Macro-porous Polymer Extraction for Offshore Produced Water Removes Dissolved and Dispersed Hydrocarbons

a report by Akzo Nobel MPP Systems

Introduction

The macro-porous polymer extraction (MPPE) technology developed in the early 1990s by Akzo Nobel removes dissolved and dispersed hydrocarbons. MPPE is basically a liquid-liquid extraction process where the extraction liquid is immobilised in a macro-porous polymer particle. This technology can remove compounds with a lower polarity than water to any level required (e.g. 99.9999% removal). The MPPE technology is applied in process water, offshore produced water, wastewater and ground water in a wide variety of markets since 1994. The first application was at Total in Harlingen (NL) where offshore-produced water and process water from the monoethylene glycol (MEG) and triethylene glycol (TEG) regeneration is treated by MPPE onshore.

Within the Oslo Paris Convention (OSPAR) for the protection of the marine environment of the North East Atlantic, European governments and industries are setting offshore emission standards for the future. This has led to testing and evaluating the MPPE technology heavily for offshore-produced water. ERT/Orkney water technology center,1 tests TOTAL,2 the Netherlands Oil and Gas Exploration and Produced Association (NOGEPA),3 NAM (Shell/Exxon),4 and Statoil.5

The MPPE technology has been, for offshore gas/condensate, proven and commercially operational since the beginning of 2002 (Total F15A).6 Two other units have started up since then: NAM K15A, and NAM K15B. In 2003, successful fieldtests on produced water from oil production took place on request of the OSPAR.9

The MPPE Process Description

In the MPPE process, hydrocarbon-contaminated water is passed through a column packed with MPPE particles (see Figure 3). The particles are porous polymer beads, which contain a specific extraction liquid. The immobilised 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 reused 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 almost 100% pure hydrocarbon phase is recovered, removed from the system and ready for recycling or disposal. The condensed aqueous phase is recycled into the system. The application

1. ERT/Orkney Water Technology Center: The removal of dissolved and dispersed organic components from produced water, ERT F92/178, 1997 (Study requested by Exxon/Mobile, TOTAL, Amanada Hess).
3. van der Kaa C C R and Petrusveki B, (Stork) (1998), Report 61944-00-32-301-2, NOGEPA (Netherlands Oil and Gas Exploration and Production Association) and Dutch Government by Inventarisation of removal techniques to reduce the benzene/heavy metal emissions from offshore platforms (in Dutch).
5. Grini P G, Statoil ASA, Tjonidheim, Hjelsvold M and S. Johnsen, SPE 74002 “Choosing Produced Water Treatment Technologies Based on Environmental Impact Reduction”, Copyright 2002, Society of Petroleum Engineers Inc. This paper was prepared for presentation at the SPE International Conference on Health, Safety and Environment in Oil and Gas Exploration and Production, held in Kuala Lumpur, Malaysia, March 2002.
of two columns allows continuous operation with simultaneous extraction and regeneration. A typical cycle is one hour of extraction and one hour of regeneration.

Separation Performance

Dissolved and dispersed components that can be removed to any level specified are:

- aromatics (benzene and xylene (BTEX));
- polyaromatic hydrocarbons (PAHs);
- naphthalenes, phenanthrenes, dibenzothiophenes (NPDs);
- aliphatics (including mineral oil up to <C20);
- TEOX/TEOC (total extractable organics);
- halogenated hydrocarbons (such as chlorinated, brominated etc.); and
- in principle all other ‘hydrophobic’ components (e.g. CS₂, THT).

In current running units, dissolved aromatics (especially benzene), PAHs, aliphatics and chlorinated hydrocarbons are removed for more than 99.99% (size of unit is tailored to required separation performance – reduction factor of one million times is feasible (= 99.9999% removal)).

With NPDs and PAHs, offshore and onshore, 99.9% removal is obtained. Onshore an industrial unit has been running since 1998, removing 3,500 ppb PAHs to n.d. level (<0.05 ppb). There has been 50% to 80% removal of:

- phenol, 50%;
- cresols (ortho-, meta-, para-) 70% to 80%; and
- alkylated phenols.

Heavier alcohols (like isobutanol), esters, ethers and other more polar compounds (like tetra hydrofuran), are removed by 40% to 80%. Some specific ethers such as dichloro-di-isopropylether (DCPE) can be removed, even at >99% level.

Inlet Conditions and Water Composition

When working with inlet temperatures for aromatics/PAHs, aliphatics removal up to 55°C to 60°C are possible. Other situations have to be viewed case by case. Inlet pressure needs to be reduced to three barg, to flow through the unit leading to an atmospheric outlet. For gas/condensate production process water the MPPE unit is placed after the degasser (flash vessel) and skimmer (basis offshore experience). For oil production-produced water, after the hydro cyclones and degasser, dissolved (heavy) metals, iron, Ca⁺⁺ (no carbonate formation) will flow through. In case of iron, limited flocculation of iron hydroxide will not affect the performance (anaerobic operation, MPPE material robustness).

Dissolved salt and other dissolved solids will flow through, as will methanol, glycols and surfactants.

With scale-corrosion inhibitors, demulsifiers and H₂S scavangers, no negative effects have been experienced.1,2,4,6–9 With Total our MPPE system is treating produced water from offshore and water from glycol regeneration onshore containing, among others, corrosion inhibitors, glycol and methanol. Current MPPE units offshore are treating produced water containing corrosion inhibitors. It also has been experienced that a major part (approximately 50%) of the inhibitor was removed with MPPE.

**Suspended Solids**

Some form of prefiltration may be required depending on the concentration. The unit is relatively robust against solids like sand, etc. There are several outlets for solids, e.g. part will be prefiltered, part will flow through, part will be removed by the hourly backwash during one of the process steps and part will be removed when material is replaced. In our offshore demonstration unit, cartridge filters are used, although other prefilters could be applied. In a long duration offshore field test no pressure drop increase over the packed bed was measured without prefiltration. Current offshore commercial units are successfully operating with standard prefilters.

**Flow Rates**

A single unit consisting of two columns can treat up to 200m³ or 250m³ per hour; for higher flow rates units will be installed parallel.

**Technical Information**

Ideally, there should be minimum operator intervention and minimum maintenance requirements. Remote control system (by telephone/modem connection) is included in combination with a fully automated MPPE unit for which only normal maintenance is required. Remote stop, start-up and other changes in process conditions are possible.

Suitable for outdoor placement, the MPPE unit can be placed in a container. With regards to equipment suitable for offshore application, in the case of a container, a 20ft container (including MPPE unit PLC, computer and prefiltration), approximately eight ton (during operation) and approximately six ton (handling weight) is used. A modular skid-mounted approach for installation on the cellar deck has also been implemented. Electricity units required are: 380–415V, maximum load 50kW, instrument air, water for steam generator and cooling water, as well as other possible options. Due to the presence of salt, possibly influenced by CO₂ content in the condensate, it is advisable to use duplex. Capacity can be tuned to the changing influent levels to obtain the required effluent, e.g. in case of a 50% higher influent concentration the same effluent level with only a 10% lower flow. At lower influent concentrations, higher flow rates can be reached. At lower capacity, level controlled operation is required (e.g. level of a buffer tank).

**Contaminant Recovery**

The recovered hydrocarbons (as a mixture) are obtained as a practically 100% pure liquid to be recycled and/or reused.

**Evidence of Confidence and Experiences**

Figures for Elf Petroland (TotalElfFina) in Harlingen onshore treatment of offshore gas produced water (since 1994) are as follows:

- six-year successful operation at three to six m³/hr;
• average concentrations of BTEX at 3,000ppm
  with peaks to 7,000 and 10,000 ppm (dispersed).

• continuous >99.9% removal of BTEX and
  aliphatics; and

• experiences published at SPE conference in
  Caracas in 1998 (SPE 46577 HM Pars/Elf

Evaluation by Orkney Water
Technology Center

• Comparison of technologies on request of Exxon,
  Amerada Hess and Total Elf Aquitaine.

• Performance was verified on oil and gas
  produced water (in 1997) during a three-month
  test with a full scale unit. The test showed
  insensitivity for corrosion inhibitors from oil
  and gas production platforms.

On request of the Dutch government and the Dutch
Oil and Gas Exploration and Production Association
(NOGEPA), the MPPE technology was evaluated by
engineering bureaus against 55 technologies and
selected as one of the best options for removing
hydrocarbons from offshore-produced water (1997).
NAM (Shell/Exxon) were in a successful four-
month offshore trial in 1999, involving:

• north Sea offshore;

• full scale unit treating all produced water
  (including water from glycol regeneration); and

• consistent continuous removal of hydrocarbons to
  meet effluent requirements with an availability of
  over 98%.

Data are published in Offshore Technology
Conference (OTC) 13217 paper (May 2001 by
Shell/Exxon and Akzo Nobel). Also listed as best
available techniques (BATs) by the OSPAR
convention for the protection of the marine
environment of the North-East Atlantic (1999):

• recommended by OSPAR and listed as best
  available technology and best environmental
  practice for produced water management on
  offshore oil and gas platforms.

Additional successful offshore demonstrations on
gas/condensate offshore-produced water were
conducted by:

• Statoil, North Sea Åsgard A condensate
  platform; and

• Shell, South China Sea, Malaysia.

And the first commercial units offshore were:

• Total F15A) April 2002;

• NAM (Shell/Exxon) K15A November 2002;

• NAM (Shell/Exxon) K15B December 2002;

• with Norsk Hydro a four-month field test on
  Troll B for evaluating the capability of the MPPE
  technology to reduce the environmental impact
  factor (poly aromatics, aromatics and aliphatics) of
  the oil produced water stream (1,250m3/) is being
  finalised; and

• successful MTBE removal tests (with a modified
  MPPE particle) from groundwater has been
  carried out with Shell in Germany.

Environmental Aspects

• Practically pure separated hydrocarbons for
  use/reuse

• Low waste of polymer
  – Long lifetime
  – Reuse of spent material

• Low energy consumption

• Low noise

• No addition of chemicals

• No emission to air

• No sludge information

• No (chemical) iron hydroxide waste

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