

Hypochlorite solutions contain oxyhalide species such as perchlorate, chlorate, and bromate that form during and after manufacture. Such oxyhalide species have the potential to contaminate finished drinking water if adequate control measures are not taken to minimize their formation during manufacture, shipment, and storage of hypochlorite solutions. This article describes the rate of formation of perchlorate in hypochlorite solutions and discusses the chemistry behind a series of control strategies that utilities and manufacturers can implement to minimize oxyhalide formation and introduction into drinking water. Factors affecting the formation of perchlorate include temperature, ionic strength, hypochlorite concentration, and the presence of transition metal ions. The authors conclude that with proper manufacture, storage conditions, and handling, formation of perchlorate, chlorate, and bromate can be minimized. If care is not taken during manufacture and storage of hypochlorite solutions, however, perchlorate, chlorate, and bromate levels can exceed health-based guidelines in drinking water.

## Perchlorate, bromate, and chlorate in hypochlorite solutions: Guidelines for utilities

Various forms of chlorine are commonly used in drinking water and water reuse applications for their ability to disinfect and maintain a residual level of disinfectant throughout the distribution system. The majority of utilities in the United States use chlorine gas during treatment, but approximately one third of all US drinking water treatment plants use bulk hypochlorite for disinfection, and around 8% use onsite hypochlorite generators or onsite generators (OSGs) during treatment (Routt et al, 2008a, 2008b). Hypochlorite solutions contain many regulated and unregulated contaminants, including bromate, chlorite, chlorate, and perchlorate (Asami et al, 2009; Greiner et al, 2008; Weinberg et al, 2003; Gordon et al, 1993).

The perchlorate ion (referred to here as perchlorate) has been identified as a contaminant of concern in hypochlorite solutions and drinking water and has drawn much attention because it is an endocrine-disrupting chemical that can affect the human thyroid system (Greer et al, 2002; York et al, 2001; Urbansky, 2000; Lamm et al, 1999). Furthermore, on the basis of both data

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A full report of this project, *Hypochlorite—An Assessment of Factors That Influence the Formation of Perchlorate and Other Contaminants* (4147), is available for free to Water Research Foundation subscribers by logging on to [www.waterfff.org](http://www.waterfff.org).

from the current study and data published elsewhere, perchlorate appears to be a ubiquitous contaminant of hypochlorite solutions, and its concentration increases significantly during storage (Asami et al, 2009; Snyder et al, 2009; Greiner et al, 2008; Snyder et al, 2005).

Hypochlorite solutions also contain chlorate, which is known to increase in concentration during storage as a function of time, temperature, and a suite of chemical factors (Adam & Gordon, 1999; Gordon et al, 1995). Chlorate has been included on the third US Environmental Protection Agency (USEPA) Contaminant Candidate List and is likely to be included in the third Unregulated Contaminant Monitoring Rule, a move that sets the stage for potential future regulation. Chlorite, a regulated drinking water contaminant and a contaminant of hypochlorite solutions, tends to remain at steady state and does not exhibit the drastic changes in concentration exhibited by chlorate and perchlorate.

Finally, bromate, yet another oxyhalide contaminant of hypochlorite solutions and a potent carcinogen, results from the oxidation of bromide via a mechanism analogous to that of chlorate (Asami et al, 2009), although its concentration remains constant once the available bromide has been converted to bromate (Snyder et al, 2009). Bromate is currently regulated in drinking water at a maximum contaminant level (MCL) of 10 µg/L.

The controversy regarding potential health effects associated with perchlorate exposure via drinking water has led to significant vacillation at the federal level and limited precautionary regulation at the state level. In 2002 the USEPA published a reference dose (RfD) for perchlorate of 0.0003 mg/kg/d, which suggested a drinking water equivalent level (DWEL) of approximately 1 µg/L (Tiemann, 2008; USEPA, 2002). In 2005 the National Academy of Sciences and USEPA updated the RfD to 0.0007 mg/kg/d with a DWEL of 24.5 µg/L (USEPA, 2006), a number based on the no observable effect level (NOEL) of 0.007 mg/kg/d for inhibition of iodide uptake determined in a human clinical trial (Greer et al, 2002). However, an Aug. 19, 2009, notice in the *Federal Register* published by the USEPA (Silva, 2009) indicated a reexamination of the perchlorate regulatory determination and the potential for a national perchlorate regulation at levels as low as 1–6 µg/L. The same document defined the relative source contribution– (RSC–) adjusted health reference level (HRL) for perchlorate at 15 µg/L (HRL = DWEL × RSC; RSC = 62%). The state of Massachusetts has already set a DWEL and an MCL of 2.0 µg/L for perchlorate (MDEP, 2006), whereas California established an MCL of 6.0 µg/L (CDPH, 2007). New Jersey had proposed an MCL of 5 µg/L (NJDEP, 2009), but the state has deferred action until

after the USEPA issues a regulatory determination (Jackson, 2011; NJDEP, 2010). In addition to drinking water, perchlorate has been detected in a variety of food products and supplements (Aribi et al, 2006; Baier-Anderson et al, 2006; Snyder et al, 2006).

To complicate matters further, proposed federal legislation (i.e., the Drinking Water System Security Act of 2009, HR 3258) may impose significant burdens on the continued use of chlorine gas (which does not lead to the introduction of perchlorate) at drinking water and wastewater utilities. This development could result in a potential increase in the use of hypochlorite during treatment (which does lead to the introduction of perchlorate). Thus, utilities may be faced with a situation in which they are required to maintain perchlorate and/or chlorate concentrations below a federal or state MCL and at the same time be under pressure to switch to hypochlorite. In other words, utilities with low levels of perchlorate in their

source water could inadvertently increase the perchlorate concentration during treatment if they switch from chlorine gas to bulk or OSG hypochlorite without taking the necessary steps to minimize perchlorate, chlorate, and bromate formation during manufacture and/or storage.

With this in mind, AWWA and the Water Research Foundation commissioned a study to investigate the factors affecting perchlorate and other oxyhalide formation in hypochlorite solutions. This project sought to understand the chemistry that could be used to predict perchlorate formation in hypochlorite solutions and to apply this information to develop a set of strategies and recommendations for utilities currently using or considering the use of bulk or OSG hypochlorite. This article discusses the implications of the chemical rate law, focusing on the guideline recommendations for utilities to minimize perchlorate formation in stored hypochlorite solutions. Although general recommendations from the research study have been discussed in *Opflow* (Stanford et al, 2009) and in the project report (Snyder et al, 2009), this article expands on each of the points and provides a more in-depth discussion. Additional data are presented regarding a comparison of bulk and OSG hypochlorite solutions obtained from participating utilities and manufacturing partners.

## MATERIALS AND METHODS

A complete discussion of all materials, analytical methods, quality assurance/quality control procedures, and experimental design is available elsewhere (Pisarenko et al, 2010; Snyder et al, 2009). Briefly, a series of experiments

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was executed during the course of this study to elucidate the mechanism of perchlorate formation and determine the factors that affect the rate of perchlorate, bromate, and chlorate formation. Because the decomposition of hypochlorite at room temperature in solutions at pH 12–13 is relatively slow—the half-life of 13% sodium hypochlorite (NaOCl) is approximately 130 days at 25°C—the bulk and OSG hypochlorite solutions ranging from 0.3–12% were incubated at controlled temperatures of 30, 40, 50, 60, and 75°C. Subsets of these solutions were spiked, diluted, and/or pH-adjusted to examine the effect of ionic strength; effect of hypochlorite, chlorite, chlorate, bromide, bromate, transition metal ion (nickel, copper, iron, manganese, and cobalt), and noble metal ion (silver, gold, platinum, palladium, and iridium) concentration; effect of pH; and relevance of the source of hypochlorite ion solutions (bulk, OSG, and calcium hypochlorite).

Throughout the course of the incubation studies, the concentration of hypochlorite, chlorate, perchlorate, bromide, and bromate, and the ionic strength of sample solutions were measured periodically (Pisarenko et al, 2010); sampling intervals were determined using predictions for hypochlorite ion decomposition rates generated by the software program Bleach 2001 (Adam et al, 2001). The incubation studies were designed to allow at least one half-life (but preferably two) of hypochlorite decomposition to occur in order to assess and quantify the rate of perchlorate ion formation. At the lowest temperature of 30°C, this resulted in incubation times of at least 130 days (half-life = 65 days at 30°C). To calculate the rates of perchlorate ion formation, the changes in measured concentration of perchlorate ion were divided by the incubation intervals. To determine the reaction order with respect to concentration of chlorate or hypochlorite ion, the natural log of the rate of perchlorate ion formation (measured experimentally) was plotted versus the natural log of each ion at various concentrations in solutions at constant chlorate or hypochlorite ion concentrations.

A detailed discussion of the steps for determining the reaction kinetics and the predictive model is included in the project report (Snyder et al, 2009).

In addition to the incubation studies for elucidation of reaction mechanism and kinetics, an occurrence survey was conducted. Hypochlorite samples as well as samples of raw, finished, and distribution system water were collected from seven participating utilities. Of these utilities, five used bulk hypochlorite, two used OSG hypochlorite, and one used chlorine gas. One participating utility (utility 7) was a wastewater treatment plant that used bulk hypochlorite for disinfection of water for nonpotable reuse. Utility 7 represented the only wastewater plant in the study and was chosen as a challenge water to determine whether the more complex matrix could affect perchlorate formation in a simulated distribution system (SDS) study. Table 1 summarizes the relevant utility descriptions.

In addition to the utilities that participated in this study, two large suppliers of OSG systems agreed to supply hypochlorite solutions from 10 additional OSG locations and/or systems, providing a total of 12 OSG hypochlorite samples, including the two from the participating utilities. Table 2 provides a description of the OSG systems; OSG 9 and 10 are cross-referenced with those in Table 1. All OSGs tested used an electrolytic conversion of a salt brine solution to hypochlorite.

Finally, one supplier of calcium hypochlorite provided freshly manufactured calcium hypochlorite in solid form. Although formation of perchlorate in a solid sample is likely to be limited, calcium hypochlorite was investigated to determine whether perchlorate was present from the manufacturing process.

## RESULTS AND DISCUSSION

**Chemical rate law.** A detailed discussion of the kinetics behind the chemical rate law for perchlorate formation is beyond the scope of this article and is available elsewhere (Snyder et al, 2009). Because the implications of

**TABLE 1** Information on utilities sampled, age of hypochlorite, and water source

Utility	Hypochlorite Source	Sampling Date	Hypochlorite Age	Water Source
1A	Bulk	01/21/2009	60%–90 days, 40%–7 days	SW
1B	OSG 9	01/21/2009	2 days since production	SW
2	Bulk	01/26/2009	34 days	SW
3	Cl <sub>2</sub> gas	01/20/2009	NA	GW, RBF
4	Bulk	01/26/2009	≥ 5 days	GW
5	OSG 10	01/29/2009	< 1 day	SW
6	Bulk	02/07/2009	≥ 12 days	OD, SW, GW
7	Bulk	01/27/2009	1–6 days	WW

Cl<sub>2</sub>—chlorine, GW—groundwater, NA—not applicable, OD—ocean desalination, OSG—onsite generator, RBF—riverbank filtration, SW—surface water, WW—tertiary treated wastewater for nonpotable reuse

perchlorate formation kinetics are integral to the research discussed in this article, however, a brief summary of the rate law is included.

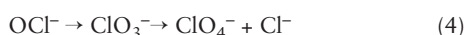
Hypochlorite ( $\text{OCl}^-$ ) is unstable and undergoes two independent modes of self-decomposition in solution (Gordon et al, 1995; Adam, 1994). In one mode, oxygen ( $\text{O}_2$ ) and chloride ( $\text{Cl}^-$ ) are formed, whereas in the other mode, chlorate ( $\text{ClO}_3^-$ ) and  $\text{Cl}^-$  are formed:



The rate of decomposition of hypochlorite to form chlorate and/or oxygen is well defined in terms of the following rate law:

$$\frac{d[\text{OCl}^-]}{3dt} = k_{\text{observed}} [\text{OCl}^-]^2 \quad (3)$$

Chlorite ( $\text{ClO}_2^-$ ) is rapidly formed as a steady-state species (equation not shown) and serves as an intermediate between hypochlorite and chlorate ions. Results from this study indicated that perchlorate ( $\text{ClO}_4^-$ ) is formed when hypochlorite and chlorate ions further react (Eq 4), thereby forming the basis of the rate law described in Eq 5:



$$\frac{d[\text{ClO}_4^-]}{dt} = k_{\text{calculated}} [\text{OCl}^-] [\text{ClO}_3^-] \quad (5)$$

What appears to be a simple rate law, however, is not trivial to deconvolute and quantify in a detailed chemical rate law. In considering the kinetics of perchlorate formation, it must be understood that the concentration of one reactant (hypochlorite) is decreasing via two possible pathways, whereas the concentration of the second reactant (chlorate) is increasing as a function of the concentration of the first reactant. To complicate matters further, a portion of the chlorate being produced is also being consumed in the production of perchlorate. Thus, the observed increase of chlorate is in reality a combined function of chlorate production and chlorate oxidation to perchlorate. Additionally, the rate of perchlorate formation is dependent on factors other than hypochlorite and chlorate concentrations including ionic strength and temperature.

Another factor that directly affects the rate of perchlorate formation is pH, although this effect is limited because most hypochlorite solutions are stored in the range of pH 11–13. Above pH 13, ionic strength effects dominate (Adam & Gordon, 1999), whereas below pH 10.5 a separate, faster hypochlorite decomposition pathway dominates. However, if the model is bound within the typical pH range of hypochlorite (pH 11–13), the effects of pH can be disregarded. Indirect factors influencing the rate of perchlorate formation include the presence of transition metal ions and the presence of bromide ions, both of which consume hypochlorite ions through catalytic decomposition (transition metal ions) or formation of hypobromite and bromate ions.

With these considerations in mind, a detailed chemical rate law was developed and validated using bulk hypochlorite solutions. Quantitative chemical rate law incor-

**TABLE 2** Description of OSGs, identification numbers, and salt source

OSG Model	Anode Material*	OSG Capacity lb/d	OSG Energy kW-h/lb FAC	Years of Service	Salt Source
1A	DSA	24	2.0	4	Unknown
1B	DSA	2,000	2.0	10	Unknown
2A	DSA	75	2.0	4	Unknown
2B	DSA	450	2.0	3	Unknown
3	DSA	750	2.0	1	Unknown
4	DSA	300	2.0	2	Unknown
5	DSA	400	2.0	†	> 99.7% as NaCl
6	DSA	180	3.5	†	> 99.7% as NaCl
7	DSA	20	3.3	†	> 99.5% as NaCl
8	DSA	10	5.2	†	> 99.5% as NaCl
9	DSA	1,200	Unknown	3	> 96% as NaCl
10	DSA	2,000	1.6–2.0	2.5, 6.5	> 99.7% as NaCl

DSA—dimensionally stabilized anode, FAC—free available chlorine, NaCl—sodium chloride, OSG—onsite generator

\*Material likely was titanium.

†Because OSG units were used only at the factory for testing, service time was much less than one year.

porates ionic strength and temperature effects in the calculated rate constant (Eq 6), which can be incorporated into Eq 5 to determine the stepwise rate of perchlorate formation (and change in concentration) as hypochlorite and chlorate concentrations change as predicted by Bleach 2001 (Adam et al, 2001). In Eq 6,  $I$  represents the ionic strength of solution,  $R$  represents the ideal gas constant, and  $T$  represents temperature (in kelvin). Eq 6 is dimensionally correct because the  $2.084 \times 10^{10}$  term is the result of dividing Boltzmann's constant ( $k$ ) by Planck's constant, resulting in units of  $k^{-1}s^{-1}$ , thereby canceling with the temperature term and leading to a per-second rate term.

$$\log(k_{\text{calculated}}) = 0.0788(I) + \log(2.084 \times 10^{10} \times T \times e^{-1.01 \times 10^5/RT} \times e^{-106/R}) \quad (6)$$

Eqs 5 and 6 were validated by using them to calculate the rate of perchlorate formation at different temperatures for bulk hypochlorite samples that varied in concentration and ionic strength. Figure 1 shows the measured perchlorate concentrations from experimental data and calculated perchlorate concentrations from Eqs 5 and 6. The calculated concentrations were fitted to a smooth line, and fixed 10% error bars were added. The data shown in Figure 1 indicate agreement of better than 10% between measured perchlorate concentration and calculated perchlorate concentration in most cases during the entire period of the holding studies. The agreement between experimental and calculated perchlorate concentrations supports the conclu-

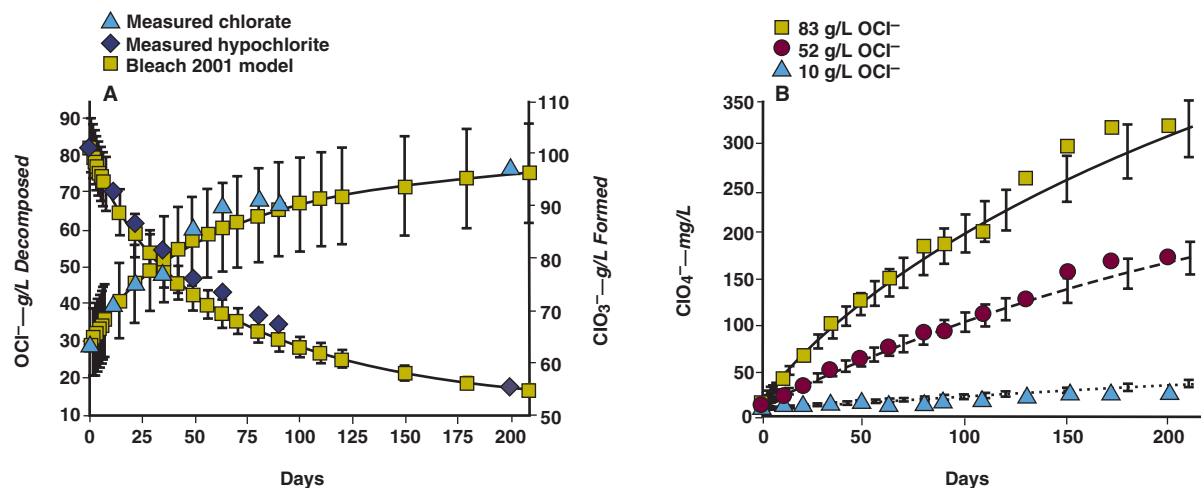
sion that the formation of perchlorate is a second-order reaction (first-order each in hypochlorite and chlorate) that is highly dependent on ionic strength and temperature. Thus, Eqs 5 and 6 can be used in conjunction with Bleach 2001 to accurately predict perchlorate concentrations as a function of time.

#### Survey of bulk, OSG, and calcium hypochlorite solutions.

The concentration of hypochlorite, perchlorate, chlorate, and bromate in the bulk samples for each of the seven utilities is shown in Table 3. Several observations can be drawn from these data.

- Only at utility 1A did perchlorate levels in the bulk hypochlorite appear to have a significant effect on the finished water concentration. Utility A's low free available chlorine (FAC) concentration (compared with other bulk hypochlorite solutions tested) and the high levels of perchlorate and chlorate could be explained by the age of the hypochlorite solution, which was a mixture of 90-day-old (60%) and 7-day-old (40%) bulk hypochlorite.
- None of the utility results were above California's 6- $\mu\text{g/L}$  MCL for perchlorate, and only two were above Massachusetts's 2- $\mu\text{g/L}$  MCL.
- Chlorate contamination from the hypochlorite solutions appeared to affect all of the utilities tested. As shown in Table 3, of the utilities tested, four had concentrations of chlorate in the finished drinking water above the 200- $\mu\text{g/L}$  (0.2-mg/L) proposed action level in California, and at one of these, the chlorate concentration was nearly twice the 800- $\mu\text{g/L}$  (0.8-mg/L) notification level recommended by the state (Howd, 2002).

**FIGURE 1** Measured and calculated decomposition of hypochlorite and formation of chlorate by software program (A) and perchlorate concentration predicted by Eqs 5 and 6 (B) at 30°C



$\text{ClO}_3^-$ —chlorate,  $\text{ClO}_4^-$ —perchlorate,  $\text{OCl}^-$ —hypochlorite

Solid lines indicate calculated concentration with  $\pm 10\%$  error bars. Software program used was Bleach 2001 (Adam et al, 2001).

- Bromate was observed at milligram-per-litre levels in all bulk hypochlorite solutions, although none of the utilities tested had finished water concentrations above the 10-µg/L bromate MCL mandated by the USEPA.

As shown in Table 4, the OSG hypochlorite samples also exhibited high variations in FAC, chlorate, and perchlorate concentrations. Eight OSG samples had < 700 mg/L of chlorate in the resulting hypochlorite solution. Bromate concentration ranged from 0.2 to 6 mg/L. Bromate concentrations are limited by the available bromide (which is rapidly converted to bromate in concentrated hypochlorite solutions) and is likely related to the amount of bromide present in the salt and/or feedwater used for hypochlorite generation. However, no discernable trends were found in the amount of perchlorate or chlorate formed by any given OSG with respect to energy consumption, OSG production capacity (pounds per day), or actual FAC concentrations. The solution for OSG 9 had the highest perchlorate concentration but was at least 48 h old when collected and may have been stored at temperatures up to 42°C. The brine solution and feedwater for OSG 9 were also at 40–42°C before electrolytic conversion.

Transition metal ion concentrations measured for this study were below detection in most of the bulk hypochlorite and OSG samples (data not shown), although utility 1A had nickel present at 0.2 mg/L, cop-

per at 0.1 mg/L, and iron concentrations approaching 10 mg/L in the hypochlorite solution. Given that metal ions have been demonstrated to have a catalytic effect on the decomposition of hypochlorite (Adam, 1994; Gordon et al, 1993), the presence of iron and nickel may have been a factor (in addition to age) in the low FAC concentration at utility 1A. Regarding the OSG hypochlorite, most brine samples showed higher levels of metal ion contamination relative to the hypochlorite product from the OSG (data not shown). This difference is likely attributable to loss of metal ions to reduction

and/or plating on the anode of the electrolytic cell. Current hypochlorite specifications recommend < 0.1 mg/L iron and < 0.05 mg/L nickel, copper, and cobalt (Gordon & Bubnis, 2000). The bulk hypochlorite sampled from utilities 1A,

4, 6, and 7 all contained at least one transition metal above the specified levels.

Transition metal ions were not measured in the calcium hypochlorite solutions. However, bromate, chlorate, and perchlorate all were measured for the 3 and 6% (as FAC) solutions of calcium hypochlorite immediately after mixing with reagent water. The 3% calcium hypochlorite solution had 390 mg/L chlorate, 27 µg/L perchlorate, and 2.4 mg/L bromate for 32 g/L FAC. The 6% calcium hypochlorite solution had 830 mg/L chlorate, 55 µg/L perchlorate, and 5.3 mg/L bromate for 61 g/L FAC.

The observed increase of chlorate is in reality a combined function of chlorate production and chlorate oxidation to perchlorate.

**TABLE 3** Summary of perchlorate, chlorate, and bromate concentrations in raw water, finished water, and hypochlorite used at participating utility locations

Utility	Source	FAC g/L	ClO <sub>4</sub> <sup>-</sup>			ClO <sub>3</sub> <sup>-</sup>			BrO <sub>3</sub> <sup>-</sup>		
			Hypo µg/L	Raw µg/L	Finished µg/L	Hypo mg/L	Raw mg/L	Finished mg/L	Hypo µg/L	Raw µg/L	Finished µg/L
1A	Bulk	87	14,000	< 0.5	3.6	19,000	0.014	0.58	24,000	< 0.5	0.5
1B	OSG 9	6.8	3,500	< 0.5	< 0.5	760	0.026	1.5	5,700	< 0.5	3.6
2	Bulk	150	670	< 0.5	< 0.5	5,900	0.005	0.019	30,000	< 0.5	< 0.5
3	Cl <sub>2</sub> gas	NA	NA	< 0.5	< 0.5	NA	< 0.003	< 0.003	NA	< 0.5	< 0.5
4	Bulk	120	220	< 0.5	< 0.5	1,800	0.13	0.20	9,000	1.3	1.4
5	OSG 10	8.7	19	2.0	2.1	780	0.008	0.16	150	< 0.5	1.3
6	Bulk	120	230	< 0.5	< 0.5	2,400	< 0.003	0.13	9,900	< 0.5	0.92
7	Bulk	130	2,000	1.6	1.2	8,000	< 0.003	0.79	7,700	< 0.5	2.6

BrO<sub>3</sub><sup>-</sup>—bromate, Cl<sub>2</sub>—chlorine, ClO<sub>3</sub><sup>-</sup>—chlorate, ClO<sub>4</sub><sup>-</sup>—perchlorate, FAC—free available chlorine, NA—not applicable, OSG—onsite generator

“Hypo” indicates hypochlorite solution. “Raw” indicates raw water entering the treatment plant. “Finished” indicates finished water leaving the treatment plant. Samples were analyzed in duplicate measurements, with average percent difference for ClO<sub>4</sub><sup>-</sup> = 2.0%, BrO<sub>3</sub><sup>-</sup> = 4.2%, and ClO<sub>3</sub><sup>-</sup> = 2.5%.



In light of the data described previously, a comparison was made by normalizing all of the contaminant concentrations to the concentration of FAC. Table 5 was created to show a relative contribution (on a basis of mass of contaminant per milligram of FAC) from each hypochlorite solution. Of the comparisons made within the limited data set collected for this project, the only trend that stood out was that the OSG hypochlorite samples consistently contributed more bromate per milligram of FAC than the fresh bulk hypochlorite solutions or the two calcium hypochlorite solutions tested. The higher levels of bromate in the OSG solutions likely were a result of bromide in the feedwater and/or salt used to make the brine solutions for electrolysis. Current NSF/ANSI 60 standards recommend no more than 0.5 µg BrO<sub>3</sub><sup>-</sup>/mg FAC (NSF/ANSI, 2005) in hypochlorite solutions. On the basis of this limit, three OSG solutions exceeded the recommendation and an additional two OSGs approached the limit (0.48 µg BrO<sub>3</sub><sup>-</sup> per mg FAC). Neither the calcium hypochlorite sample nor any of the bulk hypochlorite solutions exceeded the current bromate standard. Furthermore, only OSG 5–8 and OSG 10 used a salt with > 99.5% purity as sodium chloride (NaCl), a fact reflected in the lowest overall bromate concentrations. Thus, these data support the use of high-quality, low-bromide salts for hypochlorite generation, although further investigations quantifying purity and maximum bromide levels in salts used for OSG solutions should be performed.

Other than the relationship between salt quality and bromate formation, no consistent trends were observed. Contaminant oxyhalide concentration varied widely within and between brands, hypochlorite sources, and

production methods; this study showed no clear advantage of one over another with respect to chlorate and perchlorate concentration. Therefore, on the basis of this data set, there appears to be no straightforward way to determine what type of freshly prepared hypochlorite solution (OSG, bulk, or calcium) would result in the lowest mass loading of contaminants into the finished drinking water, an observation consistent with OSG and bulk hypochlorite data reported elsewhere (Asami et al, 2009). In light of potential perchlorate and/or chlorate regulation by federal or state agencies, investigations into methods used to minimize chlorate and perchlorate formation during OSG and bulk manufacturing processes should be of utmost importance.

**Contaminant concentrations in distribution system and SDS samples.** Perchlorate, chlorate, and bromate concentrations were also measured in the distribution system samples in order to determine whether any additional chlorate, perchlorate, or bromate had been formed. In the case of utility 2, an SDS study was used instead of collecting actual distribution system samples. Distribution system sampling locations were targeted to provide median and maximum residence times for each utility. Based on the developed model and considerations of hypochlorite concentration, temperature, pH, and ionic strength, it was not expected that any appreciable formation of chlorate, perchlorate, or bromate would be observed. Table 6 shows the results of the distribution system sampling and one SDS study.

In all cases except utility 1B, no meaningful increase in the concentration of perchlorate was observed in the distribution system. Although some chlorate data points for the distribution system were higher than in the fin-

**TABLE 4** Chlorate, bromate, and perchlorate concentration for OSG hypochlorite and brine

OSG Model	OSG Hypochlorite				Brine		
	ClO <sub>3</sub> <sup>-</sup> mg/L	BrO <sub>3</sub> <sup>-</sup> mg/L	ClO <sub>4</sub> <sup>-</sup> µg/L	FAC g/L	ClO <sub>3</sub> <sup>-</sup> mg/L	BrO <sub>3</sub> <sup>-</sup> mg/L	ClO <sub>4</sub> <sup>-</sup> µg/L
1A	140	4.1	5.4	9.7	<0.5	<0.1	<2.5
1B	240	3.8	16	8.0	<0.5	<0.1	<2.5
2A	97	5.3	8.6	6.8	<0.5	<0.1	<2.5
2B	360	3.3	410	6.9	<0.5	<0.1	<2.5
3	270	4.4	7.3	10	<0.5	<0.1	<2.5
4	1,200	2.6	40	4.5	<0.5	<0.1	<2.5
5	260	2.6	31	8.0	<0.5	<0.1	<2.5
6	180	1.4	22	5.2	<0.5	<0.1	<2.5
7	750	2.0	83	7.2	2.0	<0.1	<2.5
8	240	0.71	740	3.6	2.1	<0.1	<2.5
9	760	5.7	3,500	6.8	7.2	<0.1	65
10	780	0.15	19	8.7	<0.5	<0.1	<2.5

BrO<sub>3</sub><sup>-</sup>—bromate, ClO<sub>3</sub><sup>-</sup>—chlorate, ClO<sub>4</sub><sup>-</sup>—perchlorate, FAC—free available chlorine, OSG—onsite generator

ished water, the authors believe that this was related to the difference in hypochlorite age and dose at the time of treatment rather than a mechanistic formation of chlorate in dilute solutions (i.e., chlorinated water) in the distribution system.

The difficulty with using grab samples from a distribution system is that the hypochlorite solution used to disinfect the water is constantly changing and experiences turnover from new shipments and/or onsite generation. Therefore, in order to fully assess the behavior of chlorate, perchlorate, and bromate in distribution systems, an in-depth study with more sampling sites (and distribution systems) combined with temporal observations for a period of several months is suggested as a future research direction. However, because conditions in distribution systems

(i.e., low hypochlorite concentration, low ionic strength) are expected to be unfavorable for perchlorate formation, additional significant perchlorate formation is not anticipated.

**Implications of utility sampling and the detailed chemical rate law.** Information gathered in this study combined with the utility and OSG hypochlorite surveys provided the data and tools necessary to make qualitative and quantitative recommendations to utilities that can be used to minimize the introduction of perchlorate and bromate into finished waters. These data also helped to elucidate the factors influencing the formation of perchlorate in stored hypochlorite solutions.

The authors examined how factors such as dilution and temperature might affect the relative rate of per-

Proper management of stored hypochlorite solutions can have significant benefits in addressing for potential perchlorate compliance issues.

**TABLE 5** Relative contribution of specific contaminants on per-mass-FAC basis

Identification	Concentration in Hypochlorite Solutions				Mass of Contaminant Added per Milligram FAC		
	ClO <sub>3</sub> <sup>-</sup> mg/L	BrO <sub>3</sub> <sup>-</sup> mg/L	ClO <sub>4</sub> <sup>-</sup> µg/L	FAC g/L	ClO <sub>3</sub> <sup>-</sup> µg/mg FAC	BrO <sub>3</sub> <sup>-</sup> µg/mg FAC	ClO <sub>4</sub> <sup>-</sup> ng/mg FAC
Bulk/Utility							
1A	19,000	24	14,000	87	220	0.28	160
2	5,900	30	670	150	39	0.20	4.5
3	NA	NA	NA	NA	NA	NA	NA
4	1,800	9	220	120	15	0.08	1.8
6	2,400	10	230	120	20	0.08	1.9
7	8,000	8	2,000	130	62	0.06	15
OSG							
1A	140	4.1	5.4	9.7	14	0.42	0.6
1B	240	3.8	16	8	30	0.48	2.0
2A	97	5.3	8.6	6.8	14	0.78	1.3
2B	360	3.3	410	6.9	52	0.48	59
3	270	4.4	7.3	10	27	0.44	0.7
4	1,200	2.6	40	4.5	270	0.58	8.9
5	260	2.6	31	8	33	0.33	3.9
6	180	1.4	22	5.2	35	0.27	4.2
7	750	2	83	7.2	100	0.28	12
8	240	0.71	740	3.6	67	0.20	210
9	760	5.7	3,500	6.8	110	0.84	520
10	780	0.15	19	8.7	90	0.02	2.2
Ca(OCl) <sub>2</sub>							
1	390	2.4	27	32	12	0.08	0.8
2	830	5.3	55	61	14	0.09	0.9

BrO<sub>3</sub><sup>-</sup>—bromate, Ca(OCl)<sub>2</sub>—calcium hypochlorite, ClO<sub>3</sub><sup>-</sup>—chlorate, ClO<sub>4</sub><sup>-</sup>—perchlorate, FAC—free available chlorine, NA—not applicable, OSG—onsite generator



chlorate formation in a hypothetical bulk hypochlorite solution with a starting concentration of 2 M OCl<sup>-</sup> or approximately 13% FAC. Figure 2 shows results at 25 and 35°C. Results demonstrated the inverse relationship between hypochlorite concentration and perchlorate concentration (Figure 2, parts A and B) and showed that the mass of perchlorate added on a per-mg FAC basis increased much more rapidly than the concentration of perchlorate alone (Figure 2, parts C and D). In other words, as the hypochlorite solution ages, the concentration of hypochlorite decreases (Figure 2, parts A and B), forcing an operator to feed a higher volume of hypochlorite solution in order to achieve the target chlorine dose during treatment. Because the aged hypochlorite solution contains a greater concentration of perchlorate compared with the fresh solution (Figure 2, parts A and B), the operator would be dosing a higher volume of a solution with an elevated perchlorate concentration.

A secondary interpretation of the results shown in Figure 2 would be the ability to predict the number of days a hypochlorite solution can be stored before exceeding a given perchlorate concentration threshold. For example, storage of the hypothetical undiluted hypochlorite solution for approximately one month would result in a perchlorate concentration of approximately 0.5 µg ClO<sub>4</sub><sup>-</sup>/mg FAC. If that same utility was using a total of 6 mg/L FAC during the entire treatment process, there would be a cor-

Careful control of the quality of hypochlorite used in drinking water treatment could be equally, if not more, important for utilities operating near or above any potential federal or state maximum contaminant level resulting from source water contamination.

responding loading of 3 µg/L of perchlorate above the background concentration. Thus, at the Massachusetts MCL of 2 µg/L, the utility would be out of compliance. Had the same utility diluted the solution at a 1:2 ratio, however, the corresponding perchlorate concentration would be only 0.05 µg/L, corresponding to a loading of 0.3 µg/L of perchlorate above the background (assuming the same 6-mg/L FAC dose). Clearly, proper management of stored hypochlorite solutions can have significant benefits in addressing perchlorate compliance issues.

The calculations from Eqs 5 and 6 were used to develop Table 7, which provides a list of reduction factors, or the relative decrease in the rate of perchlorate formation for different dilution and temperature scenarios (e.g., by diluting by half and cooling the solution by 10°C, the rate of perchlorate formation would be 27 times slower than if the solution was stored undiluted at ambient temperature). The combination of Figure 2 and Table 7 should provide utilities with an applied version of the model to assist them with identifying control strategies that can be implemented in order to better control hypochlorite decomposition and perchlorate formation.

## RECOMMENDATIONS

The findings presented led to the identification of several key factors that influence the formation of perchlorate, chlorate, and bromate in hypochlorite solu-

**TABLE 6** Perchlorate, chlorate, and bromate concentrations in finished waters and distribution system samples

Utility	Residence Time A h	Residence Time B h	ClO <sub>4</sub> <sup>-</sup>			ClO <sub>3</sub> <sup>-</sup>			BrO <sub>3</sub> <sup>-</sup>		
			Finished µg/L	Distribu- tion A µg/L	Distribu- tion B µg/L	Finished mg/L	Distribu- tion A mg/L	Distribu- tion B mg/L	Finished µg/L	Distribu- tion A µg/L	Distribu- tion B µg/L
1A	36	72	3.6	< 0.5	3.1	0.58	0.59	1.2	0.5	0.80	2.9
1B	36	72	< 0.5	3.2	3.1	1.5	1.4	1.3	3.6	3.4	2.8
2	72	216	< 0.5	< 0.5	< 0.5	0.019	0.046	0.045	< 0.5	< 0.5	< 0.5
3	96	168	< 0.5	< 0.5	< 0.5	< 0.003	< 0.003	< 0.003	< 0.5	< 0.5	< 0.5
4	36	72	< 0.5	< 0.5	< 0.5	0.20	< 0.003	< 0.003	1.4	2.1	2.2
5	6	12	2.1	2.2	2.2	0.16	0.14	0.031	1.3	2.6	2.2
6	12	24	< 0.5	< 0.5	< 0.5	0.13	0.13	0.13	0.92	0.80	0.90
7*	100	150	1.2	1.2	0.90	0.79	1.6	0.82	2.6	5.9	3.2

BrO<sub>3</sub><sup>-</sup>—bromate, ClO<sub>3</sub><sup>-</sup>—chlorate, ClO<sub>4</sub><sup>-</sup>—perchlorate, SDS—simulated distribution study

\*SDS was conducted on wastewater samples instead of collecting actual distribution system samples. Sample A had free chlorine residual with no ammonia, whereas sample B had excess ammonia present, and thus free chlorine was converted entirely to chloramines.

tions. The major factors affecting perchlorate formation parallel those previously described for reducing the decomposition of bleach: temperature, ionic strength, concentration, and pH (Gordon & Bunnis, 2000; Gordon et al, 1997; Gordon et al, 1993). The information gathered during this study provided the basis for several hypothetical hypochlorite solution storage scenarios, which led to a number of quantitative and qualitative recommendations.

**Dilute stored hypochlorite solutions on delivery.** The decomposition of hypochlorite and subsequent formation of chlorate and perchlorate are dependent on hypochlorite concentration and ionic strength. Higher ionic strength and hypochlorite concentration will drive the reaction toward greater production of chlorate and perchlorate while also increasing the rate of decomposition of hypochlorite. By diluting a 2-M hypochlorite solution by a factor of 2, the rate of perchlorate formation decreases by a factor of 7 because of the combined effects of concentration and ionic strength. If the same solution

is diluted by a factor of 4, the rate of perchlorate formation decreases by a factor of 36.

**Store hypochlorite solutions at lower temperatures.** Higher temperatures speed up the chemical decomposition of bleach and the subsequent formation of chlorate and perchlorate. Every 5°C reduction in storage temperature will reduce the rate of perchlorate formation by a factor of approximately 2. Thus, it would require close to a 15°C reduction in temperature to obtain the same effect as a simple 1:2 dilution. An illustration of the relative importance of temperature and dilution is provided elsewhere (Stanford et al, 2009).

**Control the pH of stored hypochlorite solutions at pH 11–13, even after dilution.** Storage of concentrated hypochlorite solutions at pH values < 11 is not recommended because of the rapid decomposition of hypochlorite/hypochlorous acid and the consequent formation of chlorate even though this reduces the amount of perchlorate formed. When the pH is > 13, perchlorate formation is enhanced because of the ionic strength effect. Therefore, utilities should con-

**TABLE 7** Control strategies and factors reducing the rate of perchlorate formation in hypochlorite solutions at pH 12

Parameter	Ratio/Amount				
	1:1	1:2	1:4	1:6	1:10
Dilution factor	1:1	1:2	1:4	1:6	1:10
FAC—%	13	6.5	3.3	2.2	1.3
OCI <sup>-</sup> —mol/L	2.0	1.0	0.50	0.33	0.20
ClO <sub>3</sub> <sup>-</sup> —mol/L	0.05	0.025	0.013	0.0083	0.005
Ionic strength—mol/L	6	3	1.5	1	0.6
Cooling—°C	Reduction Factor for Rate of ClO <sub>4</sub> <sup>-</sup> Formation				
0 (no cooling)	1.0	6.9	36	89	270
-1	1.1	7.9	41	100	300
-2	1.3	9.0	47	120	350
-3	1.5	10	54	130	400
-4	1.7	12	62	150	450
-5	1.9	13	71	170	520
-6	2.2	15	81	200	590
-7	2.6	18	93	230	680
-8	2.9	20	110	260	780
-9	3.4	23	120	300	900
-10	3.9	27	140	350	1,000
-11	4.5	31	160	400	1,200
-12	5.1	35	190	460	1,400
-13	5.9	41	210	530	1,600
-14	6.8	47	250	610	1,800
-15	7.9	54	290	700	2,100
-16	9.1	63	330	810	2,400
-17	11	73	380	940	2,800
-18	12	84	440	1,100	3,300
-19	14	98	510	1,300	3,800
-20	17	110	600	1,500	4,400

ClO<sub>3</sub><sup>-</sup>—chlorate, ClO<sub>4</sub><sup>-</sup>—perchlorate, FAC—free available chlorine, OCI<sup>-</sup>—hypochlorite

continue to insist that manufacturer specifications include pH control in the range of 11 to 13.

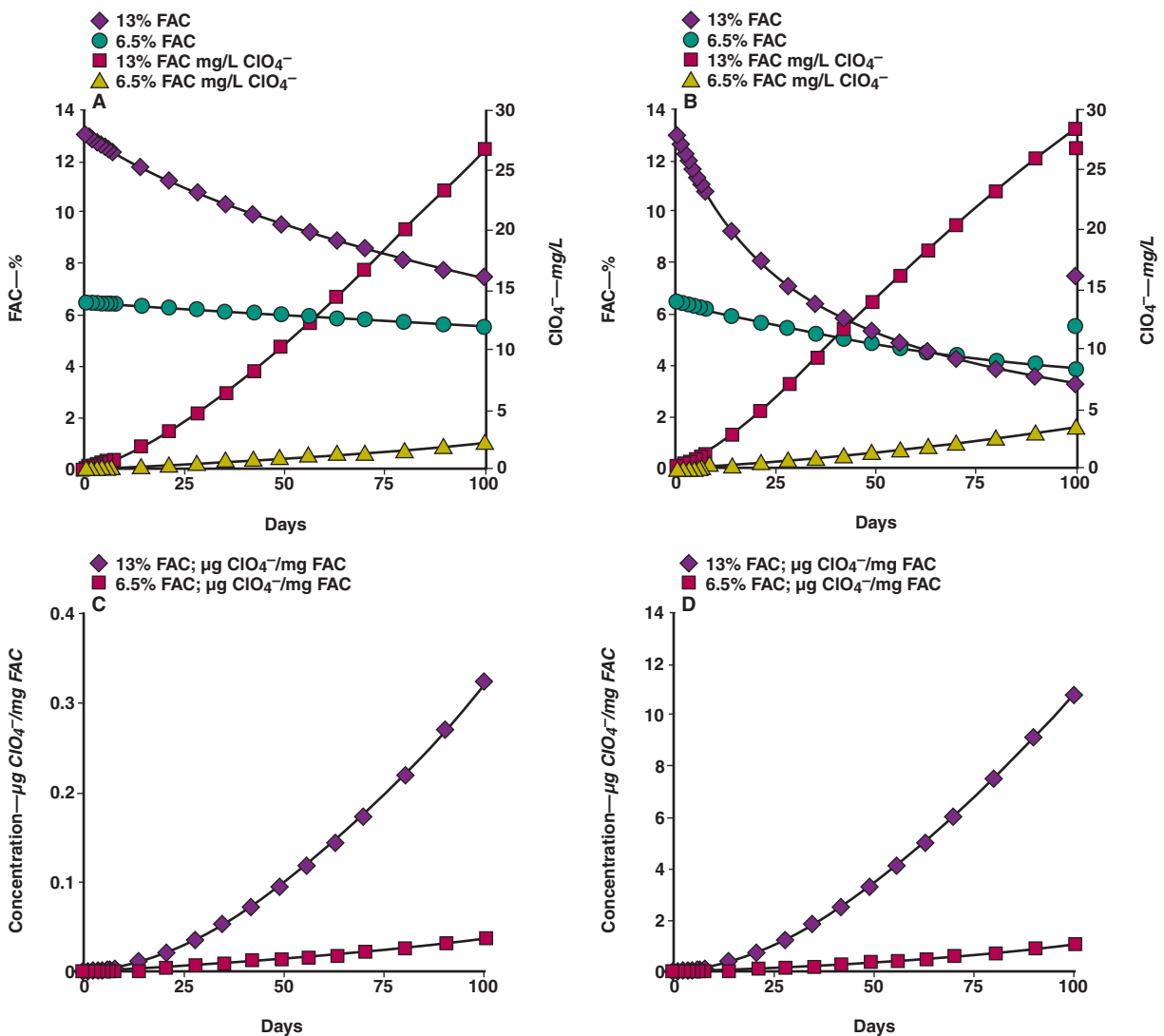
**Use OSG and calcium hypochlorite solutions as soon as possible after manufacture/preparation.** Given the typical pH range of OSG bleach (pH 9–10), such solutions should be used as soon as possible after manufacture and should not be stored for more than one to two days. Because calcium hypochlorite will also form perchlorate after dissolution in water (similar to sodium hypochlorite), only freshly prepared solutions should be used.

**Control the removal of transition metal ions by purchasing filtered hypochlorite solutions and by using low-metal ion concentration feedwater and salt for the OSG systems.** The presence of transition metal ions results in an increased

degradation rate of hypochlorite. Although this degradation is concomitant with reduced perchlorate formation, the FAC concentration is also reduced, forcing a utility to use a higher volume of bleach that in turn results in higher mass loading of contaminants such as perchlorate, chlorate, and bromate.

**Avoid extended storage times, and use fresh hypochlorite solutions when possible.** Over time, bleach will naturally decompose to produce oxygen, chlorate, and perchlorate. Shorter storage times help minimize the formation of these contaminants in the hypochlorite solution. In addition, a fresh bleach solution contains a higher concentration of hypochlorite, thus reducing the amount of solution required to obtain the target chlorine residual. Again, higher

**FIGURE 2** Relationship between hypochlorite concentration and perchlorate formation in bulk hypochlorite



ClO<sub>4</sub><sup>-</sup>—perchlorate, FAC—free available chlorine

Parts A and C represent solutions at 25°C; Parts B and D represent solutions at 35°C.

hypochlorite concentration in fresh bleach will correspond to lower concentrations of contaminants dosed.

**For utilities using OSG bleach, use high-purity salt to minimize the amount of bromide present in the brine.** Bromate formation will occur rapidly in hypochlorite solutions in the presence of bromide. By controlling the amount of bromide in the salt and source water used for onsite generation, bromate formation can be minimized.

## SUMMARY

On the basis of the information provided here, three potential sources of contamination for perchlorate and other oxyhalide ions were identified:

- background contamination from nearby agricultural activity, industrial/military sites, and/or natural deposits;
- formation during the treatment process itself (e.g., bromide conversion to bromate during ozonation); and
- via addition during the use of hypochlorite solutions containing perchlorate, chlorate, and bromate during the water treatment process.

A recent article (Russell et al, 2009) estimated that a federal perchlorate regulation of 4 µg/L would result in an annual cost of approximately \$76 million–\$140 million per year, a cost borne by only 3.4% of public water systems. The numbers generated in that report, however,

assumed that all perchlorate detected in the finished water was also present in the raw water and would need to be removed by one or more treatment technologies. Evidence from the predictive model and measured perchlorate contamination in hypochlorite solutions indicated significant potential for a 4-µg/L regulation to be exceeded. Greiner and colleagues (2008) suggested that five out of 82 bulk sodium hypochlorite solutions tested had enough perchlorate present to result in more than 4 µg/L of additional perchlorate in the finished water (above and beyond any background contamination) based on the maximum use level (MUL) of 10 mg/L FAC (NSF/ANSI, 2005). Although the 10-mg/L FAC MUL may be unrealistic for many utilities, results from the model used in the current study indicated the potential contribution of perchlorate and chlorate from hypochlorite can be significant when proper storage and handling procedures are not followed.

Therefore, careful control of the quality of hypochlorite used in drinking water treatment could be equally, if not more, important for utilities operating near or above any potential federal or state MCLs resulting from source water contamination. Furthermore, utilities should be aware that the quality of hypochlorite (i.e., perchlorate, chlorate, bromate, and metal ion concentrations) being

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delivered to their facility could be affected by the conditions under which the hypochlorite was stored after manufacture and before delivery.

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