OILFIELD TECHNOLOGY

EXPLORATION | DRILLING | PRODUCTION APRIL 2016

BANNISHING OILFIELD BACTERIA

George Nagle, BWA, USA, provides an overview of existing biocide programmes used in well maintenance.

During a market downturn in the oil and gas industry, optimising the amount of production obtained per dollar spent becomes even more critical to staying in business. Typically, one of the first areas to face a reduction in spending is exploration and drilling because of the higher risk associated with the activities compared to the return. However, costs associated with maintaining fields that are already flowing do eventually see spending cuts as well. These cuts tend to be on older wells or wells that have high water cuts or even wells that have other maintenance issues associated with them.

A persistent issue found from the beginning to the end of a well is dealing with biological species. Sometimes this can involve dealing with birds or even deer at the wellhead, but typically the overwhelming issues are dealing with microbiological life and algae. Issues revolve around clogging up systems, inhibiting production optimisation, inducing corrosion, creating system compatibility issues and finally potential issues around health and safety. Table 1 shows some commonly used biocide programmes.

Additionally, the type of microbiological life that is being treated may determine what system can work most cost-efficiently. Two typical categories are acid producing bacteria (APB) and sulfate reducing bacteria (SRB).

APBs create acid or alcohols as a part of their metabolism pathway. This can lower the overall pH of a well and lead to some corrosion. Additionally, when clusters of these bacteria form, they create a biofilm. This film coats metal surfaces and can lead to significant pitting corrosion as well as potentially restricting production flow.

APBs can thrive in oxygen rich environments, but also survive in depleted oxygen environments like wells.

Surface contamination can happen easily enough and managing these types of bacteria is acceptable. A typical measurement is a three log reduction in mass per millilitre (non-treated count to post-treated count), this is considered to be good control.

SRBs are the other major category of bacteria commonly encountered in oil and gas. Though APBs do lead to some corrosion (called microbial induced corrosion), SRBs tend to contribute to this issue in a more significant manner. Hydrogen sulfide (H_2S) is a corrosive gas formed by these bacteria. H_2S not only induces corrosion, but also is extremely hazardous to humans.

SRBs do not survive very long in oxygen environments as they are anaerobic. They utilise sulfur in place of oxygen for respiration. In well systems, sulfate can be readily available as a source for these bacteria. In terms of effective treatment, a complete kill (under 10 units/ml) is needed.

System cleaning

Starting a system clean is always ideal. It is common for a biocide to be requested for each job from a conventional, under balance and frack. However, not all biocides are equal and a lack of specificity can sometimes result in an ineffective biocide being applied. Oxidising treatments such as bleach- or bromine-based biocides tend to act quickly but also dissipate just as fast. Non-oxidising biocides tend to take more time but when combined with other chemicals or elevated temperatures they can be made ineffective.

Commonly used biocides

A commonly used oxidising biocide is sodium hypochlorite, also known as chlorine bleach. The bleach causes different proteins in the microbe's cells to group together in such a way that they become useless. Proteins are needed for almost all cellular function; the proteins that bleach acts upon are usually needed for growth and reproduction and protein denaturing takes place within moments of contact.

Even though sodium hypochlorite is a relatively quick killing treatment, it also does not have persistence in treatment. Once exposed to the open environment, it depletes rapidly. This rapid depletion of activity means it may not have the ability to make contact with the entire population in a given treatment. Field dosages can be as high as 500 - 1000 ppm and still not be able to consistently hold microbial populations in check. The oxidative properties, particularly at the elevated dosages, increase the corrosive issues within any system, but especially stainless steel.

2,2-DiBromo-3-NitriloPropionAmide (DBNPA) is typically considered to be the fastest acting biocide. Even with as little as 10 minutes of contact time, the log reduction of bacteria counts can be significant. However, any biocide showing log reductions within four hours of contact time is sufficient to protect a system. DBNPA,

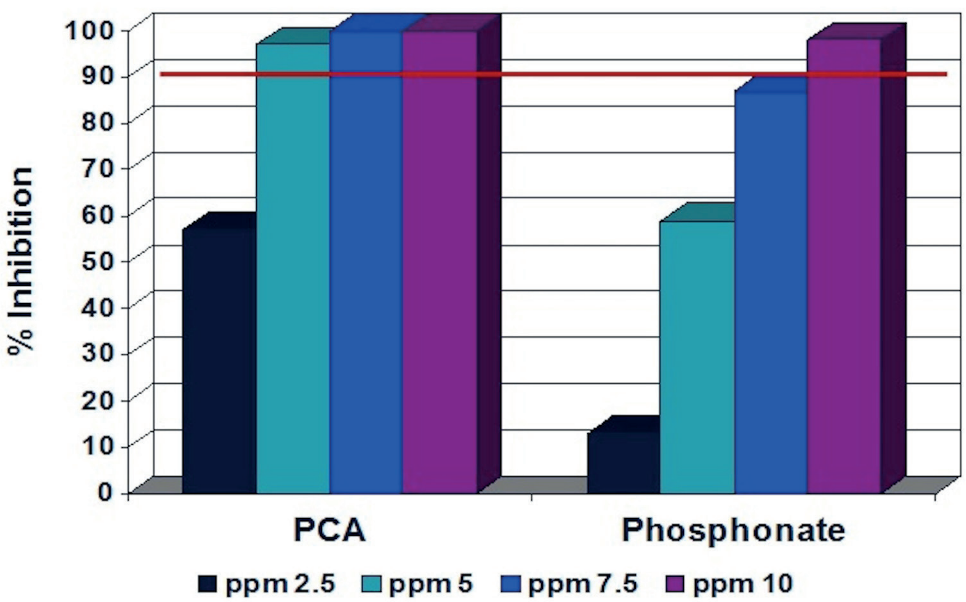

Figure 1. *Graph demonstrating that even at low dosage, polymers (e.g. PCA) are able to achieve inhibition at or above 90% in threshold inhibition testing.*

Table 1. Comparison of commonly used biocide programmes.

	2.5% TTPC/2.5% Polyquat	75% THPS	20% DBNPA	25%Glut/12% DiDAC
Dosage	250 ppm	300 ppm	200 ppm	250 ppm
Use cost	1x	1.2x	1.1x	1.25x
Kill speed	Fast	Slow	Fast	Fast
SRB performance	Excellent	Poor	Good	Good
Biofilm removal	Excellent	Poor	Poor	Good
Thermal stability	Very stable	Unknown	Poor	Breaks down
Persistency	>28 days	<7 days	<7 days	<7 days
Safe handling	Excellent	Average	Extremely poor	Poor
Gel breaker/ compatibility	Excellent	Deleterious	Poor	Deleterious
Reducing agent compatibility	Excellent	Excellent	Deactivates	Not compatible

like bleach, degrades very quickly. Additionally, it has a significantly higher health risk than other biocides. Safety is always a concern for everyone and it is important to be aware that oxidisers in general are more of a risk than non-oxidisers.

Chlorine dioxide ClO_2 is also an oxidising biocide that can be applied in a variety of situations. Thought it has been around for some time, in the past few years it has growing in popularity because of the relatively low cost and quick kill of microbes and algae. The process for making the gas onsite does have some risks. If the unit has a failure, there is potential for severe injury. Also like other oxidising biocides, they fail as temperatures exceed 80˚C and have compatibility issues with other common chemistries.

Acrolien has been starting to gain some attention because of its high efficacy in APB and SRB killing abilities. It is an extremely reactive chemistry and kills quickly, while having good biofilm removal. It also poses a high risk mitigation system be in place for the environment as well as potential contact with people.

Glutaraldehyde has been a very commonly used biocide in the field for almost half a century. It does an average job in eliminating APBs and SRBs in a system and at a relatively low cost. It is a formaldehyde-releasing chemistry and cross links proteins as a killing mechanism. As such, it has a lot of compatibility issues with amines in a system or any type of halogen. If a gel system is being used, glutaraldehyde is actually deleterious to the system. It lasts in a system longer than halogens, it also does not have extended thermal stability in systems. It is often found in combination with quaternary style biocides, but usually the quaternary biocide is doing most of the work, especially once downhole.

Tetrakis hydroxymethyl phosphunium sulfate (THPS) is often listed as a corrosion inhibitor for application purposes, though it is also used as a biocide. It provides some advantages, like most quaternary biocides, in corrosion inhibition, but also some iron sulfide scavenging. However, this is a very slow acting biocide. Like glutaraldehyde it is deleterious in gel systems and is not overly compatible with commonly found other chemistries such as anionic friction reducers. It is not a very good biofilm remover despite the improved thermostability over glutaraldehyde.

Alkyldimethylbenzyl ammonium chloride (ABDAC) and didecyl dimethyl ammonium chloride (DiDAC) are two commonly used quaternary ammonium chloride biocides. This quats are typically slower in initial kill time compared to oxidising biocides, however, they do typically achieve some levels of kill within four hours of contact time. DiDAC tends to be a little more stable and compatible then ABDAC. They are decent in controlling APB and SRB levels and have biofilm removal properties as they are surface active biocides. They kill by disrupting the cellular wall. They have a nitrogen core and this does lend itself to some foaming tendencies. There are many different blended concentrations utilising these quats with glutaraldehyde with a 2 glutaraldehyde to 1 quat being very common.

Tributyltetradecyl phosphonium chloride (TTPC) has a phosphonium core unlike the ABDAC and DiDAC, so it has a lower foaming tendency. It performs very similarly to the other quats with better thermal stability and persistency in systems. It tends to be tolerant of extreme environments such as temperature and pressure. It does not have fast performance in high TDS levels but can overcome it eventually with time or with a higher dosage.

Polyquats are also used in oil and gas. Again these types of quats perform similarly as others, but usually not as well in some of the more extreme conditions that TTPC and DiDAC can handle.

Combining biocides

Combining biocides into a dual application system has been growing in popularity. Though glutaraldehyde and quats have been used in combination for some time, those combinations have been really driven to lower costs with some lower efficacy ability as a trade off.

Looking to combine oxidising and non-oxidising biocides also achieves this but without losing efficacy. Additionally, there is not typically a lower compatibility issue either with these types of combinations. The reduction in dosing of both types of biocides, when the correct combination is selected, can sometimes be over 10 fold. This allows for a quick kill biocide treatment that also preserves.

With all of the wells that are currently being capped or that have been capped for some time, it is extremely important to apply a biocide programme and not just the cheapest out on the market. Other biocides that have been used in oil and gas are isothiazolone (and its versions), dazomet, MBT, CTAC and tris nitro. In general these biocides are used in water treatment but are not overly effective for use in oil and gas, which is why they have a relatively low use. However, during downturns in the market, they gain market share because of the very low costs. Typically these are used when a producer wants a biocide applied but has not specified what to use. It is an immediate cost cutting measure that provides little-to-no treatment. The funds spent could be better used in a combination treatment to deliver a better return on investment.

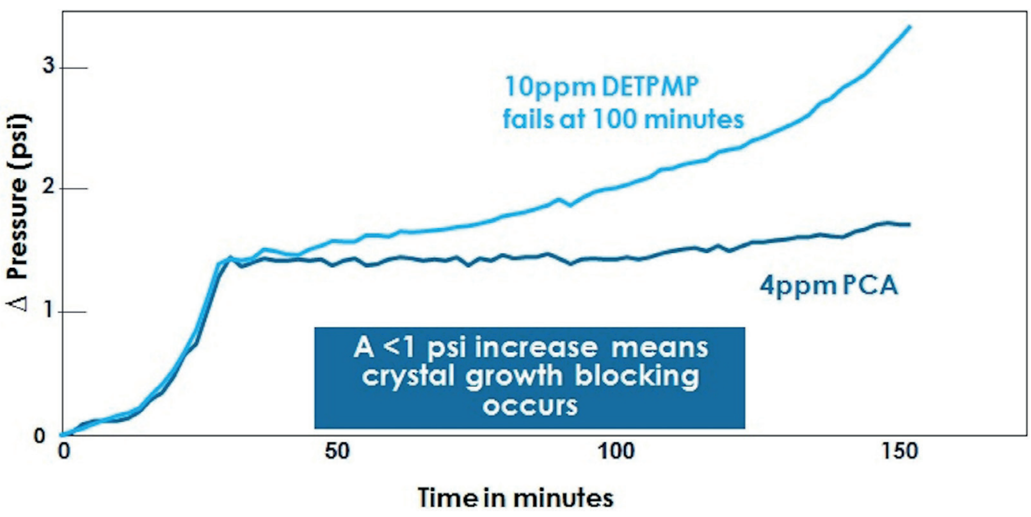

Figure 2. *Chart demonstrating that 10 ppm of phosphonates will fail before the commonly accepted 2 hour mark in a tube block test, whereas the polymer (e.g. PCA) easily surpasses this time frame. Scaling was induced for 30 minutes before adding the chemicals to demonstrate growth blocking. A delta of less than 1 psi for over 120 minutes from the kick off point indicates successful growth inhibition.*

BWA Water Additives
Tel: +1 678 802 3050
Email: americas@wateradditives.com
Web: www.wateradditives.com