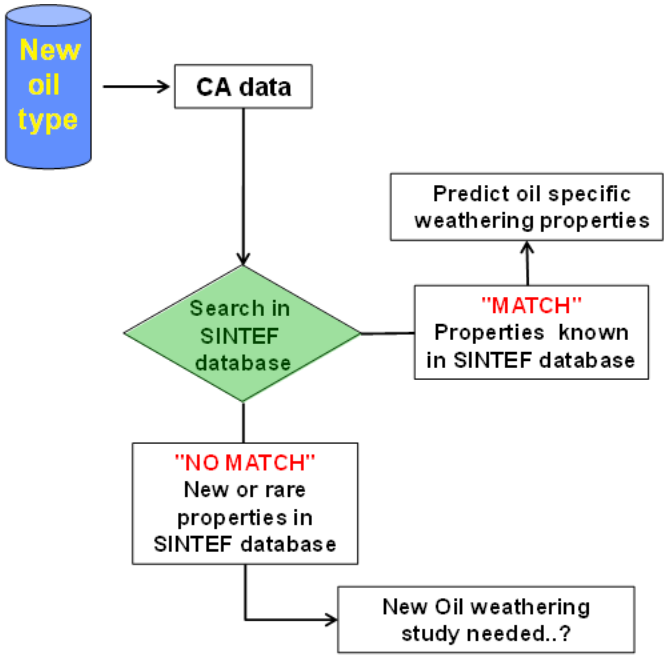
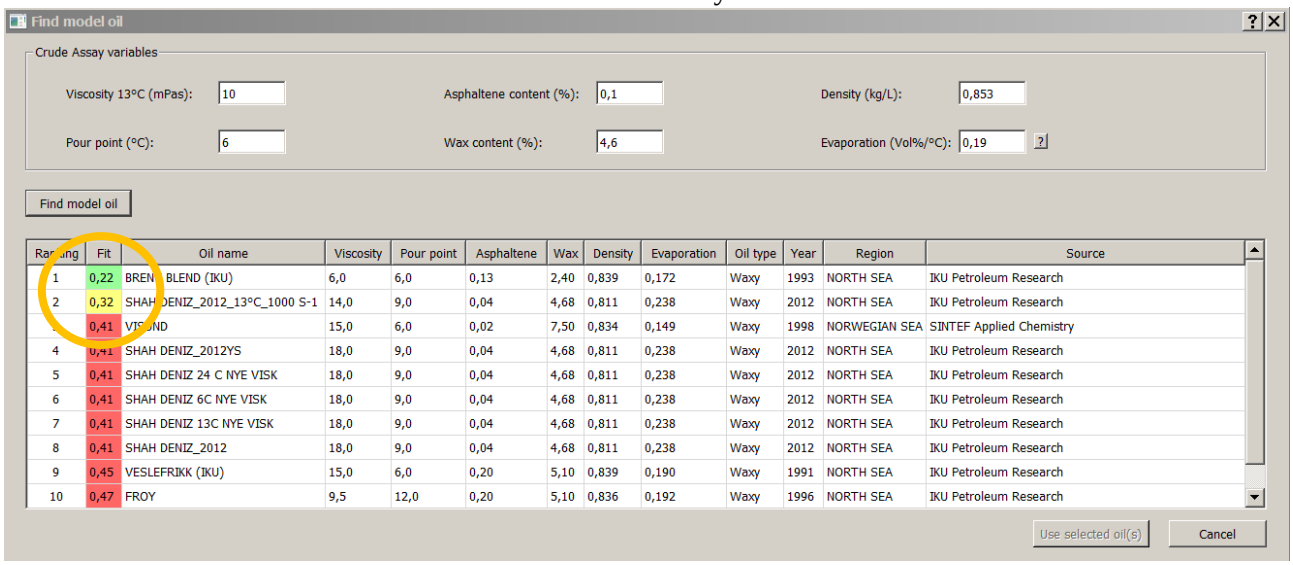


Figure 5.12: Overview of the approach based on the "Fit factor" showing how the CA data (Table 4.1) for the new oil are used to search for a model oil in the SINTEF database with existing characterised oils.

The main user interface for the "Find model oil" functionality is shown below.



Ranking	Fit	Oil name	Viscosity	Pour point	Asphaltene	Wax	Density	Evaporation	Oil type	Year	Region	Source
1	0,22	BREN BLEND (IKU)	6,0	6,0	0,13	2,40	0,839	0,172	Waxy	1993	NORTH SEA	IKU Petroleum Research
2	0,32	SHAH DENIZ_2012_13°C_1000 S-1	14,0	9,0	0,04	4,68	0,811	0,238	Waxy	2012	NORTH SEA	IKU Petroleum Research
3	0,41	VISUND	15,0	6,0	0,02	7,50	0,834	0,149	Waxy	1998	NORWEGIAN SEA	SINTEF Applied Chemistry
4	0,41	SHAH DENIZ_2012YS	18,0	9,0	0,04	4,68	0,811	0,238	Waxy	2012	NORTH SEA	IKU Petroleum Research
5	0,41	SHAH DENIZ 24 C NYE VISK	18,0	9,0	0,04	4,68	0,811	0,238	Waxy	2012	NORTH SEA	IKU Petroleum Research
6	0,41	SHAH DENIZ 6C NYE VISK	18,0	9,0	0,04	4,68	0,811	0,238	Waxy	2012	NORTH SEA	IKU Petroleum Research
7	0,41	SHAH DENIZ 13C NYE VISK	18,0	9,0	0,04	4,68	0,811	0,238	Waxy	2012	NORTH SEA	IKU Petroleum Research
8	0,41	SHAH DENIZ_2012	18,0	9,0	0,04	4,68	0,811	0,238	Waxy	2012	NORTH SEA	IKU Petroleum Research
9	0,45	VESLEFRIKK (IKU)	15,0	6,0	0,20	5,10	0,839	0,190	Waxy	1991	NORTH SEA	IKU Petroleum Research
10	0,47	FROY	9,5	12,0	0,20	5,10	0,836	0,192	Waxy	1996	NORTH SEA	IKU Petroleum Research

The fit is calculated to all the oils in the SINTEF database and the 10 oils with the closest fit appear. A colour coding indicates the degree of fit:

< 0.25: Good fit
0.26 – 0.40: Reasonable fit
> 0.40: Unsatisfactory fit

The numerical values describing the degree of fit are determined by testing similarities and differences among existing characterised oils: The ranges reflect the operational significance by evaluating weathering parameters as the evaporation, water uptake, emulsion viscosity and time window for dispersant application. This is calibrated towards oils with full weathering studies in the database. Crude oils that show a good fit to each other (< 0.25), should have similar weathering behaviour, especially for the emulsion viscosity. It is expected that the same strategy for oil spill contingency can be used for oil such similar oils. This indicates that green oils could be used as model oils for the oil represented with the inserted CA variables. The use of Yellow oils should be further investigated and use of Red oils as model oils is not recommended.

This approach using the CA variables to find a model oil could be an alternative to predicting the weathering properties from the CA variables directly, especially for those oils that fall outside the calibration of the CA module, for example condensates.

However, the boarders for the fit factor is mainly calibrated using crude oils and the uncertainty is expected to be higher when comparing condensates or very light refinery products.

5.5 Quality assurance for prediction of weathering properties on new oil types

The oil types selected for the calibration set have a broad variety of properties. Most of them are typical for the five main groups; paraffinic, waxy, naphtenic, asphaltenic and refinery products.

Despite the calibration in this study was based on a broader selection of oils, new oils could still have chemical composition (and weathering properties) which are very different from the oils used in the calibration set. Using the CA module to predict weathering properties for such oil could lead to very uncertain predictions. These oils should be identified as outliers because of high uncertainties. The CA module in SINTEF OWM will for this reason not provide predictions for these oil types, but recommend using the "Find Model Oil" option for predicting weathering properties.

A simplified message system is incorporated to help the user when predictions are based only fresh oil properties (CA data). Based on the fresh oil properties three different message categories will be displayed when running the SINTEF OWM

Red warning messages (U1-U5): Displayed if the oil properties are outside the valid range of the calibration set.

Yellow warning messages (C1-C4): Displayed if the oil properties are inside the valid range, but some combination of properties could give uncertain predictions.

Green standard message (A1): A general warning that predictions based on fresh properties only are more uncertain. Displayed if the system detects no other warning messages.

The values of the fresh oil properties defining the messages listed below (Table 5.3).

Table 5.3 Displayed warning and guiding messages.

Class	Conditions			Challenge	Examples
Unacceptable. Out of calibration range	For **BOTH** crudes and refinery products (as specified below)				
U1	Very high Visc Crude Refinery		> 2 500 >30 000	The viscosity of this oil is very high compared to the oils used in the calibration set. Cannot predict weathering properties with sufficient quality, based on fresh oil data only! Consider using the "Find Model Oil" option to select an oil with laboratory data.	
U2	Very high Wax Crude Refinery		>15 >14	The wax content of the oil is very high compared to the oils used in the calibration set. Cannot predict weathering properties with sufficient quality, based on fresh oil data only! Consider using the "Find Model Oil" option to select an oil with laboratory data.	
U3	Very high Asph Crude Refinery		>2 >10	This oil has a very high asphaltene content compared to the oils used in the calibration set. Cannot predict weathering properties with sufficient quality, based on fresh oil data only! Consider using the "Find Model Oil" option to select an oil with laboratory data.	
U4	high Vax AND Asph Crude Refinery	Vax >9 >8	Asp >1 >8	This fresh oil has a combination of high wax and high asphaltene content compared to the oils used in the calibration set. Cannot predict weathering properties with sufficient quality, based on fresh oil data only! Consider using the "Find Model Oil" option to select an oil with laboratory data.	
U5	High Evap OR Low Density	Evap > 0.25	Dens < 0.800	This is a light oil, Condensate or a light refinery product with a very high and rapid evaporation. Cannot predict weathering properties with sufficient quality, based on fresh oil data only! Consider using the "Find Model Oil" option to select a product with laboratory data.	

Use predictions with care	Only for crudes (NOT refinery products)		Challenge	
C1	low Visc AND medium Wax AND medium Evap	< 10 > 5 > 0.18	This oil has a low initial viscosity, high evaporative loss and medium wax content. The uncertainty in prediction of water uptake and emulsion viscosity could be high!	Vale, Draugen, Embla, Oseberg Sør
C2	high Visc AND	>100	This oil has high initial viscosity combined with high wax or high asphaltene content. The uncertainty in prediction of water uptake and emulsion viscosity could be high!	Elli South, Balder, Glitne, Forties, Alpine
	medium Wax OR medium asp	>5 >0,5		
C3	high Evap (evap slope)	>0.20	This oil has a high evaporative loss. The uncertainty in prediction of weathering properties, especially water uptake and emulsion viscosity, could be high!	North Star, Njord, Åsgard
C4	Borderline between "High" and "Low" wax content oil Wax AND Asp AND PP	 <4.5, 5,5> <0.15, 0,25> <-3, 3>	This oil is "borderline" between "High wax" and "Low wax" oils. The combination of wax, asphaltene and pour point influence which algorithm used for prediction viscosity. A small change in these variables could strongly influence prediction of viscosity. See user manual for further information.	
Class	**Conditions**			
	For **BOTH** crudes and refinery products			
A1	All conditions		These predictions of oil weathering are based on fresh oil properties only and could deviate from predictions based on laboratory studies!	

5.6 Crude assay module verification

To verify the performance of the extended CA module predictions were made and compared with predictions based on full laboratory studies. Weathering properties for different categories of crude oils were predicted with SINTEF OWM based on;

A: Crude assay data
B: Laboratory data from weathering study

The new extended CA module was used on a selection of oils and the results from 10 different crude oils and 4 refined products are presented here as a verification test. The oils were selected to give a realistic picture of the CA module performance. These oils are:

1. Naphtenic crudes:
Troll, Heidrun Blend and Draugen

2. Asphaltenic crudes
Balder blend (2010) and Oseberg Øst

3. Paraffinic crudes:
Gyda and Statfjord A

5. **Waxy crudes:**
Ringhorne, Elli South

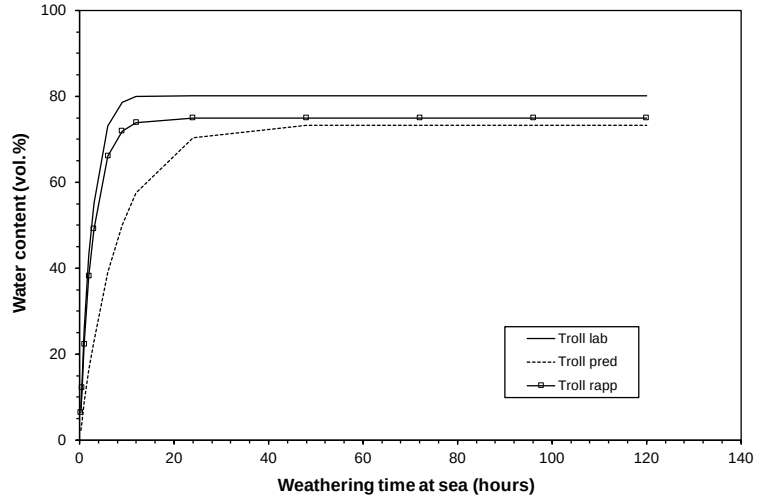
6. **Refinery products**
IF-380, IFO180, Wide range gas oil (WRG) and HDME

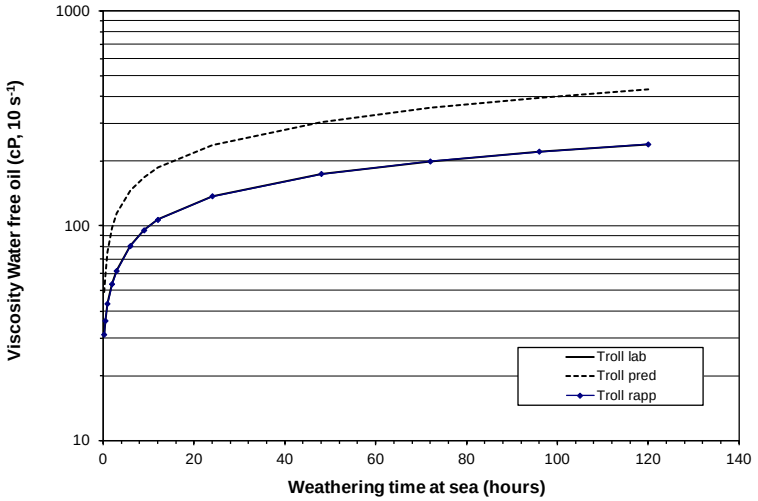
The oil listed above are used to verify the new extended CA module. Predictions of weathering properties from the SINTEF OWM (test version 9.2) based on both CA data and laboratory weathering studies are shown in Chapter 6.

For some of these weathering studies the predictions based on small-scale laboratory study are adjusted based on observations from meso-scale weathering- or from field studies. This adjustment is in most cased the water content for the emulsions which has been reduced compared to the results from small-scale laboratory studies (rotating flask apparatus). The multivariate calibration in this study has been based on the original data from the small-scale laboratory tests (see Section 5.3.2 for more details). In such cases also the adjusted results (which also are the results reported in the weathering handbooks) are presented in figures in Chapter 6 and marked as “Reported” or only “Rapp”.

6 Verification of predictions based on CA data from SINTEF Oil Weathering Model

Troll crude (message A1)





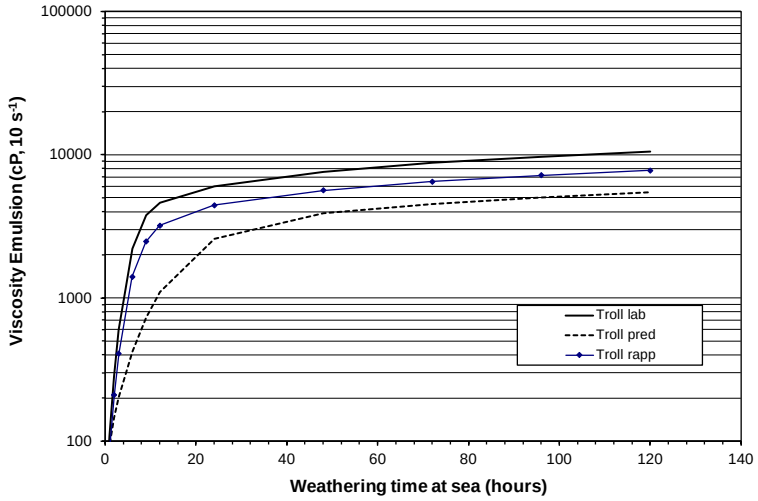
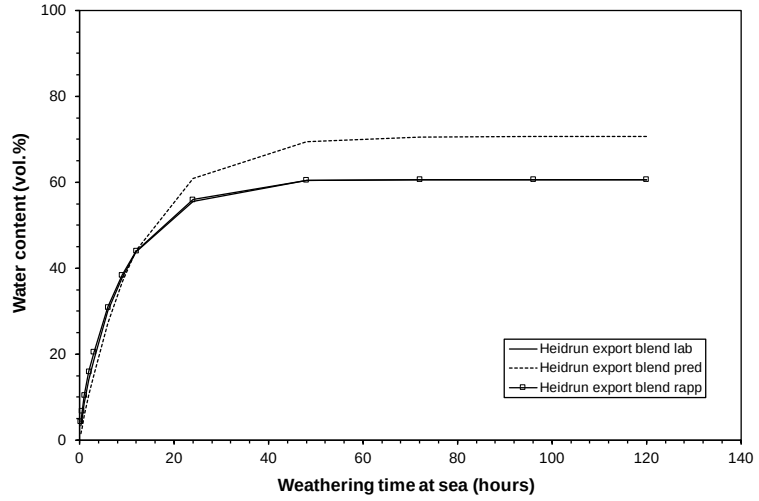
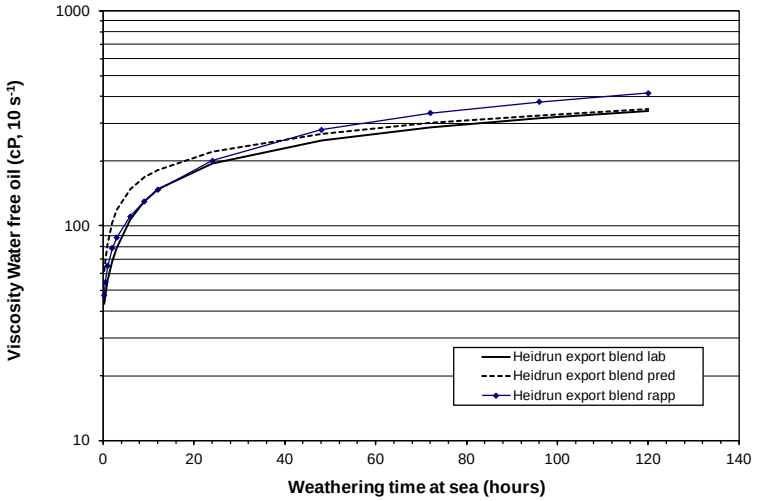


Figure 6.1 *Weathering properties for Troll crude (water uptake, water free- and emulsion viscosity) predicted based on fresh oil properties or crude assay data (pred) and lab studies (lab & rapp).*

6.1 Heidrun blend (message A1)





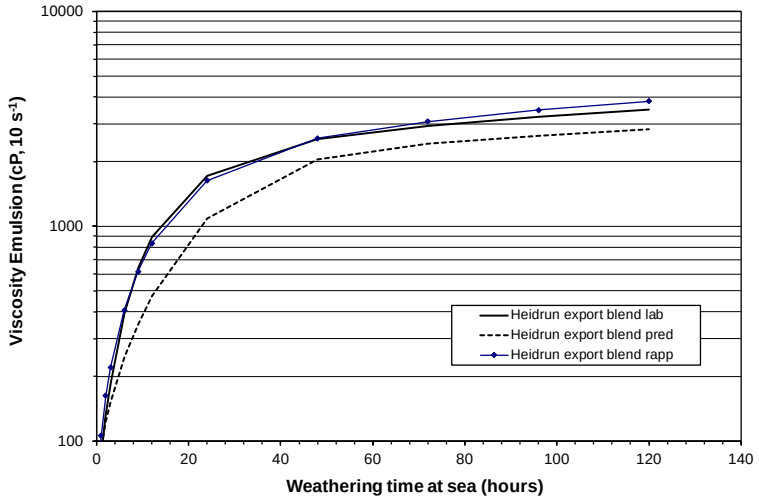
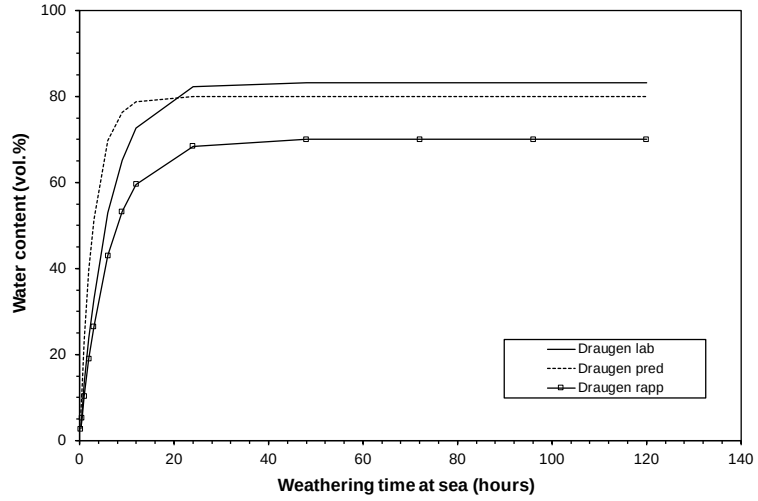
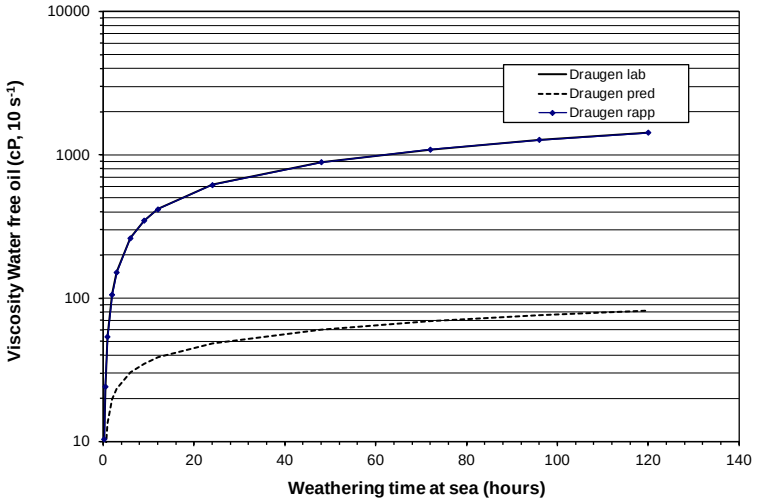


Figure 6. 6.2 Weathering properties for Heidrun blend (water uptake, water free- and emulsion viscosity) predicted based on fresh oil properties (crude assay data) and lab studies.

6.2 Draugen crude (message C1 og and A1)





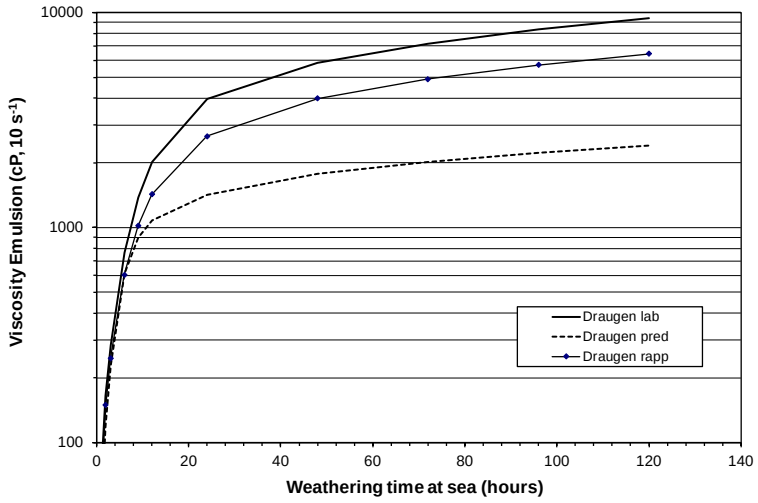
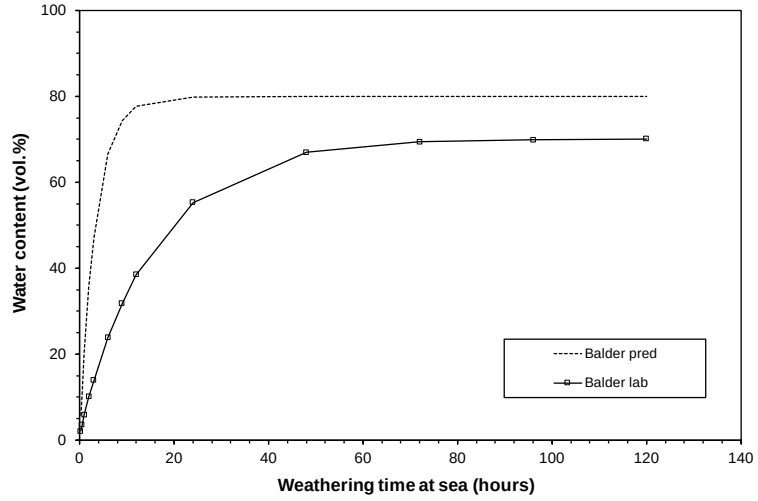
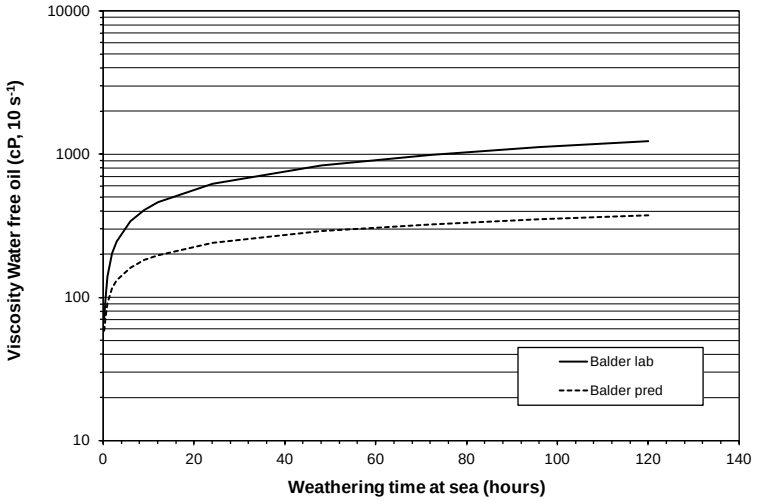


Figure 6.6.3 Weathering properties for Draugen crude (water uptake, water free- and emulsion viscosity) predicted based on fresh oil properties (crude assay data) and lab studies.

6.3 Balder blend 2010 (message: A1)





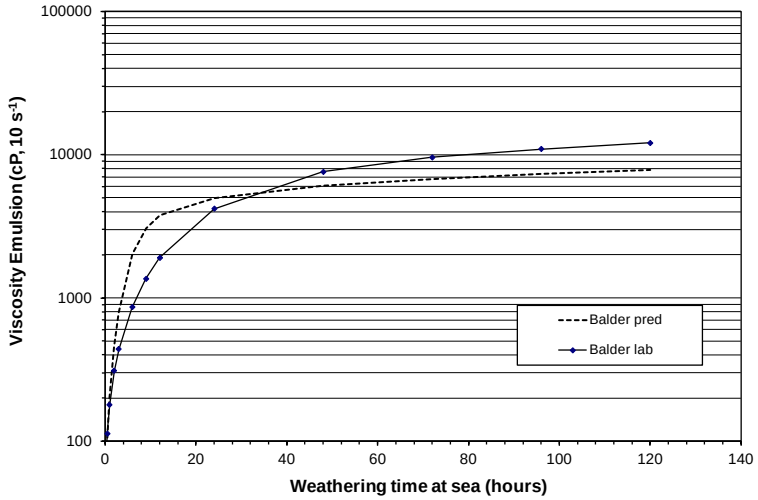
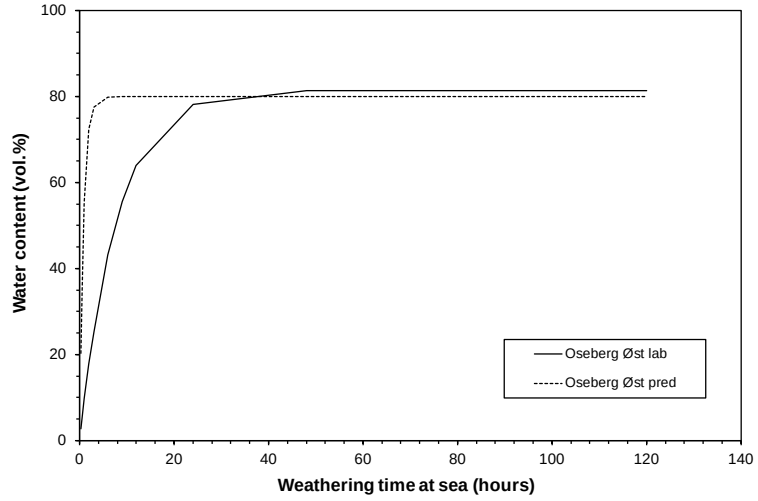
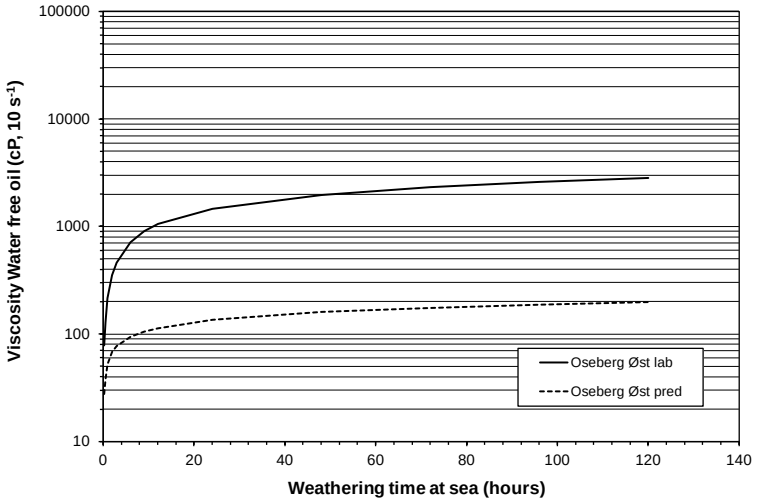


Figure 6.4 Weathering properties for Balder crude (water uptake, water free- and emulsion viscosity) predicted based on fresh oil properties (crude assay data) and lab studies.

6.4 Oseberg Øst (message: A1)





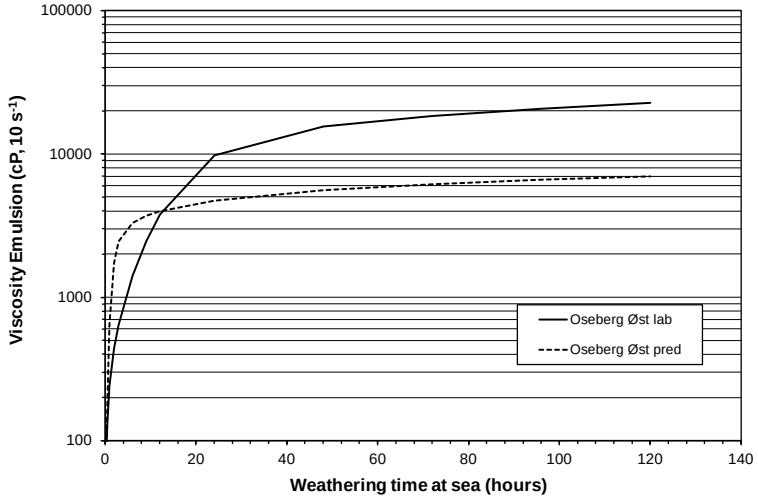
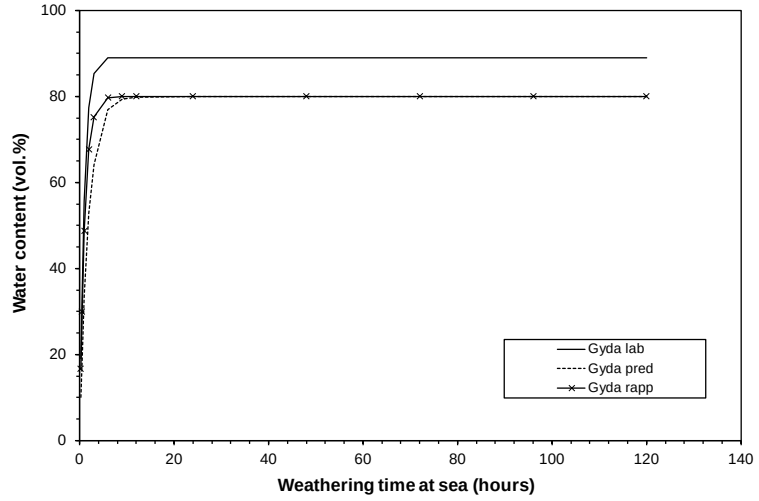
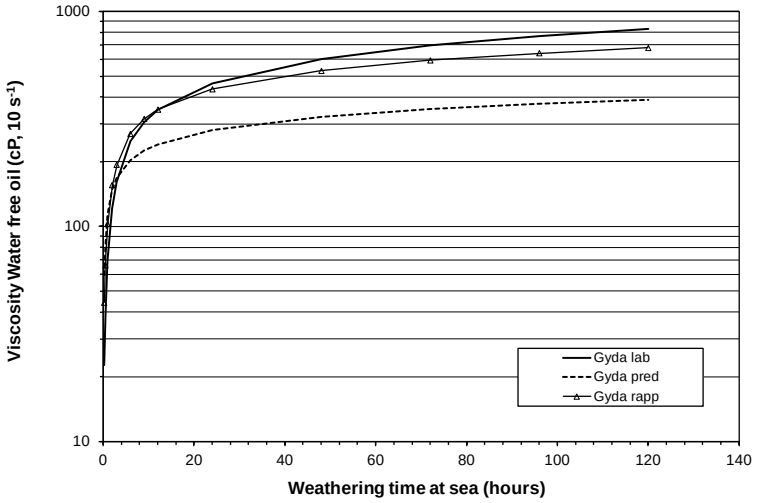


Figure 6.5 Weathering properties for Oseberg Øst (water uptake, water free- and emulsion viscosity) predicted based on fresh oil properties (crude assay data) and lab studies.

6.5 Gyda (message: C3 and A1)





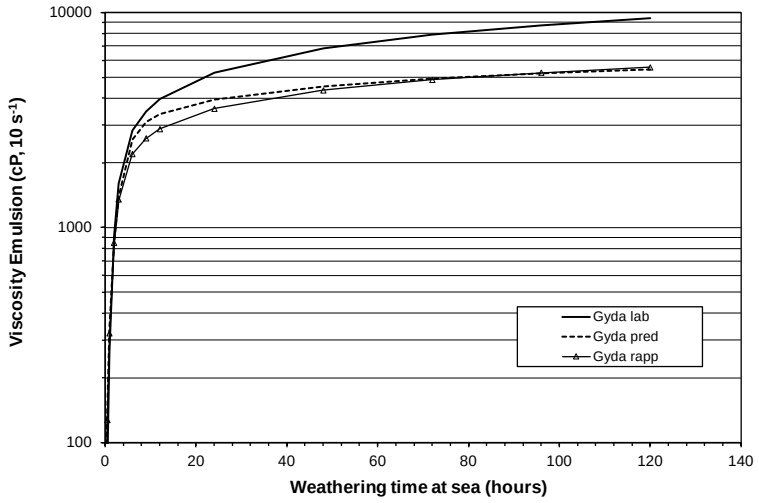
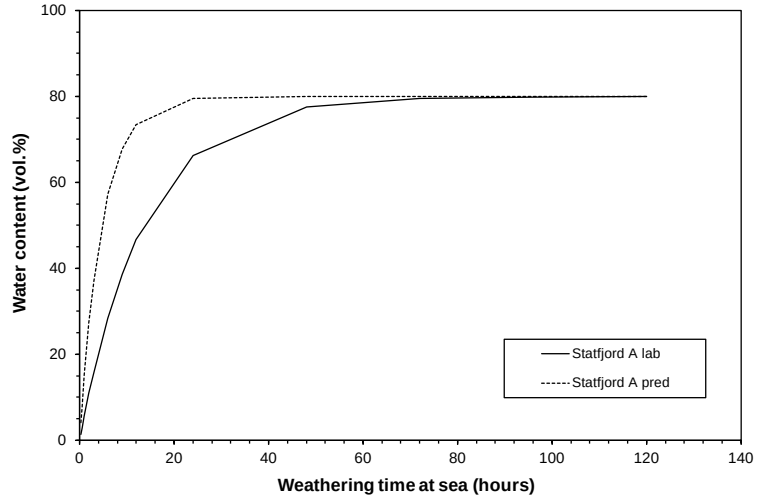
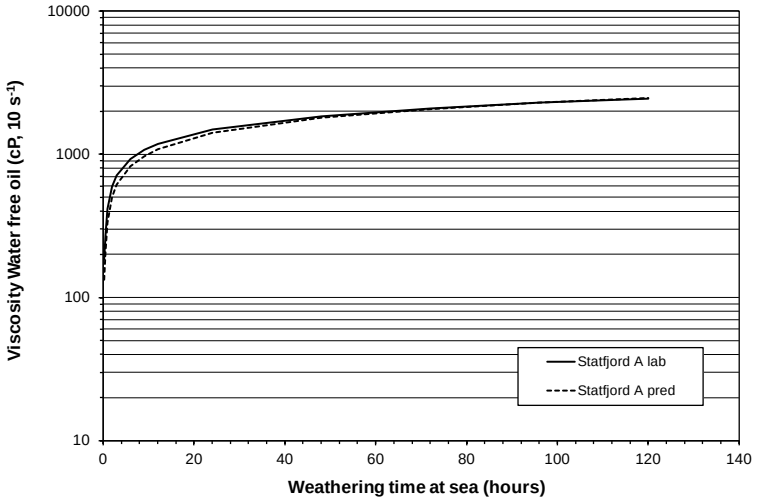


Figure 6.6 Weathering properties for Gyda crude (water uptake, water free- and emulsion viscosity) predicted based on fresh oil properties (crude assay data) and lab studies.

6.6 Statfjord A (message: A1)





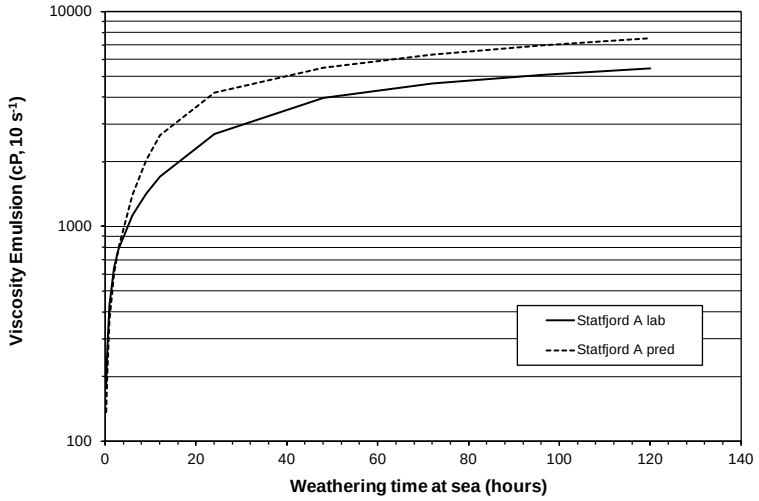
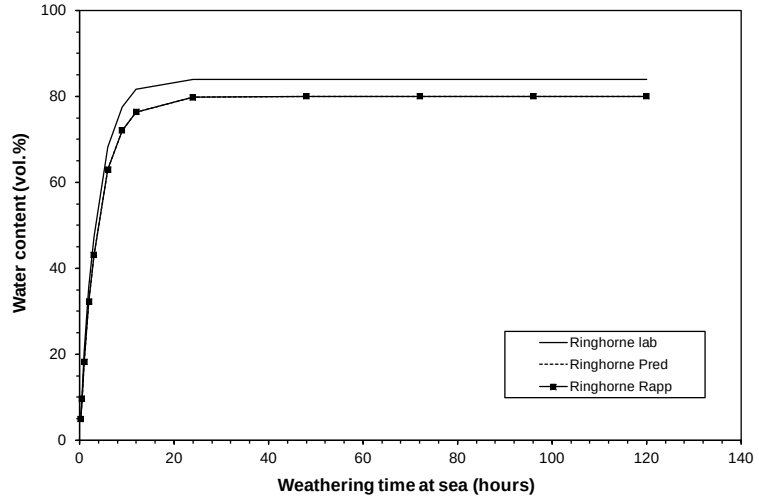
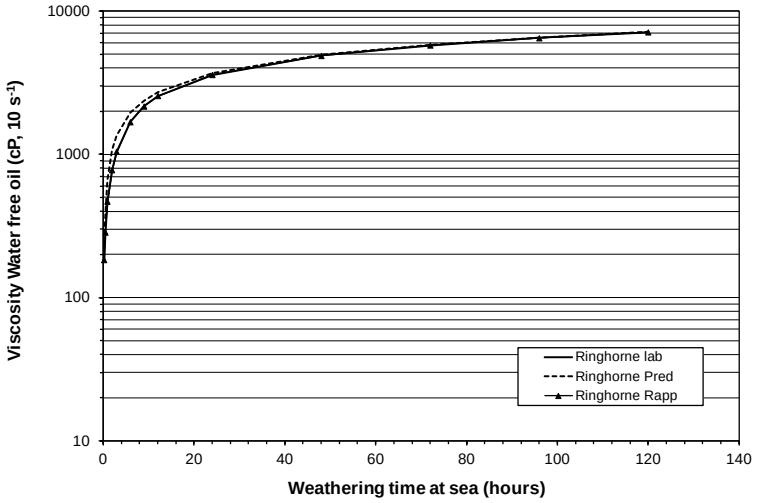


Figure 6.7 Weathering properties for Statfjord A (water uptake, water free- and emulsion viscosity) predicted based on fresh oil properties (crude assay data) and lab studies.

6.7 Ringhorne (message: A1)





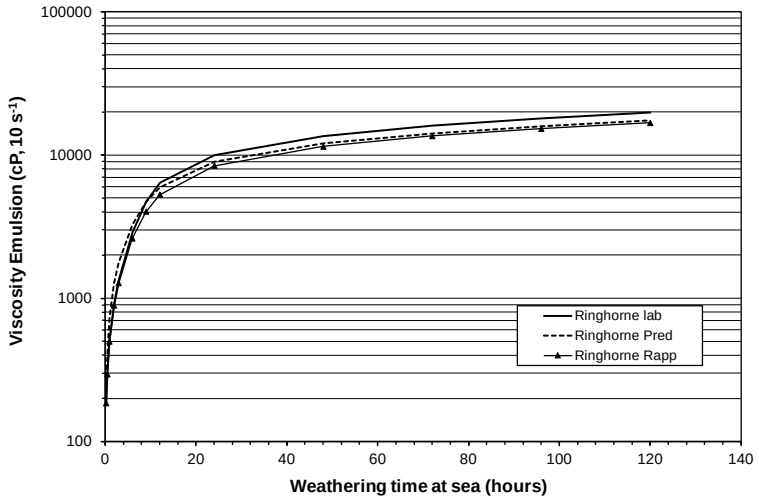
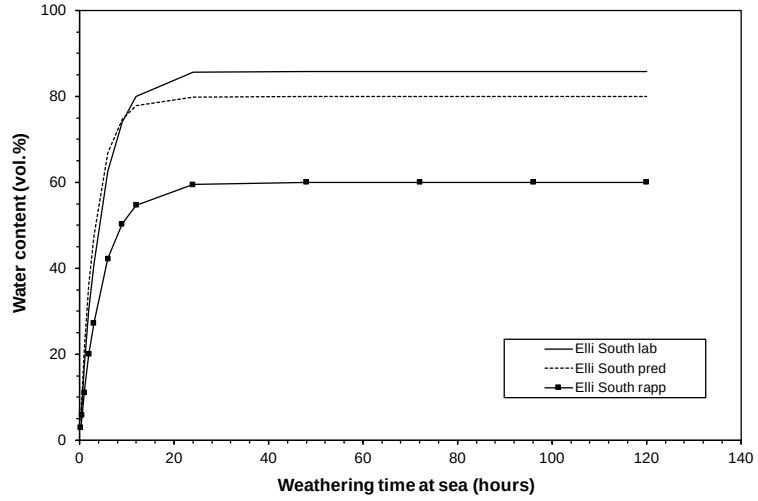
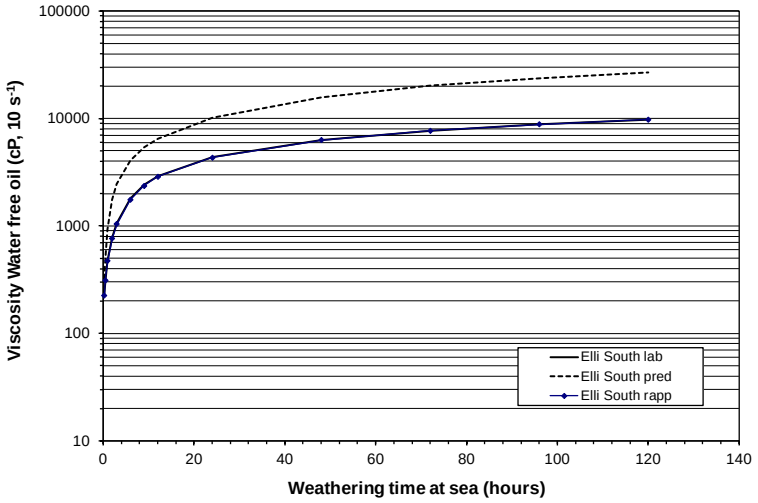


Figure 6.8 Weathering properties for Ringhorne (water uptake, water free- and emulsion viscosity) predicted based on fresh oil properties (crude assay data) and lab studies.

6.8 Elli South (message: C2 and A1)





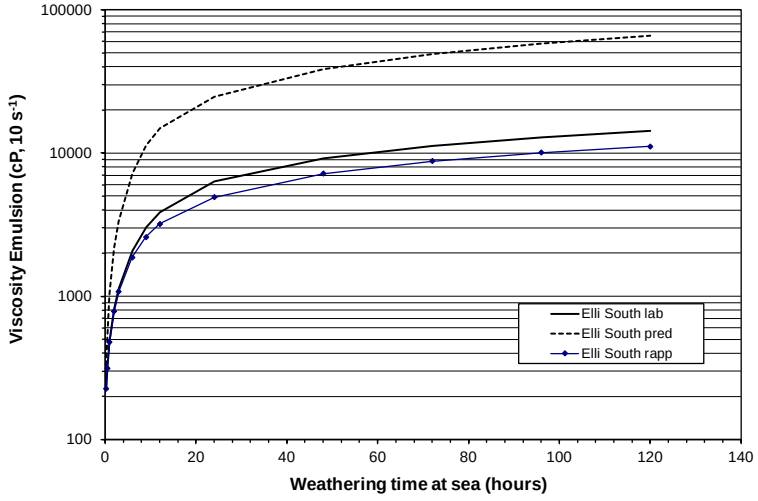


Figure 6.9 Weathering properties for Elli South (water uptake, water free- and emulsion viscosity) predicted based on fresh oil properties (crude assay data) and lab studies.

6.9 IFO180 (message: C2 and A1)

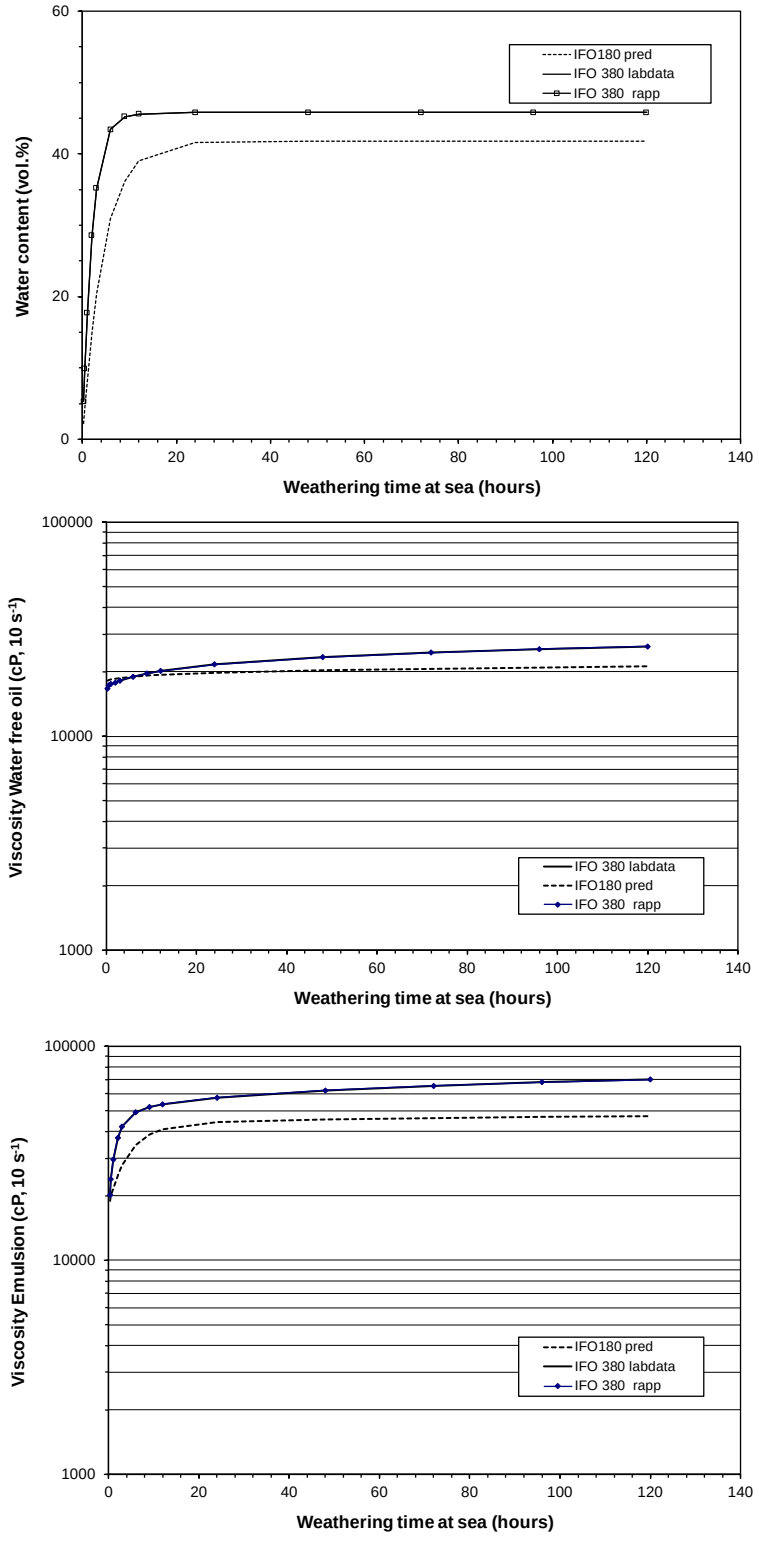


Figure 6.10 Weathering properties for IF-180 (water uptake, water free- and emulsion viscosity) predicted based on fresh oil properties (crude assay data) and lab studies.

6.10 IF380 (message: C2 and A1)

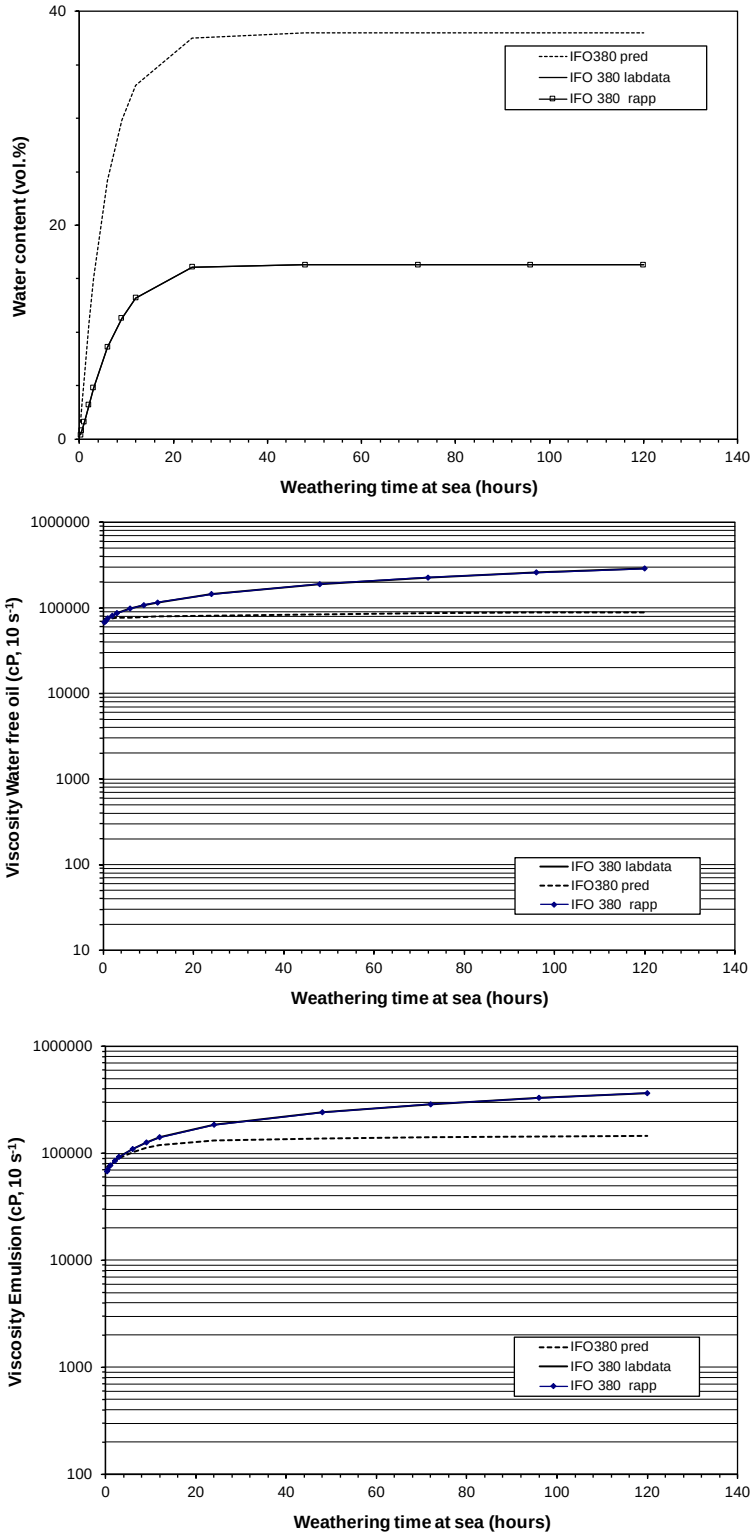


Figure 6.11 Weathering properties for IF380 (water uptake, water free- and emulsion viscosity) predicted based on fresh oil properties (crude assay data) and lab studies.

6.11 Wide Range Gasoil (message: A1)

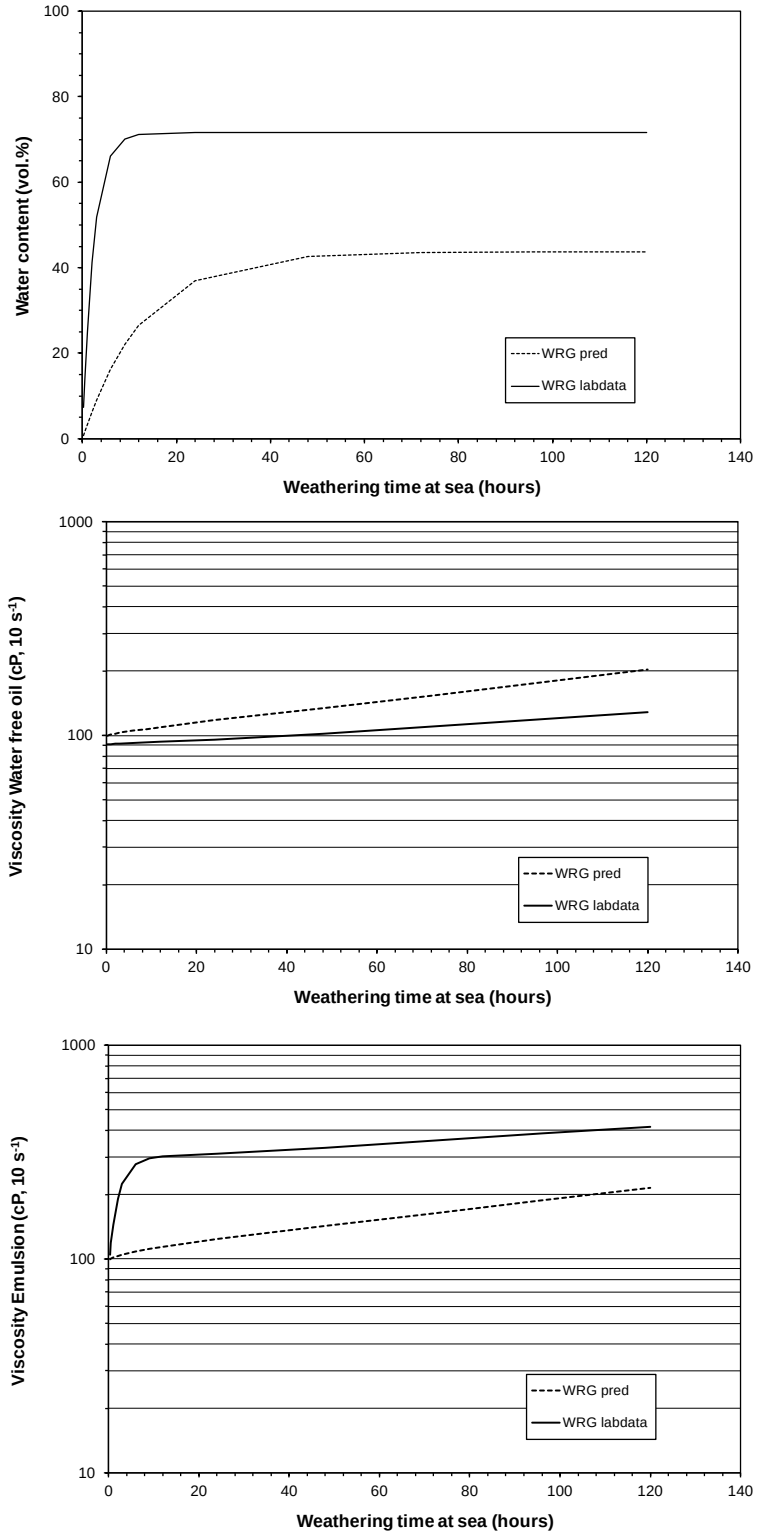


Figure 6.12 Weathering properties for WRG (water uptake, water free- and emulsion viscosity) predicted based on fresh oil properties (crude assay data) and lab studies.

6.12 HDME50 (message: C2 and A1)

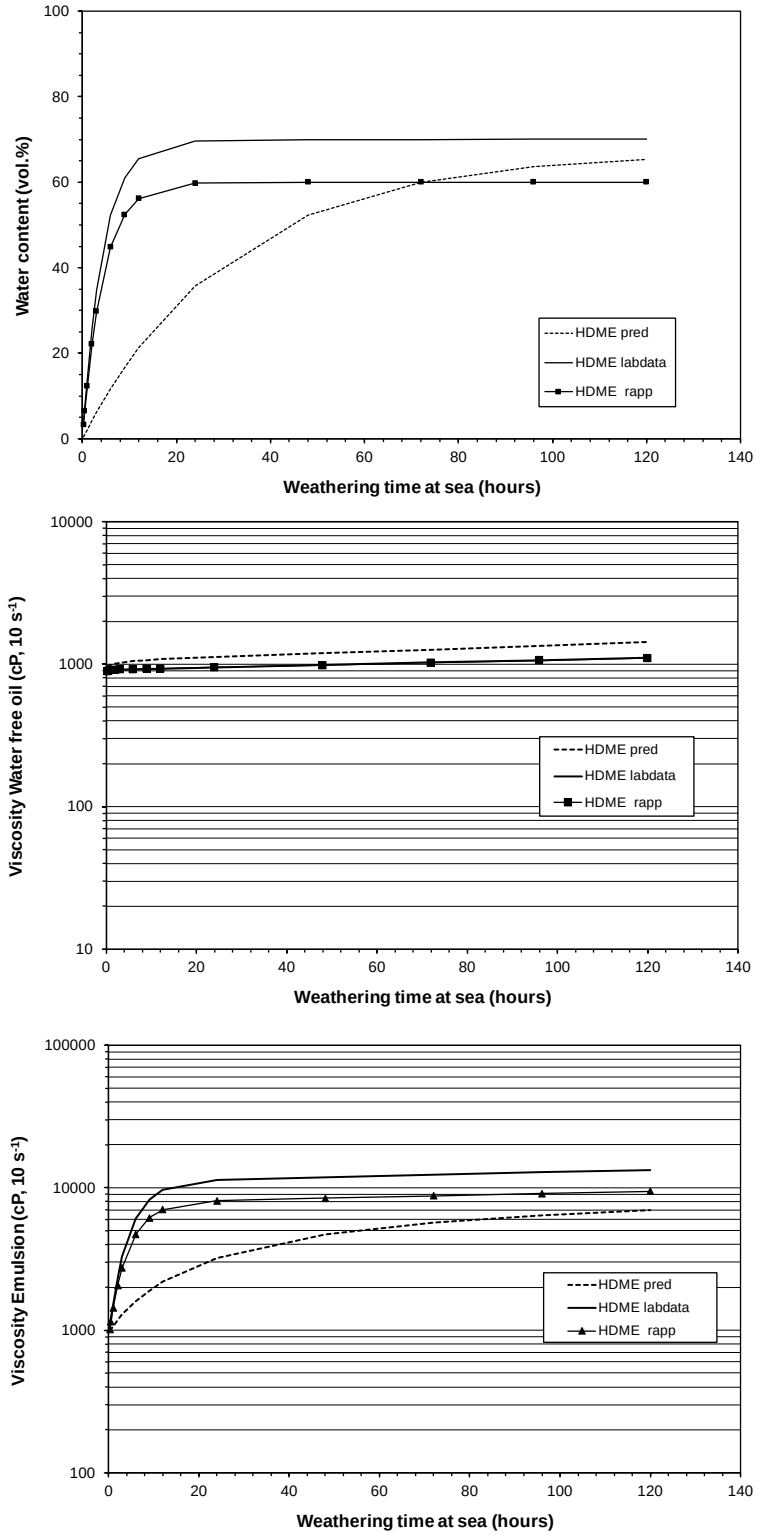


Figure 6.13 Weathering properties for HDME50 (water uptake, water free- and emulsion viscosity) predicted based on fresh oil properties (crude assay data) and lab studies.

6.13 Summary of verification based on CA data

The new CA module in SINTEF OWM was tested with a selection of crudes and refinery products. The oils are selected to cover a wide variation of the oils used to establish the algorithms and to illustrate the different warning messages (Table 5.3). The quality or deviation from the predictions based on full laboratory studies (weathering handbooks) varies strongly within the selected oils.

Naphtenic crudes:
Both Heidrun and Troll show acceptable predictions compared to predictions from a full weathering study. No warning messages are issued by OWM for these predictions.

Draugen on the other hand has a large deviation in predicted water free and emulsion viscosities. The predictions of e.g. emulsion viscosities are less than 50% of the predicted value with a full weathering study. However, a C1 warning is issued because Draugen has a very low initial viscosity (1 cP) and a very high evaporative loss.

Asphaltenic crudes:
The predictions for both water free viscosity and emulsion viscosity are generally underpredicted for the asphaltenic oils. From 30% low (emulsion viscosity) for Balder blend to approximately 50% low for Oseberg Øst. No warnings are issued for these oils.

Paraffinic crudes:
The two paraffinic candidates vary in prediction errors. Gyda underestimate the emulsion viscosity (approx. 40%), while Statjord A overestimate the same with approx. 30%. This is representative for most of the paraffinic oils which are seldom more than 50% away from values based on weathering studies.

Waxy crude:
The predictions of waxy crudes have been improved from the earlier version, mainly due to a broader variety of waxy crudes in the calibration set. Ringhorne shows very good predictions 8 < 10% off), while for Elli South the viscosity emulsions are over estimated. However, a warning is issued for Elli South (C2).

Refinery products:
Both for IF-380, IF-180 and HDME50 the CA module underestimate the emulsion viscosities. However, high emulsion viscosities in the correct range are predicted for all three oils.

- IF-180: 50 000 cP (70 000 cP based on weathering data)
- IF-380: 150 000 cP (350 000 cP based on weathering studies) and
- HDME50: 7 000 cP (9 500 cP based on weathering studies)

7 Conclusions

This report presents results from the last of several projects aiming towards an improved and simplified approach to predict weathering properties of an oil spill at sea based only on limited compositional data available from a crude assay (CA). The CA module in SINTEF OWM makes it possible to rapidly predict weathering properties for a spilled oil with a minimum of information available. A CA is a "product declaration" on crude oils and refined products (certificate of quality). CA is needed for oil trading and is for that reason available for many crude oils. The recalibration of the CA module has used an extended number of crude oils and condensates (141) including a variety of refinery products.

This approach uses a set of models or algorithms using both univariate and multivariate regression. These models predict a “synthetic” laboratory weathering data set that is used by SINTEF OWM to predict weathering properties as a function of time and environmental conditions. These models are implemented into the SINTEF OWM. A test version of OWM, version 9.2 was delivered with the draft version of this report (December 2017). A new official release of OWM (version 10) is expected during spring 2018 (mid-June 2018).

It was not possible to give predictions of acceptable quality of the lightest products like the condensates and the lightest marine gas oils. These oils are defined as oils with an evaporation slope > 0.25 OR density < 0.800. This is mainly due to the large evaporative loss for these products. When 60-70% of the product evaporates during the first hours at sea, it is difficult to predict the weathering behaviour of the residue based on properties of the fresh product. The "error message" system will tell the users that predictions are not possible for those lightest products (most condensates and light refinery products), but will guide the users to the "Find Model Oil" function. This function can be used to find a "model oil or a surrogate oil " with similar composition, which is already characterised with a weathering study.

The SINTEF OWM, when it is used with the CA module, will issue warning messages if the fresh oil properties are outside the calibrated range and predictions will not be possible. The users will also receive warning and guiding messages from the model to optimize the understanding and usefulness of the system.

The predicted properties show a good to sufficient statistical significant correlation with the measured values in the calibration set consisting of 141 different oil types in chapter 5.3. The multivariate calibration is performed with the software Unscrambler (v.10) and full cross validation is used when correlations between predicted and measured values are calculated.

The predictions from this approach should be used with care, since the uncertainty in these predictions is higher compared to predictions based on a weathering study. It is not possible to quantify this increase in uncertainty exactly, but the guiding messages should be used by the user to interpret the results. Prediction errors for oils without any warning messages generally are in the 30-50% range, but exceptions occur. For example, when predicting emulsion viscosity of a very light oil, a "warning" will be given that the predictions are more uncertain due to the high evaporative loss. Moreover, uncertainty in emulsion viscosity may have an influence on operational decisions, and the time window for dispersant application is also difficult to quantify based on this CA module approach.

This new approach should therefore not in general substitute weathering studies in relation to contingency plans or environmental risk assessments. It will, however, be a supplementary operational tool, both in preliminary contingency planning and in response operations where rapid and predictions are needed and data from laboratory weathering studies are not available.

This approach is therefore mainly developed for use in oil situations where a rapid predictions of weathering properties are needed and a laboratory weathering study is not available, e.g.

- Spills of oil types, which are only occasionally imported to Norway
- Spills of refinery products without a laboratory weathering study

- Spills of blends which rapidly and significantly changes composition
- For "re-checking" to evaluate if weathering properties have changed as a function of changing oil composition over time

8 Recommendations for future work

Blends of various crude oil types are today transported both by pipelines and by tankers from offshore production to mainland in Norway. The oils composition and ratios of the blends may change with time due to shut-down/opening of fields, reservoirs or wells, in addition to possible long-term fluctuations in the production. It will not be cost beneficial to perform weathering studies on all fraction of these combinations. The approach developed in this study could therefore be ideal mapping weathering properties for such crude oil blends.

The SINTEF OWM contains a Blend module to calculate CA properties for a blend as a part of the database Editor. This functionality was previously developed as a part of an earlier Statoil project, but has not been frequently used. The user-friendliness of this functionality should be improved.

9 References

EPA, (US - Environmental Protection Agency), 1982. Manual of practice Chemical Agents in oil spill control. EPA Report no. 600/8-82-0/0, Washington, DC.

Brandvik, P.J. and Daling, P.S, 1991, Weathering properties of the Veslefrikk crude at sea - an handbook for Statoil, IKU report no. 22.1984.00/01/91.

Brandvik, P.J., Strøm-Kristiansen, T., Lewis, A., Daling, P.S., Reed, M., Rye H., and Jensen, H., 1996a. The Norwegian Sea Trial 1995: Offshore Testing of Two Dispersant Application Systems and Simulation of an Underwater Pipeline Leakage – A Summary Paper. In: Proc. 19th Arctic Marine Oilspill Technical Seminar, Environment Canada, Ottawa, Ontario. pp. 1395-1405.

Brandvik, P.J., Strøm-Kristiansen, T., and Daling, P.S., 1996d. Weathering properties of the Frøy crude, Lillefrigg condensate and the 75:25 blend of these two products - a handbook for Elf Norge. IKU report no. 41.5135/01/96.

Brandvik, P.J., 1997. Optimisation of Oil Spill Dispersants on Weathered Oils a new Approach using Experimental Design and Multivariate Data Analysis. Dr. thesis. Norwegian University of Science and Technology, Norway. ISBN 82-7861-030-4

Daling, P.S., and Brandvik, P.J., 1991. Characterisation and prediction of the weathering properties of oils at sea - a manual for the oils investigated in the DIWO project, IKU report no: 02.0786.00/16/91. 140 p.

Daling, P.S., Ole Morten Aamo, Alun Lewis and Tove Strøm-Kristiansen, 1997: IKU oil weathering model - predicting oils' properties at sea" Publication in the Proceedings of the 1997 International Oil Spill Conference, fort Lauderdale, Florida.

Daling, P.S., T. Strøm, 1999: Weathering of Oils at Sea: Model/Field Data Comparisons. Spill Science and Technology Bulletin, Vol. 5, no. 1, pp.63-74 1999. SINTEF registration no. STF66 S99010.

Esbensen, K., Midtgaard, T., and Schönkopf, S., 1994. Multivariate Analysis in Practice, Camo AS, Trondheim. Norway.

Johansen, Ø., 1984. The Haltenbank Experiment. In: Proc. 7th Arcic Marine Oilspill Program Technical Seminar. Edmonton, Alberta. Environmental protection Service. pp. 17-36.

Leirvik, F., Wamg, U.M., Moldestad, M.Ø., Faksness, L.G. and I.K. Almås, 2004. Åsgard A, Smørbukk, Smørbukk Sør, Smørbukk kondensat/lettolje og Midgard – Egenskaper og forvitring på sjøen relatert til beredskap. Revidert Rapport, STF66 A03053

Lewis, A., Daling, P.S., Strøm-Kristiansen, T., and Brandvik, P.J., 1995a. The Behaviour of Sture Blend Crude Oil Spilled at Sea and Treated with Dispersant. In: Proc. 18th Arctic Marine Oilspill Technical Seminar, Environment Canada, Ottawa, Ontario. pp. 453-469.

Martens, H., and Næs, T., 1989. Multivariate Calibration, John Wiley and Sons, Chichester.

Strøm-kristiansen T, Knudsen, O.Ø. Singsaas, I. and Daling, P.S., 1995. The weathering properties at sea for Sture Blend, Oseberg field center and Oseberg C crudes - a weathering manual for Norsk Hydro (2nd ed.), IKU report no: 95.084, (In norwegian).

Strøm-Kristiansen, T., Daling P.S., and Brandvik P.J., 1996. NOFO 1996 Oil on water exercise - Surface oil sampling and analysis. IKU report no. 41.5164.00/03/96.

Sørstrøm S.E., (editor) 1989: Full scale experimental oil spill at Haltenbanken 1989, Data Report no: OCN89054. Oceanographic Company of Norway, Trondheim, Norway.

Walker, M. I., Lunel, T., Brandvik, P. J., Lewis, A. 1995: Emulsification processes at sea - Forties crude oil. 18th AMOP Technical Seminar, June 14-151995, Edmonton, Canada, 471-491

Appendix A: Multivariate coefficients

Prediction of maximum water uptake (%)

Regression coefficients PLS1 analysis of EM% with UNSCRAMBLER)

	B0	Topped	Res	Grav	lg-PP	Lg-Visc	Lg-Asp	Wax	Grav*lg-PP	Grav*Lg-Visc	lg-PP*Lg-Asph	lg-PP*Wax	Lg-Visc*Lg-Asph	Lg-Visc*Wax	Lg-Visc**2	Wax**2
Crude	225,620	-0,189	-0,012	-155,228	-9,605	5,679	8,420	-0,407	-10,091	3,241	7,767	0,565	-5,982	-0,023	-0,338	-0,007
Refinery	42,1977	-0,1344	0,1439	18,5520	-9,8865	0,5619	0,7627	0,5851	-15,0275	0,4361	0,5495	0,4255	0,0015	0,0630	-0,0138	0,0524

Prediction of wateruptake rate (T12)

Regression coefficients from PLS1 analysis of T12 with UNSCRAMBLER)

	B0	Topped	Res	Grav	lg-PP	Lg-Visc	Lg-Asp	Wax	Grav*lg-PP	Grav*Lg-Visc	lg-PP*Lg-Asph	lg-PP*Wax	Lg-Visc*Lg-Asph	Lg-Visc*Wax	Lg-Visc**2	Wax**2
Crude	-1,686	0,000	0,000	0,853	0,000	0,045	0,000	0,000	0,000	0,052	0,000	-0,014	0,015	0,000	0,008	0,000
Refinery	-0,9768	-0,0002	0,0002	0,6384	0,0000	0,0244	0,0290	0,0090	-0,1375	0,0245	0,0198	0,0025	0,0000	0,0035	0,0047	0,0014

Prediction of emulsion viscosity (50%)

Regression coefficients from PLS1 analysis of Visc50% with UNSCRAMBLER)

	B0	Topped	Res	Grav	lg-PP	Lg-Visc	Lg-Asp	Wax	Grav*lg-PP	Grav*Lg-Visc	lg-PP*Lg-Asph	lg-PP*Wax	Lg-Visc*Lg-Asph	Lg-Visc*Wax	Lg-Visc**2	Wax**2
Crude	0,7219	0,0010	-0,0011	2,0626	-0,1423	0,0924	0,0605	0,0061	-0,1202	0,1061	0,0070	-0,0002	0,0351	0,0025	0,0160	0,0003
Refinery	0,00	*0,0000*	*0,0000*	*0,0000*	*0,0000*	*0,0000*	*0,0000*	*0,0000*	*0,0000*	*0,0000*	*0,0000*	0,0000	0,0000	0,0000	0,0000	0,0000

Prediction of emulsion viscosity (75%)

Regression coefficients from PLS1 analysis of Visc75% with UNSCRAMBLER)

	B0	Topped	Res	Grav	lg-PP	Lg-Visc	Lg-Asp	Wax	Grav*lg-PP	Grav*Lg-Visc	lg-PP*Lg-Asph	lg-PP*Wax	Lg-Visc*Lg-Asph	Lg-Visc*Wax	Lg-Visc**2	Wax**2
Crude	0,27803	0,0013726	-0,0014443	3,049498	-0,086592	0,0634358	0,086565	0,001621	-0,0513129	0,07914744	0,03154665	-0,001882071	0,04178378	0,001177484	0,01037058	0,0001123
Refinery	0	*0,000*	*0,000*	*0,000*	*0,000*	*0,000*	*0,000*	*0,000*	*0,000*	*0,000*	*0,000*	0,000	0,000	0,000	0,000	0,000

Prediction of emulsion viscosity (max water)

Regression coefficients from PLS1 analysis of Max-water with UNSCRAMBLER)

	B0	Topped	Res	Grav	lg-PP	Lg-Visc	Lg-Asp	Wax	Grav*lg-PP	Grav*Lg-Visc	lg-PP*Lg-Asph	lg-PP*Wax	Lg-Visc*Lg-Asph	Lg-Visc*Wax	Lg-Visc**2	Wax**2
Crude	-0,2127	0,0012	-0,0012	3,2460	-0,1825	0,1053	0,1490	0,0089	-0,1456	0,1224	0,0642	0,0009	0,0513	0,0040	0,0181	0,0005
Refinery	-0,7192	-0,0062	0,0068	3,0383	-0,5758	0,1365	0,1276	0,0303	-0,4341	0,1330	0,0774	0,0328	0,0310	0,0084	0,0213	0,0012

Technology for a better society

www.sintef.no