INTERCORR2016_162

THIRD GENERATION THPS TO CONTROL SOURING AND MIC IN SIMULATED RESERVOIR CONDITIONS

Stephanie Edmunds[a], Chris Jones[b], Eder Torres[c],

Abstract

Previously published studies have investigated the use of 'water wet' pressurised sand packed bioreactors, in conditions that replicate both water injection and production well bores, to evaluate the efficacy of third generation tetrakis hydroxymethyl phosphonium sulfate (THPS) formulations for controlling souring and microbially influenced corrosion (MIC). Further studies have now been completed assessing the ability to create an oil saturated environment and the impact upon organisms such as sulfate-reducing bacteria (SRB) and sulfate-reducing archaea (SRA). This paper will review the findings from the original study and in addition present new data demonstrating the challenges that this alternative environment presents in terms of experimental design and biocide performance.

Key words: Souring, microbially influenced corrosion, MIC, Pressurised bioreactors, SRB, SRA, Third Generation THPS, tetrakis hydroxymethyl phosphonium sulfate.

Introduction

Previously a long term experimental program was initiated to explore the performance of two biocide dosing strategies for tetrakis hydroxymethyl phosphonium sulfate and to evaluate their impact on the near well bore and reservoir environments. In this innovative study conditions were created that replicated as closely as possible typical oilfield conditions and built upon previously published work to provide data demonstrating the control of mesophilic and thermophilic sulfate-reducing prokaryotes including sulfate-reducing bacteria (SRB) and sulfate-reducing archaea (SRA) (1). The study measured the impact of reservoir souring upon microbially influenced corrosion (MIC) and ascertained the influence of a chemical treatment program and its ability to limit corrosion rates, demonstrated in ''water wet'' sand packed bioreactors (2). Supplementary work has now been completed in an ''oil wetted'' bioreactors, addressing the souring remediation capability of THPS biocide formulations against either thermophilic (Phase 1) or mesophilic (Phase 2) sulfate reducing consortia, when dosed in a batch dose regime.

The generation of hydrogen sulfide (H_2S) within the reservoir matrix leading to the production of H_2S in the produced fluids is usually referred to as reservoir souring. Reservoir souring is the result of sulfate-reducing bacteria (SRB) and their metabolic activity (3).
Microbial activity on metallic surfaces resulting in severe, localized (pitting) corrosion is referred to as MIC. The problem is mainly associated with sessile bacteria creating a heterogeneous biofilm structure forcing intimate contact of the metal surface with the bacterial metabolic by-products such as H_2S, CO_2 and organic acids.

The biocide evaluated in this work was a third generation Tetrakis Hydroxymethyl Phosphonium Sulfate (THPS) based product. THPS has been successfully deployed in oilfield water injection systems for more than 20 years, and with reference to the 'water wet' study described herewith has shown that there is the potential to deploy THPS, not only as a conventional batch (shot) treatment chemical, used for highly fractured and permeable reservoirs, but also as a continuous treatment for lower permeability, mature systems where a slower matrix flow pattern is typical (4).

Methodology

Basic Methodology

Previous Study, Water Wet Bioreactors

For details of the 'water wet' bioreactor study reference should be made to the technical paper; C Jones et al., 'The Use of Realistic Physiochemical conditions to demonstrate the ability of Third Generation THPS to Control Reservoir Souring and MIC, Corrosion/2014, Paper 4042, (San Antonio, USA: NACE, 2014).

Phase 1, Oil Wet Bioreactors, Thermophilic

Overview

The Phase 1 study was carried out using two oil saturated bioreactors held at thermophilic temperatures (80˚C) to promote the establishment of a thermophilic sulfate reducing consortia. The bioreactors used, R3 and R4, were archived water saturated bioreactors which were oil saturated prior to the start of the project. The bioreactors were previously inoculated with a pure culture of *Archaeoglobus fulgidus* and effluent from another established oil saturated bioreactor. This ensured that both bioreactors were inoculated with a wide range of oil-field microorganisms prior to remediation testing.

Experimental Conditions

- Bioreactor Type: 2x 316L SS, 75 cm 1"OD
- Injection cycle: Continuous injection, 140 mL/day
- Temperature: 80˚C
- Pressure: 1000 psig
- Injection chemistry: Deaerated 100% synthetic seawater + 40 mg/L mixed volatile fatty acids (VFAs).
- Sampling: Daily bioreactor [sulfide], monthly effluent [VFA]

Phase 2, Oil Wet Bioreactors, Mesophilic

Overview

The objective of this phase of the study was to investigate and compare the efficacy of a high dose (250 ppmv) and a low dose (62.5 ppmv) of third generation under a batch dosing procedure. Two sets of corrosion monitors were fitted prior to and during biocide dosing so that differences in observed corrosion could be documented. It was considered important to allow the sulfate reducing bacteria within the bioreactors to establish a biofilm that was producing high concentrations of total sulfide as this would allow any discernible changes to be seen after biocide dosing.

Experimental Conditions

- Bioreactor Type: 2x 316L SS, 75 cm 1"OD
- Corrosion Monitor Type: 4x E235 S, 25 cm 1"OD
- Injection cycle: Continuous injection, 70 mL/day
- Bioreactor Temperature: 30˚C
- Corrosion Monitor Temperature: Ambient
- Pressure: 1000 psig
- Injection chemistry:
    - Establishment (days 6-91) – Deaerated 100% synthetic seawater + 40mg/L mixed VFAs
    - 1st Dose Period (days 91, 93, 96) – Deaerated 100% synthetic seawater + 40mg/L mixed VFAs + **250 ppmv Third Generation THPS**
    - 2nd Dose Period (days 205, 208, 210) – Deaerated 100% synthetic seawater + 40 mg/L mixed VFAs + **62.5 ppmv Third Generation THPS**
    - Recovery (days 96-205, 210-244) – Deaerated 100% synthetic seawater + 40 mg/L mixed VFAs
    - Enhanced recovery (days 244-253) – Deaerated 100% natural Irish seawater + 40 mg/L mixed VFAs

Where anaerobic injection was required (<0.1 mg/L oxygen), the injection water was sparged with oxygen-free nitrogen gas to achieve anaerobiosis. The concentration of dissolved oxygen in the injection water was analysed immediately before injection, if required after N_2 sparging, potassium metabisulphite was added to the injection water (only used at oxygen concentrations < 1mg/L). Potassium metabisulphite was not added to any water to be used for biocide injection as the reaction of this scavenger with the active biocide reduces treatment efficacy.

A metabolisable carbon source was added to the influent water in the form of mixed VFAs, which contained acetate, formate, propionate and butyrate in the ratio 100:10:5:5, respectively. 1000 mg/L stocks of each of the VFAs were made using their sodium salts (ACS

grade reagents, ≥ 99% - Sigma Aldrich UK). These stocks were QC tested via in-house ion chromatography and were diluted into the influent water to reach the desired injection concentration (40 mg/L mixed VFA).

Analysis

Water samples (10 mL) for sulfide analysis were taken daily from the sample port of each bioreactor and weekly from the corrosion monitors. Samples were collected directly onto zinc acetate which reacted with the sulfide in solution to form a zinc sulfide precipitate, preserving the total sulfide concentration of the effluent. The sulfide was then regenerated in acid for a methylene blue colourimetric test (5). This test was calibrated using the standard iodiometric sulfide titration method.

A 6ml flush of the sample line (2x sample line volume) was conducted before a sulfide sample was taken from the bioreactor. This was to ensure that no sample line contamination was affecting the bioreactor sulfide reading. After any bioreactor samples were taken, the sample port was closed and normal flow through the bioreactor and corrosion monitor was resumed.

Monthly samples for VFA analysis were taken from each bioreactor sample port to be analysed by ion chromatography. Monthly water samples were also taken and stored frozen for any future genomic analysis.

Corrosion deposit samples were taken from the corrosion monitors after their exposure period. The ‘sour’ corrosion monitors were attached for 77 days, the ‘sweet’ monitors were attached for 162 days.

Bioreactor Design

Figure 1, shows the oil wet sand packed bioreactor as used for the Phase 2 mesophillic study.

Figure 1 – Image of Oil Wet Bioreactor

Inoculation

Phase 1 Pack Matrix and Inoculum

The bioreactors used for phase 1 of this study were archived water saturated, thermophilic reactors. They were packed with low-iron sand and inoculated with a pure culture of *Archaeoglobus fulgidus* (DSMZ, Germany), a known thermophilic sulfate-reducing archaeal species.

Phase 2 Pack Matrix and Inoculum

The bioreactors were packed with an in-house sand mixture which had previously been inoculated with sulfate-reducing bacteria and had previously been in contact with biogenic sulfide. To further supplement the bioreactors with a sulfate reducing consortia, a 45 mL 'slug' of effluent from an inoculation bioreactor was injected prior to a 1 week shut-in period.

Biocide Dosing Procedure

A dosing period consisted of a 3x weekly batch injection cycle for a 4 hour contact time under continuous seawater injection. The biocide dosing procedure was as follows:

- A 5000 ppmv stock solution of third generation THPS was made in 100% synthetic seawater.
- 100 mL of influent was made with 100% synthetic seawater, added VFAs and the required volume of biocide stock to make the final concentration.
- The biocide influent was connected to the pneumatic pump, which was bled to remove any remaining regular influent.
- Injection of biocide influent was commenced and timed.
- After the contact time had expired, regular influent was connected to the pump which, again, was thoroughly bled to remove any biocide containing influent.
- Injection of regular influent commenced.
- A fresh stock solution of the biocide was made for each 4 hour injection cycle.

Result and Discussion

Water Wet Bioreactor Study

Batch (Shot) THPS dosing

The results obtained from the bioreactor train which was treated with batch injection of THPS are shown below in Figure 2.

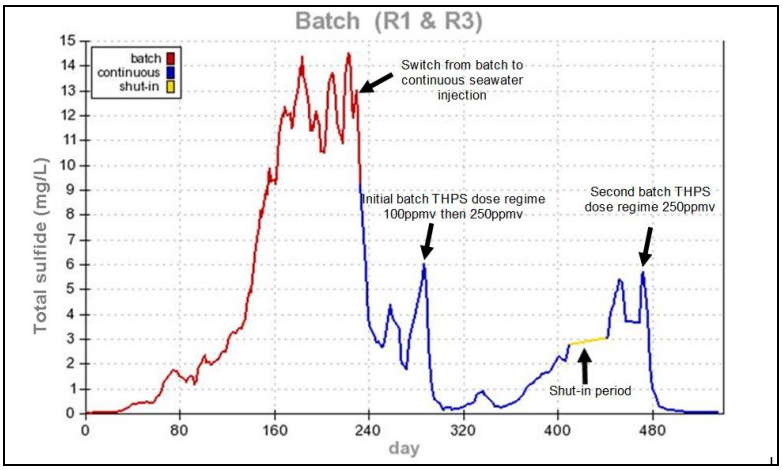

Figure 2 – Dosing of third generation THPS showing influence of batch THPS upon sulfide production (mg/L) against time (days).

Continuous THPS dosing

The results obtained from the bioreactor train which was treated with continuous injection of THPS are shown below in Figure 3.

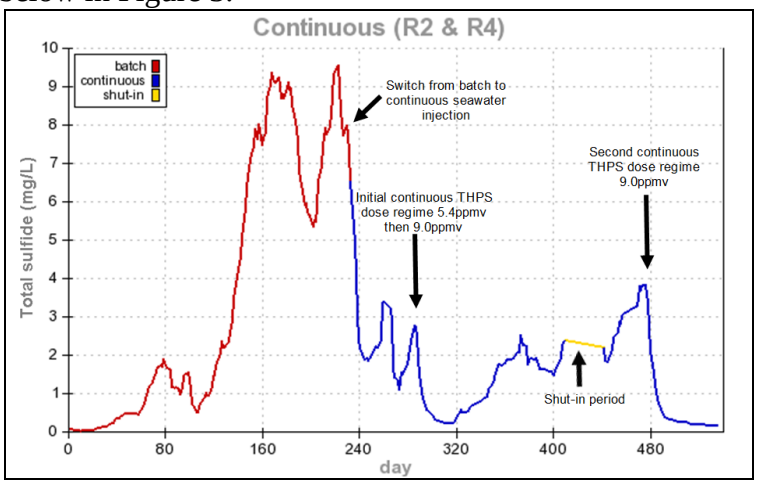

Figure 3 – Dosing of third generation THPS showing influence of continuous THPS upon sulfide production (mg/L) x time (days).

Note: Initial seawater injection was via batch injection and at day 235 seawater injection into the train changed to continuous seawater injection, resulting in a rapid decrease in sulfide concentration due to a dilution effect. At day 256 the mixed VFA concentration was doubled causing an increase in sulfide concentration. At day 289 the train was batch dosed with THPS at 100 ppmv resulting in a collapse in sulfide concentration. At day 291 the concentration of the batch dose was increased to 250 ppmv active THPS. Dosing into the train stopped ay day 301. At day 441 the mixed VFA concentration of the influent was increased to 111mg/L. At day 476 the train was dosed with influent containing 250 ppmv active THPS resulting in a reduction in sulfide concentration.

In summary the results of the water wet sand packed bioreactor study indicated that it had been possible to simulate realistic physiochemical conditions to replicate near well bore and reservoir environments. Sulfate-reducing prokaryotes had successfully been introduced into the mesophilic and thermophilic bioreactors and quantified using molecular microbiological methods such as qPCR to confirm the relative abundance of SRB and SRA populations. Biological sulfide production in the bioreactors had been shown to be dominated by the mesophilic column, with the thermophilic column appearing to be far less active. Batch and

continuous treatment programs utilising a third generation THPS product, had indicated an immediate effect on the bacterial populations with a significant reduction in H_2S production observed. Batch and continuous dosed third generation THPS had demonstrated the ability to control sessile mesophilic bacterial and thermophilic archaeal populations within water saturated bioreactor columns. Both prolonged batch (250 ppmv) and continuous (9.0 ppmv) THPS dosing reduced the corrosion rate of carbon steel as measured by low pressure MIC monitors. Prolonged (> 60 days) continuous dosing of third generation THPS was successful in reducing general corrosion as measured on a fouled LPRM probe and corrosion potential of carbon steel tubes of an in-line MIC monitor.

Oil Wet Bioreactor Studies

Phase 1 – Thermophilic Bioreactors

Figure 4 illustrates that after 54 days of continuous running, two bioreactors that had been prepared to provide a thermophilic environment were still only producing low total sulfide concentrations (< 1mg/L). A very slow increase in total sulfide production took place throughout the preparation of Phase 1 bioreactors and significant sulfide concentrations were not observed until after day 40. At their peak, the bioreactors referred to as R3 and R4 were producing 0.7 mg/L and 0.8 mg/L of total sulfide, respectively. Effluent VFA data collected during this first phase of the project indicated slow consumption within the bioreactors over the 3 month period. Maximum consumption of VFA was observed at day 50 with effluent [VFA] totalling 10 mg/L for R3 and 22.4 mg/L for R4.

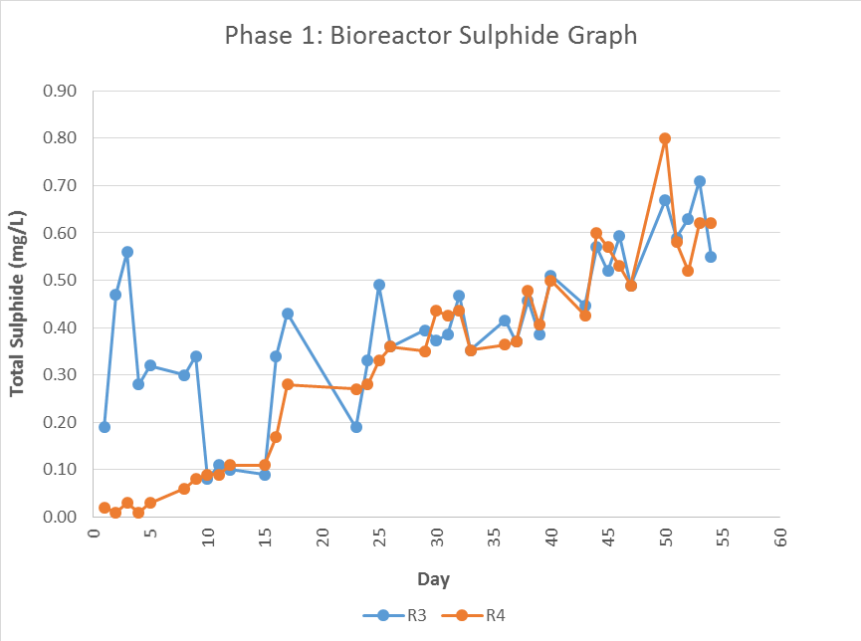

Figure 4 – Total sulfide profile of Phase 1 thermophilic bioreactors

Table 1 – Bioreactor R3 effluent VFA data

Phase 1 Day	Acetate (mg/L)	Butyrate (mg/L)	Formate (mg/L)	Propionate (mg/L)
10	30.1	1.15	0.34	1.18
26	26.5	0.59	0.10	0.75
50	9.94	0.10	0.10	0.10

Table 2 – Bioreactor R4 effluent VFA data

Phase 1 Day	Acetate (mg/L)	Butyrate (mg/L)	Formate (mg/L)	Propionate (mg/L)
10	37.4	1.60	1.50	1.45
26	25.5	0.66	1.55	0.72
50	19.7	0.10	2.46	0.10

N.B. 0.1 mg/L is the limit of detection for Acetate, Butyrate, Formate and Propionate.

The hydrogen sulfide data illustrated in Figure 4 and supported with the VFA measurements in Table 1 and 2 would appear to indicate that even after this extended establishment period a competent thermophilic sulfate- reducing microbial consortium was not established within the bioreactors.

In order to test the efficiency of third generation THPS, a minimum concentration of 5 mg/L of biogenic sulfide production from the bioreactors, plus complete consumption of VFA was required. The Phase 1 project appeared to have been unsuccessful at delivering the necessary operating conditions and it was clear that further method development would be required before a thermophilic bioreactor could be ready for use in an acceptable experimental time period.

Phase 2 – Mesophilic Bioreactors

Figure 5 illustrates that significant sulfide was detected from two bioreactors, R3 and R4, after day 6 of continuous running. Days 6 to 40 show a phase of increasing total sulfide production from both bioreactors. A total sulfide concentration plateau is reached after day 50 with a range of between 17 mg/L – 26 mg/L total sulfide. At plateau; an average sulfide concentration of 21.7mg/L was seen in bioreactor R3, whereas, a slightly lower concentration of 18.9 mg/L was seen in R4. Biocide dosing could begin once a total sulfide concentration plateau was observed.

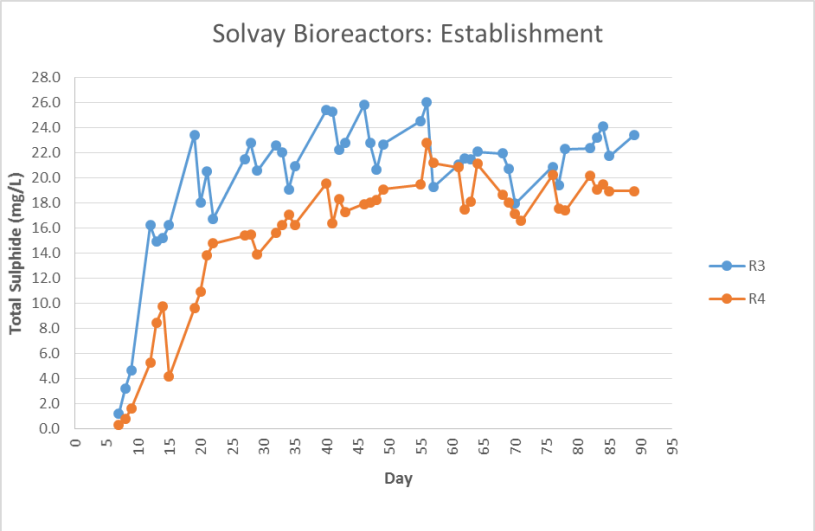

Figure 5 – Total [sulfide] production profile of bioreactors R3 and R4 prior to any biocide dosing (Days 6 – 91)

In order to determine relative SRB numbers within the bioreactors; SRB media vials (API S/W media) were inoculated from pooled bioreactor effluent. 1 mL of effluent was used to inoculate the first vial, and subsequent serial dilutions were carried out in 10-fold increments so that an approximate number of bacteria could be determined in colony-forming units per millilitre (CFU/mL). The vials were then incubated at 30˚C for 28 days. The vials were inoculated prior to biocide dosing. A positive result is indicated by the presence of a black flocculent which is formed of iron sulfide. The results of this test show that bioreactor R3 contained more SRB's prior to biocide dosing. SRB vials inoculated from R3 show positive results up to 10^6 CFU/mL, whereas vials inoculated from R4 show positive results up to 10^5 CFU/mL.

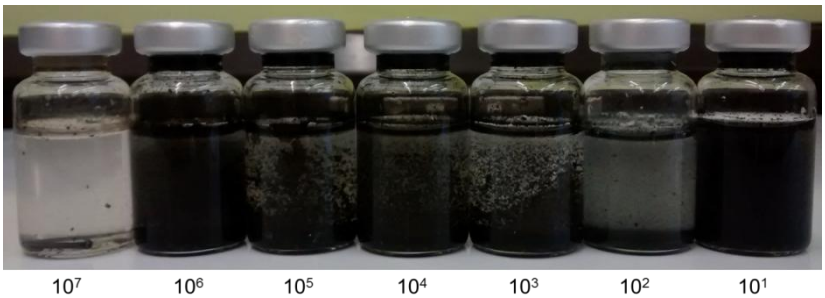

Figure 6: SRB vials inoculated from bioreactor R3 (Day 47)

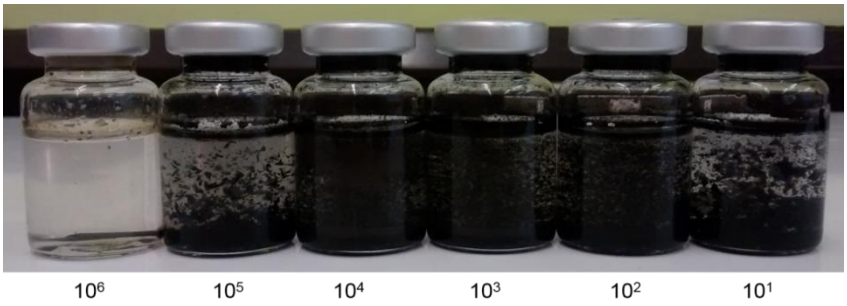

Figure 7 – SRB vials inoculated from bioreactor (Day 47)

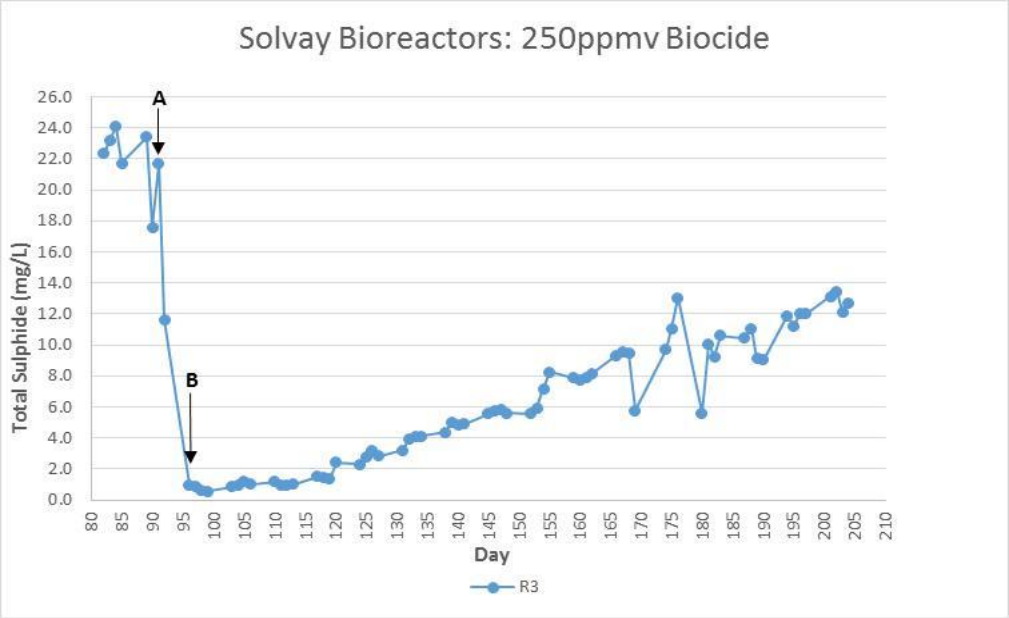

Figure 8: Total [sulfide] profile of bioreactor R3 after receiving 250ppmv biocide

N.B. Point 'A' refers to the commencement of biocide dosing. Point 'B' refers to the end of biocide dosing.

The first 4 hour biocide injection started on day 91, followed by days 93 and 96. The total sulfide produced from bioreactor R3 fell sharply after day 93. At day 99 the lowest recorded total sulfide concentration from the bioreactor was 0.6 mg/L. A gradual recovery took place between days 99 and 203 with sulfide concentrations reaching a plateau of ~12 mg/L.

Table 3 – Total sulfide produced in bioreactor R3 prior to and after third generation THPS (250 ppmv)

Bioreactor	Total sulfide before dosing (mg/L)	Total sulfide After dosing (mg/L)	% Decrease
R3	24.1	0.6	97.5

The second dose period using 62.5 ppmv of third generation THPS, started on day 205, followed by days 208 and 210. These lower concentration batch doses were applied to a

separate bioreactor, R4, that we essentially operating in a similar manner to R3. The sulfide concentration in this bioreactor when dosing at 62.5 ppmv commenced was approximately 8mg/L. At day 216 the lowest recorded H_2S concentration from bioreactors R4 was 2.0 mg/L. A very slow recovery took place between days 216 and the end of the project (day 253). The final sulfide concentrations from the bioreactor R4 was 6.0 mg/L.

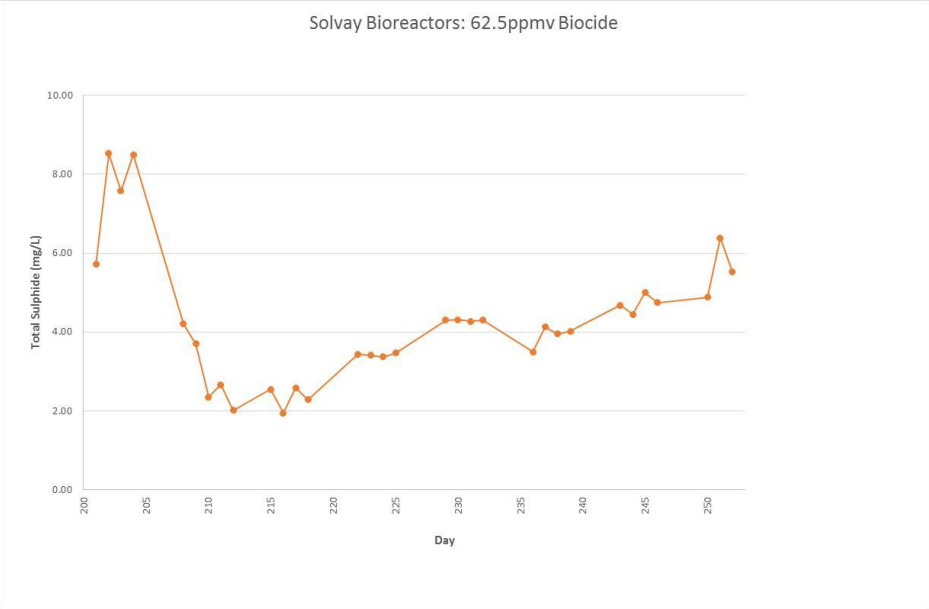

Figure 9 – Total sulfide profile of bioreactors R4 after receiving 62.5ppmv of Third Generation THPS biocide

N.B. Point 'A' refers to the commencement of biocide dosing. Point 'B' refers to the end of biocide dosing.

Figure 10 shows the individual VFA concentrations that were analysed in the effluent of the bioreactors. During establishment; effluent [VFA] was very low which coincides with the high total sulfide concentrations produced during this time, the VFA is being utilized by the bacteria.

After the first biocide dosing period, effluent [VFA] sharply increased (day 103). VFA consumption gradually increased during a 116 day recovery phase. A slight increase in effluent [VFA] was also observed after the second biocide dosing period which decreased after a 27 day recovery.

After the second biocide dose period, in order to encourage recovery, the influent chemistry was changed from fully synthetic seawater with added VFAs to fully natural Irish seawater with added VFAs. Natural seawater contains more CFU/mL of seawater microorganisms than synthetic seawater which would result in an increased rate of recovery and bacterial re-establishment within the bioreactors. No evidence of increased sulfide production took place during natural seawater injection; however, there was a slight increase in VFA consumption observed. The use of this revised influent chemistry was only possible for a very short period due to time the constraints of the project (9 days) and so would not have allowed a new biofilm to establish. It was however is interesting to note that after each biocide dosing period a lower sulfide plateau was established in the bioreactor.

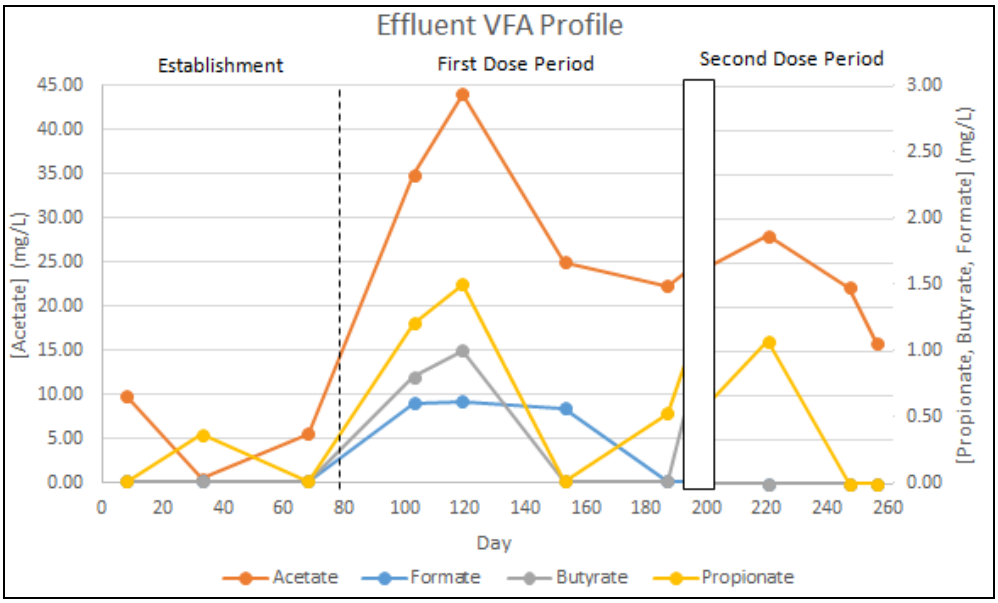

Figure 10 - Effluent VFA profile throughout the project (Establishment and First Dose; R3 and Second Dose; R4)

Corrosion Monitors

The corrosion monitors have been labelled 'sweet' and 'sour' based upon the time when installed. The 'sour' monitor was attached to the effluent stream of the bioreactor during the sour phase of the study, i.e. during establishment of the souring biomass. The 'sweet' monitor was attached during the sweet phase of the study, i.e. post biocide treatment.

The 'sour' set of corrosion monitors were attached from day 14 – 91. During this time the total sulfide measured in the corrosion monitor effluent gradually increased, in accordance with the increasing sulfide produced in the bioreactors. The sudden drop in observed sulfide at day 93 was due to the corrosion monitor being swapped out for the 'sweet' set.
The 'sweet' corrosion monitor was attached to the bioreactors from day 91 – 253. A lower total sulfide concentration was observed in the effluent of these 'sweet' monitors as less sulfide was being produced in the bioreactors during this period.

Table 4 shows the cumulative sulfide data which was injected into and sampled from the sweet and sour corrosion monitors. Both corrosion monitors scavenged a very similar percentage of sulfide; 84.6% on average. There is no significant difference in scavenged sulfide between the 'sweet' corrosion monitors that were attached during biocide dosing. Prior to biocide dosing, the 'sour' corrosion monitor was exposed to a much larger mass of sulfide.

Table 4 – Sulfide comparison data of corrosion monitors

Bioreactor	Total sulfide mass IN (mg)	Total sulfide mass OUT (mg)	Total sulfide scavenged (mg)	% Sulfide scavenged
Sour CM	65.6	11.3	54.3	82.8
Sweet CM	30.8	4.2	26.6	86.4

N.B. 'CM' – Corrosion monitor, 'Sour' – Prior to biocide dosing, 'Sweet' – After/during biocide dosing.

The Figure 11 illustrates the sulfide exposure of the corrosion monitors over time. From this we can see there is a noticeable difference in the rate of increasing sulfide exposure between the ‘sour’ and ‘sweet’ corrosion monitors.

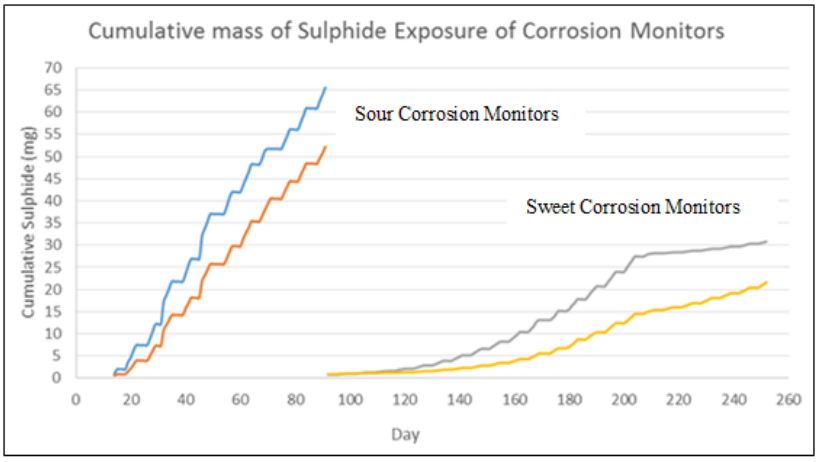

Figure 11 – Corrosion monitor sulfide exposure over time

Two sets of corrosion monitors were required so that any effects on corrosion related to Third Generation THPS could be compared. The general hypothesis was that the ‘sour’ corrosion monitors, which had been in contact with a larger total mass of sulfide at a faster rate, would show more severe signs of corrosion than the ‘sweet’ monitors. Although there were no signs of an active protective effect against corrosion, Third Generation THPS exerted a passive effect by reducing corrosion through suppressed biogenic sulfide production

Conclusions

Previously reported ‘water wet’, pressurised sand filled bioreactors had been shown to be a suitable means to simulate realistic physiochemical conditions to replicate near well bore and reservoir environments. In these studies sulfate-reducing prokaryotes had successfully been introduced into the mesophilic and thermophilic bioreactors and quantified using molecular microbiological methods such as qPCR to confirm the relative abundance of SRB and SRA populations. Biological sulfide production in the bioreactors had been shown to be dominated by the mesophilic column, with the thermophilic column appearing to be far less active. Batch and continuous treatment programs utilising a third generation THPS product, had indicated an immediate effect on the bacterial populations with a significant reduction in H_2S production observed. Both prolonged batch (250 ppmv) and continuous (9.0 ppmv) THPS dosing reduced the corrosion rate of carbon steel as measured by low pressure MIC monitors. Prolonged (> 60 days) continuous dosing of third generation THPS was successful in reducing general corrosion as measured on a fouled LPRM probe and corrosion potential of carbon steel tubes of an in-line MIC monitor.

Supplementary work has now been completed in an ‘’oil wetted’’ bioreactors, addressing the souring remediation capability of THPS Third Generation biocide formulations against either thermophilic (Phase 1) or mesophilic (Phase 2) sulfate reducing consortia, when dosed in a batch dose regime.

.

Results have indicated that establishment of a thermophilic bacterial community in a bioreactor is very difficult and time consuming to achieve and as such this approach (Phase 1) was suspended. However, it is of interest to note that a similar observation, concerning poor activity in the thermophilic column, had been made in the original 'water wet' bioreactor study and the implications for microbially influenced corrosion should be considered.

Results for the mesophilic 'oil wet' bioreactor (Phase 2) were much more informative and confirmed that a Third Generation THPS formulation can be used for souring remediation within an oil saturated, pressurised bioreactor. Furthermore it is clear from the data collected that the injection of Third Generation THPS into a biologically sour pressurised bioreactor can remediate and suppress the biogenic production of sulfide and hence reduce MIC.

There remains an interest to develop an experimental design where a pressuried thermophilic sand packed bioreactor could be shown to support a healthy population of thermophiles such as *Archaeoglobus fulgidus* (DSM 4304, DSMZ, Germany). Experiments would ideally need to monitor bacterial populations using a more sophisticated testing program, as based upon our current bioreactor studies, there is some doubt that the presence of SRP populations such as SRA can be quantified using an indirect total sulfide methodology. Experiments of this type would be extremely important if the connection between thermophilic SRP and MIC is to be made and would also assist in the selection of the most appropriate biocide mitigation program that would be effective in these challenging environments and elevated temperatures.

Acknowledgements

The Authors would like to thank Intercorr 2016 for the opportunity to present this technical paper at INTERCORR 2016, in Búzios/RJ in the month of May 2016. For permission to publish the authors thank Solvay Limited. For their valued work with pressurized sand packed bioreactors Rawwater Engineering Company Limited, UK, are recognized.

Bibliographic References

(1) C. Jones et al., "Extending Performance Boundaries with Third Generation THPS Formulations'', **Corrosion/2010**, Paper no. 10257 (San Antonio, USA: NACE, 2010).
(2) C Jones et al., ''The Use of Realistic Physiochemical conditions to demonstrate the ability of Third Generation THPS to Control Reservoir Souring and MIC'', **Corrosion/2014**, Paper 4042, (San Antonio, USA: NACE, 2014).
(3) Eden, R. D, P. J Laycock, and M. Fielder., ''**Oilfield Reservoir Souring**, Offshore Technology Report OTH 92 385,'' Health and Safety Executive, 1993.
(4) C Jones et al., "THPS: A Review of the First 25 Years, Lessons Learned, Value Created And Visions For The Future", **CORROSION/ 2012**, Paper 1505,(Salt Lake City, USA:NACE 2012).
(5) S.H. Fonselius, **"METHODS OF SEA-WATER ANALYSIS",** ed. K. Grasshof, Verlag Chemie, 1983, pp73-84.