HYPOCHLORITE—

AN ASSESSMENT OF FACTORS THAT INFLUENCE THE FORMATION OF PERCHLORATE AND OTHER CONTAMINANTS

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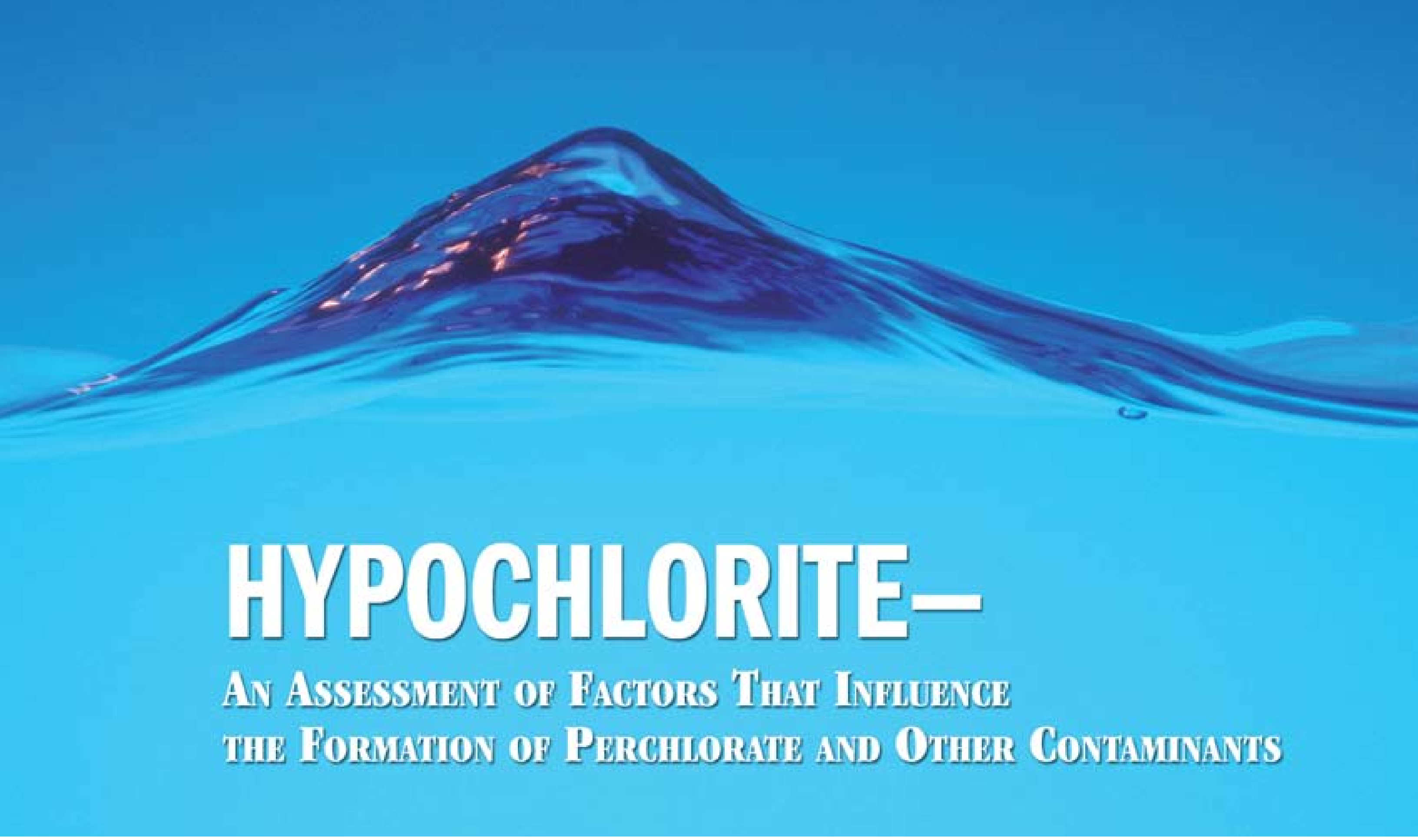

HYPOCHLORITE—

An Assessment of Factors That Influence the Formation of Perchlorate and Other Contaminants

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Jointly Funded by:
American Water Works Association,
Water Industry Technical Action Fund

and

Water Research Foundation

Published by the American Water
Works Association

American Water Works Association

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ABOUT THE FUNDING ORGANIZATIONS

American Water Works Association is the authoritative resource for knowledge, information and advocacy to improve the quality and supply of water in North America and beyond. AWWA is the largest organization of water professionals in the world. AWWA advances public health, safety and welfare by uniting the efforts of the full spectrum of the entire water community. Through our collective strength we become better stewards of water for the greatest good of the people and the environment.

The Water Research Foundation (formerly Awwa Research Foundation) is a member-supported, international, nonprofit organization that sponsors research to enable water utilities, public health agencies, and other professionals to provide safe and affordable drinking water to consumers.

Water Industry Technical Action Fund (WITAF) is administered by AWWA and is funded through member dues. WITAF funds information collection and analysis and other activities in support of sound and effective legislation, regulation, and drinking water policies and programs.

ACKNOWLEDGMENTS

This report was funded by the American Water Works Association, Water Industry Technical Action Fund (WITAF) and the Water Research Foundation. The research team greatly appreciates the diligent efforts of the Southern Nevada Water Authority's (SNWA) Applied R&D Center (ARDC). Specifically, we wish to acknowledge Oscar Quiñones, Brett Vanderford, Doug Mawhinney, and Beck Trenholm for their assistance with the development and troubleshooting of the analytical methods employed throughout this project. In addition, we would like to thank Shanon Fergusson, Elaine Go, Christy Meza, Josephine Chu, and Janie Zeigler for assistance with the sample handling and preparation. We also wish to thank David Rexing, Linda Parker, and Ron Zegers for their support and assistance through the project.

The research team would like to acknowledge Kevin M. Morley of the American Water Works Association and Alice Fulmer of the Water Research Foundation for their relentless leadership and guidance throughout the project. The team also wishes to thank the Project Advisory Committee members for their thoughtful insight and careful review of our project reports:

Gary Lynch, Park Water Company
Robert Cushing, Carollo Engineers
Andrew Eaton, MWH Laboratories
Gary Emmert, University of Memphis
Richard Sakaji, East Bay MUD

The team is especially appreciative of the support of the participating manufacturers and utilities for providing water samples, hypochlorite samples, and information regarding equipment and operations:

MIOX Corporation
Severn Trent Services
Arch Chemical

EXECUTIVE SUMMARY

INTRODUCTION

The use of chlorine for the disinfection of water has arguably saved more human lives than any other public health action in history, with a legacy dating back over 150 years. Since chlorine's first use in 1846 at a hosipital in Vienna, Austria to prevent the spread of "child bed fever", many applications of the chemical have been explored including the first full scale chlorine installation for drinking water disinfection in Chicago in 1908. During the 100 years since its use in drinking water disinfection, chlorination and filtration of drinking water has been estimated to be responsible for a 50% increase in life expectancy. Today, 98% of North American community water treatment systems use chlorine for disinfection[1],[2].

Sodium hypochlorite is a commonly used form of chlorine in drinking water and water reuse applications for its ability to disinfect and maintain a residual level of disinfectant throughout the distribution system. Approximately 1/3 of all drinking water treatment plants (DWTPs) in the United States use bulk hypochlorite for disinfection. Though the majority of liquid hypochlorite use is in the form of bulk hypochlorite delivered from regional manufacturers and/or destributors, around 8% of US DWTPs use on-site hypochlorite generators (OSG). Additionally, due to security concerns associated with chlorine gas use, additional utilities may opt or be required to switch from their current disinfection practices to bulk or OSG hypochlorite.

Hypochlorite is known to contain various impurities, including bromate, chlorate, and chlorite. These contaminants may be present during manufacturing and/or may form during transport and storage. Recently, perchlorate has been detected at elevated levels in hypochlorite solutions. Considering that perchlorate is under consideration for Federal regulation and is currently regulated in California, New Jersey, and Massachusettes[3], it is critical that contribution of perchlorate from hypochlorite solutions be quantified. Bromate is another contaminant of hypochlorite solutions that may impact drinking water quality. Although bromate is regulated by a primary enforcable standard under the Safe Drinking Water Act, the regulated level could be lowered during the 6-year review process.

With these considerations in mind, our research team developed a plan to investigate the factors impacting the formation of perchlorate, bromate, and other contaminants in hypochlorite solutions and to develop a set of guidelines to assist utilities in minimizing the formation of such contaminants. Our project objectives also included the development of a detailed chemical rate law from which predictions could be made reagarding the formation of perchlorate in a given bulk hypochlorite solution.

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[1] White, G.C. The Handbook of Chlorination, 2nd Ed. Von Nostrand Reinhold. New York, 1986.

[2] Leidholdt, R. Chlorine - "Special Agent" for Disinfecting Water. American Water Works Association. Vol. 26. No. 6. pp 40-43. June 2000.

[3] CA MCL = 6 μg/L; NJ MCL = 5 μg/L; MA MCL = 2 μg/L

RESEARCH OBJECTIVES

Based upon conversations with the Water Research Foundation Project Advisory Committee (PAC) and in accordance with specific objectives from within the AWWA RFP, the Project Team identified the following primary research objectives designed to provide the data necessary to determine the mechanisms, and to develop a predictive model, for perchlorate formation in hypochlorite solutions:

1. Determine the analytical method(s) most appropriate for measurement of oxyhalide anions in bulk hypochlorite solutions, OSG solutions, and utility water samples.

2. Determine the impact of co-occurring oxyhalide anions on the formation of perchlorate.

3. Determine the impact of pH, ionic strength, transition metals, and temperature on perchlorate formation.

4. Determine the detailed chemical rate law to predict perchlorate formation in hypochlorite solutions.

Additional secondary objectives were also developed to address concerns regarding operational considerations (i.e., hypochlorite sources, on-site generation, and other factors):

5. Compare perchlorate concentrations in bulk hypochlorite and different OSG systems, including those operated in mixed oxidant mode.

6. Determine the contribution of perchlorate in finished waters originating from hypochlorite addition.

7. Provide recommendations for water utilities to minimize the presence of perchlorate, bromate, chlorate, and chlorite in hypochlorite solutions.

RESEARCH APPROACH

In order to address the objectives outlined above, the Project Team designed a four-tiered approach to completing the project in less than one year. The specific tasks from the research approach were as follows:

Task 1: Comprehensive Literature Review
Task 2: Analysis of Impurities in Hypochlorite
  Subtask 2.1: Perchlorate in Commercially Available Hypochlorite
  Subtask 2.2: Impact of transition metals on perchlorate formation
  Subtask 2.3: Determination of Factors Related to Perchlorate Formation and Minimization in Hypochlorite
Task 3: Treatment/Manufacturing System Impact on Drinking Water
Task 4: Recommendations and Final Report

These tasks are discussed in detail in Chapter 1 of this report. In short, a detailed (though dynamic) experimental matrix was designed to test how variables such as hypochlorite concentration, chlorate concentration, ionic strength, bromide and/or bromate, transition metal ions, pH, and temperature would impact the rate of perchlorate formation. Most of the initial experiments were designed to be run at elevated temperatures (60 ºC) in order to provide rapid feedback regarding the impact of individual variables of perchlorate formation. In this manner, short incubation studies (e.g., 15 to 30 days) were used to design follow-up experiments at lower temperatures (thus longer incubation times of up to 200 days) targeting specific variables likely to have the most effect on perchlorate formation. In total, over 5000 data points were collected. These data were used to validate methods, elucidate the mechanism of perchlorate formation, build a detailed chemical rate law, and to validate the rate law on utility and OSG hypochlorite samples. Seven water treatment utilities, two OSG manufacturers, and one calcium hypochlorite supplier participated in this study, providing samples from five different bulk hypochlorite suppliers, 12 OSG systems, and one solid calcium hypochlorite sample.

REPORT OVERVIEW

This Final Report is divided into 6 Chapters, each of which is designed to carry the reader through the scientific process behind developing the “Predictive Model” and the specific recommendations for minimizing the formation of perchlorate in stored hypochlorite solutions.

- Chapter 1 contains background information on occurrence, regulation, and hypothesized mechanisms of formation for perchlorate and other regulated and non-regulated contaminants of hypochlorite solutions. This Chapter also provides a context for the current study and outlines the research approach in detail.

- Chapter 2 describes the development of analytical methods and subsequent validation of analytical methods used for the identification and quantification of perchlorate, chlorate, and bromate within concentrated hypochlorite solutions. This chapter also provides methodologies applied for other contaminants previously identified in hypochlorite.

- Chapter 3 examines the factors which influence the rate of perchlorate formation in hypochlorite solutions. Key factors identified include, hypochlorite ion concentration, chlorate ion concentration, ionic strength, and temperature.

- Chapter 4 describes the development and validation of the detailed chemical rate law which is applied for predicting the concentration of perchlorate in a given bulk hypochlorite solution.

- Chapter 5 provides the results of a survey of bulk and OSG hypochlorite solutions obtained from various manufactures and facilities for perchlorate, chlorate, and bromate. This chapter also provides the application of the rate law to predict perchlorate concentration in hypochlorite.

- Chapter 6 summarizes the findings of the study and provides recommendations to utilities on how to minimize the formation of perchlorate in bulk hypochlorite.

CONCLUSIONS

Robust analytical techniques were developed to determine the concentration of perchlorate, chlorate, and bromate in concentrated hypochlorite solutions. An LC-MS/MS method was used for all perchlorate and bromate analyses. Both LC-MS/MS and titration methods were successful for chlorate analysis; however, LC-MS/MS was found to be more robust in hypochlorite solutions with free available chlorine (FAC) $< 5\%$, while titration was found to be superior in hypochlorite solutions containing $> 5\%$ FAC.

The formation of perchlorate occurs over time as hypochlorite degrades, while bromate is rapidly formed during hypochlorite manufacturing and does not change significantly over time. The formation of perchlorate is impacted by several key factors including:

- Direct factors such as hypochlorite and chlorate concentration, ionic strength, and pH
- Indirect factors such as metal ions and bromide concentration
- Environmental factors such as temperature

Considering the variables and experimental boundaries described in this report, perchlorate formation was found to be first order in both hypochlorite and chlorate ion concentration and is highly dependent upon ionic strength and temperature. These factors were used to develop a predictive model for perchlorate that was found to agree within 10% of measured values within the boundary conditions established in this study (i.e., pH 11 – 13 and temperatures to 50º C). It should be noted, however, that in order to validate a predictive model at any temperature, a minimum of at least 1.5 half-lives are required. For the perchlorate predictive model at temperatures below 30 ºC, the time required to reach at least 1.5 half-lives would have exceeded the time allotted for the study. Thus, while the model has been validated between 30 ºC and 50 ºC, any information gathered from lower temperatures should be limited to qualitative information only until low-temperature studies can be completed.

Finally, a set of 5 bulk hypochlorite solutions, 12 OSG hypochlorite solutions, and one calcium hypochlorite sample was obtained for contaminant analysis and quantification and was used in a holding study to examine the rate of perchlorate formation in each solution. All samples tested had measurable concentrations of chlorate, perchlorate, and bromate. No specific conclusions could be made regarding differences in contaminant concentrations in bulk, OSG, and calcium hypochlorite solutions. There did appear to be, however, a link between salt quality and bromate concentration in OSG samples, suggesting that a salt of a higher purity (in this study, >99.5% as NaCl) may be useful for reducing the amount of bromate in the hypochlorite product. However, this trend needs to be further investigated before a specific recommendation on salt purity and maximum levels of bromide can be quantified. When the various solutions were aged, good correlation was observed between the rate of perchlorate formation, the concentration of hypochlorite and chlorate ions, and ionic strength. Furthermore, the "Predictive Model" was able to predict perchlorate formation in the bulk hypochlorite samples to within 20% of the measured concentration for up to 28 days at 50 ºC.

RECOMMENDATIONS

Based on the findings presented in this report, several key factors have been identified that impact the formation of perchlorate, bromate, and other contaminants in hypochlorite solutions. The major factors impacting perchlorate formation parallel those previously described for reducing the decomposition of hypochlorite: temperature, ionic strength, concentration, and pH. By using the information gathered during this study and by applying the “Predictive Model” to hypothetical liquid hypochlorite storage scenarios, several quantitative and qualitative recommendations can be made:

a. Dilute stored hypochlorite solutions upon delivery: The decomposition of hypochlorite and subsequent formation of chlorate and perchlorate is dependent upon hypochlorite concentration and ionic strength. Higher ionic strength and hypochlorite concentration will drive the reaction towards a greater production of chlorate and perchlorate while also increasing the rate of decomposition of hypochlorite. By diluting a 2 molar hypochlorite solution by a factor of 2, the rate of perchlorate formation decreases by a factor of 7 due to the combination of concentration and ionic strength effects. A four-fold dilution of a hypochlorite solution will decrease the rate of formation by 36. A ten-fold dilution of a hypochlorite solution will decrease the rate of perchlorate formation by a factor of 270.

b. Store the hypochlorite solutions at lower temperatures: Higher temperatures speed up the chemical decomposition of hypochlorite and the subsequent formation of chlorate and perchlorate. Every 5 ºC reduction in storage temperature will reduce the rate of perchlorate formation by a factor of approximately 2.

c. Control the pH of stored hypochlorite solutions at pH 11 – 13, even after dilution: Storage of concentrated hypochlorite solutions at pH values lower than 11 is not recommended due to rapid decomposition of hypochlorite ion/hypochlorous acid and the consequent formation of chlorate even though this reduces the amount of perchlorate formed. When the pH is higher than 13, perchlorate formation is enhanced due to the ionic strength effect. As such, utilities should continue to insist that manufacturer specifications include pH control in the range of 11 to 13. Given the typical pH range of OSG hypochlorite (pH 9 to 10), such solutions should be used as soon as possible after manufacture and should not be stored for more than 1-2 days.

d. Control the removal of transition metal ions by purchasing filtered hypochlorite solutions and by using low-metal ion concentration feed water for the OSG systems: The presence of transition metal ions results in an increased degradation rate of hypochlorite. While this degradation is concomitant with reduced perchlorate formation, the FAC concentration is also reduced, forcing a utility to use a higher volume of a hypochlorite solution which results in higher mass loading of contaminants such as perchlorate, chlorate, and bromate.

e. Use fresh hypochlorite solutions when possible: Over time, hypochlorite will naturally decompose to produce oxygen, chlorate, and perchlorate. Less storage time will minimize the formation of these contaminants in the hypochlorite solution. A fresh hypochlorite solution will also contain a higher concentration of hypochlorite, thereby reducing the amount of solution required to obtain the target chlorine residual. Again, higher hypochlorite concentration in a fresh hypochlorite solution will correspond to lower concentrations of contaminants dosed.

f. <u>For utilities using OSG hypochlorite, use low-bromide salt to minimize the amount of bromide present in the brine:</u> 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 on-site generation, bromate formation can be minimized.

If a utility were to combine dilution with temperature reduction, a significant impact on hypochlorite decomposition and perchlorate formation would be observed. For example, as described in Chapter 4 if a utility were to dilute a 13% bulk hypochlorite solution by a factor of 2 and also reduce the storage temperature by 10 ºC, the result would be 16 times less hypochlorite decomposition and 27 times less perchlorate formation than if the hypochlorite were stored at ambient temperatures undiluted. Chapter 4, Table 4.8 details the combined effects of temperature and dilution for various storage scenarios.

Another interpretation of the results of this study is through seasonal trends. If, for example, a utility experienced average bulk hypochlorite storage temperatures of 10 ºC in the winter and 35 ºC in the summer, the rate of perchlorate formation for 13% hypochlorite would be nearly 18 times faster in the summer. In other words, in winter that utility could expect the concentration of perchlorate concentration to increase by a factor of 10 in approximately 3 months; in summer it would increase by a factor of 10 in only 5 days. Had the hypochlorite solution been diluted by a factor of 2, the same increase in perchlorate concentration would take one month in summer and 20 months (assuming, for example, an average temperature of 10 ºC) in winter. Therefore, in order to minimize the amount of perchlorate formation in hypochlorite solutions, a combination of dilution and temperature control is recommended.

QUESTIONS FOR UTILITIES TO ASK BULK HYPOCHLORITE AND OSG SUPPLIERS

Based upon the findings of this study, a series of questions have been developed to assist utilities in developing questions that they may wish to ask hypochlorite manufacturers. While these questions are not meant to preclude or give advantage to any manufacturer or process, they are meant to help utilities obtain the information that might be of use to them in deciding how to store and handle the hypochlorite solutions that they purchase or produce on-site.

Questions for Bulk Hypochlorite Manufacturers

1. What is the temperature of the hypochlorite solution directly after manufacture?
2. At what temperature is the hypochlorite solution stored between manufacture and delivery?
3. Is there a cooling system in place to lower the temperature of the final product at the manufacturing facility?
4. Do the delivery vehicles have any cooling systems in place to hold the hypochlorite solution at a constant temperature during transport?

5. What is the concentration of hypochlorite at the time of delivery? If unknown, can the manufacturer provide the concentration of hypochlorite at the time of manufacture together with the age and storage conditions of the hypochlorite solution?
6. Do they know the concentration of bromate, chlorate, and perchlorate in the hypochlorite solutions? If so, will they provide that information?
7. What is the ionic strength of the hypochlorite solution at the time of manufacture? Does the manufacturer offer any means to reduce the ionic strength?
8. What quality of salt is used during the manufacturing process? How much bromide is present in the salt?
9. What is the concentration of transition metals (nickel, manganese, iron, cobalt, and copper) are present in the hypochlorite solution? Do these values fall within the NSF specifications for metals?
10. Does the manufacturer offer filtered hypochlorite solutions?

Questions for On-Site Generator Manufacturers

1. Does the OSG manufacturer have any specific recommendations about quality or source of salt?
2. Do they know of any specific impurities in salt that can adversely impact OSG operation or formation of contaminants in the hypochlorite solution product?
3. Does the OSG manufacturer know the range of perchlorate concentration in the final OSG solution for their various models?

Questions for Salt Suppliers

1. What is the source of the salt being delivered?
2. What is the purity (as NaCl) of the salt delivered?
3. What is the concentration of bromide in the salt?
4. What concentration of transition metals (nickel, manganese, iron, cobalt, and copper) is present in the salt?

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CHAPTER 1
INTRODUCTION

BACKGROUND

Sodium hypochlorite (a.k.a. “bleach”) is commonly used in drinking water and water reuse applications for its ability to disinfect and maintain a residual level of disinfectant throughout the distribution system. Multiple regulated contaminants exist in hypochlorite solutions including bromate, hypochlorite itself, and chlorite (Gordon, Pacey, and Bubnis 1993; Weinberg, Delcomyn, and Unnam 2003; Chlorine_Institute 2004; Asami, Kosaka, and Kunikane 2009) in addition to other unregulated oxyhalides such as chlorate and perchlorate. The presence of such oxyhalides in drinking water has become a major issue of concern for the water industry. Recently, perchlorate has been identified as a contaminant of concern in hypochlorite solutions and has received a large amount of attention as it is an endocrine disrupting compound which can impact the thyroid system of humans (Lamm, et al. 1999; Urbansky 2000a; York, et al. 2001; Greer, et al. 2002b).

Perchlorate is both a natural and anthropogenic compound: perchlorate has been found to occur naturally in the US and Chile (Dafert 1908; Jackson, et al. 2005) and has also been manufactured and used as an oxidizer for solid fuel engines, fireworks, and road flares (Davis 1940; Hampel and Leppla 1947; Simchen and Inbar-Rozem 1968; Urbansky 2000a). Chilean nitrate, a source of naturally occurring perchlorate, has been used for many years in agricultural applications in the United States. Where large quantities of perchlorate have been produced or used, perchlorate contamination of soil and water has been detected, with concentrations approaching 3,000 mg/L at former industrial sites in the Las Vegas valley. Modern analytical instrumentation has facilitated the detection of perchlorate in drinking water, dairy products, human breast milk, plants, fish, and cattle (Urbansky, et al. 2000b; Kirk, et al. 2003; Sundberg, et al. 2003; Cheng, et al. 2004; Dodds, et al. 2004; Yu, et al. 2004; Kirk, et al. 2005; Sanchez, et al. 2005; Snyder, Vanderford, and Rexing 2005). Perchlorate has also been detected in kelp (Orris, et al. 2003; Martinelango, Tian, and Dasgupta 2006), which is often used as a source of iodine in dietary supplements (Turrentine 1924; Teas, et al. 2004).

In 2002 the US EPA published a reference dose (RfD) for perchlorate of 0.00003 mg/kg/day, which would suggest drinking water equivalent level (DWEL) of approximately 1 µg/L (USEPA 2002; Tiemann 2008). In 2005 the National Academy of Sciences and the US EPA updated the RfD to 0.0007 mg/kg/day 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-day for inhibition of iodide uptake determined in a human clinical trial (Greer, et al. 2002a). Despite coming forward with an updated RfD, it is unclear whether or not perchlorate will be regulated nationally at this time (Swackhamer and Rose 2008; Tiemann 2008). However, the state of Massachusetts has set a DWEL and maximum contaminant level (MCL) of 2.0 µg/L for perchlorate (MA_DEP 2006), and California has established a MCL of 6.0 µg/L (CA_DPH 2007). Based on data from this study and data published elsewhere, perchlorate appears to be a ubiquitous contaminant of hypochlorite solutions and the perchlorate concentration in hypochlorite increases significantly over time (Greiner, et al. 2008; Asami, Kosaka, and Kunikane 2009).

Chlorate is a contaminant produced during on-site generation of hypochlorite solutions and the subsequent decomposition of hypochlorite. Chlorate is also a by-product of treatment of drinking water with chlorine dioxide (USEPA 1999; Snyder, Vanderford, and Rexing 2005).

Toxicological reports have shown that chlorate has similar toxic modes of action as the unregulated contaminant perchlorate. The state of California has set an action level for chlorate in drinking water of 800 µg/l (Drinking Water Notification Levels 2004); an action level as low as 200 µg/l has been suggested (Howd 2002). The World Health Organization has set a guideline MCL of 700 µg/L (WHO 2008). Chlorate exhibits the same mechanism of action on the thyroid as perchlorate, albeit with lower potency (USEPA 1999; Pleus 2000; Hooth, et al. 2001). Chlorate has been shown to occur in bottled water and in municipal drinking water at levels up to 270 µg/l (Snyder, Vanderford, and Rexing 2005). Chlorate occurs in drinking waters at levels much greater than those reported for perchlorate, thus, even though it is less potent than perchlorate, its toxicological relevance and occurrence is significant in holistic exposure assessments of goitrogens.

Bromate is another possible contaminant of hypochlorite solutions (Asami, Kosaka, and Kunikane 2009) and results from the oxidation of bromide to hypobromite to bromate via a mechanism analogous to that of chlorate. Bromate may also form during ozonation when bromide is oxidized by dissolved ozone in water. Bromate has been reported to be a carcinogen in mammalian studies (Kurokawa, et al. 1986; DeAngelo, et al. 1998) and is suspected to have a role in oxidative DNA damage in target organs (Ballmaier and Epe 1995; Chipman, et al. 1998). Bromate is currently regulated by the US EPA in drinking water at an MCL of 10 µg/L and is specified in hypochlorite solutions not to exceed 0.5 µg BrO_3^-/mg FAC (NSF/ANSI 2005).

Given the high likelihood of finding perchlorate (in addition to chlorate, chlorite, and bromate) in hypochlorite solutions and the widespread use of hypochlorite, the potential contribution of perchlorate from hypochlorite is a critical issue to understand. To exacerbate this situation, some utilities that once used gaseous chlorine are moving to the use of hypochlorite solutions due to homeland security concerns related to chlorine gas. The potential health impacts of perchlorate have been widely debated in the public media, and it is likely that additional states will begin to regulate perchlorate in drinking water independent of any US EPA regulatory determinations. Thus, it is vital that the water industry has the predictive tools available to understand how much perchlorate is added to drinking waters from hypochlorite and what measures can be taken to minimize the formation of perchlorate in hypochlorite solutions.

BULK HYPOCHLORITE MANUFACTURING AND USE IN DRINKING WATER TREATMENT

Of the drinking water treatment plants (DWTPs) in the United States, approximately 31% use bulk hypochlorite solutions for disinfection and 63% use chlorine gas (Routt 2008; Routt, et al. 2008). Additionally, 8% of US DWTPs use on-site generators (OSGs) for electrolytical sodium hypochlorite production from brine solutions and 8% use calcium hypochlorite (note that utilities may use more than one process for disinfection, thus numbers do not total 100%). There are multiple suppliers with multiple configurations of OSG systems including MIOX Corporation, Severn Trent (ClorTec), US Filter, and others and there are equally as many suppliers of bulk hypochlorite. It is generally manufactured by passing chlorine gas through sodium hydroxide. Sodium hydroxide is frequently produced by means of the chlor-alkali process, in which an aqueous sodium chloride solution is electrolyzed to produce chlorine gas and sodium hydroxide (Gordon, et al. 1993; Gordon, Pacey, and Bubnis 1993; Gordon, Adam, and Bubnis 1994; Gordon, Adam, and Bubnis 1995). In this context it should be noted that there are only five remaining chlor-alkali mercury cell systems still manufacturing sodium hydroxide in the United States (Oceana 2007). However, unlike the myriad configurations for OSGs, the majority of bulk hypochlorite suppliers utilize either a Powell Fabrication Generator and/or batch process. OSGs, on the other hand, vary much more widely in terms of the chemical composition of electrode materials, energy inputs, configuration, feed water quality, and salt quality. Different OSGs also have inter- and intra- brand differences. Thus, bulk hypochlorite tends to be more uniform in quality and production methods than OSG hypochlorite. Another major difference between bulk hypochlorite and OSG hypochlorite is in the concentration of hypochlorite produced: bulk hypochlorite is typically delivered as a 13% hypochlorite solution while OSG hypochlorite ranges from less than 1 % free available chlorine (FAC) to 4 % FAC.

Other sources of chlorine are available to DWTPs including calcium hypochlorite, chlorine gas, and chlorine dioxide. Calcium hypochlorite (in solid form) should, theoreticaly, have a longer shelf life than liquid hypochlorite as the decomposition of hypochlorite requires an aqueous solution. However, calcium hypochlorite is typically used only as an emergency back-up process or in small-scale operations due to increased maintenance and water hardness issues associated with its use. Chlorine dioxide is another alternative to hypochlorite which has been shown to help reduce the formation of trihalomethanes (THMs) though may be associated with increased chlorite concentration in finished water (McGuire, Lieu, and Pearthree 1999). Chlorine gas is another popular option for disinfection of drinking water and is currently used by approximately 60% of DWTPs in the United States. Because of the low concentration of dissolved chlorine gas, appreciable quantitites of perchlorate, chlorate, and chlorite are not expected to form. There are, however safety and security issues associated with handling, storage, and application. Thus, many utilities currently using chlorine gas are considering the implications of switching to the use of hypochlorite, both from a cost perspective and from a contaminant perspective.

REGULATED AND UNREGULATED CONTAMINANTS OF HYPOCHLORITE SOLUTIONS

With the differences in concentration and production processes associated with hypochlorite solutions is a concomitant difference associated with the presence and formation of contaminants. For example, small quantities of transition metal ions such as nickel(II), copper(II), manganese(II), cobalt(II) and iron(III) may be present in unfiltered finished hypochlorite solutions. Small concentrations of these ions (on the order of 1 to 2 mg/L) have been shown increase the rate of decomposition of hypochlorite by as much as 1 to 2 orders of magnitude (Gordon, Adam, and Bubnis 1994; Gordon, Adam, and Bubnis 1995) and have been hypothesized to play a catalytic role in the formation of perchlorate. Interestingly, perchlorate is also produced through an electrolytic process where chlorate may be oxidized to perchlorate (Urbansky 2000a), a distinct possibility in electrolytic hypochlorite manufacturing processes. Snyder, Vandeford, and Rexing (2005) reported that perchlorate was measurable in hypochlorite originating from an on-site hypochlorite generator. The Japanese National Institute of Public Health (JNIPH) reported that as a commercially available hypochlorite solution decayed, perchlorate concentration increased (Asami, Kosaka, and Kunikane 2007). Likewise, the JNIPH also noted that perchlorate concentration was relatively low in hypochlorite solutions produced by on-site generation. Generally speaking, however, there is little additional quantitative data regarding the concentration of perchlorate in hypochlorite solutions. To the best of our knowledge, neither have any reports been published that provide hard evidence regarding the kinetics of perchlorate formation, nor have any reports discussed ways to minimize its formation in hypochlorite.

Chlorate and chlorite, on the other hand, are well known degradation products and contaminants of hypochlorite solutions and are present in all hypochlorite (Gordon, Adam, and Bubnis 1995). Chlorate is currently unregulated at the Federal level (though the World Health Organization has set a guideline MCL of 700 μg/L) while chlorite is Federally regulated in drinking water by the US EPA with an MCL of 0.8 mg/L. Hypochlorite ion is unstable and undergoes two independent modes of self-decomposition. In one mode, oxygen and chloride are formed and in the other mode, chlorate and chloride are formed:

$$2\mathrm{OCl}^- \rightarrow \mathrm{O}_2 + 2\mathrm{Cl}^- \qquad \textbf{(1.1)}$$

$$3\mathrm{OCl}^- \rightarrow \mathrm{ClO}_3^- + 2\mathrm{Cl}^- \qquad \textbf{(1.2)}$$

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

$$\frac{d[\mathrm{OCl}^-]}{3dt} = \mathrm{k}_{\mathrm{obs}}[\mathrm{OCl}^-]^2 \qquad \textbf{(1.3)}$$

Chlorite is rapidly formed as a steady state species (not shown) in Equation 2 that serves as an intermediate between hypochlorite and chlorate. The typical half-life for decomposing 12 to 13 weight % hypochlorite (OCl^-) at room temperature (25$^{\mathrm{o}}$C) is on the order of 150 to 160 days (Gordon, et al. 1997). Changes in temperature also markedly affect the rate of decomposition of hypochlorite solutions. For example, an increase of 10 $^{\circ}$C will increase the rate of decomposition by a factor 3.5 to 4.0. As previously mentioned, 1 to 2 mg/L of transition metal ions increase the rate of decomposition of hypochlorite by as much as 1 to 2 orders of magnitude (Gordon, Adam, and Bubnis 1994; Gordon, Adam, and Bubnis 1995), thereby impacting the formation of chlorate as well. With different types of contaminants present in hypochlorite and the specific storage conditions (e.g., temperature, pH) one reaction pathway may be favored over another, thereby potentially creating more chlorate and perchlorate in the process. Furthermore, the formation of perchlorate has been hypothesized elsewhere to be a direct result of reactions between hypochlorite and chlorate as the solution decomposes (Asami, Kosaka, and Kunikane 2007; Asami, Kosaka, and Kunikane 2009).

Bromate is another contaminant typically associated with ozonation of bromide-containing waters, though it can also be found in hypochlorite solutions likely from a reaction of bromide with hypochlorite analagous to the formation of chlorate (Asami, Kosaka, and Kunikane 2009). Better refining of salts and/or source water for hypochlorite generation may help remove or reduce the introduction of bromide into the process and final product thereby greatly reducing the amount of bromate formed. It is currently unknown what impacts the presence of bromite and/or bromate will have on the decomposition of hypochlorite and the formation of chlorate and perchlorate in those solutions.

ANALYTICAL METHODS

Prior to 2005, the most commonly applied instrumental analytical technique for measurement of oxyhalide anions was ion-chromatography with conductivity detection (IC-CD). Of those, US EPA methods 300.1 and 314 using IC-CD were the most commonly used methods for the analysis of bromate and perchlorate with reporting limits of 5 µg/L for bromate and 4 µg/L for perchlorate. While IC-CD was successfully applied to many drinking waters, obtaining reliable results in more concentrated samples with higher conductivity was challenging. Furthermore, these methods suffered from potential matrix interferences when applied to environmental mixtures (Urbansky 2000b; Anderson and Wu 2002; Liu, Mou, and Heberling 2002). For example, p-chlorobenzene sulfonate, a compound often found in paints and chemical manufacturing, co-elutes with perchlorate when analyzed by US EPA method 314 (IC-CD method) and interferes with quantitation. (Johnson, Grimshaw, and Richman 2003). Some techniques used to overcome these challenges included pre-concentration steps, such as solid-phase extraction (SPE) and ion-exchange columns, and post-column reactions (derivatizations) followed by UV measurement (IC-PCR) (Inoue, et al. 1997; Bichsel and Von Gunten 1999; Nowack and von Gunten 1999; Salhi and Von Gunten 1999; Magnuson, Urbansky, and Kelty 2000; Urbansky, et al. 2000a; Wagner, et al. 2002; Kirk, et al. 2004). A more sensitive method for bromate analysis was US EPA method 317 using IC-PCR with a reporting limit around 1 µg/L though it was not applicable to other oxyhalides except chlorite. Other approved methods for bromate analysis include US EPA methods 326 and 321.8.

Other non-instrumental approaches to measuring perchlorate and other oxyhalides in aqueous media have included colorimetric determination (Bodenheimer 1955), spectrophotometric determination (Fritz 1964; Prince 1964; Cheng 1967; Weiss 1972), atomic absorption (Collinson 1968), UV absorbance (Soto, et al. 2008), amperometric titration (Clesceri, Greenberg, and Eaton 1998), and direct titration (Adam and Gordon 1995). The direct titration method relies upon the reduction of hypochlorite with sulfite, followed by sequential reduction of chlorite and chlorate ions with iodide, resulting in the stoichiometric production of iodine ions. This allows determination of these ions by iodometry, where the proportional amount of iodine for the reactions with the analyte is titrated with a standardized thiosulfate solution. One advantage of potentiometric methods over IC-CD methods is the selectivity towards specific oxyhalide anions and the ability of the method to be applied to concentrated hypochlorite solutions.

Mass spectrometry is another technique that has been applied for the detection of oxyhalide anions, most commonly in conjunction with ion-chromatography (IC-MS) or liquid chromatography (LC-MS) (Salov, et al. 1992; Urbansky, et al. 1999; Handy, et al. 2000; Koester, Beller, and Halden 2000; Magnuson, Urbansky, and Kelty 2000; Roehl, et al. 2002; Winkler, Minteer, and Willey 2004). The use of mass spectrometry for the detection of ionic compounds increased dramatically with the development of commercially available IC-MS systems (Zwiener and Frimmel 2004). In order to obtain accurate quantitation using IC-MS or LC-MS techniques, many investigators used clean-up techniques to minimize interfering compounds (Urbansky 2000b) or standard addition to compensate for suppression/enhancement artifacts (Batista, McGarvey, and Vieira 2000; Koester, Beller, and Halden 2000; Magnuson, Urbansky, and Kelty 2000). The use of tandem mass spectrometry (MS/MS) and isotope dilution can also be used to add selectivity and accuracy to oxyhalide quantitation methods. US EPA method 331.0 uses LC-MS/MS while US EPA method 332.0 uses IC-MS/MS to detect perchlorate in water, but neither was developed to identify and quantify other oxyhalides at the same time (USEPA 2005a; USEPA 2005b). A paper by Snyder et al. (2005) demonstrates that LC-MS/MS can be used to measure perchlorate together with bromate, chlorate, and iodate in OSG hypochlorite solutions (Snyder, Vanderford, and Rexing 2005). Furthermore, this paper demonstrates that, under the conditions employed, LC-MS/MS is capable of detecting perchlorate in commercial detergents – which is a significantly more challenging matrix than drinking water. This same method was later adapted to measure perchlorate in aqueous extracts of vitamins and food supplements (Snyder, et al. 2006).

RESEARCH QUESTIONS AND APPROACH

Based on the above considerations, conversations with the Water Research Foundation Project Advisory Committee, and specific objectives from within the AWWA RFP, the Project Team at SNWA identified the following additional research questions designed ultimately to assist the Project Team in determining a mechanism and predictive model for perchlorate formation in hypochlorite solutions:

1. What analytical method(s) is/are the most appropriate for measurement of oxyhalide anions in bulk hypochlorite solutions, OSG solutions, and utility water samples?

2. What hypochlorite quenching agent could be employed for use in sample preservation that would not interfere with the analysis of chlorite, chlorate, perchlorate, bromate, and metals?

3. What effects do the concentration of oxyhalide anions in addition to bromide have on the formation of perchlorate and bromate?

4. What effects do pH, ionic strength, and temperature have on perchlorate formation?

5. Do transition metals catalyze the formation of perchlorate in hypochlorite solutions?

6. Can a detailed chemical rate law be developed to predict (within 30 days of manufacture) perchlorate formation in sodium hypochlorite solutions to within +/- 10% of actual values?

7. What rate law best describes the formation of perchlorate in hypochlorite solutions and what is the reaction order with respect to hypochlorite, chlorate, and any other contributing anions?

8. Is a simple mechanism available to describe the formation of perchlorate from hypochlorite and chlorate?

Additional questions were also asked regarding operational considerations, hypochlorite sources, on-site generation, and other factors for DWTPs:

9. Is there a significant difference in the perchlorate concentration measured in fresh bulk hypochlorite and different OSG systems including those operated in mixed oxidant mode?

10. To what extend could the use of OSG or bulk hypochlorite adversely affect perchlorate concentration in finished drinking water considering the NSF 60 maximum use level (MUL) of 10 mg/L (NSF/ANSI 2005)?

11. What recommendations can be made to drinking water utilities to minimize the presence of perchlorate, bromate, chlorate, and chlorite in hypochlorite solutions used for drinking water treatment?

Research Approach

In order to answer the questions outlined above the Project Team designed a four-tiered approach to completing the project within the allowed 11-month period. The overarching objective of this study was to evaluate the magnitude of perchlorate contamination in chemically and electrochemically manufactured hypochlorite solutions, to determine the impact on finished drinking water contamination, to provide utilities with a way to predict perchlorate concentration in hypochlorite solutions, and to devise techniques to minimize the formation of perchlorate in hypochlorite solutions. The specific task outlined in the Project Proposal included the following:

Task 1: Comprehensive Literature Review
Task 2: Analysis of Impurities in Hypochlorite
    Subtask 2.1: Perchlorate in Commercially Available Hypochlorite
    Subtask 2.2: Impact of transition metals on perchlorate formation
    Subtask 2.3: Determination of Factors Related to Perchlorate Formation and Minimization in Hypochlorite
Task 3: Treatment/Manufacturing System Impact on Drinking Water
Task 4: Recommendations and Final Report

Task 1: Literature Review

The initial phase of this study involved a review of available literature regarding hypochlorite and perchlorate chemistry, analytical methodologies, and current occurrence data. A significant portion of the literature review for this study was completed prior to the Project Kickoff (May 9, 2008) and was used to identify experiments necessary in the early stages of the project. The literature review was an ongoing process during the course of the Project whereby additional papers found in the literature were used to further refine the experimental matrix and guide the completion of this Final Report.

Task 2: Impurities Analysis

This Project Team had previously developed robust analytical methodologies that were able to identify and quantify accurately and precisely perchlorate in hypochlorite solutions at sub-µg/L concentrations (Snyder, Vanderford, and Rexing 2005). The methodology utilized LC-MS/MS technology with an isotopically labeled (^{18}oxygen) perchlorate as an internal standard.

The methods developed by SNWA researchers allowed for the simultaneous, direct LC-MS/MS measurement of perchlorate, chlorate, and bromate in hypochlorite solutions and drinking water samples. However, for the purposes of understanding the factors which impact the formation of perchlorate, the decision was made to devote several weeks at the beginning of the project towards determining whether the LC-MS/MS method or the titrimetric method would provide more accurate and precise quantitation. Once the method of choice was clearly identified for use in concentrated hypochlorite solutions, then the Project Team could focus on the mechanistic studies.

Subtask 2.1: Perchlorate in Commercially Available Hypochlorite Prior to collecting, shipping, and analyzing any hypochlorite samples, the effect that preservatives / quenching agents had on the presence, formation, or decay of any species of consideration (oxyhalides, chloride, bromide, and metals) had to be quantified. The commonly used quenching agent used to treat residual hypochlorite prior to mass spectrometric measurement of perchlorate ion had been hydrogen peroxide (Urbansky 2000c). However, it was not clear that the use of peroxide would be the best quenching agent for this study. Thus, a total of seven quenching agents (hydrogen peroxide, ascorbic acid, glycine, malonic acid, oxalic acid, sodium thiosulfate, and sodium sulfite) were tested for the removal (quenching) of hypochlorite and the impact on other contaminants of concern. The criteria for the best quenching agent included ease of handling, safety, rate of reaction with hypochlorite, absence of adventitious impurities in the quenching agent, and stability.

After selection of a quenching agent and analytical method, a series of commercially available hypochlorite solutions and OSG solutions were tested for perchlorate, bromate, bromide, and transition metals. Additionally, seven utilities were asked to provide hypochlorite and treated water samples for oxyhalide and metals analysis. A commercially available 13% sodium hypochlorite solution was chosen as the baseline for kinetics studies and was aged at different dilutions with varying concentrations of chlorate, chlorite, chloride, bromide, bromate, ionic strength, pH, and transition metals. Temperatures were varied for batch studies from 30 ºC to 75 ºC. In total, over 3,800 individual data points were collected for elucidation of the mechanism described in this Report. Similarly, over 1,500 individual data points were collected from the OSG and Utility hypochlorite samples, aged at 50 ºC, and used to validate the model predictions. The study also included over 120 individual data points for the surveyed raw, finished, and distribution waters.

*Subtask 2.2****:*** *Impact of transition metals on perchlorate formation* In previous studies of the decomposition of hypochlorite to form chlorate, transition metal ions have been shown to have very important catalytic properties (Gordon, et al. 1993; Gordon, Adam, and Bubnis 1994; Gordon, Adam, and Bubnis 1995). Nickel ion, for example at the 1 – 2 mg/L level, was shown to enhance the rate of hypochlorite decomposition by more than a factor of ten. Other transition metal ions such as cobalt(II) and copper(II) may also impact the rate of hypochlorite loss though manganese(II) iron(II) seem to have little to no effect. These transitions metal ions represent those that are most likely to be present in commercial hypochlorite and potentially impact perchlorate formation. Thus, a series of experiments were also carried out as part of the concentration matrix (from Subtask 2.1) at 0.2, 2, and 20 mg/L of nickel(II), manganese(II), iron(II), cobalt(II), and copper(II). In addition, noble metals ions (Ag, Au, Ir, Pd, Pt) at 0.2 mg/L were also included as part of this task.

Subtask 2.3: Determination of Factors Related to Perchlorate Formation and Minimization in Hypochlorite This task was designed determine the factors in hypochlorite manufacturing and handling that would have the greatest impact on the formation of perchlorate in hypochlorite solutions. The Project Team used experiments from this task to assist in developing clear strategies for minimizing the formation of perchlorate in both hypochlorite manufacturing and on subsequent storage/handling. Temperature, hypochlorite concentration, and presence of metal ions were all investigated as each plays an important role in hypochlorite degradation (Gordon, Adam, and Bubnis 1994). Experiments under this task included aging hypochlorite solutions at various temperatures, pH, bromide, and metal ion concentrations, and collecting samples for perchlorate and bromate analysis as a function of time. The loss of hypochlorite and the formation of perchlorate were monitored during this portion of the study.

Task 3: Systems Impact (Influence of Hypochlorite in Perchlorate Contamination of Drinking Water)

This task was designed to provide a means for determining the degree of perchlorate contamination in finished drinking water attributable to hypochlorite. Specific experiments were designed to create a detailed chemical rate law ("Predictive Model") in order to understand the kinetic processes influencing the rate of perchlorate build-up in freshly prepared and aging hypochlorite solutions as a function of hypochlorite, chlorate, and chloride concentrations, pH, storage temperature, ionic strength, and metal ion concentration. The results of these experiments were used to develop a preliminary mathematical model from the detailed chemical rate law describing the role of each of the experimental variables in the formation of perchlorate along with the appropriate uncertainties (similar to the Adam and Gordon chlorate ion "Bleach 2001" model). The objective was to develop a "Predictive Model" that would take into account the sources of perchlorate (*e.g.,* the sodium hydroxide, the manufacturing of hypochlorite, and the continued decomposition of hypochlorite) as a function of hypochlorite, chlorate, chloride, and storage temperature and be used to assist in making specific, quantitative recommendations to utilities to minimize perchlorate formation. Additionally, several calculations were used to determine minimum, median, and maximum concentrations of perchlorate that could be expected at a typical water treatment facility based upon hypochlorite age, storage conditions (temperature and dilution), and dose.

In this phase of the project, several commercially available on-site hypochlorite generators and feed systems were also evaluated. The Project Team collected and analyzed brine streams prior to electrolytic conversion for perchlorate, chloride, metals, and other water quality constituents that may impact hypochlorite degradation and perchlorate formation. Additionally, water from the participating utilities (that also supplied hypochlorite solutions for perchlorate analysis) was used to conduct simulated distribution system (SDS) tests to determine if perchlorate would be formed in the distribution system. Actual samples from the distribution systems of participating utilities were also analyzed for perchlorate. Distribution system samples included locations having maximum chlorine contact time.

Task 4: Recommendations and Final Report

The conclusions from this research study will hopefully provide the water industry with the information needed to minimize perchlorate formation in hypochlorite solutions. Dissemination of the findings from this study include presentations and industry conferences, publication in peer-reviewed journals, and this Final Report. A complete list of recommendations for utilities using bulk hypochlorite or OSG hypochlorite can be found in the Executive Summary and in Chapter 6.

REFERENCES

Adam, Luke C. and Gilbert Gordon. 1995. Direct and Sequential Potentiometric Determination of Hypochlorite, Chlorite and Chlorate Ions When Hypochlorite Ion Is Present in Large Excess. *Analytical Chemistry*, 67 (3):535-540.

Anderson, T. A. and T. H. Wu. 2002. Extraction, Cleanup, and Analysis of the Perchlorate Anion in Tissue Samples. *Bulletin of Environmental Contamination and Toxicology*, 68 (5):684-691.

Asami, M., K. Kosaka, and S. Kunikane. 2007. Bromate, Chlorate, Chlorite, and Perchlorate in Sodium Hypochlorite Solution Used for Water Supply. *Asian Pacific Regional Exhibition, International Water Association*:10-14.

Asami, Mari, Koji Kosaka, and Soichi Kunikane. 2009. Bromate, Chlorate, Chlorite, and Perchlorate in Sodium Hypochlorite Solution Used for Water Supply. *Journal of Water Supply Research and Technology-Aqua*, 58 (2):107-117.

Ballmaier, D. and B. Epe. 1995. Oxidative Damage Induced by Potassium Bromate under Cell-Free Conditions and in Mammalian Cells. *Carcinogenesis*, 16:335-342.

Batista, Jacimaria R., Frank X. McGarvey, and Adriano Vieira. 2000. The Removal of Perchlorate from Waters Using Ion-Exchange Resins. *Perchlorate in the Environment*: 135-145.

Bichsel, Yves and Urs Von Gunten. 1999. Determination of Iodide and Iodate by Ion Chromatography with Postcolumn Reaction and UV/Visible Detection. *Analytical Chemistry*, 71 (1):34-38.

Bodenheimer, Wolf, Hannah Weiler. 1955. Colorimetric Determination of the Perchlorate Ion. *Analytical. Chemistry*, 27 (8):1293-1295.

California Department of Public Health (CA DPH). 2007. Perchlorate in Drinking Water. http://www.cdph.ca.gov/certlic/drinkingwater/pages/Perchlorate.aspx, Accessed November 14, 2008.

Cheng, Qiuqiong, Lisa Perlmutter, Philip N. Smith, Scott T. McMurry, William A. Jackson, and Todd A. Anderson. 2004. A Study on Perchlorate Exposure and Absorption in Beef Cattle. *Journal of Agricultural and Food Chemistry*, 52 (11):3456-3461.

Chipman, J.K., J.E. Davies, J.L. Parsons, J. Nair, G. O'Neill, and J.K. Fawell. 1998. DNA Oxidation by Potassium Bromate: A Direct Mechanism Linked to Lipid Peroxidation? *Toxicology*, 126:93-102.

The Chlorine Institute, Inc. 2004. Bromate in Sodium Hypochlorite Potable Water Treatment. http://www.chlorineinstitute.org/files/FileDownloads/BromateinNaOCl-PotableWaterTreatment.pdf, Accessed 04/14/09.

Clesceri, Lenore S., Arnold E. Greenberg, and Andrew D. Eaton. 1998. Standard Methods for the Examination of Water and Wastewater, 20th Edition.

Collinson, W. J., D. F. Boltz. 1968. Indirect Spectrophotometric and Atomic Absorption Spectrometric Methods Determination of Perchlorate. *Anal. Chem.*, 40 (12):1896-1898.

Dafert, F. W. 1908. The Composition of Some Chilian Caliche. *Monatshefte fuer Chemie*, 29:235-244.

Davis, Clyde O. 1940. Perchlorate Explosives, US 2190703

DeAngelo, Anthony B., Michael H. George, Steve R. Kilburn, Tanya M. Moore, and Douglas C. Wolf. 1998. Carcinogenicity of Potassium Bromate Administered in the Drinking Water to Male B6c3f1 Mice and F344/N Rats. *Toxicologic Pathology*, 26 (5):587-594.

Dodds, Eric D., John M. Kennish, Frank A. von Hippel, Richard Bernhardt, and Mark E. Hines. 2004. Quantitative Analysis of Perchlorate in Extracts of Whole Fish Homogenates by Ion Chromatography: Comparison of Suppressed Conductivity Detection and Electrospray Ionization Mass Spectrometry. *Analytical and Bioanalytical Chemistry*, 379 (5-6):881-887.

California Department of Health Services. 2004. Drinking Water Notification Levels. http://www.dhs.ca.gov/ps/ddwem/chemicals/AL/notificationlevels.htm.

Gordon, G., L. C. Adam, B. Bubnis, B. Hoyt, S. J. Gillette, and A. Wilczak. 1993. Controlling the Formation of Chlorate Ion in Liquid Hypochlorite Feedstocks. *Journal American Water Works Association*, 85 (9):89-97.

Gordon, G., G. E. Pacey, and B. Bubnis. 1993. Analytical Methods for Disinfectants and Disinfection by-Products. *Safety of Water Disinfection: Balancing Chemical and Microbial Risks*

Gordon, G., L. Adam, and B. Bubnis. 1994. *Minimizing Chlorate Ion Formation in Drinking Water When Hypochlorite Ion Is the Chlorinating Agent*, AwwaRF and AWWA Report, Denver, Colo: 195 pages.

Gordon, G., L. Adam, and Bernard Bubnis. 1995. Minimizing Chlorate Ion Formation in Drinking Water When Hypochlorite Ion Is the Chlorinating Agent. *Journal American Water Works Association,* 87 (6):97-106.

Gordon, Gilbert, Luke C. Adam, Bernard P. Bubnis, Ching Kuo, Robert S. Cushing, and Richard H. Sakaji. 1997. Predicting Liquid Bleach Decomposition. *Journal American Water Works Association,* 89 (4):142-149.

Greer, Monte A., Gay Goodman, Richard C. Pleus, and Susan E. Greer. 2002a. Health Effects Assessment for Environmental Perchlorate Contamination: The Dose Response for Inhibition of Thyroidal Radioiodine Uptake in Humans. *Environmental Health Perspectives*, 110 (9):927-937.

Greer, Monte A., Gay Goodman, Richard C. Pleus, and Susan E. Greer. 2002b. Health Effects Assessment for Environmental Perchlorate Contamination: The Dose Response for Inhibition of Thyroidal Radioiodine Uptake in Humans. *Environmental Health Perspectives*, 110 (9):927-937.

Greiner, Peter, Clif McLellan, Dale Bennett, and Angie Ewing. 2008. Occurrence of Perchlorate in Sodium Hypochlorite. *Journal American Water Works Association*, 100 (11):68–74,10.

Hampel, Clifford A. and P. W. Leppla. 1947. Production of Potassium Perchlorate. *Transactions of the Electrochemical Society, 92:10.*

Handy, Russell, David A. Barnett, Randy W. Purves, Gary Horlick, and Roger Guevremont. 2000. Determination of Nanomolar Levels of Perchlorate in Water by ESI-FAIMS-MS. *Journal of Analytical Atomic Spectrometry*, 15 (8):907-911.

Howd, Robert H. 2002. Memorandum: Proposed Action Level for Chlorate. CA Office of Environmental Health Hazard Assessment. Sacramento, CA. http://oehha.ca.gov/water/pals/chlorate.html

Inoue, Yoshinori, Tetsushi Sakai, Hiroki Kumagai, and Yuzuru Hanaoka. 1997. High Selective Determination of Bromate in Ozonized Water by Using Ion Chromatography with Postcolumn Derivatization Equipped with Reagent Preparation Device. *Analytica Chimica Acta*, 346 (3):299-305.

Jackson, W. Andrew, Srinivasa Kumar Anandam, Todd Anderson, Tom Lehman, Ken Rainwater, Srinath Rajagopalan, Moira Ridley, and Richard Tock. 2005. Perchlorate Occurrence in the Texas Southern High Plains Aquifer System. *Ground Water Monitoring & Remediation*, 25 (1):137-149.

Johnson, Jay, Dane Grimshaw, and Kent Richman. 2003. Analysis for Perchlorate by Ion Chromatography: Significant Recent Findings, American Pacific Corporation, Henderson Nevada: 10 pages.

Kirk, Andrea B., Ernest E. Smith, Kang Tian, Todd A. Anderson, and Purnendu K. Dasgupta. 2003. Perchlorate in Milk. *Environmental Science & Technology*, 37 (21):4979-4981.

Kirk, Andrea B., Ernest E. Smith, Kang Tian, Todd A. Anderson, and Purnendu K. Dasgupta. 2004. Perchlorate in Milk. *Environmental Science & Technology*, 37 (21):4979-4981.

Kirk, Andrea B., P. Kalyani Martinelango, Kang Tian, Aniruddha Dutta, Ernest E. Smith, and Purnendu K. Dasgupta. 2005. Perchlorate and Iodide in Dairy and Breast Milk. *Environmental Science & Technology*, 39 (7):2011-2017.

Koester, Carolyn J., Harry R. Beller, and Rolf U. Halden. 2000. Analysis of Perchlorate in Groundwater by Electrospray Ionization Mass Spectrometry/Mass Spectrometry. *Environmental Science & Technology*, 34:1862-1864.

Kurokawa, Yuji, Shozo Takayama, Yoichi Konishi, Yoshio Hiasa, Shogo Asahina, Michihito Takahashi, Akihiko Maekawa, and Yuzo Hayashi. 1986. Long-Term in Vivo Carcinogenicity Tests of Potassium Bromate, Sodium Hypochlorite, and Sodium Chlorite Conducted in Japan. *Environmental Health Perspectives*, 69:221-235.

Lamm, S.H., L.E. Braverman, Xiao Li Feng, K. Richman, S. Pino, and G. Howearth. 1999. Thyroid Health Status of Ammonium Perchlorate Workers: A Cross-Sectional Occupational Health Study. *Journal of Occupational and Environmental Medicine*, 41 (4):248-260.

Liu, Yongjian, Shifen Mou, and Shawn Heberling. 2002. Determination of Trace Level Bromate and Perchlorate in Drinking Water by Ion Chromatography with an Evaporative Preconcentration Technique. *Journal of Chromatography A*, 956 (1-2):85-91.

Massachusetts Department of Environmental Protection (MA DEP). 2006. Drinking Water Regulations and Standards. http://www.mass.gov/dep/water/drinking/percinfo.htm#stds.

Magnuson, Matthew L., Edward T. Urbansky, and Catherine A. Kelty. 2000. Microscale Extraction of Perchlorate in Drinking Water with Low Level Detection by Electrospray-Mass Spectrometry. *Talanta*, 52:285-291.

Magnuson, Matthew L., Edward T. Urbansky, and Catherine A. Kelty. 2000. Determination of Perchlorate at Trace Levels in Drinking Water by Ion-Pair Extraction with Electrospray Ionization Mass Spectrometry. *Analytical Chemistry*, 72 (1):25-29.

Martinelango, P. Kalyani, Kang Tian, and Purnendu K. Dasgupta. 2006. Perchlorate in Seawater. Bioconcentration of Iodide and Perchlorate by Various Seaweed Species. *Analytica Chimica Acta*, in press.

McGuire, Michael J., Nancy I. Lieu, and Marie S. Pearthree. 1999. Using Chlorite Ion to Control Nitrification. *Journal American Water Works Association*, 91 (10):52-61.

Nowack, Bernd and Urs von Gunten. 1999. Determination of Chlorate at Low µg l^{-1} Levels by Ion-Chromatography with Postcolumn Reaction. *Journal of Chromatography A*, 849 (1):209-215.

NSF/ANSI. 2005. *NSF/ANSI Standard 60: Drinking Water Treatment Chemicals - Health Effects*, NSF International, Ann Arbor, Michigan: 148 pages.

Oceana. 2007. Cleaning Up: Taking Mercury-Free Chlorine Production to the Bank, Washington, DC: 64 pages. http://www.oceana.org/north-america/what-we-do/stop-seafood-contamination/chlorine-plant-campaign

Orris, G.J., G.J. Harvey, D.T. Tsui, and J.E. Eldrige. 2003. *Preliminary Analyses for Perchlorate in Selected Natural Materials and Their Derivative Products.* U.S. Geological Survey, Open-File Report 03-314.

Roehl, R., R. Slingsby, N. Avdalovic, and P. E. Jackson. 2002. Applications of Ion Chromatography with Electrospray Mass Spectrometric Detection to the Determination of Environmental Contaminants in Water. *Journal of Chromatography A*, 956 (1-2):245-254.

Routt, J. 2008. Committee Report: Disinfection Survey, Part 1-Recent Changes, Current Practices, and Water Quality. *Journal American Water Works Association,* 100 (11):140.

Routt, Jan, Erin Mackey, Roger Noack, Laurel Passantino, Gerry Connell, Anthony Sacco, David Koch, Jim Cosman, Paul Swaim, Elliott Whitby, Andrew DeGraca, Eva Nieminski, Jim Malley, Steve Via, James Bess, Chris Cleveland, Bertrand Dusscrt, Thomas Dwyer, Tuba Ertas, Nicola Fontaine, Rodney Herrington, Dennis Greene, Charles Haas, Clayton Johnson, Suibing Liu, Dennis Mutti, Ignatius Mutoti, Keith Oxner, Dave Peters, Phyllis Posy, David Rindal, Susan Rivera, Charlotte Smith, Wayne Winsor, and Matthew Valade. 2008. Committee Report: Disinfection Survey, Part 2-Alternatives, Experiences, and Future Plans. *Journal American Water Works Association,* 100 (11):110-124,114.

Salhi, Elisabeth and Urs Von Gunten. 1999. Simultaneous Determination of Bromide, Bromate and Nitrite in Low µg l^{-1} Levels by Ion Chromatography without Sample Pretreatment. *Water Research*, 33 (15):3239-3244.

Salov, Valeri V., Jun Yoshinaga, Yasuyuki Shibata, and Masatoshi Morita. 1992. Determination of Inorganic Halogen Species by Liquid Chromatography with Inductively Coupled Argon Plasma Mass Spectrometry. *Analytical Chemistry*, 64 (20):2425-2428.

Sanchez, C. A., R. I. Krieger, N. Khandaker, R. C. Moore, K. C. Holts, and L. L. Neidel. 2005. Accumulation and Perchlorate Exposure Potential of Lettuce Produced in the Lower Colorado River Region. *Journal of Agricultural and Food Chemistry*, 53 (13):5479-5486.

Simchen, Alfred E. and Livia Inbar-Rozem. 1968. Thermal Analysis of Ammonium Perchlorate and of Its Mixtures with Inorganic Substances. *Israel Journal of Chemistry*, 6 (6):937-948.

Snyder, Shane, Brett J. Vanderford, and David J. Rexing. 2005. Trace Analysis of Bromate, Chlorate, Iodate, and Perchlorate in Natural and Bottled Waters. *Environmental Science & Technology*, 39 (12):4586-4593.

Snyder, Shane A., Richard C. Pleus, Brett J. Vanderford, and Janie C. Holady. 2006. Perchlorate and Chlorate in Dietary Supplements and Flavor Enhancing Ingredients. *Analytica Chimica Acta*, 567:23-32.

Soto, N. Ornelas, B. Horstkotte, J. G. March, P. L. Lopez de Alba, L. Lopez Martinez, and V. Cerda Martin. 2008. An Environmental Friendly Method for the Automatic Determination of Hypochlorite in Commercial Products Using Multisyringe Flow Injection Analysis. *Analytica Chimica Acta*, 611 (2):182-186.

Sundberg, Sarah E., J. Jackson Ellington, John J. Evans, Deborah A. Keys, and Jeffrey W. Fisher. 2003. Accumulation of Perchlorate in Tobacco Plants: Development of a Plant Kinetic Model. *Journal of Environmental Monitoring*, 5 (3):505-512.

Swackhamer, Deborah L. and Joan Rose. 2008. Letter to the Honorable Stephen L. Johnson, Administrator, US EPA. Office of the Administrator, Science Advisory Board. November 5, 2008, Washington, DC.

Teas, Jane, Sam Pino, Alan Critchley, and Lewis E. Braverman. 2004. Variability of Iodine Content in Common Commercially Available Edible Seaweeds. *Thyroid*, 14 (10):836-841.

Tiemann, Mary. 2008. Perchlorate Contamination of Drinking Water: Regulatory Issues and Legislative Actions. Congressional Research Service. RS21961, Washington, DC.

Turrentine, J. W. 1924. Use of Seaweed in the Prevention and Treatment of Goiter. *Endocrinology*, 8:409-419.

Urbansky, Edward T., Matthew L. Magnuson, David Freeman, and Christopher Jelks. 1999. Quantitation of Perchlorate Ion by Electrospray Ionization Mass Spectrometry (ESI-MS) Using Stable Association Complexes Wih Organic Cations and Bases to Enhance Selectivity. *Journal of Analytical Atomic Spectrometry*, 14:1861-1866.

Urbansky, Edward T. 2000a. Perchlorate in the Environment. *Environmental Science Research*, 57:299.

Urbansky, Edward T. 2000b. Quantitation of Perchlorate Ion: Practices and Advances Applied to the Analysis of Common Matrices. *Critical Reviews in Analytical Chemistry*, 30 (4):311-343.

Urbansky, Edward T. 2000c. Quantitation of Perchlorate Ion: Practices and Advances Applied to the Analysis of Common Matrices. *Critical Reviews in Analytical Chemistry* 30 (4):311-343.

Urbansky, Edward T., Baohua Gu, Matthew L. Magnuson, Gilbert M. Brown, and Catherine A. Kelly. 2000a. Survey of Bottled Waters for Perchlorate by Electrospray Ionization Mass Spectrometry (ESI-MS) and Ion Chromatography (IC). *Journal of the Science of Food and Agriculture*, 80:1798-1804.

Urbansky, Edward T., Matthew L. Magnuson, Catherine A. Kelty, and Stephanie K. Brown. 2000b. Perchlorate Uptake by Salt Cedar (*Tamarix Ramosissima*) in the Las Vegas Wash Riparian Ecosystem. *The Science of the Total Environment*, 256:227-232.

USEPA. 1999. Alternative Disinfectants and Oxidants Guidance Manual. US EPA Office of Water. EPA/815/R-99/014.

USEPA. 2002. Perchlorate Environmental Contamination: Toxicological Review and Risk Characterization (2002 External Review Draft) NCEA-1-0503, Washington, DC.

USEPA. 2005a. Method 331.0 - Determination of Perchlorate in Drinking Water by Liquid Chromatography Electrospray Ionization Mass Spectrometry. United States Environmental Protection Agency, Office of Groundwater and Drinking Water. EPA 815-R-05-007, Cincinnati, OH. http://www.epa.gov/safewater/methods/pdfs/methods/met331_0.pdf

USEPA. 2005b. Method 332.0 - Determination of Perchlorate in Drinking Water by Ion Chromatography with Suppressed Conductivity and Electrospray Ionization Mass Spectrometry. United States Environmental Protection Agency, Office of Groundwater and Drinking Water. EPA-600-R05-049, Cincinnati, OH. http://www.epa.gov/microbes/m_332_0.pdf

USEPA. 2006. Draft Regulatory Determinations Support Document for Selected Contaminants from the Second Drinking Water Contaminant Candidate List (CCL2) EPA Report 815-D-06-007, Washington, DC.

Wagner, Herbert P., Barry V. Pepich, Daniel P. Hautman, and David J. Munch. 2002. US Environmental Protection Agency Method 326.0, a New Method for Monitoring Inorganic Oxyhalides and Optimization of the Postcolumn Derivatization for the Selective Determination of Trace Levels of Bromate. *Journal of Chromatography A*, 956 (1-2):93-101.

Weinberg, H. S., C. A. Delcomyn, and V. Unnam. 2003. Bromate in Chlorinated Drinking Waters: Occurrence and Implications for Future Regulation. *Environmental Science & Technology*, 37 (14):3104-3110.

WHO. 2008. Guidelines for Drinking Water Quality, 3rd Edition Incorporating the First and Second Addenda, Volume 1, Recommendations, Geneva: 493 pages. http://www.who.int/water_sanitation_health/dwq/gdwq3rev/en/index.html

Winkler, Paul, Mark Minteer, and Janice Willey. 2004. Analysis of Perchlorate in Water and Soil by Electrospray LC/MS/MS. *Analytical Chemistry*, 76 (2):469-473.

York, Raymond G., W. Ray Brown, Michael F. Girard, and Joan S. Dollarhide. 2001. Oral (Drinking Water) Developmental Toxicity Study of Ammonium Perchlorate in New Zealand White Rabbits. *International Journal of Toxicology*, 20:199-204.

Yu, Lu , Jaclyn E. Canas, George P. Cobb, William A. Jackson, and Todd A. Anderson. 2004. Uptake of Perchlorate in Terrestrial Plants. *Ecotoxicology and Environmental Safety*, 58 (1):44-49.

Zwiener, Christian and Fritz H. Frimmel. 2004. LC-MS Analysis in the Aquatic Environment and in Water Treatment Technology - a Critical Review. Part Ii: Applications for Emerging Contaminants and Related Pollutants, Microorganisms and Humic Acids. *Analytical and Bioanalytical Chemistry*, 378 (4):862-874.

CHAPTER 2
ANALYTICAL METHODS

BACKGROUND

One of the most crucial components underlying the successful completion of this project was the validation of analytical methods for applicability in the broad array of matrices under investigation. Method validation was necessary to ensure that any empirical observations made during the course of the project could be related to precise and accurate concentrations of contaminants (within +/- 5%) in any given matrix, from 13% hypochlorite to 1% on-site generated (OSG) hypochlorite to distribution system samples with 1 ppm chlorine residual or less. Multiple analytes were identified in the initial stages of this study that had potential roles in the formation of perchlorate including transition metals (e.g., Mn, Fe, Co, Ni, and Cu), hypochlorite, chlorite, chlorate, perchlorate, bromide, and bromate. While the role of individual analytes in perchlorate (and bromate) formation could be hypothesized, good quantitation was key to the successful determination of a detailed chemical rate law. Some of the challenges in analyzing for each of the contaminants of concern included:

- Working with concentration ranges from g/L levels in concentrated hypochlorite solutions to low µg/L levels in distribution system samples, resulting in massive dilution factors (and associated error) in some cases
- High levels of hypochlorite and other salts which could potentially damage the analytical instruments
- High levels of chloride in the hypochlorite solution which can overload the liquid chromatography (LC) column and mask the presence of other analytes
- Detection of low levels of transition metals in hypochlorite solutions and distribution system samples
- Selection of a quenching agent for hypochlorite that would not contaminate or interfere with the analysis of any of the analytes of concern in the various samples collected at the SNWA laboratory or hundreds of miles away at each of the participating utility sites.

Given each of the concerns listed above, the approach for method development involved multiple steps, several of which were performed simultaneously. For the purpose of this report, however, the method development and application are listed in the most logical order for interpretation of data within the report and for future use: sample handling techniques, an overview of LC-tandem mass spectrometry (LC-MS/MS) and titrimetric methods, comparison of the methods (titration methods for use in concentrated hypochlorite solutions and LC-MS/MS for OSG and water samples), selection of a quenching agent, and metal ion quantification in hypochlorite solutions and water. For ease of use, a flow-chart summarizing the method decision making process is shown in Figure 2.1.

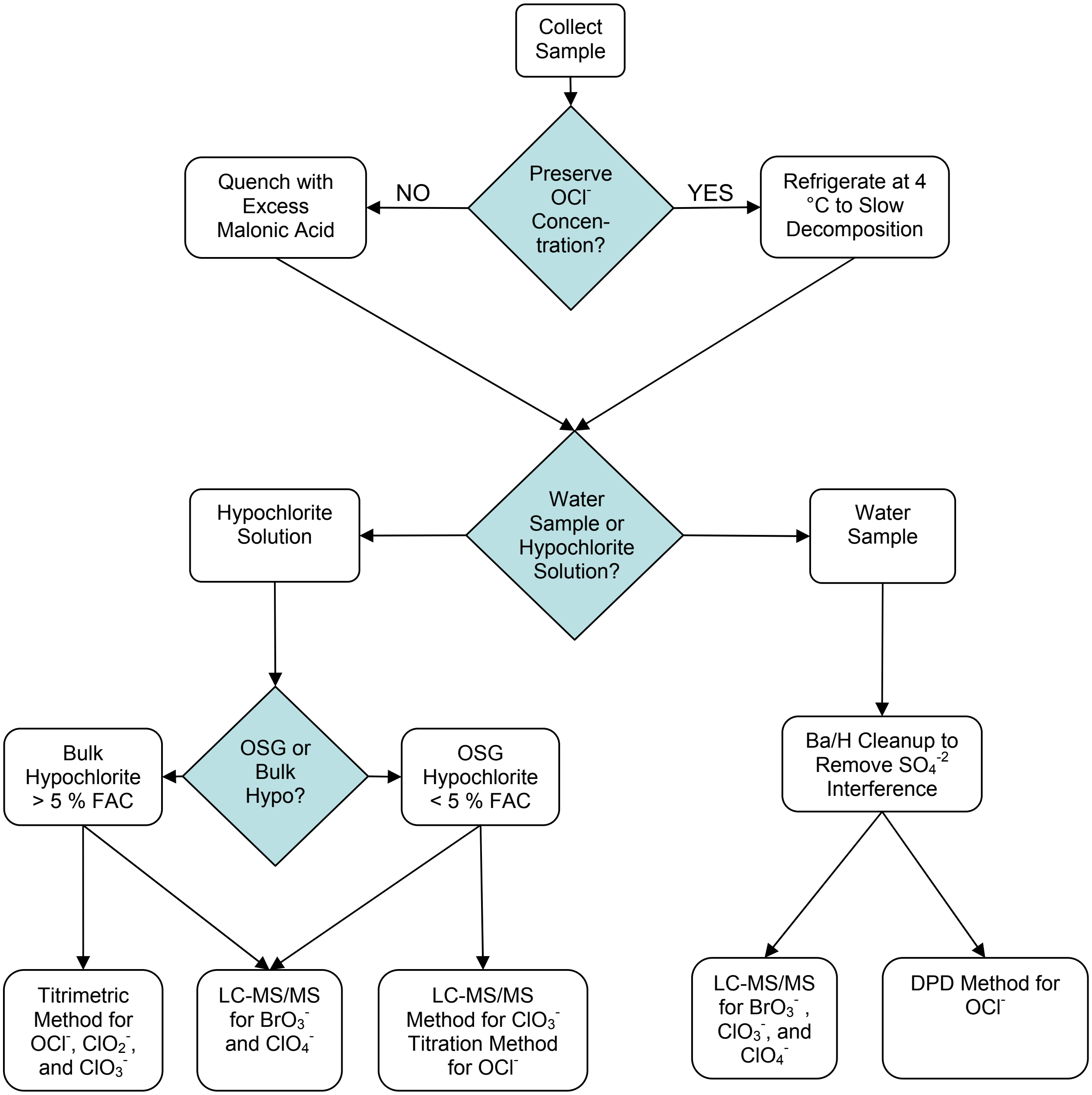

Figure 2.1 Decision tree for sample processing and analysis depending upon the type of information required and the type of sample being collected

ANALYTICAL METHODS

Sample Collection and Handling

Sodium Hypochlorite Samples

As sodium hypochlorite solutions decompose over time, thereby producing more perchlorate, controlled storage of the samples was preferred. Thus, two choices were available for this study: either quench the hypochlorite to stop subsequent formation and/or decomposition reactions or cool the samples to 4 ºC to slow reaction rates significantly below those observed at room temperature. Quenching ensures the most accurate measurements of perchlorate, chlorate, and bromate when a time-of-sampling measurement is desired. Storing samples at 4 ºC preserves hypochlorite (which is important for rate determination and modeling) and decreases the loss of hypochlorite significantly, thereby allowing the sample to be analyzed for hypochlorite in addition to chlorate, perchlorate, and bromate. Furthermore, unquenched samples can be used for holding studies to examine rates of formation of contaminants. For this study, duplicate samples were collected in acid-washed high-density polyethylene (HDPE) bottles and split: one sample was preserved with malonic acid while the other was cooled to 4 ºC and prepared for shipment on ice to the SNWA laboratory. The reaction between hypochlorite and malonic acid is mild and slow (many minutes) and no special handling was required. However, one hour of reaction time was allowed to ensure complete quenching of hypochlorite. Malonic acid was used to quench hypochlorite in a 0.75:1 mol ratio, or approximately 11 g malonic acid for every 10 g FAC expected.

Water Samples

Water samples were collected using 125 mL, acid-washed HDPE bottles that were pre-dosed with 13 µL of a 1 M malonic acid stock solution for quenching up to 10 mg/L residual hypochlorite. Sample bottles were filled, capped, and stored at 4 ºC to minimize evaporation. The perchlorate anion is very stable and does not precipitate easily, thus no pH adjustments were necessary. Once collected, the water samples were sequentially passed through one OnGuard II Ba and one OnGuard II H Cartridge (Dionex, Sunnyvale, CA) to reduce sulfate and carbonate ion concentrations. These anions have been previously shown to suppress oxyhalide concentrations when using LC-MS/MS for analysis (Snyder, Vanderford, and Rexing 2005). Care was also taken to assess the necessary cartridge capacity, as water samples have varying sulfate and carbonate ion concentrations depending on their geological background. Samples also were filtered using 0.2 µm surfactant free cellulose acetate filters (Fisher Scientific, Pittsburg, PA) to remove any suspended particulates.

LC-MS/MS Method for Bromate, Chlorate, and Perchlorate Analysis

EPA 314.0, which relies on ion chromatography (IC) coupled with conductivity detection, has long been used for the analysis of perchlorate in water. Conductivity detection is inherently a non-selective technique, as many components in aqueous mixtures are conductive, and, as a result, this method has been shown to produce false positives, where perchlorate is incorrectly identified (Johnson, Grimshaw, and Richman 2003; Mathew, Gandhi, and Hedrick 2005). This has led to the development of mass spectrometric methods for the detection and quantification of perchlorate and other oxyhalides in water (Handy, et al. 2000; Koester, Beller, and Halden 2000; Magnuson, Urbansky, and Kelty 2000; Magnuson, Urbansky, and Kelty 2000; Richardson 2002; Roehl, et al. 2002; Rickman 2003; Gandhi, Johnson, and Joe 2004; Winkler, Minteer, and Willey 2004; Zwiener and Frimmel 2004; Snyder, Vanderford, and Rexing 2005), as these methods have been shown to be much more selective and sensitive than IC-conductivity detection. In addition, the EPA has recently released two methods for the measurement of perchlorate in water, EPA 331 and 332, using LC-MS and IC-MS, respectively (USEPA 2005a; USEPA 2005b). However, due to the unique challenges being posed by the matrices of interest, this project required a method that has been proven to be reliable in very complex matrices.

In 2005, an LC-MS/MS method developed by Snyder, et al., was published that demonstrated the reliable analysis of perchlorate in water (Snyder, Vanderford, and Rexing 2005). This method was also shown to be capable of detecting perchlorate in challenging matrices such as commercial detergents and was later adapted to measure perchlorate in aqueous extracts of vitamins and food supplements (Snyder, et al. 2006). In addition, it allowed the simultaneous identification and quantification of bromate and chlorate. Therefore, it was selected as the basis for the method used in this project to measure low level concentrations of oxyhalide anions in water and OSG samples.

Although the method discussed above was based on the work by Snyder, et al., some modifications were made. Analytes were separated using a 75 x 4.6 mm Synergi Max-RP C12 column with a 4 µm pore size (Phenomenex, Torrance, CA). A binary gradient consisting of 0.1% formic acid (v/v) in water (A) and 100% methanol (B) at a flow rate of 700 µl/min was used. The gradient was as follows: 2% B held for one minute, increased linearly to 15% B by two minutes, changed to 95% B and held for four minutes, and finally changed to 2% B and held for 3 minutes. A one minute equilibration step at 2% B was used at the beginning of each run to bring the total run time per sample to 10 minutes. An injection volume of 20 µl was used for all samples.

Tandem mass spectrometry was performed using a triple-quadrupole mass spectrometer equipped with an electrospray ionization source operated in negative ion mode (Applied Biosystems, Foster City, CA). In tandem mass spectrometry, a target analyte is first ionized in the ionization source and selected for the first quadrupole. Subsequently, the precursor ion is fragmented in the second quadrupole and a representative fragment (product ion) of the precursor is selected for in the third quadrupole. The monitoring of this transition from precursor to product ion makes the mass spectrometer very selective and sensitive. For this method, the following precursor/product ion transitions were used: $^{35}ClO_4^-$ (*m/z* 99) to $^{35}ClO_3^-$(*m/z* 83) for perchlorate; $^{35}ClO_3^-$ (*m/z* 83) to $^{35}ClO_2^-$ (*m/z* 67) for chlorate; and $^{79}BrO_3^-$ (*m/z* 127) to $^{79}BrO_2^-$ (*m/z* 111) for bromate.

To ensure the proper identification of the oxyhalides, additional ion transitions of perchlorate, chlorate and bromate using naturally occurring, stable isotopes of chlorine and bromine (chlorine-37 and bromine-81) were simultaneously monitored for purposes of confirmation. The following confirmation transitions were used: $^{37}ClO_4^-$ (*m/z* 101) to $^{37}ClO_3^-$ (*m/z* 85) for perchlorate; $^{37}ClO_3^-$ (*m/z* 85) to $^{37}ClO_2^-$ (*m/z* 69) for chlorate; and $^{81}BrO_3^-$ (*m/z* 129) to $^{81}BrO_2^-$ (*m/z* 113) for bromate.

In addition, perchlorate and bromate were quantified using the isotope dilution technique. In isotope dilution, a non-radioactively labeled analog of each target compound is added to every sample and the recovery of the labeled compound is used to determine the degree of matrix interference in the sample for each target analyte (Vanderford and Snyder 2006). Because the labeled compound behaves very similarly to the unlabeled target compound, the recovery can then be used to correct for matrix interferences. For this project, labeled versions of perchlorate ($^{35}Cl^{18}O_4$) and bromate ($^{79}Br^{18}O_4$) were used that contain oxygen-18, a stable isotope of oxygen that occurs at only 0.20% in nature. As no source of oxygen-18 labeled chlorate was commercially available, it was quantified using external calibration.

Based on published results and other preliminary tests in our laboratory, the method reporting limits (MRL) for each matrix were determined and are shown in Table 2.1. (Note: The concentrated hypochlorite solution detection limits are based on a standard dilution factor of 1:100, though MRLs may be adjusted upwards for increased sample dilution.)

Table 2.1
LC-MS/MS MRLs (µg/L) for target analytes in water and hypochlorite solution

	Water	Hypochlorite solution
Perchlorate	0.05	5.0
Bromate	0.1	10
Chlorate	0.1	10

Titration Method for Hypochlorite, Chlorite, and Chlorate Analysis

While the LC-MS/MS method was validated and shown to be appropriate for use in water samples and in dilute hypochlorite solutions (i.e., OSG hypochlorite), a titrimetric technique was employed to measure oxychloride anions in bulk hypochlorite solutions. The titration technique used for this study was based in part on an older iodometric technique for chlorate determination (Equations 2.1, 2.2, and 2.3). This technique relies upon the fact that hypochlorite, chlorite, and chlorate ions react with iodide ion to produce iodine. This allows determination of chlorate but the technique is unable to differentiate chlorite and hypochlorite. The determination is based upon a proportional amount of iodine reacting with the analyte (shown below) followed by addition of excess concentrated hydrochloric acid to affect a color change, after which chlorate can then be titrated.

$$OCl^- + 3I^- + 2H^+ \rightarrow I_3^- + Cl^- + H_2O \qquad \text{pH 1.3} \qquad \textbf{(2.1)}$$

$$ClO_2^- + 6I^- + 4H^+ \rightarrow 2I_3^- + Cl^- + 2H_2O \qquad \text{pH 1.3} \qquad \textbf{(2.2)}$$

$$ClO_3^- + 9I^- + 6H^+ \rightarrow 3I_3^- + Cl^- + 6H_2O \qquad \text{6M } H^+ \qquad \textbf{(2.3)}$$

A well established way to make a standard solution of triiodide is to add a known amount of iodate to an acidic solution containing a small excess of iodide:

$$IO_3^- + 8I^- + 6H^+ \leftrightarrow 3I_3^- + 3H_2O \qquad \textbf{(2.4)}$$

The prepared standard solution of I_3^- can then be used to standardize thiosulfate and sulfite solutions:

$$I_3^- + 2S_2O_3^{2-} \rightarrow 3I^- + S_4O_6^{2-} \qquad \textbf{(2.5)}$$

$$I_3^- + SO_3^{2-} + 2OH^- \rightarrow SO_4^{2-} + 3I^- + H_2O \qquad \textbf{(2.6)}$$

Many variations of iodometric titration methods have been developed over the years. However, potentiometric titration of hypochlorite with sulfite allows selective determination of hypochlorite ion from chlorite ion (Gordon, et al. 1993; Adam 1994). This potentiometric titration technique was used and validated in previous work to study the decomposition of hypochlorite and the subsequent formation of chlorite and chlorate in concentrated hypochlorite solutions (Gordon, et al. 1993; Adam 1994; Adam and Gordon 1995; Gordon, et al. 1997). Given the previous validation and expertise within the Project Team, the potentiometric method was used for analysis of oxychloride anions in concentrated hypochlorite solutions. The sequential determinations of specific anions were carried out in five sequential steps as outlined in Equations 2.7 – 2.11:

Step 1: Titration of OCl^- at pH 10.5:

$$OCl^- + SO_3^{2-} \rightarrow SO_4^{2-} + Cl^- \qquad \textbf{(2.7)}$$

Step 2: Removal of excess SO_3^{2-} at pH 10.0 – 10.5:

$$I_3^- + SO_3^{2-} + 2OH^- \rightarrow SO_4^{2-} + 3I^- + H_2O \qquad \textbf{(2.8)}$$

Step 3: Removal of excess I_3^- at pH 9 – 10.5:

$$I_3^- + 2S_2O_3^{2-} \rightarrow 3I^- + S_4O_6^{2-} \qquad (2.\textbf{9})$$

Step 4: Determination of ClO^{2-} at pH 1.3:

$$ClO_2^- + 6I^- + 4H^+ \rightarrow 2I_3^- + Cl^- + 2H_2O \qquad \textbf{(2.10)}$$

Step 5: Determination of ClO_3^- after addition of concentrated HCl :

$$ClO_3^- + 9I^- + 6H^+ \rightarrow 3I_3^- + Cl^- + 3H_2O \qquad 6M\ H^+ \qquad \textbf{(2.11)}$$

Titrations with sulfite were carried out using a VIT 90 Video Titrator with a P101 platinum k401 SCE electrode pair (Radiometer, Copenhagen, Denmark). Titrations with thiosulfate were performed with a standard 50 mL laboratory glass burette. Concentrated hydrochloric acid (ACS reagent grade, Fisher Scientific, Pittsburg, PA) and the sample solution were purged with nitrogen gas to minimize oxidation of iodide by oxygen prior to chlorate determination. Potassium iodate standard (0.1 M) was prepared weekly using high purity (>99.4%) potassium iodate and used to standardize sulfite and thiosulfate solutions daily. Standardization by this method resulted in standard deviations of less than three parts per thousand and less than 1% relative standard deviation. The 0.2 M SO_3^{2-} solutions were prepared from ACS reagent grade sodium sulfite. The 0.1 M $S_2O_3^{2-}$ solutions were prepared from ACS reagent grade sodium thiosulfate.

ICP-MS Method for Metals Analysis in Sodium Hypochlorite Solutions

Metal ion analysis and quantification was carried out using US EPA method 200.8 on an Agilent (Palo Alto, CA) 7500c Inductively Coupled Plasma-Mass Spectrometer (ICP-MS) with an Octopole Reaction System that uses hydrogen-helium reaction gas to remove Ar-based isobaric and polyatomic oxide interferences. Internal standards were used to correct for matrix interferences. Dilutions ranging from 1:10 to 1:500 were used to reduce the impact of the high total dissolved solids (TDS) background of hypochlorite samples. Actual MRLs are summarized in Table 2.2.

Table 2.2
ICP-MS method reporting limits (µg/L) in water and hypochlorite solutions

Metal	Water*	Hypochlorite solution*
Manganese (Mn)	1.0	25
Iron (Fe)	5.0	125
Cobolt (Co)	2.0	25
Copper (Cu)	5.0	25
Nickel (Ni)	1.0	25

*Occasionally higher MRLs are shown in the text when higher dilution factors were used; the MRLs listed are the lowest level at which data are reported in the text of this report; The proportionality of MRLs between water and hypochlorite varied based on required dilution factors

Specific Conductance, Ionic Strength, and pH Measurements

Specific conductance measurements were performed using a HACH Ion-Series Conductivity/Total Dissolved Solids meter (Hach Company, Loveland, CO). A calibration was performed using a 1,000 µmho/cm standard prior to sample analysis. In most cases dilutions were required to bring the conductivity to within the linear range of the probe. Specific conductance was measured in order to determine the ionic strength of hypochlorite solutions. Ionic strength (I) was calculated from specific conductance (σ) using Equation 2.12:

$$I\ (\text{mol/L}) = 1.6 \times 10^{-5} \times \sigma\ (\mu\text{mho/cm}) \qquad \textbf{(2.12)}$$

Total dissolved solids (TDS) could also be approximated by Equation 2.13:

$$\text{TDS}\ (\text{mg/L}) \sim I * 4 \times 10^{4} \qquad \textbf{(2.13)}$$

An AP62 pH/mV Meter (Fisher Scientific, Pittsburg, PA) was used to measure sample pH. Meter calibrations using standard pH buffers (pH 4, 7, 10) was performed prior to measurements of samples.

Quality Assurance and Quality Control

Quality assurance and quality control followed EPA Method 331 for LC-MS/MS analysis and EPA Method 200.8 for metals analysis. Significant time was devoted to validate the use of the quenching agent of choice (malonic acid) and to validate the methods for applicability to each matrix (e.g., LC-MS/MS for OSG and water, titrations for bulk hypochlorite). Validation was performed using matrix spikes, blanks, and split samples for comparison.

METHOD VALIDATION

Selection of Quenching Agent

The selection of a hypochlorite quenching agent was critical for the monitoring component of this project and for experiments that were conducted off-site at a manufacturing facility. Some initial concern was raised about the potential negative impact of unquenched hypochlorite ions on the mass spectrometer, though this turned out not to be a factor and thus was not a major component in the decision making process. For any experiments performed on-site where chemical reactions/reaction rates needed to be stopped or attenuated, simply refrigerating the sample aliquots at 4 ºC significantly slowed the reaction: the half life of 13% NaOCl solution at 25 ºC is 130 days, at 4 ºC the half life is 3184 days, according to the Bleach 2001 Predictive Model (Adam, Gordon, and Pierce 2001). Thus, temporary storage of concentrated hypochlorite samples at 4 ºC (for up to several weeks) still allowed accurate determinations of hypochlorite and perchlorate concentrations. However, in cases where precise temperature control was not possible or was in question, the use of a quenching agent was necessary for the quantification of other ionic species present in the hypochlorite solutions or water sample.

A total of seven hypochlorite quenching agents were investigated for use in this project based on descriptions in the literature (Gordon 1990; Wood 1990; Sweetin 1993; Adam 1995; Liu 2003) and from current practices at the SNWA laboratory. The quenching agents tested included ascorbic acid, malonic acid, oxalic acid, glycine, sodium sulfite, sodium thiosulfate, and hydrogen peroxide. The selection of the final quenching agent was based on the following criteria:

- Safety, ease of handling, transport, and stability
- Ability to quench hypochlorite reproducibly
- No appreciable impact on bromate levels
- No appreciable impact on chlorate levels
- No appreciable impact on perchlorate levels
- Amount of transition metals present in appreciable concentration to impact analysis (i.e., contamination)
- Number of moles required and cost
- Compatibility with iodometric determination (i.e., quenching agent does not react with iodide or interfere with titration method)

Safety, Ease of Handling, Transport, and Stability

Several of the quenching agents under consideration (hydrogen peroxide, glycine, and oxalic acid) reacted vigorously with hypochlorite, causing significant loss of sample during the reaction, and/or produced heat and noxious fumes. Concentrated solutions of hydrogen peroxide (32% w/w) require special handling and quenching 10 mL of 13% sodium hypochlorite solution produced a considerable amount of heat and gas, making this quenching agent the most dangerous to use. Glycine, though relatively safe itself, reacted violently and produced a very noxious gas when reacted with hypochlorite that can potentially cause light-headedness, dizziness, and nausea. The remaining quenching agents also produced heat and gas, but to a lesser extent. Ascorbic acid reacted the least vigorously and appears to be the safest quenching agent tested. None of the quenching agents had associated transportation restrictions (other than including MSDS information with each shipping carton) with the exception of concentrated hydrogen peroxide.

Regarding stability, hydrogen peroxide and sodium sulfite in solution have limited stability and limited shelf-lives. In solution, sodium sulfite may decay by as much as 1% per hour (Adam and Gordon 1995) but may be more stable if used as a solid salt. Ascorbic acid produced marked color changes that can interfere with titrimetric analyses, both during storage of a 1 M stock solution (Figure 2.2) and after quenching of utility hypochlorite samples. Stock solution color change ranged from a colorless solution upon first preparation, to a yellow solution after 20 days of storage at 4 ºC, to a dark red solution after 37 days of storage at 4 ºC. Quenched hypochlorite solutions exhibited similar color changes due to presence of excess ascorbic acid (Figure 2.3). The development of color in quenched concentrated hypochlorite samples would interfere with the determination of chlorate ion concentration because the iodometric titration has a colorless end-point.

Figure 2.2 Stock solutions of ascorbic acid at t = zero (left), t = 20 days old (center), and t = 37 days old (right)

Figure 2.3 Quenched hypochlorite samples from utilities using ascorbic acid (left 3 bottles) and malonic acid (right bottle)

Ability to Quench Hypochlorite Reproducibly

All quenching agents tested were able to quench hypochlorite in test samples. Ascorbic acid, malonic acid, and oxalic acid were able to quench hypochlorite in different concentration and volume solutions of hypochlorite. The mole ratio of quenching agent to hypochlorite (OCl^-) was 1.2 for ascorbic acid, 0.75 for malonic acid, and 1.5 for oxalic acid. Glycine was the least reproducible quenching agent with mole ratios varying from 0.20 to 0.53; one hypothesis is that the reaction is temperature, pH, and mixing dependent and thus may produce variable results depending on sample composition and handling. Oxalic and malonic acids were the slowest reactants, requiring up to one hour for complete quenching of 13% hypochlorite solution. Sodium thiosulfate and sodium sulfite were found to quench hypochlorite reproducibly, though the sodium sulfite had to be standardized prior to use in order to determine the volume required to deliver the appropriate moles of quenching agent.

Impact on Bromate, Chlorate, and Perchlorate Measurements

In early experiments, sodium thiosulfate and sodium sulfite were observed to have an effect on the analysis of bromate by LC-MS/MS. Both bromate and the internal standard were negatively impacted by the presence of thiosulfate and sulfite. Chromatograms of the non-quenched, sulfite-quenched, and thiosulfate-quenched, 13% sodium hypochlorite samples are shown in Figures 2.4 – 2.6. The chromatograms of a non-quenched sample (Figure 2.4) versus sulfite- (Figure 2.5) and thiosulfate- (Figure 2.6) quenched samples illustrate the observed effects on LC-MS/MS analysis of bromate. In Figure 2.4, the internal standard peak height is around 300 counts (retention time 2.04 min) and effectively corrects for matrix effects, with observed average recoveries in spiked samples (n=3) at 91%. For samples quenched using sulfite and thiosulfate, peak shifts, peak attenuation (Figures 2.5, 2.6), and peak splitting (Figure 2.5) were observed. Furthermore, severe matrix suppression of both analyte and internal standard signals hindered the ability for adequate correction, yielding poor recoveries for samples quenched with thiosulfate (60%, n = 3) and no quantifiable recoveries for samples quenched with sulfite. Ascorbic acid also negatively impacted analysis of bromate. When hypochlorite solutions, quenched with ascorbic acid were analyzed, no detectible concentration of bromate was observed. Furthermore, spiked ascorbic acid-quenched hypochlorite solutions with bromate standard, showed much lower recoveries (49%, n=3) than the non-quenched hypochlorite solutions, indicating that excess ascorbic acid in fact may reduce bromate concentration (shown in Table 2.3). The observation of sulfite, thiosulfate, and ascorbic acid reduction of bromate is similar to that made by Keith *et al.* (2006) where sulfite was similarly shown to reduce bromate in gastric juices. The remaining quenching agent (malonic acid) was shown to have no impact on bromate analysis. Recovery data obtained by LC-MS/MS analysis of dilute hypochlorite samples for the remaining quenching agents are shown in Table 2.3.

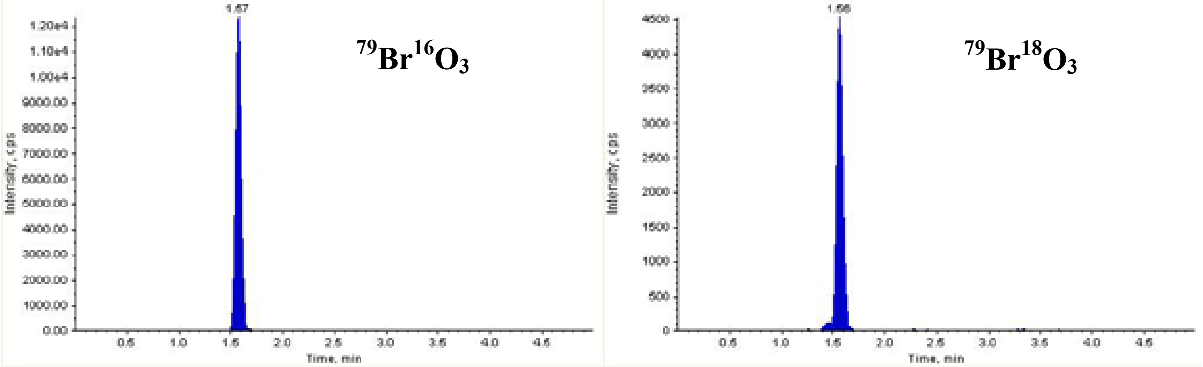

Figure 2.4 Chromatogram of bromate (left) and ^{18}O-labeled bromate (right) of a non-quenched sample of 13% sodium hypochlorite solution diluted by a factor of 1:10,000

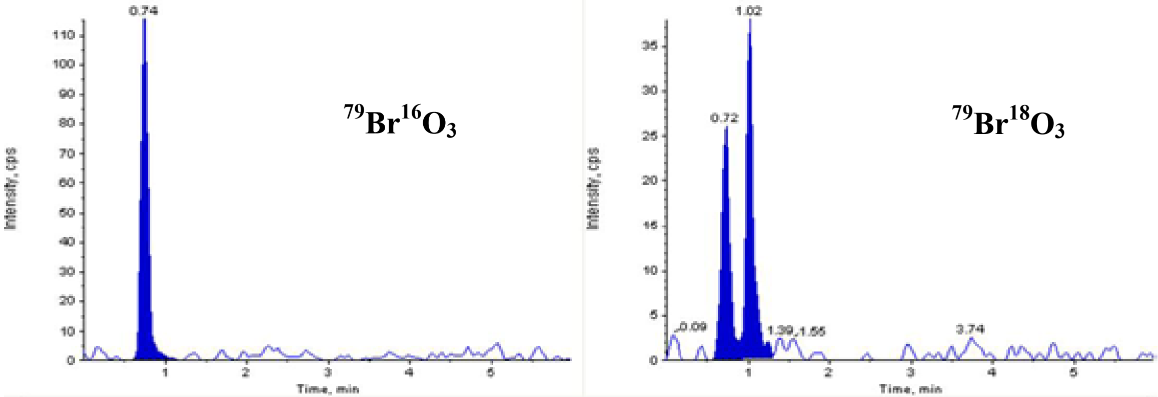

Figure 2.5 Chromatogram of bromate (left) and ^{18}O-labeled bromate (right) of a sulfite-quenched sample of 13% sodium hypochlorite solution diluted by a factor of 1:10,000

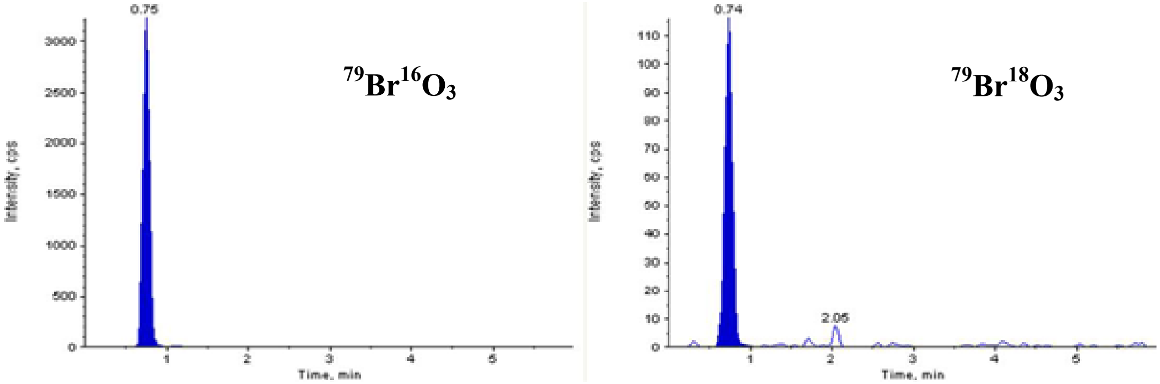

Figure 2.6 Chromatogram of bromate (left) and ^{18}O-labeled bromate (right) of a thiosulfate-quenched sample of 13% sodium hypochlorite solution diluted by a factor of 1:10,000

Table 2.3
Effects of quenching agent on analysis of chlorate, perchlorate, and bromate (n=3)

LC-MS/MS results	Non-quenched hypochlorite	Ascorbic acid	Malonic acid
Chlorate, g/L	16.1 ± 0.15	14.1 ± 0.25	15.7 ± 0.15
Chlorate recovery (matrix spike)	90.8 ± 4	96.2 ± 3	88.9 ± 0.5
Perchlorate mg/L	7.41 ± 0.10	7.42 ± 0.9	7.12 ± 0.5
Perchlorate recovery (matrix spike)	101 ± 1.8	107+1.7	104 ± 2.3
Bromate, mg/L	16.01 ± 0.25	Non-Detect	14.80 ± 0.09
Bromate recovery (matrix spike)	94.3 ± 6.5	*48.6 ± 2.2	96.7 ± 1.1

*Value based on bromate spike in non-quenched hypochlorite sample.
This indicates excess ascorbic acid may reduce bromate concentration.

Number of Moles Required and Cost

Several quenching experiments were performed in order to determine the stoichiometric amounts of quenching agent to hypochlorite required. Experiments were carried out in 13% hypochlorite and residual chlorine was measured using the DPD test. Sodium thiosulfate required the least number of moles to quench hypochlorite and was the most cost effective quenching agent ($0.11 per 10 mL of 13% hypochlorite). However due to potential interferences with the bromate analysis, sodium thiosulfate was removed from further consideration. Thus, malonic and oxalic acids remained as quenching agent candidates. Out of these two, malonic acid was the most cost-effective and required a smaller number of moles to quench sodium hypochlorite. Though costs were considered in this study for reference, it was not a major factor in the final choice of quenching agent.

Quenching Agent Decision Matrix

A generalized decision matrix is included in Table 2.4 with bold-faced text referring to reasons for rejecting a given quenching agent. Based on safety, ease of handling, transport, and stability, *glycine, hydrogen peroxide, sodium sulfite, and ascorbic acid were not recommended for quenching.* Based on negative impacts on bromate analysis, *ascorbic acid, sodium thiosulfate was not recommended for quenching.* Based on limited solubility of oxalic acid in bulk sodium hypochlorite solutions, *oxalic acid was not recommended for quenching.* Thus, malonic acid was chosen as the quenching agent of choice for experiments requiring preservation (typically for samples collected off-site and requiring shipping). For in-house experiments, the use of quenching agent was not required as the mass spectrometric and the titrimetric methods were not impacted by residual FAC; cooling the samples to 4 ºC was sufficient to slow the reactions below appreciable levels if analyzed within a 3-month window.

Table 2.4
Summary of quenching agent test results and decision-making matrix

	Quenching Agent (QA)						
	Ascorbic Acid	Glycine	Malonic Acid	Sodium Thiosulfate	Sodium Sulfite	Oxalic Acid	Hydrogen Peroxide
Stoichiometric ratio of quenching agent to FAC*	1.2	0.55	0.75	0.28	1.1	1.5	1.1
Compatible with iodometric determination?	**No**	Yes	Yes	Yes	Yes	Yes	**No**
Effect on bromate	**Decrease**	No effect	No effect	**Decrease**	**Decrease**	No effect	No effect
Effect on perchlorate	No effect	No effect	No effect	No effect	No effect	No effect	No effect
Effect on chlorate	**High bias**	N/A	No change	No change	No change	No change	N/A
Cost per 100 g	$33.60	$43.00	$25.30	$11.72	$5.96	$27.90	$32.50 / 100mL 32% w/w
g to quench 10mL 13% hypochlorite	3.97	1.82	2.48	0.93	3.64	4.97	0.70
Cost to quench 10mL of 13% hypochlorite	$1.34	$0.78	$0.63	$0.11	$0.22	$1.39	$0.65
Solution stable over time	**No**	Yes	Yes	Yes	**No**	Yes	**No**
Any related safety issues?	No	**Violent reaction**	No	No	No	**Noxious gas evolved**	**Violent reaction, hazardous**
Requires additional reagents?	No	No	No	No	No	**NaOH**	No
Soluble in hypochlorite solutions?	Yes	Yes	Yes	Yes	Yes	**No**	Yes

*FAC = Free available chlorine as measured by DPD method; Bold-faced type represents reason for rejecting a g quenching agent

Validation of LC-MS/MS Method for the Analysis of Hypochlorite Solutions

Sodium hypochlorite solutions subjected for analysis ranged from 0.35 – 13%. Thus, a robust sample preparation method had to be identified in order to ensure accurate and reproducible detection of bromate, chlorate, and perchlorate. Furthermore, sulfate, known to occur in natural water, posed a potential source of isobaric interference to the analysis of perchlorate; as such, sulfate removal techniques (e.g., barium/hydrogen cartridge filters) were used initially on unknown (i.e., utility) samples until it could be determined by analysis of an unfiltered sample that no sulfate interference existed.

Analysis of hypochlorite and hypochlorite plus chlorate, bromate, and perchlorate spikes with and without sulfate removal steps were compared to validate the clean-up steps. Sample solutions were passed sequentially through one 2.5cc OnGuard II Ba and one 2.5cc OnGuard II H Cartridge (Dionex, Sunnyvale, CA) to reduce sulfate and carbonate ion concentrations. The cartridges were conditioned by flushing and discarding 30 mL deionized water. Sample solutions were eluted typically at a flow rate of 2.0 mL/min using mechanical syringe pump and at least the first 10 mL of eluent were discarded prior to collecting a sample aliquot for analysis. The results of dilutions on measured analyte concentration with and without the clean-up step are summarized in Tables 2.5 and 2.6. There were no major differences between filtered and unfiltered samples observed that could not be explained by the dilution effects discussed below. Thus, it was decided that if sulfate interference was possible, the use of a clean-up/filtration step with Barium cartridges would not negatively impact analysis.

Table 2.5
Measured analyte concentrations with and without filtration and at different dilutions (n = 3)

		ClO_3^- (mg/L)				BrO_3^- (µg/L)				ClO_4^- (µg/L)		
	Dilution factor	**5000**	**1000**	**100**	**10**	**5000**	**1000**	**100**	**10**	**1000**	**100**	**10**
Hypochlorite, no filtration	Analyte concentration	311	291	255	113	9017	8803	7433	509	3137	3303	3290
	Std. Dev.	3.3	9.5	4.9	1.5	340	110	275	71.9	35	85	26
	RSD	1.1	3.2	1.9	1.4	3.8	1.3	3.7	14.1	1.1	2.6	0.8
Hypochlorite with Ba/H filtration	Analyte concentration	308	287	257	93.2	9283	9117	8113	3973	3070	3253	3243
	Std. Dev.	4.8	11.2	2.1	5.7	126	275	146	601	61	68	60
	RSD	1.6	3.9	0.8	6.1	1.4	3	1.8	15.1	2	2.1	1.9

Table 2.6
Spike recoveries of analytes with and without filtration and at different dilutions (n = 3)

	Dilution factor	ClO_3^-			BrO_3^-				ClO_4^-		
		5000	**1000**	**100**	**5000**	**1000**	**100**	**10**	**1000**	**100**	**10**
Hypochlorite, no filtration	% Recovery	91	200	42	100	94	86	7.7	99	96	95
	Std. Dev.	11.4	42.3	15.3	2.3	2.5	17.2	0.8	2.3	4.6	5.1
	RSD	12.5	21.7	36.4	2.2	2.7	20	10.7	2.4	4.8	5.4
Hypochlorite with Ba/H filtration	% Recovery	98	230	8.1	99	90	89	-16	100	100	100
	Std. Dev.	10.2	25.6	10.7	5.9	6.8	3.5	40.8	3.5	2.3	3.9
	RSD	10.5	11.3	132.3	6	7.5	4	250.4	3.3	2.3	3.9

In addition to the clean-up and filtration tests, a series of dilution tests were also completed in order to examine the impact of other matrix interferences (e.g., ion suppression, ion enhancement, isobaric interferences, chromatographic resolution). The analysis of perchlorate was the least impacted by sample dilution with matrix recoveries hovering around 100% for all dilutions and analyte concentrations remaining within 3% regardless of dilution factor. Thus, perchlorate analysis was able to be performed at dilutions as low as 1:10, achieving a lower MRL than originally proposed. Chlorate was typically present at levels approaching the g/L range, requiring dilutions of several orders of magnitude. Analysis of bromate was the most susceptible to the matrix effects. Interestingly, the loss in signal of the ^{18}O-labeled bromate was much higher than that of the analyte at 1:10 and 1:100 dilutions. At a 1:1000 dilution, peak-widening was significantly reduced and showed no effect on the accuracy. Examples of the chromatograms of bromate ion signal are shown in Figures 2.7 – 2.9. At a 1:100 dilution, however, the bromate peak appears to be reasonably resolved, yet the ^{18}O-labeled bromate internal standard peak is significantly impacted by matrix interferences, thereby producing an erroneous result. A higher dilution eliminated this problem. In most cases, the sensitivity of the LC-MS/MS method allowed matrix effects to be minimized by diluting the samples. Fig. 2.10 illustrates the improvement in accuracy of the analytes based on the dilution factor.

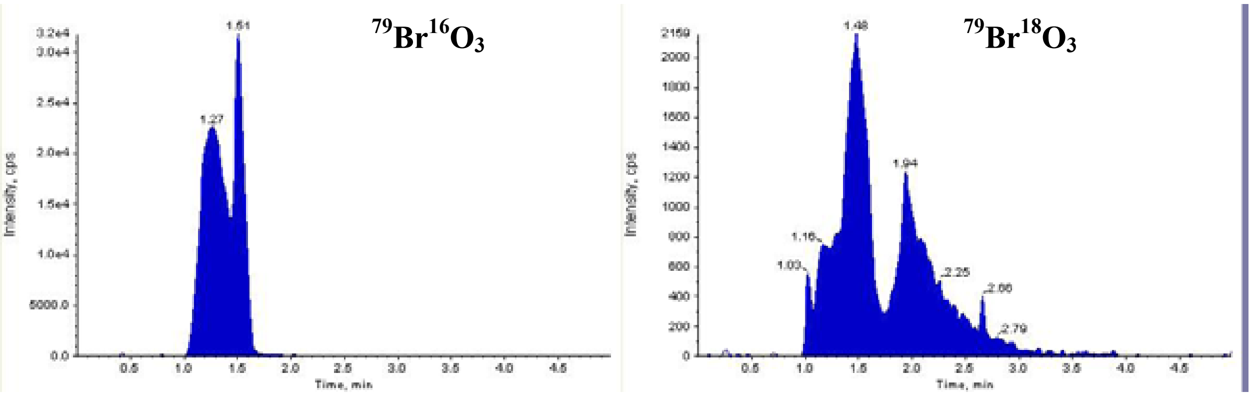

Figure 2.7 Bromate chromatogram of a sample diluted by a factor of 1:10

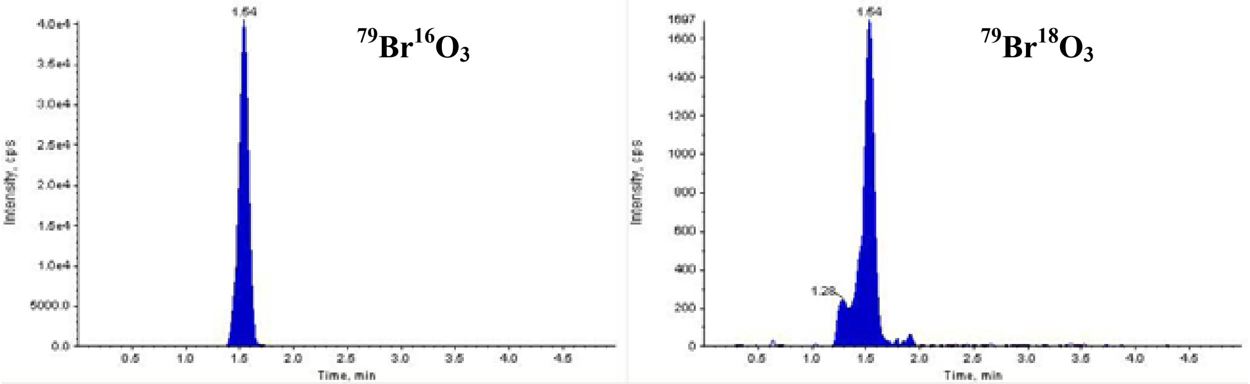

Figure 2.8 Bromate chromatogram of a sample diluted by a factor of 1:100

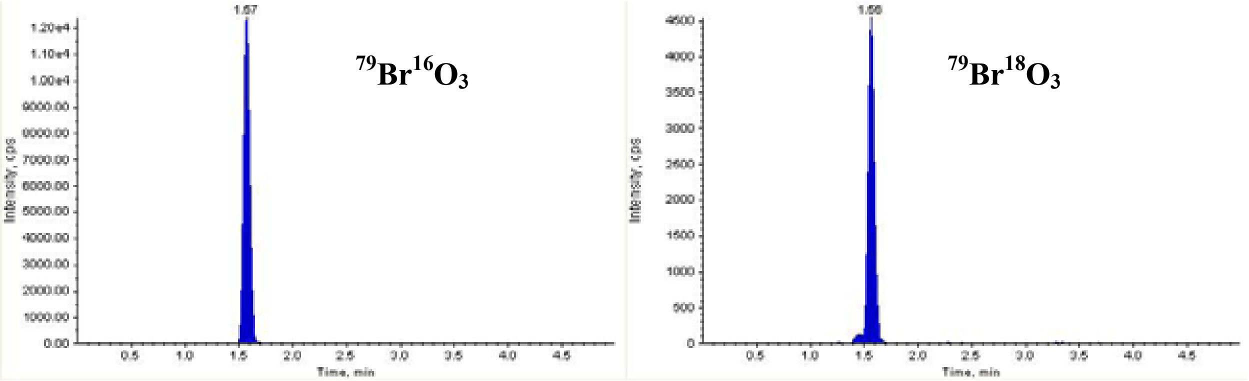

Figure 2.9 Bromate chromatogram of a sample diluted by a factor of 1:1000

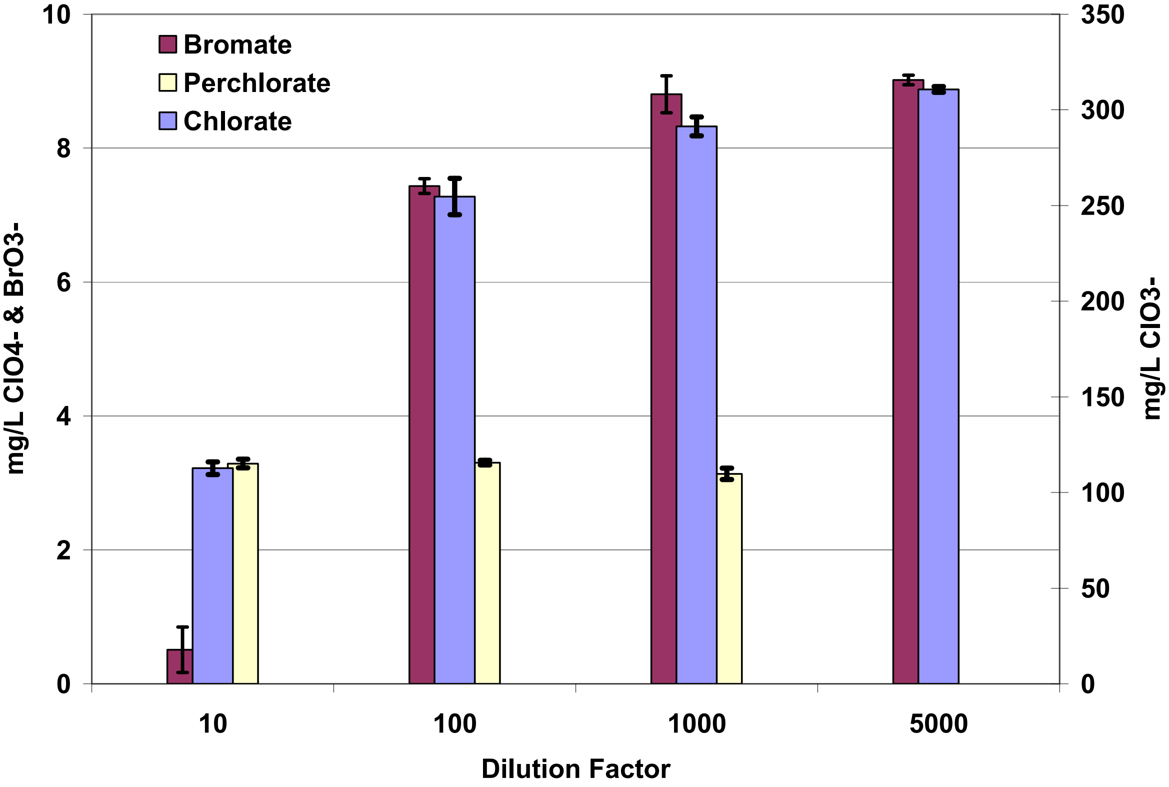

Figure 2.10 Sample concentrations of analytes measured at different dilutions

Comparison of LC-MS/MS and Titrimetric Methods: Selection Criteria for Sample Analysis

Sodium hypochlorite solutions are provided as either bulk, which is commercially available 6.5-13% as Free Available Chlorine (FAC), or as On-site Generated NaOCl that typically is 0.3-3% as FAC. Concentration of chlorate in some bulk hypochlorite samples was present at 200 g/L, thus dilutions on the order of 1:1,000,000 were needed for the LC-MS/MS analysis. In OSG hypochlorite, chlorate concentrations were typically below 1 g/L, which proved difficult to measure by iodometric titration. To determine which method (iodometric titration or LC-MS/MS) was best for chlorate analysis of either bulk or OSG sodium hypochlorite solutions, replicate samples were split and analyzed by both methods and their results compared. A comparison of the two methods for analysis of seven replicate bulk hypochlorite solutions is shown in Table 2.7.

Table 2.7
Data from the analysis of 7 replicate bulk hypochlorite solutions (13 % FAC) by LC-MS/MS and titration methods

	Unspiked hypochlorite		ClO_3^- spiked hypochlorite		% Recovery	
Replicate	LC-MS/MS	Titration	LC-MS/MS	Titration	LC-MS/MS	Titration
1	16.9	17.7	24.4	25.2	95.7	95.1
2	18.0	17.9	24.4	24.8	81.7	88.3
3	15.9	17.7	23.5	25.2	97.0	95.1
4	15.4	17.7	23.1	25.0	98.3	92.8
5	16.1	17.9	25.1	25.2	115	92.8
6	12.9	17.9	24.0	25.2	142	92.8
7	16.5	18.1	23.0	25.4	83.0	92.8
Mean	**16.0**	**17.9**	**23.9**	**25.1**	**102**	**92.8**
Std. Dev.	1.6	0.1	0.8	0.2	20.8	2.3
RSD	**9.9**	**0.8**	**3.2**	**0.7**	**20.4**	**2.4**

These results indicate that, although both methods produce similar results, titration of the concentrated hypochlorite solutions resulted in much lower relative standard deviations (RSD) than the LC-MS/MS method. The higher variability observed in the LC-MS/MS results are most likely a result of the number of dilutions in order to bring 10 – 200g/L concentrations down to the calibration curve of 5 – 500 µg/L or a dilution factor of up to 1,000,000. Carrying out serial dilutions of several orders of magnitude may have compounded errors associated with each dilution made resulting in higher variability. This variability can be visually observed from the comparison of the results from two methods of duplicate samples during a chlorate-spike experiment, shown in Fig. 2.11. It should be noted that in this context connecting lines were used for visual impact. However, in all other figures (unless otherwise noted), best-fit lines are used.

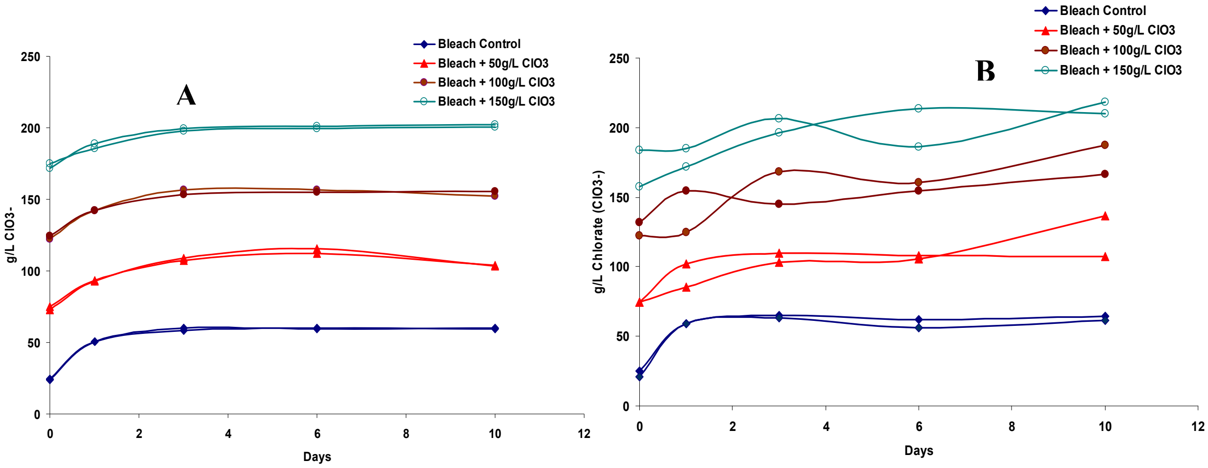

Figure 2.11 Comparison of chlorate ion concentrations measured by titration (A) and by LC-MS/MS (B) during a chlorate-spike experiment

Given these results, the iodometric titration method was used for the vast majority of bulk hypochlorite samples for the determination of chlorate ion concentration. However, for the analysis of OSG hypochlorite, the titration method could not be used as reliably. The results shown in Table 2.8 indicate poor precision for determination of chlorate at concentrations less than 1.0 g/L (10 mM).

Table 2.8
Data from the analysis of replicate OSG hypochlorite solutions with concentration of ClO_3^- at less than 1.0 g/L (< 10 mM) by iodometric titration and LC-MS/MS methods

	Titration	LC-MS/MS
Mean	**0.560**	**0.31**
Std. Dev.	0.20	0.005
RSD (%)	35.23	1.55
	(n=4)	(n=3)

Results are in g/L ClO_3^-

The iodometric determinations of chlorate concentrations at less than 1 g/L were unreliable, thus requiring analysis by LC-MS/MS. Therefore, chlorate measurements for samples from bulk hypochlorite were analyzed by iodometric titration while OSG hypochlorite solutions were analyzed by LC-MS/MS. Specifically, the iodometric titration method was used for determination of chlorate concentrations in 10 – 250 g/L range (generally in hypochlorite solutions with >5% FAC), while LC-MS/MS method was used for trace chlorate analysis in the 0.01 – 10,000 mg/L range (generally in hypochlorite solutions with <5% FAC).

REFERENCES

Adam, Luke, Gilbert Gordon, and Don Pierce. 2001. *Bleach 2001*. Miami University, Oxford, Ohio. Copyright (c) 2001 AwwaRF and AWWA.

Adam, Luke C. 1994. An Investigation of the Factors Involved in the Decomposition of Sodium Hypochlorite, A Ph.D. Dissertation, Department of Chemistry, Miami University, Oxford, OH.

Adam, Luke C. and Gilbert Gordon. 1995. Direct and Sequential Potentiometric Determination of Hypochlorite, Chlorite and Chlorate Ions When Hypochlorite Ion Is Present in Large Excess. *Analytical Chemistry*, 67 (3):535-540.

Adam, Luke C.; Gordon, Gilbert. 1995. Direct and Sequential Potentiometric Determination of Hypochlorite, Chlorite and Chlorate Ions When Hypochlorite Ion Is Present in Large Excess. *Analytical Chemistry*, 67 (3):535-540.

Gandhi, Jay, Mathew Johnson, and Hedrick Joe. 2004. Determination of Trace Level Perchlorate by Ion Chromatography-Mass Spectrometry. *LC GC North America* (Suppl. S):36-36.

Gordon, G., L. C. Adam, B. Bubnis, B. Hoyt, S. J. Gillette, and A. Wilczak. 1993. Controlling the Formation of Chlorate Ion in Liquid Hypochlorite Feedstocks. *Journal American Water Works Association*, 85 (9):89-97.

Gordon, G.: Slootmaekers, B.; Tachiuashiki, S.; Wood, D.W.III. 1990. Minimizing Chlorite Ion and Chlorate Ion in Water Treated With Chlorine Dioxide. *Journal American Water Works Association*, 82 (4):160-165.

Gordon, Gilbert, Luke C. Adam, Bernard P. Bubnis, Ching Kuo, Robert S. Cushing, and Richard H. Sakaji. 1997. Predicting Liquid Bleach Decomposition. *Journal American Water Works Association*, 89 (4):142-149.

Handy, Russell, David A. Barnett, Randy W. Purves, Gary Horlick, and Roger Guevremont. 2000. Determination of Nanomolar Levels of Perchlorate in Water by ESI-Faims-MS. *Journal of Analytical Atomic Spectrometry* 15 (8):907-911.

Johnson, Jay, Dane Grimshaw, and Kent Richman. 2003. Analysis for Perchlorate by Ion Chromatography: Significant Recent Findings, Henderson Nevada: 10 pages.

Keith, J. D., G. E. Pacey, J. A. Cotruvo, and G. Gordon. 2006. Experimental Results from the Reaction of Bromate Ion with Synthetic and Real Gastric Juices. *Toxicology*, 221(2-3):225-228.

Koester, Carolyn J., Harry R. Beller, and Rolf U. Halden. 2000. Analysis of Perchlorate in Groundwater by Electrospray Ionization Mass Spectrometry/Mass Spectrometry. *Environmental Science & Technology* 34:1862-1864.

Liu, W., Andrews, S. A., Stefan, M. I., & Bolton, J. R. . 2003. Optimal Methods for Quenching H_2O_2 Residuals Prior to UFC Testing *Water Research*, 37 (15):3697-3703.

Magnuson, Matthew L., Edward T. Urbansky, and Catherine A. Kelty. 2000. Microscale Extraction of Perchlorate in Drinking Water with Low Level Detection by Electrospray-Mass Spectrometry. *Talanta* 52:285-291.

Magnuson, Matthew L., Edward T. Urbansky, and Catherine A. Kelty. 2000. Determination of Perchlorate at Trace Levels in Drinking Water by Ion-Pair Extraction with Electrospray Ionization Mass Spectrometry. *Analytical Chemistry* 72 (1):25-29.

Mathew, Johnson, Jay Gandhi, and Joe Hedrick. 2005. Trace Level Perchlorate Analysis by Ion Chromatography-Mass Spectrometry *Journal of Chromatography A*, 1085:54-59.

Richardson, Susan D. 2002. Environmental Mass Spectrometry: Emerging Contaminants and Current Issues. *Analytical Chemistry* 74 (12):2719-2742.

Rickman, James E. 2003. LC/MS/MS Measures Perchlorate in 0.1-0.3 Ppb Range. *Trends in Analytical Chemistry* 22 (10):viii-ix.

Roehl, R., R. Slingsby, N. Avdalovic, and P. E. Jackson. 2002. Applications of Ion Chromatography with Electrospray Mass Spectrometric Detection to the Determination of Environmental Contaminants in Water. *Journal of Chromatography A* 956 (1-2):245-254.

Snyder, S. A., B. J. Vanderford, and D. J. Rexing. 2005. Trace Analysis of Bromate, Chlorate, Iodate, and Perchlorate in Natural and Bottled Waters. *Environmental Science & Technology* 39 (12):4586-4593.

Snyder, Shane A., R. C. Pleus, B. Vanderford, and J. C. Holady. 2006. Perchlorate and Chlorate in Dietary Supplements and Flavor Enhancing Ingredients. *Analytica Chimica Acta*, 567:26-32.

Sweetin, D.L. 1993. Developments in the Analytical Methodology for the Determination of Free Available Chlorine, Inorganic Chloramines, and Oxyhalogen Species. Ph.D. Dissertation, Miami University, Oxford, OH:47-69.

USEPA. 2005a. Method 331.0 - Determination of Perchlorate in Drinking Water by Liquid Chromatography Electrospray Ionization Mass Spectrometry. United States Environmental Protection Agency, Office of Groundwater and Drinking Water. EPA 815-R-05-007, Cincinnati, OH. http://www.epa.gov/safewater/methods/ pdfs/methods/met331_0.pdf

USEPA. 2005b. Method 332.0 - Determination of Perchlorate in Drinking Water by Ion Chromatography with Suppressed Conductivity and Electrospray Ionization Mass Spectrometry. United States Environmental Protection Agency, Office of Groundwater and Drinking Water. EPA-600-R05-049, Cincinnati, OH. http://www.epa.gov microbes/m_332_0.pdf

Vanderford, B. J. and Shane A. Snyder. 2006. Analysis of Pharmaceuticals in Water by Isotope Dilution Liquid Chromatography/Tandem Mass Spectrometry. *Environmental Science & Technology*, 40:7312-7320.

Winkler, Paul, Mark Minteer, and Janice Willey. 2004. Analysis of Perchlorate in Water and Soil by Electrospray LC/MS/MS. *Analytical Chemistry* 76 (2):469-473.

Wood, D.W. III. 1990. Determination of Disinfectant Residuals in Chlorine Dioxide Treated Water Using Flow Injection Analysis. Ph.D. Dissertation, Miami University, Oxford, OH:102.

Zwiener, Christian and Fritz H. Frimmel. 2004. LC-MS Analysis in the Aquatic Environment and in Water Treatment Technology — a Critical Review. Part II: Applications for Emerging Contaminants and Related Pollutants, Microorganisms and Humic Acids. *Analytical and Bioanalytical Chemistry* 378 (4):862-874.

CHAPTER 3
FACTORS IMPACTING PERCHLORATE FORMATION

BACKGROUND

The kinetics of the decomposition of the hypochlorite ion and subsequent formation of chlorite and chlorate ions in hypochlorite solutions has been well described and was the basis for much of the experimental design for this study (Gordon, et al. 1993; Adam 1994; Adam and Gordon 1995; Gordon, Adam, and Bubnis 1995; Gordon, et al. 1997; Adam and Gordon 1999). The results of the aforementioned research formed the underpinnings of the *Bleach 2001* predictive model (Adam, Gordon, and Pierce 2001), designed for bulk hypochlorite solutions in the pH range of 11 to 14 and for storage conditions with temperatures from 0 ºC to 50 ºC. The narrow pH range defined in the model is due to the fact that (1) the mechanism for hypochlorite ion decomposition is different (and the rate faster) at or below pH 10.5 and (2) most bulk hypochlorite samples used by drinking water utilities fall within the pH 11 – 14 range. The exception, of course, would be OSG hypochlorite which typically fall within the pH 9 – 10 range. The lack of applicability of the *Bleach 2001* model to OSG hypochlorite is less of a concern, however, as such solutions are typically used immediately, or at most within 48 to 72 hours of production. Thus, the work carried out for this current research study was designed around the use of bulk hypochlorite solutions in the pH 11 to 14 range in order to elucidate the mechanism of perchlorate formation.

Upon commencement of the research for this study the following facts were known about the chemistry of sodium hypochlorite solutions (Adam 1994):

1. Hypochlorite ion can decompose in the pH 11 – 14 range to form chlorate and chloride (Equation 1.1, Chapter 1) or, in the presence of a catalyst, oxygen gas and chloride (Equation 1.2, Chapter 1).

2. The rate law defining the decomposition of the hypochlorite ion in the pH 11 – 14 is defined by second order decomposition (Equation 1.3, Chapter 1).

3. The decomposition of the hypochlorite ion concomitantly results in the production of an intermediate species, the chlorite ion, which essentially remains at steady state during the production of chlorate ion.

4. The ionic strength of the hypochlorite solution impacts the rate of hypochlorite ion decomposition and subsequent chlorate ion formation; higher ionic strength favors faster reaction rates. The relationship between ionic strength, observed rate constant (k_{obs}), and the rate constant for infinite dilution (k_0, for ‘zero’ ionic strength) is defined by Equation 3.1.

$$\log k_{obs} = 0.149(I) + \log k_0 \qquad \textbf{(3.1)}$$

5. The pH of the hypochlorite solution impacts the rate of hypochlorite ion decomposition and chlorate ion formation; this reaction is minimized in the pH

11.86 – 13.00 region. At pH 14, the excess hydroxide ions contribute to the ionic strength, thereby also increasing the rate of reaction by a factor of 1.5 above that observed at pH 13.

6. Diluting hypochlorite solutions by a factor of two reduces the concentration of hypochlorite ion and ionic strength resulting in nearly a five-fold decrease in the rate of decomposition

7. The rate of hypochlorite ion decomposition increases proportionally with temperature and can be related to the zero ionic strength rate constant using the enthalpy ($\Delta H^{\ddagger}$) and entropy ($\Delta S^{\ddagger}$) of activation (Equation 3.2).

$$k_0 = 2.083 \times 10^{10}(T) \times e^{(-\Delta H^{\ddagger}/RT)} \times e^{(\Delta S^{\ddagger}/R)} \qquad \textbf{(3.2)}$$

   By storing hypochlorite solutions at 15 ºC instead of 25 ºC, the rate of decomposition decreases by a factor of 3.8; Cooling from 35 ºC to 15 ºC decreases the rate of decomposition by a factor of 14.

8. Hypochlorite ion decomposition is not impacted by the presence of carbonate or sulfate ions.

9. The presence of some transition metal ions catalyzes the decomposition of hypochlorite ions. Fe(III) and Mn(II) were shown to have no effect at concentrations of 1.1 mg/L for Mn(II) and 42 mg/L for Fe(III). Ni(II) present at 1 mg/L was able to increase the rate constant by a factor of 10, while Cu(II) at the same concentration only increased the rate constant by a factor of 1.4. However, at 10 mg/L, Cu(II) was able to increase the rate constant by a factor of 18.

With the facts listed above in mind, several hypotheses were developed to guide the experimental design:

1. The formation of perchlorate ion is a direct result of reactions between hypochlorite and chlorate ions in the following, generalized reaction:

$$OCl^- + ClO_3^- \rightarrow ClO_4^- + Cl^- \qquad \textbf{(3.3)}$$

   What was not clear, however, was the reaction order with respect to hypochlorite and chlorate ions, though it was hypothesized that the reaction would be first order in both chlorate and hypochlorite.

2. The chlorite ion, given its steady state concentration, is not likely to impact the rate of formation of perchlorate ion.

3. The presence of bromide and bromate ions will not impact the rate of formation of perchlorate ion given that bromide and bromate ions are generally present at low concentrations relative to chloride and chlorate ions.

4. Temperature and ionic strength were hypothesized to impact the rate of perchlorate ion formation in a manner analogous to that of the decomposition of hypochlorite ion and subsequent formation of chlorate ion.

5. Higher initial concentrations of hypochlorite and chlorate ions were hypothesized to increase the rate of perchlorate ion formation.

6. The role of pH is likely to be significant in perchlorate ion formation. However, given the goal of predicting perchlorate formation in bulk hypochlorite, the pH ranges suggested in the experimental design were generally in the pH 11 – 14 range.

7. The presence of transition metal ions was hypothesized to impact the rate of perchlorate ion formation, though it was unclear whether the effect would enhance or retard the rate of formation.

APPROACH

Given each of the considerations and hypotheses listed above, a series of incubation studies on commercially available sodium hypochlorite solutions were carried out in the laboratory. Two hypochlorite suppliers were used: 13% FAC from Acros Organics USA (Morris Plains, NJ) and 10–14% w/w from VWR (Brisbane, CA). Analog and digital, general-purpose, heated water baths (VWR, Brisbane, CA) were used for incubations at 30, 40, 50, 60, and 76 ºC. Temperatures were monitored daily, using glass laboratory mercury thermometer or a thermocouple thermometer with an LCD screen (Fisher Scientific, Pittsburgh, PA). Potassium bromide, Certified ACS grade (Fisher Scientific, Pittsburgh, PA); sodium bromate, 99.5% min (EMD Chemicals Inc., Gibbstown, NJ); sodium chlorate, ACS Grade, ≥99% pure (VWR, Brisbane, CA); and sodium chlorite, unstabilized, Technical Grade 80% (Acros Organics USA, Morris Plains, NJ) were added to sodium hypochlorite solutions to investigate individual and combined effects of contaminants on the decomposition of hypochlorite, formation of bromate, chlorate, and perchlorate. To adjust the pH of the sodium hypochlorite solutions, sodium hydroxide (reagent grade, ≥98%, pellets, Sigma-Aldrich, St. Louis, MO) and hydrochloric acid (ACS reagent, 37%, Sigma-Aldrich, St. Louis, MO) were used. To investigate the effects of metal ions, aliquots of 1,000 ppm Co, Cu, Fe, Ni, and Mn Standards (SPEX CertiPrep®, Inc., Metuchen, NJ) and 1,000ppm Ag, Au, Ir, Pd, and Pt Standards (Elements Inc., Shasta Lake, CA) were spiked into sodium hypochlorite solutions. Dilutions of the sodium hypochlorite solutions and preparation of standards was performed using reagent water purified using Milli-Q Gradient System (Millipore, Billerica, MA). In order to investigate factors that impact perchlorate formation, over 1,600 sample titrations and 1,600 LC-MS/MS data points were collected (not including standardization titrations and calibrations).

INVESTIGATION OF FACTORS IMPACTING PERCHLORATE FORMATION

Part of the challenge faced in designing this research study was how best to design the experiments to provide the amount of information required to determine a chemical rate law within the 9 month time line. Given the short duration of the study, the decision was made that multiple factors would need to be investigated simultaneously while still ensuring that the proper controls were in place to elucidate individual effects. Thus, at the end of the experimental phase of the study, a significant amount of deconvolution of factors/effects was required. Using the data collected from the experiments designed for this study, the individual effects of oxychloride ion concentration, bromide and bromate concentrations, metal ion concentration, ionic strength (using conductivity as a surrogate measure to calculate ionic strength), temperature, and pH were discernable. However, in presenting the results, the reader may notice some overlap between the sections and/or find questions that are raised in one section but are not fully answered until a later section. To keep this to a minimum, the factors impacting the rate of perchlorate formation are presented in the following order: hypochlorite and chlorate ion concentration effects, chlorite ion effects, metal ion effects, bromide and bromate ion effects, temperature, ionic strength, and pH.

Effects of Hypochlorite Ion and Chlorate Ion Concentrations on the Rate of Perchlorate Formation

To investigate effects of chlorate and hypochlorite ions on perchlorate formation, solutions of sodium hypochlorite were spiked with variable amounts of chlorate and hypochlorite ions and incubated at 30, 40, and 50 ºC for periods of up to 200 days. The samples were divided into three unique sets and labeled as follows:

- Constant hypochlorite concentration with variable chlorate concentrations
- Constant chlorate concentrations with variable hypochlorite concentrations
- A constant mole product of [hypochlorite] x [chlorate]

The use of sodium hypochlorite solutions with constant [OCl^-] and variable [ClO_3^-] were used to elucidate the order of the rate of perchlorate formation with respect to chlorate ion. Similarly, solutions with constant [ClO_3^-] and variable [OCl^-] concentrations were used to determine the order with respect to hypochlorite. Should the results indicate that the formation of perchlorate is first order in hypochlorite and first order in chlorate, the constant mole product results would be expected to form the same amount of perchlorate over the incubation period. Given the hypothesis that the initial rate of reaction is first order in chlorate and first order in hypochlorite (thus second order overall), the following rate law equation was proposed:

$$\frac{d[ClO_4^-]}{dt} = k_2[ClO_3^-]^m[OCl^-]^n \qquad \textbf{(3.4)}$$

Where k_2 = the apparent second order rate constant and m and n are approximately 1.

Constant Hypochlorite with Variable Chlorate at 30, 40, and 50 ºC

In this set of experiments, hypochlorite solutions were prepared having the same starting hypochlorite ion concentration[1], while additional chlorate ion was spiked at 50 g/L, 100 g/L, and

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[1] As a point of reference for discussion, a bulk hypochlorite solution of 13% FAC equates to approximately 2 M OCl^-, 103 g/L OCl^-, 149 g/L NaOCl, and/or 13.6% NaOCl (depending on specific gravity).

150 g/L. A control solution containing no additional chlorate ion above the background was also included. All samples were incubated in duplicate. The results presented in Figures 3.1 demonstrate the effects of different initial chlorate ion concentrations on formation of perchlorate ion at 30 ºC (a), at 40 ºC (b), and at 50 ºC (c). The results presented in Figures 3.2 demonstrate the effects of different initial chlorate ion concentrations on the decomposition of hypochlorite ion and formation of chlorate ion at 30 ºC (a), at 40 ºC (b), and at 50 ºC (c). The addition of chlorate to the hypochlorite solution causes a proportionate increase in perchlorate, confirming that changes in initial chlorate ion concentration affect the rate of formation of perchlorate. Casual observation of the results would point toward a reaction mechanism that is first order in chlorate (this is elucidated in more detail later).

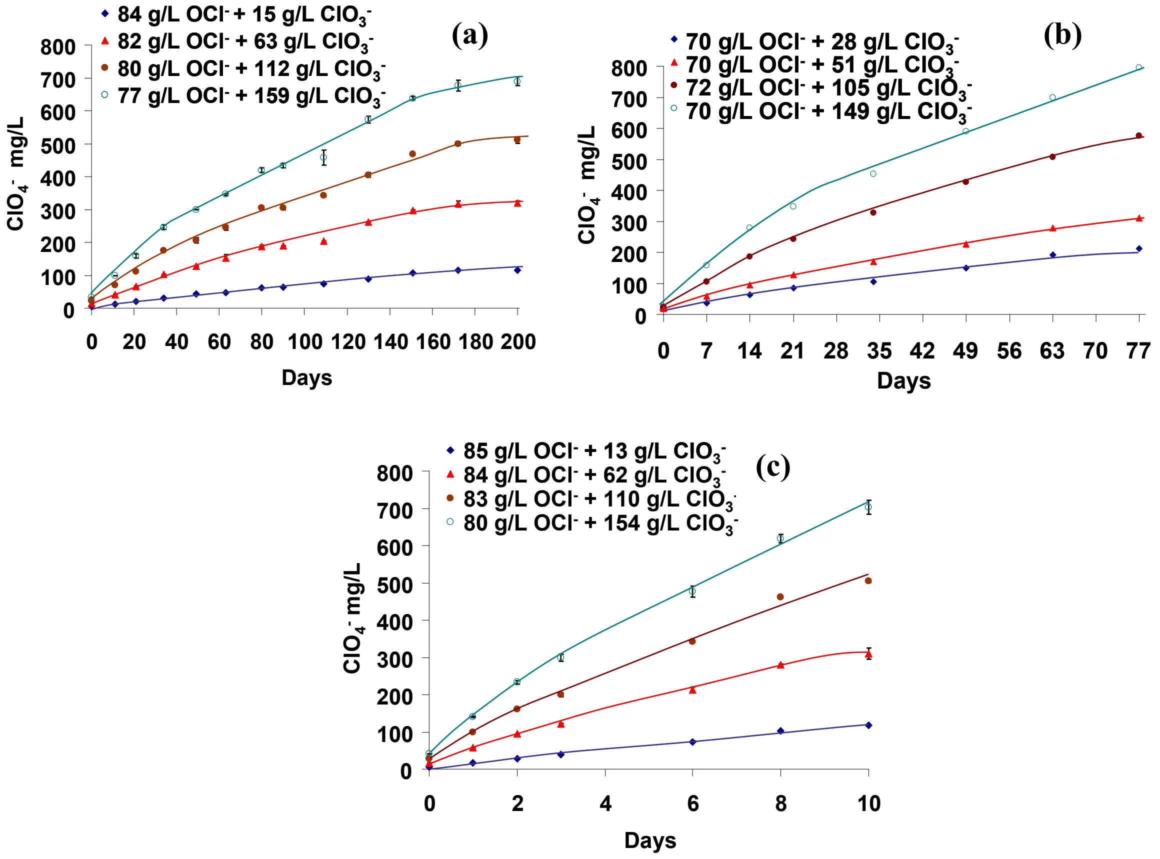


Figure 3.1 Formation of perchlorate as measured by LC-MS/MS for constant hypochlorite / variable chlorate, at (a) 30 ºC, (b) 40 ºC , and (c) 50 ºC

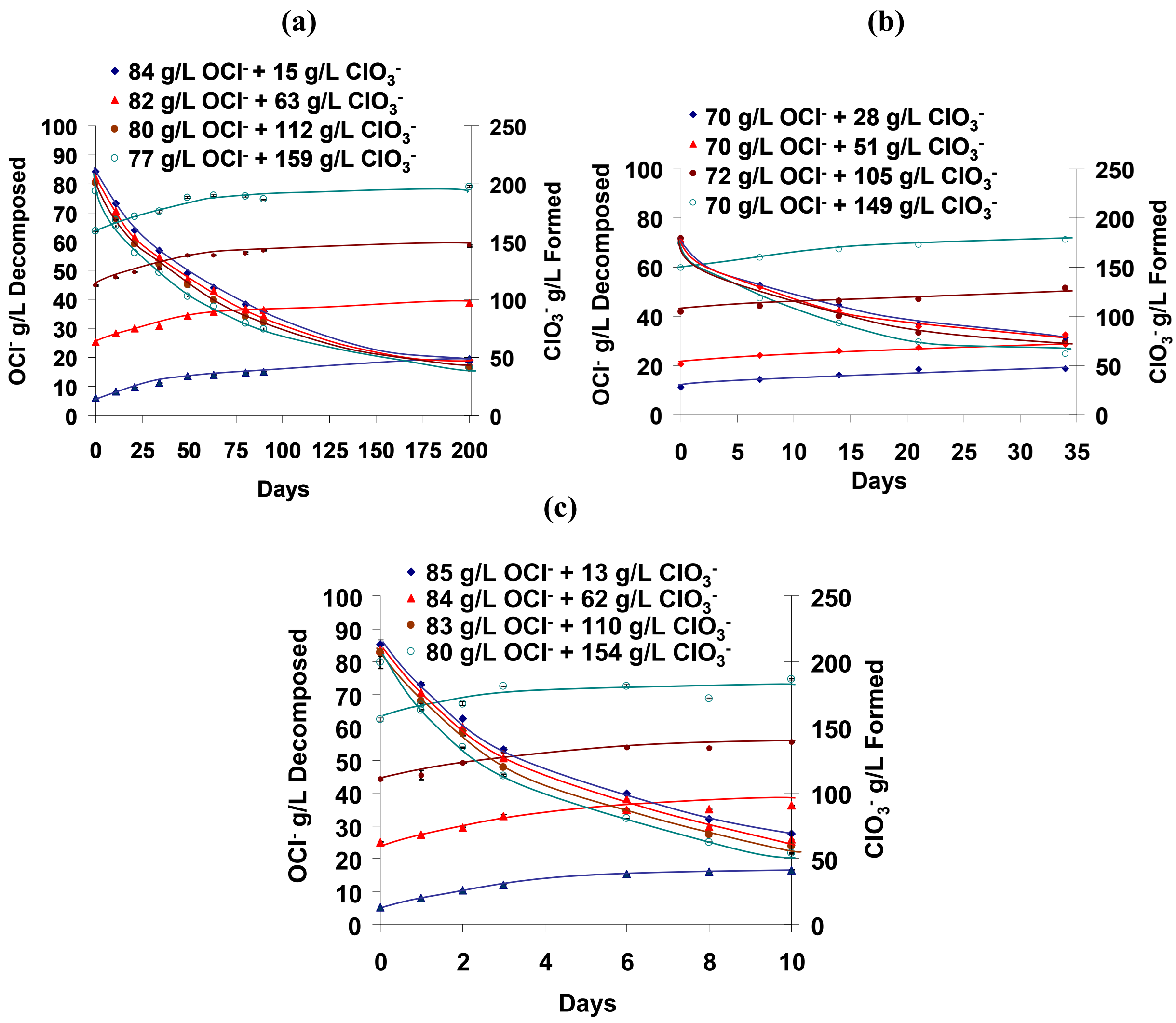


Figure 3.2 Decomposition of hypochlorite and formation of chlorate as measured by titration for constant hypochlorite/variable chlorate, at (a) 30 ºC, (b) 40 ºC (c) 50 ºC

Constant Chlorate/Variable Hypochlorite at 30, 40, and 50 ºC

Similar to the effects of variable chlorate ion concentration, the results of this data set provide evidence that changes in hypochlorite ion concentration also affects the rate of formation of perchlorate. Here, hypochlorite ion concentration was varied by dilution while appropriate amounts of sodium chlorate were added to keep chlorate ion concentration the same for all samples. Typically three or more hypochlorite ion concentrations were studied. Figure 3.3 shows plots of average concentrations of perchlorate ion (based on duplicate samples) at different temperature and associated errors of measurements at each temperature. The results presented in Figures 3.4 demonstrate the effects of different initial chlorate ion concentrations on the decomposition of hypochlorite ion and formation of chlorate ion at 30 ºC (a), at 40 ºC (b), and at 50 ºC (c). Similar to chlorate ion involvement, hypochlorite ion is also involved in formation of perchlorate; samples containing lower hypochlorite ion concentrations show less perchlorate formed.

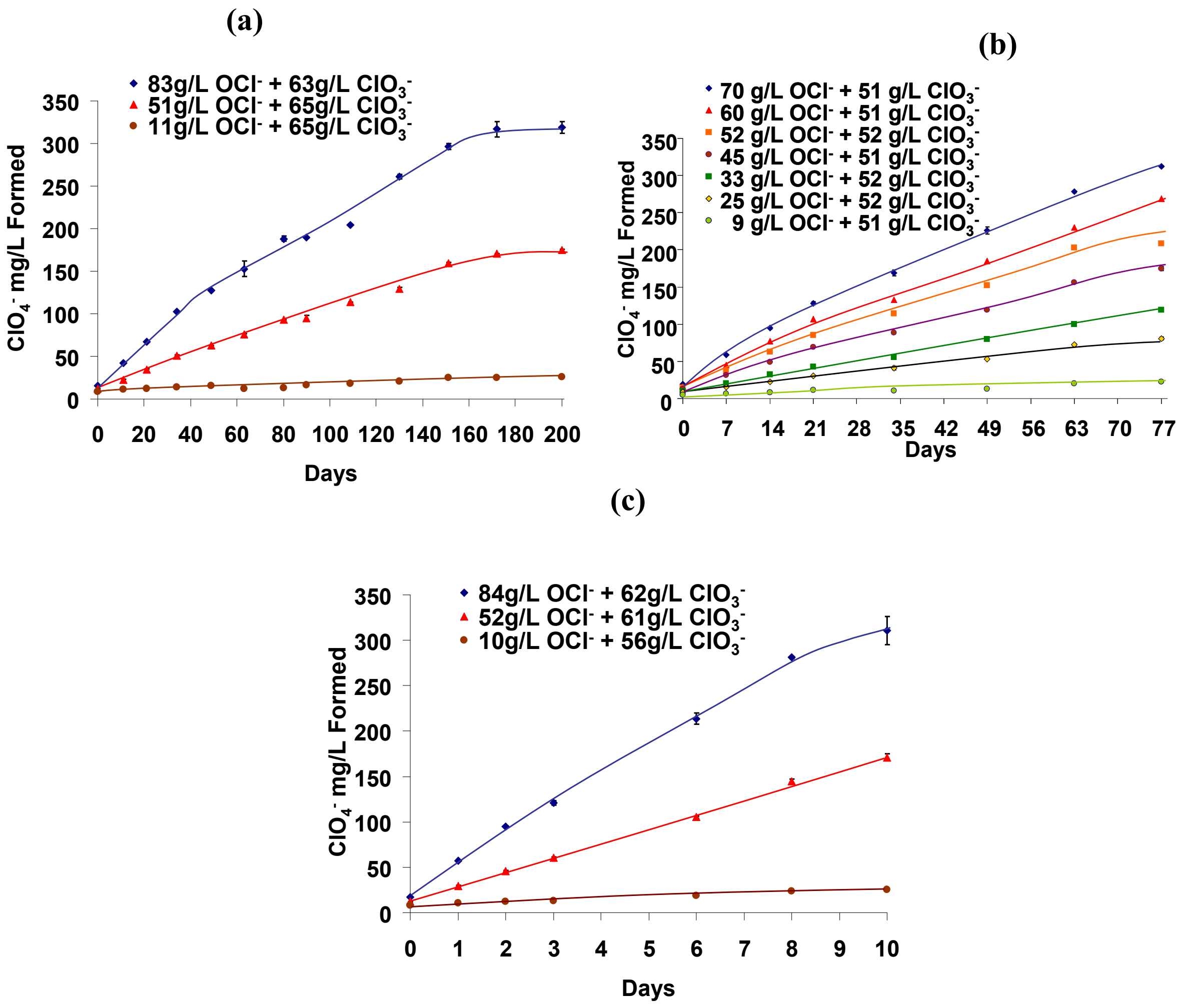


Figure 3.3 Formation of perchlorate as measured by LC-MS/MS for variable hypochlorite, constant chlorate, at (a) 30 ºC, (b) 40 ºC, and (c) 50 ºC

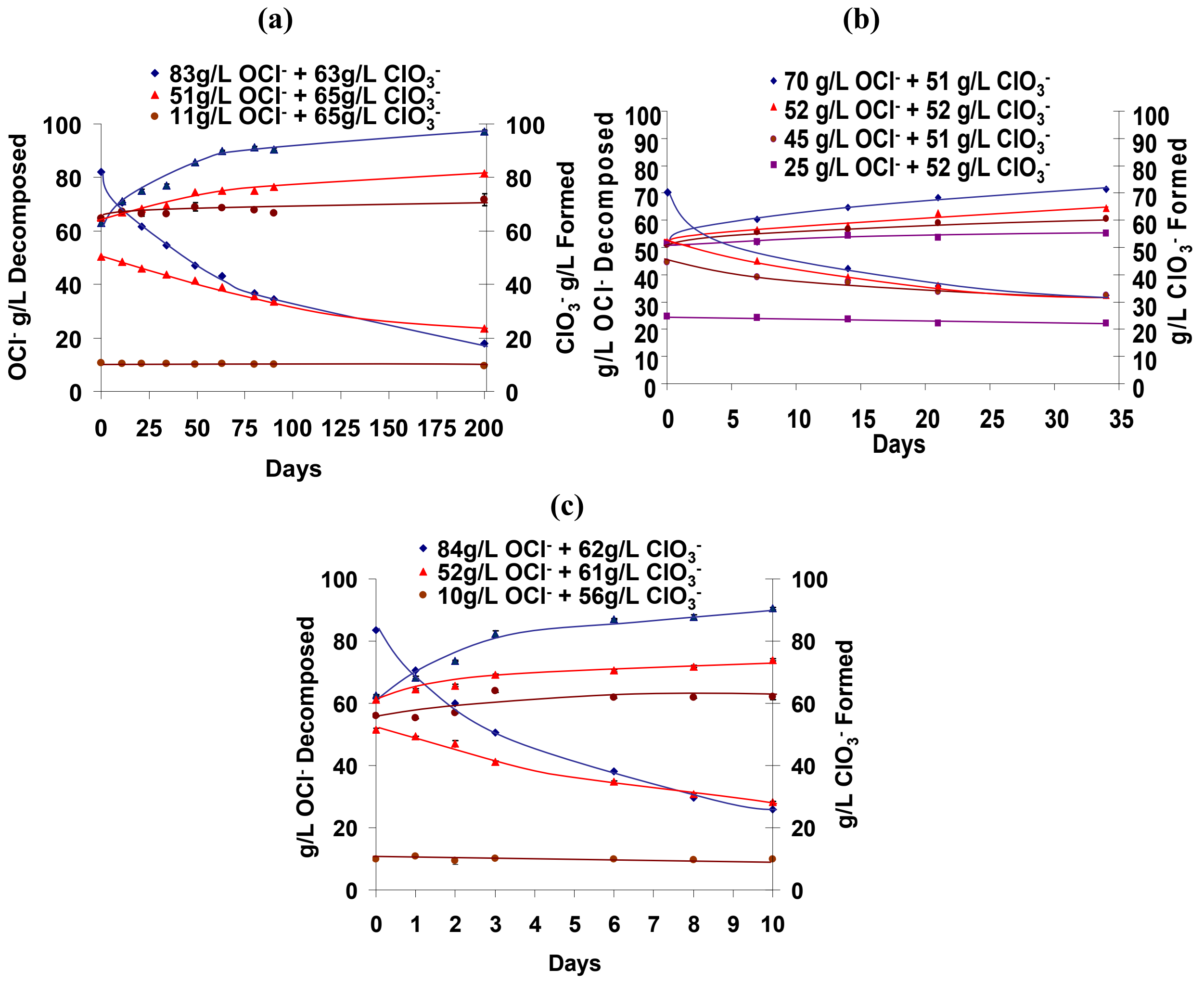


Figure 3.4 Decomposition of hypochlorite and formation of chlorate as measured by titration for variable hypochlorite / constant chlorate, at (a) 30 ºC, (b) 40 ºC, and (c) 50 ºC

Constant Molar Product of [Hypochlorite] x [Chlorate]

Because the rate of perchlorate formation appeared to be first order in chlorate and hypochlorite ions, it was expected that when the molar product was kept constant, the same rate of perchlorate formation would be observed between samples. Both hypochlorite and chlorate ion concentrations were varied in such a way that the molar product was kept constant (1.9% RSD for 30 ºC set and 13.4% RSD for 50 ºC) and the samples were incubated at 30 ºC and 50 ºC. Figure 3.5 shows plots of average concentration of perchlorate ion (based on duplicate samples) and associated errors of measurements at each temperature. Figure 3.6 shows the decomposition of hypochlorite ion and formation of chlorate ion at each temperature.

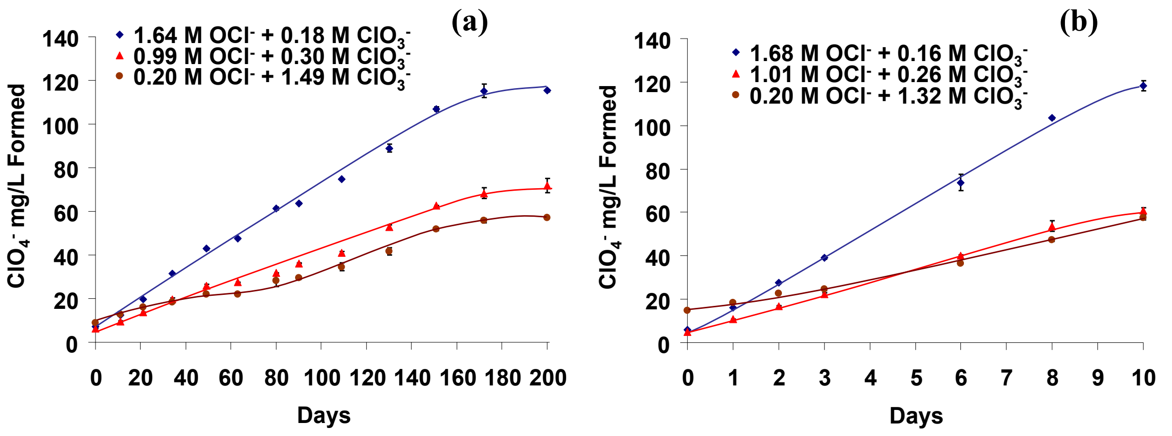


Figure 3.5: Formation of perchlorate as measured by LC-MS/MS for constant $[OCl^-] \times [ClO_3^-]$, (a) 30 °C, (b) 50 °C

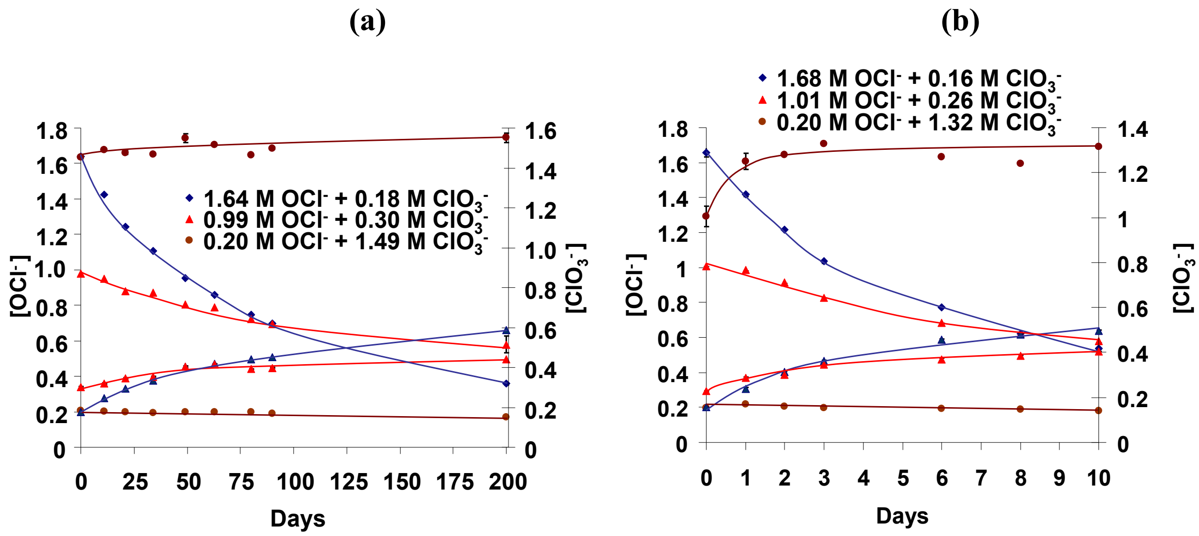


Figure 3.6 Decomposition of hypochlorite and formation of chlorate as measured by titration for constant $[OCl^-] \times [ClO_3^-]$, (a) 30 °C, (b) 50 °C

It is immediately evident from Figure 3.5 (a, b) that the assumption of first order in both hypochlorite ion and chlorate ion may have been incorrect OR that other factors (e.g., ionic strength, pH) may have been impacting the results. More perchlorate ion was formed in the sodium hypochlorite solution having higher initial hypochlorite ion concentration than those with lower concentration. The test solutions with higher initial hypochlorite ion concentration appeared to produce similar perchlorate ion concentration initially but began to deviate with time (Figure 3.6). To verify that the samples were indeed constant in molar product of $[OCl^-]$ and $[ClO_3^-]$, the measured concentrations were used to calculate the changes in molar product over time. Changes in the molar product of hypochlorite and chlorate ions over the experimental incubation period are listed in Tables 3.1 and 3.2, while the data are presented graphically in Figure 3.7.

Table 3.1

Changes in constant-molar-product experiments over incubation period at 30 ºC

Day	$[OCl^-]x[ClO_3^-]$: 1.64 M x 0.18 M	$[OCl^-]x[ClO_3^-]$: 0.99 M x 0.30 M	$[OCl^-]x[ClO_3^-]$: 0.20 M x 1.49 M
0	0.291	0.295	0.302
11	0.347	0.303	0.302
21	0.362	0.303	0.295
34	0.372	0.307	0.284
49	0.385	0.326	0.304
63	0.360	0.327	0.301
80	0.328	0.284	0.290
90	0.315	0.276	0.284
200	0.210	0.254	0.261

Table 3.2

Changes in constant-molar-product experiments over incubation period at 50 ºC

Day	$[OCl^-]x[ClO_3^-]$: 1.68M x 0.16 M	$[OCl^-]x[ClO_3^-]$: 1.01M x 0.26 M	$[OCl^-]x[ClO_3^-]$: 0.20 M x1.32 M
0	0.258	0.230	0.197
1	0.336	0.284	0.276
2	0.381	0.276	0.262
3	0.376	0.286	0.260
6	0.352	0.253	0.246
8	0.297	0.240	0.235
10	0.266	0.234	0.240

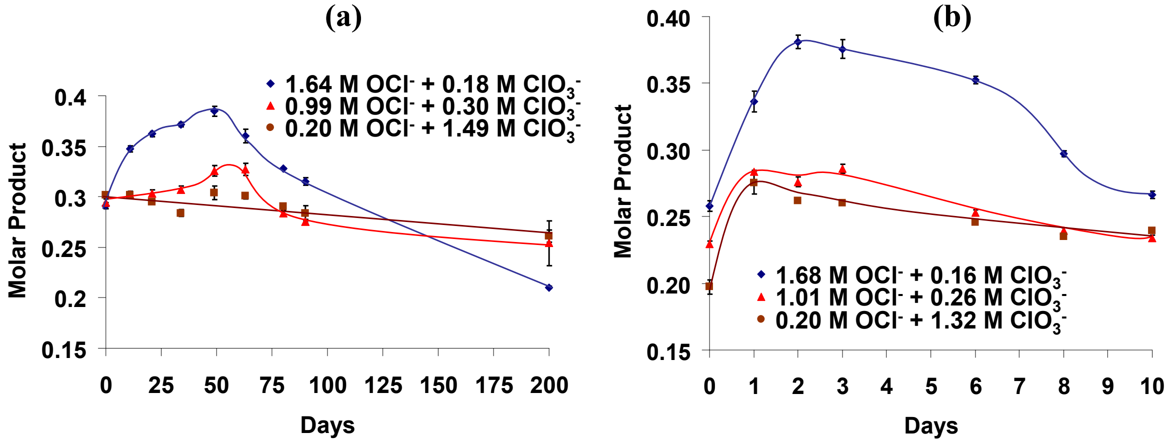


Figure 3.7 Changes in molar product of $[OCl^-]$ x $[ClO_3^-]$ (a) 30 ºC, (b) 50 ºC

The discrepancy in the perchlorate ion formation results between the three sets of constant molar-product experiments and the fact that initial molar products were within 10% suggests several possibilities: (1) The order with respect to hypochlorite may be higher than one. This can be inferred in part from the observation that in the two lowest [OCl$^-$] concentration samples, the changes in molar product were in better agreement than the high [OCl$^-$] concentration sample. Such a result suggests a dependence on hypochlorite ion concentration which is different from the dependence on chlorate ion. Thus, the order of perchlorate formation may still be one with respect to chlorate. (2) The rate of perchlorate formation may be dependent on another variable not considered during the initial design of the constant-molar-product experiments. One would expect that as a concentrated sodium hypochlorite solution is diluted (even with subsequent addition of sodium chlorate), the ionic strength and/or pH would also change. Indeed this was the case: Table 3.3 shows the ionic strength variance with dilution of the stock concentrated sodium hypochlorite solution. While pH did not vary by more than 0.8 pH units, the ionic strength varied by nearly 3 fold during dilution. Thus, ionic strength was suspected as an important factor in determination of the rate law for perchlorate formation.

Table 3.3
Ionic strength and constant-molar-product experiments at 30 and 50 ºC

30 ºC Experiment:	**[OCl$^-$]**	**[ClO$_3^-$]**	**Ionic strength (M)**	**pH**
[OCl$^-$]x[ClO$_3^-$]: 1.64M x 0.178M	1.637	0.178	6.50	12.88
[OCl$^-$]x[ClO$_3^-$]: 0.986M x 0.298M	0.977	0.302	4.23	12.69
[OCl$^-$]x[ClO$_3^-$]: 0.197M x 1.49M	0.209	1.454	2.86	12.13
			Mean	12.57± 0.39
50 ºC Experiment:				
[OCl$^-$]x[ClO$_3^-$]: 1.68M x 0.158M	1.658	0.156	6.31	12.89
[OCl$^-$]x[ClO$_3^-$]: 1.01M x 0.264M	1.008	0.228	4.20	12.69
[OCl$^-$]x[ClO$_3^-$]: 0.202M x1.32M	0.196	1.006	2.66	12.11
			Mean	12.56± 0.41

Chlorite Ion Effects

Chlorite ion concentration typically reaches steady state in hypochlorite solutions and is an intermediate in the formation of chlorate (Lister 1956; Adam, et al. 1992; Adam and Gordon 1999). Thus, when sodium chlorite is added to a sodium hypochlorite solution, chlorite ions can be expected to react with hypochlorite to produce chlorate ions based on the reactions described in Equations 3.5 and 3.6:

$$OCl^- + OCl^- \rightarrow ClO_2^- + Cl^- \qquad k_{ClO2-}\text{(slow)} \qquad \textbf{(3.5)}$$

$$OCl^- + ClO_2^- \rightarrow ClO_3^- + Cl^- \qquad k_{ClO3-}\text{ (fast)} \qquad \textbf{(3.6)}$$

To determine whether chlorite ion could represent an additional perchlorate ion formation pathway, chlorite ion was spiked at 15 g/L with and without an additional spike of chlorate ion at 100 g/L. Formation of perchlorate for the 30 ºC and 50 ºC incubation studies is shown in Figure 3.8. Figure 3.9 shows the change in perchlorate ion concentration overlaid with changes in the molar product at each temperature. Decomposition of hypochlorite ion overlaid with the formation of chlorate ion is shown in Figures 3.10. The data indicate the addition of chlorite ion does not appear to offer a substantial change in perchlorate formation beyond what would be observed from the addition of chlorate ion represented in Equations 3.5 and 3.6. This is especially evident when the molar product of chlorate and hypochlorite are considered (Figure 3.9 (a, b)), showing nearly identical changes over time.

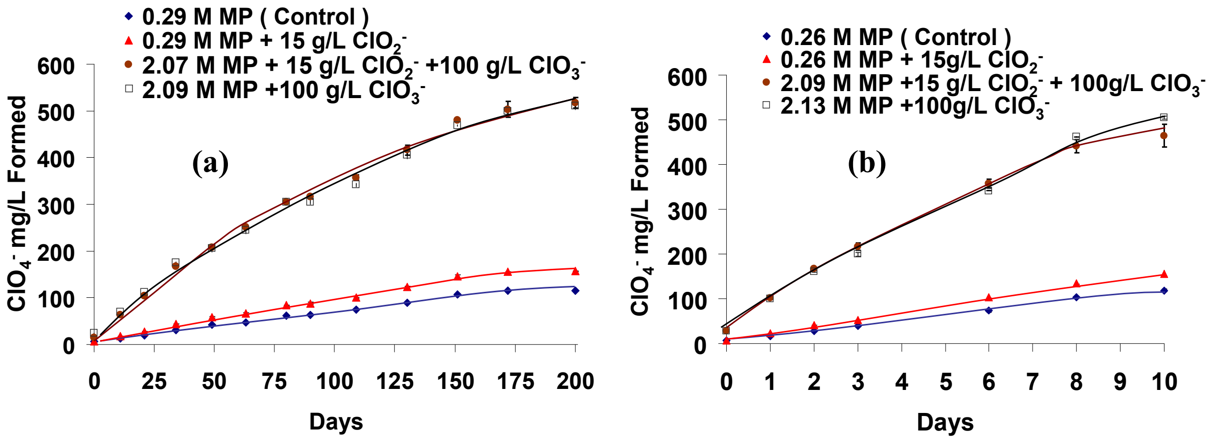


Figure 3.8 Formation of perchlorate measured by LC-MS/MS, effects of chlorite, (a) 30 ºC, (b) 50 ºC (MP = $[OCl^-]X[ClO_3^-]$)

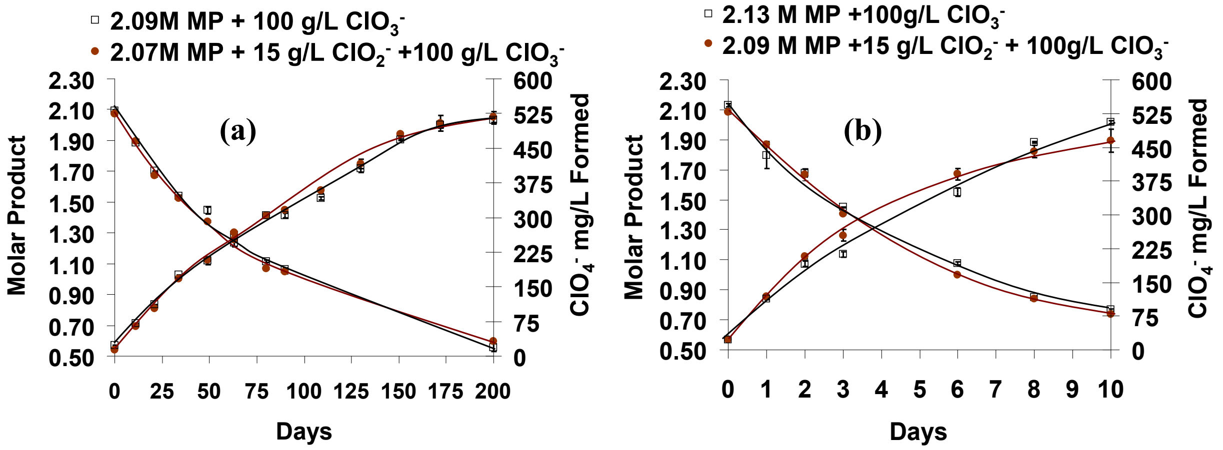


Figure 3.9 Comparison of changes in molar product (MP = $[OCl^-]X[ClO_3^-]$) over time and the concomitant formation of perchlorate, effects of chlorite, (a) 30 ºC, (b) 50 ºC

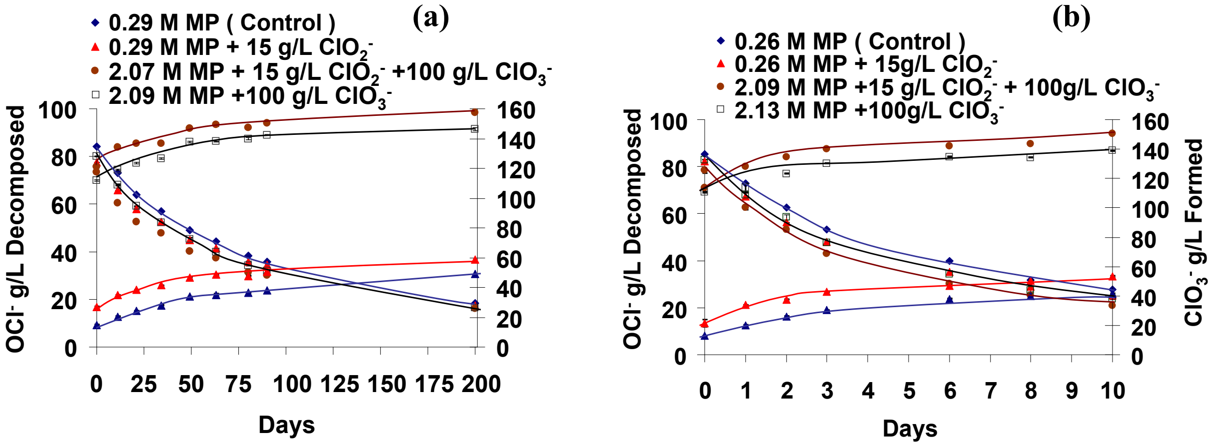


Figure 3.10 Decomposition of hypochlorite and formation of chlorate measured by titration effects of chlorite, (a) 30 ºC, (b) 50 ºC (MP = $[OCl^-]X[ClO_3^-]$)

In summary, ClO_2^- reacts with OCl^- to form ClO_3^-, affecting the formation of ClO_4^- in two ways: The first effect is due to the conversion of chlorite ion to chlorate ion, enhancing the formation of perchlorate ion. The second effect, however, occurs at the same time whereby hypochlorite ion concentration is concomitantly reduced, thus decreasing the rate of formation of perchlorate ion. The combined outcome is that more perchlorate ion formation can be observed in chlorite ion-spiked hypochlorite solutions than control solutions. However, in samples spiked with both chlorite ion and high levels of chlorate ion, this effect is not as significant. The lower accumulation of perchlorate ion correlates to observed similarities in the molar product of the chlorate ion-spiked sample and chlorite/chlorate ion-spiked sample. The addition of chlorite ion does not enhance the rate of perchlorate ion formation mechanistically, however. Thus, it was determined that chlorite ion concentration was neither a significant factor in the kinetics of perchlorate ion formation nor in determination of the chemical rate law.

Metal Ion Effects

The potential catalytic effect of transition metal ions was initially investigated at 75 ºC and evaluated the combined effects of Co^{2+}, Cu^{2+}, Fe^{3+}, Mn^{2+}, and Ni^{2+} at 20 mg/L final concentration. At this combination of temperature and concentration, the decomposition reaction of hypochlorite was too rapid to measure, and thus the effects (if any) of transition metals on the actual formation of perchlorate could not be observed. In a follow-up incubation study, 2 mg/L and 0.2 mg/L concentrations of metals were used in spiked hypochlorite solutions. Figure 3.11 (a) shows the concurrent loss of hypochlorite ion and formation of chlorate ion in the presence of transition metal ions. These results indicate that the metal ions catalyze a rapid decomposition of hypochlorite (as previously described by Adam 1994; Gordon, et al. 1997; Adam and Gordon 1999), overwhelming any possible effects that might have been observed during the catalysis of perchlorate formation. Therefore, rather than catalyzing perchlorate formation, the presence of the metal ions actually assist in the minimization of perchlorate ion formation at the expense of a loss of hypochlorite ion concentration in the hypochlorite solution as shown in Figure 3.11 (b).

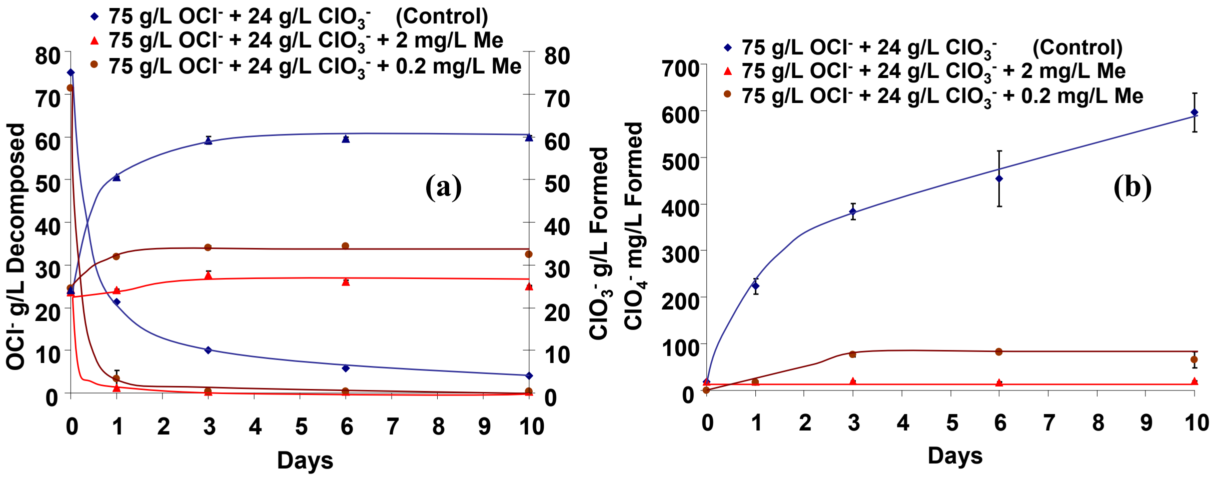


Figure 3.11 Effects of transition metals ions (Me = Co^{2+}, Cu^{2+}, Fe^{3+}, Mn^{2+}, Ni^{2+}): (a) decomposition of hypochlorite (downward sloping curves) & formation of chlorate (upper curves); (b) formation of perchlorate

The combined effects of chlorite ion, transition metals ions (Co^{2+}, Cu^{2+}, Fe^{3+}, Mn^{2+}, and Ni^{2+}), and bromide ion on formation of perchlorate and chlorate were also investigated by incubating liquid hypochlorite samples at 50 ºC with the following amounts of chlorite ion, chlorate ion, and/or transition metal ion spikes, in duplicate:

Spike 1: ClO_2^- at 15 g/L + Transition Metals Spike at 0.2 mg/L

Spike 2: ClO_2^- at 15 g/L + ClO_3^- Spike at 100g/L + Transition Metals Spike at 0.2 mg/L

Spike 3: ClO_2^- spike at 15 g/L + Br^- at 15 g/L

Figure 3.12 shows the average concentration of perchlorate vs. time for each of the spike experiments listed above. As predicted from previous experiments, the addition of chlorite with the transition metal ions does not appear to have a synergistic effect on the formation of perchlorate, though the high chlorate/chlorite ion spike was able to increase the rate of perchlorate ion production beyond that of the control (likely due to the dependence upon chlorate ion concentration).

As a follow-up experiment, noble metals ions were spiked into sodium hypochlorite solutions as a group (Ag^+, Au^+, Ir^+, Pd^+, Pt^+) at 0.2 mg/L while iridium ion was also spiked alone into a second set of solutions at 0.2 mg/L:

Spike 4: Noble Me Ions (Ag^+, Au^+, Ir^+, Pd^+, Pt^+) at 0.2 mg/L

Spike 5: Iridium Ion (Ir^+) at 0.2 mg/L

Table 3.4 provides perchlorate ion concentration results tabulated per day, showing no effect from the presence of noble metal ions on perchlorate ion formation. These data are represented graphically in Figure 3.13, lending further evidence to the lack of involvement by the tested noble metal ions on hypochlorite decomposition and perchlorate formation. Perchlorate ion concentration in spiked samples and control samples appears to be of the same statistical data set (i.e, as if replicate samples of the same hypochlorite ion solution), leading to the conclusion that the noble metal ions at 0.2 mg/L concentration have very little or no effect.

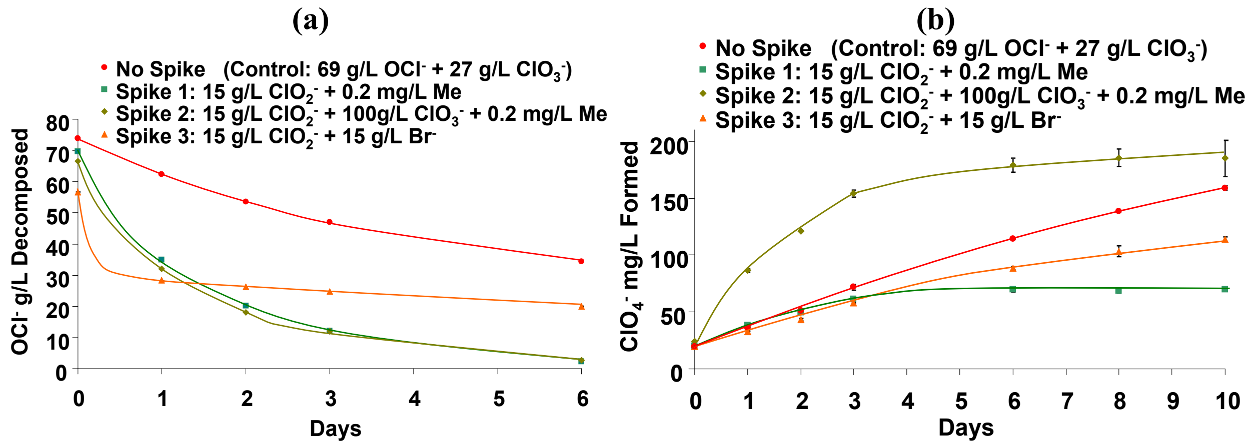


Figure 3.12 Effects of transition metals ions spikes (Me = Co^{2+}, Cu^{2+}, Fe^{3+}, Mn^{2+}, Ni^{2+}), 1.7 M hypochlorite, at 50 °C, (a) decomposition of hypochlorite; (b) formation of perchlorate

Table 3.4

Change in perchlorate concentration over the duration of incubation study 5-C with 1.7 M hypochlorite at 50 °C

Perchlorate results (mg/L)	**Day**						
	0	1	2	3	6	8	10
Spike 4: 0.2mg/L Noble Me	20.4	37.6	50.5	71.5	108	135	161
Spike 4: 0.2mg/L Noble Me (Duplicate)	20.7	37.1	52.0	70.9	112	137	150
Spike 5: 0.2mg/L Ir	19.7	40.3	54.0	69.5	115	128	161
Spike 5: 0.2mg/L Ir (Duplicate)	20.2	40.5	52.0	72.5	115	140	162
No spike: Control	20.0	34.6	52.0	74.4	114	138	157
No spike: Control (Duplicate)	19.9	37.8	50.0	69.4	115	139	161
Mean	**20.1**	**38.0**	**52.0**	**71.4**	**113**	**136**	**159**
Std. Dev.	**0.4**	**2.2**	**1.4**	**1.9**	**2.8**	**4.4**	**4.6**
RSD	**2.0**	**5.8**	**2.7**	**2.7**	**2.5**	**3.2**	**2.9**

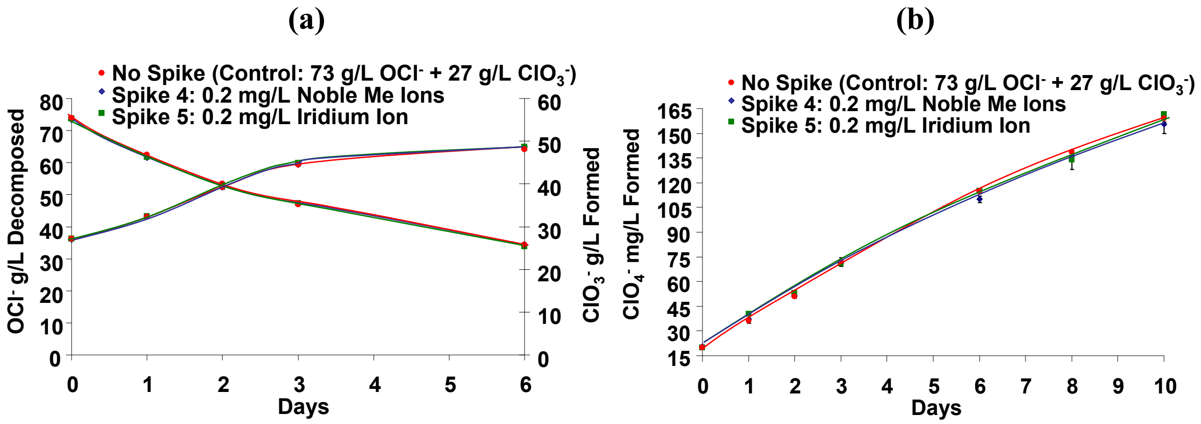


Figure 3.13 Effects of noble metals ions (Noble Me Ions =Ag^+, Au^+, Ir^+, Pd^+, Pt^+) spikes, 1.7 M hypochlorite, 50 ºC (a) decomposition of hypochlorite; (b) formation of perchlorate

In summary, transition metals are unable to enhance perchlorate ion formation because they catalyze a rapid decomposition of hypochlorite ion which is needed to form perchlorate. Thus, perchlorate can theoretically be minimized under conditions which also result in a loss of hypochlorite (though this would be disadvantageous for the utility). Chlorite and transition metals do not appear to have a synergistic effect on formation of perchlorate. Hypochlorite solutions spiked with both contaminants produced perchlorate levels significantly lower than control solution. Noble metal ions spiked at 0.2 mg/L also showed little or no effect on the amount of perchlorate formed.

Bromide and Bromate Ion Effects

The effects of bromide and bromate on formation of perchlorate, bromate, and chlorate were investigated by incubating 13% bulk hypochlorite samples at 50 °C spiked with the following amounts of bromide and/or bromate, in duplicate:

Br^- Spike at 15 g/L, BrO_3^- Spike at 15 g/L, or Br^- + BrO_3^- Spike at 15 g/L

Br^- Spike at 30 g/L, BrO_3^- Spike at 30 g/L, or Br^- + BrO_3^- Spike at 30 g/L

Bromate ion concentration over time was monitored by LC-MS/MS and is shown in Figure 3.14-(a) while the change in hypochlorite ion concentration is shown in Figure 3.14 (b). Change in perchlorate ion concentration is shown in Figure 3.15.

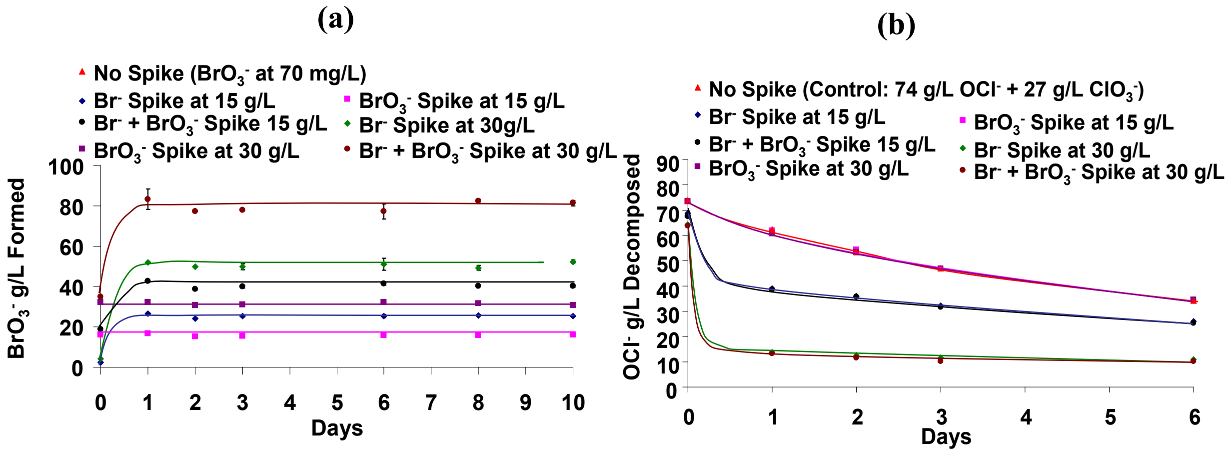


Figure 3.14: Effects of bromide and bromate, 1.7 M hypochlorite, 50 ºC, (a) formation of bromate, (b) decomposition of hypochlorite

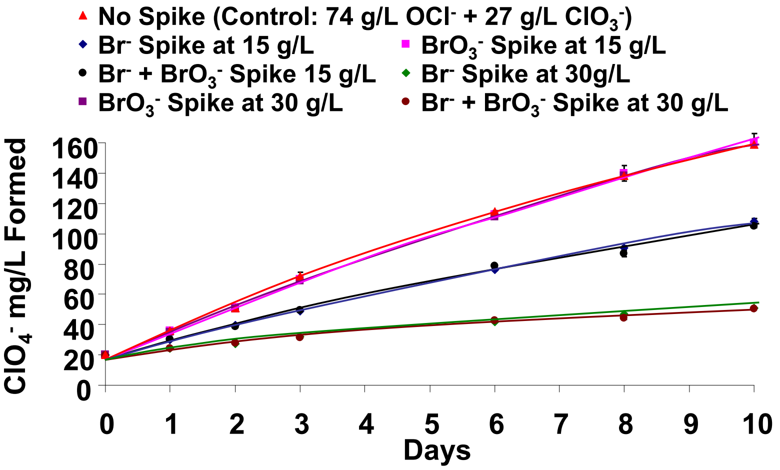
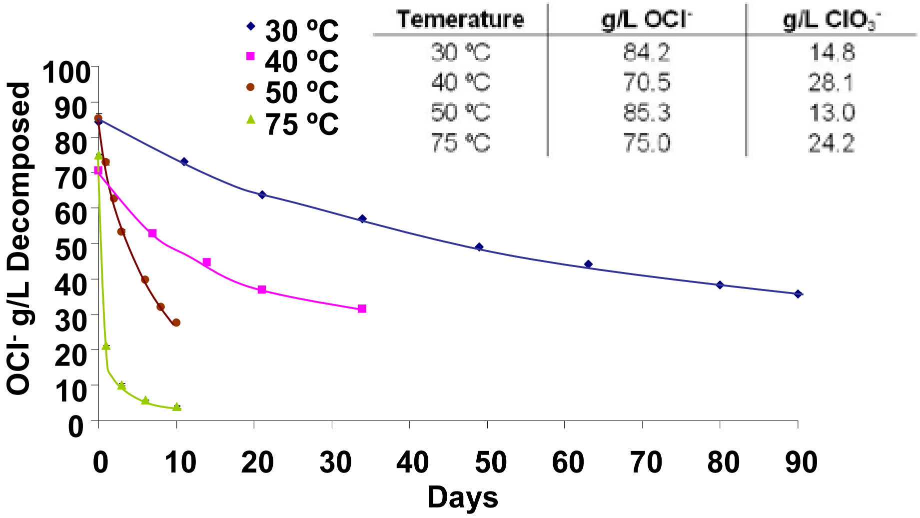


Figure 3.15 Formation of perchlorate as measured by LC-MS/MS, bromide and bromate spikes, 1.7 M hypochlorite, 50 ºC

It is clear from the data that bromide ion rapidly reacts (within 1 day) with hypochlorite ion to produce bromate, hypothetically via the formation of hypobromite in a reaction mechanism similar to that of chlorate ion. The formation of perchlorate ion over time (Figure 3.15) is largely unaffected by the presence of bromate ion in solution. The presence of bromide ion did reduce the amount of perchlorate ion formed, but is likely not directly related to bromide. Instead, the reduction in the rate of perchlorate ion formation is likely due to the loss of hypochlorite ion in a reaction of bromide to produce bromate, thereby reducing the amount of hypochlorite available to produce perchlorate. The effect of the presence of bromide ion is similar to that of the transition metals ions in the sense that both types of contaminant react with available hypochlorite to produce species different than the perchlorate (e.g., transition metal catalyze decomposition of hypochlorite to produce oxygen gas, bromide is converted to bromate), thereby reducing the available hypochlorite ion for perchlorate ion formation.

Temperature Effects

The decomposition of sodium hypochlorite solutions is strongly dependent on temperature. Both the rate of hypochlorite decomposition and the rate of chlorate formation increase with increase in temperature as observed in each of the studies listed in this Chapter (see also Figures 3.16 and 3.17) and elsewhere. The effects of temperature and ionic strength have been thoroughly investigated and a comprehensive predictive model has been developed (Adam and Gordon 1999). In this study, the effect of temperature on the formation of perchlorate ion over time was also investigated. Multiple hypochlorite solutions were incubated at temperatures ranging from 30 ºC to 75 ºC in order to quantify the relationship between perchlorate ion formation and temperature. Results of changes in perchlorate ion concentration from several of the studies are summarized in Figure 3.18 (hypochlorite and chlorate ion concentrations form the same experiments are summarized in Figures 3.16 and 3.17). Although the hypochlorite solutions varied in chlorate ion concentration, qualitatively one can still see that the rate of perchlorate ion formation is also strongly dependent on temperature. Thus, temperature effects were incorporated into the detailed chemical rate law discussed in Chapter 4.



Temerature	g/L OCl^-	g/L ClO_3^-
30 ºC	84.2	14.8
40 ºC	70.5	28.1
50 ºC	85.3	13.0
75 ºC	75.0	24.2

Figure 3.16 Decomposition of hypochlorite ion and formation of chlorate ion in sodium hypochlorite solutions stored at different temperature; (Initial concentrations of hypochlorite and chlorate are given in the right corner of the figure)

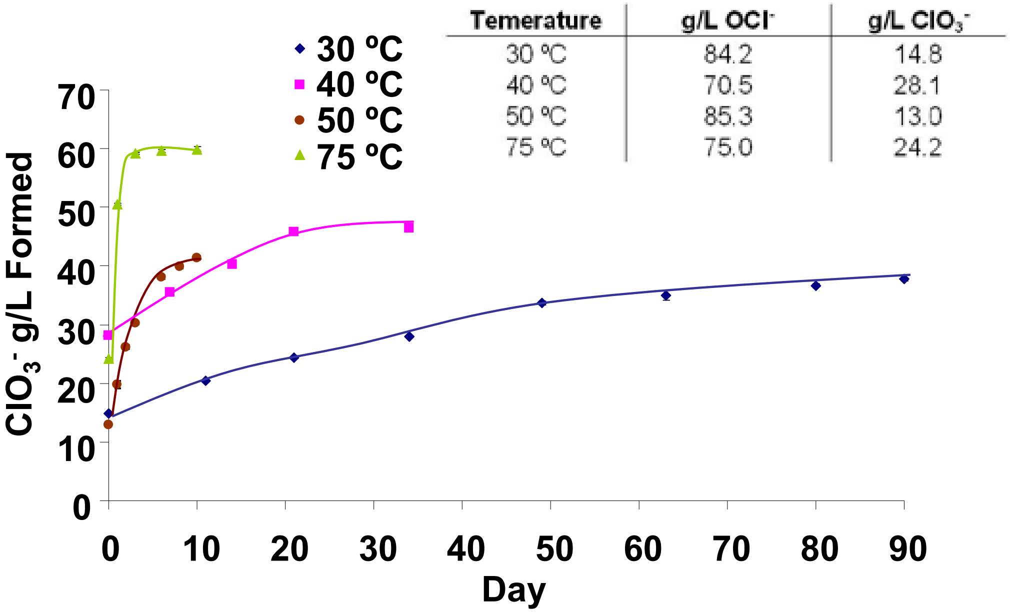


Figure 3.17 Formation of chlorate ion in sodium hypochlorite solutions stored at different temperature; (Initial concentrations of hypochlorite and chlorate are given in the right corner of the figure)

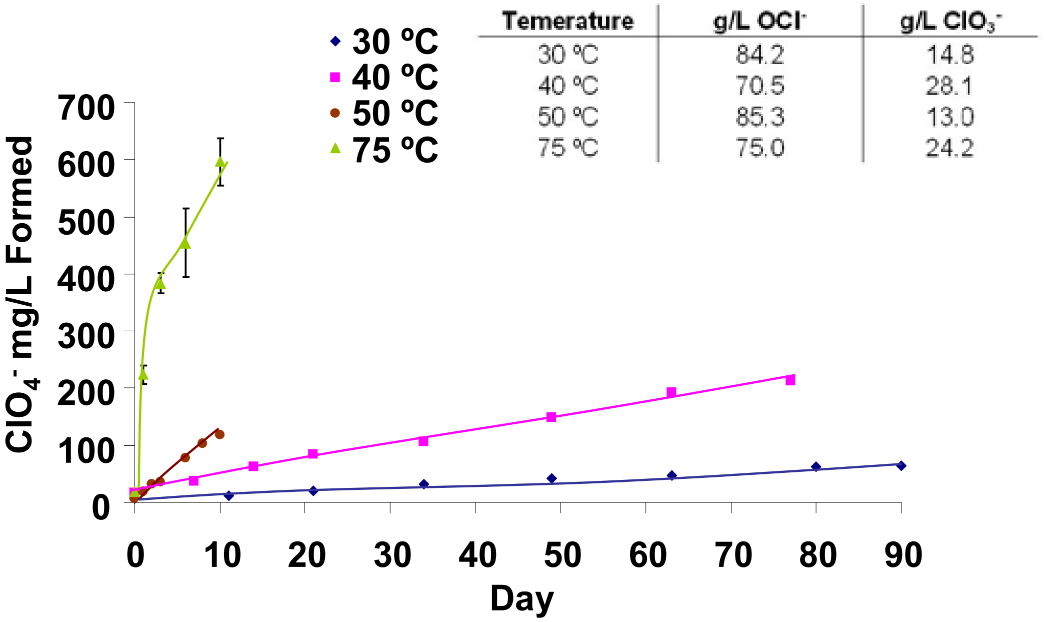


Figure 3.18 Formation of perchlorate ion in sodium hypochlorite solutions stored at different temperature; Error bars are based on difference in result of two duplicate samples; (Initial concentrations of hypochlorite and chlorate are given in the right corner of the figure)

Ionic Strength Effects

Given that higher ionic strength increases the rate of decomposition of hypochlorite ion and increases the rate of chlorate ion formation (Adam 1994; Gordon, et al. 1997; Adam and Gordon 1999), it was hypothesized that a higher ionic strength would likewise increase the rate of perchlorate ion formation. To investigate effects of ionic strength on formation of perchlorate, solutions of sodium hypochlorite were incubated at 40 ºC and 60 ºC with different ionic strengths achieved by dilution and/or spiking with sodium chloride. Three groups of samples were incubated at 40 ºC, each having varying chloride ion concentration (used to vary ionic strength), constant hypochlorite ion concentration, and a different chlorate ion concentration for each of the three groups. Another set of solutions was incubated at 60 ºC and had the same initial hypochlorite and chlorate ion concentrations but varied by sodium chloride concentration.

Figure 3.19 shows the *Bleach 2001* (Adam, Gordon, and Pierce 2001) predicted decomposition of hypochlorite ion and subsequent formation of chlorate ion when additional chloride ions are added to the solution. As expected, increasing the ionic strength by chloride ion addition increases the rates of formation of chlorate ion and disappearance of hypochlorite ion. In Figures 3.20 and 3.21, similar effects are observed on the formation of perchlorate ion with respect to ionic strength at 40 ºC and 60 ºC. In figure 3.21, the high ionic strength and high temperature resulted in a plateau of perchlorate ion concentration due to a rapid depletion of hypochlorite ion concentration. However, unlike in the metal ion experiments whereby a rapid loss of hypochlorite resulted in little additional perchlorate ion formation, here ionic strength increased the rate *and* the total amount of perchlorate ion produced in each solution. Similar impacts on hypochlorite ion, chlorate ion, and perchlorate ion concentrations were observed in each of the ionic strength – temperature paired experiments (data not shown).

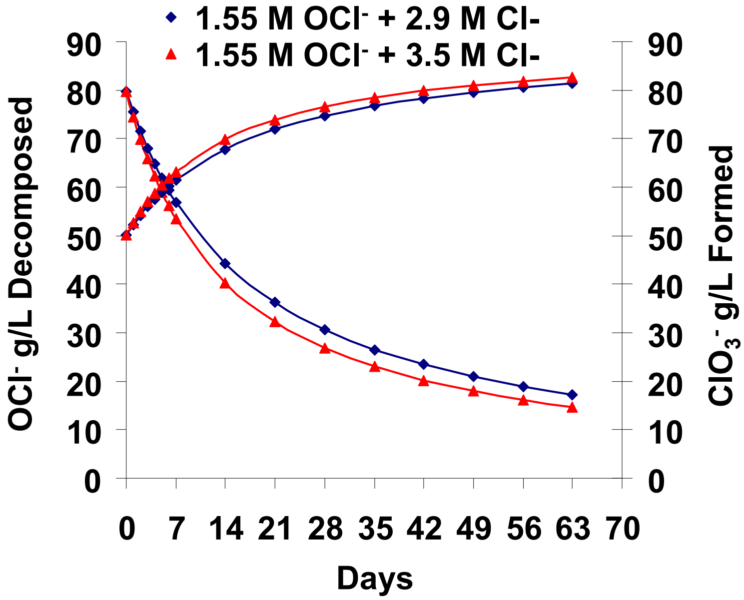


Figure 3.19 Predicted decomposition of hypochlorite ion and formation of chlorate ion in sodium hypochlorite solutions varying by concentration of chloride ion by *Bleach 2001*

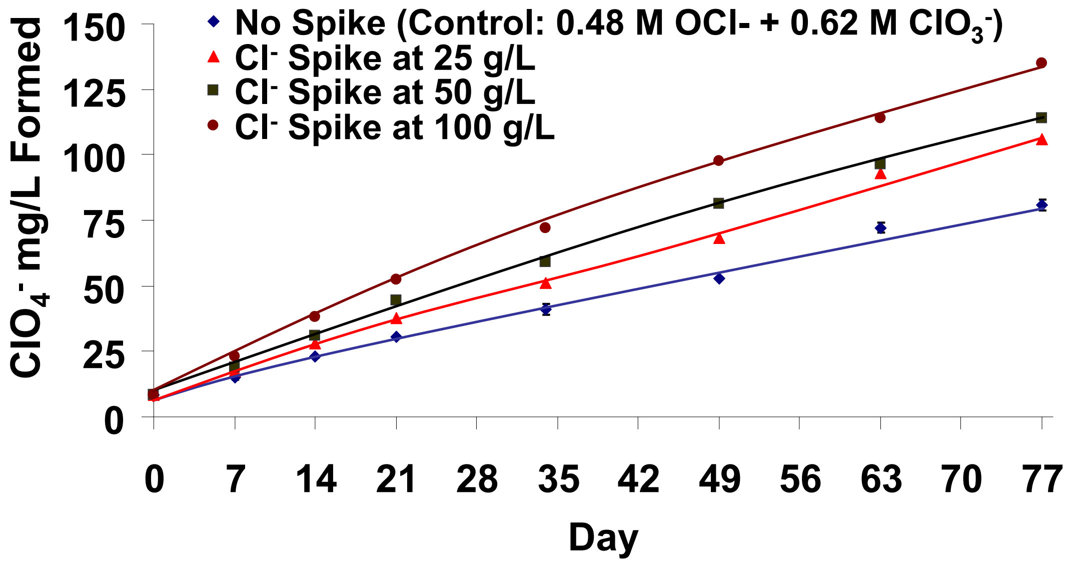


Figure 3.20 Formation of perchlorate in hypochlorite solutions spiked with variable amounts of chloride ion at 40 ºC

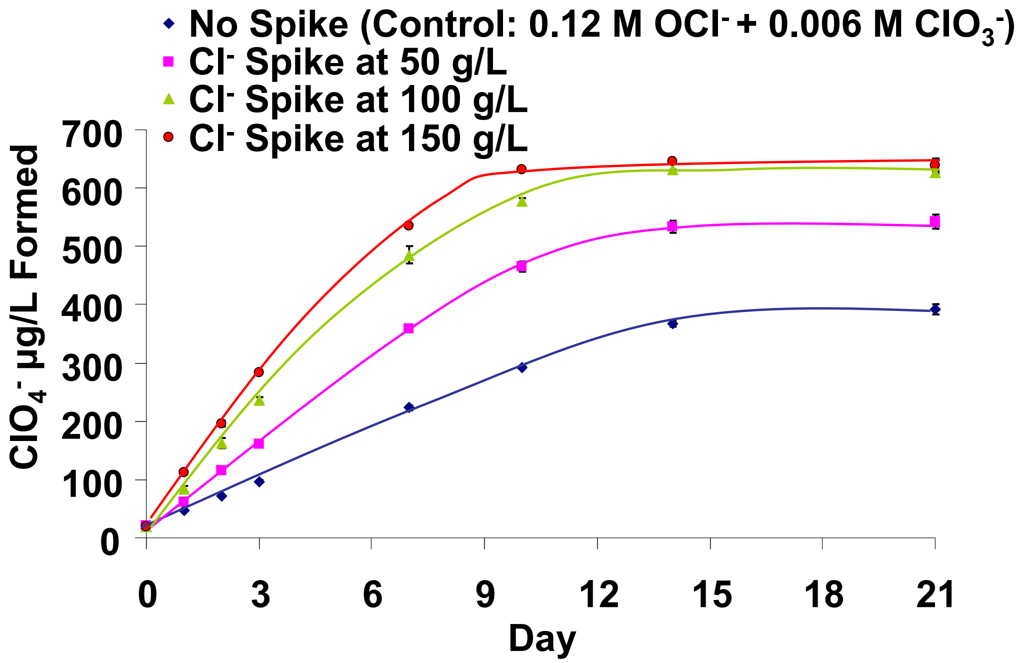


Figure 3.21 Formation of perchlorate in Hypochlorite solutions spiked with variable amounts of chloride ion at 60 ºC

Effects of pH

Sodium hypochlorite solutions are most stable in the pH 12-13 range (Adam 1994; Adam and Gordon 1999). Above pH 13, the hydroxide ion concentration exerts an ionic strength effect on the decomposition of hypochlorite ion. Below pH 11 however, an acid-catalyzed decomposition of hypochlorite ion begins to occur. At pH values lower than 10.5 this rate of decomposition continues to increase. In the pH 11 – 14 range, the decomposition of hypochlorite ion is second order in hypochlorite; in the pH 5 – 9 range, the decomposition is third order in hypochlorite. As such, there is some discontinuity that can be observed between pH of 9 and 11 in the decomposition of hypochlorite (Adam and Gordon 1999). Current guidelines recommend that sodium hypochlorite solutions should be stored in the pH 12-13 region where both the decomposition of hypochlorite ion and the formation of chlorate ion are minimized. Perchlorate ion formation, as has already been shown during the course of this report, is dependent on concentrations of hypochlorite ion, chlorate ion, and ionic strength. Thus, it is reasonable to assume that because pH affects hypochlorite ion decomposition and chlorate ion formation, pH may also affect perchlorate ion formation.

To study the pH effects on perchlorate ion formation, sodium hypochlorite solutions were prepared at three pH values (13, 11, and 9) and incubated at 40 ºC. Figure 3.22 (a) shows the changes in perchlorate ion concentration over time and Figure 3.22 (b) shows the decomposition of hypochlorite ion and formation of chlorate ion of the same sodium hypochlorite solution incubated at 40 ºC.

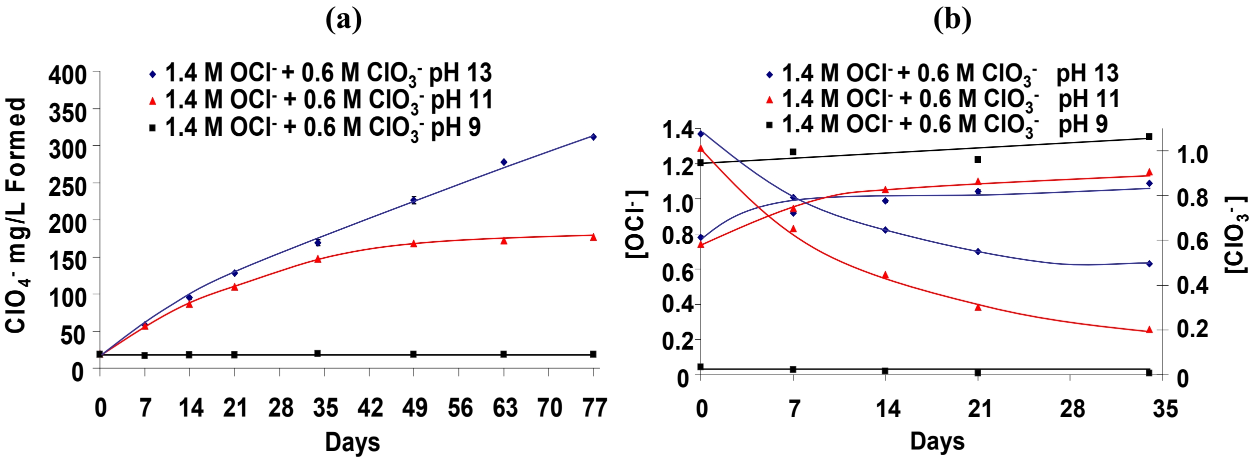


Figure 3.22 Plots of (a) perchlorate concentration vs. time; (b) hypochlorite and chlorate concentration vs. time in sodium hypochlorite solutions with initial [OCl^-] = 1.4 M and initial [ClO_3^-] =0.6 M at pH 13, 11, and 9 incubated at 40 ºC

As observed in figure 3.22 (a), the increase in perchlorate ion concentration in solution adjusted to pH 9 is not appreciable above the starting concentration. However, the data presented in Figure 3.22 (b) indicate that at pH 9 the decomposition of hypochlorite ion was so rapid that by the time of analysis only trace amounts of hypochlorite ion could be detected. Thus, the effect of pH 9 during this experiment on the rate of perchlorate ion formation was inconclusive, but indicates that decreasing the pH in concentrated sodium hypochlorite solutions may affect the rate of perchlorate formation. The same conclusion was drawn from experimental data presented in Figure 3.23 (a, b). From a practical stand point, 13% NaOCl solution at pH 12.9 has a half-life of 197 days at 25 ºC (*Bleach 2001* prediction), whereas the actual Hypochlorite solution adjusted to pH 9 decomposed in a matter of hours. Each of the pH-perchlorate figures presented here indicate that at pH values lower than 13 (which served as the control), there is less perchlorate ion formed. This result can be explained by the fact that at lower pH values the decomposition of hypochlorite ion and formation of chlorate ion are enhanced, leading to faster hypochlorite ion consumption and therefore less perchlorate ion formation.

To investigate more thoroughly the impact of pH in the 9 – 11 regions, a follow-up incubation study at 60 ºC was conducted on OSG Hypochlorite produced at SNWA (more dilute than bulk and at a lower pH) and adjusted with NaOH to vary the pH. The stock solution (control) of sodium hypochlorite had a pH of 9.35. Aliquots of this solution were adjusted to pH =10.65, 11.90 and 13.3 by addition of sodium hydroxide and then incubated at 60 ºC. As expected, the control solution at pH 9.35 had the fastest rate of hypochlorite ion decomposition, and the fastest rate of chlorate ion formation as shown in Figures 3.24 (a, b) and 3.25.

Interestingly, the rate of perchlorate ion formation was also enhanced in the sodium hypochlorite solution having an initial pH of 9.35 (Figure 3.25) though the overall perchlorate concentration at the end of the experiment was less than or the same as the other solutions tested at different pH. The hypochlorite solutions with initial pH values of 10.65 and 11.90 produced very similar amounts perchlorate ion, while solution with pH 13.30 produced more perchlorate by 21 days of incubation, and had the second fastest rate of perchlorate formation. This can be explained by the fact that the ionic strength of pH=13.30 solution was significantly higher than the rest. Table 3.5 shows ionic strength and total dissolved solids of each solution derived from specific conductance measurements.

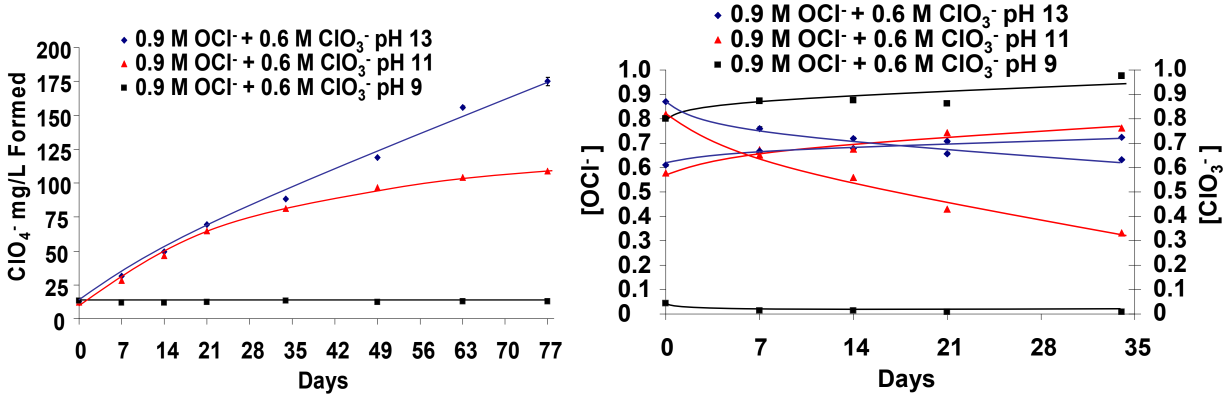

(a) (b)

Figure 3.23 Plot of (a) perchlorate concentration vs. time in sodium; (b) hypochlorite and chlorate concentration in hypochlorite solutions with initial [OCl$^-$] = 0.9 M and initial [ClO$_3^-$] = 0.6 M at pH 13, 11, and 9, incubated at 40 ºC

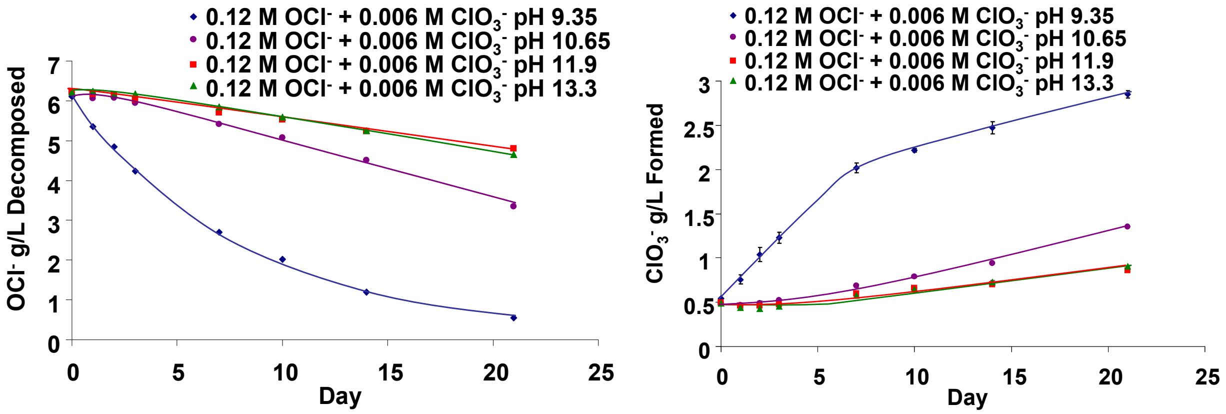

(a) (b)

Figure 3.24 Effect of pH on hypochlorite decomposition (a) and chlorate formation (b) in OSG hypochlorite solutions at 60 ºC

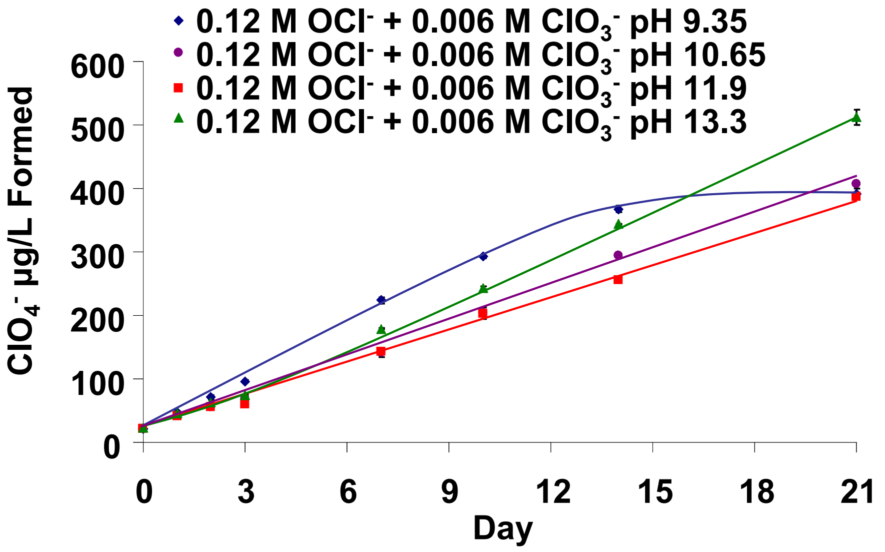


Figure 3.25 Effect of pH on perchlorate formation in OSG hypochlorite solutions at 60 ºC

Enhancement of the initial rate of perchlorate ion formation at pH 9.35 suggests that there may be a pH dependence. However, over time the amount of perchlorate produced at this pH compared to higher pH is less due to the more rapid decrease in hypochlorite ion concentration at the lower pH. From a practical standpoint, the pH effect is not significant since most of bulk sodium hypochlorite solutions have a pH above 11 and OSG Hypochlorite is rarely stored for more than 24 to 48 hours. Furthermore, the impact of ionic strength observed from adjusting the pH with sodium hydroxide points towards the issue of ionic strength acting as a "master variable" (in addition to hypochlorite ion concentration and chlorate ion concentration) that outweighs any pH effects that might be observed.

Table 3.5

Ionic strength and Total Dissolved Solids (TDS) of sodium hypochlorite solutions with initial $[OCl^-]=0.120 \pm 0.001M$ (Measured by titration), $[ClO_3^-]=0.006 \pm 0.0003$ (measured by LC-MS/MS) with pH adjusted using NaOH

pH	$[OCl^-]$	$[ClO_3^-]$	Ionic strength, M	TDS, g/L
9.35	0.118_4	0.006_5	**0.89**	**35.6**
10.65	0.120_3	0.005_9	**0.88**	**35.2**
11.9	0.120_9	0.006_0	**0.90**	**36.1**
13.3	0.120_9	0.005_8	**2.57**	**103.0**
Mean	**0.120**	**0.006_0**		
Std. Dev.	0.001	0.000_3		
RSD	1.00	4.96		

SUMMARY

The data presented in this Chapter represent the experimental work designed to determine the factors impacting perchlorate ion formation in sodium hypochlorite solutions. The effect investigated included: concentration of hypochlorite and chlorate ions, concentration of chlorite ion, metal ion effects, bromide and bromate ion effects, temperature, ionic strength, and pH. The effects of each of these factors can be grouped into four major categories: (1) Factors directly (mechanistically) impacting the rate of perchlorate formation; (2) Factors indirectly impacting the rate of perchlorate formation by changing hypochlorite ion or chlorate ion concentrations; (3) Factors having no observable effect on perchlorate formation; and (4) Environmental factors.

1. Factors directly (mechanistically) impacting the rate of perchlorate formation

    a. Hypochlorite ion concentration: higher concentration results in a faster rate of perchlorate formation

    b. Chlorate ion concentration: higher concentration results in a faster rate of perchlorate formation

    c. Ionic strength: higher ionic strength results in a faster rate of perchlorate formation

2. Factors indirectly impacting the rate of perchlorate formation by changing hypochlorite ion or chlorate ion concentrations

    a. Metal ions, rather than catalyzing perchlorate formation, actually assist in the minimization of perchlorate ion formation at the expense of a loss of hypochlorite ion concentration in the Hypochlorite solution.

    b. The presence of bromide ion reduces the rate of perchlorate ion formation by consuming hypochlorite ion for the production of bromate ion. Thus, less hypochlorite ion is available for perchlorate ion formation.

    c. Addition of chlorite ion does not enhance the rate of perchlorate ion formation mechanistically. However, chlorite did impact the concentration of hypochlorite and chlorate ions, thereby causing an incremental increase in perchlorate ion formation.

3. Factors having no observable effect on perchlorate formation

    a. BrO_3^-, Ag(I), Au(I), Ir(I), Pt(I), and Pd(I) had no observable effect either on the perchlorate formation, hypochlorite decomposition, or chlorate formation

4. Environmental factors

    a. The impact of pH clearly changes the rate of decomposition of hypochlorite ion. While it is possible that there is a mechanistic consideration in the formation of perchlorate ion, from a practical standpoint pH is considered an indirect, environmental factor that can be adjusted as needed.

b. Temperature clearly impacts the rate of perchlorate ion formation in addition to the rate of hypochlorite ion decomposition and chlorate ion formation. However, temperature can be adjusted/controlled to some extent, thus was considered an environmental factor

Based on the observations listed above, the controlling variables in the rate of perchlorate ion formation are concentration, ionic strength, temperature, and pH. From a practical standpoint, pH can be ruled out as a contributing factor because it is expected that only bulk hypochlorite solutions with a pH of 11 to 13 will be stored for any period of time. Thus, one environmental factor and three mechanistic factors remain. Any change in concentration of hypochlorite or chlorate strongly impacted the rate of perchlorate formation. However, the inclusion of constant molar product of hypochlorite and chlorite ions into the experimental matrix led to two possible scenarios: the order with respect to hypochlorite may be higher than one OR the rate of perchlorate formation may be dependent on another variable not considered during the initial design of the constant-molar-product experiments (e.g., ionic strength). Therefore, the determination of the rate law of perchlorate ion formation discussed in the next Chapter incorporates considerations of concentrations of hypochlorite and chlorate ions as well as accounting for environmental factors such as ionic strength and temperature.

REFERENCES

Adam, Luke, Gilbert Gordon, and Don Pierce. 2001. *Bleach 2001*. Miami University, Oxford, Ohio. Copyright (c) 2001 AwwaRF and AWWA.

Adam, Luke C., Istvhn Fabian, Kazunoru Suzuki, and Gilbert. Gordon. 1992. Hypochlorous Acid Decomposition in the pH 5-8 Region. *Inorganic Chemistry*, 31 (17):3534-3541.

Adam, Luke C. 1994. An Investigation of the Factors Involved in the Decomposition of Sodium Hypochlorite, A Ph.D. Dissertation, Department of Chemistry, Miami University, Oxford, OH.

Adam, Luke C. and Gilbert Gordon. 1999. Hypochlorite Ion Decomposition: Effects of Temperature, Ionic Strength, and Chloride Ion. *Inorganic Chemistry*, 38 (6):1299-1304.

Gordon, Gilbert, Luke C. Adam, Bernard P. Bubnis, Ching Kuo, Robert S. Cushing, and Richard H. Sakaji. 1997. Predicting Liquid Bleach Decomposition. *Journal American Water Works Association*, 89 (4):142-149.

Lister, M. W. 1956. Decomposition of Sodium Hypochlorite: The Uncatalyzed Reaction. *Canadian Journal of Chemistry*, 34:465.

CHAPTER 4
FORMULATION OF INITIAL MODEL FOR PREDICTING PERCHLORATE FORMATION IN HYPOCHLORITE SOLUTIONS

APPROACH

Detailed in the summary of Chapter 3 were two sets of factors controlling the rate of perchlorate formation: mechanistic factors (i.e., chlorate ion concentration, hypochlorite ion concentration, and ionic strength) and environmental factors (i.e., temperature). The results of constant molar-product (of hypochlorite and chlorate ions) experiments showed that sample solutions containing the highest concentration of hypochlorite had a faster rate of perchlorate formation and a greater concentration of perchlorate formed. This strongly suggests that either (1) the order with respect to hypochlorite is higher than one, or (2) the rate of perchlorate formation may be dependent on an additional variable such as ionic strength. Additionally, the data presented in Chapter 3 also suggested a strong temperature dependence for the rate of perchlorate formation. Therefore, in order to elucidate the chemical rate law and develop a "Predictive Model" the following approaches were taken to eliminate possibilities and determine the variables that best correlate with perchlorate formation:

1. Determine the reaction order with respect to hypochlorite and chlorate. Initially, assume the reaction order is one in both hypochlorite and chlorate.

2. If the rate constant of the rate law based on first order in each reactant does not correlate well with concentration, then consider a higher order for one or both reactants. If the order is higher than one, then a second reaction pathway (parallel or consecutive) should be considered. Determine whether a parallel reaction pathway or consecutive reaction pathway can be fitted.

3. Determine what correlations, if any, exist between ionic strength, temperature, and rate of perchlorate formation. In this case, the assumption of first order in hypochlorite and chlorate ions is initially used to convert the rate of perchlorate formation (change in perchlorate concentration per unit time) to the observed rate of formation (k_{obs}, which is the rate of formation normalized to the molar product of hypochlorite ion and chlorate ion concentrations). Only data from experiments conducted at the same, constant temperature are compared.

4. Determine the temperature dependence of the rate of perchlorate formation by using the Eyring Equation. From this, the enthalpy and entropy can be determined and later used to correct for variations in temperature.

5. Develop a model based on the established relationship between prediction of the perchlorate formation rate constant, ionic strength, and temperature.

6. Fit the experimental data using the determined rate constant based on various reaction pathways, and determine which reaction pathway provides the best fit.

DETERMINATION OF THE RATE LAW FOR PERCHLORATE ION FORMATION

Hypochlorite and chlorate ion concentrations were found to have a strong effect on the rate of perchlorate formation. An increase in concentration of either species consistently caused an increase in the rate and final amount of perchlorate formed. Other chemical species, such as bromide, chlorite, and transition metals were identified to have a direct impact on hypochlorite and chlorate, thereby causing changes in concentrations of hypochlorite or chlorate which affected perchlorate formation. Thus, the hypothesis that the formation of the perchlorate ion was a direct result of reactions between hypochlorite and chlorate ions (Equation 3.3, Chapter 3) was assumed correct.

$$OCl^- + ClO_3^- \rightarrow ClO_4^- + Cl^- \qquad \textbf{(3.3)}$$

Given that perchlorate formation was dependent on both concentrations of hypochlorite and chlorate the following rate law was proposed:

$$Rate = \frac{d[ClO_4^-]}{dt} = k_2[OCl^-]^m \times [ClO_3^-]^p \qquad \textbf{(3.4)}$$

A series of experiments were designed to determine the reaction order with respect to hypochlorite and chlorate ions (reported in Chapter 3, Figures 3.1, 3.3). In these experiments, either OCl^- or ClO_3^- concentration was varied while holding the concentration of the other reactant constant. The observed rate of perchlorate formation was then correlated with the concentration of each reactant by taking the natural log of Equation 3.4 to yield Equation 4.1:

$$\ln(Rate) = \ln k_2 + m\ln[OCl^-] + p\ln[ClO_3^-] \qquad \textbf{(4.1)}$$

The second order rate constant (k_2) and the value of the reaction order with respect to OCl^- and ClO_3^- (*m* and *p*, respectively) are determined by least squares data fitting. The next several pages are devoted to fitting natural log of the rate of perchlorate formation versus natural log of the chlorate and hypochlorite concentrations.

Order with Respect to Chlorate Ion: $\ln(\frac{dClO_4^-}{dt})$ vs. ln $[ClO_3^-]$

The order with respect to chlorate was determined by plotting the natural log of the rate of perchlorate formation against the natural log of the chlorate ion concentration in the experiments with constant hypochlorite ion concentration and variable chlorate ion concentration. The slope of the line represents the order with respect to chlorate (*p*) while the intercept is the sum of $\ln(k_2)$ and $m*\ln[OCl-]$ (Equation 4.1). Figure 4.1 (a-d) shows plots of ln(Rate) vs. $\ln[ClO_3^-]$ at different temperatures and incubation lengths. The slope and Pearson correlation coefficients (R^2) across all temperatures investigated are summarized in Table 4.1. As can be seen from Table 4.1, fitting ln[Rate] vs $\ln[ClO_3^-]$ in general produces linear correlation with an average R^2=0.9838, and average slope of 1.05 ± 0.105. This strongly suggests that the order of the reaction is first order with respect to chlorate ion.

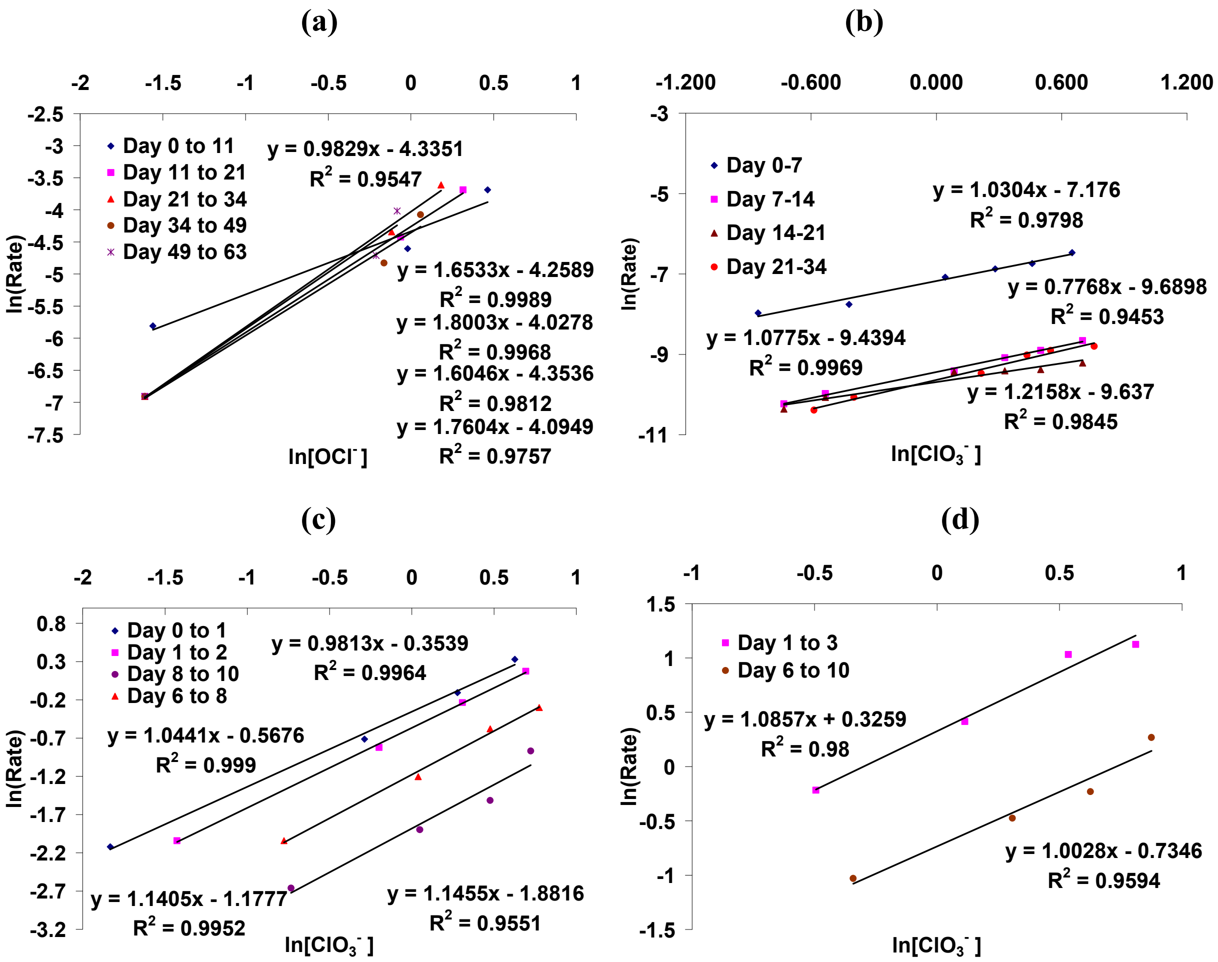


Figure 4.1 Plot of ln(Rate of perchlorate formation) vs. ln[ClO$_3^-$] at (a) 30 ºC, (b) 40 ºC, (c) 50 ºC, and (d) 75 ºC

Table 4.1
Slope and Pearson correlation coefficients for relationship between ln[Rate] and ln[ClO_3^-] at different temperatures

T, ºC	Slope	R^2
30	1.068	0.9990
30	0.999	0.9999
30	1.031	0.9983
40	1.030	0.9798
40	1.078	0.9969
40	0.777	0.9453
40	1.216	0.9845
50	0.981	0.9964
50	1.044	0.9990
50	1.146	0.9551
50	1.141	0.9952
76	1.086	0.9800
76	1.003	0.9594
Mean	**1.05 ± 0.105**	**0.9838**

Order with Respect to Hypochlorite Ion: $\ln(\frac{dClO_4^-}{dt})$ vs. ln [ClO_3^-]

The order with respect to hypochlorite was determined by plotting ln[Rate] vs ln[OCl^-] in the set of experiments with constant chlorate ion concentration and variable hypochlorite ion concentration. The slope of the line should represent the order with respect to hypochlorite (m) while the intercept is the sum of ln(k_2) and $p*\ln[ClO_3^-]$ (Equation 4.1). Figure 4.2 (a-d) shows plots of ln(Rate) vs. ln[OCl^-] at different temperatures and incubation periods. It is immediately evident from the data that the slope varies within individual experiments as well as by temperature and by time. Thus, either the order with respect to hypochlorite is greater than one or another variable is controlling the reaction rate.

Given the disagreement within the data regarding the order with respect to hypochlorite, two explanations were possible: (1) The order with respect to hypochlorite is greater than one due to second reaction pathway or (2) Another variable such as ionic strength was also impacting the rate of perchlorate formation. Thus, while new data (and data already collected) were incorporated into hypothetical considerations of higher order models in hypochlorite (with parallel or consecutive reaction pathways), additional experiments were designed to investigate the effects of ionic strength on perchlorate formation.

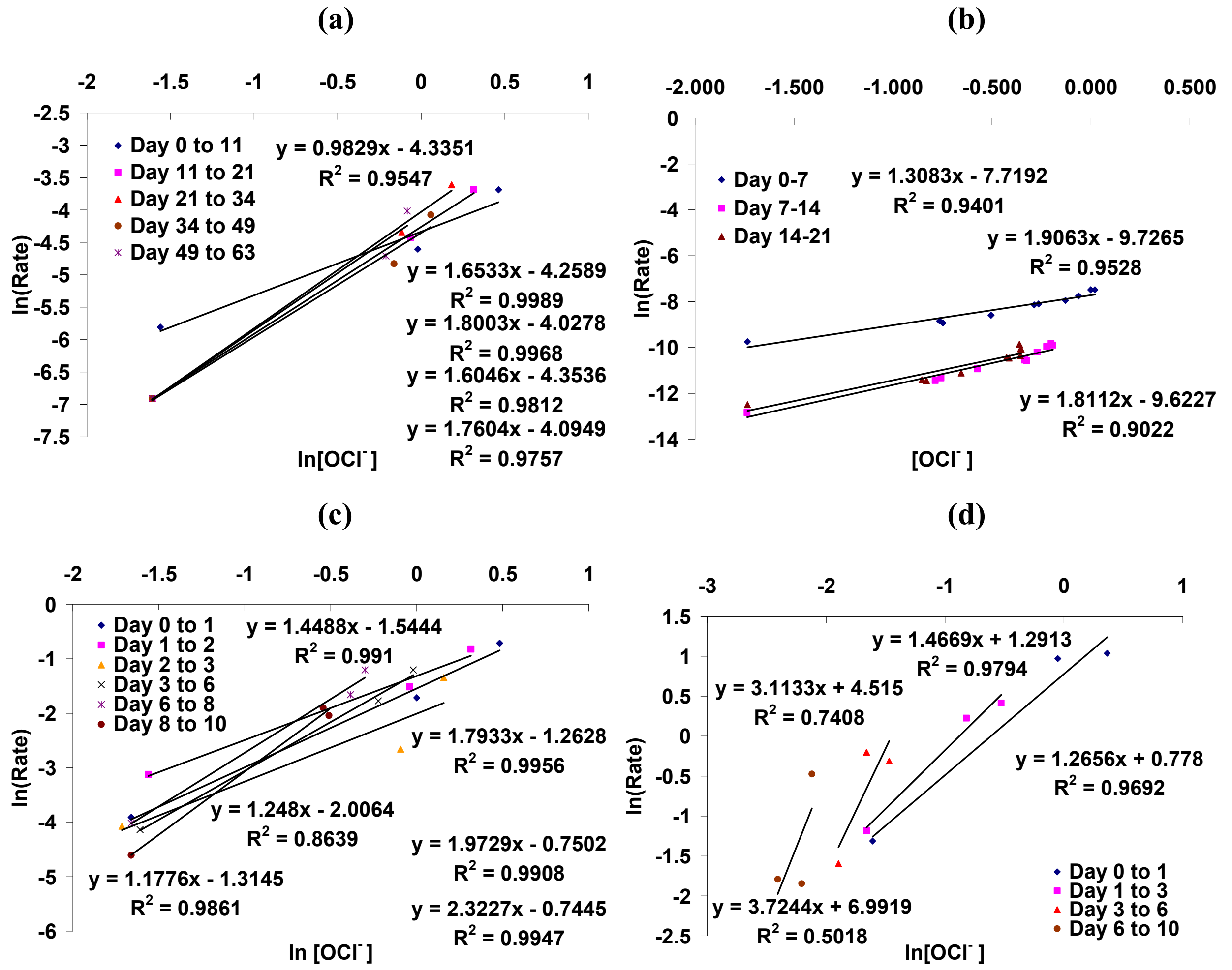


Figure 4.2 Plots of ln(Rate of perchlorate formation) vs. ln [OCl⁻] at: (a) 30 ºC , (b) 40 ºC, (c) 50 ºC, and (d) 75 ºC

Reaction Order Greater than One with Respect to Hypochlorite: Parallel or Consecutive Reaction Pathways

The variability in the order with respect to hypochlorite, suggested that the order of the perchlorate formation is higher than first order in hypochlorite ion. By taking only the initial rate of perchlorate formation from constant-chlorate-variable-hypochlorite experiments conducted at 75 ºC, 50 ºC, 40 ºC, and 30 ºC and plotting that against the log of the hypochlorite ion concentration, the slope of the line is suggestive of a reaction order of 1.6 in hypochlorite (Figure 4.3-a) and 1.0 in chlorate (Figure 4.3-b). Such an empirically-derived rate law is summarized in Equation 4.2 but does not contain any explanation of species involved in perchlorate formation nor does it take into consideration the significant contribution of ionic strength in chlorate formation (Adam and Gordon 1999) or perchlorate formation (Chapter 3).

$$Rate = \frac{d[ClO_4^-]}{dt} = k_{obs}[OCl^-]^{\sim 1.6}[ClO_3^-]^1 \qquad \textbf{(4.2)}$$

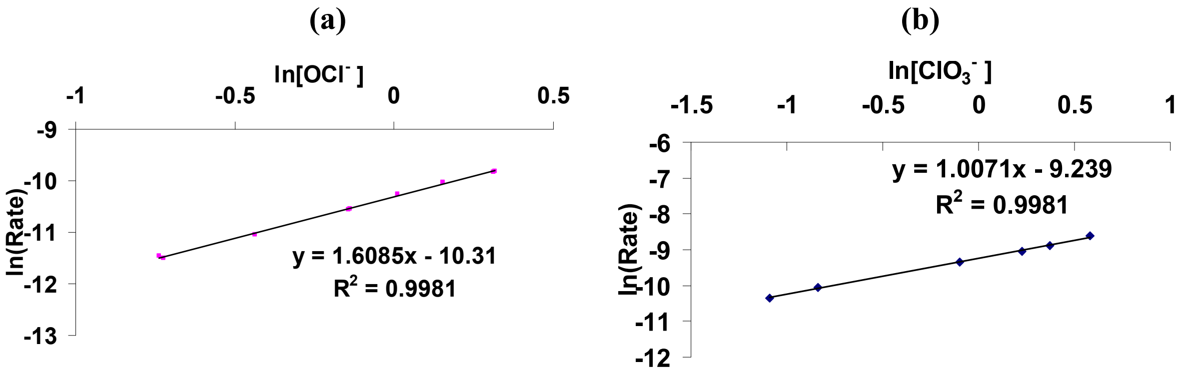


Figure 4.3 Plot of Rate vsln [OCl$^-$] (a) and ln[ClO$_3^-$] (b)

To elucidate the order with respect to hypochlorite further, and to provide more of a mechanistic explanation of the rate of formation, one area explored was the possibility of a second reaction that is second order in hypochlorite. In a parallel reaction, one pathway could be first order in hypochlorite while a second reaction could be second order in hypochlorite. In a consecutive reaction, the order with respect to hypochlorite could be second order, followed by a first order reaction (or vice versa). The hypothetical rate law equations are shown in Equation 4.3 for the parallel reaction mechanism and Equation 4.4 for the consecutive reaction mechanism.

$$Rate = \frac{dClO_4^-}{dt} = k_1[OCl^-]^1[ClO_3^-]^1 + k_2[OCl^-]^2[ClO_3^-]^1 \qquad \textbf{(4.3)}$$

$$Rate = \frac{dClO_4^-}{dt} = \frac{k_a[OCl^-]^2[ClO_3^-]^1}{1+k_b[OCl^-]^1} \qquad \textbf{(4.4)}$$

Parallel Reactions

In the investigation of a parallel reaction pathway, data from experiments that varied in concentration of hypochlorite but were constant in chlorate can be used to determine the values of k_1 and k_2. First, Equation 4.3 was rearranged by dividing by the molar product of hypochlorite and chlorate to yield Equation 4.5.

$$\frac{Rate}{[OCl^-]^1[ClO_3^-]^1} = k_1 + k_2[OCl^-]^1 \qquad \textbf{(4.5)}$$

By using Equation 4.4, when [Rate/([OCl$^-$][ClO$_3^-$])] is plotted vs. [OCl$^-$], a linear correlation will provide values of k_2 (the slope of the line) and k_1 (the intercept). Example data from the 40 ºC experiment are shown in Figure 4.4. The data shown indicate a reasonable correlation (R^2 = 0.98), but the rate law still does not account for ionic strength effects.

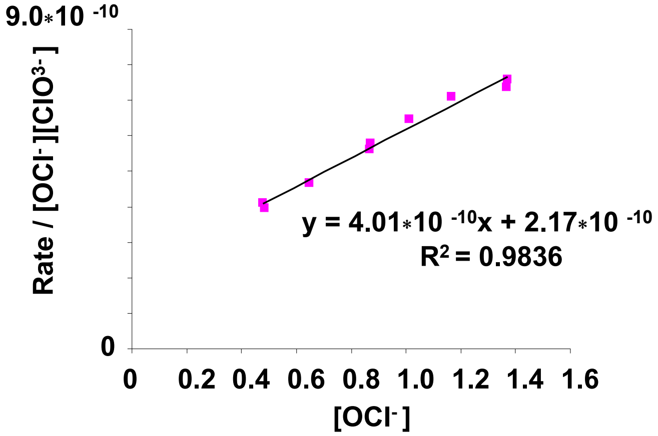


Figure 4.4 Plot of Rate/($[OCl^-][ClO_3^-]$) vs. $[OCl^-]$ at 40 ºC

Consecutive Reactions

In a consecutive reaction pathway, data from experiments that varied in concentration of hypochlorite but were constant in chlorate can also be used to determine the values of k_a and k_b. First, Equation 4.4 was rearranged to isolate hypochlorite, yielding Equation 4.6.

$$\frac{[OCl^-][ClO_3^-]}{Rate} = \frac{1}{k_a[OCl^-]} + \frac{k_b}{k_a} \qquad \textbf{(4.6)}$$

Thus, if ($[OCl^-][ClO_3^-]$)/Rate is plotted against $1/[OCl^-]$, and the correlation is linear, the slope of the line is $1/k_a$ and the intercept is the product of k_a and k_b. Example data from the 40 ºC experiment are shown in Figure 4.5. Again, a reasonable correlation of the data exists (R^2 = 0.98), though it is unclear whether this mechanism fully explains the rate of perchlorate formation, either.

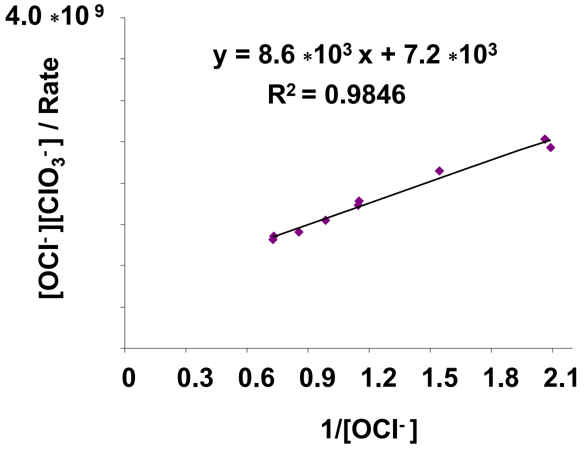


Figure 4.5 Plot of ($[OCl^-][ClO_3^-]$)/Rate vs. $1/[OCl^-]$ at 40 ºC

Ionic Strength Effect on the Observed Rate Constant

While the discussion points mentioned in the previous sections indicate the possibility of the order with respect to hypochlorite being greater than one and that either parallel or consecutive reaction pathways could be used to explain the formation of perchlorate, a simpler explanation could involve the incorporation of ionic strength into a first order reaction in both hypochlorite and chlorate (second order overall). Similar to the parallel and consecutive reaction pathways, ionic strength correlates reasonably well to the rate of perchlorate formation (Figure 4.6). With ionic strength as the simplest explanation for the deviation in observed reaction order, a measure of the variability of ionic strength across experiments was required to further quantify the relationship. Thus, an *a posteriori* measurement of ionic strength for each incubation study sample was made by taking measurements of conductivity and converting them to ionic strength by Equation 2.12. The data are compiled in Table 4.2 for the constant chlorate concentration experiments and Table 4.3 for the constant hypochlorite concentration experiments.

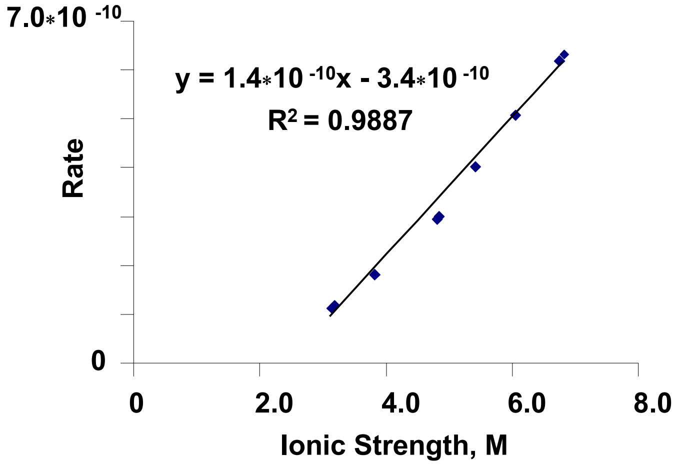


Figure 4.6 Plot of Rate of perchlorate formation vs. ionic strength at 40 ºC

Table 4.2
Variation in ionic strength of sodium hypochlorite solutions during the constant [ClO_3^-] experiment at 40 ºC

[OCl-] (M)	[ClO3-] (M)	Ionic strength (M)	pH
1.366	0.619	6.72	13.00
1.371	0.610	6.80	12.99
1.166	0.619	6.02	12.96
1.012	0.623	5.38	12.91
0.871	0.605	4.80	12.84
0.867	0.615	4.78	12.82
0.646	0.618	3.78	12.70
0.478	0.621	3.14	12.60
0.485	0.614	3.10	12.56
0.178	0.610	1.76	12.21
Mean	**0.615**	**4.63**	**12.76**
Std. Dev.	0.005	1.59	0.24
RSD	0.86	34.2	1.85

Table 4.3
Variation in ionic strength of sodium hypochlorite solutions during the constant [ClO_3^-] experiment at 40 ºC

[ClO3-] (M)	[OCl-] (M)	Ionic strength (M)	pH
1.788	1.355	7.96	12.99
1.449	1.384	7.66	12.52
1.254	1.395	7.48	12.96
0.907	1.393	7.11	12.95
0.432	1.372	6.56	12.93
0.337	1.370	6.46	12.94
Mean	**1.378**	**7.21**	**12.88**
Std. Dev.	0.014	0.55	0.16
RSD	1.02	7.64	1.26

The variability in ionic strength in the constant chlorate data set (Table 4.2) was at least 3 times higher than that in the constant hypochlorite data set (Table 4.3). These data are easily explained by the fact that the constant chlorate experiments required significant dilution of the hypochlorite solutions while the constant hypochlorite experiments only required addition of sodium chlorate. Thus, the observed variation in the sample matrix set designed to elucidate the order of the perchlorate formation reaction was irrefutably comprised of dissimilar sample matrices. As, such the ionic strength effect must be accounted for before further consideration of higher order reaction pathway.

The first step in quantifying the relationship between ionic strength and the rate of perchlorate formation was to relate the observed rate constant at a given ionic strength to a calculated rate constant at "infinite dilution" or "zero ionic strength" (k_0). The Extended Debye-Hückel Equation, also known as the Davies Equation, can be used to relate the observed rate constant (k_{obs}) to the ionic strength of the solution by Equation 4.7. This equation is also useful for relating rate constants between experiments with different ionic strength as one can determine the theoretical rate constant at "infinite dilution" (k_0 at zero ionic strength).

$$\log(k_{obs}) = 1.02 Z_M Z_N \left(\frac{I^{0.5}}{1 + I^{0.5}} - \beta I \right) + \log(k_0) \qquad \textbf{(4.7)}$$

where,

k_{obs} = observed rate constant

k_0 = rate constant at infinite dilution (zero ionic strength)

Z_M, Z_N = charges of individual reactants in rate determining step

β = experimentally determined coefficient

I = ionic strength (mol/L)

Since the product of $Z_M x Z_N$ = (-1 charge of OCl^-) x (-1 charge of ClO_3^-) = +1, Equation 4.7 becomes Equation 4.8:

$$\log(k_{obs}) = 1.02 \left(\frac{I^{0.5}}{1 + I^{0.5}} - \beta I \right) + \log(k_0) \qquad \textbf{(4.8)}$$

To simplify Equation 4.7 further, an assumption similar to one employed by Adam and Gordon (1999) in the determination of the relationship between the rate constant of hypochlorite decomposition and ionic strength was used: Equations 4.7 and 4.8 contain a "1.02 ($I^{1/2}$ / (1 + $I^{1/2}$)" term that is dominant at low ionic strength, and a 1.02 βI term that dominates at high ionic strength. If both terms are plotted as a function of ionic strength (Figure 4.7), it is evident that the "1.02 ($I^{1/2}$ / (1 + $I^{1/2}$)" term does not change as rapidly as the 1.02 βI term at ionic strength above 1M. Thus, this additional term could be removed from the equations to simplify when working above 1M. Since the majority of experiments performed during this project had an ionic strength in 1-7 M range, this simplification was used. Thus, Equation 4.8 can be further simplified to Equation 4.9.

$$\log(k_{obs}) = 1.02\beta I + \log(k_0) \qquad \textbf{(4.9)}$$

where $\log(k_0)$ is determined experimentally by fitting log (k_{obs}) vs I.

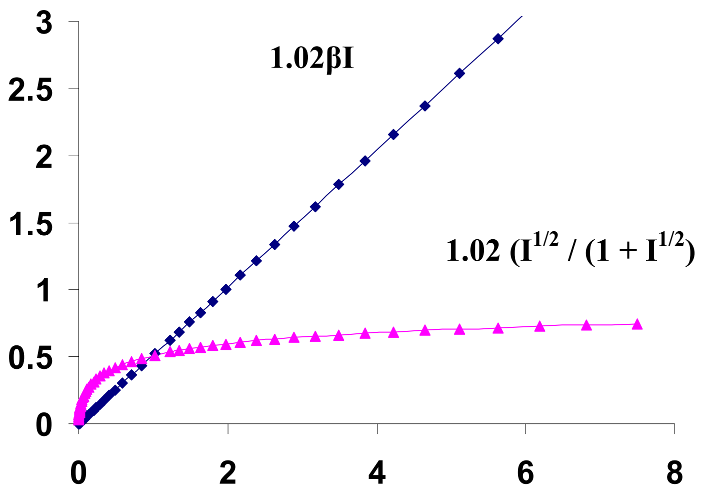


Figure 4.7 Plot of low ionic strength term [1.02 ($I^{1/2}$ / (1 + $I^{1/2}$)] and high ionic strength term [1.02 βI] as a function of ionic strength. The contribution of [1.02 βI] term becomes dominant at high ionic strength. *Assuming coefficient β value of 0.5 as an approximation.

In choosing to explore the ionic strength effect on the rate of perchlorate formation, the decision was made to use the assumption that the reaction was first order in hypochlorite and first order in chlorate in order to calculate an observed rate constant (Equation 4.10). Data from the previous incubation studies were compiled together with the ionic strength measurements and the rate of perchlorate formation was converted to the observed rate constant by dividing the average rate of initial perchlorate ion formation by the initial concentrations of hypochlorite and chlorate ions (Equation 4.10).

$$k_{obs} = \frac{\text{Rate}}{[OCl^-]\times[ClO_3^-]} \qquad \textbf{(4.10)}$$

Figure 4.8 shows the experimentally determined relationship between the rate constant and ionic strength at different temperatures. The dependence of rate constant on ionic strength increases with temperature as can be seen by increase in the slopes of the fitted lines. The slopes of the fitted lines are equal to 1.02βI and the intercepts are equal to log k_0. A summary is given in Table 4.4. The agreement of the slopes of the line between temperatures (6.35% RSD) indicate that (1) ionic strength correlates well with the rate of perchlorate formation and (2) the assumption of first order in both chlorate and hypochlorite is appropriate. Thus, ionic strength and the concentration of chlorate and hypochlorite ions were both incorporated as controlling variables in the rate of perchlorate formation.

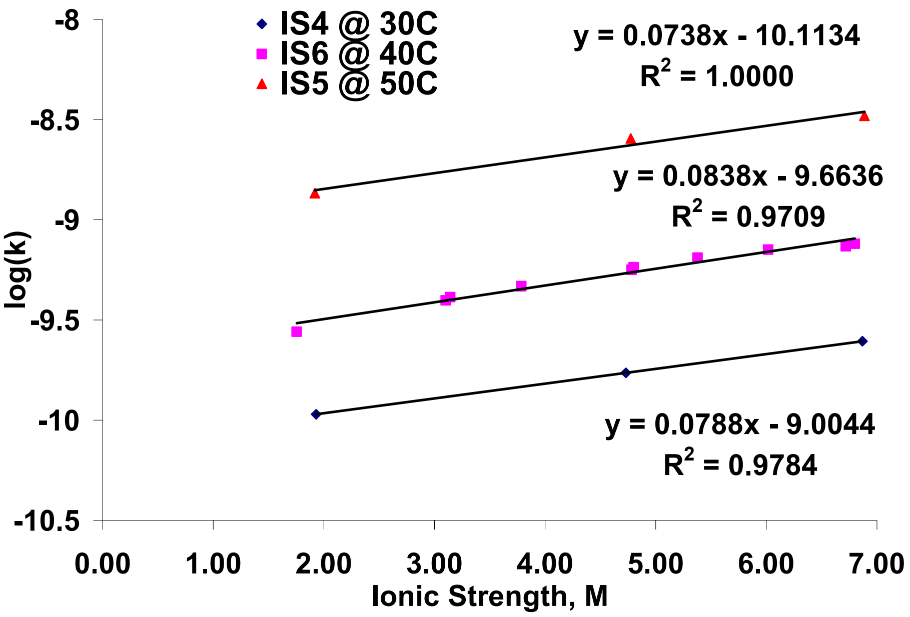


Figure 4.8 Plot of log[k_{obs}] vs. ionic strength of solution

Table 4.4

Slopes and intercept of log k_{obs} vs ionic strength-fitted lines at T = 30 ºC, 40 ºC, 50 ºC.

Temperature (ºC)	Slope	Intercept (log k_0)	k_0 in $M^{-1}s^{-1}$ (x 10^{-12})
30	0.0738	-10.1	77.0
40	0.0838	-9.66	217
50	0.0788	-9.00	990
Mean	**0.0788**		
Std. Dev.	0.005		
RSD	6.35		

Quantitation of Temperature Effects on the Rate of Perchlorate Formation

In order to combine the dependence of the observed rate constant on ionic strength and temperature, the zero ionic strength rate constant at infinite dilution (k_0) must be related to temperature dependence. Both the Arrhenius and the Eyring equations can be used to describe the temperature dependence of a reaction rate. The Arrhenius equation is applied to the kinetics of gas reactions whereas the Eyring equation (Equation 4.11), which is based on Transition State Theory, can be used for studying kinetics of reactions occurring in liquids.

$$k_0 = \frac{k_b}{h} \times T \times e^{\frac{\Delta S}{R}} \times e^{-\frac{\Delta H}{RT}} \qquad \textbf{(4.11)}$$

k_0	=	calculated from Equation 4.4	
k_b	=	Boltzmann's constant	1.381×10^{-23} J · K^{-1}
h	=	Plank's constant	6.626×10^{-34} J · s
R	=	Gas constant	8.3145 J/mol K
ΔS	=	Entropy of activation	
ΔH	=	Enthalpy of activation	

Taking the log of Equation 4.11 gives:

$$\ln(\frac{k_0}{T}) = \ln(\frac{k_b}{h}) + \frac{\Delta S}{R} - \frac{\Delta H}{RT} \qquad \textbf{(4.12)}$$

A plot of $\ln(k_0/T)$ should be a linear function of 1/T, if the data follows Equation 4.12. The slope of the line can be used to calculate ΔH and intercept can be used to calculate ΔS. Figure 4.9 shows a plot of experimentally determined $\ln(k_o/T)$ vs 1/T. Based on three points the R^2 of the line is 0.9832.

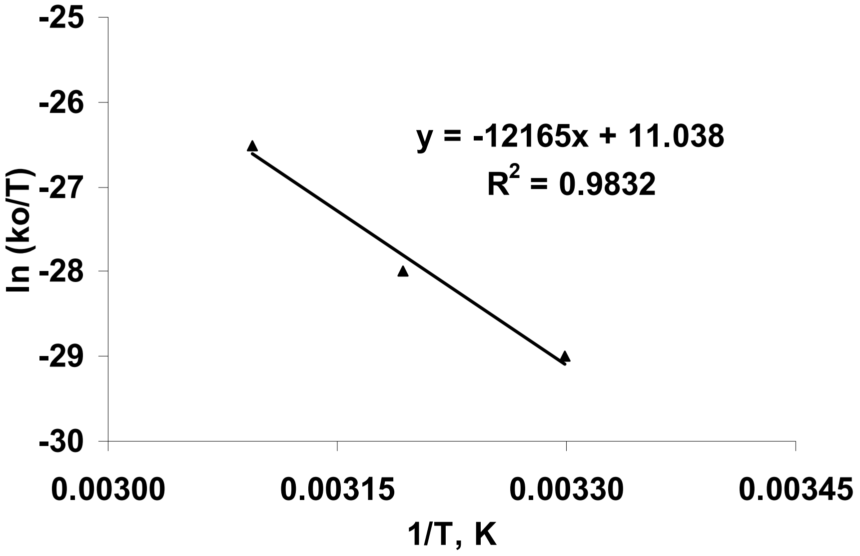


Figure 4.9 Plot of $\ln(k_o/T)$ vs 1/T for commercial hypochlorite solutions

The low Pearson correlation coefficient of 0.983 may indicate that more temperatures need to be studied and/or perhaps some temperature data points need to be repeated in order to reduce the error in the least squares estimation. However, based on the low variation observed in the fitted slopes of 6.4%, shown in Table 4.4 the Pearson correlation coefficient of 0.9832 was deemed satisfactory. The slope of the line equals ΔH / R, where the intercept equals to $\ln(k_b/T) + \Delta S/R$, based on Equation 4.12. Thus, the values of thermodynamic activation parameters for the formation of perchlorate in commercial OCl^- at infinite dilution are ΔH = 101 kJ/mol and ΔS= -106 J/mol · K.

It should be noted that, while the temperature dependence of the reaction is expected to be linear down to zero ºC, any interpretation of the model at temperatures below 30 ºC (the lowest temperature at which the model was validated) should be limited to qualitative trends only until a time when the model can be validated at lower temperatures. Typically, in order to evaluate the accuracy of a model, a minimum of 1.5 half-lives is required. At temperatures below 30 ºC, such validation was not possible given the allotted 11-month time frame of the project.

The Detailed Chemical Rate Law for Perchlorate Formation

Considering the data and results presented in the preceding sections of this Chapter there are three important findings: (1) The observed rate of perchlorate formation is dependent upon the concentration of hypochlorite and chlorate ions and the ionic strength. (2) The observed rate constant (k_{obs}) for perchlorate formation at the temperatures used in the incubation studies is related to ionic strength by a factor of 0.0788 M^{-1} (±0.005 M^{-1} or 6.35%). (3) The rate of perchlorate formation is temperature dependent. A generalized temperature *term* (relating zero ionic strength rate constant to temperature) can be derived from Equation 4.11 by incorporating the known values for ΔH and ΔS (Equation 4.13).

$$k_0 = 2.084 \times 10^{10} \times \mathrm{T} \times \mathrm{e}^{\frac{-1.01\mathrm{x}10^5}{\mathrm{RT}}} \times \mathrm{e}^{\frac{-106}{\mathrm{R}}} \qquad \textbf{(4.13)}$$

Thus, substituting a factor of 0.0788 (Table 4.4) for the 1.02βI term in Equation 4.9 and the demonstrated temperature dependence (Equation 4.13) for the k_0 term in Equation 4.9 yields a quantitative chemical rate law ("Predictive Model") that can be used to calculate the predicted rate constant (k_{calc}) of perchlorate formation at any temperature and ionic strength (Equation 4.14).

$$\log(\mathrm{k_{calc}}) = 0.0788(\mathrm{I}) + \log(2.084 \times 10^{10} \times \mathrm{T} \times \mathrm{e}^{\frac{-1.01\mathrm{x}10^5}{\mathrm{RT}}} \times \mathrm{e}^{\frac{-106}{\mathrm{R}}}) \qquad \textbf{(4.14)}$$

Thus, the predicted *rate* of perchlorate formation for any stepwise change in hypochlorite and chlorate ion concentrations can be calculated by a rearrangement of Equation 4.10 to yield Equation 4.15. By proxy, the concentration of perchlorate can also be calculated at any time point *provided the concentration of hypochlorite ion and chlorate ion can be predicted using Bleach 2001.*

$$Rate = \frac{dClO_4^-}{dt} = k_{calc} \times [OCl^-]^1 \times [ClO_3^-]^1 \qquad \textbf{(4.15)}$$

Using the "Predictive Model" shown in Equation 4.14, calculated rate constants (k_{calc}) for perchlorate formation at specific ionic strength and temperatures were compared to experimentally observed rate constants (k_{obs}) and are summarized in Table 4.5. The percent error was calculated by taking the difference between k_{calc} and k_{obs}, then dividing the difference by k_{obs} and multiplying by 100%. The average variability between observed and predicted rate constants is less than 20% across three temperatures (30 ºC, 40 ºC, and 50ºC) and with ionic strength ranging from 1.8 mol/L to 6.9 mol/L.

Table 4.5
Calculated rate constants vs. observed rate constants at variable ionic strength and temperature

T (ºC)	I (M)	k_{obs} (M^{-1} d^{-1} x 10^6)	k_{calc} (M^{-1} d^{-1} x 10^6)	Percent Error	Average % Error	R^2 (log k vs. I)
30	6.87	21.38	21.76	1.8		
30	4.73	14.88	14.76	0.8		
30	1.93	9.24	8.88	3.8	**2.1**	***1.000**
40	6.72	63.70	78.65	23.5		
40	6.80	65.51	79.82	21.9		
40	6.02	61.29	69.24	13.0		
40	5.38	55.85	61.67	10.4		
40	4.80	49.99	55.55	11.1		
40	4.78	48.59	55.35	13.9		
40	3.78	40.26	46.19	14.7		
40	3.14	35.52	41.11	15.7		
40	3.10	34.19	40.81	19.4		
40	1.76	23.87	31.96	33.9	**18**	**0.9709**
50	6.89	285.56	277.98	2.7		
50	4.77	219.79	189.46	13.8		
50	1.92	117.24	112.84	3.8	**6.7**	**0.9784**

*R^2 of 1.000 is based on 3 data points only

The agreement between the predicted experimentally determined values, given in Table 4.5, suggests that in fact the determined relationship of the rate constant on ionic strength and temperature given by Equation 4.14 can sufficiently predict the rate constants of perchlorate formation in bulk sodium hypochlorite solutions that have pH 11-13 and ionic strength of 1-7 Molar. Thus, fitting the data using more complex reaction pathways, such as a parallel or consecutive reaction pathway is simply not applicable or practical.

VALIDATION OF THE “PREDICTIVE MODEL”

To further validate the “Predictive Model”, Equation 4.14 was used to generate the rate constants needed to calculate the rate of perchlorate formation at different temperatures for several sets of samples that varied in ionic strength. The samples chosen for validation of the “Predictive Model” were bulk hypochlorite solutions used during the various incubation studies. First, *Bleach 2001* (Adam, Gordon, and Pierce 2001) was used to predict the decomposition of hypochlorite and formation of chlorate for each sample. Second, experimentally measured ionic strength, via a conductivity extrapolation, was applied to Equation 4.14 to generate rate constants of perchlorate formation at specific temperatures. Third, the obtained rate constants and the *Bleach 2001* predictions were used to predict perchlorate concentration at multiple time points during the incubation period.

Figures 4.10 and 4.11 show plots of observed and predicted (*Bleach 2001*) decomposition of hypochlorite and formation of chlorate at 30 ºC and 40 ºC. Figures 4.12 and 4.13 show the measured perchlorate concentrations and those calculated from the “Predictive Model”. The predicted concentrations were fitted to a smoothed line, and a fixed 10% error bars were added. The error bars on all figures, unless otherwise stated, are set at a fixed value of 10%.

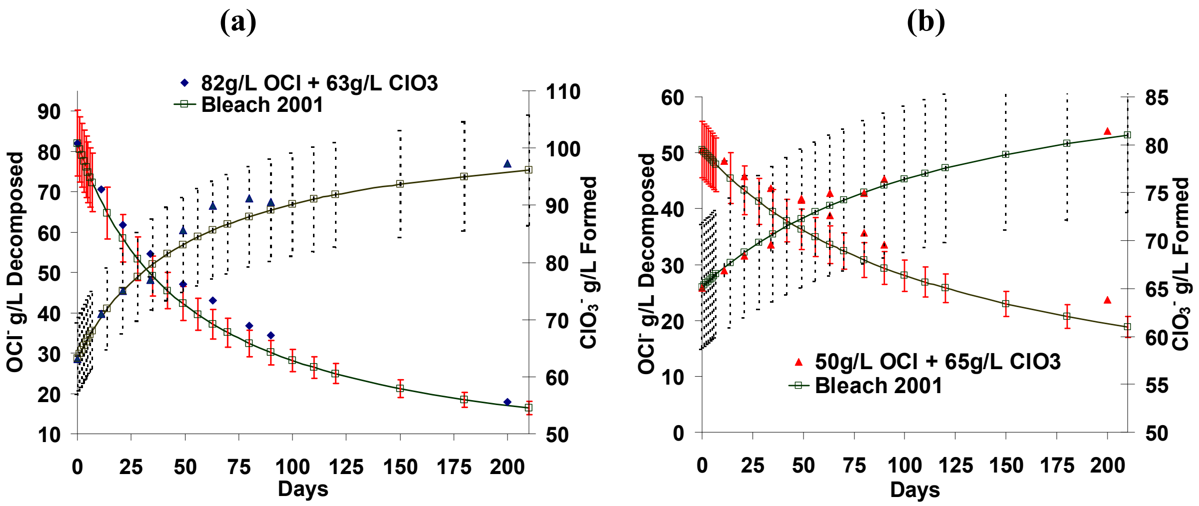


Figure 4.10 Overlaid plot of hypochlorite decomposition and chlorate formation at 30 ºC (a) initial concentration of OCl^- = 82g/L (b) Initial concentration of OCl^- = 50g/L

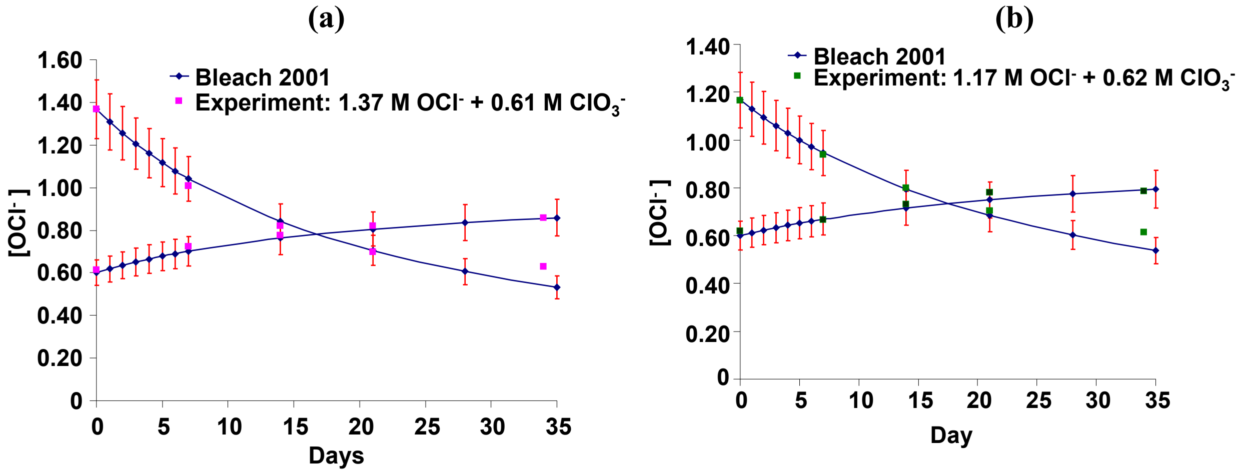


Figure 4.11 Overlaid plot of hypochlorite decomposition and chlorate formation at 40 ºC (a) initial concentration of OCl- = 1.37M (b) Initial concentration of OCl- = 1.17M

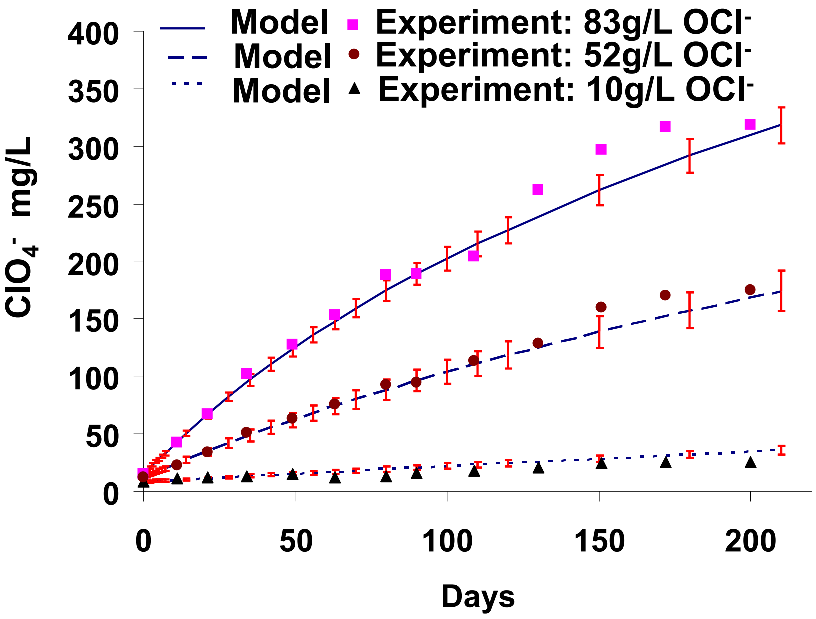


Figure 4.12 Overlaid plot of perchlorate formation experiment vs. predicted at 30 ºC

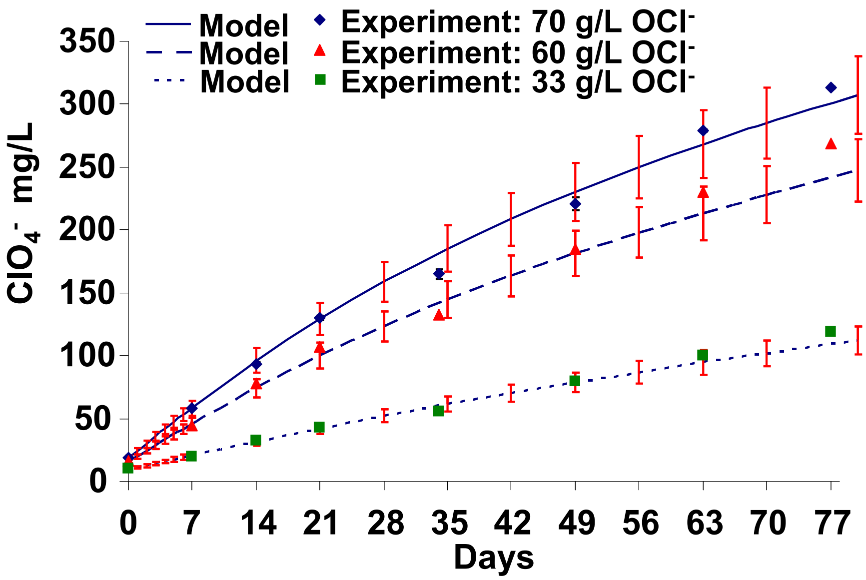


Figure 4.13 Overlaid plot of perchlorate formation experiment vs. predicted at 40 ºC

The data shown in Figures 4.12 and 4.13 indicate agreement of 10% or better between observed perchlorate concentration and measured perchlorate concentration in most cases over the entire period of the holding studies. The agreement between experimentally and predicted perchlorate concentrations supports the conclusion that the formation of perchlorate is a second order reaction (first order in hypochlorite and chlorate) that is highly dependent upon ionic strength and temperature. Furthermore, the detailed chemical rate law provided the basis for the "Predictive Model" which not only provides initial rate constants but can also be used in conjunction with *Bleach 2001* to accurately predict perchlorate concentrations as a function of time.

IMPLICATIONS

While the detailed chemical rate law is the key to understanding how factors impact the formation of perchlorate in hypochlorite solutions and can be used to predict perchlorate concentration over time, the primary goal of the "Predictive Model" is really to provide a quantitative platform from which to develop strategies that can be used to minimize perchlorate formation in hypochlorite solutions. As such, a series of hypothetical bulk hypochlorite solutions (starting concentration of 2 M OCl^- or approximately 13% FAC[1]) were used to examine how factors such as dilution and temperature might impact the amount of perchlorate formed in solution over time. Thus, Tables 4.6 – 4.8 were constructed as an aid to understand how the rate of perchlorate formation changes as a function of hypochlorite concentration, temperature, and ionic strength.

The calculations shown in Table 4.6 indicate that dilution by half causes a reduction in rate by a factor of approximately seven and dilution by 10-fold causes reduction in rate of perchlorate formation by a factor of 270. Cooling the hypochlorite solutions also provides

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[1] As a point of reference for discussion, a bulk hypochlorite solution of 13% FAC typically equates to approximately 2 M OCl^-, or 103 g/L OCl^-, or 149 g/L NaOCl, or 13.6% NaOCl (depending on the specific gravity).

significant reduction in the rate of perchlorate formation: Cooling by just 5 ºC provides approximately a 2-fold reduction in the rate of perchlorate formation, as can be seen in Table 4.7. Preserving hypochlorite from decomposition is also achieved by dilution and cooling. Thus, strategies preserving hypochlorite from decomposition, such as dilution and reduction in temperature, are also the most effective for mitigation of perchlorate formation. Table 4.8 provides a quantitative analysis of how a combined strategy of dilution and temperature reduction can slow the rate of perchlorate formation across a range of scenarios. For example, a dilution of 1:2 and a reduction of storage temperature by 10 ºC can provide a 27-fold reduction in the rate of perchlorate formation. A dilution of 1:4 with the same temperature reduction would result in 140 times slower perchlorate formation. Thus, while temperature is important in reducing perchlorate formation, it requires much more cooling to achieve the same effect as simple 1:2 or 1:4 dilutions.

Table 4.6

Predicted rate constants and Rates of perchlorate formation at variable ionic strength and temperature using the "Predictive Model"

T (ºC)	[OCl-] (M)	[ClO3-] (M)	I (M)	pH	*Bleach 2001* OCl^- $t_{1/2}$, (days)	k_{calc}, (M^{-1} d^{-1})	Calculated Rate = $[ClO_4^-]/dt$, (M/d)	*Days to reach 10uM ClO_4^-
10	2.00	0.050	6.00	12.0	1319	1.02E-06	1.02E-07	98
10	1.00	0.025	3.00	12.0	5310	5.93E-07	1.48E-08	680
10	0.20	0.005	0.60	12.0	46471	3.84E-07	3.84E-10	26000
15	2.00	0.050	6.00	12.0	610	2.19E-06	2.19E-07	46
15	1.00	0.025	3.00	12.0	2457	1.27E-06	3.18E-08	320
15	0.20	0.005	0.60	12.0	21499	8.22E-07	8.22E-10	12000
20	2.00	0.050	6.00	12.0	290	4.57E-06	4.57E-07	22
20	1.00	0.025	3.00	12.0	1167	2.65E-06	6.63E-08	150
20	0.20	0.005	0.60	12.0	10209	1.72E-06	1.72E-09	5900
25	2.00	0.050	6.00	12.0	141	9.32E-06	9.32E-07	11
25	1.00	0.025	3.00	12.0	577	5.41E-06	1.35E-07	74
25	0.20	0.005	0.60	12.0	4968	3.50E-06	3.50E-09	2900
30	2.00	0.050	6.00	12.0	70	1.86E-05	1.86E-06	5.4
30	1.00	0.025	3.00	12.0	283	1.08E-05	2.69E-07	37
30	0.20	0.005	0.60	12.0	2475	6.96E-06	6.96E-09	1400
35	2.00	0.050	6.00	12.0	36	3.61E-05	3.61E-06	2.8
35	1.00	0.025	3.00	12.0	144	2.10E-05	5.24E-07	19
35	0.20	0.005	0.60	12.0	1261	1.36E-05	1.36E-08	740

*All predictions based on starting perchlorate concentration of 1 µM; Note that the model has not been validated with experimental evidence below 30 ºC, thus values in this table should be used only as an indication of trends.

Table 4.7
Summarized effects of dilution and temperature on decomposition of hypochlorite and Rate of formation of perchlorate

Dilution:	**$-d[OCl^-]/dt$ (%)**	**x slower**	**$d[ClO_4^-]/dt$ (%)**	**x slower**
1:1	100.0	1	100.0	1
1:2	24.8	4.0	14.5	7
1:10	2.8	35.2	0.4	266

Temperature:	**$-d[OCl^-]/dt$ (%)**	**x slower**	**$d[ClO_4^-]/dt$ (%)**	**x slower**
35 °C	100	1	100	1
30	51	2.0	51	1.9
25	25	3.9	26	3.9
20	12	8.1	13	7.9
15	5.9	17	6.1	17
10	2.7	37	2.8	35

Table 4.8
Detailed table of dilution and temperature effects on the relative Rate of perchlorate formation (assumes starting temperature is 35 °C at ΔT = 0)

Dilution Factor:	**1**	**1:2**	**1:4**	**1:6**	**1:10**
Ionic Strength:	6.00	3	1.5	1	0.6
$[ClO_3^-]$ (M):	0.05	0.025	0.013	0.008	0.005
[OCl-] (M):	2.03	1.013	0.506	0.338	0.203
% FAC:	**13.05**	**6.53**	**3.26**	**2.18**	**1.31**
ΔT °C	**Reduction (X-Fold) in Rate of Perchlorate Formation**				
0	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	1000
-11	4.5	31	160	400	1200
-12	5.1	35	190	460	1400
-13	5.9	41	210	530	1600
-14	6.8	47	250	610	1800
-15	7.9	54	290	700	2100
-16	9.1	63	330	810	2400
-17	11	73	380	940	2800
-18	12	84	440	1100	3300
-19	14	98	510	1300	3800
-20	17	110	600	1500	4400

SUMMARY OF INSTRUCTIONS FOR USER APPLICATION OF THE "PREDICTIVE MODEL"

While the creation of a graphical user interface-based computer program for implementation of the predictive model was outside of the scope of this study, there are a few simple steps that can be taken to use the model directly. This section of the Report is designed to provide a simplified step-by-step set of instructions for application of the model. In order to use the predictive model, a copy of the *Bleach 2001* software is required. Such software is available from the Water Research Foundation. Additionally, this discussion assumes that the user will have a basic knowledge and understanding of how to use a spreadsheet software package such as Microsoft Excel and how best to organize data within that program. The steps to use the model are outlined below:

1. The user must know the following information about the hypochlorite solution under consideration:
    a. The initial/starting concentration (in mol/liter) of hypochlorite ion, chlorate ion, and perchlorate ion.
    b. If the concentration of perchlorate is unknown, assume "zero" for simplicity. This will lead to an underestimation of the actual perchlorate concentration but will still be useful for determining impacts of dilution and temperature variation.
    c. Ionic strength (in mol/liter). This should be measured using a conductivity probe and converted to ionic strength using Equation 2.12.
    d. The temperature at which the solution will be stored (in Kelvin).
    e. The pH of the hypochlorite solution.

2. Using *Bleach 2001* input the values for temperature, pH, hypochlorite ion concentration, and chlorate ion concentration. Allow *Bleach 2001* to calculate all other parameters. *Bleach 2001* will return a list of hypochlorite ion and chlorate ion concentrations for a specified number of days. These data should be placed into a separate spreadsheet program such as Microsoft Excel. Using a spreadsheet software package will facilitate copying formulas between worksheet cells, making the calculations simpler to repeat under varying conditions.

3. Use Equation 4.14 to calculate the rate constant (k_{calc}) for the ionic strength and storage temperature of the hypochlorite solution in question. The term "R" is the ideal gas law constant which is 8.314 J/K·mol. The term "I" is the measured ionic strength of the hypochlorite solution (mol/L). The term "T" is temperature in Kelvin (K = ºC + 273). The units of the calculated rate constant (k_{calc}) will be in L/mol/second. Note that Equation 4.14 actually return the <u>log</u>(k_{calc}), thus the user must convert to k_{calc}.

4. Convert k_{calc} into a "per day" unit: multiply k_{calc} (L/mol/sec) by a factor of 86,400 (60 seconds × 60 minutes × 24 hours) to convert to k_{calc} (L/mol/day).

5. Next, the predicted rate of perchlorate formation needs to be calculated for every incremental (per day) change in hypochlorite and chlorate ion concentration as predicted from *Bleach 2001*. Therefore, using a spreadsheet software package, Equation 4.15, and the hypochlorite and chlorate ion concentration at each increment of days (e.g., days 1, 2, 3, 5, 10, 25, 50, 100, 200), plug in the value for k_{calc}, $[OCl^-]$, and $[ClO_3^-]$ to predict the rate of perchlorate formation. The units of the rate prediction will be in mol/L/day and represents the change in perchlorate concentration per unit time.

6. Finally, the rate of perchlorate formation needs to be converted to a concentration value. This involves several steps:
    a. Input the initial (measured) concentration of perchlorate ion at day "zero" into a spreadsheet cell associated with time = zero days. If the initial concentration of perchlorate ion is unknown, use zero mol/L.
    b. For each calculated rate, multiply the rate by the number of days and add that to the predicted concentration. For example, to predict the change in perchlorate ion concentration from Day 0 to Day 1, the predicted perchlorate ion concentration at Day 1 = $\text{Rate}_{(\text{at Day 1})} \times 1\ \text{Day} + [ClO_4^-]_{(\text{at Day 0})}$.
    c. For a longer time increment (such as Day 10 to Day 25), simply adjust the number of days: the predicted perchlorate ion concentration at Day 25 = $\text{Rate}_{(\text{at Day 10})} \times 15\ \text{Days} + [ClO_4^-]_{(\text{at Day 10})}$.
    d. Continue step-wise until the perchlorate ion concentration has been calculated to the desired number of days.
    e. To convert from mol/L to µg/L, multiply the molarity of perchlorate by 99.5 g/mol × 10^6 µg/g

SUMMARY

Variation in ionic strength proved to be a significant factor impacting the rate of perchlorate formation. Establishing a relationship between the rate constant based on first order of the reaction in both hypochlorite and chlorate (second order overall) combined with ionic strength at different temperatures allowed predictions of rate constant to be made using the detailed chemical rate law described by Equation 4.14. The predicted values of the rate constant agree reasonably with the experimental values, with percent error of 2.1% for 30 ºC, 17.7% for 40 ºC and 6.75 for 50 ºC. Thus investigation of higher order reaction pathway was not applicable. This "Predictive Model" was used to predict rate constants for hypochlorite solutions varying by ionic strengths, temperatures, and concentration of hypochlorite. The predicted rate constants were used to predict initial rates of perchlorate formation, and thus the effects of dilution, temperature reduction were evaluated and strategies to mitigate perchlorate formation proposed.

REFERENCES

Adam, Luke, Gilbert Gordon, and Don Pierce. 2001. *Bleach 2001*. Miami University, Oxford, Ohio. Copyright (c) 2001 AwwaRF and AWWA.

Adam, Luke C. and Gilbert Gordon. 1999. Hypochlorite Ion Decomposition: Effects of Temperature, Ionic Strength, and Chloride Ion. *Inorganic Chemistry*, 38 **(6)**:1299-1304.

CHAPTER 5
MONITORING OF PERHLCORATE AND OTHER CONTAMINANTS IN HYPOCHLORITE SOLUTIONS

APPROACH

Given that sodium hypochlorite solutions contain contaminants such as chlorite, chlorate, perchlorate, and bromate, this portion of the study was designed (1) to examine the differences in contaminant concentration and formation between sources of hypochlorite solutions and (2) to examine the impact of those solutions on finished and distribution system water quality. Eight utilities were asked to provide samples of hypochlorite solutions (if available), to provide raw water, finished water, and distribution system samples, and to provide qualitative information regarding sources of hypochlorite, storage conditions, etc. In cases where distribution system samples were unavailable, simulated distribution system (SDS) studies were performed. Additionally, samples of brine and hypochlorite solutions from 12 on-site generator (OSG) systems made by three different manufacturers were also provided. Duplicate samples were provided from each site/source, one quenched with malonic acid at the utility upon collection, one unquenched but cooled to 4 ºC. All of the hypochlorite solutions, brine, and water samples were analyzed for perchlorate, chlorate, hypochlorite, bromate, and dissolved transition metals (Co(II), Cu(II), Fe(III), Ni(II), and Mn(II)). Hypochlorite solution samples were also aged at 50 ºC to measure the rate of hypochlorite decomposition and contaminant formation during a 30-day incubation study.

The quantitative data obtained from the analysis of the fresh and aged hypochlorite solution samples was used to assess potential impacts on finished water and to validate the "Predictive Model" developed from the detailed chemical rate law and described in Chapter 4. First, the maximum use level (MUL) approach described by NSF (NSF/ANSI 2005) was used to predict potential impacts on finished water quality. Next, the *Bleach 2001* program (Adam, Gordon, and Pierce 2001) was used to compare measured hypochlorite decomposition and chlorate formation during the incubation study with the predicted decomposition and formation by *Bleach 2001.* By comparing actual and predicted values, some insight into other possible factors (e.g., metal ions) that may have been impacting decomposition was possible. Finally, the predicted daily concentration of hypochlorite and chlorate from *Bleach 2001* was combined with the "Predictive Model" developed in Chapter 4 of this report to predict perchlorate concentration on a daily basis. Comparing the "Predictive Model" perchlorate concentration with the measured concentration of perchlorate in the aged hypochlorite samples provided additional validation of its applicability to bulk hypochlorite solutions other than those used for development of the detailed chemical rate law.

DESCRIPTION OF UTILITIES AND OSG SYSTEMS

As part of this research study, eight utilities agreed to participate by sending hypochlorite and water samples from the treatment process. Of those utilities, 5 used bulk hypochlorite, 2 used OSG hypochlorite, and 1 used chlorine gas. The participating utilities represented six states and two countries: AZ, CA, FL, GA, NV, OH, and Japan. One participating utility (Utility 8) was a wastewater treatment plant that uses bulk hypochlorite for disinfection of water for non-

Table 5.2
Description of on-site generators (OSG), identification numbers, and salt source

OSG Model	Anode Material*	OSG Capacity (PPD)	OSG Energy (kWh/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	1200	Unknown	3	>96% as NaCl
10	DSA	2,000	1.6 to 2.0	2.5, 6.5	>99.7% as NaCl

*Dimensionally Stabilized Anode (DSA), likely titanium; **OSG units only used at factory for testing, thus had << 1 year service time; *** No other information provided

Finally, one supplier of calcium hypochlorite agreed to provide freshly manufactured calcium hypochlorite in solid form. Little is known about the formation of perchlorate in solid hypochlorite, but the Project Team wanted to determine if there was perchlorate present from the manufacturing process and whether dissolved calcium hypochlorite would age any differently than sodium hypochlorite. While it is understood that calcium hypochlorite is not commonly stored in dissolved form and is typically used immediately upon dissolution, it was decided that dissolved calcium hypochlorite would be aged as a comparison to determine whether there was some other contaminant (e.g., chloride) that could potentially impact perchlorate formation. Thus, with the utility hypochlorite solutions and OSG samples, calcium hypochlorite was also aged at 50 ºC for a period of 30 days using nominal concentrations of 3% and 6% FAC.

RESULTS

Contaminants in Bulk, OSG, and Calcium Hypochlorite Solutions

The concentration of hypochlorite, perchlorate, chlorate, and bromate in the bulk samples for each of the 8 utilities is shown in Table 5.3.

- Only Utility 1-A appeared to have significant impacts on finished water concentration from the perchlorate levels in the bulk hypochlorite. The low FAC concentration at Utility 1-A (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 utilities were above California's 6 μg/L MCL for perchlorate and only two were above Massachusetts's 2 μg/L MCL.

- Chlorate contamination from the hypochlorite solutions appeared to impact all of the utilities tested. Of those utilities, three had concentrations of chlorate in the finished drinking water above the 800 μg/L notification level in California and an additional utility was at the proposed 200 μg/L action level recommended in CA (Howd 2002).

- Bromate was observed at mg/L levels in all bulk hypochlorite solutions, though none of the utilities tested had finished water concentrations over the 10 μg/L bromate MCL mandated by the US EPA.

Table 5.3
Summary of perchlorate, chlorate, and bromate concentrations in raw water, finished water, and hypochlorite used at participating utility locations

			ClO_4^-			ClO_3^-			BrO_3^-		
Utility	**Source**	**FAC (g/L)**	**Hypo (μg/L)**	**Raw (μg/L)**	**Fin. (μg/L)**	**Hypo (mg/L)**	**Raw (mg/L)**	**Fin. (mg/L)**	**Hypo (μg/L)**	**Raw (μg/L)**	**Fin. (μg/L)**
1-A	Bulk	87	14,000	<0.5	3.6	19,000	0.014	0.58	24,000	<0.5	0.5
1-B	OSG 9	6.8	3,500	<0.5	<0.5	480	0.026	1.5	2,700	<0.5	3.6
2	Bulk	150	670	<0.5	<0.5	5,900	0.005	0.019	30,000	<0.5	<0.5
4	Cl_2 Gas	n/a	n/a	<0.5	<0.5	n/a	<0.003	<0.003	n/a	<0.5	<0.5
5	Bulk	120	220	<0.5	<0.5	1,800	0.13	0.20	9,000	1.3	1.4
6	OSG 10	8.7	19	2.0	2.1	380	0.008	0.16	<100	<0.5	1.3
7	Bulk	120	230	<0.5	<0.5	2,400	<0.003	0.13	9,900	<0.5	0.92
8	Bulk	130	2,000	1.6	1.2	8,000	<0.003	0.79	7,700	<0.5	2.6

Hypo = Hypochlorite solution; Raw = Raw water entering the treatment plant; Fin = Finished water leaving treatment plant; Samples analyzed in duplicate measurements, with average % difference for: ClO_4^- 2.0%, BrO_3^- 4.2%, and ClO_3^- 2.5%.

The OSG samples also had high variations in FAC, chlorate, and perchlorate concentrations as shown in Table 5.4. All samples labeled "quenched hypochlorite" were collected at the utility in bottles pre-dosed with malonic acid. Non-quenched samples were cooled to 4 ºC and shipped with the quenched samples to the laboratory at SNWA via overnight delivery. Samples were collected directly from the OSG when possible; otherwise they were collected from dosing tanks/day tanks. The solution for OSG 9 was at least 48 hours old when collected and may have been stored at temperatures up to 42 ºC. The brine solution and feed water for OSG 9 were at 40 to 42 ºC prior to electrolytic conversion.

- Most OSGs had less than 700 μg/L chlorate present in the finished product.

- Bromate concentration ranged from 0.2 mg/L to 6 mg/L. Bromate concentrations are limited by the amount of bromide (which is rapidly converted to bromate in hypochlorite solutions) and is likely related to the amount of bromide present in the salt and/or feed water used for hypochlorite generation.

- There were no discernable trends 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.

Table 5.4
Chlorate, bromate, and perchlorate data for quenched and non-quenched samples and the feed brine to the OSG

	Quenched hypochlorite				Non-quenched hypochlorite				Brine		
OSG Model	ClO_3^- (mg/L)	BrO_3^- (mg/L)	ClO_4^- (µg/L)	FAC, (g/L)	ClO_3^- (mg/L)	BrO_3^- (mg/L)	ClO_4^- (µg/L)	FAC, (g/L)	ClO_3^- (mg/L)	BrO_3^- (mg/L)	ClO_4^- (µg/L)
1a	89	0.15	*	<0.1	140	4.1	5.4	9.7	<0.5	<0.1	<2.5
1b	320	3.0	15	2.9**	240	3.8	16	8.0	<0.5	<0.1	<2.5
2a	57	0.47	8.2	<0.1	97	5.3	8.6	6.8	<0.5	<0.1	<2.5
2b	450	2.7	380	2.6**	360	3.3	410	6.9	<0.5	<0.1	<2.5
3	240	1.7	6.6	<0.1	270	4.4	7.3	10	<0.5	<0.1	<2.5
4	1000	2.1	39	<0.1	1200	2.6	40	4.5	<0.5	<0.1	<2.5
5	220	1.1	31	<0.1	260	2.6	31	8.0	<0.5	<0.1	<2.5
6	180	0.54	21	<0.1	180	1.4	22	5.2	<0.5	<0.1	<2.5
7	610	0.32	79	<0.1	750	2.0	83	7.2	2.0	<0.1	<2.5
8	180	0.10	660	<0.1	240	0.71	740	3.6	2.1	<0.1	<2.5
9	510	5.3	3100	<0.1	760	5.7	3500	6.8	7.2	<0.1	65
10	450	0.13	19	<0.1	780	0.15	19	8.7	<0.5	<0.1	<2.5

*Sample contaminated, no perchlorate data available for unquenched hypochlorite; **Too much sample was added to the bottle provided with pre-dosed quenching agent, thus quenching was not complete

Transition metal ion concentrations measured for this study were low in most of the bulk hypochlorite (Table 5.5), OSG (Table 5.6), and brine samples (Table 5.7), though Utility 1-A had nickel present at 0.2 mg/L, copper at 0.1 mg/L and iron concentrations approaching 10 mg/L in the hypochlorite solution itself. As metals have been shown in earlier chapters and elsewhere to have a catalytic effect on the decomposition of hypochlorite, the presence of iron and nickel may have been a factor (in addition to age) in the low FAC concentration at Utility 1-A. Regarding the OSG hypochlorite, most brine samples showed higher levels of metal ion contamination relative to the hypochlorite product from the OSG. This difference is likely due to loss of metals 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 and Bubnis 2000). The bulk hypochlorite sampled from Utilities 1-A, 5, 7, and 8 all contained at least one contaminant above the specified levels.

Table 5.5
Concentrations of transition metals in utility bulk hypochlorite samples

Utility	Mn	Fe	Co (µg/L)	Ni	Cu
1-A	<100	9200	<100	200	110
1-B, OSG 9	<100	<1250	<100	<100	<100
2	<100	<500	<100	<100	<100
3	n/a	n/a	n/a	n/a	n/a
5	<100	1100	<100	<100	<100
6, OSG 10	<100	<250	<100	<100	<100
7	<100	<500	<100	110	<100
8	<100	2300	<100	<100	<100

Table 5.6
Concentrations of transition metals in OSG hypochlorite solutions

OSG	Mn	Fe	Co (µg/L)	Ni	Cu
1a	<25	<125	<25	<25	<25
1b	<25	239	<25	<25	55
2a	<25	172	<25	<25	<25
2b	<25	160	<25	<25	<25
3	<25	120	<25	<25	<25
4	<25	<125	<25	<25	<25
5	<25	<125	<25	<25	<25
6	<25	<125	<25	<25	<25
7	<25	<50	<25	<25	<25
8	<25	<50	<25	<25	<25
9	<100	<125	<100	<100	<100
10	<100	<250	<100	<100	<100

Table 5.7
Concentrations of transition metals in OSG brine solutions

OSG	Mn	Fe	Co (µg/L)	Ni	Cu
1a	45	1293	<25	30	120
1b	33	752	<25	<25	92
2a	50	1100	<25	<25	95
2b	30	630	<25	<25	92
3	29	1200	<25	27	110
4	71	400	<25	29	98
5	<25	160	<25	<25	120
6	<25	<125	<25	<25	83
7	<25	<250	<25	<25	<25
8	<25	<250	<25	<25	<25
9	<25	<125	<25	<25	<25
10	N/A	N/A	N/A	N/A	N/A

Transition metal ions were not measured in the calcium hypochlorite solutions. However, bromate, chlorate, and perchlorate were all 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.

Given the data described above, a comparison was made by normalizing all of the contaminant concentrations by the concentration of FAC. Table 5.8 was assembled to show a relative contribution (on a mass of contaminant per mg FAC basis) from each hypochlorite solution. Of the comparisons made within the limited data set collected for this project, the only trend that stands out is that the OSGs consistently contribute 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 are likely a result of bromide in the feed water and/or salt used to make the brine solutions for electrolysis. Current NSF/ANSI 60 standards recommend no more than 0.5 µg BrO_3^- per mg FAC (NSF/ANSI 2005) in hypochlorite solutions. Based on this limit, three OSG solutions exceed the recommendation and an additional two OSGs approached the limit (0.48 µg BrO_3^- per mg FAC). Neither the calcium hypochlorite sample nor any of the bulk hypochlorite solutions exceeded the current bromate standard. Furthermore, only OSGs 5-8 and OSG 10 used a salt with greater than 99.5% purity (as 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, though further investigations detailing specific recommendations should be performed.

Other than the bromate observation, there are no consistent trends and contaminant concentrations vary widely within and between brands, hypochlorite sources, and production methods. Thus, from this limited data set collected during this project, there does not appear to be a 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 which is consistent with OSG and bulk hypochlorite data reported elsewhere (Asami, Kosaka, and Kunikane 2009).

Table 5.8
Relative contribution of specific contaminants on a per-mass-FAC basis

		Concentration in hypochlorite solutions				Mass of contaminant added per mg FAC		
		ClO_3^- (mg/L)	BrO_3^- (mg/L)	ClO_4^- (µg/L)	FAC (g/L)	ClO_3^- (µg/mg FAC)	BrO_3^- (ng/mg FAC)	ClO_4^- (ng/mg FAC)
Bulk	1-A	19,000	24	14,000	87	220	280	160
	2	5,900	30	670	150	39	200	4.5
	4	n/a	n/a	n/a	n/a	n/a	n/a	n/a
	5	1,800	9	220	120	15	75	1.8
	7	2,400	10	230	120	20	83	1.9
	8	8,000	8	2,000	130	62	59	15
OSG	1a	140	4.1	5.4	9.7	14	420	0.6
	1b	240	3.8	16	8	30	480	2.0
	2a	97	5.3	8.6	6.8	14	780	1.3
	2b	360	3.3	410	6.9	52	480	59
	3	270	4.4	7.3	10	27	440	0.7
	4	1200	2.6	40	4.5	270	580	8.9
	5	260	2.6	31	8	33	330	3.9
	6	180	1.4	22	5.2	35	270	4.2
	7	750	2	83	7.2	100	280	12
	8	240	0.71	740	3.6	67	200	210
	9	760	5.7	3500	6.8	110	840	520
	10	780	0.15	19	8.7	90	17	2.2
Cal Hypo	Cal 1	390.0	2.40	27.0	32	12	75	0.8
	Cal 2	830.0	5.30	55.0	61	14	87	0.9

Contaminant Concentrations in Distribution System and SDS Samples

The concentration of perchlorate, chlorate, and bromate was also measured in the distribution system samples in order to determine whether there was any additional chlorate, perchlorate, or bromate formation. In the case of Utility 2, a SDS study was used instead of collecting actual distribution system samples. Distribution system sampling locations were targeted to give a median residence time and a maximum residence time for each utility. Based on the model developed in Chapter 4 and the considerations of hypochlorite ion concentration, temperature, pH, and ionic strength it was not expected that any appreciable formation of chlorate, perchlorate, or bromate would be observed. The results of the distribution system sampling and SDS studies are shown in Table 5.9.

Table 5.9
Perchlorate, chlorate, and bromate concentrations in finished waters and distribution system samples

Utility	Res. time A (hrs)	Res. time B (hrs)	ClO_4^- Fin. (µg/L)	ClO_4^- Dist. A (µg/L)	ClO_4^- Dist. B (µg/L)	ClO_3^- Fin. (mg/L)	ClO_3^- Dist. A (mg/L)	ClO_3^- Dist. B (mg/L)	BrO_3^- Fin. (µg/L)	BrO_3^- Dist. A (µg/L)	BrO_3^- Dist. B (µg/L)
1-A	36	72	3.6	<0.5	3.1	0.58	0.59	1.2	0.5	0.80	2.9
1-B	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
4	96	168	<0.5	<0.5	<0.5	<0.003	<0.003	<0.003	<0.5	<0.5	<0.5
5	36	72	<0.5	<0.5	<0.5	0.20	<0.003	<0.003	1.4	2.1	2.2
6	6	12	2.1	2.2	2.2	0.16	0.14	0.031	1.3	2.6	2.2
7	12	24	<0.5	<0.5	<0.5	0.13	0.13	0.13	0.92	0.80	0.90
8*	100	150	1.2	1.2	0.90	0.79	1.6	0.82	2.6	5.9	3.2

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

In all cases except Utility 1-A, the concentration of contaminants did not increase in the distribution system. The difficulty in using grab samples from distribution system is that the hypochlorite solution used to disinfect the water is constantly changing and experiences turnover from new shipments and/or on-site generation. Thus, in order to assess behavior of chlorate, perchlorate, and bromate in distribution systems an in-depth study with more sampling sites (and distribution systems) combined with temporal observations over a period of several months is suggested as a future research direction.

Holding Studies for Bulk, OSG, and Calcium Hypochlorite Solutions

Each of the unquenched OSG solutions collected for this study was held at 50 ºC for a period of 30 days while periodic aliquots of the solution were collected for analysis of ionic strength, pH, and concentration of hypochlorite, chlorate, perchlorate, and bromate. Data for the oxyhalides were grouped by manufacturer and graphed against holding time (Figures 5.1, 5.2, and 5.3). As expected, samples with high initial hypochlorite concentrations (e.g., OSG 1a and OSG3, Figure 5.1) also showed higher overall perchlorate formation relative to starting concentration and those with low initial hypochlorite concentration (e.g., OSG 4, Figure 5.1) showed the lowest overall perchlorate formation relative to the starting concentration. Measurements of bromate concentration had a high degree of variability because sample dilutions were made to target chlorate and perchlorate; thus, bromate analysis was not optimized for utility OSG and bulk hypochlorite holding study and the data are not shown. However, bromate concentrations in all OSG and bulk hypochlorite samples did not appear to suggest a trend of increasing or decreasing concentration. Such observation is supported in the bromide/bromate studies discussed in Chapter 3 (most bromate formation is likely to occur during on-site generation or very shortly thereafter).

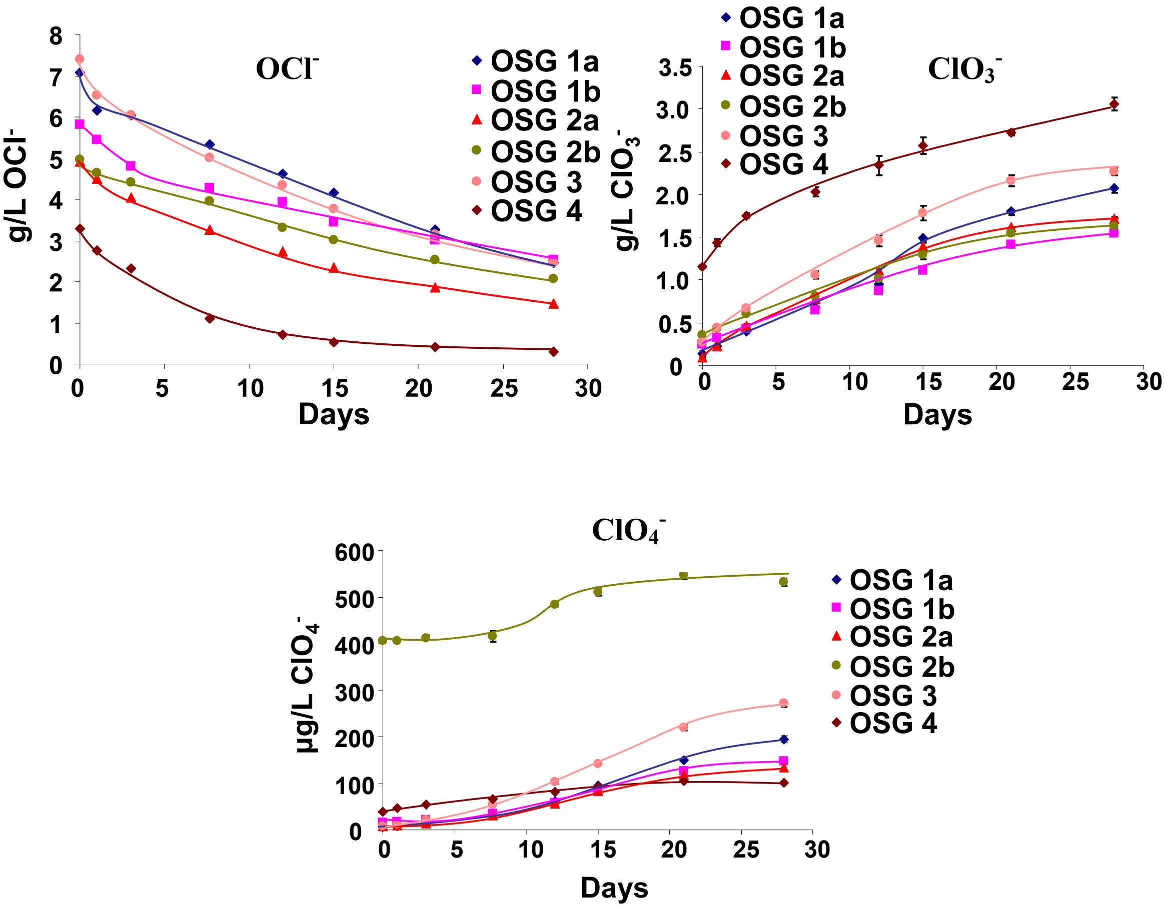

Figure 5.1 Hypochlorite, chlorate, and perchlorate concentrations during 50 ºC holding study for six OSG samples from the same OSG manufacturer (different models)

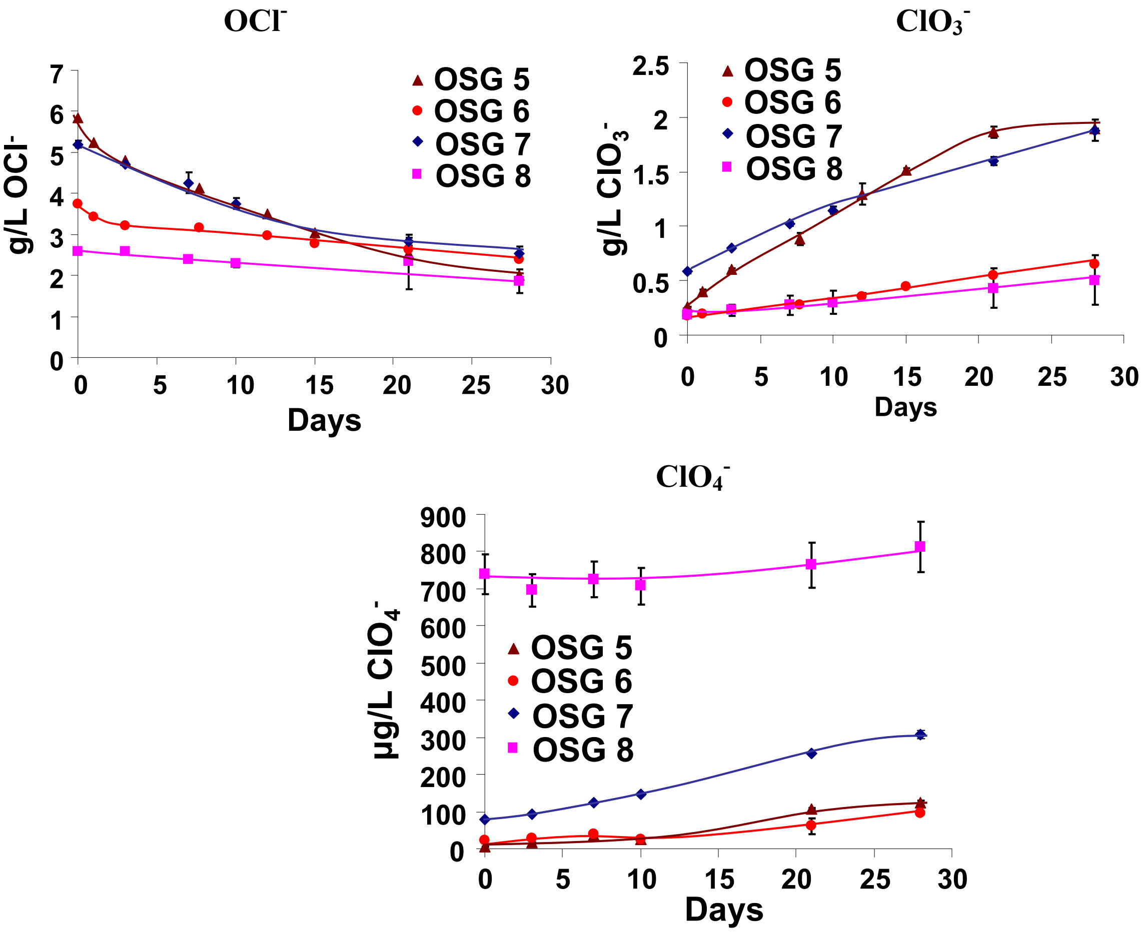

Figure 5.2 Hypochlorite, chlorate, and perchlorate concentrations during 50 ºC holding study for 4 OSG samples from the same OSG manufacturer (different models)

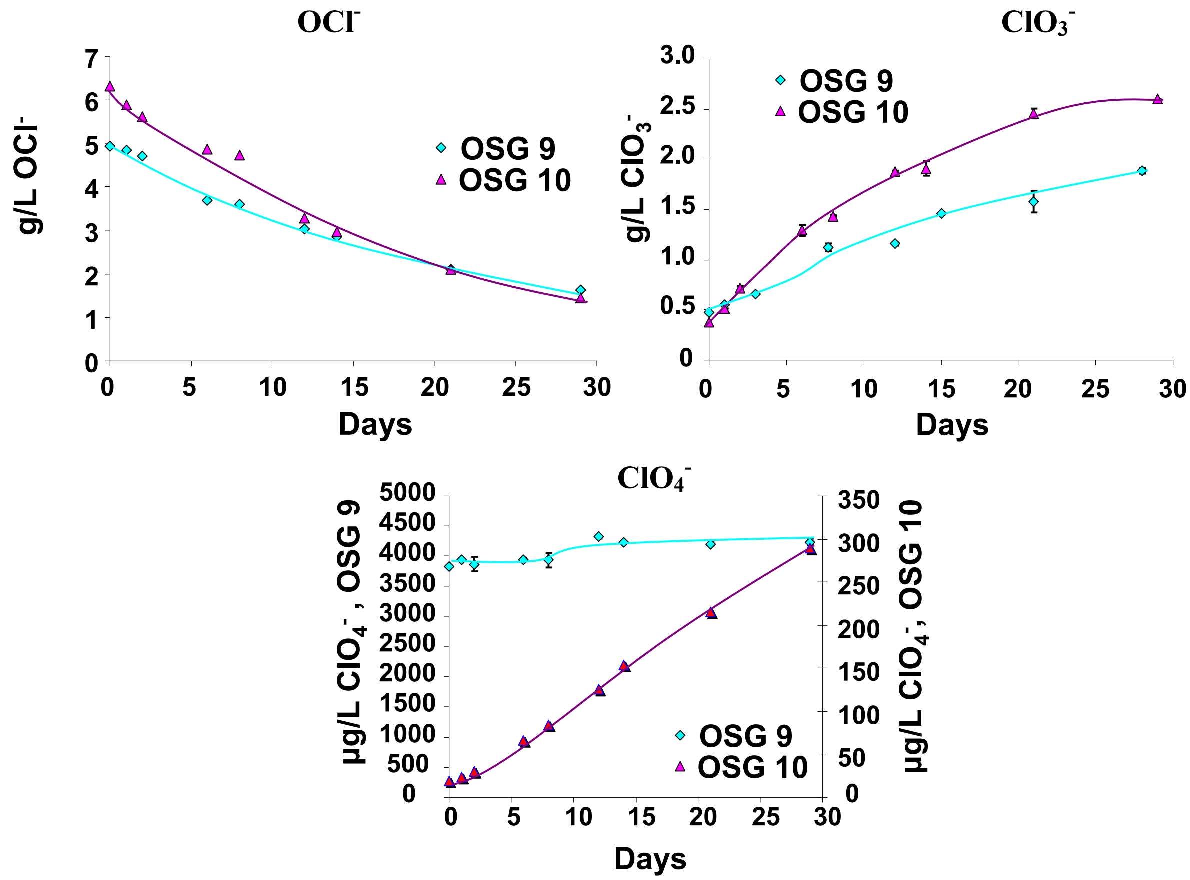

Figure 5.3 Hypochlorite, chlorate, and perchlorate concentrations during 50 ºC holding study for the two utility-provided OSG samples

The hypochlorite samples from the utilities were similarly aged at 50 ºC and analyzed for changes in hypochlorite, chlorate, perchlorate, and bromate concentrations (Figure 5.4). In all cases a higher initial hypochlorite concentration corresponded to higher rate of chlorate and perchlorate formation. Another interesting observation is the relative magnitude of perchlorate formation in the OSG samples versus the bulk hypochlorite samples. There is significantly less chlorate and perchlorate formation in the aging OSG samples than the aging bulk hypochlorite samples, a fact easily explained by the difference in starting concentration of hypochlorite and predicted by the reaction kinetics.

Similar to the bulk and OSG hypochlorite solutions, the two calcium hypochlorite solutions (3% and 6% FAC) were aged at 50 ºC and 60 ºC. The data from these two incubation studies are summarized in Figure 5.5. Upon examination of the data there were no major deviations from the trends observed in the bulk and OSG hypochlorite solutions: Increased temperature and increased starting concentration of hypochlorite both increased the rate of chlorate and perchlorate formation.

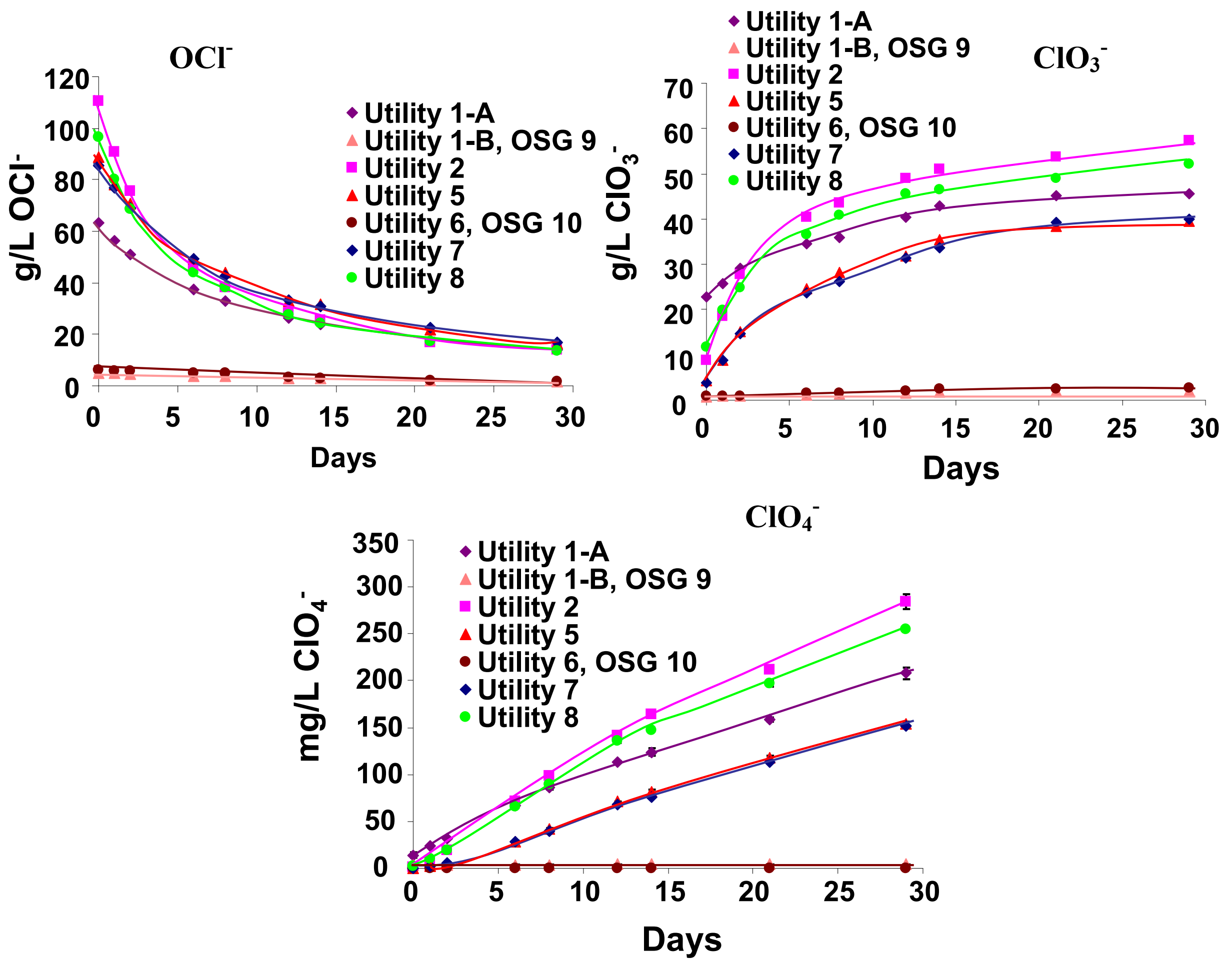

Figure 5.4 Hypochlorite, chlorate, and perchlorate concentrations during 50 ºC holding study for all Utility hypochlorite samples

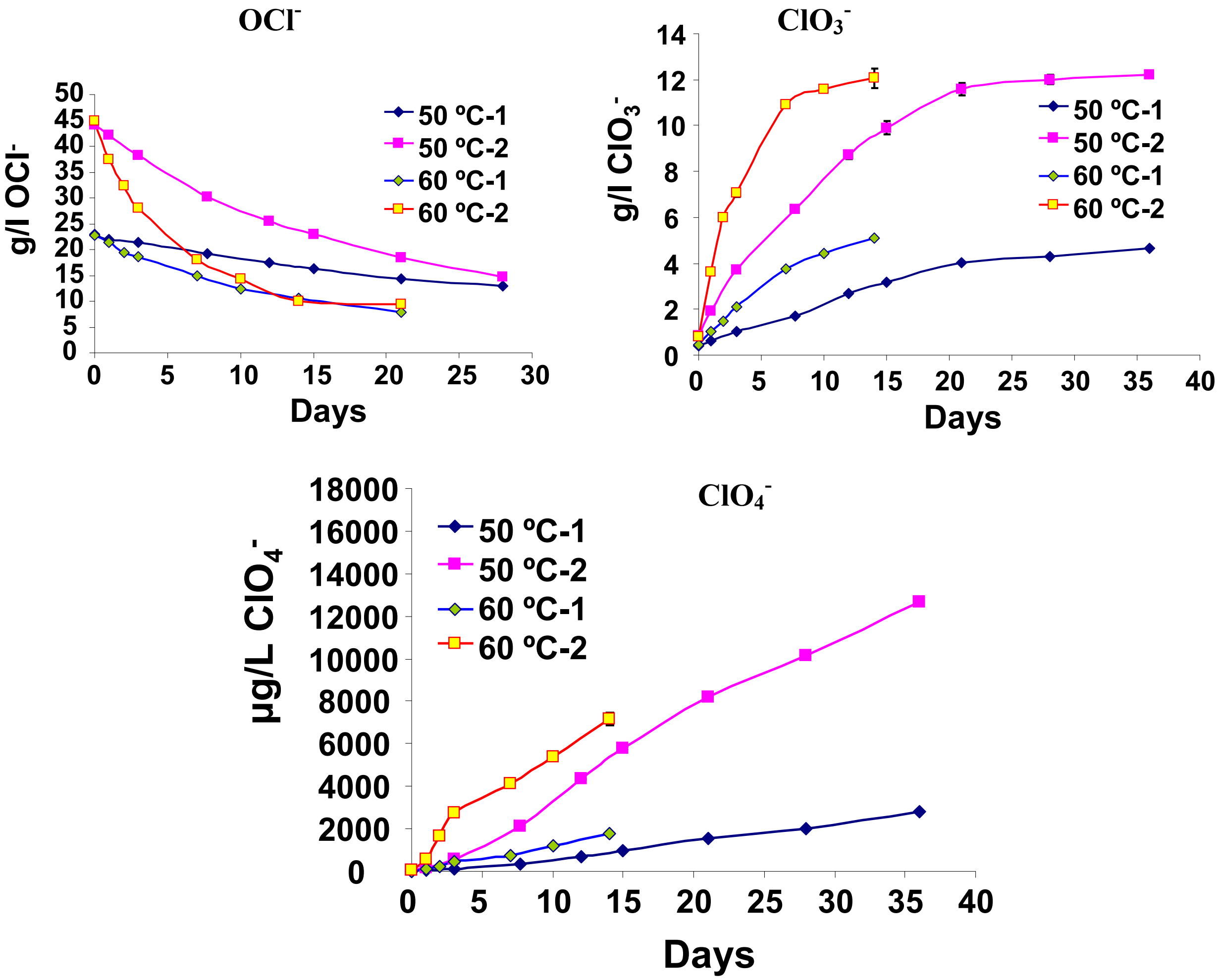

Figure 5.5 Calcium hypochlorite solutions aged at 50 ºC and 60 ºC with 3% FAC (Cal Hypo 1: 50 ºC-1, 60 ºC -1) and 6% FAC (Cal Hypo 2: 50 ºC-2, 60 ºC -2)

Comparison of Measured vs. Predicted Concentration using MUL

The MUL of 10 mg/L was used to estimate the maximum amount of contaminants that could be dosed into the finished water via hypochlorite addition. The calculation of MUL followed the equations listed below and relied upon the measured concentration of specific contaminants (e.g., chlorate, perchlorate, bromate) in the hypochlorite to be dosed into the water plus the concentration of each contaminant in the raw water:

$$\text{Volume}_{\text{hypo dosed}} = \frac{10\text{ mg/L} \times 1\text{ L}}{\text{FAC}_{\text{hypo dosed}}\text{ (mg/L)}} \tag{5.1}$$

$$\text{Max. Conc.}_{\text{MUL,10}} = \frac{\text{Volume}_{\text{hypo dosed}} \times [\text{Contaminant}]_{\text{hypo dosed}}}{1\text{L}} + [\text{Contaminant}]_{\text{raw water}} \tag{5.2}$$

The maximum expected concentrations of each contaminant based on the MUL approach are listed in Table 5.10. In most cases, the MUL calculated concentrations in the finished water did not match the measured finished water concentrations of chlorate, perchlorate, or bromate though they did provide a conservative estimate. The premise behind the MUL is that it provides for a conservative calculation by *overestimating* the concentration of a contaminant in the finished water by assuming the maximum amount of hypochlorite that would be used at any given facility. While this is a reasonable approach, it is limited in its predictive ability because it does not take into consideration other potential sources of contaminants (e.g., oxidation of bromide to bromate during ozonation) or sinks of contaminants (e.g., ion exchange sites on filter media). Underestimation of contaminant concentrations by >20% occurred 5 times (once for perchlorate, twice for chlorate, twice for bromate). Such observations are consistent with attempts published elsewhere at using injection ratios (similar to MUL but using actual dosing quantities) to predict finished water concentrations of chlorate and perchlorate (Asami, Kosaka, and Kunikane 2007; Asami, Kosaka, and Kunikane 2009). Thus, it is not clear whether using the MUL would be a good tool to predict actual contaminant concentrations in drinking water nor would it be beneficial to use as a "normalization" technique as suggested elsewhere (Greiner, et al. 2008). However, if combined with an understanding of the treatment process at any given facility it may be able to provide a reasonable estimation of maximum expected contaminant concentrations.

Table 5.10
Comparison of measured and calculated concentrations of contaminants in finished water samples from participating utilities

			ClO_4^-			ClO_3^-			BrO_3^-	
Utility	FAC g/L	Hypo (µg/L)	MUL* (µg/L)	Meas.** (µg/L)	Hypo (mg/L)	MUL* (mg/L)	Meas.** (mg/L)	Hypo (µg/L)	MUL* (µg/L)	Meas.** (µg/L)
1-A	87	14000	1.9	3.6	19000	2.2	0.58	24000	3.0	0.5
1-B	6.8	3500	5.4	<0.5	480	0.7	1.5	2700	4.2	3.6
2	150	670	0.3	<0.5	5900	0.4	0.019	30000	2.3	<0.5
4	Cl_2 Gas	n/a	n/a	<0.5	n/a	n/a	<0.003	n/a	n/a	<0.5
5	120	220	0.3	<0.5	1800	0.3	0.20	9000	2.1	1.4
6	8.7	20	2.0	2.1	380	0.4	0.16	50	0.3	1.3
7	120	230	0.3	<0.5	2400	0.2	0.13	9900	1.1	0.92
8	130	2000	1.8	1.2	8000	0.6	0.79	7700	0.8	2.6

*Estimated concentration in finished water based on maximum use level (MUL) of 10 mg/L FAC as Cl_2; **Measured concentration in finished water; Refer to Table 5.3 for raw water concentrations (when raw water concentration was < MRL, a value of ½ the MRL was used in the MUL calculation)

Measured vs. Predicted Concentrations of OCl^- and ClO_3^- in Hypochlorite using *Bleach 2001*

The *Bleach 2001* (Adam, Gordon, and Pierce 2001) model was applied to the aged utility bulk hypochlorite samples for verification that hypochlorite decomposition and chlorate formation was occurring as expected. Four of the five Utility bulk hypochlorite samples were selected for use in this modeling exercise. OSG hypochlorite samples were not used in this exercise as they typically have pH values in the range 9 – 10; the *Bleach 2001* model does not predict below pH 11 because the recommendation for utilities is to store liquid hypochlorite at pH 11 – 13. Thus, running a simulation of OSG hypochlorite decomposition was not applicable. The starting concentration, pH, and holding temperature for the bulk hypochlorite solutions are summarized in Table 5.11. Figure 5.6 shows overlaid plots of hypochlorite decomposition and chlorate formation of measured vs. predicted concentrations for four Utility bulk hypochlorite samples.

Table 5.11
Initial concentrations, pH, and temperature values entered into *Bleach 2001*

Utility	pH	OCl^- (g/L)	ClO_3^- (g/L)	Temperature (ºC)
1-A	12.84	63.1	22.8	50
2	13.25	110.7	8.73	50
5	12.90	89.0	4.37	50
8	13.11	96.7	11.6	50

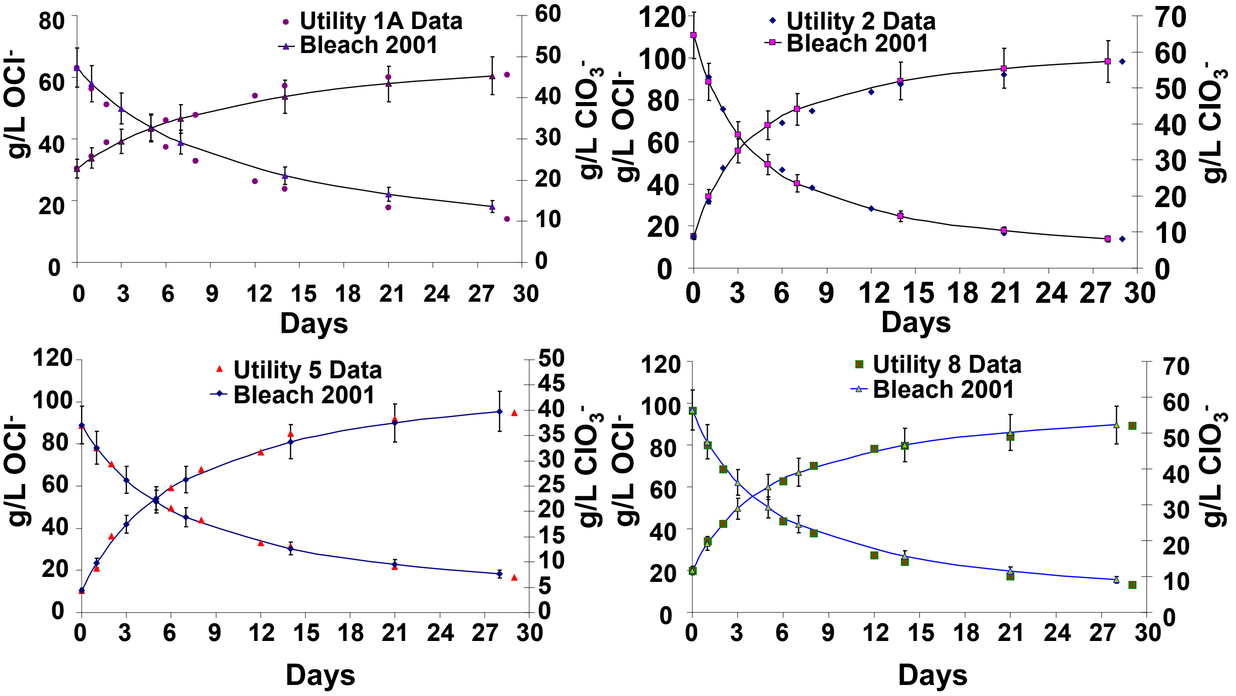

Figure 5.6 Measured vs. predicted concentrations of OCl^- and ClO_3^- in hypochlorite using *Bleach 2001:* Utility 1A, 2, 5, and 8 aged at 50 ºC; Error bars are 10% of predicted value

In general, the measured decomposition of sodium hypochlorite samples from the utilities showed excellent agreement (within 5 to 10 %) with the *Bleach 2001* predicted decomposition with the exception of Utility 1-A differing by up to 25%. The plot of the Utility 1-A sample in Figure 5.6 shows that hypochlorite decomposed faster than expected, possibly resulting from the presence of iron at 9.2 mg/L, copper at 0.1 mg/L, and nickel at 0.2 mg/L (Table 5.5) in the hypochlorite solution. Otherwise, the agreement between measured concentrations and predicted concentrations was acceptable. Therefore, considering that the chemical model for predicting perchlorate concentration over time requires an input of predicted hypochlorite and chlorate concentrations, it was determined that *Bleach 2001* could be used to generate those predicted concentrations for use in perchlorate modeling.

Measured vs. Predicted Concentrations of ClO_4^- in Hypochlorite using the "Predictive Model"

The "Predictive Model" from the detailed chemical rate law of perchlorate formation described in Chapter 4 of this report was also applied to the aged bulk hypochlorite samples selected for *Bleach 2001* testing. This application of the "Predictive Model" was used in order to validate its ability to predict perchlorate concentrations in hypochlorite solutions other than those used to develop the model. As an additional exercise, the rate of perchlorate formation and the observed rate constant were calculated for each hypochlorite solution and are summarized in Table 5.12. As seen, the rate of perchlorate formation appears to be impacted by a combination of ionic strength, concentration of hypochlorite, and concentration of chlorate, indicating that each factor is indeed important to include in the "Predictive Model".

Table 5.12

Observed rate and rate constant of perchlorate formation in bulk sodium hypochlorite solutions received from participating utilities

Utility	pH	[OCl-] (mol/L)	[ClO3-] (mol/L)	I (mol/L)	Observed *Rate ($\times 10^{-6}$)	**k_{obs} ($\times 10^{-6}$)
1-A	12.84	1.226	0.228	5.74	100	363
2	13.25	2.152	0.071	6.47	76	499
5	12.9	1.729	0.022	4.86	19	506
7	13.13	1.661	0.029	4.95	21	427
8	13.11	1.879	0.096	6.26	78	429

*Rate in units of mol ClO_4^- / L / d; **k in units of L / mol ClO_4^- / d

(Utilities 1-B and 6 were OSG samples; Utility 3 was not sampled; Utility 4 used Cl_2 gas)

Comparing the measured concentration of perchlorate over time with the predicted perchlorate concentration provides the best evidence of the validity of the "Predictive Model". Figure 5.7 shows overlaid plots of average measured concentration of perchlorate over time vs. predicted concentration in bulk hypochlorite samples. The error bars in Figure 5.7 have been arbitrarily set at ± 10%. The formation of perchlorate in most samples was predicted to within ± 10% of the actual values. This demonstrates that the "Predictive Model" is a useful way to approximate the formation of perchlorate in bulk hypochlorite solutions. Moreover, this exercise demonstrates that the "Predictive Model" can be used to make specific recommendations to utilities based on predicted behavior that will assist in minimizing perchlorate formation during storage.

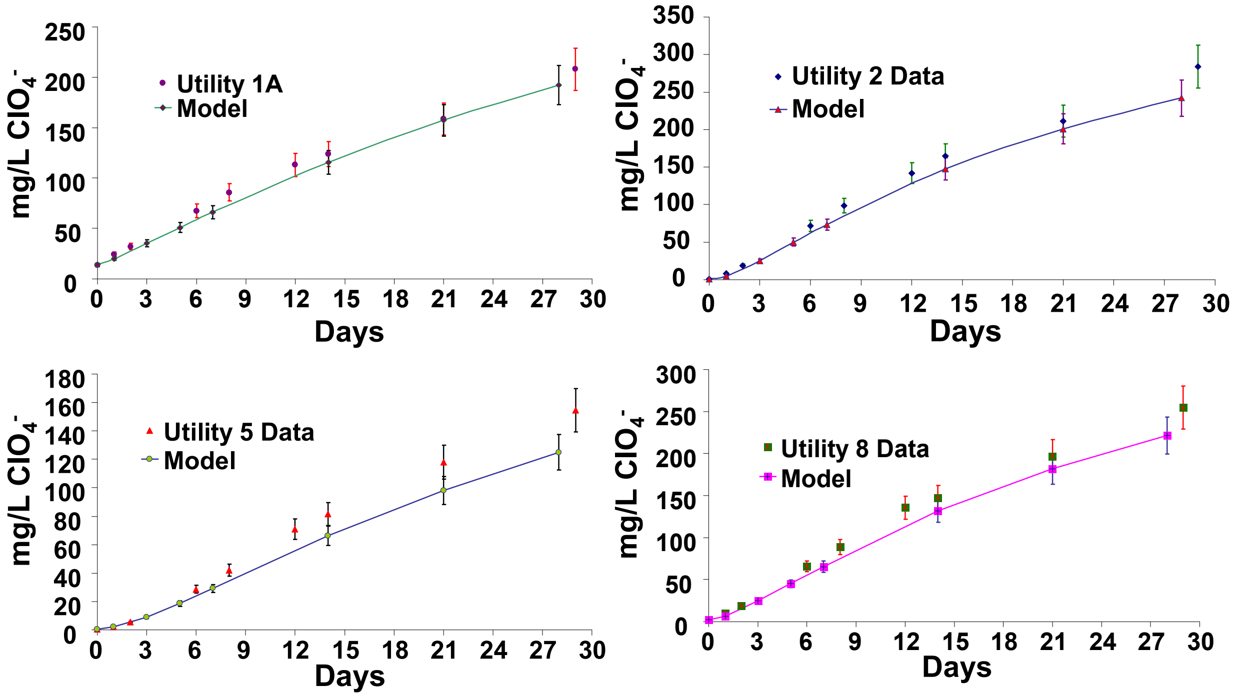

Figure 5.7 Measured vs. predicted concentrations of ClO_4^- in hypochlorite using the Predictive Model: Utility 1, 2, 5, and 8 aged at 50 ºC; Error bars are +/- 10%

Finally, in a demonstration of the importance of the "master variables" (ionic strength and concentration of chlorate and hypochlorite), the observed rate of perchlorate formation in each of the bulk hypochlorite, OSG, and calcium hypochlorite was plotted against ionic strength (Figure 5.8) and the molar product (Figure 5.9). Table 5.13 lists the observed rate and rate constants for the OSG and calcium hypochlorite solutions. While the correlation was reasonable for the constant molar product, a significant amount of variability was introduced with the OSG solutions, likely a function of their low pH range (pH 8.8 to 9.8). When the OSG samples are removed (Figures 5.10 and 5.11), a much better correlation (as reflected by the R^2 values) is observed between the observed rate and ionic strength and the observed rate and molar product. The remaining variability in the ionic strength plot (Figure 5.11) may be explained by the use of a surrogate for ionic strength (i.e., conductivity) rather than the true ionic strength of the solution.

Table 5.13
Observed rate and rate constants of perchlorate formation in OSG hypochlorite and calcium hypochlorite solutions

	I (mol/L)	pH	[OCl-] (mol/L)	[ClO3-] (mol/L)	Observed *Rate (x 10^{-9})	**k_{obs} (x 10^{-6})
OSG 1a	0.669	9.36	0.137	0.0016	68	300
OSG 1b	0.589	9.26	0.113	0.0029	47	140
OSG 2a	0.945	9.12	0.096	0.0012	45	410
OSG 2b	0.526	9.23	0.097	0.0043	46	110
OSG 3	0.682	9.28	0.144	0.0032	95	200
OSG 4	0.502	8.77	0.064	0.0139	22	25
OSG 5	1.15	9.06	0.113	0.0031	72	200
OSG 6	0.546	9.41	0.073	0.0021	15	96
OSG 7	0.923	9.47	0.101	0.0070	82	120
OSG 8a	0.280	9.28	0.052	0.0024	31	250
OSG 8b	0.250	9.84	0.049	0.0020	22	220
OSG 9	0.828	9.38	0.096	0.0057	140	260
OSG 10	0.882	9.36	0.123	0.0045	94	170
CalHypo1 @ 50 ºC	0.748	11.2	0.446	0.0047	389	187
CalHypo2 @ 50 ºC	1.38	11.5	0.859	0.0099	2700	319
CalHypo1 @ 60 ºC	0.748	11.4	0.443	0.0052	540	235
CalHypo2 @ 60 ºC	1.38	11.5	0.874	0.0099	3500	409

*Rate in units of mol ClO_4^- / L / d;
**k in units of L / mol ClO_4^- / d

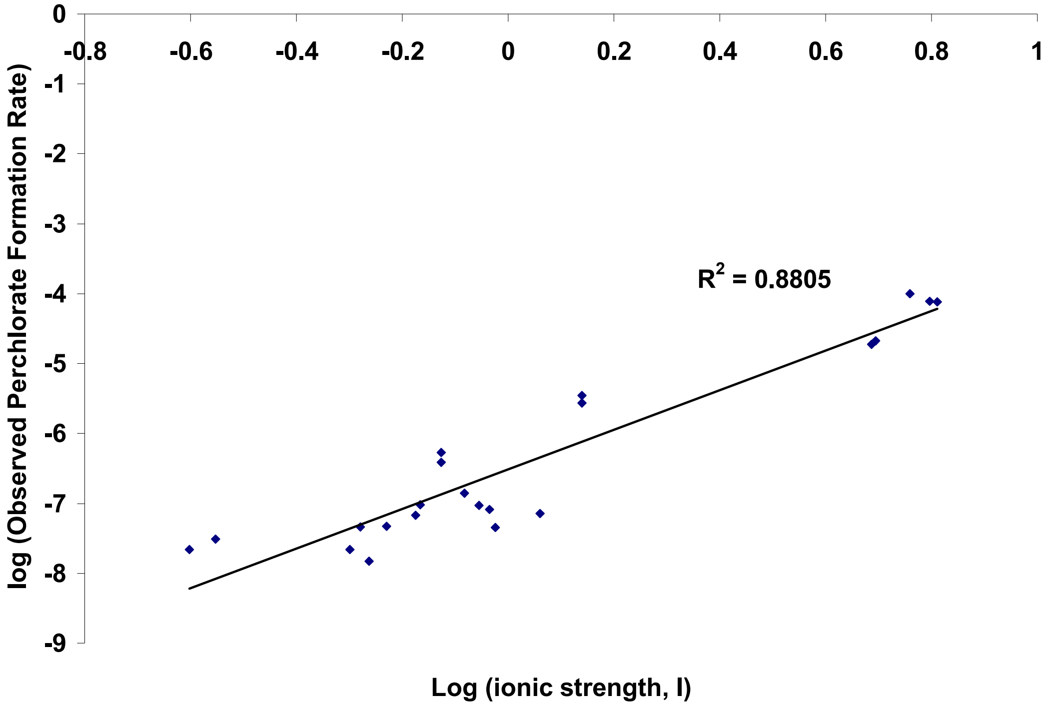

Figure 5.8 Relationship between observed rate of perchlorate formation and ionic strength for bulk, OSG, and calcium hypochlorite samples

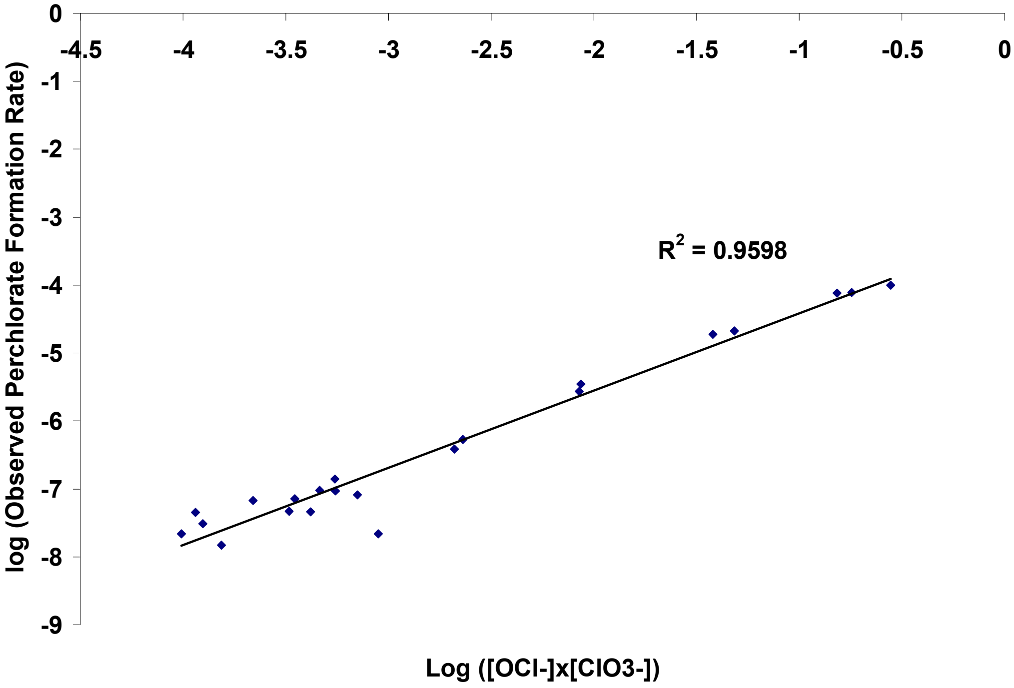

Figure 5.9 Relationship between observed rate of perchlorate formation and the molar product of hypochlorite and chlorate for bulk, OSG, and calcium hypochlorite samples

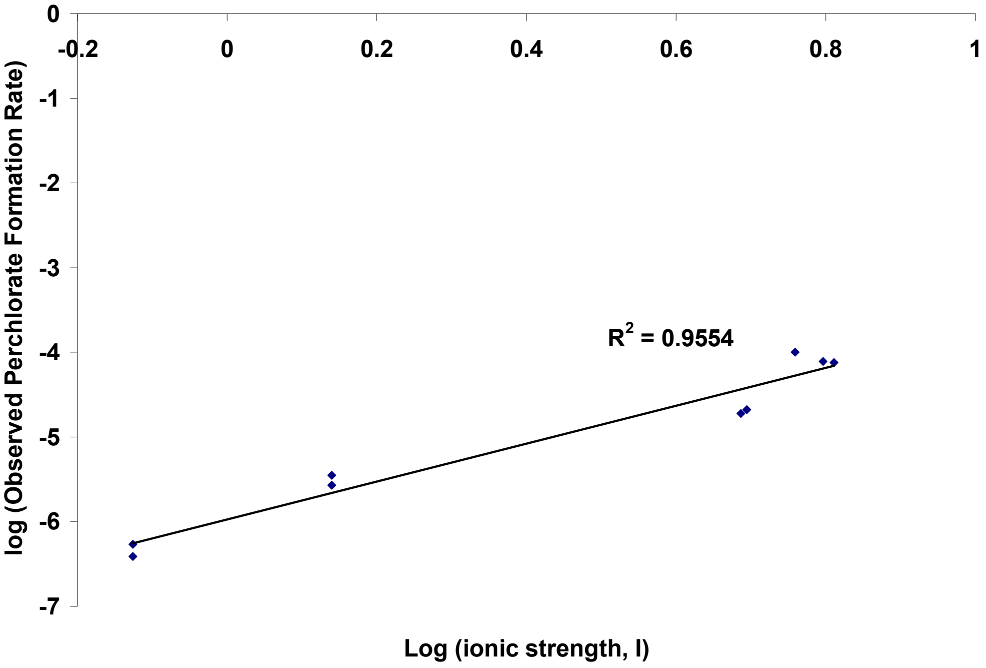

Figure 5.10 Relationship between observed rate of perchlorate formation and ionic strength for bulk and calcium hypochlorite samples only

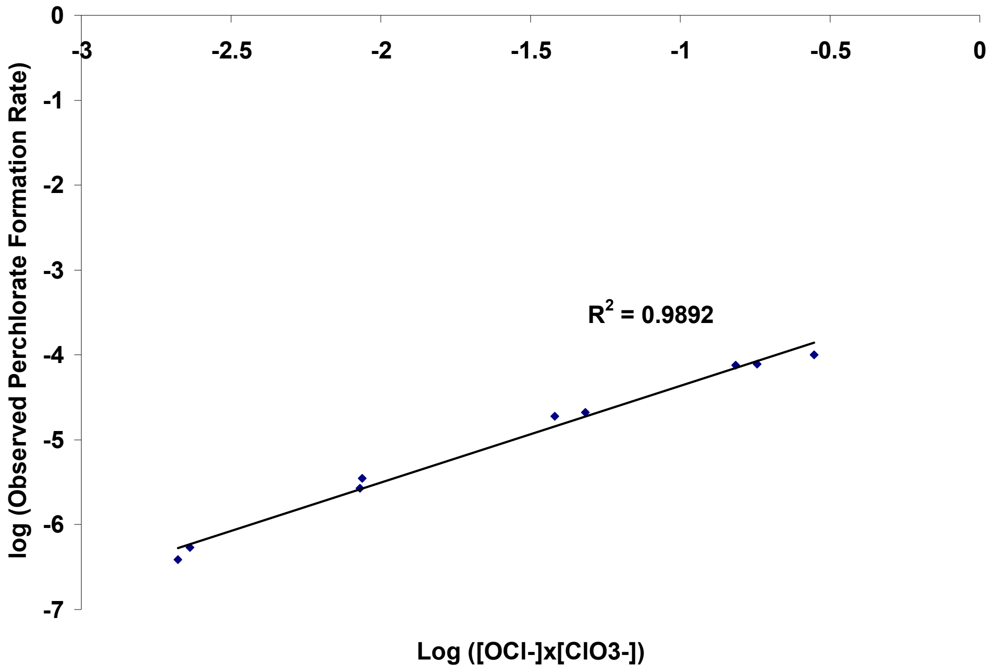

Figure 5.11 Relationship between observed rate of perchlorate formation and the molar product of hypochlorite and chlorate for bulk and calcium hypochlorite samples only

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SUMMARY

In summary, the detailed chemical rate law (i.e., "Predictive Model") can be applied to bulk sodium hypochlorite solutions in conjunction with *Bleach 2001* to predict perchlorate formation over time at various temperatures and ionic strength. The model is only applicable to bulk sodium hypochlorite in pH 11-13 range due to the design of *Bleach 2001* working only within the specifications for bulk hypochlorite solutions. At the high temperature selected for aging the bulk hypochlorite samples (50 ºC), the "Predictive Model" was able in 3 out of 4 cases to predict actual perchlorate concentrations within 10% of the measured value. Furthermore, observed rates of perchlorate formation in bulk hypochlorite and calcium hypochlorite solutions correlated well with ionic strength and the molar product of hypochlorite and chlorate.

The errors in correlation and prediction observed could be due to the use of a surrogate (i.e., conductivity) for ionic strength instead of true ionic strength. The only way to determine the "true" ionic strength would be to measure the concentration of each cation and anion in the solution and then sum their individual concentrations into a combined ionic molarity. Such an undertaking would be impractical at best for an individual utility wanting to estimate what impact different storage scenarios would have on perchlorate formation. Thus, in bulk hypochlorite solutions that vary widely in quality and starting concentration of each contaminant, using conductivity as a surrogate provides an appropriate and useful surrogate for ionic strength. Furthermore, the model has demonstrated its ability to predict the *trends* of perchlorate formation which, from a utility perspective, is the most useful information to guide the decision making about how best to store bulk hypochlorite solutions.

REFERENCES

Adam, Luke, Gilbert Gordon, and Don Pierce. 2001. *Bleach 2001*. Miami University, Oxford, Ohio. Copyright (c) 2001 AwwaRF and AWWA.

Asami, M., K. Kosaka, and S. Kunikane. 2007. Bromate, Chlorate, Chlorite, and Perchlorate in Sodium Hypochlorite Solution Used for Water Supply. *Asian Pacific Regional Exhibition, International Water Association*:10-14.

Asami, Mari, Koji Kosaka, and Soichi Kunikane. 2009. Bromate, Chlorate, Chlorite, and Perchlorate in Sodium Hypochlorite Solution Used for Water Supply. *Journal of Water Supply Research and Technology-Aqua*, 58 **(2)**:107-117.

Gordon, Gilbert, Luke C. Adam, Bernard P. Bubnis, Ching Kuo, Robert S. Cushing, and Richard H. Sakaji. 1997. Predicting Liquid Bleach Decomposition. *Journal American Water Works Association*, 89 **(4)**:142-149.

Gordon, Gilbert and Bernard Bubnis. 2000. Sodium Hypochlorite Specifications. *Proceedings of the AWWA Annual Conference*; 123-125; CD ROM W-12, 7, 12 pp

Greiner, Peter, Clif McLellan, Dale Bennett, and Angie Ewing. 2008. Occurrence of Perchlorate in Sodium Hypochlorite. *American Water Works Association Journal*, 100 **(11)**:68-74,10.

Howd, Robert H. 2002. Memorandum: Proposed Action Level for Chlorate. CA Office of Environmental Health Hazard Assessment. Sacramento, CA. http://oehha.ca.gov/water/pals/chlorate.html

Kosaka, Koji, Mari Asami, Yukiko Matsuoka, Masahiro Kamoshita, Shoichi Kunikane. 2007. Occurrence of Perchlorate in Drinking Water Sources of Metropolitan Area in Japan. *Water Research*, 41:3474 – 3482.

NSF/ANSI, (NSF International/American National Institute of Standards). 2005. NSF/ANSI Standard 60. Drinking Water Treatment Chemicals - Health Effects, NSF International, Ann Arbor, Michigan: 148 pages.

CHAPTER 6
CONCLUSIONS AND SUMMARY

DISCUSSION

In the first part of this study, two methods were validated for the analysis of perchlorate and chlorate in hypochlorite solutions: titration and LC-MS/MS. The titration method was better suited for use with concentrated (>5% FAC) hypochlorite solutions while the LC-MS/MS method was better suited for use with lower concentration (<5%) hypochlorite and water samples. Bromate was quantified using LC-MS/MS and transition metals were quantified using ICP-MS. Malonic acid was found to be the most reliable and appropriate quenching agent for use in the study, providing no measurable interference in analysis, no problems associated with storage, and no major safety issues associated with shipping, handling, and the quenching reaction itself.

The methods developed in the early stages of the study were used to investigate factors impacting the rate of formation of perchlorate and bromate in hypochlorite solutions. Bromate was found to form within one to two days of introduction of bromide into hypochlorite solutions. Furthermore, bulk hypochlorite and OSG samples received from utilities showed little-to-no additional bromate formation. Thus, the data suggest that nearly all bromate is formed during manufacture or shortly thereafter. Perchlorate formation, on the other hand, was slow enough to measure and was impacted by several sets of factors: (1) Direct (mechanistic) factors including hypochlorite ion concentration, chlorate ion concentration, and ionic strength. (2) Indirect factors including the presence of metal ions and the presence of bromide ion. (3) Environmental factors including pH and temperature. While it is possible to argue that pH is really a mechanistic factor and that ionic strength is really an environmental factor, their effects were categorized as such to simplify discussion of the detailed chemical rate law. Bromide and metal ions were found to impact the formation of perchlorate indirectly by enhancing the loss of hypochlorite, either through decomposition (catalyzed by metals) or formation of bromate. The effect of pH was important, but in the pH 11 – 13 range was not shown to be a major factor in perchlorate formation.

After separating the factors impacting the rate of perchlorate formation, a detailed chemical rate law describing the dependence of perchlorate formation on ionic strength, hypochlorite ion concentration, chlorate ion concentration, and temperature was developed. While initial data indicated the rate of perchlorate formation may have been greater than second order and a result of parallel or consecutive mechanisms, ionic strength turned out to be the "master variable" controlling the reaction rate. As such, the formation of perchlorate is first order in hypochlorite and chlorate ion concentration and is highly dependent upon ionic strength and temperature. Thus, the detailed chemical rate law was used as a "Predictive Model" to predict perchlorate concentration to within 10% of the measured perchlorate concentration in multiple bulk hypochlorite samples aged at different temperatures for up to 200 days. Furthermore, the "Predictive Model" was then used to develop a set of quantitative recommendations for utilities to use to minimize the amount of perchlorate formation in stored bulk hypochlorite solutions. It should be noted, however, that given the time limitation of the study, the model was not validated on real samples below 30 ºC. Thus, any predictions below 30 ºC should be limited to a qualitative assessment of how dilution and temperature changes impact perchlorate formation rather than an exact prediction of the actual concentration of perchlorate expected.

Finally, a set of 5 bulk hypochlorite solutions, 12 OSG hypochlorite solutions, and one calcium hypochlorite sample was obtained for contaminant analysis and quantification and was used in a holding study to examine the rate of perchlorate formation in each solution. All samples tested had measurable concentrations of chlorate, perchlorate, and bromate. No specific conclusions could be made regarding differences in contaminant concentrations in bulk, OSG, and calcium hypochlorite solutions. There did appear to be, however, a link between salt quality and bromate concentration in OSG samples, suggesting that a salt of a higher purity (in this study, >99.5% as NaCl) may be useful for reducing the amount of bromate in the hypochlorite product. However, this trend needs to be further investigated before a specific recommendation on salt purity and maximum levels of bromide can be quantified. When the various solutions were aged, good correlation was observed between the rate of perchlorate formation, the concentration of hypochlorite and chlorate ions, and ionic strength. Furthermore, the "Predictive Model" was able to predict perchlorate formation in the commercial bulk hypochlorite samples to within 20% of the measured concentration for up to 28 days at 50 ºC.

RECOMMENDATIONS

Based on the findings presented in this report, several key factors have been identified that impact the formation of perchlorate, bromate, and other contaminants in hypochlorite solutions. The major factors impacting perchlorate formation parallel those previously described for reducing the decomposition of hypochlorite: temperature, ionic strength, concentration, and pH. By using the information gathered during this study and by applying the "Predictive Model" to hypothetical liquid hypochlorite storage scenarios, several quantitative and qualitative recommendations can be made:

a. <u>Dilute stored hypochlorite solutions upon delivery:</u> The decomposition of hypochlorite and subsequent formation of chlorate and perchlorate is dependent upon hypochlorite concentration and ionic strength. Higher ionic strength and hypochlorite concentration will drive the reaction towards a greater production of chlorate and perchlorate while also increasing the rate of decomposition of hypochlorite. By diluting a 2 molar hypochlorite solution by a factor of 2, the rate of perchlorate formation decreases by a factor of 7 due to the combination of concentration and ionic strength effects A four-fold dilution of a hypochlorite solution will decrease the rate of formation by 36. A ten-fold dilution of a hypochlorite solution will decrease the rate of perchlorate formation by a factor of 270.

b. <u>Store the hypochlorite solutions at lower temperatures:</u> Higher temperatures speed up the chemical decomposition of hypochlorite and the subsequent formation of chlorate and perchlorate. Every 5 ºC reduction in storage temperature will reduce the rate of perchlorate formation by a factor of approximately 2.

c. <u>Control the pH of stored hypochlorite solutions at pH 11 – 13, even after dilution</u>: Storage of concentrated hypochlorite solutions at pH values lower than 11 is not recommended due to rapid decomposition of hypochlorite ion/hypochlorous acid and the consequent formation of chlorate even though this reduces the amount of perchlorate formed. When the pH is higher than 13, perchlorate formation is enhanced due to the ionic strength effect. As such, utilities should continue to insist that manufacturer specifications include pH control in the range of 11 to 13. Given the typical pH range of OSG hypochlorite (pH 9 to 10), such solutions should be used as soon as possible after manufacture and should not be stored for more than 1-2 days.

d. <u>Control the removal of transition metal ions by purchasing filtered hypochlorite solutions and by using low-metal ion concentration feed water for the OSG systems</u>: The presence of transition metal ions results in an increased degradation rate of hypochlorite. While this degradation is concomitant with reduced perchlorate formation, the FAC concentration is also reduced, forcing a utility to use a higher volume of a hypochlorite solution which results in higher mass loading of contaminants such as perchlorate, chlorate, and bromate.

e. <u>Use fresh hypochlorite solutions when possible:</u> Over time, hypochlorite will naturally decompose to produce oxygen, chlorate, and perchlorate. Less storage time will minimize the formation of these contaminants in the hypochlorite solution. A fresh hypochlorite solution will also contain a higher concentration of hypochlorite, thereby reducing the amount of solution required to obtain the target chlorine residual. Again, higher hypochlorite concentration in a fresh hypochlorite solution will correspond to lower concentrations of contaminants dosed.

f. <u>For utilities using OSG hypochlorite, use a low-bromide salt to minimize the amount of bromide present in the brine:</u> 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 on-site generation, bromate formation can be minimized.

If a utility were to combine dilution with temperature reduction, a significant impact on hypochlorite decomposition and perchlorate formation would be observed. For example, as described in Chapter 4 if a utility were to dilute a 13% bulk hypochlorite solution by a factor of 2 and also reduce the storage temperature by 10 ºC, the result would be 16 times less hypochlorite decomposition and 27 times less perchlorate formation than if the hypochlorite were stored at ambient temperatures undiluted.

Another interpretation of the results of this study is through seasonal trends. If, for example, a utility experienced average bulk hypochlorite storage temperatures of 10 ºC in the winter and 35 ºC in the summer, the rate of perchlorate formation for 13% hypochlorite would be nearly 18 times faster in the summer. In other words, in winter that utility could expect the concentration of perchlorate concentration to increase by a factor of 10 in approximately 3 months; in summer it would increase by a factor of 10 in only 5 days. Had the hypochlorite solution been diluted by a factor of 2, the same increase in perchlorate concentration would take one month in summer and 20 months (assuming, for example, an average temperature of 10 ºC) in winter. Therefore, in order to minimize the amount of perchlorate formation in hypochlorite solutions, a combination of dilution and temperature control is recommended.

FUTURE WORK

While the “Predictive Model” is appropriate for use in bulk hypochlorite solutions, it would be interesting to build in a pH dependence to assist with predictions for OSG hypochlorite which may have pH values in the range of 9 to 10. Also, according to Adam and Gordon (1999), some chloride ion-specific dependence exists within the mechanism of chlorate formation. The direct impact of chloride ion formation (other than in its use to increase ionic strength) was not investigated. Thus, future studies examining the impact of chloride ion on perchlorate formation may be investigated. Furthermore, ionic strength was measured by a surrogate, conductivity, and thus does not reflect the “true” ionic strength of the solution. The detailed chemical rate law incorporates the measured “ionic strength”, but may benefit from the incorporation of the “true” ionic strength. As such, future studies are also recommended which may address this issue. The relationship between salt purity and bromate formation during OSG production of hypochlorite needs to be quantified and should be investigated more thoroughly. Finally, in order to 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 over a period of several months is suggested as a future research direction. Such information may indicate whether any contaminant violations could occur in distribution systems with high temperatures and long residence times.

REFERENCES

Adam, Luke C. and Gilbert Gordon. 1999. Hypochlorite Ion Decomposition: Effects of Temperature, Ionic Strength, and Chloride Ion. *Inorganic Chemistry*, 38 **(6)**:1299-1304.

LIST OF ABBREVIATIONS

Abbreviation	Description
$\Delta H^{\ddagger}$	Enthalpy of Activation
$\Delta S^{\ddagger}$	Entropy of Activation
ACS	American Chemical Society
ARDC	Applied Research and Development Center
AWWA	American Water Works Association
CA DPH	California Department of Public Health
DNA	Deoxyribonucleic Acid
DSA	Dimensionally Stabilized Anode
DWEL	Drinking Water Equivalent Level
DWTP	Drinking Water Treatment Plant
EPA	*See US EPA*
FAC	Free Available Chlorine
GW	Groundwater
HDPE	High Density Polyethylene
I	Ionic Strength
IC-CD	Ion Chromatography with Conductivity Detection
IC-MS/MS	Ion Chromatography with Tandem Mass Spectrometry
IC-PCR	Ion Chromatography with Post Column Reaction
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
JNIPH	Japanese National Institute of Public Health
k_0	Rate Constant at Zero Ionic Strength
k_2	Hypothetical Second Order Rate Constant
k_b	Boltzmann's Constant
k_{calc}	Calculated Rate Constant
k_{obs}	Observed Rate Constant
LC-MS	Liquid Chromatography with Mass Spectrometry
LC-MS/MS	Liquid Chromatography with Tandem Mass Spectrometry
M	Molarity (mol/L)
MA DEP	Massachusetts Department of Environmental Protection
MCL	Maximum Contaminant Level
MP	Molar Product
MRL	Method Reporting Limit
MS/MS	Tandem Mass Spectrometry

Abbreviation	Description
NOEL	No Observable Effect Level
NSF/ANSI	NSF International/American National Standards Institute
OD	Ocean Desalination
OSG	On-Site Generator
PAC	Project Advisory Committee
PPD	Pounds Per Day
R	Ideal Gas Law Constant
R^2	Pearson Correlation Coefficient Squared
RfD	Reference Dose
RFP	Request for Proposals
RSD	Relative Standard Deviation
SDS	Simulated Distribution System
SNWA	Southern Nevada Water Authority
SPE	Solid Phase Extraction
SW	Surface Water
t	Time
T	Temperature
TDS	Total Dissolved Solids
THMs	Trihalomethanes
US	United States
US EPA	United States Environmental Protection Agency
UV	Ultraviolet Light
v/v	volume/volume
WHO	World Health Organization
WW	Tertiary Treated Wastewater