

Biocide Evaluation and Optimization for Produced Water Pipelines by Testing on System-Specific High-Risk Microorganism

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ABSTRACT

Corrosion management is essential to secure integrity and reduce downtime. In 2010, extensive corrosion was observed in a carbon steel separator at the South Arne facility. Biocide dosing and microbial monitoring have been ongoing since. To provide the necessary knowledge for selection of the optimal biocide treatment at South Arne, culprit microorganisms were identified and enumerated. Methanogens were identified to be dominant in the system, with as major representative the genus *Methanothermococcus*, thus this was enriched and grown as biofilm in a specially designed Multiwell Plate Assay. This method allows for numerous chemical dosages and combinations tests to verify biocide efficiency and potential synergies with other production chemicals. The effect and compatibility of glutaraldehyde, THPS and H₂S scavenger on system-derived biofilm in produced water (PW) was studied.

The triazine-based H₂S scavenger, up to 1000 ppm, promotes activity and supports growth of methanogens. When biofilms were exposed to combinations of triazine-based H₂S scavenger and biocide, the biocide effects were reduced. Thus, increased biocide dosages were needed to reduce microbial growth and obtain a similar effect to treatments consisting solely of biocide. The combination of regular system monitoring, identification of culprit microorganisms, and specified biocide efficiency evaluation provides valuable knowledge and in-depth understanding of which corrosive microorganisms survive the given biocide treatment, prompting further improvements and increasingly specific and efficient corrective actions.

Key words: Methanogens, *Methanothermococcus*, Biofilm, Microbial influenced Corrosion (MIC), MIC risk management, Microbial community structure analysis, Next Generation Sequencing (NGS), THPS, Glutaraldehyde, H₂S scavenger, Biocide, Produced water.

INTRODUCTION

Original platform-design-life for the South Arne facility, in the Danish sector of the North Sea, was 10 years of service. The platform is now in its 20th year of oil, gas and water production, with related challenges to system integrity. The platform's original design only accounted for CO₂ and H₂S corrosion; microbial influenced corrosion (MIC) and microbial management were not included in the asset's integrity management plan. Since 2010, when extensive corrosion was observed in a carbon steel separator, microbial numbers of MIC indicator microorganisms have become an important input factor in the risk-based corrosion monitoring program.¹ The microbial monitoring program includes detection and quantification of high-risk MIC microorganisms: Sulphate-reducing *Bacteria* (SRB), Sulphate-reducing *Archaea* (SRA), and methanogens, using the microbial molecular method (MMM) qPCR. Additionally, as part of the lifetime extension of the installations, carbon steel has been replaced with duplex piping and vessels have been coated or recoated with epoxy-based coating. Further, biocide is dosed in the injected water (IW) and PW system, to control MIC risk and corrosion in vessels, water zones, and pipelines.

The biocide program has been modified multiple times, with periods of increased frequency and doses; however, the compatibility of the active ingredient downstream in the PW system, interaction with other production chemicals², and the efficiency against troublesome organisms had not been evaluated. Reoccurring high levels of microorganisms, leading to a high-risk of fouling, as well as presence of high-risk MIC microorganisms, especially methanogens, prompted a process of re-evaluation and optimization of the biocide treatment strategy. The aim of the optimization process is not only to contribute to secure integrity and reduce down-time, but also to reduce environmental impact and, ultimately, costs.

Testing and evaluating efficacy and compatibility of a biocide with on-site chemicals and conditions is necessary because there are many interactions among production chemicals that can downregulate and reduce their forecasted impact^{2,3}. The microbial groups present, and their behaviors also need to be realistically simulated because they influence biocide efficacy. For example, microorganisms that attach to surfaces as biofilms are more difficult to combat with biocides than microorganisms that thrive in the water phase. The cost of system-specific testing is often covered by the daily savings achieved through correct dosing.⁴

While the response of SRB to biocides has been extensively tested⁴, little information is available on the response of methanogens to biocides. For the South Arne, where dominant microbial groups are methanogens, a system-specific laboratory test was designed to provide the knowledge necessary to select the optimal biocide treatment. The intent of the test was to investigate the compatibility of two biocides (glutaraldehyde and THPS) with the PW system and their efficiency against the predominant MIC microorganism (*Methanothermococcus* sp.) at different dosages. First, the microbial community composition in the produced water system was investigated by Next Generation Sequencing (NGS) in order to identify the dominant troublesome microbial groups in the system, which persisted in the PW vessels and did not respond to the mitigation treatment in place at the time. Second, the dominant genus, accounting for more than 91 % of the sequences detected in the degasser and coalescer (Figure 5) was enriched from a PW system sample and grown as biofilm in the laboratory. Third, the efficacy of different biocide treatments was tested in produced water on the biofilm with a DTI Multiwell

Plate Assay [†] reflecting system conditions. This procedure allows numerous dosages and combinations to be studied in one experiment, which leads to highly representative results and simultaneously reduces testing costs. ²

The test performed was an enrichment of only the dominating methanogen group, due to its persistence and very high relative abundance throughout the PW system, especially in the degasser and coalescer (Figure 5). The most relevant group should be targeted by the biocide treatment.

EXPERIMENTAL PROCEDURE

Site and Sampling

South Arne operates with a sulphate-reduced and nano-filtered seawater injection, with re-injection of produced water to increase the recovery of oil from the formation. Biocide is applied both upstream of the deaerator (not shown) and to the produced water system downstream of the production manifold in the separation train, which is composed of five main vessels (1st, 2nd, and 3rd stage separators, coalescer and degasser) (illustrated in Figure 1) that are included in the MIC monitoring program.

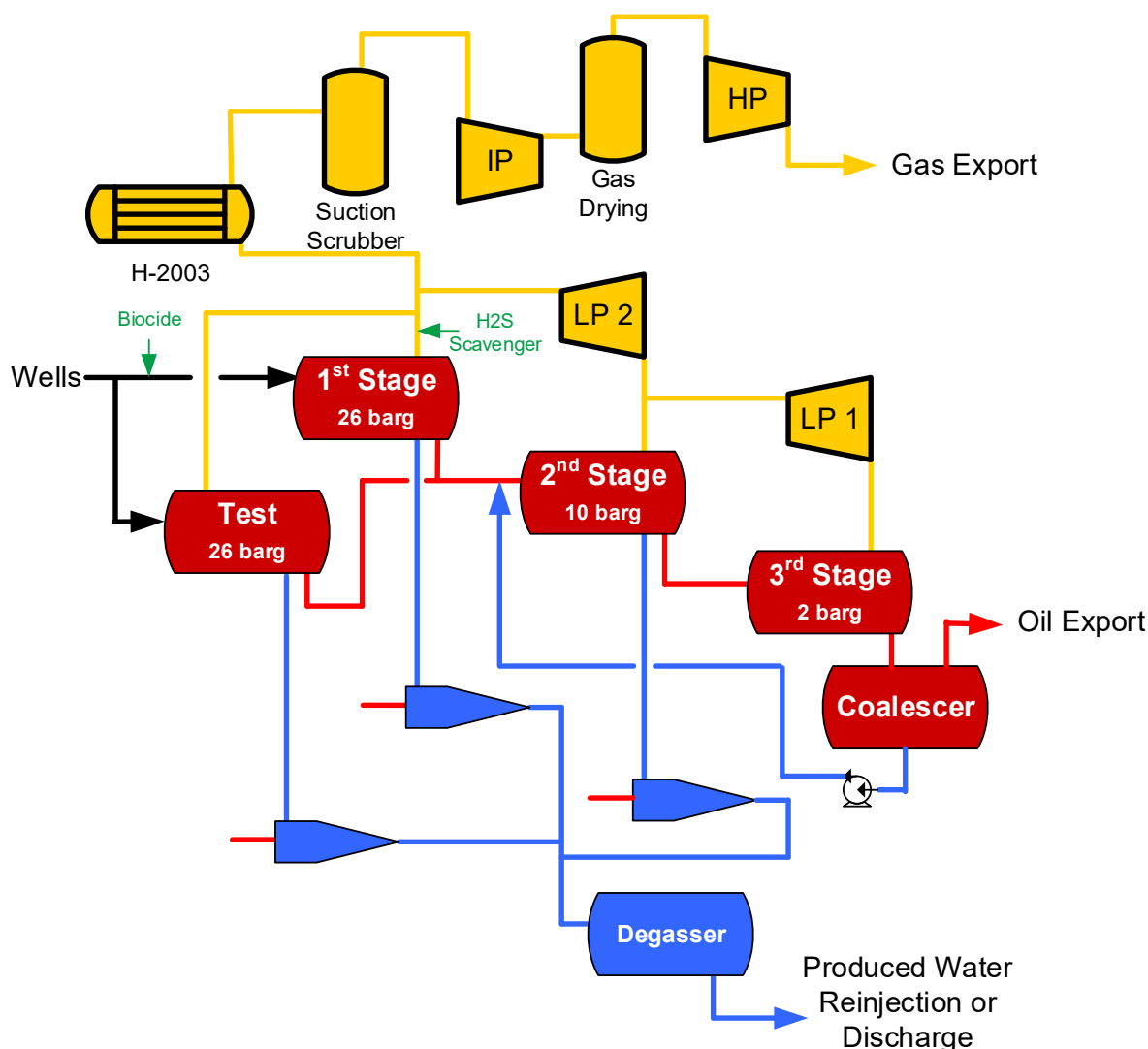


Figure1: Schematic overview of the separation process on South Arne and injection points for chemicals.

[†] Trade name

Molecular methods for characterization of system microorganisms

Prokaryotic numbers, total numbers of Bacteria and Archaea, were enumerated by quantitative Polymerase Chain Reaction (qPCR) targeting the gene for 16S rRNA, which is present in all Bacteria and Archaea. Sulphate-reducing Bacteria (SRB) and Archaea (SRA) were quantified by qPCR targeting the *dsrAB* gene, which is present in all sulphate-reducing prokaryotes (SRP). Methane producing Archaea were quantified using qPCR targeting the gene encoding the Methyl-Coenzyme M Reductase (MCR) genes.

The activity of cells in immediately fixated samples was measured by determining the RNA content by RT-qPCR targeting 16S rRNA molecules for each of the specific groups cited in the previous paragraph.

Microbial community structure analysis (also noted NGS) was investigated by targeting and amplifying 16S rRNA gene sequences of Bacteria (region V1-3) and Archaea (V4-V6). Samples were subsequently sequenced using MiSeq Reagent kit v3[†], 600 cycles (Illumina, USA) following the standard guidelines for preparing and loading samples on the MiSeq Illumina MiSeq 2x300bp PE[†] technology and sequencing of bacterial and archaeal 16S rRNA genes. Taxonomy was assigned by the RDP classifier^{†5} as implemented in the `parallel_assign_taxonomy_rdp.py` script in QIIME^{†6}, using the MiDAS database v.1.20^{†7}.⁷ The results were analyzed in R^{†8} through the RStudio IDE[†] using the `ampvis` package v.1.9.1^{†9}.

Enrichment of system microorganisms

Subsamples from the South Arne PW degasser (V-4006) were inoculated to individual culture bottles and left for growth at 45 °C. Subsamples from culture bottles with positive growth were frequently transferred to fresh growth medium. Growth was verified by turbidity of the culture, microscopy, overpressure of the headspace (indicating gas production) and methane (CH₄) detection in the culture headspace by gas chromatography (GC) measurements. An enrichment with methane production was evaluated for microbial community composition by 16S rRNA gene sequencing (NGS), using Illumina MiSeq (described in the previous section).

Biocide efficacy against system-specific methanogenic biofilm

Figure 2 gives an overview of the methodology applied to evaluate biocide efficacy against the lab-grown system-specific methanogenic biofilm. An enrichment culture was diluted and distributed in multiwell plates under anaerobic conditions and incubated at 45°C. Measures were taken to avoid evaporation from the wells during incubation, especially for the wells placed at the edge of the plates. The amount of established biofilm was measured after 1, 2, 3, 4, and 7 days to identify when the biofilm was actively growing and when the biofilm matured (data not shown). The biocide testing was conducted after 2 days because the methanogenic biofilm was actively growing at that time.

After 2 days with methanogenic biofilm establishment, the nutrient broth was carefully removed and replaced with filter sterilized-anaerobic PW, either with or without chemicals. The PW was applied to simulate field conditions and enable potential cross-binding of active compounds in the biocides with other compounds in the produced water.

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