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WATER MANAGEMENT

Singlet oxygen-generating treatment technology achieves sustainable operations, helps operators meet production goals

A new chemistry solution, first developed for the food and beverage industry, provides an environmentally safe and economical alternative for upstream water treatment without the hazards or cost of traditional oxidizers or conventional biocides.

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While water use has always been an issue, it was only in the late 1990s that unchecked water use in the oil field became a concern, with the industry competing with agriculture and cities for clean water supplies. Hydraulically fracturing shale formations brought the country energy independence, but it also highlighted the large amount of water needed to successfully execute the process.

In the last decade, this was further exacerbated by investors wanting greener, more environmentally friendly companies to invest in. The perfect nexus of environmental stewardship, innovative technology and good business practices brought scientists' thinking out of the box while adapting technologies from other industries.

Traditional water treatment. Microbial control has always been a primary concern for completion water. Water sourced from traditional water storage facilities, such as pits and ponds, requires effective microbial control prior to introduction to the wellbore, as this is essential for a healthy formation. Choosing the wrong solution for water treatment can result in expensive damage to equipment, a high bacteria load pumped downhole, and a potentially sour well.

Traditional oil and gas microbial treatment solutions can be divided into two types. One involves oxidizers that provide economical, fast bacteria control. However, many companies frown upon oxidizers, since the most common of them is chlorine dioxide, a volatile, flammable gas that presents significant exposure hazards to wellsite personnel and accelerates corrosion.

The second type includes conventional biocides and preservatives, such as glutaraldehyde (glut), quaternary ammonium compounds (quat), glut-quat blends and aldehyde-releasing compounds. These conventional chemistries provide a longer-lasting solution but are more expensive and slower-acting, and users cannot obtain immediate feedback on efficacy.

A new chemical oxidant technology, initially developed for the food and beverage industry, contains a 5.8% solution of sodium peracetate, formulated to deliver large concentrations of reactive oxygen species (ROS), which enhance product performance. This unique oxidant provides a safe, economical alternative for upstream water treatment without the hazards or cost of traditional oxidizers or conventional biocides. The new oxidant provides rapid treatment and can be combined with the complementary use of conventional biocides for long lasting results.

Originally developed for industrial water treatment, reuse and sanitization, this new oxidant technology was first proposed for the food and beverage industry, where it needed to clear numerous regulatory hurdles before adoption. However, a faster-to-market approach was provided by early adopters in an industry typically not known for fast adaptation of new technology: the oil patch.

Chemistry. At the well site, on-demand production of the new oxidant occurs by reacting three stable, non-flammable feedstocks together in a specific process to create the unique formulation. This formulation continuously transforms "activated" peracetate into a combination of reactive oxygen species (ROS), including singlet oxygen, which is molecular oxygen in an excited state. Formulated in water, the ROS "supercharges" the oxidative activity of the parent peracetate (without the use of light or catalysts for activation). The active peracetate-singlet oxygen solution is generated on site, due to its short half-life (approximately 1.5 hours (hr) for concentrate), in contrast to chlorine dioxide that is generated on site, because it's too dangerous to transport.

The combination of reactive oxidizing species provides enhanced performance while generating a significant oxidation-reduction potential signature that can be monitored and correlated to concentration or efficacy in a treatment process. By its nature, singlet oxygen is short-lived in water and reacts quickly with certain kinds of materials but not with others. This unique selectivity, in comparison to hydroxyl radical, ozone or chlorine, allows it to do specific jobs in the presence of materials, including salinity, oil, polymers and numerous water treatment chemicals. This allows you to selectively target the oxidation of unwanted materials. You do not necessarily want to break down everything that is in the water; for example, a friction-reducing polymer necessary for a successful frac treatment.

Since this new treatment technology is primarily a dilute solution of a peracetate salt, it is an inherently safer oxidation chemistry that is essentially non-volatile and odorless. The peracetate-singlet oxygen solution is dosed into the water stream, automatically, at the prescribed proportion for the current flowrate and water quality, based on data from in-line flowmeters and oxidation reduction potential (ORP) sensors. Oxygen is slowly released from any unconsumed oxidant, leaving non-toxic, biodegradable residuals that are generally recognized as safe (GRAS designated by the FDA).

Laboratory testing. The selective reactivity of peracetate-singlet oxygen chemistry is beneficial for avoiding corrosion and degradation of equipment and materials. The inherent selectivity makes the chemistry less aggressive toward sensitive metals, polymers and elastomers. Extensive lab testing established the selectivity of the formulation to target contaminants over other materials.

A recent study compared the corrosion rates between the standard benchmark of dissolved oxygen (DO), chlorine dioxide, a peracetic acid product and the peracetate-singlet oxygen formulation at similar active oxidant concentrations. Relative comparisons were made under controlled conditions in temperature-controlled, circulating immersion baths equipped with automated make-up chemical feeds in a laboratory setting.

Corrosion coupons prepared from high-pressure-pumping pipe sections were provided by a third-party oilfield services company. Three coupons, representing three pipe types/alloys, were designated by a coating color on

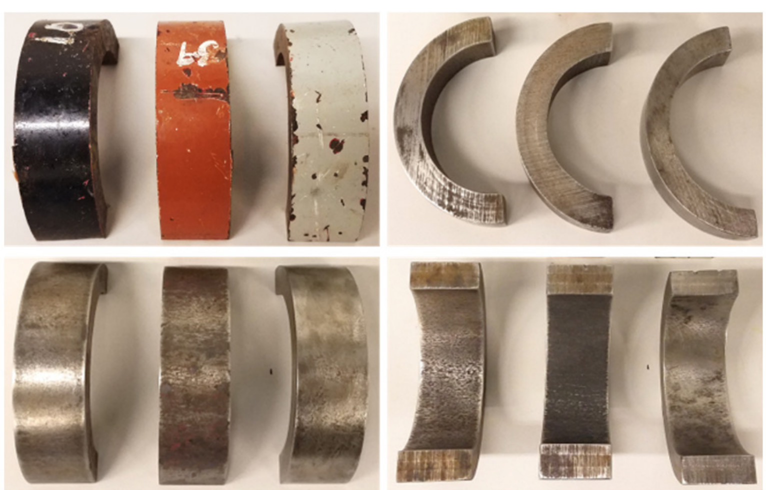

Fig. 1. Three coupon types tested: before preparation (top left panel) and after preparation.

Fig. 2. Coupons after 400 hr of exposure prior to cleaning. Black, brown and grey types, left to right. Dissolved oxygen (top row). Peracetate-singlet oxygen (second row), chlorine dioxide (third row), peracetic acid (bottom row).

Table 1. Corrosion reduction in steel alloys, using peracetate-singlet oxygen

	Corrosion range	Condition
Air exposed coupons	2.3 to 3.1 mpy (0.094 to 0.13 lb/ft^2/yr)	Minor pitting
Peracetate-singlet oxygen	2.5 to 4.3 mpy (0.10 to 0.17 lb/ft^2/yr)	Minor pitting
Chlorine dioxide	14.0 to 15.4 mpy (0.57 to 0.63 lb/ft^2/yr)	Moderate to severe pitting
Peracetic acid	23.7 to 24.5 mpy (0.97 to 1.0 lb/ft^2/yr)	Severe pitting

the outer surface of the pipe (black, brown, and grey) and subjected to each test bath condition. One set of three coupons prepared for testing is shown in Fig. 1.

Three pipe types/alloys were selected and tested to compare corrosion rates, extent of pitting, and other behavior when exposed to 5% brine solutions containing oxidants in circulating immersion baths at 115°F. The control bath contained dissolved oxygen from air (average near 4.3 mg/L O2), while comparisons were made for the peracetate-singlet oxygen formulation (average near 10 ppm active peracetate), chlorine dioxide (average near 9 ppm active ClO2) and peracetic acid product (average near 8 ppm active PAA). Three coupon types were thoroughly cleaned and exposed to each of the three chemistry conditions for a total of 400 hr.

During the tests, the air exposed coupons passivated with ferric oxide mixed with a thin layer of mineral scale, while the peracetate-singlet oxygen formulation-exposed coupons passivated with ferrous oxide mixed with a thin layer of mineral scale. The ClO2 and PAA exposed coupons did not passivate significantly and experienced the most severe corrosion. After 400 hr, the coupons were cleaned to remove iron oxides and scale deposits, measured for weight loss, and evaluated for pitting. The results are shown in Fig. 2 and Table 1.

Testing has shown that peracetate-singlet oxygen, when compared to other oxidizing water treatment technologies, effectively reduces corrosion in steel alloys used in pressure-pumping equipment for hydraulic fracturing operations, Table 1.

WELLSITE TREATMENT

Water treatment for hydraulic fracturing. Untreated water laden with bacteria can cause problems in the formation and with the equipment. If left untreated, the bacteria will multiply downhole, thus increasing the problems. A

Table 2. Peracetate-singlet oxygen risk vs. traditional water treatment options

	HIGHLY CORROSIVE	OXIDIZING HAZARD	FLAMMABLE	ENVIRONMENTAL HAZARD	IRRITANT, ACUTE TOXICITY	TOXIC
Peracetate-Singlet Oxygen	—	—	—	—	—	—
Chlorine Dioxide	X	X	X	—	X	X
Peracetic Acid	X	—	X	X	X	—
Chlorine Bleach	X	—	—	X	—	—

During actual application, peracetate-singlet oxygen technology provides lower risk compared to traditional water treatment options.

peracetate-singlet oxygen chemistry treats water used during hydraulic fracturing, so the water does not contain bacteria that can contaminate the formation or damage equipment. Water is treated on the surface prior to the frac job. The supply reservoir can also be treated for faster, more persistent bacteria control.

Produced water treatment for reuse. Ideally all produced water—water returning back uphole after the frac treatment—should be treated for reuse on the next frac job. Peracetate-singlet oxygen chemistry provides microbial control to treat water produced by the frac treatment, removing microbes and other contaminants from downhole, so they are not introduced into another well.

Water treatment prior to injection. A third, lesser use involves treating produced water before it is injected in saltwater disposal wells (SWD), Table 2. Peracetate-singlet oxygen chemistry can remove bacteria from wastewater before it is injected in saltwater disposal wells. Bacteria can cause corrosion and souring in the SWD system, necessitating equipment repair and replacement.

During actual application, peracetate-singlet oxygen provides lower risk, compared to traditional water treatment options. (Hazards showing empty cells in the table are not applicable to the listed chemical.)

CASE HISTORY

A major E&P operator, working from a multi-well horizontal pad in the Permian basin, identified a problem with high amounts of corrosion on its service provider's frac iron, causing frequent equipment repair and replacement. Clean Chemistry was engaged to confirm the cause of the corrosion and the relation to the water quality being used. It was found that the chemistry being pumped caused a lower pH in the fluid and was a factor leading to the corrosion. Additionally, chemical residue left after the treatment caused corrosion. The company recommended a treatment program of its proprietary formulation of peracetate-singlet oxygen, along with an advanced wellsite dosing skid containing internal software to improve service quality with leading accountability and data transparency.

This alternative resulted in a safer, more effective water treatment program for both efficacy and cost to the operator. The client's previous frac program used water treatment with peracetic acid rates of 100 or more ppm concentration of active ingredients. The product decreased the active product use to 15 to 20 ppm and achieved better results that retained the pH level of frac treatment water, left no detrimental residual chemical amount, and reduced equipment corrosion. It also helped maintain the performance of the friction reducer.

Results were enhanced by an onsite dosing skid more advanced than current competitor units. The onsite dosing program uses proprietary software for automated onsite generation and introduction of the chemistry into the water stream. Service quality is enhanced by an array of inline sensors that provide instant data for elite-level service quality. Key performance indicators are monitored in real time by a 24/7 dedicated quality team to ensure job performance is maintained, and operations run smoothly throughout the job.

The result was less repair and replacement of frac iron, as well as effective, quality water treatment. Cost savings were also realized by using a safer, more effective chemistry for water treatment. The client was satisfied with the results and plans on using this solution for other wells in the area.

BENEFITS

A scarcity of clean, fresh ground water will only become more acute in the future. Reducing freshwater use at the wellsite will remove competition with agriculture and municipalities for this valuable commodity. Benefits will also be achieved through equipment protection, decreased costs and environmental protection, plus the added benefit of no residual effects.

Asset protection. Better microbial control reduces equipment contamination and corrosion that can lead to costly equipment repair or replacement. This is especially true during frac treatments, where harmful ingredients in the water can contaminate the large amounts of iron, pipe and casing that are exposed to the water. The new chemistry also removes biofilms that can clog injectors on waterfloods.

Wellsite economics. Lower amounts of produced water injected into disposal wells will decrease associated transportation costs. This includes the actual transportation costs (trucks or pipelines), the injection process and regulatory and permitting costs. The process lowers toxicity levels of treated water and removes contaminants that can quickly clog disposal wells.

Environmental. The new process does not contain chlorine, chlorate, chlorite, chloride, sulfate or phosphates. It contributes less organic carbon than peracetic acid and avoids formation of trihalomethanes (THM), haloacetic acids (HAA) or other toxic halogenated organics. These attributes ensure lower environmental impacts and help to meet limits on salts, phosphorus, BOD and disinfection byproducts.

Fig. 3. Innovative trailer-mounted treatment unit.

Table 3. Trailer specifications.

Trailer dimensions	8 ft x 20 ft
Chemical pump rate range (per pump)	0.5 gpm @ 125 psi 0.8 gpm @ 100 psi 1.5 gal/min @ 50 psi
Power requirements	25-kW generator 30 and 50 A connections
Pump configurations (eight total pumps)	2 to 4 peracetate-singlet oxygen 4 to 6 other chemicals or additives
Treatment capacity	200+ bbl/min

No residual effects. Any residual material is readily biodegradable and is not persistent in the environment. According to the FDA designation, the residual material is generally recognized as safe (GRAS). It does not directly form toxic halogenated, chlorinated byproducts from water treatment, especially in drinking water.

Singlet oxygen-generating treatment technology also can be adapted for use in paper mills, in water cooling systems and in the food and beverage industry.

TRAILER MOUNTED SYSTEM

A new trailer-mounted system, introduced in Q2 of 2023, provides a simpler, smaller equipment footprint, with less capital investment for water treatment to any project site regardless of location, **Fig. 3.** The enhanced trailer design includes a proprietary equipment package, while a standard design means the unit is easily manufactured to meet the demand of water treatment in any industry, **Table 3.**

The new mobile treatment trailer has several key features that enhance water treatment in the field, including:

Chemical dosing capacity. Chemical dosing pumps (up to eight) for oxidants, preservative biocides, scale inhibitors, clay control, surfactants and more. Chemicals can be dosed directly into the water stream, and the chemistry can be mixed to fit the special job requirements. Chemical rates and makeup can be changed to match changing job parameters or changes in the treatment plan. A single trailer unit can service zipper and simulfracs with high water use rates.

Automation. Inline quality sensors and pump flowmeters track quality and control precise chemical treatment. Dedicated flowmeters control and monitor chemical consumption.

Connectivity. Real-time reporting includes cloud-backed tracking of treatment performance data from inline water quality sensors, chemical generation statistics and automated daily reports.

Autonomous, remotely monitored operation. All Clean Chemistry water treatment trailers incorporate remote monitoring and control by QA/QC specialists. Specialists can intervene remotely for continuous treatment in case of system alerts and alarms. Currently, most trailers for frac-on-the-fly water treatment jobs are staffed, while most of the jobs for treating produced water are unmanned.

Simplified logistics and deployment. The new trailer-mounted system means jobs are more easily scheduled, and crews and trailer are kept busy. Units can pick up and go to the next location; maintenance is performed in the field. Units can be on site for as long as needed, from several weeks to several months. The trailer can be set up in as little as 4 to 6 hr, if necessary.

VALUE PROPOSITION

It is more cost-effective and sustainable to use recycled water, compared to acquiring fresh water and/or disposing of produced water. A sound water treatment program that can be used in any area negates the disparity of water cost in different regions. Water reuse lowers the cost of operations, so there is more budget to make water treatment more economically feasible. Peracetate-singlet oxygen is a safer, greener and more effective oxidation chemistry, compared to traditional oxidizers and preservative chemistries. **WO**

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