Pennsylvania AWWA
American Water Works Association

DE NORA
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Status of Chlorate Regulations & Impact at Water Treatment Plants

Pennsylvania Annual AWWA Conference
Hershey, PA
April 18, 2018

ELECTRODE TECHNOLOGIES & WATER TECHNOLOGIES

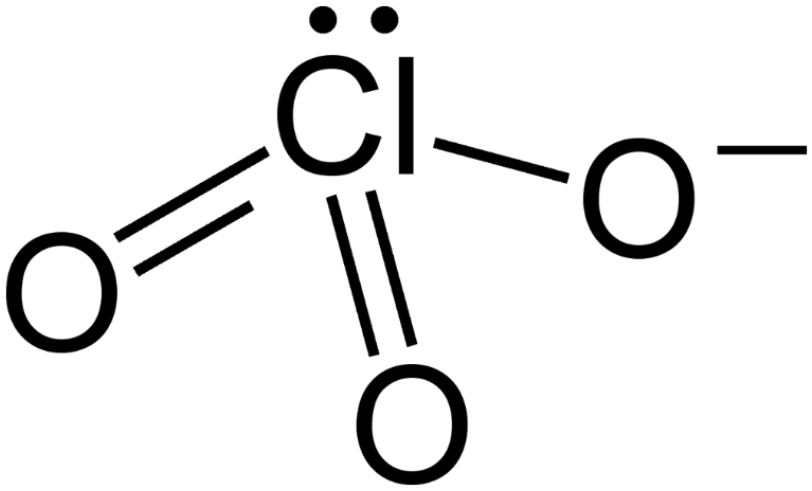


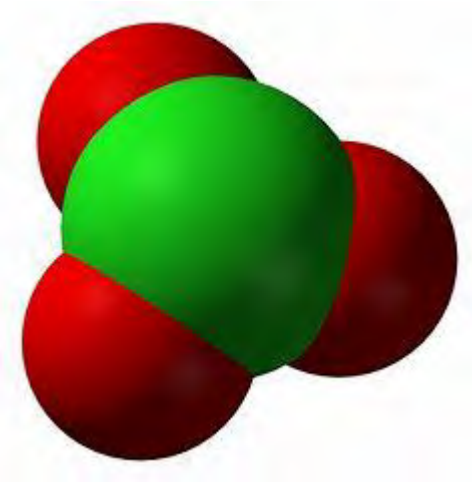



Background on Chlorate

What is Chlorate?

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).





Chlorate Likely to be Regulated

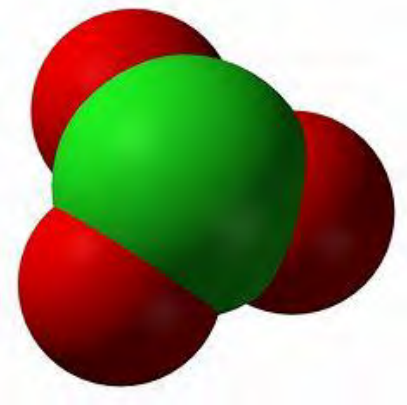
Chlorate (ClO_3^-) is on the EPA's Third Chemical Contaminant List (CCL3)

- 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.

Currently, not regulated in the United States and there is no enforceable Maximum Contaminant Limit (MCL).

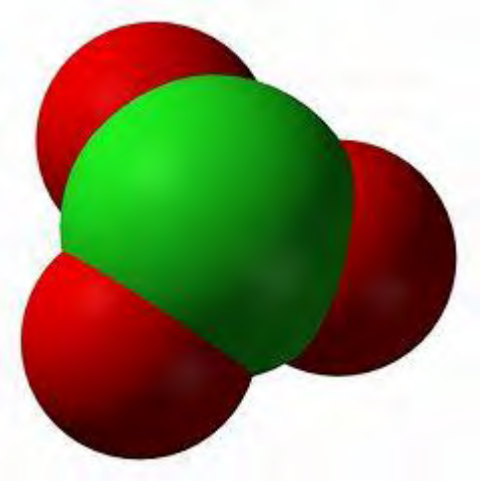
- Canada MCL is 1.0 mg/l (1000µg/l)
- WHO recommends a chlorate limit of 0.7 mg/l (700 µg/l)

- 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 0.7 mg/l (700 µg/l) in the US.



Chlorate - Future Regulatory Challenge

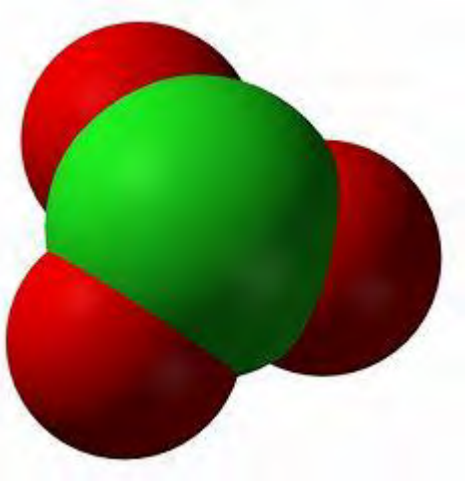
- While 210 µg/l is established by the EPA as a health reference level, it is conjectured that the EPA will not establish such a low level as it will seriously impact the viability of using delivered bulk hypochlorite in the marketplace.
- A level of 210 µg/l is also predicted to impact 34% of utilities using On-Site Generation.



Factors Influencing Chlorate Formation

- Time (storage time)
- Storage Temperature
- Hypochlorite concentration

The higher or longer any of these are, the more chlorate that will form



Chlorine efficacy challenges

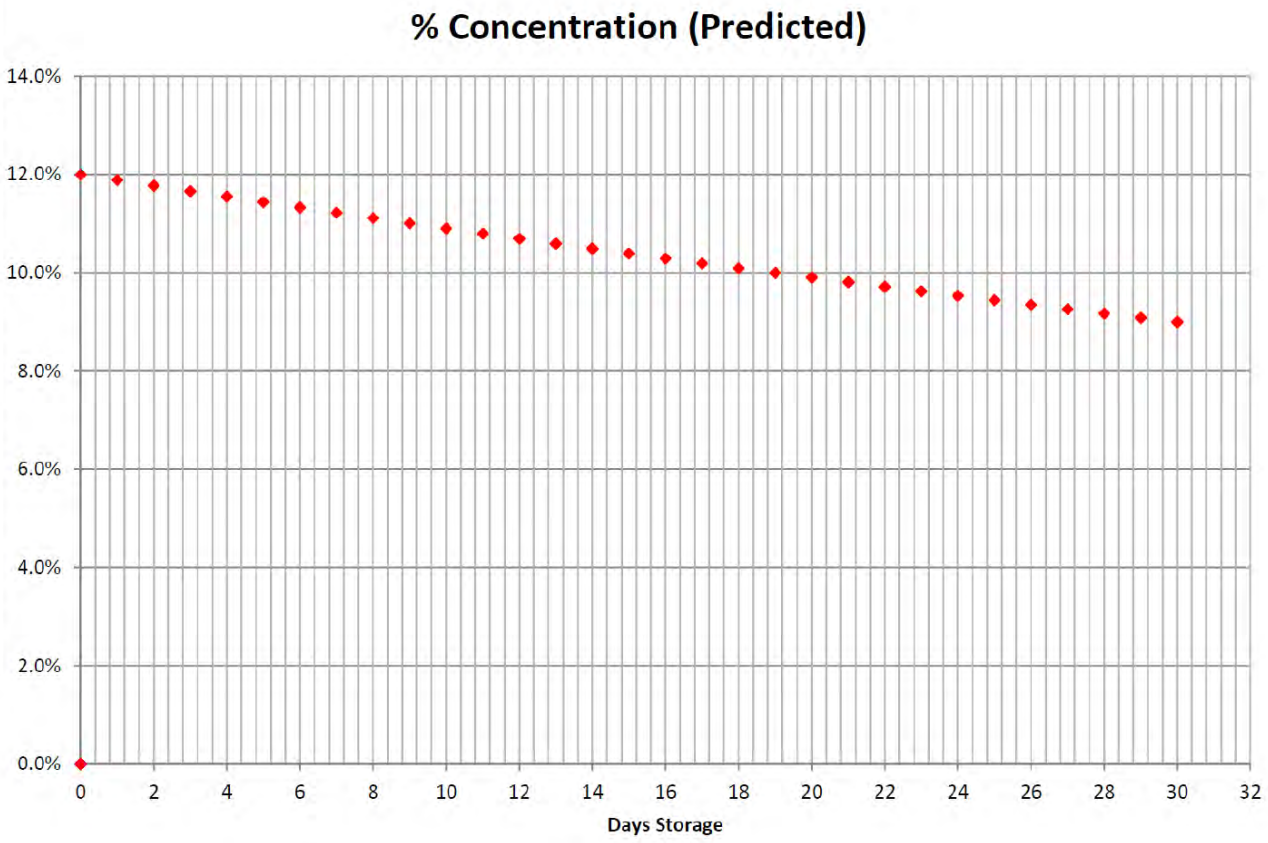
MIOX The SAFEST WATER In The World

Degradation Calculator

Days of Storage:	30
% Concentration:	12.00%
Temperature:	90 °F

% Concentration (Predicted)	Days	% Lose in Concentration
11.22%	7	6.50%
10.39%	15	13.42%
8.99%	30	25.04%
6.74%	60	43.81%

Days Storage:	% Concentration (Predicted)
0	12.00%
1	11.89%
2	11.77%
3	11.66%
4	11.55%
5	11.44%
6	11.33%
7	11.22%
8	11.11%
9	11.01%
10	10.90%
11	10.80%
12	10.69%
13	10.59%
14	10.49%
15	10.39%
16	10.29%
17	10.19%
18	10.09%
19	10.00%
20	9.90%
21	9.81%
22	9.71%
23	9.62%
24	9.53%
25	9.44%
26	9.35%
27	9.26%
28	9.17%
29	9.08%
30	8.99%



Chlorine efficacy challenges

MIOX The SAFEST WATER In The World

Degradation Calculator

Days of Storage:	30	
% Concentration:	0.50%	
Temperature:	90	°F

% Concentration (Predicted)	Days	% Lose in Concentration
0.50%	7	0.01%
0.50%	15	0.02%
0.50%	30	0.04%
0.50%	60	0.07%

Days Storage:	% Concentration (Predicted)
0	0.50%
1	0.50%
2	0.50%
3	0.50%
4	0.50%
5	0.50%
6	0.50%
7	0.50%
8	0.50%
9	0.50%
10	0.50%
11	0.50%
12	0.50%
13	0.50%
14	0.50%
15	0.50%
16	0.50%
17	0.50%
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22	0.50%
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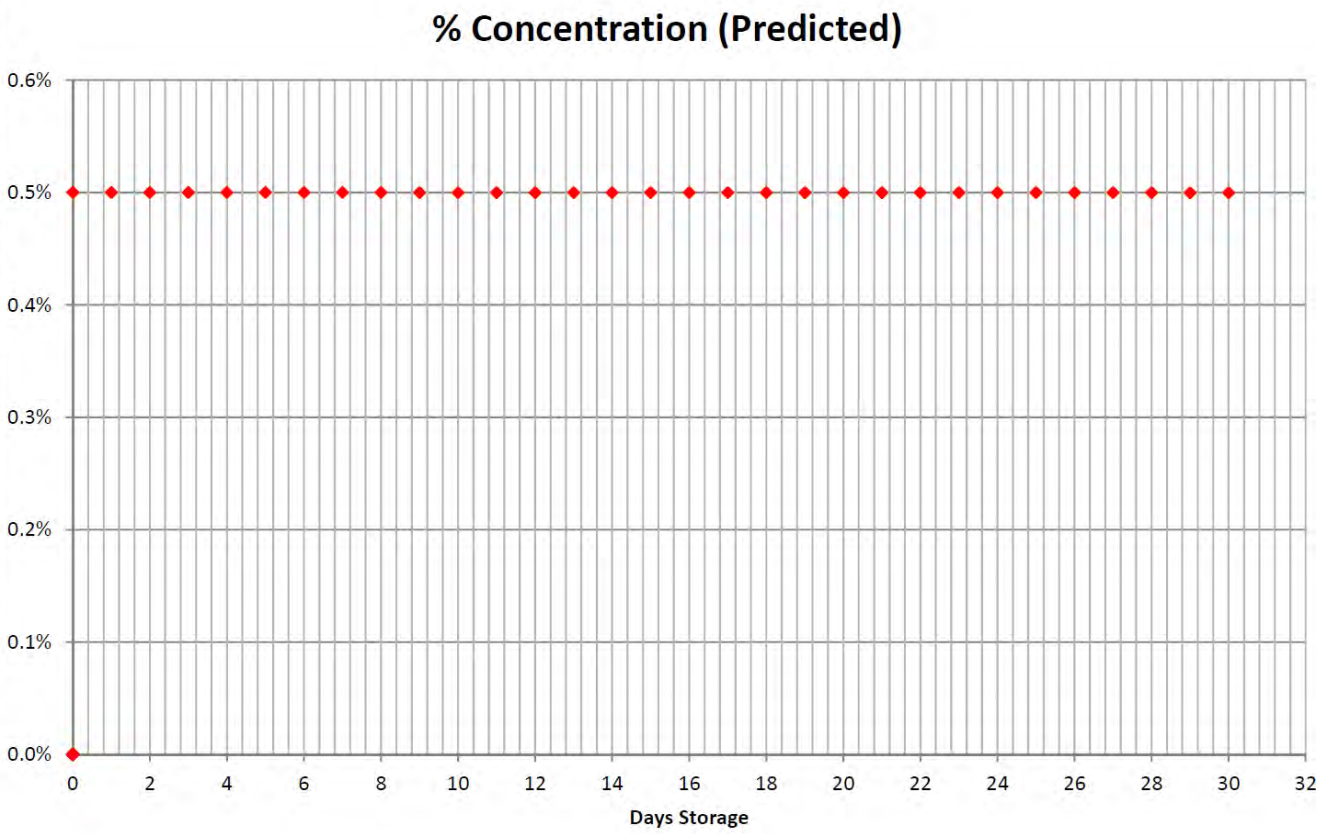
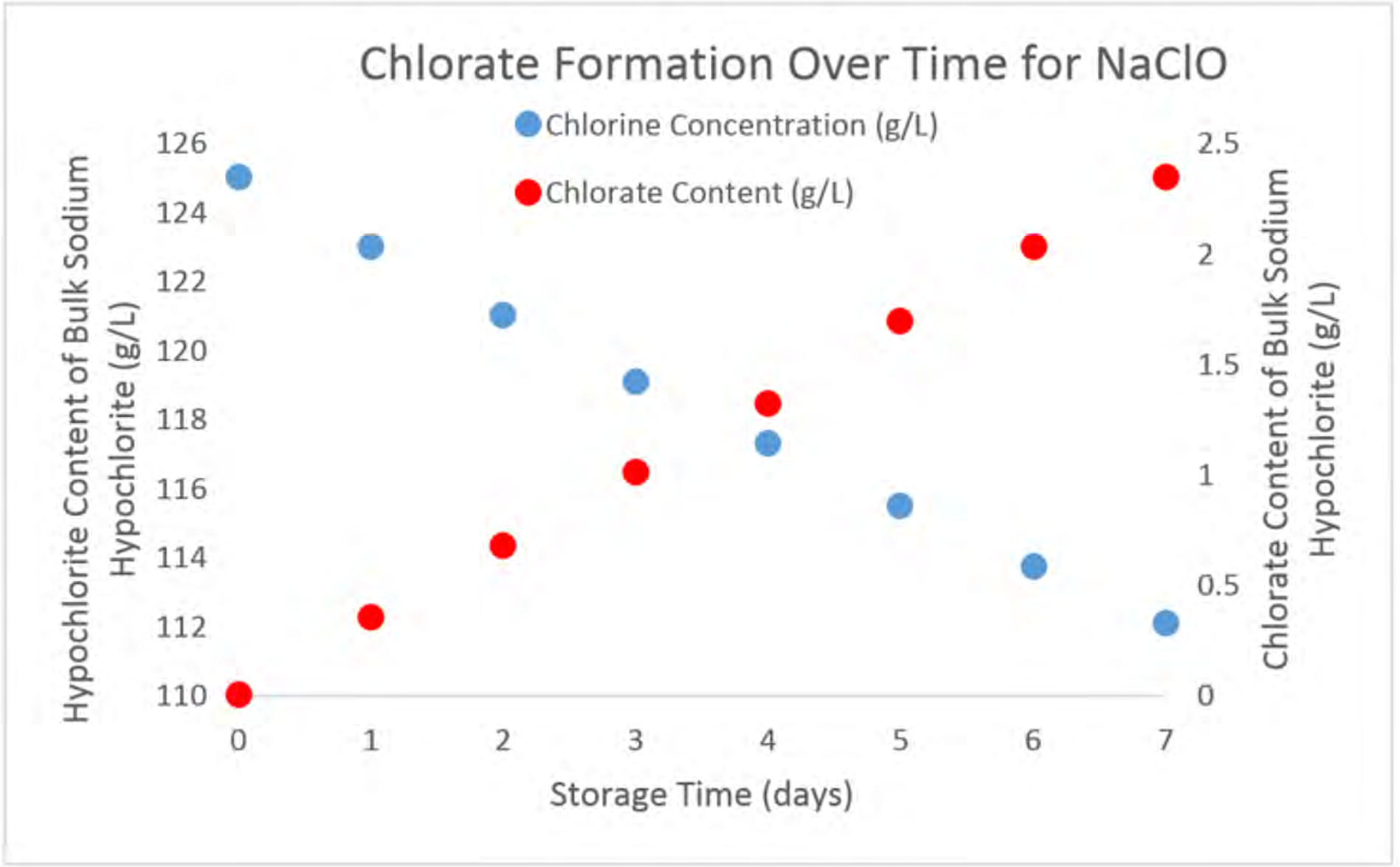
25	0.50%
26	0.50%
27	0.50%
28	0.50%
29	0.50%
30	0.50%



Chlorine degradation vs. FAC concentration

Days of Storage				
%FAC	7	15	30	60
15.0	13.43	11.83	9.33	5.81
13.0	11.91	10.78	8.93	6.14
12.0	11.22	10.39	8.99	6.74
5.0	4.93	4.84	4.71	4.14
1.0	1.0	1.0	1.0	0.9
0.5	0.5	0.5	0.5	0.5

Chlorate formation vs. Time

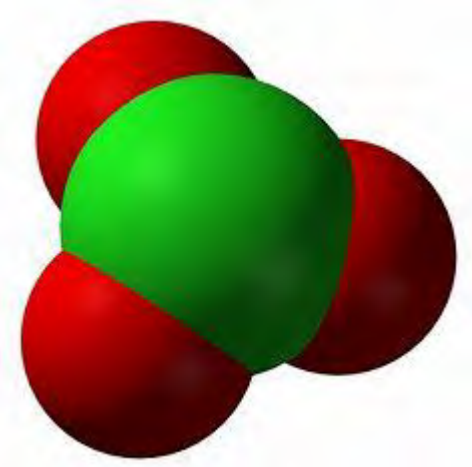


Chlorate Impacts on Bulk Hypochlorite

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.
- Purchase 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!!!!!



What About 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 hypochlorite is produced is generated using salt.

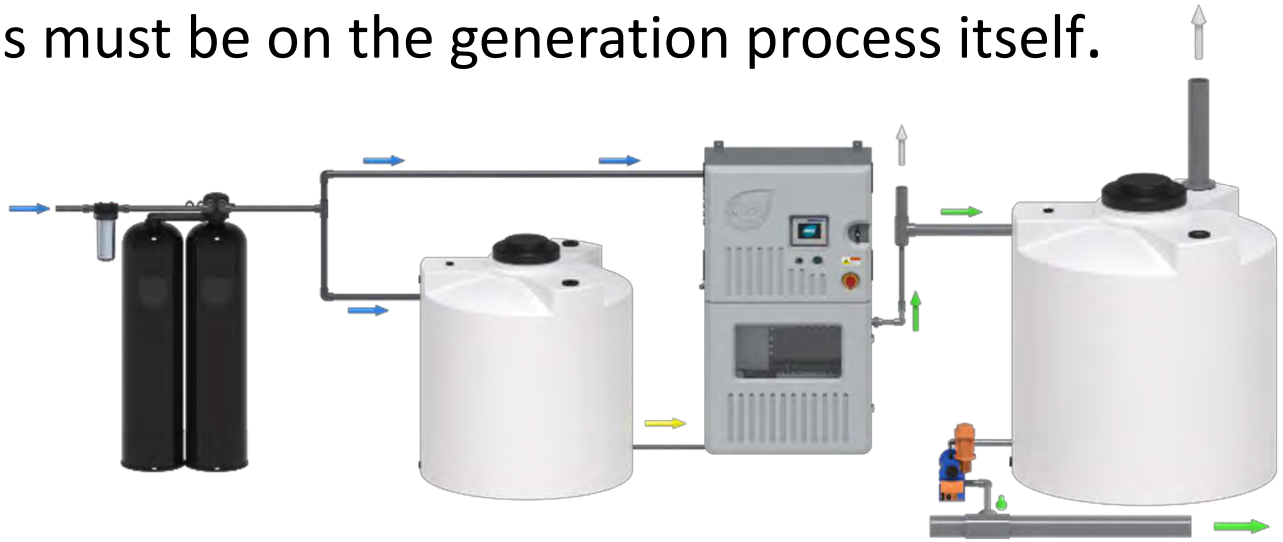
Chlorate Impacts on On-Site Generation

- Chlorate ions are produced as an undesirable side reaction of the electrochemical process.
- In the process, a portion of the hypochlorous acid or hypochlorite ions are oxidized at the anode to produce chlorate ions.
- Research to date on chlorate production by installed commercial electrolytic OSG systems has not found any correlation between OSG brand, age, capacity, or a variety of operational conditions.

Theoretical Advantages of On-Site

- Generated on-site – always fresh.
- <1% chlorine concentration = very slow degradation rate.
- Modular in nature
  - as regulations change, upgrades are simple and easy to implement.

- These are all valid – and minimize the degradation – so focus must be on the generation process itself.



Why Use On-Site Generation?

Safety is One Major Reason

OSG

HAND SANITIZER

SODIUM HYPOCHLORITE

CHLORINE GAS

Regulations

- Trend toward the safest solution
- Limit on hazardous chemical storage

Incidents

- Fairly recent near miss of Cl_2 leak at two large industrial facilities (US)

Sustainability

- Less trucks, lower carbon footprint
- Water conservation, less chemicals

Operational Cost is Another…

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

Salt		Electricity		Operational Cost
 $0.36	+	 $0.18	=	MIOX Cost ~$0.54
3 lbs salt at $0.12/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

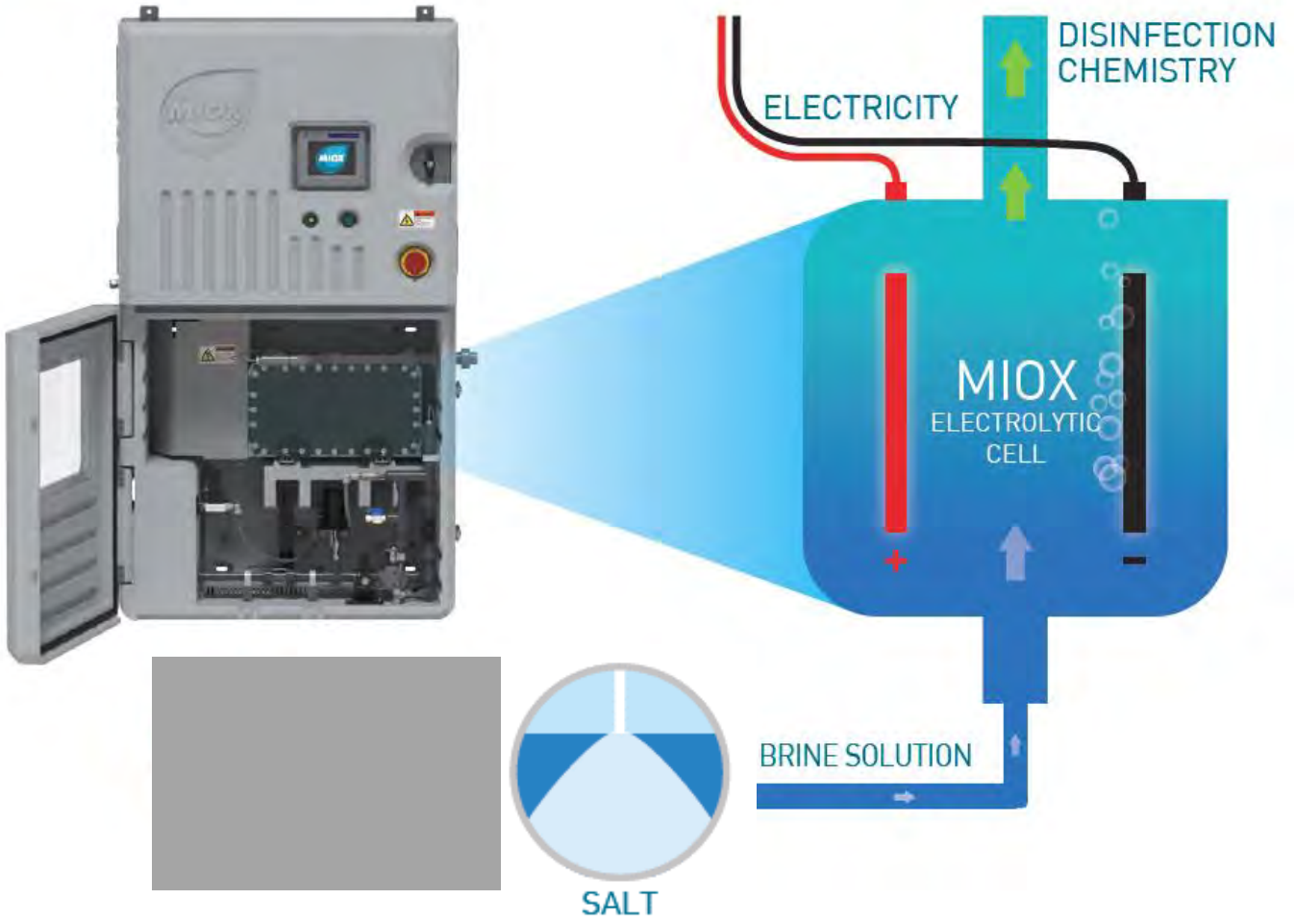
How Does It Work?

Process Flow

- Softened water to electrolytic cell and brine tank
- Salt and water mix in brine tank to form saturated brine
- Saturated brine enters the electrolytic cell
- Electrical current is passed through the electrolytic cell producing oxidant
- Hydrogen gas produced during the electrolysis process is vented outside
- Oxidant solution leaves the electrolytic cell and is stored in the oxidant tank
- Oxidant solution is dosed into the treatment process by a metering pump
- OSG turns ON/OFF from a signal located inside the oxidant tank

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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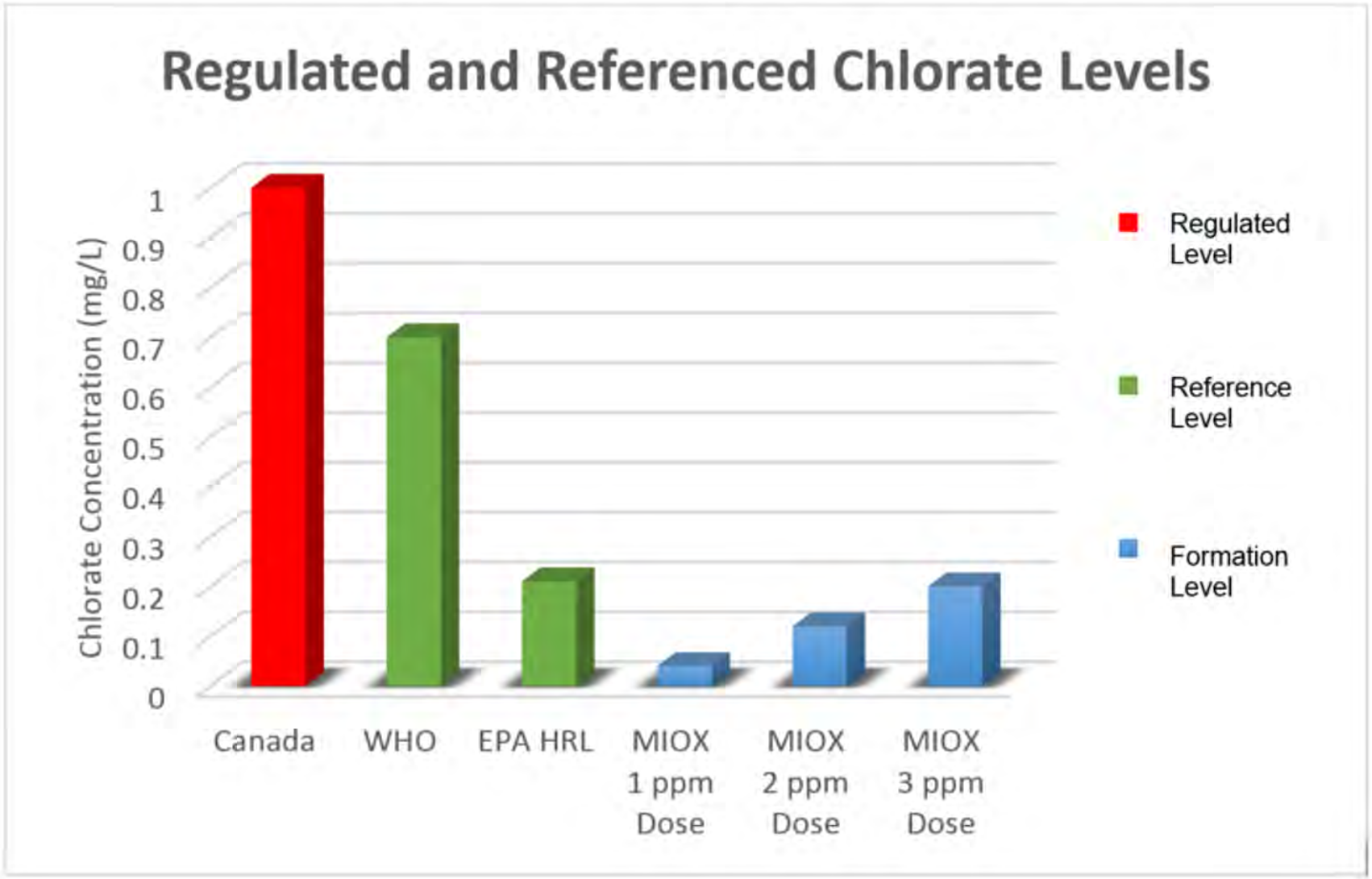
If you stop here, you have a hypochlorite generator…

…But if you add more power…

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

Theoretical Advantages of On-Site



Current Status

- De Nora recently acquired MIOX on February 1, 2019
- Prior to acquisition both De Nora and MIOX were independently investigating impacts of chlorate in on-site generation
- Current efforts are to integrate work done by each entity
- De Nora is actively conducting research in to the mechanisms resulting in the production of chlorate during electrolysis to ensure our products will be able to meet future chlorate regulatory requirements.

Thank You for Your Time…….
Questions?

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