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Microbial Solutions Treat Frac Water

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HOUSTON–Because the water used in hydraulic fracturing operations typically is not potable, it is a common source of problematic bacteria such as sulfate-reducing bacteria (SRB) and acid-producing bacteria (APB). Controlling micro-organisms during the completion of hydraulically fractured wells is a significant component in the successful development of a production system.

Detrimental bacteria such SRB introduced into the reservoir during the completion process can facilitate biogenic sulfide production, resulting in the souring of production fluids and gas, iron sulfide formation, and SRB-associated microbiologically influenced corrosion. Adequate treatment is necessary to mitigate the possibility that detrimental bacteria can establish colonies in the wellbore and formation, causing operational issues and increasing operating costs. Once SRBs have established colonies and begin producing sulfide, reaching the impacted formation areas with a remedial biocide treatment post-completion is usually cost-prohibitive.

Biological control programs in Marcellus Shale well completions are particularly important because of the lower formation temperatures, which can provide optimal growth conditions for many bacteria, including moderately thermophillic SRB and APB. Halo-tolerant and halophilic bacteria have been shown to proliferate in producing wells. Moreover, environmentally efficient use of water in the Marcellus play has increased dramatically the reuse of produced and flowback water for hydraulic fracturing. This situation allows for the possibility that bacteria can make multiple trips down hole and back again in the absence of effective treatment programs.

Biocides are dosed routinely at low levels into fracturing fluids to control microbe populations and subsequent adverse effects associated with bacterial activity. Biocides, by their nature and intended purpose, are not tolerated well by certain aquatic organisms. In an effort to improve the ecological profile of the microbiological control program in fracturing operations, a treatment system was developed for Marcellus Shale wells using nitrate and nonhazardous live nitrate-reducing bacteria (NRB) to control SRB. Nitrates stimulate the metabolic activity of NRB.

Live NRB–selected for tolerance to Marcellus temperature and salinity properties–and the nitrate solution were added to the fracturing fluids as an alternative to biocides to treat multiple horizontal Marcellus wells. NRB can mitigate SRB activity by consuming the limited carbon resources available (competitive exclusion), direct SRB metabolic inhibition, and direct oxidation of sulfide or indirect oxidation through nitrite and sulfide interaction.

The primary objective of adding a proprietary mixture of live NRB and nitrate to the fracturing fluid system was to ensure that NRB and SRB competition would occur after completing the Marcellus wells. The wells were monitored for periods ranging from three to 18 months, depending on the date of completion. Treatment efficacy was evaluated by comparing data from the NRB and nitrate-treated wells with data collected from wells completed in the same manner, and in some cases on the same pad, with a biocide that historically exhibited good microbial control. Compared with successful biocide applications, the results demonstrate that NRB and nitrate treatment is similarly effective at controlling SRB activity.

First Fracturing Application

Although proven effective in controlling SRB in continuously applied methods in several waterflood projects around the world, nitrate-based programs had not been applied previously to hydraulic fracturing. The water used for Marcellus fracturing operations can originate from multiple sources, including flow back and produced water, and water from streams, rivers and other nonpotable sources. The quantities and types of NRB in these fluids are largely unknown. The success of a competitive exclusion program for hydraulic fracturing is predicated on having sufficient numbers of NRBs capable of surviving under reservoir conditions.

Consequently, the Marcellus program used a liquid solution containing concentrated active, naturally occurring NRBs with the propensity to survive under downhole conditions. Aqueous sodium nitrate was dosed to act as the terminal electron acceptor for the NRB metabolic pathway.

The NRB strains were selected for their capacity to metabolize in the temperature and salinity ranges characteristic of the Marcellus. Different proprietary strains were applied as an aqueous solution, depending on the total dissolved solids of the well completion fluids. The NRB/nitrate treatment program represented a significant compatibility increase with aquatic organisms from biological control methods, compared with conventional biocides.

The live NRB solution and aqueous sodium nitrate were injected into a manifold, where water from on-site tanks flowed to the blender tub. A target dosage was identified and maintained, based on the bulk water pumping rates. From the blender, the fluids containing the NRB/nitrate treatment were pumped down the wellbore and into the formation.

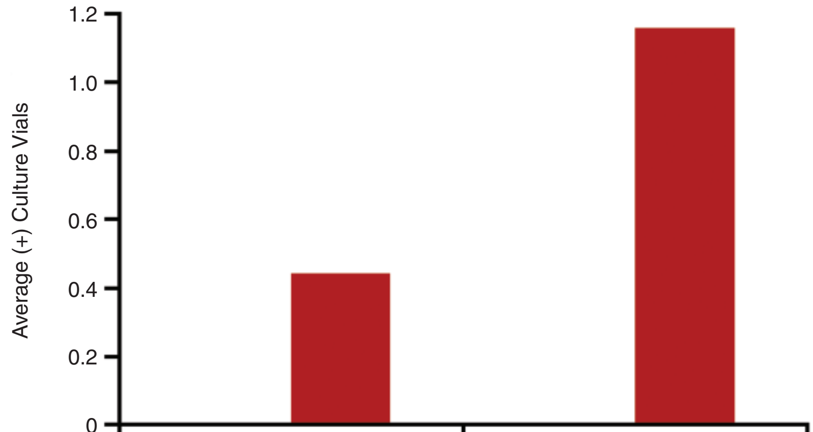
The treatment rationale helped ensure that the fracturing process would push NRB/nitrate into the fractured formation zones. This same basic application method was used for all three well pads discussed in this article. Pads A and C used a combination of freshwater and produced water for completion. Pad B used only freshwater.

Pad C wells were treated only with NRB/nitrate (no biocide). Pads A and B had some wells treated with the NRB/nitrate system and some wells treated with a conventional biocide program consisting of 50 percent active glutaraldehyde and 76 percent active dimethyl oxazolidine (DMO) co-injection. This biocide program had been used in more than 100 completed Marcellus wells, and historically had provided effective microbial control.

Genetic identification and characterization of NRB bacteria using pyrosequencing techniques was performed on pad C (NRB/nitrate treatment only). The genomic population analysis relied on 454 pyrosequencing methods and blasting alignment to 16s rDNA. Bacteria culturing

FIGURE 2

Average Post-Fracture Bacteria Populations (Biocide versus NRB/Nitrate Wells)

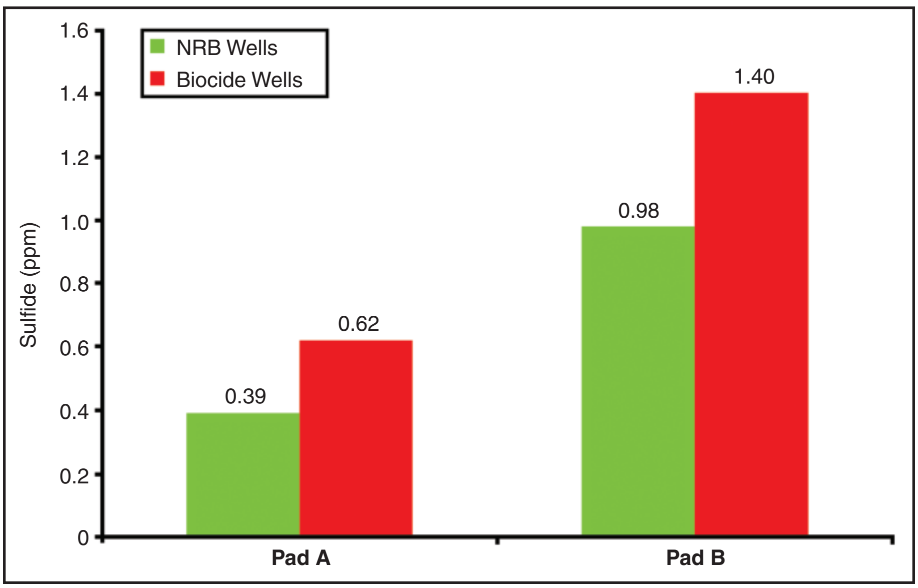


	NRB Wells	Biocide Wells
Average SRB	0	0
Average APB	0.44	1.156

was performed at the well site according to the NACE TMO-194 standard (2004). Serial dilution was performed by selecting total dissolved solids of the sampled water (by refractometer) using appropriately matched culture media. A dilution series of eight vials per series was used for serial dilution. Modified Postgate's B media were used to detect SRB, and phenol red dextrose (PRD) was used to detect APB. A custom media formula was used to cultivate NRB.

FIGURE 1

Average Post-Fracture Sulfide Gas Concentrations (Biocide versus NRB/Nitrate Wells)



Ion exchange chromatography was used to quantify nitrates and volatile fatty acids (VFAs) in the source water, flow back, and production fluids. VFAs are generally the carbon source types metabolized by problematic bacteria. VFAs are typically products of organic matter degraded by microbes, and are naturally ubiquitous in rivers, streams and ponds. When VFA resources are limited, NRB and SRB must compete for these metabolites.

The VFAs tested were propionate, valerate, butyrate and acetate with 0.125-milligram/liter detection limits. The nitrate analysis detection limit was 0.025 mg/l. Sulfide was measured using colorimetric gas indicator tubes. A gas collection bulb was attached to the sample point before measurement, creating a gas retention space for sampling by the vacuum. The tubes were graduated and read at the time of sampling.

Treatment Results

Pads A and B contained wells treated with both NRB/nitrate and biocide. Wells on Pad A were completed before pad B, so they were monitored up to 26 months after hydraulic fracturing, compared with 19 months for pad B wells. The average sulfide produced from both pads during this time was calculated for NRB/nitrate and glutaraldehyde/DMO-treated wells (Figure 1).

Pad A exhibited generally lower gas phase sulfide than pad B. In both cases,

FIGURE 3A

Pad A VFA Concentrations (Biocide versus NRB/Nitrate Wells)

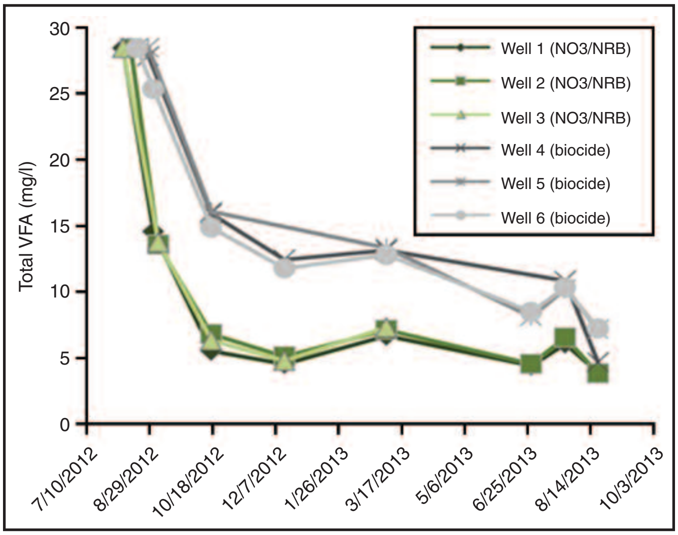
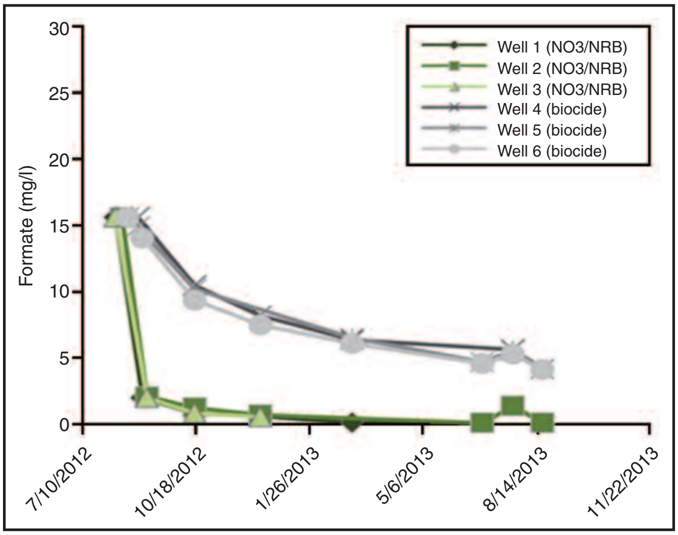


FIGURE 3B

Pad A Formate Concentrations (Biocide versus NRB/Nitrate Wells)



biocide-treated wells produced higher concentrations of sulfide compared with NRB/nitrate-treated wells. This difference amounted to 37.1 percent less sulfide for pad A and 30 percent less sulfide for pad B. The average sulfide for pad A NRB/nitrate wells was 0.39 parts per million compared with 0.62 ppm for pad A biocide-treated wells. Pad B produced more than twice this amount, with 0.98 ppm sulfide for NRB/nitrate wells and 1.4 ppm sulfide for biocide wells. For both pads, the NRB/nitrate treatment maintained average sulfide concentrations under 1 ppm.

Source waters were measured from 10^4 to greater than 10^6 colony-forming-units per milliliter (cfu/ml) for both APB and SRB populations during the completion of both pads. The bacterial samples were collected from on-site tanks. Post-completion, the wells were monitored regularly for bacterial populations for 12 months on pad A and eight months on pad B. Throughout the course of monitoring, no NRB/nitrate- or biocide-treated well tested positive for SRB growth. The number of positive culture vials in serial dilution sets for both pads were averaged.

Further classification was made to separate NRB/nitrate- and biocide-treated wells to help determine bacteria populations (Figure 2). In serial dilution sets of bacteria culture media, the NRB/nitrate wells turned 0.44 PRD vials for APB growth, on average. The biocide wells on these pads turned more than twice that amount at 1.156 positive PRD vials for APB growth. The average of all wells for SRB growth was zero, indicating that the NRB/nitrate and biocide programs were equally successful in controlling SRB activity.

NRB bacteria were cultivated successfully on the NRB/nitrate-treated wells, and the quantified populations ranged from 10^1 to 10^3 cfu/ml detected at the wellheads for pads A, B and C. Genetic identification by means of pyrosequencing was performed on NRB cultures from a NRB/nitrate-treated well on pad C. The results indicated that the same proprietary NRB bacterial species used to complete the well were the dominant species cultivated during production.

VFAs were tracked for 16 wells on pads A and B. Pad A is a six-well pad, with three wells treated with glutaraldehyde/DMO biocide and three wells treated with NRB/nitrate. The horizontal sections of these wells were in opposite directions of the respective treatment programs to help minimize the chances of cross-communication between individual wells with

FIGURE 4

Pad B VFA Concentrations (Biocide versus NRB/Nitrate Wells)

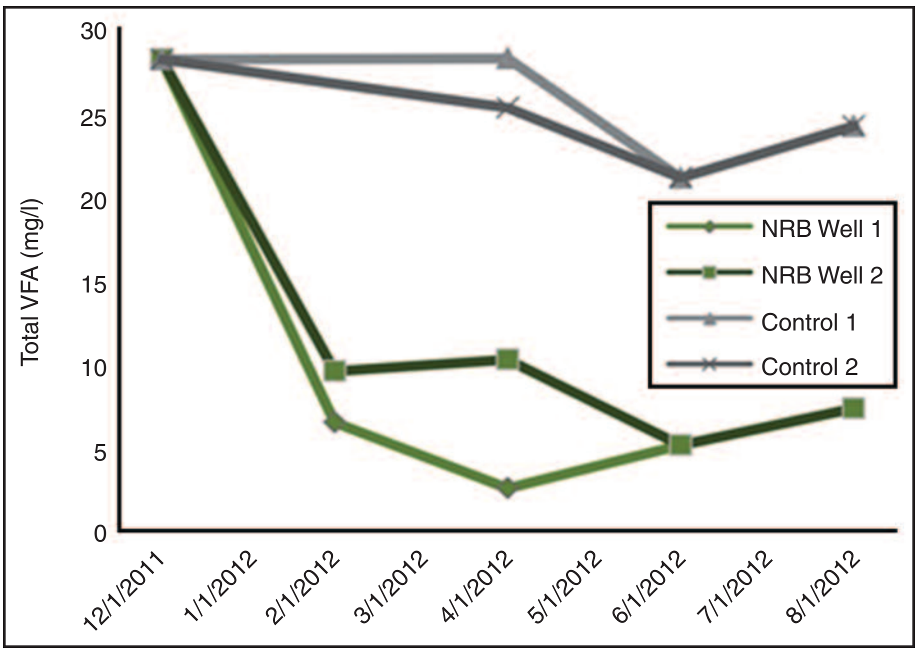


FIGURE 5A

Pad A Nitrate Concentrations (NRB/Nitrate Wells)

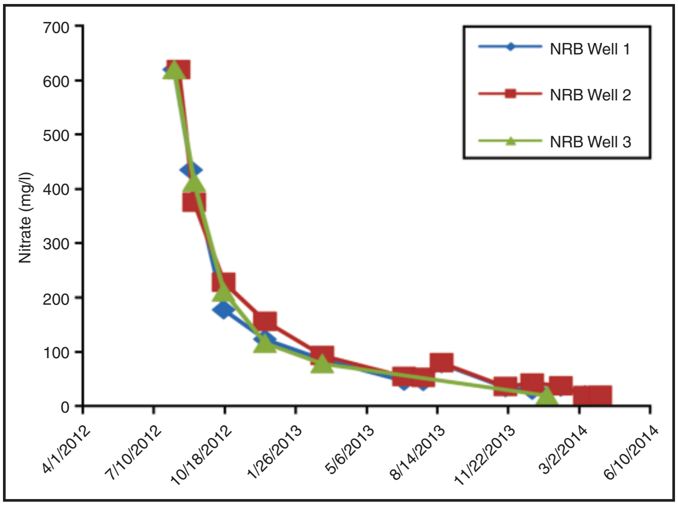
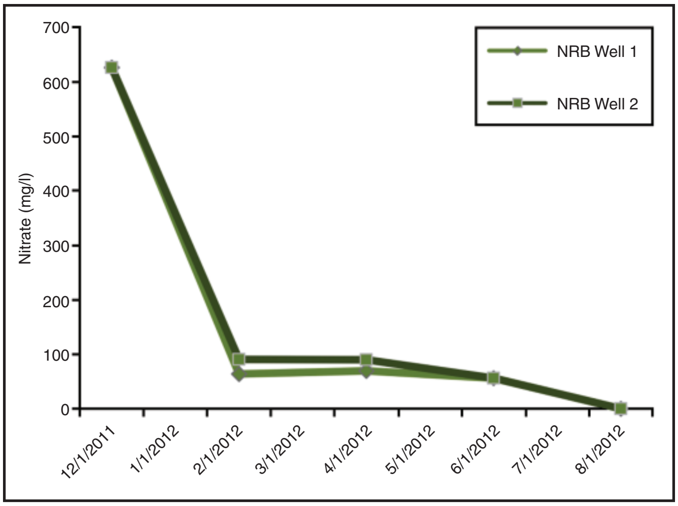


FIGURE 5B

Pad B Nitrate Concentrations (NRB/Nitrate Wells)



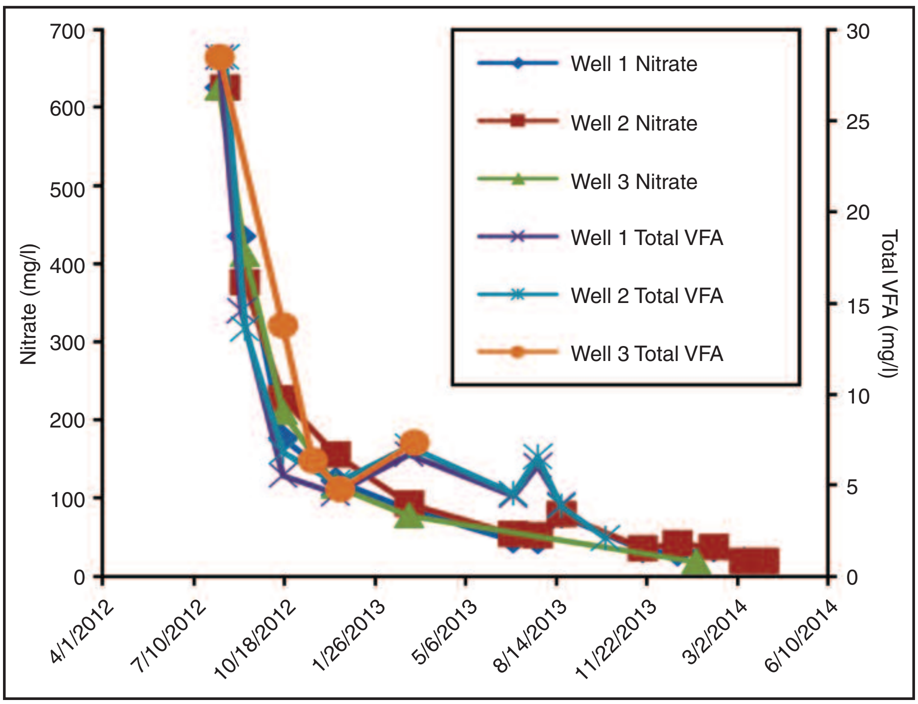
comparable treatments. All six wells were tracked for VFA for more than one year (Figure 3A). The source water for the wells was a mixture of approximately 30 percent produced water and ≈70 percent freshwater by volume. The water mixture contained an average of 28.45 mg/l of total VFA (as tested from tanks before injection).

VFA concentrations decreased for both NRB/nitrate- and biocide-treated wells, but the reduction in NRB/nitrate wells was greater (nearly 80 percent two months after completion when the wells were flowed back compared with 50 percent for biocide-treated wells). Two months after completion, NRB/nitrate wells established low VFA levels, and NRB metabolic activity seemed to slow as these concentrations were maintained up to one year. Biocide well VFA readings continued to slowly decrease over the 10 months following flow back.

Although propionate, valerate, butyrate, and acetate were investigated, formate was the principle organic found in pad A. The rapid loss of formate occurring in the production waters of NRB/nitrate-treated wells was maintained up to one year (Figure 3B). Analysis of formate performed one year after the completion date determined that the concentration had dropped below the detectable limit of 0.250 ppm. Conversely, formate levels were between 4.13 and 4.19 ppm on the biocide-treated wells after one year of production.

FIGURE 6

Pad A VFA versus Nitrate (NRB/Nitrate Wells)



Significant Decrease

Pad B contained 10 wells, two of which were treated with NRB/nitrate and eight with glutaraldehyde/DMO biocide. Four wells were tracked for VFA levels (two treated with NRB/nitrate and two with biocide). VFA concentrations were monitored throughout an eight-month interval (Figure 4). Testing of the freshwater used to complete the wells indicated an average of 28.1 mg/l total VFA being injected into the wells.

Two months after completion, the wells were flowed back, and VFA concentrations in the two NRB wells were decreased significantly (by 66 and 77 percent, indicating strong metabolic activity). A large VFA reduction at flow back was not observed in pad B biocide-treated wells. Instead, the wells exhibited a gradual and minimal decrease in VFA (from 28.1 to 24.14 mg/l) throughout the eight-month monitoring period.

Nitrate concentrations were measured on pad A wells for six months and pad B wells for eight months for wells that received the NRB/nitrate treatments. As flow back proceeded, nitrite levels tapered off. Nitrate concentrations dropped below 100 mg/l within two months of completion on pad B. On pad A, nitrate was detected at less than 100 mg/l seven months after production began. Nitrate was recovered in low levels after a year in two of the three wells tested from pad A. Pad B no longer contained nitrate eight months following completion (Figures 5A and 5B).

Because similar trends were apparent from VFA and nitrate residuals, both were plotted for pad A. Overall, VFA and nitrate reduction trends through NRB metabolic activity were in good agreement (Figure 6).

More than 100 hydraulically fractured Marcellus wells have now been treated using live NRB strains in conjunction with sodium nitrate. The NRB/nitrate system has achieved equal-to-biocide control of wellhead souring as measured by gas phase sulfide and SRB populations. In fact, the NRB/nitrate-treated wells investigated during this study produced 30 percent less sulfide on average than conventional biocide-treated wells. General field monitoring has not recovered SRB in the NRB/nitrate-treated Marcellus wells, and low levels of sulfide have been maintained.

NRB/nitrate treatment offers an ecologically improved alternative to biocide if applied properly in a compatible field (i.e., sustainable total dissolved solids concentrations, temperatures, and low-porosity shale). No small measure of the success of the Marcellus applications should be attributed to using a specialized NRB strain tolerant of reservoir conditions. Without these proven strains, the addition of nitrate could have been ineffective in mitigating souring and microbiologically influenced corrosion.

Future work will include testing NRB/nitrate applications in other North American shales in addition to increasing the number of strains available for treatment applications. ❒

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