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The Impact of Sludge in Treatment of Flowback/Produced Water with Chlorine Dioxide: A Case History

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The Produced Water Society

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PureLine

Outline

- What Is ClO_2 and Why Is It Used in HF?
- Species in Produced Water That React with ClO_2
- Reaction Stoichiometry & Kinetics
- What Happens to ClO_2 Residual
- How Much ClO_2 / Contact Time Required for Bacterial Inactivation
- Penetration of Organics (polysaccharides) by ClO_2
- Setup with Working Tanks
- Response of Real-Time Generator Control to Dirty Working Tanks
- How ClO_2 Interacts with Sludge
- What Happens if ClO_2 Is Fed Based Solely on Bulk Water Demand
- Conclusions

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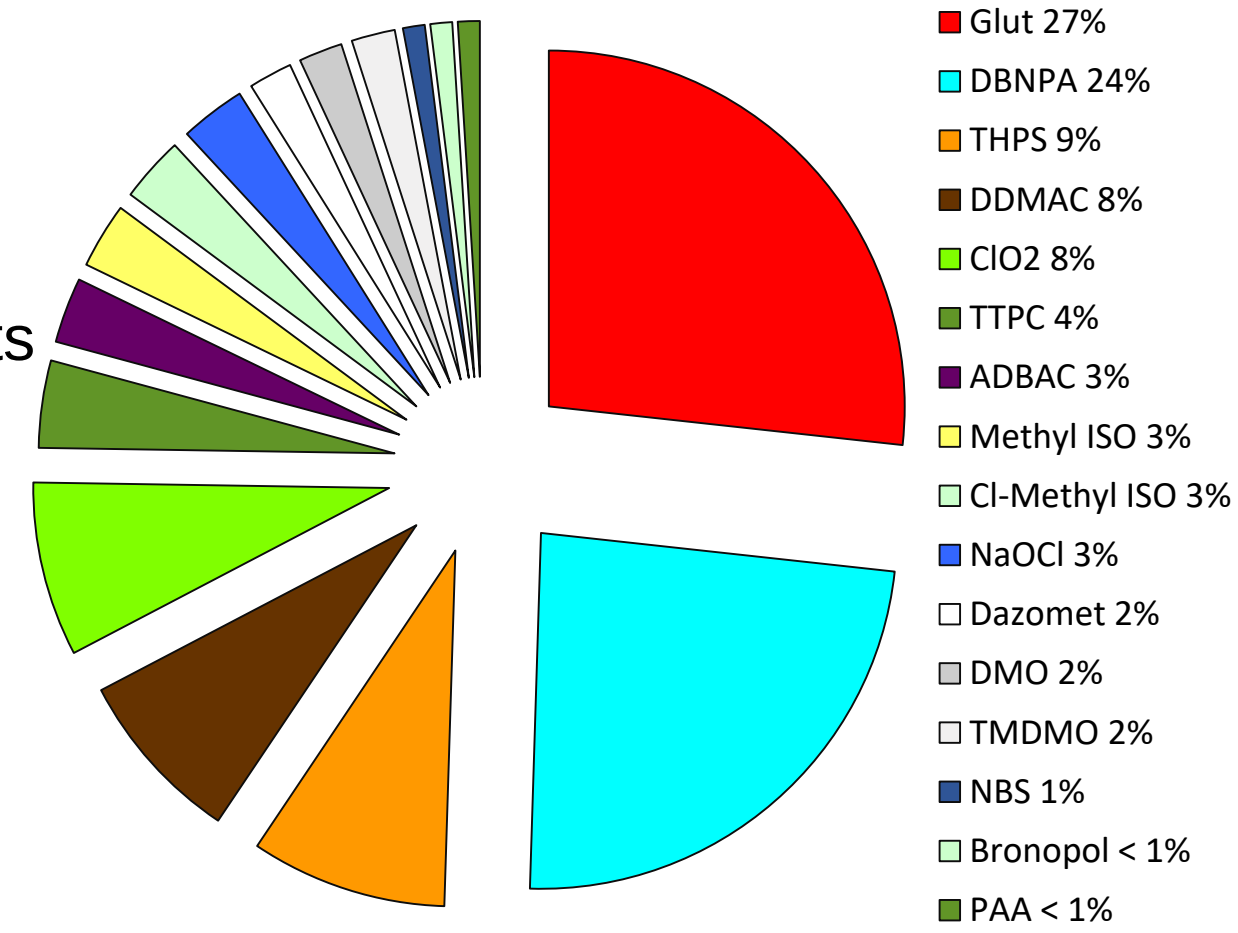
What Is ClO_2 and Why Is It Used in Hydraulic Fracturing

- A gas at ambient temp that is very soluble in water
- Very selective reaction chemistry
- Very effective oxidant and biocide
- Penetrates biomass, amorphous deposits
- Effective at produced water pHs
- Generated at point of use
  - Oxidation of Chlorite (ClO^{-2})
  - Reduction of Chlorate (ClO^{-3})



FracFocus Chemical Disclosure Registry, 2013, http://fracfocus.org/.

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Components of Produced Water That React with ClO_2

Some Species in F/P Water Which Create a Demand for ClO_2		
H_2S, HS^-, and S^{-2}	Organic Disulfides	Manganese
Thiosulfate	Sulfites	Unsaturated hydrocarbons
Mercaptans	Reduced sulfur compounds	Aromatic hydrocarbons
Organic sulfides	Iron	Tertiary amines

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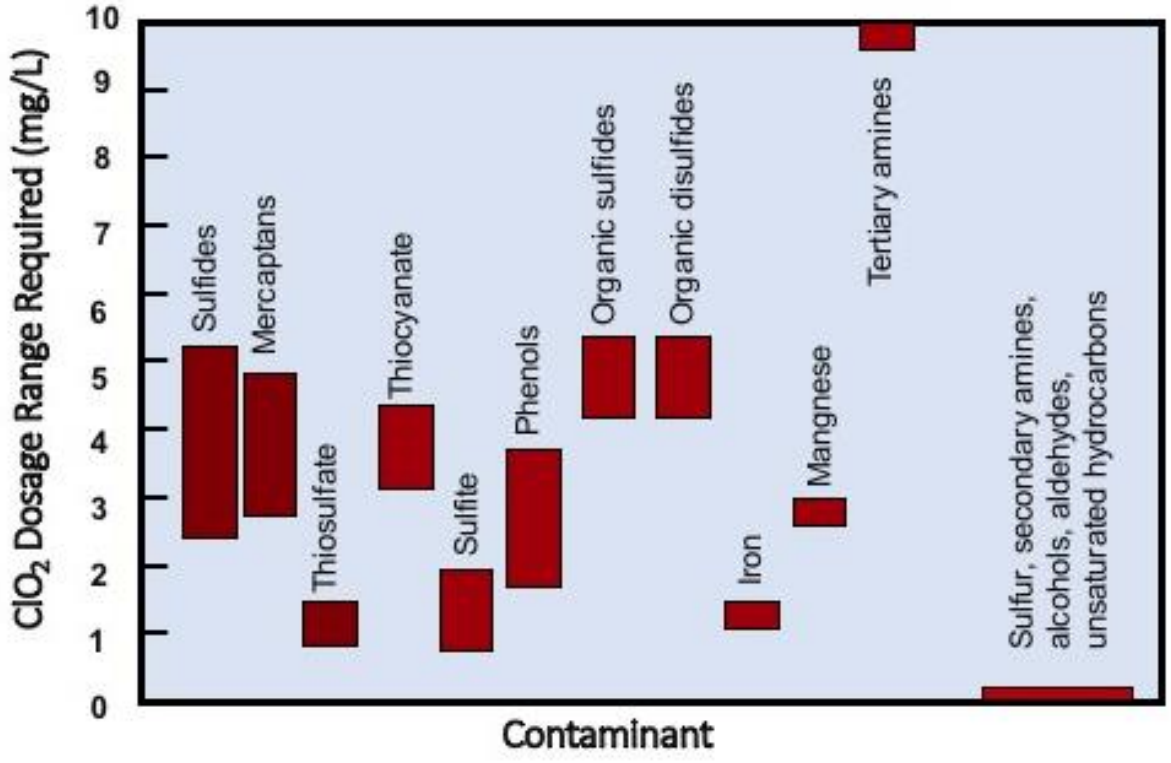
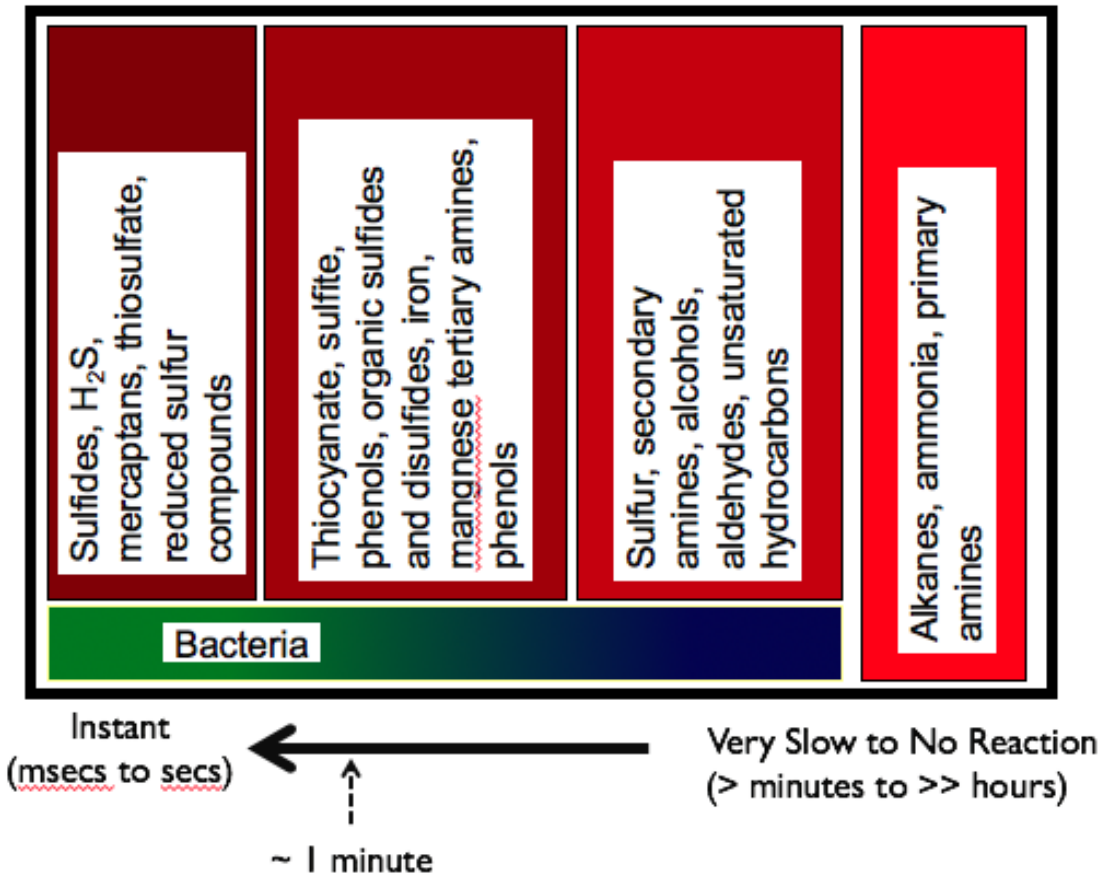
ClO_2 Reaction Stoichiometry & Kinetics

Stoichiometry



Kinetics



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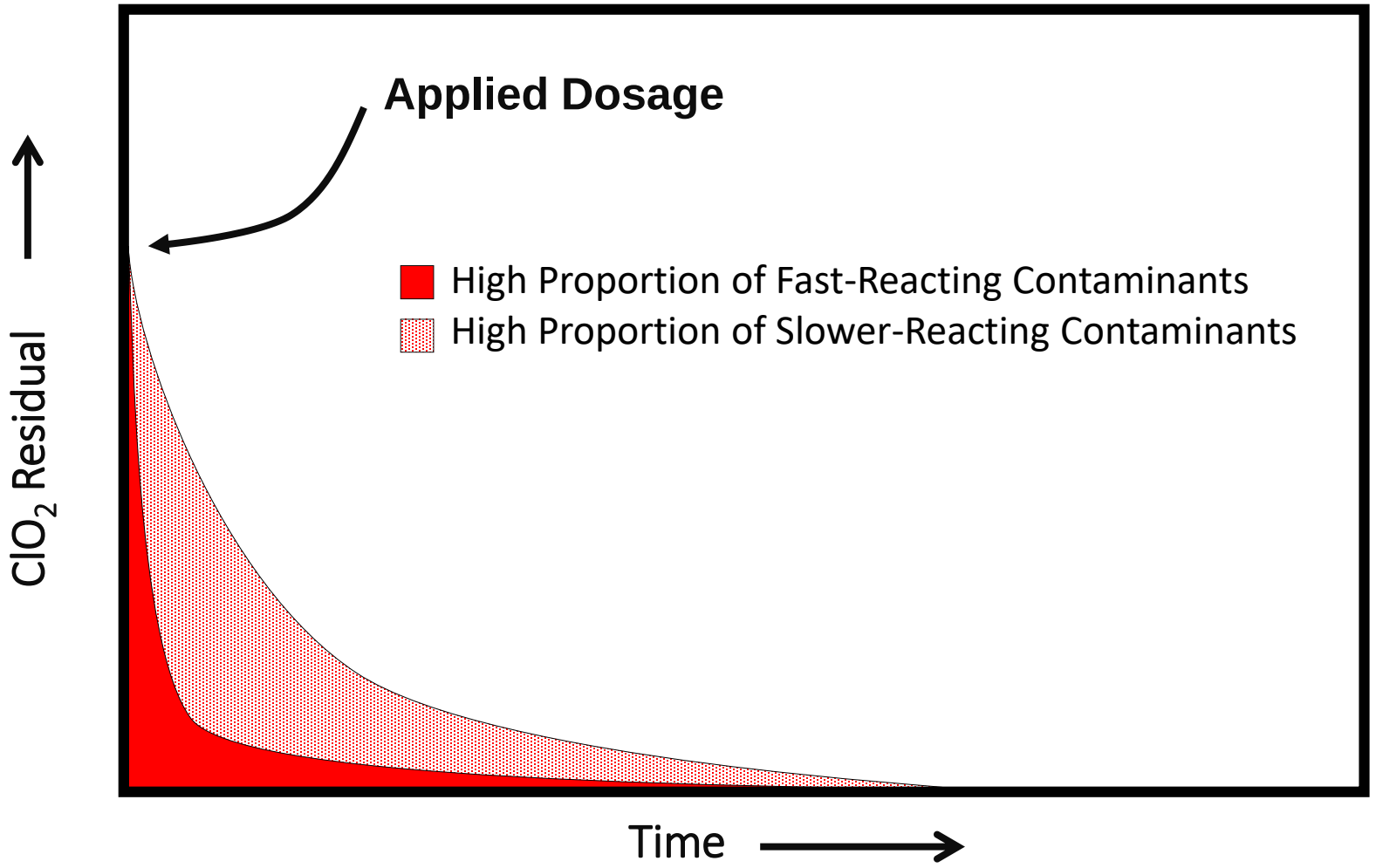
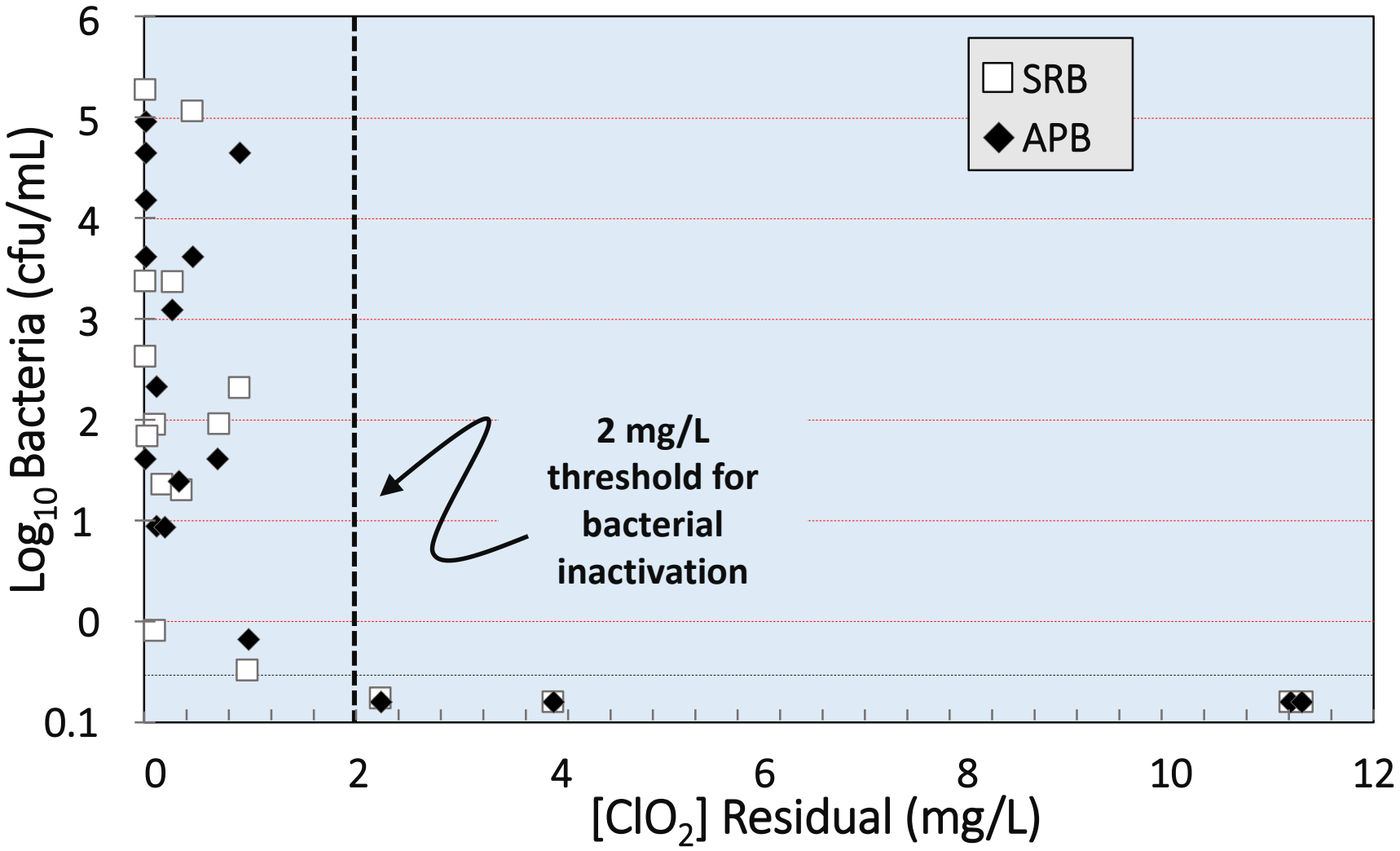
What Happens to ClO_2 Residual



Residual ClO_2 Required for Bacterial Inactivation



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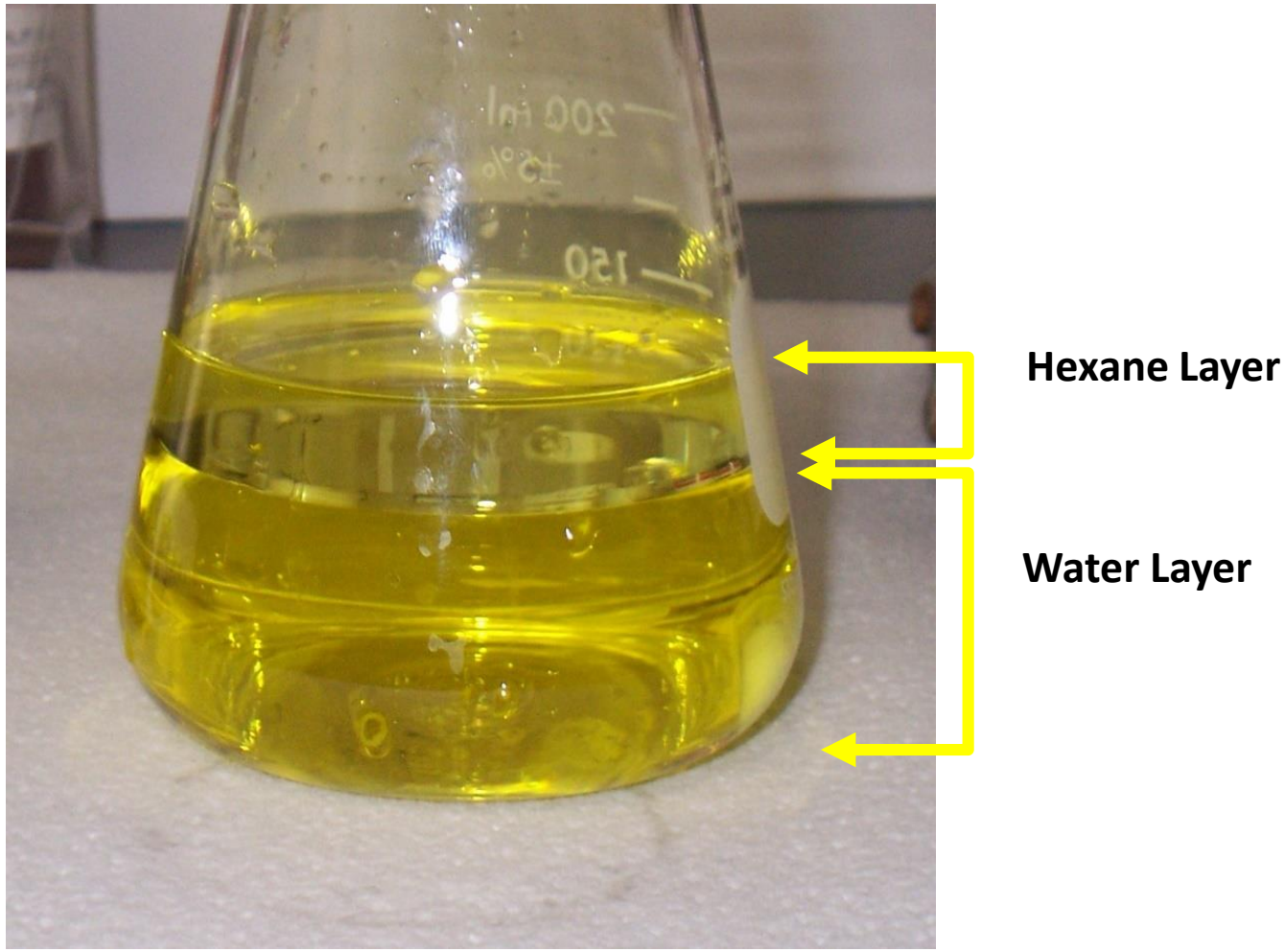
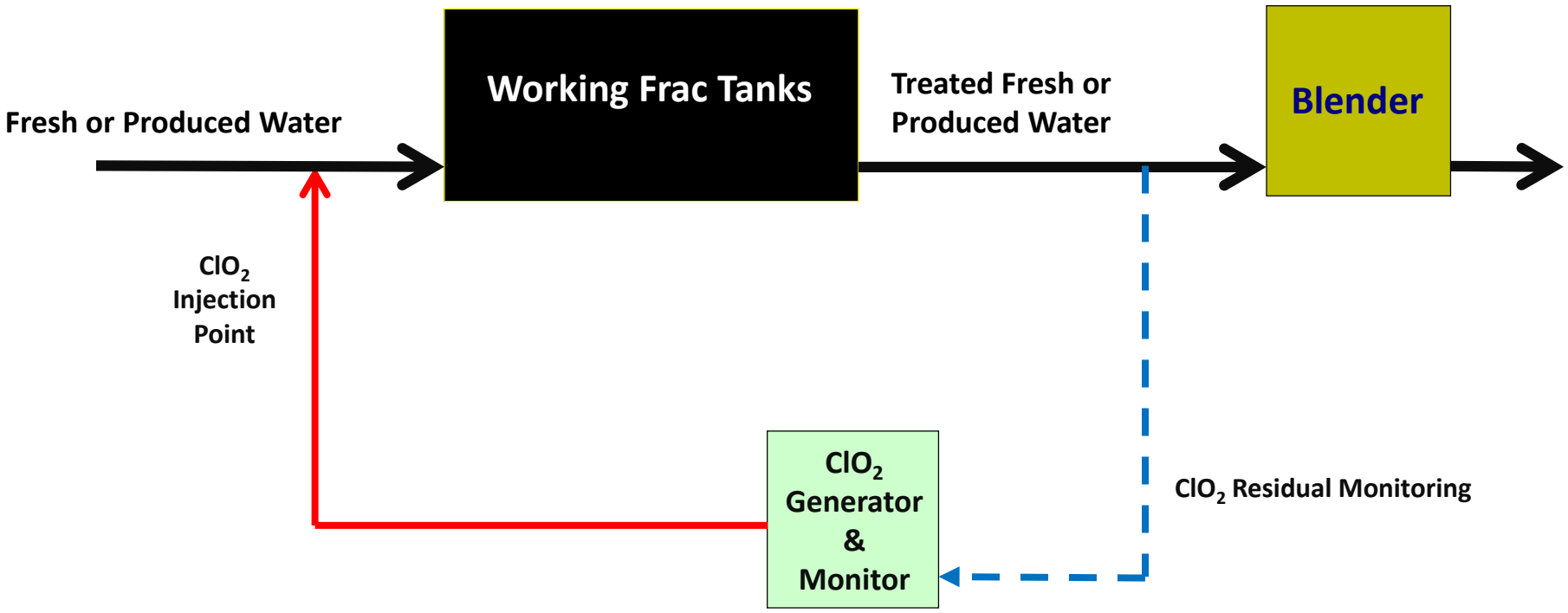
ClO_2 Penetrates Organics (Biofilm)

ClO_2 is uncharged. ClO_2 is relatively non-polar. It is ~ 4X more soluble in cyclohexane than it is in water.



Caveat

Setup with Working Tanks



- Typical Fresh Water Dosage ~1.5 – 10 ppm (~ 3 – 5 ppm residual)
- Typical Produced Water Dosage ~ 10 - 150 ppm (every application is different)

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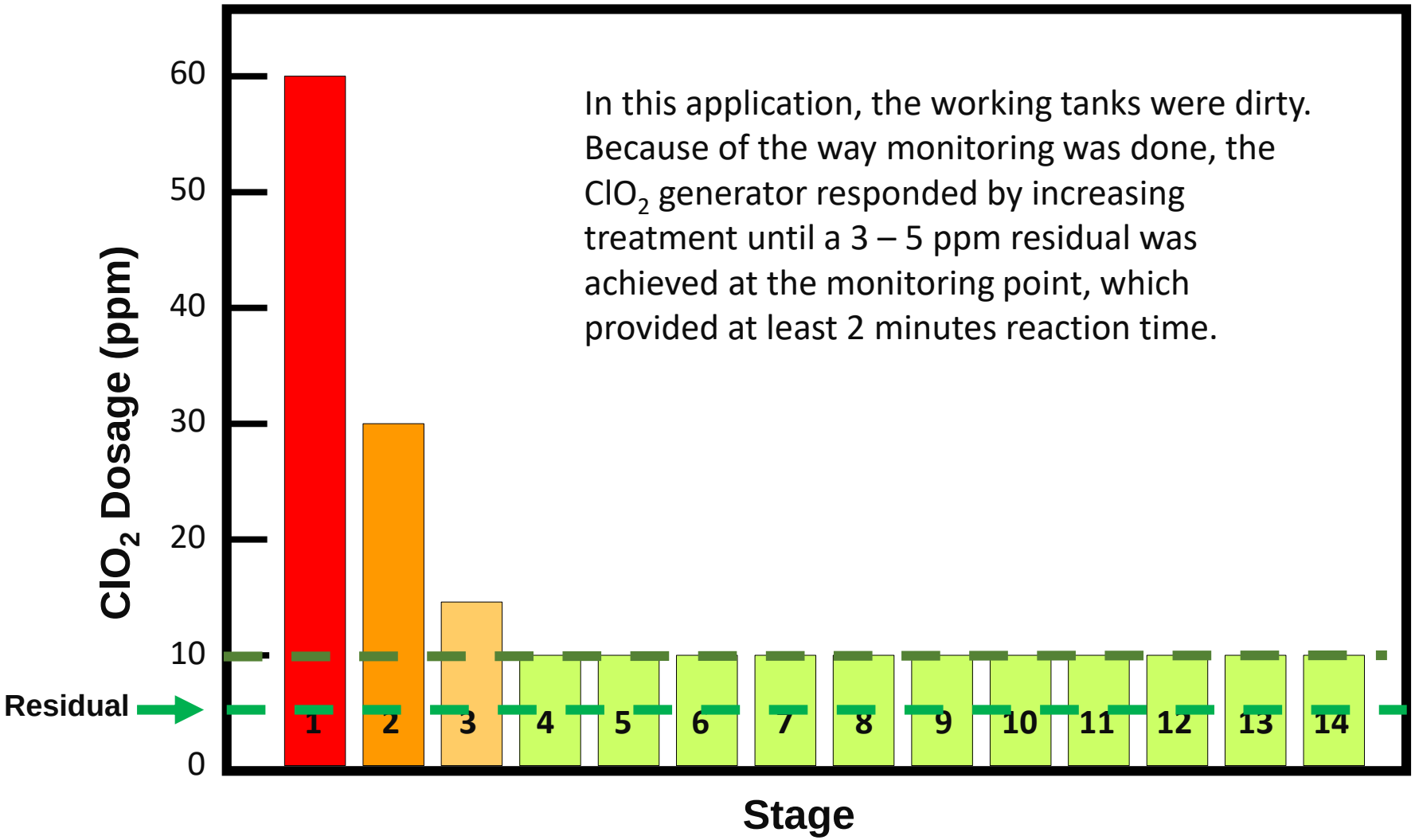
Response of Real-Time Generator Control to Dirty Working Tanks



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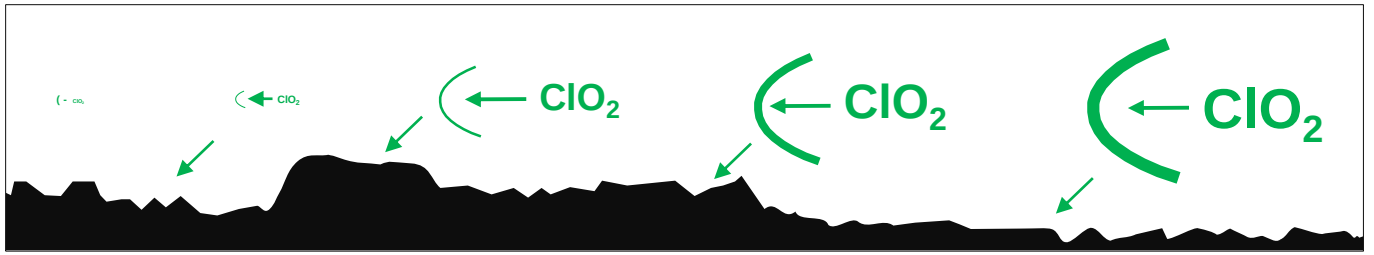
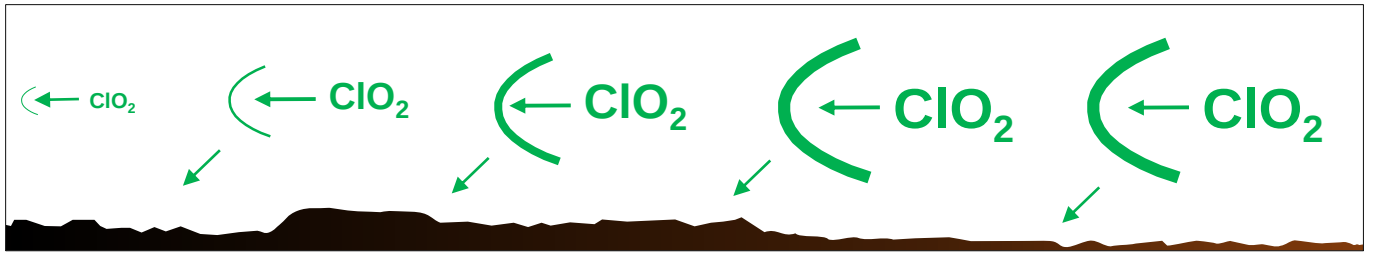
How ClO_2 Interacts with Sludge

Stage 1

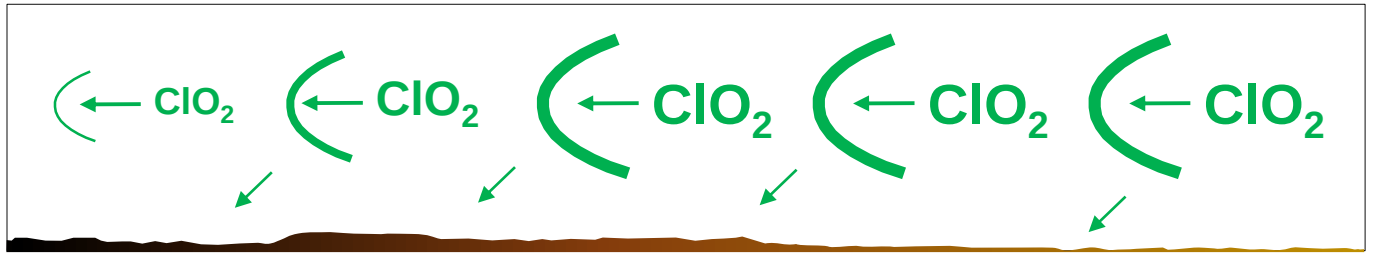


Bulk Water Demand Met

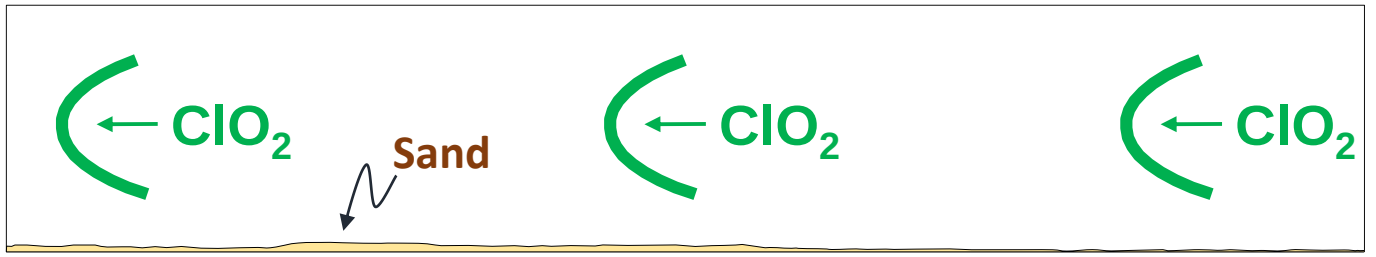
Stage 2



Stage 3



Stage 4 - 14



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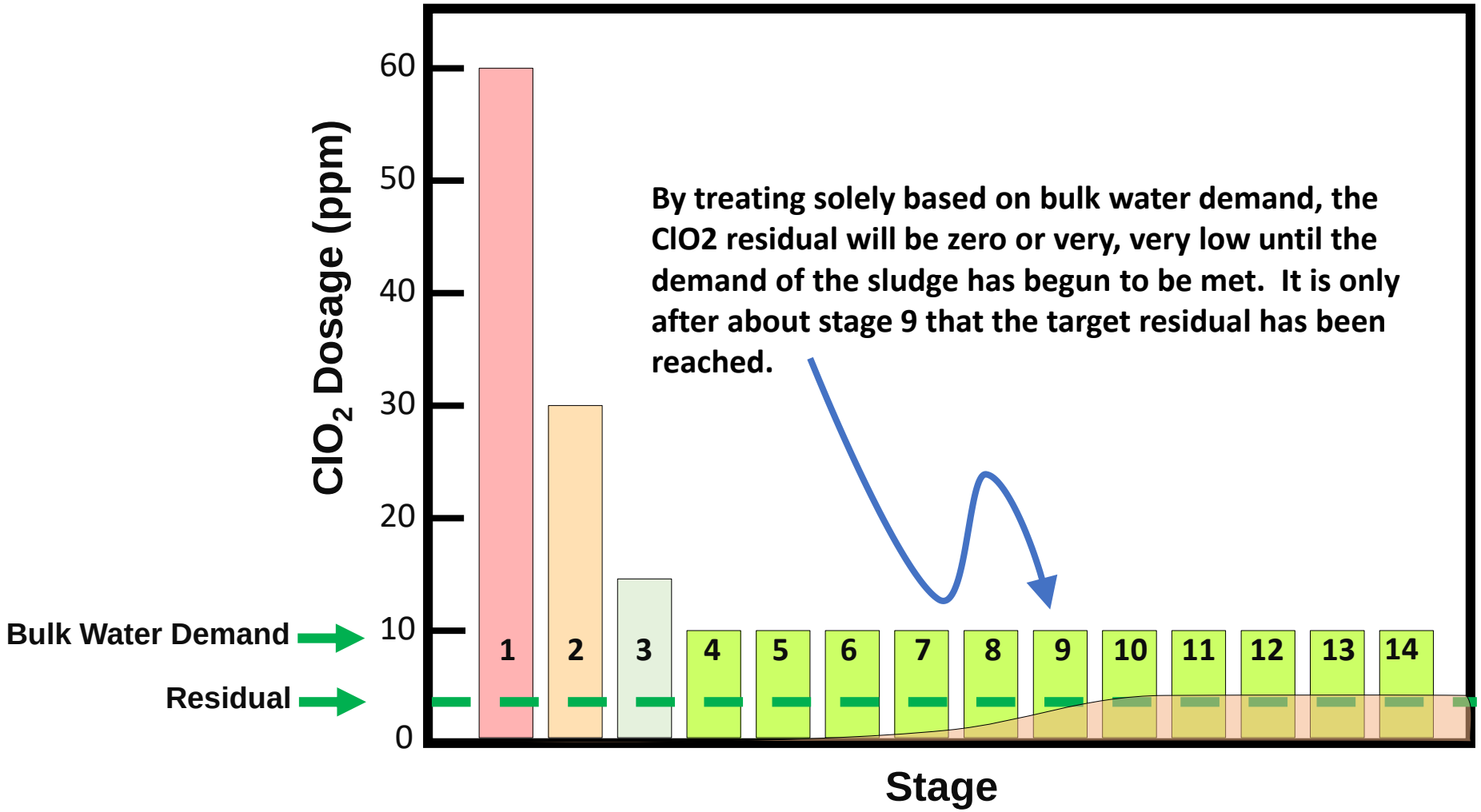
What Happens if ClO_2 Is Fed Based Solely on Bulk Water Demand



Conclusions:

- ClO_2 – Effective on Bacteria & Biofilm
- ClO_2 – Kinetics & Stoichiometries
- ClO_2 – 2 ppm residual for Minimum of 2 minutes
- ClO_2 – Bulk Water Demand vs. Biofilm Demand vs. Sludge Demand
- Importance of Real-Time Monitoring and Control
- What Happens If.....

- What Happens Next....