FIELD-PROVEN REMOVAL OF DISSOLVED AND DISPERSED HYDROCARBONS AT COMMERCIAL SCALE FROM OFFSHORE PRODUCED WATER BY THE MACRO POROUS POLYMER-EXTRACTION TECHNOLOGY

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ABSTRACT

During offshore production of gas, condensate and oil, water is co-produced in significant amounts and discharged into the sea. For dispersed oil ("free oil") emission standards of 40 ppm or higher are applied, depending on local legislation. However, for dissolved hydrocarbons such as Benzene, Toluene, Ethyl, Ethylbenzene, Xylene etc. (Aromatics), Polycyclic Aromatic Hydrocarbons (PAH's), alkylphenols no emission limits are set. Dissolved hydrocarbon concentrations can go up to 100 ppm level in oil produced water and 500 –1000 ppm levels in gas produced water. Both Oil & Gas Industry and Governments in various countries have addressed this issue and set targets but despite considerable effort no agreed reductions have been obtained, mainly due to the lack of suitable and reliable technologies. Within the framework of OSPAR (Oslo Paris Convention for the Protection of the Maritime Environment of the North East Atlantic) alternative techniques (55), have been evaluated by the Dutch Oil & Gas Industry in the course of the nineties. In this study Macro Porous Polymer Extraction (MPPE) came out as a promising option. Subsequent testing and evaluation by the ERT/Orkney Water Technology Center, and offshore field tests of NAM (Shell/Exxon) and Statoil Åsgard A, has led to the first commercial MPPE offshore applications in 2002. Removal efficiencies of 99% have been reported on both aromatic (BTEX) and polycyclicaromatic hydrocarbons (PAH's). For dispersed aliphatics 50 to 99% removal has been obtained depending on the composition. Next to the separation performance the main issue in offshore application is the effect of the water composition (water environment) on the steady long term separation performance. It shows that the presence of salt, heavy metals, alcohols (glycols) and surfactant containing chemicals (like corrosion, scale inhibitors etc.) do not negatively influence the separation performance, while solids can be adequately dealt with. There are strong indications that offshore produced water with temperatures up to 60° C can be treated with the MPPE technology. For Gas and Gas condensate platforms the MPPE unit size is small enough for installment on existing platforms. For oil platforms this is also considered for streams up to 300 m³/hr while sizes for 1000 m³/hr levels are challenging and currently being investigated.

1 INTRODUCTION

During the production of gas, condensate and oil, water is co-produced in significant amounts. When producing gas and oil, offshore, this produced water normally is discharged into the sea. To minimize possible negative impact on the environment, maximum concentration limits have been defined for components which may be present in the disposed water. In the North Sea the government has restricted the amount of aliphatic (dispersed) hydrocarbons in produced water discharged into the sea: the monthly average should remain below 40 mg/l.

Fig. 1 – Internal structure of the Macro Porous Polymer
Dissolved Hydrocarbons. Next to the dispersed hydrocarbons however, there are two other groups of components present in overboard water, heavy metals and dissolved hydrocarbons of which heavy metals are outside the scope of this paper and of less concern than the dissolved hydrocarbons. The dissolved hydrocarbons generally consist of aromatic hydrocarbons (up to hundreds of ppm), polycyclicaromatic hydrocarbons (PAH), and alkyl phenols (both on ppb levels). All these components are of major concern to the oil & gas industry and government with respect to the environmental impact.

The Dutch Oil & Gas Exploration and Production Association (NOGEPA), and the Dutch government have made an agreement in the middle of the nineties to cope with the problem of dissolved hydrocarbon emissions in the Dutch part of the North Sea. In this agreement, targets are set for a reduction in the volume of organics yearly discharged overboard. For the aromatics the agreement stipulates a reduction of 60% in the year 2000 compared to the level in 1990. Despite considerable effort, the gas/oil producing companies have not been successful in obtaining the required reduction, mainly due to the lack of suitable and reliable technologies, which can be applied offshore. On request of the NOGEPA, Stork Engineering Consultancy B.V. performed a study [Ref. 1] into techniques for reducing heavy metals and aromatic hydrocarbons emission on offshore locations. Out of the 55, one of the most promising techniques was found to be the Macro Porous Polymer Extraction process of Akzo Nobel. This was also recognized by the OSPAR (Oslo-Paris) Convention for the protection of the marine environment of the North East Atlantic who has listed the MPPE technology as Best Available Technology (BAT) for oil and gas produced water.

Based on the above, the MPPE technique was subsequently tested by NAM Business Unit Offshore on one of their gas offshore platforms (L2) [Ref. 2] in the first half of 1999. Later (in 2001), additional field trials were held in the North Sea (Statoil Asgard A) [Ref. 3] and the South China Sea. Previously (1997) the MPPE technology was also tested and verified for treating oil & gas produced water by ERT/Orkney Water Technology Center [Ref. 4] on request of the Oil & Gas Offshore Industry. Since 2002 two commercial industrial size units are operating successfully in the North Sea (TotalFinaElf, F15A) and NAM K15A (Shell/Exxon). Additional offshore MPPE units are currently under construction and options for more have been made. This paper describes the offshore experience with the MPPE process in the performed field tests and subsequent commercial MPPE units. In addition, a MPPE process description is given and other experiences with the MPPE technology, relevant to offshore application, are highlighted.

2 MPPE TECHNOLOGY

2.1 The MPPE particles

A scanning electron microscopic (SEM) photograph of Macro Porous Polymer particles is shown in Fig. 1. The porous polymer particles have a diameter of 1000 micron, with pore sizes of 0.1-10 micron. The porosity is 70 to 80%.

These polymers were initially developed as controlled release media in medical applications. The application in water treatment started in 1991. Initially the macroporous polymer was used for absorbing dispersed oil from water. Initiated by the oil and gas industry the idea emerged to develop a medium to remove dissolved hydrocarbons from water by immobilizing an extraction liquid in the pores of the polymer and so this (patented) MPPE Technology was developed by the mid nineties.

2.2 Limits of current used technologies in offshore

This request by the oil and gas industry is a logical development following their aim of reducing the emission of hydrocarbons in wastewater. Especially in offshore, the removal of dissolved hydrocarbons is the main problem as these cannot be separated by gravity. The concentrations in offshore discharged water can be in the hundreds of ppm for dissolved hydrocarbons while at the same time the dispersed are meeting levels of 18 to 40 ppm (=equal to current standards in the various regions in the world). Generally present gravity based separation techniques cannot reach lower dispersed oil levels than 30 ppm because of small dispersed droplet sizes (< 20 µm).
2.3 The MPPE Process description

In the MPPE process hydrocarbon contaminated water is passed through a column packed with MPPE particles (figure 2).

Fig. 2 - Schematic Overview of Macro Porous Polymer Extraction Process

The particles are porous polymer beads, which contain a specific extraction liquid. The immobilized extraction liquid removes the hydrocarbon components from the water. Only the hydrocarbon components, which have a high affinity for the extraction liquid, are removed. The purified water can either be re-used or discharged. Periodical in-situ regeneration of the extraction liquid is accomplished by stripping the hydrocarbons with low pressure steam. The stripped hydrocarbons are condensed and then separated from the water phase by gravity. The practically 100% pure hydrocarbon phase is recovered, removed from the system and ready for recycle or disposal. The condensed aqueous phase is recycled to the system. The application of two columns allows continuous operation with simultaneous extraction and regeneration. A typical cycle is one hour extraction and one hour regeneration.

2.3 Applicability

The components that can be removed with above described MPPE technique need to have an affinity (i.e. partition coefficient) for the extraction liquid compared to water in order to allow extraction.

Examples of hydrophobic components are aliphatic hydrocarbons, aromatic hydrocarbons (benzene, toluene) and halogenated hydrocarbons such as chlorinated hydrocarbons.

The removal efficiency that can be realized with MPPE is very high, as a result of the high number of mass transfer stages in the packed bed (high specific area for mass transfer) and in-situ separation of extraction liquid and purified water. Removal efficiencies up to 99.9999% (concentration reduction factor of $10^6$) have been achieved in both pilot and full-scale units. Some examples of components are presented in table 1.

3 PRODUCED WATER COMPOSITION

When producing a gas field the composition of the produced water will depend on its origin:
- formation water originating from the produced reservoir below gas/water contact
- connate water present around the formation in the gas reservoir
- equilibrium water condensed from the gas phase due to pressure and temperature reduction. While producing the gas, the formed water is being mixed with the liquid hydrocarbon phase (being a mixture of different organic components such as longer alkanes, aromatics and polycyclic aromatics). In general water and the hydrocarbon phase are immiscible, but various components e.g. aromatics such as Benzene, Toluene, Ethyl benzene and Xylene) are dissolved in the water phase and can reach up to levels of 1500 ppm (or more). Additionally, the separated water phase will contain minor quantities (up to
150 ppm) of the immiscible hydrocarbons (mainly aliphatics) in the form of droplets with a size between 1 and 10 micron.

The same goes for produced water coming from offshore oil production. Generally these water streams contain lower levels of dissolved aromatics (e.g. 50 to a few hundred ppm) than gas produced water while dispersed aliphatics may vary between 40 to 100 ppm.

Table 1 - Examples of components removable with an MPPE system

<table>
<thead>
<tr>
<th>Aromatic and Aliphatic Compounds</th>
<th>Halogenated/Chlorinated Compounds</th>
<th>Polyaromatic Hydrocarbons</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>Monochloromethane</td>
<td>PCBs</td>
</tr>
<tr>
<td>Toluene</td>
<td>Dichloromethane</td>
<td>Naphthalene</td>
</tr>
<tr>
<td>Ethyl Benzene</td>
<td>Trichloromethane</td>
<td>Acenaphthylene</td>
</tr>
<tr>
<td>Xylene(s)</td>
<td>Tetrachloromethane</td>
<td>Acenaphthene</td>
</tr>
<tr>
<td>Cumene</td>
<td>Dichloroethane (1,1 &amp; 1,2)</td>
<td>Fluorene</td>
</tr>
<tr>
<td>Limonene</td>
<td>Trichloroethane</td>
<td>Phenanthrene</td>
</tr>
<tr>
<td>Nitrobenzene</td>
<td>Tetrachloroethane</td>
<td>Anthracene</td>
</tr>
<tr>
<td>Cresol(s)</td>
<td>Chloroethylene</td>
<td>Fluoranethene</td>
</tr>
<tr>
<td>Higher alkylated phenols</td>
<td>Dichloroethylene</td>
<td>Pyrene</td>
</tr>
<tr>
<td>Octanol</td>
<td>Trichloroethylene</td>
<td>Benz(a) anthracene</td>
</tr>
<tr>
<td>Nonanol</td>
<td>Tetrachloroethylene</td>
<td>Chrysene</td>
</tr>
<tr>
<td>Decanol</td>
<td>Chloropropane</td>
<td>Dibenzo thiophene</td>
</tr>
<tr>
<td>Hexane</td>
<td>Chlorobutadiene</td>
<td>Etc.</td>
</tr>
<tr>
<td>Heptane</td>
<td>Hexachlorobutadiene</td>
<td></td>
</tr>
<tr>
<td>MIBK</td>
<td>Monochlorobenzene</td>
<td></td>
</tr>
<tr>
<td>TetraHydroThiophene</td>
<td>Dichlorobenzene</td>
<td></td>
</tr>
<tr>
<td>CS₂</td>
<td>Chlorobenzenes</td>
<td></td>
</tr>
<tr>
<td>Tetramethyltetrahydrofuran</td>
<td>Chloroaphtalene</td>
<td></td>
</tr>
<tr>
<td>Etc.</td>
<td>Hexachlorocyclohexane</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Monochlorophenol</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Dichlorophenol</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Trichlorophenol</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Dichloro-di-isopropylether</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Dioxins</td>
<td></td>
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<tr>
<td></td>
<td>Etc.</td>
<td></td>
</tr>
</tbody>
</table>

4 CHOICES FOR EMISSION REDUCTION

To reduce the volume of aromatics in the discharged water three different approaches can be used:
1. Avoid water production from the well;
The production of formation water and connate water may be controlled, but equilibrium water due to condensation will always form at surface.
2. Water injection back into the well;
After surface separation of the water and the hydrocarbon phase, the water is not discharged into the sea, but feedback to a formation below the surface. This technique is only possible when a well is available for disposing the water.
3. Removal of hydrocarbons from the water;
This can be done at several places, from the well bottom, up to the end of the system where the water is discharged overboard. The removal technologies of the dispersed phase are normally based upon gravitational force and are widely used in the gas and oil producing industry. The removal techniques for aromatics are more complex and are hardly applied in oil and gas industry. The MPPE technology is applied on the platform just before water is discharged overboard.
5 MPPE PERFORMANCE

Based on offshore experience with commercially installed units, long duration full-scale field trials and many years of experience onshore with process streams comparable to offshore produced water, some major observations/conclusions can be made on the key issues in offshore produced water treatment with the MPPE technology.

5.1 Separation Performance

Separation Performances have been measured by (1) formal legally authorised analysis methods like NEN-6675 (with Freon extraction and triple peak infra-red method), and APHA 5520 B (measuring mainly higher boiling components) and (2) by gaschromatographical methods (GC) sometimes combined with mass spectrometer. It showed that both NEN and APHA were not appropriate, detailed and accurate enough so that for the performance interpretation the GC analysis data from third party Starlabs were used.

5.1.1 Aromatic Hydrocarbons

The MPPE process showed consistent removal performance for all BTEX components (Benzene, Toluene, Ethylbenzene, Xylene) meeting continuously the effluent requirements. Consistent required removal efficiencies from application to application varied from 90% to 99.99%. No negative effects of salt, heavy metal and other present polyaromatic and aliphatic hydrocarbons were measured.

Benzene generally is the key component (highest concentration and most difficult to remove) and determines the size of the equipment. The longest onshore experience in BTEX removal is 9 years.

5.1.2 Polycyclic Aromatic Hydrocarbons (PAH’s)

In all offshore and onshore applications and field tests containing PAH and NPD’s (Naphtalenes, Phenanthrenes, Dibenzothiophenes) a consistent high removal efficiency was measured of 98 to 99.99% levels. Onshore experience in PAH’s removal is more than 5 years (99.9% removal at 4000 ppb level)

5.1.3 Aliphatic Hydrocarbons

In practice it is shown that all dissolved aliphatics are removed. However aliphatic solubility is low, especially above C₁₀ chainlength. The removal effectiveness of the MPPE technology for the dispersed (non dissolved) aliphatics depends on the chainlength and becomes difficult from C₂₀ upwards. Removal of total dispersed hydrocarbons varied from case to case from 50% to 99%. For oil produced water streams > 50% of total aliphatic removal were measured.

5.2 Water composition effects

Second to the question whether a technology can remove the target compounds from water at all, the main issue is always the effect of the water composition that again is varying in quality and quantity as a function of time. Below are the MPPE experiences with various compounds present in offshore produced water.

Dissolved salt flow through the MPPE unit with no negative effects on the separation performance.

Dissolved metals / heavy metals (e.g. cadmium, chrome, nickel, mercury, zinc, iron, calcium) flow through without negative effects. No calcium carbonate formation was found. As the MPPE process is principally anaerobic, no inhibiting ironhydroxide formation was found (iron concentrations up to 50 ppm).

Lower alcohols like methanol, glycol etc. flow through without harming the process.

Higher alcohols (alkylated phenols, C₄ alcohols and higher) esters and ethers will be partially removed on levels of e.g. 20-80% depending on the chainlength, with no negative effect on the separation of the target compounds.
Surfactants containing chemicals like corrosion inhibitors, scale inhibitors, H₂S scavengers etc. have had no detrimental effects on the separation performance. A sudden surfactant breakthrough due to misoperation during one of the field trials [Ref. 2] resulted in a short time performance dip to 93% and was recovered to above 99% immediately after normal operation was restored (Fig. 3). Also removal of some corrosion inhibitor components were measured (up to 50%). It goes without saying that the effect of these surfactant containing chemicals always needs special attention as variations in quantity and quality are numerous. Suspended solids do not deteriorate the separation performance as such but they may have an effect on the pressure drop over the MPPE column in the longer term. This is a.o. depending on particle size, type of solid (e.g. sand, tar etc.). A good robustness has been shown in practice so far. In principle there are four outlets of solids, (1) part will flow through the column, (2) part will be sedimented in a buffer tank following the hourly backwash, (3) part will be prefiltered and (4) part will accumulate in the bed and will be removed during periodical (≥ 1 year) exchange of the MPPE material. Nevertheless it needs attention and should be addressed. So far solids did not cause major problems in commercial MPPE units on Gas plattforms and oil produced water field tests.

Fig. 3 – BTEX removal (log scale) during MPPE offshore field test
1: Temporary drop to 81% removal due to steam minimation experiments
2: Temporary drop to 93-94% removal due to a sudden breakthrough (very high concentration) of a surfactant containing chemical
5.3 Space and footprint

The size of the MPPE unit is determined by flowrate, target compounds to be removed and the reduction factor. Gas production platforms have limited produced water flow rates. Up to 15-20 m$^3$/hr MPPE units including auxiliary equipment can be built in a standard 20 ft high cube containers (if requested, see Fig. 4). This size is accessible to practically all offshore gas production platforms. Skidmounted MPPE units to be delivered in modules for construction on e.g. cellar decks accessible part by part through narrow passages are also possible. On oil production platforms produced water flow rates vary widely from hundreds to thousands of m$^3$/hr. Depending on space available it is case by case required to assess the applicability of the MPPE technology (See Fig. 5). MPPE units for flow rates on 1000 m$^3$/hr levels are at this moment investigated by prospects. MPPE unit sizes for flow rates up to 300 m$^3$/hr are not prohibitive for offshore applications (footprint 42 m$^2$; height 10 m).

Fig. 4 – MPPE offshore unit for gas platforms

Fig. 5 – The dual-column MPPE system is sized for the project-specific combination of flow and removal requirements.

5.4 Water temperature effect

The extraction performance decreases principally at higher temperatures. However, the measurable effect is depending on the extent that a component can be extracted and the temperature increase. In the group compounds aromatics, polyaromatics and aliphatics, there are indications in running investigations that influent temperatures up to 60$^\circ$ C are possible without major consequences for these groups of compounds.
5.5 Performance guarantee / remote control

All MPPE units are fully automated and provided with remote control facilities, which makes it possible to shut down, start up and change process conditions from e.g. onshore. This facility has proven to be an effective and efficient tool to adequately support offshore operations in problem analysis, troubleshooting, adapting process conditions to different influent conditions etc. The remote control facility can be operated from long distances with a mobile telephone and a laptop. These provision and services form an integral part of the operational lifetime Performance Guarantee concept (at a fixed annual fee) that goes with the delivery of the MPPE unit. Also included in the Performance Guarantee concept are the periodical MPPE material exchanges, making the annual operating costs independent of the exchange frequencies.

6 POSITIONING MPPE IN THE PROCESS WATER TREATMENT

The influent of the MPPE process on Gas platform is taken from the third compartment of the skimmer vessel (see Fig. 6). This stream is filtered before treated in the MPPE unit and discharged as overboard water.

On oil platforms mainly two options are considered, (1) replacement of hydrocyclones and (2) positioning after the hydrocyclones. These positions are evaluated case by case and depend among others on the water composition.

Fig. 6 – Scheme of liquid production on gas platform, including MPPE tie-in

7 ENVIRONMENTAL ASPECTS

Due to the nature of the MPPE process the following aspects can be highlighted with regard to the environmental impact:

- Hydrocarbons are separated in practically pure form, ready for (re)use/recycle into the product stream.
- Low waste of polymer due to the long lifetime and reuse of spent material.
- Low energy consumption.
- No addition of chemicals.
- No emission to air.
- No sludge formation and no iron hydroxide (chemical) waste.
- Long lifetime of equipment and small footprint.
- Low noise level.
8 OTHER INDUSTRIAL APPLICATIONS

The unit at Total Fina Elf E&P [Ref. 5] Nederland was the first industrial application of the MPPE technology. Ever since 1994, more than 20 industrial applications have been implemented in The Netherlands, Germany, France and the USA, and over 50 successful onsite field-tests (on and offshore) with mobile MPPE units have been carried out. Of all current applications 60% is in processwater and/or wastewater and 40% in groundwater. In the latter application MPPE has been proven to be very well suited as a separation technique in DNAPL removal (Alameda California [Ref. 6 and 7]). (DNAPL=Dense Non Aqueous Phase Layers). DNAPLs consist of heavy chlorinated compounds heavier than water with very low solubility, requiring decades of pump-and-treat to be removed. By adding a surfactant up to 5% to the groundwater, solubility can be increased from a few mg/l to e.g. 50,000 mg/l MPPE has proven in practice to reduce these influent concentrations levels with 95 to 99%. In this way decades of treatment can be reduced to months or one to two years. This factual experience is very important also for offshore applications where often surface active chemicals such as corrosion inhibitors, oil/water separation chemicals are being used. Offshore experience started with the test and evaluation by ERT/Orkney Water Technology Center [Ref. 4], followed by the long duration tests with NAM (Shell/Exxon) in 1997 [Ref. 2], Statoil [Ref. 3] and in the South China Sea, both in 2001. Two commercial offshore units (TotalFinaElf and NAM) are on stream since 2002 and others are under construction.

REFERENCES


