

Chlorine Dioxide

Impacting and Reducing Microbial Induced Corrosion

ICoTA Roundtable Presentation
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remote

Extending Life of Coiled Tubing

- Throughout operations success can be measured by extending fatigue life of coiled tubing
- Primary consideration is made for metallurgy selection, pressure during operating conditions, and fluids management
- Localized damage is not always mechanical in nature but biological make-up of the fluid will also lead to string failure causing microbial induced corrosion



Water Resources

- Fresh water is very abundant in Canada but not always accessible
- Produced water is wastefully sent to disposal at higher costs than biocide treatments
- Produced water needs to be stored to have enough volume for large scale completions, creating lots of time for biofilms to form
- Risk of using produced water creating hydrogen sulfide from sulfate reducing bacteria (SRB) and harboring iron sulfide, etc.

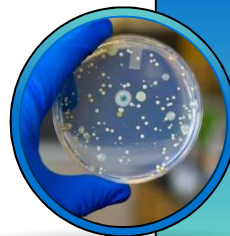


Chlorine Dioxide Applications



Municipal Water

- Potable water disinfection
- Wastewater oxidation
- Flume water



Microbial Control

- Process water microbial control
- *Legionella* control
- Mollusk control
- Paper slimicide
- Zebra mussel control



Odor Abatement / Control

- Rendering odor control
- Wastewater deodorization
- NOx oxidation
- SOx oxidation



Food & Manufacturing

- Hard surface sanitizer
- Fruit & vegetable processing
- Brewing & beverage
- Ethanol fermentation



Industrial Utilities

- Oil & gas hydraulic fracturing
- Cooling tower
- Ammonia plants
- Pulp bleaching

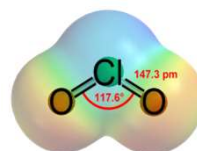


Industrial Process Waters

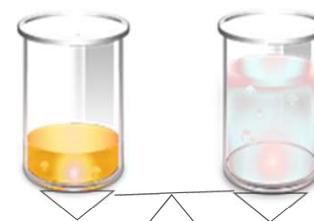
- RO membrane
- RO/NF/UF/MF



Chlorine Dioxide Properties



2.4x heavier than air



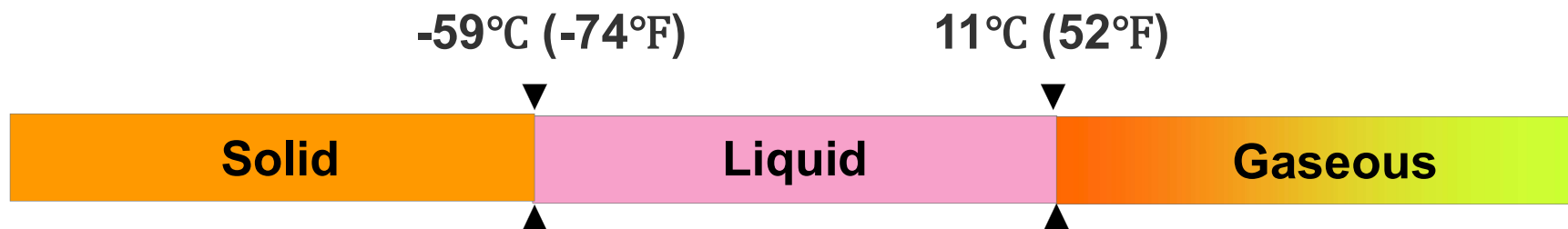
Chemical Formula: ClO_2

Molar mass: 67.453g/mol

Molar absorptivity (360nm): 1250 (M-cm)⁻¹

Specific Gravity of liquid at 0°C: 1.64

Odor Threshold is 0.1 ppm

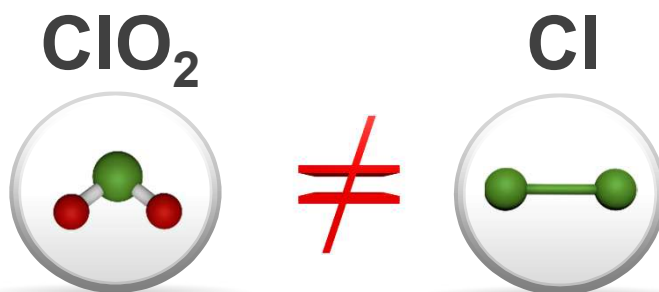


Chlorine Dioxide Properties

CHLORITE + BLEACH + ACID

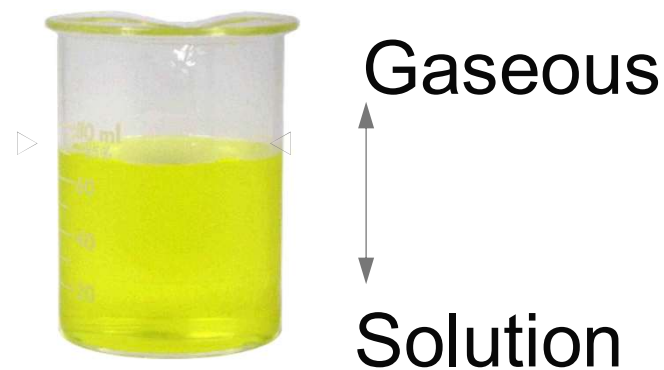
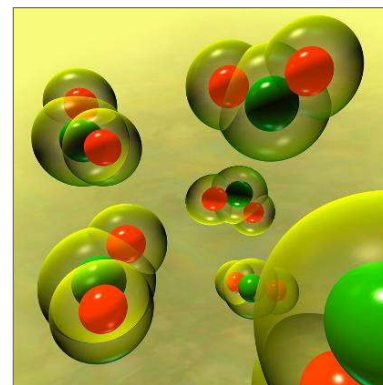


While Chlorine Dioxide (ClO_2) has Chlorine in its name, its chemistry is radically different than elemental chlorine. One atom makes all the difference.

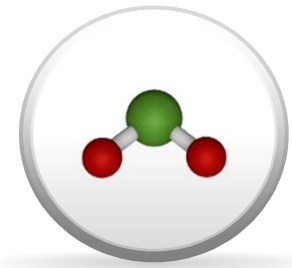


Chlorine Dioxide Properties

- Exhibits a yellow-green color, becoming more red as concentration increase
- Effective over wide pH range (2-10)
- Has an odor similar to chlorine
- Highly soluble in water
- Selective Oxidation
- Selective Rapid Reaction



Coiled Tubing Applications



- Small dose chemical requirements
- Low residual does not interfere with other chemistries
- Generated on-the-fly for real time disinfection
- Reduce microbial influenced corrosion on equipment and tubulars
 - Oxidizes Iron Sulfide (FeS)
 - Oxidizes Hydrogen Sulfide (H₂S)
 - Penetrates & Removes biofilm
 - Kills Bacteria (SRB, APB, IRB)



Oxidation Potential

Chlorine Dioxide mild oxidizer and powerful biocide

Standard Oxidation Potentials of Various Oxidants

Oxidant Species Capacity	Formula	Oxidation Potential Eo(Volts)	Oxidation
Hydroxyl free radical	OH ⁻	2.80	2e ⁻
Ozone	O ₃	2.07	2e ⁻
Hydrogen peroxide	H ₂ O ₂	1.76	2e ⁻
Permanganate ion	MnO ₄ ⁻	1.68	3e ⁻
Chlorous acid	HClO ₂	~1.6	4e ⁻
Hypochlorous acid	HOCl	1.49	2e ⁻
Molecular Chlorine	Cl ₂	1.36	2e ⁻
Hypobromous acid	HOBr	1.33	2e ⁻
Molecular Bromine	Br ₂	1.07	2e ⁻
Hypoiodous acid	HOI	0.99	2e ⁻
Chlorine dioxide	ClO ₂	0.95	5e ⁻
Molecular Iodine	I ₂	0.54	2e ⁻
Oxygen	O ₂	0.40	2e ⁻
Hypochlorite Ion	ClO ⁻	<0.50	2e ⁻



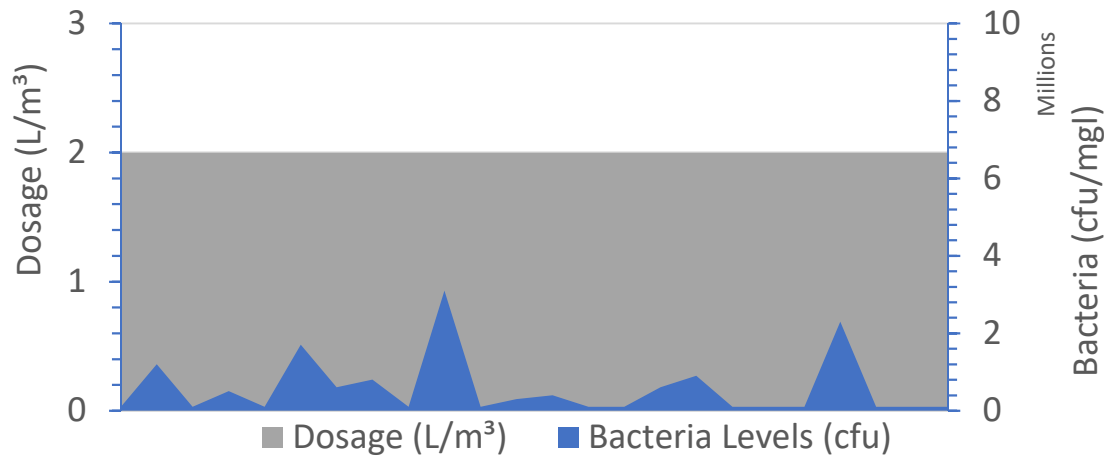
Biocide Comparison

	Bacteria Kill Efficacy @ PMRA Approved Dose	Fast Reaction Time	Duration of Protection	Effective pH Range	Low Toxicity to Enviro (includes by-prod)	Low Cost per Cube >3,000 m ³	Low Cost @ PMRA Effective Dose
ClO ₂	<div>High</div> <div>↑</div> <div>Low</div>	●●●●●	●●	●●●●●	●●●●●	●●●●	●●●●●
Glut		●●●	●●●	●●●	●	●●●	●●●●
Bronopol		●	●●●●●	●●●	●●	●	●●
THPS		●●	●●●	●●●	●●●	●●●	●●●
Quat		●●	●●●	●●●	●	●●●	●●
DBNPA		●●●●	●	●	●	●●●●●	●

●●●●● = Exceptional, ● = Marginal



Optimizing Treatments

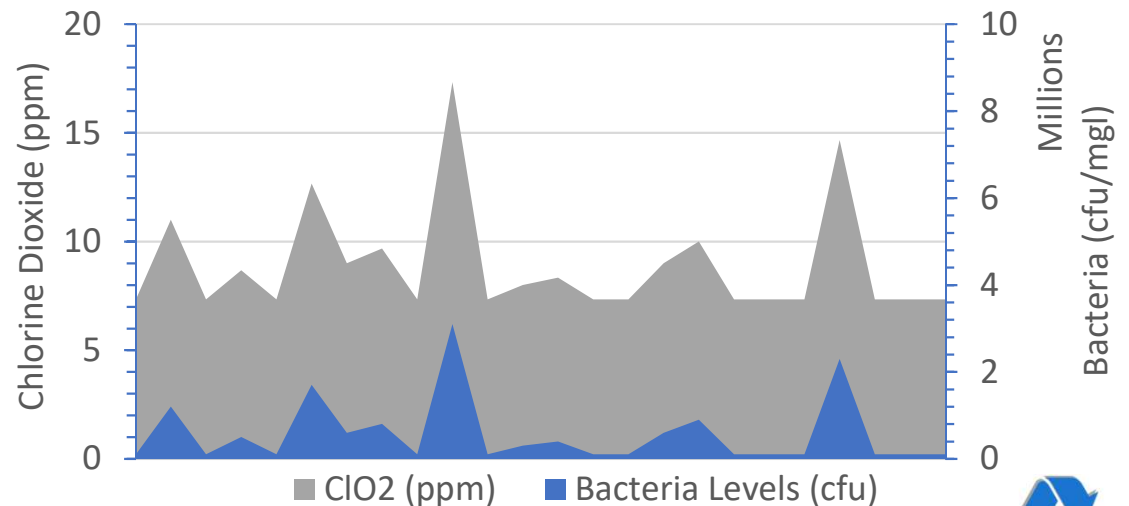


Traditional

- Single point dosage assume all water quality is the same

On-the-Fly

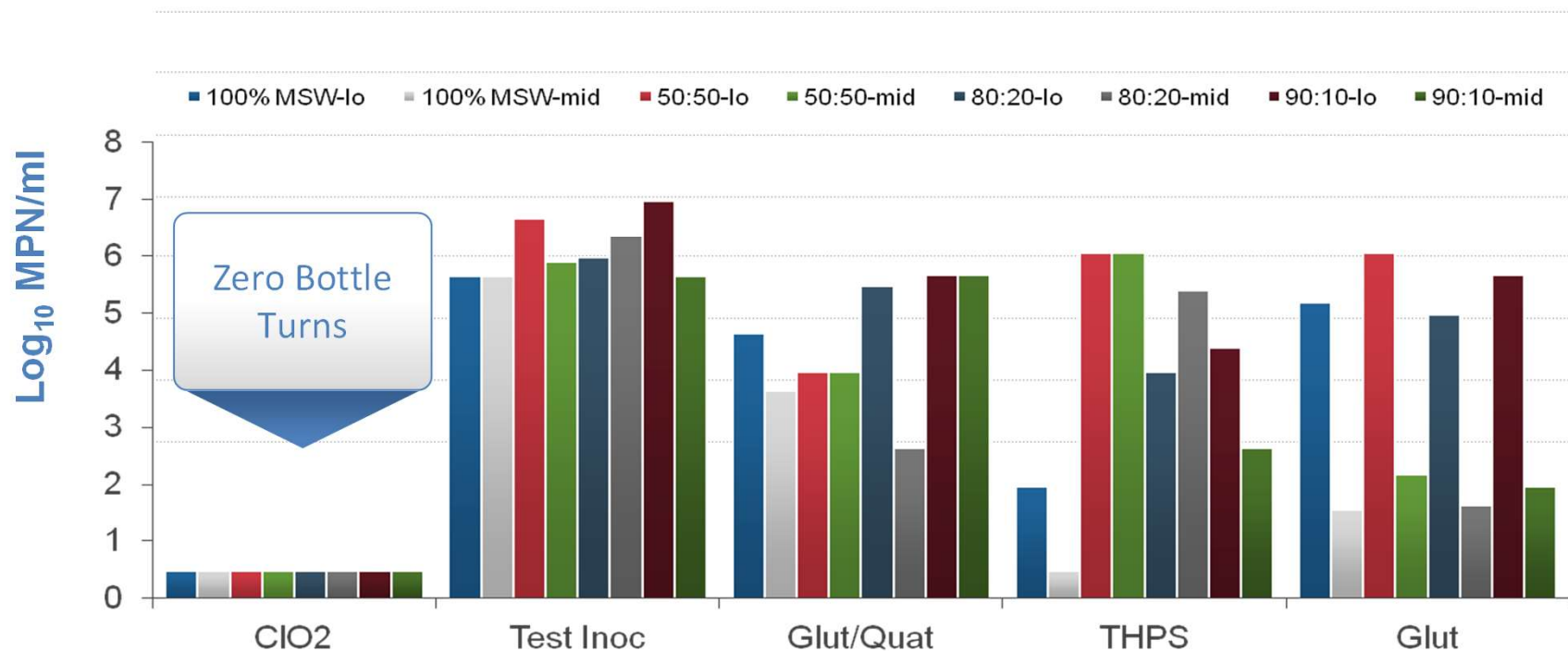
- Method adjusts for water quality changes using instrumentation from Chlorine Dioxide Generator



ClO₂ Short-Term Time-Kill Study

**Performance: Lab ClO₂ vs Nonoxidizing Biocides (SPE174560)
Surviving SRBs After 30 Minute Contact Time**

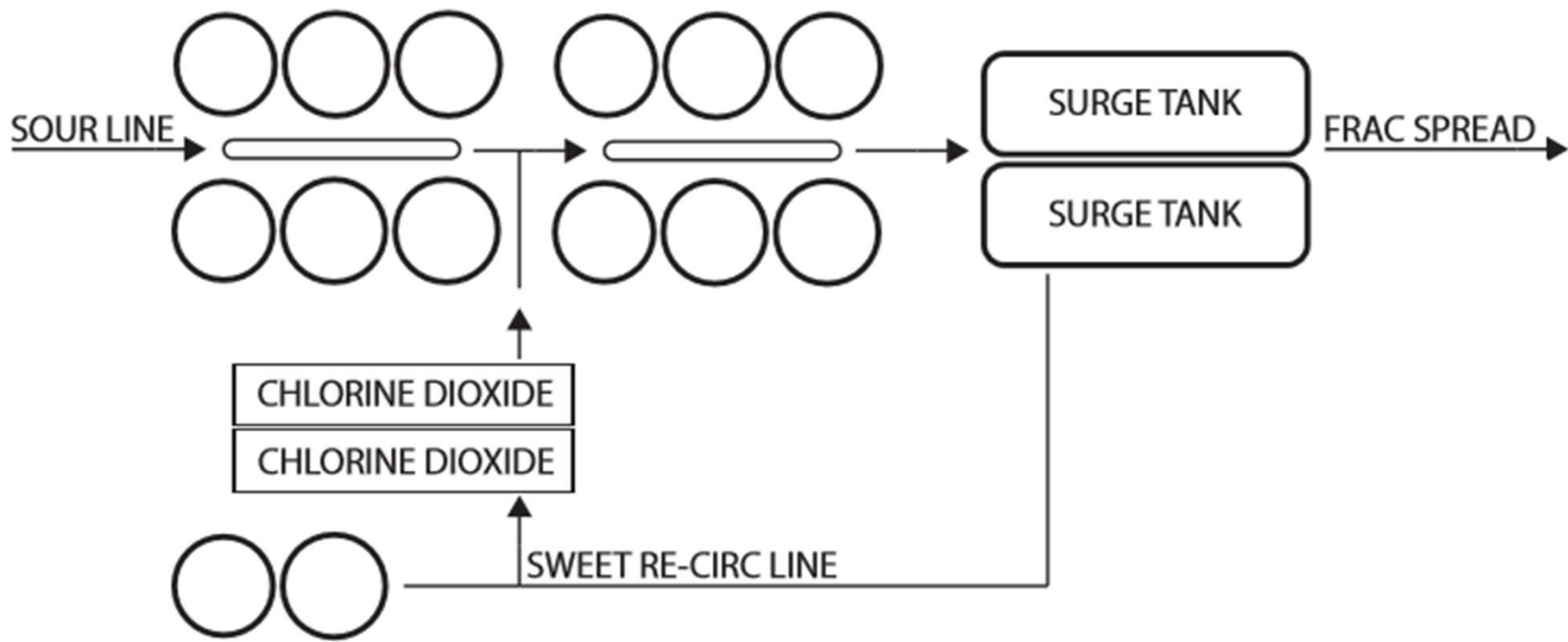
Microbial Efficacy: Marcellus Shale Water
Sulfate-Reducing Bacteria (SRB)



**All ClO₂ test results were below the level of detection
(i.e., <3.0 CFU/ml or 0.48 log/ml)**



Layout



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