

# **Controlling Bromate, Chlorate, and Perchlorate in Sodium Hypochlorite used for drinking water treatment**

**Dave Purkiss, NSF International**  
**The Chlorine Institute's 2013 Technology Symposium**

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# Controlling Bromate, Chlorate and Perchlorate Formation

- **Bromate:**
  - Common impurity in sodium hypochlorite, established when first produced.
- **Chlorate and Perchlorate:**
  - Concentrations are low in fresh hypochlorite.
  - Significant concentrations can develop in storage.
  - Steps can be taken to slow the breakdown of hypochlorite → chlorate → perchlorate.

# Standards

**AWWA B-300 Hypochlorites** - being revised to contain recommended storage and handling practices to limit bromate, chlorate and perchlorate formation.

**NSF/ANSI Standard 60** –revised to contain:

- Evaluation criteria for perchlorate, and chlorate.
- Born on date.
- Any repackaging dates.
- Lower pass/fail criteria for bromate.

# NSF/ANSI Standard 60

## Drinking Water Treatment Chemicals

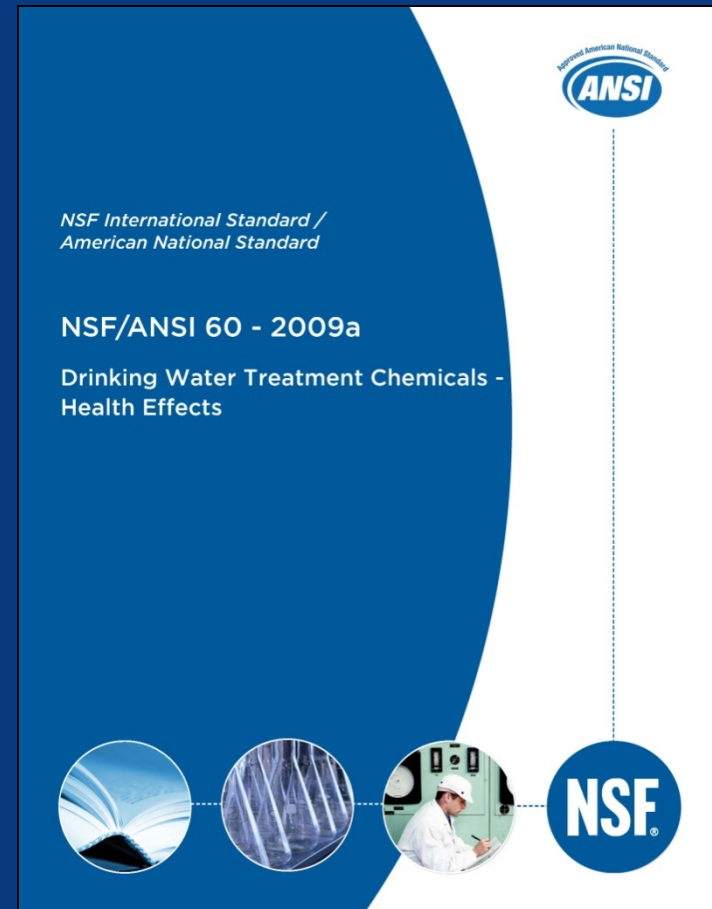
### - Health Effects.

- Developed to ensure treatment chemicals do not add unsafe levels of chemicals or contaminants to drinking water.
  - Chemical is safe at its maximum use level.
  - Contaminants associated with the chemical are below maximum allowable levels.

# NSF/ANSI Standard 60

Covers all categories of treatment chemicals

- Coagulation and flocculation
- Corrosion and scale control
- Disinfection and oxidation
- Algicides, Fluoridation, Well drilling, Cleaning, Well pump lubricants



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# Testing of Product to NSF Standard 60

- Product dosed into water at 10 times maximum use level.
- Chemical analyses conducted for various contaminants.
- Evaluation of each detected chemical concentration to SPAC.
  - SPAC = single product allowable level.
  - SPAC typically is 1/10 total allowable level.
- **Example for arsenic**
  - MAC = 10 ppb
  - SPAC = 1 ppb

[CL] The residual levels of chlorine (hypochlorite ion and hypochlorous acid), chlorine dioxide, chlorate ion, chloramine and disinfection by-products shall be monitored in the finished drinking water to ensure compliance to all applicable regulations.

## Advance Chemicals Ltd.

2023 Kingsway Road  
Port Coquitlam, BC V3C 1S9  
Canada

[Free call](#)

[Visit this company's website](#)

**Facility : Port Coquitlam, British Columbia, Canada**

### Sodium Hypochlorite[CL]

*Trade Designation*

Advance 12A

Advance Bleach

*Product Function*

Disinfection & Oxidation

Disinfection & Oxidation

*Max Use*

97mg/L

194mg/L

[CL] The residual levels of chlorine (hypochlorite ion and hypochlorous acid), chlorine dioxide, chlorate ion, chloramine and disinfection by-products shall be monitored in the finished drinking water to ensure compliance to all applicable regulations.

## Alexander Chemical Corporation

1001 Butterfield Road

# Bromate

- Bromide ions are in the salt that make both chlorine and sodium hydroxide.
- Virtually all of the bromide in in these two chemicals quickly becomes  $\text{BrO}_3$  at the pH of  $\text{NaOCl}$ .
- Some plants can change salt sources; some are limited to salt they have available
- Current technology cannot easily or economically remove bromate or its precursor from the initial salt, the two reactants, or the final hypochlorite



# Bromate

NSF results on sodium hypochlorite testing between 2004 – 2011 (886 samples)

## Concentration of bromate in undiluted hypochlorite (mg/kg)

| Minimum | Maximum | Mean |
|---------|---------|------|
| 2.0     | 313     | 31   |

## Concentration of bromate in drinking water from hypochlorite dosed at max use level (ppb)

| Minimum | Maximum | Mean |
|---------|---------|------|
| 0.15    | 26      | 2.5  |

# Bromate

## NSF/ANSI Standard 60

- HC IMAC = 10 ppb
- Two (2) known sources :
  - bromide in source water converted to bromate by UV or ozone
  - sodium hypochlorite
- Adding 1 additional safety factor gives source factor of 3.
- **SPAC** =  $10 \text{ ppb} / 3 = 3 \text{ ppb}$

# Bromate

## NSF/ANSI Standard 60

However, a significant number of sodium hypochlorite mfrs could not meet the 3 ppb level for bromate.

- SPAC for bromate set at **5 ppb** in 2000.
- SPAC is being reduced to **3 ppb** in 2013.

Bear in mind the typical NSF 60 certified maximum use level for hypochlorite is equivalent to 10 mg/L chlorine. Covers total amount of chemical that would be dosed in a treatment train.

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## Alexander Chemical Corporation

1901 Butterfield Road

# Bromate

- Bromate can also form in sodium hypochlorite produced from onsite generators (OSG)
- Bromide in salt is also precursor in OSG
- Criteria recently added for OSG salts in NSF 60
  - 54 mg/kg limit for bromide in salt (default)

Based on assumption that 3.0 ug/L bromate will be produced from 3.5 lbs of NaCl containing 54 mg/kg bromide with 15 gallons of water to produce via electrolysis 1 pound of free available chlorine (FAC) equivalent disinfectant and dosed at to effect a 10 mg/L FAC in the finished drinking water.

# Bromide Concentration in Salt

Salt with higher bromide concentration can be used as long as total dose of hypochlorite is low enough to not exceed a 3 ppb contribution of bromate.

| OSG Hypochlorite Dose (FAC) | Bromide Content in Salt (mg/kg) |
|-----------------------------|---------------------------------|
| 10 mg/L                     | 54 (default)                    |
| 7.5 mg/L                    | 81                              |
| 5.0 mg/L                    | 108                             |

Std 60: *“In all instances where compliance with this standard is indicated for a product use in electrolytic sodium hypochlorite generators (e.g. product packaging, product literature, certification listings), an indication of the maximum bromide concentration specification and associated maximum feed concentration of chlorine attested by this standard shall also be indicated.”*

# Perchlorate and Chlorate

- Concentrations are low in fresh hypochlorite.
- Significant concentrations can develop in storage.
- Steps can be taken to slow the breakdown

hypochlorite → chlorate → perchlorate

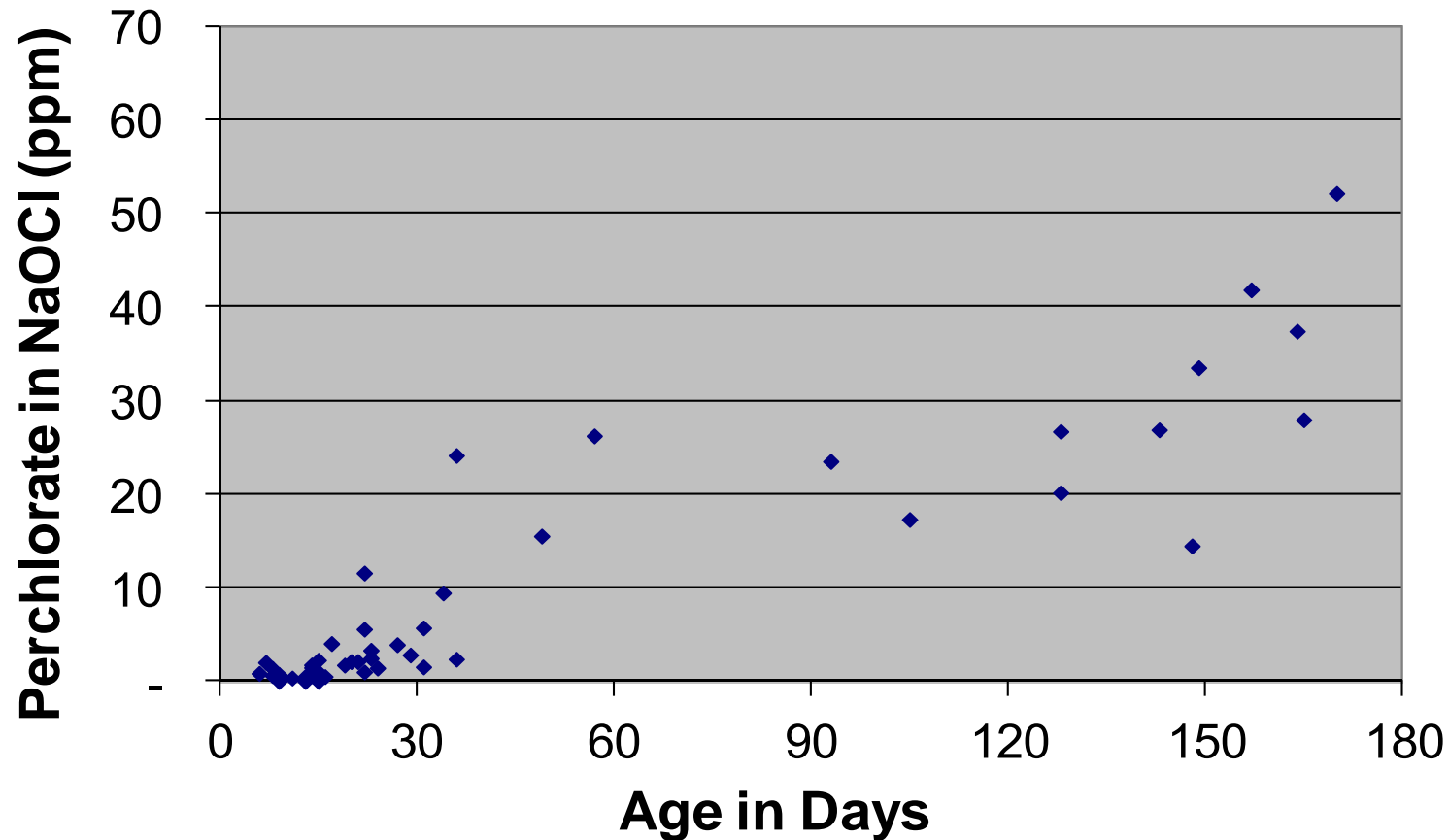
# NSF Study on Perchlorate Occurrence

Selected a wide variety of treatment chemicals that are currently certified to NSF 60.

- 164 chemical samples from 102 mfrs.
- 37 different chemical types.
- Found perchlorate in two chemical types
  - Sodium hydroxide (found limited)
  - Sodium hypochlorite (found all)



# Effect of Age on Perchlorate in NaOCl NSF 60 Treatment Chemicals



# Occurrence in NaOCl

Typical maximum use level for 12.5% NaOCl solution is 84 mg/L (10 ppm total chlorine equivalents).

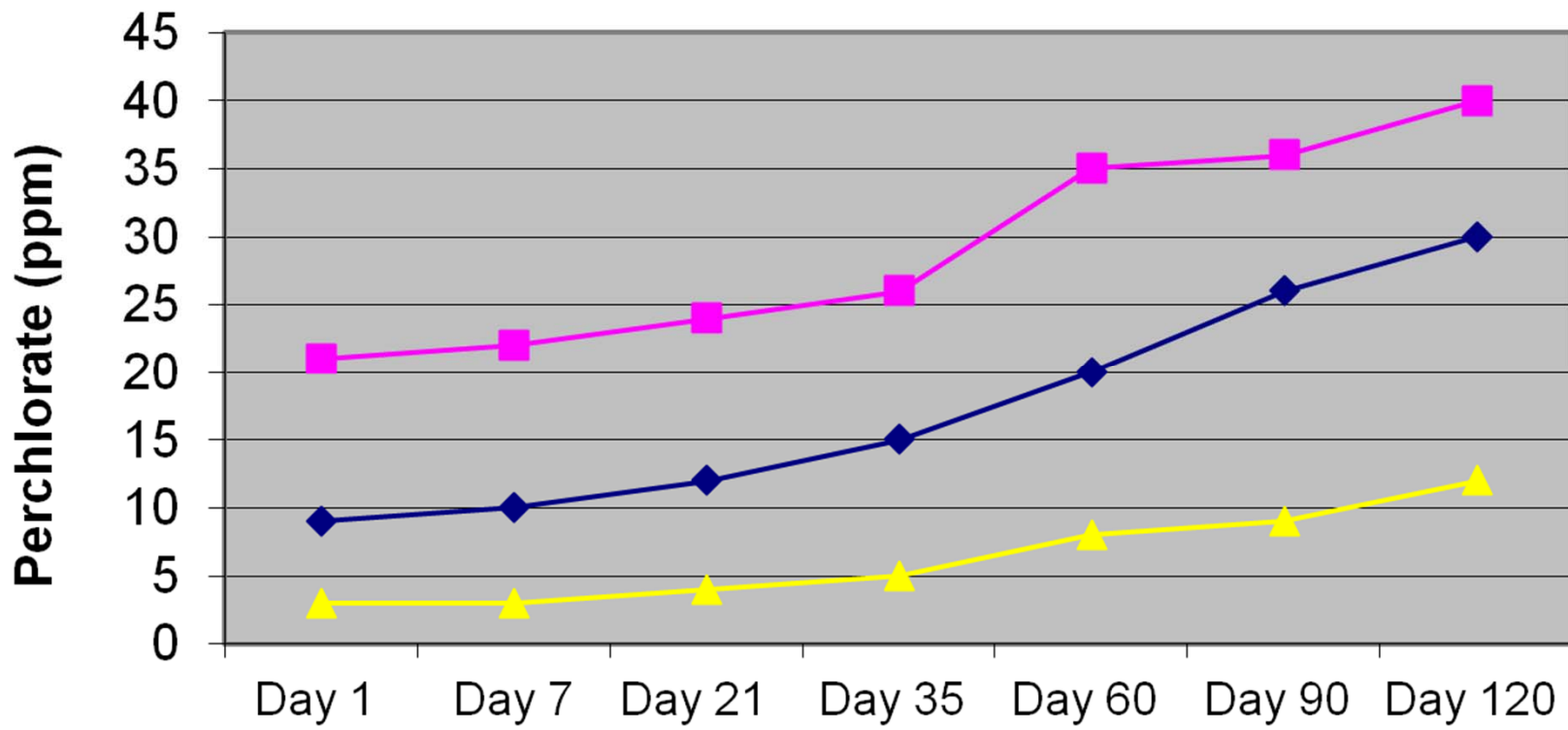
## Example:

- 12.5% NaOCl solution
- Dosed at 84 mg/L to drinking water (10 mg/L FAC)
- If perchlorate in NaOCl was 12 ppm
- Perchlorate in finished drinking water = 1.0 ppb

# Age of NaOCl and Perchlorate Concentration in Product

- All samples under 30 days old would contribute less than 1.0 ppb to drinking water if used at maximum use level.
- 83% of samples less than 90 days old would contribute less than 1.0 ppb to drinking water if used at the maximum use level.

# Pool Chlorine Perchlorate in product (ppm) Time from purchase



# New Requirements for Perchlorate in NSF/ANSI 60

- **Requirements address:**
  - Concentration of perchlorate as new product is shipped from manufacturers.
  - Require production date and any repackage date on product container.
  - Reference AWWA B-300 recommended storage and handling practices.

# Current Drinking Water Regulatory Requirements - Perchlorate

## Health Canada/USEPA

- No current HC Guideline
- No current US federal regulation for perchlorate in drinking water. EPA is developing a standard.
- EPA Draft HRL = 15 ppb.

## US States

- CA MCL 6 ppb, MA MCL 2 ppb
- Other states with MCLs, action levels, or guidance criteria.

# New Requirements for Perchlorate in NSF/ANSI 60

## SPAC for perchlorate.

- Based on draft EPA HRL = 15 ppb.
- Total of known sources = 2.
  - Contaminated source water.
  - Hypochlorite.
- Add 1 unknown source for a factor of 3.
- $15 \text{ ppb} / 3 = 5 \text{ ppb}$ .

# New Requirements for Perchlorate in NSF/ANSI 60

Optional lower criteria (SPAC) can be chosen by manufacturer to meet state or provincial regulations:

- **Based on CA MCL = 6 ppb.**
  - SPAC = 2 ppb.
- **Based on MA MCL = 2 ppb.**
  - SPAC = 0.7 ppb.
- **Supplier can choose Certification to local regulation = X.**
  - SPAC = X/3.



# Current Drinking Water Regulatory Requirements - Chlorate

## Health Canada

- Drinking Water Guideline of 1ppm.

## USEPA

- No current federal regulation for chlorate in drinking water.

# Chlorate and NSF 60

## – NSF 60 SPAC:

- Health Canada Guideline of 1 ppm.
- Known sources = 3.
  - Contaminated source water.
  - Hypochlorite.
  - Chlorine dioxide or ozonation of chlorinated water.
- Add 1 unknown source for a factor of 4
- **SPAC = 0.2 ppm** (0.3 ppm being considered)

# Chlorate and Perchlorate NSF 60

- Levels of chlorate and perchlorate in fresh hypochlorite solutions that are NSF 60 certified should be low.
- Products are quenched upon sampling at manufacturing site.
- Born on date and B-300 recommendations will be useful for Operators to gauge the age and potential for development of significant levels.

## AWWA / WRF Sponsored Study

Southern Nevada Water Authority completed a study in 2009.

Results published in *Hypochlorite – An Assessment of Factors That Influence the Formation of Perchlorate and Other Contaminants*.

*Available at:*

[www.awwa.org/files/GovtPublicAffairs/PDF/HypochloriteAssess.pdf](http://www.awwa.org/files/GovtPublicAffairs/PDF/HypochloriteAssess.pdf)

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# AWWA/WRF Sponsored Study

Surveyed occurrence at utilities including:

- Onsite generators.
- Bulk Hypochlorite.
- Calcium hypochlorite.

# AWWA/WRF Sponsored Study

Found perchlorate formation occurred overtime influenced by:

- Hypochlorite and chlorate concentration
- Ionic strength
- pH
- Temperature
- Metal ions

# AWWA Recommendations

Study recommendations are being published in Annex to AWWA B-300.

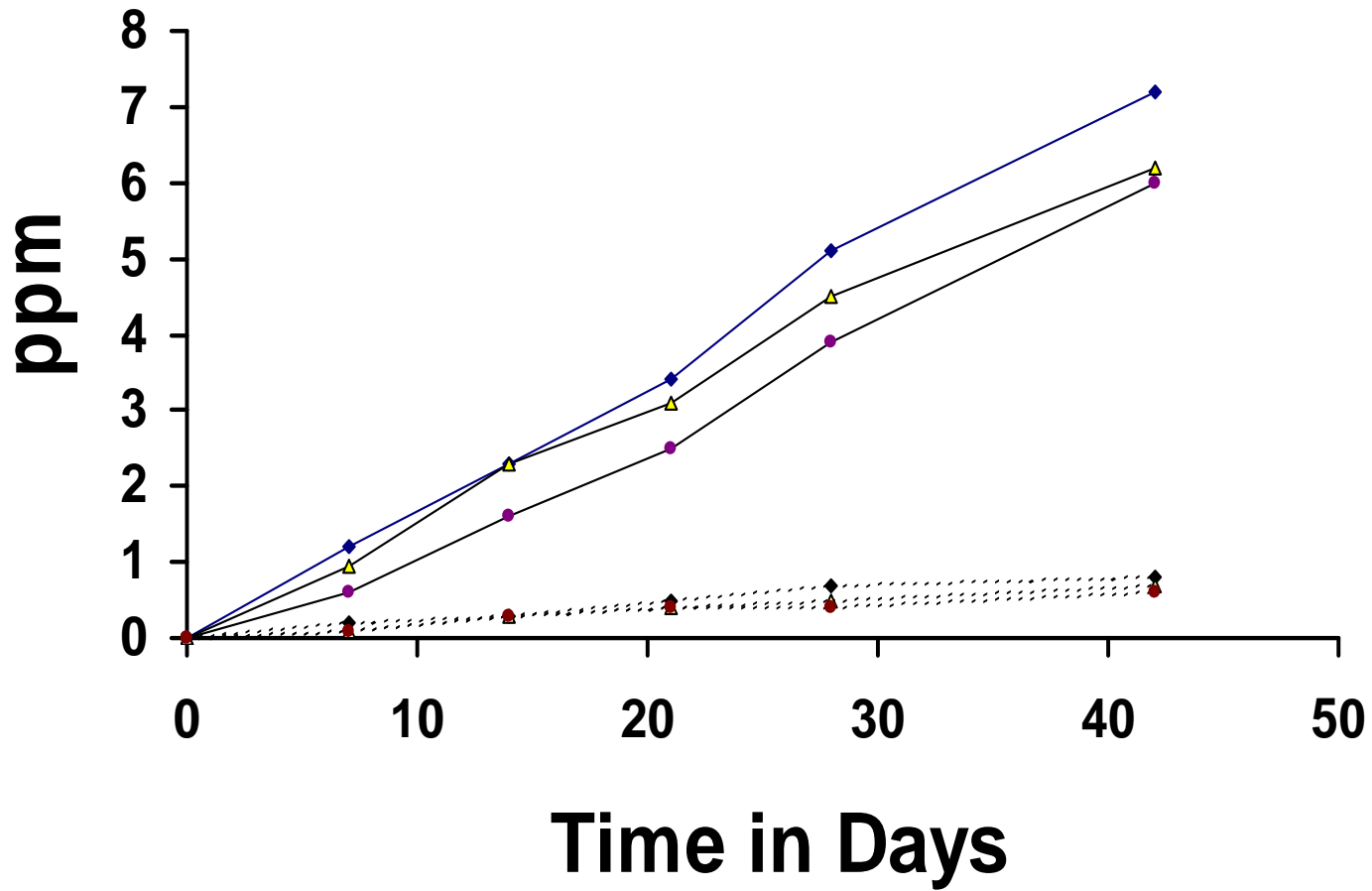
1) Dilute hypochlorite solutions on delivery.

Diluting a 15% solution by a factor of 2 decreases:

- Perchlorate formation by a factor of 7.
- Chlorate by a factor of 5.

# Perchlorate in NaOCl

Comparison of Perchlorate formation Rates Between Full Strength and 1:2 Diluted NaOCl





# AWWA Recommendations

2) Reduce storage temperature.

Every 5 degree reduction in temperature reduces the rate of decomposition by a factor of 2.

# AWWA Recommendations

3) Control the pH between 11 and 13.

Below 11 chlorate formation increases. Above 13 perchlorate formation increases. On site generators typically are between pH 9 to 10 and should be used within 1 to 2 days.

# AWWA Recommendations

- 4) Control the concentration of transition metal ions.
  - Purchase filtered sodium hypochlorite solutions.
  - Use low metal ion concentration feed water for onsite generators.

## AWWA Recommendations

- 5) Use fresh hypochlorite solutions when possible.
- 6) Use a low bromide salt in onsite generators to reduce the formation of bromate.


# AWWA Hypochlorite Assessment Tool

The screenshot shows the AWWA website homepage. At the top, there is a navigation bar with links for 'Contact Us', 'Advertise With Us', 'Sourcebook', and 'Site Map'. Below this is the AWWA logo and tagline 'The Authoritative Resource on Safe Water'. A search bar is located on the right side of the header. The main navigation menu includes 'Home', 'Membership and Sections', 'AWWA Bookstore', 'Conferences and Education', 'Professional and Technical Resources', 'Government and Public Affairs', 'Publications', and 'About AWWA'. The 'Professional and Technical Resources' menu is expanded, listing items such as 'Technical & Educational Council Resources', 'Communities & Resource Pages', 'AWWA Standards', 'AWWA Manuals', 'Career Center', 'Work for Water', 'Sustainable Water Utilities', 'Operator Assistance', 'Partnership for Safe Water', 'Utility Management', 'WaterWiser', 'Global Resources', 'Discussion Forums', and 'Hypochlorite Assessment Tool'. The main content area features a 'Water Treatment Plant Design' banner, a 'Quick Poll' section with a question about hydrant colors and radio button options, a 'News' section with several articles including 'EPA webcast to...', 'AWWA, WEF collaboration...', 'AWWA supports...', 'Funds offered to build local disaster resilience', and 'New EPA drinking water chief named', and 'AWWA Announcements' with a link to 'AWWA design staff recognized'. On the right side, there is a 'Welcome Please Log In' box with a 'Log In' button, an 'ACE<sup>12</sup>' logo, a 'BURIED NO LONGER' report link, and a 'Career center' logo. A dark blue box at the bottom right contains the text 'Want the strongest'.


<http://www.awwa.org/>



# AWWA Hypochlorite Assessment Tool

 American Water Works Association  
The Authoritative Resource on Safe Water

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### Hypochlorite Assessment Model

Welcome, Peter  
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Initial Hypochlorite (OCI<sup>-</sup>) 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<sub>3</sub><sup>-</sup>):  g/L

Initial Sodium Chloride (NaCl):  mol/L

Initial Perchlorate (ClO<sub>4</sub><sup>-</sup>):  mg/L

Specific Conductance:  μmho/cm

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

**Optional Input**  
*The following inputs are optional but provide additional interpretation*

Expected Chlorine (Cl<sub>2</sub>) Dose:  mg FAC/L finished water

Chlorate (ClO<sub>3</sub><sup>-</sup>) MCL:  mg/L

Perchlorate (ClO<sub>4</sub><sup>-</sup>) 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 predictive formation, not regulatory compliance.

<http://www.awwa.org/>

# AWWA Hypochlorite Assessment Tool

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## Hypochlorite Assessment Model

**Inputs:**

|   |   |                |
|---|---|----------------|
| Initial Hypochlorite (OCl <sup>-</sup> ) Concentration*: 12.5 NaOCl (% w/w) | Initial Chlorate (ClO <sub>3</sub> <sup>-</sup> ): 0.002 g/L      | 0.002 g/L      |
| pH (default 12.5): 12.5   | Initial Sodium Chloride (NaCl): 1.99 mol/L                        | 1.99 mol/L     |
|   | Initial Perchlorate (ClO <sub>4</sub> <sup>-</sup> ): 0.0597 mg/L | 0.0597 mg/L    |
| Specific Gravity (S.G.): 1.185  | Specific Conductance: 250720 μmho/cm                              | 250720 μmho/cm |

**Results:**

Hypochlorite and Chlorate
Hypochlorite and Perchlorate
Residual Chlorate and Perchlorate

Hypochlorite half-life at Temperature 1: 150 days

| Days | °C | NaOCl (% w/w) | ClO <sub>3</sub> <sup>-</sup> (g/L) | ClO <sub>4</sub> <sup>-</sup> (mg/L) | ClO <sub>3</sub> <sup>-</sup> (mg/mg FAC) | ClO <sub>4</sub> <sup>-</sup> (μg/mg FAC) | Residual ClO <sub>3</sub> <sup>-</sup> (mg/L) | Residual ClO <sub>4</sub> <sup>-</sup> (mg/L) | O <sub>2</sub> (L) |
|------|----|---------------|-------------------------------------|--------------------------------------|---|---|---|---|--------------------|
| 0    | 25 | 12.5          | 0.002                               | 0.06                                 | 0   | 0   | 0   | 0   | 0                  |
| 1    | 25 | 12.417        | 0.342                               | 0.06                                 | 0.002                                     | 0   | 0.002   | 0   | 0.011              |
| 2    | 25 | 12.335        | 0.678                               | 0.066                                | 0.005                                     | 0   | 0.005   | 0   | 0.022              |
| 3    | 25 | 12.254        | 1.01                                | 0.079                                | 0.007                                     | 0.001                                     | 0.007   | 0   | 0.032              |
| 4    | 25 | 12.175        | 1.337                               | 0.098                                | 0.01                                      | 0.001                                     | 0.01  | 0   | 0.043              |
| 5    | 25 | 12.096        | 1.659                               | 0.122                                | 0.012                                     | 0.001                                     | 0.012   | 0   | 0.053              |
| 6    | 25 | 12.018        | 1.978                               | 0.153                                | 0.015                                     | 0.001                                     | 0.015   | 0   | 0.064              |
| 7    | 25 | 11.941        | 2.293                               | 0.189                                | 0.017                                     | 0.001                                     | 0.017   | 0   | 0.074              |

<http://www.awwa.org/>



# Summary

## Hypochlorite will contain

- Bromate
- Chlorate
- Perchlorate

## Manage concentrations

- Follow AWWA B-300 recommendations
- Use chemicals within certified maximum use levels



# Summary

## Hypochlorite certified to NSF 60 requires:

- Contributes  $\leq$  3-5 ppb bromate
- Contributes  $\leq$  200-300 ppb chlorate
- Contributes  $\leq$  5 ppb perchlorate (or lower as indicated)

## Salt for OSG certified to NSF 60 requires:

- Contributes  $\leq$  3 ppb bromate  
( $\leq$  54 mg/kg bromide for 10 ppm FAC dose)

# Contact Info:

**Dave Purkiss**

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