Summer 2017

Chlorate Formation In On-Site Hypochlorite Generation Facilities: Effects Of Temperature, pH, And Storage Times

Lukas Simon Kriem

Recommended Citation

Kriem, Lukas Simon, "Chlorate Formation In On-Site Hypochlorite Generation Facilities: Effects Of Temperature, pH, And Storage Times" (2017). *MSU Graduate Theses*. 3191.
https://bearworks.missouristate.edu/theses/3191

CHLORATE FORMATION IN ON-SITE HYPOCHLORITE GENERATION FACILITIES: EFFECTS OF TEMPERATURE, PH, AND STORAGE TIMES

A Master's Thesis
Presented to
The Graduate College of
Missouri State University

In Partial Fulfillment
Of the Requirements for the Degree
Master of Science, Chemistry

By
Lukas Simon Kriem
August 2017

CHLORATE FORMATION IN ON-SITE HYPOCHLORITE GENERATION FACILITIES: EFFECTS OF TEMPERATURE, PH, AND STORAGE TIMES

Chemistry

Missouri State University, August 2017

Master of Science

Lukas Simon Kriem

ABSTRACT

Drinking water is one of the fundamental pillars of modern society, and it is crucial that pathogen-free drinking water be provided to communities. Currently, one third of all drinking water in the U.S. is being disinfected using hypochlorite and the number is rising. However, use of hypochlorite is facing the issue of a hypochlorite byproduct, chlorate ion, which at high concentrations is considered a health risk to humans. During and after its electrolytic generation process, hypochlorite may go through a disproportionation reaction to form chlorate and chloride, a process which is thermodynamically favored. Even though chlorate in drinking water is not regulated yet, the EPA is in the process of regulating chlorate concentrations in the near future. Therefore, it is important to track current concentrations and put mechanisms in place to efficiently reduce chlorate concentrations in generated hypochlorite solutions as well as in drinking water. The purpose of this research was to evaluate the influence of three different parameters in the generation process: pH, temperature and storage time, and also to assess the influence of pH and temperature adjustments during the generation process. Additionally, this research should provide general guidelines on how to reduce chlorate concentrations in on-site generation processes. In all cases, chlorate was observed to increase with time, but increases were less pronounced when storage temperature was decreased and when storage pH was increased. Effects of adjusting pH and temperature during the generation process were not clearly determined in the experimental work.

KEYWORDS: chlorate, chlorate formation, on-site hypochlorite generation, hypochlorite decomposition, electrochemistry, environmental chemistry

This abstract is approved as to form and content

Richard N. Biagioni
Chairperson, Advisory Committee
Missouri State University

CHLORATE FORMATION IN ON-SITE HYPOCHLORITE GENERATION FACILITIES: EFFECTS OF TEMPERATURE, PH, AND STORAGE TIMES

By

Lukas Simon Kriem

A Master's Thesis
Submitted to the Graduate College
Of Missouri State University
In Partial Fulfillment of the Requirements
For the Degree of Master of Science, Chemistry

August 2017

Approved:

Dr. Richard N. Biagioni

Dr. Todd Brewer

Dr. Adam Wanekaya

Dr. Keiichi Yoshimatsu

Dr. Julie Masterson: Dean, Graduate College

ACKNOWLEDGEMENTS

Danke an meine Eltern, Freunde und Professoren.

TABLE OF CONTENTS

LIST OF TABLES

TABLE OF FIGURES

INTRODUCTION

Chlorate, ClO_3^-, is an ion that may be formed as a byproduct of the water disinfection process. Chlorate has become of concern in recent decades due to the observation of its presence at significant concentrations in drinking water. The United States Environmental Protection Agency (USEPA) has evaluated chlorate concentrations in drinking water throughout the U.S. and is in the process of determining a regulatory concentration for public drinking water systems.

Due to this impending regulation, it is important to recognize chlorate's important health effects, its occurrences in United States drinking water systems, and the factors that control its introduction into drinking water. Some of the factors controlling chlorate formation have been well-researched in the laboratory setting, but, appropriate application of the findings to water treatment have not been developed. Because chlorate has been observed throughout U.S. drinking water systems, understanding the control of chlorate is an issue on the national scale.

History

Chlorate salts (calcium, potassium and sodium chlorate) have been used commercially in agriculture since their registration as inorganic salt herbicides in 1966. Chlorate in drinking water was first evaluated starting in 1987 when the USEPA conducted a field study which lasted almost four years. Chlorate specifically caught the USEPA's attention due to its use in agriculture and runoff from crop fields. Additionally, chlorate was detected and described as a drinking water disinfection by-product due to its formation in the decomposition of hypochlorite to chlorate. Data from this study indicated significant concentrations of chlorate in drinking water. Only a limited number of treatment plants were sampled, insufficient to provide representative data, but the studies gave the USEPA an insight into the presence of chlorate in drinking water.

In 1996, chlorate was included as part of the USEPA's Information Collection Rule (ICR) study. The main focus of the ICR was to collect samples from 300 public water systems and over 100,000 customers over an 18-month period in order to create a nationwide database. In addition, this study included comparison of concentrations from different disinfection methods to determine if there was a direct correlation between chlorate concentrations and disinfection methods. The results of this study established the first Health Reference Level (HRL) to be 210 μg/L of chlorate (see Health Effects and Levels).

Starting nearly ten years later, the USEPA's Unregulated Contaminant Monitoring Rule 3 (UCMR3) study is the most recent data collection, and is also the biggest data collection thus far. In this study, more than 20,000 samples from various treatment plants were included that use any of the four treatment methods: chlorine dioxide, off-site bulk hypochlorite, on-site hypochlorite, or gaseous chlorine. For this study, the USEPA selected a reference concentration of 210 μg/L chlorate (same as the HRL), suggesting that regulations in the future may adopt this number.

Currently, chlorate concentrations (along with concentrations of other disinfection byproducts including bromate, chlorite, and perchlorate) are being reviewed by the USEPA under the Six-Year Review. *(20, 22, 23, 24)*

Health Effects and Levels

A number of studies have investigated both acute and long-term health effects of chlorate. *(1)* In terms of absorption and metabolism, chlorate is quickly absorbed by the gastrointestinal tract. *(19)* Chlorate does not target a specific organ, but rather is distributed throughout the whole body. *(24)*

Chlorate is distributed in the tissues in different concentrations that were determined by Abdel-Rahman et al. in 1982 in a study where rats were injected with 5 mg/L of chlorate. They concluded that more than 90% of the initial dose left the body through urine and was not accumulated in the body. The highest concentrations of chlorate were found in plasma with 0.68% and packed cells with 0.57%. *(19)* Other sites of accumulation were also kidneys, lungs, stomach, duodenum, ileum, liver, spleen, bone marrow, testes, skin and carcass. *(1, 24)*

The LD_{50} dose (the amount of sodium chlorate needed to kill 50 percent of a population within a specific time period) of sodium chlorate is believed to be 800 mg/kg. *(1)* Below the LD_{50} dose, local irritations of the gastrointestinal tract can appear. *(1)* Other frequent observations include hemolysis and methemoglobin formation, which is then also followed by intravascular coagulation. *(1)* Currently, the studies conducted do not show any carcinogenic activity for humans and thus is not considered a carcinogen. *(7, 19, 21)*

In the early 2000s, results of short term tests were reported by the National Toxicology Program. *(18)* Ten volunteers ingested 1000 mL of different chlorate concentrations (0.01, 0.1, 0.5, 1.0, 1.8 and 2.4 mg/L) over a 3-day period. In all volunteers, only a slight change in serum bilirubin, iron and methemoglobin were observed. *(18)* Since these changes were minor, the authors concluded that chlorate at the levels tested would not have any serious physiological effect for the volunteers. Additionally, Canada's federal health department came to a similar conclusion and summarized that in human volunteers, a chlorate dose of 0.036 mg/kg/day for 12 weeks did not result in any adverse effects. *(16)*

The database and number of studies that consider the long-term effects of chlorate are not as extensive as for other DBPs. However, a well-conducted 90-day study showed that there is a no-observed-adverse-effect-level (NOAEL) of 30 mg/kg per day. This amount is congruent with the chlorate's minimal effects on thyroid colloids in low concentrations. *(7,16)* From this concentration, a good tolerable dose intake estimation was made considering a 1000× uncertainty factor (×10 for interspecies variation; ×10 for intraspecies variation; ×10 to account for the short duration of the study). This factor results in a tolerable dose intake of 0.03 mg/kg/day which has been a widely-accepted concentration and supports the previous studies and their results. *(18, 19)*

Important levels that were considered in the UCMR3 included the minimum reporting level (MRL) and HRLs. The levels reported are 20 μg/L for MRL and 210 μg/L for HRL. In this case, it is vital to specifically discuss HRLs and their importance, and to clarify why different agencies (USEPA, Health Canada, World Health Organization) have established different values. Generally speaking, any HRL is dependent on four parameters: chronic reference dose, volume of drinking water consumed, adult body weight, and relative source contribution. The chronic reference dose was determined based on the benchmark dose level that was stated by the National Toxicology Program in December 2005 and was accepted to be 0.09 mg/kg/day, adjusted with an uncertainty factor of 30% to be 0.03 mg/kg/day. World Health Organization (WHO) and the USEPA both determined a total drinking water consumption of 2 L/day/person, while Health Canada (HC) adapted a consumption rate of 1.5 L/day/person. HC and USEPA used an adult weight of 70 kg for their calculations while WHO used 60 kg. However, the biggest difference between HC, WHO and the USEPA is the relative source contribution. While HC and WHO established a relative source contribution of chlorate in drinking water to be 80% (20% from food), the USEPA only attributes 20% to drinking water (80% from food). This is the reason why the HRL from the USEPA is so much smaller than the value from HC and WHO (see T1). *(18)*

Table 1. Different parameters considered for the calculation of HRL for three different organizations (WHO, HC, USEPA)

Parameter	Health Organizations		
	WHO	HC	USEPA
BMDL	0.09mg/kg/day	0.09mg/kg/day	0.09mg/kg/day
Uncertainty factor	0.3	0.3	0.3
Chronic reference level	0.03mg/kg/day	0.03mg/kg/day	0.03mg/kg/day
Consumed Volume	2L/day	1.5L/day	2L/day
Adult body weight	60kg	70kg	70kg
Relative source contribution	80%	80%	20%
Conversion factor	1000 µg/mg	1000 µg/mg	1000 µg/mg
HRL	720 µg/L	1120 µg/L	210 µg/L

Other HRL examples include Europe (1000 µg/L), Japan (600 µg/L) and Costa Rica (200 µg/L). The different concentrations underline the difficulty of determining a reasonable concentration by the USEPA and the final HRL value may be subject to further discussions.

Example calculation USEPA:

$$\text{HRL} = 0.03\frac{mg}{kg \bullet day} \text{ x } \frac{day}{2L} \text{ x } 70\text{kg x } \frac{1000\mu g}{1mg} \text{ x } 0.2 = 210\ \mu\text{g/L}$$

Occurrence in the U.S.

Sodium chlorate is a common non-selective herbicide especially in the Midwest and South Central regions in the U.S., although its use has declined dramatically over the past decades. The influence on drinking water from agricultural use of chlorate is rather negligible as the only link between agriculture and drinking water is surface water which may be used as a drinking water source. Furthermore, agricultural sodium chlorate is not considered a major contributor to chlorate in the environment since it only makes up 2% of the total sodium chlorate use. *(4, 14)*

Most recent data collected by the UCMR3 show a large range in chlorate concentrations throughout the U.S. (see F1) High population regions (e.g., coastal areas) generally have more PWSs and therefore include more sampling sites. *(5, 14)* However, sites with highly elevated chlorate concentrations appear throughout the country. *(4, 23)*

In the most recent UCMR3 data summary (July 2016, UCMR3, 2016), a total of 62,414 samples were collected. Out of these samples, 34,239 showed chlorate concentrations above the MRL. Of these 34,239 samples, 9,741 samples exceeded the reference concentration of 210µg/L, a total of 15.6% of all samples in the study (62,414 samples). In addition, samples were compared to the total PWS used for the data collection. Here, 4,918 PWS (number of PWS that showed chlorate concentrations, where the number is not equivalent to all the sampled PWS) showed reportable concentrations of chlorate (chlorate concentration above 20 µg/L) in their water, and of these, 1,896 PWS (38.6% of PWS with reportable concentrations) showed concentrations above the reference concentration. *(14, 23)* Because it is likely that the USEPA will select 210 µg/L as its regulatory limit, the large percentage of PWSs exceeding this limit highlights why chlorate control is an important issue. *(4, 5)*

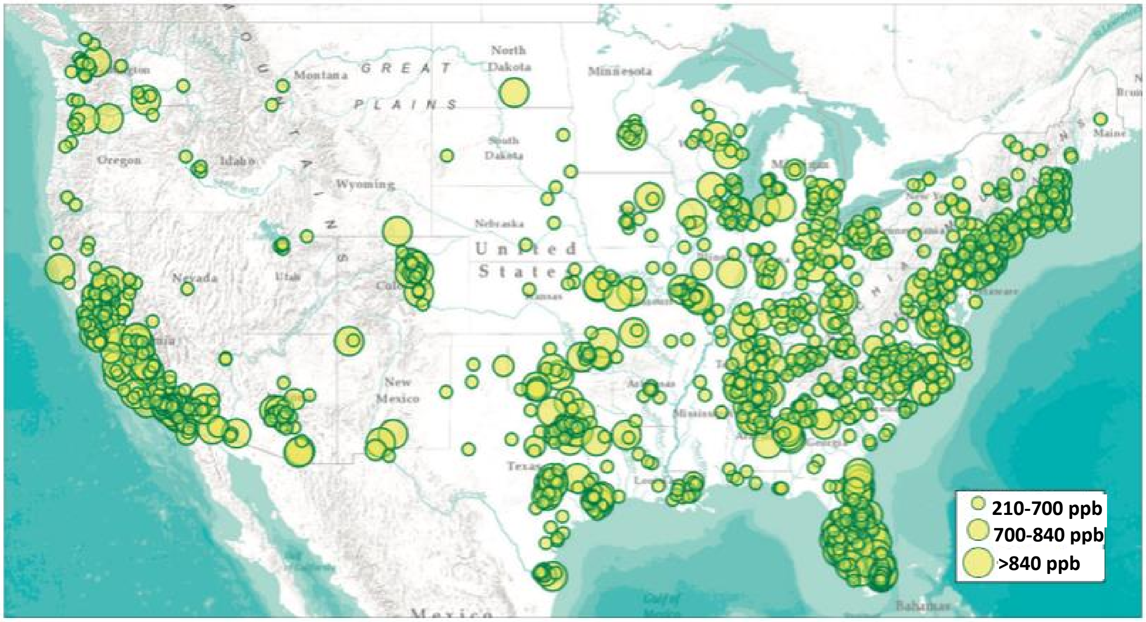

Figure 1. Location and concentrations of UCMR3 database. *(14)*

A factor that may contribute to high chlorate in PWSs is temperature. Chlorate is commonly found as a disinfection by-product (DBP) in water treatment processes (see next section). Generally, higher temperatures increase bacteria concentrations in the water treated at PWSs. Thus, higher temperatures of source waters require that greater volumes of disinfectant be fed into the treatment systems. Since chlorate is a disinfection byproduct, higher disinfection use may lead directly to increased chlorate concentrations in drinking water.

Another factor that possibly explains higher chlorate concentrations in the northeast region is the age of pipe systems in cities. Many of these pipe systems are overaged, some being over 100 years old. To account for aging pipe systems and the need to maintain residual disinfection from the treatment plant to the homes, the disinfectant is increased at the plant to ensure enough residual disinfectant throughout the system. *(4, 5)* Again, because of the direct relationship between disinfectant and chlorate the expected chlorate concentration exceeds the HRL in many cases. (F1) *(14, 23)*

Seasonal changes in concentrations are another important factor that has been detected over the past years. F2 and F3 summarize results for reporting sites where there were four quarterly sampling event measurements (SEs) during the year so that a locational running annual average (LRAA) could be determined. These SEs were collected throughout the year for sites that used surface water (SW), groundwater under the direct influence of surface water (GWUDI), or mixed water. *(14)* The data were divided into two groups: PWS that showed a maximum of > 210 μg/L, and those for which remained < 210 μg/L throughout the measurement period. The plots show SE:LRAA ratios for every month and disinfection system. *(5)* Here, a SE:LRAA of 1 indicates that the chlorate concentration for that particular sampling event was equal to the site's average chlorate concentration. *(4, 23)*

For sites where concentrations remained below 210 μg/L for the entire year, the variation in SE:LRAA over time shows only subtle seasonal variations, with only modest increases in the ratios during the summer and early fall months. (F2). In contrast, sample sites that had maximum concentrations > 210 µg/L showed a very distinct seasonal variation with clear increases in chlorate concentrations in the months of June-October (F3). This may be partially due to increased disinfectant fed into the system, but also faster degradation of disinfectant to chlorate in warmer temperatures. *(14)*

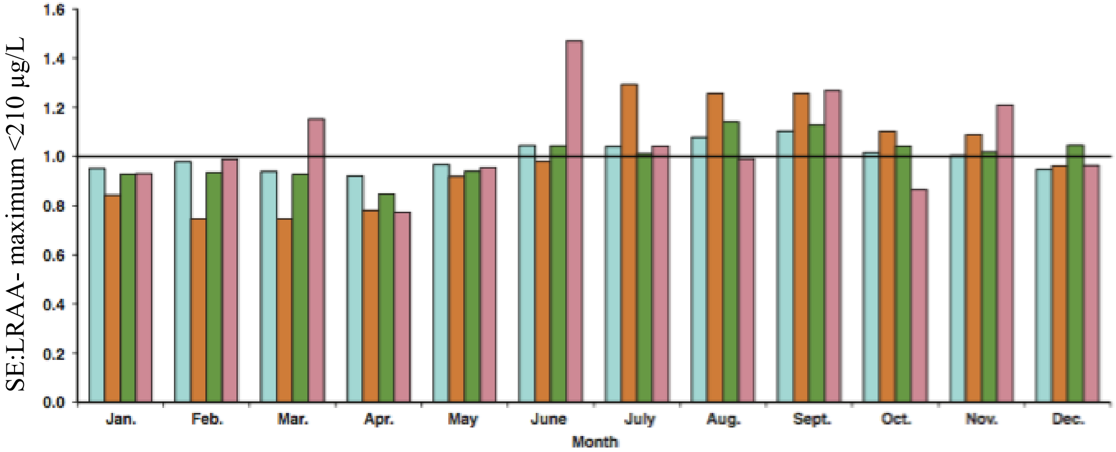

Figure 2. Monthly averages of SE:LRAA for surface water, GWUDI or MX for all four SE. Sample sites with a maximum of < 210 µg/L. Light blue = gaseous chlorine, orange = offsite hypochlorite, green = onsite hypochlorite, pink = chlorine dioxide *(14)*

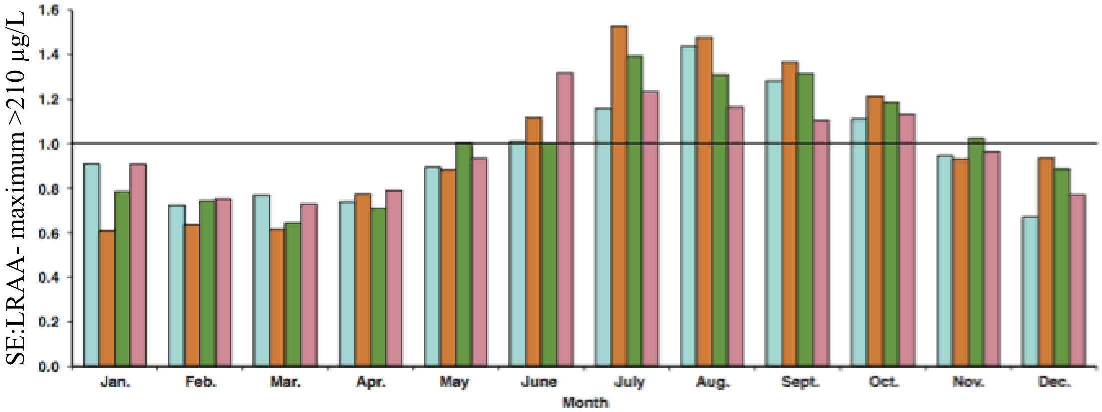

Figure 3. Monthly averages of SE:LRAA for surface water, GWUDI or MX for all four SE. Sample sites with a maximum of > 210 µg/L. Light blue = gaseous chlorine, orange = offsite hypochlorite, green = onsite hypochlorite, pink = chlorine dioxide *(14)*

Chlorination and Challenges

There are six common water disinfection methods established by the USEPA (T2): chlorine dioxide, sodium hypochlorite, gaseous chlorine, chloramines (from a non-hypochlorite source), ozone and ultraviolet light (UV). The last three disinfection processes are not further considered in this paper since they do not show any formation of chlorate at any point. Although gaseous chlorine and chlorine dioxide often show increased amounts of chlorate in water they are not discussed in this paper.

Table 2. Total number of samples in the UCMR3 and their disinfection type (PWS= Public Water Systems).

Disinfectant type	Count of PWS
*Sodium Hypochlorite	22433
*Gaseous Chlorine	18074
*Chloramines	11597
*Chlorine Dioxide	1936
*UV Light	1013
*Ozone	1787
No Disinfectant	2414
All other types	593
GRAND TOTAL	59847

*EPA approved disinfectants

This research was conducted on the Springfield, MO, water system, a PWS that used on-site hypochlorite for disinfection. This PWS showed elevated chlorate formation during the UCMR3. The research focuses on sodium hypochlorite as a water disinfectant because sodium hypochlorite not only is associated with significant amounts of chlorate in samples but it is also one of the most commonly used disinfectant types (around 39% of all collected samples came from treatment systems that used either on-site or off-site sodium hypochlorite for its disinfection) and its use is becoming more common because there is a push towards sodium hypochlorite systems. Hence, it is important to consider the evaluation of sodium hypochlorite systems in regards of chlorate in drinking water. *(24, 25)*

Gaseous Chlorine Versus Sodium Hypochlorite

The use of chlorine gas has been decreasing mostly due to safety, effluent toxicity, air emissions and the potential for use of chlorine gas for terrorism. Other characteristics for both treatment methods are considered and the advantages and disadvantages of each are shown in the table below (T3).

Table 3. Advantages and Disadvantages for using different disinfection types.

Disinfection type	Advantages	Disadvantages
Chlorine Gas	• highly effective against most pathogens • "residual" protection for drinking water • most reliable operationally • very cost-effective	• by-product formation (THMs, HAAs) • special operator training • regulatory requirements by the USEPA
Sodium hypochlorite	• highly effective against most pathogens • "residual" protection for drinking water • less training required for operators • fewer regulations by the USEPA	• limited shelf-life • same by-products as chlorine gas but also chlorate • higher chemical cost • corrosive • crystallization and clogging of pipes

Sodium hypochlorite generation systems require a rather high capital cost, but many utilities make the switch from chlorine gas to sodium hypochlorite due to safety concerns for their employees and the surrounding public.

The disinfection mechanism is not fully understood but it is believed to follow the same mechanisms as chlorine gas (which also produces HClO when dissolved in water). Chlorine's modes of actions are believed to involve different sites in microorganisms. Biological inactivation can appear via multiple different mechanisms in the organisms, including: oxidation of sulfhydryl enzymes and amino acids, ring chlorination of amino acids, loss of intracellular contents, decreased uptake of nutrients, inhibition of protein synthesis, decreased oxygen uptake, oxidation of respiratory components, decreased adenosine triphosphate production, and breaks in DNA and depressed DNA synthesis. Any of these results in the destruction of the microorganism, and disinfection with hypochlorite is usually attributed to a combination of multiple mechanisms. *(11)*

Another great advantage of using hypochlorite as a disinfectant is its ability to disinfect effectively even at low concentrations. It only takes a few milligrams per liter to disinfect water in treatment facilities. This gives the operators a benefit as they do not need to feed substantial volumes to have acceptable disinfection.

The disinfection power of hypochlorite is somewhat pH dependent. Hypochlorous acid and hypochlorite ion are related by the acid dissociation:

$$HClO \rightleftharpoons H^+ + ClO^- \qquad pK_a = 7.54 \qquad \text{(A)}$$

The species distribution is illustrated in F4. Hypochlorous acid, a neutral species, is more effective in disinfection than hypochlorite ions. The figure shows that equal amounts of neutral hypochlorous acid and of hypochlorite ions are present at a pH of

7.54. *(2, 3, 6)* This equilibrium is not only important for its application in the disinfection process but also in the hypochlorite decomposition process (see below).

Hypochlorite Generation

Contribution in a solution

pH-level

Figure 4. Relationship between hypochlorous acid (HOCl) and hypochlorite ions (OCl) as a function of pH.

Sodium hypochlorite generation can be separated into on-site and off-site generation systems. With on-site generation, the sodium hypochlorite is produced at the end-use facility and used within days or weeks for disinfection. *(22)* In comparison, off-site generation involves an independent manufacturer that produces sodium hypochlorite at its facility and then transports it to the end user. With off-site generation, the sodium hypochlorite solution tends to be more concentrated and the solution may be stored for longer periods of time before delivery. *(17)* T4 shows a comparison of off-site versus on-site generation sources for hypochlorite. *(23)*

There are two commons types of generators: high-strength and low-strength hypochlorite generation systems. Usually high-strength systems are used by contractors that produce sodium hypochlorite off-site and then deliver it on-site. Sodium hypochlorite concentrations are a higher (normally around 15%) and are then diluted on-site before use in disinfection. These systems electrolyze an aqueous mixture of NaOH and NaCl together to form hypochlorite at high concentrations. However, this type of system is not part of this study.

Table 4. Advantages and Disadvantages of using different hypochlorite generation processes.

Generation type	Advantages	Disadvantages
Off-site Hypochlorite Generation	• low capital cost • simple application to the system	• tank corrosion • variable costs • safety • product degradation • product quality
On-site Hypochlorite Generation	• generation of 10-12% (high strength system) or 0.8% (low strength system) NaClO • high stability of salt pricing	• high capital cost • brine waste • high level of complexity • hydrogen generation

In comparison, low strength systems are typically used on-site because they only generate hypochlorite concentrations below 1%.

The reaction for electrolytic hypochlorite formation is rather simple. A diluted salt solution is fed into an electrolytic cell which then produces the oxidant by using a current. The anode and cathode half-reactions are:

$$\text{Anode: } 2\,Cl^- + H_2O \rightarrow Cl_2 + 2e^- \qquad \text{(B)}$$

Cathode: $Cl_2 + H_2O \rightarrow Cl^- + HClO + H^+$ (C)

Combination of HClO from the anode and hydroxide ion from the cathode result in the reaction,

$HClO + OH^- \rightarrow ClO^- + H_2O$ (D)

The overall reaction is:

$Cl^- + H_2O \rightarrow ClO^- + H_2$ (E)

Under typical electrolysis conditions, some chlorate is produced by direct oxidation of chloride or hypochlorite at the anode:

$Cl^- + 3H_2O \rightarrow ClO_3^- + 6H^+ + 6e^-$ (F)

$ClO^- + 2H_2O \rightarrow ClO_3^- + 4H^+ + 4e^-$ (G)

According to Jung et al. *(15),* about 13% of chloride can be converted to chlorate.

Underlying Chemistry

Prior to discussing the conversion of hypochlorite to chlorate in on-site hypochlorite systems, it will be helpful to discuss some of the underlying chemistry. The hypochlorous acid – hypochlorite ion acid-base equilibrium (with $pK_a = 7.54$) was introduced earlier. Chloric acid, $HClO_3$, is a strong acid so the dominant species within normal pH ranges is ClO_3^-. Chlorite, ClO_2^-, is generally a minor species in these systems. It is the anion from chlorous acid, $HClO_2$, which is fully dissociated in the pH range of interest to this study.

Key electrochemical relationships between species include the following: *(26)*

$ClO^- + H_2O + 2e^- \rightleftharpoons Cl^- + 2OH^-$ $E° = 0.890$ V (H)

$ClO_2^- + H_2O + 2e^- \rightleftharpoons ClO^- + 2OH^-$ $E° = 0.681$ V (I)

$$ClO_3^- + H_2O + 2e^- \rightleftharpoons ClO_2^- + 2OH^- \qquad E° = 0.271\ V \qquad (J)$$

$$ClO_3^- + 2H_2O + 4e^- \rightleftharpoons ClO^- + 4OH^- \qquad E° = 0.476\ V \qquad (K)$$

Therefore, the disproportionation of ClO^- into Cl^- and ClO_3^- is based on equations (H) and (K):

$$3ClO^- \rightleftharpoons 2Cl^- + ClO_3^- \qquad E° = 0.414 \qquad (L)$$

This is a net four electron transfer, so its equilibrium constant is:

$$K = 10^{\left(\frac{4\times 0.414V}{0.0592V}\right)} = 10^{30.0} = 1\times 10^{30}$$

The very large equilibrium constant implies that the disproportionation reaction is highly favored and, at equilibrium, hypochlorite should be quantitatively decomposed into chloride and chlorate. (For solutions below pH 7.5 where HClO, rather than ClO^-, dominates, the details of the analysis are a bit different, but the same conclusion holds throughout the pH range relevant to water treatment). The fact that hypochlorite solutions can be synthesized and stored implies that hypochlorite's disproportionation is relatively slow: its decomposition is limited by kinetic rather than equilibrium factors. *(8, 9)*

Chlorite, ClO_2^-, is the intermediate species between ClO^- and ClO_3^-. Its overall disproportionation reaction based on equations (I) and (J) is:

$$2\ ClO_2^- \rightleftharpoons ClO^- + ClO_3^- \qquad E° = 0.410 \qquad (M)$$

Given the E° value for this net 2-electron reaction, its equilibrium constant is 7×10^{13}. Hence, chlorite should be a minor species in these mixtures.

A number of studies have addressed the kinetics of hypochlorite disproportionation. A mechanism described in the beginning of the 20th century and was first proposed by Foerster and Dolch, was based on a two-step mechanism for the formation of chlorate: *(10)*

$$ClO^- + ClO^- \longrightarrow ClO_2^- + Cl^- \text{ (slow step)} \qquad \text{(N)}$$

$$ClO_2^- + ClO^- \longrightarrow ClO_3^- + Cl^- \text{ (fast step)} \qquad \text{(O)}$$

The net reaction for the formation can be described as followed:

$$3ClO^- \longrightarrow ClO_3^- + 2Cl^- \qquad \text{(P)}$$

Since the second reaction occurs rapidly, chlorite (ClO_2^-) is almost instantaneously converted into chlorate. This rapid conversion reduces the buildup of chlorite in drinking water and does not have to be considered as an important DBP. However, it has a vital part in the mechanism of chlorate formation.

At a pH between 5-9, significant amounts of both HClO and OCl^- are present in solution, and the decomposition is better represented by the following reaction:

$$2HOCl + ClO^- \longrightarrow ClO_3^- + 2Cl^- + 2H^+ \qquad \text{(Q)}$$

Adam and Gordon (3) showed that in this pH range, the rate follows:

$$-d([HOCl] + [OCl^-])/3dt = k_{obs}[HOCl]^2[OCl^-] \qquad \text{(R)}$$

Here, the rate of formation is proportional to the square of hypochlorous acid concentration and the hypochlorite ion concentration to the first power. *(2, 3, 6, 22, 23)*

For this rate law, the maximum rate of chlorate formation is expected when the ratio of $[HOCl]/[OCl^-]$ is equal to 2. Using the $pK_a = 7.54$, maximum rate of decomposition has is at a pH= 7.24 and decreases with a pH change in either direction. This agrees with Figure 5, which shows the decrease in the chlorate formation rate with increasing pH as the $[HOCl]/[OCl^-]$ decreases.

A number of studies also describe temperature effects on the rate of chlorate formation. As expected (and discussed more below), increasing temperatures increase rates. Adam and Gordon report increasing ionic strength also increasing rates of reactions. *(3)* For the second-order rate constant, they reported the ionic strength (μ) dependence on the rate constant as:

$$\log k_2 = 0.146\,\mu + \log k_{\infty} \qquad \text{(S)}$$

This predicts that increasing the ionic strength from $\mu = 1.0$ to $\mu = 1.5$ would increase the observed rate constant by approximately 18% (based on the contribution of the 0.146μ term to the calculation of k_2). Thus, ionic strength changes may be responsible for moderate changes in decomposition rates. *(3, 13)*

Controlling Chlorate Formation

Many publications conclude that the rate of decomposition of chlorate can be reduced pre-formation (up through the electrolysis step) and/or post-formation (after electrolysis) by controlling the following parameters: pH, temperature, storage concentration, storage time, ionic strength and transition metals impurities (shown in T5).

As part of this research, only pH, temperature and storage time were considered as adjustable parameters in the pre- and post-formation of hypochlorite. The rationale for selection of these parameters is based on the recognition that any changes must be practical for implementation in a functioning water treatment plant that utilizes on-site hypochlorite generation.

Hypochlorite solutions, whether produced off- or on-site, may be stored for prolonged periods of time because water systems must be assured of adequate disinfectant supplies even in the event of disruptions in deliveries or production. Storage time seems to be an important factor in water treatment and is even more so important for off-site generation systems. This is due to higher hypochlorite concentrations. Sodium hypochlorite solutions from off-site generation systems may have been stored at the manufacturer site for some time before being shipped and may then be stored additionally on-site. However, off-site generated hypochlorite solutions are normally at elevated pH levels (above 11.0) where chlorate formation is very slow. *(8, 9)*

Regardless of the system, the shorter the storage time the less decomposition of hypochlorite to chlorate is observed. However, time in the distribution system (after treatment) is not expected to be important: when hypochlorite is fed into the water system it experiences a dilution factor of about 1:1,000. With this great dilution, the rate of hypochlorite decomposition goes towards zero because the rate of chlorate formation depends on total hypochlorite cubed (intermediate pH range) or squared (higher pH range). This means that once the hypochlorite is in the distribution system, the formation of chlorate is negligible. *(13)* The more important factor to consider is time the concentrated solution is in the storage tank. The rate law for sodium hypochlorite decomposition also predicts that a dilution of sodium hypochlorite by a factor of two will decrease the rate of decomposition hypochlorite by four to eight (depending on the pH range). *(23)*

Table 5. Parameters influencing formation of chlorate and whether they are important for post- and/or pre-formation.

Parameter	Pre-formation	Post-formation
pH-level	●	●
Temperature	●	●
Storage concentration		●
Storage time		●
Ionic strength	●	●
Transition metals	●	●

As discussed in the preceding section, previous research has demonstrated that there is a relationship between the pH of a sample and the decomposition rate in the near neutral pH range. *(3, 13)* Rates of chlorate formation are much higher in the range between pH 5 to 9 than at a higher pH range, so decomposition of hypochlorite in post-formation is most rapid when stored in the mid pH range. *(2)* As pH is adjusted to pH > 9.5, the chlorate formation slows down and some chlorite buildup is observed (F5). *(2, 3, 13)*

Gordon, Adam, and Bubnis tested the effects of increased hydroxide concentrations on the formation rate of chlorate. Decomposition rates for hypochlorite solutions with varying amounts of added caustic soda were evaluated. As shown in F6, increased caustic soda concentrations decreased the decomposition rate of hypochlorite and, at the same time, decreased the formation of chlorate ions in the solution. This is very consistent with the kinetics of chlorate formation mentioned earlier *(2, 3, 13)*. These results reflect the effects of post-formation pH adjustment.

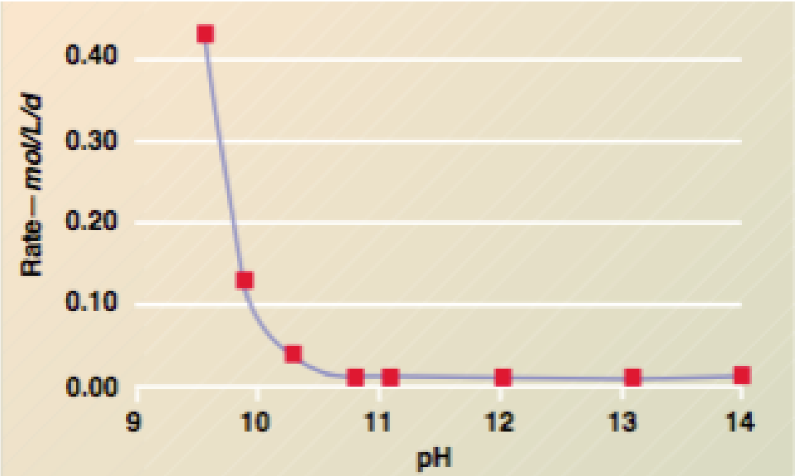

Figure 5. Rate of decomposition at different pH levels ranging from 9.5 to 14. *(13)*

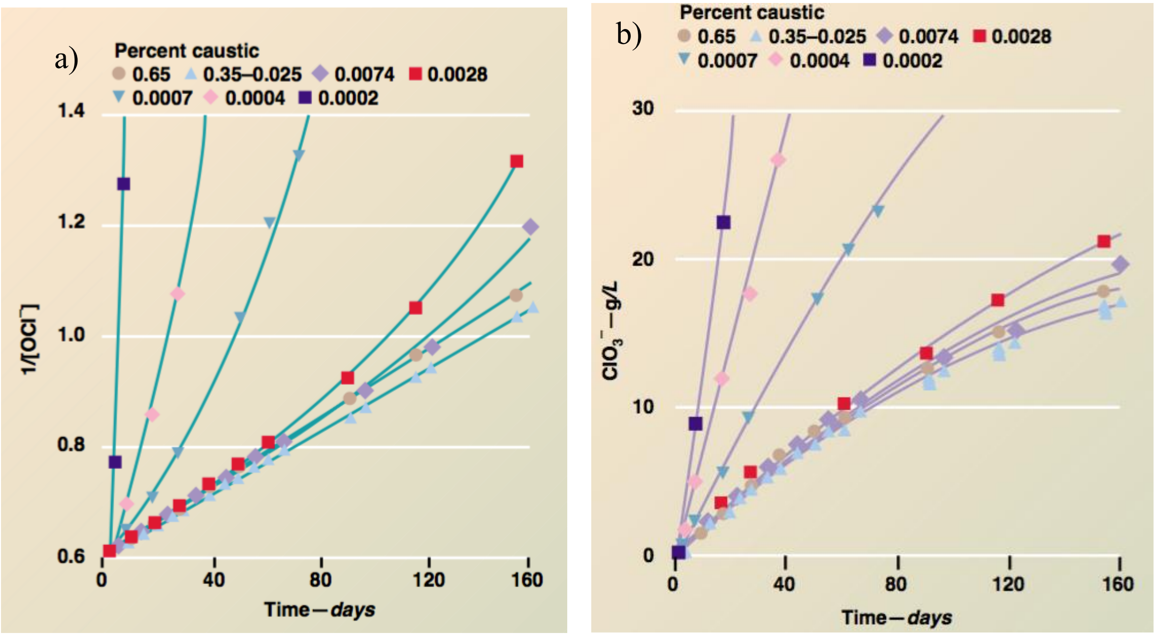

Figure 6. a) hypochlorite decomposition at various caustic soda (NaOH) concentrations with [OCl]= 1.64M; b) chlorate ions formed as a function of time [OCl}= 1.64M. *(13)*

It is not fully understood how chlorate concentrations behave if pH is changed before generation. Jung et al showed that chlorate formation rose with increasing pH, up to pH 7.2, and then remained constant up to pH 9 (the upper pH limit of the study). The proposed reason for that is that, at low pH levels, the dominant species in the solution is hypochlorous acid, (F4) does not contribute as much to the chlorate formation as hypochlorite ions do. *(15)* Jung's results were specifically for Ti/Pt electrodes with relatively low salt concentrations and moderate current densities, so their direct application to the current investigation may be limited.

The last factor that will have an effect on chlorate formation is temperature. As discussed earlier, publications have clearly established a strong correlation between temperature and rates of hypochlorite decomposition and chlorate formation (F7).

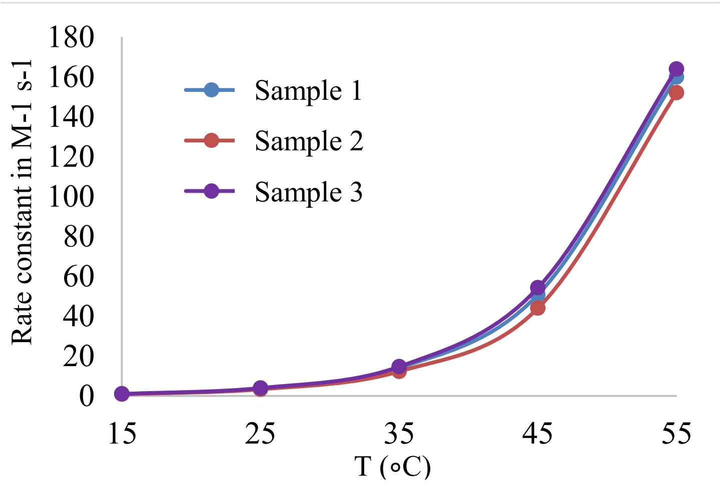

Figure 7. Effects of temperature on the formation rate constant of chlorate for three different samples with an ionic strength of 3.727 *(3)*.

The following relationship *(3)* can be used to model the rates in chlorate formation in the pH range above 11 with increasing temperature:

$$\log k_2 = 0.149\mu + \log[2.083 \times 10^{10} T \exp(-0.1018 \times 10^5/RT) \exp(-56.5/R)] \qquad (T)$$

(Where k_2 = rate constant, μ = ionic strength of solution, T = temperature and R = gas constant)

This equation (T) predicts experimental rate constants (F7) within an average error of < 5%. This is in agreement with experimental findings in other publications. *(3, 4)* The relationship described applies to behavior at pH ≥ 11 where Foerster and Dolch *(10)* mechanism dominates. It is not strictly applicable to the pH 7 – 11 range most relevant to this study, but is illustrative of the influence of temperature on chlorate decomposition rates. At this point, there do not appear to be any published studies detailing the temperature dependence of hypochlorite decomposition in the pH 7 – 11 range.

Study Objectives

The objective of this research is to analyze the parameters responsible for chlorate formation in operational settings. The publications discussed earlier studied the effects of temperature, pH and storage times under lab conditions, but there is little information available based on the applicability for an operational setting. Thus, it is important to look at the aforementioned parameters in the context of operational capability and in the formation of hypochlorite using electrolytic cells. Parameters for chlorate formation in electrolytic cells will be considered pre- and post-hypochlorite generation and will be discussed in relation to its feasibility and application for treatment conditions. Of particular concern is that any alterations in conditions do not adversely affect the quantity of hypochlorite produced, the key chemical required for the disinfection process.

Post-generation adjustments cannot reduce the concentration of chlorate produced by electrolysis in the generation step. *(6)* The primary goal of adjusting parameters post-generation is simply to stop or slow down the decomposition reaction resulting in chlorate formation.

Systems

The experiment was conducted in cooperation with City Utilities of Springfield, MO. Springfield is located in southwest Missouri and has a population of around 165,000 and a service area population of around 230,000. The city of Springfield is provided with drinking water by two municipally-owned facilities, James River and water pump stations: Blackman Water Treatment Plant (BWTP) and Fulbright Water Treatment Plant (FWTP). BWTP provides drinking water for about 150,000 Springfield residents while FWTP provides water for the remaining 80,000 people.

From 1980 to 2013, BWTP used gaseous chlorine as its disinfection method. BWTP switched to an on-site sodium hypochlorite generation system in April 2013. FWTP completed its switch to on-site sodium hypochlorite in late October 2016 (the changeover started at the beginning of August 2016). Both plants use generator systems from PSI On-Site Disinfection. BWTP uses three Microclor® Model MC-1600 skid systems, each rated to produce 1,600 pounds (725 kg) per day of free chlorine as sodium hypochlorite. FWTP uses three Microclor® Model MC-800 skid systems capable of producing up to 800 pounds (360 kg) per day of free chlorine as sodium hypochlorite. The material used for the electrodes is titanium with DSA (dimensionally stable anodes) proprietary coating for best sodium hypochlorite generation (F8). Both systems are able to produce approximately 0.8% sodium hypochlorite under optimal settings. The systems typically operate under the conditions in T6, but are not strictly limited to all of these settings.

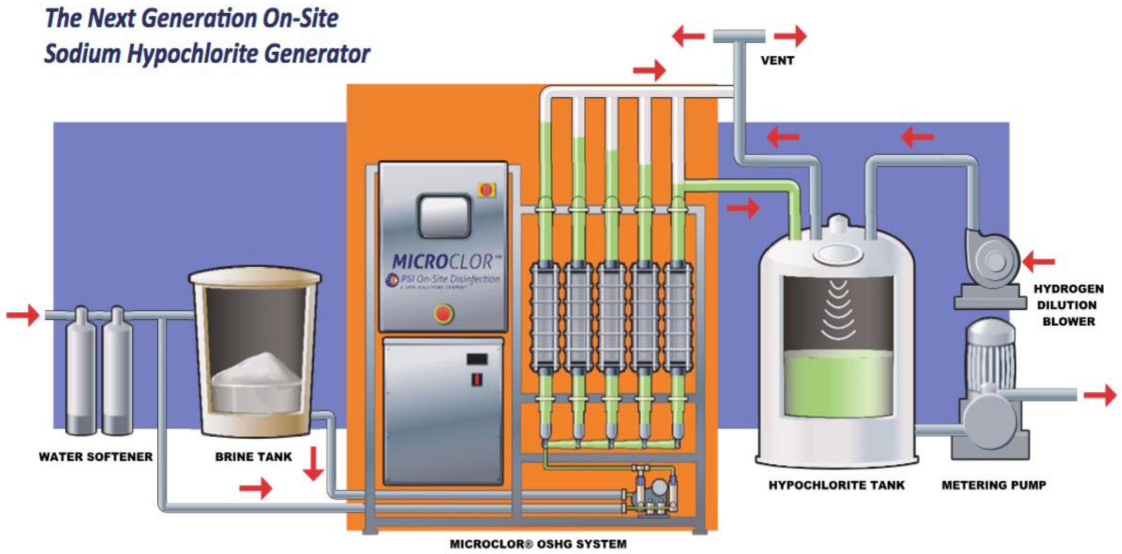

Figure 8 Schematic of sodium hypochlorite formation system using a PSI Generator (http://www.4psi.net/microclor-diagram.php)

Under typical operating conditions, the hypochlorite emerging from the generation system is somewhat warmer than the supply water, with outlet temperatures of around 35°C. The hypochlorite solution is directed into one of three 150,000 L storage tanks for BWTP, or one of the four 75,000 L storage tanks for FWTP. *(12)* These are not temperature controlled, but because of the containers' large volumes and the high heat capacity of aqueous solutions, the hypochlorite solutions tend to remain at elevated temperatures.

Table 6. Operation settings for the two sodium hypochlorite generation systems of interest.

Operation settings	Blackman WTP	Fulbright WTP
Potable water source	James River, Fellows Lake	Fulbright Spring, McDaniel Lake
Potable water temperature	20℃	20℃
Potable water pH	7.8 to 8.2	7.4 to 7.8
Brine Flow	5.3 L/min	2.8 L/min
Cell Flow	53.0 L/min	30.3 L/min
Current on the system*	450 amp	250 amp
Free Chlorine produced	0.6 to 0.8%	0.75 to 0.85 %

*current to the power supply with 240 VAC

Sodium hypochlorite is injected into the treatment system at a concentration between 2-10 ppm depending on the disinfection demand corresponding to a 800 to 4,000-fold dilution of the stored hypochlorite. Water from the two treatment plants flow into the same City of Springfield water distribution system. The residence time of treated water in the distribution system varies with location. The longest residence time sites in the system have been identified as the Expedia site for FWTP and the Evans Road site for BWTP (see F9).

Overview of Key Analytical Methods

Ion chromatography is the most commonly used method for measuring chlorate concentrations. A schematic of a typical ion chromatograph (IC) can be found below in

F10. The sample is then injected into an eluent (mobile phase) typically containing KOH or a mix of $NaHCO_3$ and Na_2CO_3. The mixture is pumped through a separation column containing a stationary phase composed of porous resins with fixed charge-carrying groups using a high pressure non-metallic pump. After separation, the sample then runs through an electrolytic eluent conductivity suppressor and is then detected and made visible with a data management instrument.

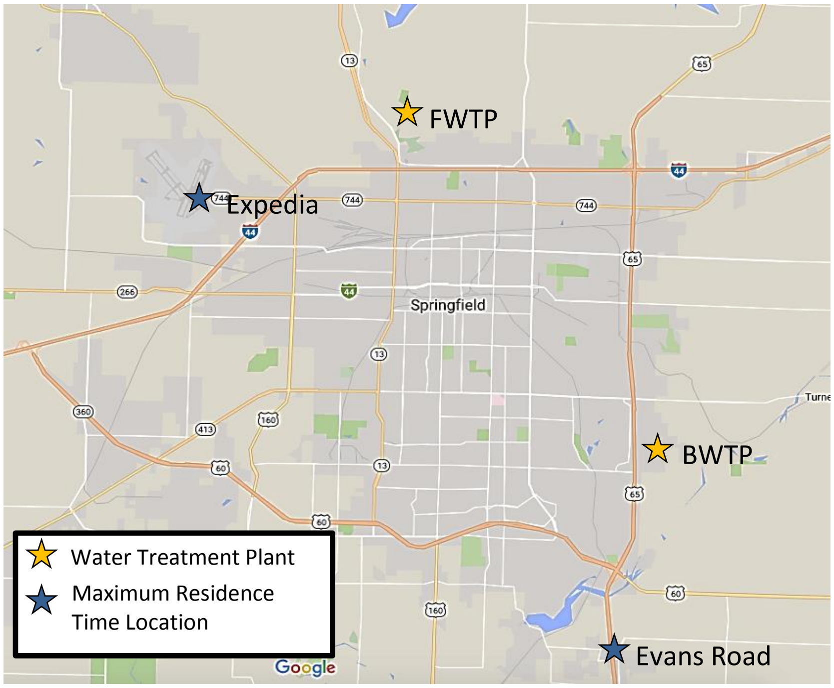

Figure 9. Locations of water treatment plants and maximum residence locations in Springfield, MO.

Free chlorine was determined using a colorimetric method based on the reaction of free chlorine with DPD (N,N-diethyl-p-phenylenediamine), which is oxidized to form a highly colored Würster dye (radical species) which absorbs at $\lambda = 520$ nm.

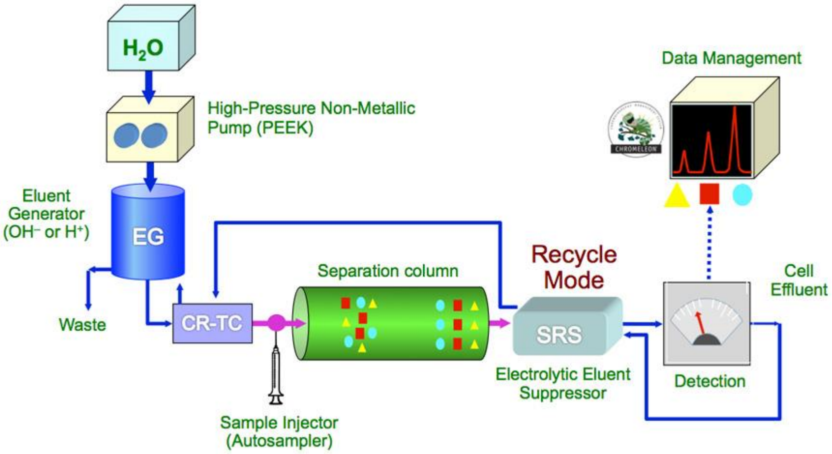

Figure 10. Schematic of a typical Ion Exchange Chromatograph. (http://www.chromacademy.com/Introduction_to_Ion_Chromatography_Essential_Guide.html)

METHODS

Instrumental Method Details

For the detection of chlorate concentrations, a ThermoScientific™ Dionex™ ICS-5000+ Capillary HPIC™ System with Chromeleon 7.0 software was used. The detection method for chlorate was Method 300.1 published by the USEPA.

The analytical column was a Dionex IonPac AS22 packed column, 250 mm long with a 2 mm inner diameter, along with a 50 mm long 2 mm diameter guard column. The A22 stationary phase is a porous resin functionalized with alkanol quaternary ammonium groups for ultralow hydrophobicity. The column's capacity is 52.5 μeq/column.

Additionally, the system was operated under the following conditions:

Detector: Suppressed Conductivity Detector, Dionex CD20
Suppressor: ASRS-2mm, external source electrolytic mode, 4 mA current
Eluent: 2.3 mmol Na_2CO_3, 0.7 mmol $NaHCO_3$
Eluent flow: 0.3 mL/min
Sample loop: 10 μL
System Backpressure: 1300 psi
Analysis time: 15 min

A small detection window was needed for this analysis. Chloride was present in high concentrations in the sample since only a small part of chloride ions reacted to form hypochlorite ions. Thus, the conductivity due to chloride is very high compared to chlorate's conductivity. Additionally, the chloride peak and chlorate peak were in close proximity to each other and the detection window had to be adjusted to only show the chlorate peak in an effort to keep chlorate from being dwarfed by the chloride peak (F11). Samples from the generators, storage tanks, and generation studies had to be diluted (typically 500-fold) to fit the calibration range. Samples from the distribution system were injected without any dilutions.

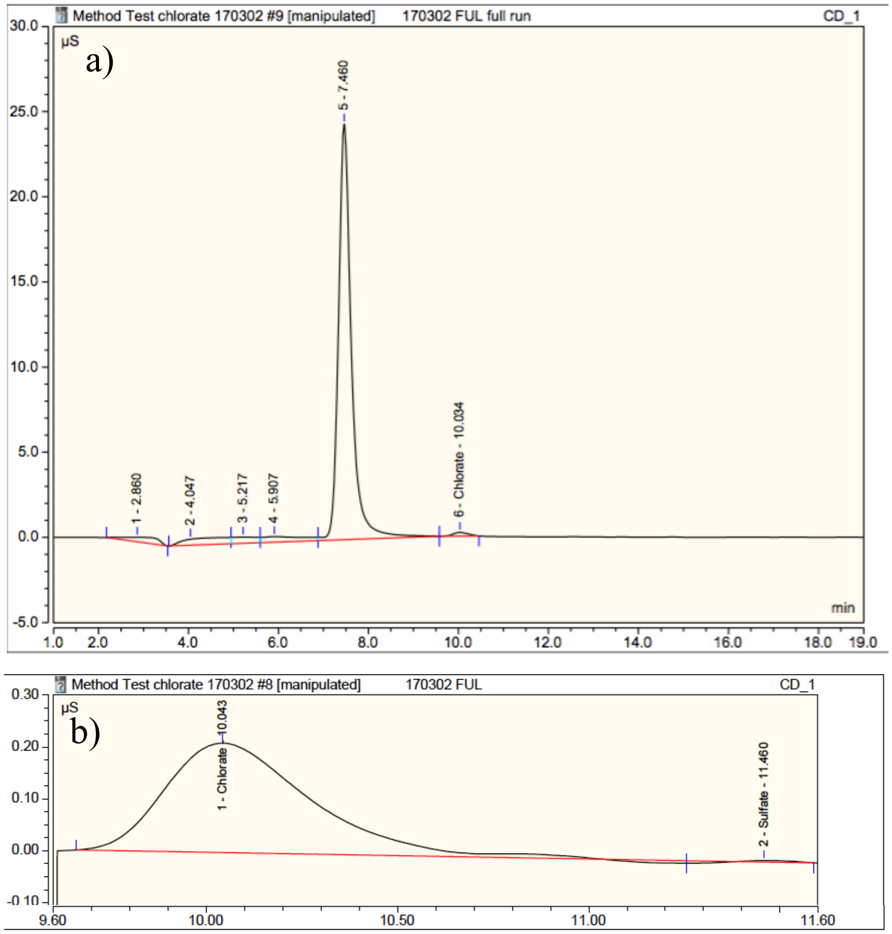

Figure 11. Chromatograph using Dionex ICS-5000+. a) chromatograph with detections times 1-19min. First peak shows a chloride peak, second shows a chlorate peak. b) chromatograph with adjusted detection times of 9.6-11.6min where the first peak shows chlorate.

Analysis of pH levels were conducted using a Mettler Toledo SevenGo™ pH meter. Free chlorine was determined using a Hach Pocket Colorimeter™ II using a SwifTest™ DPD Reagent. Samples directly from generators were typically diluted at a 1:10,000 ratio (two sequential 1:100 dilutions) to get to the instruments' range.

Preliminary Treatment System Sampling

Chlorate samples for the sodium hypochlorite generators were collected right after the formation process in the generators. Additional sample points in the plant were: First basin (1), second basin (2), after the filter system before distribution (3), potable water in the generator building that is used for generation (4), after the water softener (5), and in the hypochlorite storage tanks (6). (F12)

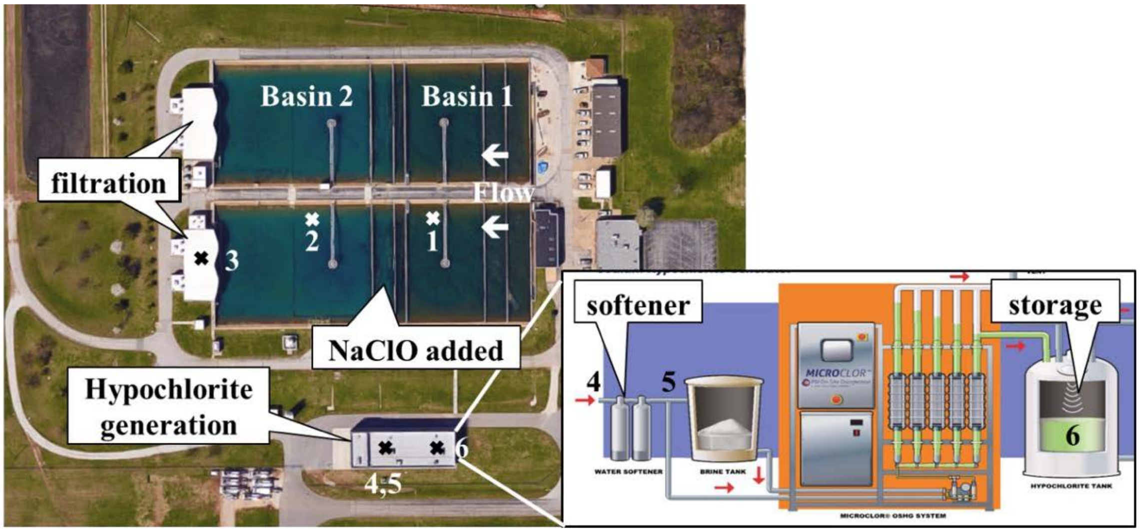

Figure 12. Sample points at BWTP.

In addition, samples were collected at the maximum residence times in the water system (Expedia serves as the maximum residence location for FWTP, Evans Road serves as the maximum residence location for BWTP). (F9)

Post-Generation Study: Age, Temperature and pH Studies

For the study, fresh sodium hypochlorite samples were collected from running generator systems at BWTP and FWTP (9 samples each for FWTP and BWTP). Samples were collected in white 1000 mL Nalgene bottles to eliminate the influence of light on chlorate formation. For the age study, no further changes were made. For the temperature study, one sample was put into a refrigerator and kept at 5°C, another one was kept at 21°C and the third was put in an incubator at 35°C. For the pH study, the pH of the sodium hypochlorite solutions were adjusted using 1M sodium hydroxide (NaOH). One sample was not adjusted and kept at its original pH of around 9.2. A second sample was adjusted to a pH 10.0 and a third sample to pH 11.0. Data collection started one day after the initial collection day (day 0) and is labeled as day 1. The pH, free chlorine concentration, and chlorate concentration of each sample was measured regularly over a 28 day period, a time period chosen to reflect storage times for on-site generated hypochlorite.

Pre-Generation Study: Temperature and pH Level

To study effects of adjusting parameters before sodium hypochlorite generation, the residential sodium hypochlorite generator Breeze 540 by Saline Generating System was used. This system generates sodium hypochlorite in the same process as the PSI systems except it is smaller in size and it is easier to modify the generator’s settings. According to the manufacturer’s specifications, the system is designed to generate up to 1.35 pounds of free chlorine per day, equivalent to about 25 g free chlorine per hour. The generator, as configured by the manufacturer, is designed to be part of a high flow volume / low free chlorine concentration system for chlorination of swimming pools. The electrodes consisted of a similar type of material as the PSI generators (titanium with DSA coating).

For these studies, the system’s flow chamber was replaced by a PVC chamber to allow circulation of a relatively small volume of solution (F13,F14), allowing generation of higher concentrations of free chlorine in short periods of time.

Solutions for the runs were made using softened water and brine solution from BWTP and mixed at a 12:1 ratio to ensure a similar solution concentration compared to the generator systems at BWTP and FWTP in order to imitate their production settings as much as possible.

A total volume of 2500 mL of solution was pumped through the reaction chamber using a peristaltic pump (Masterflex Easy Load II, Cole Parmer) with a pump rate of 325ml/min. The solution was cycled through the cell for a total time of 60 min (total number of cycles are about 10). Samples were collected before and after the run. Temperature, pH values and free chlorine concentrations were determined immediately after collection (see procedure for post-generation study). Samples were brought to BWTP for IC analysis to determine chlorate concentrations.

pH adjustments to the brine solution were made by adding the following solutions: 10 mM sodium carbonate, 10mM sodium bicarbonate and 10 mM sodium hydroxide. In all cases, the change was performed before every run. The carbonate and bicarbonate solutions were prepared by adding solid reagents, and the sodium hydroxide solution by adding 1 M NaOH solution. The solutions were then used for the specific runs.

The cold run was performed by cooling the solution to 10°C initially and was then cycled through the system for 60 min (F13,F14).

Every prepared brine solution (diluted 1:12) was used for two runs. One run was performed without changing any parameters (which served as a baseline reading). The second run was then performed with the changed parameters (NaOH, $NaHCO_3$, Na_2CO_3, temperature) to compare the concentrations to the unchanged run.

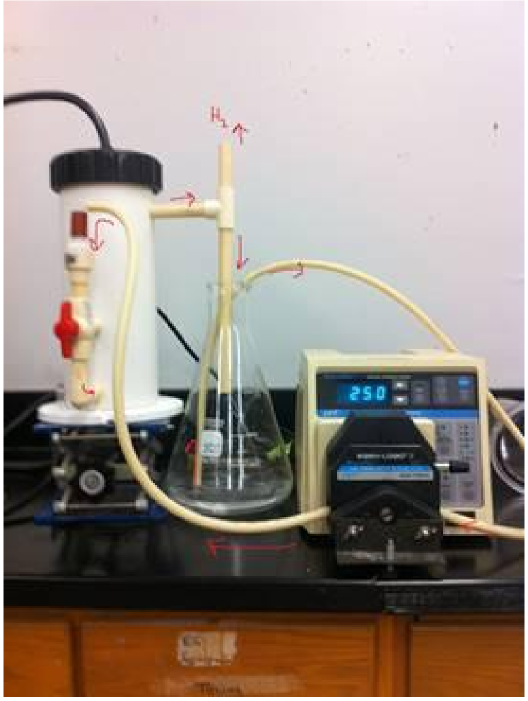

Figure 13. Picture of the setup of the Saline Generating System Breeze 540.

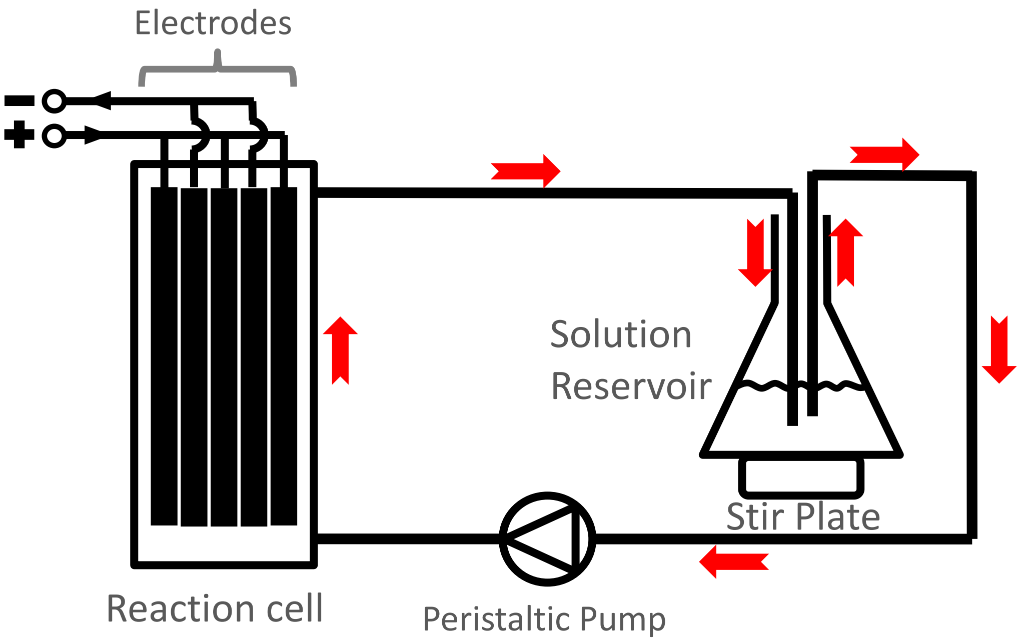

Figure 14. Schematic of the pool generator setup

The system had no provisions for temperature control. Modifications to allow temperature control were planned. However, difficulties with the power supply (overheating, leading ultimately to failure of control circuitry) made it impossible to implement the modifications.

RESULTS

Samplinmg of Different Locations at BWTP

Samples were collected throughout BWTP. (AA) The results show that the first basin does not contain any chlorate because it is raw water that is not disinfected. Basin #2 shows chlorate concentrations because samples were collected after disinfection of the drinking water. However, elevated chlorate concentrations were found in the outlet of the hypochlorite generation system (average chlorate concentration 365 ppm) as well as in storage tank #2 (average chlorate concentration 590 ppm). Based on these observations, it can be concluded that chlorate formation occurs in the generation system and storage.

Maximum Residence Study

The Evans Road and Expedia sampling sites evaluated here correspond to the maximum residence locations (locations furthest from the water treatment plant) for BWTP and FWTP, respectively. Maximum residence locations were selected because the UCMR3 study used maximum residence locations for its data collection. The samples, collected over a 2-month period, showed elevated concentrations of chlorate in drinking water (AB, F15). Four samples from the Evans Road site showed concentrations above 210 ppb, the concentration chosen as a reference value because it is likely to be the concentration at which chlorate will be regulated. All samples collected from Evans Road exceeded 100 ppb.

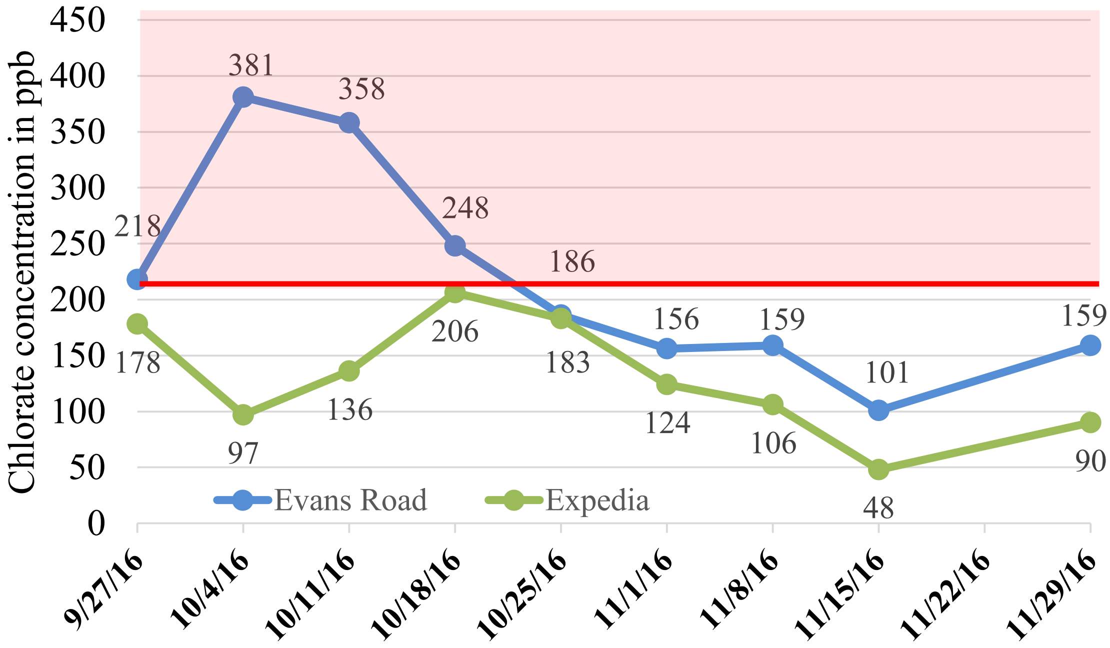

Figure 15. Chlorate concentrations at two different maximum residence locations. Drinking water at Evans Road is provided by BWTP. Drinking water at Expedia is from FWTP.

Chlorate concentrations for the Expedia location samples ranged from 48 to 206 ppb, with none exceeding 210 ppb. However, the study time when samples were collected included the time period (early August 2016 to late October 2016) when FWTP switched its treatment system from chlorine gas (not expected to introduce chlorate) to on-site sodium hypochlorite, using a mix of chlorine gas and sodium hypochlorite during the transition.

Post-Generation Study

Effects of Storage Time Adjustments. According to the study of the influence of storage time on chlorate formation, the pH (F16, AC), free chlorine concentration (F17, AD), and chlorate concentration (F18, AE) all change with time. For the plots (F16-18),

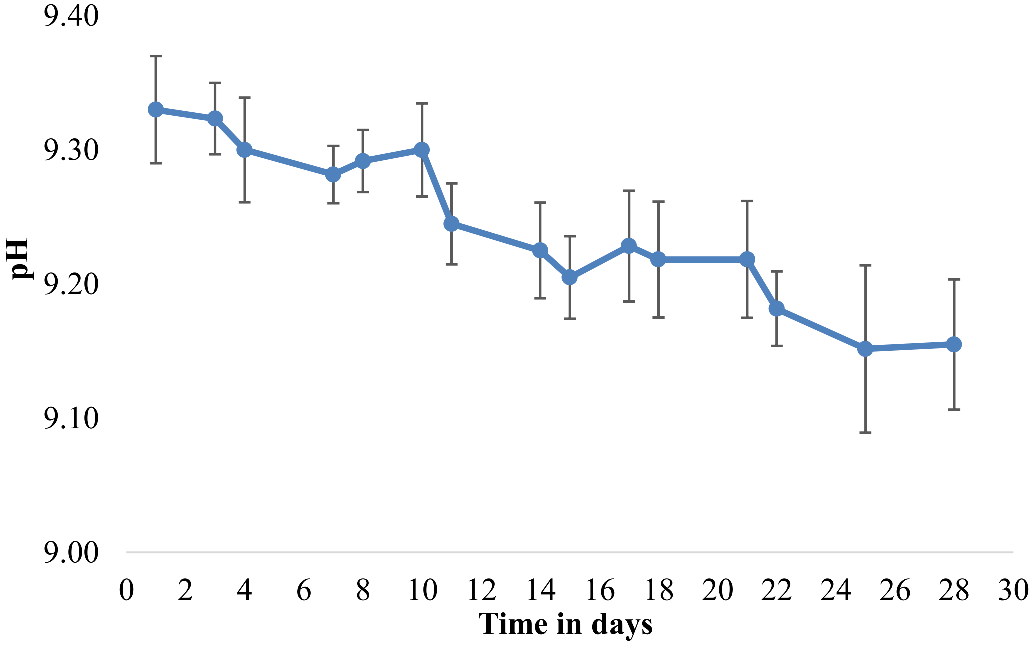

Figure 16. Change in pH levels compared to Day 1 values for a total of six different samples over a 28-day time period; error bars represent one standard deviation.

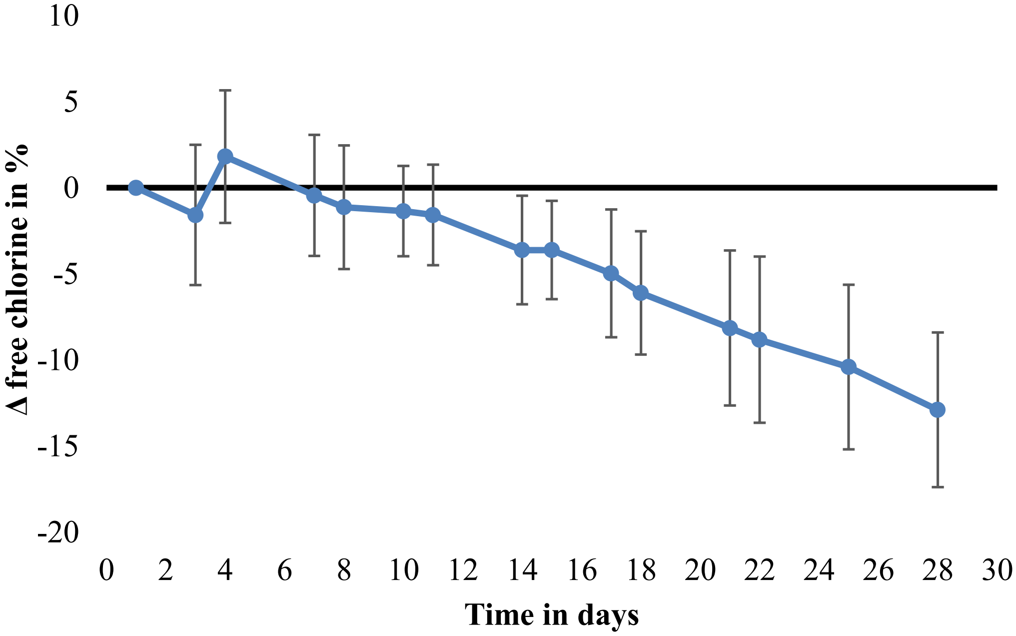

Figure 17. Change in free chlorine concentration compared to Day 1 values for a total of six samples compared to their initial free chlorine concentration over a 28-day period, in percent; error bars represent one standard deviation.

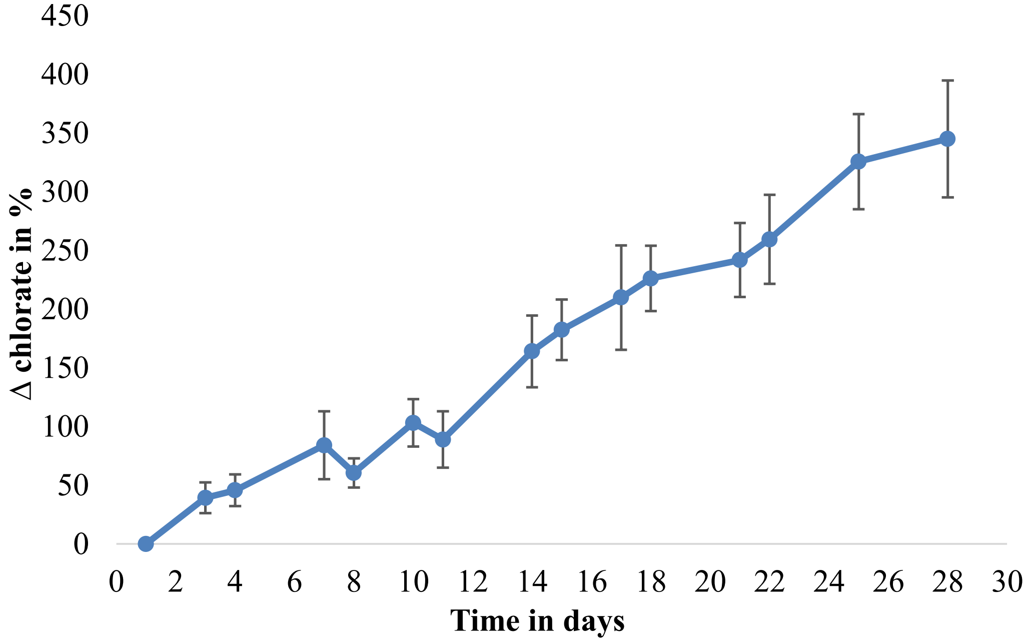

Figure 18. Change in chlorate concentration compared to the Day 1 values over a 28-day period, in percent; error bars represent one standard deviation.

all six collected samples (both BWTP and FWTP) were error bars equivalent to one standard deviation were added to compare result.

Figure 16 shows the pH change over the 28 day duration for the six samples. All samples show an initial pH of 9.3 ± 0.05. Over this specific period a pH change can be observed for all six samples with an ending pH of 9.15 ± 0.07. Even though there is not a completely consistent decrease in pH, a clear trend can be observed for the samples. This trend can be explained by looking at concentrations of free chlorine and chlorate.

The free chlorine plots and chlorate plots show concentration changes compared to the initial concentration (where the initial concentration is considered as 0% change). Initial free chlorine concentrations averaged 6900 ppm for BWTP and 7900 ppm for FWTP. These dropped to average values of 6300 ppm at BWTP and 6600 ppm at BWTP.

The decrease in free chlorine was not consistent for all samples and ranges from ~7% (BWTP) to ~18% for (FWTP).

However, the decomposition of free chlorine would also decrease the sample's pH to a small extent. A 30% drop in OCl^- would change the pH by about 0.08 (by changing the $HClO:OCl^-$ ratio). In addition, the decomposition of free chlorine enhances chlorate concentration.

The average initial chlorate concentrations were 128 ppm for BWTP and 214 ppm for FWTP. After the 28-day period these concentrations increased to 586 ppm (average at BWTP) and 915 ppm (average at FWTP). Chlorate concentration increases ranged from 293% (BWTP) up to a maximum of 410% (BWTP).

Effects of Temperature Adjustments. Samples from both BWTP and FWTP were held at a range of temperatures (5°C, 21°C, and 35°C) and monitored for a 28 day period. For both cold and intermediate temperatures the pH dropped only slightly over the experimental duration. (F19, AF) The pH for intermediate temperature had a slightly lower final pH compared to the cold temperature (intermediate temperature final pH levels of 9.17 (FWTP) and 9.20 (BWTP), cold temperature final pH levels of 9.37 (FWTP) and 9.38 (BWTP)).

The biggest decrease in pH can be observed for warm temperature (35°C) samples. For both systems, the pH dropped by at least 0.5 units (FWTP: 0.52 units; BWTP: 0.59 units).

Free chlorine concentrations (F20, AG) were essentially stable at 5°C. Both systems showed minor losses of free chlorine at intermediate temperature, with a 10%

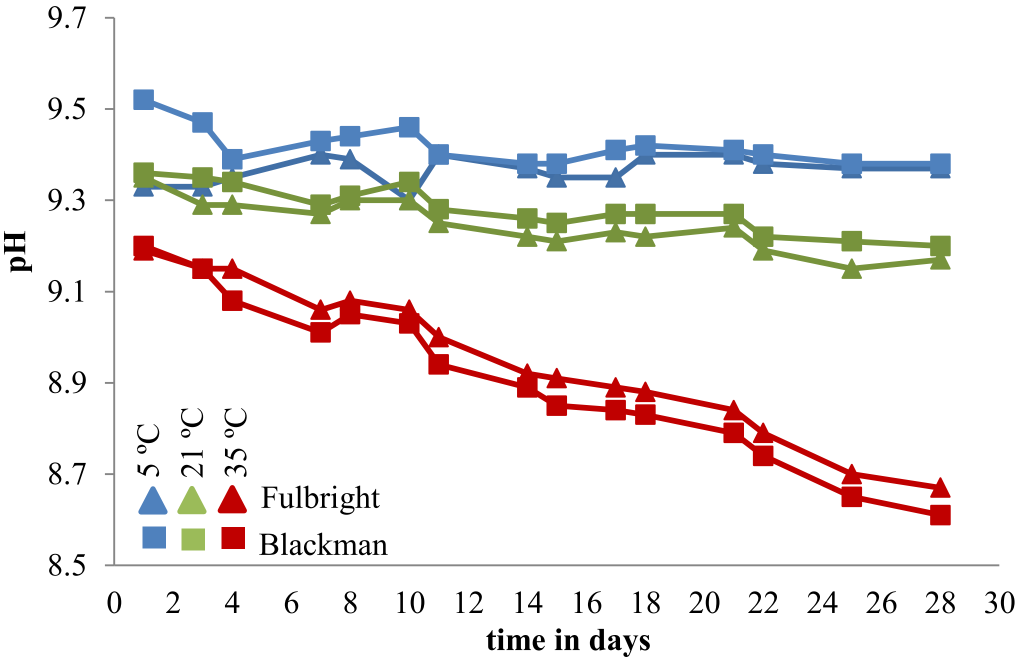

Figure 19. Change in pH levels compared to Day 1 values for the two sodium hypochlorite generators at 5 ºC (blue), 21 ºC (green) and 35 ºC (red) over a 28-day period.

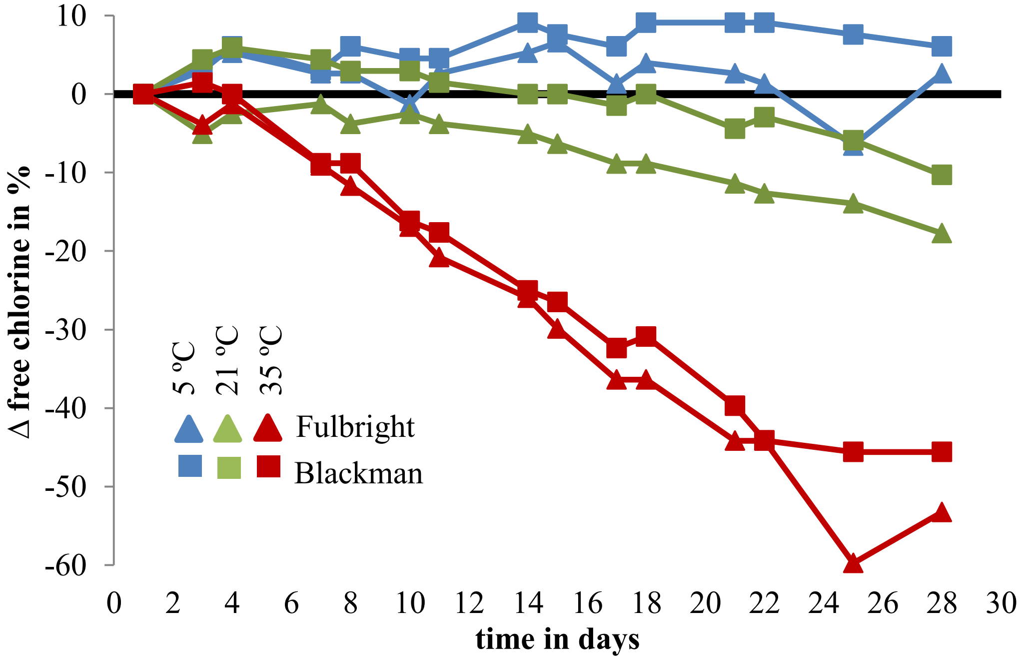

Figure 20. Change in free chlorine concentrations compared to Day 1 values for the two sodium hypochlorite generators at 5 ºC (blue), 21 ºC (green) and 35 ºC (red) over a 28-day period (in percent) in comparison to the initial concentration.

drop for BWTP and 18% drop for FWTP in comparison to their initial free chlorine concentration. There were big decreases in free chlorine concentrations for both BWTP (46%) and FWTP (53%) at high temperatures. Again, the trends in free chlorine are similar to the trends in pH for the same samples, with the greatest decreases occurring at the highest temperature.

Chlorate results (F21, AH) showed that BWTP had a lower initial chlorate concentration with around 121-146 ppm, compared to 194-257 ppm for FWTP. At 5°C, chlorate concentration increases by approximately 60%, compared to their initial concentration for both locations. At intermediate temperatures, for both sites the chlorate concentrations had increased by about 380% over 28 days, despite FWTP's higher initial chlorate concentration. The biggest change can be observed for both warm temperature samples. Chlorate concentrations for FWTP increased by about 800%, while BWTP increased by almost 1200%. FWTP had an initial chlorate concentration of 257 ppm and showed a final concentration of 2350 ppm, and increase of nearly 2100 ppm. In comparison, BWTP started with 145 ppm and ended at 1892 ppm after the 28-day period, and increase of about 1750 ppm. In absolute terms, FWTP showed a higher chlorate concentration increases compared to BWTP after 28 days.

Overall, the BWTP had a higher percent increase in chlorate concentration than FWTP, but it showed lower free chlorine concentrations compared to FWTP. For pH levels, no distinct change can be seen between the two systems.

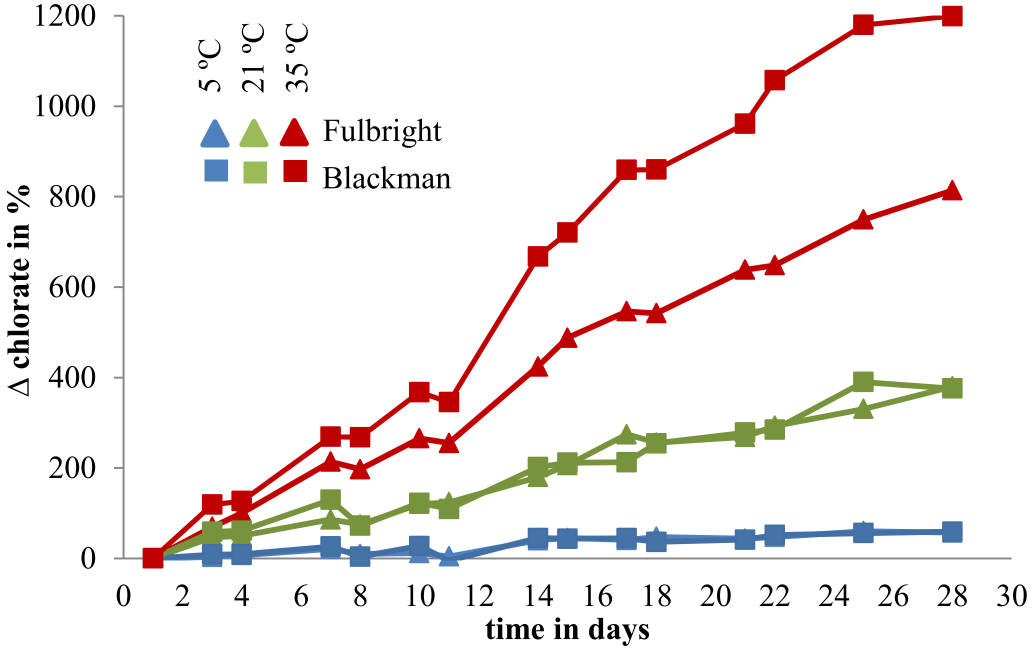

Figure 21. Change in chlorate concentrations compared to Day 1 values for the two sodium hypochlorite generators at 5 ºC (blue), 21 ºC (green) and 35 ºC (red) over a 28-day period (in percent) in comparison to the initial concentration.

Effects of pH adjustments. The effects of initial pH adjustments (to pH 11.3 or 10.3, or unadjusted at pH 9.2) on samples from both treatment systems were followed for 28 days (F22, AI). For each initial pH, the solution pH remain nearly constant throughout the whole study since they have been adjusted initially at day 0.

Considering free chlorine concentrations there is no clear trend (F23, AJ). The samples with pH ~9.2 shows a slight decrease in free chlorine concentration (FWTP: 15%, BWTP: 7%). For a pH of ~10.3, there were slight rises in free chlorine. These concentrations increased mostly in the first two days and then remained constant until the end of the study, suggesting that a low initial reading may have skewed the results. At pH 11.3, FWTP showed a decrease of 4% while BWTP showed a minimal increase of less than 2%.

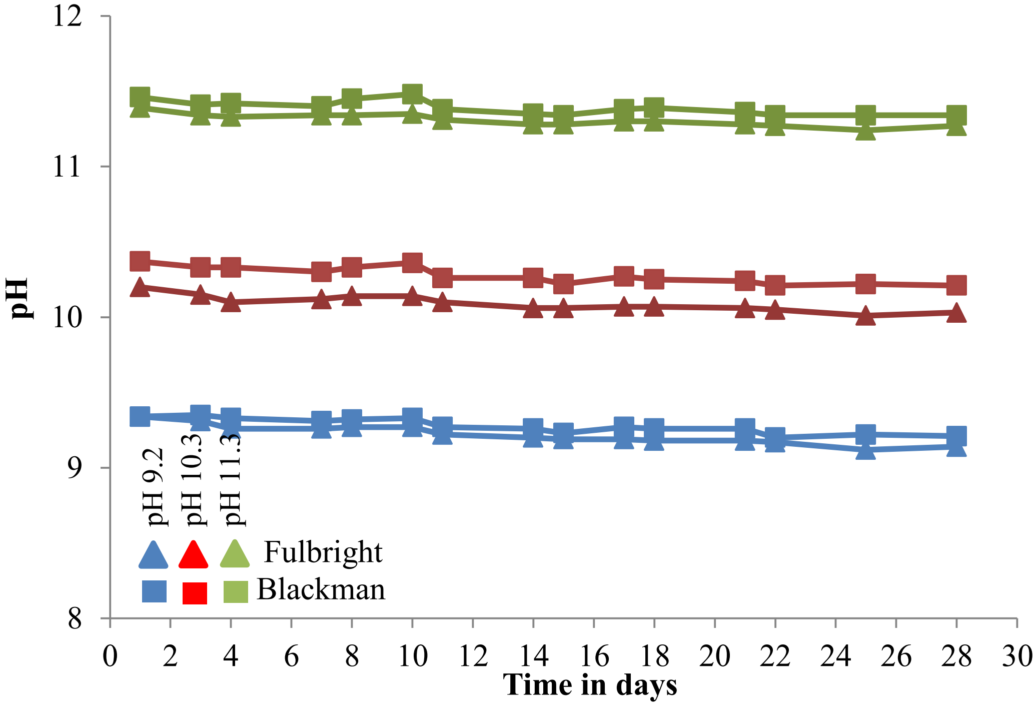

Figure 22. pH compared to the Day 1 values for the two sodium hypochlorite generators after adjustment to pH 9.2 (blue), ~10.3 (red) and ~11.3 (green) over a 28-day period.

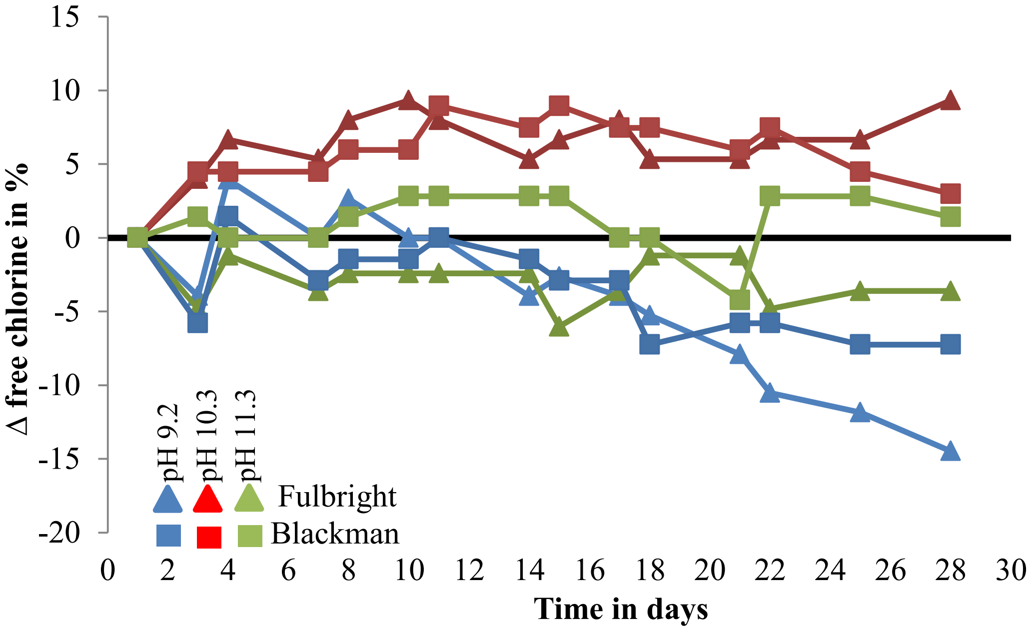

Figure 23. Change in free chlorine concentrations compared to the Day 1 values for the two sodium hypochlorite generators for adjusted pH levels ~9.2 (blue), ~10.3 (red) and ~11.3 ºC (green) over a 28-day period in percent in comparison to the initial concentration.

Chlorate concentrations show modest increases for the higher pH samples and a pronounced increase for the lowest pH samples, (F24, AK) At pH ~11.3 an increase of 50% can be observed for both systems. pH ~10.3 had elevated chlorate concentrations of 112% (FWTP) and 129% (BWTP). The biggest increase in chlorate concentration was observed at the pH ~9.2. Here, FWTP showed an increase of 310% and BWTP showed an increase of 410%. It should be noted that the initial chlorate concentrations for BWTP were lower (110-130 ppm) compared to FWTP (190- 210 ppm). The final chlorate concentrations were also higher for FWTP (334 ppm, 399 ppm and 885 ppm) than BWTP (168 ppm, 281 ppm and 650 ppm). So, although the percent increase at BWTP was greater than at FWTP, the greater absolute increase in chlorate concentration was observed for FWTP.

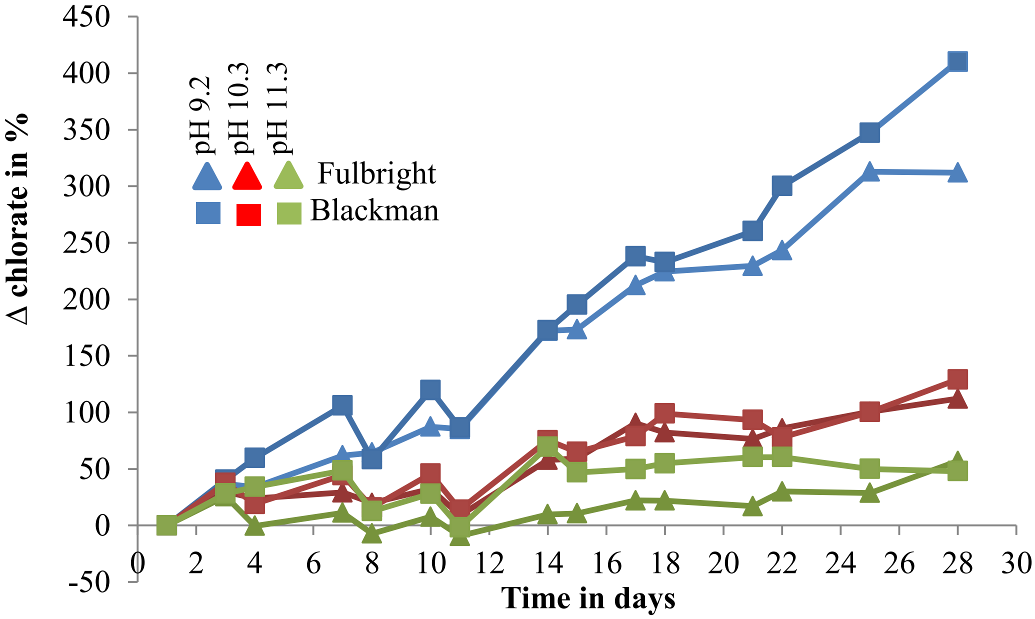

Figure 24. Change in chlorate concentrations compared to the Day 1 values for the two sodium hypochlorite generators for adjusted pH-level ~9.2 (blue), ~10.3 (red) and ~11.3 (green) over a 28-day period in percent in comparison to the initial concentration.

Pre-Generation Study

Changing parameters in pre-generation using the Breeze540 generation system resulted in alterations in chlorate concentrations (F25, AL). For every altered parameter a duplicate was run without alterations that serves as a control run in order to create two points of data for every parameter. The 0% line in F24 represents no difference in chlorate concentration compared to the baseline run.

Adding 10 mmol of sodium hydroxide per liter of brine mixture had almost no effect on chlorate concentration (1% and 6% increase). For sodium bicarbonate, increased chlorate concentrations were observed (33% and 46%). Sodium carbonate was the parameter change that showed the highest increase in chlorate concentration when added to the brine solution (58% and 78%).

The only decrease in chlorate concentration was observed for a temperature adjustment with an initial temperature of 21°C for the baseline run and a final temperature of ~55°C. In comparison, the cold runs started at 11°C and 6°C and increased to temperatures of ~55°C for both runs. Both samples showed a decrease in chlorate concentration of 21% (baseline run: 455 ppm; 11°C: 361 ppm) and 24% (baseline run: 401 ppm; 11°C: 306 ppm).

A complication in interpreting these results stems from significant delays between sampling and chlorate measurements made necessary by the need for service to the IC system.

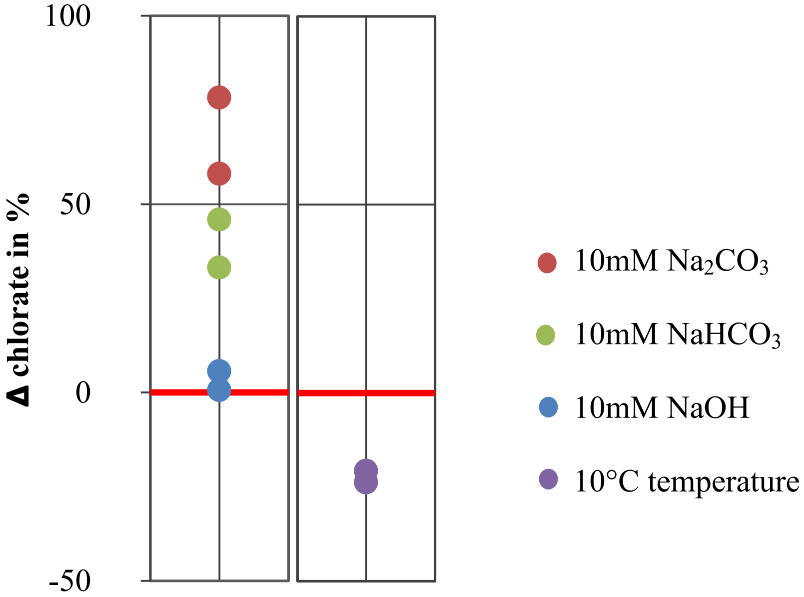

Figure 25. Change in chlorate concentrations for the pool generator for the addition of sodium carbonate, sodium bicarbonate, sodium hydroxide and an initial temperature of 10C in comparison to the initial concentration.

DISCUSSION

Operational Adjustments

The main purpose of this research was to determine and evaluate operational solutions to effectively decrease chlorate concentrations in drinking water. The study's goal was to make adjustments from an application basis. Many studies have focused on research under lab conditions (samples of deionized water spiked with chlorate), but the research from an application base has restrictions on the range of variable that are considered in this paper.

First, it is important that changes in parameters do not reduce the quantity of free chlorine produced. There is a need to effectively change parameters while still providing an adequate supply of free chlorine for the disinfection purpose of drinking water. Also, there are limitations to the adjustment of pH in the generation process. The chlorine generation system has a specific pH range for optimal hypochlorite generation. Operating the system at a pH below or above the range could result in decreased electrode lifetime, decreased hypochlorite generation, or loss of warranties provided by the manufacturer. Finally, there are also practical limitations to temperature changes. Because of the large requirement of water and the temperature rise occurring primarily within the generation apparatus (not amenable to modifications), and the high heat capacity of that water involved, the ability to control temperature is limited.

This study showed trends comparable to previous reports, but it also has substantial differences that will be discussed. The maximum residence study for BWTP and FWTP established that chlorate concentrations still exceed the amount of 210 ppb and thus have to be addressed. From an operational perspective, two possible options to reduce chlorate can be considered which can be achieved by changes pre- and post-generation. It can be assumed that there is a relationship between hypochlorite decomposition and chlorate formation.

For future simplicity, it can be expected that, on average, the electrolysis apparatus generates a product solution of 8,000 ppm of hypochlorite and 500 ppm of chlorate which then goes into the storage tanks. One approach to decrease chlorate concentrations in drinking water would be to reduce chlorate concentrations in the storage tanks (see next sections).

One opportunity to have a decrease in chlorate in water is to modify the disinfection process so that less hypochlorite is required. This might be achieved with the construction of a clear well at BWTP. A clear well can be generally defined as a reservoir for storing large quantities of drinking water of high quantities to accommodate fluctuations in water demands and thus the changing filtration rate with varying demand. Whereas FWTP has been using a clear well for many decades, BWTP is hoping to use one by the end of 2018. A clear well would provide longer chlorine contact time for the disinfection. Because of the longer disinfectant contact time, it is possible to feed hypochlorite further down in the water treatment process. This gives the flocculating agent more time to eliminate fungi, bacteria and viruses resulting in a lower hypochlorite demand for disinfection. Consequently, hypochlorite requirements could be lowered significantly while still providing the same level of disinfection. Because chlorate's source is hypochlorite disinfectant, reducing hypochlorite additions would reduce chlorate proportionally.

Relationship of Changes in Free Chlorine with Chlorate

The overall stoichiometric relationship between hypochlorite and chlorate is based on the following reaction.

$3\ ClO^- \rightleftharpoons 2Cl^- + ClO_3^-$

Hence, there should be a direct relationship between the decrease in free chlorine concentration (expressed as equivalent free Cl_2 in g/L or %) and increase in chlorate (expressed as mass ClO_3^-/L, commonly as ppm). The quantitative relationship between a 1.0 g free chlorine (0.10% or 1000 ppm) loss per liter and the expected chlorate increase is:

$$\frac{1g\ Cl_2}{1L} \times \frac{1\ mole\ Cl_2}{70.906g\ Cl_2} \times \frac{1\ mole\ ClO_3^-}{3\ mole\ Cl_2} \times \frac{83.451\ g\ ClO_3^-}{1\ mole\ ClO_3^-} = \frac{0.392gClO_3^-}{1L}$$

$$\equiv\ 392\ ppm\ ClO_3^-$$

Table 7 presents comparisons between observed changes in free chlorine and chlorate, and in expected chlorate increases based on the relationships discussed above. For example, for hypochlorite produced at FWTP, the free chlorine dropped by 1000 ppm (0.10%) over the course of 28 days, while the chlorate concentration increased by 579 ppm. The increase in chlorate concentration based on hypochlorite decomposition is 392 ppm. Hence, the observed chlorate increase is much larger than expected:

$$\frac{579\ ppm\ ClO_3^-}{392\ ppm\ ClO_3^-} \times\ 100\% = 148\%$$

T7 and T8 summarizes all results for comparisons over a range of conditions previously considered.

Table 7. Contribution of hypochlorite decomposition to chlorate concentration at FWTP.

Run		Measured values (ppm)		Theoretical value (ppm)	contribution in %
		Δ free Cl-	Δ chlorate	chlorate	
Storage Time		1000	579	392	148
Temperature	5C	*			
	21C	1400	737	549	134
	35C	4100	2095	1608	130
pH	9	1100	670	432	155
	10				
	11	300	121	118	103

* calculations not possible because the final free chlorine concentration was bigger than the initial

Table 8. Contribution of hypochlorite decomposition to chlorate concentration at BWTP.

Run		Measured values (ppm)		Theoretical value (ppm)	contribution in %
		Δ free Cl-	Δ chlorate	chlorate	
Storage Time		**			
Temperature	5C	*			
	21C	700	455	275	166
	35C	2900	1746	1138	153
pH	9	500	523	196	267
	10	*			
	11	*			

* calculations not possible because the final free chlorine concentration was bigger than the initial

**data for BWTP storage time included in FWTP data

The results show that chlorate concentration increases in the sample were much greater than predicted based on the observed loss of free chlorine. This can be explained based on the times that concentrations were determined. While free chlorine concentrations were measured almost instantaneously after collection, chlorate determination was somewhat delayed, allowing more hypochlorite to disproportionate. The one example with good agreement between predicted and actual chlorate concentration increase is the sample at adjusted to pH 11, where the disproportionation reaction is pretty much completely quenched. Hence, it is likely that some portion of observed chlorate concentration increases reflect experimental artifacts. If the experiment were repeated, some measure should be taken to limit further hypochlorite decomposition, e.g., the sample pH should be raised, or the solution diluted substantially, in order to stop hypochlorite decomposition.

Reducing Chlorate by Altering Storage Time in Post-Generation

From a cost perspective, changing storage time would be the most affordable solution to prevent chlorate formation. Collected data show that keeping storage time under seven days would limit increasing the chlorate concentrations to a maximum of 50%. This approach would require more frequent generation but would have an effect to control chlorate concentrations in the tanks. (13, 23) The main limitation is that this approach would require reduction in the amount of hypochlorite held in reserve, which could be problematic should there be any interruption in the hypochlorite generation.

A variant on the approach would be to dilute the hypochlorite as soon as it is produced. Diluting the solution would have two beneficial effects:

1. Decrease of solution temperature in tanks (see effects of temperature)
2. dilution of the solutions reduces chlorate formation rate.

In addition, a greater volume of hypochlorite would be required for disinfection, so the storage time would be reduced. The main practical drawback of dilution is that the hypochlorite solution would only be half as strong, so twice as much would be required to achieve the same disinfection. In order to have the same total disinfectant capacity, storage tanks need to be doubled (increasing storage time) or hypochlorite would need to be generated twice as frequently.

Reducing Chlorate by Altering pH in Post-Generation

Previous publications suggested that the rate of chlorate formation is reduced significantly at pH ≥ 10. (2, 3, 13) The data collected for this project showed that an increase of pH effectively reduced chlorate formation over time. pH adjustments in the drinking water industry are typically achieved with the use of sodium carbonate or sometimes sodium hydroxide. However, the use of either compound would require increased capital cost. As an example, hypochlorite solutions were adjusted to a pH 10 and 11 by using 1N sodium hydroxide. Considering the solution's buffering capacity (water used to prepare the brine is softened to remove Ca^{2+} and Mg^{2+}, but the softening does not remove HCO_3^- or CO_3^{2-}, anions that contribute to alkalinity), it takes 3 mL of sodium hydroxide per liter of solution to change the solution's pH to 10 and 7 mL to change it to pH 11. Additionally, increasing pH increases the possibility of corrosion not only in storage tanks but also in the pipe system.

At increased pH, the disproportionation reaction is still thermodynamically favorable but the reaction rate slows down with increasing pH. As discussed, the disproportionation reaction shows its highest rate at a pH of 7.24 (Equation 9) and declines with increasing pH. (2, 3)

Controlling Chlorate by Altering Temperature in Post-Generation

Warm temperature samples show the most rapid increases in chlorate concentration throughout the 28-day period, with up to a 200% increase after seven days. Normally, samples taken after the generation process show temperatures at around 35°C, which is consistent with the temperature study at warm temperature. Also, there is minimal temperature drop in the storage tanks due to their insulation capability, allowing the temperature of 35°C to remain consistent for long periods of time.

Using the temperature study and comparing concentration after seven days for the 35°C and 21°C, it can be concluded that decreasing the temperature to 21°C could reduce the rate of formation by half compared to 35°C samples. (3, 4) This rate is still not ideal but would at least slow down chlorate formation. A drop of temperature post-generation could be achieved by either using dilutions of the hypochlorite (see above) or cooling the solution. Cooling the solution can be achieved using a heat exchanger (high cost to effectively cool solution) or using potable water as a cooling agent in some way.

It is known that cooling the solution has an impact on the disproportionation reaction. At lower temperatures, the disproportionation reaction slows down significantly, which reduces chlorate concentrations.

Effects of Pre-Generation Adjustments

A modified commercial pool generator was chosen to identify the effects of parameter changes in pre-generation for several reasons:

1. The system is smaller than the units used by City Utilities to generate less hypochlorite solution.
2. The pool generator gives the opportunity to change parameters without impacting the water treatment process

3. The pool generator requires less maintenance
4. It was portable.

Even though electrolysis was the driving factor in hypochlorite generation, different characteristics made it difficult to directly compare the pool generator with City Utilities system. One major difference was the current densities on the electrodes' surfaces. Calculations were made for both systems.

PSI Microclor® Models MC-1500 and MC-800:
Flow rate: 15 gal/min ≅ 1 L/s
Hypochlorite generation: 0.8% $NaClO^-$ = 8 g/L NaClO
Total area of anodes: 50,600 cm^3

$$\frac{1\ L}{1\ s} \times \frac{8\ g\ \mathrm{ClO}-}{1\ L} \times \frac{1\ mole\ Na\mathrm{ClO}}{74.44\ g\ Na\mathrm{ClO}} \cong \frac{0.11\ moles\ Na\mathrm{ClO}}{1s}$$

0.11 moles NaClO/s = 0.22 moles e^-/s

$$\frac{0.22\ Me^-}{1\ s} \times \frac{96485\ coulomb}{1\ moles\ e^-} \cong \frac{2.1\times 10^4\ coulomb}{1s} = 2.1\times 10^4\ A$$

$$\frac{2.1\times 10^4 A}{50600\ cm^2} \cong 0.41\ A/cm^2$$

Saline Generating System Breeze 540:
Flow rate: 325 mL/min ≅ 0.005 L/s
Hypochlorite generation: 0.7% NaClO = 7 g/L NaClO
Total area of anodes: 500 cm^3
Cycling time: 1h = 3600sec

$$\frac{7\ g\ Na\mathrm{ClO}}{1\ L} \times \frac{1\ mole\ Na\mathrm{ClO}}{74.44\ g\ Na\mathrm{ClO}} \times 2.5L \cong 0.24\ moles\ NaClO$$

0.24 moles NaClO = 0.48 moles e^-

$$0.48\ Me^- \times \frac{96485\ coulomb}{1\ moles\ e^-} \div 3600sec \cong \frac{12.86\ coulomb}{1s} = 12.86\ A$$

$$\frac{12.86\ A}{500\ cm^2} \cong 0.026\ A/cm^2$$

Looking at the above calculation, it can be concluded that the current density for the PSI Microclor® is 16 times higher than for the Breeze Saline Generating System. It is believed that the formation reaction for chlorate happens at close proximity to the anode surface.

For the mechanism of hypochlorite formation, oxidation reactions at the anode convert two chloride ions into chlorine gas which reacts with water to form hypochlorous acid and hydrochloric acid.

$$Cl_2 + H_2O \longrightarrow HClO + H^+ + Cl^- \qquad \text{(S)}$$

On the anode surface, high amounts of hydrogen ions are produced as part of the formation mechanism of hypochlorite, thus creating a very acidic environment on the electrode's surface. Adding sodium bicarbonate, sodium carbonate or sodium hydroxide to the brine mixture will increase the pH of the feed solution but will not have much effect on the pH on the electrodes surface.

Adding sodium hydroxide to the brine mixture did not have any effect on the observed chlorate concentration. In contrast, observed chlorate increased upon addition of either bicarbonate or carbonate. One potential explanation for increased chlorate concentration with the use of sodium bicarbonate is its buffering capacity which could lower the product's pH where hypochlorite decomposition would be faster. The increase of chlorate upon adding carbonate is not clear. The pH should be high enough that chlorate formation slows down. It is also possible that the high chlorate concentrations measured for some samples reflected artifacts due to delays between sample collection and IC analysis.

Considering the issue with increasing pH at the anode's surface, using sodium carbonate and bicarbonate, another possibility could be to lower the pH of the solution to drive the pH at the surface to an even more acidic pH. This could result in moving the pH substantially below 7.0, away from the pH with the highest formation rate and thus reducing it. This concept was not considered in this research paper as it is not preferable from an application perspective due to corrosion issues. Another problem associated with low pH is that the equilibrium of the reaction would shift towards the formation of hypochlorous acid and also releasing chlorine gas as a byproduct of the equilibrium shift.

The only parameter change that showed a decrease in chlorate concentration was a change in temperature. At low temperature, the disproportionation reaction slows down which makes the reaction very temperature dependent. Even though it was not tested in this research it can be assumed that the disproportionation is the slowest for a solution of 0°C and increases with increasing temperature. This assumption needs further research to confirm the dependency of temperature for the system. At this point, it cannot be determined whether the lower chlorate concentration reflects less production of chlorate from the electrolysis, per se, or suppressed disproportionation in the solution.

Even though the data collected from the pool generator lines up well with the theory, the effects of artifacts need to be discussed as well. Throughout the runs of 60 min, temperatures increased to about 50°C and were about 15°C higher than what was observed for the PSI Microclor® systems. This same temperature increase also appeared at low temperature runs that started at decreased initial temperatures. Furthermore, it is possible that evaporative loss of solution could have had an influence because of high solution temperatures, but this may only be minor.

Overall, the data show a trend that lowering solution temperature in pre-generation can have a great influence on chlorate concentration but it is necessary to investigate the effects of temperature and eliminate the specific artifacts. Even though current densities of the different systems do not coincide with each other, the Breeze Saline Generating System can be used as a good reference for altering parameters that can be applied to the PSI Microclor® systems.

CONCLUSION

Chlorate in drinking water appears rather commonly throughout the U.S. with varying concentrations. Chlorate is a disinfection byproduct of hypochlorite generation. Springfield, MO, which uses on-site hypochlorite generation systems, is facing the issue of producing high concentrations of chlorate in their drinking water above a possible HRL of 210 µg/L. This concentration was exceeded several times in the past year.

With the move by the USEPA to regulate chlorate concentrations in drinking water, this research is very important to understanding the mechanisms behind chlorate formation in on-site generation systems and in evaluating what parameters can have a positive impact on chlorate reduction. Being able to successfully demonstrate how to reduce chlorate in drinking water can have a big influence on PWS that are using some kind of hypochlorite as their disinfectant.

Different possibilities of reducing chlorate formation were considered and evaluated. Reduced storage time, low temperatures and high pH were identified to lower decomposition rates of hypochlorite in post-generation. Decreasing storage time reduces the time for hypochlorite decomposition. From an application perspective, it is important to reduce storage time as much as possible.

A correlation has been found between hypochlorite decomposition rates and solution temperatures. Low temperatures (10°C) reduce hypochlorite decomposition while high temperatures (35°C) increase hypochlorite decomposition compared to room temperature (21°C). Previous publications looked at chlorate formation under lab conditions. This research showed that findings from these publications can also be applied to settings with a more complex matrix.

Furthermore, increasing pH of hypochlorite solutions also has a positive effect on reducing decomposition rates and also agrees with findings from previous publications. Increasing the solution pH to 11 during storage almost stopped the decomposition of hypochlorite, maintained free chlorine strength, and prevented significant increases in chlorate concentration.

Additionally, an increased solution pH using sodium carbonate and sodium bicarbonate in pre-generation showed an increase in chlorate concentration, but no effect on chlorate concentration was observed by changing the pH using sodium hydroxide. A decrease in solution temperature appeared to reduce chlorate concentrations. Overall, changes in temperature for pre- and post-generation as well as reduced storage time in post-generation are showing the most promising effect in reducing decomposition rates from an operational perspective, but the results and conclusions are suspect due to potential artifacts.

It needs to be emphasized that adjustments made in post-generation do not reduce chlorate concentrations. Its purpose is to reduce hypochlorite decomposition rates to minimize further increases in chlorate concentration.

Results from adjustments in post-generation were successful and agree with findings from previous papers. The\results are a good representation of the hypothesis and underline the success of this research. Results from adjustments in pre-generations did not yield comparable results for several reasons. First, little data was gathered and only one duplicate was collected for every adjustment. This makes it difficult to determine the correctness of this experiment. Also, artifacts of the instrumentation set up may have skewed the results. Additionally, throughout the test runs for pre-generation adjustments some instrumentation error was observed. Since the Breeze Saline Generating System was not manufactured for the production of high hypochlorite concentrations, the instrument increased in temperature and caused melting of some of the insulation which required a modification of the instrument setup. Because the experimental system was not stable, obtaining reproducible data comparable over multiple runs was not possible.

If adjustments in pre-generation are considered in future research, it may be advisable to purchase a complete hypochlorite generation system that is able to withstand changes in parameters and provide data closer to the application settings. This purchase, however, would require some capital cost. Also, the system may lose its warranty by changing some of the parameters considered.

Using the current system setup of the Breeze Saline Generating System, more data points on the effect of temperature changes in pre-generation will be required in order to make a better statement regarding control of chlorate formaition. It is crucial to eliminate artifacts in the system setup to remove the influence of other undesirable parameter changes. To eliminate the artifact of temperature in the pH run it is necessary to keep the solution temperature close to the initial temperature. Putting the reaction chamber into a temperature controlled water bath may prevent the increase in temperature. This also applies to the temperature runs.

BIBLIOGRAPHY

(1) Abdel-Rahman, M.; Couri, D.; Bull, R. Metabolism and Pharmacokinetics of Alternate Drinking Water Disinfectants. *Environmental Health Perspectives* **1982,** 46, 19-23.

(2) Adam, L.; Fábián, I.; Suzuki, K.; Gordon, G. Hypochlorous acid decomposition in the pH 5-8 region. *Inorganic Chemistry* **1992**, *31*(17), 3534-3541.

(3) Adam, L.; Gordon, G. (1999). Hypochlorite Ion Decomposition: Effects of Temperature, Ionic Strength, and Chloride Ion. *Inorg. Chemistry* **1999,** 38(6), 1299-1304.

(4) Alfredo K.; Adams C.; Eaton A.; Roberson J.; Stanford B. The Potential Regulatory Implications of Chlorate. *American Water Works Association*, **2014,** 1-26.

(5) Alfredo, K.; Stanford, B.; Roberson, J.; Eaton, A. Chlorate Challenges for Water Systems. *Journal-American Water Works Association* **2015,** 107, 187-196.

(6) Boal, A. Tech Brief- On-site Generation of disinfectants. *National Environmental Service Center*, **2009,** 9(1), 1-4.

(7) Couri, D.; Abdel-Rahman, M.; Bull, R. (1982). Toxicological effects of chlorine dioxide, chlorite and chlorate. *Environmental Health Perspectives* **1982,** 46, 13-17.

(8) Czarnetzki, L. Aspects of electrochemical production of hypochlorite and chlorate. *Technische Universiteit Eindhoven*. **1989,** 1-166.

(9) Czarnetzki, L.; Janssen, L. Formation of hypochlorite, chlorate and oxygen during NaCl electrolysis from alkaline solutions at an RuO2/TiO2anode. *J. of Applied Electrochemistry* **1992,** 22(4), 315-324.

(10) Foerster, F.; Dolch, P. Elektrochemie wässriger Lösungen. *Z. Elektrochem,* **1917**, 23, 137.

(11) Gerba, C.; Rusin P. Relationship between the use of antiseptics/disinfectants and the development of antimicrobial resistance. *Association for Professional in Infection Control and Epidemiology*, **2001,** 187-194. In: Rutala WA, ed. Disinfection, sterilization and antisepsis: principles and practices in healthcare facilities. Washington, DC.

(12) Gonce, N.; Voudrias, E.A. Removal of chlorite and chlorate ions from water using granular activated carbon. *Water Research* **1994,** 28(5), 1059-1069.

(13) Gordon, G.; Bubnis, B.; Adam, L. Minimizing Chlorate Ion Formation. *Journal-American Water Works Association* **1995,** 87(6), 97-106.

(14) Gorzalski, A.; Spiesman, A. Insights on Chlorate Occurrence, Intra-system Variability, and Source Water Concentrations. *Journal-American Water Works Association* **2015,** 107(11), 613-626.

(15) Jung, Y.; Baek, K.; Oh, B.; Kang, J. An investigation of the formation of chlorate and perchlorate during electrolysis using Pt/Ti electrodes: The effects of pH and reactive oxygen species and the results of kinetic studies. *Water Research* **2010,** 44(18), 5345-5355.

(16) Lubbers, J.; Chauhan, S.; Bianchine, J. Controlled clinical evaluations of chlorine dioxide, chlorite and chlorate in man. *Fundamental and Applied Toxicology* **1981,** 1(4), 334-338.

(17) n.a. Chlorite and Chlorate in Drinking-water – background document for development of WHO Guidelines for Drinking-water Quality. *World Health Organization* **2005,** 1-23.

(18) n.a. NTP Technical Report on the Toxicology of Sodium Chlorate. *National Toxicology Program* **2005,** 1-156.

(19) n.a. Guidelines for Canadian Drinking Water Quality: Guideline Technical Document — Chlorite and Chlorate. *Water Quality and Health Bureau, Healthy Environments and Consumer Safety Branch* **2008,** 1-44.

(20) Rivera S.; Matousek R. AWWA Manual M65- Overview. *American Water Works Association* **2015,** 1-9.

(21) Rutala, W.; Weber, D. Guideline for Disinfection and Sterilization in Healthcare Facilities. *Center For Disease Control and Prevention* **2008,** 1-158.

(22) Stanford, B.; Pisarenko, A.; Dryer, D.; Ziegler-Holady, J.; Gamage, S., et al. Chlorate, perchlorate, and bromate in onsite-generated hypochlorite systems. *Journal - American Water Works Association* **2013,** 105(3), 93-102.

(23) Stanford, B., Pisarenko A., Snyder S., Gordon G. Perchlorate, bromate and chlorate in hypochlorite solutions: Guidelines for utilities. *American Water Works Association* **2011,** 103(6), 1-13.

(24) USEPA. Inorganic Chlorates Facts. *United Environmental Protection Agency* **2008,** 1-7.

(25) USEPA. The Third Unregulated Contaminant Monitoring Role (UCMR 3): Data Summary, July 2016. 1-12.

(26) Wardman, Peter. Reduction Potentials of One Electron Couples Involving Free Radicals in Aqueous Solution. *Journal of Physical and Chemical Reference Data* **1989,** 18(4), 1637-1755.

APPENDICES

Appendix A. Chlorate concentrations in ppm at different locations throughout the treatment process at BWTP.

Sampling events	First Basin	Second Basin	Post Filter	Potable Water	Water Softener	Hypochlorite Generation System	Storage Tank #2
1	0	0.16	0.15	0.23	0.16	248	413
2	0	0.14	0.15	0.21	0.14	587	491
3	0	0.10	0.11	0.23	0.19	541	510
4	0	0.09	0.10	0.15	0.13	444	591
5	0	0.11	0.10	0.15	0.11	332	575
6	0	0.08	0.09	0.16	0.11	221	537
7	0	0.07	0.08	0.13	0.00	200	539
8	0	0.08	0.08	0.15	0.10	346	259

Appendix B. Chlorate concentrations in ppm for the two different maximum residence locations.

Date	Evans Rd	Expedia
3/18/2013	78.0	23.1
9/30/2013	149	149
12/16/2013	202	112
3/25/2014	213	76.5
4/1/2014	179	81.3
6/24/2014	523	285
9/30/2016	218	178
10/4/2016	381	97.3
10/11/2016	358	136
10/18/2016	248	206
10/25/2016	186	183
11/1/2016	156	124
11/8/2016	159	106
11/15/2016	101	48.2
11/29/2016	159	90.1

Appendix C. pH-levels for the storage time runs over a 28-day period.

	Fulbright WTP			Blackman WTP				
Day	Run 1	Run 2	Run 3	Run 1	Run 2	Run 3	Average	std. dev.
1	9.34	9.34	9.35	9.25	9.34	9.36	9.33	0.040
3	9.30	9.31	9.29	9.34	9.35	9.35	9.32	0.027
4	9.25	9.26	9.29	9.33	9.33	9.34	9.30	0.039
7	9.26	9.26	9.27	9.30	9.31	9.29	9.28	0.021
8	9.26	9.27	9.30	9.29	9.32	9.31	9.29	0.023
10	9.25	9.27	9.30	9.31	9.33	9.34	9.30	0.035
11	9.20	9.22	9.25	9.25	9.27	9.28	9.25	0.030
14	9.17	9.20	9.22	9.24	9.26	9.26	9.23	0.036
15	9.17	9.19	9.21	9.18	9.23	9.25	9.21	0.031
17	9.17	9.19	9.23	9.24	9.27	9.27	9.23	0.041
18	9.16	9.18	9.22	9.22	9.26	9.27	9.22	0.043
21	9.17	9.18	9.24	9.19	9.26	9.27	9.22	0.044
22	9.14	9.17	9.19	9.17	9.20	9.22	9.18	0.028
25	9.05	9.12	9.15	9.16	9.22	9.21	9.15	0.062
28	9.08	9.14	9.17	9.13	9.21	9.20	9.16	0.048

Appendix D. Free Chlorine concentrations in percent (top) and change in free chlorine in percent (bottom) for the storage time runs over a 28-day period.

	Fulbright WTP			Blackman WTP			
Day	Run 1	Run 2	Run 3	Run 1	Run 2	Run 3	Average
1	0.81	0.76	0.79	0.69	0.69	0.68	0.74
3	0.81	0.73	0.75	0.70	0.65	0.71	0.73
4	0.79	0.79	0.77	0.73	0.70	0.72	0.75
7	0.77	0.76	0.78	0.71	0.67	0.71	0.73
8	0.76	0.78	0.76	0.69	0.68	0.70	0.73
10	0.77	0.76	0.77	0.68	0.68	0.70	0.73
11	0.76	0.76	0.76	0.69	0.69	0.69	0.73
14	0.74	0.73	0.75	0.68	0.68	0.68	0.71
15	0.75	0.74	0.74	0.68	0.67	0.68	0.71
17	0.73	0.73	0.72	0.68	0.67	0.67	0.70
18	0.73	0.72	0.72	0.66	0.64	0.68	0.69
21	0.69	0.70	0.70	0.67	0.65	0.65	0.68
22	0.69	0.68	0.69	0.66	0.65	0.66	0.67
25	0.68	0.66	0.68	0.65	0.65	0.64	0.66
28	0.67	0.65	0.65	0.63	0.64	0.61	0.64

	Fulbright WTP			Blackman WTP				
Day	Run 1	Run 2	Run 3	Run 1	Run 2	Run 3	Average %	Std. dev.
1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3	0.00	-3.95	-5.06	1.45	-5.80	4.41	-1.58	4.08
4	-2.47	3.95	-2.53	5.80	1.45	5.88	1.81	3.85
7	-4.94	0.00	-1.27	2.90	-2.90	4.41	-0.45	3.51
8	-6.17	2.63	-3.80	0.00	-1.45	2.94	-1.13	3.59
10	-4.94	0.00	-2.53	-1.45	-1.45	2.94	-1.36	2.62
11	-6.17	0.00	-3.80	0.00	0.00	1.47	-1.58	2.92
14	-8.64	-3.95	-5.06	-1.45	-1.45	0.00	-3.62	3.15
15	-7.41	-2.63	-6.33	-1.45	-2.90	0.00	-3.62	2.86
17	-9.88	-3.95	-8.86	-1.45	-2.90	-1.47	-4.98	3.71
18	-9.88	-5.26	-8.86	-4.35	-7.25	0.00	-6.11	3.58
21	-14.8	-7.89	-11.4	-2.90	-5.80	-4.41	-8.14	4.51
22	-14.8	-10.5	-12.7	-4.35	-5.80	-2.94	-8.82	4.83
25	-16.1	-13.2	-13.9	-5.80	-5.80	-5.88	-10.4	4.78
28	-17.3	-14.5	-17.7	-8.70	-7.25	-10.3	-12.9	4.49

Appendix E. Chlorate concentrations in ppm (top) and change in chlorate concentration in percent (bottom) for the storage time runs over a 28-day period.

	Fulbright WTP			Blackman WTP			
Day	Run 1	Run 2	Run 3	Run 1	Run 2	Run 3	Average
1	232	215	194	135	128	121	171
3	278	294	285	180	179	192	235
4	298	288	290	191	204	195	244
7	363	348	361	222	263	278	306
8	332	353	339	203	202	209	273
10	410	402	427	259	280	270	341
11	381	398	434	222	238	254	321
14	500	585	543	327	348	365	445
15	579	587	594	349	376	377	477
17	587	671	726	363	431	378	526
18	664	697	690	410	424	429	552
21	697	708	714	425	459	458	577
22	721	738	762	439	510	466	606
25	865	887	835	541	570	593	715
28	928	885	931	530	651	576	750

	Fulbright WTP			Blackman WTP				
Day	Run 1	Run 2	Run 3	Run 1	Run 2	Run 3	Average %	std. dev.
1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.0
3	20	37	47	33	40	59	39.3	13
4	28	34	50	41	60	61	45.7	13
7	57	62	86	64	106	130	84.2	29
8	43	64	75	51	59	72	60.7	12
10	77	87	120	92	120	123	103	20
11	64	85	124	64	86	110	88.8	24
14	115	172	180	143	173	202	164	31
15	149	173	206	159	195	212	182	26
17	153	212	274	169	238	213	210	44
18	186	225	256	204	233	255	226	28
21	200	230	269	215	260	278	242	32
22	210	243	293	225	300	285	260	38
25	272	313	330	301	347	390	326	41
28	300	312	380	293	410	376	345	50

Appendix F. pH levels for the temperature runs over a 28-day period.

	Fulbright WTP			Blackman WTP		
Days	5°C	21°C	35°C	5°C	21°C	35°C
1	9.33	9.35	9.19	9.52	9.36	9.20
3	9.33	9.29	9.15	9.47	9.35	9.15
4	9.35	9.29	9.15	9.39	9.34	9.08
7	9.40	9.27	9.06	9.43	9.29	9.01
8	9.39	9.30	9.08	9.44	9.31	9.05
10	9.30	9.30	9.06	9.46	9.34	9.03
11	9.40	9.25	9.00	9.40	9.28	8.94
14	9.37	9.22	8.92	9.38	9.26	8.89
15	9.35	9.21	8.91	9.38	9.25	8.85
17	9.35	9.23	8.89	9.41	9.27	8.84
18	9.40	9.22	8.88	9.42	9.27	8.83
21	9.40	9.24	8.84	9.41	9.27	8.79
22	9.38	9.19	8.79	9.40	9.22	8.74
25	9.37	9.15	8.70	9.38	9.21	8.65
28	9.37	9.17	8.67	9.38	9.20	8.61

Appendix G. Free chlorine concentrations in percent (top) and change in free chlorine in percent (bottom) for the temperature runs over a 28-day period.

	Fulbright WTP			Blackman WTP		
Days	5°C	21°C	35°C	5°C	21°C	35°C
1	0.76	0.79	0.77	0.66	0.68	0.68
3	0.79	0.75	0.74	0.68	0.71	0.69
4	0.80	0.77	0.76	0.70	0.72	0.68
7	0.78	0.78	0.70	0.68	0.71	0.62
8	0.78	0.76	0.68	0.70	0.70	0.62
10	0.75	0.77	0.64	0.69	0.70	0.57
11	0.78	0.76	0.61	0.69	0.69	0.56
14	0.80	0.75	0.57	0.72	0.68	0.51
15	0.81	0.74	0.54	0.71	0.68	0.50
17	0.77	0.72	0.49	0.70	0.67	0.46
18	0.79	0.72	0.49	0.72	0.68	0.47
21	0.78	0.70	0.43	0.72	0.65	0.41
22	0.77	0.69	0.43	0.72	0.66	0.38
25	0.71	0.68	0.31	0.71	0.64	0.37
28	0.78	0.65	0.36	0.74	0.61	0.37

	Fulbright WTP			Blackman WTP		
Days	5°C	21°C	35°C	5°C	21°C	35°C
1	0.00	0.00	0.00	0.00	0.00	0.00
3	3.95	-5.06	-3.90	3.03	4.41	1.47
4	5.26	-2.53	-1.30	6.06	5.88	0.00
7	2.63	-1.27	-9.09	3.03	4.41	-8.82
8	2.63	-3.80	-11.7	6.06	2.94	-8.82
10	-1.32	-2.53	-16.9	4.55	2.94	-16.2
11	2.63	-3.80	-20.8	4.55	1.47	-17.7
14	5.26	-5.06	-26.0	9.09	0.00	-25.0
15	6.58	-6.33	-29.9	7.58	0.00	-26.5
17	1.32	-8.86	-36.4	6.06	-1.47	-32.4
18	3.95	-8.86	-36.4	9.09	0.00	-30.9
21	2.63	-11.4	-44.2	9.09	-4.41	-39.7
22	1.32	-12.7	-44.2	9.09	-2.94	-44.1
25	-6.58	-13.9	-59.7	7.58	-5.88	-45.6
28	2.63	-17.7	-53.3	12.1	-10.3	-45.6

Appendix H. Chlorate concentrations in ppm (top) and change in chlorate concentration in percent (bottom) for the temperature runs over a 28-day period.

	Fulbright WTP			Blackman WTP		
Days	5°C	21°C	35°C	5°C	21°C	35°C
1	188	194	257	124	121	146
3	194	285	436	135	192	319
4	201	290	516	135	195	330
7	227	361	808	156	278	537
8	206	339	765	129	209	536
10	210	427	940	158	270	681
11	196	434	914	118	254	649
14	263	543	1349	180	365	1120
15	272	594	1513	178	377	1200
17	264	726	1663	179	378	1400
18	277	690	1653	169	429	1400
21	270	714	1900	175	458	1550
22	277	762	1926	188	466	1690
25	301	835	2186	193	593	1860
28	295	931	2352	197	576	1890

	Fulbright WTP			Blackman WTP		
Days	5°C	21°C	35°C	5°C	21°C	35°C
1	0.00	0.00	0.00	0.00	0.00	0.00
3	3.30	46.8	69.5	8.67	59.0	119
4	7.20	49.9	101	8.80	61.1	127
7	20.9	86.0	214	26.2	130	269
8	9.56	74.7	197	4.11	72.4	268
10	11.8	120	265	27.4	123	368
11	4.19	124	255	-4.93	110	345
14	40.1	180	424	45.0	202	668
15	45.1	206	488	43.7	212	721
17	40.8	274	546	44.5	213	859
18	47.6	256	542	36.7	255	860
21	43.7	269	638	41.5	278	961
22	47.4	293	648	51.7	285	1060
25	60.3	330	750	55.9	390	1180
28	57.2	380	814	59.1	376	1200

Appendix I. pH levels for the pH runs over a 28-day period.

	Fulbright WTP			Blackman WTP		
Days	pH=9	pH=10	pH=11	pH=9	pH=10	pH=11
1	9.34	10.20	11.39	9.34	10.37	11.46
3	9.31	10.15	11.34	9.35	10.33	11.41
4	9.26	10.10	11.33	9.33	10.33	11.42
7	9.26	10.12	11.34	9.31	10.30	11.40
8	9.27	10.14	11.34	9.32	10.33	11.45
10	9.27	10.14	11.35	9.33	10.36	11.48
11	9.22	10.10	11.31	9.27	10.26	11.38
14	9.2	10.06	11.28	9.26	10.26	11.35
15	9.19	10.06	11.28	9.23	10.22	11.34
17	9.19	10.07	11.30	9.27	10.27	11.38
18	9.18	10.07	11.30	9.26	10.25	11.39
21	9.18	10.06	11.28	9.26	10.24	11.36
22	9.17	10.05	11.27	9.20	10.21	11.34
25	9.12	10.01	11.24	9.22	10.22	11.34
28	9.14	10.03	11.27	9.21	10.21	11.34

Appendix J. Free chlorine concentrations in percent (top) and change in free chlorine in percent (bottom) for the pH runs over a 28-day period.

	Fulbright WTP			Blackman WTP		
Days	pH=9	pH=10	pH=11	pH=9	pH=10	pH=11
1	0.76	0.75	0.83	0.69	0.67	0.71
3	0.73	0.78	0.79	0.65	0.70	0.72
4	0.79	0.80	0.82	0.70	0.70	0.71
7	0.76	0.79	0.80	0.67	0.70	0.71
8	0.78	0.81	0.81	0.68	0.71	0.72
10	0.76	0.82	0.81	0.68	0.71	0.73
11	0.76	0.81	0.81	0.69	0.73	0.73
14	0.73	0.79	0.81	0.68	0.72	0.73
15	0.74	0.80	0.78	0.67	0.73	0.73
17	0.73	0.81	0.80	0.67	0.72	0.71
18	0.72	0.79	0.82	0.64	0.72	0.71
21	0.70	0.79	0.82	0.65	0.71	0.68
22	0.68	0.80	0.79	0.65	0.72	0.73
25	0.67	0.80	0.80	0.64	0.70	0.73
28	0.65	0.82	0.80	0.64	0.69	0.72

	Fulbright WTP			Blackman WTP		
Days	pH=9	pH=10	pH=11	pH=9	pH=10	pH=11
1	0.00	0.00	0.00	0.00	0.00	0.00
3	-3.95	4.00	-4.82	-5.80	4.48	1.41
4	3.95	6.67	-1.20	1.45	4.48	0.00
7	0.00	5.33	-3.61	-2.90	4.48	0.00
8	2.63	8.00	-2.41	-1.45	5.97	1.41
10	0.00	9.33	-2.41	-1.45	5.97	2.82
11	0.00	8.00	-2.41	0.00	8.96	2.82
14	-3.95	5.33	-2.41	-1.45	7.46	2.82
15	-2.63	6.67	-6.02	-2.90	8.96	2.82
17	-3.95	8.00	-3.61	-2.90	7.46	0.00
18	-5.26	5.33	-1.20	-7.25	7.46	0.00
21	-7.89	5.33	-1.20	-5.80	5.97	-4.23
22	-10.5	6.67	-4.82	-5.80	7.46	2.82
25	-11.8	6.67	-3.61	-7.25	4.48	2.82
28	-14.5	9.33	-3.61	-7.25	2.99	1.41

Appendix K. Chlorate concentrations in ppm (top) and change in chlorate in percent (bottom) for the pH runs over a 28-day period.

	Fulbright WTP			Blackman WTP		
Days	pH=9	pH=10	pH=11	pH=9	pH=10	pH=11
1	215	188	213	128	123	114
3	294	244	268	179	169	146
4	288	233	212	204	146	152
7	348	243	237	263	177	169
8	353	225	198	202	142	128
10	402	249	229	280	179	145
11	398	205	193	238	140	112
14	585	297	234	348	215	193
15	587	299	236	376	202	167
17	671	358	260	431	219	170
18	697	343	260	424	244	176
21	708	332	249	459	237	182
22	738	349	277	510	218	182
25	887	377	274	570	246	233
28	885	399	334	651	281	168

	Fulbright WTP			Blackman WTP		
Days	pH=9	pH=10	pH=11	pH=9	pH=10	pH=11
1	0.00	0.00	0.00	0.00	0.00	0.00
3	37.0	29.9	25.9	40.4	37.6	28.2
4	33.8	23.8	-0.31	59.6	19.1	34.1
7	61.9	29.2	11.2	106	44.5	48.6
8	64.5	19.9	-7.11	58.6	15.8	12.6
10	87.3	32.3	7.71	120	45.8	28.0
11	85.3	8.80	-9.33	86.5	13.9	-1.70
14	172	58.0	10.7	173	75.3	69.7
15	173	59.3	10.7	195	65.0	46.8
17	212	90.4	22.1	238	78.9	49.9
18	225	82.3	22.0	233	98.9	55.0
21	230	76.4	17.0	260	93.3	60.5
22	243	85.8	30.0	300	77.9	60.4
25	313	101	28.7	347	100	105
28	312	112	56.9	410	129	48.0

Appendix L. Pre-Generation runs.

Setting	Initial		Final				
	T (◦C)	pH	T (◦C)	pH	Free Cl (%)	Chlorate (ppm)	Chlorate change (%)
Unchanged	24.3	8.5	56.4	9.23	0.63	309	
10mmol NaOH	23.7	9.5	56.8	9.42	0.65	311	0.68
Unchanged	20.1	7.81	52.3	9.39	0.81	369	
10mmol NaOH	21.1	11.01	52.2	10.54	0.74	390	5.69
Unchanged	21.7	8.19	52.2	9.25	0.77	331	
10mmol Na2CO3	21.6	10.34	21.6	10.05	0.77	523	58.1
Unchanged	24	8.27	54.3	9.11	0.71	350	
10mmol Na2CO3	24.9	10.08	51.5	9.88	0.66	625	78.3
Unchanged	22.1	8.27	54.2	9.27	0.57	364	
10mmol NaHCO3	22.1	7.84	53.4	9.04	0.51	485	33.2
Unchanged	21.3	8.18	53.5	9.65	0.54	425	
10mmol NaHCO3	19.4	8.23	51.3	9.35	0.47	532	25.0
Unchanged	21.9	8.13	54.4	9.72	0.78	456	
10°C temperature	11.4	8.04	48.1	9.43	0.8	361	-20.8
Unchanged	21.5	8.16	55.5	9.6	0.73	401	
10°C temperature	6.5	8	53.7	9.52	0.8	306	-23.8