Removal of Toxic Contents from Gas/Condensate Produced Water by the Macro Porous Polymer Extraction Technology

SPE Workshop

SPE Oil and Gas Effluent Discharge Management Workshop

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Jan Bart Kok – Veolia MPP Systems

Port of Spain, Trinidad and Tobago
30 June – 1 July 2015
“Look at present and future discharge requirements to decide now on your produced water treatment”

- Authorities / O&G companies
- Discharge requirements
- Technology chosen

- Technology chosen
- Examples including Prelude
- MPPE Technology

Discharge requirements → Technology window
Present and future discharge performance → Design/Construction
Fishing / swimming and oil / gas production

Six countries
Six languages
Six cultures
Six policies

All:
• Fishing
• Swimming
• Digging for oil and gas
Emission Regulations 70’s → present / future

- North East Atlantic / North Sea (OSPAR)
  - 1978: 40 ppm dispersed oil (PARCOM)
  - 2007: 30 ppm dispersed oil (OSPAR)
  - 2010 - today: Risk Based Approach (OSPAR)

Individual countries

- The Netherlands: Reduction Benzene / Aromatic discharge
  - 1994: Covenant Industry and Government
    Benzene / Aromatic reduction of 80% in 2000 vs. 1990
  - 1999: MPPE fieldtest NAM (Shell/Exxon) offshore L2 (OTC paper)

- Norway
  - 2002: Zero Harmful Discharge in 2005 (ZHD)
  - Environmental Impact Factor (EIF)
## Oil & Gas produced water composition

<table>
<thead>
<tr>
<th>Hydrocarbons</th>
<th>Less polar</th>
<th>More polar</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dispersed Floating</td>
<td>Aliphatics: 200-1300 ppm</td>
<td>Negligible</td>
</tr>
<tr>
<td>(sheen)</td>
<td>Separators / flotation “Standard”: 40 ppm</td>
<td></td>
</tr>
<tr>
<td></td>
<td>“Advanced”: 10-30 ppm</td>
<td></td>
</tr>
</tbody>
</table>
## Oil & Gas produced water composition

<table>
<thead>
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<td>“Advanced”: 10-30 ppm</td>
<td></td>
</tr>
<tr>
<td><strong>Dissolved Not floating</strong></td>
<td>Aliphatics</td>
<td>Alcohols / Methanol / Glycol</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Carboxylic acids</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Hundreds of ppm</td>
</tr>
<tr>
<td><strong>“Non Toxic”</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Toxic</strong></td>
<td>Aromatics</td>
<td>Alkyl Phenols</td>
</tr>
<tr>
<td><strong>Carcinogenic</strong></td>
<td>BTEX 200 – 3,000 ppm</td>
<td>Ten – Hundreds ppb</td>
</tr>
<tr>
<td><strong>Mutagenic</strong></td>
<td>PAHs 200 – 80,000 ppb</td>
<td></td>
</tr>
</tbody>
</table>
## Produced Water composition

<table>
<thead>
<tr>
<th>Compounds</th>
<th>ppm</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dispersed oil</td>
<td>200 - 1,000 (gas)</td>
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</tr>
<tr>
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<td></td>
<td></td>
</tr>
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<td></td>
</tr>
<tr>
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<td></td>
<td>B</td>
</tr>
<tr>
<td>Toxic:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>- Benzene</td>
<td></td>
<td>T</td>
</tr>
<tr>
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<td></td>
<td>E</td>
</tr>
<tr>
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<td></td>
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<td>APh</td>
</tr>
<tr>
<td>Dissolved hydrocarbons</td>
<td></td>
<td>Polar</td>
</tr>
<tr>
<td>Readily Biodegradable</td>
<td>hundreds</td>
<td></td>
</tr>
<tr>
<td>Polar</td>
<td></td>
<td></td>
</tr>
<tr>
<td>- Acids</td>
<td></td>
<td></td>
</tr>
<tr>
<td>- Alcohols (Methanol)</td>
<td></td>
<td></td>
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</tbody>
</table>
Environmental Impact Factor Norway

- Investigation Norwegian Offshore Industry (Statoil / Hydro end 90’s)
  - Impact of Individual compounds on Environment

- Type of molecules and concentration determine Impact on Environment

- The more toxic, non biodegradable molecules:
  - The higher multiplication factors to reflect the environmental impact

- Environmental Impact Factor:
  - Specific groups of molecules are expressed in % of the total 100% Environmental Impact
  - Of that particular produced water stream
  - In that particular environment
### Produced Water composition

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<tr>
<th>Compounds</th>
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<th>EIF*(2)</th>
<th>EIF*(3)</th>
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* EIF = Environmental Impact Factor
Risk Based Approach (OSPAR)

Prioritizing mitigation actions on those substances that pose the greatest risk to the environment

- **Substances**: differentiate in wastewater constituents
  - Toxic / non biodegradable
  - Non toxic / biodegradable

- **Location**: differentiate in discharge environment
  - Dilution (current speed, depth etc.)
  - Capability for biodegradation (cold vs. warm seawater)

- **Approach**:
  - Identify specific toxic constituents and their fate
  - Focus water treatment on these target constituents
  - ZHD: Zero Harmful Discharge to the environment
  - More cost efficient than meeting absolute discharge limits on generic parameters (COD, TOC)
Statoil Kollsnes Phenomena

- Treating offshore Produced Water of 4 platforms
- Start up extra platform (Kvitesebjørn) Q4 2004
  - Equal TOC levels!
  - Bioactivity ceased! Q1 2005
- MPPE installed Q2 2005
- Biotreatment recovered within three months Q3 2005
Statoil Kollsnes conclusions

- Equal TOC levels but Bio ceased?
- 20 – 100 times more and varying BTEX contents (600 ppm)
- 10 – 50 times more PAHs
- Poisoned biological mass
- BTEX > 12 mg/l could be toxic to biological mass

Biotreatment recovered because MPPE removes:
- Aliphatics (dispersed oil) > 99%
- BTEX > 99%
- PAHs > 99%
- Alkyl Phenols ~ 30%
Statoil Kollsnes Norway

MPPE

- An MPPE unit was rented May 2005.
Statoil Kollsnes permanent unit Norway
Reduction of toxic content is a powerful concept

- Environment Impact Factor / Risk Based Approach

Importance of toxicity removal is proven in practice

- Gas produced water $\rightarrow$ toxic contents kills bio treatment

What about Offshore Produced Water Composition?
## Gas Produced

<table>
<thead>
<tr>
<th>Flow rates ( (m^3/h) )</th>
<th>Gas produced</th>
<th>Oil produced</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(&lt; 5 – 150)</td>
<td>(100 – &gt; 1000)</td>
</tr>
</tbody>
</table>

## Oil Produced

### Inlet data measured in practice (ppm)

- **Aliphatic HC (dispersed oil)**: \(300 – 1400\) \(\text{ppm}\) \(\rightarrow\) \(40 – 100\) \(\text{ppm}\)
- **Aromatics (BTEX)**: \(300 – 3000\) \(\text{ppm}\) \(\rightarrow\) \(30 – 70\) \(\text{ppm}\)
- **PAHs**: \(4 – 80\) \(\text{ppm}\) \(\rightarrow\) \(0.5 – 2\) \(\text{ppm}\)
- **TPH/THC**: \(700 – 4000\) \(\text{ppm}\) \(\rightarrow\) \(< 200\) \(\text{ppm}\)

### Typical goals

**“Old”:**
- **Dispersed oil**: \(< 30\) \(\text{ppm}\) \(\rightarrow\) \(< 30\) \(\text{ppm}\)

**“New”:**
- **Dispersed and dissolved, Aliphatics (oil), BTEX, PAHs, (TPH)**: \(< 10 – 30\) \(\text{ppm}\)
- **Toxic Hydrocarbons**: Zero Harmful Discharge (ZHD)

*TPH: Total Petroleum Hydro Carbons*
When MPPE for gas / condensate / LNG?

Law / Drive authorities / Drive companies

Front runner: Norway 2005: Zero Harmful Discharge (ZHD)
- EIF = Environmental Impact Factor

Follower: OSPAR – North Sea
- Risk based approach

Australia:
- 2006: < 50 ppm dispersed oil
- 2007: < 30 ppm dispersed oil
- > 2007: < 30 ppm dispersed and dissolved hydrocarbons = ZHD*

Recent: Egypt: ZHD, law 4
- Israel: ZHD
- East Africa: ZHD
- Indonesia: ZHD

* ZHD: Zero Harmful Discharge
## Discharge limits seen in MPPE tenders / inquiries

<table>
<thead>
<tr>
<th>Location</th>
<th>BTEX (ppm)</th>
<th>PAH (ppb)</th>
<th>Aliphatics (ppm)</th>
<th>Total HC (ppm)</th>
<th>Hg (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Australia 1</td>
<td>15</td>
<td>15</td>
<td>30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Australia 2</td>
<td></td>
<td></td>
<td></td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>Australia 3</td>
<td></td>
<td></td>
<td>5</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Australia 4</td>
<td></td>
<td></td>
<td></td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Australia 5</td>
<td></td>
<td></td>
<td>10</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>East Africa 1</td>
<td>5</td>
<td>5</td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>East Africa 2</td>
<td>5</td>
<td>5</td>
<td>10</td>
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<td>East Africa 3</td>
<td>0.5</td>
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<td>10</td>
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<td>East Africa 4</td>
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<tr>
<td>Indonesia 1</td>
<td>15</td>
<td>15</td>
<td>15</td>
<td>30</td>
<td>0.01</td>
</tr>
<tr>
<td>Indonesia 2</td>
<td>15</td>
<td>10</td>
<td>25</td>
<td>25</td>
<td>0.01</td>
</tr>
<tr>
<td>Malyasia 1</td>
<td>10</td>
<td>10</td>
<td>20</td>
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<tr>
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<td>15</td>
<td>5</td>
<td>20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mediterranean 2</td>
<td>1</td>
<td>0.2</td>
<td>15</td>
<td>20</td>
<td></td>
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Compounds

Dispersed oil = 200 - 1,000 (gas)
Dispersed hydrocarbons =
Dispersed Aliphatics = floating

Dissolved hydrocarbons Toxic:
Toxic:
- Benzene
- Toluene
- Ethyl benzene
- Xylene
- PAHs and NPDs 4 - 80
- Alkyl Phenols 0.1 - 0.2

Dissolved hydrocarbons Readily Biodegradable
Polar:
- Acids
- Alcohols (Methanol)
# Gas / Condensate and LNG produced water treatment

1. **Gas production**: produced water after separator / degasser

2. **Gas drying (glycol)**: MEG REGEN produced water

## MPPE for removal of 1 + 2:

1. **Dispersed oil (aliphatics)**: 200 - 1,400 ppm: > 99%
2. **Dissolved and dispersed aromatics (BTEX)**: 300 - 3,000 ppm: > 99%
3. **PAHs**: 4 - 80 ppm: > 99%
4. **Alkyl Phenols**: ppb levels: ~ 30%
5. **Chemicals**: ppb / ppm: ~ 20 - 50%
6. **Environmental Impact Factor**: 95 - 99%
Intermediate conclusions 2/2

Reduction of toxic content is a powerful concept
- Environmental Impact Factor / Risk Based Approach

Importance of toxicity removal is proven in Practice:
- Gas produced water: toxic contents kills bio treatment
- Gas/condensate/FLNG PW 10-20 x more toxic than oil PW
- Growing trend to remove dispersed and dissolved toxic hydrocarbons (TPH)
- MPPE creates a Zero Harmful Discharge

- Real life examples? FLNG?
- MPPE technology?
- Conclusions??
Since June 1994
- Offshore Gas Produced water
- Condensed water MEGREGEN unit
- Aromatics/PAHs
  - Dissolved /dispersed 1,500 – 3000 ppm
  - Dispersed oil (aliphatics) 160 – 350 ppm
- Total removal 3350 to < 0.5 ppm
- Flow 4 m³/hr

Since June 1997: Added
- Produced water from other Gas locations
- Rainwater / run off water
- Groundwater
- 6 m³/hr

Column size (m):
d = 0.8, h = 2.0
Offshore gas produced water

Removal dispersed, dissolved Aliphatics, Aromatics, and PAHs

Fulfilling TOTAL’s environmental goal beyond present legal requirements

MPPE unit installed partially over the platform edge
Ormen Lange Project
- Makes Norway world’s largest exporter of natural gas
- 100 kilometer from the northwest coast of Norway

MPPE Unit removes:
- Dispersed oil (aliphatics)
- Dissolved and dispersed aromatics (BTEX)
- Poly Aromatics (PAHs)
- Flow rate 70 m³/h
Location Pluto LNG Burrup plant

- Burrup, Peninsula, Western Australia
MPPE Unit removes the:
- Dispersed oil (aliphatics)
- Dissolved and dispersed aromatics (BTEX)
- Poly Aromatics (PAHs)
- Total MPPE Unit capacity 43 m³/hr
- 2 parallel column trains guarantee 100% redundant extraction capability

- Pluto Project increases the Natural gas production with approximately 25%
- Veolia supplied a total Effluent water Treatment Package consisting of:
  - CPI, MPPE unit, Chiller, MBR, Oxidation/ozone, Activated Carbon & Demin unit.
- On stream in 2011

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Inpex Ichthys project
Inpex Ichthys project
3D Model Inpex ICHTHYS MPPE unit
2 x 90m$^3$/h
Shell Prelude Floating LNG

- Gas treatment + liquefaction
- LNG and condensate off loading
- 488m x 74m: largest floating structure
- Avoids: pipelines, coastal modifications, land use
- Lower environmental footprint
- Flexibility to relocate and reuse
Shell Prelude Floating LNG
MPPE in hull
Shell FLNG Prelude

MPPE for produced water treatment

- Capacity 140 m³/h
- Compact
- Located in “dead” space hull
- Redundant extraction capacity
  → 2 x 2 columns)
- No additional up- or downstream treatment units
MPPE for produced water treatment

- MPPE material exchange by column exchange
- Redundant extraction capacity → 2 x 2 columns
- Continuous operation possible during MPPE material exchange
- Option with two hatches possible
Shell FLNG Prelude

FOB Rotterdam,
The Netherlands
MPP structure
MPPE process (1)

- **Extraction**
  - Water/hydrocarbons
  - Condensed steam recycle

- **Stripping**
  - Condensor
  - Hydrocarbons

Steam is shown at the top, entering the process, while water is shown at the bottom, exiting the process.
MPPE process (2)

Organics and water

Extraction

Condensed water recycle

Steam

Stripping

Condenser

Separator

Heavy Organics for reuse

Light Organics for reuse

Clean water
MPPE Features

- High reduction factor
- Reduction factor independent of inlet concentration
- Robust against water environment (surfactants, salts, pH range 3-9 etc.)
- Predictable separation performance
  (with a lifetime performance guarantee)
- Coping with unexpected higher inlet concentrations than design
  - 10% lower flow: 50% higher inlet possible
  - Lower influent: higher flow possible
- Capacity flexibility
  - Turn up / down ratio e.g. 0 to 150% of design capacity
- Batchwise operation; Immediate performance at start up
- Separated hydrocarbons (~100% pure) for (re)use
- No waste stream, no air emission
- 100% recovery of water and hydrocarbons
MPPE Robustness Design / Actual

BTEX

BTEX

Aliphatics

Aliphatics

ppm (mg/l)

In

Out

In

Out

In

Out

In

Out

Design

Actual

Design

Actual

Society of Petroleum Engineers
Most toxic next to TPH: Mercury

- NAM offshore field test 1999 (OTC paper)
- Bench Mark studies 2011 - 2012
- Cadmium, lead, nickels: 0.0001 – 0.014 ppb
- Mercury inlet: 3 – 120 ppb
- Cases with Mercury removal %
  a. 5 years: 81 – 85 %
  b. 8 years: > 92 %
  c. 9 years: 98 – 99.0 %
  d. 10 years: 83 – 98 %
Conclusions

Reduction of toxic content is a powerful concept
- Environment Impact Factor / Risk Based Approach

Importance of toxicity removal is proven in practice
- Gas produced water: toxic contents kills bio treatment
- Gas/condensate/FLNG PW: 10 - 20 x more toxic than oil PW
- Growing trend to remove dispersed and dissolved toxic hydrocarbons (TPH)
- Flotation technologies (hydrocyclones, CFU) unable to remove toxic content

MPPE
- Creates Zero Harmful Discharge (ZHD)
- Proven in offshore produced water treatment (> 20 years)
- Positioning in ‘dead’ spaces; FLNG: inside hull or topside
- Structural mercury removal observed (being studied and optimized)
THANKS

QUESTIONS?