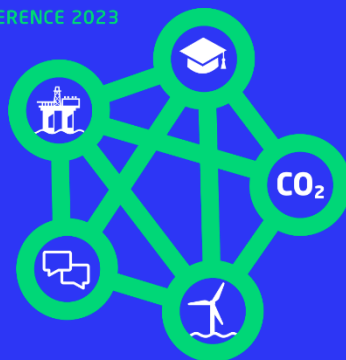


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Lene Hjelm Poulsen  
Hamid Nick

# Poster Award Ceremony





# 7 Poster Awards



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# Audience Favorite Award

# 39

**Bridging Analytical Gaps: Produced Water Characterization of Contaminants and Their Eco-Toxicity**

Neri Bonciani<sup>1</sup>, Matteo Ottaviani<sup>1</sup>, Emil H. Bohr<sup>2</sup>, Markus V. Strange<sup>3</sup>, Jixin Qiao<sup>3</sup>, Lars M. Skjolding<sup>3</sup>, Karen L. Feilberg<sup>3</sup>

**DTU**

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<sup>2</sup> DTU Aqua, Kemitorvet 202, Kgs Lyngby (Denmark)  
<sup>3</sup> DTU Sustain, Byngstrøgsvet 115, Kgs Lyngby (Denmark)

**Introduction**

Exploiting subsurface reservoirs for oil production and, in later life, CO2 sequestration yields substantial amounts of produced water (PW). This water originates as a formation brine contaminated by oil-related compounds and production additives (including anti-scaling agents, H2S scavengers, and biocides). Most offshore production platforms discharge this wastewater entirely into the sea column, observing a limiting value relating to dispersed oil-in-water only. Hence, there is a great need to understand the environmental impact of the remainder of the constituents water only. Hence, there is a great need to understand the environmental impact of the remainder of the constituents water only. Hence, there is a great need to understand the environmental impact of the remainder of the constituents water only. (Environmental Impact Factor per each substance).

**1. Organics in PW**

Naturally occurring compounds in PW (as BTEX) and chemicals as formaldehyde releaser, glutaraldehyde and secondary ammonium compounds (QAC) are the greatest contributors to the environmental impact factor (EIF) in PW discharge. These compounds are hardly ever monitored and regulated and their concentration in the discharged PW is usually unknown. However our work has achieved effective analytical ways to measure those concerning compounds, BTEX and other alkylated aromatics are extracted with Dynamic Headspace (DHS) method and trapped in granular charcoal. Aldehydes are derivatized with O-(2,3,4,5,6-Pentafluorobenzyl)formaldehyde (PFBA) and measured with GC-MS. Moreover, QAC are analyzed through LC-ESI-MS with previous SPE pre-concentration and separation. Experiments on targeted extract on 24h with DHS are subject to eco-toxicity tests on different trophic levels and the toxicity decrease is evaluated.

	V87	V86	V84	V21
Formaldehyde (µg/L)	22.5	21.0	19.2	20.5
Glutaraldehyde (µg/L)	2.3	1.9	<LOD	<LOD

**2. Inorganics in PW**

PW comprises a variety of suspended solids, radionuclides, and metals. Traditionally, the presence of trace and heavy metals in PW has been underestimated, with more attention being given to toxic organic compounds. Currently, there is a significant research gap concerning the features of metals and metalloids in Danish PWs. Understanding the composition of trace metals in produced water is crucial, not only for geochemical mapping but also for environmental monitoring purposes. Given the great temporal variability in metal concentrations, relying on a single sample collection is inadequate and potentially misleading. In this work, we have used ICP-OES and ICP-MS to overcome the complexity of the sample and characterize unfiltered PW sample and evaluate the relative difference among sampling days. Potassium-210 extraction from PW and analysis via alpha-spectrometry has been also performed, to assess the magnitude of PW alpha-emitters input into the sea.

**3. Eco-toxicity tests**

Volatile compounds as formaldehyde and glutaraldehyde have shown to be greater toxicity contributors, after performing dynamic head space removal experiments. Significant differences are shown below if we compare bacteria's EC50 of various PW samples, as they are more affected by biocide content variations in PW. Pityri- and zoogloeation (respectively algae and copepods) are showing much lower EC50 values, thus PW is more toxic to them and their response to different PW samples is not as diverse as the bacteria's.

**Conclusions**

In conclusion, the knowledge gap about minor components in PW has been partially filled. Single sampling for monitoring or environmental purposes is not representative enough, due to daily variations of those components (organic and inorganic). To achieve a zero-harmful discharge, it is imperative to continuously monitor all substances in produced water that raise environmental concerns. This will help mitigate environmental impact, safeguard public health, ensure adherence to forthcoming environmental regulations, and enhance the efficacy of water treatment processes for the safe disposal or recycling of produced water.

BlueNord nordsefonden

- Neri Bonciani
- Matteo Ottaviani
- Emil H Bohr
- Markus Strange
- Jixin Qiao
- Lars Skjolding
- Karen Feilberg

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# The Best Awards

# 33

- Alessandro Perrucci
- Alaa Khalil
- Sarah Huckelkamp
- Sofie Askjaer Hass
- Maria Nymann
- Sergey Kucheryavskii
- Jens Muff
- Marco Maschietti

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### Innovative approach for H<sub>2</sub>S scavenging in offshore oil and gas: MEA-triazine recovery and hydrothermal oxidation of spent scavengers.

Alessandro Perrucci<sup>1</sup>, Alaa Khalil<sup>1</sup>, Sarah Hückelkamp<sup>2</sup>, Sofie Askjær Hass<sup>2</sup>, Maria Nymann Christensen<sup>2</sup>, Sergey Kucheryavskiy<sup>1</sup>, Jens Muff<sup>1</sup>, Marco Maschietti<sup>1</sup>

<sup>1</sup>Aalborg University, Department of Chemistry and Bioscience, Section of Chemical Engineering; <sup>2</sup>Aquarden Technologies

#### Challenge

- Aqueous solutions of MEA-triazine (HET) utilized in large excess to remove H<sub>2</sub>S from the gas.
- Large amount of unspent HET: 35 – 105 g/L in the Spent and Unspent Scavengers (SUS).
- Excessive use of MEA-triazine: high operational costs and high environmental impact.
- MEA-triazine: often more than 50% of total expenditure of oilfield chemicals.
- SUS: up to 20% of the Environmental Impact Factor (EIF) of offshore O&G water discharge in the North Sea.

#### Objectives

- Develop a membrane-based process for MEA-triazine recovery.
- Develop a Hydrothermal Oxidation (HTO) Process for on-site treatment of the spent scavengers before discharge into the sea.
- Develop a method based on Raman Spectroscopy (RS) to analyze SUS on-line.

#### Filtration Experiment Major Results

- The nanofiltration membrane (NF270) rejects HET up to 75%.
- The separation of the unspent scavenger (HET) from the spent scavenger (dithiazine, DTZ) is possible!
- The membrane maintains a high permeate flux of 21 LMH at 10 bar.
- No evidence of fouling up to 24 hours of operation.

#### Raman spectroscopy Major Results

SUS samples: HET, MEA, DTZ

Raman spectra of the main aqueous SUS components

- The selected peaks for HET, MEA, and DTZ are clearly observable in the reaction spectra.
- The possibility of quantifying the unspent scavenger (HET) on-line is envisaged, together with other key species (monoethanolamine, thiadiazine, dithiazine).

#### Novel approach

#### Hydrothermal Oxidation Major Results

- Operability of continuous – flow HTO proved for diluted SUS feeds with Chemical Oxygen Demand (COD) up to 105 g/L.
- COD reduction up to 95%.
- Autothermal reaction at steady-state conditions (no external heating needed).
- No pH drop below 6.95 during the HTO reactions (no corrosion risk).

Test	#1	#2	#3	#4	#5
T [°C]	350	325	325	280	325
p [bar]	240±3	241±3	239±3	238±3	239±1
v [L/h]	0.6	0.6	0.54	0.6	0.6
COD <sub>in</sub> [g/L]	32.4	26.9	101.2	95.4	105
DRE <sub>COD</sub> [%]	93.4	93.4	95.3	92.8	95.4

#### Key Message

- Installing a nanofiltration unit is expected to reduce MEA-triazine consumption from 40% to 72% for installations operating with scavenger dosages from 12 to 40 kg/kg.
- This result can be achieved with a small (one/two cascade modules less than 2 m long) and cheap (< 50 000 EUR) membrane unit.
- Raman Spectroscopy can be used for on-line monitoring of SUS.
- HTO can reduce the COD of the wastewater up to 95%.

#### Acknowledgements

This project was financially supported by the Danish Offshore Technology Centre under the Produced Water Management programme.

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# The Best Awards

# 27

**Inhibition capability of black tea extract (BTE) on 1Cr steel in Oil and gas Industry: experimental and molecular modelling studies**

\* Ghada Shaban<sup>1</sup>, Kiril Borisov<sup>1</sup>, Martin Andersson<sup>1</sup>, Rajan Ambat<sup>1</sup>  
<sup>1</sup>Denmark Technical University of Denmark, Produktionstorvet 425, Kongens Lyngby, 2800 Denmark \*ghshaga@dtu.dk

**Introduction**  
 For corrosion mitigation in oil & gas and CO<sub>2</sub> storage related applications, the injection of inhibitors is one of the most efficient and economical approaches. We focus on finding green and environmentally friendly organic molecules as corrosion inhibitor replacing presently used inhibitor chemistries. Since, there is a need for a better understanding of inhibition process of different compounds of inhibitor. Also, there is a growing recognition of the potential in reusing waste as a source of potential corrosion inhibitor, which can be interesting from economic point of view. Therefore, Focused on low alloy carbon steel, our project highlights black tea extract (BTE) as a promising inhibitor chemistry.

**II. Project motivation and research objectives**

- Systematically perform molecular modelling study of BTE inhibitor chemistry.
- Identify the key molecule within the BTE responsible for the inhibition properties will be identified and modelled for calculating adsorption energy.
- Comprehensively understand the correlation between the inhibitive ability of BTE on CO<sub>2</sub> corrosion resistance of 1Cr steels and operational parameters such as temperature, pH, inhibitor's concentration.
- Propose the mechanisms responsible for the inhibition effect.

**III. Materials and methods**

**Tea extraction**

- The extraction process was performed using the aqueous solvent method.
- Over heating chamber with force variation with force variation.
- Yield: 30%

**Electrochemical setup**

**Specimens**  
 1Cr steel

**Electrolyte solution**  
 1 wt % NaCl solution saturated with CO<sub>2</sub>

**Electrochemical tests**  
 DC polarization, AC impedance and immersion methods.

**Surface characterization and phase analysis**  
 SEM, EDX, and AFM

**Chemical analysis**  
 GC-MS, FTIR, and IR

**IV. Results**

**Optimized geometry of Component on Fe(110)**

**Adsorption energy values on Fe(110) surfaces using DFT**

Molecule	Chemical structure	Adsorption energy (eV)	E <sub>ads</sub> (kJ/mol)
Water	<chem>O</chem>	-0.18	-17
Ethanol	<chem>CCO</chem>	-0.25	-23
Formic acid	<chem>C=O</chem>	-0.35	-32
Acetic acid	<chem>CC(=O)O</chem>	-0.45	-41
Propionic acid	<chem>CCC(=O)O</chem>	-0.55	-50
Butyric acid	<chem>CCCC(=O)O</chem>	-0.65	-59
Pentanoic acid	<chem>CCCCC(=O)O</chem>	-0.75	-68
Hexanoic acid	<chem>CCCCCC(=O)O</chem>	-0.85	-77
Heptanoic acid	<chem>CCCCCC(=O)O</chem>	-0.95	-86
Octanoic acid	<chem>CCCCCCC(=O)O</chem>	-1.05	-95
Nonanoic acid	<chem>CCCCCCC(=O)O</chem>	-1.15	-104
Decanoic acid	<chem>CCCCCCCC(=O)O</chem>	-1.25	-113

**Macro-surface analysis of inhibited and corroded samples**

**SEM images of inhibited and corroded samples**

**VI. UV-Vis absorbance and FTIR**

**Electrochemical technique**

**IV. Conclusions**

- The results showed that the inhibitor protects materials from corrosion, therefore changing the morphology and properties of the formed corrosion layers, increase efficiency by increasing inhibitor's concentration and temperature, likely due to higher surface coverage and stronger adsorption to the steel.
- Molecular modelling and isotherm study.
- Surface, as confirmed by molecular modelling technique showed the formation of chelate complexes on surface, as confirmed by FTIR spectroscopy technique showed the corrosion protective behavior of BTE.
- Fourier Transform Infrared Spectroscopy technique showed the corrosion protective behavior of BTE.
- poly phenols' molecules with iron, which might contribute to the corrosion protective behavior of BTE.

- Ghada Shaban
- Kiril Andersson
- Rajan Ambat

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# The Best Awards

# 43

DTU Offshore  
Danish Offshore Technology Center

## Metal-organic frameworks as oxygen scavengers

SENSORS & FUNCTIONAL MATERIALS

Per Reichert<sup>1</sup>, Simon I. Andersen<sup>1</sup>, Ali A. Eftekhari<sup>1</sup>, Kasper S. Pedersen<sup>2</sup>, and Jonas Sundberg<sup>1</sup>

<sup>1</sup> Danish Offshore Technology Center, Technical University of Denmark, 2800 Kongens Lyngby, Denmark  
<sup>2</sup> DTU Chemistry, Technical University of Denmark, 2800 Kongens Lyngby, Denmark

**Motivation and Background** Produced water reinjection is an important tool to reduce the environmental impact of offshore oil production sites by avoiding discharge. To maintain constant flow rates, produced water is mixed with seawater, which contains high levels of dissolved oxygen. Untreated this leads to well corrosion and bacterial growth. We aim to develop new metal-organic frameworks (MOFs) for the chemisorption of oxygen from gas and aqueous phase. With their high porosity and reusable character, MOFs are incredibly potent to replace oxygen scavenging chemicals, increase eco-efficiency and reduce the overall environmental impact factor (EIF) of offshore oil and gas production.

Figure 1: Left: Schematic model of the produced water treatment on oil and gas platforms offshore, including possible risks. Right: blueprint of a metal-organic framework (MOF) with the implementation of a cobalt site into the organic linker, and typical archetype oxo-metal clusters as metal nodes suitable for O<sub>2</sub> absorption in gas and aqueous phase.

**Metal-organic frameworks**

- ➔ Porous coordination polymers, formed by self-assembly of metal-nodes and organic linkers.
- ➔ Their permanent porosity greatly facilitates adsorptive processes and rapid mass transfer.
- ➔ Our newly proposed MOFs integrates O<sub>2</sub> binding within its organic linkers. A shift of functionality from the nodes to the linkers will enable selective and reversible binding of dissolved oxygen.
- ➔ With their reusable properties, metal-organic frameworks are incredibly potent for oxygen adsorption.

Figure 2: Scanning electron microscopy image of target MOF.

**Reactor design**  
Dual packed bed reactor setup.

- ➔ One active bed (1).
- ➔ Parallel regeneration.
- ➔ Regeneration by passing heated deoxygenated water above the critical temperature through the saturated bed (2/3).

Figure 3: Left: Dual packed bed reactor setup; right: Computational calculations for an experimental model developed to support the design of a pilot reactor leading to a full-scale unit. Diagrams show the development of fluid velocity (a), column weight (b), absorption efficiency (c), cycle time (d) in regard to the diameter of the reactor.

**References**

[1] Cook et al., Chem. Rev., 2013, 113, 734. [2] James et al., Chem. Soc. Rev., 2003, 32, 276. [3] Yazhi et al., Chem. Rev., 2012, 112, 2.

**Acknowledgements**

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- Per Reichert
- Simon Andersen
- Ali Eftekhari
- Kasper Pedersen
- Jonas Sundberg

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# The Best Awards


# 45



**DTU**  
Danish Offshore Technology Center

Maksim Kurbasov, Tinku Saikia, Karen Louise Feilberg, Gisle Øye

Analyzing Key Factors Impacting Near-Wellbore Permeability Reduction in Produced Water Injection: Insights from Core Flooding and Microfluidic Analysis



**NTNU**  
Norwegian University of Science and Technology

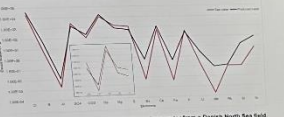
**Introduction**

Offshore oil and gas operations in the Danish North Sea generate substantial volumes of produced water alongside comparatively limited oil production, as reported by the Danish Energy Agency in 2022. Specifically, 30.8 billion m<sup>3</sup> of reservoir water was produced, whereas only 3.7 billion m<sup>3</sup> of oil was extracted. The disposal of this contaminated water presents a significant challenge for petroleum companies, primarily due to spatial constraints on offshore platforms.

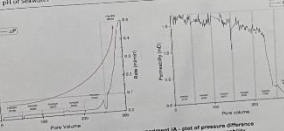
Two primary approaches are typically employed to address this issue. The first method involves discharging produced water into the North Sea and the second is re-injecting the water into the reservoir as part of the water injection/pressure support. Discharging to sea unfortunately contributes to considerable pollution due to the presence of crude oil and production chemical residue (including spent scavenger, biocide, anti-scaling chemicals, PAHs etc.) in the produced water.

Re-injection of this complex water is associated with risks of reservoir damage due to the clogging of the pore space. Enhanced comprehension of the intricate processes occurring within the channelled space in the reservoir rock offers a promising avenue for optimizing produced water re-injection technology and extending the operational lifespan of these injection wells.

**Core Flooding experiments**



Characteristic	Value
Porosity and pore volume of core	35%, 5.74 mD
Length of core	21.68 cm
Diameter of Core	36.3 mm
Radius of borehole	From 100% SW to 100% PW
Width 10% steps (every 10 pore volumes)	
Dissolved oxygen of Produced water	5%
Dissolved oxygen of Seawater	80.6%
The pH of Produced water	7.83
The pH of Seawater	7.94




**Screening of inorganic precipitates**

**Glass micromodel - flooding**


Characteristic	Value
Permeability	2.1 Darcy
Porosity	52%
Pore Volume	2.3 μl
Flow rate	0.61 μl/min
Temperature	28 °C
Magnification	20X - 40X

**Step 1**  
100% Sea water. 45 Pore volumes of sea water was injected into the chip to condition it. No clogging was observed.

**Step 2**  
80% Produced water and 20% Sea Water injected. 850 Pore volumes (1.36 μl) total. Images taken after every 100 PV injection.




**Biofilm Formation**



(1) Stage indicates free floating biofilm producing bacteria that adhere to the surface. (2) Stage forms colonization made EPS, and the attachment becomes irreversible. (3) Stage biofilm is formed and the in situ ecosystem is growing by creating water channels allowing the water to keep the biofilm hydrated and nourished. (4) Stage studies critical environmental factors such as the mass or requirement of the biofilm, that either disperses or colonizes on surfaces further down.

**Screening of inorganic precipitates**

**Examination of sediment on the flow surface using an optical microscope**



3D and SEM study of the formed sediment was carried out when sediment was washed and when pumping produced water and the water each different ratio through a solution flow.

As a result of the study, it was determined that the formation and development of a sediment layer, which was observed and is a consequence of the permeability loss. Currently, preparations are underway to conduct further investigations.

Reference to Figure 10(a), (b), (c) and (d) in the text.

**Conclusions**

According to the studies, the main reason for the decrease in reservoir permeability when re-injecting produced water is the precipitation of inorganic sediments in the form of the mineral Fe<sub>2</sub>O<sub>3</sub>. But it is also worth noting that the decrease in permeability and clogging of the channel space is affected by the formation of biofilm as a result of the activity of bacteria located in the produced water.

**Contact information**

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- Gisle Oye

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## Poster Award

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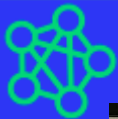
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# The Best of the Best Award

# 22

- Magdalena Skowrya
- M. Echarri
- Y. Ivanova
- K. Ravnkilde
- C Frederiksen
- A Skov



**DTU**

## Temporary abandonment of oil wells using pumpable, polymer-based plug

M.M. Skowrya<sup>1</sup>, M. Echarri<sup>1</sup>, Y.D. Ivanova<sup>2</sup>, K.M. Ravnkilde<sup>3</sup>, C.H. Frederiksen<sup>2</sup>, A.L. Skov<sup>1</sup>

<sup>1</sup> Danish Polymer Centre, DTU Chemical and Biochemical Engineering  
<sup>2</sup> Danish Offshore Technology Centre, DTU

**1 Challenge**

**What is the problem?**

- Denmark phases out fossil fuel extraction by 2050
- Increased focus on oil well **plug & abandonment** topic
- Time-consuming** and very **costly** operations
- Current solutions are **harmful** to the environment

**2 Solution**

**How could the problem be solved?**

- A temporary, pumpable **polymer tubing plug** that **reduces the pressure** buildup prior to abandonment and mitigates the risk for the rig entry

**3 Materials**

Functionalized Polymer containing double bonds (C=C) + Cross-linker monomer of increased functionality + Free-radical initiator thermal initiator + Hydrophobic filler

Liquid → Δ, 24h → Solid

**Cross-linked polymer plug & CT scans**

CT scans of the plug at different stages: (a) Plug before use, (b) Plug after use, (c) Plug after use, (d) Plug after use.

Labels: pumpable, non-toxic, thermally stable, pressure resistant.

**Rheological behavior**

**Cross-linking time** and **Viscosity** graphs.

- The formulation remains liquid at room temperature for 20h
- The polymer **sets fast** at high temperatures
- Shear-thinning** material
- Pumpable with equipment existing on the platform

**Environmental assessment**

Material	Biodegradability (EN 13430)	Biodegradability (EN 13430)	Biodegradability (EN 13430)	Test for ready biodegradability (Level 1)
Polymer	>100	>100	>100	Not pass
Resin	>100	56-540	>100	Not pass
Initiator	>100	25-38	>100	Not pass
Additive	>100	>100	>100	Not pass

- No requirement to label for aquatic toxicity
- No compounds recognized as potentially bioaccumulating
- Not readily biodegradable, however, different aim here

**Thermogravimetric analysis**

- The material must remain stable at the temperature present in high-pressure & high temperature (HPHT) oil wells
- Thermally stable polymer** in the intended working temperature (20-300°C)
- Thermal decomposition at 400 °C

**Water pressure test**

The polymer plug is prepared under high water pressure and high temperature (50 °C) for 24 h. The resistance of the polymer plug to seawater pressure is tested by a water pressure test.

The polymer by itself can withstand pressure of 55 bar and 55 bar once crosslinked under a steel tubing.

The resistance test at the polymer steel interface, including an adhesion challenge.

**4 Conclusions**

- Polymer** material for temporary plugging of oil wells is being developed
- Uniform structure** confirmed in CT scans
- Non-toxic** material - safe to handle and transport
- Adequate rheological behavior**, long working time at room temperature and fast crosslinking at downhole temperatures
- High thermal stability**
- Ability to withstand water pressure up to **145 bar**
- Adhesion challenge**, improvement of polymer-steel bonds

**Reservoir**  
High pressure  
High temperature

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