DUPONT™ CHLORINE DIOXIDE

ClO_2 WORKS IN THE OILFIELD!

ClO_2 WORKS IN THE OILFIELD!

Chlorine dioxide (ClO_2) is a powerful biocide that has been used commercially in the oilfield for over 25 years to control microbiological activity, prevent souring by H_2S and improve flow assurance. With the rapid development of unconventional shale gas and hydraulic fracturing, ClO_2 has emerged as a leading microbiological control technology for frac water disinfection.

ClO_2 is an optimal solution for on the fly treatment of hydraulic fracturing water because it:

- Is highly effective on both bacteria and spores
- Requires lower dosages than other technology
- Allows real time monitoring and control
- Has a proven and sustainable Safety, Health, and Environmental footprint

DuPont, a global provider of chlorine dioxide technology, is a proven leader in water disinfection and the safe application of ClO_2. With 60 years of global ClO_2 experience DuPont has been well positioned to meet the rapidly developing needs of this demanding application in the oilfield.

HIGHLY EFFECTIVE ON BACTERIA AND SPORES

ClO_2 is proven to be highly effective at killing both live bacteria and their spores. With the rise of hydraulic fracturing and its increasing water requirements, the need for improved microbial control in the oilfield has never been more important. Flow back and produced waters in many areas test positive for microbes and once sweet formation waters are becoming increasingly sour due to the presence of microbes. The sources of microbial contamination are diverse but there is no doubt that traditional microbial control programs are not eliminating all of the contamination concerns. The risk of microbial induced souring, accelerated corrosion and reduced hydrocarbon flow rates are very real and every effort to improve microbial disinfection needs to be evaluated.

Many microbes are spore formers and can survive in harsh environments, both on the surface and in the formation. Some are facultative organisms, which metabolize with or without combined oxygen. Many microbes can survive as spores and then be transported in equipment, piping, and waters that are moved from one field to another. Because the sources of microbial contamination are diverse, the initial treatment focus needs to be on what can be controlled. Because fracturing activities are purposefully intrusive, it is clear that the focus should be to maximize the microbial control of surface operations to prevent future contamination of formations.

ClO_2 is best suited to accomplish this microbial control. Traditional oilfield biocides either do not affect spores[1], require exceptionally high concentrations (2% or greater), operate under very specific limited conditions, and / or require hours of contact time before deactivating spores. By contrast, ClO_2 deactivates spores[2] at much lower concentrations and with much less contact time. This means that when treating with ClO_2, disinfection can be completed within the residence time allowed for during fracturing surface operations.

Studies conducted by Taylor and Berg both support the use of chlorine dioxide to reduce or eliminate difficult to kill slime formers such as sulfate reducing bacteria (SRBs).[3,4] ClO_2 not only quickly and effectively kills SRBs but also oxidizes the H_2S they produce, reducing the sour in the formation water which further reduces corrosion concerns.

Downhole conditions impact the performance of biocides. Once inside the formation, dilution of all biocides will occur at some point. When dilution occurs, a less than lethal dose of biocide is being applied, reducing the killing efficacy, especially at the outside edge of the treatment zone.

For traditional biocides, this dilution effect allows development of biocide resistance or tolerance in the microbes that survive. Over time these survivors migrate back into the treated formation with the flow and are more difficult to kill next time. However, it is generally recognized that ClO_2 does not give microbes adequate time to shift their metabolic function in an attempt to survive; therefore, biocidal resistance is not an issues with ClO_2 treatment.

REQUIRES LOWER DOSAGE THAN OTHER TECHNOLOGIES

Chlorine dioxide is a highly selective and very rapid acting oxidant used effectively in a wide range of applications from drinking water to wastewater. It is important to emphasize that ClO_2 is different from other traditional oxidizers, such as hypochlorite. The concentration of the active hypochlorite solutions are pH-dependent and therefore effectiveness is pH-impacted. ClO_2 is a dissolved gas in solution and once formed its concentration and performance is not pH dependent. It is a neutral molecule giving it greater selectivity of reaction; therefore, it easily penetrates the microbial cell wall via diffusion and performs its oxidative function on the metabolic biochemical components of the microbe.

ClO_2, unlike other oxidizers, is actually used preferentially in highly contaminated water systems because it does not react with most organic contaminants in the water. In many applications this means it can be used before or after filtration to provide both oxidation and disinfection at lower dosages than required for other biocides. In industrial waste water applications, ClO_2 is typically applied at much lower concentrations than hypochlorite solutions. ClO_2 is used to oxidize large reactive organic molecules like phenols and may oxidize unbroken polymer gels found in flowback water.

In oilfield fracturing, the typical water disinfection dose with ClO_2 would be 100 times lower than the effective dose of traditional oil and gas biocides. This has both economic and sustainability implications. The selectivity and mode of action of ClO_2 make it uniquely suited to work at low concentrations and provide economic advantages over many traditional biocide programs.

REAL TIME MONITORING AND CONTROL

Inadequate microbial control has significant impacts on corrosion rates and creates both economic cost and sustainability concerns. SRBs are the primary cause of microbial-induced corrosion. Traditional biocide treatment methods for SRBs rely upon best guess application rates from previous field results, which are not adjusted for real time variation in water quality or chemical analysis.

ClO_2 is a rapid acting, oxidizing biocide, and as a result it can be monitored based on established residual analysis in "real time" to ensure the proper dose is achieved to meet the disinfection performance requirements in the water. It is generated on site, on demand, and dosed at the rate required, based on real time analytical feedback. Therefore, disinfection performance can be controlled, optimized, and customized to reduce costs and environmental impact.

PROVEN SAFETY, HEALTH & ENVIRONMENTAL FOOTPRINT

When properly generated and applied, ClO_2 does not form Absorbable Organic Halides (AOX) and does not contribute to the formation of Trihalomethanes (THMs). AOX and THMs are disinfection by-products (DBP's) associated with substitution reactions of halogens [Cl, F, Br] with organic molecules typically found in many waters. Care must be taken in drawing conclusions after reviewing literature references and studies around the performance of ClO_2, as all chlorine dioxide is not the same in quality. Unfortunately the generation of poor quality ClO_2 stock solutions can and has resulted in incorrect conclusions. As stated by Gilbert Gordon, "Impurities in the generator effluent can react with ClO_2 and substantially lower the concentration of stored ClO_2 or potentially form unwanted by-products."[5] Generation systems that have poor control in the lab or in the field can have un-reacted chlorine which can enter into substitution reactions generating low levels of AOX or THMs. DuPont offers chlorine dioxide generation systems that can be precisely adjusted to ensure that minimal to no excess chlorine is available, with a 95% to 98% yield efficiency.

ClO_2 by-products will ultimately revert to form sodium chloride (table salt) at levels which are insignificant when compared to the natural salt levels found downhole.

ClO_2 is also widely used in drinking water disinfection systems around the world and is approved for this use by the U. S. Environmental Protect Agency (U.S. EPA) and World Health Organization (WHO). ClO_2 is also approved by the U.S. Food and Drug Administration (FDA) for direct food contact in a wide variety of applications, which include poultry, red meat and fruit and vegetable sanitization applications.

The U.S. EPA regulates the use of biocides as antimicrobial pesticides. However, these regulations do not speak to the concept of "sustainability"[6]. Sustainability goes beyond minimal legal performance. When making choices one must evaluate the merits beyond the minimum requirements.

Companies are developing internal rating systems or scales to gage the environmental risk of a given chemistry for use in oil and gas operations. The use of DuPont™ Clorine Dioxide as a biocide for oil and gas operations has scored very well in these ratings systems. For example, in one large oil and gas service company's rating system, DuPont™ ClO_2 scores zero for environment risk in oil and gas operations which is the best rating possible. Additionally, ClO_2 is the primary treatment option in numerous municipal drinking water applications, which emphasizes the environmental benefits of this application. This is no real surprise given that ClO_2 is the primary treatment option in numerous municipal drinking water applications.

Using the precursor chemical, sodium chlorite, ClO_2 is produced on-site in a reactor. In addition to supplying the precursor chemical product, DuPont has over 40 years of experience providing engineering expertise to a broad range of industry around the globe for the efficient generation chlorine dioxide. Engineering expertise and practical application know-how are invaluable in providing reliable technology to complement other injection and dilution processes at the oilfield site. Not all biocide suppliers are able to match the combined engineering, chemical and microbiological depth brought by DuPont.

Every biocide technology carries with it certain risks and responsibilities. One responsibility is the reporting of Incidents to the Office of Pesticide Programs (OPP) of the EPA. Some in the industry have tried to portray ClO_2 as unsafe. All chemistries have hazards to respect and ClO_2 is no different. However, for comparison, over the 18-year period of 1992 thru 2010, ClO_2 had ~16 times fewer incidents reported than the most commonly used oilfield biocide over similar volumes shipped.

ClO_2 WORKS IN THE OILFIELD

ClO_2 is an economical, selective, rapid-acting oxidizing biocide that is well suited to microbial disinfection of hydraulic fracturing waters. Chlorine dioxide, used in fracturing water disinfection, is an effective and innovative technology shift from other established applications as well as an opportunity to greatly reduce the environmental footprint associated with traditional microbial biocides used in the oilfield today.

DuPont is a global provider of chlorine dioxide products and related technologies used in disinfecting, sanitizing, and odor control applications. DuPont provides chlorine dioxide technology solutions for a wide variety of markets, including oil and gas, and provides equipment and raw materials for our customers' use in producing chlorine dioxide. In particular, DuPont customers benefit from our deep expertise in chlorine dioxide chemistry, generation and application knowledge. Additionally, DuPont continues to lead the way for safe and consistent application of ClO_2 in the oilfield industry through the DuPont™ OXYCHLOR® Certified Partner Program.

ABOUT DUPONT

Founded in 1802, DuPont puts science to work by creating sustainable solutions essential to a better, safer, healthier life for people everywhere. Operating in approximately 90 countries, DuPont offers a wide range of innovative products and services for markets including agriculture, nutrition, electronics, communications, safety and protection, home and construction, transportation and apparel.

For more information, please visit the www.chlorinedioxide.dupont.com website.

The miracles of science™

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