Solving the Impact of High Toxic Loads in the Produced Water at the Kollsnes Gas Terminal by Applying the MPPE Technology

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1 INTRODUCTION

The Kollsnes gas processing facilities is located at Kollsnes west of Bergen in Norway. The Kollsnes gas plant was started up in 1996 and is owned by Gassled with Gasco as operator and Statoil ASA as technical service provider.

The plant treats gas from the Troll, Visund and Kvitebjørn offshore fields in the North Sea at a rate of up to 130 million standard cubic meters (scm) per day. See map overview in figure 1.

The Kollsnes plant separates natural gas liquids (NGL) from the methane-rich gas, and compresses the latter for pumping by large compressors through various pipelines to continental Europe.

The Vest process pipeline carries the NGL phase from the Kollsnes facility to Statoil’s Mongstad refinery for further fractionation into propane, butanes and naphtha. Gas from Kollsnes is transported to continental Europe through four pipeline systems. An overall picture of the plant is given in figure 2.

As a part of the operation of the pipeline from the offshore fields, monoethylene glycol (MEG) is added to prevent hydrate formation and for corrosion control. Periodically methanol is also added at Troll B & C platforms in connection with start-up of new production wells. Associated water transported together with the gas, is separated from the gas at Kollsnes. This water contains MEG, methanol and residue of condensate. MEG is further recovered in a
regeneration plant for reuse offshore, but small amounts of MEG follow the produced / process waste stream from the regeneration plant.

To prevent any negative environmental effects in the recipient, all waste streams from MEG regeneration as well as the separated condensed water from the gas goes to treatment. The treatment plant has a biological stage for removal of readily biodegradable organic materials, and a stage for separation of the sludge (micro-organisms) produced by the biodegradation process.

The waste water plant consists of two storage tanks TA301 and TA318 for buffer and de-aeration, pre-treatment with centrifuges and filtration to remove free oil, an aerobe biological reactor (TA320), sludge separation (TA306) and final polishing in sand filters (TA310). Miscellaneous chemicals (iron sulphate, Antifoam agent, polymer, phosphoric acid and ammonia) are also added to the process on a continuous and intermittent rate. See figure 3.

Figure 3, Water plant schematic

2 Start-up of the Kvitebjørn field

Kvitebjørn is a gas condensate field developed with an integrated accommodation, drilling and process facility with a steel jacket, see picture 4. Rich gas is transported in a dedicated pipeline to Kollsnes, while condensate is transported in a pipeline to the Troll Oil Pipeline for onward transport to Mongstad. Kvitebjørn is operated by Statoil ASA. Estimated production in 2006 is 54,000 barrels of oil per day, 6,7 billion scm of gas per year and 0,31 million tones of NGL per year[1].

Gas with associated NGL and condensed water from the Kvitebjørn field was tied-in to the gas plant autumn 2004. Very soon after start-up, the total organic content (TOC) in the waste water outlet started to increase, especially MeOH content in aerobe biological reactor (TA320).. This happened without any increase in the total organic load to the inlet buffer tank of the produced water treatment plant. In January 2005 the biological activity had almost ceased. The oxygen uptake was minimal and the biological sludge was most likely poisoned.
2.1 Identifying the problem

The biological treatment plant was no longer able to treat MeOH and MEG even with the same chemical oxygen demand (COD) load as before. Oxygen measurements within the sludge indicated a very low oxygen uptake. It was also difficult to maintain the sludge concentration in the bioreactor TA320. It was concluded that either the sludge was poisoned or nutrient was lacking. It should here be mentioned that nutrients have to be added on a continuous basis at the Kollsnes plant.

Several water samples were taken at multiple locations in the plant. These samples were further analyzed for different components that could be potentially toxic for the sludge.

Further the nutrient addition was checked to be ensured that an excessive volume was added and that the system performed as expected. Nothing wrong was found in the nutrient addition system.

Different chemicals that were added both to the plant as well as to the offshore platforms were also investigated. It was concluded that none of the chemicals used could explain the observed behavior of the plant.

The sludge and water analysis from the Troll field and the Kvitebjørn fields gave the following results:

- Water from the Kvitebjørn field had significant higher BTEX, PAH and phenol concentration compared to water from the Troll field. Up to 20 – 100 times more BTEX from Kvitebjørn compared to Troll was measured. Concentrations up to 600 mg/l were observed. PAH concentrations was 10 times higher, the C₂ and C₄ phenols was 10 to 50 times higher.

- Water going out of the bio reactor had a very high BTEX content. The accumulated BTEX concentration in the bioreactor had become most likely toxic for the bio mass. The water analysis indicated also a high content of C₂ and C₄ phenols.

- The BTEX content did vary a lot over time and it is not unlikely that even higher contents than measured occurred during the initial start-up period of Kvitebjørn.

- The metal content in the water and sludge was not very high and it is not likely that this has been the cause of the problems.

It was thus concluded that the bio mass had been poisoned most likely by high contents of BTEX, Phenols and PAHs during start-up of Kvitebjørn.

In order to confirm this conclusion further in the problem solving process, toxicity analysis of the water was performed before and after bubbling of nitrogen gas (500 to 1000 liter gas per liter water). TOC, BTEX and Microtox were analyzed before and after nitrogen bubbling. These results indicated that nearly all the water was highly toxic and confirmed as well that the Kvitebjørn water was more toxic than the Troll water.
The measured toxicity was reduced after nitrogen bubbling which supported the suspicion that BTEX and other volatile organic components were the cause of the problems.

The treated water from vessel TA310 also had a BTEX level that could be toxic for microorganisms in an active sludge system. The ESIS database [2] indicates an EC50 of 13 mg/l is given for similar bacteria but no data is given for bacteria in a MeOH and MEG environment. The absolute toxicity level will also be a function of the pre-adoption of the bio culture.

Waste water to the biological treatment had to be stopped in February 2005. The bioreactor was from this point fed only with pure water, MEG and MeOH to try to rebuild the bio culture. The waste water had further to be shipped for external cleaning at a high cost.

Several technical solutions to the problem were investigated. It was during this process decided to try the MPPE technology from Akzo Nobel MPP Systems. In May 2005 a MPPE unit was introduced upstream the biological treatment plant in a trial to remove the toxic components present in the water. See picture 5.

2.2 Introducing the MPPE technology

The MPPE (Macro Porous Polymer-Extraction) process from Akzo Nobel MPP Systems in the Netherlands has been available for purification of ground water, process water and offshore produced water for several years [3] [4]. In the MPPE water treatment process, hydrocarbon-contaminated water is passed through a column packed with MPPE particles. See picture 6. The particles are porous polymer beads that contain a specific extraction liquid. The immobilized extraction liquid removes the hydrocarbon components from the process water. The purified water can either be reused or discharged.

Periodical in-situ regeneration of the extraction liquid is accomplished by stripping the hydrocarbons using low pressure steam. The stripped hydrocarbons are then condensed and separated from the water phase by gravity. The almost 100% pure hydrocarbon phase is recovered, removed from the system and left ready for recycling or disposal.

The condensed aqueous phase is recycled into the system. The application of two columns allows continuous operation with simultaneous extraction and regeneration. A typical cycle is one hour of extraction and one hour of regeneration. Figure 7a shows a simplified flow-sheet of the MPPE process and picture 7b a photo of a full-scale MPPE installation.
According to Akzo Nobel the MPPE technology can reduce dissolved and dispersed hydrocarbons such as aliphatics, aromatics (BTEX), polyaromatic and halogenated (chlorinated) hydrocarbons with up to 99.9999 % removal.

MPPE technology can be applied for treatment of offshore produced water, process water, wastewater and ground water in a wide variety of markets including the offshore, gas and oil, chemical, coatings and pharmaceutical industries. MPPE can withstand complex produced water environments containing salt, methanol, glycols, corrosion inhibitors, scale inhibitors, H₂S scavengers, demulsifies, defoamers and dissolved (heavy) metals.

More than 25 commercial units have been in operation since 1994 [5] making the MPPE process a well proven technology. Statoil has previous to Kollsnes tested the MPPE system on produced water at the Åsgard A platform. The tests went well and removal efficiencies of more than 99.4 % were obtained for the BTEX compounds [6].

The installed MPPE skid on Kollsnes was installed upstream the bio reactor to try to protect it from high loads of BTEX, PAH and phenols. See figure 8.
Picture 9 and 10 show pictures of the internal steam generation and collection drum for the condensed hydrocarbon phase.
2.3 Results

Measurements have been regularly taken the 16 months the rental MPPE unit has been in operation. The following curves represent the removal efficiency measured by the laboratories used. The BTEX removal is given in figure 11.

The removal of BTEX has been in the area between 95 and 100% dependent on the laboratory used. It is clearly a challenge to both sample and analyze the BTEX content in a consistent matter. The MPPE mobile unit (mobile unit No. IV) that was available at the moment of request, is a unit with a fixed separation capacity (MPPE quantity). The removal effectiveness that could be expected based on process design calculations prior to sending the unit to Kollsnes was around 98% for BTEX. This demonstrates that the calculated performance of the MPPE mobile unit was well in line with the measured separation performance over the 16 months operation so far. As expected the efficiency has been slowly degraded during the first year of operation by 2 – 3%. The slow reduction of the separation performance over time is due to a combination of factors like reduction of packed bed efficiency, slow loss of extraction liquid etc. This slow reduction in separation performance makes it easy to plan MPPE material exchange well ahead e.g. during general plant shutdowns.

PAH removal shows a more inconsistent behavior than BTEX, although the efficiency has been in general very good and varies between 95 and 99%. Removal efficiency as function of time is given in figure 12. The behavior of the PAH is mainly determined by Naphtalene, the most soluble component of all PAHs. The removal effectiveness of naphthalene remained > 99%. The overall removal performance for PAH based on process design calculations was expected to be > 99%. The anomaly of the lower measured separation of the PAH versus BTEX, and the improvement of the separation performance over time can be explained by the tendency of PAH to stick to (very fine) particles and/or to be present as very fine particles. This was demonstrated in the laboratory where solid filtration of samples showed a removal of PAH. Removal of “dissolved” PAH with MPPE was well above > 99%. The improvement in PAH removal performance over time can be very well explained by an improving filtration effect over time of the pre-filtration / MPPE columns combination.
The phenol reduction has quite rapidly been reduced to no effect. This is given in figure 13.
2.4 Conclusions and recommendation for future projects

During the first 16 months of operation the MPPE unit has performed well within Statoil’s expectation. The bio culture has been adequately protected against high concentrations of PAH and BTEX which could be of toxic levels. The waste water treatment plant has run without problems after the MPPE unit was installed.

The availability for the unit has in general been very high.

For future tie-ins the BTEX, PAH and Phenol content in the produced water must either be analyzed or calculated.

Calculations based on the initial reservoir pressure and temperature could be done assumed equilibrium between the hydrocarbon and water phase and a given hydrocarbon composition.

If the toxic load is expected to be higher than the bio-culture is expected to handle, MPPE should be evaluated as a mitigating technical solution to the plant design.

3 NOTATION

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<tr>
<th>TOC</th>
<th>Total Organic Carbon</th>
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<tbody>
<tr>
<td>NGL</td>
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<tr>
<td>MeOH</td>
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<tr>
<td>COD</td>
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</tr>
<tr>
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<td>PAH</td>
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<tr>
<td>MPPE</td>
<td>Macro Porous Polymer Extraction</td>
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4 REFERENCES