Managing Hypochlorite to Reduce Chlorate Formation: A Utility Case Study

KIMBERLY GUPTA, PE
PORTLAND WATER BUREAU

CO-AUTHOR: YONE AKAGI, PE

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PORTLAND WATER BUREAU
FROM FOREST TO FAUCET

Presentation Outline

- Background on chlorate
- Factors affecting chlorate formation
- PWB's experience with chlorate
  - UCMR Results
  - Study evaluating chlorate formation in low salt hypo vs standard hypo

Why Do We Care About Chlorate?

- Chlorate is an unregulated disinfectant by product that occurs when using hypochlorite or chlorine dioxide for disinfection
- Chemicals used for drinking water treatment is the dominant source of exposure to chlorate
  - Chlorate compounds are also used in agriculture as herbicides or desiccants
- Route of toxicity is through ingestion and inhalation
  - Decrease thyroid function
  - Impairment of blood's ability to carry oxygen
  - Some toxicological reports have shown that chlorate has similar toxic modes of action as perchlorate
- Widespread in drinking water at relevant concentrations

Chlorate Regulations

There is no federal regulation for chlorate in drinking water at this time

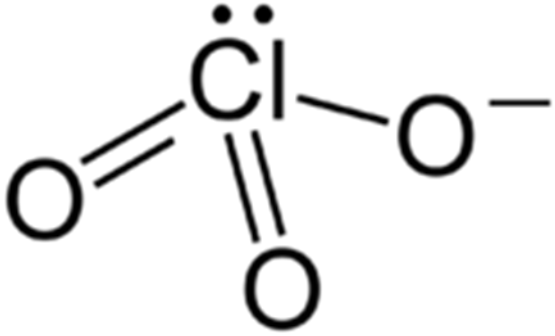
- EPA has established a Health Reference of 210 µg/L

California has set an action level for chlorate at 700 ug/L

WHO: 0.7 mg/L provisional guideline

Canada: 1 mg/L Maximum Acceptable Concentration

Control of chlorate formation is best since there are no widely accepted treatment methods for chlorate



Chlorate Occurrence (ICR)

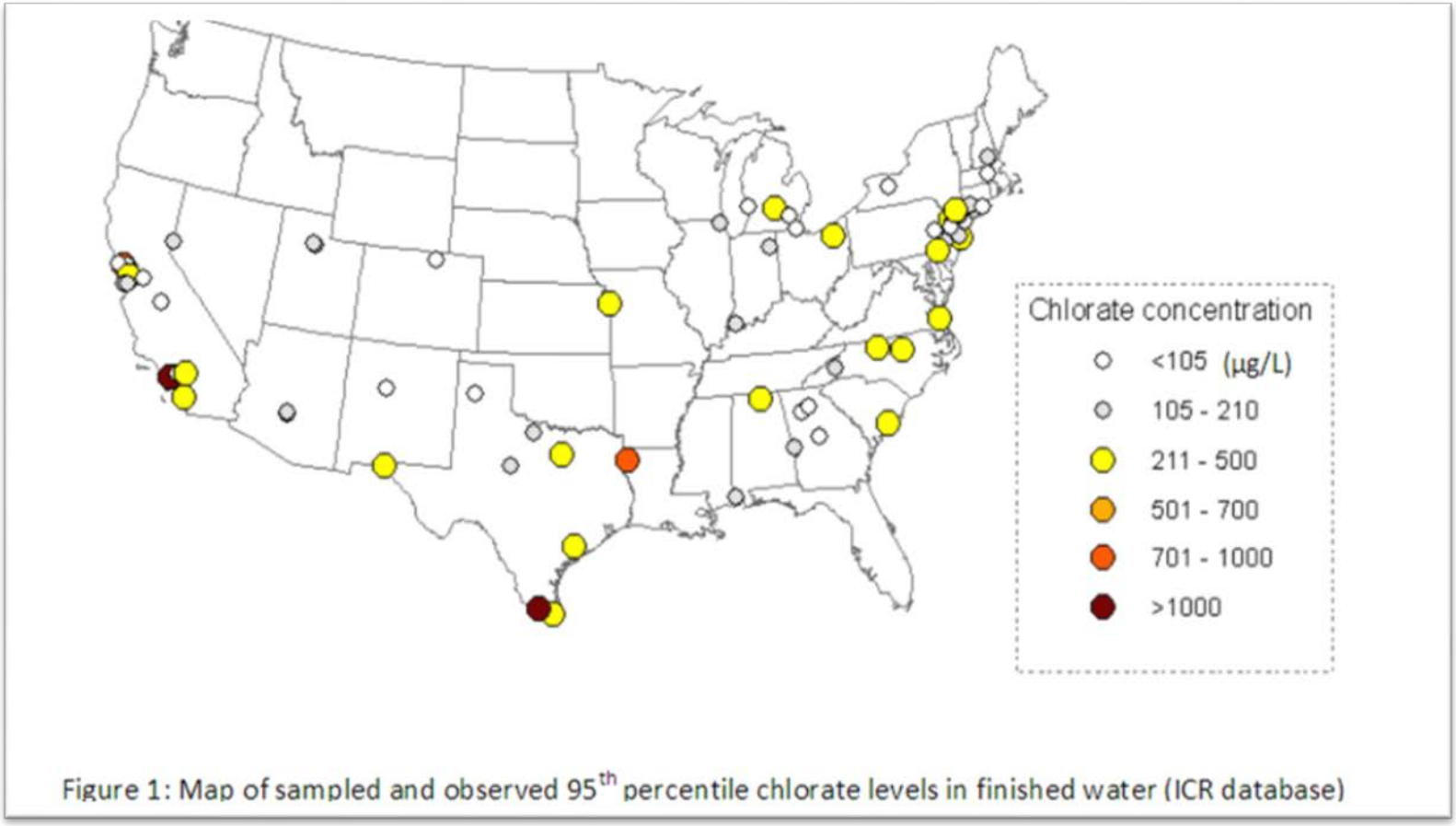


Figure 1: Map of sampled and observed 95th percentile chlorate levels in finished water (ICR database)

Source: Alfredo et al., 2014

Chlorate Occurrence: ICR and UCMR3

Among 47 Common Systems	Measurements	Chlorine Dioxide: Number of Samples[1]	Chlorine Dioxide: Percent of Total	Hypochlorite: Number of Samples[2]	Hypochlorite: Percent of Total
DBP ICR	**Total Number of Samples**	**581**	--	**114**	--
DBP ICR	Detections > 210 µg/L	112	19.3%	14	12.3%
DBP ICR	Detections > 420 µg/L	13	2.2%	2	1.8%
DBP ICR	Detections > 630 µg/L	1	0.2%	1	0.9%
UCMR 3	**Total Number of Samples**	**168**	--	**203**	--
UCMR 3	Detections > 210 µg/L	67	39.9%	55	27.1%
UCMR 3	Detections > 420 µg/L	20	11.9%	13	6.4%
UCMR 3	Detections > 630 µg/L	8	4.8%	2	1.0%

Source: Six-Year Review 3 Technical Support Document for Chlorate (EPA, 2016)

Chlorate Occurrence: UCMR

Threshold Concentration	National Estimate of Number of Sample Locations with Locational Average Concentration > Threshold (Percent[1])	National Estimate (in million) Population Served by Sample Locations with Locational Average Concentration > Threshold (Percent[1])
> HRL (210 µg/L)	24,868 (16.59%)	52 (17.43%)
> 2xHRL (420 µg/L)	10,168 (6.78%)	15 (5.06%)
> 3xHRL (630 µg/L)	5,124 (3.42%)	6 (2.00%)

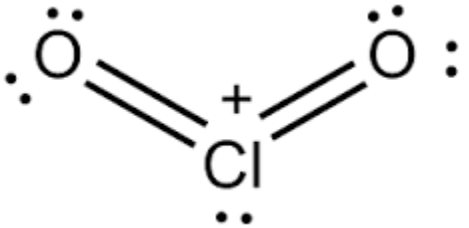
Source: Six-Year Review 3 Technical Support Document for Chlorate (EPA, 2016)

Chlorate Formation

Disinfection with the following:

- Chlorine dioxide
- Bulk hypochlorite
- On-site generated hypochlorite

Ozonation/UV treatment of chlorinated waters can lead to chlorate formation



Sodium Hypochlorite

Sodium hypochlorite is a commonly used source of chlorine for water treatment

- Has been estimated that approximately 31% of WTPs use bulk hypochlorite for disinfection (Snyder et al., 2009)
- Use has increased due to safety concerns regarding transporting and storing chlorine gas

It is effective, relatively easy to use, and readily available

Sodium Hypochlorite Continued

There are a number of disadvantages to using sodium hypochlorite

- Multiple contaminants can occur in hypochlorite solutions including bromate, chlorite, chlorate, and perchlorate
- Sodium hypochlorite decomposes with time, heat, and exposure to metals such as iron, copper, nickel, etc.
- As hypochlorite degrades, perchlorate and chlorate are formed

Factors Contributing to the Formation of Chlorate in Hypochlorite Solutions

Hypochlorite strength

- Higher strength solutions will form more chlorate

pH

- pH range to reduce chlorate formation is 11-13

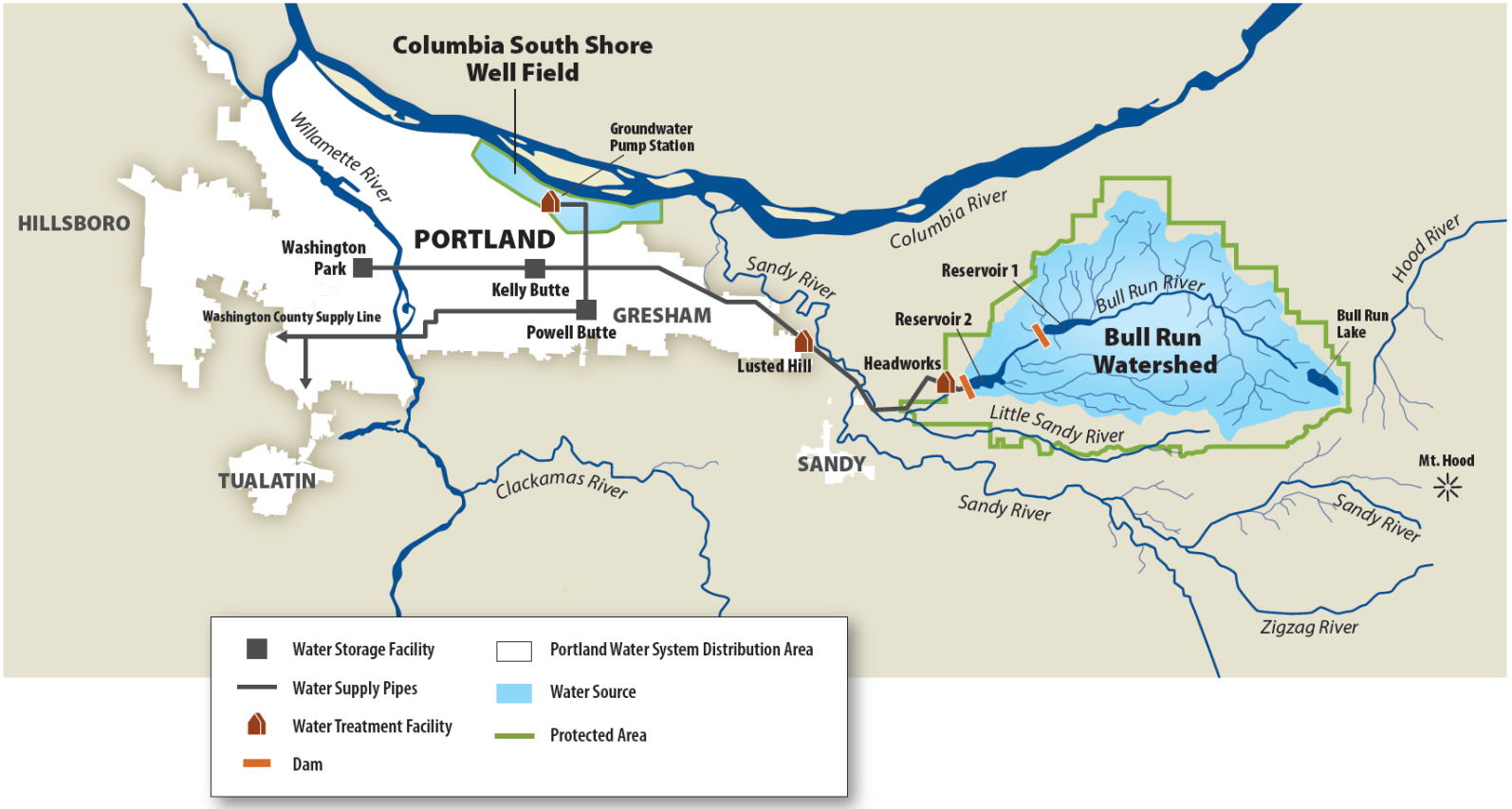
Ionic strength

- Higher ionic strength favors higher reaction rates

Presence of some metals

- Some metals such as iron will increase the decomposition rate of hypochlorite

Portland Water Bureau Overview



- Serves approximately 966,000 people – approximately 25% of Oregon
- 20 wholesaler customers which comprise approximately 42% of system demand

Monitoring Hypochlorite in the PWB's System – UCMR3 Results

- As part of UCMR3, Portland tested primary and backup supplies for chlorate
- Treated water from the surface water supply was non-detectable for chlorate in any of the samples
- A chlorate concentration of 3000 µg/L was measured in treated water from the groundwater supply

What Happened?

The groundwater facility is an emergency source of supply so it must be able to be brought online as soon as possible

- Sodium hypochlorite must be stored on site at the groundwater treatment facility at all times

Chlorate formation is a function of time

- As the solution ages, chlorate increases and FAC decreases

Implemented Strategies to Decrease Chlorate Formation

- Dilute hypochlorite solutions immediately after delivery ✓
  - Diluting a 2M solution in half decreases the formation of chlorate by a factor of 7
- Ensure pH of 11-13 of stored hypochlorite solutions (even after dilutions) ✓
- Ensure transition metal ions are low (purchase filtered hypochlorite solutions) ✓
- Tightened the hypochlorite specification to improve initial hypochlorite conditions ✓
- Store hypochlorite solutions at low temperatures (60°F/15°C recommended)
  - Decreasing the storage temperature by 5C decreases formation by a factor of 2

High Strength Low Salt Hypochlorite

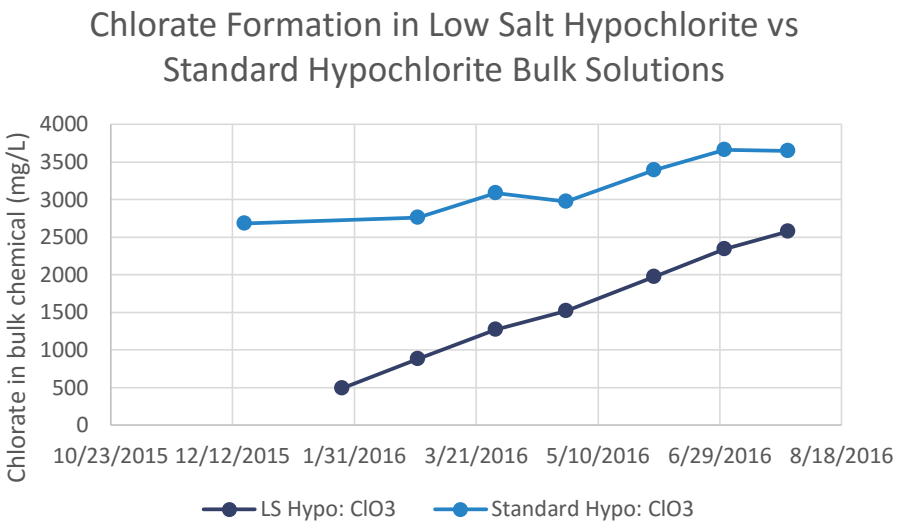
According to the vendor, the high strength, reduced salt hypochlorite would improve the half life of the sodium hypochlorite by a factor of 2 compared to traditional sodium hypochlorite at the same concentration and temperature

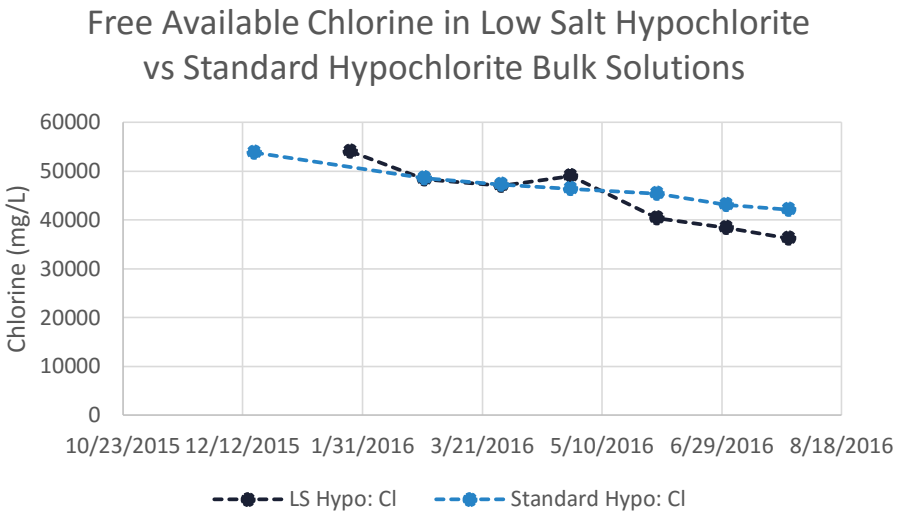
Reduced salt in the sodium hypochlorite makes the product approximately 2 times more stable than standard hypochlorite

We conducted a trial to evaluate this

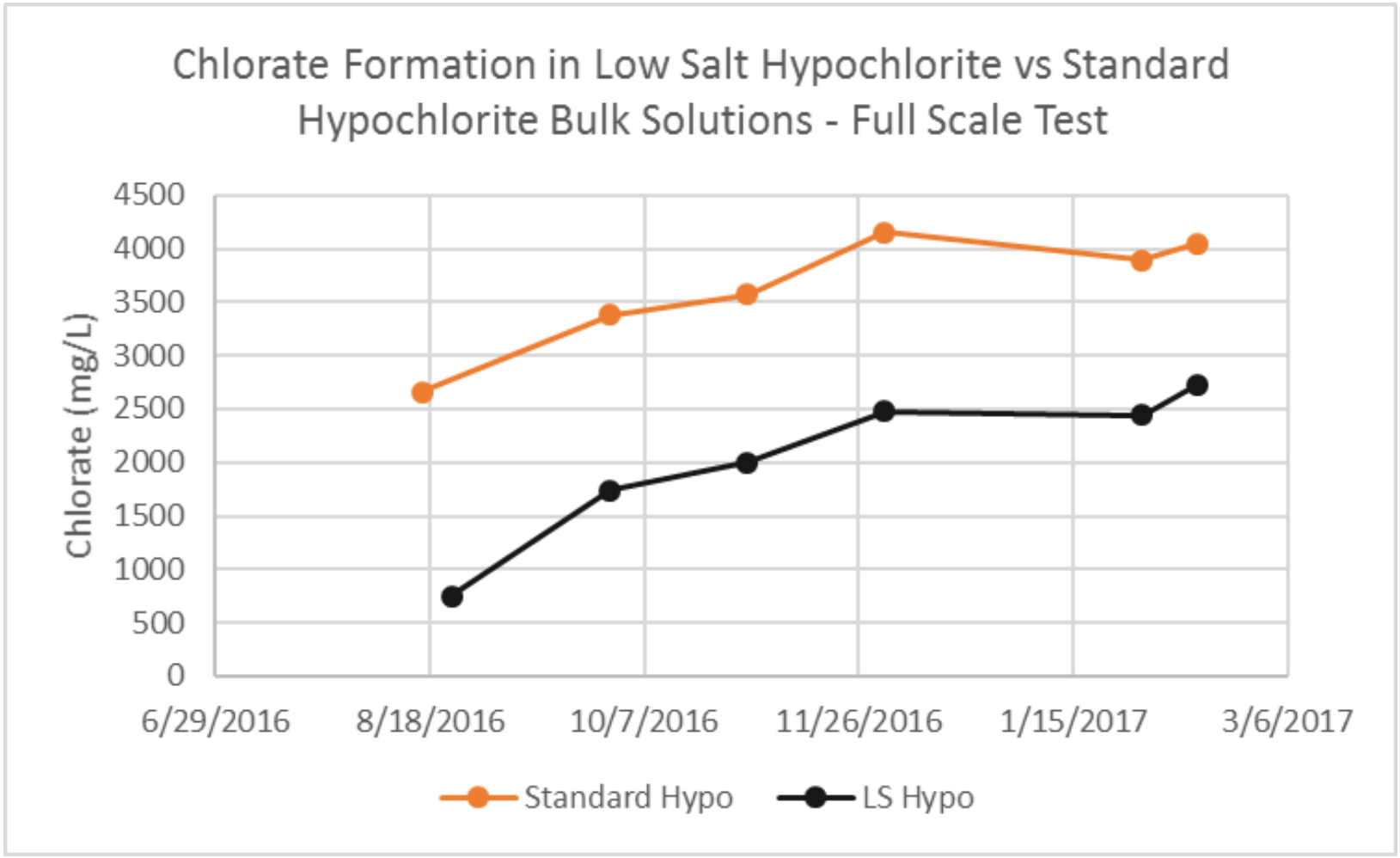
Results: Low Salt vs Standard Hypochlorite

- Obtained 5 gallons of low salt hypochlorite from the vendor
- At the same time, we ordered a new shipment of our standard hypochlorite
- Stored the low salt hypo near our existing hypochlorite storage tanks
- Sampled the low salt and standard hypochlorite each month and analyzed for chlorate, pH, and FAC





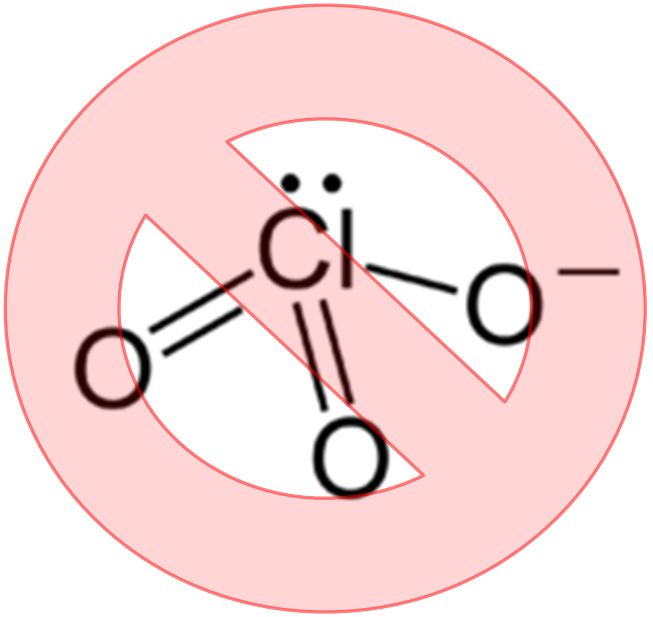
Results: Low Salt vs Standard Hypochlorite - Full Scale Test



Recommendations Based on Our Experience

Implement strategies to reduce chlorate formation

- Use fresh hypochlorite when possible
- Dilute hypochlorite upon delivery
- Store at lower temperatures
- Control the pH (11-13)
- Control the removal of metals that increase hypochlorite degradation



Recommendations Based on Our Experience

Double check your hypochlorite specifications

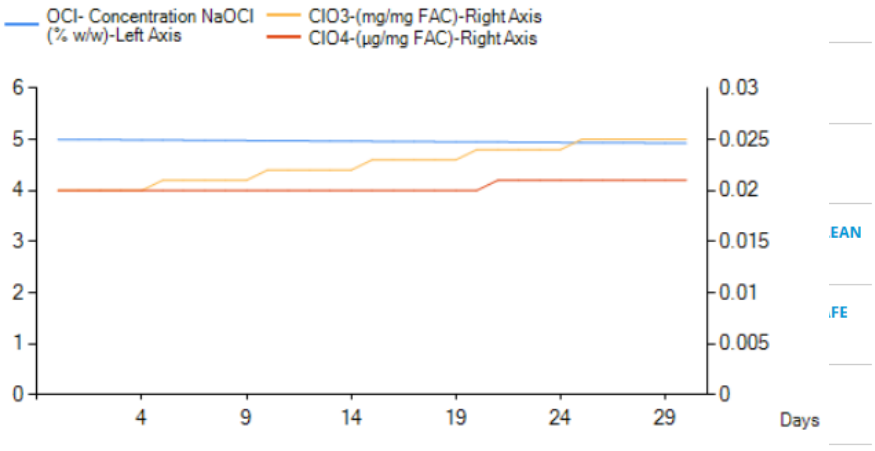
Estimate the chlorate formation potential of your hypochlorite

- Determine how long it takes you to use up a batch of your hypochlorite
- Use the AWWA chlorate tool to estimate how much chlorate (and perchlorate) the hypochlorite you have onsite is producing
- Use the tool to determine various dilutions to help reduce chlorate formation
- Monitor to ensure your assumptions were correct

Resources

There are a lot of very helpful resources out there on this topic

- AWWA hypochlorite assessment tool



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Home > Resources & Tools > Water and Wastewater Utility Management > Hypochlorite Assessment Model

Hypochlorite Assessment Model

Initial Hypochlorite (OCl^-) Concentration*: [ ] NaOCl (% w/w) ▾ Specific Gravity (S.G.): [ ]

pH (default 12.5): [ ]

Temperature 1*: [ ] Duration: [ ] Days

Temperature 2 (optional): [ ] Duration: [ ] Days

Temperature 3 (optional): [ ] Duration: [ ] Days

Temperature 4 (optional): [ ] Duration: [ ] Days

Temperature Unit of measure: (•) °C(default) ( ) °F

Initial Concentration

Initial Chlorate (ClO_3^-): [ ] g/L

Initial Sodium Chloride (NaCl): [ ] mol/L

Initial Perchlorate (ClO_4^-): [ ] mg/L

Specific Conductance: [ ] µmho/cm

If the following fields are left blank, default values will be assumed.

Optional Input

The following inputs are optional but provide additional interpretation

Expected Chlorine (Cl_2) Dose: [ ] mg FAC/L finished water

Chlorate (ClO_3^-) MCL: [ ] mg/L

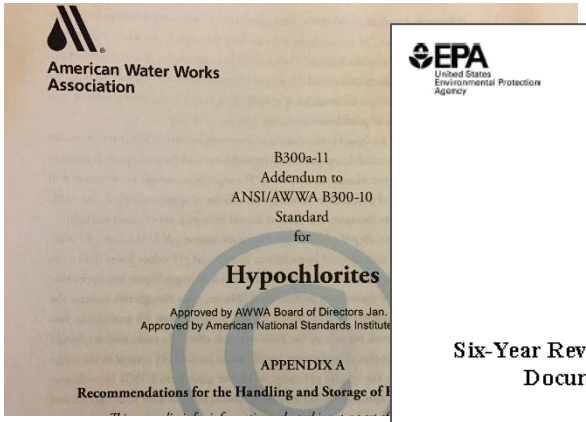
Perchlorate (ClO_4^-) MCL: [ ] mg/L

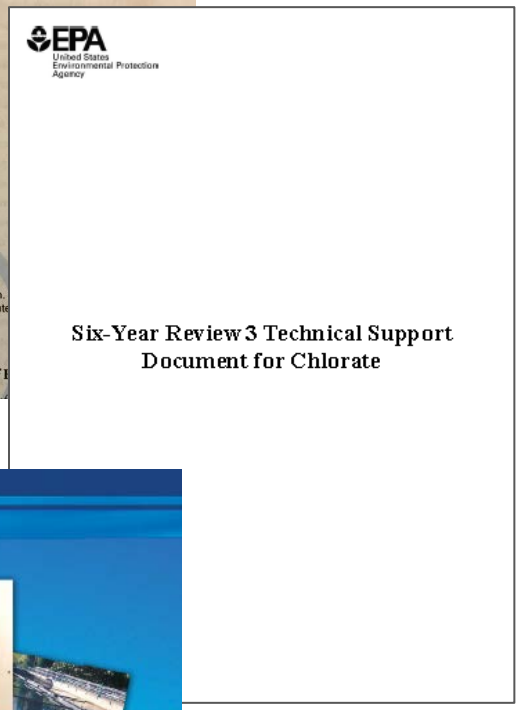
The Hypochlorite Assessment Model assumes no responsibility for individual's understanding of state and local Maximum Contaminant Level (MCL) standards. The model is designed for predicting formation, not regulatory compliance.

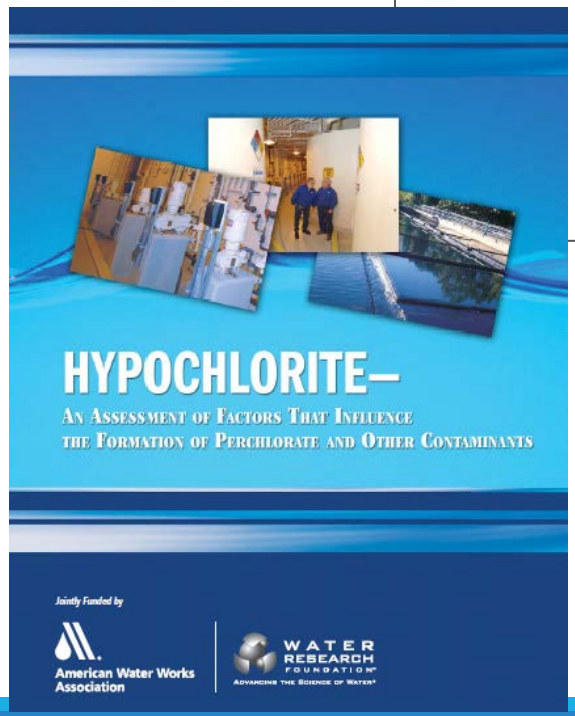
Calculate Reset

Resources Continued

- AWWA Journal Articles and WaterRF Studies
- AWWA Standard on Hypochlorite Storage
- EPA 6 year review on chlorate
- Water RF and AWWA Reports



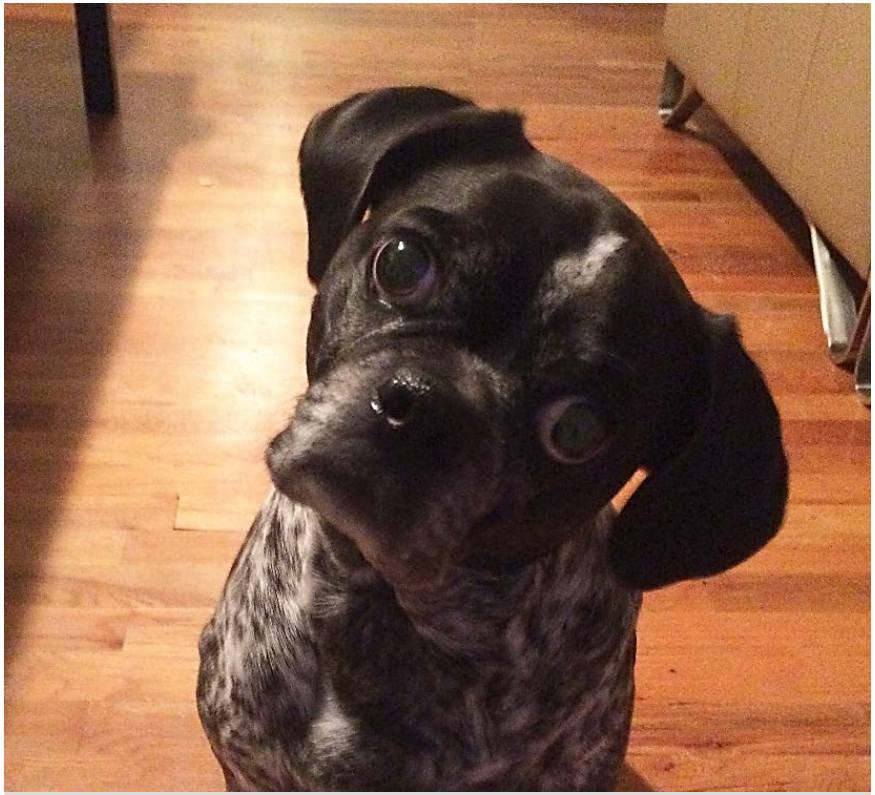




Next Steps

- Continue practicing strategies to minimize chlorate formation in bulk hypochlorite
- Consider switching to a low salt hypochlorite
- Continue monitoring our hypochlorite as we receive it and monthly to ensure that chlorate concentrations do not reach unacceptable levels

QUESTIONS?



Contact information
Kimberly Gupta
Portland Water Bureau
Kimberly.gupta@portlandoregon.gov