Produced water challenges

Influence of production chemicals on flocculation

Thesis Report for

Master of Offshore Environmental Engineering

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Abstract

Produced water is the largest volume waste from offshore oil and gas exploration and production processes. Water in varying quantities is always produced along with oil, and has to be separated from the oil. The quantity of "produced water" generally increases substantially with the age of the oil field. Produced water handling tactic depends on the composition of produced water, location, quantity and the availability of resources.

This thesis describes practical, economical, technological and environmental aspects of produced water management, an incorporated part of the oilfield development plan. The water can either be injected into the formations or treated. Advantages and disadvantages of different options for produced water minimizing technologies are discussed.

Water is mostly discharged to sea. Treatment of produced water has been attempted and is proven to be an effective option for produced water handling. After treatment it, however, still contains traces of oil and chemicals. In addition, some oil is discharged with displacement water. Reducing environmental impact of produced water discharges is the major aim of each oil and gas production field.

In Norway PW discharge is under strict authority of the Pollution Act, which gives permits for discharge to the environment, The Oslo-Paris convention, OSPAR, is the most important international agreement regulating discharges to the sea and protecting marine environment of the north-east Atlantic. OSPAR stipulates that the maximum discharge limit is 30 ppm OIW for the petroleum companies operating in the North-East Atlantic. In order to meet zero environmental harmful discharges a produced water management tool Environmental Impact Factor (EIF) was developed.

When choosing produced water treatment technologies, focus is on the major contributor for the total environmental impact. Experience has shown that the major contributors to EIF are dispersed oil, volatile aromatics, heavy aromatics, alkylated phenols, and different process chemicals.

The majority of available technologies will remove dispersed oil and some are also able to reduce the aromatic components as well as oil-soluble chemicals from the produced water. But the performance is highly dependent on process variables at each installation. Chemicals

used in scale squeeze operations are often acidic in nature. Highly charged chemicals also disturb the separation regime established in the system. Effect of production chemicals (corrosion / scaling inhibitors) on flocculation process is a problem that has been focused on in this thesis. Experiments with turbidity and particle size distribution measurements were performed with purpose to study how the production chemicals influence oil/water separation efficiency. Synthetic produced water, some selected chemicals (corrosion/scaling inhibitors), and CFG (natural flocculating agent) and Floctreat (flocculant received from Clariant Oil Services) were used in the experiments. Operating conditions such as temperature (55-60 °C) and pH (6.2) of produced water were stated.

CFG showed good flocculation effectiveness while Floctreat was not equally successful in these experiments.

Results indicated that both corrosion inhibitors and scaling inhibitors have an effect on separation efficiency. Concentration of added chemical is also an important factor in flocculation. Depending on type and concentration of chemicals, production chemicals will typically decrease or increase separation efficiency.

Contents

Abbreviations

API	American Petroleum Institute
BCF	Bioconcentration Factor
BOD	Biological Oxygen Demand
BS&W	Basic Sediment and Water
BTEX	Benzene, Toluene, Ethylbenzene, and o-, m-, and p-Xylene
BWPD	Barrels of Water per day
CETCO	Colloid Environmental Technologies Company
CFU	Compact Flotation Unit
CI	corrosion inhibitor
CMR	carcinogen, mutagen, peproductive toxicity
DD	degree of deacetylation
DGF	Dissolved Gas Flotation
DO	Dissolved Oxygen
DREAM	Dose Related Risk and Effect Assessement Model
EC	Effect Concentration
EIF	Environmental Impact Factor
EPA	Environmental Protection Agency
GAB	General Aerobic Bacteria
GanB	General Anaerobic Bacteria
HELCOM	Helsinki Commission
HOB	Hydrocarbon Oxidizing Bacteria
HP	High Pressure
LC	Lethal Concentration
MPPE	Macro Porous Polymer Extraction
MW	Molecular Weight
NETL	National Energy Technology Laboratory
NOEC	No Observable Effect Concentration
NPD	Naphtalene, Phenanthrene and Dibenzothiophene
NTU	Nephelometric Turbidity Units
OECD	Organization for Economic Co-operation and Development

OiW	Oil-in-Water
OLF	Oljeindustriens Landsforening (Norwegian Oil Industry Association)
OSPAR	Oslo/Paris convention
OTU	Offshore Treatment Unit
PAH	Polycyclic Aromatic Hydrocarbons
PEC	Predicted Environmental Concentration
PLONOR	Pose Little Or No Risk to the Marine Environment
PNEC	Predicted No Effect Concentration
PTB	pounds of salt per thousand barrels of oil
PW	Produced Water
PWT	Produced Water Treatment
REACH	Registration, Evaluation, Authorization and restriction of the Chemicals
SAR	Sodium Adsorption Ratio
SPB	Sulphur Reducing Bacteria
SPE	Society of Petroleum Engineers
SOB	Sulphur Oxidizing Bacteria
TDS	Total Dissolved Solids
ThOD	Theoretical Oxygen Demand
TOC	Total Organic Carbon
TORR™	Total Oil Remediation and Recovery Trademark
WIO	Water-in Oil
WOR	Water –Oil-Ratio
WOC	Water-Oil-Contact

Chapter 1

Introduction

The theoretical part of this thesis covers challenges relating to produced water and the environment. This includes water composition and characteristics, as well as minimizing volume of produced water (PW) and treatment technologies. Knowledge of emulsion theory is essential in choosing of produced water treatment methods.

Practical part of the thesis consists of research of realistic concentration of Oil in Water, (OiW) following experiments of removal of the oil by using flocculation method. CFG is a natural flocculant, and the topic of this research is to investigate how CFG works in the presence of production chemicals.

1.1 General overview

Produced water is the largest volume waste from offshore oil and gas exploration and production processes. It consists of formation water, which is water naturally present in the reservoir, and/or in case of gas production, condensed water. In addition, the effluent stream from oil production process can also contain:

— seawater that has to be injected to maintain reservoir pressure and that has broken through to production wells

— occasionally some smaller oily streams like displacement water from oil storage facilities, process and drainage water (Ray and Engelhardt, 1992)

Water in varying quantities is always produced along with oil, and has to be separated from the oil. The quantity of "produced water" generally increases substantially with the age of the oil field. Oil reservoirs frequently contain large volumes of water. Nowadays produced water is no longer a simple waste stream.

Globally, oil wells produce about 220 million BWPD (barrels of water per day)—roughly three barrels of water for every barrel of oil (Water Management, Halliburton, 2009). In older fields, the water "cut," or ratio-of-water-to-oil, can be 95% or higher. In 2007 the

amount of produced water generated on the Norwegian Continental Shelf was 183 million cubic meter (Annual report and accounts 2007, StatoilHydro). This was an increase of 5% compared with 2006.

One report published in 2007 illustrated the cost using a typical North Sea field of 50 wells, with each well producing 5,000 bbl of water per day. The daily water handling cost for the oilfield (if the cost of treating each barrel is $0.50) would equate to $125,000 (SPE International Symposium on Oilfield Chemistry, Houston, 2007). Managing this produced water is a great challenges and costs to operators.

The figure below demonstrates the large increase in the water/oil ratio when the oilfield reach maturity and water by far becomes the major fraction of the production.
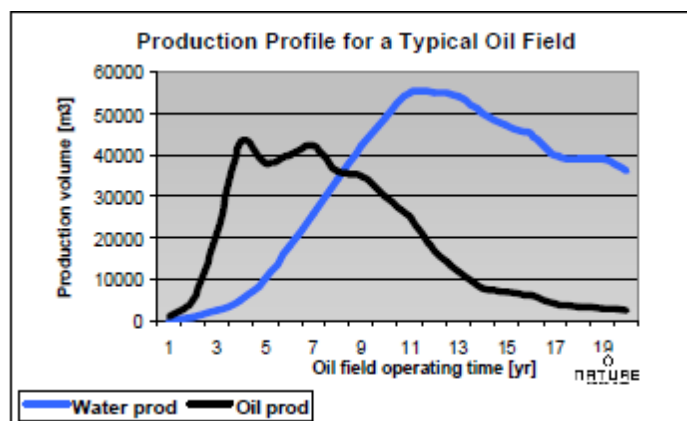
Figure 1: Typical production profile for an oilfield in the North East Atlantic
(Nature technology solutions, 2009)

The water can either be injected into the formation or treated. In 2003, about 14 per cent (Norwegian Pollution Control Authority, 2008) of the produced water was injected. The amount of produced water discharged into the sea was 162 million cubic meters, an increase of 12% (Figure 2). In other words most of the water is discharged to the sea. Even after treatment, it still contains traces of oil and chemicals. In addition, some oil is discharged with displacement water.
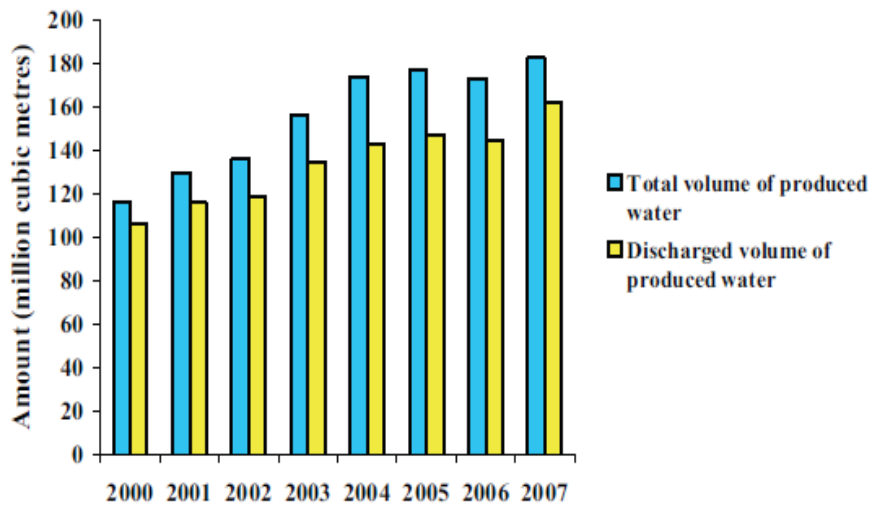
Figure 2: Amounts of produced water on the Norwegian Continental Shelf (OLF, 2007)

1.2 Constituents in produced water

Oil fields usually start producing reservoir water at a rather early stage of production at low water to oil ratios. As fields mature, later, the ratio between water and oil can reach high values (up to 10:1), and the composition of the reservoir water changes. However, oil fields production is often enhanced by water injection, to maintain the reservoir pressure. Injected water dilutes the formation water and the discharged produced water progressively approaches the injected water in composition and character (OGP, 2005).

Table 1 below surveys the average data of Produced Water characteristics.

Table 1: Typical Produced Water Characteristics (OLF, 1992)

Oil-in-Water	
-Normal	100-500 mg/L (free oil)
-Maximum (Upset Conditions)	3000 mg/L (free oil)
Total Suspended Solids	2 mg/L normal
(Excluding oil)	3000mg/L extreme maximum
Temperature	50-90°C
pH	5.1 to 7.0

Specific Gravity at 15°C	1.03 to 1.15
Sulphide as H_2S	0-1000 mg/L
Dissolved Oxygen	Nil
Dissolved CO_2	50-2000 mg/L
Salinity	2.4 to 20% (wt)

***These are conditions of the water after the inlet separator (1st. stage separator)

The related crude oil property ranges are for information:

Density at 15°C: 0.78 to 0.88

API Gravity: 30 - 50°

Produced water is basically a mixture of formation water and injected water and also contains smaller quantities of:

- ➢ Dissolved organics (included hydrocarbons)
- ➢ Traces of heavy metals
- ➢ Dissolved minerals
- ➢ Suspended oil (non-polar)
- ➢ Solids (sand, silt)
- ➢ Bacteria
- ➢ Production chemicals

Depending on many factors produced water characteristics and physical properties vary considerably. These factors are: the geographic location of the field, the geological formation with which the produced water has been in contact for thousands of years, and the type of hydrocarbon product being produced. Produced water properties and volume can even vary throughout the lifetime of the reservoir. Oil and grease are the constituents of produced water that receive the most attention in both onshore and offshore operations, while salt content (expressed as salinity, conductivity, or total dissolved solids [TDS]) is also a primary constituent of concern in onshore operations. In addition, produced water contains many organic and inorganic compounds that can lead to toxicity. Some of these are naturally occurring in the produced water while others are related to chemicals that have been added for well-control purposes. These vary greatly from location to location and even over time in the same well.

The constituents of produced water can be classified into the following groups:

➢ Inorganic components

➢ Organic components

➢ Production and processing chemicals

➢ Other substances and properties

1.2.1 Inorganic components

As it mentioned above, properties of produced water can vary depending on geographical and geological factors and probably age of the oilfield. Formation water has similar properties to seawater, but normally has higher salinity and lower pH. When seawater is injected, composition of produced water will eventually change.

Dissolved salts are the major inorganic constituents of produced water, but salinity can vary from almost fresh – the condensed water, to saturated (up to 300 ppt) with a chloride content of about 14 times that of seawater (3rd International Petroleum Environmental Conference, Albuquerque, 1996). The chloride content of the discharges varies from almost fresh – the condensed water, to salty formation water. In North Sea the concentration of total dissolved salts can have values between 3 g/l and far above the average concentration in seawater.

Table 2: Produced water characteristics (Ray and Engelhardt, 1992)

Produced water parameters	pH	Chloride (g/l)	Temperature (°C)
Oil fields			
Brent	6-7.7	12.4-14.8	3-80
Other northern	6-7.7	14.7-16.9	
Sentral North Sea	6-7.7	81.0-100	
Gas fields			
UK sector	3.5-5.5	0.1-277	10-50
Dutch sector	3.8-5.5	0.1-189	13-45
North Sea seawater	8.1	18.8-19.5	3-17

The data in Table 2 illustrates that the effluents from different fields have very variable pH values and salinities. Consider that the temperature of produced water can be very different (3-80°C) depending on the field.

Table 3 lists the average concentration values of some of the major anionic constituents in produced water and in seawater.

Table 3: Major inorganic constituents in produced water, the average concentration (mg/l) (OGP, 1994)

Component	World-wide discharge average	North Sea discharge average	World-wide seawater average
Bicarbonate	771	615	28
Chloride	60874	44630	19000
Sulphate	325	814	900
Sulphide	140	-	-
Nitrate	1	1	0.67
Phosphate	0	0	0.09

The main inorganic components, which are thought to be environmental concern, are metals. Over the last 10 years, studies to determine the concentrations of trace metals in formation and produced water, sampling and analysis methodologies improved considerably. The most interest has metals: cadmium, copper, nickel, arsenic, chromium, lead, mercury, and zinc (Table 4).

Because of different factors (geological characteristics, gas or oil production, mature/quite new production field, corrosion of galvanized equipment occurring) the results are variable.

Table 4: Tons of heavy metals discharged into the North Sea (OLF, 2007)

Metal	2000	2001	2002	2003	2004	2005	2006	2007
Arsenic	0.080	0.052	0.104	0.013	0.144	0.057	0.073	0.063
Cadmium	0.103	0.035	0.055	0.012	0.010	0.006	0.010	0.008
Copper	4.790	4.290	3.230	3.090	1.760	1.080	1.780	1.930
Lead	23.800	2.450	4.180	1.940	1.100	1.630	2.290	2.230
Chromium	1.180	1.030	0.694	0.809	0.580	0.458	0.482	0.538

Mercury	0.116	0.016	0.020	0.007	0.005	0.004	0.005	0.003
Nickel	0.248	0.204	0.335	-	-	-	-	-
Zinc	3.570	1.840	4.510	-	-	-	-	-

1.2.2 Organic constituents

- ✓ Dispersed oil
- ✓ Dissolved organic compounds

Oil contents a wide spectrum of compounds, mostly hydrocarbons, which can have very various properties (such as solubility, molecular weight and structural complexity). Therefore oil is present in PW both as dispersed droplets and in the dissolved phase.

The amount of dispersed oil in a PW depends on:

- ✓ Oil density
- ✓ Shear history of the droplet
- ✓ Amount of oil coalescence
- ✓ Interfacial tension between the water and the oil

1.2.2.1 Dispersed oil

In order to limit the discharge of oil in produced water into the sea is decided to measure it. Although the oil content in PW varies from platform to platform, the overall concentration of dispersed oil in produced water discharged to the North Sea is relatively stable. From 01.01.2007 the goal performance standard for dispersed oil is 30 mg/l as monthly average (OSPAR, 2001).
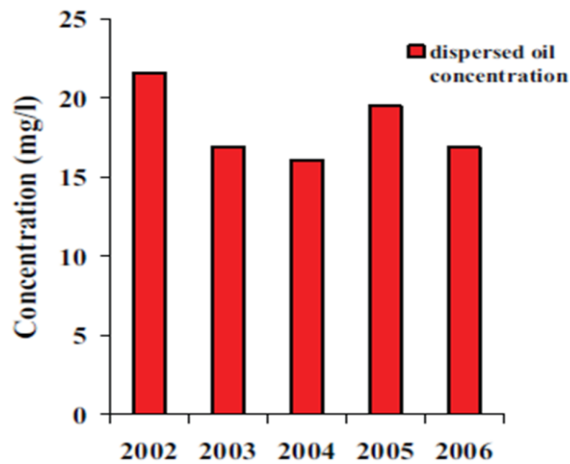
Figure 3: Average concentrations of dispersed oil discharged with PW in the Norwegian sector (compiled from OLF, 2007)
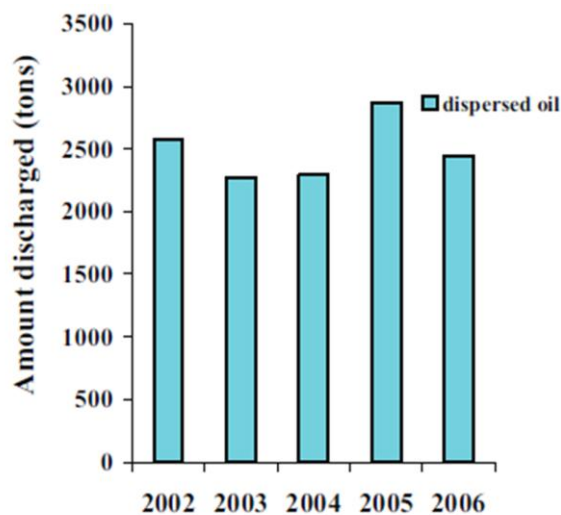
Figure 4: Amounts of dispersed oil discharged with PW in the Norwegian sector (OLF, 2007)

Dissolved organic compounds that may be in the produced water stream include aliphatic hydrocarbons, carboxylic acids, phenols and low molecular weight aromatics. The concentration and nature of soluble organics depends upon type of oil and some technological factors, such as the stage of production and artificial lift techniques.

Contribution and concentration of specific organic compounds in produced water is given in Table 5.

Table 5: The contribution from specific organic compounds in produced water (OLF, 2007) and concentration for North Sea sector (OLF Env. Programme, Project D01)

Organic compound	Contribution (%)	Concentration (mg/l)(North Sea)
Carboxylic acids	93.6	30-800 (typical 300)
BTEX	4.8	0-20 (typical 8)
Phenols	0.5	1-11 (typical 5)
EPA PAHs	0.13	0-4 (typical 1.5)
Alkylphenols (C1-C3)	0.89	0-6 (typical 1)
Alkylphenols (C4-C9)	0.03	0-30 (typical 5)

1.2.2.2 Carboxylic acids

Carboxylic (fatty) acids represent the biggest group among all organic compounds in PW and account for most of the total organic carbon content (TOC) of produced water. Acetic acid is present in the highest concentration. Carboxylic acids are not considered to be environmentally harmful. The total amount of carboxylic acids discharged on the Norwegian Continental Shelf in 2007 increased by 3% compared with the quantity discharged in 2006 (Figure 5).
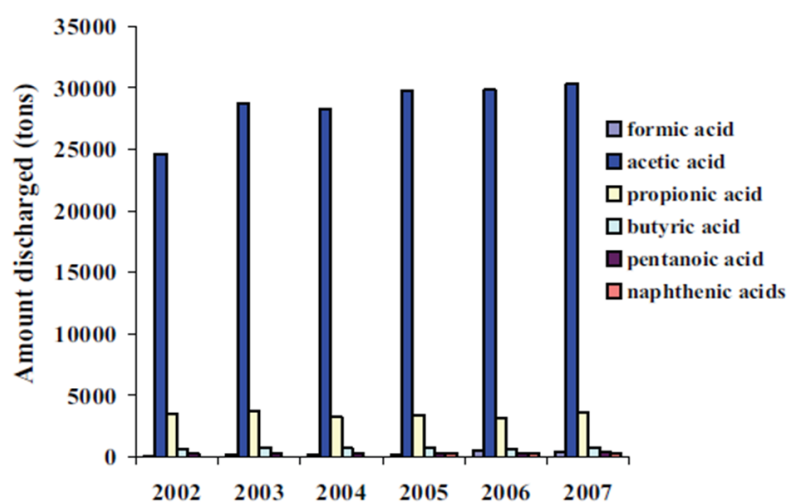
Figure 5: Amounts of carboxylic acids discharged on the Norwegian Continental Shelf (OLF, 2007)

1.2.2.3 Phenols

Phenols are the second largest group of dissolved organics in produced water, and phenol is the most abundant compound in this group (Table 6). Solubility of alkylphenols decreases with increasing MW. Studies on C4-C9 phenols have indicated effects on hormone balance and reduced reproduction abilities in cod exposed to alkylated phenols (endocrine disruptors). These compounds are also believed to bioaccumulate.

Table 6: Average concentrations of phenols (mg/l) in PW discharged in the Norwegian sector. Source OLF, 2007

Type of compound	2002	2003	2004	2005	2006	2007
Phenol	2047.8	1366.9	1449.2	1155.1	1239.5	1315.1
Alkylphenols C1-C3	1651.9	2086.5	1947.9	1749.9	2320.9	2108.7
Alkylphenols C4-C5	66.7	74.9	89.7	90.1	107.5	77.3
Alkylphenols C6-C9	2.2	2.9	1.5	2.0	0.9	1.0

1.2.2.4 Aromatic compounds

Aromatic compounds are divided into the following groups due to their wide range of concentrations in PW, and differences in possible effect on the environment:

— **BTEX**: Benzene, Toluene, Ethylbenzene and Xylenes- monocyclic aromatic compounds (ortho, meta and para isomers)
— **NPD**: Naphtalene, Phenanthrene and Dibenzothiophene, as well as their C1-C3 alkyl homologues- 2-3 ring aromatic compounds
— **PAH**: Polycyclic Aromatic Hydrocarbons, represented b the 16 EPA PAHs (except naphthalene and phenanthrene)

Table 7: Amounts of aromatic compounds (tons) discharged in the Norwegian sector (OLF, 2007)

Group of compounds	2002	2003	2004	2005	2006	2007
BTEX	1089	861	1485	1479	1644	1826
NPD	146	142	170	163	154	124
EPA PAHs (excluding NPD)	1.2	1.8	1.6	1.9	1.7	1.1

BTEX are found in the highest concentrations among aromatic compounds in PW (Table 7). BTEX compounds are relatively soluble in water (the solubility of benzene is about 1400 mg/L and xylenes about 120 mg/L); highly volatile and are biodegraded rapidly in the water environment. Though toxicity increases with increasing molecular weight.

NPDs represented by naphthalene (most abundant compound) and its alkyl homologues (C1-C3 naphthalene, phenanthrene, C1-C3 phenanthrene, dibenzothiophene, C1-C3 dibenzothiophene. Compared with the high molecular weight PAHs, naphthalenes have lower bioaccumulation potential and are rapidly biodegraded in the aquatic environment. However, dibenzothiophenes are moderately toxic, but not mutagenic or carcinogenic.

PAHs are the less water-soluble fraction of aromatic compounds with higher molecular weight and therefore the higher potential for bioaccumulation in marine organisms. PAHs are expected to be associated with particulates and oil droplets in the produced water. Their toxicity is variable and depends on the particular compound, exposure (acute or chronic) and the nature of the organism exposed to PAHs. Although they represent only a small fraction of the aromatic compounds in produced water, they are of environmental concern, due to possible mutagenic, carcinogenic or teratogenic effects. In addition, some PAHs may be endocrine disruptors. Higher molecular weight PAHs are thought to be more toxic to marine life than lower molecular weight aromatics. PAHs can be biodegraded, but at relatively low rates. During the microbial degradation of PAHs, compounds more toxic than the parent compounds are often produced. These intermediate metabolic products may also be mutagenic or carcinogenic even if their parent compounds are not.

1.2.3 Bacteria

In general, bacteria come under the heading of micro organisms and are commonly found in both natural and industrial systems. By definition, the organisms are too small to be seen by the unaided eye, generally being less than 0.1 mm in diameter. Also under this general heading are protozoa, algae, fungi and viruses. Of all the micro organisms, however, it is the bacteria which have the biggest impact in the oil industry.

"Bacteria that are responsible for many problems in the oil industry may be broadly classified as either sessile (attached to surfaces associated with biofilms) or planktonic (free floating). This classification may be further refined by considering the main types of organisms likely to be encountered in a produced water injection system.

The predominant types are:

- Sulphate-Reducing Bacteria (SRB)
- Iron bacteria
- Slime Formers (Include General Aerobic Bacteria (GAB), and General Anaerobic Bacteria (GanB))
- Sulphur Oxidising Bacterial (SOB)
- Hydrocarbon Oxidising Bacteria (HOB)

Of these, the type most relevant to oxygen free produced water is the SRB.

SRB form a physiological and ecological assemblage of diverse types of strictly anaerobic bacteria. They have in common the ability to "activate" sulphate and reduce it to hydrogen sulphide in dissimilatory energy conserving reactions. In doing so, they are responsible for souring reservoirs.

SRB can tolerate temperatures from -5°C to approximately 100°C and show considerable adaptability to new temperature conditions. They tolerate pH values from 5 to 9.5, a wide range of osmotic conditions and can be grown under a hydrostatic pressure of up to 500 atmospheres." (OLF, 1992)

1.2.4 Production chemicals

Process chemicals are used in oil and gas production for specific purposes to enhance treatment and reduce or mitigate different types of operating problems. In general, they can be one of four types:

- Fouling problem (deposition of any unwanted matter in a system)
- This type includes scales, corrosion products, wax (paraffin), asphaltenes, biofouling, and gas hydrates

- Foams, emulsions, and viscous flow (caused by physical properties of the fluid)
- Corrosion problem (affects the safety of workforce and the structural integrity of the facilities)
- Environmental or economic problems. Examples: hydrogen sulfide has environmental and economic consequences; discharge of oily water can damage the environment.

Large numbers of special additives uses in the production to enhance performance. Many of these chemicals are more soluble in oil than in produced water and as a result remain mostly in oil phase. Other (water-soluble) chemicals concentrate in produced water phase, and are disposed with it. Consequently, added chemicals influence the quantity that may be discharged in the produced water stream.

Factors affecting the choice of production chemicals are:

- performance
- price
- stability
- health and safety in handling and storage
- environmental restrictions
- compatibility issues

Oilfield production chemicals which are required to triumph over or minimize the effects of the production problems and used on different stages of a process are listed in the Table 8 below:

Table 8: Production chemicals

Acidity Control	Coolant	Hydraulic Fluid
Antifoam	Corrosion Inhibitor	Hydrogen Sulfide Scavenger
Asphaltene	Demulsifier	Oxygen Scavenger
Asphaltene Inhibitor	Deoiler	Sand control
Control of Naphthenate and other carboxylate fouling	Detergent/Cleaning Fluid	Scale Dissolver
Biocide	Dispersant	Scale Inhibitor
Carrier Solvent	Drag Reducing Agent	Water Clarifier
Coagulant	Dye	Wax Dissolver
	Flocculant	Wax Inhibitor
	Gas Hydrate Inhibitor	Other

The table below divides the chemicals into two main groups based on the way they are added/enter the process.

Table 9: Additional Chemicals Used in Connection with the Production (OLF, 1993)

Group 1: Chemicals that may be squeezed into the formation (or otherwise added batchwise):	Corrosion inhibitors
	Scaling inhibitors
	Biocides
Group 2: Chemicals added into the riser pipe or on the platform continually:	Emulsion breakers
	Reverse emulsion breakers
	Coagulants
	Flocculants
	Antifoams
	Wax- and asphaltene-treating agents
	(Biocides)

Chemicals in the first group are water soluble and a major fraction of the scale inhibitor, at the order of one tenth of at least one type corrosion inhibitor and roughly one quarter of some biocides used in the topside process equipment, can be found in the produced water. The last group has little water solubility, and should not occur in the water stream if they are applied optimally.

The increased volume of produced water handled in petroleum production operations is becoming a most important concern, particularly with the opportunity of further fall in the oil content allowed in the discharged water, as well as the fact that produced water contains a number of undesirable toxic components. Handling this increasing quantity of water is of prime concern to all oil companies wherever they operate. Chapter 2 exposes different aspects of produced water management.

Chapter 2

PW management

Produced water management requires consideration of all issues influencing the performance of produced water treatment. Analysis of produced water's quality and identifying of presence and amount of constituents is the first step in PW management.

"Oil/water separation technology traditionally used offshore is sensitive to variations in water quality, and some of the technologies are also sensitive to large variations in flow conditions and content of solids. Predictable conditions are often needed for optimum performance of several of the technologies applied. Operational aspects are important for the performance. Integration of oil operating conditions (production chemicals, recirculation of rejects, scale control programs, operation of separators, etc.) with the produced water treatment is important for the performance of the treatment technology." (Eilen Vik, 2007)

This chapter describes practical, economical, technological and environmental aspects of produced water management. As it mentioned in the first chapter produced water is a global challenge of oil production. Therefore produced water management is an incorporated part of the oilfield development plan. What seems to be a good solution on one field not even is an option on another.

 "Produced water handling methodology depends on the composition of produced water, location, quantity and the availability of resources**.**

Some of the options available to the oil and gas operator for managing produced water might include the following:

1. *Avoid production of water onto the surface* – Using polymer gels that block water contributing fissures or fractures or Downhole Water Separators which separate water from oil or gas streams downhole and reinject it into suitable formations. This option eliminates waste water and is one of the more elegant solutions, but is not always possible.

2. *Inject produced water* – Inject the produced water into the same formation or another suitable formation; involves transportation of produced water from the producing to the injection site. Treatment of the injectate to reduce fouling and scaling agents and bacteria might be necessary. However, it can be unbeneficial due high cost.

3. *Discharge produced water* – Treat the produced water to meet onshore or offshore discharge regulations. In some cases the treatment of produced water might not be necessary.

4. *Reuse in oil and gas operations* – Treat the produced water to meet the quality required to use it for drilling, stimulation, and workover operations.

5. *Consume in beneficial use* – In some cases, significant treatment of produced water is required to meet the quality required for beneficial uses such as irrigation, rangeland restoration, cattle and animal consumption, and drinking water for private use or in public water systems."(J.Daniel Arthur, P.E.Bruce G.Langhus, C.P.G. Chirag Patel, 2005)

The headlines of this and the next chapters are:

- ✓ Produced water minimizing and disposal options
- ✓ Produced water treatment

2.1 Produced water minimizing options

- ❖ Water shut-off
- ❖ Separation on the Platform and Discharge to Sea
- ❖ Reinjection to Reservoirs
- ❖ Downhole Separation and Reinjection of the water
- ❖ Subsea/Seabed Separation and Water Reinjection

2.1.1 Water shut-off

Selective Water Shut-Off in the Reservoir

- mechanical shut-off
- chemical shut-off

Mechanical Water Shut-Off

Mechanical methods are mostly used in water shut-off operations. The perforated section of the well, which is placed in the water-producing section of the reservoir, is partially plugged, using cement. This technical method is applicable both on oil and gas production, and there is normally no need for any additional facilities on the platform for this operation.

However, the reduction in produced water discharges will be a direct result of the degree of success in installing the cement plug in the well.

Chemical (Polyacrimide) Water Shut-Off

Chemical shut-off methods are less common than mechanical methods. However, polyacrimide water shut-off is one option that can be used. Polyacylamide will then be injected into the reservoir together with Chrome (III) and Aluminium (II) in order to form a stable gel. This gel will settle in the reservoir so that vertical communication between the zones will be limited and reduce the amount of produced water.

This method will require a chemical injection system installed on the production facility.

2.1.2 Separation on the Platform and Discharge to Sea

This option is listed as an alternative among others for produced water management. "This is however, the traditional way of handling of produced water and on the Norwegian continental shelf, this is how approximately 92% of produced water is managed.

Oil, gas and water are produced from the reservoir, into the well and through the well up to the installation's topside. On the topside a processing train separates the bulk of oil, gas and water into separate streams through several separation stages. The water stream then is directed to a committed water processing plant for further treatment." (Trygve Husveg, 2002)

Before the water is discharged to sea, PW is treated primarily by removing the oil. Oil recovered in this way is fed back to the oil treatment facilities and sold together with ordinary crude. The other substances, which are harmful and must be removed, such as heavy metals, aromatic substances and phenols, may lead to end products that need to be handled and deposited in an environmentally safe manner. The treatment of produced water on installations is done by means of physical facilities such as flotation tanks, separators, hydrocyclones and centrifuges. Depending on the process selected there will always be oil residues in the water. The discharge requirement of oil in the water is 30 mg per liter.

"Among the most relevant treatment technologies for use offshore Norway are:

— Methods for making small drops of oil melt together into bigger drops so that the oil can more easily be separated from the water in the separation process
— A method where the oil components are captured by the condensate, which is mixed with the produced water
— Methods consisting of different types of filter which can remove oil and other components from the water

Some of the treatment methods can also remove other organic components, particles, chemical residue and heavy metal from the produced water." (Environment 2001- The Norwegian Petroleum Sector)

2.1.3 Reinjection to Reservoirs

The same source (Environment 2001- The Norwegian Petroleum Sector) has more about this alternative:

"The reinjection of produced water is an important option because it can do away with the discharge of oil and chemicals from produced water. However, this option is dependent on the specific reservoir condition and it can therefore not be applied everywhere. If the decision is made early in the planning phase of a new field to reinject the produced water, then the extra cost of reinjection will be much lower than if it is implemented at a later

stage. A decision to reinject produced water to provide pressure support and boost production may only marginally increase the investment cost of a new installation and cause no or a very limited increase in the emission to air. If the produced water for some reason cannot be used as pressure support and a separate injection well must be drilled this would mean considerable extra investments and an increase in the emission to air. On existing installations it may be possible to convert to reinjection without major outlays, if conditions allow it. In the Norwegian sector more than ten fields reinject produced water or have plans to do so, and this option is being considered at several other fields. It is expected that the amount of produced water that is reinjected will increase in the coming years."

Reinjection of produced water is based on conventional technology. Research in this domain is therefore directed more against effects of the injection, in the reservoir that receives the produced water. To identify alternative injection sites, or water receptors, other than the producing reservoir, might also be important.

Effects of produced water reinjection:

"Globally, produced water reinjection has been evaluated and practiced for many years. In most cases the produced water reinjection activity has been on individual wells and has not included mixing with seawater prior to injection. The experiences from these trials have been variable. In most cases some loss in infectivity has been seen, in some cases the problems observed have been more severe; i.e. accelerated reservoir souring and increased scaling have also been noted.

Experiences from offshore fields stress the need for a better understanding of the mechanisms that influence the impact of produced water reinjection. Industry acceptance of combined produced water/seawater reinjection as a viable option in field development concepts, and industry confidence in any predictive modeling capability will be greatly enhanced by full scale implementations of such schemes, with appropriate documentation and verification of models through the results observed." (Mark Reed and Ståle Johnson, 1996)

When effects of produced water reinjection are to be assessed, one has to determine reservoir, process and environmental aspects like:

- ➤ Injectivity
- ➤ Scaling potential
- ➤ Souring potential
- ➤ Corrosion potential
- ➤ Environmental impact

2.1.4 Downhole Separation and Water Reinjection

"By using downhole separation the produced water is separated down in the well and reinjected.

The main aim of downhole separation is to avoid handling large quantities of water on the installation by moving the process down into the production well. This also prevents the capacity of the processing system becoming a problem when the water production increases. This can help prolong a field's lifetime and so enhance the oil production. At the same time the use of chemicals is reduced because of improved separation conditions and by avoiding discharges through water reinjection. This process removes almost all of the water from the production flow." (Environment 2001- The Norwegian Petroleum Sector)

Selected from OLF minute (2001): Norsk Hydro has completed tests on downhole separation with realistic/real fluids under high pressure and high temperature. The tests show that in one step of separation, "reinjection quality"-water and raw oil with less than 0.5 % water can be achieved. This can be achieved even if the separator is not located in a 100 % horizontal position. System tests for the running of a separator, control system and turbine pump have also been carried out. An installation test on Ullrigg is closed. Of today, there is not enough interest in the licenses to continue develop this solution, and there are neither plans of finding a well suitable for a pilot installation.

In the OSPAR draft (2002), the removal efficiency is described in this way: "The reduction of harmful substances as a result of the downhole separation technique cannot be expressed in a figure because of the large number of variables, including the WOR (Water-Oil-ratio). The WOR can be increased with 85-97 % to a WOR of 1-3." It is further indicated a maximum reduction of the production of formation water to be about 50 %. This also gives a measure

about the potential for reduction of dissolved and dispersed oil and heavy metals. Due to lower volumes of produced water a reduction in use of production chemicals are also indicated to be as high as 50 %.

 "The most obvious effect of downhole separation technology is the reduction of process equipment required topside. Since the total water production at the surface is reduced, less and smaller process equipment is needed for the liquid separation. Production with a downhole separator opens for new and favorable options in terms of production:

• The pressure drop in the well can be reduced, due to removal of the dense phase

• Selective reinjection can enhance the reservoir recovery and maintain the reservoir pressure

• Dynamic control of the water-oil contact (WOC-control) through dual completion and reinjection of the separated water in the aquifer may reduce or eliminate water production due to water coning and thus improve oil recovery." (Mark Reed and Ståle Johnson, 1996)

2.1.5 Subsea/Seabed Separation and Water Reinjection

"Seabed separation involves separating the produced water from the well flow at the seabed, so that only oil and gas are transported up to the production installation. This method will reduce the amount of water requiring treatment on the installation. The separated water is for the most part reinjected. Discharges at the seabed would only result in minor discharges of chemicals because of the reduced need of corrosion and hydrate inhibitors on the surface. In order that this technology is to become a real environmental alternative to downhole separation, the water must be reinjected and possibly provide pressure support at those fields where this is possible." (Environment 2001- The Norwegian Petroleum Sector)

2.1.5.1 Troll Pilot

"During the summer of 2000, a subsea separation station, the Troll Pilot was completed and installed at the Norsk Hydro operated Troll Field. Troll Pilot is the first subsea water

separation facility ever built and it is installed on a water depth of 350 meters. Troll Pilot separates water from the wellstream and re-injects the water into the formation." (Environment 2001- The Norwegian Petroleum Sector)

"Troll Pilot is meant to remove bulk quantities of water from the well stream of the production line in the Troll field and to re-inject the separated water into the same formation through a water injection well. The wellstream consisting of oil, water and gas is directed into a 3 phase's gravity separator on a seabed structure. Oil and gas are mixed again and routed to Troll C in a common pipe. The separated water is taken off and injected in the injection well with the help of a pump." (Troll Pilot, Internal TFE report, 2002)

Conclusion on the Troll Pilot:

"As a pilot, Troll Pilot first objective was to qualify seabed water separation and reinjection technology. One can say that, by the end of year 2001, this objective has been fulfilled. The separation objectives have been met; oil in injection water content is 700 ppm and water accounts for 2 to 3 % to the volume of the outlet stream, using no chemical injection."

2.1.6 Advantages and Disadvantages of Water Minimizing Technology

In general, it can be claimed that water production reducing technologies/methods in the reservoir, well or sub-sea, offers the following benefits when being introduced:

- Increasing hydrocarbon production capacity on topsides
- Saving water treatment facilities or capacities on these
- Reduce the extent of oil-water emulsions and related problems
- Huge hydrodynamic benefits in deepwater flow lines
- Reduce the need for adding chemicals (corrosion and scale inhibitors)
- Environmental effects – reduced rates of water discharges

These benefits will probably grow larger and larger as development of deepwater fields and distant satellite fields become more and more topical.

The lack of experience from water minimizing technologies in operation is a main drawback for the further progress in this domain. Major effort must be paid in developing and implementing these technologies in order to establish necessary knowledge of the operability. To be a prioritized technology, a water minimizing method must exhibit an improvement in the comprehensive picture of efficiency, reliability, safety and economy, compared to traditional technology. (The content of this and the next sections are adapted from Trygve Husveg's PhD report 2002)

2.1.6.1 Advantages of Produced Water Minimizing Technology

The potential benefits of subsea water separation, downhole water separation - or water blocking of zones in the reservoir, can more extensively/detailed be listed as the following items:

- Production with reduced water production may extend field lifetime and increase oil recovery, due to improved well performance and reservoir flow conditions. A well producing at conditions where the well normally would be shut down, due to high water production rate, can in many cases continue to produce with lower water production.

- The use of a water minimizing technology reduces the required space for liquid separation equipment on the surface. Thus more space is available for other activities on the surface or smaller production vessels can be used.

- Lower flow to the platform due to water reduction might allow downsizing off pipes and risers.

- The physical conditions for down hole and subsea separation are favourable for oil/water separation compared with conditions at the surface. Thus, a hydrocyclone operating at bottom hole conditions, for example, is expected to have a higher efficiency than a hydrocyclone operating at the surface. (Due to the fluid being exposed to lower/fewer shear forces and to higher temperature and pressure)

- Hydrostatic pressure drop in the vertical portions of the well is reduced by removing the produced water as far upstream as possible, due to water being denser than oil. This benefit increases with increasing water depth.

- In the cases where the natural gas-liquid ratio is less than the optimum gas-liquid ratio a technology/method of reducing water production can create an artificial lift similar to gas lift.

- The use of water minimizing technologies can reduce the use of (toxic) production chemicals such as corrosion inhibitors, hydrates inhibitors and flocculators.

- By reinjecting of the produced water, (downhole and subsea separation) bringing large volumes of water to the surface is avoided, pressure decline is reduced and enhanced water displacement of oil is achieved.

- Environmental effects when discharges of produced water to the sea are reduced. For the methods of downhole separation and subsea separation the produced water is injected into its original reservoir or into a disposal well in another reservoir.) When water zones are selectively blocked or shut off, the water production is reduced. Today's limit of 40mg/l oil in water indicates the oil discharge reduction potential.

Most of these advantages are respectively increasing with increasing water cuts, and some with increasing water depth.

2.1.6.2 Disadvantages of Produced Water Minimizing Technology:

- Being subsea, downhole or even in the reservoir (when blocking of zones), monitoring the behavior and efficiency of the water minimizing technology/method might be very hard to perform. Online, reliable water-in-oil or oil-in-water monitors do not exist for subsea or downhole application. (Neither do they for topside application)

- Optimal operational control of subsea and downhole separation equipment might be an impracticable task for the distant topside controller. This is also due to the lack of monitoring instruments. Sufficient control might be achieved however.

- Maintenance of downhole and subsea equipment is both time forcing and expensive operations. Restricted access at the equipment and the need for supporting activities (ROV etc.) when carrying out the physical work, also complicate the situation.

- Reliability is a keyword for equipment in offshore petroleum production. Since reliability to a large degree is a function of monitoring, access and maintenance factors, the reliability of subsea and downhole separation equipment is uncertain.

- Safety of novel equipment or of conventional equipment placed in a new environment will always be a subject of discussion. In petroleum production safety criteria are very strict giving the opportunity to try and fail low chance. Safety is also safety for material values and even small mistakes can lead to large economical consequences for the operator.

- Economy: Novel technology is usually expensive. Subsea and downhole separation solutions are in most cases unrealistic economical options for implementation or replacement on existing or old fields.

- The temperature drop in the tubing and riser will in the case of a lower water share in the flow be higher. Water is by thermodynamic reasons capable of keeping the heat better. A lower temperature increases the risk wax and hydrate formation. This effect will increase with increasing water/reservoir depth. Better insulation on tubes might be required.

Not only the last one but also several of these disadvantages will respectively increase with an increasing water depth.

2.1.7 Sidetracking to Zones with a higher Fraction of Oil

Sidetracking is another method that can be used to reduce water production. If a well is producing too much water due to changed or difficult reservoir conditions, the well can be sidetracked. Then the internals of the well must be pulled out before a diverted "sidetrack" is drilled. The "new" well is drilled from somewhere above the production zone in the existing well, towards a favorable zone somewhere else in the reservoir. This is a heavy and costly operation that, of course, forces the production of the actual well to be closed down. A special drilling vessel will probably also be required for such an operation. The efficiency of sidetracking will be a direct result of how successful the drilling operation is in finding a zone in the reservoir with less water access to the new production zone.

No experience data on this subject has been found.

2.1.8 Challenges and Research

In general the research in the domain of produced water minimizing (or about options for production) is initiated because:

- There is a need for upgrading the produced water treatment facility on existing installations
- New developments and installations are planned
- Evaluations of reservoir characteristics and of the production/injection balance are performed (in order to optimize production)
- There is a need to push forward the knowledge and technology for marginal field developments
- There is a need to find a cost-effective solution to the potential environmental problems associated with the discharges of large volumes of produced water

"It is a challenge to reduce environmentally-harmful discharges to sea without this leading to higher energy consumption and increased emissions to air. It is necessary to undertake an overall evaluation of the different measures, while at the same time taking into account conditions specific to the different fields. Good knowledge about the reservoir and hydrocarbon flow may make it possible to place wells in a manner that contributes to reducing the production of water. Process optimization is another option requiring integration of know-how from different skills and operating environments. Several different technological options exist at the moment. But as several of these technologies have not been tested and undergone qualification, it remains a challenge to decide which method should be selected for a particular field. In this context cooperation and shearing lessons learnt could be very important in finding solutions based on cost/utility considerations. On many installations several smaller measures have been introduced which collectively can contribute considerably to discharge reductions. It could be very useful to share this knowledge and the lessons learnt."(Environment 2001- The Norwegian Petroleum Sector)

2.2 Produced water treatment

Produced water needs to be treated. Treatment of produced water has been attempted and is proven to be an effective option for produced water handling. Studies conducted to identify, verify and compile existing and newly developed techniques demonstrate the economical benefits of produced water treatment. Treating oilfield water can help facilitate additional water management options for operators such as beneficial uses that in the short and long term can potentially provide certain community and economic advantages. Treated produced water has the potential to be a valuable product rather than a waste. The treatment of produced water is a necessity before the majority of the conventional produced waters can be applied to other uses.

2.2.1 Aims of PWT

The general objectives for operators when they plan produced water treatment are:

- ✓ *"De-oiling* – Removal of free and dispersed oil and grease present in produced water
- ✓ *Soluble organics removal* – Removal of dissolved organics
- ✓ *Disinfection* – Removal of bacteria, microorganisms, algae, etc.
- ✓ *Suspended solids removal* – Removal of suspended particles, sand, turbidity, etc.
- ✓ *Dissolved gas removal* – Removal of light hydrocarbon gases, carbon dioxide, hydrogen sulfide, etc.
- ✓ *Desalination or demineralization* – Removal of dissolved salts, sulfates, nitrates, contaminants, scaling agents, etc.
- ✓ *Softening* – Removal of excess water hardness
- ✓ *Sodium Adsorption Ratio (SAR) adjustment* – Addition of calcium or magnesium ions into the produced water to adjust sodicity levels prior to irrigation
- ✓ *Miscellaneous* – Naturally occurring radioactive materials (NORM) removal" (J.Daniel Arthur, P.E.Bruce G.Langhus, C.P.G. Chirag Patel, 2005)

New produced water treatment technologies satisfying the environmental targets are CTour, Epcon CFU, Cetco CrudeSep/CrudeSorb, Akzo Nobel MPPE, Earth Canada total oil removal and recovery system (TORRTM, Opus Maxim CFU), filtration technologies (Microsieves, Media and Nutshell filtration and Membrane technologies) and oxidation technologies. Otherwise there are some conventional methods that are still in use in oil production due different reasons (mostly economical).

2.2.2 Factors influencing selection of PWT technologies

When choosing produced water treatment technologies, one should focus on the major contribute to the total environmental impact. The compounds of interest are: PAH, NPD (naphtalenes, phenanthrenes and dibenzo-thiophenes), BTEX (Bensene, Toluene, Ethylbenzene and Xylene), phenol, alkyated phenols, metals, and added chemicals. The later being substances such as: production chemicals, corrosion-, scale-, and hydrate-inhibitors, separation chemicals, and H_2S scavenger. Experience has shown that the major contributes to the EIF are dispersed oil, volatile aromatics, heavy aromatics, alkylated phenols, and process chemicals.

Depending on the produced water characteristics and the degree of treatment required will be selected the most suitable treatment system.

Produced water treatment can be divided into two groups:

- mechanical
- chemical

Mechanical treatment includes separation by using different equipment such as filters, separators, hydrocyclones, coalesces, centrifuges, membranes, skim tanks and gas flotation units. There are various types of filters (media filter, carbon filter, disposable cartridge filter) which can be used on different stages of separation. Similarly there are many types of membrane systems and techniques utilize a good performance in PW treatment.

"Chemical treatment may be required for a variety of reasons:

- ➢ to assist the separation of oil emulsions from the produced water in the primary separation by adding of a "reverse emulsion breaker" or de-oiler chemical upstream
- ➢ to increase the efficiency of the media filtration process by addition of a flocculants upstream
- ➢ to minimize scale formation by dosing scale inhibitor upstream of the primary separation process
- ➢ to minimize bacterial growth by slug dosing biocides
- ➢ to assist in the separation of water emulsion breaker upstream of a reject streams from both separation stages by dosing an emulsion breaker upstream of a reject stream clarifier" (OSPAR Draft 2002)

2.2.3 PW treatment technologies

The management and disposal of produced water represent the single largest waste stream challenge facing the oil and gas production industry. There are a lot of techniques that are already in use to handle produced water which are divided in 3 groups:

- ✓ Physical separation
- ✓ Enhanced separation
- ✓ Alternative separation

Table 10 below shows principles, equipment and separation efficiency of a couple of PW treatment technologies.

Table 10: Produced water treatment technologies (Data is gathered from different sources)

Method	Principles	Equipments	Droplet size separated	Hydrocarbon removal efficiencies
PHYSICAL SEPARATION				
Media filter	Filtration	Media	>2 µm	5 -25 mg/l

Dissolved Gas flotation (DGF)	Use higher velocity of small gas particles to	Dissolved gas	20 µm	70 – 95 % removal, 10 – 40 mg/l
Induced gas flotation	Gas bubbles cause oil and solids to rise to the surface	Gas bubbles	≥20 µm	80 -90 % 40 mg/l
Tilted plate separator	Coalescense	Corrugated plastic plates	≥60 µm	60 -150 mg/l
Combined plate separator and DGF	Coalescense	TPS and DGF	>40 µm	80 -90 %
Static hydrocyclones	Centifugual separation based on size, shape, and	Static hydrocyclones	10-15 µm	80 – 95 % removal, 20-30 mg/l
Coalescer	Coalescence, bringing the droplets together	Coalescer	>2 µm	95-99 % 10 mg/l
Disposable cartridge filter	Saturation of oleophilic cartridge elements	Oleophilic elements	0.05-1 µm	90 % 10 mg/l
Centrifuges	Gravitation	Centrifuges	>2 µm	84-99 % 5-25mg/l
ENHANCED SEPARATION				
Pect-F	By using fibre materials increase the oil droplet sizes in the	Fibre material	10-15 µm	50 % compared with hydro-cyclones
Mares Tail	Coalescence of oil droplets	Suspended free floating fibre tails in a spool	10-15 µm	65%
ALTERNATIVE SEPARATION				
Membrane technology	Membrane acts as a very specific filter (barrier) that will let water flow through, while it catches suspended	Multi media membrane	Depends on membrane type (up to < 1µm)	10 mg/l ²
Carbon filter	Adsorption	Granular activated carbon	>0.5 µm	< 1 mg/l

MPPE	Liquid-liquid extraction and steam stripping	Solid matrix	>0.1-10 µm	80-85 %
Epcon CFU	Is a separation unit where flotation, degassing and slow centrifugal forces in	CFU unit	5 µm	60-80 % removal, < 10 mg/l
CTour	Using liquid-luquid extraction to removing dispersed oil and PAH	Scrubber, Mixers, Hydrocyclones	5 µm	80 % removal, 5 mg/l
Biological treatment	Biodegradation	bacteria	2 µm	87-90%
Northern Treatment	Flocculation	OTU Offshore Treatment Unit	5 µm	5 mg/l
Cetco Oilfield services	Flocculation Coagulation	Hi-Flow Treatment unit	<3 mg/l	98 %

2.2.4 CETCO

CETCO Oilfield Services offers a wide range of liquid coagulants and flocculants that provide an economical yet highly efficient option in treating high volume waste streams. Their innovative liquid format of these products reduces operator involvement by allowing for easy automation of the entire treatment process. CETCO developed these easy to apply line of products especially for the removal of emulsified oils, suspended solids, insoluble BOD/COD, and metals from wastewater. For over 30 years, CETCOs bentonite clay-based, dry, chemical flocculants have cleaned industrial wastewater in one simple step.

CETCO introduces Hi-Flow, a patented process for removing free or partially soluble oils from wastewater. Originally designed for treating high rates of produced water in the oilfield industry, this new smaller version of our Hi-Flow system is now available for applications in the industrial sector. The same physical and chemical characteristics used on the platforms

were designed and engineered into a unit that can run 5-15 gallons per minute. (CETCO Oilfield Services)

Whole the studies and research, improvement of management and technologies have one purpose, namely environment safety. Chapter 3 describes the ways to achieve this objective.

Chapter 3

Environment

The reducing of environmental impact of produced water discharges is the major aim of each oil/gas production field together with restriction authority.

3.1 Regulations and requirements. OSPAR

When the production cannot be eliminated, the water has to be treated and disposed off. During the last years we have seen an enormous increase in amount of production and discharge of produced water. Therefore is tighter focus on environmental effects today, the important subject for oil companies.

In Norway PW discharge is under the restriction authority of the Pollution Act, which gives permits for discharge to the environment and internationally by Oslo-Paris convention, OSPAR, the most important international agreement regulating discharges to the sea is the convention for the protection of the marine environment of the north-east Atlantic. This convention aims to prevent pollution of these discharges and to protect them from being harmed by human activities.

 OSPAR has agreed that the maximum discharge limit is reduced to 30 ppm OIW for the petroleum companies operating in the North-East Atlantic. Also 15% reduction in tonnage of oil discharged to sea by 2007 from 2000 baseline. This is by country (not installation) and includes both dissolved and dispersed oil. There shall be no harmful discharges from any new installation, and existing installations shall continuously work against a practically achievable zero environmental discharge. The zero discharge can be achieved by a constant reduction of environmental destructive discharges against a realistic zero level, where the environmental harm depends on the content of potentially environmental damaging chemicals in addition to time and place for the discharge.

3.1.2 OSPAR tests

Ecotoxicity tests recognized by OSPAR and by Norwegian Pollution authorities:

- Phytoplankton: Skeletonema costatum, with other word Algae test (ISO/DIS 10253) – all chemicals
- Marine biodegradation test (OECD 306) – all chemicals
- Bioaccumulation testing – calculations

Algae test (concentration series of chemicals prepared in algal growth medium): algal cultures incubated in each concentration of chemicals and in pure growth medium (controls) at 20°C for 72 hours. Inhibition of algal growth measured as reduction in vivo chlorophyll fluorescence (EC-concentrations). Hence will EC-50 concentrations be determined (conc. of chemicals inhibiting algal growth by 50 %).

Marine biodegradation test (BOD)

Normal seawater used as source for bacterial degradation of chemicals, which are in normal seawater (supplied with essential inorganic nutrients) to a concentration of 2 mg/L. Testing occurs in   air-tight BOD (biological oxygen demand) bottles in 5-28 days at 20°C. Oxygen consumption measured at intervals as the difference between DO in seawater without and with chemicals. Biodegradation determined as % of a theoretical oxygen demand (ThOD) for the chemical.

Bioaccumulation test is a chemical test to determine the distribution of a chemical between two immiscible phases; octanol and water. The bioconcentration factor is a part of risk assessment determination. Bioconcentration is defined as the net result of uptake, distribution, and elimination of a compound in an organism due to exposure via water; whereas bioaccumulation includes exposure from both food and water (Frost et al. 1998, section 4.1). The bioconcentration factor (BCF) expresses the ratio between the concentration in organisms and the aqueous concentration. Therefore, the aqueous concentration, which is lethal to 50% of the population (LC50), depends strongly on the BCF.

Descriptions:

> LC50 - Lethal Concentration 50 is the concentration of a chemical which kills 50% of a sample population.

> EC50 - Effect concentration 50 is the concentration of a chemical at which a predetermined level of effect occurs to 50% of a sample population.

Criteria used for the classification of chemicals with regard to the aquatic environment are presented in Table 11.

Table 11: An overview of criteria used for the classification of chemicals with regard to the aquatic environment (Tatjana Tišler, Ph. D., 2003)

Fish 96-hour LC_{50} (mg/L) or daphnids 48-hour EC_{50} (mg/L) or algae 72-hour IC_{50} (mg/L)	Ready Biodegradability (RB)	Bioaccumulation potential Log $P_{ow} \geq 3$ or BCF$\geq$100	Classification R phrases Danger symbol (N)
≤1	NO	YES/NO	R50/53
	YES	YES	N
≤1	YES	NO	R50
			N
1-10	NO	YES/NO	R51/53
	YES	YES	N
10-100	NO	YES/NO	R52/53
	YES	NO	No classification*
Not available	NO	YES	R53
	YES	NO	No classification*

* A substance is not classified if it has either a proven potential to degrade rapidly in the aquatic ecosystem or an absence of chronic toxicity at the concentration of 1.0 mg/L (NOEC >1 mg/L in a prolonged toxicity study with daphnia or fish).

3.2 Environmental Impact Factor (EIF) Produced water

When selecting PW treatment technologies, reduced environmental impact is the important aim. The method used for quantifying this impact on the Norwegian sector is the

Environmental Impact Factor, EIF, which relies on DREAM (Dose Related Risk and Effect Assessement Model). This method is computerized in a tool that calculates the quantity of the environmental risk associated to a certain volume of water into the sea from each of a number of chemical component groups that are present in produced water. As well it is a device for identification of the most environmental beneficial and cost effective measures for reduction of harmful discharges to the sea. Furthermore, EIF is a management tool for selecting and documenting best environmental practice used by all offshore operators on the Norwegian Continental Shelf since 2000.

"The environmental risk, expressed as the EIF, is based on a comparison between the expected real concentration in the discharge area in question and the concentration that represents the lower impact limit for a representative selection of components in the produced water, a so-called PEC/PNEC factor." (NETL)

PEC = Predicted Environmental Concentration

PNEC = Predicted No Effect Concentration.

Data on the composition and flow of produced water discharges are necessary for EIF model calculations. This model simulates the spreading of a discharge and calculates the risk of a dangerous effect in the recipient. Comparison of concentration of compounds (PEC) with the concentration where no effect is expected (PNEC) is used to perform risk calculation.

The environmental risk for each component (group) is the relationship between the predicted environmental concentration (PEC) and the PNEC value. For composite discharges the total environmental risk is calculated as the sum of the environmental risks for each component (group).

When the relationship between the PEC and PNEC is calculated as being less than one for the accumulated discharges, the environmental risk to the recipient is regarded as acceptable.

The PNEC value of a substance is calculated on the basis of the most sensitive species for which impact data are available. The lowest available impact value, whether acute (EC50/LC50) or chronic (NOEC) is divided by a safety factor. The size of the safety factor is determined by the amount of the data describing the impacts and by whether data on acute

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and chronic effects are available. In addition, each component is weighted to take account of other effects than chronic and acute toxicity, such as degradability and bioaccumulation.

In order to obtain a basis for defining treatment targets and assessment of technologies,

EIF calculations were employed to estimate the concentration levels of naturally occurring components in produced water that would give a discharge with no harmful effect.

An EIF = 1 or lower was defined as "zero harmful discharge" for the purpose of this evaluation.

The EIF describes the water volumes exceeding a resultant (and weighted) PEC/PNEC = 1. This water volume, i.e. the model, has a geographical resolution of 100m*100m*10 m (0.01 km_2*0.01km). A further description of the EIF and the detailed method for calculating the EIF is provided by the EIF guidelines.

Example: The EIF for a discharge is related to a recipient water volume of 100000 m3 (a grid with cells of 100 x 100 x 10 m) and is the volume of water with a risk > 5 % divided by 100000. The reported EIF is the maximum value calculated for the 30- day period (Melin, 2005a).

3.3 Impact of discharges of PW

Environmental data for 2007 (Statoil Hydro annual report 2007)

NORWEGIAN CONTINENTAL SHELF (includes the UK sector of Statfjord): …………..	Produced water 157 mill scm
DISCHARGES TO WATER	
Produced water ………………………………………..	139 mill scm
Oil in oily water [1] …………………………………….	1,320 tones, 8.6 mg/l (2006: 15.9 mg/l)
Unintentional oil spills [2] ……………………………	4,484 m^3

Produced water injected in the ground ……….	19 mill m^3
Chemicals: [3] process/production…………………	30,200 tones
Drilling/well……………………………………………	67,800 tones
Other unintentional spills [4] **………………………**	5,263 m^3
WASTE [5]	
Non-hazardous waste total………………………	14,900 tones
Non-hazardous waste for recovery………….	12,200 tones
Non-hazardous waste recovery rate………..	82 %
Hazardous waste total………………………………	102,000 tones
Hazardous waste for recovery…………………	77,500 tones
Hazardous waste recovery rate……………….	76 %

[1] Includes oil from produced water, drainage water, ballast water and jetting

[2] The volume is dominated by one incident on Statfjord A totaling 4,400 m3

[3] Includes 87,200 tones of water and green chemicals/substances

[4] The volume is dominated by one drilling fluid spill on Visund estimated at 5,000 m3

[5] Includes waste from the onshore base operations. Waste related to drilling totals 91,400 tones

Little is known about the effects of discharges containing the chemicals which are used in oil and gas production, due largely to insufficient research but also the complex nature of some of the chemical cocktails involved. The many chemical constituents found in produced water,

can present a threat to aquatic life when they are discharged. Especially if they are present either individually or collectively in high concentrations.

Depending on where it is discharged, produced water can have different potential impacts. For example, discharges to small streams are usually having a larger environmental impact in comparison with discharges made to the open ocean by virtue of the dilution that takes place following discharge. Regulatory agencies have documented the potential impacts that discharges of produced water can have on the environment and have forbidden discharges in most onshore or near-shore locations.

For a long time the only governmental regulation and rules for PW discharges in petroleum sector has been concerning concentration of non-polar oil in water (OIW). It has been given little notice to dissolved organics.

But at this time there is wide agreement within governments, oil production industry and scientists that focus should currently be on dissolved organic components, heavy metals and production chemicals. Results of numerous different studies and research are severe and have triggered further investigations of possible consequences of PW discharges for living organisms.

The results of field-specific EIF-calculations show that the most significant contributors to environmental risk commonly are the water-soluble oil fraction; essentially alkylated phenols and polycyclic aromatic hydrocarbons (PAHs). In some cases specific production chemicals also give an important contribution to the risk of environmental damaging effects.

3.4 Green chemicals

3.4.1 Coloring code and OSPAR PLONOR list

Coloring code for offshore chemicals (black, red, green and yellow) is used in Norwegian regulations are relating to chemicals to be used in the oil industry and requirements for environmental monitoring of the petroleum activities on the Norwegian Continental Shelf.

The substances are classified as follows:

- **Black**: Chemicals which basically cannot be discharged. Permits are given in special cases.
- **Red**: Chemicals which pose an environmental hazard and should therefore be replaced. Permits are given on condition that special priority is given to identifying substitutes for these substances.
- **Yellow**: Chemicals in use but not included in any of the other categories. Normally permitted without specific conditions
- **Green**: Chemicals on the list from the OSPAR PLONOR list which are permitted without specific conditions.

OSPAR's **PLONOR**-List is a positive list of chemicals used in offshore-installations, which are considered to pose little or no risk to the Environment" (PLONOR). The substances on this list are mainly inorganic alkali or earth alkali salts and organic substances with rapid biodegradation like short chain alcohols. For use of chemicals mentioned on this list, data requirements are lower than for other non listed substances.

The OSPAR PLONOR list includes:

- Inorganic salts that are naturally occurring/constituents of seawater (excluding salts of heavy metals)
- Minerals those are not soluble in seawater
- Organic substances that meet the following criteria: no CMR (carcinogen, mutagen, reproductive toxicity) properties and LC50 or EC50 > 100 mg/L and Log Pow <3 or BCR <100 or MW>1,000 and substance is readily biodegradable according to OECD 306 or equivalent (seawater biodegradation tests)
- Other organic substances that are non-water soluble (e.g., nutshells and fibers)

The OSPAR PLONOR criteria includes both negative (e.g., no CMR properties) and positive criteria, e.g., acute toxicity of LC50 (lethal concentration) or EC50 (effective concentration) > 100 mg/L.

"If the chemical is not on the PLONOR list, further evaluation is needed. The chemical is required to be substituted if it meets criteria listed below and a less hazardous (or preferably non-hazardous) substitute is available:

a) It is in OSPAR List of Chemicals for Priority Action; or

b) It is considered by the authority, to which the application has been made, to be of equivalent concern for the marine environment as substances covered by the previous sub-paragraph; or

c) is inorganic and has a LC50[3] or EC 50[4] less than 1 mg/L; or

d) Has a biodegradation less than 20% during 28 days; or

e) Meets two of the following three criteria:

  (i) Biodegradation in 28 days less than 70% (OECD 301A, 301E) or less than 60% (OECD 301B, 301C, 301F, 306);

  (ii) Bioaccumulation log $Pow_5 \geq 3$ or $BCF_6 > 100$ and considering molecular weight;

  (iii) Toxicity LC50 < 10mg/L or EC50 < 10mg/L" (HELSINKI COMMISSION, 2008)

Classification	Category
Water	Green
Chemicals on the PLONOR List	Green
Hormone-disruptive substances	1 (Black)
Chemicals on the priority list in White Paper No. 25 (2002-2003)	2 (Black)
Biodegradability < 20% and low Pow ≥ 5	3 (Black)
Biodegradability <20% and toxicity EC50 or LC50 $\leq$10 mg/l	4 (Black)
Two of three categories: biodegradability < 60%, log Pow $\geq$3,	

EC50 or LC50≤10 mg/l	6 (Red)
Inorganic and EC50 or LC50≤1 mg/l	7 (Red)
Biodegradability<20%	8 (Red)
Other chemicals	Yellow

(HELCOM, 2008)

3.4.2 Green versus good

The target of the OSPAR Commission Hazardous Substances Strategy is to prevent pollution of the maritime area by continuously reducing discharges, emissions and losses of harmful substances. The ultimate aim is to achieve concentrations in the marine environment near background values for naturally occurring substances and close to zero for synthetic substances. The Commission will implement this Strategy progressively by making endeavor to achieve these objectives by the year 2020. OSPAR has already identified a List of Substances of Possible Concern.

In November 2004 the European Commission approved new Commissioners and has opened the way for the European Parliament to finalize its EU Chemicals Policy. The Registration, Evaluation, Authorization and restriction of the Chemicals (REACH) has the potential for significant reduction of substances for all speciality chemical products including those used in the petroleum industry.

One of the stated objectives of the European Commission of REACH is to motivate innovation in the chemical industry through the development of alternative substances as substitutes for existing chemicals.

Biodegradation of additives is a key environmental performance pointer used by many regulators as a classification tool to grant a pass/fail status to a product, or otherwise, use in some kind of ranking system.

Surfactants are a good example of an area where technical performance (emulsion stability or breaking performance, antifoaming properties, corrosion inhibitor or cleaning power) may be in conflict with environmental performance. Fish and algae appear to be most

affected by toxicity of surfactants. Toxicity in fish occurs via impact on respiratory organs via interference with permeability (cell breakdown). In this respect, charged (anionic/cationic) surfactants seem to have the greatest disruptive potential, with cationic surfactants being especially toxic.

There is anecdotal evidence from the field that "green" chemicals are often perceived as being less effective than their conventional counterparts, even though the redesign of the chemicals to accommodate changes in regulatory requirements may present opportunities to improve technical performance.

A good example of redesign for environmental reasons resulting in performance improvement was a product that was designed for wellbore clean-ups, pit cleaning and, when diluted, washing down the rig (Figure 6).

New cleaning material improved biodegradability performance compared to existing product
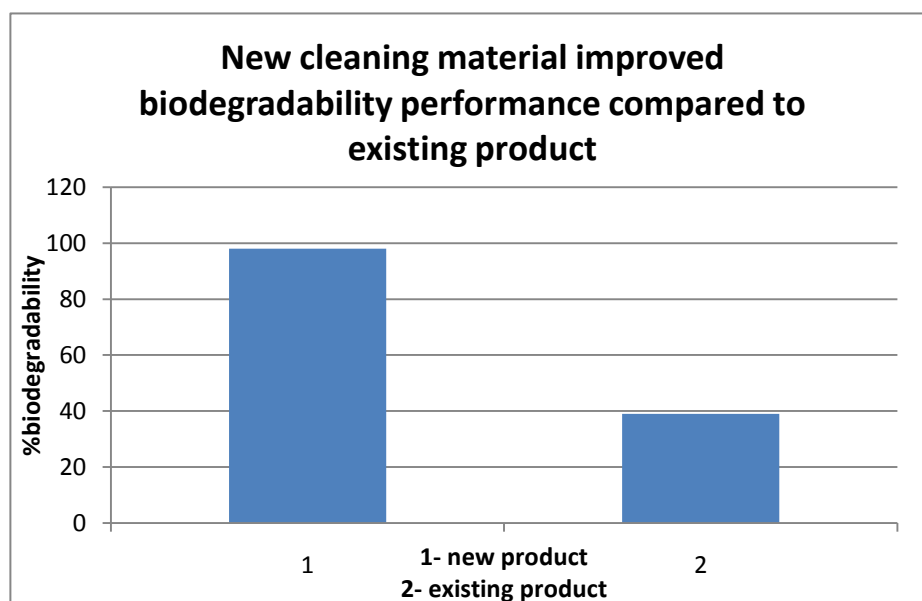
Figure 6 Biodegradability of existing and new products (Proceeding of the Chemistry in the Oil Industry IX Symposium, 2005)

Conclusions

➢ Toxicity of materials can be associated with the extent to which materials are chemically active

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- The more stable a product is in response to temperature-related effects, the less likely it will be readily biodegradable

- Re-design of products to accumulate changes in environmental regulations does necessarily lead to a decrease in performance

- Economics, technical performance, client preferences and material availability are important factors to consider in addition to regulatory compliance

- In some areas, regulations may be driven by politics as well as a good science. This, and other factors such as oceanography, can contribute to discrepancies between regulations in different areas. (Proceeding of the Chemistry in the Oil Industry IX Symposium, 2005)

How the oil/water separation occurs and the factors influence the separation process will be revealed and demonstrated in chapter 4.

Chapter 4

Oil/Water Separation

Nearly all crude oil producers need to separate produced water from oil. Eventually it is necessary to separate entrained oil from produced water too. Both of these separation processes can be able with many different types of equipment, pressurized or atmospheric, and in many different ways. Some of these are more efficient than others. This chapter covers short presentation of oil/water separation, Stoke's law and emulsion theory.

4.1 From 1-st separator to Refinery Waste Water Treatment

The wellstream components need to be separated by using separators. The first step of the production process involves separating the oil, gas, and water into singular streams where they can be managed properly. This is normally accomplished by gravity separation in a horizontal or vertical separator. For a typical oilfield, with high liquid production, the horizontal separator is by far the most common.

Separators can be 2-phase (oil/water) or 3-phase (gas/oil/water). The 1-st stage of separation is always 3-phase, if water is present. The remaining stages can be 3-phase (oil,water&gas) or 2-phase (oil&gas).

Separators equipped with different internal components for enhancing of separation and control devices (Figures 7 and 8).
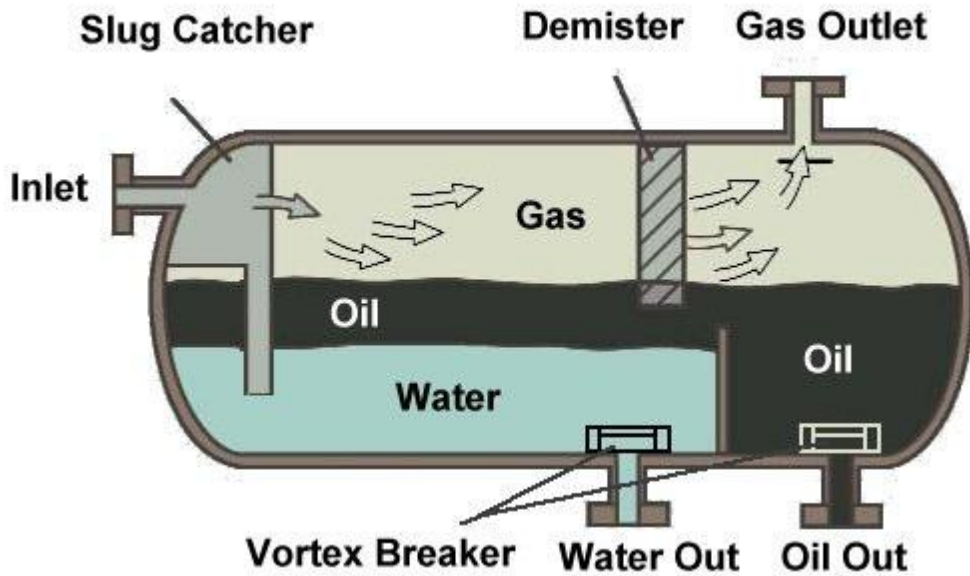
Figure 7: Horizontal three-phase separator (Oil and gas production handbook, 2006)
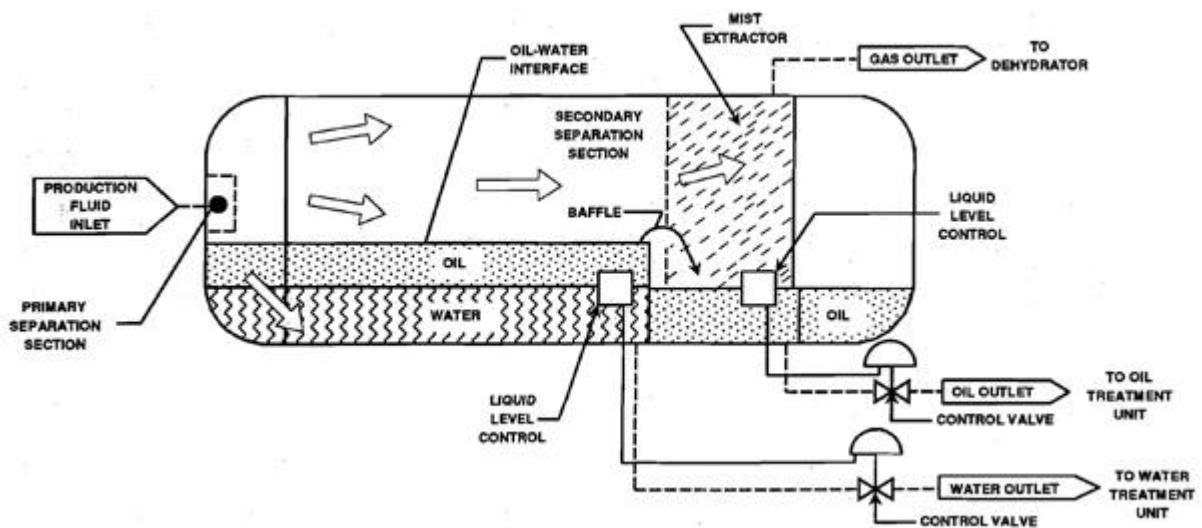
Figure 8: Scheme of 3-phase separator with internals (NETL)

4.2 Stoke's law

The API separator is a gravity separation device designed by using Stoke's law to define the rise velocity of oil droplets based on their density and size. The static separation of immiscible fluids (fluids that are not soluble in one another), in this case oil and water,

and/or suspended solids, can be predicted by applying Stoke's law of physical separation. Predicting static separation is very straight forward. An example is predicting the separation of gravel dumped into a tank of water. The tank is "static", which means there is no motion inside. By applying Stoke's law anyone can calculate how long it will take for the gavel to reach the bottom of the tank. It is obvious that the gravel will settle to the bottom because gravel is heavier than water. It is logical that the larger, heavier pieces of gravel will settle (separate) faster, and the smaller, lighter pieces will settle (separate) slower. An understanding this simple principle is a good beginning to understanding "gravity separation" and Stoke's law.

$$V = D^2g(r_p - r_f)/18\mu$$

V= velocity of rise/settling (cm sec^{-1})

g = acceleration of gravity (cm sec^{-2})

D = "equivalent" diameter of particle (cm)

r_p = density of particle (g cm^{-3})

r_f = density of medium (g cm^{-3})

μ = viscosity of medium (dyne sec cm^{-2})

Note that this equation is for spherical particles with Reynolds number less than 1 in a continuous viscous fluid (laminar flow).

The design of the separator is based on the specific gravity difference between the oil and the wastewater because that difference is much smaller than the specific gravity difference between the suspended solids and water.

4.3 Specifications of raw and treated oil on different stages of separation

The following scheme demonstrates the whole separation process. Green vertical arrows up show separated gas.
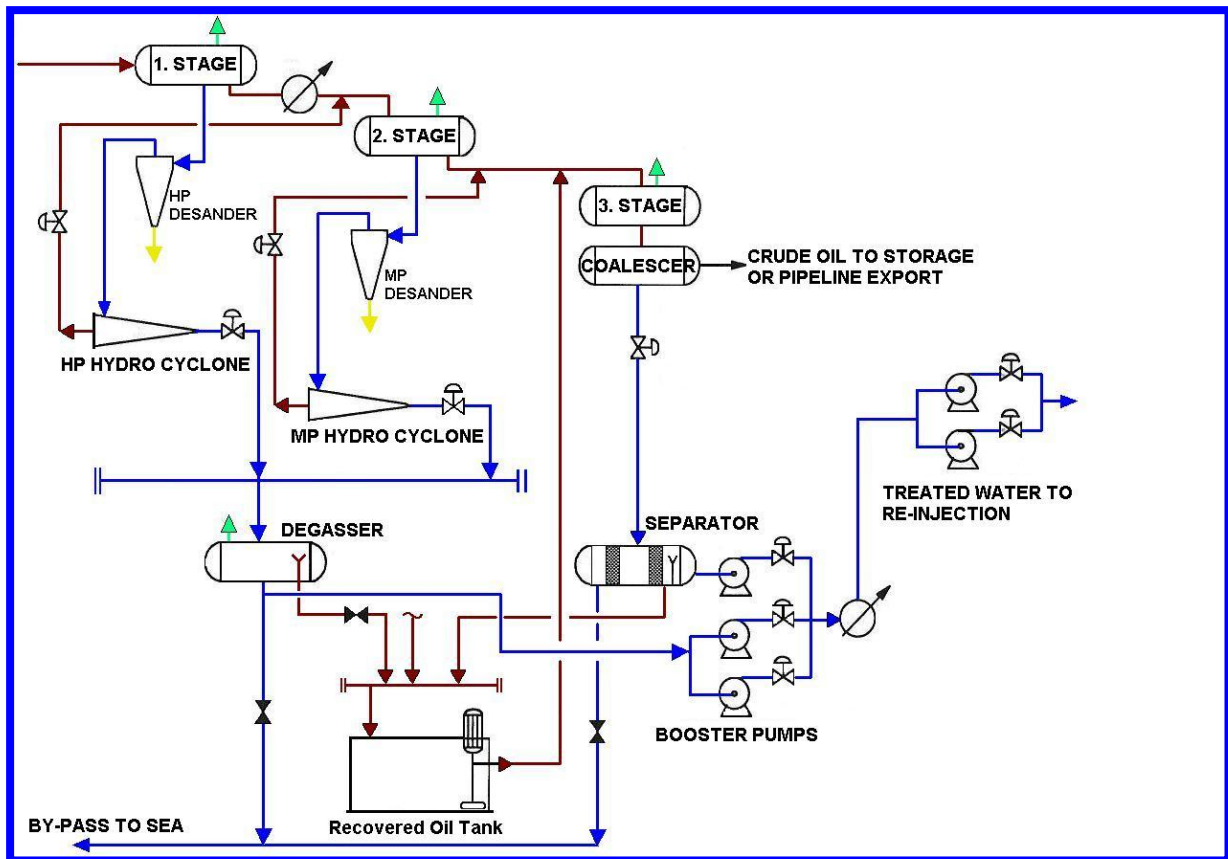
Figure 9: Produced water treatment (NTS, 2010)

Raw crude oil has the following materials present:

- Water: present in two forms: free water (30%) and emulsions (10%)

- Salt: 50,000-250,000 mg/L formation water

- Gas: dissolved gas (600 scf/bbl crude oil)

- H_2S: 70 ppm

Treated crude oils have the following final specifications:

- Water: 0.3 vol% maximum

- Salt: 10 lbs (as NaCl) per 1000 barrels of oil

- H_2S: 70 ppm

- Vapor pressure: 10 psig (4-5 psi RVP)

In gravity separation the well flow is fed into a horizontal vessel. The retention period is typically 5 minutes, allowing the gas to bubble out, water to settle at the bottom and oil to be taken out in the middle. The pressure is often reduced in several stages (high pressure

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separator, low pressure separator etc.) to allow controlled separation of volatile components. Once separation is done, each stream undergoes the proper processing for further field treatment.

As mentioned the production choke reduces will pressure to the HP manifold and **first stage separator** to about 3-5 MPa (30-50 times atmospheric pressure). Inlet temperature is often in the range of 100-150 degrees C. Frequently the water cut (percentage water in the well flow) is almost 40% which quite high. In the first stage separator, the water content is typically reduced to less than 5%.

In the **second stage separator** the pressure is now around 1 MPa (10 atmospheres) and temperature below 100 degrees C. The water content will be reduced to below 2%.

The final separator is a two phase separator, also called a flash-drum. The pressure is now reduced to about atmospheric pressure (100 kPa) so that the last heavy gas components will boil out.

After the third stage separator, the oil can go to a **coalescer** for final removal of water. In this unit the water content can be reduced to below 0.1%. The coalescer is completely filled with liquid: water at the bottom and oil on top. Inside electrodes form an electric field to break surface bonds between conductive water and isolating oil in an oil water emulsion.

Various paths are used to manage the produced water.

Water from the separators and coalescers first goes to a **sand cyclone**, which removes most of the sand. The sand is further washed before it is discharged. The water then goes to a **hydrocyclone**, a centrifugal separator that will remove oil drops. The hydrocyclone creates a standing vortex where oil collects in the middle and water is forced to the side. Finally the water is collected in the **water de-gassing drum**. Dispersed gas will slowly rise to the surface and pull remaining oil droplets to the surface by flotation.

The surface oil film is drained, and the produced water possibly can be discharged to sea. Recovered oil in the water treatment system is typically recycled to the third stage separator.

Oil leaving the 3-rd stage separator does not generally meet the purchaser's specifications. Oil may still contain between 10% and 15% water that exists mostly as emulsified water. The presence of this salt water presents serious corrosion and scaling problems in transportation and refinery operations.

Water remaining in the oil is known as the basic sediments and water (BS&W). A maximum of 1% BS&W and in some cases less than 0.5% BS&W is acceptable. The limit on the salt content of the remnant water in oils is usually in the range of 10 to 15 PTB (pounds of salt per thousand barrels of oil). If these specifications are not met, then further treatment of the oil leaving the separator will be needed. Such treatment involves emulsion treatment/dehydration and desalting processes.

4.4 Emulsions

4.4.1 Factors affecting particles sizes in emulsions

In addition, most chemical additives used in oilfield operations also have the effect of reducing particle sizes. Examples are:

— Emulsion breakers when high instantaneous dosages are applied;
— Corrosion Inhibitors. These chemicals often depend on water wetting surface active agents to clean organic deposits from the corrosion sites. These powerful surface active agents (surfactants) promote very stable oil-water and oil-water - solids emulsions.
— Scale Inhibitors. Both organic and inorganic scale inhibitors are formulated to disperse solids, preventing agglomeration. This is the exact opposite from coalescence (droplet or particle size growth). While stable dispersions are not defined as emulsions, the results are much the same, since the dispersants prevent coalescence (droplet or particle size growth).
— Acids: Acids are used for well stimulation. By definition, acids have very low pH values. A low pH environment promotes dispersion. Therefore, droplet and particle coalescence will not normally occur in low pH environments. Acids applied in oilfield production operations nearly always contain surface-active

chemicals used to remove the oily deposits from the reservoir rock and scale the acids are designed to attack. These surfactants promote chemically stable emulsions, and this problem is enhanced further by the presence of the very small (usually less than one micron) solids particles carried back to surface treating facilities by spent acids.

Chemically stabilized emulsions add time to the physical separation, as has been described in the preceding explanation of Stoke's law.

4.4.2 Introduction and definition

"Produced water may be produced as "free" water (i.e., water that will settle out fairly rapidly), and it may be produced in the form of an emulsion. A regular oilfield emulsion is a dispersion of water droplets in oil.

Emulsions can create high-pressure drops in flow lines, lead to an increase in demulsifier use, and sometimes cause trips or upsets in wet-crude handling facilities. The problem is usually at its worst during the winter because of lower surface temperatures. These emulsions must be treated to remove the dispersed water and associated inorganic salts to meet crude specifications for transportation, storage, and export and to reduce corrosion and catalyst poisoning in downstream processing facilities.

Emulsions occur in almost all phases of oil production and processing: inside reservoirs, wellbores, and wellheads; at wet-crude handling facilities and gas/oil separation plants; and during transportation through pipelines, crude storage, and petroleum processing.

An emulsion is dispersion (droplets) of one liquid in another immiscible liquid. The phase that is present in the form of droplets is the dispersed or internal phase, and the phase in which the droplets are suspended is called the continuous or external phase. For produced oilfield emulsions, one of the liquids is aqueous and the other is crude oil. The amount of water that emulsifies with crude oil varies widely from facility to facility. It can be less than 1% and sometimes greater than 80%." (Petroleum Engineering Handbook—Vol. I)

4.4.3 Types of emulsions

- ✓ water-in-oil
- ✓ oil-in-water
- ✓ multiple or complex emulsions

In the oil industry, water-in-oil emulsions (WIO) are more frequent; therefore, the oil-in-water emulsions (OIW) are sometimes referred to as "reverse" emulsions.

Multiple emulsions are more complex and consist of tiny droplets suspended in bigger droplets that are suspended in a continuous phase.

Emulsions are also can be divided in

- ➤ macroemulsions (dispersed droplets size are larger than 0.1 μm; thermodynamically unstable, that means separation of the two phases over time)
- ➤ microemulsions (droplet size less than 10 nm; thermodynamically stable)

4.4.4 Origins of emulsions

Sufficient mixing and the presence of an emulsifier (used to stabilize emulsions) cause the formation of crude oil emulsions. The amount of mixing and quantity of emulsifying agent will influence on size of dispersed water droplets in oil. The water droplets can vary in size from less than 1 μm to more than 1000 μm.

4.4.5 Physical properties and characteristics

Oilfield emulsions are characterized by several properties including appearance and color, BS&W, droplet size, and bulk and interfacial viscosities.

Basic Sediment and Water. BS&W is the solids and aqueous fraction of an emulsion. It is also referred to as BSW, bottom settlings and water, or bottom solids and water. The most

common method for the determination of oil, water, and solids consists of adding a small overdose of a demulsifier to an emulsion, centrifuging it, and allowing it to stand.

Viscosity of Emulsions. Emulsion viscosity can be considerably larger than the viscosity of either the oil or the water since emulsions show non-Newtonian behavior. This performance is a result of droplet crowding or structural viscosity. A fluid is considered non-Newtonian when its viscosity is a function of shear rate. At a certain volume fraction of the water phase (water cut), oilfield emulsions behave as shear-thinning or pseudoplastic fluids (i.e., as shear rate increases, viscosity decreases).

The viscosity of emulsions depends on several factors: viscosities of oil and water, volume fraction of water dispersed, droplet-size distribution, temperature, shear rate, and amount of solids present.

The viscosity of the emulsion can be substantially higher than the viscosity of the oil or water at a given temperature. Temperature also has a significant effect on emulsion viscosity.

4.4.6 Stability of emulsions

"From a purely thermodynamic point of view, an emulsion is an unstable system because there is a natural tendency for a liquid/liquid system to separate and reduce its interfacial area and, hence, its interfacial energy. However, most emulsions demonstrate kinetic stability (i.e., they are stable over a period of time). Produced oilfield emulsions are classified on the basis of their degree of kinetic stability. Loose emulsions separate in a few minutes, and the separated water is free water. Medium emulsions separate in tens of minutes. Tight emulsions separate (sometimes only partially) in hours or even days.

Produced oilfield emulsions are stabilized by films that form around the water droplets at the oil/water interface. These films are believed to result from the adsorption of high-molecular-weight polar molecules that are interfacial active (surfactant-like behavior). These films enhance the stability of an emulsion by increasing the interfacial viscosity.

The factors that affect interfacial films and, therefore, the emulsion stability are heavy polar fractions in the crude oil; solids, including organic (asphaltenes, waxes) and inorganic (clays,

scales, corrosion products, etc.) materials; temperature; droplet size and droplet-size distribution; pH of the brine; and brine composition.

These include asphaltenes, resins, and oil-soluble organic acids (e.g., naphthenic, carboxylic) and bases. These compounds are the main constituents of the interfacial films surrounding the water droplets that give emulsions their stability.

Solid particles stabilize emulsions by diffusing to the oil/water interface, where they form rigid films that can sterically inhibit the coalescence of emulsion droplets. Furthermore, solid particles at the interface may be electrically charged, which may also enhance the stability of the emulsion.

Particles must be much smaller than the size of the emulsion droplets to act as emulsion stabilizers.

When solids are wetted by the oil and water (intermediate wettability), they agglomerate at the interface and retard coalescence. These particles must be repositioned into either the oil or water for coalescence to take place. This process requires energy and provides a barrier to coalescence.

The role of colloidal solid particles in emulsion stability and the mechanisms involved are summarized in the following points:

- The particles must be present at the oil/water interface before any stabilization can take place
- The ability of the solids to form a rigid, protective film encapsulating the water droplets is important for stabilizing these emulsions
- Water-wet particles tend to stabilize oil-in-water emulsions, and oil-wet particles stabilize water-in-oil emulsions

As it mentioned previously, temperature has the most important affect on the oil viscosity. Increasing of temperature leads to a decrease in the oil viscosity. This is because the temperature increases the thermal energy of the droplets and, therefore, increases the frequency of drop collisions. It also reduces the interfacial viscosity, which results in a faster film-drainage rate and faster drop coalescence.

Effect of drop size to emulsions stability is mentioned earlier in this chapter.

pH. The pH of water has a strong influence on emulsion stability. The stabilizing, rigid emulsion film contains organic acids and bases, asphaltenes with ionizable groups, and solids.

Adding inorganic acids and bases strongly influences their ionization in the interfacial films and radically changes the physical properties of the films. The pH of water affects the rigidity of the interfacial films. It was reported that interfacial films formed by asphaltenes are strongest in acids (low pH) and become progressively weaker as the pH is increased. In alkaline medium, the films become very weak or are converted to mobile films. The films formed by resins are strongest in base and weakest in acid medium. Solids in the emulsions can be made oil-wet by asphaltenes, an effect that is stronger in an acidic than in a basic medium. These partially oil-wet solids tend to stabilize water-in-oil emulsions.

pH also influences the type of emulsion formed. Acid or low pH generally produces waterin-oil emulsions (corresponding to oil-wetting solid films), whereas basic or high pH produces oil-in-water emulsions (corresponding to water-wetting mobile soap films).

Brine composition

- Brine composition (alkalinity in particular because of a buffering effect) is intimately tied to the pH in determining the stabilizing properties of the interfacial films
- Brines with high Ca++ ions and a high Ca++/Mg++ ratio form nonrelaxing, rigid films around the water droplets, resulting in stable emulsions
- Higher concentration of divalent ions and high pH result in reduced emulsion stability

4.4.7 Demulsification

Demulsification is the breaking of a crude oil emulsion into oil and water phases. From a process point of view, the oil producer is interested in three aspects of demulsification: the rate or the speed at which this separation takes place, the amount of water left in the crude oil after separation, and the quality of separated water for disposal. A fast rate of separation,

a low value of residual water in the crude oil, and a low value of oil in the disposal water are obviously desirable. Produced oil generally has to meet company and pipeline specifications. For example, the oil shipped from wet-crude handling facilities must not contain more than 0.2% BS&W and 10 pounds of salt per thousand barrels of crude oil. This standard depends on company and pipeline specifications. The salt is insoluble in oil and associated with residual water in the treated crude. Low BS&W and salt content is required to reduce corrosion and deposition of salts. The primary concern in refineries is to remove inorganic salts from the crude oil before they cause corrosion or other detrimental effects in refinery equipment. The salts are removed by washing or desalting the crude oil with relatively fresh water.

The interfacial film, which is the most reason for emulsion stability, must be destroyed and the droplets made to coalesce. Therefore, destabilizing or breaking emulsions is linked directly to the removal of this interfacial film. The factors that affect the interfacial film and, consequently, the stability of the emulsions were discussed earlier. The factors that enhance or speed up emulsion breaking are discussed here.

Temperature. Application of heat promotes oil/water separation and accelerates the treating process. An increase in temperature has the following effects.

- Reduces the viscosity of the oil
- Increases the mobility of the water droplets
- Increases the settling rate of water droplets
- Increases droplet collisions and favors coalescence
- Weakens or ruptures the film on water droplets because of water expansion and enhances film drainage and coalescence
- Increases the difference in densities of the fluids that further enhances water-settling time and separation

An economic analysis should be performed that takes into consideration factors such as heating costs, reduced treating time, and residual water in the crude.

Very high shear is detrimental and should be avoided. High shear causes violent mixing of oil and water and leads to smaller droplet sizes. Smaller droplets are relatively more stable than

larger droplets; therefore, measures that increase shearing of the crude oil should be avoided or minimized where possible. However, a certain amount of shear is required for mixing the chemical demulsifier into the bulk of the emulsion.

Solids have a strong tendency to stabilize emulsions, especially if they are present as fines or when they are wetted by both oil and water. Removing the solids or their source is sometimes all that is required for eliminating or reducing the emulsion problem. Oil-wet solids stabilize water-in-oil emulsions. Water-wet solids can also be made oil-wet with a coating of heavy polar materials and can participate effectively in the stabilization of water-in-oil emulsions.

Because **emulsifying agents** are necessary in the stabilization of emulsions, controlling them allows for their destabilization and resolution.

Mechanisms Involved in Demulsification, Flocculation or Aggregation

- Water content in the emulsion. The rate of flocculation is higher when the water cut is higher
- Temperature of the emulsion is high. Temperature increases the thermal energy of the droplets and increases their collision probability, thus leading to flocculation
- Viscosity of the oil is low, which reduces the settling time and increases the flocculation rate
- Density difference between oil and water is high, which increases the sedimentation rate
- An electrostatic field is applied. This increases the movement of droplets toward the electrodes, where they aggregate

Coalescence. Coalescence is the second step in demulsification. During coalescence, water droplets fuse or coalesce together to form a larger drop. This is an irreversible process that leads to a decrease in the number of water droplets and eventually to complete demulsification.

Coalescence is enhanced by the following factors:

- High rate of flocculation increases the collision frequency between droplets

- The absence of mechanically strong films that stabilize emulsions
- High interfacial tension. The system tries to reduce its interfacial free energy by coalescing
- High water cut increases the frequency of collisions between droplets
- Low interfacial viscosity enhances film drainage and drop coalescence
- Chemical demulsifiers convert solid films to mobile soap films that are weak and can be ruptured easily, which promotes coalescence
- High temperatures reduce the oil and interfacial viscosities and increase the droplet collision frequency

Sedimentation or Creaming. Sedimentation is the process in which water droplets settle down in an emulsion because of their higher density. Its inverse process, creaming, is the rising of oil droplets in the water phase. Sedimentation and creaming are driven by the density difference between oil and water and may not result in the breaking of an emulsion. Unresolved emulsion droplets accumulate at the oil/water interface in surface equipment and form an emulsion pad or rag layer. A pad in surface equipment causes several problems including the following.

- Occupies space in the separation tank and effectively reduces the retention or separation time
- Increases the BS&W of the treated oil
- Increases the residual oil in the treated water
- Increases arcing incidences or equipment upset frequency
- Creates a barrier for water droplets and solids migrating down into the bulk water layer

Emulsion pads are caused or exacerbated by ineffective demulsifier (unable to resolve the emulsion); insufficient demulsifier (insufficient quantities to break the emulsion effectively); other chemicals that nullify the effect of the demulsifier; low temperatures; and the presence of accumulating solids. Because emulsion pads cause several operational problems, their cause should be determined and appropriate actions taken to eliminate them.

4.4.8 Methods of Emulsion Breaking or Demulsification

- Adding chemical demulsifiers

- Increasing the temperature of the emulsion

- Applying electrostatic fields that promote coalescence

- Reducing the flow velocity that allows gravitational separation of oil, water, and gas. This is generally accomplished in large-volume separators and desalters

4.4.8.1 Thermal Methods

Heating reduces the oil viscosity and increases the water-settling rates.

Increased temperatures also result in the destabilization of the rigid films because of reduced interfacial viscosity. Furthermore, the coalescence frequency of water droplets is increased because of the higher thermal energy of the droplets. In other words, heat accelerates emulsion breaking; however, it very rarely resolves the emulsion problem alone. Increasing the temperature has some negative effects. First, it costs money to heat the emulsion stream. Second, heating can result in the loss of light ends from the crude oil, reducing its API gravity and the treated oil volume. Finally, increasing the temperature leads to an increased tendency toward some forms of scale deposition and an increased potential for corrosion in treating vessels.

The application of heat for emulsion breaking should be based on an overall economic analysis of the treatment facility. The cost-effectiveness of adding heat should be balanced against longer treatment time (larger separator), loss of light ends and a resultant lower oil-product price, chemical costs, and the costs of electrostatic grid installation or retrofitting.

4.4.8.2 Mechanical Methods

There is a wide variety of mechanical equipment available for breaking oilfield emulsions including free-water knockout drums, two- and three-phase separators (low- and high-pressure traps), desalters, settling tanks, etc.

Free-Water Knockout Drums. Free-water knockout drums separate the free water from the crude oil/water mixture.

Production Traps or Three-Phase Separators. Three-phase separators or production traps are used to separate the produced fluids into oil, water, and gas. These separators are described earlier in this report.

Desalters. The oil from the separator is generally still contains unacceptably high levels of water and solids). It must be further treated to meet crude specifications.

For the refinery, the salt level must be further reduced. Refinery crude should contain no more that a specified amount of inorganic solids (salts). This is generally expressed in pounds per thousand barrels. The industry standard is 1 pound per thousand barrels. The removal of the salts, along with the remaining water, is the process of desalting.

Desalters are normally designed as either one-stage or multistage desalters. Generally, desalters use a combination of chemical addition, electrostatic treating, and settling time. The retention time is based on a certain oil specification for a given product rate. Also, fresh water (wash water) is added with the chemicals to reduce the concentrations of dissolved salt (by diluting) in the treated water and, hence, the outgoing crude.

4.4.8.3 Electrical Methods

Electrostatic grids are sometimes used for emulsion treatment. Highvoltage electricity (electrostatic grids) is often an effective means of breaking emulsions. It is generally theorized that water droplets have an associated net charge, and when an electric field is applied, the droplets move about rapidly and collide with each other and coalesce.

Electrostatic dehydration generally is used with chemical and heat addition. Invariably, the use of electrostatic dehydration results in reduced heat requirements. Lower temperatures result in fuel economy, reduced problems with scale and corrosion formation, and reduced light-end loss. Electrostatic grids can also lead to a reduction in the use of emulsion-breaking chemicals.

The one limitation of electrostatic dehydration is shorting/arcing, which generally happens when excess water is present. Recent designs in electrostatic grids have eliminated shorting/arcing.

4.4.8.4 Chemical Methods

The most common method of emulsion treatment is adding demulsifiers. These chemicals are designed to neutralize the stabilizing effect of emulsifying agents.

Selection of the right demulsifier is cruicial to emulsion breaking. Demulsifier chemicals contain the following components: solvents, surface-active ingredients, and flocculants. Solvents, such as benzene, toluene, xylene, short-chain alcohols, and heavy aromatic naptha, are generally carriers for the active ingredients of the demulsifier.

Some solvents change the solubility conditions of the natural emulsifiers (e.g., asphaltenes) that are accumulated at the oil/brine interface. These solvents dissolve the indigenous surface-active agents back into the bulk phase, affecting the properties of the interfacial film that can facilitate coalescence and water separation.

Surface-active ingredients are chemicals that have surface-active properties characterized by hydrophilic-lipophilic balance (HLB) values. For a definition and description of HLB, see Ref.5. The HLB scale varies from 0 to 20. A low HLB value refers to a hydrophilic or water-soluble surfactant. In general, natural emulsifiers that stabilize a water-in-oil emulsion exhibit an HLB value in the range of 3 to 8. Thus, demulsifiers with a high HLB value will destabilize these emulsions.

Flocculants are chemicals that flocculate the water droplets and facilitate coalescence. A detailed process for selecting the appropriate demulsifier chemicals includes the following steps.

- Characterization of the crude oil and contaminants includes the API gravity of the crude oil, type and composition of oil and brine, inorganic solids, amount and type of salts, contaminant type and amounts

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- Evaluation of operational data includes production rates, treating-vessel capabilities (residence time, electrostatic grids, temperature limitations, etc.), operating pressures and temperatures, chemical dosage equipment and injection points, sampling locations, maintenance frequency, and wash-water rates
- Evaluation of emulsion-breaking performance: past experience and operating data including oil, water, and solids content during different tests; composition and quality of interface fluids; operating costs; and amounts of water generated and its disposal

Mixing/Agitation. For the demulsifier to work effectively, it must make intimate contact with the emulsion and reach the oil/water interface. Adequate mixing or agitation must be provided to thoroughly mix the chemical into the emulsion. This agitation promotes droplet coalescence; therefore, the point at which the demulsifier is added is critical. Once the emulsion has broken, agitation should be kept to a minimum to prevent re-emulsification.

Dosage. The amount of chemical added is also important. Too little demulsifier will leave the emulsion unresolved. Conversely, a large dose of demulsifier (an overtreat condition) may be detrimental.

On the basis of an evaluation of the literature, the demulsifier rates quoted vary from less than 10 to more than 100 ppm (based on total production rates). These numbers are provided for primary or secondary oil-recovery emulsions.

During tertiary oil recovery (especially during surfactant or micellar flooding), demulsifier rates typically can be in the hundreds of ppm and even higher in extreme cases.

Factors Affecting Demulsifier Efficiency. Several factors affect demulsifier performance including temperature, pH, type of crude oil, brine composition, and droplet size and distribution.

As described previously, an increase in temperature results in a decrease in emulsion stability, and, hence, a lower dosage of demulsifier is required. pH also affects demulsifier performance.

Generally, basic pH promotes oil-in-water emulsions and acidic pH produces water-in-oil emulsions.

High pH, therefore, helps in destabilizing water-in-oil emulsions. It has also been reported that basic pH reduces demulsifier dosage13 requirements.

Demulsifiers that work for a given emulsion may be completely ineffective for another.

Demulsifiers are typically formulated with polymeric chains of ethylene oxides and polypropylene oxides of alcohol, ethoxylated phenols, ethoxylated alcohols and amines, ethoxylated resins, ethoxylated nonylphenols, polyhydric alcohols, and sulphonic acid salts. Commercial demulsifiers may contain one or more types of active ingredient. There is a wide variation within the active ingredient type as well. For example, the molecular weight and structure of the ethylene or propylene oxides can be changed to affect a complete range of solubilities, HLBs, charge neutralization tendencies, solids-wetting characteristics, and costs.

Many chemical additives reduce or inhibit the rate of buildup of interfacial films. The best demulsifiers should possess both types of film modifying behavior: displacement of components in rigid interfacial films and inhibition of the formation of the rigid films.

An increase in demulsification rate is generally observed with increasing demulsifier concentration up to a critical concentration (the critical aggregation concentration). This is attributed to a monolayer adsorption of the demulsifier at the interface (simultaneously displacing the indigenous crude oil surfactant film).

Higher concentrations beyond this critical concentration (overdosing) result in two different types of behavior. Type I behavior is the leveling of the demulsification rate with increased demulsifier concentration. This type of behavior is attributed to the formation of a liquid crystalline phase. Type II behavior is a reduction in demulsification rate with increased demulsifier concentration.

The solubility of the demulsifier in oil and water, or its partitioning, is also very crucial in determining the effectiveness of the demulsifier. The partitioning of the surfactant is measured either by the partition coefficient or by its HLB value.

Demulsifiers that are soluble in water only (low partition coefficient or low HLB) are not very effective in breaking water-in-oil emulsions. Oil solubility is important because oil forms the continuous phase, permits a thorough distribution of the demulsifier in the emulsion, and affects its diffusion to the oil/ water interface.

To ensure good overall performance, a demulsifier should meet the following criteria.

- Dissolve in the continuous oil phase
- Have a concentration large enough to diffuse to the oil/water interface. However, it should not be higher than the critical aggregate concentration
- Partition into the water phase (partition coefficient close to unity)
- Possess a high rate of adsorption at the interface
- Have an interfacial activity high enough to suppress the IFT gradient, thus accelerating the rate of film drainage and promoting coalescence."(Fanchi J.R., 2006)

Nevertheless flocculation is an effective emulsion breaking method and whereas a Produced Water Treatment method. More about this process reveals in chapter 5.

Chapter 5

Flocculation

5.1 Introduction

Produced water is a colloidal solution, where the contaminants are dispersed throughout the water phase. Flocculation is a process where colloids (dispersed fine particles sized 5-200 nm) come out of suspension in the form of floc or flakes. The floc may then float to the top of the liquid, settle to the bottom of the liquid, or can be readily filtered from the liquid.

Destabilization (flocculation) of the produced water can be achieved by naturalizing the electrostatic barrier. To enhance this process adjusting the pH or adding salts can be done. When repulsive forces are low, the dispersed particles can flocculate because of electric attraction between particles. Chemical adding will destabilize the colloid solution by affecting the particles charge. Chemicals that promote flocculation by causing colloids and other suspended particles in liquids to form a floc are called flocculants, or flocculating agents.

Many flocculants are multivalent cations such as aluminum, calcium, iron or magnesium. These positively charged molecules interact with negatively charged particles and molecules to reduce the barriers to aggregation. In addition, many of these chemicals, under appropriate pH and other conditions such as temperature and salinity, react with water to form insoluble hydroxides which, upon precipitating, link together to form long chains or meshes, physically trapping small particles into the larger floc.

Long-chain polymer flocculants, such as modified polyacrylamides, are manufactured and sold by the flocculant producing business. These can be supplied in dry or liquid form for use in the flocculation process. The most common liquid polyacrylamide is supplied as an emulsion with 10-40% actives and the rest is a carrier fluid, surfactants and latex. Emulsion polymers require activation to invert the emulsion and allow the electrolyte groups to be exposed. (Wikipedia)

5.2 Stoke's law for flocculation

It is questionable because Stoke's law is only valid for an impermeable sphere. Since a floc is of highly porous structure, the ambient fluid will penetrate the floc; the settling speed of the floc is, therefore, higher than that of an impermeable particle with the same size and the same effective density as the floc (Huang H, 1993).

However, Stoke's law is working in sedimentation process after flocculation. "Small oil droplets will settle much slower than large oil droplets. Field experience has shown that the oil droplet size distribution often has a peak around 10 – 15 mm and thus the volume of oil droplets below 10 mm can be quite significant.

According to Stoke's law, the settling velocity is proportional to the square of the oil droplet diameter and to the g-force applied.

Oil droplet size is crucial to separation and it is imperative that the selected equipment is suitably effective. The smaller the droplets, the lower are their settling velocity. The separation equipment can be made more effective by increasing the g-force applied on the oil droplets. It may also be possible to increase the settling velocity of the oil droplets by flocculating them into larger agglomerates." (SPE 56643)

5.3 CFG

CFG is flocculating agent; consists of a mix of a clay mineral bentonite and Sodium Pyrophosphate.

Clay minerals represent a flocculation agent with large surface area and chemical reactive area. The characteristics common to all clay minerals derive from their chemical composition, layered structure, and size. Clay minerals all have a great affinity for water. Some swell easily and may double in thickness when wet. Most have the ability to soak up ions (electrically charged atoms and molecules) from a solution and release the ions later when conditions change.

5.3.1 Bentonite

Bentonite clay, also referred to as Montmorillonite, is sedimentary clay composed of weathered and aged volcanic ash. The largest and most active deposits come from Wyoming and Montana in the US (Mountain Rose Herbs stocks a Wyoming variety).
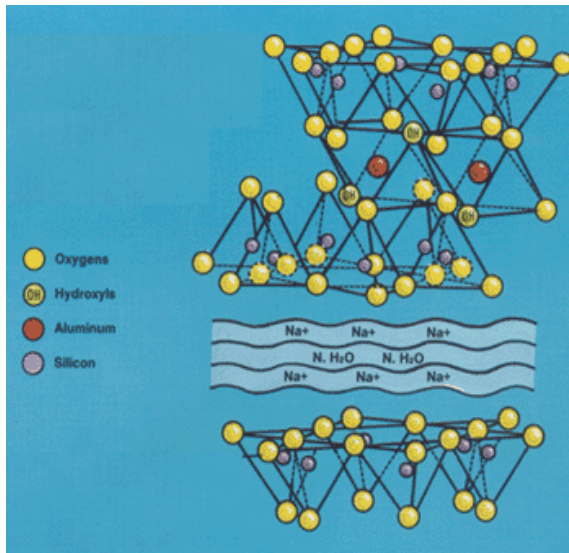
Figure 10: Chemical structure of Bentonite   Figure 11: Bentonite

The special properties of bentonite are an ability to form thixotrophic gels with water, an ability to absorb large quantities of water with an accompanying increase in volume of as much as 12–15 times its dry bulk, and a high cation exchange capacity.

Bentonite has complicated, non-stoichiometric structure – $2[(Al_{1.67} Mg_{0.33})(Si_{3.5} Al_{0.5})O_{10} (OH)_2]$. It is 3-layer clay with 1 aluminium oxide sheet surrounded by 2 silicon oxide sheets. The internal Al sheet and external Si oxide sheets share oxygen atoms. The basic crystal structure of smectites is an octahedral alumina sheet between two tetrahedral silica sheets. Atoms in these sheets common to both layers are oxygens. These three-layer units are stacked one above another with oxygens in neighbouring layers adjacent to each other. This produces a weak bond, allowing water and other polar molecules to enter between layers and induce an expansion of the mineral structure. In the tetrahedral coordination, silicon may be substituted by aluminium and possibly phosphorus; in the octahedral coordination, aluminium may be substituted by magnesium, iron, lithium, chromium,zinc, or nickel.

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Substitutions of silicon by cations produce an excess of negative charges in the lattice, which is balanced by cations (Na+, K+, Mg2+, Ca2+) in the interlayer space. These cations are exchangeable due to their loose binding and, together with broken bonds (approximately 20% of exchange capacity), give montmorillonite a rather high (about 100 meq/100 g) cation exchange capacity, which is little affected by particle size. This cation exchange capacity allows the mineral to bind not only inorganic cations such as caesium but also organic cations such as the herbicides diquat, paraquat (Weber et al., 1965), and striazines (Weber, 1970), and even bio-organic particles such as rheoviruses (Lipson & Stotzky, 1983) and proteins (Potter & Stollerman, 1961), which appear to act as cations. Variation in exchangeable cations affects the maximum amount of water uptake and swelling. These are greatest with sodium and least with potassium and magnesium.

The swelling type bentonite when dispersed in water separates into suspendible flakes which are all finer than 0.5 micron. Calcium bentonite yields about 35% finer than 0.5 micron. Calcium bentonite yields about 35% finer than 0.5 microns. The difference in bentonite and other clays lies in lattice structure. The sheets of atoms in bentonite are much thinner and more easily separable in water. That is why bentonite occupies more surface area than other clays. This property is known as dispersibility, which is unique to swelling type of bentonite.

5.3.2 Sodium pyrophosphate

Sodium pyrophosphate is polymer with a high molecular weight (611.770386 [g/mol]), and has a formula $Na_6O_{18}P_6$, has formal zero charge. It is a white powder or granular.
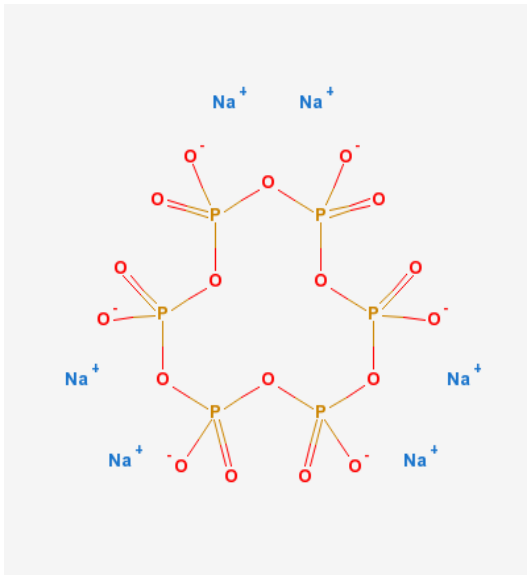
Figure 12: Sodium pyrophosphate (chemical structure)   Figure13: Sodium pyrophosphate

When mixing CFG with water, the components will easy solve in the water phase, creating Wyoming Bentonite clay colloid particles with positive and negative charges. The Sodium Meta Pyrophosphate will act as deflocculant on the Bentonite and adsorb onto the positive charges.

5.3.3 Chitosan (clariant)

Together with CFG chitosan will be used in flocculation.

From Wikipedia*: Chitosan is produced commercially by deacetylation of chitin, which is the structural element in the exoskeleton of crustaceans (crabs, shrimp, etc.) and cell walls of fungi. The degree of deacetylation (%DD) can be determined by NMR spectroscopy, and the %DD in commercial chitosans is in the range 60-100 %.*

The amino group in chitosan has a pKa value of ~6.5, thus, chitosan is positively charged and soluble in acidic to neutral solution with a charge density dependent on pH and the %DA-value. This makes chitosan a bioadhesive which readily binds to negatively charged surfaces. Chitosan is biocompatible and biodegradable.

Chitosan can also be used in water processing engineering as a part of a filtration process. Chitosan causes the fine sediment particles to bind together and is subsequently removed

with the sediment during sand filtration. Chitosan also removes phosphorus, heavy minerals, and oils from the water.

In combination with bentonite, chitosan is an ideal substance to use in flocculation process.

5.4 Factors possible affecting flocculation

Production chemicals remaining in PW will be in focus in this chapter. As it shown in the Table "Additional Chemicals Used in Connection with the Production", corrosion inhibitors, scale inhibitors and biocides, that may be squeezed into the formation, and are water soluble, can be found in the produced water. The presence of the production chemicals can truly affect the flocculation process. To be more precisely, their concentration and charge are the most significant factors that can influence the flocs formation.

Production chemicals

Corrosion inhibitors- water soluble fluids. These compounds are prepared by reacting a polyoxylated starting material with elemental sulfur. These compounds perform better in aqueous systems than their nonoxylated analogs. The concentration range is usually in the 10-500 ppm range, based on the weight of the water in the system. Often they are cationic.

Scale inhibitors concentrations vary from 50 to 100 mg/L. Mostly they have anionic charge.

Biocides: Cationic or neutral charge.

— Nitrate concentration is 5-50 ppm
— Diammonium salts of tetrahydrophthalic acid or methyl-tetrahydrophthalic acid – 25-75 ppm
— Oxidizing biocides, such as chlorine/hypochlorite – (up to 30 minutes)
— Organic biocides are characterized by high "speed-of-kill" properties, usually required relatively high-dosage concentrations, often in the range 400-500 ppm

Demulsifies: concentration 1-max 5000 ppm, preferable 1-1000 ppm (Malcolm's book: 1-500 ppm. Nonionic, ionic)

Antifoamers: mostly used silicone oils, 2/3 ppm. Catalyst poison (refinery).

The flocculant is typically added to the raw water in an amount suitable to flocculate suspended matter. In most cases large particles, flocs, are removed via settling in a clarifier and are recollected as sludge. Occasionally, clarifier upsets cause cationic polymer "carry-over". In such instances, cationic polymers may interfere with the performance of anionic polymers used as precipitation inhibitors and dispersant in the water treatment formulation. (Source: 4th Int. Symposium on Inorganic Phosphate Materials, Germany, July 2002)

Production chemicals' solubility in oil and water

"Control of mineral scales is through chemical treatment alone. All of the chemicals are used for control of mineral scales work by interfering with crystal growth. There are three common types of chemical compounds used for this purpose, phosphate esters, phosphonates, and acid polymers. All **scale inhibitors** are highly water-soluble and will stay with the produced water to discharge." (Hayward Gordon Ltd, 2008)

Emulsion breakers (for instance polyether type) are oil/water soluble or soluble in both water and oil.
For normal emulsion uses oil-soluble emulsion breakers, for reverse- water soluble, but oil solubility of these can increase with increasing of pH.

Corrosion inhibitors (CI) are also oil- or water soluble.

"Oil soluble corrosion inhibitors are most commonly used since they are usually the most effective at providing a stable, durable film. The concentration of active ingredient in bulk corrosion inhibitors is usually 30 - 40%. The remaining material (inert ingredients) is usually a hydrocarbon based solvent like heavy aromatic naphtha. When improved water solubility is required, dispersants or surfactants may be added, or water soluble corrosion inhibitors such as quaternary amines can be used. Oil soluble inhibitors will follow the oil stream to the refinery and water-soluble inhibitors will stay with the water phase." (Hayward Gordon Ltd, 2008)

Water soluble CI have 0.2-5 ppm (90%>1) LC_{50} concentration, while oil soluble CI have 2-1000 ppm (90%>5) LC_{50} (S. T. Orszulik, 2008)

Chapter 6

Experiments

This chapter contains two parts: tests with turbidity measurements and tests with particle size distribution measurements.

During the experiments synthetic produced water was prepared. Eilen Vik from Aquateam (personal communication) recommended using seawater and adding needed amount of oil to get the synthetic produced water. This way produced water will contain the ions that are normally present in produced water.

Seawater from Sola beach was used in our experiments. 1µm filter removed suspended particles (living microorganisms, sand and other) from the seawater.

Oil for testing was received from Ula and Ekofisk platforms through Clariant. Also, Clariant had acquired production chemicals for testing. Because of limited time it was decided to use only a few of the chemicals; and in the second part of experiments mostly Ekofisk oil was used (Ula oil was used just for purpose of comparing).

6.1 Turbidity measurements

This is the first section of the experimental part of this Thesis. Produced water contains suspended solids consisting of particles of many different sizes. During flocculation large suspended particles (flocs) settle rapidly to the bottom of the container due to high mass (Stokes's law). Very small particles, however, will settle only very slowly or not at all. Turbidimeters will measure water turbidity (cloudiness of water caused by suspended particles and colloids. The units of turbidity are called Nephelometric Turbidity Units (NTU). Turbidity measurement is a key test of water quality.

6.1.1 Materials and methods

Preparation of flocculant CFG

- 18 g Bentonite dissolved in 200 ml water and mixing 1.5 hours
- Afterwards 9 g Na Pyrophosphonate was added and mixed again

During tests we used 0.5-3 mg/L of CFG. Total Solids (TS) content was 135 g/L.

Chitosan

- 1 g Chitosan dissolved in 2M HCl (100mL) by using magnet mixing for 24 hours

In tests was used 0.5 mg/L of chitosan. TS = 10 g/L.

Preparation of synthetic produced water:

- 800 ml seawater was heated to 60 °C
- Mixed with 0.2 mg Ula/Ekofisk oil (250ppm) by using high shear mixer Silverson (16000 rpm) for 5 min
- Ula/Ekofisk oil Specific Gravity 0.8384

Operating conditions: pH = 6.2, salinity = 5%, temperature = 55-60°C

Jar-test mixing: after each added chemical use max (180 rpm) speed for 45 sec.

Concentration of chemicals used in the tests: Floctreat – 10-100 ppm

Corrosion inhibitor (CRW) 25-100 ppm

Scale inhibitor (scaletreat) 10-100 ppm

Corrosion inhibitors list: CRW 85194, CRW 85348, CRW 85270, CRW 85593, CRW 85282

Scale inhibitors list: Scaletreat 10-551, Scaletreat 10-555, Scaletreat 10-550, Scaletreat 10-553, Scaletreat 10-554, Scaletreat 10-552

Flocculants list: Floctreat (received also from Clariant Oil Services) and CF (that was prepared in the laboratory)

6.1.2 Results

Results from the turbidity measurements tests are presented in tables 12-17 and Figures 14-25. First experiments was performed using Ula oil, afterwards- Ekofisk oil. Each of chemicals

were used individually. In the tables and figures chemicals expressed as chemical # (1-6). Some pictures taken during the tests are available in Appendix.

Jar-test 1 (Ula oil)

Oily water's turbidity before flocculation is 43.8 NTU.

Floctreat's results (without added other chemicals): 10 ppm – 14.9 NTU

50 ppm – 17.1 NTU

100 ppm - 17.8 NTU

Chemical 1 = CRW 85194 (corrosion inhibitor)

Chemical 2 = CRW 85270 (corrosion inhibitor)

Table 12: Data from Jar-test 1

CFG mg/L	Flocculation without chemicals presence	Flocculation with chemical 1			Flocculation with chemical 2		
		25 ppm	50 ppm	100 ppm	25 ppm	50 ppm	100 ppm
	Turbidity	Turbidity	Turbidity	Turbidity	Turbidity	Turbidity	Turbidity
0.5	27.3	40.0	44.0	60.6	25.3	66.7	69.7
1	14.2	26.6	33.8	38.5	22.8	59.0	61.1
2	11.3	17.3	22.5	32.5	21.0	41.3	38.3
2.5	10.4	11.5	16.0	22.8	13.9	33.4	23.4
3	5.3	4.7	6.8	13.3	12.0	10.3	10.4

The data from Table 12 demonstrated in Figures 14 and 15.
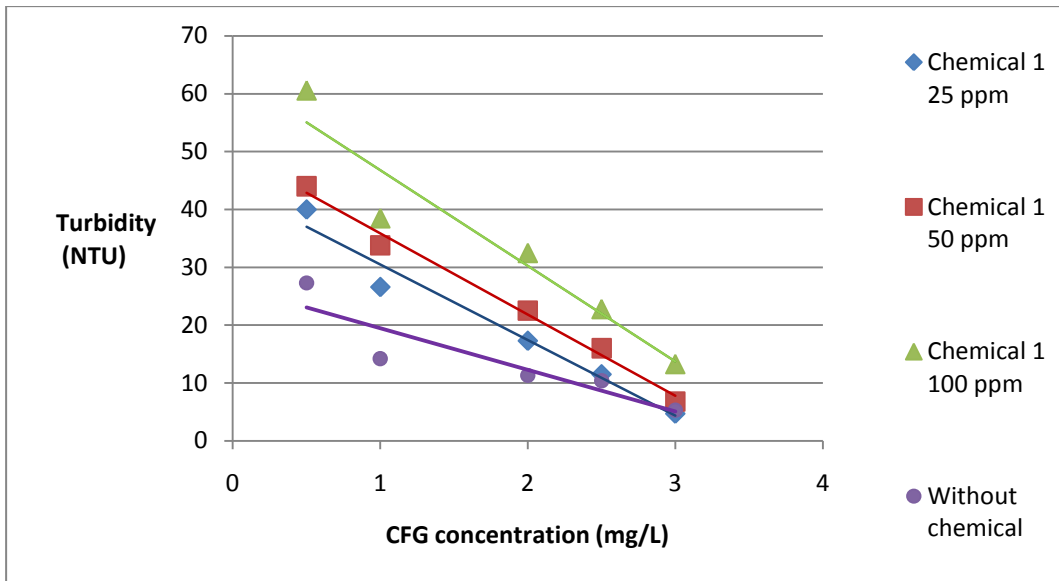
Figure 14: Results from Jar-test 1
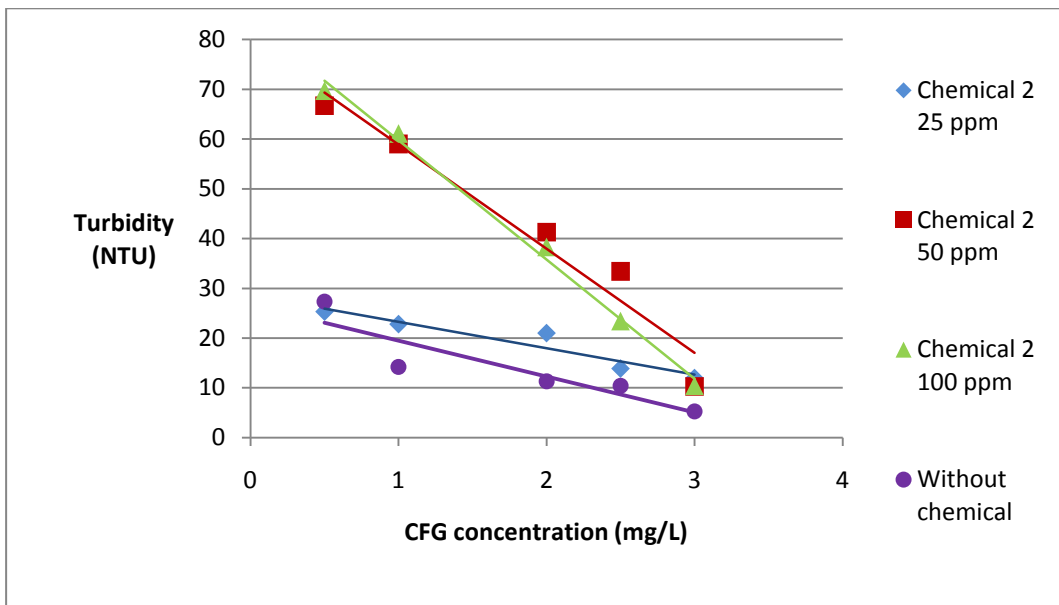
Figure 15: Results from Jar-test 1

Jar-test 2 (Ula oil)

Chemical 3 = CRW 85593 (corrosion inhibitor)

Chemical 4 = scaletreat 10-551 (scale inhibitor)

Table 13: Results from Jar-test 2

CFG mg/L	Flocculation without chemicals presence	Flocculation with chemical 3			Flocculation with chemical 4		
		25 ppm	50 ppm	100 ppm	10 ppm	50 ppm	100 ppm
	Turbidity	Turbidity	Turbidity	Turbidity	Turbidity	Turbidity	Turbidity
0.5	27.3	33.8	40.3	32.4	35.7	35.2	18.1
1	14.2	20.2	29.0	26.2	39.2	37.5	16.9
2	11.3	16.4	17.5	10.0	25.1	22.0	7.1
2.5	10.4	8.8	7.7	6.4	15.6	8.76	5.8
3	5.3	4.8	3.9	3.4	13.1	7.3	4.6

The data from Table 13 is demonstrated in Figures 16 and 17.
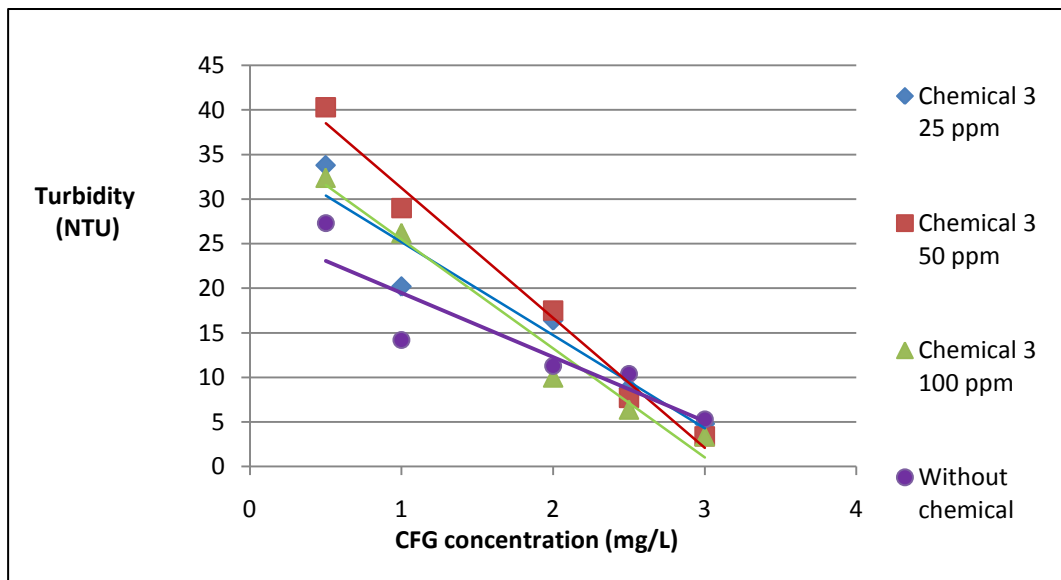
Figure 16: Results from Jar-test 2

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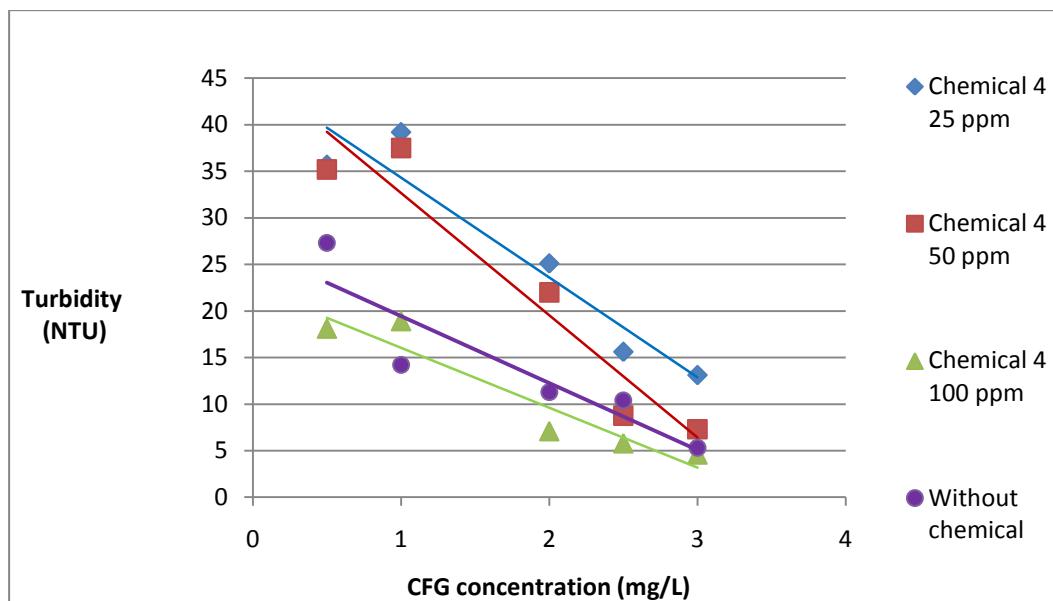
Figure 17: Results from Jar-test 2

Jar-test 3 (Ula oil)

Chemical 5 = scaletreat 10-550 (scale inhibitor)

Chemical 6 = scaletreat 10-554 (scale inhibitor)

Table 14: Results from Jar-test 3

CFG mg/L	Flocculation without chemicals presence	Flocculation with chemical 5			Flocculation with chemical 6		
	Turbidity	10 ppm	50 ppm	100 ppm	10 ppm	50 ppm	100 ppm
		Turbidity	Turbidity	Turbidity	Turbidity	Turbidity	Turbidity
0.5	27.3	31.8	34.4	52.5	36.1	36.6	42.1
1	14.2	30.9	23.8	43.3	28.3	36.1	23.4
2	11.3	28.1	18.8	20.6	11.4	34.2	21.1
2.5	10.4	17.4	11.0	7.9	8.3	12.6	6.9
3	5.3	10.2	8.3	7.5	3.1	8.6	6.4

The data from Table 14 is demonstrated in Figures 18 and 19.
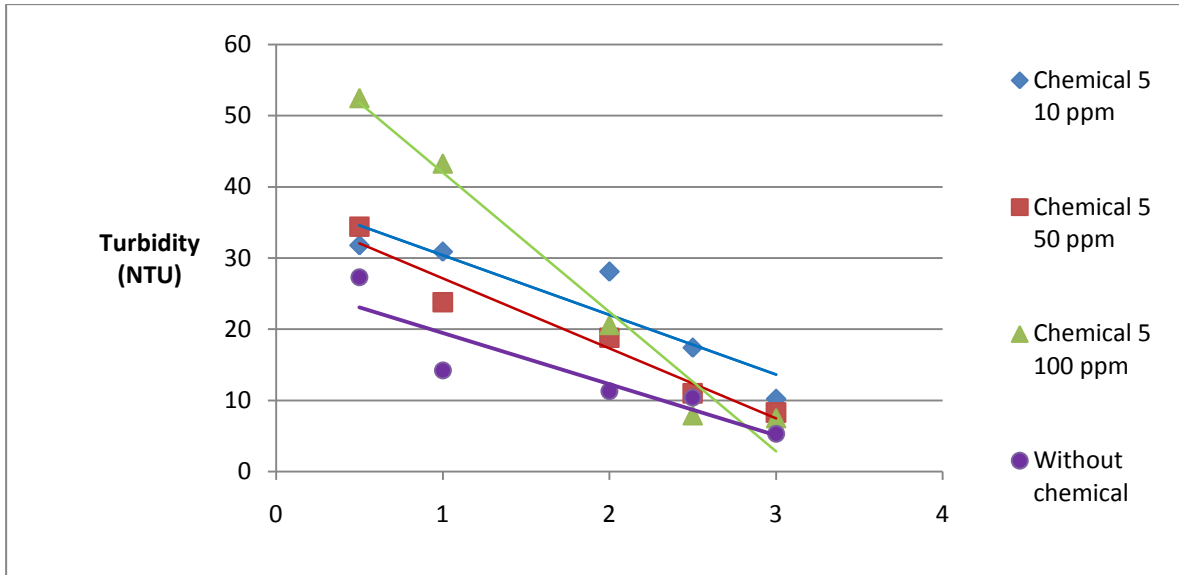
Figure 18: Results from Jar-test 3
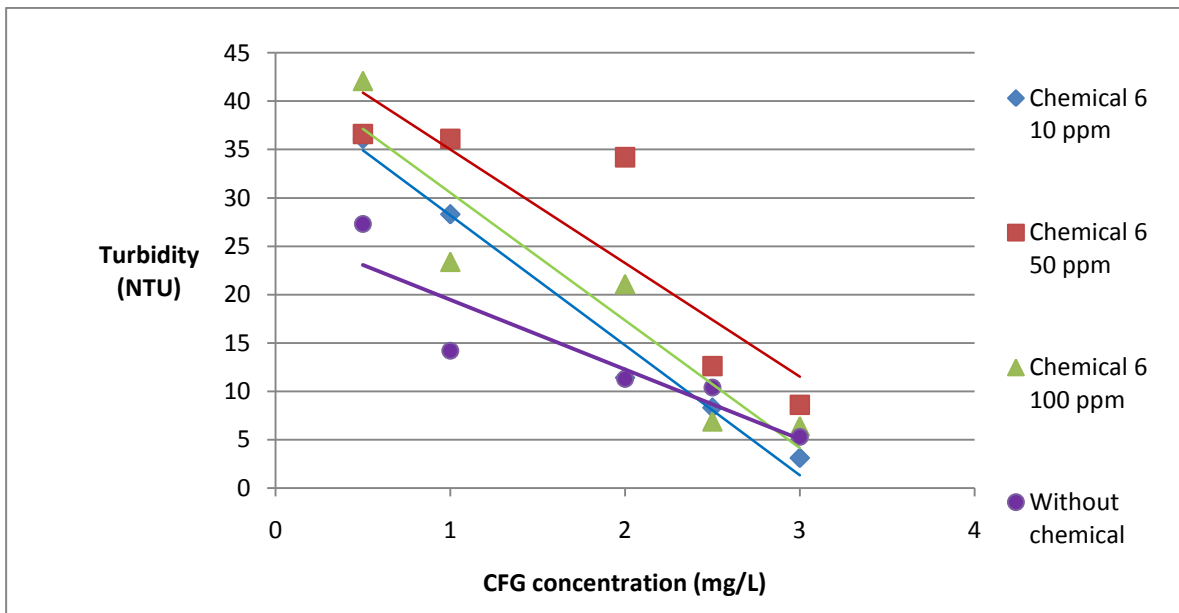
Figure 19: Results from Jar-test 3

Jar-test 4 (Ekofisk oil)

Oily water's turbidity before flocculation is 75.7 NTU

Chemical 1 = CRW 85194 (corrosion inhibitor)

Chemical 2 = CRW 85270 (corrosion inhibitor)

Table 15: Results from Jar-test 4

CFG mg/L	Flocculation without chemicals presence	Flocculation with chemical 1			Flocculation with chemical 2		
		25 ppm	50 ppm	100 ppm	25 ppm	50 ppm	100 ppm
	Turbidity	Turbidity	Turbidity	Turbidity	Turbidity	Turbidity	Turbidity
0.5	37.0	65.8	38.0	59.7	38.2	62.2	85.7
1	10.6	27.5	18.0	23.1	18.3	25.8	32.8
2	8.6	18.6	14.5	20.6	13.5	25.1	29.0
2.5	5.9	11.3	11.1	10.5	11.5	18.9	21.3
3	4.6	8.0	4.6	4.7	10.4	11.4	12.3

The data from Table 15 is demonstrated in Figures 20 and 21.
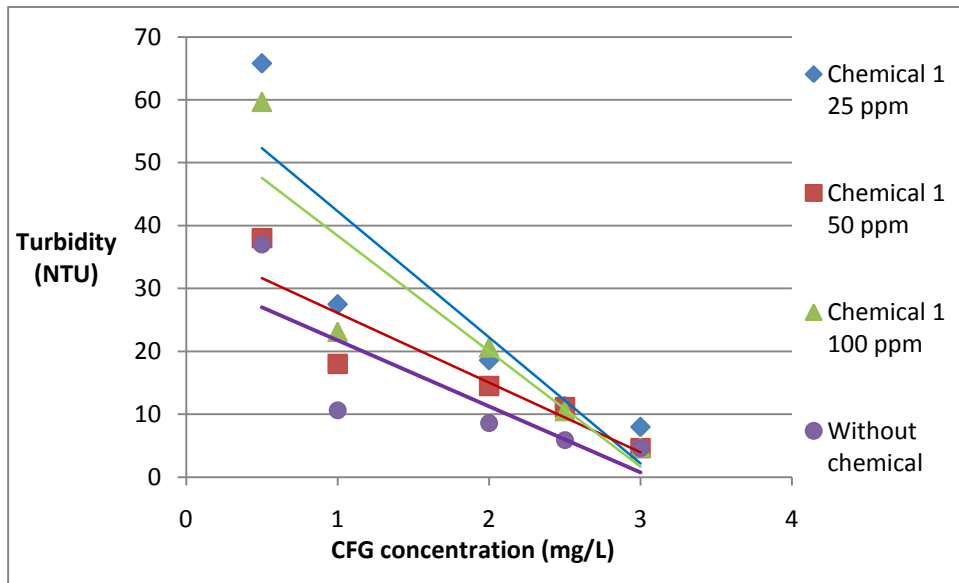
Figure 20: Jar test 4 results
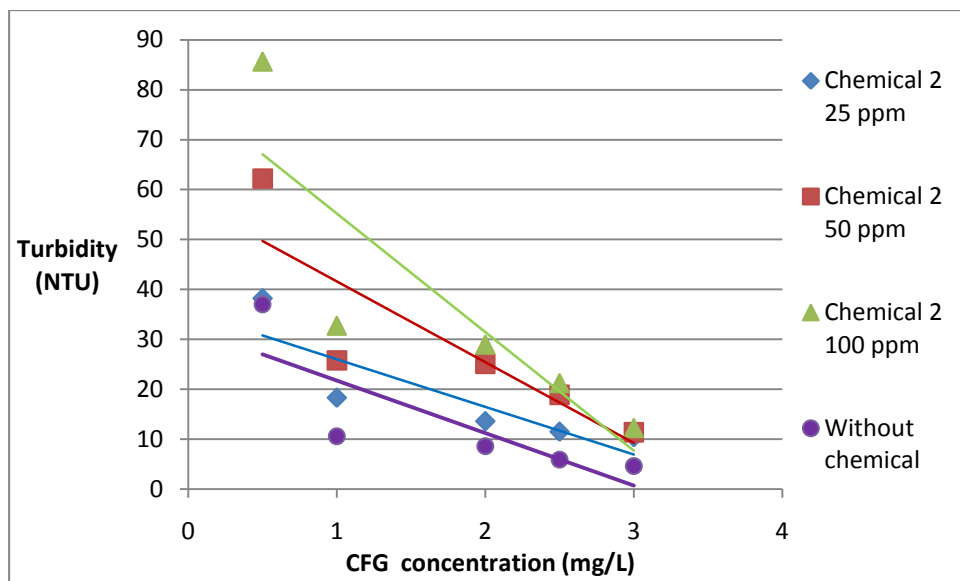
Figure 21: Results from Jar test 4

Jar-test 5 (Ekofisk oil)

Chemical 3 = CRW 85593(corrosion inhibitor)

Chemical 4 = scaletreat 10-551 (scale inhibitor)

Table 16: Results from Jar-test 5

CFG mg/L	Flocculation without chemicals presence	Flocculation with chemical 3			Flocculation with chemical 4		
		25 ppm	50 ppm	100 ppm	10 ppm	50 ppm	100 ppm
	Turbidity	Turbidity	Turbidity	Turbidity	Turbidity	Turbidity	Turbidity
0.5	37.0	45.6	45.1	51.8	31.4	17.2	11.0
1	10.6	17.0	34.7	22.0	17.1	15.8	8.7
2	8.6	13.1	19.4	19.6	9.5	6.1	6.6
2.5	5.9	9.1	16.9	14.4	9.2	5.5	4.5
3	4.6	9.1	7.3	4.7	5.6	5.1	2.2

The data from Table 16 is demonstrated in Figures 22 and 23.
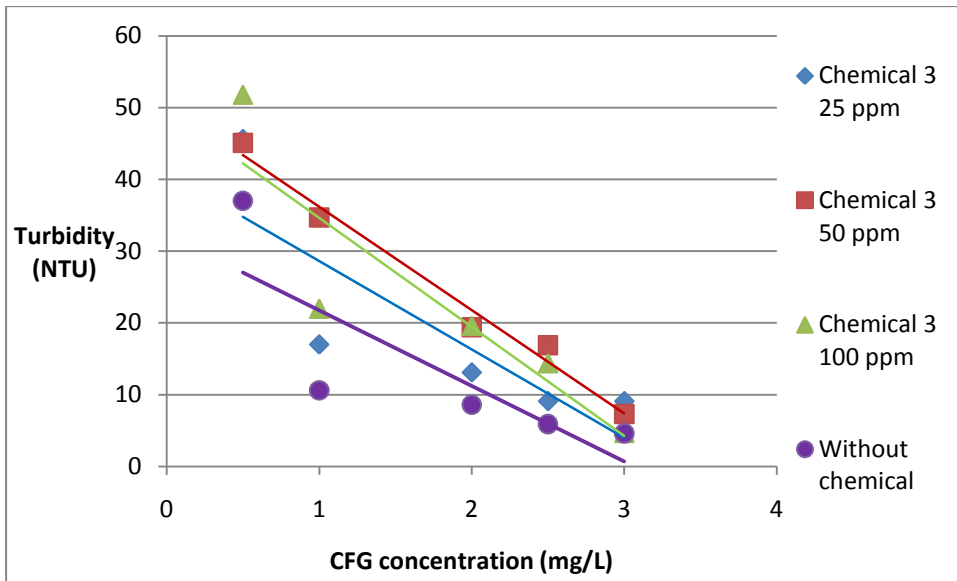
Figure 22: Results from Jar-test 5
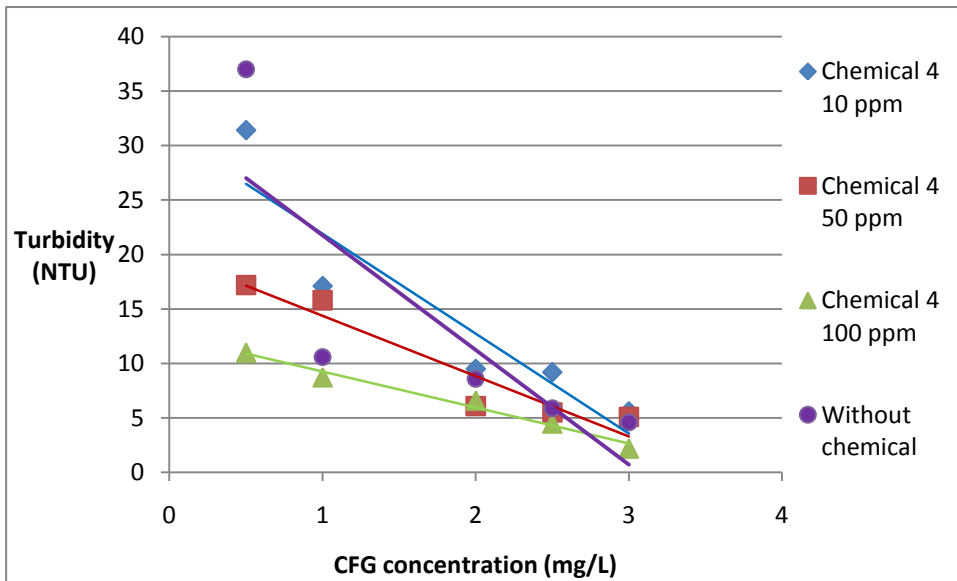
Figure 23: Results from Jar-test 5

Jar-test 6 (Ekofisk oil)

Chemical 5 = scaletreat 10-550 (scale inhibitor)

Chemical 6 = scaletreat 10-554 (scale inhibitor)

Table 14: Results from Jar-test 17

CFG mg/L	Flocculation without chemicals presence	Flocculation with chemical 5			Flocculation with chemical 6		
		10 ppm	50 ppm	100 ppm	10 ppm	50 ppm	100 ppm
	Turbidity	Turbidity	Turbidity	Turbidity	Turbidity	Turbidity	Turbidity
0.5	37.0	35.1	26.8	17.2	50.3	68.8	58.5
1	10.6	10.1	8.7	6.8	6.7	20.2	11.1
2	8.6	4.8	4.8	6.2	6.7	7.3	7.9
2.5	5.9	3.2	4.5	5.5	5.6	5.7	7.2
3	4.6	3.1	4.3	5.4	3.5	6.4	3.8

The data from Table 17 is demonstrated in Figures 24 and 25.
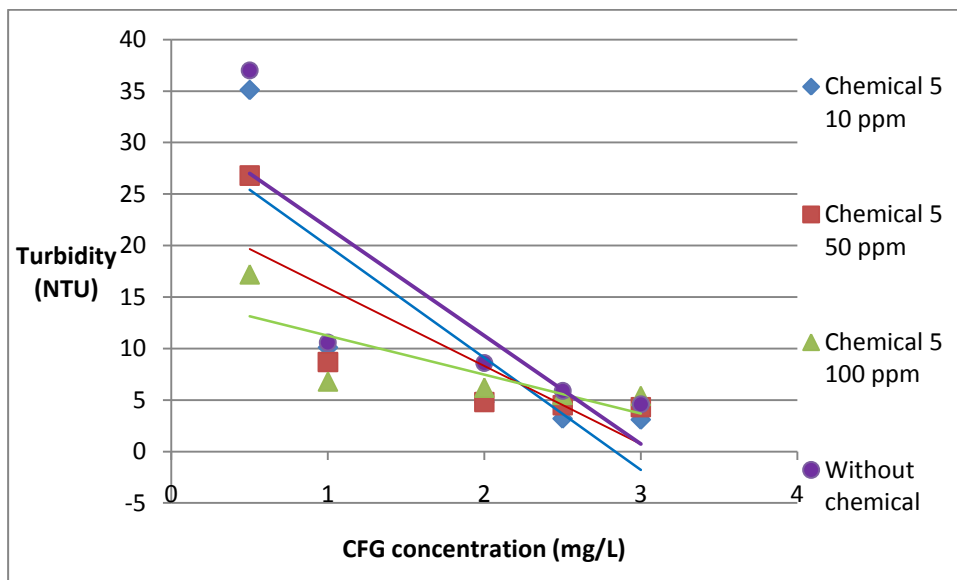
Figure 24: Results from Jar-test 6

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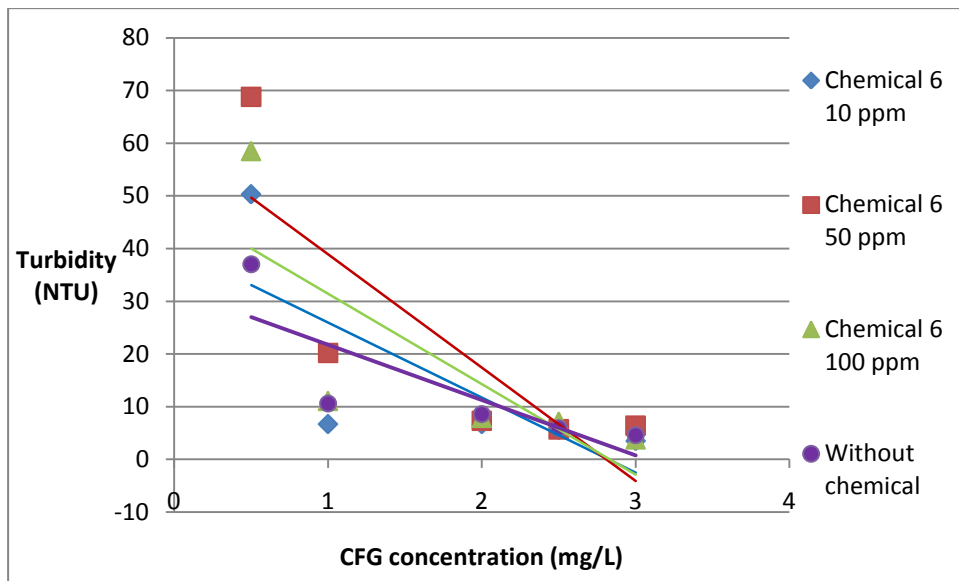
Figure 25: Results from Jar-test 6

6.1.3 Discussion and conclusion

From the results of tests with turbidity measurements it is fully possible to prove that production chemicals have an effect on the flocculation process with CFG used as a flocculant. Floctreat from Clariant did not give visible results, and further use of Floctreat was discontinued. Separation efficiency depends on concentration of chemicals as well as on concentration of CFG. Variation of separation score can be explained from difference of chemicals. Even though it is not possible to get more information about chemical structure of the chemicals that were used in the tests, it is completely clear that the presence of production chemicals will typically decrease or enhance separation efficiency depending on concentration of these and the concentration of flocculants. It means that for some concentrations the production chemicals can promote flocculation and take on function as a flocculating agent. This is possible only in presence of high concentration of CFG. Lower than 2 mg/L concentrations of flocculant when production chemicals are present, provide increased turbidity compared with flocculation process without chemicals presence.

The lack of knowledge about chemical structure of the chemicals is a main disadvantage in analysis of the tests results. It could be interesting to discuss the charge and molecular weight of chemicals components to get a full picture over aggregation process.

6.2 Tests with particle size measuring

This part of the experiments was done with Mastersizer 2000 (Figure 26) created by Malvern Instruments for particle size analysis. Malvern was one of the early pioneers of laser diffraction technology.

6.2.1 Mastersizer 2000

Principles of measurement

The diffraction light pattern (He-Ne laser) is dependent on the particle size. The laser diffraction pattern is measured and correlated to the particle size distribution based on Fraunhofer or Mie theory. The last one predicts the light scattering behavior of all materials under all conditions. The use of Mie theory presupposes knowledge of the light refractive index of the particles and the dispersion media and the imaginary part of the refractive index of the particles.

Figure 26: Mastersizer 2000.

Parameters and applications

Volume particle size distribution (0.02 – 2000 μm)

6.2.2 Tests forecast

The results from tests using Mastersizer 2000 include thousands of measurements. They were sorted and some made accessible in Appendix part (tables with data and figures with frequency curves).

The tests are divided in groups:

➢ Making stable oil-in water emulsions

- ➢ Flocculation without chemicals
- ➢ Flocculation with chemicals
    - ❖ Flocculation with corrosion inhibitor (CI)
    - ❖ Flocculation with scale inhibitor (SI)
    - ❖ Flocculation with both CI and SI
- ➢ Flocculation with/without chemicals by Floctreat (flocculant from Clariant)
- ➢ Shear forces
- ➢ A closer look on flocculation process during the first minutes

Chemicals that are used in tests are:
- ✓ CRW 85194 (corrosion inhib.), called here from CI 1
- ✓ CRW 85270 (corrosion inhib.), CI 2
- ✓ CRW 85593(corrosion inhib.), CI 3
- ✓ Scaletreat 10-550, SI 1
- ✓ Scaletreat 10-551, SI 2
- ✓ Scaletreat 10-554, SI 3

During the experiments oily water was always prepared with concentration of 250 ppm of oil (mostly Ekofisk, fewer times Ula).

6.2.3 Making stable oil-in-water emulsions

Chapter 4 covered emulsions theory and described factors affecting the stability of emulsion. Effect of very shear forces is mentioned previously in this report. High shear causes violent mixing of oil and water and leads to smaller droplet sizes. Smaller droplets are relatively more stable than larger droplets.

During the experiments OIW emulsions were made (just like in turbidity measurement-tests, see in sub-chapter 6.1) by using Silverson mixer. With Mastersizer it was possible to measure particle size distribution and check the stability of emulsions.

After numerous tests it was concluded that the emulsions made during experiments, were stable and independent of mixing residence time. Table 1 in Appendix present data from the

tests with measurements of samples done instantly after the mixing, measurements of the same sample after a short period of time (2-5 min) and measurements after various mixing residence times. The results are roughly similar. That means that stability of emulsion does not change with time (meaning in a short period of time like 1-1.5 hours) and does not depend on mixing time. All other factors (temperature, pH, used materials and method) were the same in the tests.

Figure 27 below shows measurements record of synthetic produced water with 250 ppm Ekofisk.
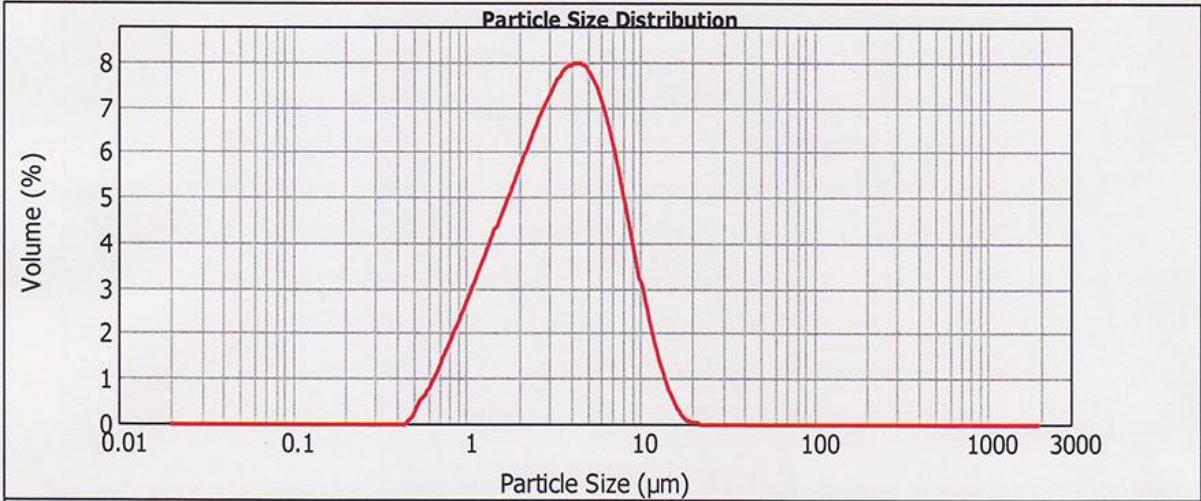
Figure 27: Oily water (250 ppm Ekofisk)

Table 18 shows the average data from tests "Making of stable emulsions".

Table 18: Stable emulsions OIW (average data)

Average results Ekofisk/Ula 250 ppm	d (0.1)	d (0.5)	d (0.9)	D[3, 2]- Surface weighted	D[4, 3]- Volume weighted	Result 8-10 µm
Ekofisk 1	1.263	3.393	9.372	2.593	4.532	5.805
Ekofisk 2	1.205	3.506	9.530	2.562	4.620	6.244
Ula (5 min)	1.353	3.825	10.475	2.831	5.029	7.488

Descriptions:

Ekofisk 1 – several measurements of the same sample during 1-1.5 hours

Ekofisk 2 – measurements of some samples with 1-5 minutes mixing residence time

Ula (5 min) - measurements of sample with 5-minutes mixing

D (0, 5), **D (0, 1)** and **D (0, 9)** are standard **percentile** readings from the analysis.

- **D(0, 5)** is the size in microns at which 50% of the sample is smaller and 50% is larger. This value is also known as the Mass Median Diameter (MMD) or the median of the volume distribution. Emulsions with D (O, 5) under 5 µm are mostly stable.

- **D (0, 1)** is the size of particle below which 10% of the sample lies.

- **D (0, 9)** is the size of particle below which 90% of the sample lies.

- **D [4, 3]** is the **Volume Weighted Mean** or Mass Moment Mean Diameter.

- **D [3, 2]** is the **Surface Weighted Mean**, also known as the Surface Area Moment Mean Diameter.

- Result 8-10 µm shows volume of particles with size 8-10 µm in %.

Concentration of oil ranged between 115 and 141 ppm, when ideally this should be 250 ppm. This can be explained by the fact that some amount of oil can be lost when during the mixing when oil attaches itself to surfaces such as the container and the mixer.

6.2.4 Flocculation without chemicals

The emulsions which were prepared in previous experiments were used in floc- tests without chemicals. CFG was used as flocculating agent in different concentrations (from 0.5 mg/L to 3 mg/L); fixed chitosan 0.5 mg/L; preparation of these is described in 6.1.

The data given in Table 19 below contains selected records (otherwise there are a lot of data from floc tests with variable numbers depending on when the measure was taken). Later (in 6.2.2.5) it will be explained the possible reason of these differences.

Table 19: Various concentrations of flocculant used in floc tests

Floc test CFG	D (0, 1)	D (0, 5)	D (0, 9)	D [3, 2] - Surface weighted mean	D [4, 3] - Volume weighted mean	Result 8.00μm-10.00μm
0.5 mg/L	46.782	178.283	441.194	31.557	214.268	0.330
1 mg/L	55.091	185.298	676.327	56.831	298.232	0.191
2 mg/L	115.308	396.215	827.410	235.156	436.763	0.000
2.5 mg/L	137.679	464.597	1084.545	279.894	546.275	0.000
3 mg/L	157.265	685.100	1355.179	339.409	728.824	0.000
OIW (Ekofisk)	1.213	3.548	8.360	2.559	4.274	6.161

The table contains the data for oily water (for comparing reason). Without doubt the full separation occurs after adding the flocculant: droplet size increases dramatically.

The Figure 28 below presents the data from the Table 19. Different colors indicate the results of experiments:

— OiW Ekofisk 250 ppm   — Floc test CFG 2 mg/L

— Floc test CFG 0.5 mg/L   — Floc test CFG 2.5 mg/L

— Floc test CFG 1 mg/L   — Floc test CFG 3 mg/L
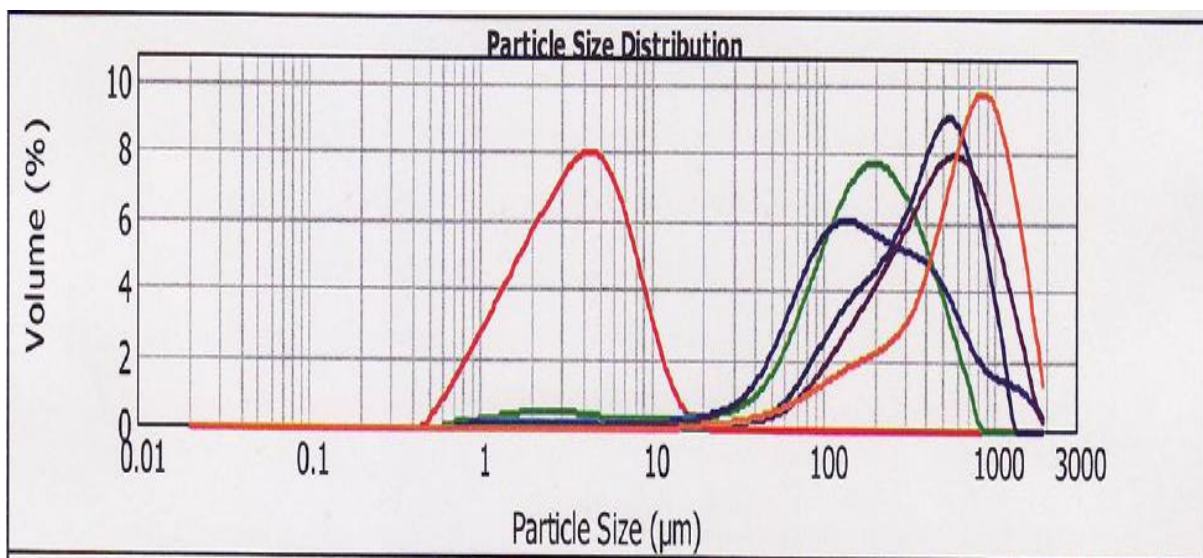
Figire 28: Flocculation with CFG (0.5-3 mg/L)

6.2.5 Flocculation with chemicals

- ➢ Flocculation with corrosion inhibitor (CI)
- ➢ Flocculation with scale inhibitor (SI)
- ➢ Flocculation with both CI and SI

6.2.5.1 Flocculation with corrosion inhibitors (CI)

Table 20 contains the data from floc tests with corrosion inhibitors (CI 1-CI 3). Oily water (250 ppm Ekofisk) and flocculation without chemical are included for comparing purpose.

Table 20: Flocculation with CI

Floc test with CI (1 mg/L CFG, OIW Ekofisk)		D (0, 1)	D (0, 5)	D (0, 9)	D [3, 2] - Surface weighted mean	D [4, 3] - Volume weighted mean	Result 8.00µm-10.00µm
CI 1 (25 ppm)	Average result	60.157	197.932	534.244	18.809	253.674	0.309
	First result	67.726	212.717	573.927	56.223	271.684	0.202
CI 1 (50 ppm)	Average result	40.810	129.335	360.334	39.845	172.040	0.230
	First result	45.049	140.719	397.361	54.668	185.593	0.238
CI 1 (100 ppm)	Average result	43.082	117.138	320.567	40.235	155.899	0.286
	First result	50.871	169.568	547.014	71.268	242.620	0.184
Floc test without chemical (average) 1 mg/L CFG		55.091	185.298	676.327	56.831	298.232	0.191
CI 2 (25 ppm)	Average result	75.266	247.012	779.542	88.556	350.115	0.115
	First result	65.373	191.127	508.099	61.431	250.184	0.134
CI 2 (50 ppm)	Average result	118.407	612.341	1213.955	288.517	642.928	0.000
	First result	95.368	277.152	619.837	187.727	321.408	0.000
CI 2 (100 ppm)	Average result	47.405	131.859	446.826	47.949	200.314	0.211
	First result	41.251	101.323	219.484	35.865	116.766	0.246
Floc test without chemical (average) 1 mg/L CFG		55.091	185.298	676.327	56.831	298.232	0.191

CI 3 (25 ppm)	Average result	107.945	785.662	1425.787	251.590	791.396	0.012
	First result	85.466	686.213	1363.032	148.299	709.615	0.078
CI 3 (50 ppm)	Average result	57.279	461.515	1076.645	67.264	516.441	0.022
	First result	51.152	409.788	976.125	60.888	462.360	0.025
CI 3 (100 ppm)	Average result	187.536	737.759	1404.806	334.710	776.280	0.000
	First result	155.213	737.895	1411.852	313.522	773.120	0.000
Floc test without chemical (average) 1 mg/L CFG		55.091	185.298	676.327	56.831	298.232	0.191
OIW (Ekofisk)		1.310	3.217	6.985	2.533	3.766	3.985

Each sample was measured several times with 20-30 seconds between measurements; therefore in Table 20 represented averaged results and the very first measuring data. Analyzing of data leads to conclusion that corrosion inhibitors are typically enhance or does not disturb very much the oil/water separation.

Figure 29 represents the data of flocculation test with corrosion inhibitor (CI 3)

— Floc test CFG (1 mg/L), without chemical

— Floc test CI 3 (100 ppm) + CFG (1 mg /L)
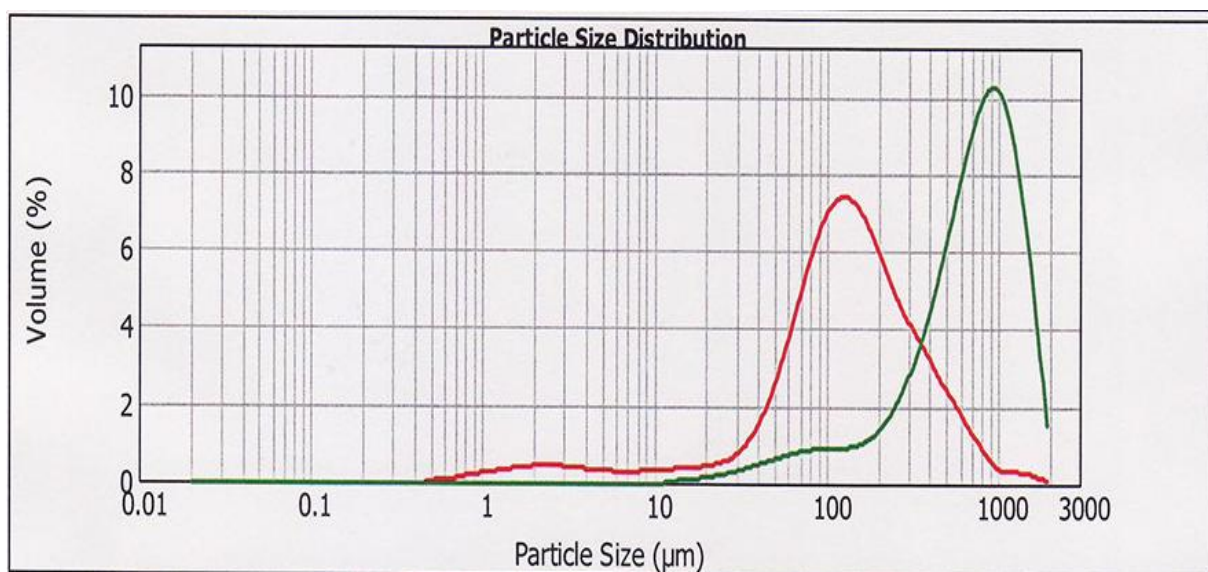
Figure 29: Flocculation with corrosion inhibitor

6.2.5.2 Flocculation with scale inhibitor (SI)

In these experiments the chemical is dissolved in water before mixing with oil because scale inhibitors should be added to water before injection, as a result SI dissolves in water before it comes in contact with oil. Therefore in Table 21, showing the data from floc tests with scale inhibitors (SI 1-SI 3), with red text is written SI # (concentration) + concentration oil. As in previous case oily water and flocculation without chemical are included for comparing purpose. The same applies for average and first result as well.

Table 21: Floc tests with scaling inhibitors.

Floc test 1 mg/L CFG, 250 ppm Ekofisk		D (0, 1)	D (0, 5)	D (0, 9)	D [3, 2] - Surface weighted mean	D [4, 3] - Volume weighted mean	Result 8.00μm-10.00μm
SI 1 (25 ppm) + 250 ppm Ekofisk		1.101	3.020	10.006	2.323	4.469	5.605
SI 1 (25 ppm)	Average result	62.364	412.024	1107.558	79.306	503.093	0.150
	First result	57.724	215.960	648.287	49.650	291.690	0.192
SI 1 (100 ppm) + 250 ppm Ekofisk		1.111	2.678	8.060	2.198	3.759	4.247
SI 1 (100 ppm)	Average result	85.927	579.849	1196.354	112.990	617.393	0.095
	First result	56.092	250.450	672.460	59.267	312.555	0.167
Floc test without chemical (average) 1 mg/L CFG		55.091	185.298	676.327	56.831	298.232	0.191
SI 2 (25 ppm) + 250 ppm Ekofisk		1.184	3.255	8.575	2.455	4.187	5.897
SI 2 (25 ppm)	Average result	59.460	215.192	552.086	39.804	273.515	0.419
	First result	52.560	195.933	447.263	35.987	226.641	0.308
SI 2 (50 ppm) + 250 ppm Ekofisk		1.244	3.564	7.584	2.586	4.054	5.438
SI 2 (50 ppm)	Average result	122.499	735.875	1367.016	166.179	753.572	0.091
	First result	70.842	326.524	755.226	73.631	372.175	0.207
SI 2 (100 ppm) + 250 ppm Ekofisk		1.120	2.943	8.918	2.305	4.152	5.012
SI 2	Average result	109.578	633.831	1275.578	251.592	670.943	0.000

(100 ppm)	First result	120.333	743.520	1371.722	302.662	764.769	0.000
Floc test without chemical (average) 1 mg/L CFG		55.091	185.298	676.327	56.831	298.232	0.191
SI 3 (25 ppm)+ 250 ppm Ekofisk		1.244	3.472	7.297	2.553	3.933	4.837
SI 3 (25 ppm)	Average result	70.635	427.135	1109.198	72.150	512.813	0.136
	First result	111.289	661.724	1282.000	281.131	687.245	0.000
SI 3 (100 ppm)+ 250 ppm Ekofisk		1.230	3.509	7.711	2.556	4.064	5.587
SI 3 (100 ppm)	Average result	70.789	498.115	115.541	78.606	549.465	0.219
	First result	86.353	687.367	1384.039	101.964	705.508	0.144
Floc test without chemical (average) 1 mg/L CFG		55.091	185.298	676.327	56.831	298.232	0.191

From the data presented in Table 21 above one can consider that some of scaling inhibitors (for instance SI 2) disturb the flocculation process in low concentration and enhance with higher concentrations. The others show the opposite result.

The Figure 30 below shows diagrams made on the data from flocculation with scaling inhibitor (SI 2, 50 ppm) in the sample.

— Floc test CFG (1 mg/L), without chemical   — Floc test SI 2 (50 ppm) + CFG (mg /L)
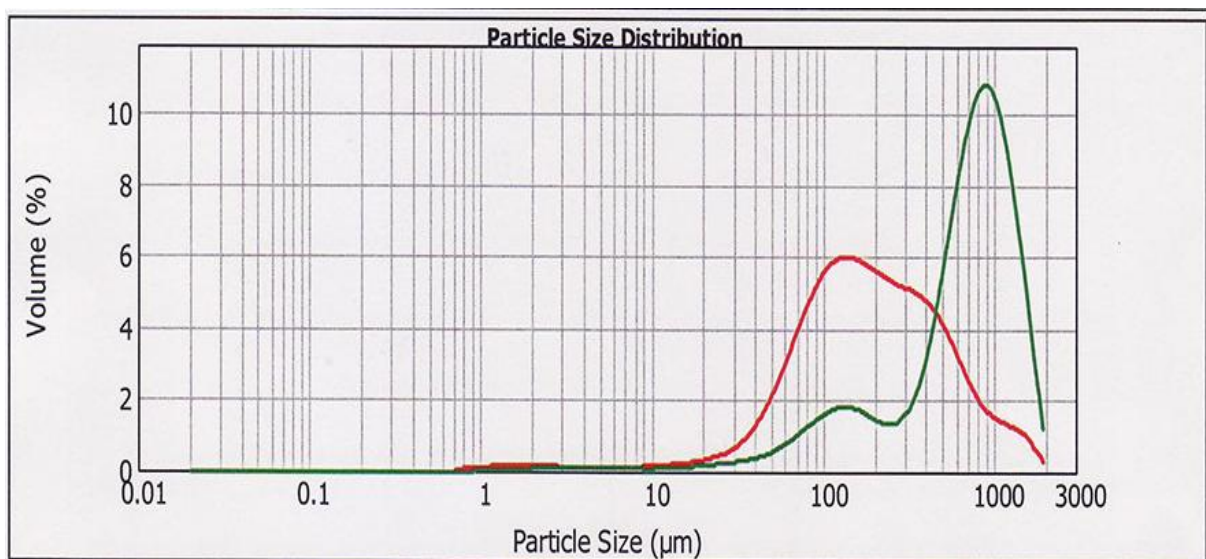
Figure 30: Flocculation with scaling inhibitor

6.2.5.3 Flocculation with both CI and SI

This part includes experiments where both corrosion inhibitors and scale inhibitors were added to sample before flocculation process. Due to high number of probable combinations and a lot of measured data (if all 6 chemicals were tested), was decided to use only a few of the chemicals and some various concentrations.

Table 22: Floc test with combination of scale inhibitor SI 1 and corrosion inhibitors CI 2 and CI 3

Floc test		D (0, 1)	D (0, 5)	D (0, 9)	D [3, 2] - Surface weighted mean	D [4, 3] - Volume weighted mean	Result 8.00µm- 10.00µm
SI 1 (25 ppm) + 250 ppm Ekofisk		1.101	3.020	10.006	2.323	4.469	5.605
Floc test without chemical (average) 1 mg/L CFG		55.091	185.298	676.327	56.831	298.232	0.191
SI 1 (25 ppm) + 250 ppm Ekofisk + 1 mg/L CFG	Average result	62.364	412.024	1107.558	79.306	503.093	0.150
	First result	57.724	215.960	648.287	49.650	291.690	0.192
SI 1 (25 ppm) + 250 ppm Ekofisk + CI 2 (25 ppm) + 1mg/L CFG	Average result	136.716	736.977	1391.357	252.686	764.072	0.009
	First result	95.177	412.048	984.028	208.896	481.439	0.064
SI 1 (25 ppm) + 250 ppm Ekofisk + CI 2 (50 ppm) + 1 mg/L CFG	Average result	128.637	742.799	1447.200	268.419	768.003	0.011
	First result	76.062	241.628	586.914	88.284	290.685	0.108
SI 1 (25 ppm) + 250 ppm Ekofisk + CI 2 (100 ppm) + 1mg/L CFG	Average result	97.155	630.152	1271.088	132.419	663.069	0.027
	First result	73.543	361.992	926.051	91.141	435.188	0.109
SI 1 (25 ppm) + 250 ppm Ekofisk + CI 3 (25 ppm) + 1 mg/L CFG	Average result	101.678	627.420	1269.118	125.060	660.034	0.048
	First result	92.104	413.766	858.185	202.572	444.927	0.104
SI 1 (25 ppm) + 250 ppm Ekofisk + CI 3 (50 ppm) + 1 mg/L CFG	Average result	71.259	454.118	1125.845	65.701	529.321	0.083
	First result	104.459	538.947	1161.958	246.789	593.502	0.000
SI 1 (25 ppm) + 250 ppm Ekofisk + CI 3 (100 ppm) + 1 mg/L CFG	Average result	109.741	737.598	1360.689	106.471	753.641	0.034
	First result	188.350	734.695	1362.148	363.090	770.070	0.000

		D (0, 1)	D (0, 5)	D (0, 9)	D [3, 2] - Surface weighted mean	D [4, 3] - Volume weighted mean	Result 8.00μm-10.00μm
SI 1 (100 ppm) + 250 ppm Ekofisk		1.111	2.678	8.060	2.198	3.759	4.247
Floc test without chemical (average) 1 mg/L CFG		55.091	185.298	676.327	56.831	298.232	0.191
SI 1 (100 ppm) + 250 ppm Ekofisk + 1 mg/L CFG	Average result	85.927	579.849	1196.354	112.990	617.393	0.095
	First result	56.092	250.450	672.460	59.267	312.555	0.167
SI 1 (100 ppm) + 250 ppm Ekofisk + CI 2 (25 ppm) + 1 mg/L CFG	Average result	68.185	354.796	688.336	87.565	367.722	0.083
	First result	54.179	151.441	372.813	56.871	185.451	0.162
SI 1 (100 ppm) + 250 ppm Ekofisk + CI 2 (50 ppm) + 1 mg/L CFG	Average result	66.548	423.595	1177.280	75.241	526.878	0.089
	First result	42.302	136.013	367.064	36.557	173.670	0.215
SI 1 (100 ppm) + 250 ppm Ekofisk + CI 2 (100 ppm) + 1 mg/L CFG	Average result	71.730	467.093	1140.978	74.467	538.836	0.088
	First result	47.233	156.982	444.945	43.703	204.802	0.206
SI 1 (100 ppm) + 250 ppm Ekofisk + CI 3 (25 ppm) + 1mg/L CFG	Average result	79.367	527.979	1239.693	79.274	593.623	0.092
	First result	55.506	167.058	468.102	51.827	224.712	0.181
SI 1 (100 ppm) + 250 ppm Ekofisk + CI 3 (50 ppm) + 1 mg/L CFG	Average result	89.559	701.875	1401.204	110.494	716.948	0.054
	First result	44.741	137.073	355.813	38.278	171.680	0.229
SI 1 (100 ppm) + 250 ppm Ekofisk + CI 3 (100 ppm) + 1 mg/L CFG	Average result	108.202	730.203	1425.999	110.129	750.789	0.026
	First result	81.043	338.956	1018.583	109.717	455.646	0.114

Table 23: Floc test with combination of scale inhibitor SI 2 and corrosion inhibitors CI 2 and CI 3

Floc test		D (0, 1)	D (0, 5)	D (0, 9)	D [3, 2] - Surface weighted mean	D [4, 3] - Volume weighted mean	Result 8.00μm-10.00μm
SI 2 (25 ppm) + 250 ppm Ekofisk		1.184	3.255	8.575	2.455	4.187	5.897
Floc test without chemical (average) 1 mg/L CFG		55.091	185.298	676.327	56.831	298.232	0.191
SI 2 (25 ppm) + 250 ppm Ekofisk + 1 mg/L CFG	Average result	59.460	215.192	552.086	39.804	273.515	0.419
	First result	52.560	195.933	447.263	35.987	226.641	0.308

SI 2 (25 ppm) + 250 ppm Ekofisk + CI 2 (25 ppm) + 1 mg/L CFG	Average result	60.558	341.189	1037.385	44.615	453.097	0.133
	First result	88.234	517.499	1206.495	92.081	585.116	0.000
SI 2 (25 ppm) + 250 ppm Ekofisk + CI 2 (50 ppm) +1 mg/L CFG	Average result	39.986	195.346	575.833	39.217	260.072	0.284
	First result	30.202	116.559	290.720	27.959	140.924	0.386
SI 2 (25 ppm) + 250 ppm Ekofisk + CI 2 (100 ppm) + 1 mg/L CFG	Average result	88.021	531.724	1169.031	151.372	583.948	0.041
	First result	71.621	351.531	756.755	89.219	383.827	0.113
SI 2 (50 ppm) + 250 ppm Ekofisk		1.198	3.893	9.168	2.639	4.639	7.856
Floc test without chemical (average) 1 mg/L CFG		55.091	185.298	676.327	56.831	298.232	0.191
SI 2 (50 ppm) + 250 ppm Ekofisk + 1 mg/L CFG	Average result	122.499	735.875	1367.016	166.179	753.572	0.091
	First result	70.842	326.524	755.226	73.631	372.175	0.207
SI 2 (50 ppm) + 250 ppm Ekofisk + CI 2 (25 ppm) + 1 mg/L CFG	Average result	84.275	697.383	1425.593	56.810	724.209	0.132
	First result	155.350	786.114	1442.657	359.195	808.865	0.000
SI 2 (50 ppm) + 250 ppm Ekofisk + CI 2 (50 ppm) + 1 mg/L CFG	Average result	29.587	122.816	581.919	33.392	224.306	0.325
	First result	20.358	68.028	158.856	20.046	90.079	0.538
SI 2 (50 ppm) + 250 ppm Ekofisk + CI 2 (100 ppm) + 1 mg/L CFG	Average result	32.306	104.575	320.447	27.828	144.847	0.388
	First result	27.133	82.950	191.556	21.666	103.086	0.506
SI 2 (50 ppm) + 250 ppm Ekofisk + CI 3 (25 ppm) + 1 mg/L CFG	Average result	115.652	689.045	1368.693	174.259	723.274	0.022
	First result	96.823	474.011	1039.288	217.809	522.619	0.000
SI 2 (50 ppm) + 250 ppm Ekofisk + CI 3 (50 ppm) + 1 mg/L CFG	Average result	56.943	332.520	1044.930	56.131	446.965	0.195
	First result	40.156	129.586	430.478	31.721	184.990	0.319
SI 2 (50 ppm) + 250 ppm Ekofisk + CI 3 (100 ppm) + 1 mg/L CFG	Average result	91.302	722.496	1440.145	105.174	740.388	0.041
	First result	166.810	872.449	1513.179	381.554	873.081	0.000

The Figures 31 and 32 present the measurements data of flocculating process with both corrosion inhibitors and scaling inhibitors.

— Floc test CFG (1 mg/L), without chemical

— Floc test SI 2 (50 ppm) + CFG (1 mg/L)

— Floc test SI 2 (50 ppm) + CI 2 (50 ppm) + CFG (1 mg/L)

— Floc test SI 2 (50 ppm) + CI 2 (100 ppm) + CFG (1 mg/L)
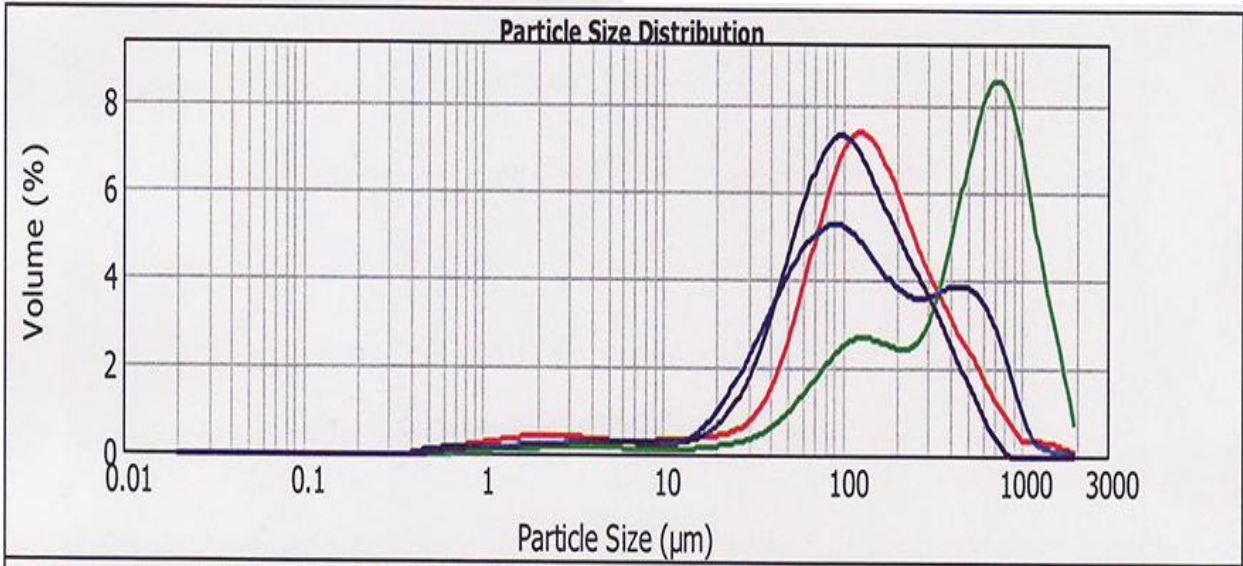
Figure 31: Flocculation with both SI and CI

— Floc test CFG (1 mg/L), without chemical

— Floc test SI 2 (100 ppm) + CFG (1 mg/L)

— Floc test SI 2 (100 ppm) + CI 3 (25 ppm) + CFG (1 mg/L)

— Floc test SI 2 (100 ppm) + CI 3 (50 ppm) + CFG (1 mg/L)

— Floc test SI 2 (100 ppm) + CI 3 (100 ppm) + CFG (1 mg/L)
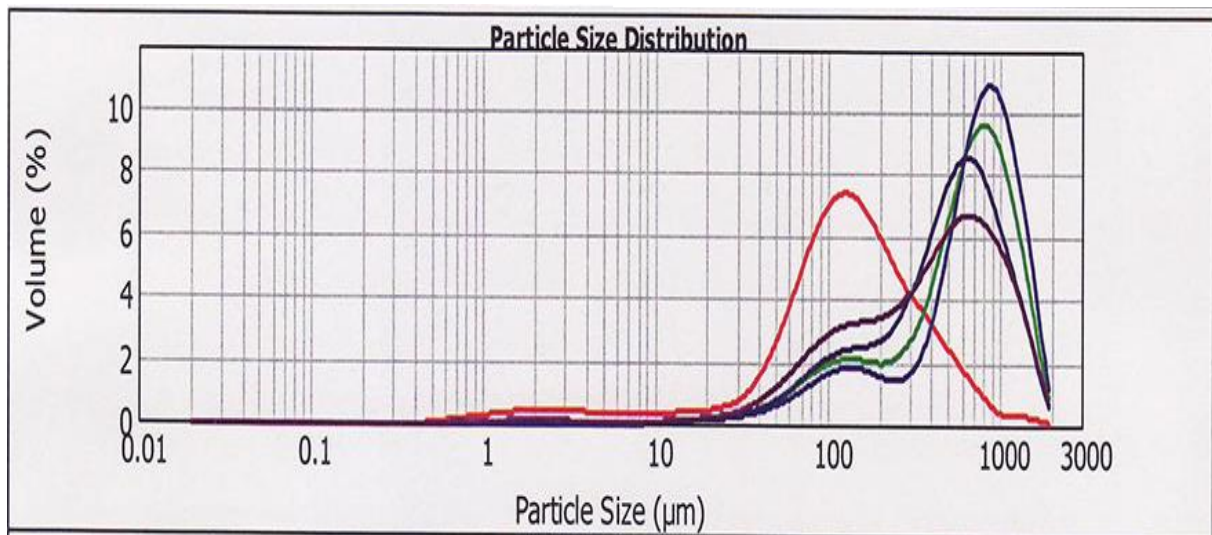
Figure 32: Flocculation with both SI and CI

From the tables and figures above one can see that both corrosion inhibitors and scale inhibitors have variable effect on flocculation, individually and in combination. Some scaling inhibitors in combination with some of corrosion inhibitors increase separation efficiency. But higher concentration of CI in presence of SI (example: SI 2 (50 ppm) + CI 2 (50/100 ppm)) can lead to lowering the separation.

6.2.6 Flocculation with/without chemicals by Floctreat

Flocculant, received from Clariant Oil Services, named Floctreat was used in the tests with comparing intention. This flocculating agent did not give representative results in all tests, except a few. In most tests floctreat gave no visible oil-water separation. Reason for that could be that the method used in experiments and some conditions such as oil droplet size in OIW, mixing-method, was probably not feasible for that type of flocculant. Measurement data from Mastersizer 2000 confirms that this floctreat does not work like CFG does. In comparison with oily water particle size data, measurements of tests with floctreat does not gives almost any difference, except when OIW has D (0, 5) higher than 5 μm. After an intense shaking a sample gets some waxy floating particles, this fact gives sometimes very large variation between particle sizes.

Table 24 demonstrates some measurement data of experiments with floctreat.

Table 24: Floc test with floctreat

Floc test	D (0, 1)	D (0, 5)	D (0, 9)	D [3, 2] - Surface weighted mean	D [4, 3] - Volume weighted mean	Result 8.00μm-10.00μm
OIW (Ekofisk)	1.422	6.611	14.204	3.566	7.271	12.711
OIW (Ekofisk)+ 100 ppm Floctreat	1.557	8.320	20.711	4.129	9.889	10.648
OIW (Ekofisk) *	2.288	12.926	22.431	6.188	13.193	10.595
OIW (Ekofisk)+ 100 ppm Floctreat	7.948	45.379	99.953	11.621	49.578	2.672
SI 1 (25 ppm) + 250 ppm Ekofisk	1.243	2.802	5.841	2.298	3.257	2.045
SI 1 (25 ppm) + 250 ppm Ekofisk + 200 ppm Floctreat	1.192	5.166	13.043	2.906	6.228	10.560
SI 1 (100 ppm) + 250 ppm Ekofisk	1.109	2.682	8.143	2.200	3.799	4.234
SI 1 (100 ppm) + 250 ppm Ekofisk+ 100 ppm Floctreat	2.259	11.434	1307.747	5.861	288.499	10.918
SI 2 (50 ppm) + 250 ppm Ekofisk	1.128	3.779	9.491	2.529	4.660	7.744
Chemical 5 50 ppm + 250 ppm Ekofisk + 100 ppm Floctreat	4.271	39.868	159.051	9.170	67.203	2.925
SI 2 (100 ppm) + 250 ppm Ekofisk	1.124	2.942	8.924	2.309	4.164	4.942
SI 2 (100 ppm) + 250 ppm Ekofisk + 100 ppm Floctreat	3.263	65.858	848.378	10.471	238.111	2.334
SI 2 (100 ppm) + 250 ppm Ekofisk + CI 2 (100 ppm) + 100	0.946	2.538	9.264	1.992	4.303	3.079
SI 2 (100 ppm) + 250 ppm Ekofisk + CI 3 (50 ppm) + 100 ppm	1.079	7.797	588.891	3.136	132.820	2.991

* Meaning that this emulsion was made with a purpose, used share force was lower, such as the D (0, 5) becomes higher than 5 μm. To get understanding of Floctreat's behavior was tried various ways.

The table above shows that Floctreat separates oil from water in very low degree. Probably the reason of that can be in mixing method. Surprisingly in some of the tests Floctreat got a little better result. No other possibly explanation of the strange behavior of this flocculating agent is suggested.

6.2.7 Shear forces

The droplet size is the key parameter determining the kinetics of emulsion destabilization. The role of shear forces in making of stable emulsion is demonstrated in 6.2.3. Shear forces acting on droplets gradually break them up into many smaller droplets. Hence subjecting flocculated emulsions to shear forces causes a breakdown of the flocs. Even though it happens, after a short period of time the flocs are seems to be restored. The evidence is in Table 25 below. The table presents the data of measurements of a flocculating sample (containing: 100 ppm scale inhibitor (SI 3) dissolved in seawater, added 250 ppm Ekofisk oil, mixed with Silverson, added 1.5 mg/L flocculant (CFG) and 0.5 mg/L chitosan) that are mixed with Silverson again in order to damage the flocs. The first column shows the date and time of measuring.

Table 25: The data of measurements of flocculating sample after shear mixing

Measurement date/time		D (0, 1)	D (0, 5)	D (0, 9)	D [3, 2] - Surface weighted mean	D [4, 3] - Volume weighted mean	Result 8.00μm-10.00μm
Floc test 04.05.2010 13:00		54.819	440.528	1167.297	67.221	532.566	0.257
The same sample after violent mixing	04.05.2010 13:06	2.296	34.651	153.693	6.714	62.118	2.761
	04.05.2010 13:06	3.921	70.718	298.691	9.443	113.540	1.895
	04.05.2010 13:07	7.403	113.291	455.955	13.101	177.702	1.361
	04.05.2010 13:07	11.623	167.672	503.770	16.683	218.693	1.047
	04.05.2010 13:08	19.254	255.775	660.820	22.307	309.875	0.770
	04.05.2010 13:08	39.212	348.305	822.232	32.059	393.435	0.537
	04.05.2010 13:09	62.424	426.420	799.251	40.886	427.544	0.406
	04.05.2010 13:09	59.958	398.179	994.420	40.750	472.912	0.423
	04.05.2010 13:09	87.817	563.428	1273.028	57.470	628.732	0.313
	04.05.2010 13:10	72.982	439.949	955.845	48.324	482.392	0.370

6.2.8 A closer look on flocculation process during the first minutes

During experiments it was noted that flocculation occurred in the sample through measuring. Mastersizer 2000 measured two times in a minute. The data of each

measurement regularly could be contrasting. Therefore it became attractive to take a closer look on flocculation, to analyze these different data. Table 26 shows measurement data of some flocculating sample the first minutes. More complete table is available in appendix.

Table 26: Measurement data of periodically measurements of flocculation sample the first 4-5 minutes. In the first column are noted date and time of measuring.

Floc test Date/time	D (0, 1)	D (0, 5)	D (0, 9)	D [3, 2]	D [4, 3]	8.00µm- 10.00µm	Obscuration
10.05.2010 15:30	88.234	517.499	1206.495	92.081	585.116	0.000	24.93
10.05.2010 15:31	74.533	374.982	706.268	68.907	379.307	0.109	24.38
10.05.2010 15:31	65.895	358.004	965.259	52.884	443.224	0.134	21.24
10.05.2010 15:32	55.810	284.593	914.560	40.537	399.340	0.162	19.50
10.05.2010 15:32	51.929	256.033	1041.011	34.746	424.714	0.167	18.69
10.05.2010 15:33	54.572	275.852	1086.943	37.123	429.354	0.172	18.89
10.05.2010 15:33	51.380	291.455	1115.759	34.752	448.322	0.178	18.38
10.05.2010 15:34	56.088	352.702	1254.693	38.657	515.397	0.142	18.20
10.05.2010 16:51	155.350	786.114	1442.657	359.195	808.865	0.000	32.45
10.05.2010 16:52	330.244	974.587	1567.009	500.831	973.953	0.000	34.86
10.05.2010 16:52	176.389	890.706	1510.192	175.443	896.239	0.000	32.82
10.05.2010 16:53	162.865	948.980	1554.853	385.505	926.607	0.000	24.54
10.05.2010 16:53	182.905	1013.808	1590.847	141.873	988.989	0.000	24.72
10.05.2010 16:54	84.474	755.195	1447.614	54.985	758.196	0.155	20.87
10.05.2010 16:54	77.781	670.153	1416.792	51.494	705.967	0.174	21.43
10.05.2010 16:55	55.728	455.769	1166.746	34.884	537.424	0.244	19.89
10.05.2010 16:55	32.595	290.264	780.050	23.035	353.983	0.357	19.39
10.05.2010 16:56	30.754	252.298	623.971	21.637	291.872	0.385	19.60
10.05.2010 17:18	166.810	872.449	1513.179	381.554	873.081	0.000	24.24
10.05.2010 17:19	271.693	956.881	1551.907	468.884	956.389	0.000	27.04
10.05.2010 17:19	120.962	773.678	1441.357	290.516	782.515	0.000	16.26
10.05.2010 17:20	168.643	942.250	1538.529	391.406	929.576	0.000	17.84
10.05.2010 17:20	671.894	1129.492	1609.975	643.800	1116.141	0.000	32.54
10.05.2010 17:21	113.930	802.277	1455.366	290.572	806.165	0.000	14.51
10.05.2010 17:21	230.287	859.500	1487.865	401.278	873.185	0.000	22.83
10.05.2010 17:22	43.637	251.804	743.633	38.302	338.938	0.129	11.40
10.05.2010 17:22	46.099	267.513	777.234	40.254	353.890	0.132	11.24
10.05.2010 17:23	44.420	258.223	896.166	38.621	374.000	0.150	11.15

All measurements were preceded by background measuring (seawater in this case) which plays important role in the measurements, for example to detect the concentration of the sample and obscuration. The sample concentration is controlled by monitoring the obscuration of the laser beam caused by the sample.

Obscuration (the last column in the table 26) is simply the fraction of light "lost" from the main beam when the sample is introduced. Or with another words, it is a measure of the amount of laser light lost due to the introduction of the sample into the analyzer beam.

The obscuration term can be expressed mathematically:

$$O_b = 1 - L_s/L_b$$

Ls is the light intensity measured in the central detector when a sample is present in the cell, L_b is the same but with clean dispersant (here: seawater)

Obscuration is usually expressed as a percentage: 100 x Ob.

An ideal range is between 3 and 20%, depending on the sample and dispersion unit used. 20-50 % is usable, but there is a danger of multiple scattering.

Since the flocculating sample is a sample with unstable concentration, it is really possible that obscuration is changing during measuring. The user-manual to Mastersizer 2000 does not recommend to measure samples before the obscuration is stabilized (3-20). While stabilization of obscuration indicates that the sample has properly dispersed. However, it was essential to take measurements immediately after adding of chemicals and rapid mixing.

If the obscuration decreases the size of the particles within the sample may be increasing; either the sample is sticking together or the particles are actually swelling due to the dispersant. Other causes could be the larger particles settling out due to high weight (sedimentation).

If obscuration increases rapidly, particles may be attaching themselves to the cell windows due to surface charges. This means material is in the laser beam continuously and the obscuration appears to increase.

6.3 Conclusion

The main objective of this thesis was to research a possible influence of production chemicals on the effect on flocculation. In this work experiments with particle size distribution measurements using synthetic produced water were been performed. Numerical results based on several experiments are presented and analyzed. Each test was performed at identical operating conditions and flocculating residence time.

The following observations were made:

- Stability of emulsion does not change with time (meaning in a short period of time like 1-1.5 hours) and does not depend on mixing time.
- Separation efficiency increases with increasing flocculant (in this case- CFG) concentrations.
- Corrosion inhibitors typically enhance or do not disturb the oil/water separation.
- Some scale inhibitors disturb the flocculation process at low concentrations, and enhance at higher concentrations. Other inhibitors show the opposite result.
- Both corrosion inhibitors and scale inhibitors have variable effect on flocculation, individually and in combination. Some scale inhibitors in combination with some corrosion inhibitors increase separation efficiency. But higher concentration of CI in presence of SI can lead to poor separation.
- Various concentrations of production chemicals have varying effect on floc formation.
- Floctreat separates poorly oil from water. Surprisingly in some of the tests Floctreat gave a little better result. Probably the reason for that can be in mixing method. However, the results from using Floctreat are far away from using CFG.
- Subjecting flocculated emulsions to shear forces causesa breakdown of flocs. After a short period, however, the flocs seem to be restored (this can be because of CFG presence, at CFG is a flocculant with high performance).
- Changes in particle sizes and instability in concentration of sample during flocculation lead to changes of obscuration value. Increasing or decreasing of obscuration indicates that particles may attache to the cell windows due to surface charges, or the size of the particles within the sample may be increasing respectively.

6.4 Suggestions for further research

In order to understand better how the production chemicals influence the flocculation the following aspects must be further addressed:

➢ Investigate effects of production chemicals on oil/water separation with focus on various concentrations and combinations of added chemicals

➢ Research the effect of production chemicals with attention to charges of components presence and added to produced water

➢ Study rheology and behavior of aggregating OiW emulsion related to droplet-droplet interactions in presence of various concentrations and combinations of added chemicals and flocculant

➢ Use another (one or more) flocculating agent with purpose of comparing CFG, and probably confirm that CFG is the better flocculant with high performance and not harmful to environment

➢ Review experiments in larger scale (pilot): This thesis used synthetic produced water and all tests can have deviation from offshore tests with real produced water, dissolved production chemicals and the right environment

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Appendix

I: Total Solids (TS) calculation for CFG and Chitosan

a) 18 g Bentonite and 9 g Na Pyrophosphonate per 200 ml water gives 135 g TS per L

$(18 + 9) \cdot 5 = 135$ g TS/L

b) 1 g Chitosan per 100 ml HCl gives 10 g TS per L

$1 \cdot 10 = 10$ g TS/L

II: Tables

Table 1: Measurement data oily water (Ekofisk/Ula 250 ppm)

Ekofisk/Ula 250 ppm	d (0.1)	d (0.5)	d (0.9)	D[3, 2]-Surface weighted mean	D[4, 3]-Volume weighted mean	Result 8-10 µm
Test Ekofisk 250 ppm 21.04 16:46:27	1.151	3.604	8.257	2.503	4.246	6.301
Test Ekofisk 250 ppm 26.04 13:22:48	1.200	3.590	11.542	2.608	5.169	6.859
Test Ekofisk 250 ppm 26.04 13:23:14	1.264	3.533	10.983	2.661	5.012	6.718
Test Ekofisk 250 ppm 26.04 13:23:39	1.263	3.535	11.007	2.661	5.018	6.673
Test Ekofisk 250 ppm 26.04 13:24:04	1.265	3.559	11.189	2.673	5.081	6.745
Test Ekofisk 250 ppm 26.04 13:24:30	1.262	3.539	10.924	2.659	4.977	6.760
Test Ekofisk 250 ppm 26.04 14:50:35	1.268	3.129	9.779	2.534	4.491	5.266
Test Ekofisk 250 ppm 26.04 14:51:26	1.267	3.155	9.853	2.541	4.513	5.425
Test Ekofisk 250 ppm 26.04 14:51:01	1.267	3.140	9.684	2.533	4.461	5.358
Test Ekofisk 250 ppm 27.04 16:59:06	1.213	3.548	8.360	2.559	4.274	6.161
Test Ekofisk 250 ppm 27.04 16:59:32	1.299	3.566	7.962	2.648	4.193	5.776
Test Ekofisk 250 ppm 27.04 17:57:50	1.310	3.217	6.985	2.533	3.766	3.985

	D (0, 1)	D (0, 5)	D (0, 9)	D [3, 2]	D [4, 3]	Obscuration
Test Ekofisk 250 ppm 27.04 17:58:15	1.395	3.237	6.703	2.611	3.721	3.441
Average results	1.263	3.393	9.372	2.593	4.532	5.805
Test Ekofisk 250 ppm 3 min, 30.04 15:43:08	1.277	3.861	9.036	2.729	4.634	7.035
Test Ekofisk 250 ppm 4 min, 30.04 15:46:20	1.265	3.696	8.788	2.662	4.478	6.625
Test Ekofisk 250 ppm 5 min, 30.04 15:49:02	1.206	3.351	8.736	2.502	4.305	5.668
Test Ekofisk 250 ppm 5 min, 30.04 15:49:27	1.205	3.347	8.801	2.501	4.326	5.634
Test Ekofisk 250 ppm 1 min, 1.05 13:04:27	1.184	3.538	10.384	2.561	4.899	6.328
Test Ekofisk 250 ppm 1 min, 1.05 13:04:53	1.184	3.537	10.101	2.556	4.798	6.406
Test Ekofisk 250 ppm 1 min, 1.05 13:05:18	1.186	3.553	10.253	2.566	4.837	6.494
Test Ekofisk 250 ppm 2 min, 1.05 13:07:14	1.181	3.335	10.127	2.500	4.684	5.954
Test Ekofisk 250 ppm 2 min, 1.05 13:07:40	1.180	3.351	9.912	2.500	4.624	6.050
Average results	1.205	3.506	9.530	2.562	4.620	6.244
Test Ula 250 ppm 5 min 28.04 16:40:57	1.333	3.881	9.808	2.808	4.858	7.609
Test Ula 250 ppm 5 min 28.04 16:41:23	1.332	3.868	9.676	2.800	4.801	7.627
Test Ula 250 ppm 5 min 28.04 18:40:54	1.313	3.784	11.673	2.798	5.324	7.245
Test Ula 250 ppm 5 min 28.04 18:41:20	1.395	3.803	10.629	2.879	5.068	7.473
Test Ula 250 ppm 5 min 28.04 18:41:26	1.390	3.782	10.752	2.872	5.094	7.485
Average results	1.353	3.825	10.475	2.831	5.029	7.488

Table 2: Measurement data of flocculating sample the first 4-5 minutes. In the first column are noted date and time of measuring.

Floc test Date/time	D (0, 1)	D (0, 5)	D (0, 9)	D [3, 2]	D [4, 3]	8.00µm-10.00µm	Obscuration

10.05.2010 15:30	88.234	517.499	1206.495	92.081	585.116	0.000	24.93
10.05.2010 15:31	74.533	374.982	706.268	68.907	379.307	0.109	24.38
10.05.2010 15:31	65.895	358.004	965.259	52.884	443.224	0.134	21.24
10.05.2010 15:32	55.810	284.593	914.560	40.537	399.340	0.162	19.50
10.05.2010 15:32	51.929	256.033	1041.011	34.746	424.714	0.167	18.69
10.05.2010 15:33	54.572	275.852	1086.943	37.123	429.354	0.172	18.89
10.05.2010 15:33	51.380	291.455	1115.759	34.752	448.322	0.178	18.38
10.05.2010 15:34	56.088	352.702	1254.693	38.657	515.397	0.142	18.20
10.05.2010 15:42	30.202	116.559	290.720	27.959	140.924	0.386	32.18
10.05.2010 15:42	31.460	122.908	323.267	29.558	153.073	0.353	31.94
10.05.2010 15:43	37.250	159.010	460.679	36.404	208.655	0.303	32.48
10.05.2010 15:44	40.776	202.927	513.067	40.327	242.569	0.289	32.53
10.05.2010 15:45	39.023	192.286	540.223	37.657	245.856	0.310	30.87
10.05.2010 15:45	41.926	232.328	553.087	41.644	265.332	0.285	30.92
10.05.2010 15:46	45.669	266.554	637.553	46.313	305.297	0.246	30.63
10.05.2010 15:46	51.370	320.912	778.380	55.264	375.149	0.211	30.73
10.05.2010 15:47	47.166	308.975	718.148	48.029	344.425	0.223	29.85
10.05.2010 15:47	45.651	271.522	682.241	45.355	319.485	0.238	29.18
10.05.2010 15:53	71.621	351.531	756.755	89.219	383.827	0.113	43.41
10.05.2010 15:53	70.962	351.708	1061.870	88.452	469.193	0.113	39.68
10.05.2010 15:54	81.637	470.427	1211.769	105.276	564.767	0.091	35.71
10.05.2010 15:54	95.859	572.667	1268.781	238.677	630.765	0.000	33.58
10.05.2010 15:55	81.227	497.533	1072.401	96.289	538.507	0.093	30.47
10.05.2010 15:56	97.223	591.706	1208.412	245.766	625.437	0.000	26.41
10.05.2010 15:57	93.514	567.737	1119.587	236.042	589.610	0.000	25.83
10.05.2010 15:57	87.509	536.249	1088.282	225.726	567.441	0.000	25.60
10.05.2010 15:58	107.688	689.852	1327.453	281.051	714.937	0.000	24.93
10.05.2010 15:58	122.278	728.940	1358.308	314.377	754.996	0.000	24.71

10.05.2010 16:51	155.350	786.114	1442.657	359.195	808.865	0.000	32.45
10.05.2010 16:52	330.244	974.587	1567.009	500.831	973.953	0.000	34.86
10.05.2010 16:52	176.389	890.706	1510.192	175.443	896.239	0.000	32.82
10.05.2010 16:53	162.865	948.980	1554.853	385.505	926.607	0.000	24.54
10.05.2010 16:53	182.905	1013.808	1590.847	141.873	988.989	0.000	24.72
10.05.2010 16:54	84.474	755.195	1447.614	54.985	758.196	0.155	20.87
10.05.2010 16:54	77.781	670.153	1416.792	51.494	705.967	0.174	21.43
10.05.2010 16:55	55.728	455.769	1166.746	34.884	537.424	0.244	19.89
10.05.2010 16:55	32.595	290.264	780.050	23.035	353.983	0.357	19.39
10.05.2010 16:56	30.754	252.298	623.971	21.637	291.872	0.385	19.60
10.05.2010 17:00	96.823	474.011	1039.288	217.809	522.619	0.000	27.85
10.05.2010 17:00	112.468	625.255	1247.398	272.024	661.581	0.000	25.72
10.05.2010 17:01	133.395	730.943	1339.308	325.574	753.695	0.000	23.69
10.05.2010 17:01	161.502	884.663	1515.269	375.305	881.085	0.000	24.17
10.05.2010 17:02	114.913	727.876	1410.299	146.104	754.181	0.000	20.07
10.05.2010 17:02	138.279	728.944	1430.202	310.637	766.450	0.000	20.42
10.05.2010 17:03	141.276	836.337	1489.062	179.881	834.994	0.000	19.85
10.05.2010 17:03	174.262	841.820	1465.041	382.238	854.106	0.000	22.55
10.05.2010 17:04	86.883	578.120	1287.909	85.552	640.600	0.109	17.65
10.05.2010 17:04	80.330	487.703	1168.123	74.324	563.432	0.113	17.65
10.05.2010 17:09	40.156	129.586	430.478	31.721	184.990	0.319	38.79
10.05.2010 17:10	43.972	157.578	486.583	37.346	217.803	0.294	38.95
10.05.2010 17:10	48.829	223.524	565.215	43.902	268.149	0.250	38.67
10.05.2010 17:11	57.364	324.738	1063.546	57.681	454.587	0.186	37.45
10.05.2010 17:11	52.345	259.304	810.980	47.575	357.568	0.224	36.26
10.05.2010 17:12	60.439	362.841	1178.285	61.579	496.457	0.179	36.39
10.05.2010 17:12	70.009	492.422	1178.759	77.158	560.207	0.148	35.83
10.05.2010 17:13	73.310	500.360	1182.854	81.728	567.605	0.133	35.81
10.05.2010 17:13	88.572	627.700	1354.286	112.601	680.571	0.111	36.16

10.05.2010 17:14	92.796	640.065	1314.125	119.028	681.712	0.103	35.78
10.05.2010 17:18	166.810	872.449	1513.179	381.554	873.081	0.000	24.24
10.05.2010 17:19	271.693	956.881	1551.907	468.884	956.389	0.000	27.04
10.05.2010 17:19	120.962	773.678	1441.357	290.516	782.515	0.000	16.26
10.05.2010 17:20	168.643	942.250	1538.529	391.406	929.576	0.000	17.84
10.05.2010 17:20	671.894	1129.492	1609.975	643.800	1116.141	0.000	32.54
10.05.2010 17:21	113.930	802.277	1455.366	290.572	806.165	0.000	14.51
10.05.2010 17:21	230.287	859.500	1487.865	401.278	873.185	0.000	22.83
10.05.2010 17:22	43.637	251.804	743.633	38.302	338.938	0.129	11.40
10.05.2010 17:22	46.099	267.513	777.234	40.254	353.890	0.132	11.24
10.05.2010 17:23	44.420	258.223	896.166	38.621	374.000	0.150	11.15

III: Pictures taken during flocculation the first 30 seconds of mixing

Descriptions:

Pictures 1, 4, 6: samples without chemical, flocculant-CF

Pictures 2, 5, 7: sample with chemical, flocculant-CF

Picture 3: sample without chemical, flocculant- Floctreat

1   2

3
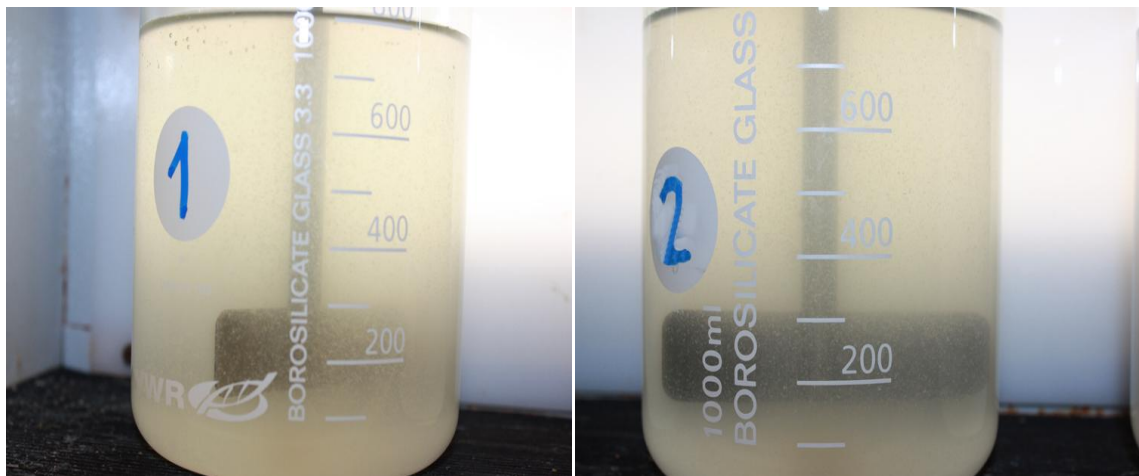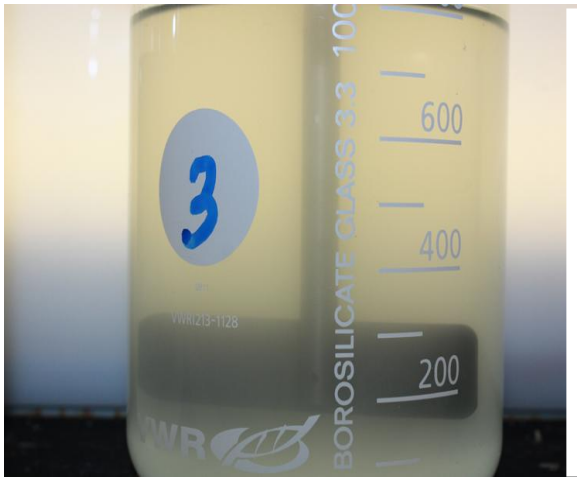
1-sample without chemical (flocculant-CF)

2-sample with chemical (flocculant- CF)

3-sample without chemical (floctreat)

Concentrations of CF:
pictures 1, 2 - 0.5 ml/L
pictures 4, 5 - 1 ml/L
pictures 6, 7 - 2 ml/L

4

5

6

7

VI: Malvern records

Result analysis reports for:

    1: Test Ekofisk 250 ppm

    2: Floc test CFG 0.5-3 ml/L

    3: Floc test with corrosion inhibitor

    4: Floc test with scaling inhibitor

    5: Floc test with both chemical

    6: Floc test with both chemical

MASTERSIZER 2000

Result Analysis Report

Sample Name: Test Ekofisk 250 ppm	**SOP Name:**	**Measured:** 27. april 2010 16:59:06
Sample Source & type: A	**Measured by:** Administrator	**Analysed:** 27. april 2010 16:59:07
Sample bulk lot ref:	**Result Source:** Edited	

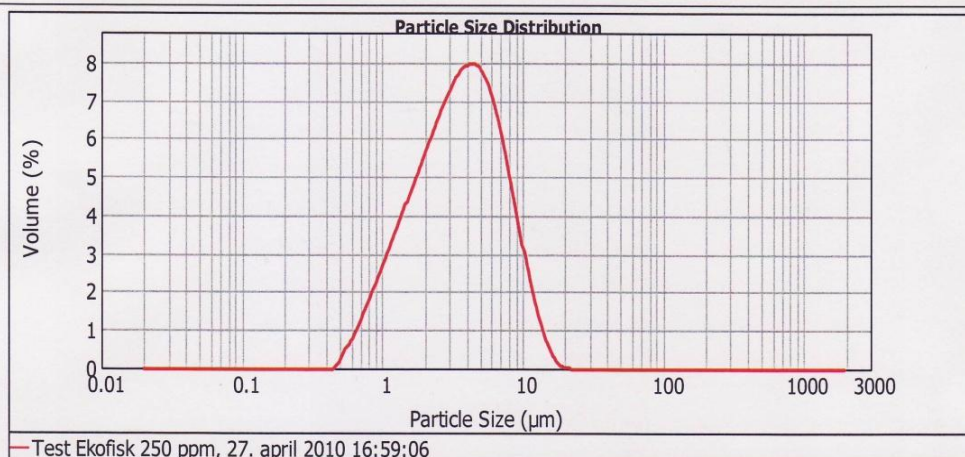|			
Particle Name: Default	**Accessory Name:** Hydro 2000MU (A)	**Analysis model:** General purpose	**Sensitivity:** Normal
Particle RI: 1.520	**Absorption:** 0.1	**Size range:** 0.020 to 2000.000 um	**Obscuration:** 21.82 %
Dispersant Name: Water	**Dispersant RI:** 1.330	**Weighted Residual:** 2.380 %	**Result Emulation:** Off

Concentration: 0.0087 %Vol	**Span :** 2.015	**Uniformity:** 0.63	**Result units:** Volume
Specific Surface Area: 2.34 m²/g	**Surface Weighted Mean D[3,2]:** 2.559 um	**Vol. Weighted Mean D[4,3]:** 4.274 um	

d(0.1): 1.213 um **d(0.5): 3.548 um** **d(0.9): 8.360 um**

Particle Size Distribution — Volume (%) vs Particle Size (µm)

— Test Ekofisk 250 ppm, 27. april 2010 16:59:06

Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %
0.010	0.00	0.105	0.00	1.096	3.00	11.482	1.54	120.226	0.00	1258.925	0.00
0.011	0.00	0.120	0.00	1.259	3.52	13.183	0.83	138.038	0.00	1445.440	0.00
0.013	0.00	0.138	0.00	1.445	4.05	15.136	0.37	158.489	0.00	1659.587	0.00
0.015	0.00	0.158	0.00	1.660	4.59	17.378	0.08	181.970	0.00	1905.461	0.00
0.017	0.00	0.182	0.00	1.905	5.12	19.953	0.01	208.930	0.00	2187.762	0.00
0.020	0.00	0.209	0.00	2.188	5.65	22.909	0.00	239.883	0.00	2511.886	0.00
0.023	0.00	0.240	0.00	2.512	6.15	26.303	0.00	275.423	0.00	2884.032	0.00
0.026	0.00	0.275	0.00	2.884	6.61	30.200	0.00	316.228	0.00	3311.311	0.00
0.030	0.00	0.316	0.00	3.311	6.97	34.674	0.00	363.078	0.00	3801.894	0.00
0.035	0.00	0.363	0.00	3.802	7.18	39.811	0.00	416.869	0.00	4365.158	0.00
0.040	0.00	0.417	0.00	4.365	7.17	45.709	0.00	478.630	0.00	5011.872	0.00
0.046	0.00	0.479	0.00	5.012	6.90	52.481	0.00	549.541	0.00	5754.399	0.00
0.052	0.00	0.550	0.23	5.754	6.35	60.256	0.00	630.957	0.00	6606.934	0.00
0.060	0.00	0.631	0.62	6.607	5.55	69.183	0.00	724.436	0.00	7585.776	0.00
0.069	0.00	0.724	1.04	7.586	4.55	79.433	0.00	831.764	0.00	8709.636	0.00
0.079	0.00	0.832	1.50	8.710	3.49	91.201	0.00	954.993	0.00	10000.000	0.00
0.091	0.00	0.955	1.98	10.000	2.44	104.713	0.00	1096.478	0.00		
0.105	0.00	1.096	2.49	11.482		120.226	0.00	1258.925	0.00		

Operator notes:

1: Test Ekofisk 250 ppm

MASTERSIZER 2000

Result Analysis Report

Sample Name: Floc test CF 3 mL/L, (Ekofisk)	**SOP Name:**	**Measured:** 24. april 2010 15:34:52
Sample Source & type: F	**Measured by:** Administrator	**Analysed:** 24. april 2010 15:34:53
Sample bulk lot ref:	**Result Source:** Edited	

Particle Name: Default	**Accessory Name:** Hydro 2000MU (A)	**Analysis model:** General purpose	**Sensitivity:** Normal
Particle RI: 1.520	**Absorption:** 0.1	**Size range:** 0.020 to 2000.000 um	**Obscuration:** 56.08 %
Dispersant Name: Water	**Dispersant RI:** 1.330	**Weighted Residual:** 2.772 %	**Result Emulation:** Off

Concentration: 3.9380 %Vol	**Span :** 1.749	**Uniformity:** 0.529	**Result units:** Volume
Specific Surface Area: 0.0177 m²/g	**Surface Weighted Mean D[3,2]:** 339.409 um	**Vol. Weighted Mean D[4,3]:** 728.824 um	

d(0.1):   157.265   um   **d(0.5):   685.100   um**   **d(0.9): 1355.179   um**

Particle Size Distribution
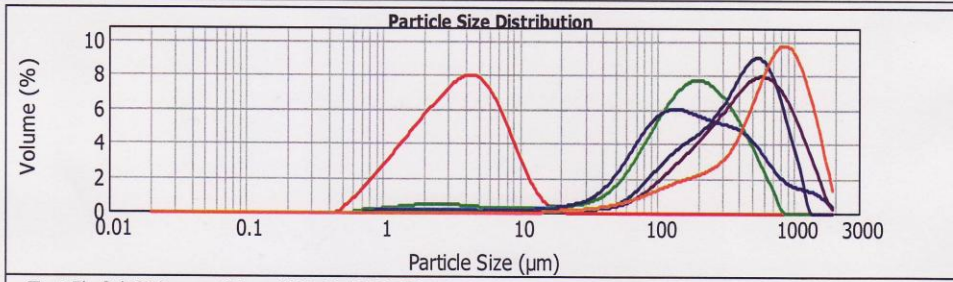
- Test Ekofisk 250 ppm, 27. april 2010 16:59:06
- Floc test CF 0.5 mL/L, (Ekofisk), 24. april 2010 15:44:14
- Floc test CF 1 mL/L (Ekofisk), 22. april 2010 15:37:58
- Floc test CF 2 mL/L (Ekofisk), 21. april 2010 17:10:05
- Floc test CF 2.5 mL/L, (Ekofisk), 24. april 2010 15:26:31
- Floc test CF 3 mL/L, (Ekofisk), 24. april 2010 15:34:52

Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %
0.010	0.00	0.105	0.00	1.096	0.00	11.482	0.00	120.226	1.47	1258.925	6.03
0.011	0.00	0.120	0.00	1.259	0.00	13.183	0.00	138.038	1.64	1445.440	4.38
0.013	0.00	0.138	0.00	1.445	0.00	15.136	0.04	158.489	1.78	1659.587	2.43
0.015	0.00	0.158	0.00	1.660	0.00	17.378	0.08	181.970	1.92	1905.461	0.57
0.017	0.00	0.182	0.00	1.905	0.00	19.953	0.10	208.930	2.07	2187.762	0.00
0.020	0.00	0.209	0.00	2.188	0.00	22.909	0.13	239.883	2.28	2511.886	0.00
0.023	0.00	0.240	0.00	2.512	0.00	26.303	0.17	275.423	2.61	2884.032	0.00
0.026	0.00	0.275	0.00	2.884	0.00	30.200	0.21	316.228	3.12	3311.311	0.00
0.030	0.00	0.316	0.00	3.311	0.00	34.674	0.26	363.078	3.84	3801.894	0.00
0.035	0.00	0.363	0.00	3.802	0.00	39.811	0.33	416.869	4.78	4365.158	0.00
0.040	0.00	0.417	0.00	4.365	0.00	45.709	0.41	478.630	5.87	5011.872	0.00
0.046	0.00	0.479	0.00	5.012	0.00	52.481	0.51	549.541	6.99	5754.399	0.00
0.052	0.00	0.550	0.00	5.754	0.00	60.256	0.63	630.957	7.97	6606.934	0.00
0.060	0.00	0.631	0.00	6.607	0.00	69.183	0.77	724.436	8.63	7585.776	0.00
0.069	0.00	0.724	0.00	7.586	0.00	79.433	0.94	831.764	8.80	8709.636	0.00
0.079	0.00	0.832	0.00	8.710	0.00	91.201	1.11	954.993	8.40	10000.000	
0.091	0.00	0.955	0.00	10.000	0.00	104.713	1.30	1096.478	7.44		
0.105		1.096		11.482		120.226		1258.925			

Operator notes:

2: Floc test CFG 0.5-3 ml/L

MASTERSIZER 2000

Result Analysis Report

Sample Name: Averaged Result chem 3 100 ppm+ CF	**SOP Name:**	**Measured:** 4. mai 2010 16:45:30
Sample Source & type:	**Measured by:** Administrator	**Analysed:** 4. mai 2010 16:45:31
Sample bulk lot ref:	**Result Source:** Averaged	

Particle Name: Default	**Accessory Name:** Hydro 2000MU (A)	**Analysis model:** General purpose	**Sensitivity:** Normal
Particle RI: 1.520	**Absorption:** 0.1	**Size range:** 0.020 to 2000.000 um	**Obscuration:** 27.23 %
Dispersant Name: Water	**Dispersant RI:** 1.330	**Weighted Residual:** 3.890 %	**Result Emulation:** Off

Concentration: 1.4996 %Vol	**Span :** 1.650	**Uniformity:** 0.495	**Result units:** Volume
Specific Surface Area: 0.0179 m²/g	**Surface Weighted Mean D[3,2]:** 334.710 um	**Vol. Weighted Mean D[4,3]:** 776.280 um	

d(0.1): 187.536 um   **d(0.5): 737.759 um**   **d(0.9): 1404.806 um**

Particle Size Distribution
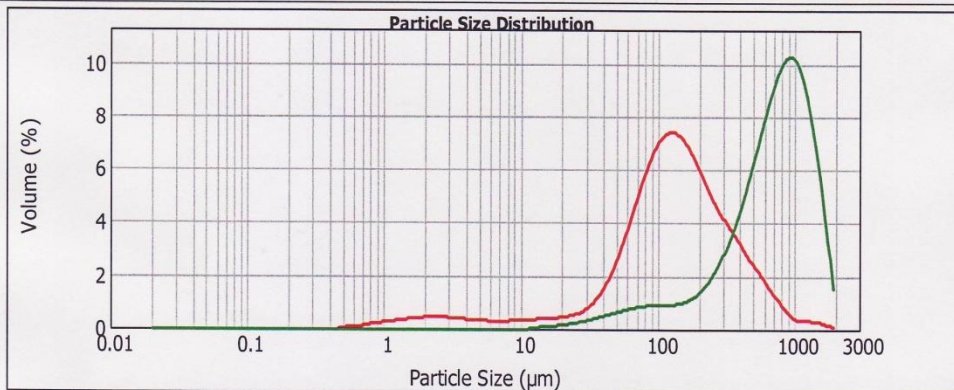
— Averaged Result 1 cf, 22. april 2010 15:37:33
— Averaged Result chem 3 100 ppm+ CF 100 ppm, 4. mai 2010 16:45:30

Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %
0.010	0.00	0.105	0.00	1.096	0.00	11.482	0.02	120.226	0.83	1258.925	6.97
0.011	0.00	0.120	0.00	1.259	0.00	13.183	0.06	138.038	0.87	1445.440	5.15
0.013	0.00	0.138	0.00	1.445	0.00	15.136	0.08	158.489	0.96	1659.587	2.88
0.015	0.00	0.158	0.00	1.660	0.00	17.378	0.11	181.970	1.14	1905.461	0.68
0.017	0.00	0.182	0.00	1.905	0.00	19.953	0.15	208.930	1.42	2187.762	0.00
0.020	0.00	0.209	0.00	2.188	0.00	22.909	0.20	239.883	1.83	2511.886	0.00
0.023	0.00	0.240	0.00	2.512	0.00	26.303	0.25	275.423	2.37	2884.032	0.00
0.026	0.00	0.275	0.00	2.884	0.00	30.200	0.32	316.228	3.05	3311.311	0.00
0.030	0.00	0.316	0.00	3.311	0.00	34.674	0.39	363.078	3.86	3801.894	0.00
0.035	0.00	0.363	0.00	3.802	0.00	39.811	0.47	416.869	4.80	4365.158	0.00
0.040	0.00	0.417	0.00	4.365	0.00	45.709	0.55	478.630	5.82	5011.872	0.00
0.046	0.00	0.479	0.00	5.012	0.00	52.481	0.63	549.541	6.90	5754.399	0.00
0.052	0.00	0.550	0.00	5.754	0.00	60.256	0.70	630.957	7.92	6606.934	0.00
0.060	0.00	0.631	0.00	6.607	0.00	69.183	0.75	724.436	8.75	7585.776	0.00
0.069	0.00	0.724	0.00	7.586	0.00	79.433	0.79	831.764	9.21	8709.636	0.00
0.079	0.00	0.832	0.00	8.710	0.00	91.201	0.81	954.993	9.12	10000.000	0.00
0.091	0.00	0.955	0.00	10.000	0.00	104.713	0.82	1096.478	9.12		
0.105		1.096		11.482		120.226		1258.925	8.36		

Operator notes: *Average of 7 measurements from Floc test with chemical.mea*

Malvern Instruments Ltd.
Malvern, UK
Tel := +[44] (0) 1684-892456 Fax +[44] (0) 1684-892789

Mastersizer 2000 Ver. 5.60
Serial Number : MAL1042031

File name: Print nå.mea
Record Number: 52
25.05.2010 18:01:55

3: Floc test with corrosion inhibitor (chem. 3 = CI 3), 100 ppm

MASTERSIZER 2000

Result Analysis Report

Sample Name: Averaged Result 5 50 + CF	**SOP Name:**	**Measured:** 10. mai 2010 16:44:01
Sample Source & type:	**Measured by:** Administrator	**Analysed:** 10. mai 2010 16:44:02
Sample bulk lot ref:	**Result Source:** Averaged	

Particle Name: Default	**Accessory Name:** Hydro 2000MU (A)	**Analysis model:** General purpose	**Sensitivity:** Normal
Particle RI: 1.520	**Absorption:** 0.1	**Size range:** 0.020 to 2000.000 um	**Obscuration:** 36.71 %
Dispersant Name: Water	**Dispersant RI:** 1.330	**Weighted Residual:** 4.598 %	**Result Emulation:** Off

Concentration: 1.3197 %Vol	**Span :** 1.691	**Uniformity:** 0.496	**Result units:** Volume
Specific Surface Area: 0.0361 m²/g	**Surface Weighted Mean D[3,2]:** 166.179 um	**Vol. Weighted Mean D[4,3]:** 753.572 um	

d(0.1):   122.499   um   **d(0.5):   735.875   um**   **d(0.9):   1367.016   um**

— Floc test CF 1 mL/L (Ekofisk), 22. april 2010 15:37:58
— Averaged Result 5 50 + CF, 10. mai 2010 16:44:01

Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %
0.010	0.00	0.105	0.00	1.096	0.01	120.226	0.07	120.226	1.62	1258.925	6.58
0.011	0.00	0.120	0.00	1.259	0.02	13.183	0.09	138.038	1.61	1445.440	4.63
0.013	0.00	0.138	0.00	1.445	0.03	15.136	0.11	158.489	1.51	1659.587	2.41
0.015	0.00	0.158	0.00	1.660	0.05	17.378	0.13	181.970	1.36	1905.461	0.53
0.017	0.00	0.182	0.00	1.905	0.06	19.953	0.15	208.930	1.23	2187.762	0.00
0.020	0.00	0.209	0.00	2.188	0.06	22.909	0.18	239.883	1.19	2511.886	0.00
0.023	0.00	0.240	0.00	2.512	0.07	26.303	0.21	275.423	1.37	2884.032	0.00
0.026	0.00	0.275	0.00	2.884	0.07	30.200	0.25	316.228	1.85	3311.311	0.00
0.030	0.00	0.316	0.00	3.311	0.07	34.674	0.30	363.078	2.71	3801.894	0.00
0.035	0.00	0.363	0.00	3.802	0.07	39.811	0.37	416.869	3.93	4365.158	0.00
0.040	0.00	0.417	0.00	4.365	0.07	45.709	0.47	478.630	5.41	5011.872	0.00
0.046	0.00	0.479	0.00	5.012	0.07	52.481	0.60	549.541	6.99	5754.399	0.00
0.052	0.00	0.550	0.00	5.754	0.07	60.256	0.78	630.957	8.41	6606.934	0.00
0.060	0.00	0.631	0.00	6.607	0.06	69.183	0.98	724.436	9.42	7585.776	0.00
0.069	0.00	0.724	0.00	7.586	0.06	79.433	1.20	831.764	9.79	8709.636	0.00
0.079	0.00	0.832	0.00	8.710	0.06	91.201	1.39	954.993	9.40	10000.000	0.00
0.091	0.00	0.955	0.00	10.000	0.06	104.713	1.55	1096.478	8.27		
0.105		1.096	0.01	11.482		120.226		1258.925			

Operator notes: *Average of 10 measurements from 10.05.mea*

4: Floc test with scaling inhibitor SI 5 (50 ppm)

5: Floc test with both chemical: scaling inhibitor SI 2 (50 ppm) and corrosion inhibitor CI 2 (50, 100 ppm)

MASTERSIZER 2000

Result Analysis Report

Sample Name:
Averaged Result 5 100+ 3 100

Sample Source & type:

Sample bulk lot ref:

SOP Name:

Measured by:
Administrator

Result Source:
Averaged

Measured:
10. mai 2010 18:26:13

Analysed:
10. mai 2010 18:26:14

Particle Name:
Default

Particle RI:
1.520

Dispersant Name:
Water

Accessory Name:
Hydro 2000MU (A)

Absorption:
0.1

Dispersant RI:
1.330

Analysis model:
General purpose

Size range:
0.020 to 2000.000 um

Weighted Residual:
1.528 %

Sensitivity:
Normal

Obscuration:
33.53 %

Result Emulation:
Off

Concentration:
0.6343 %Vol

Specific Surface Area:
0.0682 m²/g

Span :
2.511

Surface Weighted Mean D[3,2]:
87.986 um

Uniformity:
0.787

Vol. Weighted Mean D[4,3]:
527.569 um

Result units:
Volume

d(0.1): 77.148 um   **d(0.5): 428.986 um**   **d(0.9): 1154.209 um**

Particle Size Distribution
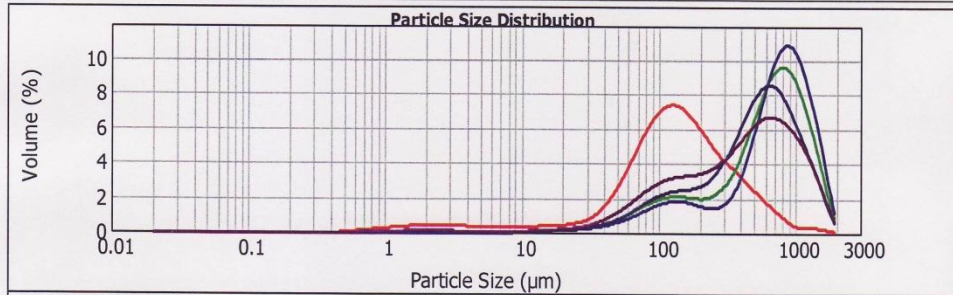
— Averaged Result 1 cf, 22. april 2010 15:37:33
— Averaged Result 5 100 cf, 10. mai 2010 17:41:19
— Averaged Result 5 100+3 25, 10. mai 2010 18:12:14
— Averaged Result 5 100+3 50, 10. mai 2010 18:18:46
— Averaged Result 5 100+ 3 100, 10. mai 2010 18:26:13

Size (μm)	Volume In %	Size (μm)	Volume In %	Size (μm)	Volume In %
0.010	0.00	0.105	0.00	1.096	0.08
0.011	0.00	0.120	0.00	1.259	0.08
0.013	0.00	0.138	0.00	1.445	0.09
0.015	0.00	0.158	0.00	1.660	0.09
0.017	0.00	0.182	0.00	1.905	0.10
0.020	0.00	0.209	0.00	2.188	0.10
0.023	0.00	0.240	0.00	2.512	0.09
0.026	0.00	0.275	0.00	2.884	0.09
0.030	0.00	0.316	0.00	3.311	0.08
0.035	0.00	0.363	0.00	3.802	0.07
0.040	0.00	0.417	0.00	4.365	0.06
0.046	0.00	0.479	0.00	5.012	0.05
0.052	0.00	0.550	0.00	5.754	0.04
0.060	0.00	0.631	0.01	6.607	0.03
0.069	0.00	0.724	0.02	7.586	0.04
0.079	0.00	0.832	0.05	8.710	0.05
0.091	0.00	0.955	0.07	10.000	0.08
0.105		1.096		11.482	

Size (μm)	Volume In %	Size (μm)	Volume In %	Size (μm)	Volume In %
11.482	0.09	120.226	2.87	1258.925	3.41
13.183	0.11	138.038	2.94	1445.440	2.39
15.136	0.14	158.489	2.98	1659.587	1.29
17.378	0.17	181.970	3.04	1905.461	0.30
19.953	0.21	208.930	3.16	2187.762	0.00
22.909	0.27	239.883	3.38	2511.886	0.00
26.303	0.34	275.423	3.72	2884.032	0.00
30.200	0.45	316.228	4.18	3311.311	0.00
34.674	0.59	363.078	4.70	3801.894	0.00
39.811	0.78	416.869	5.23	4365.158	0.00
45.709	1.02	478.630	5.68	5011.872	0.00
52.481	1.31	549.541	5.98	5754.399	0.00
60.256	1.63	630.957	6.05	6606.934	0.00
69.183	1.96	724.436	5.89	7585.776	0.00
79.433	2.27	831.764	5.54	8709.636	0.00
91.201	2.54	954.993	5.00	10000.000	
104.713	2.74	1096.478	4.30		
120.226		1258.925			

Operator notes: *Average of 10 measurements from 10.05.mea*

6: Floc test with both chemical: scaling inhibitor SI 2 (100 ppm) and corrosion inhibitor CI 3 (25, 50, 100 ppm)