TOTAL

ENVIRONMENTAL ASPECT OF EOR CHEMICALS

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Presented at FORCE - EOR Competence Building Workshop
6. November 2013

PRESENTATION OUTLINE

- **Problems with offshore EOR projects**
  - OSPAR convention
  - Polymer EOR environmental challenges

- **R&D to meet the challenge**
  - Characterization of environmental impacts
  - Possibility to reduce the environmental impacts
    - PWRI
    - Treatment before discharge
    - Polymer recovery which requires sludge management

OSPAR CONVENTION

The Convention for the Protection of the marine Environment of the North-East Atlantic (the 'OSPAR Convention')

- **Open for signature at the Ministerial Meeting of the Oslo and Paris Commissions in Paris on 22 September 1992**

Signed and ratified by all of the Contracting Parties to the original Oslo or Paris Conventions

- **Belgium, Denmark, the European Community, Finland, France, Germany, Iceland, Ireland, the Netherlands, Norway, Portugal, Spain, Sweden and the United Kingdom of Great Britain and Northern Ireland) and by Luxembourg and Switzerland.**

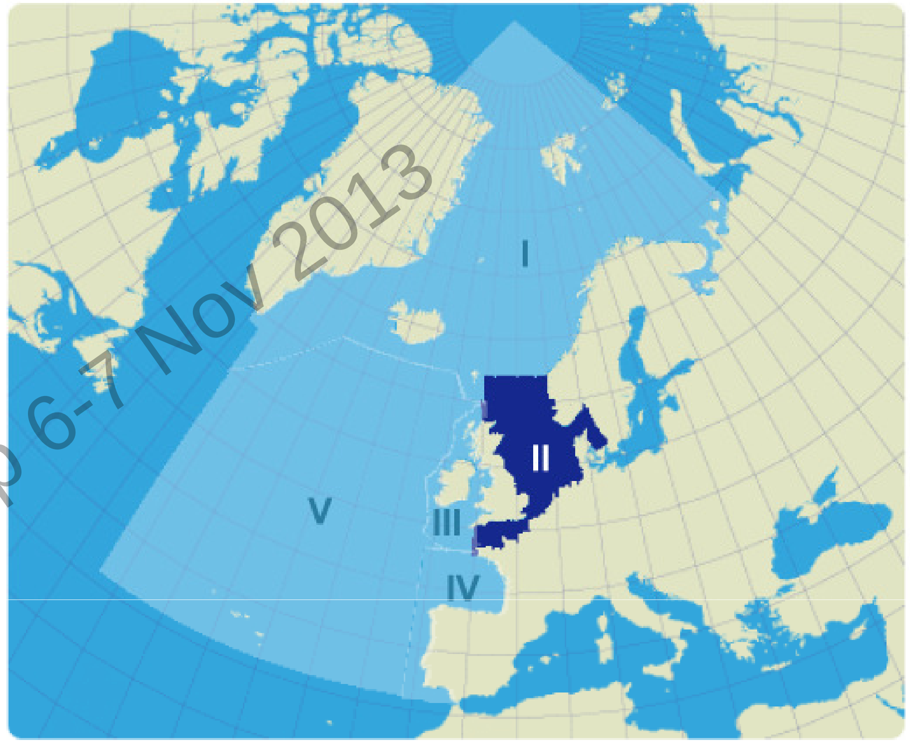
The OSPAR Convention entered into force on 25 March 1998

☞ **Precautionary principle**

☞ **Best Available Techniques (BAT)**

☞ **Best Environmental Practice (BEP)**

The North East Atlantic



The North East Atlantic

Region I	Arctic Waters
Region II	Greater North Sea
Region III	Celtic Seas
Region IV	Bay of Biscay and Iberian Coast
Region V	Wider Atlantic

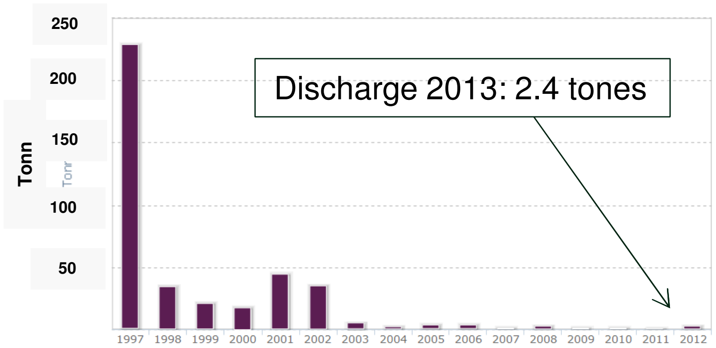
Region 2: The Greater North Sea is one of the busiest maritime areas. Offshore activities related to the exploitation of oil and gas reserves, and maritime traffic are very important. Two of the world's largest ports are situated on the North Sea coast, and the coastal zone is used intensively for recreation. The Greater North Sea is surrounded by densely populated, highly industrialised countries.

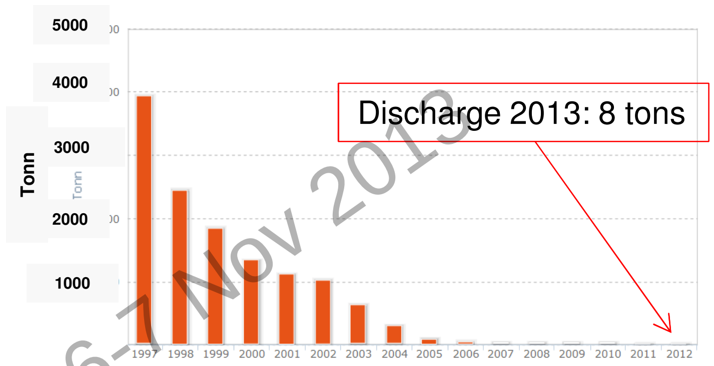
Hazard assessment of offshore chemicals (OSPAR and Norwegian regulations)

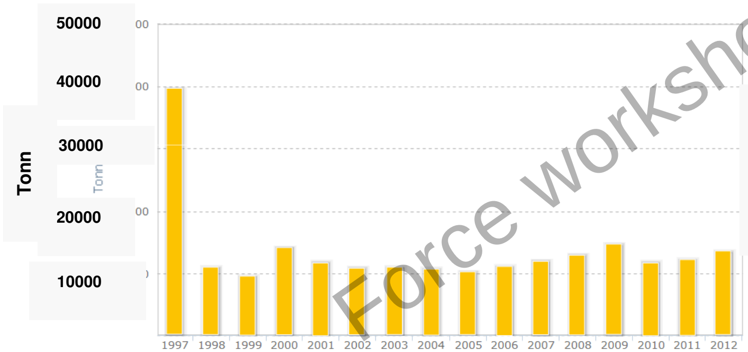
Classification of exploration and production chemicals

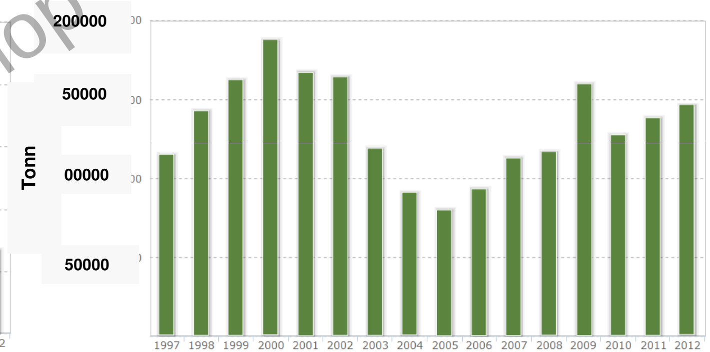
Category	*Criteria – Ecotoxicity tests*	*Actions*
Black	■Priority list (Stortingsmelding Nr. 25) ■OSPAR List of Chemicals for Priority Action ■Both low biodegradability and high bioaccumulation (BOD28 < 20 %, and Log POW ≥ 5) ■Low biodegradability and toxic (BOD28 < 20 %, and EC50 or LC50 ≤ 10 mg/L) ■Compounds expected to be carcinogenic/mutagenic or harmful to reproduction	Not discharged
Red	■Inorganic chemicals with high toxicity (EC50 or LC50 ≤ 1 mg/L) ■Organic chemicals with low biodegradability (BOD28 < 20 %) ■Organic chemicals or mixtures which meet 2 of the 3 following criteria: Biodegradability < 60 %, or bioaccumulation potential (Log POW ≥ 5, or toxicity of EC50 or LC50 ≤ 10 mg/L)	Phased out or replaced
Yellow	■Include compounds which based on their characteristics are not defined as RED or BLACK, and ■NOT included in the PLONOR list	Accepted
Green	■Chemicals expected to have NO environmental effects ■PLONOR list	Testing not required

CHEMICAL DISCHARGE ON NORWEGIAN CONTINENTAL SHELF









☞ **99% + of the discharge are green and yellow chemicals today**

Reference case – Medium size polymer EOR project:

20% of the annual produced water (~20 MSm3) containing 200 ppm of HPAM

⇒ ~ 800 tons per year discharge of red chemical

OSPAR'S PLONOR LIST

OSPAR COMMISSION

Protecting and conserving the North-East Atlantic and its resources

OSPAR List of Substances Used and Discharged Offshore which Are Considered to Pose Little or No Risk to the Environment (PLONOR)

OSPAR Agreement 2012-06 (Replacing Agreement 2004-10)
Revised February 2013 to correct footnote cross-references

Substances in the PLONOR list

1. The list at Appendix 1 contains substances whose use and discharge offshore is subject to expert judgement by the competent national authority of Contracting Parties. These substances do not normally need to be strongly regulated as, from assessment of their intrinsic properties, the OSPAR Commission considers that they pose little or no risk to the environment.

Criteria for inclusion of substances in the PLONOR list

2. Requests to the Offshore Industry Committee for inclusion of new substances on this list should be accompanied by the appropriate data required to undertake a prior assessment. The data required and the acceptance criteria are the following:

Categories	Minimum data required for assessment	Acceptance criteria
All substances, including inorganic salts (naturally occurring or constituents of seawater)[i], and natural organic substances which are non-water soluble (e.g. nutshells, fibres etc.)	Parts 1 and 3 of HOCNF shall be completed, supported by the Safety Data Sheets if necessary. CAS-number(s) shall be provided if they exist	- Classification with risk phrases according to Council Directive 67/548/EEC, Annex VI does not lead to any of the following risk phrases: R50, R50/53, R51, R51/53, 52, R52/53, R53[ii]. - The substance is not Carcinogenic (cat 1 & 2)[iii], Mutagenic (cat 1 & 2)[iii] or Toxic for Reproduction (Cat 1, 2 & 3)[iii]
		Classification with hazard statements according to Council Regulation 1272/2008, Annex VI does not lead to any of the following hazard statements: H400, H410, H411, H412, H413[ii]. The substance is not Carcinogenic (cat 1A & 1B)[iii], Mutagenic (cat 1A & 1B)[iii] or Toxic for Reproduction (Cat 1A, 1B & 2)[iii]

OIC 2012 Revision of OSPAR List of Substances Used and Discharged Offshore which Are Considered to Pose Little or No Risk to the Environment (PLONOR)

CAS Number	EINECS Number	Substance / Synonyms[v]
64-19-7	200-580-7	Acetic acid
1335-30-4 12141-46-7 12068-56-3 1318-93-0	215-628-2 235-253-8 235-102-6 215-288-5	Aluminium silicate Aluminium silicate (Al_2SiO_5) Aluminium silicate ($Al_6Si_2O_{13}$) Aluminium silicate (Montmorillonite)
10043-01-3	233-135-0	Aluminium sulphate
7722-76-1 10124-31-9	231-764-5 233-330-0	Ammonium dihydrogen phosphate ($(NH_4)H_2PO_4$) Ammonium acid phosphate / phosphoric acid, ammonium salt ($NH_3.xH_3$ PO_4)
10192-30-0	233-469-7	Ammonium bisulphite
12125-02-9	235-186-4	Ammonium chloride
1336-21-6	215-647-6	Ammonium hydroxide
10196-04-0	233-484-9	Ammonium sulphite
12168-85-3	235-336-9	Tricalcium silicate
57-13-6	200-315-5	Urea
-	-	Vegetable fibre
1318-00-9	-	Vermiculite
68608-58-2 92129-93-6	271-787-8	Whey, Protein-free Whey lactose low Whey permeate
-	-	Wood fibres
11138-66-2	234-394-2	Xanthan gum
-	Polymer	High MW hydroxy ethyl cellulose polymer
-	Polymer	Hydroxypropylated cross-linked corn starch

TOTAL

EOR – ENVIRONMENTAL CONCERNS

EOR polymers (likely also surfactants) are a red chemicals

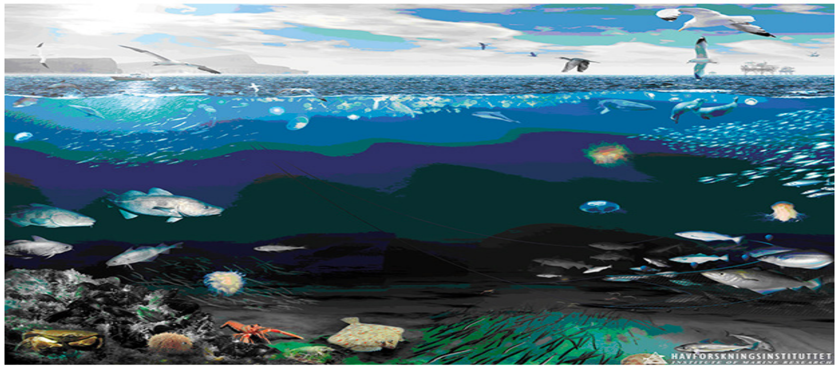
- Low degradation (less than 20% degradation during 28 days according to HOCNF* testing protocol)

Handling of back produced EOR chemicals

- PWRI** is the best and required solution to avoid environmental impact
- Discharge of produced water containing EOR chemicals may happen due to for example failure or irregularity of the re-injection facilities
- Recovery of polymer from produced water, but large sludge needs disposal management

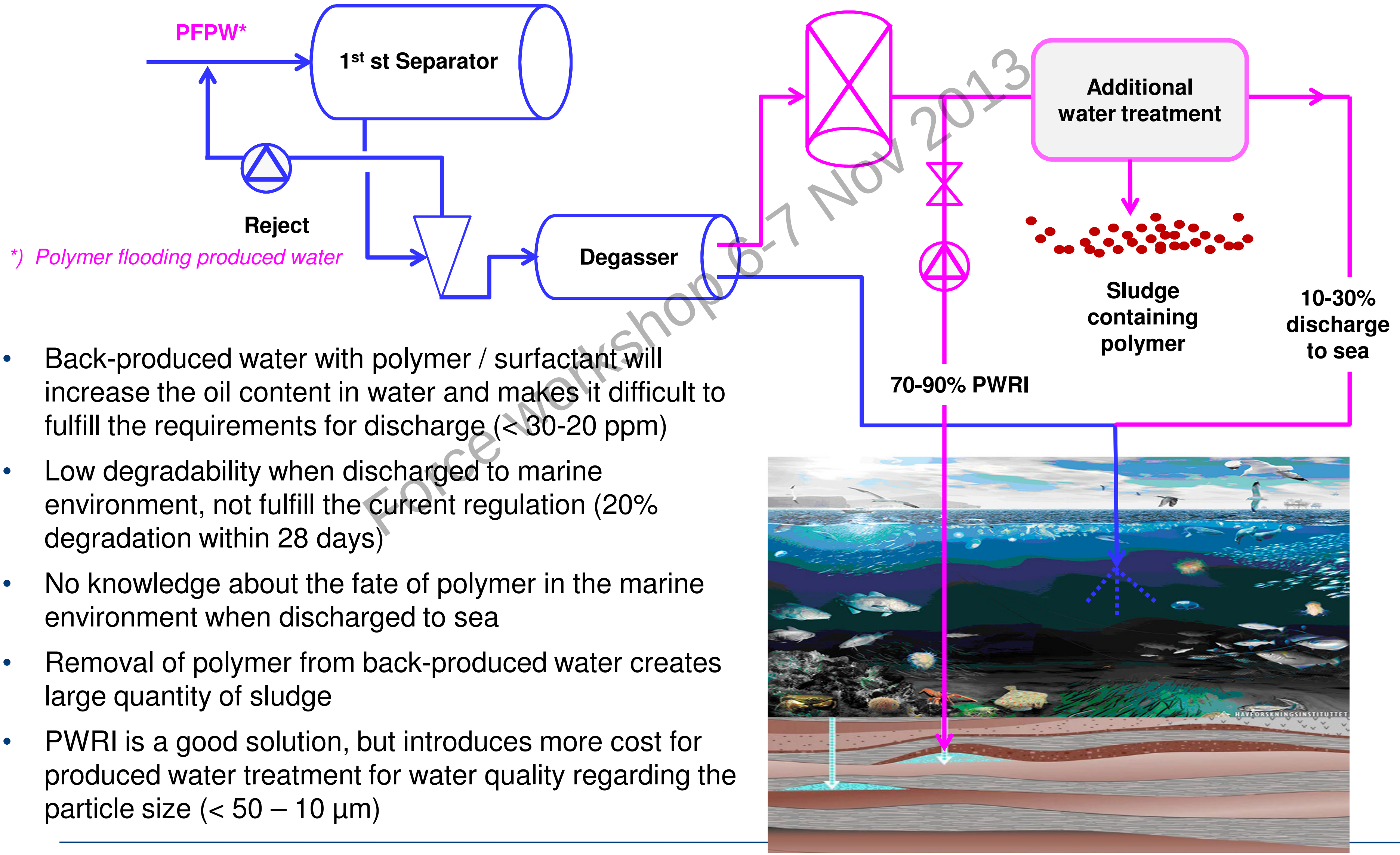
Discharge of fresh EOR solution to sea may be unavoidable

- Discharge of disqualified fresh solutions
- Discharge due to accident during transport from shore to field



**) Harmonized Offshore Chemical Notification Format*
***) Produced water reinjection*

POLYMER EOR - ADDITIONAL CHALLENGE TO WATER TREATMENT



- Back-produced water with polymer / surfactant will increase the oil content in water and makes it difficult to fulfill the requirements for discharge (< 30-20 ppm)
- Low degradability when discharged to marine environment, not fulfill the current regulation (20% degradation within 28 days)
- No knowledge about the fate of polymer in the marine environment when discharged to sea
- Removal of polymer from back-produced water creates large quantity of sludge
- PWRI is a good solution, but introduces more cost for produced water treatment for water quality regarding the particle size (< 50 – 10 µm)

ONGOING R&D: CHARACTERIZATION OF ENVIRONMENTAL IMPACTS

SINTEF aquateam

Statoil

TOTAL

JIP - ENVIRONMENTAL ASPECT OF EOR CHEMICALS

Phase 1 - 2009 – 2011 (SINTEF)
Phase 2 – 2012 – 2013 (Aquateam)
Phase 3 under preparation for 2013 - 2014

Objectives

- The overall aim of this project is to qualify chemicals for use as offshore EOR chemicals in an environmentally acceptable manner.

Scope of work:

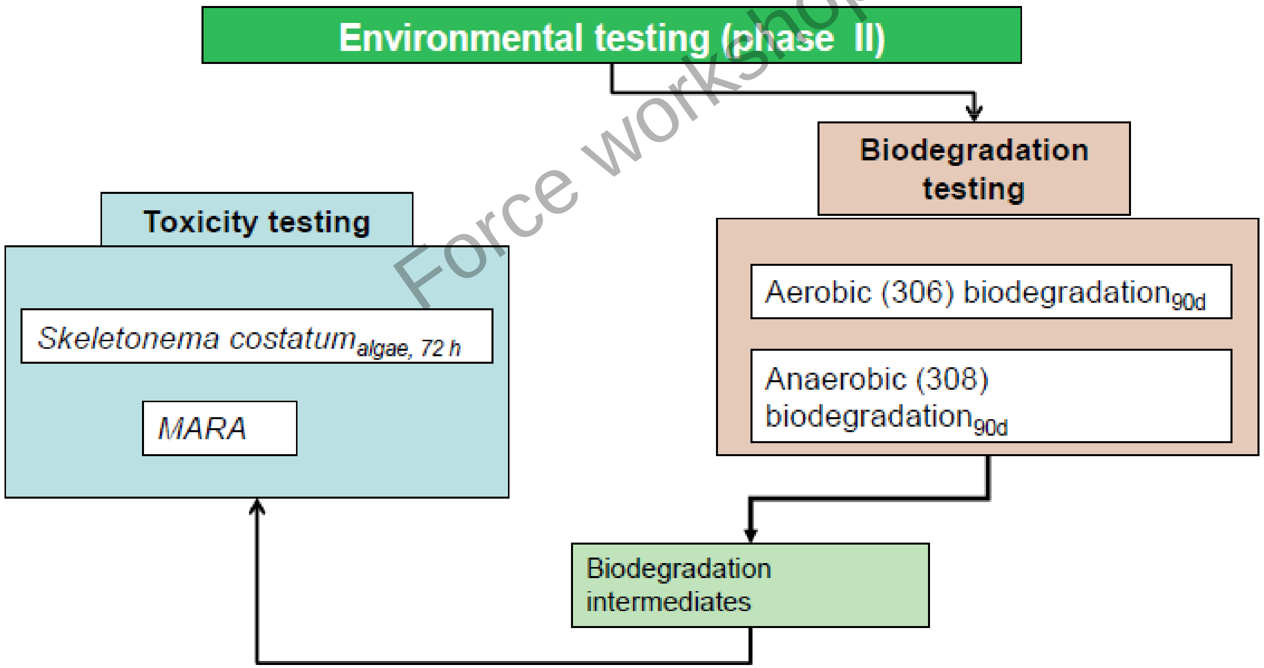
- Environmental testing of produced water containing back-produced polymer and establish the environmental impact
- Establish analytical procedures and method for residual polymer analysis
- Identify feasible PFPW treatment technology

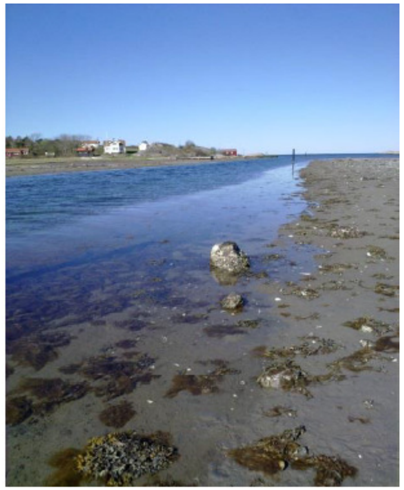
ENVIRONMENTAL TESTING

2 types of bio-degradation testing

- ***Aerobic*** – simulate HPAM in suspension in water column
- ***Anaerobic*** – simulate HPAM has sunk and accumulated at sea bottom there is sediment and lack of oxygen.

Simple toxicity testing





ONGOING R&D:
POSSIBLE WATER TREATMENT METHODS

Produced water reinjection (PWRI)

- **Water quality requirements depend on the PWRI strategy**

  ⇒ Most restrict when injection to reservoir with matrix mode

  ⇒ Max Total Suspended Solid (TSS), Cut size, etc

Degradation of polymer in PFPW before discharge

- **Mechanical degradation**
- **Oxidation**

Polymer recovery from PFPW

- **Flocculation / Coagulation**
- **Ultra filtering**

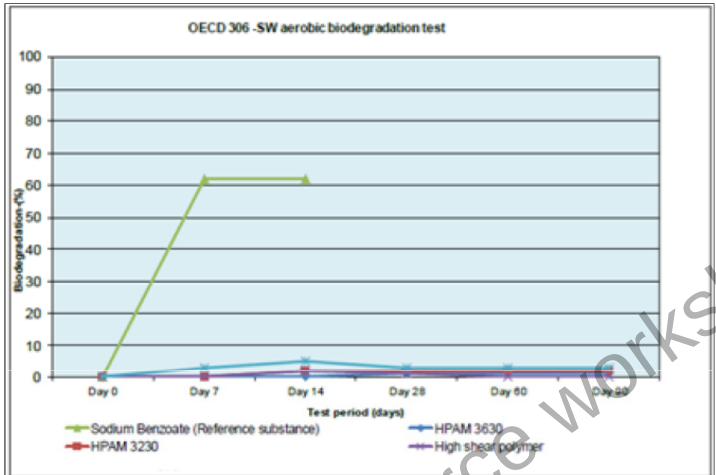
=> Sludge management

TOTAL

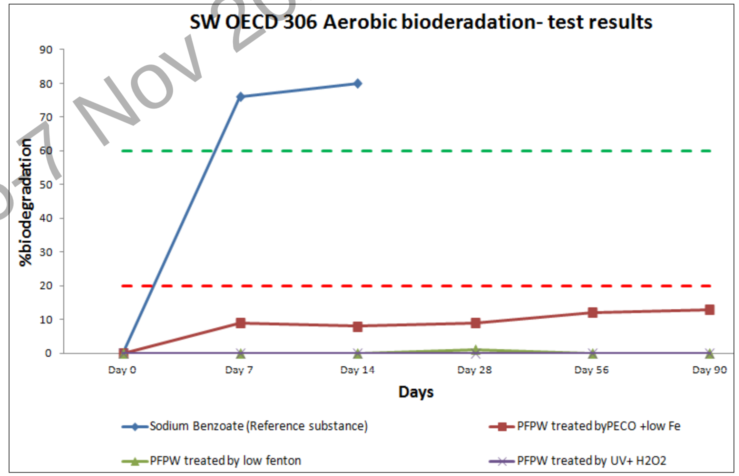
PRELIMINARY TEST RESULTS OF BIODEGRADATION OF POLYMER

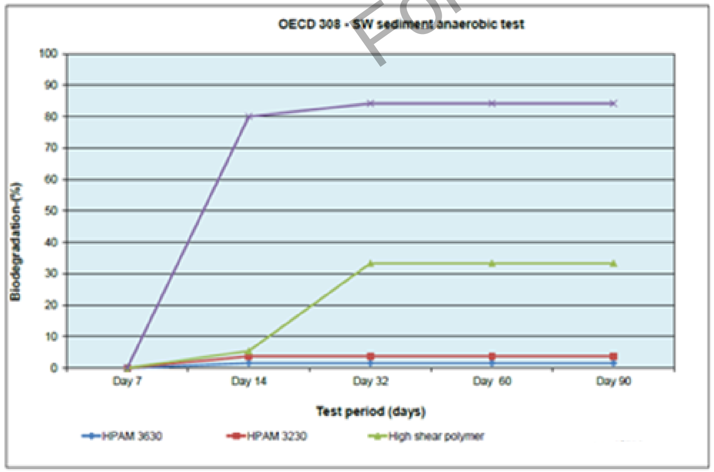
SINTEF aquateam
Statoil
TOTAL

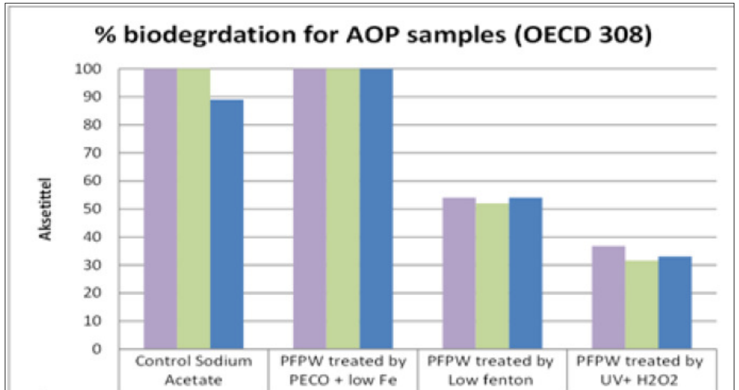
Aerobic biodegradation testing
(OECD 306)



Anaerobic biodegradation testing
(OECD 308)







	Control Sodium Acetate	PFPW treated by PECO + low Fe	PFPW treated by Low fenton	PFPW treated by UV+ H2O2
Day 34	100	100	54	37
Day 56	100	100	52	32
Day 69	89	100	54	33

ADVANCED OXIDATION (AOP) FOR POLYMER DEGRADATION

Oxidation processes tested in the project:

Oxidant / Processes	Viscosity Reduction	Polymer removal (by precipitation or filtering)	Mineralization (HPAM transformed to CO2 + other comp)
NaClO	Slow	No	No
Fenton	Very fast	> 95 %	No
Zydox(ClO2)	Negligible	No	No
Photooxidation			
UV	Fast	No	No
UV+H2O2	Very fast	Up to 15 %	Up to 15%
UV+Fenton	Very fast	> 90 %	Up to 30%
UV+TiO2	Fast	Less than 10 %	Less than 10%
PECO (from AquaMost)			
PECO	Fast	No	No
PECO+Fe	Very fast	> 95 %	Up to 40%
WaterDiam			
BDD	Slow	No	No
BDD+UV	Fast	No	No
BDD+Fe+UV	Fast	> 95 %	No
Steel electrode	Slow	Up to 30%	No
Fenton + Nano Filtration	Very fast	> 95 % by filtration	No

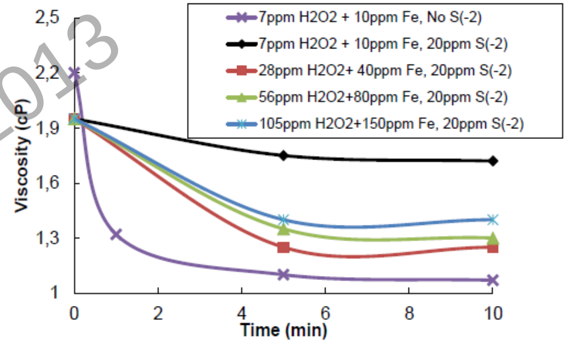
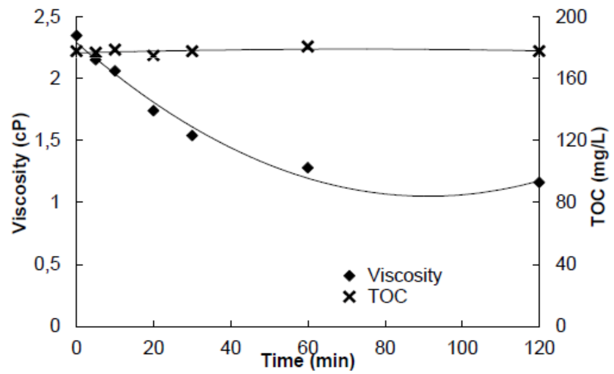
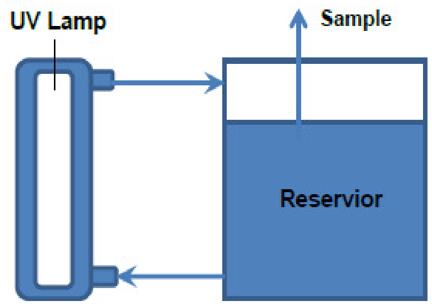


Figure 42. Effect of S(-2) on HPAM degradation





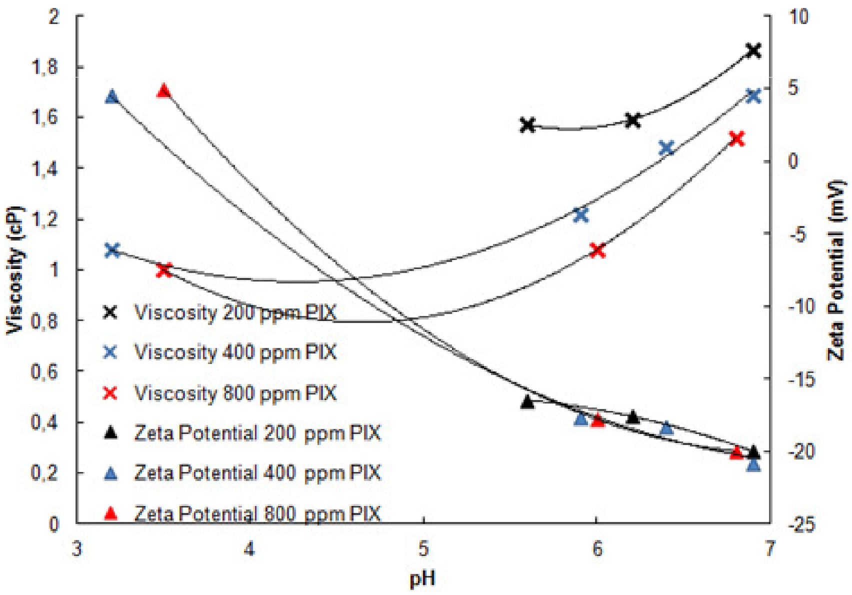
FLOCCULATION & COAGULATION

Chemical	HPAM removal	Minimal effective dosage	Sludge generation	Sludge generation* (mg/l)	TOC in solution (mg/l)
PAX	Over 95%	200 mg/l	Yes	578**	~10
PIX	Over 95%	200 mg/l	Yes	382	~10
SNF Polymers	Up to 90%, based on viscosity	500 mg/l	Yes	hard to estimate	up to 400
Sorbfloc®	Not observed	Not applicable	Little	Not applicable	Not applicable

*) Assuming that all metallic components precipitate.
**) Gives 0.578 kg sludge pr Sm3 of water.

Main conclusions from testing:

- Relatively high dosage is needed
- More testing needed for optimization
- Other flocculates and coagulants should be tested
- Must develop sludge handling strategy



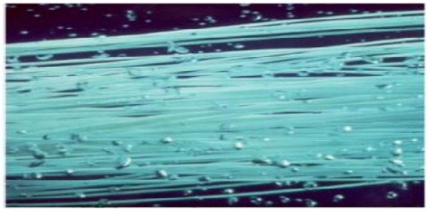
PWRI – KEY PARAMETERS

Reinjection in matrix mode in shallow unconsolidated reservoir

Key Performance Parameter	Requirement	Ceramic Membrane	Centrifugation
OIW (Oil In Water)	< 10 ppm	< 5 ppm	< 5-10 ppm
TSS (Total Suspended Solids)	< 1 mg/L	< 1 mg/L	< 1 mg/L
Cut size	< 2 µm	< 0.1 µm	< 2 µm
Temperature	50°C	< 150°C	NA

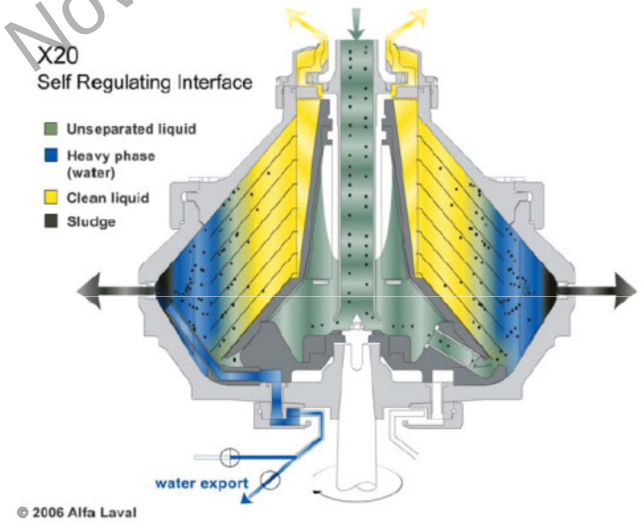
PWRI – PFPW WATER TREATMENT

Membranes



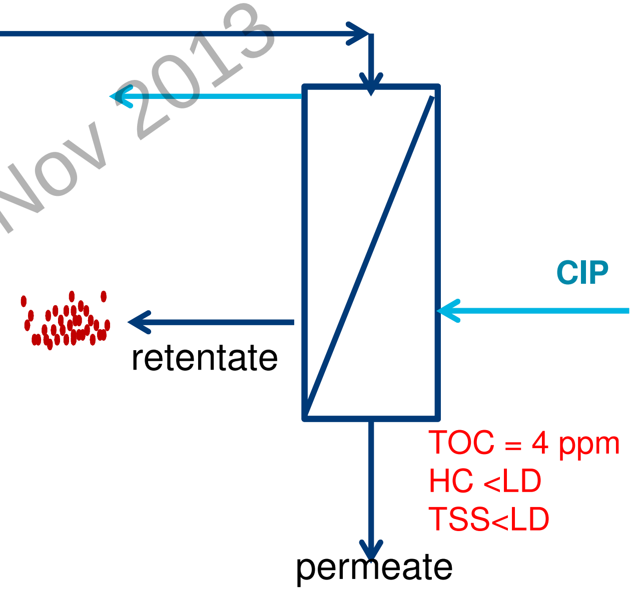
OR

Centrifugation



CASE STUDY – SLUDGE MANAGEMENT FOR CEOR WATER TREATMENT – FILTRATION

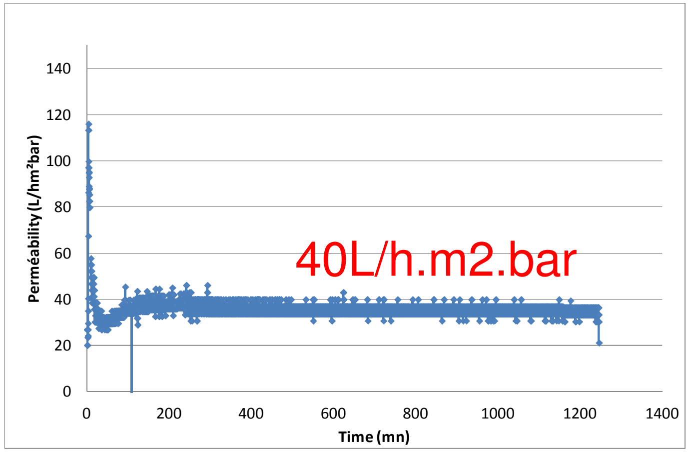
500 ppm polymer
+
50 ppm oil
+
20 ppm particles



Q retentate = 10% Flux
Qs* retentate #10% Flux
Dryness # 2%

SLUDGE Content:
98% water
Polymer 5000ppm
Oil 40ppm
Particles 20ppm

* s= Sludge



CASE STUDY – COAGULATION

500ppm polymer
+
50ppm oil
+
20ppm particles

500ppm FeCl3

1 hour
sedimentation

Polymer 400ppm
Particles

Polymer
Oil
Particles

Qs = depending of sludge separation
Dryness # 3 to 5% (for decantation)

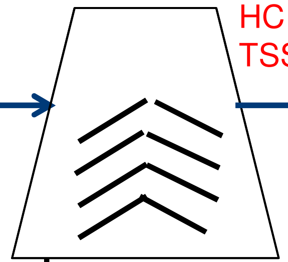
SLUDGE Content
Polymer 400ppm
Oil
Particles

+ Daily
Coagulant
consumption

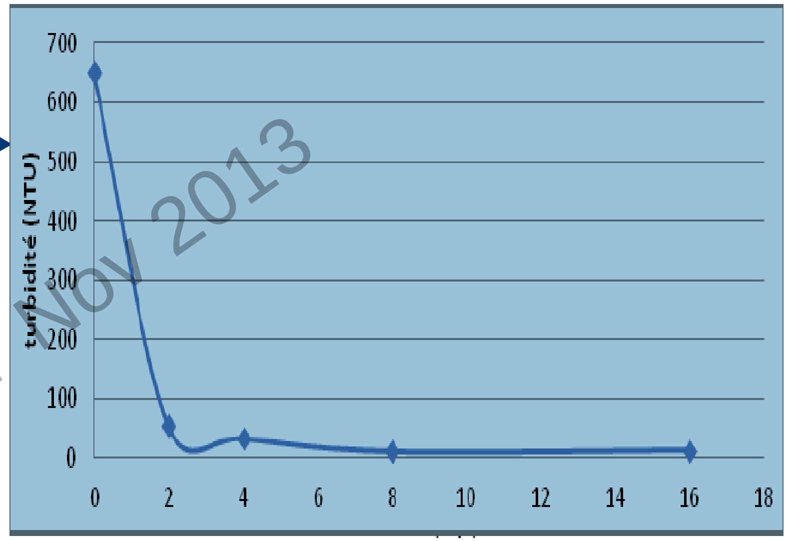
* s= Sludge

CASE STUDY – CENTRIFUGATION TECHNOLOGIES

500 ppm polymer
+
50 ppm oil
+
20 ppm particles



TOC # 200 ppm
HC <LD
TSS<LD



Turbidity = f(time) min

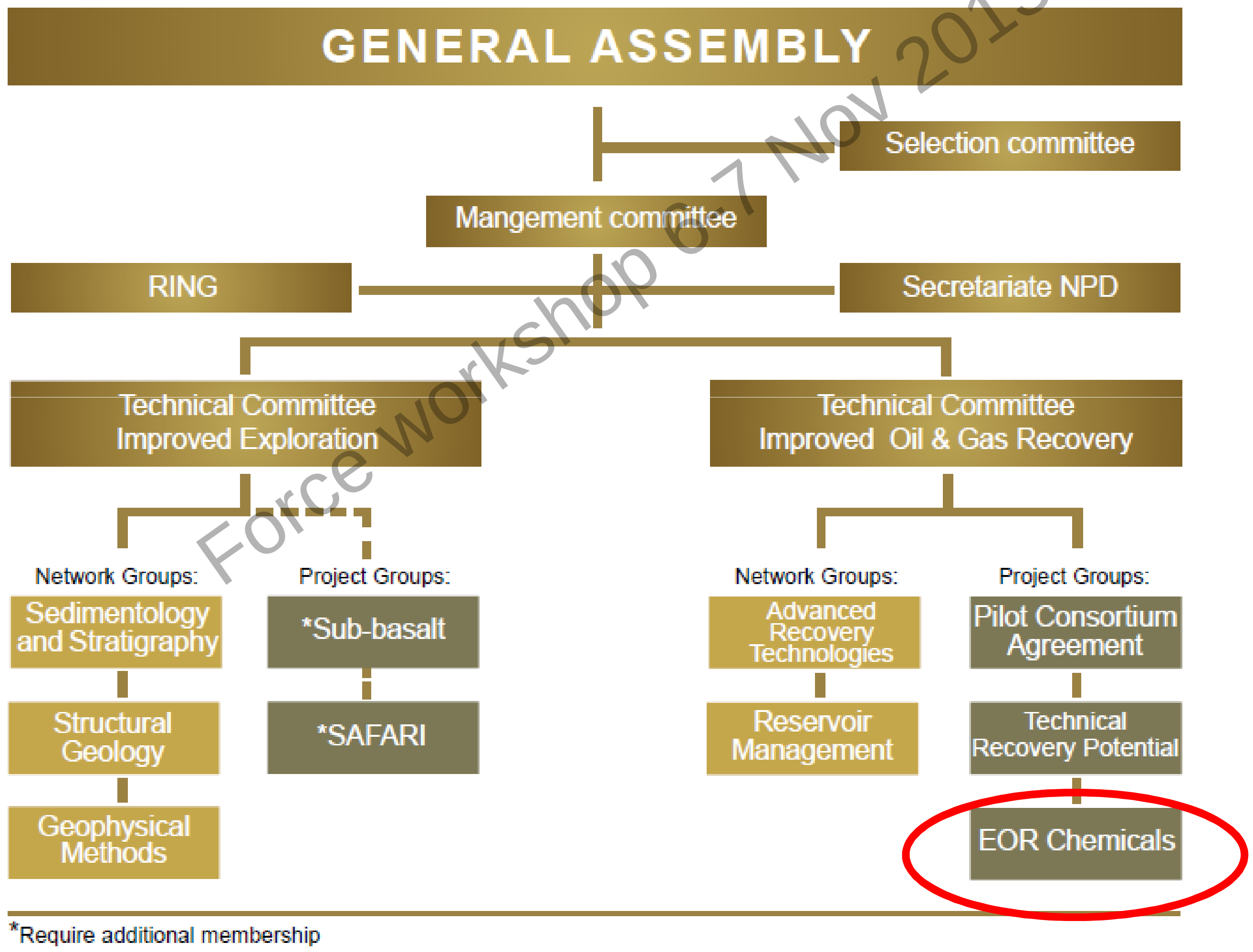
Polymer 0ppm
Oil 40ppm
Particles 20ppm

Qs # 10% Flux
Dryness # 15 to 30%

* s= Sludge

FORCE – REPORT FROM GROUP 'EOR CHEMICALS'

FORCE - A cooperation forum – Membership from 30+ E&P companies



FORCE – REPORT FROM GROUP 'EOR CHEMICALS'

FORCE – EOR Chemical group

- Project goals:
  - Assess the environmental impact and risk related to utilization of EOR chemicals during platform operations, reservoir flow and discharge of produced water. Recommend guidelines for safe and environmental offshore handling of EOR chemicals .
- Group members:
  - NPD – Norwegian Petroleum Directorate
  - KLIF – Norwegian Climate and Polution Authority
  - Oil companies: Shell, Statoil, Total, Petoro
  - Research Inistitutes: CIPR

Report to be published to general public in 2011:

"Assessment of Environmental Impact from EOR Chemicals for the Norwegian Continental Shelf"

- Assessment of potential environmental impact of HPAM / Surfactant in marine environment
- Estimations of potential discharge from field scale studies: Polymer flooding case / PASF case
- Importance of detection and monitoring

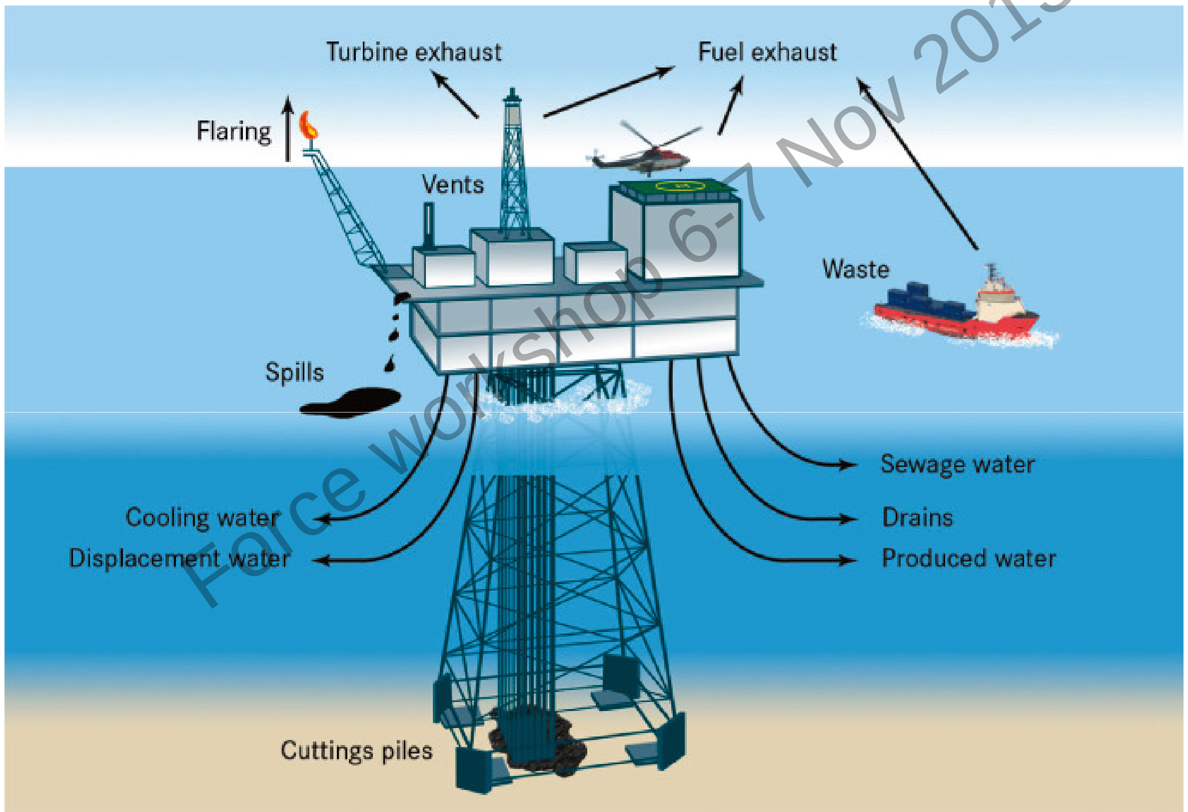
FORCE – REPORT FROM GROUP 'EOR CHEMICALS'

FORCE

Assessment of Environmental Impact from EOR Chemicals for the Norwegian Continental Shelf

Table of contents

TOTAL ENVIRONMENTAL IMPACT
=> NEED FOR LIFE CYCLE EVALUATION



SUMMARY AND CONCLUSIONS

- **Polymer as EOR chemical is red chemical**

  ➔ Cannot be discharged to marine environment according to the environmental regulation in Norway

- **Polymer flooding EOR requires additional strategy for handling of the back-produced water**

  ➔ Polymer recovery generates large quantity of sludge

  ➔ Conventional centrifuge method does not allow separation of polymer from PFPW. However, it might be applied for PWRI.

- **Discharge PFPW might be feasible**

  ➔ Anaerobic biodegradation may degrade polymer fast enough but requires reduction of the polymer chain length before discharge

  ➔ AOP looks promising for degradation of polymer, more research is needed for energy efficiency of AOP

  ➔ More research needed to understand the behavior of polymer when discharged to sea