Enhanced Removal of Suspended Solids and Residual Oil in Produced Water by Chlorine Dioxide

Greg Simpson, PhD & Zhengkai (Zack) Li, PhD PE

PureLine Treatment Systems
Bensenville, IL, U.S.A.

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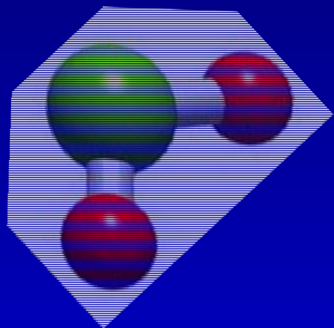
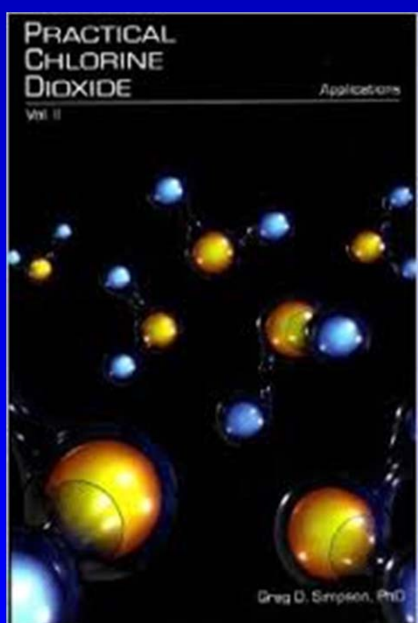
Outline

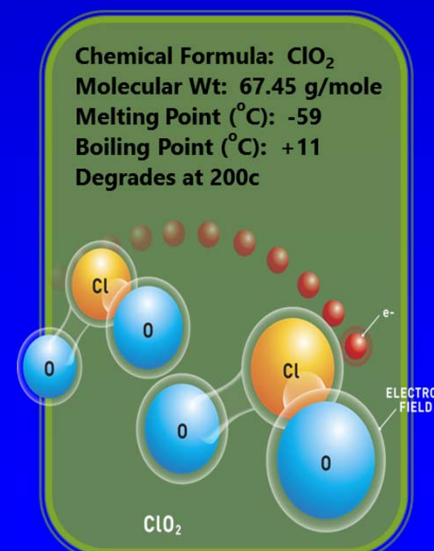
- Part I. Background of ClO_2
  - What is ClO_2?
  - Where is ClO_2 Used?
  - What are the mechanisms of ClO_2?
- Part II. ClO_2 Treatment of Produced Water
  - Use of ClO_2 as Potent Biocide
  - Use of ClO_2 as Robust Oxidant
  - Role in Removal of SS and Residual Oil

Introduction of ClO_2





- A stable free radical present as gas at ambient temperature
- A true dissolved gas in solution, but not react with water
- 2.5 times the oxidizing capacity of Chlorine
- A strong oxidizer with a very selective reaction chemistry
- A potent disinfectant, sterilant and biocide
- Must be generated at point of use
  - Oxidation of Chlorite (ClO_2^-)
  - Reduction of Chlorate (ClO_3^-)
- Effective at a broad range of pH
- Approved by EPA, FDA, and WHO



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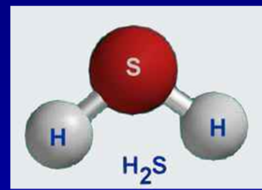
Applications of ClO_2

Legionella Control



Destroy Sulfides

Oil & Gas

Ballast Water

Where is Chlorine Dioxide Used?

Odor Control

Food Processing

Potable Water

Beverage Industry

Chill Loops and Cooling Towers

Fruit and Vegetable Wash

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Problematic Species in O&G vs. Efficacy of ClO_2

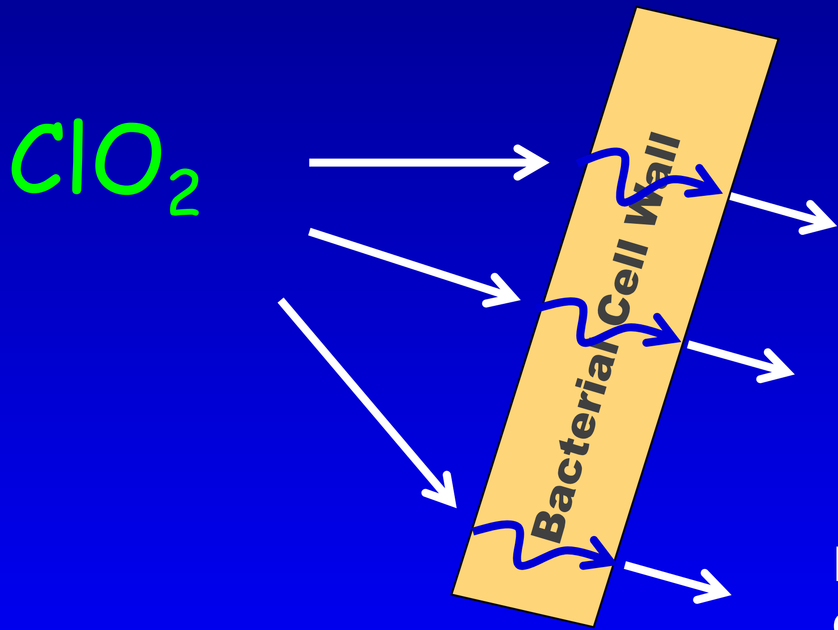
Species	Problems	ClO_2 Effectiveness
Bacteria	Corrosion, Clogging, Production of H_2S	Very Effective
Biofilm	Corrosion, Clogging	Very Effective
H_2S	Corrosion, Souring of Reservoir	Very Effective
FeS	Corrosion, Clogging	Very Effective
Hardness Salts	Deposit/Scale, Clogging	No Direct Effect
Barium Salts	Deposit Formation, Clogging	No Direct Effect
NORM	Environmental	Effective *

* Mason, J., Block, R. and Knippers, M., "Reduction of Naturally Occurring Radioactive Material Disposal Volume by Chemical and Physical Treatment," SPE 24563, 67th Annual Technical Conference and Exhibition of the Society of Petroleum Engineers, Washington, DC, October 4-7, 1992

ClO_2 & Bacteria

1. Penetration

Penetration of the cell wall – Rate limiting step



The bacterial cell wall thickness varies. Spores are much more resistant to disinfection than bacteria

ClO_2 was chosen to inactivate anthrax spores in DC

It is the penetration factor that makes one bacterium more or less resistant to inactivation.[1,2]

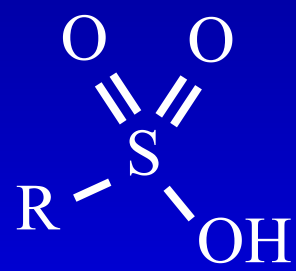
1. McDonnell, G. and Russell, A., "Antiseptics and Disinfectants: Activity, Action, and Resistance," *Clinical Microbiology Reviews*, 12(1), 147(1999).
2. Ingols, R. and Ridenour, G., "Chemical Properties of Chlorine Dioxide," *Journal of the American Water Works Association*, 40, 1207(1948).

ClO_2 & Bacteria

2. Oxidation of Vital Cell Components

Amino acids
Proteins
Enzymes

very fast

ClO_2 + R-S-H → 

(Reduced Sulfides) (Oxidized Sulfones)

- The affinity of ClO_2 for reduced sulfur compounds, specifically the thiol group (-SH), could be an important mode of bacterial disinfection [1,2, 3]

[1] Green, D. and Stumpf, P., "The Mode of Action of Chlorine," *Journal of the American Water Works Association*, 38, 1301(November, 1946).

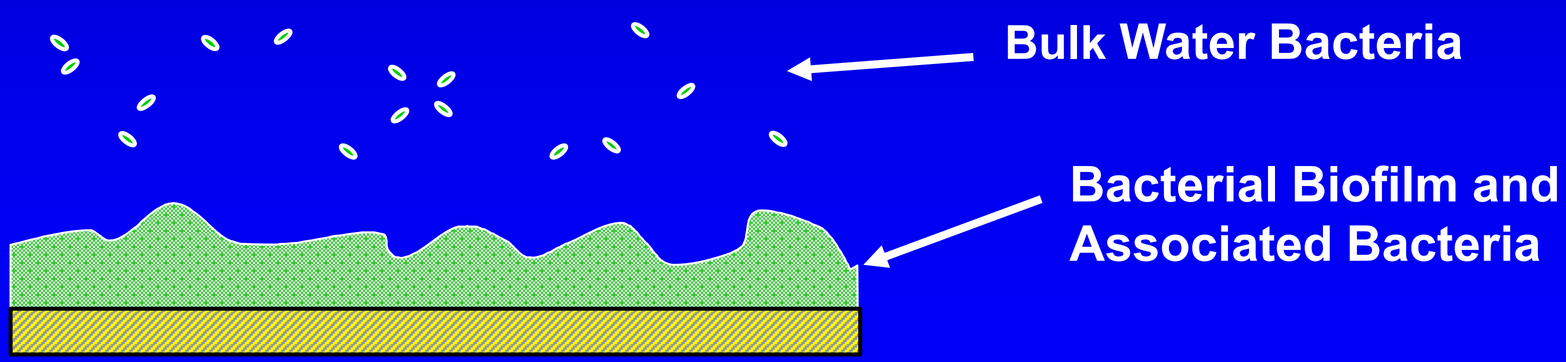
[2] Knox W., Stumpf, P., Green, D., and Auerbach, V., "The Inhibition of Sulfhydryl Enzymes as the Basis of the Bacterial Action of Chlorine," *Journal of Bacteriology*, 55,451 (1948).

[3] Ison, A., Odeh, I. N., & Margerum, D. W. (2006). Kinetics and mechanisms of chlorine dioxide and chlorite oxidations of cysteine and glutathione. *Inorganic chemistry*, 45(21), 8768-8775.

ClO_2 & Biofilm

ClO_2 reacts with...

1. Planktonic bacteria in the bulk water
2. Biofilm and Sessile Bacteria on system surfaces. For ClO_2, one ***<u>must</u>*** account for surface demand.



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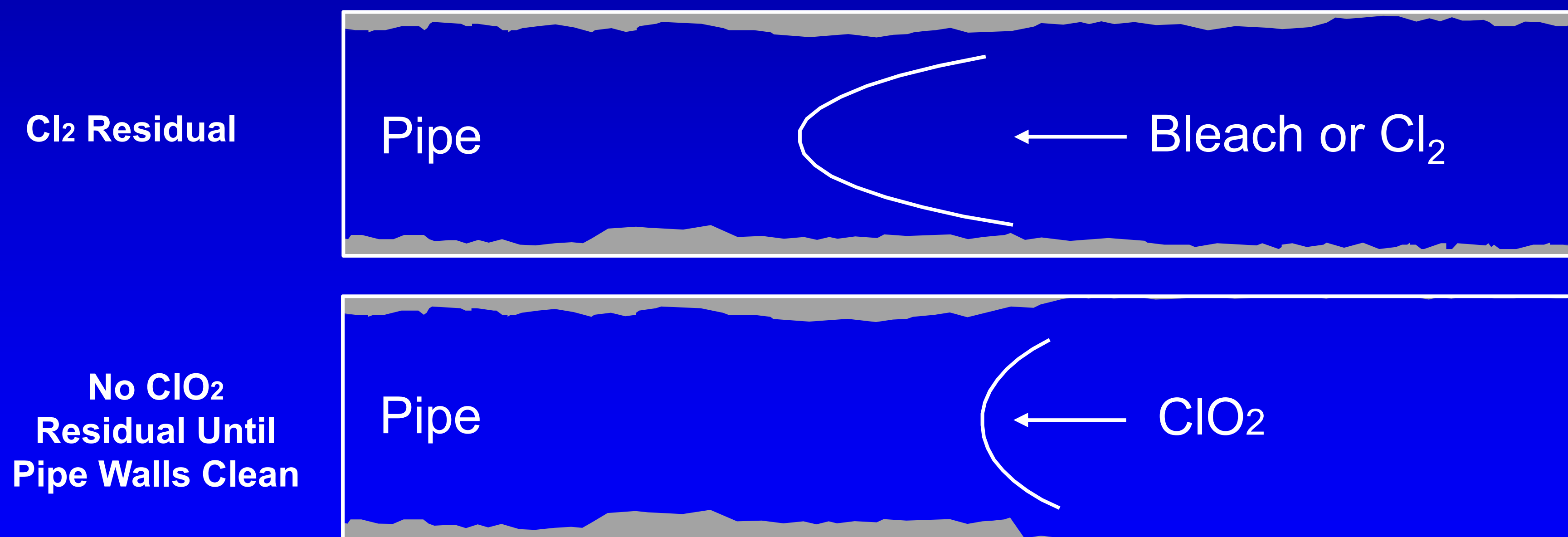
ClO_2 & Biofilm

1. Proves much more effective in biofilm disinfection than Cl_2.
2. Exhibits very low effective C*T- values compared to Cl_2.



Hosni, A.A., Shane, W.T., Szabo, J.G. and Bishop, P.L., "The disinfection efficacy of chlorine and chlorine dioxide as disinfectants of B. globigii, a surrogate for B. anthracis, in water networks: a comparative study," *Canadian Journal of Civil Engineering*, 36: 732-737, 2009.

Reactions of ClO_2 with H_2S or FeS

$$5H_2S + 8ClO_2 + 4H_2O \rightarrow 5H_2SO_4 + 8HCl$$

Stoichiometric ClO_2 in acidic solution

Strong Mineral Acids

$$2H_2S + 2ClO_2 \rightarrow H_2SO_4 + 2HCl + S°$$

Insufficient ClO_2 in neutral to alkaline solution

Elemental Sulfur Possible

$$5FeS + 9ClO_2 + 2H_2O \rightarrow 5Fe^{3+} + 5SO_4^{2-} + 9Cl^{-} + 4H^{+}$$

Converts insoluble FeS to ferric iron – a water treatment agent

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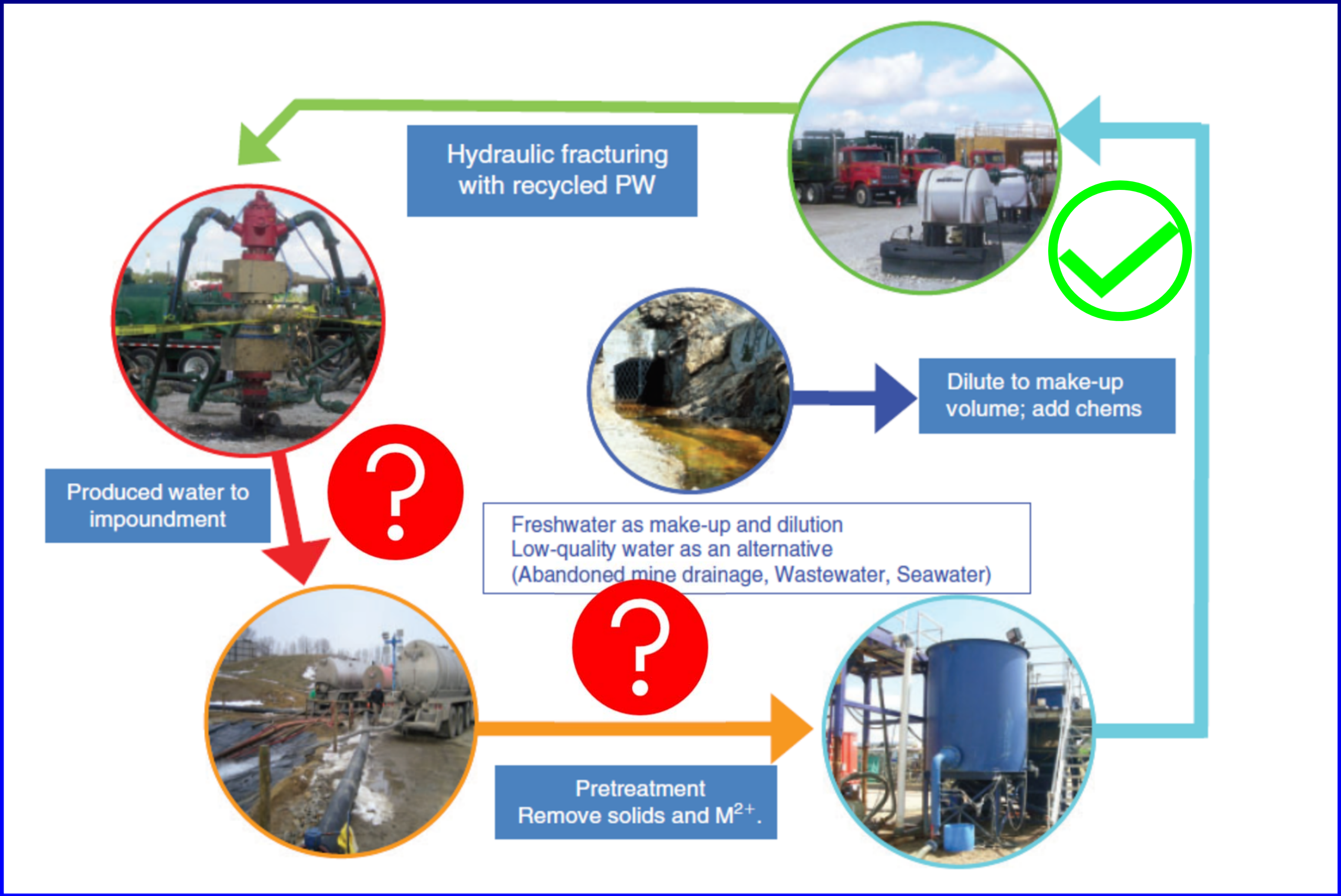
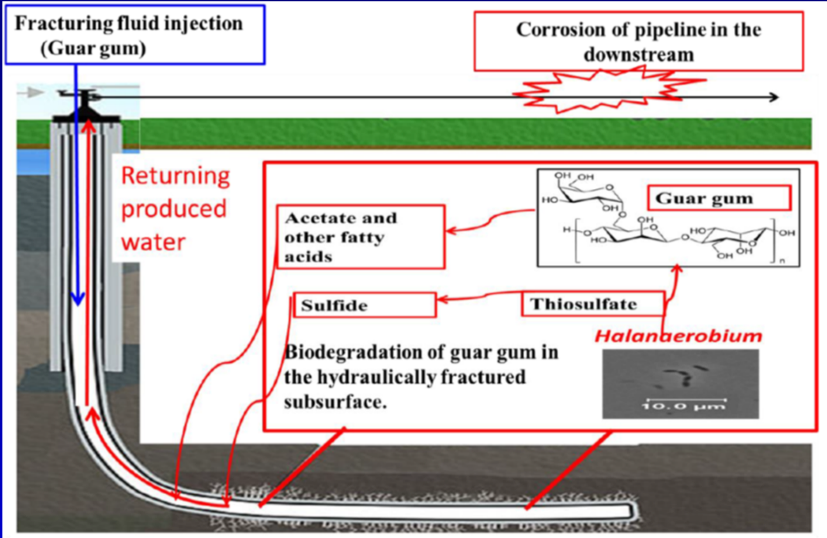
Produced Water Management Challenges*



* Gregory, K. and Mohan, A.M. 2015. Current perspective on produced water management challenges during hydraulic fracturing for oil and gas recovery. *Environ. Chem.*, 12, 261–266

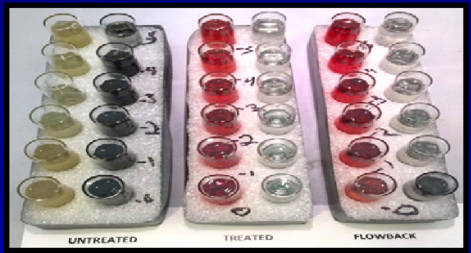
Common Contaminants in Produced Water

- Microorganisms
  - Degrade the quality of oil and gas
  - Microbiologically Influenced Corrosion
  - Plug formation with biofilms
- Suspended Solid, Residual Oil
  - Foul water treatment systems
  - Cause expensive maintenance operations for injection wells
- Iron Sulfide
  - Decrease production rates by plugging the formations, and corrosion of well casing and tubing
  - Stabilize emulsions at oil/water interface, and make it very difficult process to separate oil/water/solids



Liang et al., 2016. *Frontiers in Microbiology*

Roles of Chlorine Dioxide in Produced Water Treatment



#1. Biocide

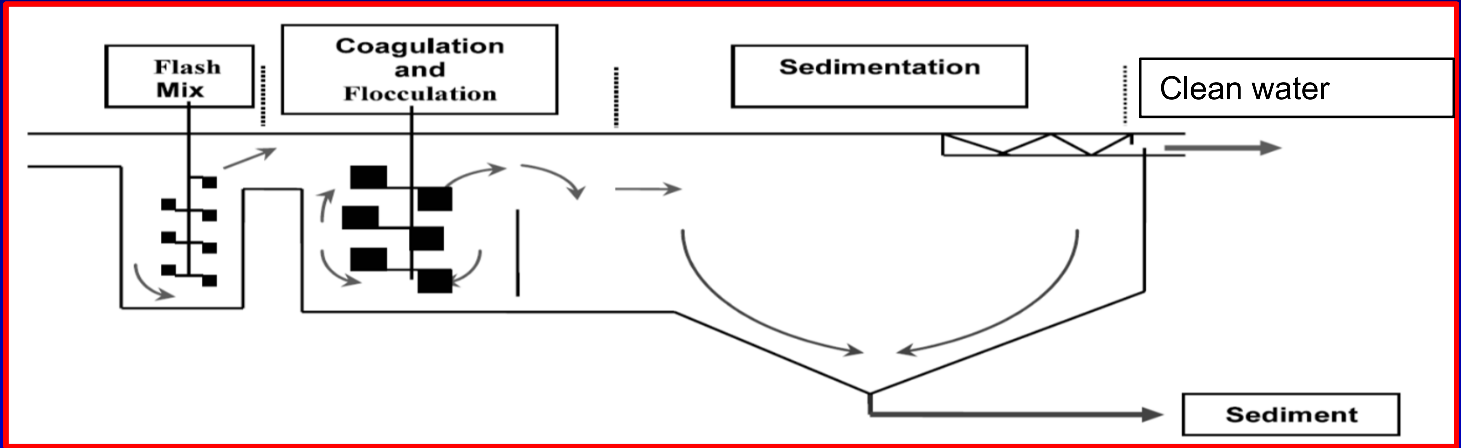
- Drastic distinction of microbial communities in produced waters and other source waters - must be considered for disinfection
- Halo- and thermophilic Anaerobes predominant in produced water – Tolerant to non-oxidizing biocide but susceptible to oxidizing biocide

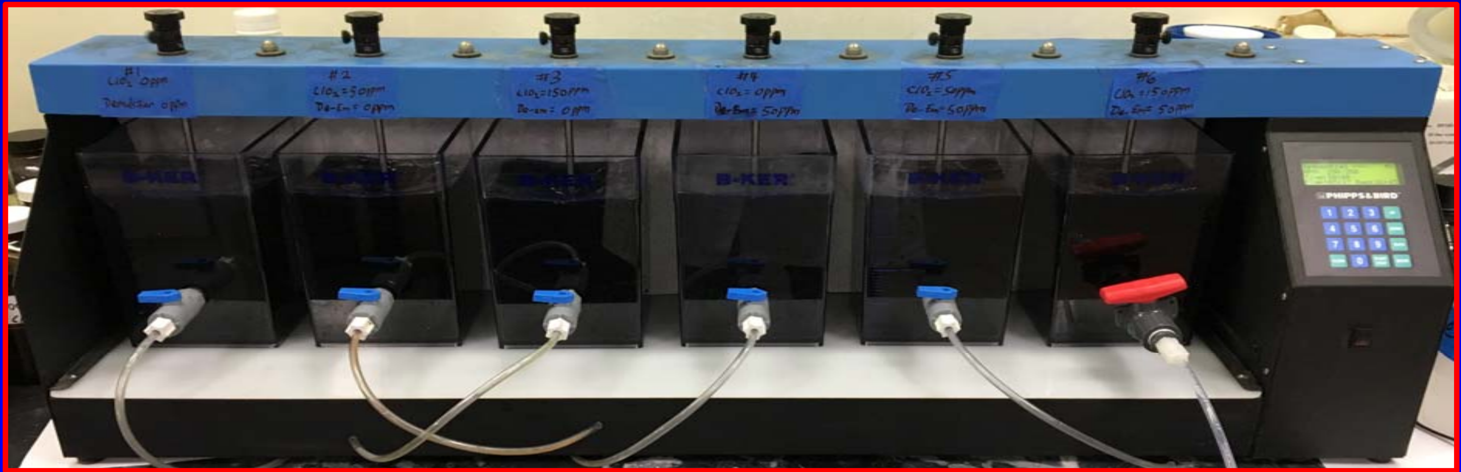
#2. Oxidant

- Oxidize FeS to break up the oil-in-water emulsions; oxidized $Fe(OH)_3$ serve as coagulant to enhance flocculation and sedimentation
- Oxidation of organic compounds (e.g. aromatic amines, phenols, and polyacrylamide breakdown products) to reduce FOG in water

To investigate the impact of chlorine dioxide on enhanced removal of residual oil and SS from produced waters

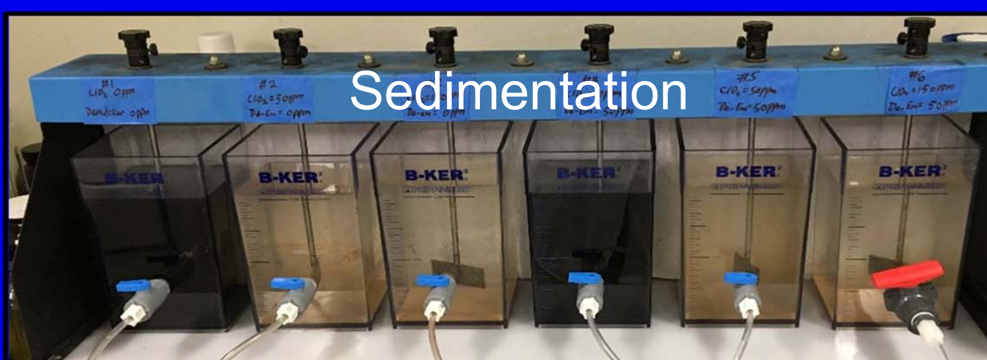
Testing Apparatus





- **Mixing conditions:** 250 rpm for 30 min to disperse oil; 150 rpm for 5 min, 20 rpm for 20 min, and 0 rpm for 30 min
- **Measured Parameters**: pH, ORP, Temperature, density, ClO_2 residual, total sulfides, ferrous iron, total iron, TSS, and residual oil

Testing Procedure



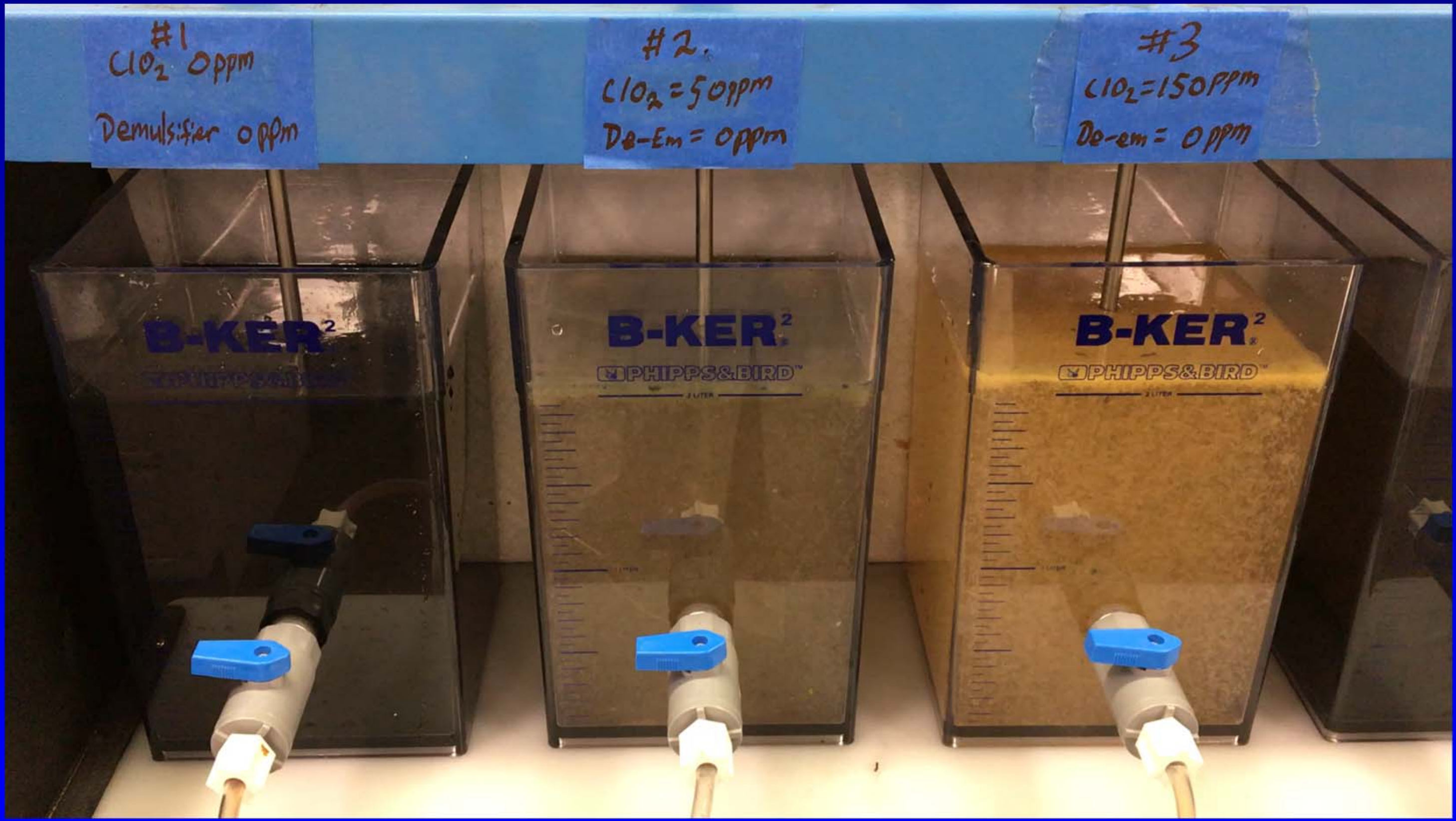
Test conditions

Test No	Produced Water
Test (1)	Raw produced water (RPW)
Test (2)	PW Amended with Gasoline
Test (3)	PW Amended with Diesel
Test (4)	PW Amended with Motor Oil

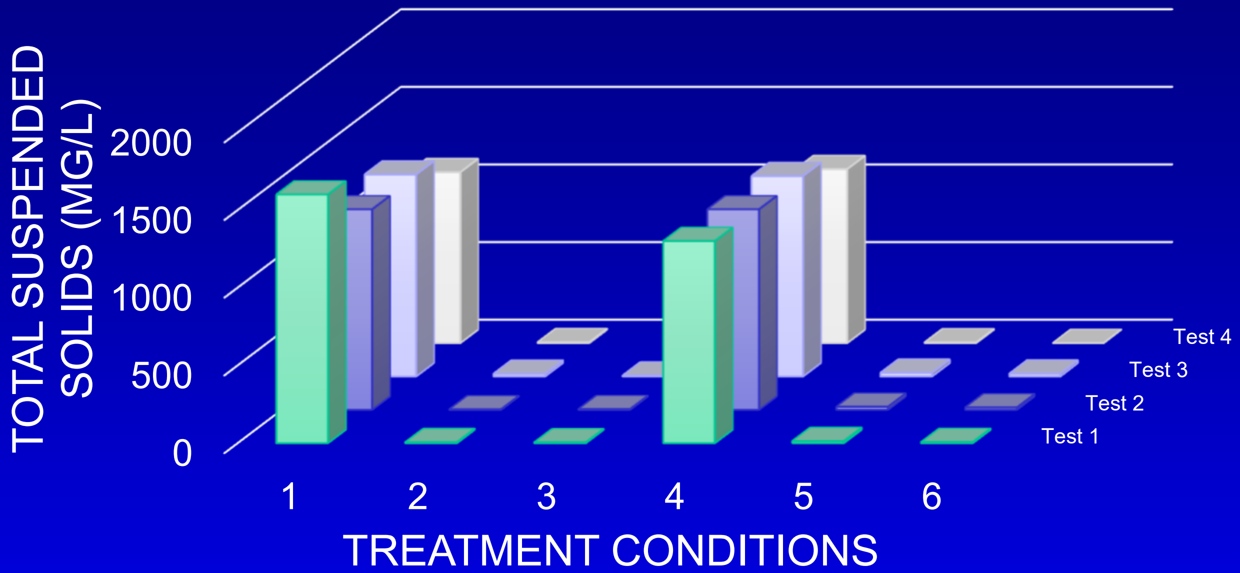
Treatment conditions

Jar No	ClO_2 (ppm)	De-Emulsifier (ppm)
(1)	0	0
(2)	50	0
(3)	150	0
(4)	0	50
(5)	50	50
(6)	150	50

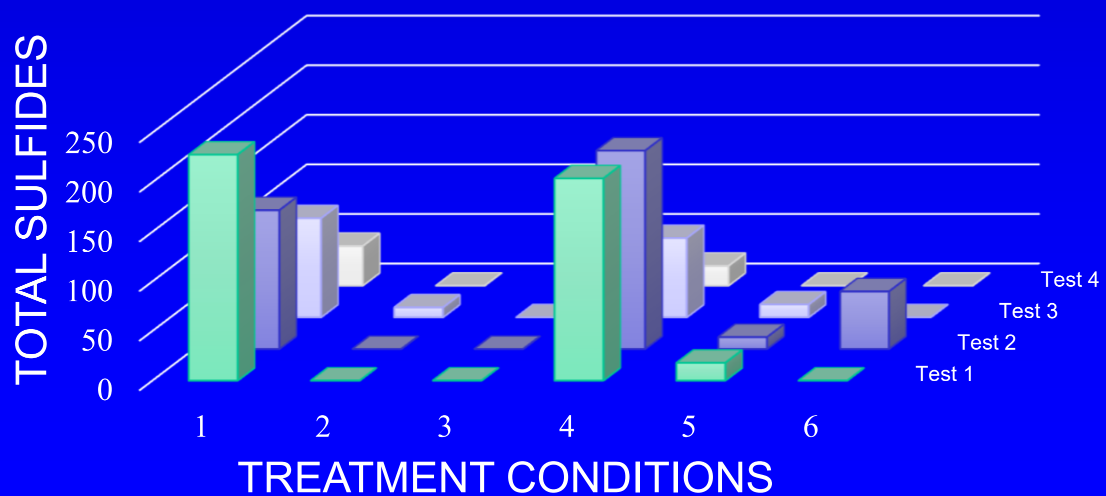
Reaction and Flocculation



TSS & Total Sulfides



Test#	TSS (ppm)
(1)	1540
(2)	1550
(3)	1740
(4)	1620



Test#	S^{2-}(ppb)
(1)	270
(2)	180
(3)	410
(4)	650

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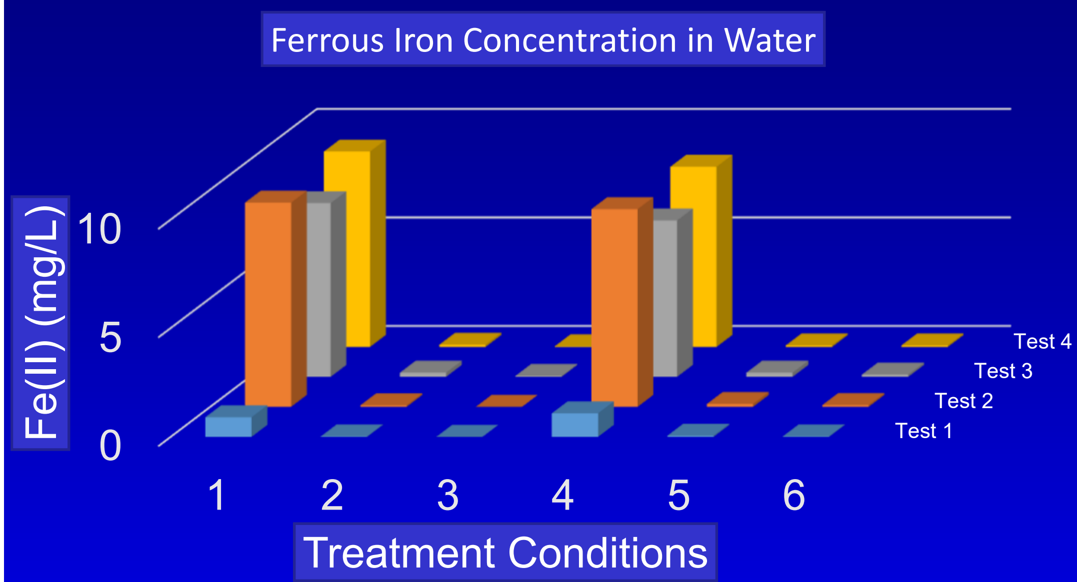
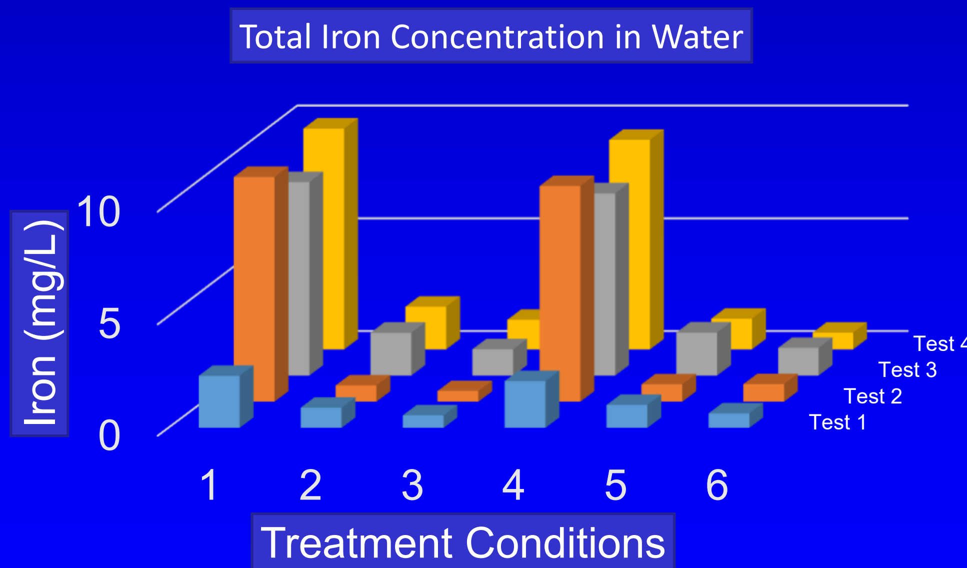
Iron Removal



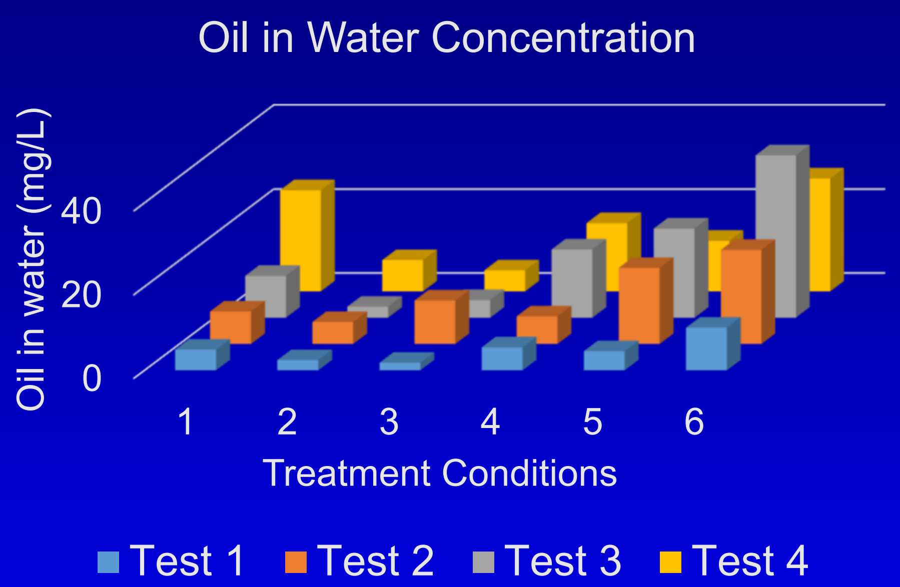
Test	ICP-AES
(1)	13.8 mg/L
(2)	14.7 mg/L
(3)	14.1 mg/L
(4)	13.7 mg/L

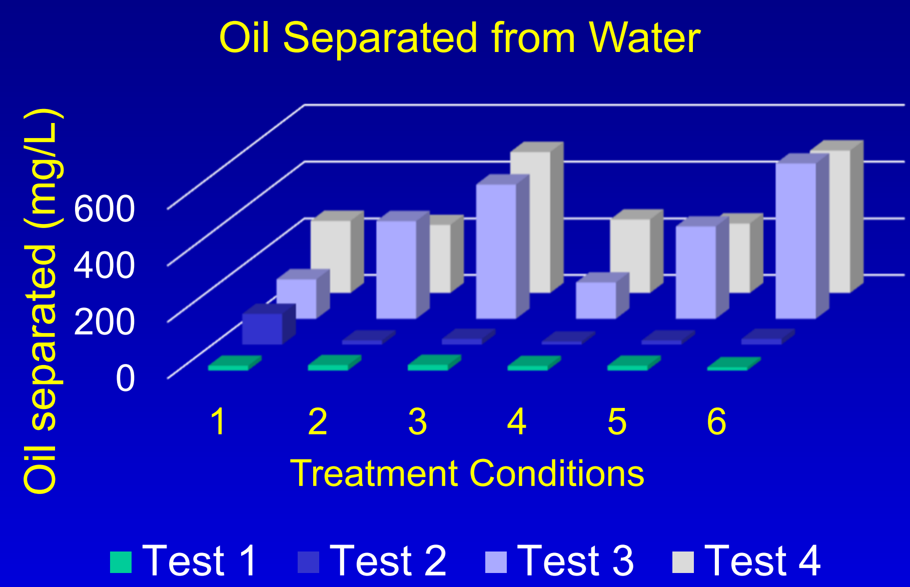


For three oil-amended tests:

- w/o ClO_2: η (Fe) ≤ 43%
- with ClO_2 : η (Fe) ≥ 86 %

Oil – Water Separation



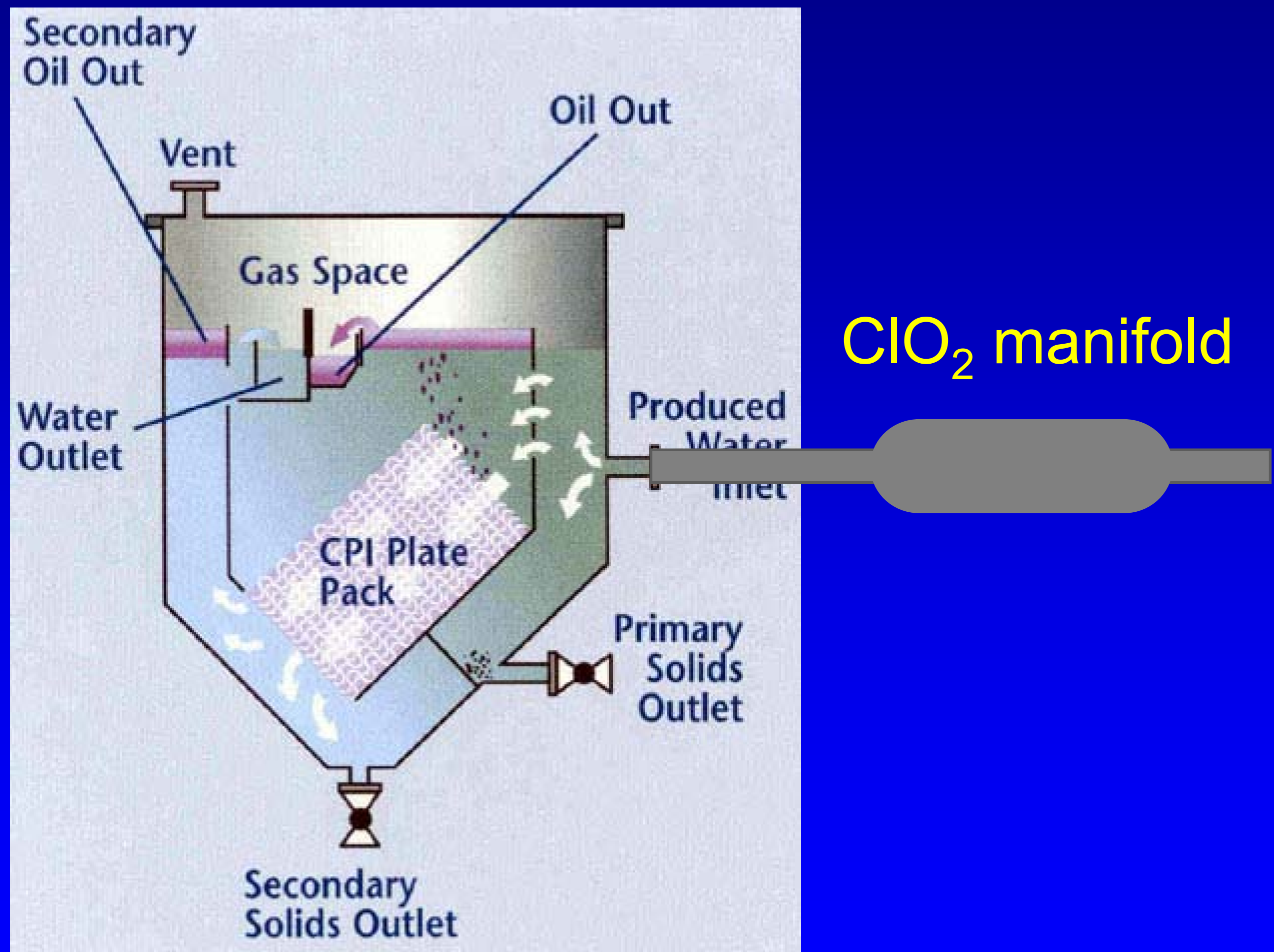


Treatment conditions	ClO2	Demulsifier	Diesel Oil		Motor Oil	
Jar#	(ppm)	(ppm)	W (%)	S (%)	W (%)	S (%)
1	0	0	0%	0%	0%	0%
2	50	0	-74%	**147%** ↑	-69%	-5%
3	150	0	-58%	**239%** ↑↑	-79%	**95%** ↑
4	0	50	63%	-8%	-32%	2%
5	50	50	113%	**134%** ↑	-50%	-4%
6	150	50	287%	**292%** ↑↑	12%	**97%** ↑

Summary of Results

- ClO_2 treatment removed TSS by > 99 %;
- ClO_2 treatment removed iron by > 86%;
- ClO_2 treatment removed sulfides by > 90%.
- ClO_2 treatment at both 50 ppm and 150 ppm levels enhanced oil-water separation for the tested diesel oil
- ClO_2 treatment at 150 ppm level also enhanced oil-water separation efficiency for the tested motor oil
- Commercial de-emulsifier at 50 ppm level has no significant effect in oil-water separation efficiency
- Tests with other sources of produced water confirmed positive correlation of ClO_2 dosage and total FOG reduction from water

Integration of ClO_2 Treatment into Existing Units*



* Source: https://www.netl.doe.gov/research/coal/crosscutting/pwmis/tech-desc/physep

Conclusions

- Produced waters are contaminated with bacteria and biofilm, hydrogen sulfides and iron sulfides, residual emulsions, etc.
  - These cause operational challenges such as clogging and corrosion, wear of facilities, and environmental compliance issues
- Chlorine dioxide can provide effective treatment, both as a potent biocide and as an oxidant
  - ClO_2 treatment very effectively removes iron and sulfides, controls TSS and residual oil, and improves the overall water quality of the produced water for reuse and recycle
- Best management practice may integrate chlorine dioxide into an existing or a new treatment system
  - Benefits include clean water, reduced footprint, savings on operational and capital costs, elimination of hydrogen sulfides, mitigation of corrosion, and good for the environment

Thank you!

Supplementary Slides

How is ClO_2 Made?

- ClO2 is produced in two ways
  1. Reduction of chlorate ion (ClO_3^-)

Chlorate/Peroxide + Sulfuric Acid

$$NaClO_3 + \frac{1}{2} H_2O_2 + \frac{1}{2} H_2SO_4$$

$$\Rightarrow ClO_2 + \frac{1}{2} O_2 + \frac{1}{2} Na_2SO_4 + H_2O$$

Cl (+5)

Cl (+4)

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How is ClO_2 Made?

- ClO2 is produced in two ways
  2. Oxidation of chlorite ion (ClO_2^-)

Acid-Chlorite (1000 lbs/day max)

$5NaClO_2 + 4HCl \Rightarrow 4ClO_2 + 5NaCl + 2H_2O$

Acid-Bleach-Chlorite (up to 50,000 lbs/day)

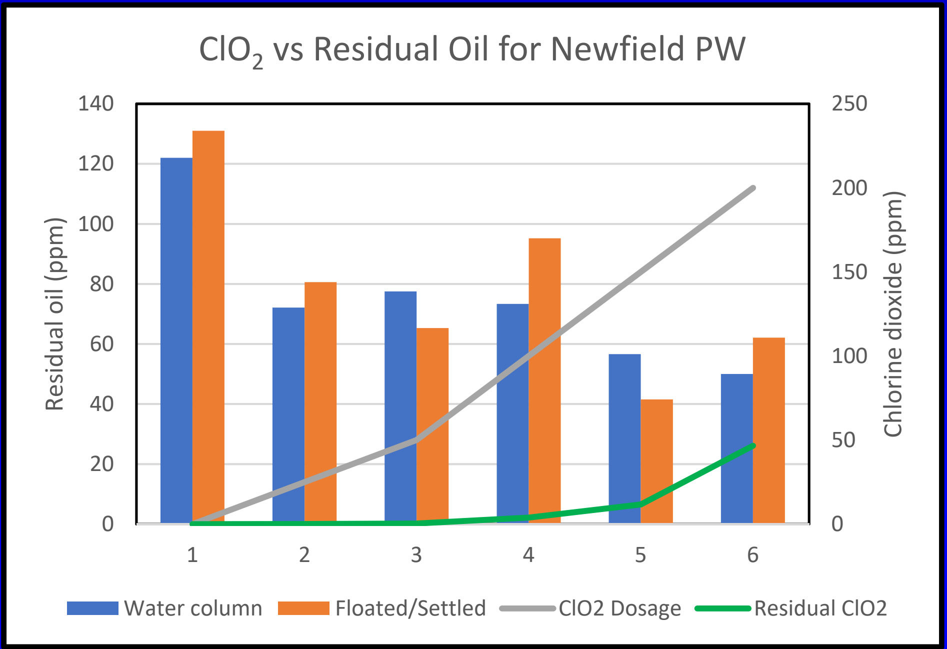
$2NaClO_2 + HOCl + HCl \Rightarrow 2ClO_2 + 2NaCl + H_2O$

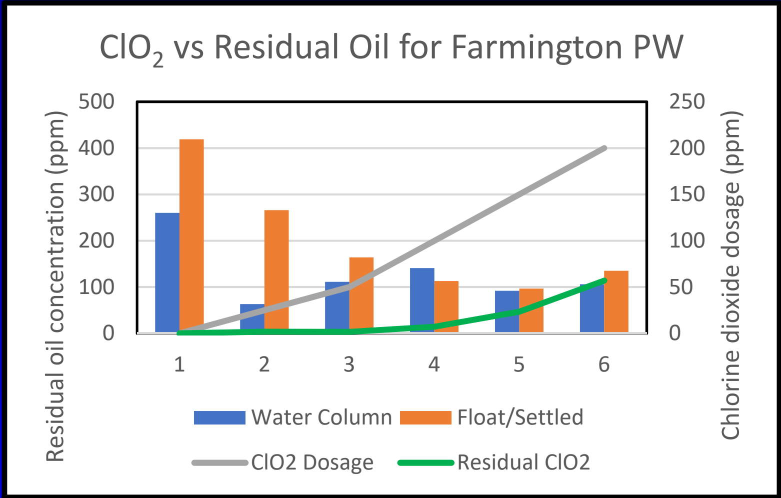
Cl (+3) **Cl (+4)**

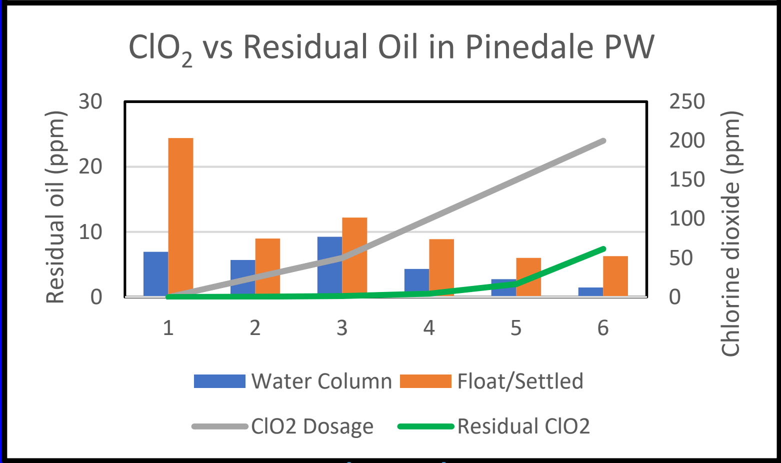
Other PW Tests

RPW Test#	Hardness (As CaCO3 mg/L)	Na (mg/L)	K (mg/L)	Mg (mg/L)	Ca (mg/L)	Sr (mg/L)	Ba (mg/L)	Iron (mg/L)	Mn (mg/L)	B (mg/l)	P (mg/l)
5 (N2)	68	2,010	42.8	3.55	21	4	0.903	0.786	ND	12.4	0.57
6 (F2)	360	3,860	37	23.2	106	17	7.38	21.6	0.644	1.43	0.755
7 (P1)	59	1,120	13.3	2.54	19	2	5.8	16.6	0.424	2.37	ND

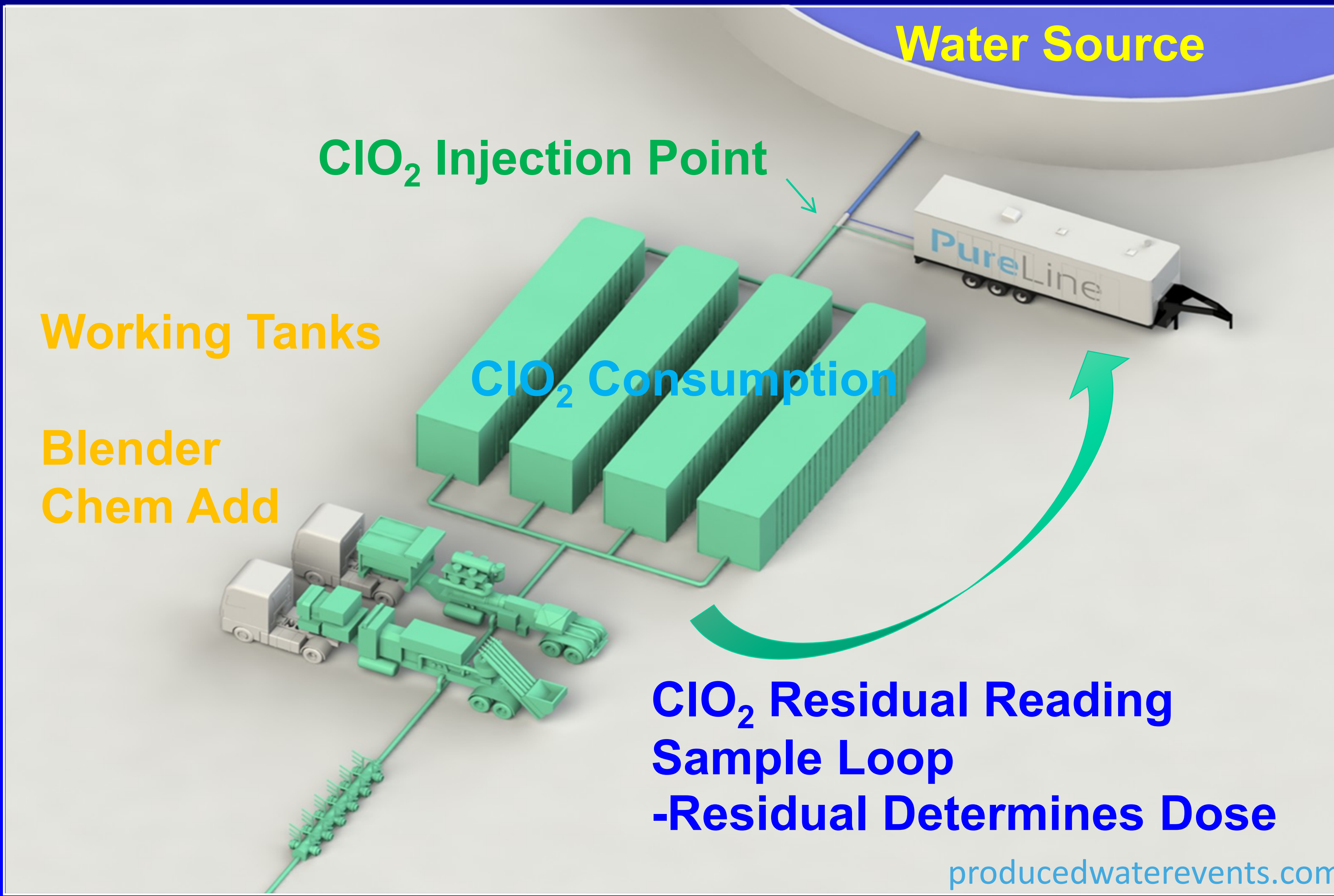
RPW Test#	Alkalinity (mg/L)	Chloride (mg/L)	Oil (mg/L)	SO_4^{2-} (mg/L)	TDS (mg/L)	TSS (mg/L)
5 (N2)	1200	3,620	161.0	101	7,600	120
6 (F2)	539	6,030	113	194	11,700	508
7 (P3)	355	2,050	15.5	ND	4,460	122



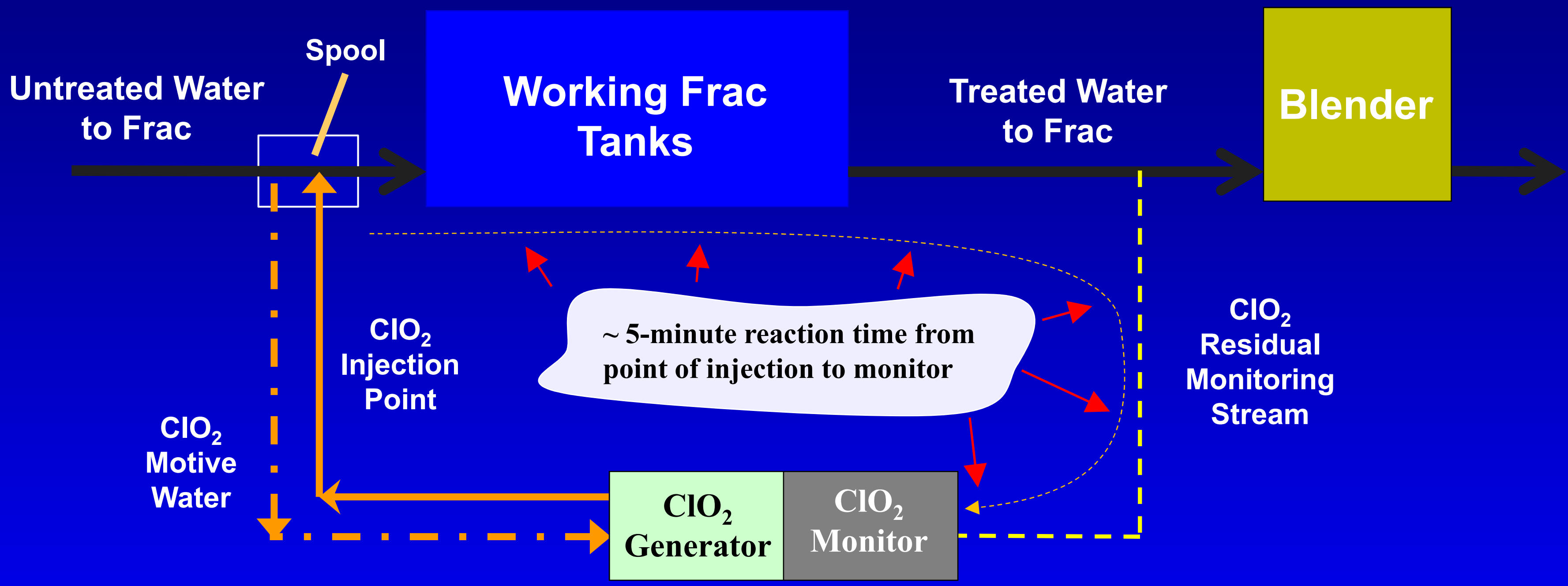




ClO_2 On the Pad - Holistic Biocide Treatment

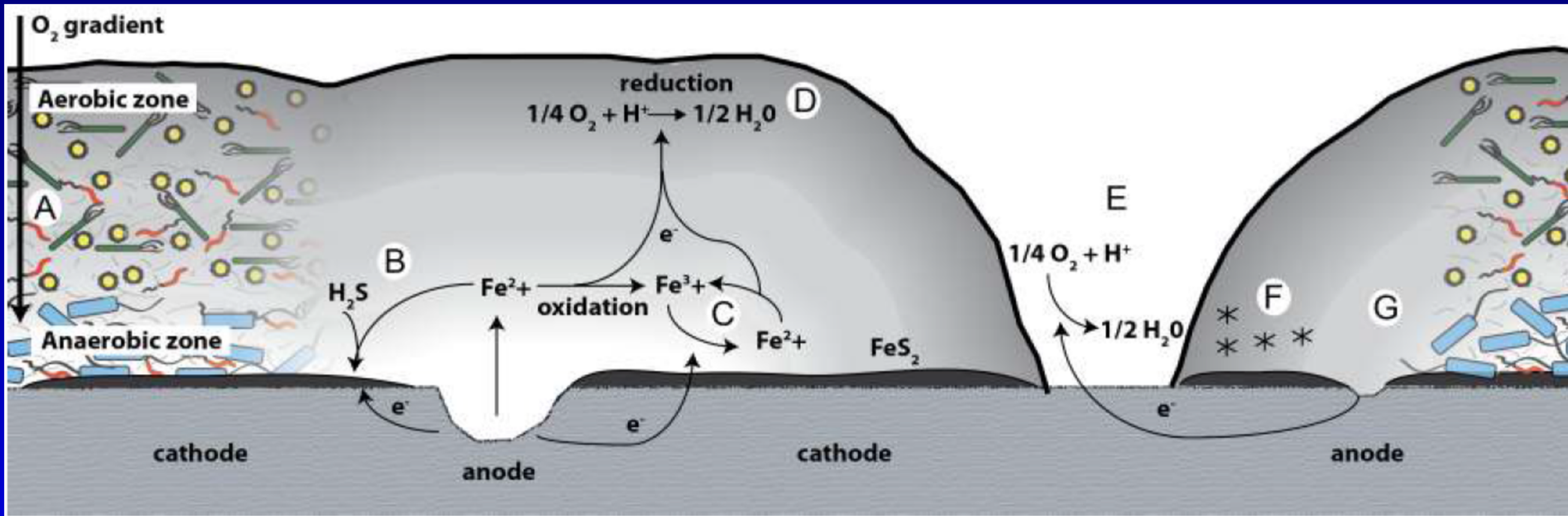


Injection / Monitoring



- Typical Fresh Water Dosage ~ 5 – 10 ppm (~ 3 – 5 ppm residual)
- Typical Produced Water Dosage ~ 10 - 150 ppm (every application is different)

Corrosion of Biofilm*



- (A) create anaerobic zones
- (B) concentrate corrosive chemicals
- (C) concentrate ferrous ions
- (D) conduct electron away from surface
- (E) create differential aeration zones
- (F) bind corrosion promoters
- (G) disrupt passivating film

* Li, K., Whitfield, M. & Van Vliet, K. (2013). Beating the bugs: roles of microbial biofilms in corrosion. Corrosion Reviews, 31(3-6), 73-84

Eckert, R. B. "Emphasis on biofilms can improve mitigation of microbiologically influenced corrosion in oil and gas industry." Corrosion Engineering, Science and Technology 50.3 (2015): 163-168.