CONTINUOUS-DOSAGE CHLORINE DIOXIDE TREATMENT FOR OILFIELD WATERS:

COST-EFFECTIVE MANAGEMENT OF BACTERIA IN PRODUCED AND INJECTED WATER

GLOBAL
INDUSTRIAL
WATER

EXECUTIVE SUMMARY

The negative impact of anaerobic bacteria on oilfield profitability is significant, resulting in

- souring of recovered oil and gas;
- bacteriological contamination of produced water;
- creation of troublesome biofilm that decrease permeability;
- and the corrosion and scaling of oilfield equipment.

With a long history of use in municipal water treatment and food processing, chlorine dioxide is well known as a powerful biocide which is also safe and environmentally friendly.

The latest developments in large-scale, onsite production of chlorine dioxide make it possible to engineer continuous dosage of chlorine dioxide to oilfield produced water in general, and reinjected water in particular.

By using continual rather than burst dosage of chlorine dioxide in reinjected water, oilfield operators can now achieve highly efficacious management of anaerobic bacteria and improve oilfield profitability.

KEY CHALLENGE:
MANAGING ANAEROBIC BACTERIA THAT IMPACT OILFIELD PROFITABILITY

There are three types of microorganisms commonly found in water used in oil fields: algae, fungi and bacteria. Among these, bacteria present the most significant problems for oilfield operators.

Anaerobic and aerobic bacteria occur naturally in geological formations and are also added whenever water is injected during fraccing and when produced water is reinjected into wells. Dispersed oil, as well as gellants commonly added to frac fluids, also provide bacteria with a ready and highly nutritious food source.

Bacteria – or more precisely, the results of bacterial metabolism reacting with other oilfield chemistries – are harmful to the oil extraction process in several ways. This is primarily because they promote **corrosion**, increase **souring** and **scaling**, and decrease **permeability**.

Anaerobic bacteria:

A major impact on oilfield profitability due to corrosion, souring and decreased permeability

- Anaerobic bacteria create **biofilm**, thin layers of bacterial slime which attach to pipes, pumps, filters, heat exchangers, etc., used in oilfield systems. Biofilm impacts oilfield profitability by corroding metal pipes and fittings, fouling systems and impairing heat transfer. Biofilm also affects permeability by clogging the free flow of water, oil and gas in underground formations and filter systems. Bacteria living under the protective layers of biofilm are normally not affected by biocidal treatments commonly used in the oil industry.

- Anaerobic bacteria promote **souring**, as sulfate-reducing bacteria (SRB) are the primary producers of **hydrogen sulfide (H_2S)**. Reinjected produced water, with its high concentrations of biogenic hydrogen sulfide, effectively turn sweet oil sour. The effects of the souring process – in addition to **corrosion, excess solids and emulsion** – are that hydrogen sulfide must be removed from natural gas prior to sale.

Hydrogen sulfide gas: a toxic result of bacterial souring

- In addition to being highly corrosive, the hydrogen sulfide gas is also extremely **toxic**. Clear and colorless, hydrogen sulfide smells like rotten eggs at low concentrations (3-5 ppm). At concentration of just 150 ppm, however, hydrogen sulfide paralyzes the olfactory nerve. At concentrations above 700 ppm, it is rapidly fatal.

Scaling and rock plugging

- Anaerobic bacteria exacerbate **scale formation** in pipe and well systems. Waters high in sulfates, when injected into reservoirs, mix with barium and strontium to form supersaturated barium and strontium sulfate. As pressure decreases in the vicinity of production wells, precipitation occurs and scale is formed. The results are **clogging of production pipes and rock plugging** around the well.
- Iron-reducing bacteria (IRB), can make environments suitable for SRBs and often coexist with SRBs in complex relationships. IRBs react with iron, which is relatively insoluble, to reduce it to ferrous iron, which is soluble and easily reacts with organic compounds. The results are **corrosion of pipes, pumps and fittings.**

TRADITIONAL METHODS OF OILFIELD BACTERIA MANAGEMENT

Oil and gas producers are keen to reduce the levels of anaerobic and aerobic bacteria in wells, and usually do so by batch biocidal treatment of reinjected produced water.

Operators use a variety of biocides to manage bacterial growth downhole and at surface. These include acrolein, glutaraldehyde, quaternary amines, gaseous chlorine, chlorine dioxide and sodium hypochlorite solution. While these traditional methods help reduce SRBs, at least temporarily, they all have particular strengths and weaknesses relative to a wider range of issues that are relevant in evaluating oilfield biocides.

Constant or burst delivery makes a difference

Furthermore, traditional methods rely on bolus (batch) dosage rather than continuous dosage. This results in uneven levels of biocidal protection and necessitates reliable test procedures to indicate when retreatment is necessary.

Effective oilfield bacterial management has a range of success criteria:

One-off reduction of anaerobic bacteria: only one of several success criteria

- Overall biocidal efficiency against anaerobic and aerobic bacteria
- Direct reaction with hydrogen sulfide
- Ability to penetrate biofilm

- Prevention of scaling
- Converts ferrous iron to filterable ferric oxide
- Injection method - continuous or batch (bolus)
- Compatibility with other fracture fluid additives (for example, gellants, viscosifiers, friction reducers)
- Operational complexity: transportation, storage, manpower, training
- Environmental impact
- Costs (installation, operating, total costs of ownership)

Chlorine dioxide provides overall best-in-class biocidal protection

Table 1: Comparison of oilfield biocides

	Acrolein	Glutaraldehyde	Quaternary amines	Gaseous chlorine	Hypochlorite	Chlorine dioxide
Reacts with hydrogen sulfide	yes	no	no	no	yes	yes
Penetrates biofilm	no	no	no	no	no	yes
Converts ferrous iron to hydrogen ferrix oxide	no	no	no	yes	yes	yes
Human toxicity concerns	high	high	medium	high	medium	low
Environmental concerns	high	high	medium	high	medium	low

CHLORINE DIOXIDE FOR OILFIELD USE

Chlorine dioxide excels as an oilfield biocide, but has seen limited use until now

Despite being a highly effective biocide with definite environmental advantages, the use of chlorine dioxide in oilfields until now has been limited by two factors: difficulties in transporting chlorine dioxide to oilfields, and the costs of establishing and maintaining a chlorine dioxide treatment regimen.

Chlorine dioxide is a volatile gas that cannot be compressed or stored and is never shipped in its pure state due to the risk of explosion. In lower concentrations, however, such as those produced in onsite generation, chlorine dioxide is considered to be much safer than most alternatives.

Thus, chlorine dioxide for water treatment is always generated on site, and only in diluted form. In the past, this has meant that oilfield operators were dependent on mobile production units to create sufficient amounts of chlorine dioxide for bacterial management.

On site production of chlorine dioxide: three methods

There are three methods available for creating chlorine dioxide suitable for use onsite in oilfields. All three methods require setting up a mobile production unit on site, and all produce chlorine dioxide suitable for "bolus", or non-continuous injection.

Three-chemical method:

- Inputs: hydrochloric or sulfuric acid, chlorine gas or sodium hypochlorite, and sodium chlorite
- Advantages: Capable of high volumes; lowest capital investment
- Disadvantages: Risk of exposure to acids and chlorine gas which are highly toxic, corrosive and require special transportation, storage and trained operators ; produced chlorine dioxide has low ph levels that can cause corrosion. Large quantities of chemical and multiple storage vessels are required for this process, in excess of 15 lbs. chemical per lb. ClO_2 produced.

- Two-chemical method:

- Inputs: hydrochloric or sulfuric acid, and sodium chlorite
- Advantages: Capable of high volumes; next lowest capital investment
- Disadvantages: Risk of exposure to acids and chlorine gas which are highly toxic, corrosive and require special transportation, storage and trained operators ; produced chlorine dioxide has low ph levels that can cause corrosion. This method has the second highest consumption of chemical per unit of ClO_2 produced.

One-chemical method:

- Inputs: sodium chlorite (electrolysis)
- Advantages: Produces a very pure form of chlorine dioxide; simple logistics – just one, safe ingredient that can be stored easily; produced chlorine dioxide is ph neutral; best suited for continuous treatment; capable of high volumes, as low as 6.3 lbs. chemical consumed/ lb. ClO_2. This dramatically reduces transportation and storage requirements vs. the competing technologies.

One-chemical method presents the most advantages for oil producers

- Disadvantages: Higher initial capital costs

While the bolus method is highly effective in temporarily controlling underground bacteria, it lasts only as long as the concentration of chlorine dioxide remains at a sufficient level. This presented oilfield operators with three problems:

1. The effects of the bolus wear out with time. Production variables and off-gassing make it difficult to maintain effective levels of chlorine dioxide in wells over a longer period. Failure to maintain continual levels of biocide in the well allows the dead bacteria to be consumed as food by surviving organisms, accelerating the creation of biofilms and bacteria due to the lack of growth controlling bioicide.

Previously, wider oilfield use of ClO_2 was prevented by the difficulties and costs of using the bolus method

2. Costs were too high. The expense of transporting, setting up and operating a mobile production unit to deliver a burst, or "bolus", of chlorine dioxide to distant oilfields was multiplied by the fact that the procedure has to be repeated numerous times over the life of the oilfield, and not always on a predictable basis.

3. Oilfield operators who wanted to use chlorine dioxide had to depend on outside suppliers.

Overall, oilfield operator experience with the bolus method of chlorine dioxide bacterial management was often either wide variations in bacterial levels, with concomitant problems with souring and corrosion, or unpredictable costs.

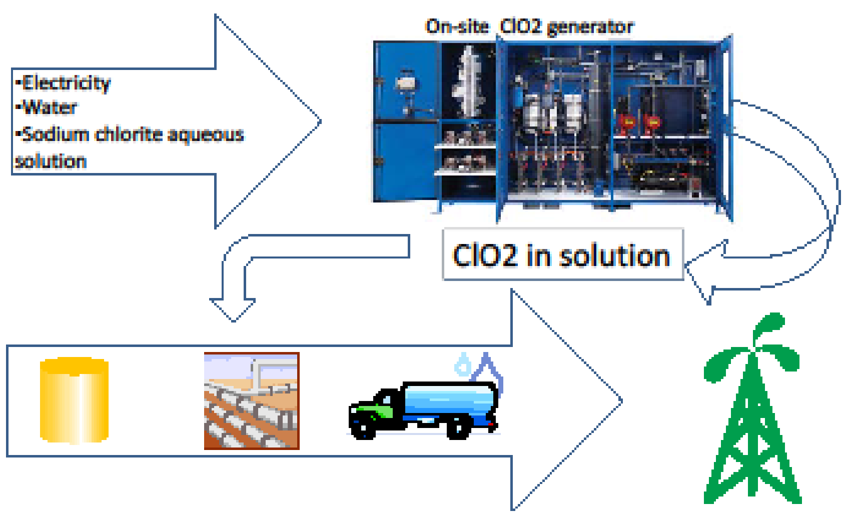
New: Continuous ClO_2 dosage in oilfields

Continuous dosage of chlorine dioxide in the petroleum industry is relatively new, and has only become feasible since a new generation of containerized chlorine dioxide generators, capable of producing 100 lbs or more per day has been developed.

The containerized production unit contains all equipment necessary to produce a consistent supply of chlorine dioxide in remote locations.

Illustration 1: Schematic overview of onsite ClO_2 production

Continuous onsite ClO_2 generation depends on just 3 simple inputs



As illustrated above, the new generation of onsite chlorine dioxide production takes place in a containerized production unit with just three inputs: feed water, sodium chlorite liquid and electricity.

Feed water quality is not critical, as the unit includes particle filters and a high-capacity reverse osmosis purifier. Sodium chlorite powder can be trucked to the site in bulk tankers or totes. Electrical requirements are 3 phase, 480v.

The onsite unit produces chlorine dioxide in a 25% or 31% dilution. This chlorine dioxide solution is then added to produced water – either in reservoirs, pipelines or tank trucks – before being reinjected into wells.

ENVIRONMENTAL IMPACT

Produced water is, without comparison, the single largest waste product associated with the exploration for and production of oil and gas.

Produced water: a growing environmental challenge...

In a young well, the amount of produced water is low and oil production is high. As time goes on, this ratio changes, as oil production decreases and water production increases. Worldwide, the ratio of water to oil is estimated to be between 2:1 and 3:1. In the US, where many wells have already matured past peak production, this ratio is 7:1 on average, and even reaches 50:1 in many older wells.

It is estimated that in the US alone, oil and gas wells generate approximately 15-20 billion bbl (barrels; 1 bbl = 42 U.S. gallons) per year. The rest of the world produces more than 50 billion bbl annually.

...facing increased scrutiny from EPA and other regulators

The treatment and/or disposal of such massive volumes of produced water has major environmental consequences that are coming under increased scrutiny by the EPA and other regulatory bodies.

Reinjection of produced water is commonly seen as the disposal method with the smallest environmental impact. Since reinjected produced water is often treated with a biocide to manage bacterial growth in the reservoir, the environmental effects of biocides used in produced water are also coming under increased scrutiny.

Produced water is often used in hydraulic fracturing. Because hydraulic fracturing is used in many coal bed methane (CBM) production areas, and because most CBMs are fully or partially located within areas that are designated as having groundwater suitable for human consumption (Underground Sources of Drinking Water, or

USDWs) by the EPA, the public focus on fracking fluids and how these might affect USDWs is expected to increase in the future.

CHLORINE DIOXIDE IN BRIEF

In concentrated form, ClO_2 cannot be transported and is thus always generated on site

Chlorine dioxide (ClO_2) is a gas that is well known as powerful disinfectant in municipal water treatment facilities and in food processing industries. It is also used industrially for bleaching wood pulp and flour.

The chlorine dioxide molecule is relatively small, volatile, and very energetic. It is stable in dilute solution, but unstable in concentrated form. Thus, chlorine dioxide is almost always used as a dissolved gas in water in concentrations that range from 0.5 to 10 grams per liter. Because transportation of concentrated chlorine dioxide is not safe, chlorine dioxide is almost always produced on site.

Chlorine dioxide differs from chlorine and other oxidizing biocides in that it doesn't hydrolyze in water. ClO_2 remains a true gas in solution, allowing it to be used at lower concentrations with a higher level of efficacy. This small molecule penetrates the biofilm wall where it degrades to two salts, chlorite and chlorate. When the chlorine dioxide/ chlorite has penetrated deep enough into the biofilm, it encounters acidic hydrogen sulfide, which reacts with the chlorite to form new chlorine dioxide, inside the biofilm. This action/ reaction with the chlorine dioxide degrading then being reformed into new ClO_2 inside the biofilm is the process that makes ClO_2 the best possible solution when dealing with biofilm issues. When the biofilm has been eliminated, a clean surface will be left behind; should a biofilm get a start, the residual chlorine dioxide at low concentrations will ensure its control.

ClO_2 is highly stable in aqueous solution, making it ideal for oilfield use

A safe biocide with a broad range of applications

ClO_2 is a highly effective biocide that kills bacteria, viruses, algae, fungi and protozoa.

Used properly, ClO_2has little or no effect on humans, animals or fish cells and is safe to use. For example, ClO_2 has been approved for use in the processing of USDA organic and kosher foodstuffs.

A powerful yet safe disinfectant and biocide

ClO_2 is unsurpassed in disinfecting throughout a water system – also in "dead end" areas. For this reason, ClO_2 is often used to disinfect both municipal water systems as well as water systems in hospitals, where germs such as Legionella can prove to be stubbornly resistant to other biocides, chlorine in particular.

Furthermore, chlorine dioxide does not affect taste or form toxic chloramines or haloforms (THM).

Chlorine dioxide is neither chlorine nor chlorine gas

Though similar in name to the element *chlorine*, the compound *chlorine dioxide* (ClO_2) has very different properties and applications.

Importantly, chlorine dioxide is highly soluble and is stable in dilute aqueous solutions. In fact, a key advantage of chlorine dioxide for the oil industry is its high solubility in water. Chlorine dioxide is approximately ten times more soluble in water than chlorine.

Other key differences between chlorine and chlorine dioxide are:

- $ClO_2$is a more effective biocide than the chlorine.
- Unlike chlorine or other oxidants, ClO_2penetrates biofilm and is effective in disinfecting organisms under this. (delete? Stated above)
- ClO_2 is effective at much lower concentrations than chlorine: just <5 ppm
- Unlike chlorine, ClO_2maintains its molecular form in a broad pH range. ClO_2 works at pH 2-10, while chlorine loses its sanitizing ability >pH7.5
- ClO_2 does not form chloramines – as does chlorine
- ClO2 does not give off chlorine taste or odors

$ClO_2$is a more effective biocide than the chlorine – and differs in many ways

Continuous-dosage chlorine dioxide treatment for oilfield waters
September, 2009

• ClO2 is tolerant of high organic loads, while chlorine is rapidly consumed by organics

This white paper draws on information from:

The National Energy Technology Laboratory (NETL), part of DOE's national laboratory system (www.netl.doe.gov)

The Argonne National Laboratory's "A White Paper Describing Produced Water from Production of Crude Oil, Natural Gas, and Coal Bed Methane," by Veil, J.A., M.G. Puder, D. Elcock, and R.J. Redweik, Jr., 2004

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