

Innovative Biocide Blend Solves Microbial Contamination Issues in Oil and Gas Applications

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ABSTRACT

Detailed comparative efficacy laboratory studies were conducted using relevant field conditions which highlighted the excellent performance of this new biocide compared to other commonly used oil and gas biocides. Results showed that the biguanide polyammonium blend provided quick and persistent biocidal activity against a range of bacteria, including acid producing and sulfate reducing bacteria at low concentrations. The blend was also compatible with additives typically found in oil and gas stimulation fluid packages and worked over a broad range of pH, TDS, and temperatures, indicating broad fluid and environmental compatibility across a wide range of oil and gas applications. In addition, results show strong performance advantages against corrosion causing biofilms. These results were verified in a field trial that confirmed the biocidal performance of the biguanide-polyammonium blend against biofilm in a produced water processing facility.

Key words: biocide, non-oxidizing biocide, biofilm, oil and gas, hydraulic fracturing, stimulation, production, hydrothermal stability, biguanide polyammonium-blend, BPAB

INTRODUCTION

Microbial contamination in the development of unconventional oil and gas formations can cause numerous problems, including formation plugging, microbial induced corrosion, and well souring, all of which can have a negative effect on well productivity and quality of oil and gas. The most common method to control microbial contamination during stimulation of unconventional oil and gas formations is through the use of biocides. Traditional oil and gas biocides such as glutaraldehyde/quaternary ammonium blends struggle to provide effective microbial control under the severe conditions encountered during stimulation

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of unconventional oil and gas formations. Glutaraldehyde decomposes and becomes ineffective at high temperatures and monomeric quats adsorb to sand and are deactivated.^{1,2} The innovative biguanide polyammonium blend (BPAB) described in this paper was specifically developed to provide improved microbial control under these severe conditions. It's performance against biofilm presents opportunities in additional oil and gas segments such as production and pipeline applications. In addition to improved microbial control, the biguanide polyammonium blend has an excellent HSE profile with very low risk for eye and skin irritation, skin sensitization, or inhalation toxicity demonstrating that it is safer to handle than other biocides.³

EXPERIMENTAL PROCEDURE

Biocidal Efficacy Testing

Microbial Strains

The following bacteria were used in this study: The general-aerobic bacteria (GAB) *Pseudomonas aeruginosa* (ATCC 15442), 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.

Inoculum Preparation

Pseudomonas aeruginosa and *Klebsiella aerogenes*: A small portion of growth was removed from a slant or plate and was suspended in sterile saline. One milliliter of this suspension was spread evenly on the surface of a plate of plate count agar and incubated overnight at 37°C. Plates were harvested by adding 10 ml of sterile saline, agitating gently with a sterile loop. The suspension was diluted with sterile saline to produce an inoculum containing approximately 10⁸ CFU/ml.

Desulfovibrio vulgaris: One milliliter of growth was removed from a culture vial using a sterile syringe and suspended in a new 1% API SRB media vial. The vial was incubated overnight at 37°C. 1 milliliter was drawn from the overnight vial and added to a fresh media vial. This vial serves as the inoculum containing approximately 10⁶ CFU/mL.

Biocide Preparation

The following biocides were used in this study: Bellacide® 364[†], which contains 6.4% of biguanide-polyammonium blend (BPAB); 12.5% glutaraldehyde, 1.2% alkyl dimethyl benzyl ammonium chloride, and 1.8% didecyl dimethyl ammonium chloride (GQ1); 25% glutaraldehyde (GA); 25.7% glutaraldehyde, 5% alkyl dimethyl benzyl ammonium chloride, and 7.5% didecyl dimethyl ammonium chloride (GQ2); 20% tetrakis(hydroxymethyl) phosphonium sulfate (THPS); 20% alkyl dimethyl benzyl ammonium chloride (ADBAC) and 10% didecyl dimethyl ammonium chloride (DDAC). Stock solutions of biocides were prepared as weight percent solutions in distilled water.

Anaerobic Efficacy Test

Glass vials containing 35 ml of sterile brine were prepared, and 35 µl of the APB strain *E. aerogenes* and 0.4 ml of the SRB strain *D. vulgaris* were added. In some experiments sterile sand was added to some of the glass vials. At time zero, appropriate volumes of biocide stock solution were added to each of the reaction vials except one, which served as a negative control. At the desired time points 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

[†] Trade Name

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by transferring 1 ml to a new media vial to make a 1:10 dilution and repeating this step out to seven vials in total. After completion of the serial dilutions for each reaction, the plastic flat holding the 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 determined for each condition.

Thermal Stability Test

Biocides were added to vials containing 35 ml of sterile brine (pH 7.4, 112,000 ppm TDS). One vial of each biocide was stored at either room temperature or at 95°C for 48 hours. After 48 hours had passed, the vials incubated at 95°C were removed from the oven and allowed to cool to room temperature. When the vials had cooled, 35 µl of the APB strain *E. aerogenes* and 0.4 ml of the SRB strain *D. vulgaris* were added to each vial. At four hours following addition of the bacteria, serial dilutions were made of each vial according to the procedure for the anaerobic efficacy test described above, and the media vials were incubated at 37°C for 72 hours. Following this incubation, the number of media vials that exhibited positive bacterial growth via color change was determined for each condition.

Biofilm Preparation

Biofilm samples were generated on stainless steel coupons (approximate dimensions: 2.6 cm L x 1.1 cm W x 0.1 cm H) using a chemostat-type system set up for once through flow as described previously.⁴ The coupons were degreased by washing in acetone. The coupons were placed in a beaker and enough acetone was added so that all the coupons were covered. The coupons were briefly agitated, and the acetone was then decanted. The coupons were then inserted lengthwise into a soft PVC holder. Each PVC holder held eight coupons. Three loaded PVC holders were stacked one on top of the other in a 250 ml chromatography column (4.8 cm W x 15 cm H). The column was connected at the bottom to a pump and reservoir. The reservoir was filled with synthetic brine. The composition of the synthetic brine was as follows: NaCl, 12.50 g/l; KCl, 0.17 g/l; MgCl₂ · 6H₂O, 0.25 g/l; CaCl₂ · 2H₂O, 0.72 g/l; SrCl₂ · 6H₂O, 0.07 g/l; BaCl₂ · 2H₂O, 0.01 g/l; Na₂SO₄, 0.19 g/l; and NaHCO₃, 1.23 mg/l. The pump was adjusted to deliver 5 ml per minute. A 0.3% filter sterilized glucose solution was injected into the synthetic water prior to the column using a syringe pump at a rate determined to yield 10 mg/l glucose. As the column was filling, a sufficient amount of the *Pseudomonas aeruginosa* or *Klebsiella aerogenes* inoculum was added to the column to yield an initial bacterial count of 10³ CFU/ml and the outlet end piece was attached to the column. Once the column was completely filled with brine the pumps were stopped and the column was allowed to sit overnight. After the overnight incubation the pumps were restarted, and the system was run continuously.

Biofilm Efficacy Test

After 3 days of continuous operation, the pumps were stopped, and individual coupons were aseptically removed from the column and placed in test tubes containing 10 ml of sterile brine. Biocide was added to the test tubes in an amount calculated to give the desired concentration and the test tubes were then incubated with shaking (300 rpm) for the desired contact time. An untreated test tube served as a control. At the desired times, the coupons were removed from the test tube, rinsed with 10 ml of sterile saline (to remove any planktonic microorganisms that may be present in the water adhering to the coupon), and placed in fresh tubes of 10 ml sterile saline. The tubes were then sonicated for five minutes on high using a Vevor Ultrasonic Cleaner Model PS-30A. After sonication, viable microorganisms were enumerated by standard pour plating of dilutions made in sterile saline using plate count agar. Plates were incubated for 48 hours at 37°C. Results were reported as colony forming units (CFU)/cm².

Field Trial

A Robbins Device-type biofilm monitoring unit was installed at a produced water processing facility located in the Piceance basin. The water in this system has a pH of 6.60 and a total dissolved solids content of ~25,000 ppm. The biofilm monitoring unit has 12 removable coupon holders which were loaded