ARCTIC
RESPONSE
TECHNOLOGY
OIL SPILL PREPAREDNESS

DISPERSANT TESTING UNDER REALISTIC CONDITIONS

TASK 2.2 / TASK 4

FINAL REPORT

EXECUTIVE SUMMARY

The objective of this research program was to assess the efficiency of mineral fine to disperse crude oil under artic conditions.

In a first stage, a total of 150 laboratory tests were performed to select the most efficient clay (kaolinite, barite, calcite or bentonite) and to define the MOR (Mineral Oil Ratio) and mixing condition which enable OMA (Oil Mineral Aggregates) formation. The dispersion rates of four oils (Grane, Alaska North Slope, Troll and Oseberg) were assessed at two salinities (5 and 35 ppt). Dispersion was characterized in term of oil concentration in the water column and median OMA size (d0,5) after one hour of resting time. The results obtained during the first stage highlighted that calcite can be considered as the best candidate at MOR 2/5. High mixing energy is required for OMA formation in the water column and then, after test completion, a very low energy is sufficient to avoid the OMA to resurface. Additional tests were performed to assess the combination of mineral fine with dispersant at 2 Dispersant to Oil Ratios (DOR). These tests confirmed that calcite can be considered as the best candidate for OMA formation. Moreover, it was clear that using dispersant for low viscous oils (<23 mPa.S @ 5°C) did not enhance significantly the dispersion compared with results obtained while a mineral was used alone (except for Troll crude oil @ MOR 1/10).

In a second stage, two tests were performed in Cedre's flume tank. The oil dispersion using Corexit 9500 have been compared with oil dispersion using bentonite at MOR 1/10. The oil was weathered in the flume for 18 hours before dispersant or mineral application. The dispersion efficiency was very low for both conditions and reached 21% and 2% respectively for dispersion and mineral treatment. Without agitation, OMA were observed at the water surface and needed slight agitation to resuspend in the water column.

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1. INTRODUCTION

As a task 2.2 of the project “Dispersant testing under realistic conditions”, Cedre is in charge of the oil-mineral aggregates (OMAs) tests which were completed in its flume tank.

For this test program, the Arctic JIP requested bentonite to be used as fine mineral in this program. This mineral is a component of most drilling muds used for exploration, development, and production drilling worldwide and especially in Artic where bentonite is available in bulk. TOTAL oil company provided bentonite samples to Cedre.

To prepare the flume test program, Cedre proposed to conduct a short and simple preliminary laboratory testing program. The results of these preliminary tests were presented in a progress report in January 2015 (Annex 1) and discussed during a February 12, 2015conference call and a meeting in March 2015 (Interspill 2015).

These preliminary tests were conducted between December 2014 and January 2015 on Alaska North Slope (ANS) using the dispersant Finasol OSR 52. The results suggested that mixing energy is a key parameter in the oil dispersion using mineral fines. It was necessary to use very high energy to produce OMA with a neutral buoyancy. The low results observed in the modified IFP test were due to an insufficient energy even when tuned “high”. In order to forecast what could occur with higher energy such as the energy obtained with a ship propeller, additional tests were performed in a beaker with a magnetic stirrer in a first step and then with an Ultraturax in a second step. In this condition, formation of aggregates was observed and the dispersion appeared to be significantly higher. Finally, in order to simulate what could occur in the flume test during the next stage of the experimental study, tests were carried out in a large tank (1 m^3) using the electric propeller which is already used by Sintef and SL Ross for the flume tests.

During the February 12, 2015 conference call, it was proposed to conduct new tests with barite instead of bentonite. Barite is commonly used as weighting agent in drilling mud and could be interesting in case of floating OMA as observed during the tests with ANS and bentonite. Qualitative tests were performed with ANS and Grane at laboratory scale and in the large tank of 1m^3 using the propeller. No OMA formation was observed and the mineral sank immediately without any aggregates in the water column even if the energy was applied for a long time.

During the March 2015 meeting between the Arctic JIP, Sintef and Cedre, it was agreed to conduct additional tests at laboratory scale to assess the influence of mineral nature (bentonite and calcite) and oil nature (4 crude oils).

2. EXPERIMENTS AT LABORATORY SCALE

2.1 OBJECTIVES

These additional tests were performed to better define the experimental conditions that will be used during the pilot scale experiment in the flume test.

2.2 MATERIALS AND METHODS

2.2.1 Fine Minerals

The two types of fine minerals used were Bentonite and Calcite from Total and Sigma Aldrich respectively. The main properties of the fines are summarized in the table below.

Table 1: Fines main properties.

	Color	Density (g/ml)	Particle size range (µm)	CEC (*) Meq/100g
Bentonite	Green	1.02	60 – 180	100
Calcite	White	2.93	5 – 50	10

(*) CEC : cation exchange capacity.

All the solutions of fines were prepared in distilled water at a concentration of 10 000 ppm prior to use.

2.2.2 Oil properties

Four crude oils were used: Grane, Alaska North Slope, Troll and Oseberg. Table 2 and figure 1 present physic- chemical properties and SARA fractionation of each oil.

Table 2: physical and chemical properties of the four crude oils tested.

Oil	Density at 5°C (g/ml)	Viscosity at 5°C (mPa.s) (10 s-1)	Evaporative losses (%wt.) 150/200/250°C
ANS	0.874	23	18.5 / 28.4 / 39.5
Troll	0.852	10	16.8 / 26.5 / 36.8
Oseberg	0.825	13	26.3 / 35.2 / 49.1
Grane	0.930	635	1.7 / 4.8 / 11.3

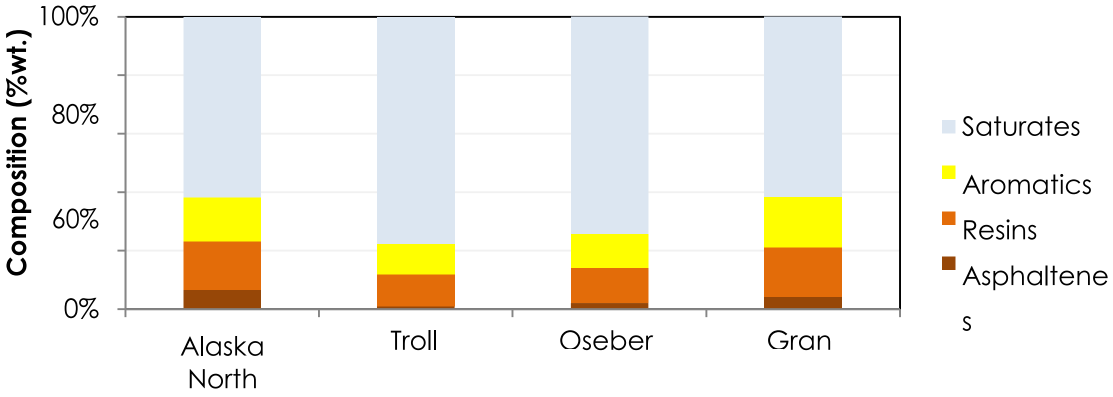


Figure 1: results of SARA fractionation of the four crude oils.

All the experiments were performed on the oil topped at 150°C.

2.2.3 Laboratory test protocol

All the laboratory experiments were duplicated and conducted at 2 +/- 1°C.The 35ppt experiments were performed using filtered and sterilized (UV) natural sea water provided by Oceanopolis (public ocean parc - Brest). Water salinity of 5 ppt was reached by dilution of the natural sea water with distilled water.

In a beaker containing 300 ml of water, 500 mg of oil were added at the water surface with a syringe. After addition of fine minerals and/or dispersant the mixture was submitted to a 1 minute high energy mixing (Ultraturrax®). The whole solution was transferred into a graduated separatory funnel. After an hour of resting time, the fraction below the water surface (250 mL) and the water surface (50 ml) were collected in two separated flasks. The oil content and OMA particle size were measured in both fractions. The water samples were sonicated, extracted with methylene chloride and dried on sodium sulfate. The oil concentration was analyzed with a UV-visible spectrometer (Evolution 600 UV-VIS, Thermo Fisher Scientific) previously calibrated. The absorbance of the solvents extracts was compared to standard solutions of each oil.

The particle size distribution in both fractions was analyzed with a laser diffraction analyzer (Malvern Instruments, Mastersizer 2000). Sampling was performed using a peristaltic pump placed after the measuring cell to avoid droplets coalescence.

Table 1 presents the experimental matrix.

Table 1. Experimental parameters

Water volume (ml)	300
Type of oil	Grane, ANS, Oseberg, Troll
Oil quantity (mg)	500
Type of mineral	Bentonite, Calcite
Mineral/Oil weight ratio (MOR)	2 :5, 1 :5, 1 :10
Mixing time (min)	1
Salinity	3, 35 ppt

2.3 RESULTS

2.3.1 Qualitative tests with barite at pilot scale

All the results of the tests presented hereafter are detailed in appendix 2.

As agreed during the February 12, 2015 conference call, additional qualitative tests were conducted in March 2015 with a new mineral in order to produce negatively buoyant OMA. Barite was selected as it is commonly used as a weighting agent. The mineral was ordered from Sigma Aldrich. The pictures below present a comparison of two tests conducted in the 1m^3 tank on ANS topped at 150°C with bentonite and barite. For these two tests, 125 mL of oil and 25 g of suspended mineral (MOR 1/5) were used. Agitation was created using the wash propeller set at its highest speed for 15 minutes.

Release of oil (125mL) in the 1m^3 tank

Oil slick before mineral addition

Addition of **Barite** (MOR 1/5)

Addition of **Bentonite** (MOR 1/5)

Very high level of agitation with the propeller

Very high level of agitation with the propeller

After 15 minutes of agitation, oil resurfaced immediately even with low agitation. No OMA observed.

After 15 minutes of vigorous agitation, oil resurfaced partially, OMA were observed and remained in the water column if low agitation was applied.

Figure 2: comparison of ANS dispersion between Barite and Bentonite at pilot scale.

In addition, quantitative tests were performed at laboratory scale with Barite and ANS. Only 3% of oil was measured in the water column after one hour rest time. Due to the low efficiency of dispersion using barite, it was decided to continue the experimental matrix with bentonite and calcite.

2.3.2 Quantitative tests at laboratory scale with seawater (35 ppt)

All the results are detailed in appendix 2.

2.3.2.1 *Grane*

Figure 3 presents the percentage of oil remaining in the water column after one minute of very high mixing energy and one hour resting time. This amount of oil can be considered as neutral or negative buoyant OMA while the amount of oil resurfacing is considered as positive buoyant particles. Figure 4 presents the median diameter of the OMA in the water column after 1 minute of high mixing energy and one hour resting time. Conclusions of these results are:

- percentage of oil remaining in the water column never exceeded 20% with bentonite and 27% using calcite without a significant difference between the two minerals,

- using Bentonite, percentage of oil in the water column increased significantly with MOR, however, no significant difference appeared between MOR 1/5 and MOR 2/5,
- using Calcite, percentage of oil in the water column increased significantly with MOR, however, no significant difference appeared between MOR 1/5 and MOR 2/5,
- median diameter of particles in suspension in the water column were lower than 81µm using calcite and 67µm using bentonite,
- median diameter of particles did not differ between surface and water column while using calcite whatever the MOR,
- using Bentonite, median diameter of particles were smaller with MOR 1/10 and were very close between surface and water column samples.

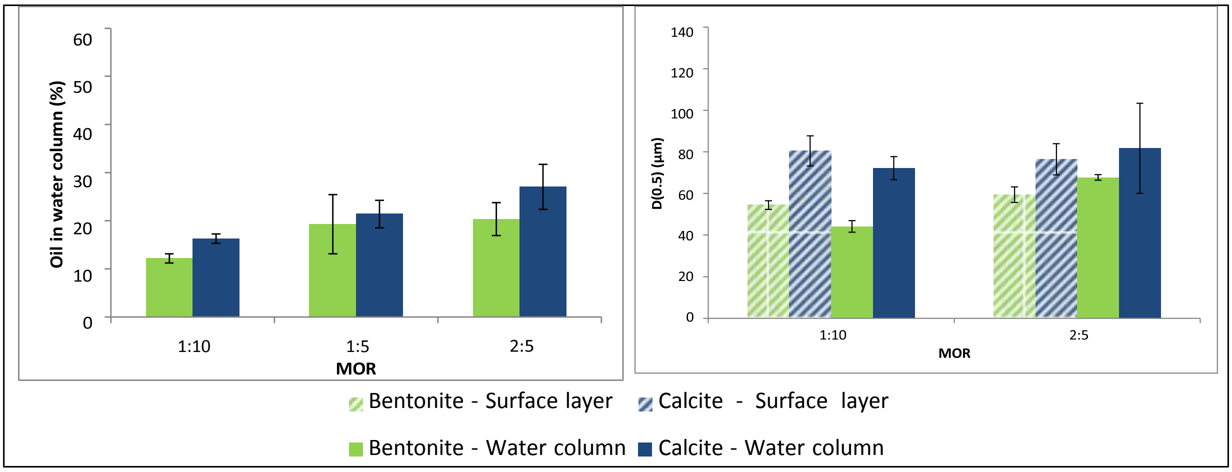


Figure 3. Percentage of Grane oil in the water column after one hour resting time.

Figure 4. Median diameter (µm) of OMA in the water column after one hour resting time.

2.3.2.2 *Alaska North Slope (ANS)*

Figure 5 and figure 6 present the results obtained with the ANS in seawater. Conclusions of these results are:

- percentage of oil remaining in the water column never exceeded 31% using bentonite and 42% with calcite with a significant difference between the two minerals,
- using Calcite, percentage of oil in the water column increased significantly with MOR,
- using Bentonite, percentage of oil in the water column increased significantly with MOR, however, no significant difference appeared for a MOR higher than 1/5,
- median diameter of particles in suspension in the water column were lower than 70µm using Bentonite and 61 µm using Calcite,
- median diameter of particle trended to increase with MOR whatever the water sample and mineral use,

- using Calcite, median diameter of particles in both surface and water columns were smaller than using Bentonite.

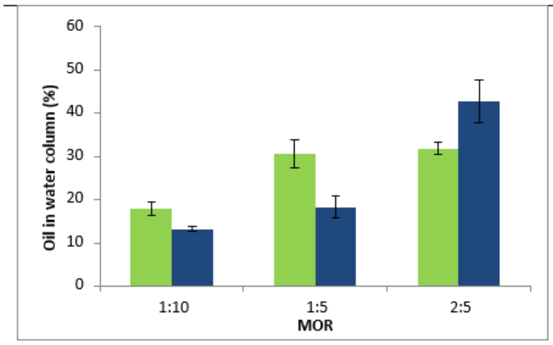


Figure 5. Percentage of ANS oil in the water column after one hour resting time.

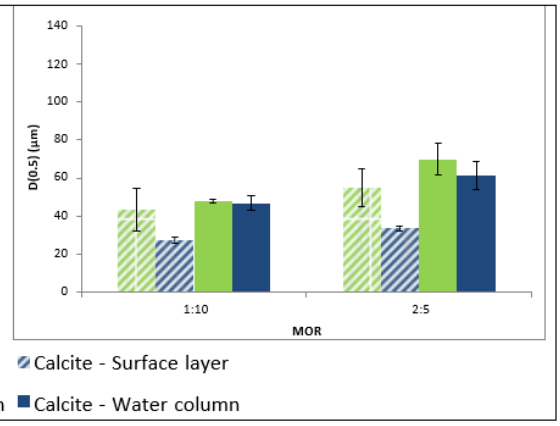


Figure 6. Median diameter (µm) of OMA in the water column after one hour resting time.

2.3.2.3 *Troll*

Figure 7 and figure 8 present the results obtained with the Troll crude oil in seawater. Conclusions of these results are:

- percentage of oil remaining in the water column never exceeded 12% using bentonite and 27% with calcite with a significant difference between the two minerals,
- using Calcite, percentage of oil in the water column increased significantly with MOR without a significant difference between MOR 1/5 and MOR 2/5,
- using Bentonite, percentage of oil in the water column increased with MOR, until a threshold limit obtained with a MOR of 1/5,
- median diameter of particles in suspension in the water column were lower than 61µm using bentonite and 78 µm using calcite,
- using Bentonite, median diameter of particles increased if MOR increased
- using Calcite, median diameter of particles in the water column decreased with MOR and remained stable in the water surface samples.

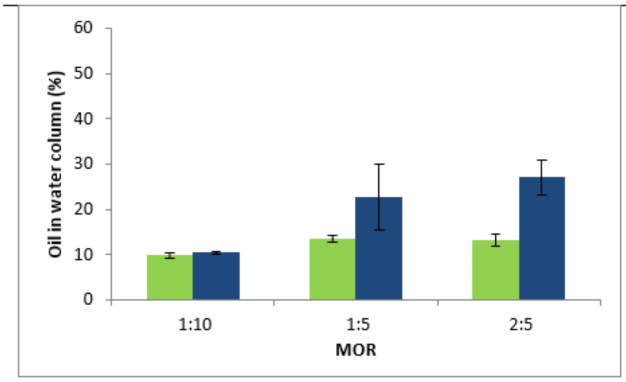


Figure 7. Percentage of Troll oil in the water column after one hour resting time.

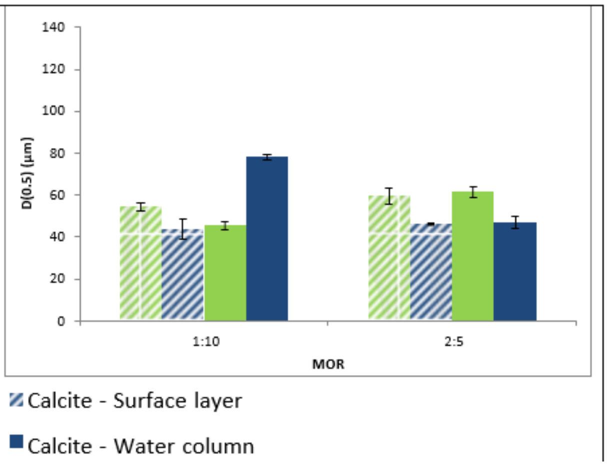


Figure 8. Median diameter (µm) of OMA in the water column after one hour resting time.

2.3.2.4 *Oseberg*

Figure 9 and figure 10 present the results obtained with the Oseberg crude oil in seawater. Conclusions of these results are:

- percentage of oil remaining in the water column never exceeded 20% using Bentonite and 34% with Calcite with a significant difference between the two minerals for MOR 2/5,
- using Calcite, percentage of oil in the water column increased significantly with MOR without a significant difference between MOR 1/10 and MOR 1/5,
- using Bentonite, percentage of oil in the water column increased significantly with MOR from 13% to 20% for MOR 2/5,
- median diameter of particles in suspension in the water column were lower than 74µm using bentonite and 53 µm using calcite,
- using Bentonite and Calcite, median diameter of particles in both surface and water column samples increased if MOR increased.

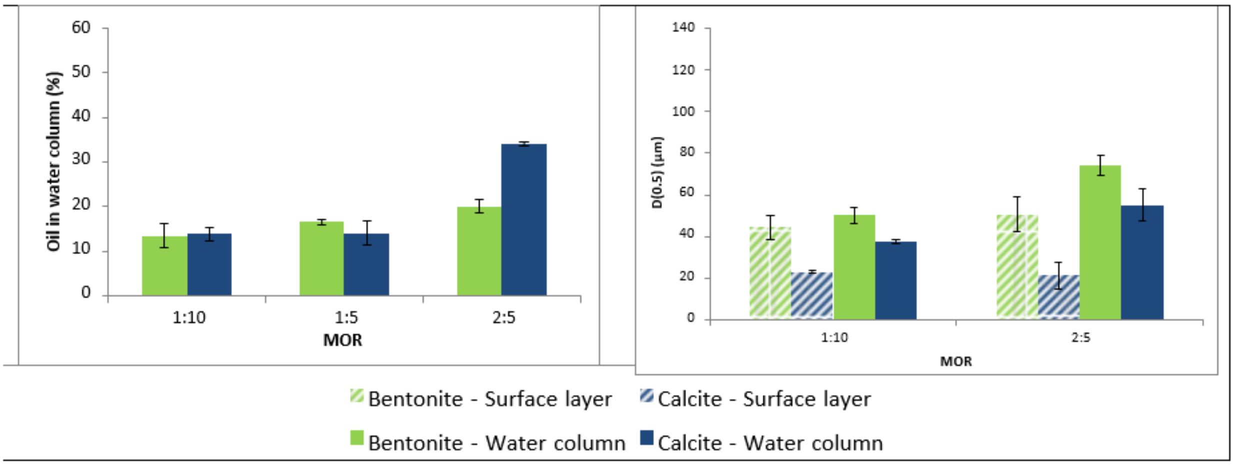


Figure 9. Percentage of Oseberg oil in the water column after one hour resting time.

Figure 10. Median diameter (µm) of OMA in the water column after one hour resting time.

2.3.3 *Tests at laboratory scale with freshwater (5 ppt)*

2.3.3.1 *Grane*

Figure 11 and figure 12 present the results obtained with the Grane crude oil in freshwater (5 ppt). Conclusions of these results are:

- percentage of oil remaining in the water column never exceeded 46% using Bentonite and 22% with Calcite with a significant difference between the two minerals,
- using Calcite, percentage of oil in the water column trended to increase with MOR however without a significant difference between MOR 1/5 and MOR 2/5.
- using Bentonite, percentage of oil in the water column increased significantly with MOR,

- median diameter of particles in suspension in the water column were lower than 55µm using bentonite and 109 µm using calcite,
- in the surface sample, median diameter of particles were lower than 124µm for Calcite and62 µm for Bentonite,
- using Calcite, median diameter of particles in the water column decreased with MOR and increase in the surface samples,
- using Bentonite, there is a slight increase of median diameter of particles in the water column and a slight decrease of particles in the surface samples while increasing MOR.

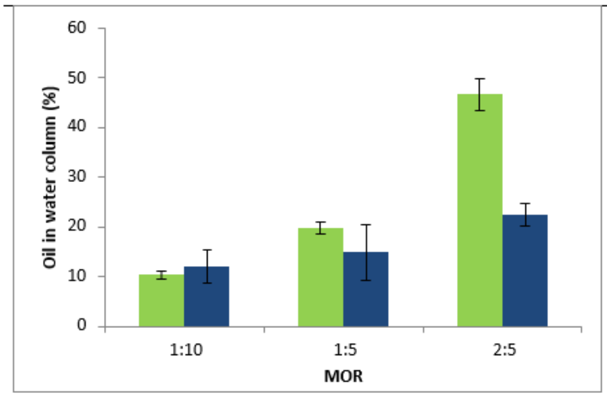


Figure 11. Percentage of Grane oil in the water column after one hour resting time.

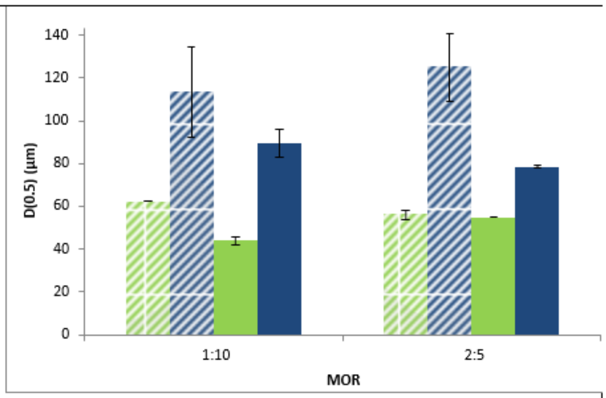


Figure 12. Median diameter (µm) of OMA in the water column after one hour resting time.

2.3.3.2 *Alaska North Slope (ANS)*

Figure 13 and figure 14 present the results obtained with the ANS crude oil in freshwater (5 ppt). Conclusions of these results are:

- percentage of oil remaining in the water column never exceeded 46% using Bentonite and 44% with Calcite with a significant difference between the two minerals at MOR 1/5 and 2/5,
- using Calcite, percentage of oil in the water column increased significantly according to the MOR,
- using Bentonite, percentage of oil in the water column did not differ between MOR 1/10 and MOR 2/5. Surprisingly, percentage of oil were significantly higher while using intermediate MOR 1/5,
- median diameter of particles in suspension in the water column were lower than 51µm using bentonite and 107 µm using calcite and did not change while increasing MOR,
- in the surface sample, median diameter of particles did not differ significantly from water column sample while using bentonite,
- in the surface sample, while using calcite, median diameter of particles trend to be higher with MOR 1/10 (however with a high standard deviation) and did not differ for MOR 2/5.

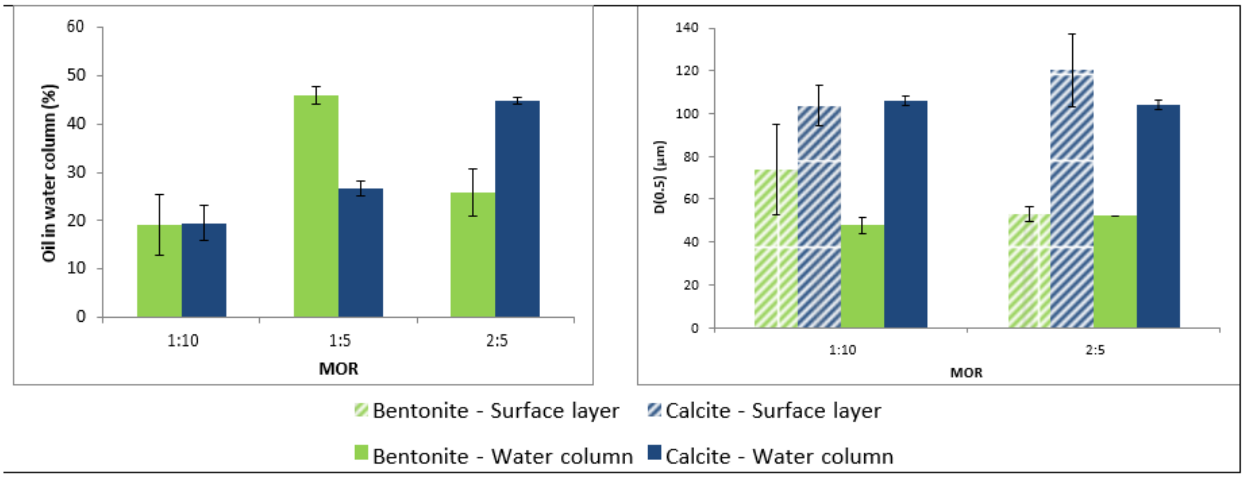


Figure 13. Percentage of ANS oil in the water column after one hour resting time.

Figure 14. Median diameter (µm) of OMA in the water column after one hour resting time.

2.3.3.3 *Troll*

Figure 15 and figure 16 present the results obtained with the Troll crude oil in freshwater (5 ppt). Conclusions of these results are:

- percentage of oil remaining in the water column never exceeded 49% using Bentonite and 37% with Calcite without a significant difference between the two minerals,
- using Calcite and Bentonite, percentage of oil in the water column increased significantly according to the MOR (except for MOR 1/5 with bentonite),
- median diameter of particles in suspension in the water column were lower than 56µm using Bentonite and 72 µm using Calcite with a slight increase while increasing MOR,
- in the surface sample, median diameter were lower than 108µm for Calcite and 62 µm for Bentonite and did not differ while increasing MOR.

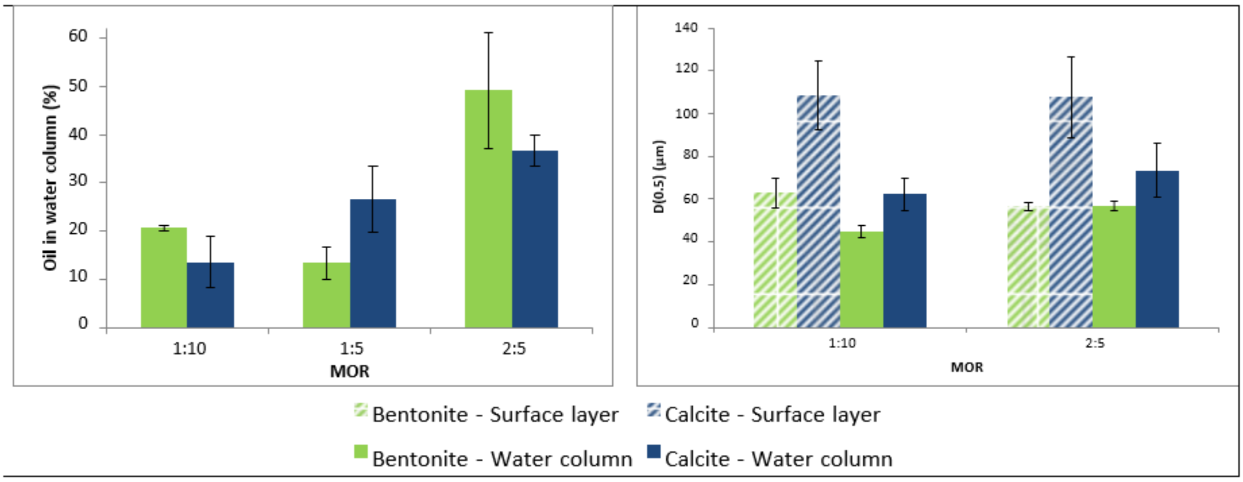


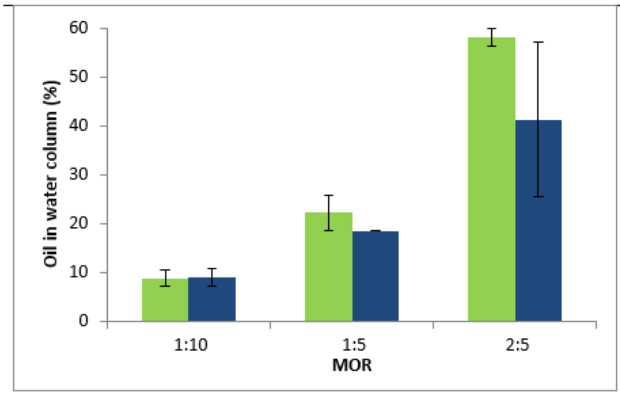
Figure 15. Percentage of Troll oil in the water column after one hour resting time.

Figure 16. Median diameter (µm) of OMA in the water column after one hour resting time.

2.3.3.4 *Oseberg*

Figure 17 and figure 18 present the results obtained with the Oseberg crude oil in freshwater (5 ppt). Conclusions of these results are:

- percentage of oil remaining in the water column never exceeded 59% using Bentonite and 41% with Calcite without a significant difference between the two minerals,
- using Calcite and Bentonite, percentage of oil in the water column increased significantly according to the MOR tested,
- in the surface sample, median diameter of particles were lower than 100µm for Calcite and 55 µm for Bentonite,
- median diameter of particles in suspension in the water column were lower than 55µm using Bentonite and 64 µm using Calcite,
- using Calcite, median diameter of particles at the surface decreased significantly while increasing MOR and did not differ significantly for particles in suspension in the water column.
- using Bentonite there is no difference of median diameter of particle size between surface sample and water column and there is a slight increase of particles while increasing MOR.



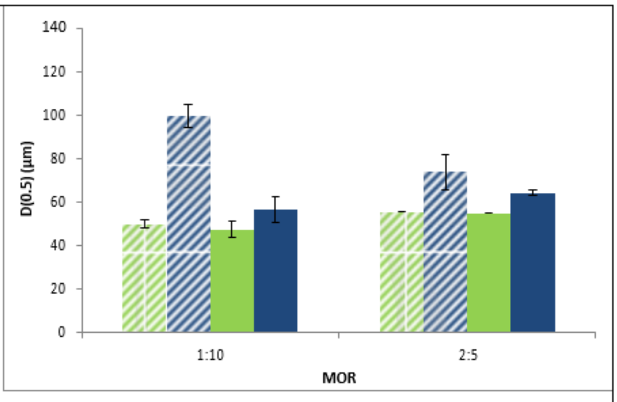


Figure 17. Percentage of Oseberg oil in the water column after one hour resting time.

Figure 18. Median diameter (µm) of OMA in the water column after one hour resting time.

2.3.4 Visual observations during laboratory scale experiment

Pictures and video of the tests were done during the experimental work. Following pictures (figure 19) were taken after completion of a laboratory test conducted with Grane and bentonite in seawater at MOR 1/5. Slight agitation of the surface was sufficient to "resuspend" the OMA concentrated at the surface after the one hour resting time. In the same way, the OMA with a negative buoyancy were easily "resuspended" with a very low energy provided for example by a magnetic stir bar. If higher energy was applied, the large aggregates (500

µm) observed at the surface in the following two first pictures broke immediately into smaller particles.

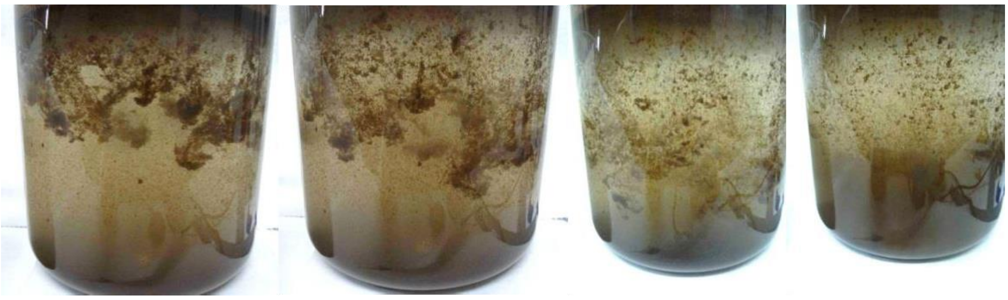


Figure 19. Example of OMA easily resuspended in the water column with a slight surface agitation: Grane and bentonite in seawater at MOR 1:5.

2.3.5 Additional tests

2.3.5.1 Assessment of the influence of mineral nature and particle size

In order to assess the potential influence of the mineral particle size on the OMA formation, it was agreed during the meeting held in Vancouver (June 4th, 2015) to conduct additional test with a new bentonite or calcite at a different particle size range than already used. Different potential supplier were contacted and a bentonite at particle size range of 5-50µm was found and available in stock (SigmaAldrich).

These tests were performed at laboratory scale with seawater. The first tests were conducted on Troll and Oseberg oils. As the results and influence of mineral size were not clear, tests with Grane and ANS were also conducted. Medan diameters of particles were also measured for these tests. The results are not presented as the values were systematically around 20 µm suggesting that particles measured were mainly bentonite particles alone without any oil droplets.

The results obtained with the four oils are presented in figure 20. For Grane and ANS, no significant difference between bentonite and calcite appeared for MOR 1/10 and 1/5. For the highest MOR, Calcite enhanced significantly the dispersion and the percentage of oil measured in the water column. While testing Troll dispersion, there were no significant differences of results between the two minerals tested. For the Oseberg oil, better results were obtained with Calcite and the differences were significant for the lowest and highest MOR.

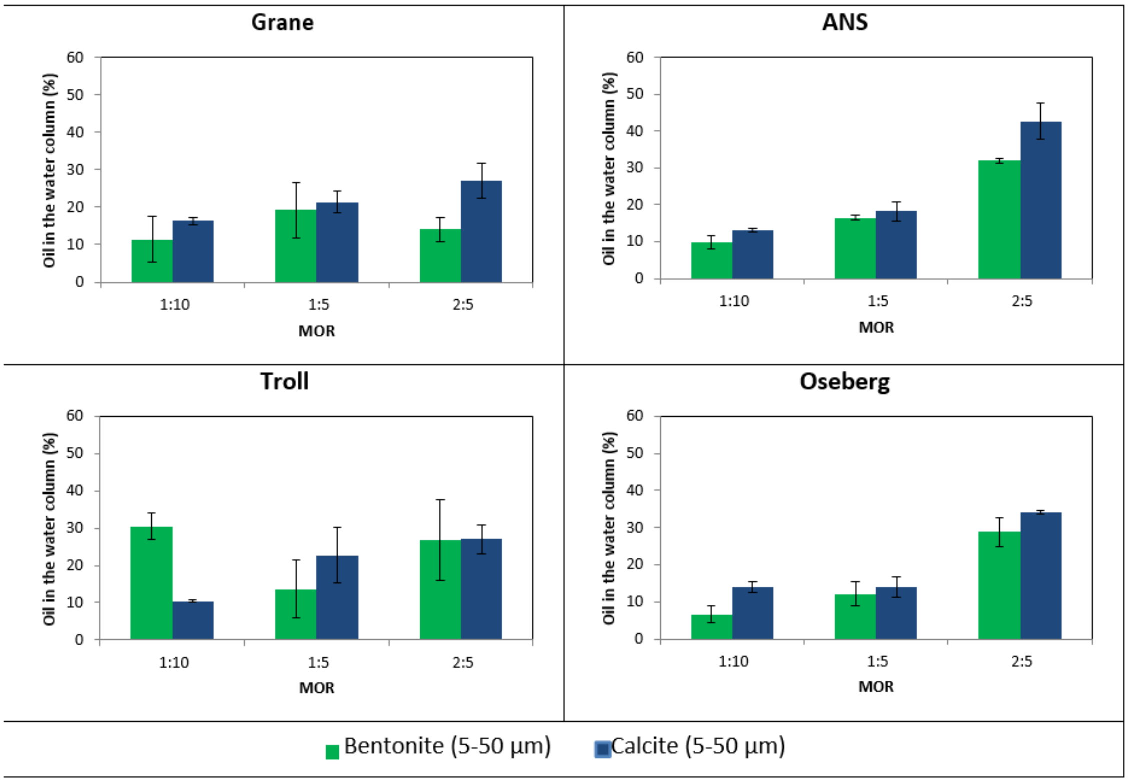


Figure 20. Comparison of percentage of oil in the water column for tests conducted with Bentonite and Calcite with a similar particle size range (5-50 µm)

2.3.5.2 *Assessment of dispersion with a combination of dispersant and mineral*

As already done during the preliminary tests, the influence of dispersant addition was also assessed at laboratory scale. The results presented in the following figures were obtained with seawater (35 ppt) using Corexit 9500 for two DOR: 1/50 and 1/25. Globally, these results confirmed that the use of Calcite enhances the oil dispersion compared with Bentonite especially for the highest MOR 2/5.

These results provided additional information:

- Whatever minerals and oils, results obtained with MOR 1/5 or 2/5 without dispersant are very close or higher than the results obtained with dispersant alone at DOR 1/25 or 1/50.
- For most of the tests performed with a combination of bentonite and dispersant, the use of dispersant combined with bentonite did not enhance the oil dispersion.
- Considering the tests with Calcite and Grane, combination of mineral with dispersant increased significantly the oil dispersion. There was no differences of results between DOR 1/25 and 1/50.
- Considering the tests with Calcite with the three other oils, the differences of oil dispersion were less clear while using dispersant. This is probably due to the

difference of viscosity between these four oils: lowest viscosities for ANS, Troll and Oseberg compared to Grane oil.

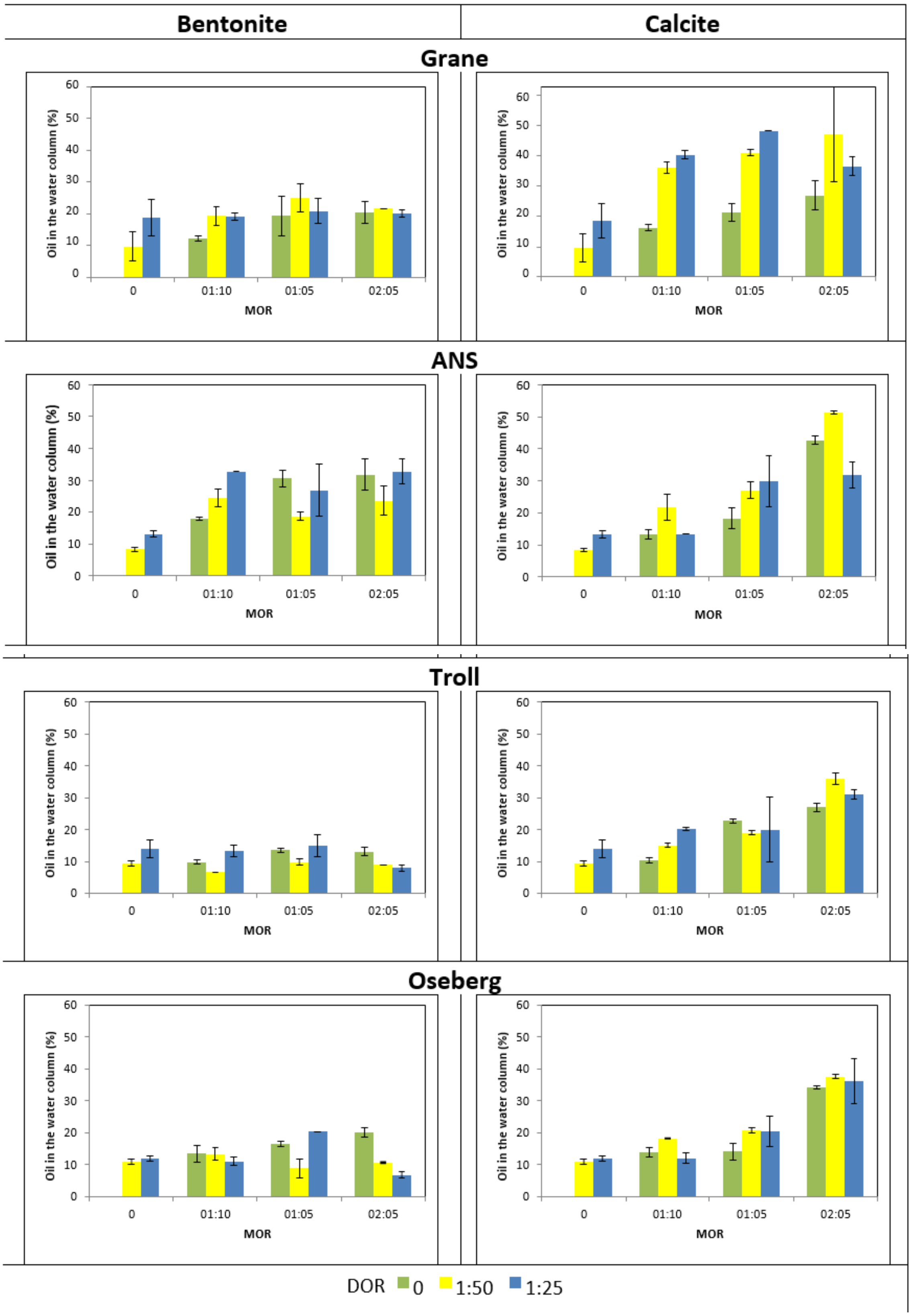


Figure 21. Percentage of oil in water column using dispersant at two DOR (1/50, 1/25).

2.4 CONCLUSIONS OF EXPERIMENTS AT LABORATORY SCALE

The aim of this part of the project "Dispersant testing under realistic conditions" was to assess the influence of mineral in the dispersion of oil and OMA formation. According to the results obtained during the preliminary testing (report Cedre, R.15.04, January 2015) and the results from the additional tests presented in the current report, the conclusions are:

General observation using different types of mineral fines:

- OMA formation required very high mixing energy to be observed.
- After one hour resting time, OMA were found at the surface, water column and bottom of laboratory beaker.
- Surfacing OMA were easily "resuspended" in the water column with an extremely low mixing energy suggesting a neutral buoyancy of these aggregates.
- Large OMA were observed at the surface after one hour resting time and broke easily if mixing energy was applied in the beaker.
- Barite did not enhanced oil dispersion while no dispersant is used and is therefore not adapted for OMA formation.

Oil measured in the water column

- In terms of percentage of oil in the water column, Calcite trended to give better results than Bentonite especially in seawater. In freshwater, the difference was less clear without statistical analyses.
- Increasing MOR enhance the OMA formation and percentage of oil in the water column.
- Experiment conducted with freshwater gave better results in terms of percentage of oil measured in the water column: this is due to the difference of density between seawater and freshwater as all the OMA with a density between 1.000 and 1.025 were present in the water column for freshwater testing while they were probably resurfacing for the seawater testing.

Median particle diameter

- Concerning the median diameter of particles in the water column whatever the minerals and oil tested, the highest diameter was 80µm for seawater testing and 100µm for freshwater testing.
- Concerning the particles found in the surface sample whatever the minerals and oil tested, the median diameter were logically higher than in the water column but were still below 80µm for seawater tests and 120 µm for freshwater tests. Such particles are therefore easily redispersed in the water column even with a very low mixing energy.
- In freshwater, median diameter of particles (surface or water column) trended to be smaller for Bentonite than for Calcite. In seawater, the difference were not significant.

- In freshwater using bentonite, median diameter of particles (surface or water column) did not change while increasing MOR. In seawater, median diameter trended to increase with MOR.
- In both seawater and freshwater, using calcite, there is no significant tendency between the different tests conducted: in some cases, median diameter increased with MOR and in others, median diameter decreased.

Additional tests were conducted on a new Bentonite characterized by a similar particle size range to Calcite mineral to assess the influence of mineral type on oil dispersion. Globally, the results obtained did not highlight a significant difference between Bentonite and Calcite except for highest MOR for two oils (Grane and ANS). However, the results of the tests including the use of dispersant gave interesting results and highlighted that Calcite can be considered as the best candidate for OMA formation and oil dispersion with mineral.

Moreover, it was clear that using dispersant for low viscous oils (<23 mPa.S @ 5°C) did not enhance significantly the dispersion compared with results obtained while a mineral was used alone.

According to the tests performed since the beginning of the project and the results obtained during the laboratory tests presented in the present report:

- Calcite can be considered as the best candidate for additional experiments,
- Better results were obtained with MOR 2/5,
- High mixing energy is required for OMA formation in the water column,
- Very low mixing is recommended after test completion to highlight the neutral buoyancy of OMA.

Therefore, to confirm the laboratory tests, we suggest the following test matrix (table 3) to be conducted at pilot scale in a flume test. It is suggested to start the tests using high wave energy mixing followed by propeller wash mixing: preliminary tests were already performed in Cedre flume test in order to test and to validate the cooling device developed for this study. During the two tests performed (pictures in annex 3), we observed that low energy mixing was not necessary as it did not provide enough energy for OMA formation.

Table 3. Suggested test matrix for experiment at pilot scale.

Oils	Weathering	Dispersant	DOR	MOR	Energy (**)	Ice coverage	Salinity
Grane Troll ANS Oseberg	6 hrs (*)	Corexit 9500	0 1/50 1/25	2/5	H/Prop wash	80%	35 ppt

(*): according to SINTEF – SL Ross report (April 2015)

(**): start with High energy followed by propeller wash energy then very low energy. Dispersant effectiveness is reported after each period.

3. EXPERIMENTS AT PILOT SCALE

As requested by the Arctic JIP, Cedre compared the dispersion of a weathered crude oil (Alaska North Slope) using 2 protocols:

- Addition of a dispersant (Corexit 9500) (DOR: 1/20)
- Addition of a mineral fine (bentonite) (MOR: 1/10).

3.1 Material & methods

3.1.1 Oil

Table 4 and 5 present the properties and evaporative losses during artificial weathering for the ANS crude oil.

Table 4. Properties of Alaska North Slope crude oil.

Cedre reference	**Oil type**	**Oil viscosity (*) (mPas @ 2°C / 10s-1)**	**Oil viscosity (*) (mPas @ 2°C / 100s-1)**	**Oil density (2°C) (**)**
HC-14-091	ANS crude oil	40	37	0,887

(*) conducted using Haake VT550

(**) ASTM D5002 « Standard Test Method for Density and Relative Density of Crude Oils by Digital Density Analyzer » using an Anton Paar DMA 5000 densimeter.

Table 5. ANS evaporative loss from artificial weathering.

Oil type	150°C +	200°C +	250°C +
ANS	15,1	28,4	33,9

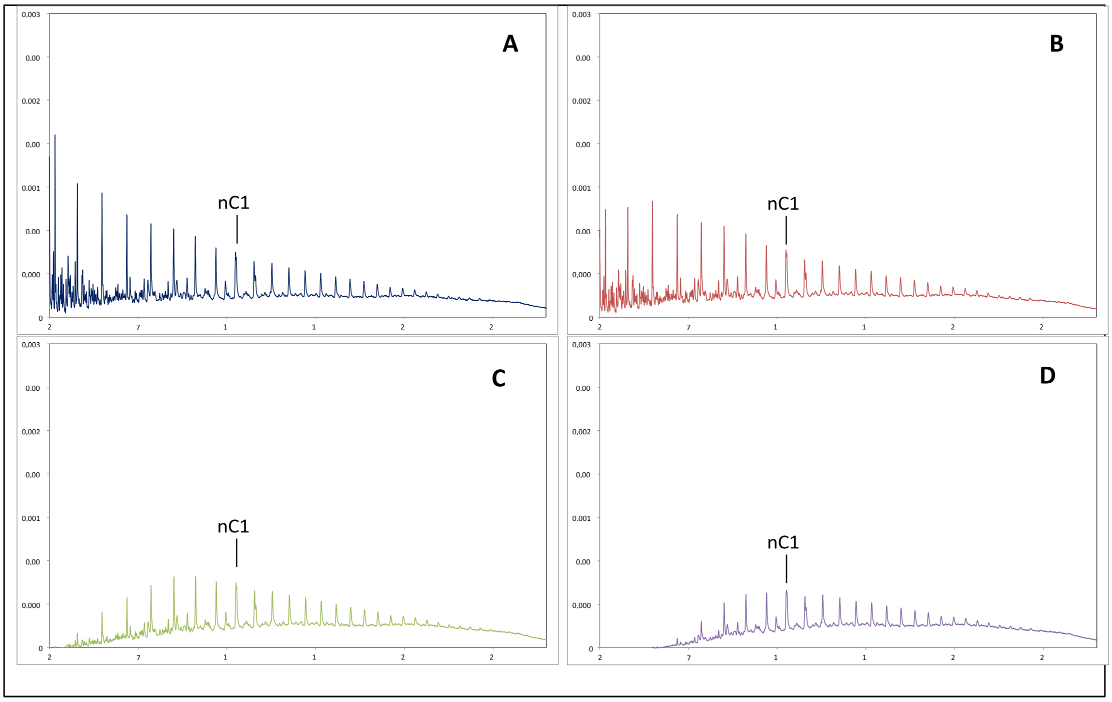


Figure 22. GCFID chromatograms of ANS (A)/ ANS 150°C+ (B) / ANS 200°C+ (C) / ANS 250°C+ (D).

3.1.2 Cedre flume: Polludrome

Details of the *Polludrome* (figure 23) are given in the table 6.

Table 6. Cedre flume details

Flume (circulation) length inner wall	16.4 m
Flume (circulation) length outer wall	20.2 m
Flume height	1.4 m
Flume width	0.6 m
Seawater depth	0.90 m
Surface area	8 m^2
Seawater volume	7.2 m^3
Containment area	1 m^2
Seawater temperature	-1 to 1°C
Dispersant applicator	Wagner 450
Nozzle size applicator	0,5 mm
Oil volume	1L
Particle size analyser	Malvern Mastersizer 2000
Propeller	MinnKota Endura 30 (20 cm depth)
Efficiency measurements	SFUV (AU10 Turner design) & grab samples (every 10 minutes)
Frequency wave maker (LE) (*)	350 rpm (wave maker engine) / 15 rpm (wave maker) (wave amplitude = 3 cm)
Wind speed	1.2 m/s

(*) settings defined during intercalibration studies between Sintef, SL Ross and Cedre flume. (Report Cedre R.13.51.C).

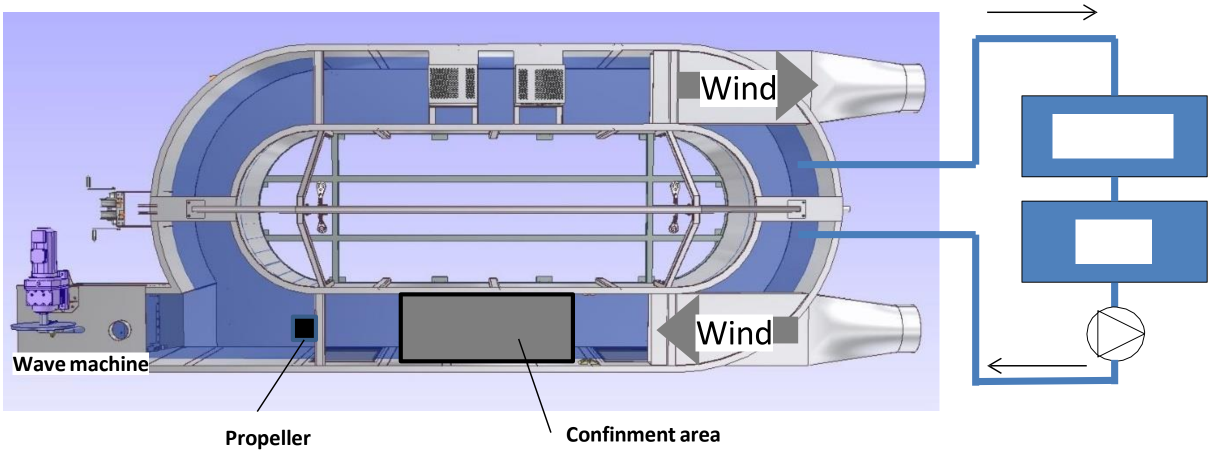


Figure 23. Cedre flume (*Polludrome*) in weathering time configuration (reversed wind).

Size distribution of ice blocks is detailed in table 7.

Table 7. Size distribution of ice blocks in Cedre flume. ....

Total area	Ice blocks size (cm)	50% ice	
		Number	Area (m2)
$8m^2$	20 x 20	19	0.75
	10 x 10	166	1.66
	5 x 5	632	1.58
$1m^2$	20 x 20	5	0.20
	10 x 10	20	0.20
	5 x 5	40	0.10

3.1.3 Testing conditions

At the end of each run, a second propeller energy regime was conducted in order to assess the influence of an additional energy regime on the dispersion efficiency.

Table 8. Experimental matrix of tests performed at Cedre.

Test ID	Oil	Dispersant / Mineral Fine	Ice coverage (%)	Salinity (ppt)	Weathering time (h)	DOR / MOR	Energy
ANS 1	ANS	Bentonite	50	35	18	1 : 10	L/Prop/L/Prop
ANS 2	ANS	Corexit 9500	50	35	18	1 : 20	L/Prop/L/Prop

3.1.4 Testing protocol

3.1.1.1 Oil weathering

- PTFE "walls" were placed in the flume to obtain a $1m^2$ area
- Ice blocks were added in this confinement area
- 1L of ANS crude oil was added in the confinement area between the ice blocks
- Wave maker and wind generator (1.2 m/s reversed to waves) were turned on
- After 18 hours of weathering; oil was sampled for analysis (viscosity, density, water content, evaporation (GCFID analysis)).

It must be noticed that for the two tests, the oil weathering was initiated at 4.00pm. As part of ice blocks melted during the weathering time, additional ice blocks were added at two different times (10.00pm and 8.00am the day after).

It was not possible to ensure the ice concentration during the night. Therefore, it would have been easier to work with PE blocks during the weathering stage to ensure that during the 18 hours of weathering, there is no evolution of oil slick thickness - and evaporation - due to the ice blocks melting.

3.1.5 Dispersant / mineral fine application

The protocol used was:

- Waves and wind were turned off
- Ice blocks were added in the Polludrome

- Test #1: Solution of Bentonite (10 000 ppm) was applied using a watering can.
- Test #2: Dispersant was applied (using Wagner 450 with a 0.5 mm nozzle diameter) on the oil located between the ice blocks.
- PTFE walls were removed and waves (LE) and wind (same direction) were turned on for 30 minutes.

3.1.6 *Energy input*

The following protocol was used for each test:

- Low energy for 18 hours prior to dispersant / mineral fine application
- No energy during dispersant / mineral fin application
- Low energy for 30 minutes after dispersant / mineral fine application
- Propeller energy for 10 minutes
- Low energy for 30 minutes
- Propeller energy for 10 minutes
- Low energy until the end of the test

3.2 RESULTS

3.2.1 *Influence of Weathering*

Table 9 gives the oil properties after 18 hours of weathering in Cedre flume. Water content was measured using Dean Stark according to ISO 3733 norm. Evaporation was calculated after GC-FID analysis (figure 24) and calibration with residues from artificial weathering (Table 2). Oil samples were collected after 18 hours of weathering and before dispersant / bentonite application.

We observed different weathering rates between the two tests especially for viscosities and densities which are significantly higher for the test #2. The differences between the emulsification and the evaporation rates are lower. These differences are probably due to a problem with the PTFE "walls" used to confine the slick during the 18 hours of weathering. At the end of the weathering time, we observed some oil (≈ 200 mL) out of the confinement area for the test #2 which therefore influenced the slick thickness and probably increased its weathering. However, it seems that evaporation rates are quite similar to those obtained by SL Ross / Sintef.

Table 9. Oil properties after 18 hours of weathering.

Test ID	Dispersant / Mineral Fine	Oil viscosity (mPa.s@2°C)		Oil density (@2°C)	Water content (%) (*)	Evaporation (%)
		10s-1	100s-1			
ANS 1	Bentonite	2900	2025	0,955	43	20,3
ANS 2	Corexit 9500	8200	7923	0,989	47	24

(*) conducted according to the ISO 3733 Dean & Stark method, equivalent to the ASTM D95-05 (2010) Standard Test Method for Water in Petroleum Products and Bituminous Materials by Distillation.

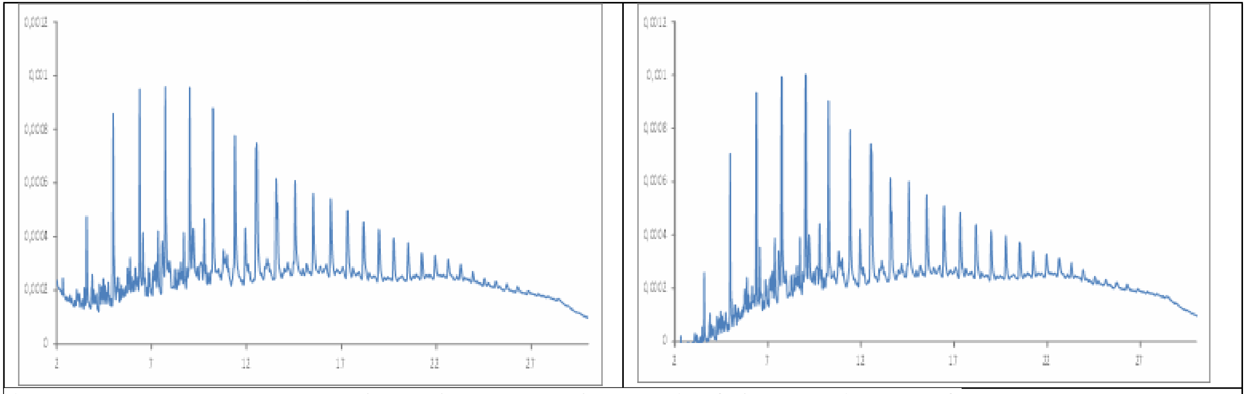


Figure 24. GCFID chromatograms of ANS after 18 hours of weathering (left ANS 1 / right ANS 2).

3.2.2 Dispersion with Corexit 9500

Figure 25 presents the oil concentration measured in the water column during the test. SFUV (AU 10 – Turner design) recording was started immediately after dispersant application. Data were recorded every 3 seconds. SFUV was previously calibrated with crude oil. In addition, during the test, grab samples were collected every 10 minutes in order to confirm (and correct if necessary) the SFUV results. Oil concentrations in the grab samples were determined by colorimetric analysis using a calibration curve conducted with a sample of oil after each 18 hours of weathering.

Dispersant effectiveness was calculated using the oil concentration data and corrected according to evaporation rate measured.

From 10 to 30 minutes, oil was detected periodically in the water column. This periodic variation of oil concentration with an amplitude decreasing with time was already observed at Cedre during the intercalibration study. It corresponds to the movement of the dispersed oil plume in the water column which homogenizes progressively in the whole water volume. After a first propeller energy period, the average dispersant effectiveness reached 16.3%. After the second propeller energy period, the dispersant effectiveness increased to reach 21.4%. There was no influence of the second use of the propeller as the oil concentration in the water column started to increase slightly before the propeller was started.

During this test, the oil concentration before and after the propeller energy regime did not changed significantly. It suggests that propeller does not increase chemical dispersion of oil.

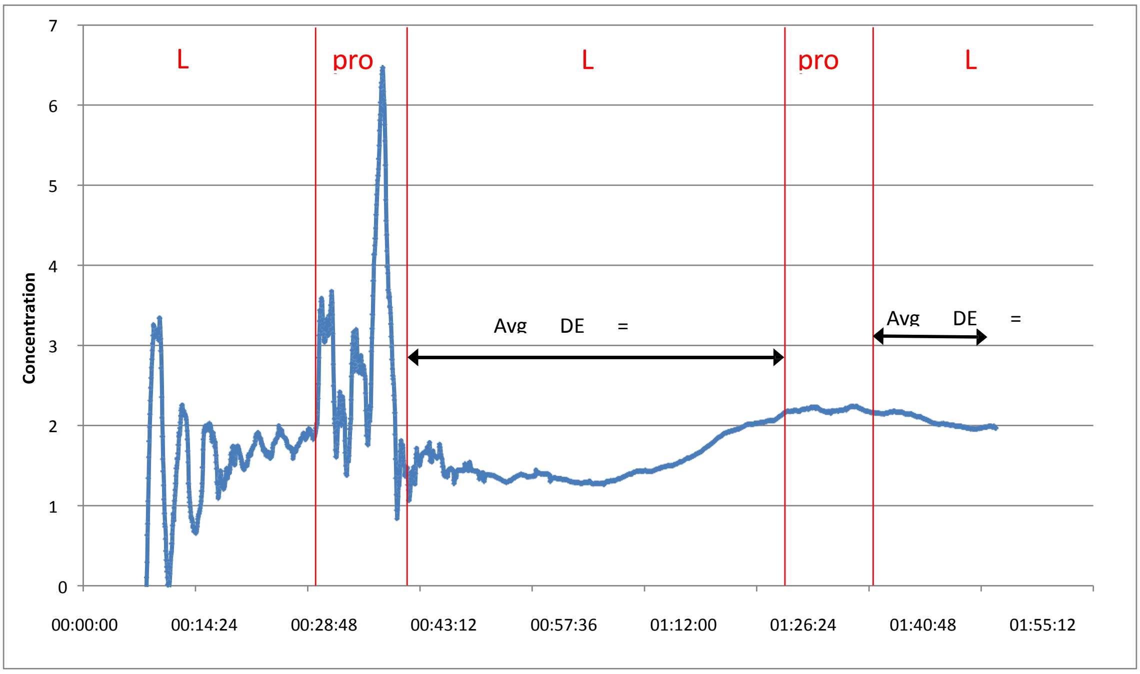


Figure 25. Oil concentration in water column (ANS + Corexit 9500, DOR: 1/20).

Simultaneously with oil concentration, oil droplet size was measured using a Malvern Mastersizer 2000. During this test, a lot of erroneous data grouped around 700 µm were recorded and not considered. This was probably due to the presence of a large volume of small pieces of ice in the water column which mask the presence of oil droplets.

Figure 26 presents the evolution of d50% during the test with Corexit 9500. 5 minutes after the propeller was started, oil droplets were detected during an average of 25 minutes with a d50% between 2 and 60 µm.

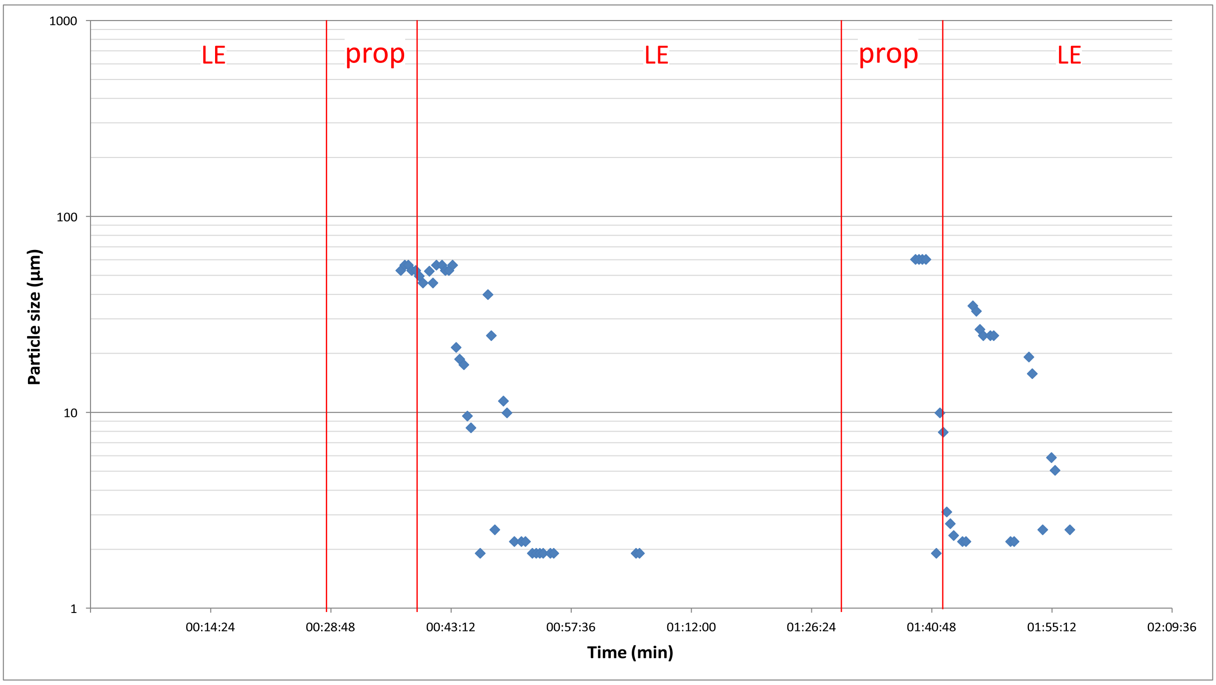


Figure 26. Droplet size evolution (ANS + Corexit 9500, DOR: 1/20).

3.2.3 Dispersion with Bentonite

Figure 27 presents the oil concentration measured in the water column during the tests conducted with bentonite. 16 minutes after bentonite application, oil was detected at very low concentration suggesting a very low dispersion effectiveness of bentonite at low energy level. 5 minutes after the propeller was turned on, the concentration of oil reached 3 to 5 ppm. 5 minutes after the propeller was turned off, the oil concentration decreased immediately to less than 1 ppm. During the 2nd propeller energy regime, oil was detected in the

water column at a concentration comprised between 3 and 16 ppm. Immediately after the propeller energy period, the oil concentration decreased to less than 2 ppm. At the end of the test, the increase of oil concentration suggests that the whole volume of the flume test was not completely homogenized.

These results suggest that without a very high energy period, the oil dispersion with a mineral fine is not observed. While propeller is turn on, oil is dispersed in the water column. As soon as the propeller is stopped, oil mineral aggregates are not present in the water column but at water surface. Low energy regime is not sufficient to resuspend these aggregates in the water column. It would have been interesting to study the behaviour of these aggregates at high energy level.

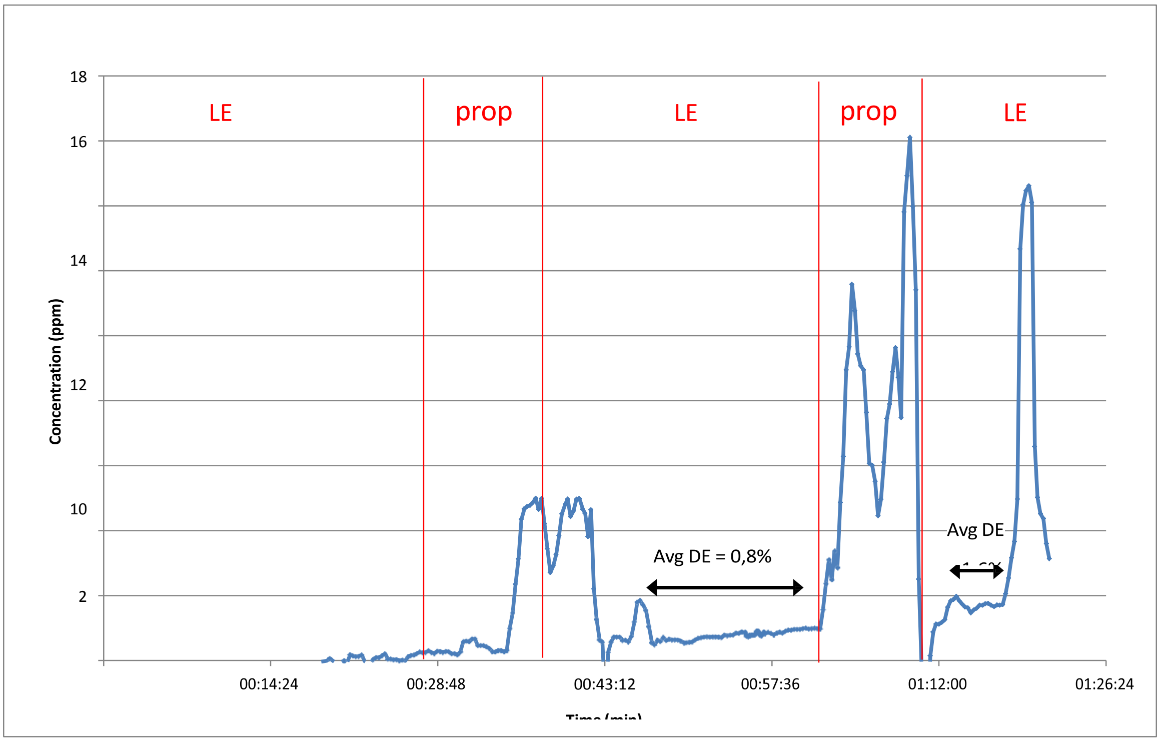


Figure 27. Oil concentration in water column (ANS + Bentonite, MOR: 1/10).

Figure 28 presents the d50% measured during the test conducted with bentonite. Before the propeller energy period, large aggregates of bentonite with a diameter higher than 1 cm (like snow) and smaller aggregates were observed visually in the water column (figure 29). At low energy regime, these aggregates of bentonite particles were sinking slowly few seconds after bentonite application. Smallest aggregates (between 300 and 500 µm) were measured (Figure 28) while the biggest were probably too brittle and broke in the hose connecting the Polludrome to the Malvern.

Even if the propeller was turned on, the particle size remained at a range between 300 and 700 µm and did not change after the second propeller energy period.

Considering the SFUV results, these large aggregates were mainly composed of bentonite alone and oil but at a very low concentration.

At the end of the test, the surface of the flume was recovered with a brown mixture of emulsified oil (due to prop mixing) and mineral fine (figure 30). One sample of water surface was collected for observation (figure 31 and 32). After few seconds without agitation, all the aggregates were observed at the surface. No particles were observed at the bottom. After a very slight agitation (figure 31), the aggregates resuspended in the water column. This was observed during the previous experiment performed at lab scale with very high level of energy (Ultraturrax).

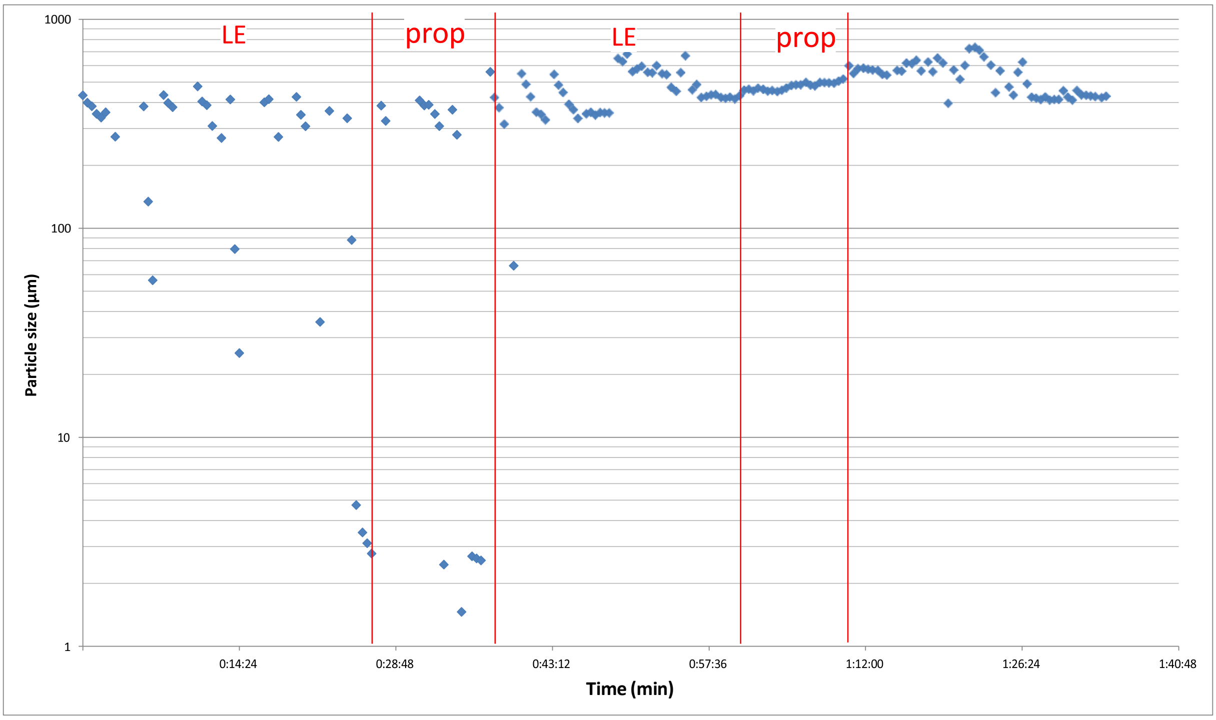


Figure 28. Particle size evolution (ANS + Bentonite, MOR: 1/10).

Figure 29. Bentonite aggregates sinking at the beginning of the test.

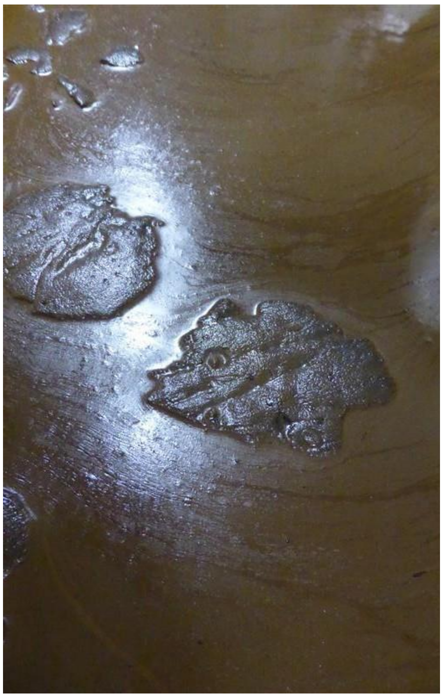


Figure 30. Water surface at the end of the test.

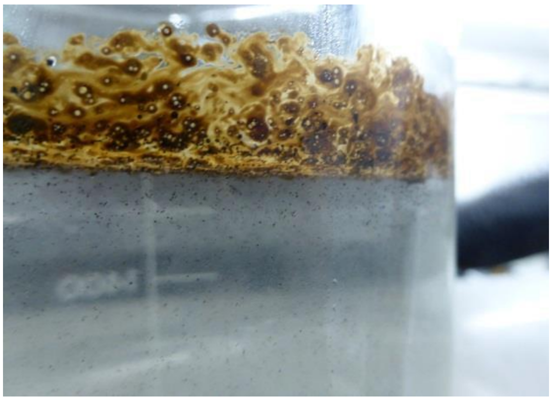


Figure 31. Sample of water surface.

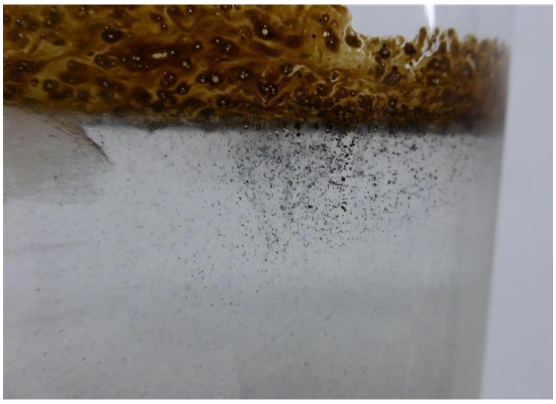


Figure 32. Oil Mineral Aggregates resuspended after slight agitation

3.3 CONCLUSION

Two tests of dispersion were conducted in Cedre's flume test in order to compare the oil dispersion with Corexit 9500 and oil dispersion with a mineral fine (Bentonite). The mains conclusions are:

- Using dispersant, DE reached 21%.
- Using bentonite, DE did not exceed 2%.
- Without agitation, OMA were observed at the water surface and needed agitation to resuspend in the water column

3.4 FUTURE TESTS

We recommend to conduct additional tests:

- Test with high energy regime for 10 minutes immediately after bentonite application in order to enhance the contact between mechanically dispersed oil and bentonite then low energy for 60 minutes to follow the OMA behavior in the water column(Test #3: HE /LE)
- Test with propeller energy regime for 10 minutes immediately after bentonite application in order to enhance the contact between mechanically dispersed oil and bentonite then Low energy for additional 60 minutes to follow the OMA behavior in the water column (Test #4: Prop/LE)
- Test with lighter crude oil and probably easily dispersible. According to SL Ross / Sintef results, Oseberg or Troll appear to be good candidates.

For these additional tests, we recommend to use PE blocks during the weathering time to ensure a constant oil thickness.

APPENDIX 1

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Centre de documentation, de recherche
et d'expérimentations sur les pollutions accidentelles des eaux
*Centre of Documentation, Research
and Experimentation on Accidental Water Pollution*

OGP International Association of Oil & Gas Producers

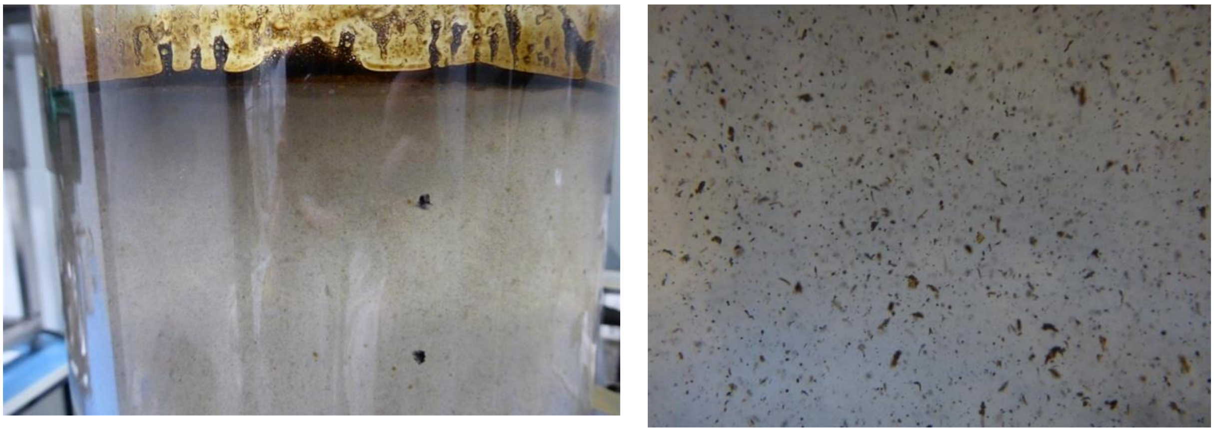
OGP-JIP 6 Arctic

DISPERSANT TESTING UNDER REALISTIC CONDITIONS

Task 2.2 / Task 4

Preliminary laboratory tests program

PROGRESS REPORT



R.15.04.C/5614 CA/RJ/FXM January 2015

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Références Contrat / *Contract references* : OGP
Proposal P14036 – April 2014 / Agreement dated May, 25th, 2014

OGP-JIP 6 ARCTIC

DISPERSANT TESTING UNDER REALISTIC CONDITIONS.

Task 2.2 / Task 4

Preliminary laboratory tests program

Progress report

Rédigé par / *Written by* : Cathy AUDEGOND *validated*	**Relu par** / *Read by* : Ronan JEZEQUEL François MERLIN *validated*	**Contrôlé par** / *Checked by* : Georges PEIGNE Stéphane LE FLOCH *validated*

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1. INTRODUCTION

As a task 2.2 of the project “Dispersant testing under realistic conditions”, Cedre is in charge of the oil-mineral aggregates (OMAs) tests which will be completed in its flume test.

For this test program, OGP requested bentonite to be used as fine mineral in this program. In this respect, as part of OGP, TOTAL oil Company provided bentonite samples to Cedre.

In order to prepare the flume test program Cedre proposed to conduct a short and simple preliminary laboratory testing program.

The results of these laboratory preliminary tests are summarized here.

2. OBJECTIVES

This laboratory program aimed at preparing the flume testing program to be conducted at Cedre using mineral fines, as planned in Task 2.2 and 4. This program intended to give information on the effect of the mineral type and concentration and of the mixing conditions (energy) on the OMA formation.

In the past, most of the work on OMA had been carried out using Kaolinite which is thereby well documented. Conversely, the use of bentonite had not been studied yet. Accordingly this preliminary test program was completed on these two mineral fines, Kaolinite acting as a reference.

3. PRINCIPLE

Preliminary laboratory tests were performed using a modified version of the IFP test in which dispersant efficiency assessment can be conducted under low or high mixing energy. Low energy refers to standard condition of IFP protocol while high energy refers to doubled low energy.

The test matrix is given in Table 1. The tests were performed using Alaskan North Slope crude. Finasol OSR 52 was added with a DOR equal to 1:20 and fine minerals with a MOR equal to 1:5 prepared as a solution in water. A large separating funnel (5L) was used instead of the beaker used in the IFP protocol (Figure 1). After half an hour rest time, the dispersion stability was assessed. The whole water collected through the overflow was separated into 3 parts: the 5% lower, the 90% in between and the 5% upper. The amount of oil in the samples was measured in each part after extraction with methylene chloride.

Figure 1. Cedre modified IFP test apparatus.

4. RESULTS

a. Modified IFP tests

Results, presented in Table 2, suggest that:

- Dispersant alone: 48% of oil is dispersed in the water column
- Kaolinite alone: no dispersion observed even at high energy (same results obtained with oil alone)
- Bentonite alone: very poor dispersion, possibly slightly higher than kaolinite alone even at high energy
- Kaolinite + dispersant: kaolinite improves the dispersion (65%)
- Bentonite + dispersant: bentonite reduces the dispersant efficiency (14%).

Table 2 - Results expressed in terms of efficiency of the IFP test (%).

		Test # 1	Test # 2	**Mean**
Dispersant	Low energy	51	45	**48**
Dispersant + Kaolinite	Low energy	69	60	**65**
Kaolinite alone	Low energy	1	1	**1**
	High energy	1	1	**1**
Dispersant + Bentonite	Low energy	17	12	**14**
Bentonite	High energy	3	3	**3**
Oil alone	Low energy	1	1	**1**
	High energy	1	0	**1**

Concerning the distribution of dispersed oil in the water column (figure 2):

- Using only dispersant, 75% of the oil is dispersed in the mid water column and approximately 20% of oil is measured in the 5% upper of the funnel,
- Using kaolinite and dispersant, approximately 43% is measured in the 5% upper of the funnel and 50% in the mid water column
- Using bentonite and dispersant, the dispersed oil is observed in the 3 parts of the water column (25% in the 5% upper of the funnel, 57% in the mid water column and 18% at the bottom).

This suggests that using bentonite, the aggregates observed (see figure 3) are denser than those obtained with kaolinite.

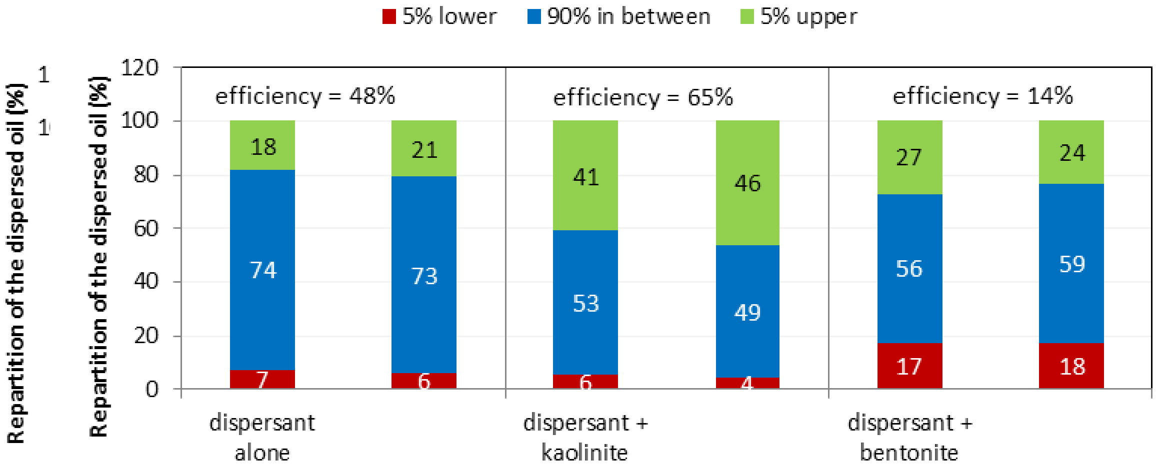

Figure 2 - Repartition of dispersed oil in the 3 parts of the separating funnel.

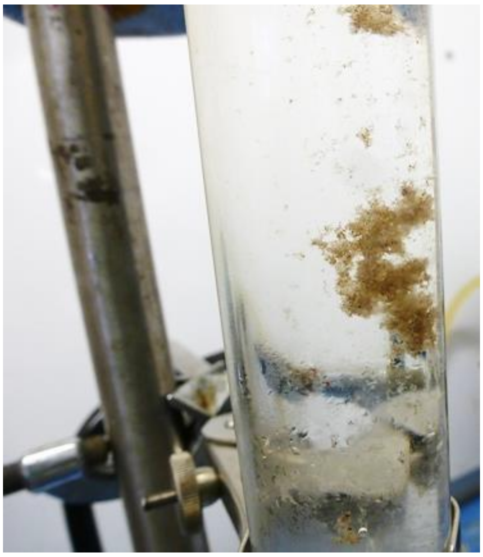

Figure 3 - OMAs collected in the separating funnel

5. Additional tests with higher energy

Even if the IFP test results obtained with bentonite alone were low, formation of OMA was clearly observed in the test tank, which unfortunately did not pass through the overflow located at the bottom of the tank.

More, even when tuned at higher energy, the turbulence in the IFP test does not represent the strong mixing energy which can be achieved with a ship propeller.

Possibly the IFP test is not well appropriate to describe the dispersion of oil with fine minerals. Therefore, additional tests were performed in a beaker using a higher energy than in the IFP test.

a. Tests with magnetic stirrer

In a beaker containing sea water and a known amount of crude oil, a solution of bentonite was added to the oil while mixing was performed with a magnetic stirrer. Water samples were collected in the 5 cm under the surface layer (top) (surface oil excluded), in the middle of the water column (water column) and in the bottom of the tank (bottom) (OMA settled at the bottom were excluded). Oil concentrations were measured in all the samples, the results are presented in Figure 4.

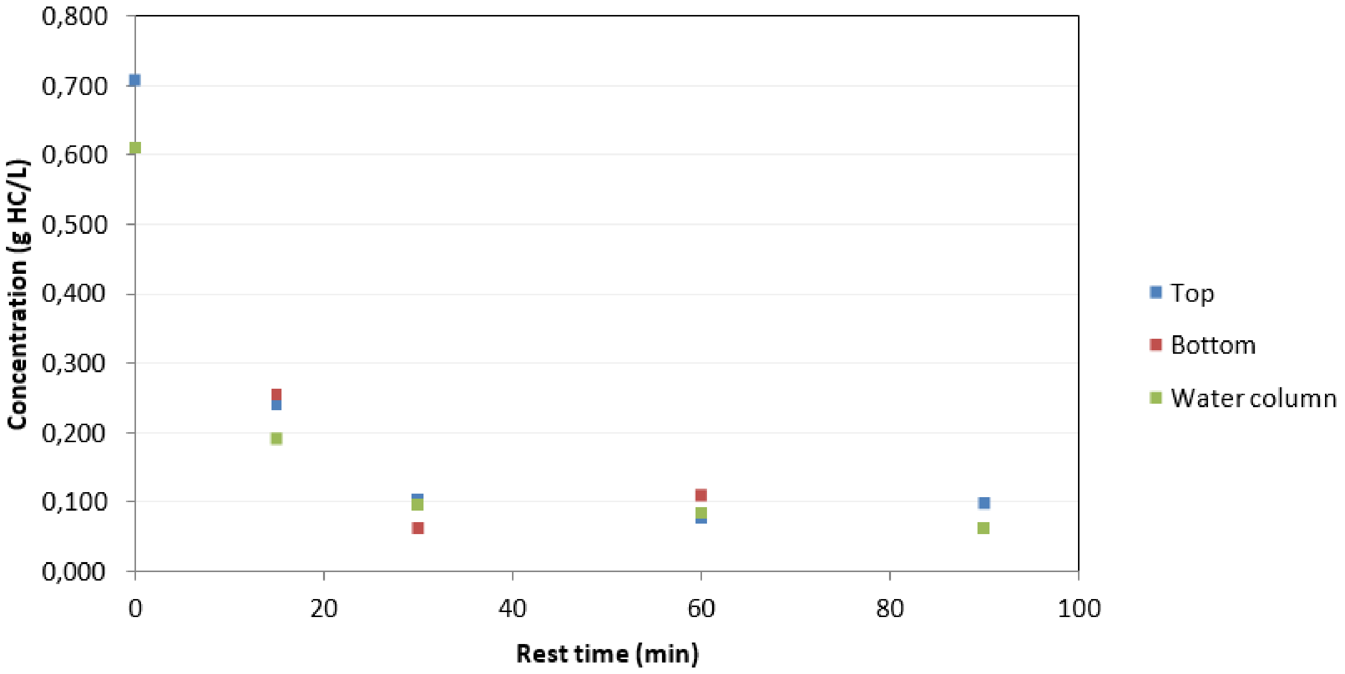

Figure 4 - Concentration of dispersed oil after a 15, 30, 60 and 90 rest time.

After half an hour rest time, a few quantity of oil remains in the water column. Even if the bentonite and the oil were well mixed (formation of OMAs actually observed), almost all of the OMAs formed can be found at the water surface after 30 minutes. However, even after 90 minutes of rest time, it could be observed that the OMAs were likely to return in suspension in the water column if a low stirring energy was applied.

b. Tests with high shear rate mixer

Finally, additional qualitative tests were performed with a very high energy mixing (using a high shear rate mixer - *Ultraturax*). In this condition, it was observed that the oil dispersed was distributed in the whole water column and kept stable even after one hour rest time.

6. CONCLUSION

These preliminary tests suggest that mixing energy is a key parameter in the oil dispersion using mineral fines. It was necessary to use high energy to produce OMA which remain in the water column. The low result observed in the modified IFP may be due to an insufficient energy even when tuned "high"

In order to forecast what could occur with higher energy such as the energy obtained with a ship propeller, we decided to perform additional tests in a beaker with a magnetic stirrer in a first step and then with an Ultraturax. In this condition, formation of aggregates was observed and the dispersion appeared to be higher.

Finally, in order to simulate what will occur in the flume test during the next stage of the experimental study, tests were carried out in a large tank (1 m^3) using the electric propeller (as agreed between Sintef, SLRoss and Cedre). These tests are still ongoing.

7. TIMELINE

Task 2.2:

Week 10: first flume test with bentonite (task 2.2) (two tests per week).

Week 24: completion of tests with bentonite (on the basis of 30 tests).

Week 26 - 27: draft report of task 2.2.

Task 4: Timescale and number of tests will be confirmed according to results of task 2.2.

Week 29: first tests with new OMA (task 4.4).

Week 35: completion of tests with new OMA (task 4.4).

Week 38 - 39: draft report.

APPENDIX 2

Oil	Salinity	Mineral	MOR	%oil water column +/- Std. dev.	D0,5 (µm) water column	D0,5 (µm) surface layer
1:10	10,4 +/- 0,7		44 ± 2	62 ± 2		
Grane	5 ppt	Bentonite	1:5	19,8 +/- 1,2	55 ± 1	66 ± 11
			2:5	46,6 +/- 3,3	55 ± 0,1	56 ± 2
		Calcite	1:10	12,0 +/- 3,3	90 ± 1	113 ± 16
			1:5	14,9 +/- 5,7	109 ± 7	100 ± 10
			2:5	22,5 +/- 2,2	79 ± 6	125 ± 21
	35 ppt	Bentonite	1:10	12,2 +/- 1,0	44 ± 3	54 ± 2
			1:5	19,3 +/- 6,2		
			2:5	20,3 +/- 3,4	68 ± 1	59 ± 4
		Calcite	1:10	16,3 +/- 1,0	72 ± 6	80 ± 7
			1:5	21,4 +/- 2,9		
			2:5	27,0 +/- 4,7	82 ± 22	76 ± 7
Troll	5 ppt	Bentonite	1:10	20,7 +/- 0,5	45 ± 3	63 ± 7
			1:5	13,4 +/- 3,4	54 ± 0,4	61 ± 3
			2:5	49,1 +/- 12	57 ± 2	57 ± 2
		Calcite	1:10	13,6 +/- 5,4	62 ± 13	108 ± 19
			1:5	26,6 +/- 6,9	54 ± 7	146 ± 19
			2:5	36,7 +/- 3,2	74 ± 7	108 ± 16
	35 ppt	Bentonite	1:10	9,8 +/- 0,7	45 ± 2	54 ± 2
			1:5	13,5 +/- 0,7		
			2:5	13,1 +/- 1,3	62 ± 3	59 ± 4
		Calcite	1:10	10,4 +/- 0,3	78 ± 1	44 ± 5
			1:5	22,7 +/- 7,4		
			2:5	27,0 +/- 3,8	47 ± 3	46 ± 1
ANS	5 ppt	Bentonite	1:10	19,1 +/- 6,4	48 ± 4	74 ± 21
			1:5	46,0 +/- 1,8	51 ± 0,4	73 ± 13
			2:5	25,8 +/- 4,9	52 ± 0,1	53 ± 4
		Calcite	1:10	19,5 +/- 3,5	106 ± 2	104 ± 17
			1:5	26,7 +/- 1,6	99 ± 6	108 ± 13
			2:5	44,8 +/- 0,7	104 ± 2	120 ± 9
	35 ppt	Bentonite	1:10	17,9 +/- 1,5	48 ± 1	44 ± 11
			1:5	30,6 +/- 3,2		
			2:5	31,8 +/- 1,3	70 ± 8	55 ± 10
		Calcite	1:10	13,2 +/- 0,5	47 ± 4	27 ± 2
			1:5	18,3 +/- 2,6		
			2:5	42,7 +/- 5,0	61 ± 7	34 ± 1
Oseberg	5 ppt	Bentonite	1:10	8,8 +/- 1,7	48 ± 4	50 ± 0
			1:5	22,2 +/- 3,7	50 ± 3	52 ± 2
			2:5	58,2 +/- 1,8	55 ± 0,3	56 ± 2
		Calcite	1:10	9,0 +/- 1,9	57 ± 1	100 ± 8
			1:5	18,6 +/- 0,1	66 ± 4	76 ± 9
			2:5	41,4 +/-15,8	64 ± 6	74 ± 5
	35 ppt	Bentonite	1:10	13,5 +/- 2,7	50 ± 4	45 ± 6
			1:5	16,6 +/- 0,7		
			2:5	20,1 +/- 1,5	74 ± 5	51 ± 9
		Calcite	1:10	13,9 +/- 1,5	38 ± 1	23 ± 1
			1:5	14,0 +/- 2,7		
			2:5	34,1 +/- 0,4	55 ± 8	21 ± 6

APPENDIX 3

Pictures of preliminary tests in polludrome.