

A New High Performance Biguanide Polyammonium-Based Blend for Control of Microbiological Fouling in Oil and Gas Stimulation

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ABSTRACT

Microbial fouling in oil and gas stimulation has been shown to cause a multitude of problems, including formation plugging, hydrogen sulfide (H₂S) exposure, microbial induced corrosion, and well souring, all of which can have deleterious effects on well production and quality of oil and gas. In order to determine the most appropriate biocide to mitigate these issues, end users must take many factors into consideration, such as basic biocidal activity, fluid composition, environmental compatibility, and user safety. Additionally, with an increased reliance on recycling and reuse of flowback water, microbiological control in stimulation has become more challenging given the current market push for reduced use of fresh water. Recycled or higher solids waters can carry more bacteria, thus require higher treatment rates when using conventional non-oxidizing biocides. This paper presents a biguanide polyammonium-based blend biocide composed of polyhexamethylene biguanide and a polyquaternary ammonium compound that was designed to meet the performance and market challenges in the current oil and gas stimulation dynamic. Results showed that the biguanide polyammonium-based blend provided quick and persistent biocidal activity against a range of bacteria, including acid producing and sulfate reducing bacteria, at low concentrations, indicating effective biocidal capability. The biguanide polyammonium-based blend was also compatible with additives found in typical oil and gas stimulation fluid packages and worked over a broad range of pH, TDS, and temperatures, indicating broad fluid and environmental compatibility across oil and gas stimulation applications. In addition, there are no open pour restrictions, demonstrating that the biguanide polyammonium-based blend is safer to handle than other biocides. These results were verified in multiple oil and gas stimulation field assessments confirming the validity of the laboratory bench top evaluation.

Key words: biocide, non-oxidizing biocide, oil and gas, hydraulic fracturing, stimulation, chemical compatibility, hydrothermal stability, biguanide polyammonium-blend, BPAB, total dissolved solids

INTRODUCTION

There are many factors to take into consideration when designing and implementing a stimulation fluid package for a new stimulation site. End users must consider fluid composition, environmental compatibility, and user safety to name a few.^{1,2} Additionally, with an increased reliance on recycling and reuse of flowback water, chemical integrity has become more challenging given the current market push of reduced use of 100% fresh water. This is especially important in northern and eastern basins in the USA where produced water contains higher solids than in other regions. Thus, every component needs to work well with each other and with external environmental factors, and they also need to be sound choices that specifically work for each individual stimulation site.

Not only does one need to study the overall set up and design of the stimulation, but also the specifics around each component that will go downhole. When it comes to chemicals pumped downhole, end users will need to look at many variables when considering compatibility.^{1,3} One issue of chemical selection that needs to be considered is the downhole environment, mainly how high the downhole temperature is going to be and whether the component will be able to maintain its chemical integrity at that high of a temperature. Another consideration is overall compatibility with other chemical components of the fracturing fluid. Not only does the chemical need to not negatively interfere with other chemical actions, but there should be no negative interference with its own action. Finally, another variable that needs serious consideration is the water chemistry of the water going downhole. Source water can be clean, low total dissolved solids (TDS) fresh water, purely recycled water with high concentrations of impurities, low pH, and high TDS, or any potential variable concentration of the two together. With the increase of mainly recycled water use, other factors start to come into play such as higher solids that can require higher treatment rates of scale inhibitors, biocides, and other chemical components or complete exchange to more niche products that are specifically compatible in such waters.

When choosing a biocide, it is well understood that microbial fouling in oil and gas stimulation causes a multitude of problems, including formation plugging, H₂S exposure, microbial induced corrosion, and well souring, all of which have deleterious effects on well production and quality of oil and gas.⁴⁻⁹ Importantly to note, with an increased reliance on recycled water comes an increase in solids in said waters, and high solids water are known to carry more challenging bacterial communities and the possibility of higher biocidal treatment rates.¹⁰⁻¹⁴ Thus, choosing the best biocide for the specific environmental, chemical, safety, and reasonable dose requirements of a stimulation site is imperative.

Keeping these criteria in mind, in this study, numerous biocide blends were screened for basic efficacy, extreme environmental efficacy and stability, chemical compatibility, and personnel safety that currently affects stimulation end users.

EXPERIMENTAL PROCEDURE

Efficacy Testing

Biocide Blends

The following biocides were used in this study for blends:

Alkyl dimethyl benzyl ammonium chloride (ADBAC), 2-bromo-2-nitropropane-1,3-diol (BNPD), dodecylguanidine hydrochloride (DGH), didecyl dimethyl ammonium chloride (DDAC), dimethyl oxazolidine (DMO), glutaraldehyde (GA), polyhexamethylene biguanide (PHMB), tetrakis(hydroxymethyl)phosphonium sulfate (THPS), tributyl tetradecyl phosphonium chloride (TTPC), and Poly[oxyethylene(dimethyliminio)ethylene(dimethyliminio)ethylenedichloride] (PQ).

Blend	Composition	Blend	Composition	Blend	Composition	Blend	Composition
1	ADBAC/BNPD	6	BNPD/GA	11	DDAC/DMO	16	GA/TTPC
2	ADBAC/DGH	7	BNPD/PHMB	12	DDAC/TTPC	17	GA/PQ
3	ADBAC/DMO	8	BNPD/PQ	13	DMO/PHMB	18	PHMB/TTPC
4	ADBAC/TTPC	9	DGH/GA	14	DMO/TTPC	19	PHMB/PQ
5	ADBAC/PQ	10	DGH/TTPC	15	DMO/PQ	20	THPS/PQ

Table 1. Screening Biocide Blend Compositions

Microbial Strains

The following bacteria were used in this study: The acid-producing bacteria (APB) strain *Enterobacter aerogenes* (ATCC 13045) and the sulfate-reducing bacteria (SRB) strain *Desulfovibrio vulgaris* (ATCC 7757). Stock cultures of the bacterial strains were maintained on plate count agar and 1% API SRB media, respectively.

Reagent Preparation

The following biocides were used in this study: Bellacide® 364[†], which contains 6.4% of a biguanide polyammonium-blend (BPAB) and a glutaraldehyde/quaternary ammonium compound blend, which contains 12.5% glutaraldehyde, 1.2% alkyl dimethyl benzyl ammonium chloride, and 1.8% didecyl dimethyl ammonium chloride (12:3 G/Q). Stock solutions of biocides were prepared in distilled water.

Other reagents used include a proprietary anionic friction reducer; a proprietary cationic friction reducer; Ammonium persulfate and sodium chlorite, oxidative breakers; Sodium bisulfite and sodium sulfide, reducing agents; a proprietary non-emulsifying agent; and a proprietary scale inhibitor. Stock solutions of chemical reagents were prepared in distilled water.

Anaerobic Efficacy Test

For laboratory testing, glass vials containing 35 mL of sterile variable pH (6.5 – 10) + variable % NaCl buffer (10K – 100K TDS) were prepared, and 35 µL of the APB strain *E. aerogenes* and 0.4 mL of the SRB strain *D. vulgaris* were added. For field water testing, sterile glass vials with 35 mL of collected field water with indigenous bacteria were prepared. At time zero, appropriate volumes of biocide stock solution were added to each of the reaction vials except one, which served as a control. For compatibility testing with other chemical components, appropriate volumes of chemical stock solutions were also added to each reaction vial with biocide treatment as well as one vial with no biocide treatment as to determine if there were any deleterious effects of the chemical itself on the bacteria. This was either done with a single chemical component or multiple chemical components. At the desired time points (1, 4, and 24 hours, for example) following incubation at room temperature, 1 mL of each reaction solution was transferred using a sterile syringe to a sealed media vial containing SRB or APB growth media. Serial dilutions of this new solution were made by transferring 1 mL to a new media vial to make a 1:10 dilution and repeating this step out to eight vials in total. After completion of the serial dilutions for each reaction, the plastic flat holding both APB and SRB media vials was placed in a 37°C incubator for 72 hours. Following this incubation, the number of media vials that exhibited positive bacterial growth via color change was counted for each reaction.

Thermal Stability Test

The biocidal efficacy of the four biocide solutions were tested under two temperature conditions over a time course of 28 days. For each biocide, stock solutions were prepared in pH 9 phosphate buffer

[†] Trade Name

containing 1% NaCl (20K TDS). One bottle of each solution was stored at either room temperature or at 80°C for the duration of the study. On Day 0, three reaction vials containing 35 mL of sterile pH 7 buffer and another three containing 35 mL of pH 9 buffer were set up, and to each were added 35 µL of APB and 0.4 mL of SRB overnight cultures. At time point T0, an appropriate amount of the room temperature or 80°C biocide stock solution was added to two of the three reaction vials of corresponding pH. The third reaction vial did not contain biocide and served as the control. At the desired time points following addition of the biocide, serial dilutions were made of each reaction according to the procedure for anaerobic studies outlined above, and the APB and SRB media vials were incubated at 37°C for 72 hours. This procedure was repeated on Days 1 and 28.

Biocidal Efficacy at pH 10.5

Glass vials containing 35 mL of sterile pH 10.5 + 2% NaCl buffer (30K TDS) were first prepared, then stock solutions of biocide were added at the desired concentrations and incubated for 1 hour at room temperature. Following this incubation period, the pH of each solution was adjusted to pH 8 by adding 5-6 drops of concentrated (33% w/w) HCl, before inoculating with 35 µL of APB and 0.4 mL of SRB overnight cultures at time T0. At time points of 1, 4, and 24 hours, serial dilutions from each reaction solution were made, and the resulting media vials were incubated for 72 hours at 35°C.

Oxidative Breaker Compatibility Testing

The stability of oxidative breakers in the presence of biocide was determined by measuring and comparing either ammonium persulfate or sodium chlorite concentrations in control and mixed solutions over a time course. For each test, two solutions of either ammonium persulfate or sodium chlorite at a concentration yielding 120 ppm or 200 ppm active by weight, respectively, were first prepared in pH 10.5 phosphate buffer containing 2% NaCl (30,000 ppm total dissolved solids [TDS]). One of the solutions served as the control, while biocide was added to the other at the desired concentration for testing of each biocidal blend and incubated at 80°C. At time T0, the ammonium persulfate or sodium chlorite concentrations in each solution were determined using either a colorimetric kit for sodium persulfate or a colorimetric sodium chlorite test kit and subsequently measured at time points of 10 minutes, 30 minutes, 1 hour, 2 hours, and 4 hours.

Case Studies

Trial wells were completed under normal stimulation procedures with a dose of 0.25 GPT of BPAB. Treatment of water for drill-out operations occurred at the beginning of the drill out and whenever the water is changed to minimize post frac contamination of wells, offset wells followed current standard practice for drill-out water biocide treatment. Water sampling was required on wells during the completion and at regular intervals during flowback. Samples were acquired for testing during and after completion for analysis. Sample analysis included SRB and APB serial dilution vial bottle turns. Sampling included (where possible): source water prior to biocidal treatment (untreated stimulation water), source water post-biocidal treatment in the blender prior to stimulation (pre-stimulation treatment water), 30-day post-stimulation flowback water, 60-day post-stimulation flowback water, and 90-day post-stimulation flowback water. Basic well information collected included: US basin location, stimulation fluid type, and water source.

RESULTS

Prior to any laboratory or field testing, to address pre-criteria for biocide development blend selection, a matrix was created that considered novelty of blend combination, cost to develop, material feasibility, and basic miscibility using eleven separate biocides. Thus, the matrix started with fifty-five blend options that were reduced to twenty blends that then went on to laboratory efficacy screening.