PA-AWWA 70th Annual Conference

Pocono Manor, PA

Utilization of Mixed Oxidants to Improve Residual & Overall Water Quality in Distribution Systems

May 10, 2018

Pennsylvania AWWA
American Water Works Association

What are Mixed Oxidants?

Mixed Oxidants are Produced by On-site Generation

- On-site generation is when basic, simple chemicals are used to generate chemical at the point of use
- In this case, the chemical produced is a chlorine-based disinfectant generated using salt

Why Use On-Site Generation?

Safety is One Major Reason

- Regulations
  - Trend toward the safest solution
  - Limit on hazardous chemical storage
- Incidents
  - Recent near miss of Cl_2 leak at two large industrial facilities South East US
  - Chlorine dioxide related fatalities: GM plant in 2014, Midland TX Oilfield 2016
- Sustainability
  - Less trucks, lower carbon footprint
  - Water conservation, less chemicals

Operational Cost is Another…

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To produce 1 lb of 100% Free Available Chlorine
equivalent to 1 gallons of 12.5% hypo

Salt		Electricity		Operational Cost
$0.30	+	$0.18	=	MIOX Cost ~$0.50
3 lbs salt at $0.10/lbs (or delivered brine)		2.5 kW-hr power at $0.07/kW-hr		Equivalent to 1 gallon of delivered 12.5% sodium hypochlorite ~$0.10 addt'l including parts maintenance

Equivalent Operational Cost

12.5% Sodium Hypochlorite	**$0.65 ~ $2.50**
Chlorine Gas	**$0.40 ~ $.75**

and Performance is the Third

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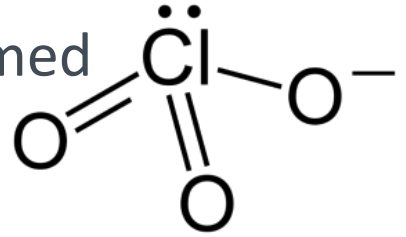
- Mixed Oxidants outperform typical bleach generators by providing enhanced behaviors

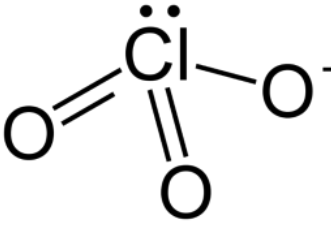
Future Challenges - Chlorate

- Chlorate (ClO_3^-) is on the EPA's Third Chemical Contaminant List (CCL3)
  - indicating that the intention of the Environmental Protection Agency (EPA) to review chlorate as a potential candidate for regulation under the Safe Drinking Water Act.
- Chlorate is suspected to have negative health impacts such as thyroid issues, reduced hemoglobin production, and reduced weight gain.
- Chlorate is a highly oxidized form of chlorine, can be introduced to a water source as an industrial or agricultural contaminant or into a finished water as a disinfection byproduct (DBP).
- As a DBP, chlorate can result from water disinfection with bulk sodium hypochlorite, chlorine dioxide, or hypochlorite formed through electrolytic on-site generation (OSG) systems.



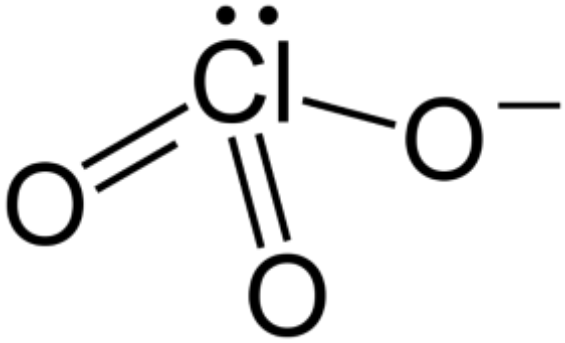
Future Challenges - Chlorate

- Currently, chlorate in drinking water is not regulated in the United States and there is no enforceable Maximum Contaminant Limit (MCL).
  - Canada MCL is 1.0 mg/L (1000µg/L).
  - The World Health Organization (WHO) recommends a chlorate limit of 0.7 mg/L (700 µg/L)
- While no final recommendation has been promulgated, literature on the topic indicated that the regulation may fall within the range of 0.21 mg/L (210 µg/L) to 0.8 mg/L (800 µg/L) in the US.
- While 210 µg/L as established by the EPA as a health reference level, it is conjectured that the EPA will not establish such a low level as it will seriously impact the viability of using delivered bulk hypochlorite in the marketplace.



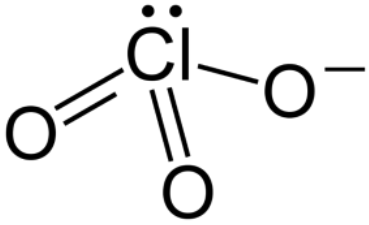
Chlorate Impacts on Bulk Hypochlorite

- To limit chlorate formation, users of bulk hypochlorite may need to:
  - Move storage indoor, if not already located there.
  - Cool the room where the hypochlorite is stored to retard degradation.
  - Require “born-on dating” from the manufacturers to ensure freshness.
  - Limit storage volumes.
  - Purchasing lower concentrations to slow the degradation.
  - Dilute the concentrated hypochlorite once it has been delivered to the treatment plant.
- All of these will have significant cost impacts!!!!!



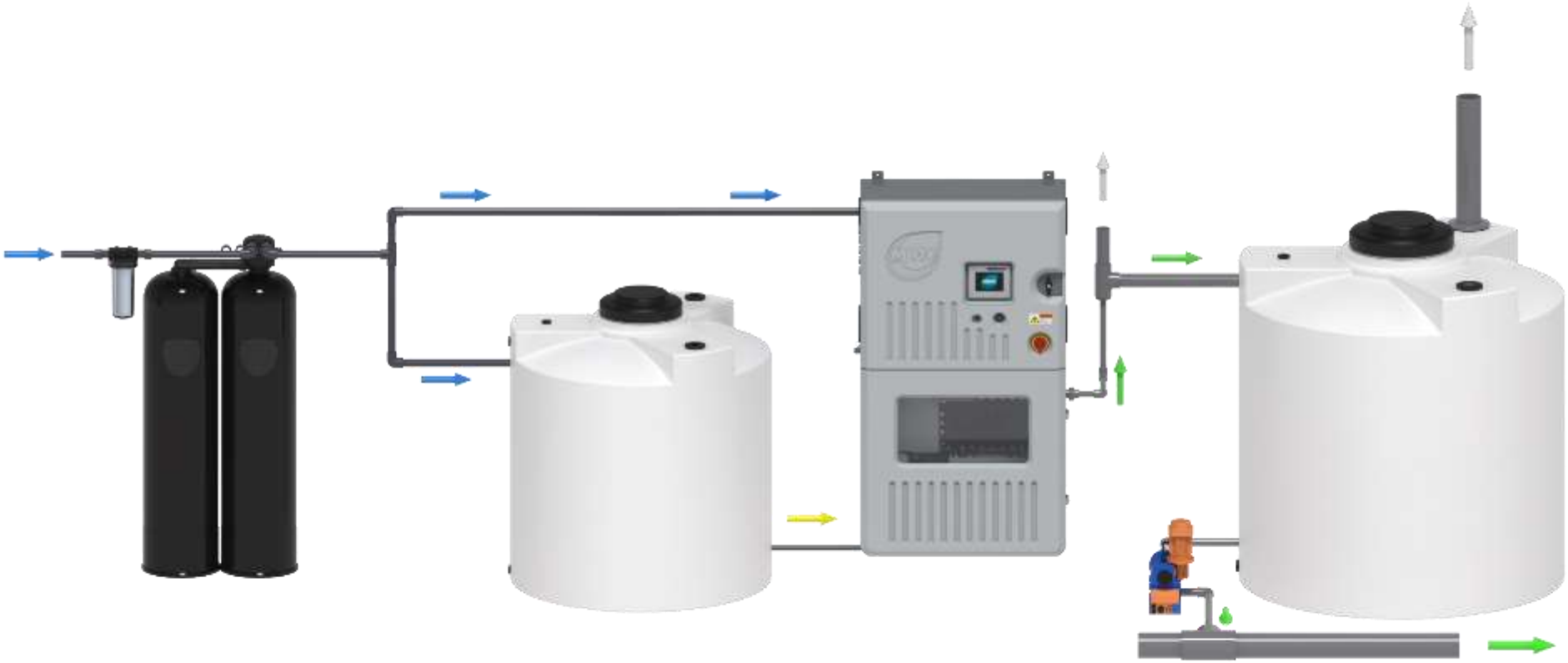
“Future Proof” Against Chlorate with OSG

- Testing shows MIOX’s RIO OSG systems typically produce less than 40 micrograms per milligram of free available chlorine (FAC).
- Even at a high FAC dose of 5 mg/L, the expected chlorate concentration in the treated water will be less than 200 µg/L.
- Water treatment plants usually dose 2 – 3 mg/L FAC so chlorate content will likely be half of the lowest contemplated chlorate regulatory limit.
- Generated on-site – always fresh.
- Less than 1% chlorine concentration = very slow degradation rate.
- Modular in nature
  - as regulations change, upgrades are simple and easy to implement.



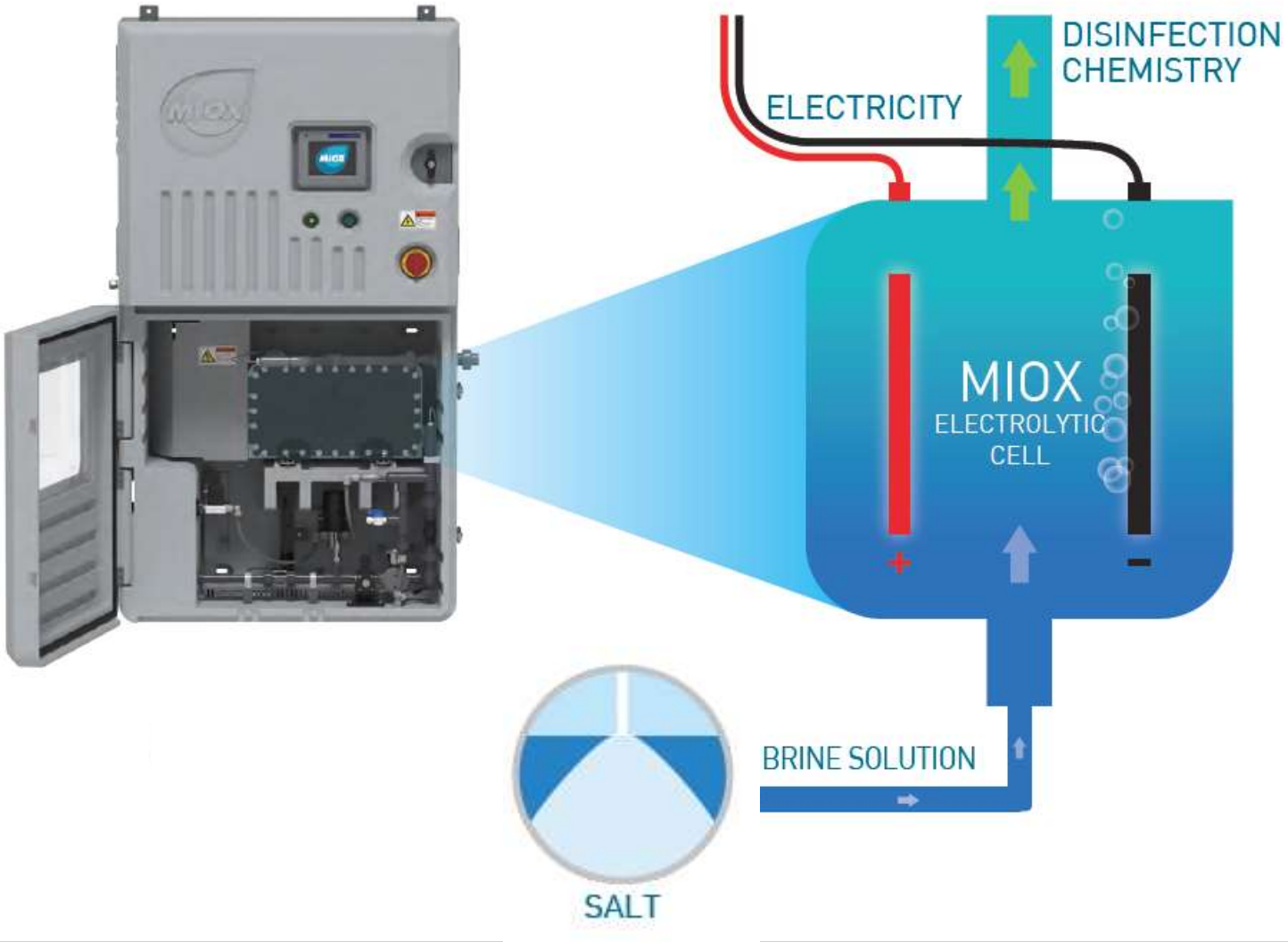
How Does It Work?

Typical Process Flow



MIOX ELECTROLYSIS PROCESS

The electrolytic cell of a MIOX on-site chemical generator uses salt combined with water and electricity to generate disinfectant at the point of use.



Cell Reactions

- **Anode Primary Reaction (+ Side): $2\ Cl^- \rightarrow Cl_2 + 2\ e^-$**
- **Cathode Reaction (- Side): $2\ H_2O + 2\ e^- \rightarrow H_2\uparrow + 2\ OH^-$**
- **Chlorine Hydrolysis Reaction: $Cl_2 + H_2O \rightarrow HOCl + Cl^- + H^+$**
- **HOCl Equilibrium Reaction: $HOCl \leftrightarrow OCl^- + H^+$ (depends on pH)**

If you stop here, you have a hypochlorite generator…

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…But if you add more power…

- **Anode Secondary Reaction (+ Side): $2\ OH^- \rightarrow H_2O_2 + 2\ e^-$**

Performance and Benefits of Mixed Oxidants

Municipal Water Treatment

- The peroxide component in Mixed Oxidant Solution (MOS) enhances the performance of the chlorine
  - Superior microorganism inactivation
  - Control/Eliminate biofilm
  - Reduced coagulant consumption
  - Longer-lasting residual
  - Reduced formation of DBPs, AOX
  - Accelerated breakpoint chlorination - Improved taste and odor
  - Cost effective removal of Ammonia and Sulfides
  - Faster oxidation of manganese

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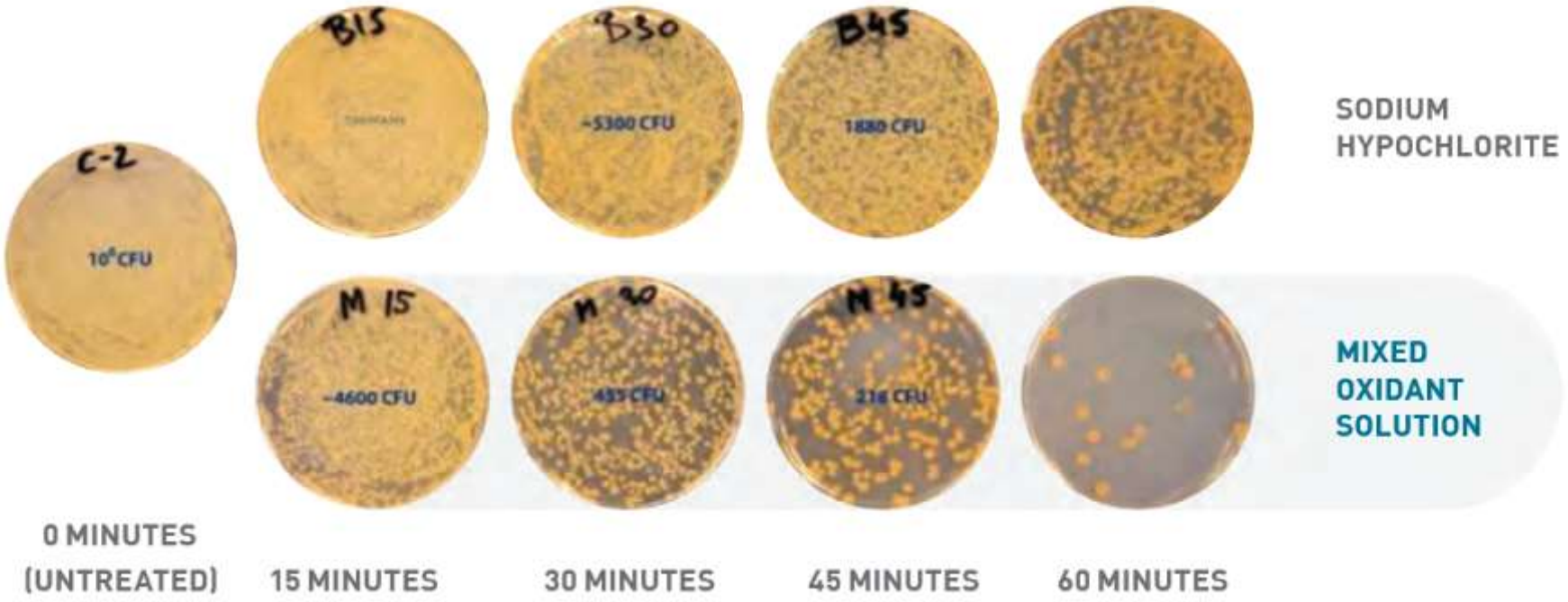
- Produces more powerful disinfectant than Hypochlorite
- More power is derived from Hydrogen Peroxide in solution with Hypochlorite in 24-48 hrs

Centers for Disease Control and Prevention (US CDC) verifies MIOX Mixed Oxidant Solution (MOS) is more effective than bleach for inactivating very tough to kill spores like Bacillus Globigii.



Biofilm Creates Multiple Challenges

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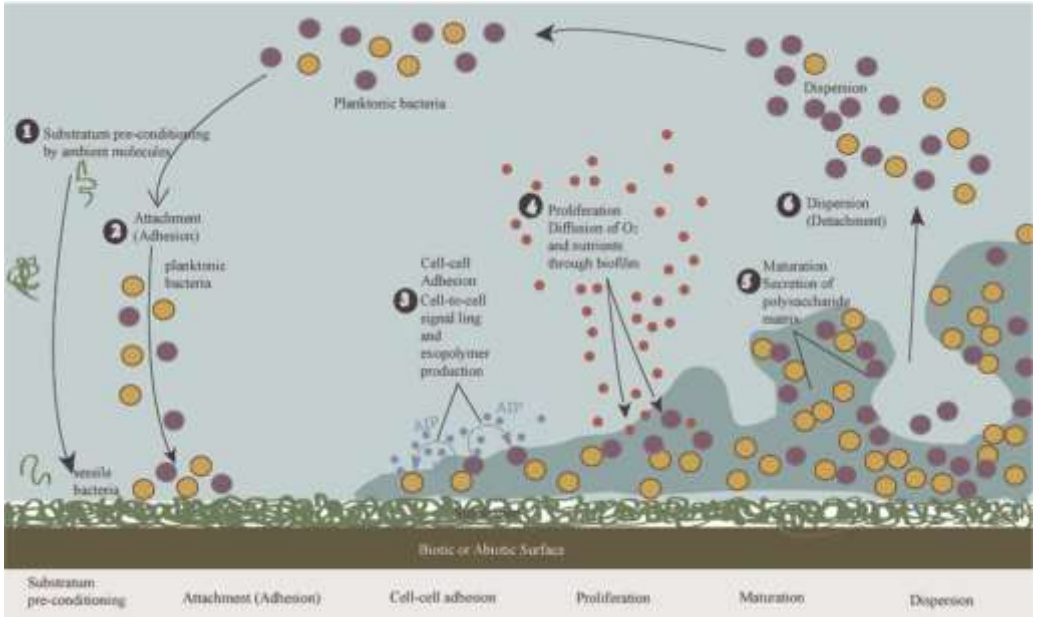
- Acts as an oxidant demand (consumes chlorine)
- Provides an additional carbon source

- *Therefore - High chlorine + more organics = DBP troubles*

Why is Biofilm so Hard to Control?

- Bacteria secrete it for several reasons
  - Helps transport nutrients to the organisms
  - Helps transport waste from the organisms
  - Protects the organisms from adverse environmental conditions
    - Example: Chlorine!!!



Biofilm Harbors Legionella & Corrosion

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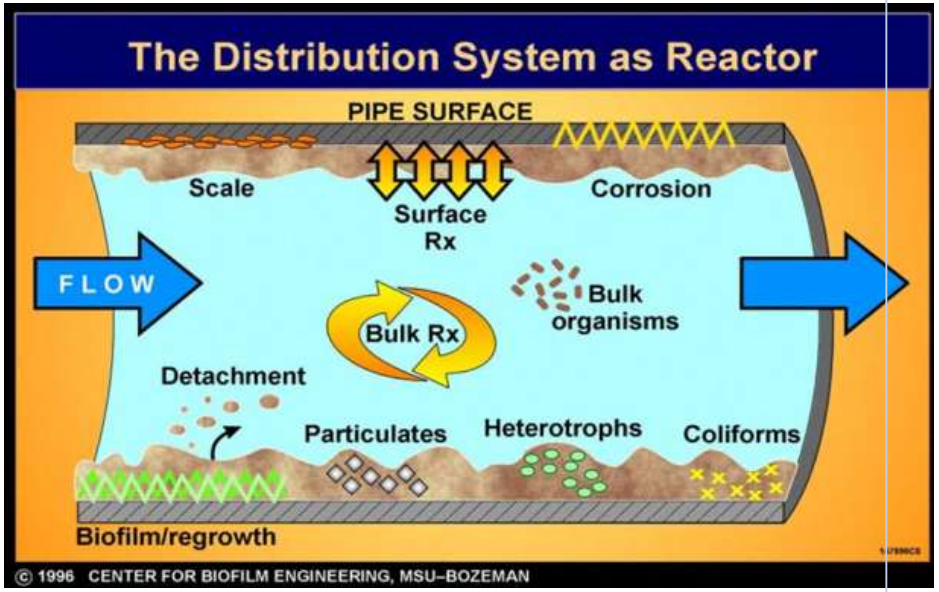
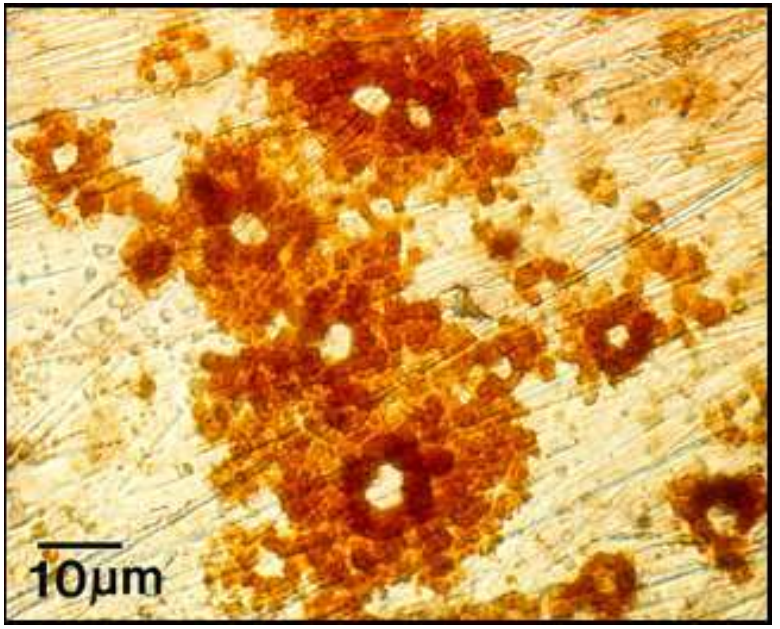
Biofilm Harbors Organisms



Although Hypochlorite and other proprietary biocides inactivates Legionella, it cannot inactivate Legionella in the Biofilm

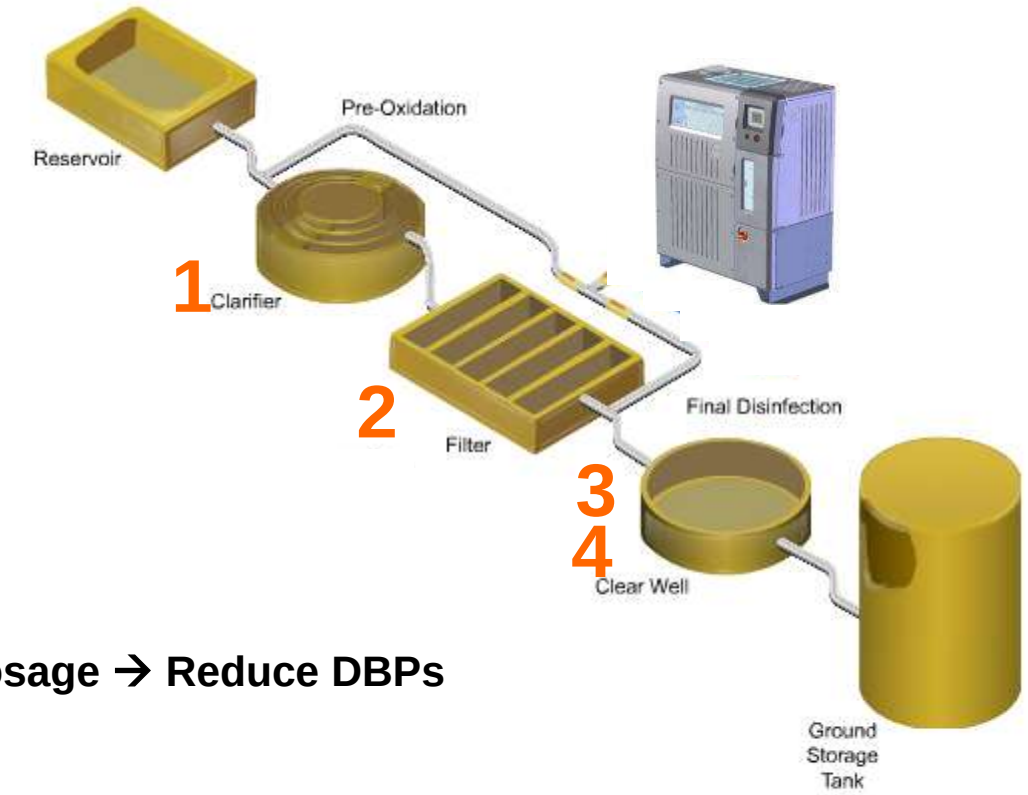
Microbially Influenced Corrosion (MIC)



Pitting corrosion on 316S stainless steel*

Where MOS Fits In

Typical Drinking Water Treatment Facility Layout



- **Control/Eliminate biofilm**
- **Reduce Demand → Reduce Dosage → Reduce DBPs**
- **Longer-lasting residual**
- **Accelerated breakpoint chlorination - Improved taste and odor**
- **Reduced coagulant consumption**

1. **Pre-oxidation**
2. **MF/UF Pre-feed**
3. **Clean in Place (CIP)**
4. **Final Disinfection**

Biofilm Removal Across Many Applications

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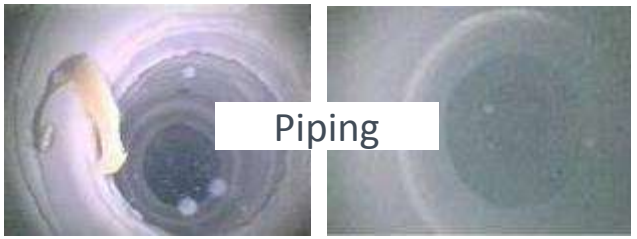
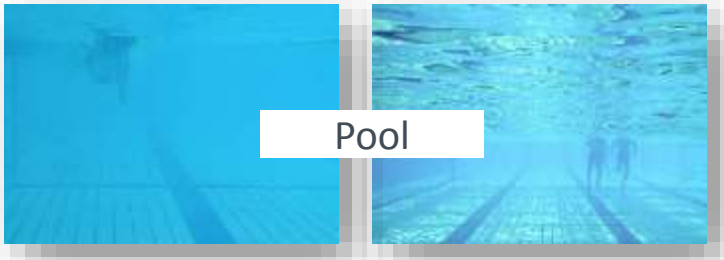
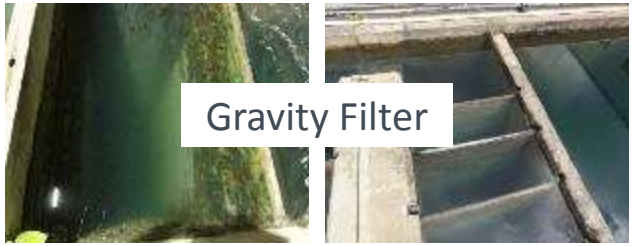

Piping


Pool


Condenser


Frac Pond


Gravity Filter


Hot Tub


Cooling


HVAC

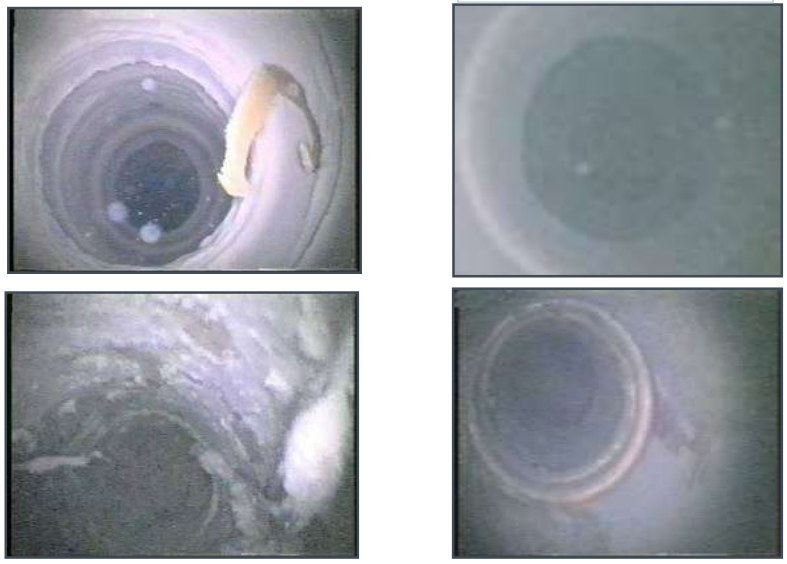
Cost Safety Control

CASE STUDY

Spa in Japan previously using **Bulk Hypochlorite** 1.5 mg/L had Legionella cases. In 5 hours of Mixed Oxidant solution biofilm started sloughing

BEFORE MOS

22 days AFTER MOS



- **Extensive biofilm**
- **Legionella CFU >5**
- **Dose: 1.5 mg/L Hypo**
- **Residual: 0.2 mg/L**

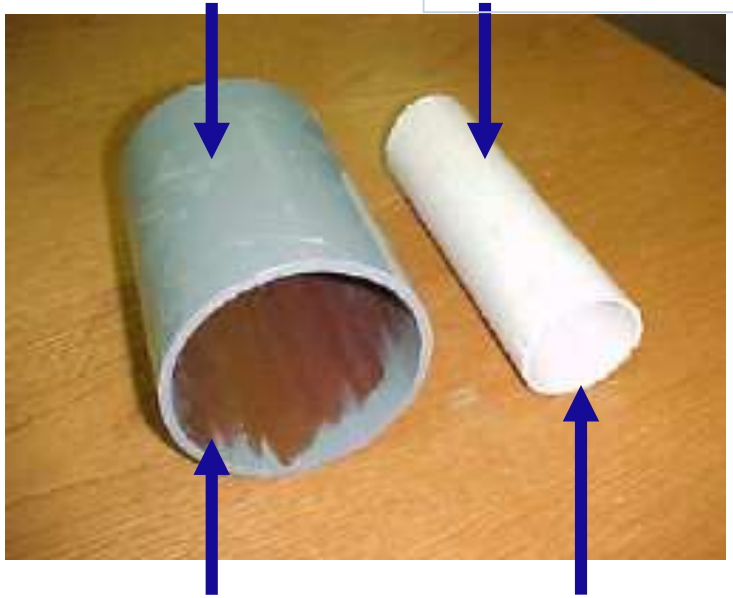
- **Biofilm eliminated**
- **No bacterial hits**
- **Dose: 0.6 mg/L Hypo**
- **Residual: 0.4 mg/L**

CASE STUDY

A city in Texas was using **Gas Chlorine** where brown biofilm slime on pipes in distribution system commonly noticed.

BEFORE MOS

1 Year AFTER MOS



Distance from Treatment Plant: **200 feet**

Distance from Treatment Plant: **1/2 mile**

Lower Disinfection Byproduct Formation

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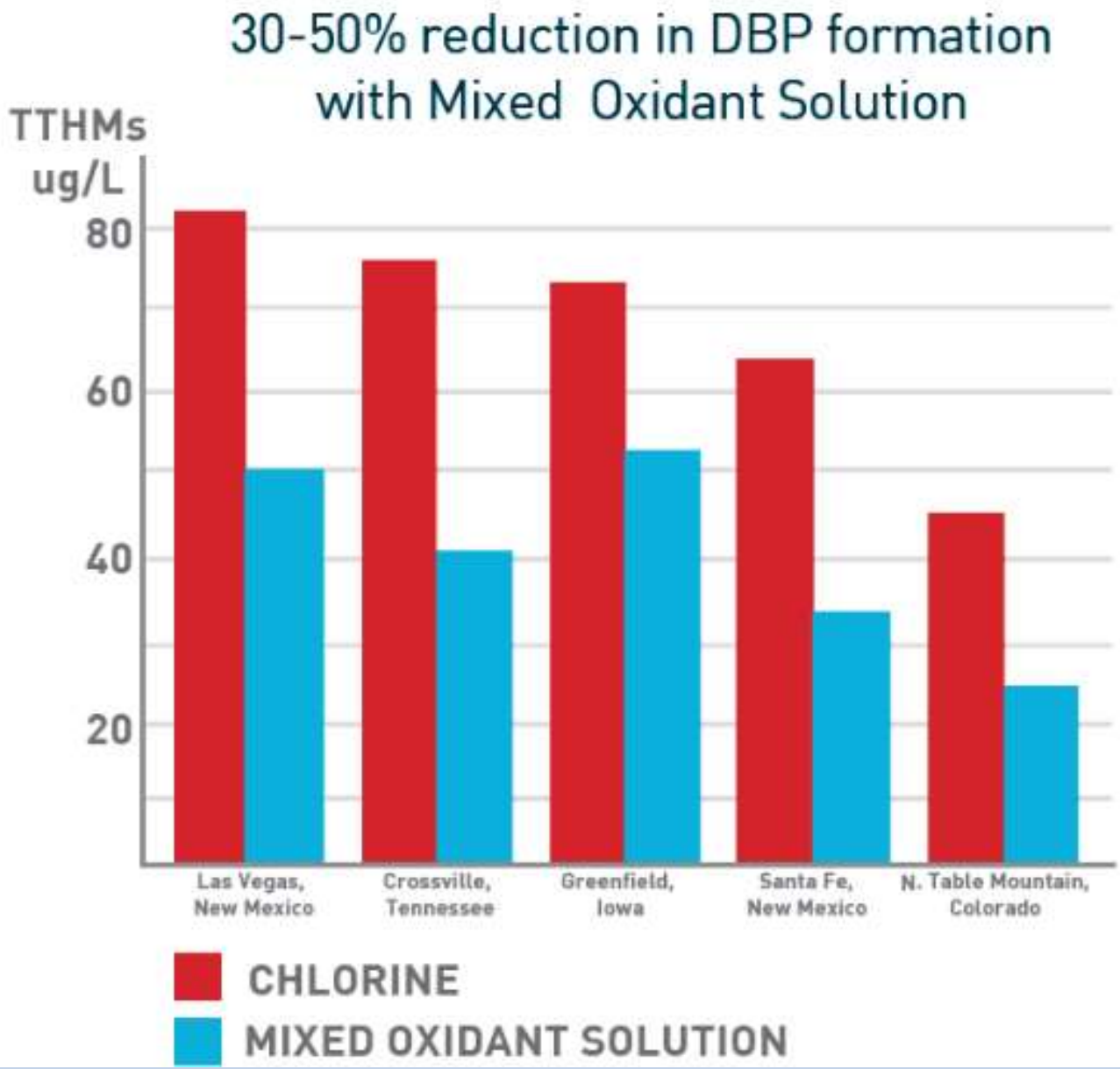

Reduced Dose + Higher residuals

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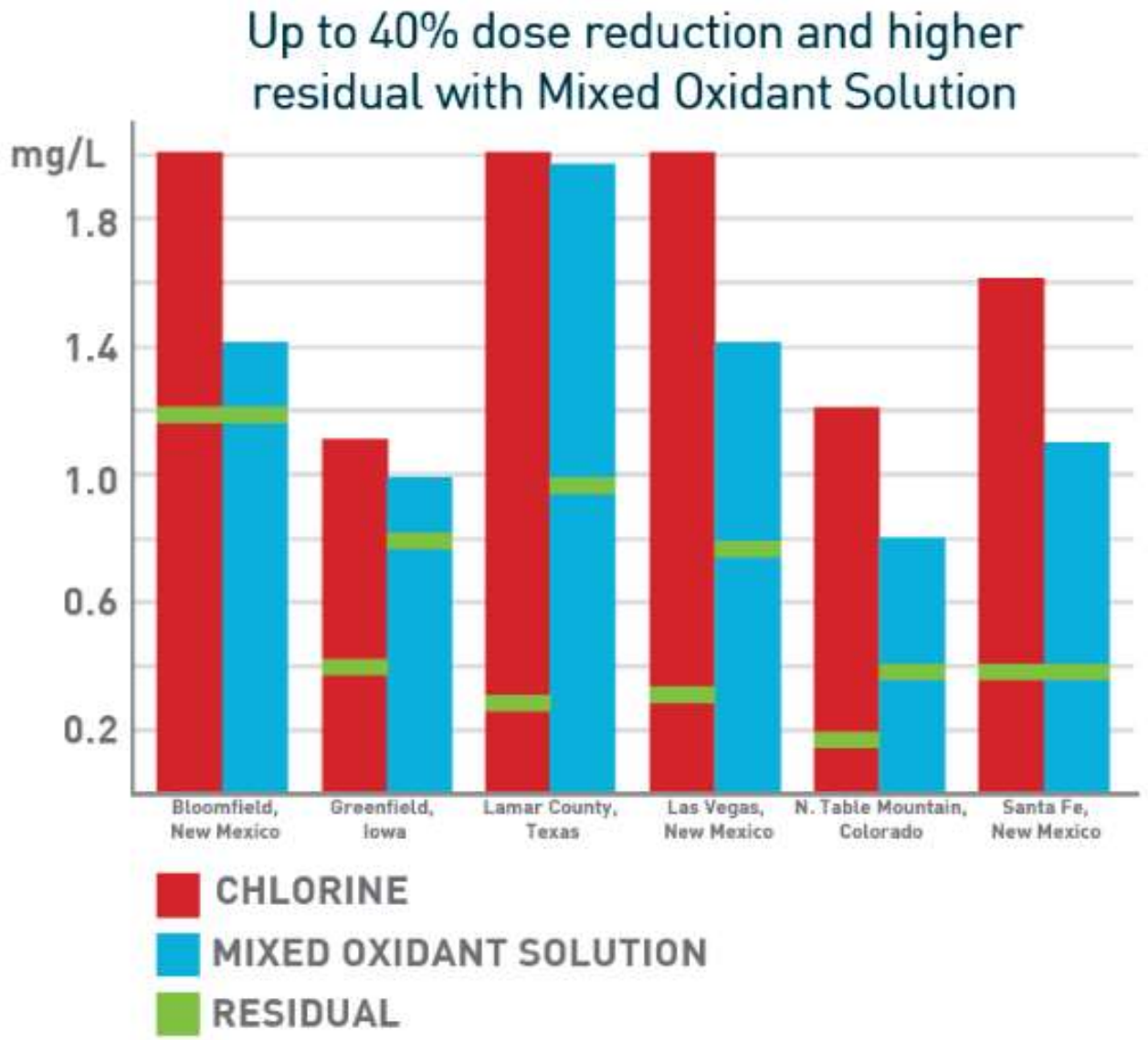
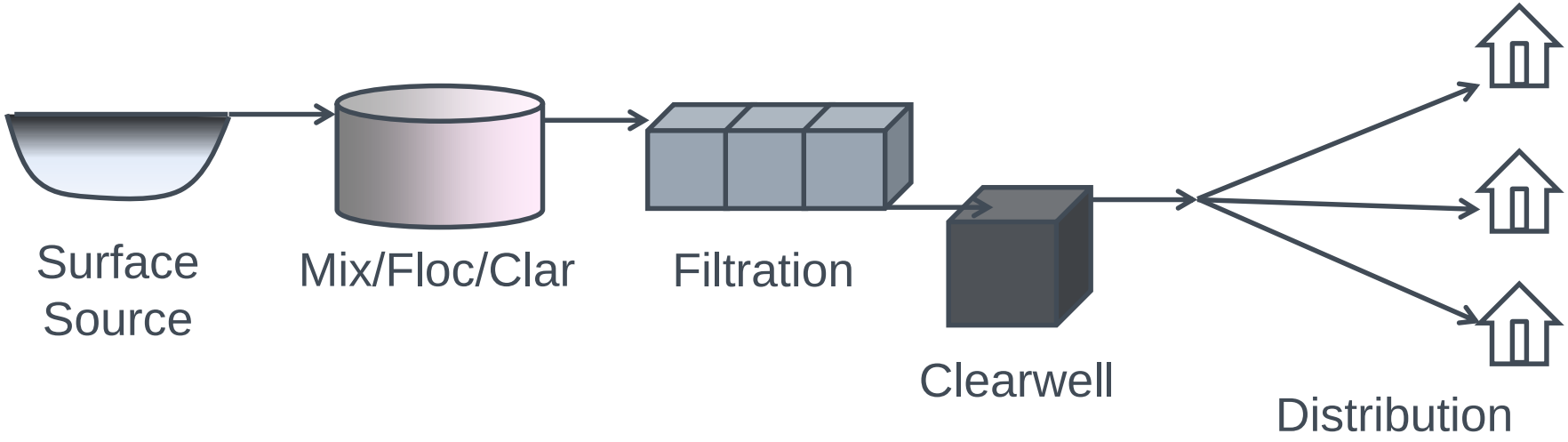


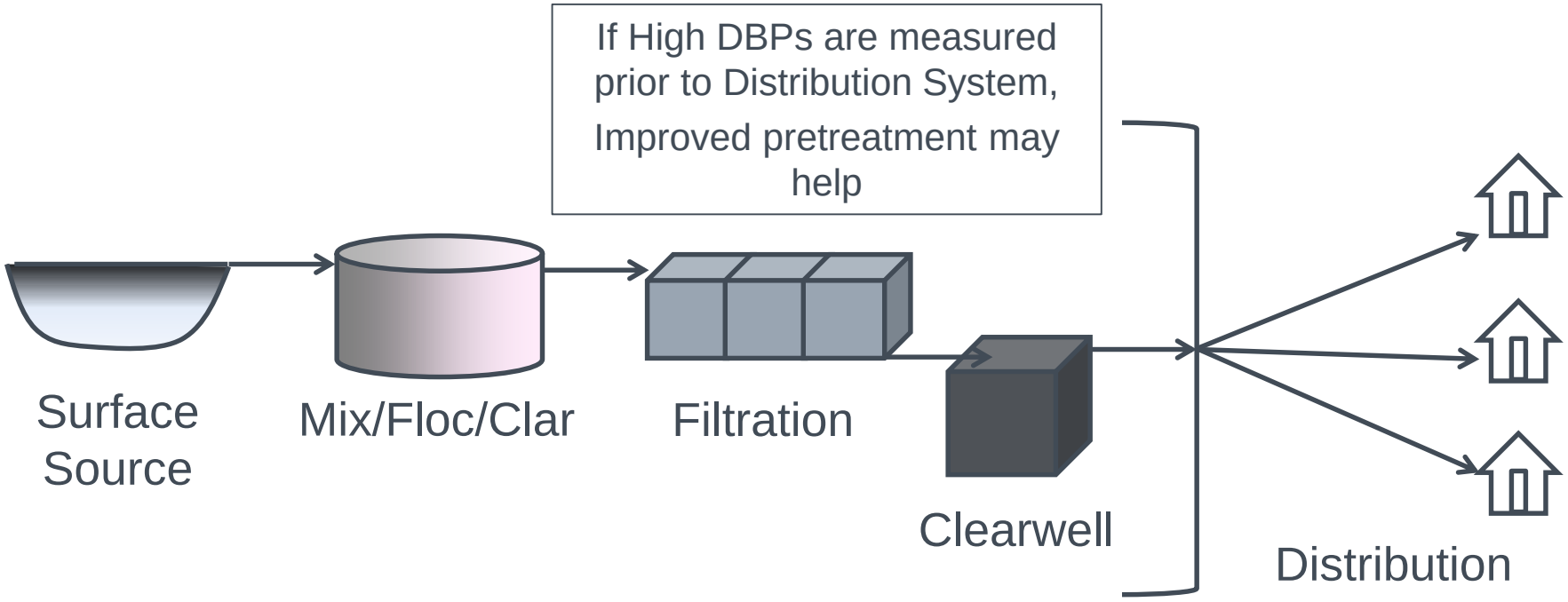
Disinfection By-Product Formation Reduction

- DBP troubleshooting can help identify if MOS makes sense…



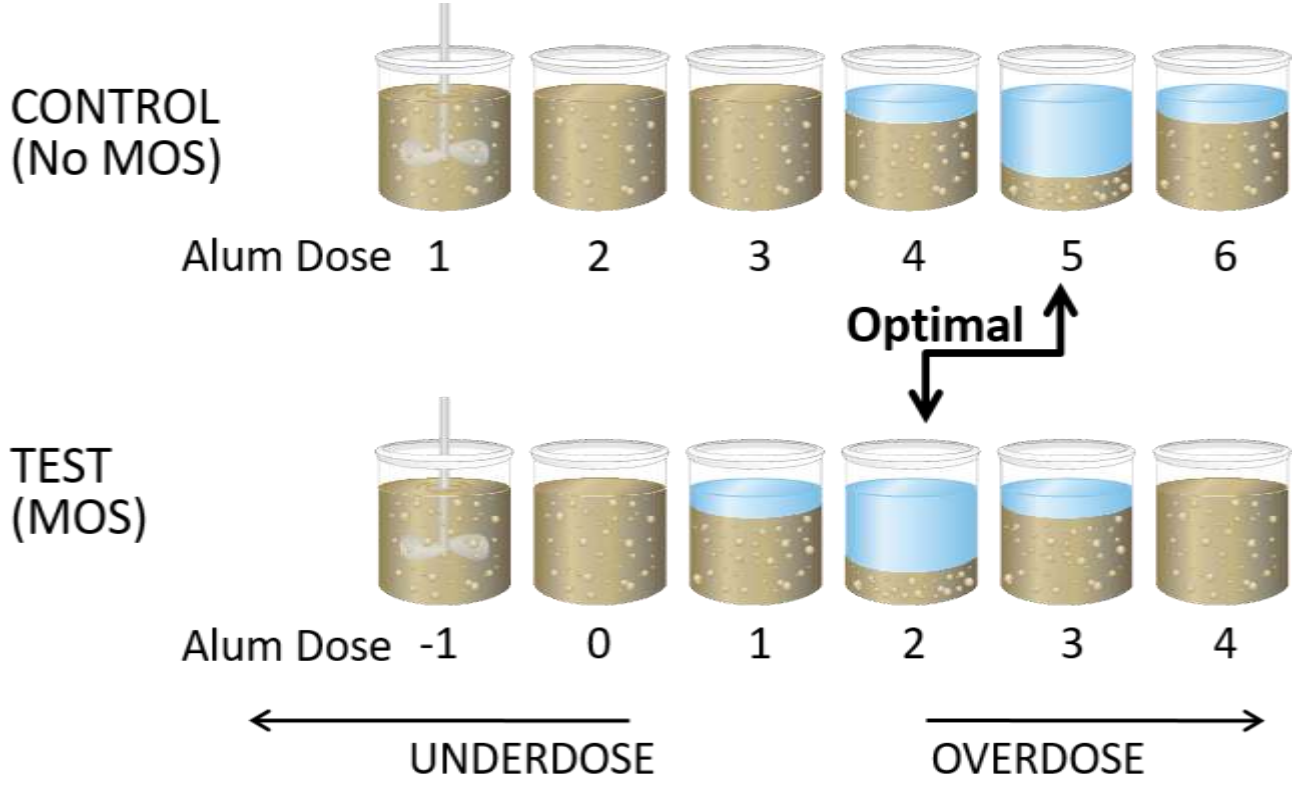
Disinfection By-Product Formation Reduction

- DBP troubleshooting can help identify way forward…



Microflocculation Effect May Improve Organic Matter Reduction and Reduce Coagulant Cost

- Effect can improve removal and settleability at a lower effective dose
- Enhanced DOC removal can lead to lower formation potential



Reduce Coagulant Usage by up to 40%

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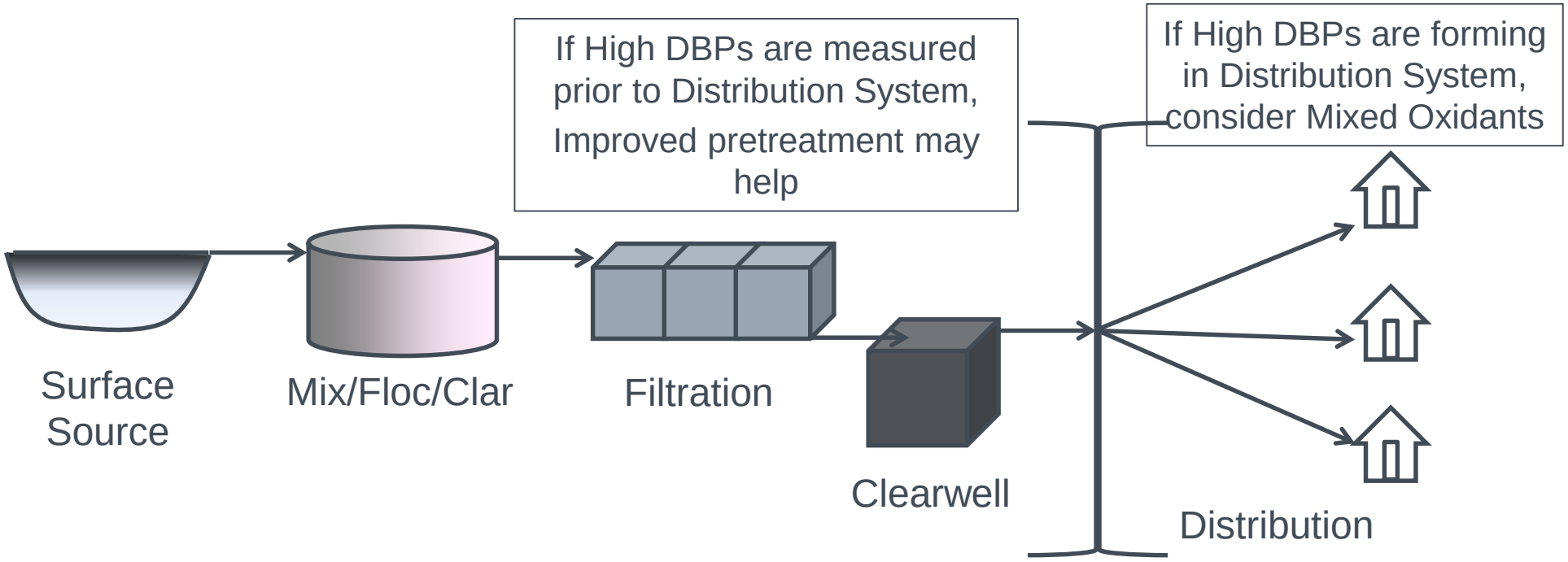
	COAGULANT CONSUMPTION			EFFLUENT TURBIDITY - ntu		
INSTALLATION SITE	PREVIOUS DOSE	CURRENT DOSE	PERCENT REDUCTION	PREVIOUS LEVELS	CURRENT LEVELS	PERCENT REDUCTION
Crossville, Tennessee	90 GPD	70 GPD	22%	N/A	N/A	N/A
Greenfield, Iowa	14.7 mg/L	8.9 mg/L	40%	0.107	0.065	39%
Las Vegas, New Mexico	10.5 mg/L	7.5 mg/L	29%	0.07	0.03	57%
Santa Fe, New Mexico	90 mg/L	54 mg/L	40%	0.60	0.18	70%
Midwest United States	N/A	N/A	N/A	2.0	0.4	80%

Disinfection By-Product Formation Reduction

- DBP troubleshooting can help identify way forward…



Some Additional Testing Can Help Decide

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DBP Formation Potential (DBPFP) can help tell you what is going on:

- This would be done on the filtered water before the clearwell or storage. This should be timed to emulate the distribution timing expected during the worst DBP formation times of the year. For example, if you have calculated that the distribution system has a residence time of 24 hours at the test point, the DBPFP test should have a hold time of 24 hours.
- This should then also be compared to the actual DBPs as measured at the test point.
- Ideally, you will take a sample at your testing point after the same residence time, so that you are comparing roughly the same water.

Some Additional Testing Can Help Decide

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DBP Formation Potential (DBPFP) can help tell you what is going on:

Scenario 1

If the DBPFP is say 40 ppb, but the sample from the furthest test location is 100 ppb, then you know the distribution system is strongly contributing to the formation.

This is usually due to the presence of biofilm in the distribution system acting as an additional carbon source. In this case, this is a textbook case of where MOS can be of significant value.

Some Additional Testing Can Help Decide

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DBP Formation Potential (DBPFP) can help tell you what is going on:

Scenario 2

If the DBPFP is high, say 85 ppb, and the sample at the furthest point is something like 90 ppb, then the distribution system is pretty clean.

Therefore more focus should be given to improving the pretreatment to reduce the DBP precursors coming through the water treatment plant.

Some Additional Testing Can Help Decide

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DBP Formation Potential (DBPFP) can help tell you what is going on:

Scenario 3

If the DBPFP is high, say 85 ppb, and the sample returns at something like 125 ppb, then you know that both the precursors and the distribution system are contributing to the problem and both areas should be targeted for improvement – once again, and ideal case where MOS could be used.

Case Studies

Paducah Water, Paducah, KY

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Contact: Ricky Gilbert, Plant Superintendent

Plant Capacity: 20 MGD

System: (3) RIO M5 SC (900#FAC/day)

Prior Disinfection: Chlorine Gas

Installation Date: February 2015

Source Water: Surface

Application: Pretreatment
Final Disinfection

Benefits: Safety, TTHM reduction, chlorine residual enhancement,

They no longer re-chlorinate at four (4) booster stations in their distribution since switching to MOS

Prestonsburg Utility Commission, KY

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Contact: Donald Compton, WTP/WWTP Manager

Plant Capacity: 5 MGD

System: MIOX- 5001 (2004) RIO-M5 SC (2014) & RIO-S M900 (2018)

Total Capacity: 1200# FAC/day

Prior Disinfection: Chlorine Gas

Installation Date: August 2004

System Upgrades: 2014, 2018

Source Water: Surface

Application: Pretreatment, Final Disinfection

Benefits: Safety, TTHM reduction, chlorine residual enhancement

Danville WTP, Danville, KY

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Contact: Andy Tompkins,WTP Superintendent

Plant Capacity: 10 MGD

System: (3) RIO-M5 SC (900#FAC/day)

Prior Disinfection: Chlorine Gas

Installation Date: Legacy MIOX units initially installed in 2002 were replaced in 2016 & 17

Source Water: Surface

Application: Pretreatment, Final Disinfection

Benefits: Safety, Reduced Liability, TTHM reduction, chlorine residual enhancement,

They no longer re-chlorinate at five (5) booster stations in their distribution system since switching to MOS

Holiday Hills WTP

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Holiday Hills WTP
Crossville, TN

System: Two (2) RIO-M3
Total Capacity: 360 #FAC/day
Installation Date: July 2008
Applications: Surface Water Final Disinfection, DBP Reduction, Chlorine Residual Improvement

50% reduction in TTHM & HAA after first year in operation.
The original MIOX system was installed in 2000 & upgraded to RIO units in 2008

Laguna Beach County Water District

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Summit Reservoir (600K gallons)
Hastie Reservoir (1.95 M gal)
Laguna Beach, CA

System: One (1) VAULT M15
Total Capacity: 15 #FAC/day
Installation Date: March 2016
Source Water: Purchased Surface
Applications: Reservoir Residual Management; DBP Reduction, Chlorine Residual Improvement, Residual Stability

District has reported that water quality improved & residual benefits have extended to other reservoirs in system.

MIOX Wide Range of Generators

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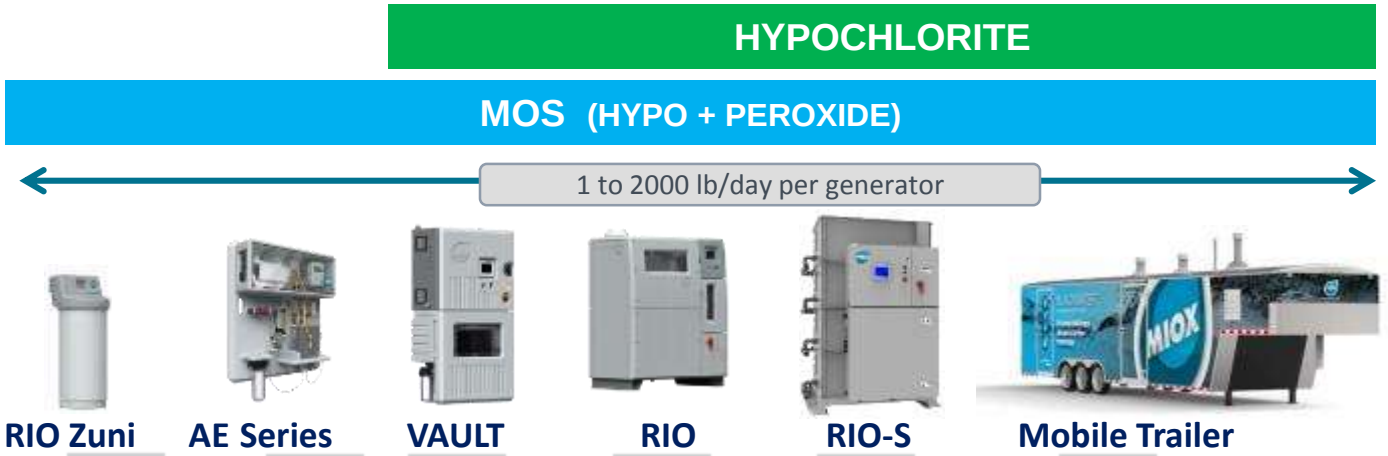

Thank You for Your Time…….

Questions?

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