Best Management Practices for Sodium Hypochlorite

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OTCO 49th Annual Water Workshop

March 23, 2011

Controlling Bromate, Chlorate and Perchlorate Contamination

- Bromate is a common contaminant in sodium hypochlorite.
- Chlorate and perchlorate concentrations are low in fresh hypochlorite.
- Significant concentrations of chlorate and perchlorate can develop in storage.
- Certain 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 Standard 60 – being revised to contain:

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

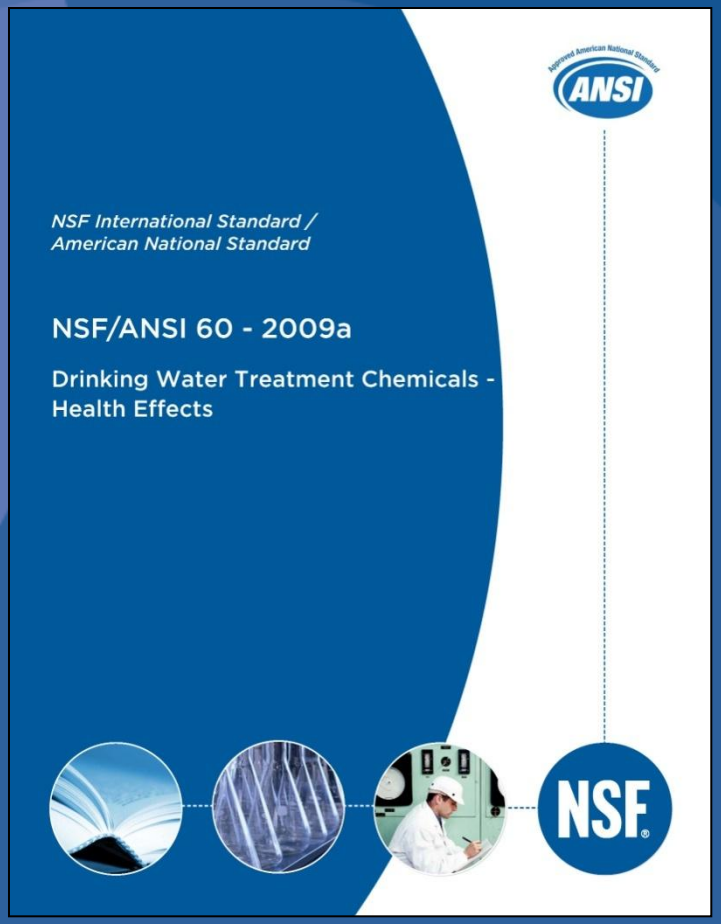
NSF/ANSI Standard 60

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



Certification to NSF/ANSI Standard 60

- Toxicology review of chemical formulation.
- Inspection of the manufacturing facility to verify formulation and collect samples.
- Testing of the chemical.
- Toxicology evaluation of results.
- If product meets requirements:
  - Package can bear the NSF 60 Mark
  - Listings at http://www.nsf.org

Testing of Product to NSF 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.
- For example, the arsenic MCL = 10 ppb

  so the SPAC for arsenic= 1 ppb

Certification to NSF/ANSI Standard 60

- **If a number of known sources of a contaminant are limited, the SPAC can be greater than 1/10 of MCL.**
- Bromate MCL = 10 ppb
- Two known sources :
  - bromide in source water converted to bromate by UV or Ozone.
  - sodium hypochlorite .
- Adding 1 additional safety factor gives source safety factor of 3.
- SPAC = 10 ppb/3 = 3 ppb

NSF/ANSI Standard 60

Hypochlorite and Bromate

- However, a significant number of sodium hypochlorite mfrs could not meet the 3 ppb level for bromate.
- SPAC for bromate set at 5ppb in 2000.
- SPAC is being reduced to 3ppb 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.

NSF/ANSI Standard 60

Hypochlorite

- Historically NSF 60 required sodium hypochlorite to be evaluated for heavy metals and VOCs.
- Bromate was added in 2000.
- Perchlorate and chlorate are being added in 2011.

NSF/ANSI Standard 60

Hypochlorite and Chlorate and Perchlorate

- CA DHS reported in 2005 that a water utility found traces of perchlorate in sodium hypochlorite.
- MA DEP published a report in 2005, showing levels of perchlorate can increase with the age of sodium hypochlorite.

MA DEP 2005

State of MA DEP report:

- Found perchlorate in hypochlorite solutions used at water treatment plants.
- Highest levels 4000 ppb in residual amounts in storage tank.
- New delivery was at 0.2 ppb.
- Aging this over 26 days increased to:
  - 6750 ppb at room temperature.
  - 1000 ppb at 5^{o}C.

Current Drinking Water Regulatory Requirements - Perchlorate

USEPA

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

States

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

NSF Study on Perchlorate Occurrence

- NSF selected a wide variety of treatment chemicals that are currently certified to NSF 60.
- 164 different chemical samples from 102 mfrs.
- 37 different chemical types.
- Found perchlorate in Sodium Hydroxide (NaOH) and Sodium Hypochlorite (NaOCl).

Method

- NSF utilized modified EPA 331.0 LC/MS/MS for analysis.
- Once samples received stored in 40 mL amber bottles in dark at 23 +/- 2^{o}C
- Detection level was 1 ppb in water.

Occurrence in NaOH

- 27 samples of NaOH were analyzed.
- 22 samples were ND.
- 5 samples ranged from 110 ug/kg to 900 ug/kg in product.
- Potential contribution to water was only 0.12 ppb if the sample with the highest detection was used at its maximum use level.
- Conclusion: Perchlorate not an issue for NaOH based on our testing to date.

Occurrence in NaOCl

- 82 samples of NaOCl were analyzed.
- 7 samples were ND.
- Samples ranged from ND to 300 ppm in product.
- Potential contribution to water was 28 ppb if the sample with the highest detection was used at its maximum use level.

Occurrence in NaOCl

- Typical maximum use level for 12.5% NaOCl solution is 84 mg/L (10ppm total chlorine equivalents).
  - For this product, 12 ppm of perchlorate in product would equate to 1.0 ppb in finished drinking water.

Perchlorate Occurrence in NaOCl

ppm in Product	# SAMPLES	% Samples
ND	7	9%
>ND to 12	42	51%
>12 to 60	30	36%
>60 to 96	0	0
>96 (96,144,300)	3	4%
Totals	82	100%

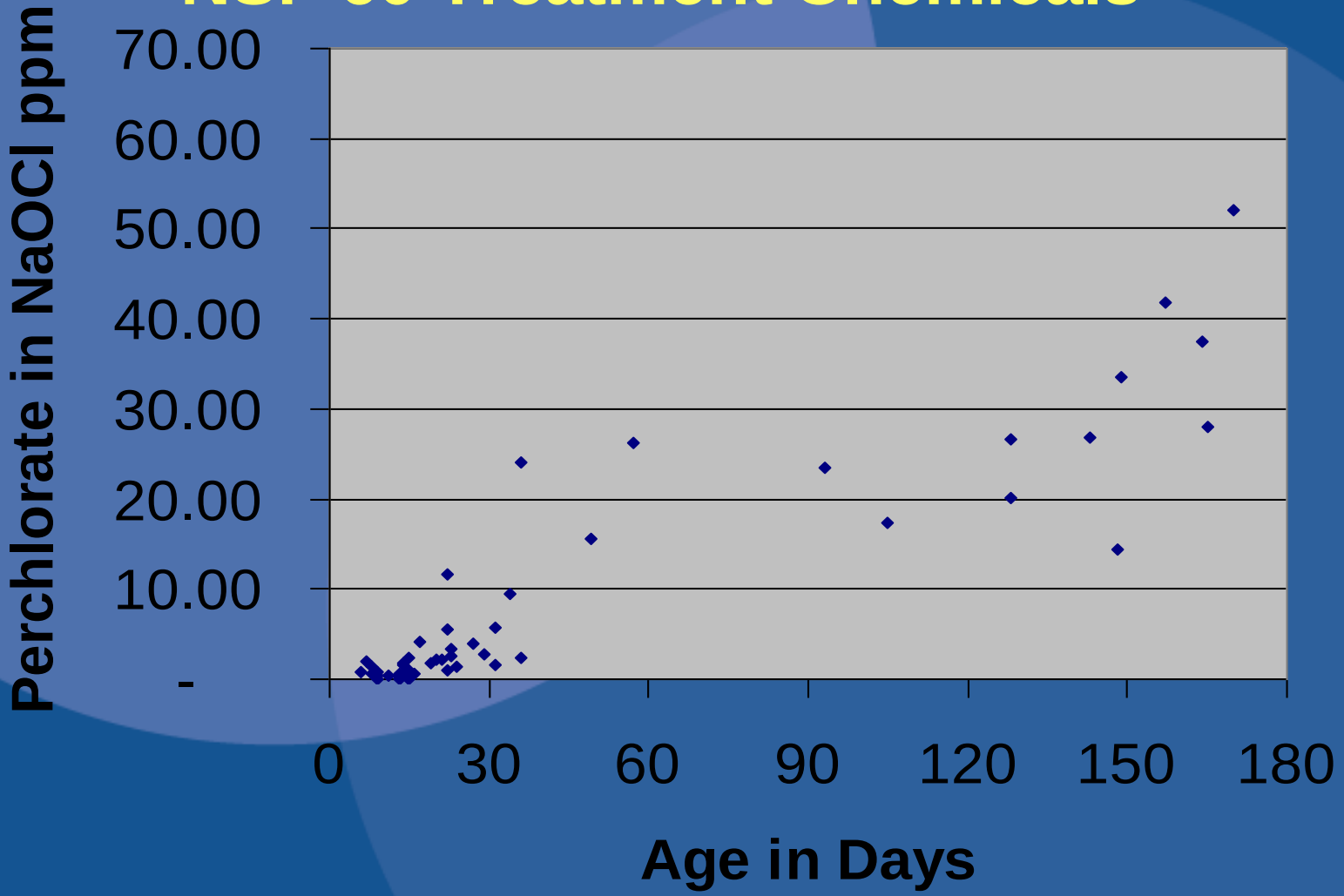
Age of NaOCl and Perchlorate Concentration in Product

Age of NaOCl in days	# samples	Perchlorate >12ppm	% less than 12ppm	% greater than 12ppm
≤ 30 days	33	0	100	0
> 30 - <45	32	1	97	3
45 - <60	25	2	92	8
60 - <90	24	4	83	17
> 90	32	27	16	84

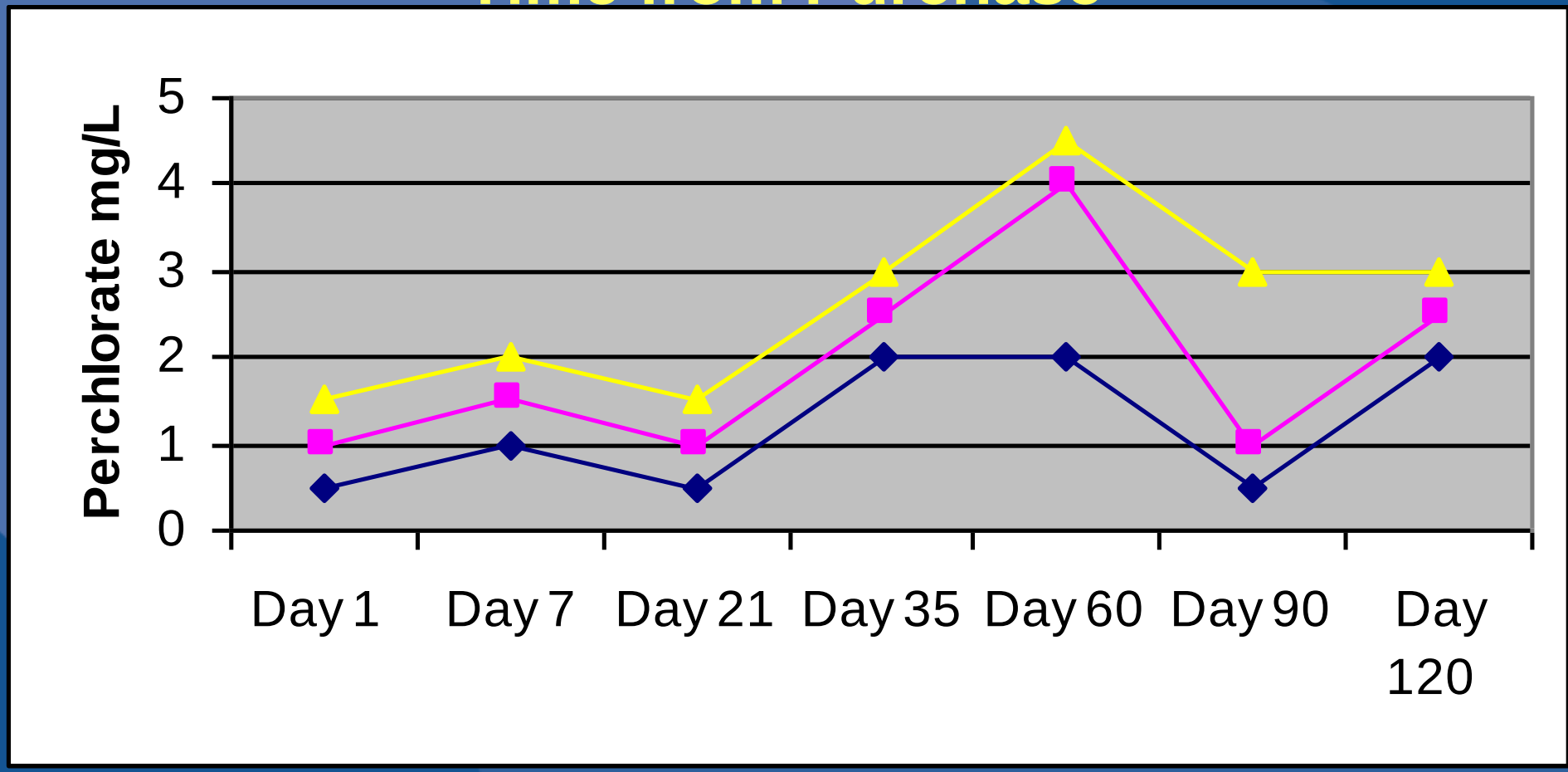
Age of NaOCl and Perchlorate Concentration in Product

- 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.

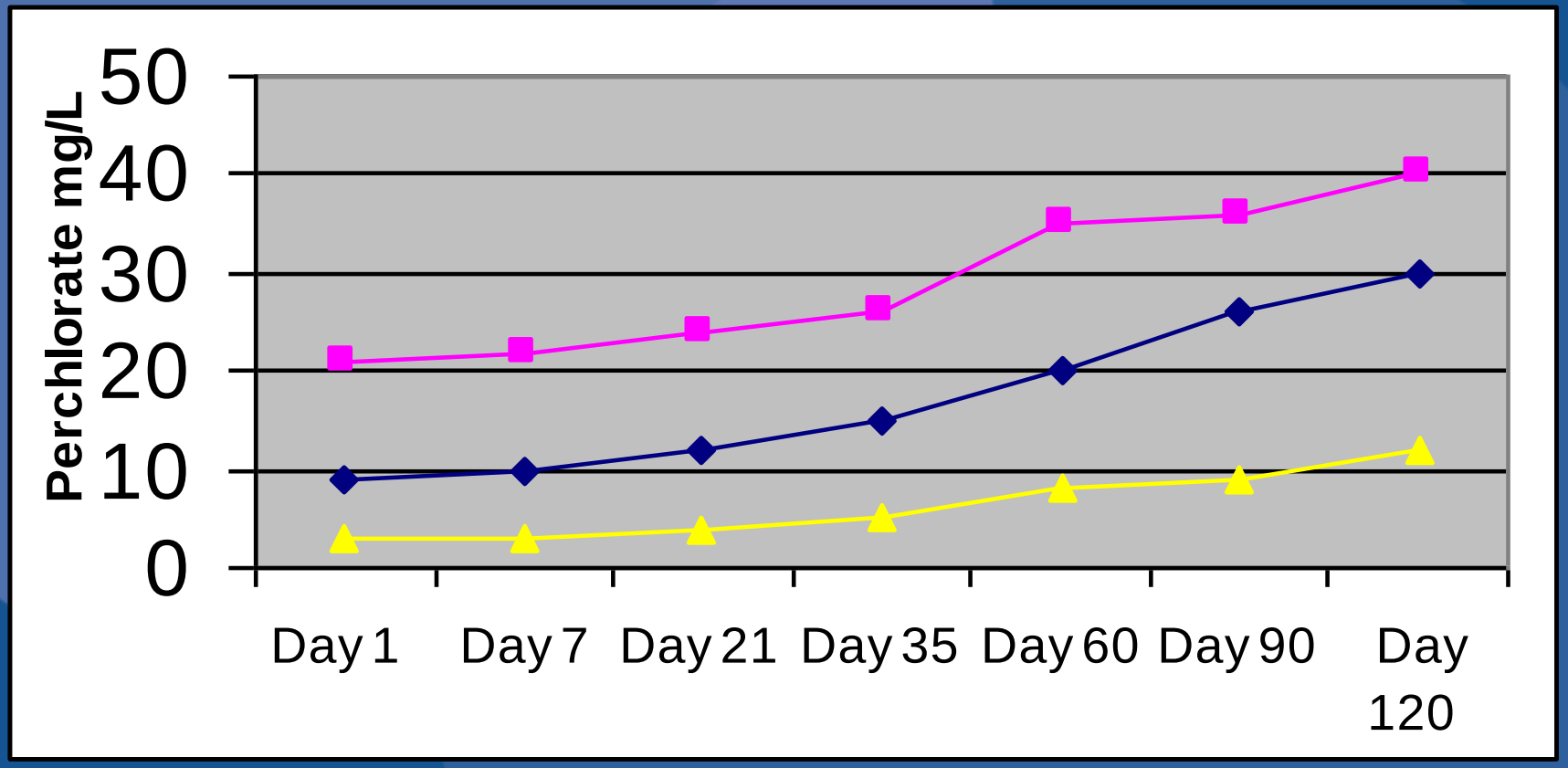
Effect of Age on Perchlorate in NaOCl NSF 60 Treatment Chemicals



Laundry Bleach
Perchlorate in product (ppm)
Time from Purchase

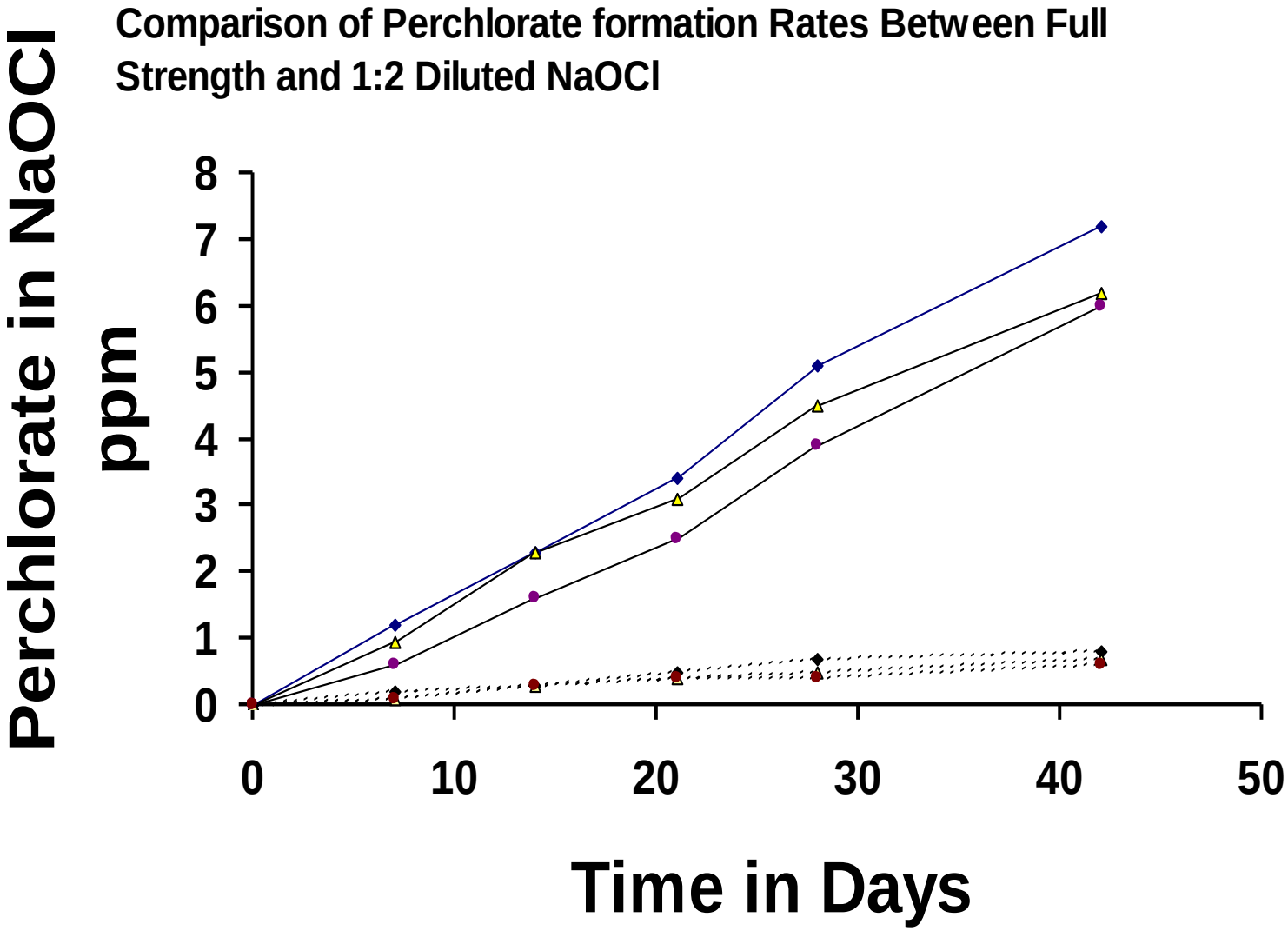


Perchlorate in Pool Chlorine ppm (Time from purchase)



Sodium Hypochlorite Decomposition

- Hypochlorite decomposes into chlorite, oxygen, and chlorate overtime.
- pH, concentration, metal ions, and temperature are factors.
- Dilution of NaOCl by ½ decreases chlorate formation by 5x.
- A 10^{o} C increase in temp will increase decomposition by 3.5x.
- Is the same true for perchlorate formation?


Comparison of Perchlorate formation Rates Between Full Strength and 1:2 Diluted NaOCl
Perchlorate in NaOCl ppm
0
1
2
3
4
5
6
7
8
0
10
20
30
40
50
Time in Days

Conclusions from NSF Study

- NSF has only found perchlorate in NaOH and NaOCl.
- Negligible perchlorate contribution from NaOH.
- Negligible perchlorate contribution from most NaOCl used within 45 days of manufacture.
- Small systems or utilities that store for longer periods should use precautions.

Conclusions from NSF Study

- Current storage precautions for NaOCl should also reduce perchlorate formation:
  - Diluting and storing in dark at cool temperatures reduces chlorate and perchlorate formation.
  - Storage tanks and piping should be emptied and flushed routinely.

New Requirements for Perchlorate NSF 60 - 2011

- NSF 60 requirements will 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 (currently being drafted and balloted into B-300).

Perchlorate and NSF 60

NSF 60 requirements will address:

- SPAC for perchlorate.
- Based on draft EPA HRL = 15 ppb.
- Total of known sources = 2.
  - Ozone.
  - Hypochlorite.
- Add 1 unknown source of a factor of 3.
- 15 ppb/3 = 5 ppb.

Perchlorate and NSF 60

Optional lower criteria can be chosen by manufacturer to meet state regulations:

- Based on CA MCL = 6ppb.
  - SPAC = 2ppb.
- Based on MA MCL = 2ppb.
  - SPAC = 0.7ppb.

Current Drinking Water Regulatory Requirements - Chlorate

USEPA

- No current federal regulation for chlorate in drinking water.

Health Canada

- Drinking Water Guideline of 1ppm.

Chlorate and NSF 60

- NSF 60 SPAC for chlorate:
  - Based on Health Canada Guideline of 1ppm.
  - Total of known sources = 3.
    - Hypochlorite.
    - Ozone.
    - Chlorine dioxide.
    - Add 1 unknown source of a factor of 4.
  - 1ppm/4 = 0.25 ppm.
  - Rounds to 0.2ppm (200ppb).

Chlorate and Perchlorate NSF 60

- Expecting very few issues with chlorate and perchlorate in fresh hypochlorite solutions that are NSF 60 certified.
- 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

AWWA/WRF Sponsored Study

Surveyed occurence 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 to be 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.

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 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.

NSF 60 will be investigating setting Bromide levels for NSF 60 certified salt.

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