

Why are Glutaraldehyde/Quaternary Ammonium Biocides So Common in Hydraulic Fracturing and Are They Being Used Appropriately?

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ABSTRACT

Biocides are utilized in hydraulic fracturing operations to prevent or remediate biofouling, souring, and Microbially Influenced Corrosion (MIC). Biofouling occurs when microorganisms form biofilms on shale or proppant surfaces, thus impeding the flow of hydrocarbons. Biofilms on piping and other equipment can lead to MIC and is linked to corrosion failures estimated to cost the industry billions of dollars. Lastly, microorganisms present in fracturing fluids often produce hydrogen sulfide thereby threatening the health and safety of workers and reducing the value of hydrocarbons produced.

Glutaraldehyde (Glut) and quaternary ammonium compounds (QAC) are the two most common non-oxidative biocides used in hydraulic fracturing. In general, glut and QAC are added at the blender during completions to inactivate microorganisms present in water and other injected fluids. Glut and QAC are sometimes used by themselves but are most often added in combination due to the belief that a combination of the two works better than each active individually. This paper will address the strengths and limitations of both glut and QAC, their applications, and compatibility with other additives in hydraulic fracturing.

Key words: glutaraldehyde, quaternary ammonium, biocide, microbial contamination, biofilm, Microbially Influenced Corrosion (MIC)

INTRODUCTION

Oil and gas operations worldwide are impacted by the presence of microorganisms. A variety of microorganisms can be found in the oilfield, dependent on the type of operation, geology, location, water source and water treatment utilized. Biocides are used in all stages of oil and gas development to control microorganisms and their detrimental impacts on production such as corrosion, biofouling, and souring. A wide number of biocides are used to control microorganisms, ranging from oxidizing biocides that react quickly but leave no residual activity, to preservatives which act slowly, but provide antimicrobial activity for weeks or months at a time. The spectrum of biocides used in oil and gas are covered by several excellent reviews and will not be detailed in this paper.^{1, 2, 3}

The two most common biocides used in hydraulic fracturing operations are glutaraldehyde (glut) and quaternary ammonium compounds ("quats" or QAC). Glut and QAC are common due to their broad availability and effectiveness at low concentrations. Glutaraldehyde is applied at levels ranging from 50-150 ppm active ingredient (a.i.) as these concentrations provide sufficient activity to inactivate bacteria rapidly within a variety of matrices (waters and other fluids). QAC are applied at levels ranging from 15-50 ppm as these levels are inhibitory to bacteria and higher levels lead to foaming and pumping difficulties. Given these dose ranges, a wide number of combination products are available at ratios ranging from 1:2 to 6:1 glutaraldehyde to QAC.

Glutaraldehyde is widely used in both conventional and unconventional oil and gas operations either alone or in combination with quaternary ammonium compounds. Structurally, glutaraldehyde is a dialdehyde that exerts biocidal activity by reacting with primary or secondary amines present on the bacterial cell surface. Glutaraldehyde inactivates bacteria by impeding the activity of the cell wall, quickly (minutes to hours) leading to cell death. In general, glutaraldehyde is compatible with most other oilfield chemistries, but will react with bisulfite-based oxygen scavengers or primary/secondary amines.

Quaternary ammonium compounds (QACs) are a group of biocides in which four alkyl groups are attached to a central, positively charged, nitrogen. Several "generations" of QACs have been developed since their early use, each with slight benefit over previous chemistries.⁴ QACs are surface active and act by lysing the cell membrane allowing intracellular contents to leak out. QACs inactivate bacteria rapidly but are ineffective in high salinity waters or in the presence of fluid additives such as anionic friction reducers. Two different QAC are most common in the oil and gas industry: alkyl dimethyl benzyl ammonium chloride (ADBAC) and didecyl dimethyl ammonium chloride (DDAC).

The goal of this work was to investigate the performance of glutaraldehyde and quaternary ammonium compounds both alone and in combination to determine their appropriate use in hydraulic fracturing.

EXPERIMENTAL PROCEDURES

Materials

Water Samples.

Biocide experiments were conducted in water samples obtained from oil and gas operations in the United States. Both fresh and produced waters were collected and analyzed for pH, total dissolved solids (TDS), and ion content (when available). Water samples were stored at 4 °C prior to use. Experiments were conducted in fresh water alone (pH 7.08, TDS ~0.1%) and a 3:1 combination of fresh water and produced water (pH 7.68, TDS ~3.3%). This TDS was selected in order to ensure viability of microorganisms utilized in these experiments. Increased salinity would likely further reduce the effectiveness of QAC. Additional experiments were conducted in fresh water and 3:1 fresh to produced

water amended with either 1000 parts per million (ppm) v/v anionic friction reducer or a combination of 1000 ppm friction reducer and 10% w/v proppant sand (40-70 mesh).

Biocides and Other Chemicals.

The following individual biocides were selected for use in this study: glutaraldehyde (glut), didecyl dimethyl ammonium chloride (DDAC), and alkyl dimethyl benzyl ammonium chloride (ADBAC). Proppant sand (40-70 mesh) and anionic polyacrylamide friction reducer were sourced from service company partners.

Microorganisms.

Laboratory strains of bacteria were utilized for challenge studies. These included *Escherichia coli* ATCC 8739, *Enterobacter aerogenes* ATCC 13048, and *Pseudomonas aeruginosa* ATCC 13552. Bacteria were cultured on trypticase soy agar plates at 30 °C, stored at 4 °C, and sub-cultured periodically for the duration of the study.

Methods

Efficacy Experiments.

Biocide efficacy against a single challenge of bacteria was determined by dispensing 10 ml of water sample into sterile vials. Stock solutions of glut and QAC were prepared by dilution in sterile deionized water. Mixtures of 5.6:1 glut:QAC were prepared as stock solutions and diluted. Biocides were dispensed into water samples at desired concentrations. Bacteria were cultured in tryptic soy broth (TSB) overnight at 30 °C, mixed 1:1:1 and diluted 1:10 in sterile phosphate buffer. The bacterial inoculum was added to each water sample at 1:100 to give approximately 10^5 - 10^6 colony forming units (CFU)/ml bacteria in each water sample. Aliquots were withdrawn periodically, residual biocide neutralized, and viable bacteria estimated at select time points by a most probable number (MPN) technique as previously described.⁵ Experiments were carried out in test matrices consisting of fresh water, 3:1 fresh to produced water, both waters with 1000 ppm friction reducer, and both waters with 1000 ppm friction reducer and 10% w/v proppant added.

RESULTS

Efficacy Experiments – Fresh Water.

Experiments were conducted by adding glut, ADBAC, and DDAC at 0, 25, 50, and 100 parts per million (ppm) active ingredient (a.i.) to fresh water samples. Bacteria were added as described above and samples taken to enumerate surviving bacteria at 15, 50, 60 minutes, and 4 hours after addition. Results are plotted as the log number of viable cells per milliliter during each time point. The limit of detection for the MPN assay was approximately $1.48 \log_{10}$ cells/ml.

As can be seen in Figure 1, glut, ADBAC, and DDAC all successfully reduced the level of bacteria in fresh water during the course of the experiment. Glut reduced the level of bacteria almost completely ($>4 \log_{10}$) by 15 minutes after bacterial addition at all concentrations tested (25, 50, and 100 ppm a.i.). ADBAC performed almost as well with a reduction in bacteria to below the detection limit at 50 and 100 ppm. At 25 ppm active ingredient, ADBAC was able to reduce the levels of bacteria from 1-3 log at each time point. On the other hand, DDAC did not perform as well as either glut or ADBAC alone. DDAC at 25, 50, and 100 ppm produced only a 1-2 $\log_{10}$ reduction at 15 minutes, 30 minutes, and 1 hour after addition. After 4 hours however, all levels of DDAC resulted in reduction of bacteria to below the detection limit.

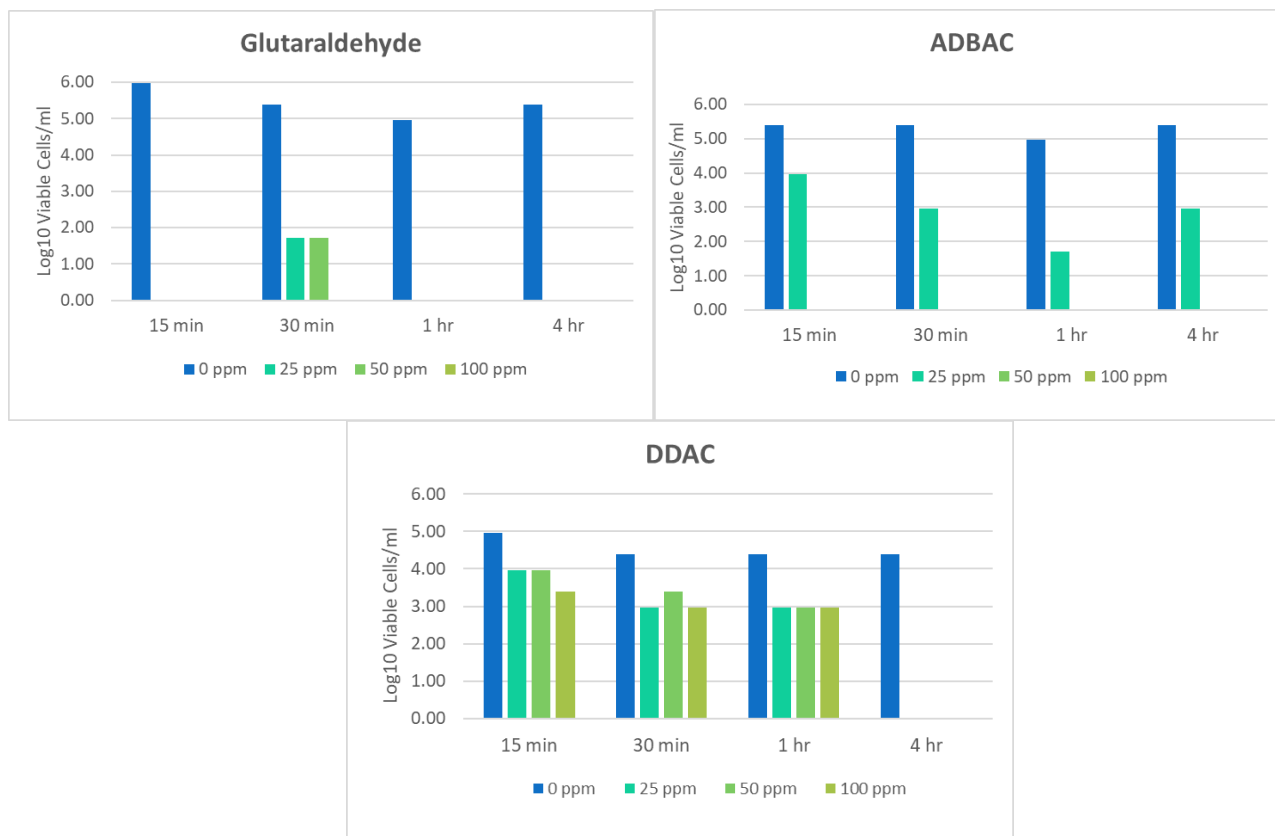
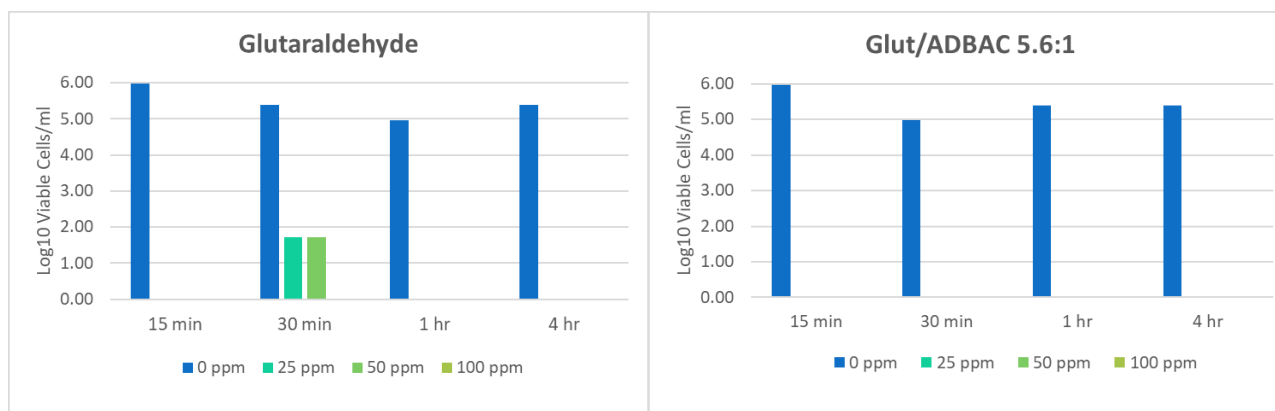


Figure 1: Response of aerobic bacteria to glutaraldehyde, ADBAC, and DDAC in fresh water.

In the next challenge experiment, glutaraldehyde alone was compared to the performance of combinations of glut with ADBAC and glut with DDAC at a ratio of 5.6:1. Biocides were again added to water samples and then challenged with bacteria as previously described. Results can be found in Figure 2. The combination of glut with ADBAC at 5.6:1 and glut with DDAC at 5.6:1 performed similarly to glutaraldehyde alone (Figure 2) in that bacteria were reduced from approx. 10^6 cells/ml to below the detection limit within 15 minutes at all concentrations tested (25, 50, 100 ppm a.i.).

Collectively, results from experiments in fresh water indicate that glut, ADBAC, and DDAC perform well and are capable of inactivating added bacteria within a short time period. Combination products of glut and ADBAC or DDAC at a ratio of 5.6:1 performed better than each biocide individually.



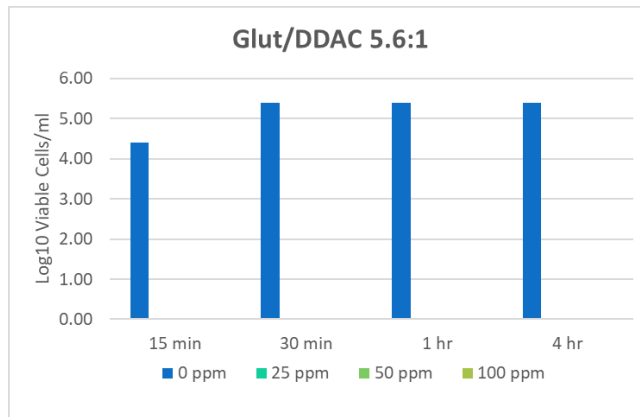


Figure 2: Response of aerobic bacteria to glutaraldehyde, 5.6:1 glut:ADBAC, and 5.6:1 glut:DDAC in fresh water.

Efficacy Experiments – Fresh:Produced Water (3:1).

Additional challenge experiments were conducted in a 3:1 mixture of fresh and produced water. This ratio was selected as it results in a water matrix at approximately 3% TDS which is common in hydraulic fracturing completions. Experiments were conducted exactly as those in fresh water. Results can be found in Figures 3 and 4.

Figure 3 represents the response of bacteria to 0, 25, 50, and 100 ppm of glut, ADBAC, and DDAC in 3:1 fresh to produced water. Glutaraldehyde performs well, resulting in complete inactivation of added bacteria at all time points with 50 and 100 ppm a.i. ADBAC and DDAC do not perform as well as glutaraldehyde in 3:1 fresh to produced water. This is as expected given previously published data on the loss of efficacy of QAC in saline environments.¹

