Few things are certain in the oil and gas industry. Prices, profits and prospects are easily affected by the health of the global economy, politics, taxes, regulations, extreme weather and more. Even with an increase in oil prices, companies are still not profiting as they would hope to from hydraulic fracturing. So, it is understandable that operators continue to look for cost-saving advantages.

Unfortunately, some cost-cutting measures can place entire wells at risk. This is especially true when it comes to the selection and use of biocides. Every operator and completion engineer is aware of the water-intensive nature of their work, but not all fully understand the ongoing threat and impact of microbial contamination. Uncontrolled microbial proliferation can negatively impact production rates, asset integrity and even the quality and market value of hydrocarbons (Figure 1).

Crucially, an effective biocide programme is a relatively small investment, typically less than 0.5% of overall fracturing operation costs. Careful, intelligent selection and deployment of registered biocides for every phase of hydraulic fracturing – preparing the water topside, decontaminating the well, and protecting the reservoir – enhances production and protects...
hydrocarbon quality over the entire lifecycle of a well. Therefore, it is important to understand the difference between the cost of any single biocide versus the total cost to treat a well. Confusion over this difference has led to troubling trends.

**Less is not more**

There are three aspects of the ‘less is more’ trend being witnessed at fracturing sites today. First is the notion that the least expensive biocide option – in particular, chlorine dioxide (ClO₂) and tributyl tetradecyl phosphonium chloride (TTPC) – will address all of a well’s microbial control needs. Second is the application of lower biocide doses. These two trends suggest that many operators do not fully recognise the value of an integrated biocides programme that goes beyond topside quick-kill treatments. There is no ‘silver bullet’ technology available that can provide microbial control during every phase of hydraulic fracturing operations (Figure 2).

The reason ClO₂ has such a short line on the efficacy chart is because it is a highly reactive, quick-kill, topside biocide that is rapidly consumed through chemical interactions with other frac fluid additives. This in turn leaves less ClO₂ to kill bacteria after its initial use. In addition, any ClO₂ residuals that remain quickly lose efficacy downhole because the chemistry is prone to degrading at high temperatures. It may be less costly, but ClO₂ is not a ‘silver bullet’.

Neither is TTPC, another popular biocide choice among the advocates of ‘less is more’. While its kill speed in topside applications is well known, the efficacy of TTPC is diminished by its incompatibility with proppants and anionic additives, such as friction reducers. TTPC also presents a foaming issue that can cause complications on the job site. Downhole, TTPC’s incompatibility with proppants remains an acute problem, but there are several other issues regarding its effectiveness. Most importantly, TTPC is a surface-active biocide that almost immediately adsorbs onto shale, causing it to lose efficacy quickly.

### Glutaraldehyde and glutaraldehyde-quaternary ammonium

Operators analysing Figure 2 may conclude that glutaraldehyde (glut) and blends of glutaraldehyde and quaternary ammonium (glut-quats) are ‘silver bullet’ biocides. Not quite, but these two biocides have become popular choices for good reasons. From topside to downhole, glut has proven to be one of the most versatile biocides available. It is efficacious throughout the preparation and decontamination phases, with short-term effectiveness as a protective biocide.

Glut-quat compounds provide a noticeable increase in kill speed, and they are widely used in hydraulic fracturing and other water-intensive applications. These synergistic combinations are highly effective in controlling bacteria, and are ideally suited to meet the diverse demands of most oilfield applications.

The efficacy of glut-quats was a driving force behind the development of the AQUCAR™ 714 water treatment microbiocide, an aqueous biocide blend that combines the robust ability of glut and glut-quats. It is especially effective for controlling both slime-forming and sulfate-reducing varieties of bacteria in oil and gas operations. Glut-quat blends are noted for their ease of use in the field and for their ability to improve the performance of surface-active biocides. For example, foaming is reduced when compared to using a quat alone. Additional benefits of glut-quat biocides include efficacy over a broad pH and temperature range, greater operational sustainability, compatibility with the most commonly used frac fluid additives, enhanced production and cost effectiveness. A reduction in sessile microorganism populations – known to cause corrosion, reduce heat exchange efficiency and block the flow of hydrocarbons out of the reservoir – is also seen.

More recently, two advanced glut-quat products were launched, specifically designed for the cold-weather environments found in Canada and the Bakken and Marcellus Basins, among others. Winterised with methanol, AQUCAR™ TN 250 LT and AQUCAR™ 7140 LT water treatment microbiocides can help operators extend microbial control down to -40˚F. The former, when co-dosed with glutaraldehyde or 2,2-dibromo-3-nitrilopropionamide (DBNPA) can reduce and delay the impact of souring, microbial induced corrosion, biofouling and plugging. The latter is compatible with many fracturing fluid additives, making it effective in controlling slime-forming and sulfate-reducing varieties of bacteria.

### Unregistered, non-genuine glut and glut-quat biocides

A third aspect of the ‘less is more’ trend in oilfield biocides is the appearance of less expensive, unregistered, unbranded or falsely branded glut and glut-quat compounds in the market. It has become more common for unvetted vendors to offer smaller hydraulic fracturing operators cheap biocides. These vendors typically sell glut and glut-quat because of their popularity, and because they cost more than inexpensive quick-kill biocides, like ClO₂, and TTPC.

Of greater concern for operations is the fact that these vendors have been known to sell non-genuine products mixed with less effective aldehydes, such as formaldehyde or glyoxal, labelling the products falsely as glut. Now available worldwide, the risks are potentially high for workers and the environment when mislabelled chemicals – especially ones containing carcinogens – are handled. This is because non-genuine products may have significantly different toxicological properties over the entire lifecycle of a well.
properties that can harm workers and the environment, and they have been proven to fall short in both efficacy and sustainability.

Smaller operators can unknowingly fall prey to this emerging black market. With the goal to get wells into operation as quickly and inexpensively as possible, they may only know that glut and glut-quat are generally versatile and effective. Some may not even look at the label, ask where the biocide is made, or question whether it is registered. Some may only care about the low sticker price.

There are many dangers involved with trusting unregistered biocides of unknown origin – including their efficacy, safety and environmental impact. Therefore, it is critical that companies ensure they are using genuine glut that complies with approved safe-handling guidelines. It requires approximately one year for biocides to be tested and approved for use by the US Environmental Protection Agency (EPA) and Canada’s Pest Management Regulatory Agency (PMRA). In the US, biocides must be registered under the Federal Insecticide, Fungicide and Rodenticide Act (FIFRA), Section 40 CFE 152.15(a) as well.

Oilfield operators should also know that genuine glut is neither a carcinogen, mutagen nor a reproductive toxicant. It is readily biodegradable and does not bioaccumulate. DuPont Microbial Control has developed and validated new analytical methods to help oilfield operators distinguish genuine glut from non-genuine products. These methods include a field-deployable, easy-to-use test kit that provides rapid detection.

Without the confidence of a branded, registered, EPA- or PMRA-approved biocide, operators simply cannot be certain of a biocide’s content or safety. If it does not contain the indicated amount of glut or glut-quat, it may not provide the microbial control protection needed to keep operations going and protect hydrocarbon quality. Additionally, if it is a false glut containing aldehydes, it can be dangerous for operators to use and harmful to the environment. Finally, if the EPA or PMRA decides to audit a well, users of unregistered biocides may be subject to stiff fines and possible criminal charges.

Better outcomes
When it comes to oilfield biocides, ‘less’ almost always means less: less productivity, less asset value, less hydrocarbon value and less profits. Moreover, short-sighted decisions to cut corners without understanding the impact on operational efficiency can cost operators greatly. Despite the initial lower cost of CIO₂, TTPC and black-market biocides, fully-tested and registered biocides end up costing 10 – 50% less to control microbes over time, while protecting an operator’s investment. Buying from reliable, established biocide suppliers provides operators with technical expertise, integrated microbial control programme advice, regulatory assurance and assistance, and – ultimately – peace of mind.

By identifying key biocide trends in the oil and gas industry today – including demystifying seemingly effective, lower-cost ‘silver bullets’, discussing the impact of lower biocide dosing on operations, and creating awareness of the growing black market for unregistered products – key learning and best practices can be established to help operators address or avoid challenges, while moving forward with proven strategies that help increase well production and improve profitability in the long-run.