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Successful Treatment of a Corrosive Acetic Acid Producing Halophile that is Averse to Culture Media

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ABSTRACT

Here, we coupled successive rounds of molecular microbial methods (MMM) to calibrate adenosine triphosphate (ATP) readings to trend *Halanaerobium* fouling in unconventional wells. ATP was then used to drive a biocide efficacy study, which resulted in selecting a glutaraldehyde/quaternary amine (quat) blend. This selection was partly supported by literature searches, which showed that quats have been effective on *Halanaerobium*. ATP monitoring was then used to direct the success of a downhole biocide treatment program for horizontal wells. Since sessile samples were not routinely available, planktonic samples were used. Over two years of reviewing the treatment results of approximately 30 wells in a single lease, where multiple sample points were available, we found that most treatments were successful in returning/or maintaining wells within KPIs. The operator has experienced reduced failures and currently relies on MMM supported ATP to monitor multiple leases where *Halanaerobium* is present.

Key words: Adenosine Triphosphate (ATP), Molecular Microbial Methods (MMM), *Halanaerobium*, Biocide, Polymerase Chain Reaction (PCR), Microbially Influenced Corrosion (MIC)

INTRODUCTION

The development of shale plays has introduced large water quantities to diverse downhole environments.¹ The most recent reduction in oil price has put more focus on produced water reuse since “clean” frack water sources (e.g. potable, municipal) tend to be non-economical.² Compounding the problem, in some cases operators have used less effective, underdosed, or forgone a completion biocide treatment to save on cost. The downhole environment has been shown to act as a selection pressure on microbial diversity.³ Given time, this in turn leads to a higher biological load in unconventional wells. This reservoir entrenchment of microorganisms leads to souring, plugging by biomass or iron sulfide, and corrosion.⁴ These problems persist downhole, as well as in downstream production, creating a health and safety concern. The cost of poor biological treatment during the frack becomes poor return on investment during production in the form of workovers and producing well down time.

Sulfate reducing bacteria (SRB) and acid producing bacteria (APB) are usually the suspected culprits in the oil patch for souring and corrosion. This is, in large part, due to their presence being readily and routinely accessible through culturing. Culture media, known colloquially as bug bottles, are known to only allow for the growth of <1% of organisms present and require 14-28 days for detection.⁵ However, recent studies have shown that a guar-utilizing acetic acid producing bacteria can lead to corrosion and, under the right conditions, souring.⁶ It was previously reported that this organism (at least in part) is not compatible to conventional culture media.⁷ Therefore, it is difficult to unambiguously detect this microbe without the use of molecular microbial methods (MMM). Historically, MMM typically required a 4 week turnaround period, and a high per sample cost (approximately 100X the cost of using culture media) which has limited widespread application.⁸ In the past few years, MMM market maturity in the O & G industry has resulted in these costs being reduced ten-fold and data can be returned to the customer in as soon as 2 weeks’ time.

A field was identified in the Permian basin that showed well failure developing on the order of 1 month post tubing replacement. Given the field’s aggressive and frequent failure rate, a disconnect was identified between microbial risk assessments from serial dilution results and actual failure rates. In this field, modified Postgate B medium and phenol red dextrose medium were found to give microbial counts ranging from below detectable limits (BDL) to 10² APB and/or SRB cells per mL of sample. These levels are lower than typical industry limits used to indicate fouling.⁹ Using a form of MMM, next generation sequencing, a *Halanaerobium* organism was identified as prevalent (found in at least ~50% of sites) and abundant (up to 88.2%) in the operator’s field. For a field-wide biocide program, a microbial assay must be able to give results quickly so that operators can assess and react to the failure threat. Such a method should be able to act as a translation to MMM for strategic application of biocides. ATP testing measures microbe activity levels by processing energy molecules into a luminescence. ATP methods are low cost, fast (15 min for 1 sample) and robust “tail-gate technology.” However, results are non-specific for cell type making interpretation difficult.¹⁰

Given the dominance of *Halanaerobium* in this West Texas (WTX) field, it was understood that the bulk of microbial activity/population could be attributed to this genus. The use of culture media testing on site was abandoned, and a successful biocide program was created by ranking fouling through the use of 16S rRNA gene-based qPCR and ATP assays. By combining ATP with MMM, an ATP key performance indicator (KPI) was calibrated and was field specific. Wells that presented an ATP assay above the minimum threshold (100 pg/ml cATP) in wellhead produced fluids received workover biocide treatment. Those assets that showed a 10-fold increase in ATP over the established KPI (>1000 pg/ml cATP) were treated on a high priority schedule.

An ATP-based efficacy test was carried out and resulted in a glut/quat product blend being chosen for well workovers. A lease was monitored for approximately 2 years. The majority (~66%) of the well treatments were successful in achieving less than the established ATP KPI, and the operator recorded major reductions in failure frequencies. The operator has implemented this treatment program field-wide into multiple leases and this approach continues to adequately maintain asset integrity.

EXPERIMENTAL PROCEDURE

Field Sampling Procedure

Samples were taken from well head production via ½" valves. Pressure was determined before clearing debris by flowing into a discard vessel. Collection bottles were overflowed briefly (approx. 30 sec.) and capped with minimum head space. Sample processing and preservation were carried out at well.

Adenosine Triphosphate Analysis

Microbial activity in waters were recorded by measuring the adenosine tri-phosphate (ATP) present in well sample or aliquots (efficacy study). Water sample was filtered to capture microbes, washed, and then lysed into a stabilization buffer. The collected ATP was then used to power luciferase and light was detected via a luminometer. An ATP control was processed for calibration. The amount of light detected is directly proportional to microbial activity contained within the sample. The sample was processed at the well head up to the lysing step, placed on ice, and then processed at the regional lab.

Microbial Molecular Methods

The MMM sample was preserved by adding site water sample to a third-party proprietary preservative solution. The MMM samples were stored in the DNA preservative on location (2 parts sample: 3 parts preservative) at the time of sampling and shipped for third-party analysis within 48 hours. Nucleic acid was purified using a lysing modified standard method.¹¹ Third party lab performed amplification and next generation sequencing utilizing a proprietary next generation sequencing method.¹² The qPCR samples were probed for total bacteria. Next generation sequencing (NGS) was analyzed to the genus taxonomic rank.

Periodic Surveys

Field surveys were carried out over 2 years across multiple leases. Surveys I & II were carried out in the first quarter of year 1. Survey III was carried out in the first quarter of year 2, while Survey IV was completed in the fourth quarter of year 2. Surveys I & II contained 30 samples each. Survey III was made up of 36 samples and Survey IV sampled 10 sites.

The initial two surveys (I & II) were used to build the ATP KPI surveys. Surveys III and IV were collected after treatment was initiated for at least 6 months. Survey IV was targeted to Field A, a field that received the earliest biocide treatments. Genera that showed at least 10% abundance were included for analysis. This cut off was selected since multiple genera were found to be within this order of magnitude and so were given priority over genera with lower percent order magnitude (i.e. vs 1%; 0.1%). Other genera can be found upon request.

Biocide Efficacy Study

An efficacy study was performed using a representative well from Field A in order to test against naturally present flora. Water was separated into known aliquots and independently received low (200ppm active) or high dosages (500ppm active). Aliquot was given 4, 24, and 168 hours contact time while a no chemical control was retained. Results were tabulated at each contact time to provide percent reduction relative to no chemical control.

Well Treatment

Biocide applications were made on horizontal well assets based on ATP KPI, and reaction to initial biocide treatment. Historical well information was considered when available. Initial applications utilized a pill of treated fluid to be pumped down the annulus and allowed to produce back up the pumping system. Secondary applications had a larger pill size and subsequent larger biocide load that were allowed soak for 8-24 hours prior to returning the well to production. In persistent cases where lateral heel fouling was suspected, a chemical solids remediation pill plus a biocide was then applied

and spotted over the heel section for 8-12 hours before returning well to production. Biocide application rates were within label limits for application and were decided upon by higher activity (ATP level) receiving closer to the maximum allowed dosage.

RESULTS

The field was initially surveyed by taking 30 samples from wells, transfer pumps, vessels, and flowlines. qPCR and DNA sequencing analyses were carried out by a third-party laboratory which employed NGS techniques. Maximum abundance was reported from a single site across each individual survey. Average abundance was taken for specified taxa across all the samples in an individual survey. Taxa was reported at genus level. In several cases taxa was reported with similarity, if available. Unclassified genera were reported at the most specific taxonomic rank available, or “unclassified” was used if not available.

Survey I: Before Treatment

It was found that in the majority of samples, *Halanaerobium* was overrepresented when comparing percent abundance. This genera showed a 45.5% maximum abundance in a single sample with an 14.8% abundance average across all samples. The next five genera showed 43.8% *Thermotoga*, 37.7% *Petrotoga*, 36.8% *Halanaerobium*/unclassified, 36.5% *Archaeoglobi*/Thermococci, and 35.0% *Halomonas*, while the average percent lowered to 2.3%, 2.4%, 2.1%, 3.9% and 2.3%, respectively.

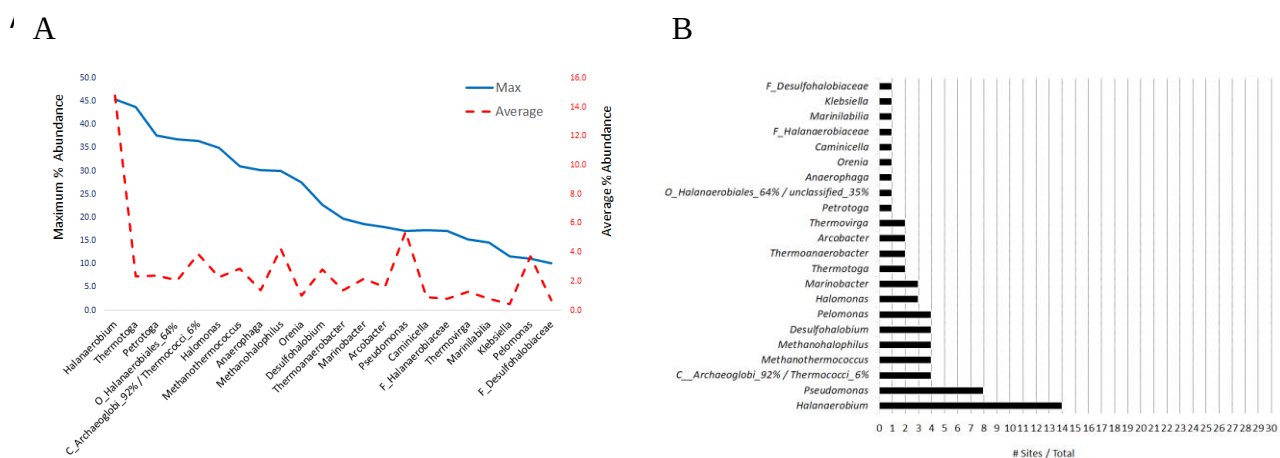


Figure 1: A: Maximum Abundance and Average Abundance. B: Genera prevalence based on abundance cutoff (10%).

The frequency of taxa in the sample locations showed *Halanaerobium* represented in 14/30 sites. At 8/30 sites, the genus *Pseudomonas* was present. Several taxa appeared within 4/30 sites; these were *C_Archaeoglobi_92%/Thermococci_6%*, or *Methanothermococcus*, *Methanohalophilus*, *Desulfotomobacter*, and *Pelomonas*.

Survey II: Before Treatment

Within the second survey of 30 samples, *Halanaerobium* genera showed a 88.2% maximum abundance in a single sample with a 32.8% average. The next five genera showed 66.7% *Petrotoga*, 49.1% *Desulfotomobacter*, 41.6% *Unclassified*, 40.6% *Clostridium*, and 37.5% *Methanohalophilus*, while the average percent lowered to 11.6%, 4.8%, 4.5%, 8.3% and 1.7%.