# OILFIELD TECHNOLOGY

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## RESERVOIR SOURING MITIGATION

# Removing sour

**Jennifer Knopf and Ulf W. Naatz, Vink Chemicals, Germany, and Matt Streets, Rawwater, UK,** outline the options available to mitigate the challenges of reservoir souring.

The injection of large volumes of water into oil and gas reservoirs for maintaining reservoir pressure is typically applied during secondary and tertiary stages of conventional production and oil and gas recovery. Over the lifetime of the well, such sulfate-containing water from various sources – including seawater, aquifer water or produced water reinjection – may lead to the establishment of mature microbial communities in the vicinity of the injection well or deep in the rock channels. The onset of complex metabolic processes causes a raft of problems for the operator. One particular challenge is

# the taste

referred to as ‘reservoir souring’, which is the process chiefly dominated by sulfate reducing bacteria (SRB) and sulfate reducing archaea (SRA) utilising various sulfate sources and eventually forming reduced sulfur species, namely hydrogen sulfide ($H_2S$). If not properly controlled, souring can become a costly process with both top and bottom-line impacts, and can eventually render an oilfield economically unprofitable.

In contrast to wells producing crude oil that contains naturally occurring hydrogen sulfide, wells that produce biogenic $H_2S$ tell a history of failed microbiological control during drilling, production and/or shut-in periods. Sulfate reducing microorganisms are readily introduced to the uncontaminated subsurface as a result of operational processes if not protected properly by a best practice treatment programme.

As an example, a large onshore oilfield in North Africa turned from a sweet production asset to a sour oilfield within less than a decade. This was due to wells having to be abandoned by the operator during a civil war without having the time to implement industry best practice shut-in procedures for microbiological control (preservation). Therefore, produced crude increased from less than 10 ppm (w/w) $H_2S$ in the past to over 800 ppm (w/w) more recently, with the oilfield now producing about 150 kg of biogenically formed $H_2S$ every hour.

The consequences of souring include:

- $H_2S$ formation.
- Immediate HSE risk for field personnel.
- Loss of productivity.
- The high expense of $H_2S$ scavengers.

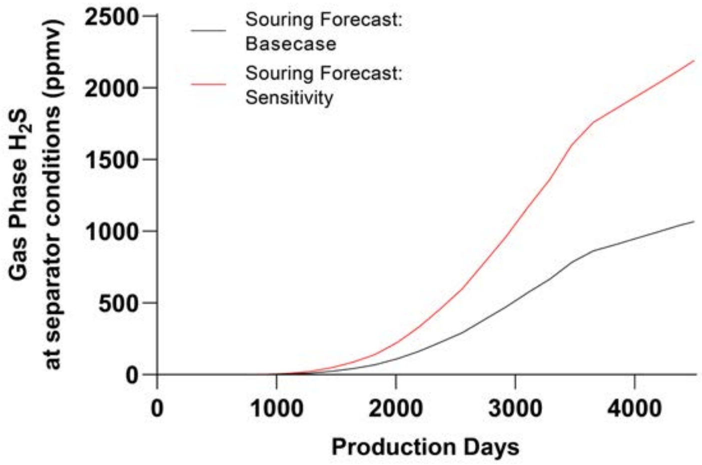


**Figure 1.** *Basecase and sensitivity forecasts – an example of output souring profiles from Rawwater's souring forecasting model, DynamicTVS©.*

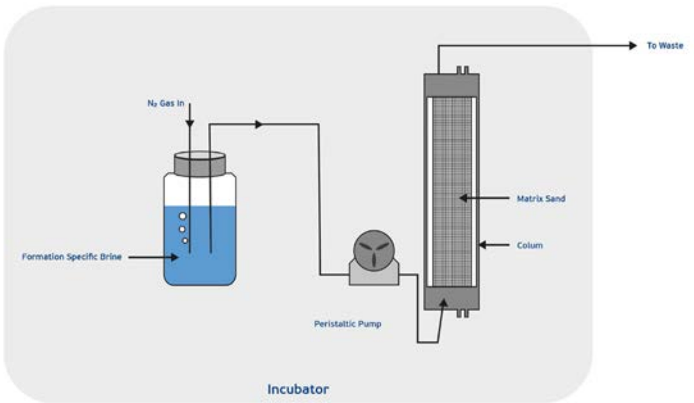


**Figure 2.** *FFUBR test set-up.*

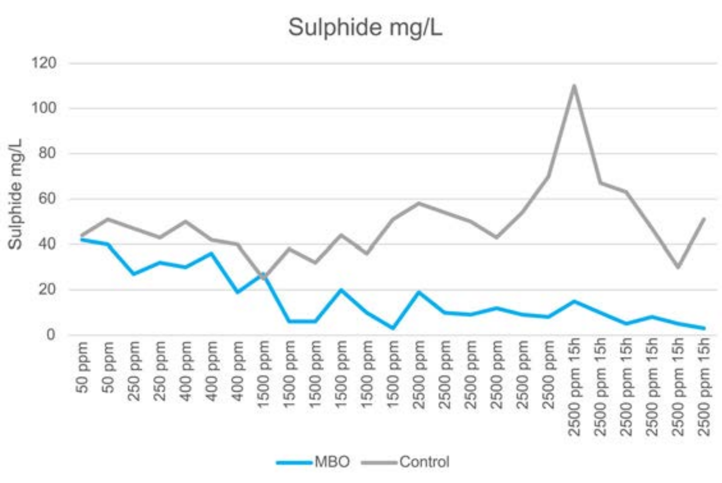


**Figure 3.** *Sulfide measurements.*

- Damage to production facilities, as well as leaks and spills.
- Biofilm and plugging.
- Formation damage.
- The replacement of assets from microbiological influenced corrosion (MIC).
- Reduction in oil quality and lost value from sour hydrocarbon production.
- Unwanted attention from investors, media, regulators and the public.

## Recent trends in mitigation programmes

The first step in a reactive mitigation strategy is the implementation of a $H_2S$ scavenger treatment programme to quickly bring the sour crude to export specifications. However, the mass of $H_2S$ produced from the large North African oilfield described previously demonstrates the enormous consumption of scavenger required to remove this high $H_2S$ load. Established organic, non-reversible scavenger chemistries rarely act in a 1:1 stoichiometric reaction path and typically come as a 40 – 60% aqueous solution (for example MEA-triazine). Thus, the volumes of scavengers brought to the field accordingly may be high. The field produces 150 kg $H_2S$/hr, which results in 3600 kg $H_2S$/day. For treatment of 3600 kg $H_2S$/day, with a typical treatment rate of 3 ppm scavenger: 1 ppm $H_2S$, 10.8 t of a scavenger (100% active product) would be required. Industry standard scavengers come diluted, containing 40% active, which increases the needed scavenger volume to 27 t scavenger (40%) per day.

Taking the chemicals cost for a permanent $H_2S$ scavenger treatment into account, it appears logical to alternatively (and sometimes additionally) focus on the root causes of biogenically formed $H_2S$, firstly the biofilm, and secondly, the volume and quality of the injection water. In the first case, a specifically designed biocide treatment for the well and its near wellbore area may be a sustainable and cost-effective solution compared to a permanent, continuous $H_2S$ scavenger treatment. However, if the biofilm has spread deep into the formation, any cost-effective biocide treatment will be ineffective, and the potential risk of formation damage during deep squeeze treatments may be considered too high. Alternative treatments may employ specific treatment of the injection water to control or alter the primary metabolic processes by SRBs within the formation during the transit of the water from the injection well to the producing well (i.e. biocides or nitrate). Another mitigation strategy is the removal or significant reduction of the sulfate content from the source water prior to injection. This is typically achieved by implementing membrane technologies or other water pre-treatment methods which facilitate the precipitation of the sulfate ion. Coupled with scale control, this methodology has been shown to significantly reduce sulfate reducing activity in the downhole formation, but like other water injection treatment strategies, the effects are only visible upon breakthrough of the injection water, which can take months or even years.

## Reservoir souring modelling

Rawwater Engineering Company Ltd. (Rawwater), as a third-party, independent specialist in oilfield reservoir souring, supports Vink Chemicals in oilfield reservoir souring modelling and high-pressure laboratory simulations.

Predicting the appearance and severity of sour fluid production through computer models is crucial for making significant technical and economic decisions related to field development and material selection. Whilst the intricacies of modelling microbial sour gas production are complex, a credible souring forecasting model should describe four key mechanisms:

- Cooling of an oilfield reservoir as a result of waterflooding.
- The opportunity for the growth of sulfate-reducing microorganisms in the waterflood.

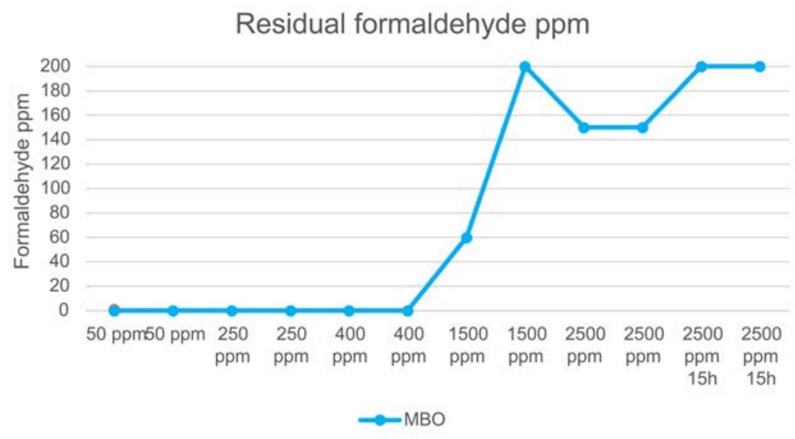


***Figure 4.*** *Detection of residual formaldehyde.*

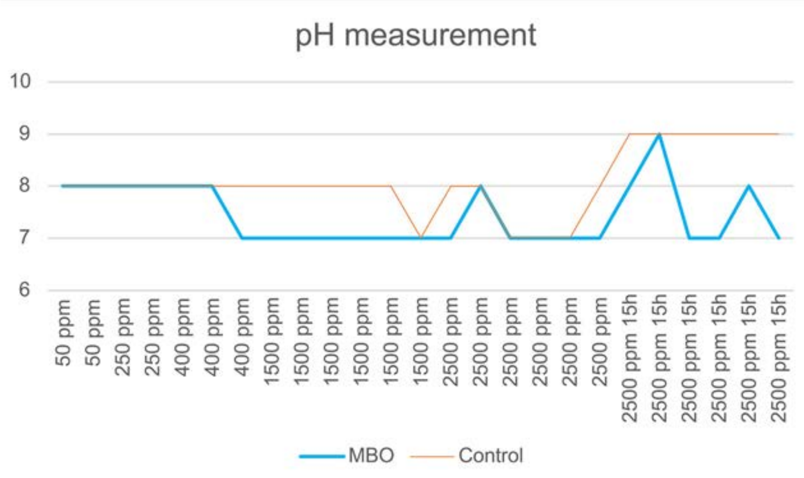


***Figure 5.*** *pH measurements.*

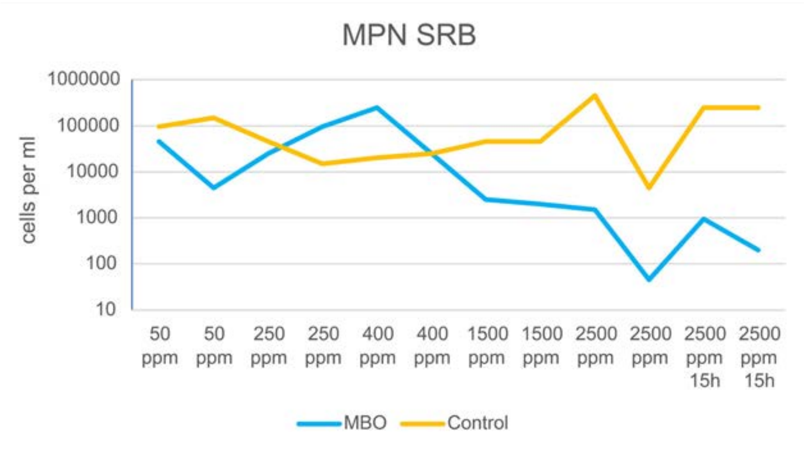


***Figure 6.*** *Most probable number of SRB. This graph demonstrates that the biocide MBO successfully reduced the SRB count at a higher dosage rate by 2 – 3 log.*

- Transport of the hydrogen sulfide from the 'downhole bioreactor' created to the production well(s).
- The partitioning of the sulfide species at specified pressure and temperature conditions at the production facilities.

Souring modelling is also vastly improved through the ease at which history matching of field $H_2S$ data can be conducted, as well as sensitivity analysis and processing under short computational turnaround times. Over the past 30+ years, numerous mathematical souring models of varying dimensions have been created to aid in forecasting the potential for microbial oilfield reservoir souring (Figure 1).

One of these models was the DynamicTVS© souring forecasting tool which is owned and operated by Rawwater. Initially developed in the late 1980s, the souring module, which was first published in 1993, interfaces with 4D simulators which can be operated by various industry disciplines without the need for a background in reservoir engineering. As part of their continual development, tools such as the DynamicTVS model and the ESSS 'SourSimRL' simulator, use asset data and field observations, as well as kinetic data from laboratory-based, high-pressure bioreactor studies like those conducted at Rawwater, to further improve and advance their souring forecasting capabilities. In summary, oilfield reservoir souring forecasting and modelling contribute to improved operational efficiency, reduced costs, enhanced safety, environmental compliance, and optimised reservoir management throughout the lifecycles of oilfields.

## Souring mitigation techniques

As mentioned previously, an exclusive topside $H_2S$ treatment is not always the most economical solution. A successful treatment lies in additionally addressing the root cause, microbiologically-formed $H_2S$. Controlling reservoir souring requires the use of an effective biocide that can reduce contamination and prevent significant bacteria growth. Traditional biocides for microbial mitigation are typically implemented under short-lived, high-dose applications. Long term protection biocides for microbial control aim to achieve long-term preservation and are key to more successful production operation and extended asset life. Vink Chemicals' biocide grotan® OX is suitable for both short-term and longer-term strategies so operators can plan and be assured of smooth well operation. Such biocides can:

- Control CAPEX, reduce operating/high maintenance costs, and ultimately avoid well shutdown.
- Improve efficiency in reducing SRB – the main source of $H_2S$ souring.
- Ensure fast acting and long-lasting biocidal activity for short-term disinfections and long-term preservation.
- Offer water and oil soluble properties to multiphase environments.
- Offer a wide pH tolerance for variety of oil and gas environments.

## Laboratory souring simulation: bioreactor test

### Summary

In this experimental setup, the biocide grotan OX (MBO, 3,3′-methylenebis (5-methyl-oxazolidine), CAS: 66204-44-2) showed significant biocidal efficacy. The performance was demonstrated by the reduction of SRB, GHB and APB bacterial counts and the reduction of sulfide levels. This test demonstrated that MBO is a suitable candidate for a cost-effective reservoir souring treatment programme. The testing was performed by the third-party lab, Intertek UK laboratories.

### Test set-up

One biocidal product was assayed against general heterotrophic bacteria (GHB), acid-producing general heterotrophic bacteria (APB) and sulfate reducing bacteria (SRB) to compare the efficiency of its biocidal action. For this testing, fixed film up flow bioreactors (FFUBRs) were utilised (Figure 2). The packing matrix used was sand, saturated with seawater (35 000 TDS – already set-up), and then eluted with the same water containing SRB and GHB (in-house cultures). Set-up consisted of three FFUBRs at 50°C. After a period of microbial community establishment, treatment commenced with the lowest test concentration under pulse treatment, once a week for two weeks before increasing the concentration in increments. The efficacy of the chemicals was tested by measuring various parameters throughout the course of testing such as pH and sulfide at the inlet and outlet. At the end of each phase (pulse treatment), bacterial enumerations were performed on the outlet fluids by MPN culture methods, as well as residual formaldehyde measurements. The NACE International Standard TMO 194-2014 was used as a guideline in the design of these tests.

### Methodology

Samples were collected on a regular basis on the outlet of the FFUBR, with periodical sampling on the inlet to determine various parameters:

- Sulfide assay by XION 500 and pH at the outlet.
- Bacterial enumerations on the outlet fluids by MPN culture methods.
- Residual biocide at the outlet – using the semi quantitative formaldehyde test kit from Quantofix™.

### Results

A significant decrease in sulfide concentration was achieved by the biocide MBO (Figure 3). There are two effects behind the drop in sulfide concentration: the scavenging of sulfide and the reduction of active SRB, which significantly reduced sulfide production. The successful decrease in sulfide concentration indicates good efficacy of MBO.

Residual ppm(w) formaldehyde was detected during treatment with MBO (Figure 4). This observation indicated that there was an excess of MBO available after scavenging the $H_2S$ present, providing sufficient free formaldehyde for biocidal control.

The pH values of the test media did not change significantly during the test period (Figure 5). This indicated a strongly buffered system that is not significantly affected by the addition of alkaline chemicals.

## Conclusion

The biocidal active ingredient MBO, 3,3′-methylenebis(5-methyloxazolidine), showed good performance against high levels of contamination with SRB, GHB, and APB (Figures 6 – 8). In addition, the amount of sulfide was significantly reduced. Unreacted, unconsumed formaldehyde residues were detected, indicating excess dosing, meaning dose rates can be optimised and reduced. This test setup simulated a worst-case sour reservoir scenario, with a strongly

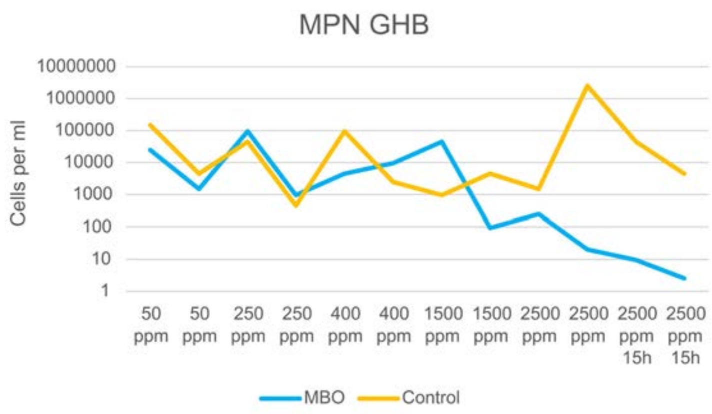


**Figure 7.** *Most probable number of GHB. As can be seen, MBO was able to significantly reduce the GHB count at higher doses.*

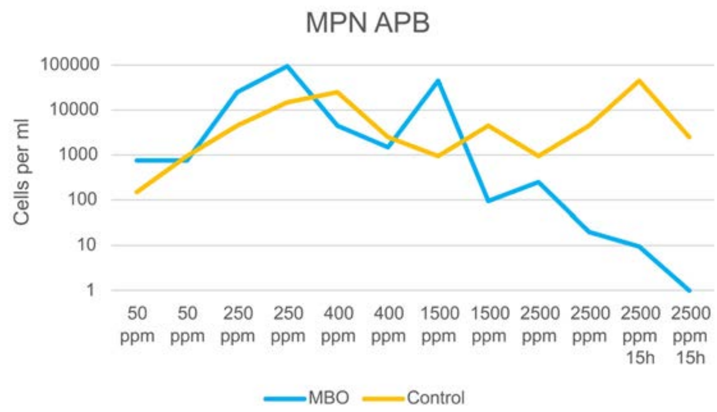


**Figure 8.** *Most probable number of APB. The biocide MBO was able to reduce the APB count to an acceptable level.*

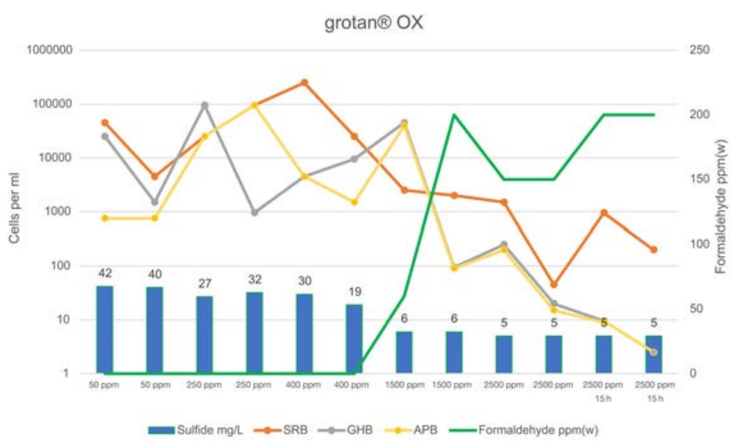


**Figure 9.** *Overview of collected lab data (sulfide/residual formaldehyde/MPN SRB, GHB, APB).*

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