

A Field Study into the Mitigation of Severe Downhole Microbiologically Influenced Corrosion of Oxygen Contaminated Hydro-Fracked Unconventional Oil Reservoirs

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ABSTRACT

The mitigation of downhole, dissolved oxygen (DO) accelerated, microbiologically influenced corrosion (MIC) in hydro-fracked, oxygen contaminated, relatively high temperature, unconventional reservoirs is challenging. Additionally, little research has been published in the area. The mitigation of downhole MIC in this type of well is complicated by the reality that mechanical cleaning is not yet possible; therefore, downhole MIC mitigation is solely dependent on chemical applications. DO-accelerated, downhole corrosion is also more difficult to control in high TDS (total dissolved solids) producing wells with complex water chemistries. Furthermore, the hydrofracking process typically introduces oxygen which accelerates corrosion. In this case-study, an oilfield in Alberta, which had been experiencing severe downhole corrosion, was the subject of a comprehensive corrosion investigation, which identified MIC as the most significant corrosion mechanism. Downhole water chemistry, oxygen contamination levels, ATP determination, and 16S DNA sequencing were used to identify those specific wells which had quantifiable, carbon steel, MIC degradation issues. Several wells had high concentrations of sulfate-reducing bacteria (SRB) and methanogenic microorganisms as well as elevated dissolved sulfide concentrations. Once the problematic wells were identified, biocide and corrosion inhibitor programs were optimized in cooperation with the client and their oilfield chemical provider to effectively mitigate downhole corrosion.

Key words: microbiologically influenced corrosion, sulfate-reducing bacteria, methanogen, dissolved oxygen, downhole tubing, DBNPA, cocodiamine

INTRODUCTION

MIC is a well known and firmly established threat to the integrity of oil and gas production and transmission infrastructure.¹ Numerous case studies and reports have been published outlining severe corrosion rates and failures due to MIC in oil and gas production lines, separators, storage tanks and pipelines.² Sulfate-reducing bacteria (SRB) and methanogens are typically the most prevalent microorganisms found in severely corrosive MIC scenarios in the oil and gas industry.^{3,4} Under mesophilic conditions, like those found in the oil and gas surface production infrastructure, mentioned above, SRB and methanogen mediated MIC is a common occurrence in conventional oil and gas production. However, many of the new wells being drilled in North America are relatively deep (1-2 km), horizontally fractured unconventional oil wells with downhole temperatures ranging from 50-80°C.

A Canadian oil and gas company produces light oil (API gravity = 36.5) and gas from the Montney and Charlie Lake formations in northwestern Alberta, Canada. The producer experienced a failure in the Mulligan field 12-19-081-08-W6M pipeline, which carries a high water cut emulsion to the 14-23 battery. A materials engineering and testing company determined that MIC was likely the predominant mechanism of corrosion in the pipeline based on the observation of tubercles, pit morphology and XRD analysis of the corrosion products. However, it must be noted here that pit morphology is no longer used to confirm the occurrence of MIC as other corrosion mechanisms can cause morphologies similar to those previously attributed to MIC. The XRD did reveal the presence of mackinawite, which can be caused by SRB mediated MIC, and also made up a significant percentage of the corrosion product sample from the pits. It should be noted that the 12-19-081-08 W6M pipeline sample was received in a dry state by the materials engineering and testing company; therefore, no reliable microbiological testing could be performed to determine whether a corrosive microbial community was present.

Two corrosion engineering service companies were retained to identify the corrosion mechanism(s) which led to the 12-19-081-08-W6M pipeline failure as well as the downhole corrosion issues that were beginning to occur, and likely contributed to the 12-19-081-08-W6M pipeline failure. This developed into a three field-wide assessment of the produced fluids in order to determine the mechanism(s) of downhole corrosion. Full water chemistry was employed along with ATP testing, and next generation sequencing (NGS) to determine if MIC was one of the major corrosion mechanisms causing downhole corrosion issues in the three fields (Spirit River, Mulligan, and Earring). Once MIC was identified as a leading or major integrity threat, collaborative work between the operator, the chemical vendor and the SMEs began to optimize the downhole chemical treatment program to mitigate corrosion.

EXPERIMENTAL PROCEDURE

Water Chemistry

Emulsion samples were collected from wellheads (for those wells identified in the scope of work) in 1 litre (L) polypropylene sample bottles. If any of the candidate wells were on test, a water sample was collected from the downstream test separator. Alkalinity, dissolved CO₂, dissolved H₂S, dissolved O₂, as well as ferrous and total iron concentrations were determined in the water of the emulsion samples with chemical test kits. These test kits employ several colorimetric methods to determine the concentrations of the analytes mentioned above.

- An acid titrant with a bromocresol green/methyl red indicator was used to determine **total alkalinity**.
- A caustic titrant with a phenolphthalein pH indicator was used to determine **dissolved CO₂** concentrations.
- The methylene blue method was used to determine the **dissolved sulfide** concentrations.

- **Dissolved Oxygen (DO)** concentrations in the 0-40 ppb range were determined with the Rhodazine D method. DO concentrations in the 1-12 ppm range were determined with the indigo carmine method.
- The Phenanthroline method was used to determine **ferrous and total iron** concentrations.
- The **pH** of produced water was determined with pH paper.

Several chemical parameters of the produced water samples including total dissolved solids (TDS), formic acid, acetic acid, propionic acid, manganese and sulfate concentrations were determined by an industrial analytical lab.

Microbiological Assessment

Microbial cell concentrations in produced water samples were determined with a commercially available ATP test kit.

Produced water samples were stored on ice and freight forwarded to a molecular biology lab for DNA extraction, qPCR amplification, and 16S rRNA gene sequencing on the Illumina platform. Microbial community profiles for selected water samples were generated from the sequencing results.

RESULTS AND DISCUSSION

Produced Water Chemistry Corrosivity Assessment

Produced water samples were collected from wells in the three fields under investigation. The wells of interest in the Spirit River, Mulligan and Earring fields are below in Table 1.

Table 1

Legal Sub-Division (LSD) Descriptions of the Wells in the Scope of Work in the Three Operating Fields

	Field		
	Spirit River	Mulligan	Earring
LSD (Legal Sub-Division)	4-15-078-07-W6M	12-07-081-07-W6M	12-03-083-08-W6M
	2-16-078-07-W6M	9-9-081-07-W6M	15-26-082-08-W6M
	102/16-09-078-07-W6M	8-19-081-07-W6M	
	13-36-078-07-W6M	102/5-36-081-08-W6M	
	14-36-078-07-W6M	12-20-081-07-W6M	
	15-36-078-07-W6M	100/5-36-081-08-W6M	

Several water chemistry parameters were determined and their contributions to corrosion were assessed. The water chemistry parameters assessed were iron to manganese ratios, dissolved CO₂, H₂S and O₂ concentrations, sulfate concentrations, organic acid concentrations, alkalinity, TDS and pH.

To determine whether corrosion was active in the wells under investigation, iron to manganese ratios were determined. In sweet systems an Fe:Mn ratio > 60:1 suggests active corrosion may be occurring downhole or at surface. In cases where H₂S is present, a ratio of > 40:1 suggests active corrosion may likely be occurring. Several wells in the three fields had iron to manganese ratios in excess of 40:1; however, elevated iron-to-manganese ratios did not necessarily correlate with severe downhole corrosion scenarios observed in the three fields (Table 2). For instance, Mulligan wells 102/5-36-081-08-W6M, 12-20-081-07-W6M and 100/5-36-081-08-W6M had severe downhole corrosion resulting in well workovers; however, the iron to manganese ratios for these wells were not elevated (Table 2). The fact that iron-to-manganese ratios were a poor metric for determining whether downhole corrosion was occurring was

attributed to the formation of adherent, insoluble corrosion products, which either remained as a corrosion scale or crust on the metal surface or broke off into pieces in the produced fluid.

Table 2
Iron-to-Manganese Ratios in Spirit River, Mulligan and Earring Wells in 2017 and 2018. Wells with Bolded Iron-to-Manganese Ratios Likely had Active Corrosion

Field	Well (W6M)	Pad	Fe ^{TOTAL} : Mn Ratio				
			Dec '17	Feb '18	April '18	June '18	Aug '18
Spirit River	4-15-078-07	08-21	-	-	-	-	66:1
	2-16-078-07	08-21	17:1	163:1	10:1	56:1	29:1
	102/16-09-078-07	08-21	-	-	22:1	26:1	-
	13-36-078-07	14-25	57:1	169:1	42:1	112:1	60:1
	14-36-078-07	14-25	-	-	-	-	-
	15-36-078-07	14-25	-	-	44:1	-	-
Mulligan	12-07-081-07	15-08	174:1	333:1	28:1	-	71:1
	9-9-081-07	15-08	45:1	42:1	-	99:1	37:1
	8-19-081-07	5-30	2:1	2:1	9:1	-	2:1
	102/05-36-081-08	5-30	-	21:1	4:1	7:1	13:1
	12-20-081-07	5-30	-	-	-	8:1	-
	100/05-36-081-08	5-30	-	87:1	37:1	-	21:1
Earring	12-03-083-08	11-34	59:1	69:1	47:1	97:1	49:1
	15-26-082-08	11-34	61:1	66:1	100:1	85:1	43:1

The average TDS concentration in the produced water from the wells under investigation in the three fields was 84,720 ppm (Table 3), and because the TDS was relatively high, the conductivity was also high, approximately 90,000 $\mu\text{S}/\text{cm}$ in most produced waters. The high conductivity contributed to the corrosivity of the produced water.

The average alkalinity (as CaCO_3) in the produced waters was 295 ppm with a maximum of 714 ppm (Table 3). Although the average alkalinities in the fields were relatively low, scaling was an issue in the three fields and scale inhibitors were used on several wells. For instance, XRD analysis of solids obtained from downhole equipment in the Mulligan field revealed that a significant percentage of the solids were made up of dolomite ($\text{CaMg}(\text{CO}_3)_2$). Therefore, the alkalinity was not contributing to the formation of protective scales. Dissolved CO_2 concentrations in the produced waters averaged 182 ppm (Table 3) and reached a maximum of 380 ppm in one well. Because dissolved CO_2 concentrations were relatively low, CO_2 or sweet corrosion was not considered to be a major driving corrosion mechanism downhole. The average pH of the produced waters in Spirit River, Mulligan and Earring was 7.

Sulfate concentrations in the produced waters averaged 5067 ppm (Table 3) and were more than sufficient for biogenic sulfide production. The average sulfide concentration in the produced waters was determined to be 3 ppm and the maximum value determined was 10 ppm (Table 3). However, it should be noted that these sulfide concentrations were determined from wellhead samples, at ambient pressure and temperature, with colorimetric test kits. Based on downhole data from the Charlie Lake formation, the dissolved sulfide concentration at the pump intake could have been as high as 1100 ppm at 115 bar and 50°C. The high downhole sulfide concentrations contributed to corrosion of the downhole equipment but also likely contributed to the corrosion failure of the 12-09-081-08-W6M pipeline. XRD analysis of corrosion product found in the through-wall pit revealed that 46% of the corrosion product was made up of the iron sulfide minerals greigite, mackinawite and pyrite. Although significant sulfide concentrations

were found in several wells, it was not clear at the outset of the corrosion investigation whether the sulfide was being biogenically produced or the sulfide had existed in the reservoir over geological time and that bacteria played no role in sulfide production.

As stated previously, the client produces a light crude oil emulsion from unconventional hydraulically fractured wells in the Charlie Lake geological formation of northwestern Alberta. The wells are drilled vertically to a depth of 1.3 km and then whipstocked horizontally for another approximately 1.9 km. The water used to hydraulically fracture the wells was fresh water typically obtained from ponds and low spots in the terrain surrounding the fracking operation. The oxygen content in the water being used to frac a well in the Spirit River area was greater than 12 ppm (as measured in December 2017), which exceeded the range of the test kit. The frack water is typically treated with chlorine dioxide (ClO₂) disinfectant and a biocide before the fracturing process to reduce the bacterial load in the frack water. Oxygen scavengers are not used to remove oxygen from the frack water because oxygen scavengers are typically incompatible with the biocides and disinfectants being used and the quantity of oxygen scavenger required to treat the large volume of water used would be cost prohibitive. Even though the wells were shut-in for several weeks before they were flowed back, trace levels of oxygen are routinely found in the produced waters for months after production begins. Oxygen was found in the produced waters of wells in all three operating areas. Dissolved oxygen concentrations for Spirit River wells 13-36-078-07-W6M and 15-36-078-07-W6M were 1 ppm and 25 ppb, respectively. The dissolved oxygen concentration for Earring well 15-26-082-08-W6M was 17.5 ppb. The dissolved oxygen concentrations for Mulligan wells 102/5-36-081-08-W6M, 12-20-081-07-W6M and 100/5-36-081-08-W6M were greater than 40 ppb and less than 1 ppm. Dissolved oxygen concentrations greater than 10 ppb can cause and accelerate internal corrosion; therefore, it is likely that oxygen was a contributing factor to the downhole corrosion observed in the wells under investigation. Furthermore, it is also likely that the oxygen in the produced water reacted with the sulfide to form elemental sulfur which is extremely corrosive and could have contributed to corrosion.⁵

Table 3
Water Chemistry Parameters for Spirit River, Mulligan and Earring Fields

Water Chemistry Parameter	Average (ppm)	Minimum (ppm)	Maximum (ppm)
TDS	84720	57000	114300
Alkalinity	295	93	714
CO ₂	182	57	380
SO ₄ ²⁻	5067	2929	7888
H ₂ S	3	0	10

Organic acid concentrations were determined for several wellhead samples in all three production fields. Formic, acetic, and propionic acid concentrations were determined in these samples. Significant concentrations of acetic acid were found in Spirit River wells 4-15-078-07-W6M (620 ppm), 13-36-078-07-W6M (1000 ppm) and 2-16-078-07-W6M (670 ppm), Mulligan wells 102/05-36-081-08-W6M (670 ppm), 100/05-36-081-08-W6M (750 ppm), 12-20-081-07-W6M (300 ppm) and 8-19-081-07-W6M (320 ppm), and Earring wells 12-03-083-08-W6M (340 ppm) and 15-26-082-08-W6M (640 ppm). Significant concentrations of formic acid were not detected in these samples. Propionic acid was detected in low concentrations (≤110 ppm) in Spirit River wells 13-36-078-07-W6M, 4-15-078-07-W6M, 2-16-078-07-W6M and Earring well 15-26-082-08-W6M. The presence of acetic and propionic acid in these produced waters suggested that hydrocarbon degradation was occurring. These organic acids may also have been metabolized by SRB to produce sulfide.

Microbial Cell Concentrations and Community Profiles in Produced Waters

Microbial cell concentrations in produced waters were quantified by ATP determination for the wells under investigation. Rather than reporting colony forming units per mL (CFU/mL) as is customary for serial dilutions, microbial equivalents (ME) per mL are reported for ATP determination of microbial cell concentrations. A threshold of 10^4 ME/mL was chosen for microbial cell concentrations and over this threshold, the microbial cell concentrations would be considered high and below this threshold, the cell concentrations would be considered moderate or low. Several wells in Spirit River, Mulligan and Earring had high microbial cell concentrations at some point during the corrosion investigation. Spirit River wells 4-15-078-07-W6M, 2-16-078-07-W6M, 13-36-078-07-W6M and 15-36-078-07-W6M had high microbial cell concentrations (Figure 1 below). All Mulligan wells had high microbial cell concentrations (Figure 2). In the Earring field, 15-26-082-08-W6M had high microbial cell concentrations (Figure 3). However, it is not only necessary to determine whether a produced water sample has high microbial cell concentrations, it is also necessary to determine the metabolic capabilities of the microorganisms and how they would contribute to corrosion to conclude that MIC is occurring downhole.

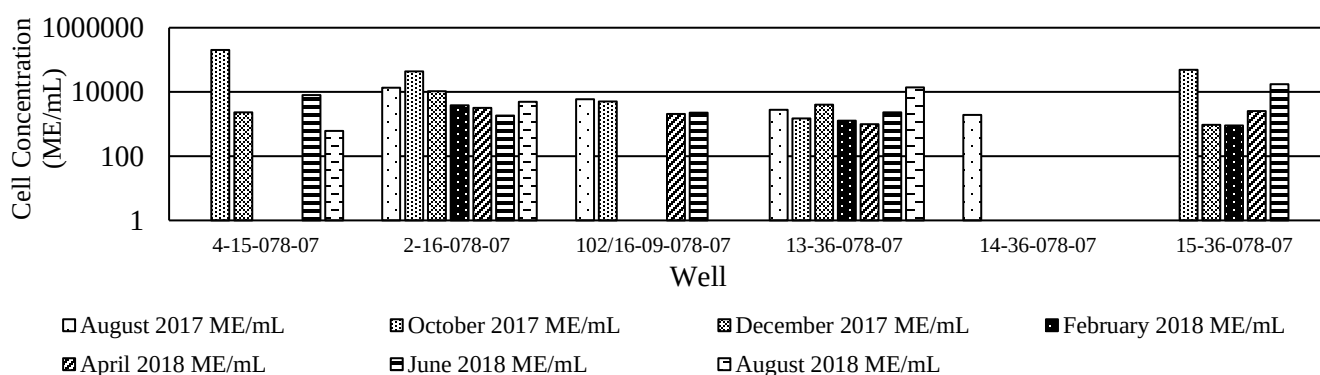


Figure 1: Cell concentrations in microbial equivalents (ME) per mL detected in wells sampled during 2017 and 2018 through ATP determination in the Spirit River field. Cell concentrations over 10^4 ME/mL are high, concentrations below this are moderate or low.

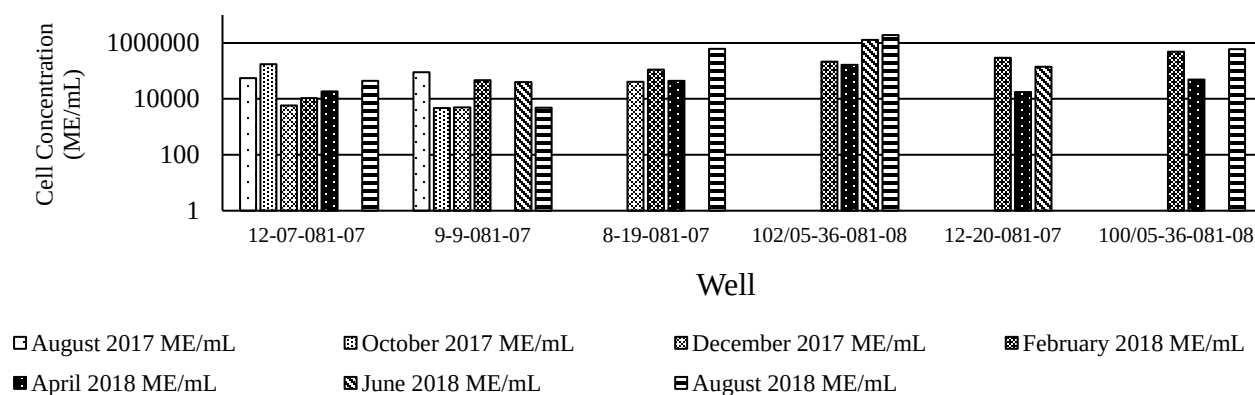


Figure 2: Cell concentrations in microbial equivalents (ME) per mL detected in wells sampled during 2017 and 2018 through ATP determination in the Mulligan field. Cell concentrations over 10^4 ME/mL are high, concentrations below this are moderate or low.