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AN INVESTIGATION OF CHLORATE AND PERCHLORATE IN ONSITE-GENERATED HYPOCHLORITE

by

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ABSTRACT

AN INVESTIGATION OF CHLORATE AND PERCHLORATE IN ONSITE-GENERATED HYPOCHLORITE

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The University of Texas at Arlington, 2016

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This investigation evaluated the occurrence and concentration of chlorate and perchlorate in two low-strength onsite-generated hypochlorite systems in the DFW Metroplex, and attempted to correlate their concentrations to operating conditions and input materials of the generation process. Chlorate and perchlorate are disinfectant byproducts found in drinking water treated with hypochlorite and are known to pose potential health problems. Hypochlorite samples were quenched to remove chlorine and then analyzed using ion chromatography to determine the byproduct concentration. Results showed a correlation between byproduct concentration and the density of the solution as well as with the chlorine concentration. Other factors, such as pH, did not appear to significantly affect the byproduct concentration. The measured levels of chlorate and perchlorate in the hypochlorite generation systems studied are currently not high enough

to pose serious health effects, but future federal regulation may require water treatment facilities to take an active approach to limit the contaminants.

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CHAPTER 1

INTRODUCTION

Chlorine is a common disinfectant used across the United States to disinfect water for drinking purposes. Chlorine-based disinfectants come in various forms and differ based on their cost, ease of application, and their tendency to form unhealthy byproducts. Currently, liquefied chlorine gas is the most widely used disinfectant for water treatment plants in the US, as it is easy to use and relatively inexpensive. However, liquefied chlorine gas presents many safety concerns, especially when stored in water treatment facilities located in highly populated areas, as it is highly toxic. Due to the Environmental Protection Agency’s Risk management plan and pressure by the US Department of Homeland Security, water treatment plants are shifting away from the use of liquefied chlorine gas and are beginning to use hypochlorite solutions to disinfect drinking water.

Hypochlorite solutions commonly come in two forms, high-strength hypochlorite, and low-strength hypochlorite. High-strength hypochlorite is generally produced by an external supplier at a concentration of approximately 10-12% Cl_2 and is then transported to the water treatment facility where it is stored until needed. Low-strength hypochlorite is generally produced at the water treatment facility and is known as onsite generated (OSG) hypochlorite. OSG hypochlorite is produced through the electrolysis of brine and softened water, resulting in a 0.5% to 1.2% hypochlorite solution, depending on the generator manufacturer. The disinfectant is either sent directly to the water supply, or is stored at the water treatment facility until required. Unlike disinfection using liquefied chlorine gas, disinfection using hypochlorite is known to introduce disinfection byproducts in the finished water because the impurities exist in the disinfectant itself rather than forming through reactions between the disinfectant and compounds in the water. Two byproducts found in finished hypochlorite solutions are chlorate and perchlorate, both of which are known to pose serious health risks. Though the byproducts are not currently federally regulated, the EPA is expected to begin regulating the concentration of both byproducts in the near future.

The formation of chlorate and perchlorate in low-strength OSG hypochlorite solutions is currently not fully understood. To comply with the potential regulation of chlorate and perchlorate by the EPA, knowledge of why these byproducts form, and how to limit their formation will be important information to water treatment facilities. This study aims to correlate operating conditions and input materials of onsite generated low-strength hypochlorite disinfection systems, such as water temperature, quality and quantity of the brine solution, and the quality of the water used, to the presence and concentration of chlorate and perchlorate found in the resulting hypochlorite solution.

Additionally, this research will attempt to correlate the operating conditions and input materials with the resulting concentration of chlorine in the hypochlorite solution. In order to reach the required residual chlorine content in finished water, operators add hypochlorite until they achieve the required residual. However, if the chlorine content of the hypochlorite concentration is lower than the expected concentration given by the manufacturer of the generation systems, operators must add more of the hypochlorite solution to the water. This practice is inefficient as it requires more hypochlorite solution, meaning more energy expenditures, to achieve the same amount of residual chlorine in treated water and also adds more of the disinfectant byproducts to the water supply than if hypochlorite solutions with the expected chlorine concentrations were used. Therefore, this investigation will attempt to correlate the chlorine concentration of the resulting hypochlorite solution to operating conditions in order to increase the efficiency of the systems and to limit the concentration of byproducts found in the finished water.

CHAPTER 2

LITERATURE REVIEW

2.1 Overview of Chlorate and Perchlorate

Chlorate and perchlorate are both under investigation for potential adverse health effects in humans. Health effects of both byproducts have been extensively tested using laboratory animals, but tests involving human subjects are limited.

2.1.1 Disinfection Byproducts: Chlorate

Chlorate compounds are strong oxidizers and have several industrial applications such as in the manufacture of dyes, explosives, matches, and herbicides, and also as a bleaching agent for paper and textiles (WHO, 2005, USEPA, 2014a, Alfredo et al., 2014). The chlorate ion is present as a disinfection byproduct from the degradation of high and low-strength hypochlorite solutions during generation and also due to the degradation of high-strength hypochlorite during storage (Garcia-Villanova et al., 2010, USEPA, 2014a, Alfredo et al., 2014, WHO, 2005). Several tests involving animal subjects have been performed, to determine the health effects of habitual chlorate intake. In animal tests involving rats, chronic intake of the chlorate ion is strongly linked to blood and thyroid problems. The chlorate ion is known to inhibit iodine uptake by the thyroid, reducing the production of the thyroid hormone (Alfredo et al., 2014, Righi et al., 2012, USEPA, 2014a). In another case study, rats undergoing subchronic exposure to the chlorate ion experienced decreased hemoglobin and red blood cell counts, thyroid colloid depletion, and follicular cell hypertrophy (USEPA, 2014a). To investigate the effect of the chlorate ion on human health, 60 male volunteers consumed different concentrations of the chlorate ion over a period of 12 weeks with an additional observation period of 8 weeks (WHO, 2005, Lubbers et al., 1982, Alfredo et al., 2014). In this test, the intake of the chlorate ion did not reveal physiologically significant affects. The results from this study were used to determine the no observed adverse effect level (NOAEL) based on the highest dosage level of 2.4 mg/L (Alfredo et al., 2014). However, one area of concern is the effect chronic chlorate intake will have on sensitive groups of the population, such as people with thyroid or blood problems, pregnant women, developing children, and fetuses (USEPA, 2014a). Further research is needed to evaluate the extent of the effect the chlorate ion on sensitive groups, but several studies suggest that the consumption of the chlorate ion affects sensitive groups more strongly than the average population.

2.1.2 Disinfection Byproducts: Perchlorate

Perchlorate is a naturally occurring anion that forms in the atmosphere and is deposited by rain and snowfall events. The perchlorate ion also forms as hypochlorite solutions degrade either during storage, or during the generation of hypochlorite through electrolysis (WHO, 2015, Snyder et al., 2009). Like chlorate, perchlorate is a powerful oxidizer and is used commercially in rocket fuels, airbags, and road flares. Perchlorate is also used in medicines to treat overactive thyroid disorders (WHO, 2015). The perchlorate ion is commonly found in water, cow and animal milk, and produce as a result of anthropogenic sources (Kirk 2006, WHO, 2015). Perchlorate is of concern, as it is known to negatively affect the thyroid, inhibiting the thyroid's ability to uptake iodide, potentially resulting in hypothyroidism. Hypothyroidism can negatively affect the structural and brain development during early childhood, and for adults, hypothyroidism negatively affects many of the body systems including the cardiovascular, gastrointestinal, and reproductive systems (WHO, 2015, Pisarenko et al., 2010, Kirk, 2006). In animals tests, the long term exposure of rats to perchlorate salts in drinking water with concentrations ranging from 10-12 g/L resulted in the growth of thyroid tumors. Other similar studies have shown little correlation between perchlorate exposure and significant adverse health effects in the test animals (WHO, 2015).

2.2 Regulatory Limits of Chlorate and Perchlorate

Chlorate is currently unregulated by the EPA. However, chlorate is on the Contaminant Candidate List (CCL) and has a health reference level of 210 µg/L (USEPA, 2014a, Breytus, 2015, Stanford et al., 2013). As a contaminant candidate, the chlorate ion may come under regulation in the coming years and face a positive regulatory determination. The Office of Environmental Health Hazard Assessment of California issued a proposed action level for chlorate of 200 µg/l, which is a non-enforceable standard on the contaminant (Stanford et al., 2013, Alfredo et al., 2014, Howd 2002). Additionally, the World Health Organization set the provisional guideline of 700 µg/L for chlorate (Stanford et al., 2013, Alfredo et al., 2014, WHO, 2005). In early 2011, the USEPA made the determination to regulate perchlorate and is currently in the process of introducing a national primary drinking water regulation (USEPA, 2014a). The EPA has established an interim Lifetime Drinking Water Health Advisory for perchlorate of 15 µg/L, based on the no observed adverse effect level on pregnant mothers (Health and Ecological Criteria Division, 2008, USEPA, 2012). Also, the states of California and Massachusetts regulate perchlorate at 6 µg/L and 2 µg/L respectively (Stanford et al., 2013, USEPA 2012,. California EPA, 2016, MassDEP 2002). It is important to note that regulatory agencies at the state and federal level do not want to water treatment facilities to risk inadequate disinfection of water in order to comply the maximum contaminant levels for chlorate and perchlorate, thus many of the guidelines for byproduct concentrations are not yet mandatory.

2.3 Previous Investigations of OSG Systems

Despite potential future regulation, research shows that currently a significant number of water treatment facilities would exceed recommended levels for chlorate and perchlorate. In a study by Stanford et al, 6 of 12 OSG systems investigated would have exceeded the 210 μg/L health reference level by the EPA for chlorate for a chlorine dose of 5 mg/L and at a chlorine dose of 10 mg/L, 10 of 12 systems would have exceeded the reference level (Stanford et al., 2013). Additionally, past research has shown that each OSG system exhibits a high variability in its production of chlorine, chlorate, and perchlorate when compared to other generators and also, at different sampling times for the same generator (Stanford et al., 2013, Stanford et al., 2011). Both chlorate and perchlorate are extremely difficult to remove from existing water supplies, as both anions are highly stable in water. Therefore, it is important to minimize their production, instead of attempting to remove the contaminants (WHO, 2015, Gordon et al., 1995, WHO, 2005, Garcia-Villanova, 2010). The variability in production outputs and difficulty in removing the disinfection byproducts after production leads to concerns, as there is a lack of evidence correlating concentrations of the chlorate and perchlorate ions to operating conditions, generator types, and the quality of input materials (Stanford et al., 2011, Stanford et al., 2013). In view of the potential regulation of chlorate and perchlorate, if methods of minimizing the production of these contaminants are not developed, water treatment facilities may find themselves unable to comply with acceptable contaminant limits.

2.4 Mechanism of Low-Strength Hypochlorite Generation by Electrolysis

Water treatment facilities using OSG hypochlorite electrolyze a brine solution and water to produce low-strength hypochlorite (0.5%~1.2% Cl_2). In the electrolysis process, electricity is passed between two conductive rods or electrodes, separating ions in the solution based on their charge. In the case of OSG systems, brine, a saturated salt solution, is mixed with softened water and is passed through the electrolysis system. In the solution, salt is present in its ionic form as follows:

$$NaCl_{(s)} + H_2O \rightarrow Na^{+}{}_{(aq)} + Cl^{-}{}_{(aq)} + H_2O$$

As electricity is passed through the system, one plate, the cathode, becomes negatively charged and another plate, the anode, becomes positively charged. The cathode, being negatively charged, attracts the positive ions of the solutions, known as cations. The anode, being positively charged, attracts the negative ions of the solution, known as anions (http://aquarius.umaine.edu/). In the electrolysis of salt water, several intermediate oxidation/reduction reactions occur before the final hypochlorite solution is produced. The reactions are summarized as follows (Abdul-Wahab et al., 2009At the anode, chlorine ions are oxidized to produce chlorine:

$$2Cl^{-} \rightarrow 2Cl_2 + 2e^{-}$$

The resulting chlorine is quickly hydrolyzed into hypochlorous acid and hydrochloric acid:

$$Cl_2 + H_2O \rightarrow HOCl + HCl$$

At the cathode, the sodium ion is reduced:

$$Na^{+} + e^{-} \rightarrow Na$$

The resulting sodium quickly reacts with water:

$$Na^{+} + H_2O \rightarrow 0.5H_2 + NaOH$$

The products of the anode and cathode then react:

$$HCl + NaOH \rightarrow NaCl + H_2O$$

$$HOCl + NaOH \rightarrow NaOCl + H_2O$$

The net overall reaction is as follows:

$$NaCl_{(s)} + H_2O_{(l)} \rightarrow e^{-} \rightarrow NaOCl_{(aq)} + H_{2(g)}$$

The resulting hydrogen gas is highly explosive in its pressurized, concentrated form and therefore, is vented off the resulting sodium hypochlorite solution to the atmosphere. The following figure shows a visual representation of hypochlorite generation using electrolysis (Abdul-Wahab et al., 2009).

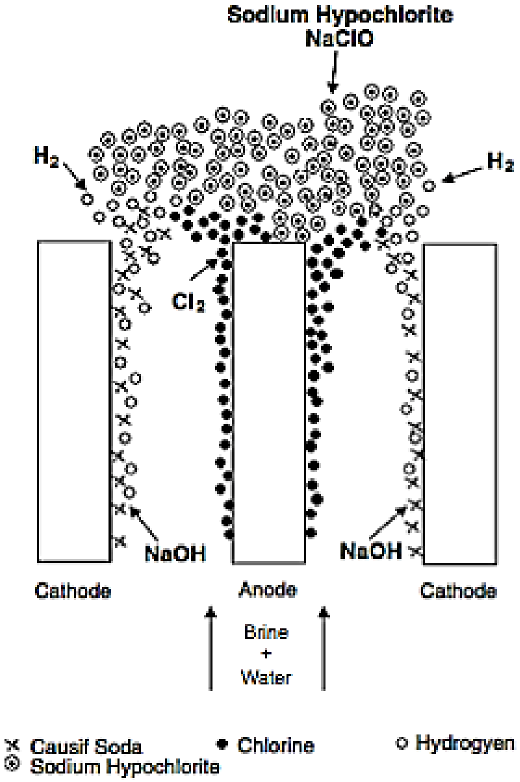

Figure 2.1: Visual Representation of the Generation of Sodium Hypochlorite

During the electrolysis process, the amount of sodium chloride converted into sodium hypochlorite is directly related to the amount of electricity passed through the system (Abdul-Wahab et al., 2009). In onsite generation systems, the hypochlorite is generally present in concentrations between 0.5% and 1.2% chlorine.

2.5 Reaction Kinetics of the Formation of Chlorate and Perchlorate

Chlorate and perchlorate are the end products of successive oxidation reactions of chlorine oxyanions ultimately converting the hypochlorite ion to perchlorate (Hubler et al., 2014).

$$OCl^- \rightarrow ClO_2{}^- \rightarrow ClO_3{}^- \rightarrow ClO_4{}^-$$

The rate at which hypochlorite degrades into chlorate and perchlorate is affected by conditions such as pH, temperature, current density, and concentration of chloride in the solution during electrolysis (Stanford et al., 2011, Hubler et al., 2014, Adam, 1994, Gordon et al., 1995). However, it is unclear if these conditions affect the breakdown of high and low-strength hypochlorite solutions to the same extent. The hypochlorite ion is first converted into the chlorite ion in the following net reaction (Hubler et al., 2014, Garcia-Villanova et al., 2010):

$$2ClO^- \rightarrow Cl^- + ClO_2{}^-$$

Afterwards, the chlorite ion reacts with the hypochlorite ion and quickly forms chlorate and the chloride ion (Hubler et al 2014):

$$ClO^- + ClO_2{}^- \rightarrow Cl^- + ClO_3{}^-$$

Thus, the overall reaction series converting the hypochlorite ion into the chlorate ion is summarized as follows (Stanford et al., 2011, Gordon et al., 1995):

$$3OCl^- \rightarrow ClO_3{}^- + 2Cl^-$$

The perchlorate ion is then formed from the anodic oxidation of chlorate to perchlorate through interactions with chlorate and hypochlorite (Stanford et al., 2011, Jung et al., 2010, Munichandraiah et al., 1987):

$$ClO_3^- \rightarrow ClO_4^- + Cl^-$$

Perchlorate formation therefore is also affected by the concentration of the chlorate ion in the solution.

2.6 Factors Affecting Hypochlorite Degradation

Both chlorate and perchlorate are formed from the degradation of the hypochlorite ion in OSG hypochlorite solutions. Therefore, chlorate and perchlorate concentration in OSG hypochlorite solutions are a result of the extent of degradation of the hypochlorite solution. The stability of the hypochlorite ion is known to be connected with the pH of the solution, the temperature of the solution, the overall concentration of the hypochlorite, and the exposure of the solution to light (Garcia-Villanova et al., 2010, Stanford et al., 2011). Hypochlorite decomposition is minimized at a pH of 11.86-13 (Breytus, 2015, Garcia-Villanova et al., 2010, Stanford et al., 2011). However, it is important to note that the conversion of chlorate to perchlorate within this pH range is affected more by the ionic strength of the solution rather than the pH of the solution (Munichandraiah et al., 1987, Stanford et al., 2011, Jung et al., 2010). Additionally, solutions with high hypochlorite concentrations tend to be less stable than solutions with lower concentrations (<10% chlorine) (Garcia-Villanova et al., 2010, Snyder et al., 2009). Temperature also plays an important role in the decomposition of hypochlorite and formation of chlorate with higher temperatures increasing the rate of decomposition (Breytus, 2015, Stanford et al., 2011).

Again, it is unclear if these conditions affect the breakdown of high and low-strength hypochlorite solutions to the same extent.

CHAPTER 3

METHODOLOGY

3.1 Drinking Water Treatment Facilities

Two drinking water facilities utilizing OSG hypochlorite systems were analyzed in this study. The two plants, known as Facility 1 and 2 for the purposes of this study, both use ClorTec® OSG hypochlorite systems with a capacity of 1500 pounds per day. Both facilities had an average maximum storage time of 2-3 days in the storage tanks, with storage time being lower in the summer due to a higher water demand.

3.2 Sample Collection

In an attempt to correlate the presence of chlorate and perchlorate in finished OSG hypochlorite, the water to brine ratio was adjusted and adequate time was given for the system to stabilize. After stabilization, samples were taken from a sampling port at the end of the electrolysis tank. Upon collection from the electrolysis tank, each sample was measured for density, temperature, and pH. Additionally, samples were taken from storage tanks at the OSG facilities from sampling ports to evaluate the effect of storage on chlorine, chlorate, and perchlorate concentration. The samples were collected in high-density polyethylene (HDPE) bottles and transported to the laboratory in an ice chest. In the laboratory, the samples were stored in the laboratory refrigerator at approximately 4° Celsius.

3.3 Chlorine Measurement

Each sample was measured for chlorine content within a 1-week period after collection from the treatment facility. The Hach® DR/890 Colorimeter used to determine chlorine content in this study is only able to measure up to 10 mg/L total chlorine content. Therefore, as the expected chlorine content of 0.8%, as given by the manufacturer of the OSG systems, results in a total chlorine concentration of approximately 8000 mg/L, each sample was diluted by a ratio of 1:1000 before testing for chlorine (Breytus, 2015, Severen Trent Water Purification, Inc., 2011).

Figure 3.1: Measurement of Chlorine Using DPD Hach® Kit

The final concentration measured by the Hach® Colorimeter is multiplied by 1000 to find the chlorine concentration in the undiluted solution. The high dilution factor leads to significant variability and only provides accurate measurements up to two significant digits. However, for the scope of this study, a high degree of accuracy in the determination of the chlorine content is not required. Each sample was tested in triplicate to eliminate the effect of errors. Dilutions were made in either 100 mL or 50 mL volumetric flasks at a 1:1000 dilution ratio with ultra-pure Mili-Q water.

3.4 Quenching of Samples

The removal of chlorine from the sample, a process known as quenching, is necessary in ion chromatography as the chlorine harms the columns in the ion chromatograph (Breytus, 2015). Additionally, quenching is necessary to prevent further degradation of the sodium hypochlorite, maintaining the original concentrations of chlorate and perchlorate in the sample (Stanford et al., 2013).

3.4.1 Selection of Quenching Agent

There are several different quenching agents available to remove residual chlorine from the hypochlorite. However, only certain agents remove the chlorine in a way that does not interfere with the ion chromatograph readings. From prior studies, both malonic acid and hydrogen peroxide function well as quenching agents. However, previous studies suggest that quenching residual chlorine with hydrogen peroxide is more compatible with the USEPA's Method 300.1 for measuring inorganic anions in drinking water and thus, hydrogen peroxide was chosen as the quenching agent for the purposes of this study (Stanford et al., 2013, Breytus, 2015, USEPA 1997). Hydrogen peroxide and chlorine react on a 1:1 molar ratio, consuming 1 mole of hydrogen peroxide per 1 mole of chlorine. Therefore, using the estimated chlorine content from the treatment facility, the approximate amount of hydrogen peroxide needed to complete the reaction is calculated. However, the reaction of hydrogen peroxide with chloride is both exothermic and rapid. Therefore, the complete quenching of chlorine in the sample can be visually observed when no more bubbles are noticed after the addition of a 20-µL aliquot of hydrogen peroxide. As hydrogen peroxide degrades over time, the exact strength may be different than its original strength and so the calculated amount of hydrogen peroxide for the quenching may be different than the actual amount required (Pisarenko et al., 2010, Breytus, 2015). In order to ensure that the chlorine was completely removed, the visual method was adopted and hydrogen peroxide was added until the addition of a 20-µL aliquot of hydrogen peroxide produced no more bubbles, indicating that the reaction was complete. Hydrogen peroxide has the same damaging effect on the ion chromatograph as chlorine so after the quenching of the chlorine it is necessary to remove the residual hydrogen peroxide. Residual hydrogen peroxide was catalytically removed with a small portion of manganese dioxide, which has been used previously in the removal of residual hydrogen peroxide (Breytus, 2015).

3.4.2 Quenching Procedure

1. A 5 mL pipet is used to measure approximately 10 mL of room temperature hypochlorite sample to a 50 mL beaker. A small magnetic stirrer is placed into the beaker.
2. Hydrogen peroxide (approximately 30% by weight) is added in 20 µL portions until the reaction is over, noted by the lack of bubbles after the addition of a 20 µL aliquot of hydrogen peroxide.

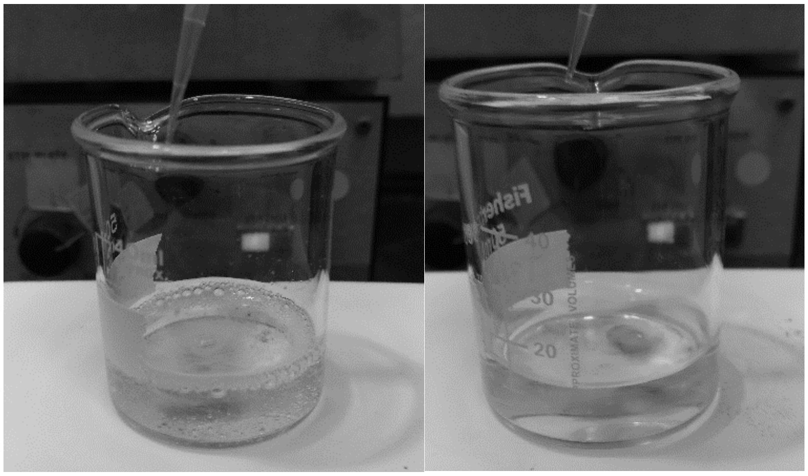

Figure 3.2: Quenching Residual Chlorine with Hydrogen Peroxide. Left: vigorous exothermic reaction upon addition of hydrogen peroxide; Right: completed reaction

3. To remove the residual, unreacted hydrogen peroxide from the sample, a small amount of manganese dioxide of approximately 1.5 mg is added to the sample. The sample is then set on slow mixing overnight.
4. The sample is then transferred to a 10 mL volumetric flask and the sample volume is raised to the 10 mL mark with Mili-Q water used to wash out the sample from the reaction beaker.
5. After the volume is raised back to 10 mL, the quenched sample is then passed through a 0.45 μm syringe filter to remove the manganese dioxide. After filtration, the samples are stored in the laboratory refrigerator.

3.5 Sample Preparation

Chlorate and perchlorate occur in hypochlorite solutions at concentrations that differ by a factor of 100. Chloride is present in hypochlorite solutions at high concentrations relative to chlorate and has a retention time slightly shorter than chlorate. This leads to peak interference between the chloride and chlorate peaks during measurement. In order to separate the peaks, the samples were diluted by a factor of 10 when testing for chlorate. Perchlorate, however, has a long retention time in the chromatograph so peak interference is not an issue. Additionally, if the samples for perchlorate were diluted, it is likely that the perchlorate peak will be undetectable as perchlorate is generally present in low concentrations. Therefore, in order to test for the concentration of perchlorate in the hypochlorite samples, the samples were not diluted.

3.6 Preparation of Standard Solutions

Based on prior studies of OSG systems, the expected chlorate and perchlorate concentrations ranged from 100-1200 mg/L and 10-100 µg/L, respectively. Due to laboratory constraints, perchlorate could only be measured down to 1 ppm, or 100 µg/L, so standards were prepared accordingly, with 100 µg/L being the lowest concentration of perchlorate for the standards. Standards were prepared by diluting high concentration stock solutions of chlorate and perchlorate with ultra-pure Mili-Q water to achieve the desired concentration. During testing, if the measured concentration fell out of the range of the standards, either the hypochlorite sample was diluted, or another set of 5 standards were created within the range of the sample concentration.

3.7 Calibration Curves

Calibration curves were created by running the standard solution in the ion chromatograph and plotting the area under the peak against the known concentration. A separate calibration curve was plotted each time a set of samples were run in the ion chromatograph to ensure that the measurements for the samples were made under the same conditions as that of the standards. This gives greater accuracy and reliability of the results. There are two options for the y-intercept when creating the calibration curve through regression analysis.

1. Force the y-intercept to equal zero
2. Allowing regression analysis to choose best-fit line with a non-zero y-intercept.

According to Dolan et al, statistical guidelines determine which option is best and will provide the most reliable results. The Standard Error of the y-intercept (SE_y) is determined using the LINEST function in Excel and is used to determine the better of the two options by the following guidelines:

if y-intercept > SE_y set b=y-intercept value

if y-intercept ≤ SE_y set b=0

This method will improve the accuracy of the regression model and reduce the error in the calibration curve (Dolan, 2009a).

3.7.1 Chlorate Calibration Curve

Calibration curves were plotted with a minimum of 5 points. The known concentration of the standard was plotted against the area under the peak from the ion chromatograph.

Table 3.1: Concentration vs. Peak Area of Chlorate

Standards	
Chlorate Concentration (ppm)	Peak Area (µS*min)
10	0.611
30	1.9816
50	3.4781
70	5.1944
90	6.9142
100	7.9045

Excel was used to calculate the following statistical parameters from the ion chromatograph data:

Table 3.2: Regression Analysis Performed for Chlorate Calibration Curve Using Excel

slope	12.2726
y-intercept	4.9807
SE_y	1.6767
R^2	0.9971

Since the y-intercept is greater than SE_y, the y-intercept will not be forced to zero in the regression analysis, therefore:

y-intercept=4.9807

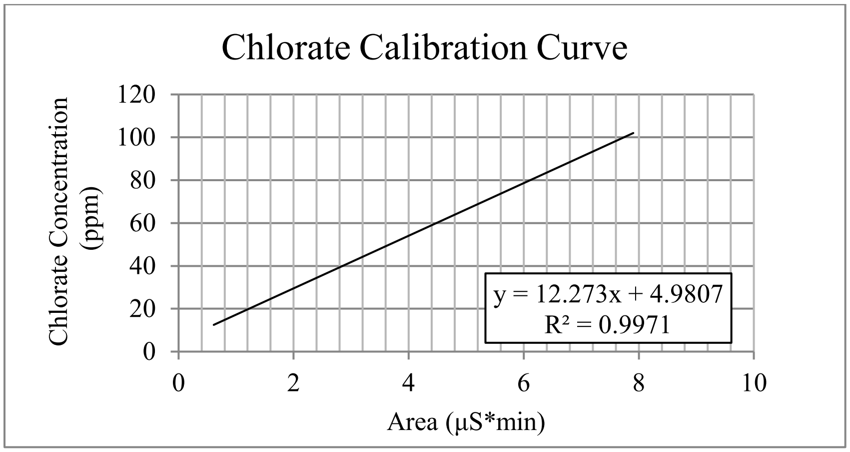

Figure 3.3: Sample Chlorate Calibration Curve

Similar analysis was performed for each of the chlorate calibration curves. For each curve, the y-intercept value was greater than the Standard Error of the y-intercept (SE_y), and so the y-intercept was not forced to zero.

3.7.2 Perchlorate Calibration Curve

Calibration curves were plotted with a minimum of 5 points. The known concentration of the standard was plotted against the area under the peak from the ion chromatograph

Table 3.4: Concentration vs. Peak Area of Perchlorate

Standards	
Perchlorate Concentration (ppm)	Peak Area (µS*min)
1	0.0414
3	0.1382
5	0.2542
7	0.3849
9	0.4931
10	0.5268

Excel was used to calculate the following statistical parameters from the ion chromatograph data:

Table 3.5: Regression Analysis Performed for Perchlorate Calibration Curve Using Excel

slope	17.8270
y-intercept	0.3706
SE_y	0.1747
R^2	0.9970

Since the y-intercept is greater than SE_y, the y-intercept will not be forced to zero in the regression analysis, therefore:

y-intercept=0.3706

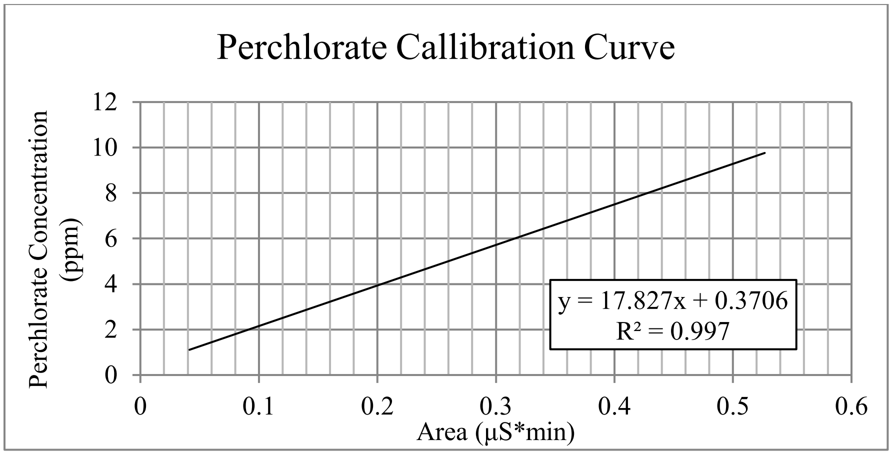

Figure 3.4: Sample Perchlorate Calibration Curve

3.8 Limit of Detection

To determine the instrumental limit of detection for the ion chromatograph, the two common methods of visual evaluation of the analyte peak and the determination of the standard deviation of the response and the slope were both used and the conservative value was adopted as the limit of detection. Visual evaluation relies on the operator to determine if a peak is reasonable discernable, and thus, this method will produce variability depending on the analyst. The standard deviation of the response and the slope is a statistical method that relies on the overall performance of the calibration curve (Dolan, 2009b). The following formula is used to determine the limit of detection using the the standard deviation of the response and the slope method:

$$LOD = \frac{3.3 \times \sigma}{S'}$$

S=slope of the calibration curve

σ=Standard Error of the y-intercept of calibration curve

3.8.1 Limit of Detection: Chlorate

Visual Evaluation:

Previous studies with the ion chromatograph used in this experiment show that the lowest chlorate concentration at which a peak was detectable is approximately 0.03 ppm.

Standard deviation of the response and the slope method:

Given S=12.2726 and σ =1.6767

$$LOD = \frac{3.3 \times \sigma}{S'} = \frac{3.3 \times 1.6767}{12.2726} = 0.451 ppm$$

The more conservative value of 0.451 ppm was the LOD value for chlorate for the purposes of this experiment. For each calibration curve created, there is a separate LOD value. However, as the measured concentrations of chlorate are far above each of the LOD values, the results are not out of range.

3.8.2 Limit of Detection: Perchlorate

Visual Evaluation:

Previous studies with the ion chromatograph used in this experiment show that the lowest chlorate concentration at which a peak was detectable is approximately 0.25 ppm.

Standard deviation of the response and the slope method:

Given S=17.8270 and σ =0.1747

$$LOD = \frac{3.3 \times \sigma}{S'} = \frac{3.3 \times 0.1747}{17.8270} = 0.0323ppm$$

The more conservative value of 0.25 ppm was the LOD value for perchlorate for the purposes of this experiment.

3.9 Spike Recovery Analysis

Due to the fact that the ion chromatograph quantifies the concentration of an unknown sample by comparing the peak of the unknown to the peak of a standard, the measured values from the chromatograph are merely relative measurements. For this reason, spike recoveries are necessary to determine if the ion chromatograph is functioning properly. To determine the instrumental ability to accurately measure actual concentrations hypochlorite samples were spiked with a known volume and concentration of the standard solution. In this study, three samples, each in triplicate, were spiked with three different concentrations. Then, both the spiked and unspiked samples were analyzed using the ion chromatograph. The spike recovery was then determined by the following formula:

$$\%recovery = \frac{spiked\ sample\ concentration(ppm) - sample\ concentration(ppm)}{standard\ added\ concentration(ppm)}$$

High spike recoveries indicate a high degree of accuracy of the measurements made by the ion chromatograph. For the purposes of this study, spike recoveries of 90% are considered acceptable.

The spike recoveries for each sample tested were within 5% of complete recovery. This is a very acceptable recovery of the spike and it is concluded that the ion chromatograph provides accurate results.

Table 3.6: Spike Recovery Analysis for Hypochlorite Samples Spiked with the Standard

	Measured Chlorate Concentration (ppm)		
	Sample 1	Sample 2	Sample 3
Not Spiked	25.70	25.28	21.94
Spiked 1	33.09	34.08	31.48
Spiked 2	32.53	34.35	31.68
Spiked 3	33.08	34.22	31.58
Spiked Average	32.90	34.22	31.58
Standard Deviation	0.26	0.11	0.08
Concentration Difference (ppm)	7.20	8.94	9.64
% Recovery	102.92	99.31	96.38
%RSD	0.80	0.32	0.26

CHAPTER 4

EXPERIMENTAL DATA

4.1 Facility Overview

The two water treatment facilities, known as Facility 1 and 2 for the purposes of this study, both use OSG hypochlorite to disinfect drinking water. Samples were collected from the facilities during the months of January, February, and March.

4.1.1 Hypochlorite Generation System

The hypochlorite generation systems of both Facility 1 and Facility 2 were of the same capacity and were from the same manufacturer. The hypochlorite generation system of this study was made of two electrolytic cells, each with a capacity of 750 pounds per day. The water flow is divided between the two cells, with the operator in control of the amount of flow to each cell. The brine flow is also an operator-controlled parameter to an extent. Brine flow into the electrolysis system is not pump-controlled and relies heavily on a venturi section to draw the brine solution into the system. The venturi draws up the brine solution into the system by the water flow rate into the first electrolytic cell (Water Flow 1) and thus, the brine flow is related to the flow of water into the first electrolytic cell

Additionally, the Operation and Maintenance manual from the manufacturer provided the optimum flow rates for the water and brine going into the hypochlorite generator. The recommended total water flow rate is 14.45 gpm and the recommended brine flow rate is 1.17 gpm. According to the manufacturer, these flow rates should result in a hypochlorite solution of 0.8% Cl_2. However, when these flow rates were applied to the hypochlorite generators studied in this investigation, the concentration of the hypochlorite solution never reached the expected concentrations. Additionally, there was a discrepancy of approximately 30% in the measured values of the chlorine content when the hypochlorite solutions were measured by the water treatment facility and when they were measured in the UTA lab.

4.1.2 Input Material Quality and Storage Time

Both facilities used softened water for electrolysis as softened water lacks the hardness that produces a buildup of calcium and magnesium deposits. Also, high quality salt is used to decrease the presence of ions other than sodium and chlorine in the electrolysis process as these can lead to other disinfectant byproducts such as bromate. Finally, both facilities reported an average storage time in tank of approximately 2-3 days, depending on the time of year. During the summer months when the water demand is higher, the storage duration is shorter.

Table 4.1: Input Material Quality and Storage Time for Facilities 1 and 2

	Inlet Water Quality	Brine Quality	Average Storage Time in Tank
Facility 1	Membrane-filtered, softened water	food grade salt + softened water	2-3 days (shorter in summer months)
Facility 2	Softened water passed through carbon filters to remove chlorine	food grade salt + softened water	2-3 days (shorter in summer months)

4.1.3 Operating Conditions and Sample Characteristics

Both facilities monitored and controlled the temperature of the inlet water. The optimal temperature range for the inlet water, according to the manufacturer, is 50-70 °F. The voltage and amperage of the system are controlled by the sensory equipment of the system and are not controlled by the operator. However, according to the manufacturer, both of these parameters are dependent on the salt concentration in the electrolytic cells of the system. For each facility, one sample was collected from the hypochlorite storage tank and 3 samples were collected from the sampling port of the hypochlorite generator, each from a different operating condition.

Table 4.2: Operating Conditions for Facilities 1 and 2

	Facility 1			Facility 2		
Operating Condition (OC)	OC1	OC2	OC3	OC1	OC2	OC3
Water Flow 1 (gpm)	5.8	6.9	7	8.3	7.2	8.4
Water Flow 2 (gpm)	7.2	7.1	7.2	7.4	7.2	5.85
Brine Flow (gpm)	1.3	1.4	1.1	1.25	0.85	1.5
Inlet Water Temp. (°F)	50-70	50-70	50-70	49	49	49
Voltage (Volts)	88	87	93	101	108	95
Amperage (Amps)	1280	1280	1275	1277	1275	1280

The density of the samples was determined by performing a hydrometer analysis and recording the temperature of the solution. The density of the sample was then found using a set of curves provided by the manufacturer that correlated the hydrometer reading and temperature of the solution to the solution density. According to the manufacturer, the target density for the system in study is 24 g/L. None of the samples tested for density reached the target density for the system. It should be noted that the pH of the samples from Facility 1 was measured at the laboratory several weeks after collection, not upon collection of the samples, as was the case for the pH measurements for Facility 2. Additionally, the average temperature of the samples taken from the sampling port from each facility are approximately 20 °F in difference. According to the operator of Facility 2, high sample temperature is a result of buildup on the main electrodes at the ends of the electrolysis cells and that when the electrode is acid-washed regularly to remove the buildup, the temperature of the sample is lower.

Table 4.3: Sample Characteristics for Facilities 1 and 2

	Location of Sample Collection	Operating Condition	pH	Density of Sample (g/L)	Temperature of Sample (°F)
Facility 1	Storage Tank	n/a	8.73	n/a	ambient
	Sampling Port	OC1	8.73	20	120
	Sampling Port	OC2	9.05	23	115
	Sampling Port	OC3	9.09	17.5	120
Facility 2	Storage Tank	n/a	9.10	n/a	ambient
	Sampling Port	OC1	9.48	18.5	94
	Sampling Port	OC2	9.59	13.5	95
	Sampling Port	OC3	9.42	21	98

4.2 Free Available Chlorine

Samples were measured in triplicate for chlorine content using the Hach® Digital Colorimeter. Averages and standard deviations for all samples from both facilities are shown in Table 4.4. In order for the chlorine content of the samples to fall within the range of the colorimeter, the sample was diluted by a 1:1000 ratio. The target chlorine concentration for both facilities is 0.8% chlorine.

Table 4.4: Average Chlorine Concentration of Samples from Facilities 1 and 2

Facility	Location of Sample Collection	Operating Condition	Average Chlorine Concentration (%)	Standard deviation
Facility 1	Storage Tank	n/a	0.62	0.047
	Sampling Port	OC1	0.69	0.047
	Sampling Port	OC2	0.69	0.094
	Sampling Port	OC3	0.64	0.047
Facility 2	Storage Tank	n/a	0.57	0.121
	Sampling Port	OC1	0.62	0.090
	Sampling Port	OC2	0.57	0.170
	Sampling Port	OC3	0.71	0.160

4.3 Chlorate Concentration

Quenched samples were first diluted by a factor of 10 and then analyzed in the ion chromatograph. In this study, chlorate had a retention time of approximately 7.7 minutes.

The concentration of the chlorate tested was determined using the calibration curve as the standard. Then, to get the actual concentration of the chlorate in the hypochlorite sample, the measured concentration was multiplied by a factor of 10. The average concentrations of the chlorate ion in the hypochlorite samples are listed in the following table along with the standard deviations.

Table 4.5: Average Chlorate Concentrations of Samples Collected from Facilities 1 and 2

	Location of Sample Collection	Operating Condition	Average Chlorate Concentration (ppm)	Standard deviation
Facility 1	Storage Tank	n/a	246.3025	2.4027
	Sampling Port	OC1	251.5138	0.7609
	Sampling Port	OC2	220.7822	1.0133
	Sampling Port	OC3	290.4069	4.2217
Facility 2	Storage Tank	n/a	296.3831	0.9255
	Sampling Port	OC1	202.1968	1.2683
	Sampling Port	OC2	302.7360	3.1243
	Sampling Port	OC3	191.5641	0.6648

4.4 Perchlorate Concentration

Previous studies show that perchlorate is present in hypochlorite solutions at a much smaller concentration than chlorate and thus, dilution of the quenched hypochlorite samples would likely make the perchlorate concentration fall out of the limit of detection. Furthermore, the retention time of perchlorate in the ion chromatograph is approximately 39 minutes so peak interference from the chloride ion, which was a problem for chlorate measurement, does not affect the perchlorate peak. Therefore, when measuring for perchlorate, the quenched hypochlorite samples were not diluted when analyzed in the ion chromatograph. However, the perchlorate ion produced no detectable peak during analysis. This does not indicate that there is no perchlorate in the sample, but rather that the concentration is too small to be measured using these methods. However, when constructing the calibration curve for perchlorate, concentrations of perchlorate as small as one part per million (ppm) were detected. Therefore, although the exact concentration of perchlorate in the sample could not be determined, it is concluded that the concentration is less than one ppm.

CHAPTER 5

DISCUSSION OF RESULTS

5.1 Chlorine Concentration: Expected Versus Measured

The Operation and Maintenance manual from the manufacturer, ClorTec® provided the recommended flow rates for the water and brine going into the electrolytic cells. The recommended total water flow rate is 14.45 gpm, with 50% going to each electrolytic cell, and the recommended brine flow rate is 1.17 gpm. According to the manufacturer, these flow rates should result in a hypochlorite solution of 0.8% Cl_2. However, when these flow rates were applied to the hypochlorite generators studied in this investigation, the concentration of chlorine in the hypochlorite solution never reached the expected concentration. Additionally, there was a discrepancy of approximately 30% between the measured chlorine concentrations by the water treatment facility and when they were measured in the University of Texas at Arlington environmental lab. The Hach® DPD method used in this study to measure the chlorine content at UTA was validated using a standard concentration of chlorine. Also, the results provided by the Hach® Colorimeter were precise for each of the samples tested, so it is unlikely that an experimental error is responsible for the discrepancy. Currently it is unclear where the error lies, whether in the procedure followed by the water treatment facilities, or in some other area.

5.2 Trends

The results from both facilities were analyzed for trends relating the chlorate and chlorine concentration to parameters such as density, pH, retention time, and the solution temperature. Perchlorate concentration was not analyzed for trends, as the perchlorate concentration was undetectable due to laboratory constraints. Trends for the facilities were analyzed on an individual basis as variables such as the age of the generator, the entering water temperature, and the cleanliness of the electrodes were out of the control of this investigation and may skew the results if the facilities were analyzed together.

Table 5.1: Summary of Sample Characteristics and Measured Values for Facility 1 and 2

	Facility 1				Facility 2			
Sample Location	Tank	Sample Port	Sample Port	Sample Port	Tank	Sample Port	Sample Port	Sample Port
Operating Condition	n/a	OC1	OC2	OC3	n/a	OC1	OC2	OC3
Chlorate (ppm)	246.3	251.5	220.8	290.4	296.4	202.2	302.7	191.6
Chlorine mg/L	6166.7	6933.3	6933.3	6366.7	5716.7	6216.7	5733.3	7066.7
Density (g/L)	n/a	20.0	23.0	17.5	n/a	18.5	13.5	21.0
Retention Time (min)	n/a	11.0	10.5	10.3	n/a	9.4	10.5	10.2
Solution Temperature (°F)	Ambient	120.0	115.0	120.0	Ambient	94.0	95.0	98.0
pH	8.7	8.7	9.1	9.1	9.1	9.5	9.6	9.4

5.3 Density Relations

5.3.1 Chlorate Concentration and Solution Density

Both facilities exhibited clear trends between the chlorate concentration and the density during generation. This trend may occur because when there is a high mass transfer of the brine ions near the anode surface, intermediate byproduct formation, such as chlorate and perchlorate, is minimized

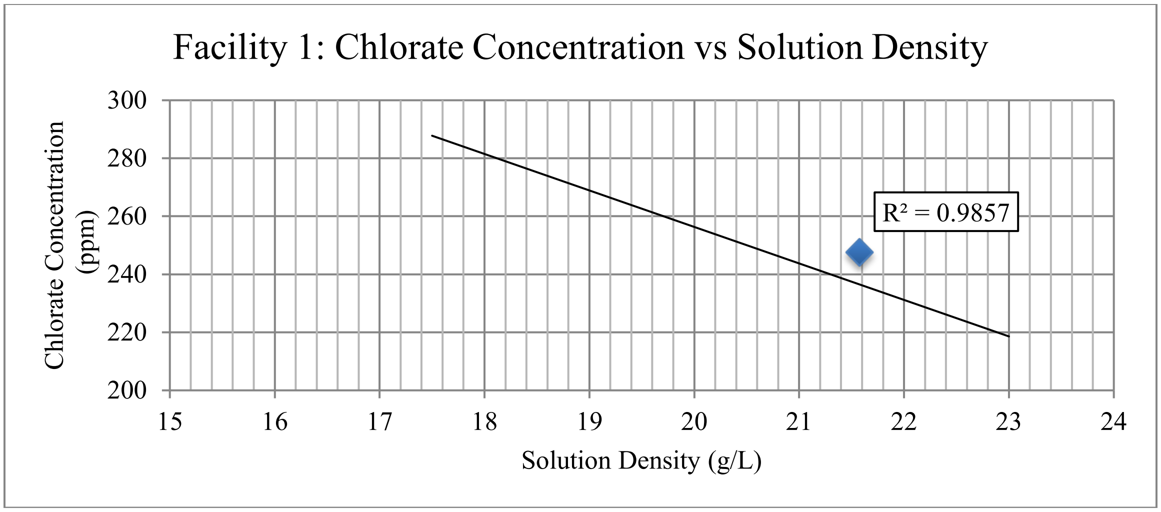

Figure 5.1: Relation of Chlorate Concentration and Solution Density for Samples from Facility 1

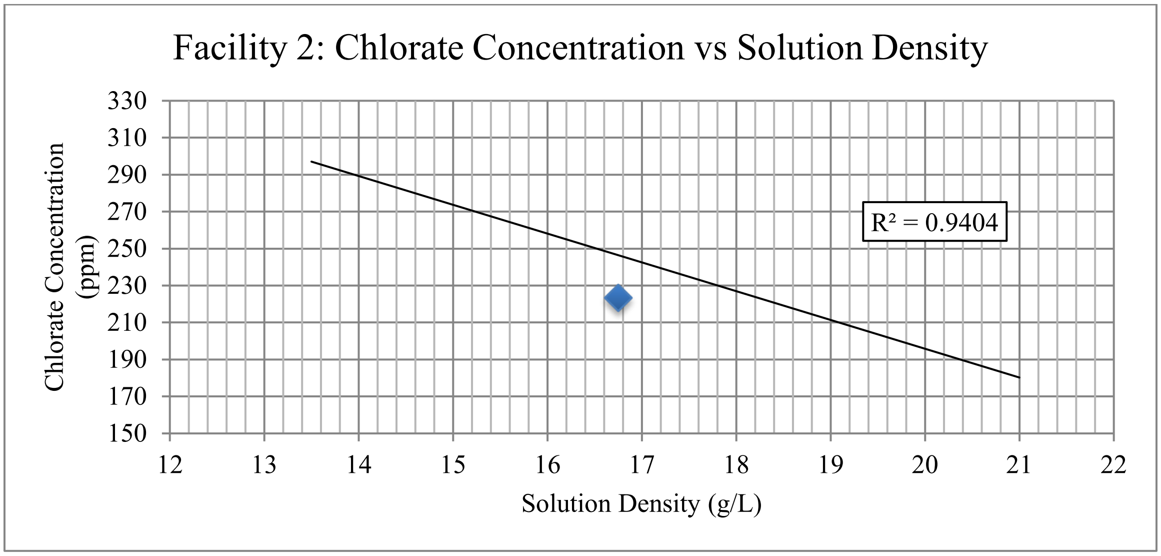

Figure 5.2: Relation of Chlorate Concentration and Solution Density for Samples from Facility 2

5.3.2 Chlorine Concentration and Solution Density

Additionally, higher brine flows were correlated with higher chlorine concentrations in the finished hypochlorite solutions. This trend may be due to the fact that at higher brine flows, the system can more efficiently convert the sodium and chloride ions into sodium hypochlorite. Also, due to the high mass transfer rate of the brine solution, byproducts formed form the degradation of the hypochlorite may be less, resulting in a higher chlorine concentration.

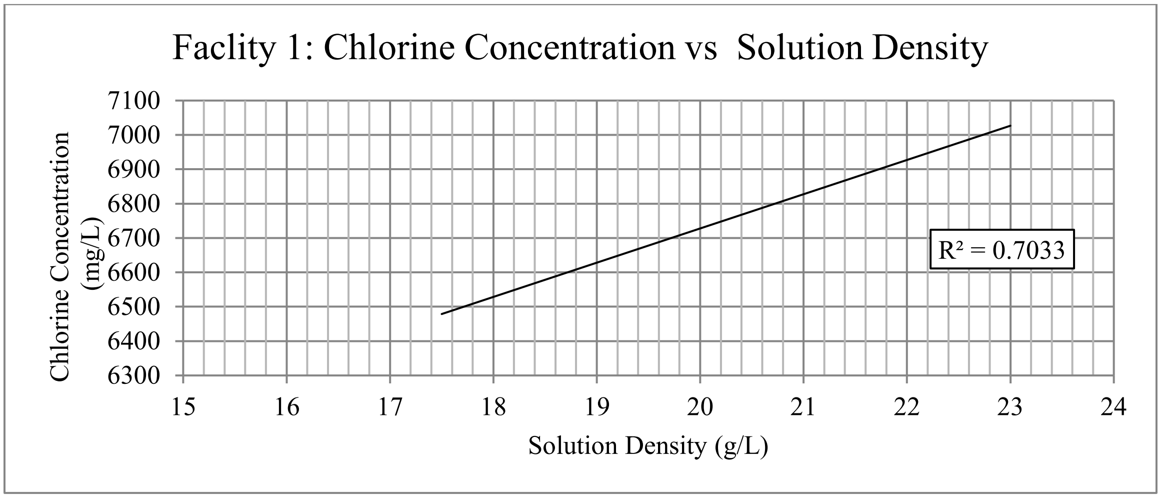

Figure 5.3: Relation of Chlorine Concentration and Solution Density for Samples from Facility 1

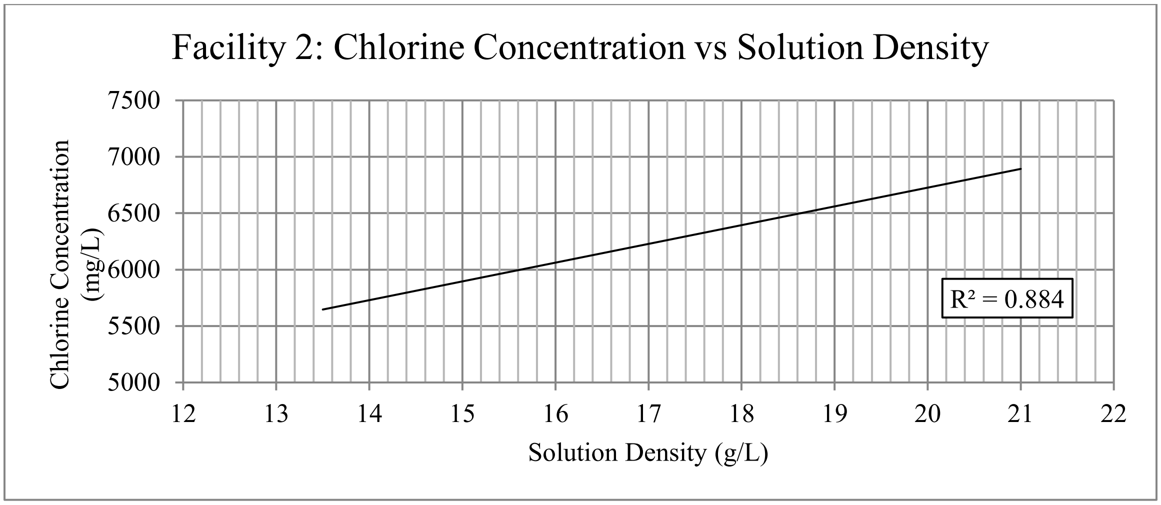

Figure 5.4: Relation of Chlorine Concentration and Solution Density for Samples from Facility 2

5.4 pH Relations

Based on the results of this study, pH does not appear to affect the chlorate or chlorine concentration of the resulting hypochlorite solution.

5.4.1 Chlorate Concentration and pH

No clear trends between the chlorate concentration and pH were observed for either facility. Based on the results of this study, it appears that the pH of the resulting low-strength hypochlorite solution does not greatly affect the degradation of hypochlorite into chlorate. However, due to the limited number of samples analyzed in this investigation, more testing is needed before determining the effect of pH on low-strength hypochlorite solutions.

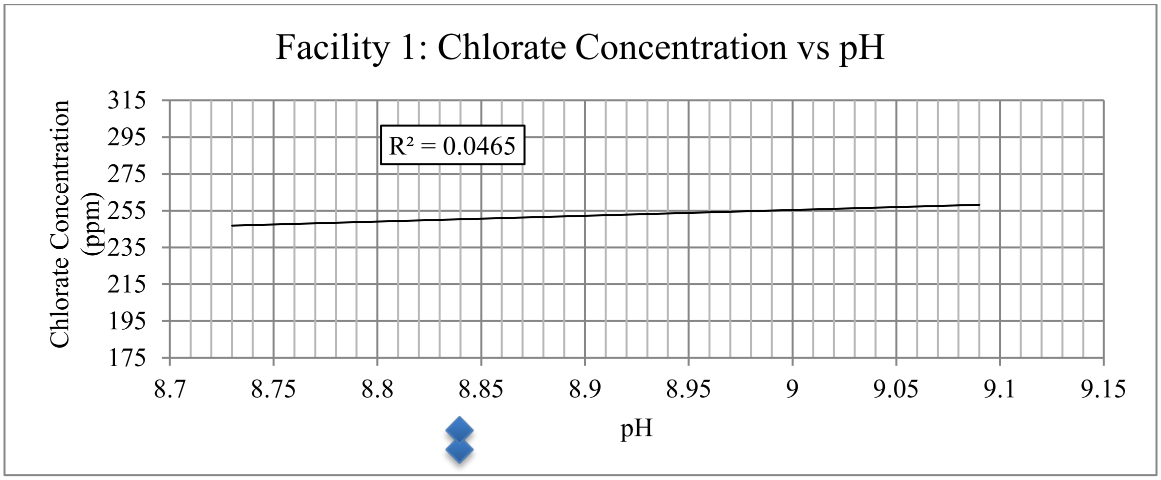

Figure 5.5: Relation of Chlorate Concentration and pH for Samples from Facility 1

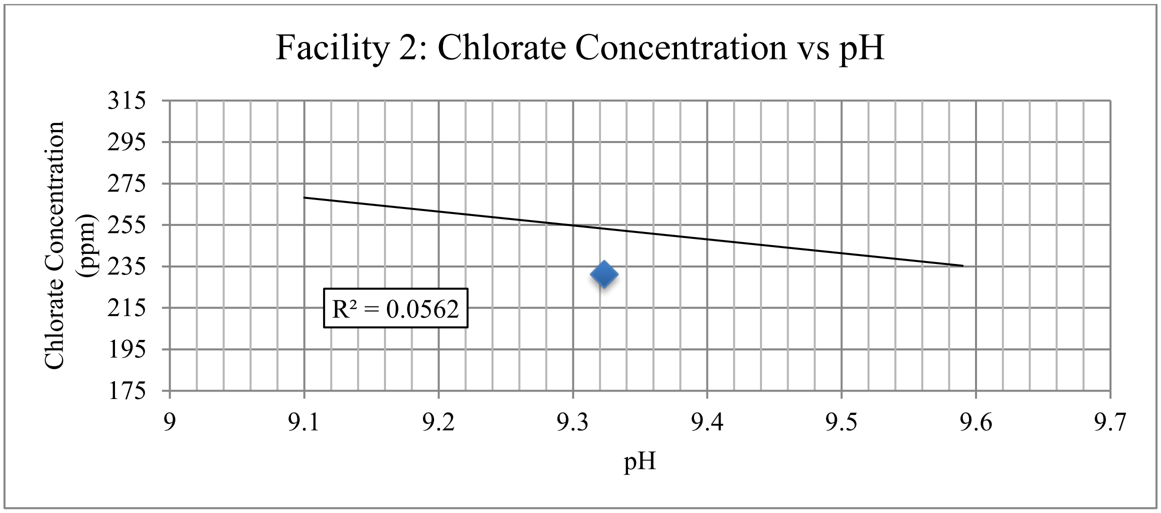

Figure 5.6: Relation of Chlorate Concentration and pH for Samples from Facility 2

5.4.2 Chlorine Concentration and pH

No clear trends between the chlorine concentration and pH were observed for either facility. Based on the results of this study, it appears that the pH of the resulting low-strength hypochlorite solution does not greatly affect the amount of chlorine formed during the electrolysis process. However, due to the limited number of samples analyzed in this investigation, more testing is needed before determining the effect of pH on chlorine production by electrolysis.

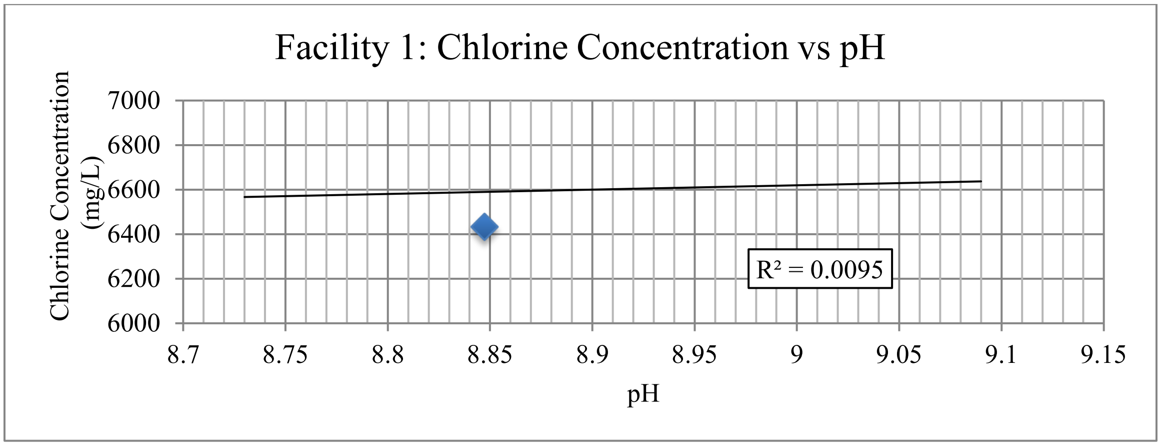

Figure 5.7: Relation of Chlorine Concentration and pH for Samples from Facility 1

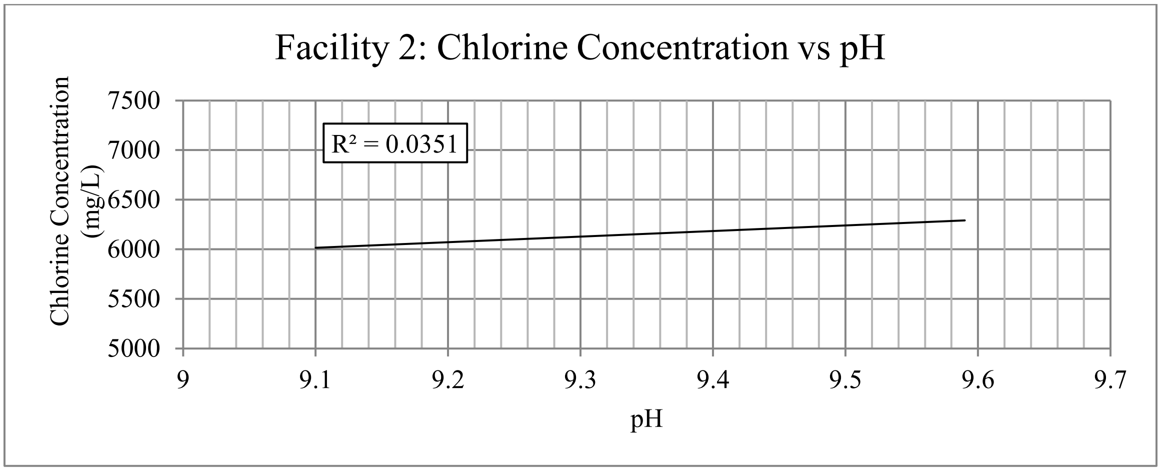

Figure 5.8: Relation of Chlorine Concentration and pH for Samples from Facility 2

5.5 Solution Temperature Relations

The resulting solution temperature varied by approximately 20 °F between the two facilities, with temperature variations within each facility varying only by about 5 °F for the different operating conditions. The chlorate and chlorine concentrations of both plants were analyzed for trends related to the solution temperatures.

5.5.1 Chlorate Concentration and Solution Temperature

The resulting solution temperature after electrolysis does not appear the impact the final chlorate concentration based on the results of this investigation. The temperature of the resulting solution may be affected more by the condition of the electrolysis equipment rather by operating conditions, resulting in large temperature variations between generators and small temperature variations within the same generator.

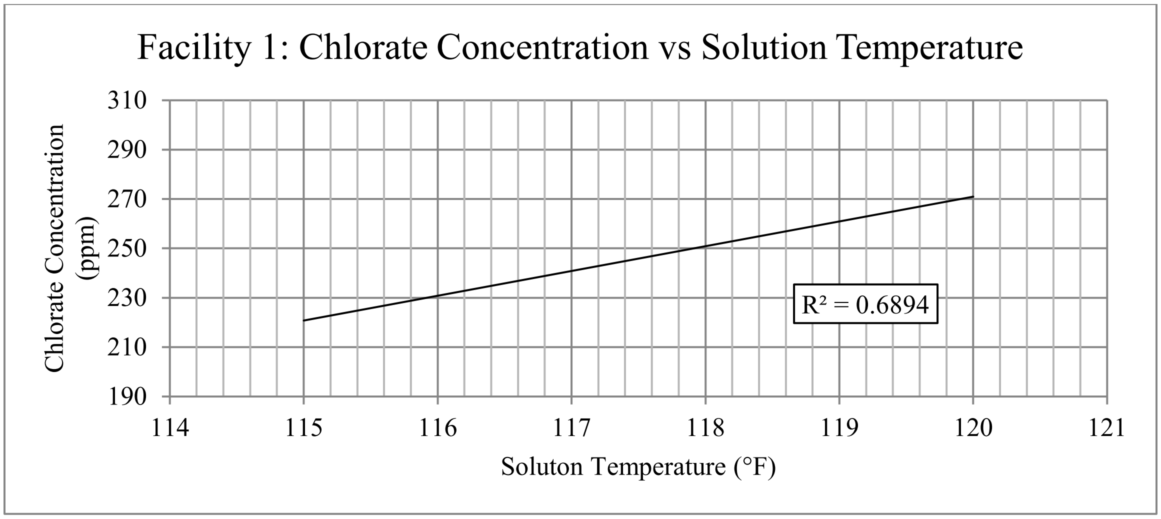

Figure 5.9: Relation of Chlorate Concentration and Solution Temperature for Samples from Facility 1

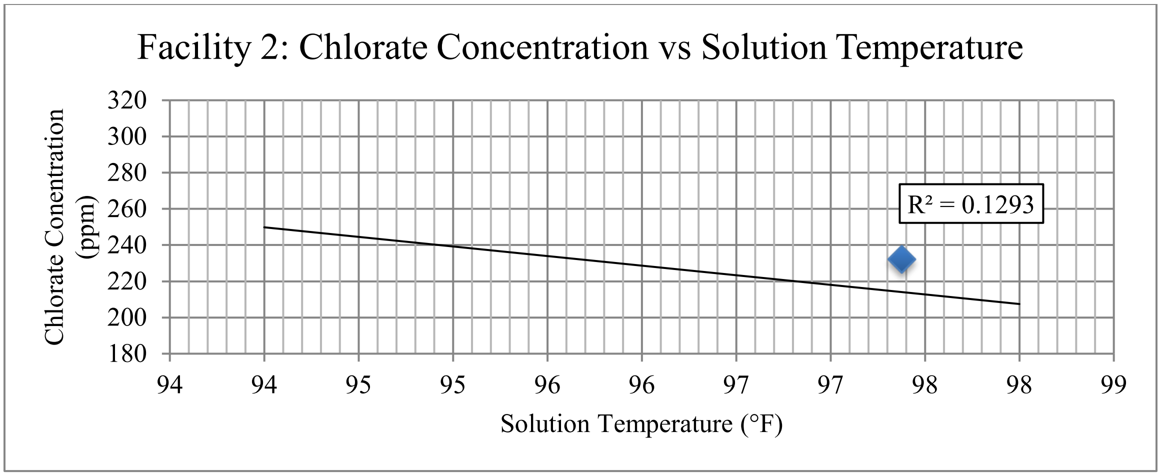

Figure 5.10: Relation of Chlorate Concentration and Solution Temperature for Samples from Facility 2

5.5.2 Chlorine Concentration and Solution Temperature

Chlorine concentration also did not appear to be affected by the resulting solution temperature. However, it is unclear if lower solution temperatures will produce higher chlorine concentrations due to the small data set of this study. A larger data set is required to better understand the correlation, if one exists, of chlorine concentration and solution temperature.

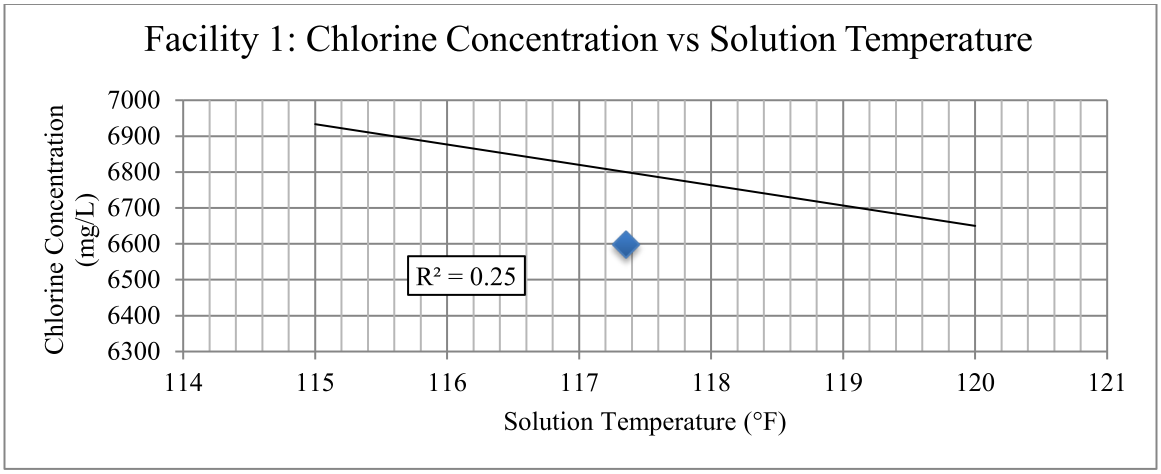

Figure 5.11: Relation of Chlorine Concentration and Solution Temperature for Samples from Facility 1

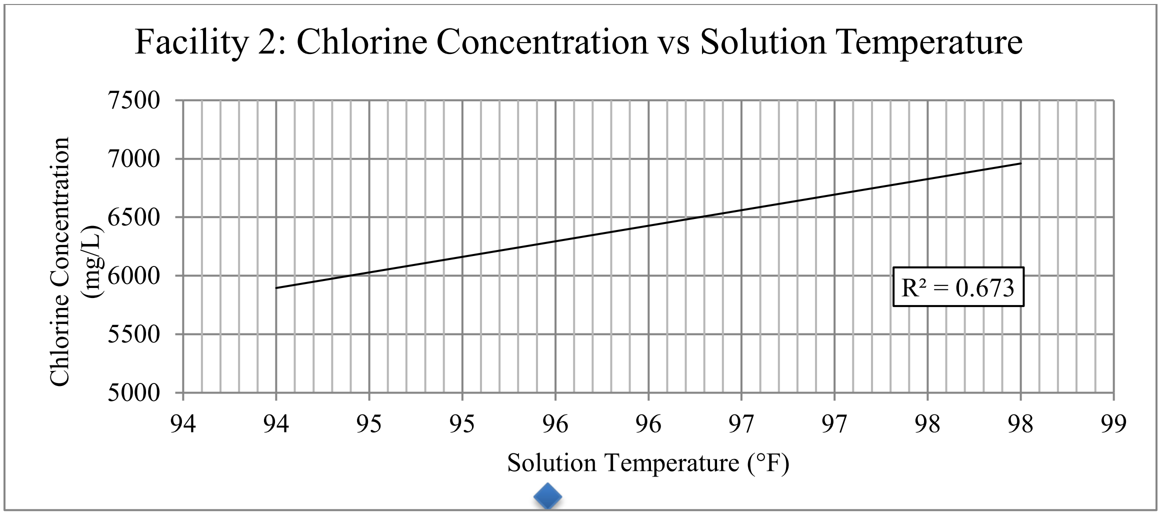

Figure 5.12: Relation of Chlorine Concentration and Solution Temperature for Samples from Facility 2

5.6 Retention Time Relations

Both facilities were evaluated for the effect of retention time on the resulting concentrations of chlorate and chlorine. It is expected that a lengthy retention time would produce larger concentrations of chlorate due to potential for more side reactions at the anode after the production of the hypochlorite. Also, it is expected that short retention times would result in low chlorine levels as the complete conversion of the brine to hypochlorite may not have sufficient time to occur.

5.6.1 Chlorate Concentration and Retention Time

Based on the results of this study, there was no significant correlation between chlorate concentration and retention time. However, it is possible that a correlation exists between chlorate concentration and retention time but that other factors affects chlorate production more and therefore govern in this situation. Further research is needed to determine the effect of retention time on chlorate production.

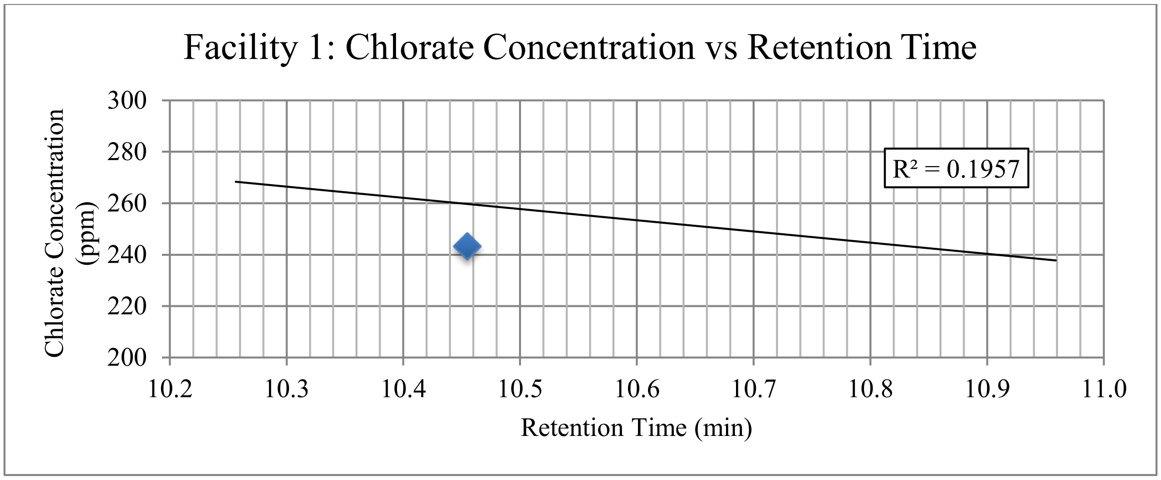

Figure 5.13: Relation of Chlorate Concentration and Retention Time During Electrolysis for Samples from Facility 1

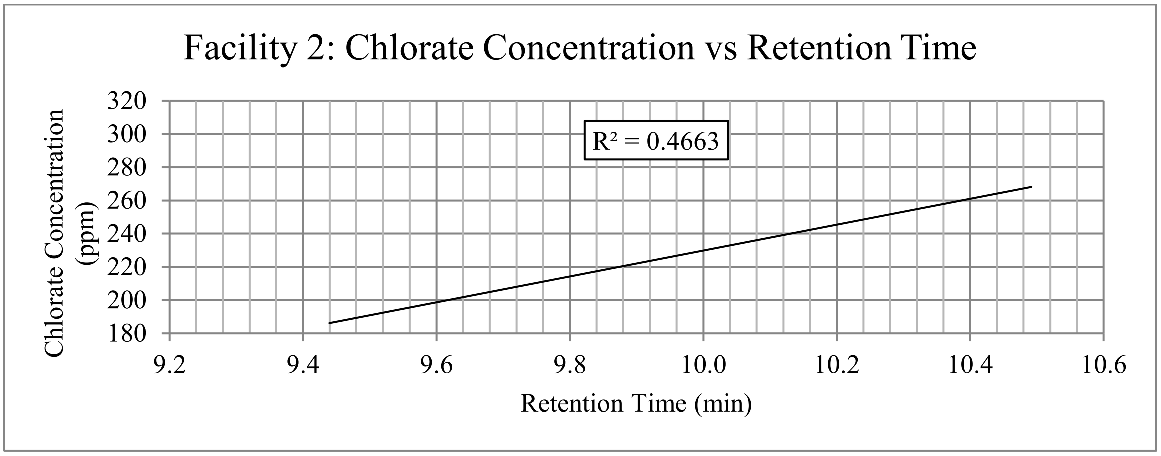

Figure 5.14: Relation of Chlorate Concentration and Retention Time During Electrolysis for Samples from Facility 2

5.6.2 Chlorine Concentration and Retention Time

Based on the results of this study, there was no significant correlation between chlorine concentration and retention time. Chlorine production may be affected more by the mass flow rate of the brine and therefore shows little correlation with retention time. More research is needed to fully understand if chlorine concentration and retention time are correlated.

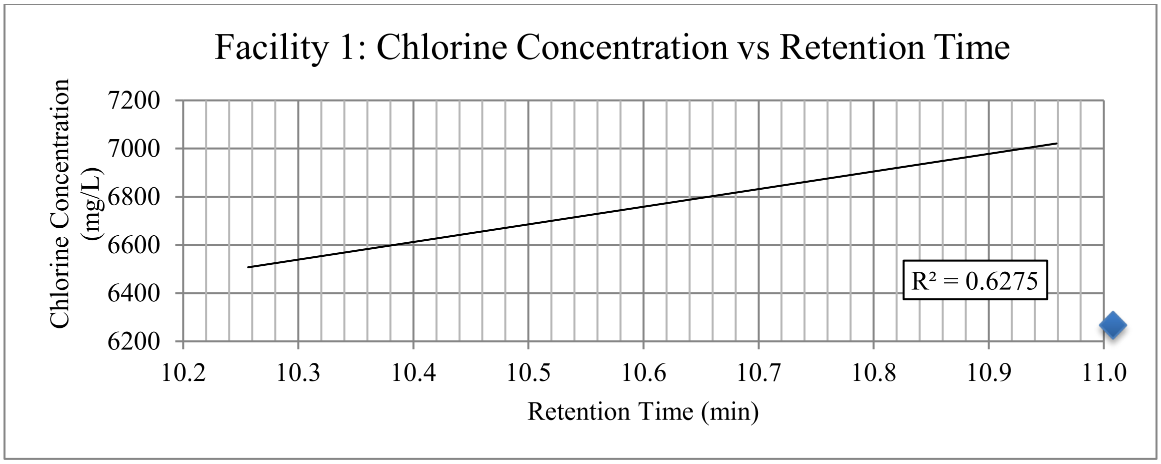

Figure 5.15: Relation of Chlorine Concentration and Retention Time During Electrolysis for Samples from Facility 1

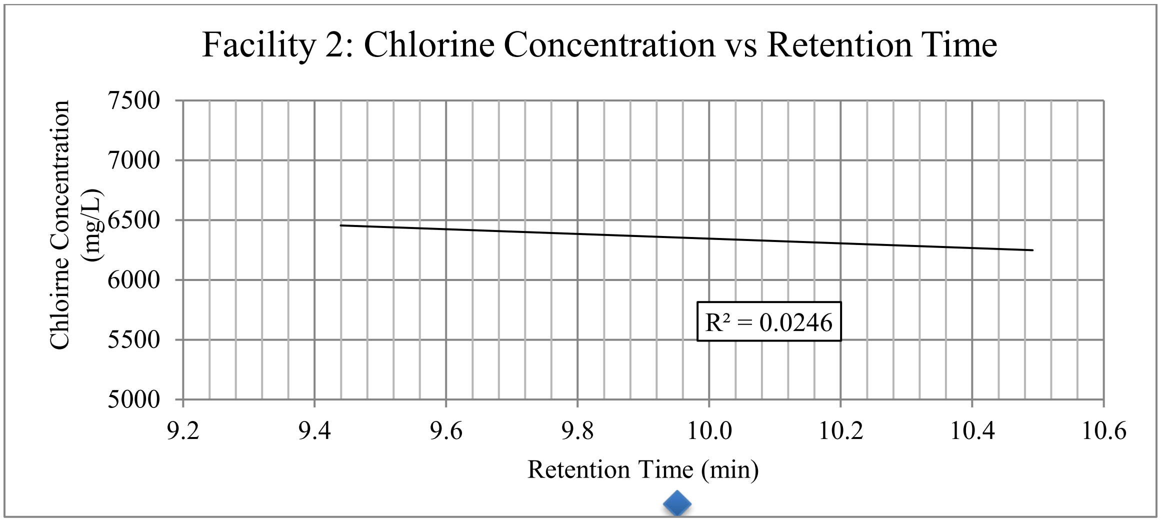

Figure 5.16: Relation of Chlorine Concentration and Retention Time During Electrolysis for Samples from Facility 2

5.7 Chlorate and Chlorine Concentration

Additionally, both facilities were analyzed for correlations between chlorate concentration and chlorine concentration. Chlorate concentrations were, on average, lower for samples with high chlorine contents.

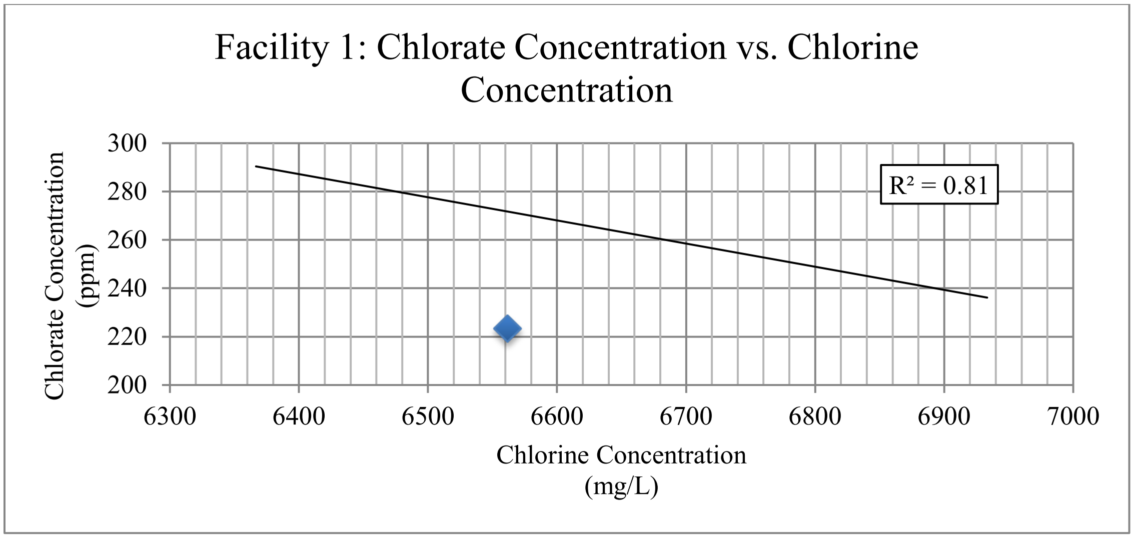

Figure 5.17: Relation of Chlorate and Chlorine Concentration for Samples Collected from Facility 1

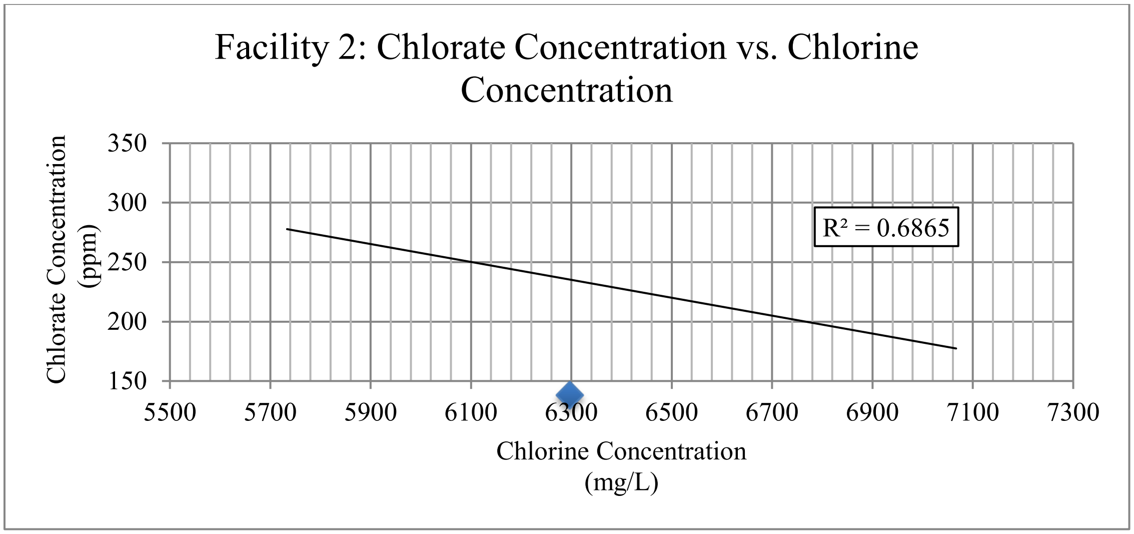

Figure 5.18: Relation of Chlorate and Chlorine Concentration for Samples Collected from Facility 2

Since both chlorate and chlorine concentrations are measured values resulting from different operating conditions, the correlation between chlorate and chlorine is not used to determine ways to limit chlorate production. However, the correlation is important as it augments the need for efficient production of chorine at the optimal concentration as given by the generator manufacturer, ClorTec®. Based on observed correlations, chlorate concentration is lower at higher chlorine concentrations. Therefore, when operators add hypochlorite solutions with the optimal chlorine content to finished water, the final concentration of chlorate in drinking water will likely be lower than if operators added hypochlorite solution with a lower than optimal chlorine concentration.

5.8 Chlorate Concentration in Finished Drinking Water

Based on a chlorine dose of 5 mg/L, 3 of the 8 samples tested would have exceeded the most conservative maximum contaminant levels of 200 μg/L and 210 μg/L of chlorate given by the Office of Environmental Health Hazard Assessment of California and the EPA, respectively. Additionally, though the exact concentration of perchlorate is unknown due to the limits of the equipment employed for testing, the concentration is known to be below 1 ppm. Therefore, it is unlikely that the perchlorate concentration in the finished water will exceed the maximum contaminant levels for perchlorate.

Table 5.2: Chlorate Concentrations in Finished Water at a Chlorine Dosage of 5 mg/L

		In Hypochlorite Solution		In Finished Water
Facility	Operating Condition	Chlorate (ppm)	Chlorine (mg/L)	Chlorate (μg/L)
Facility 1	n/a-Tank	246.30	6167	199.70
	OC1	251.51	6933	181.38
	OC2	220.78	6933	159.22
	OC3	290.41	6367	228.07
Facility 2	n/a-Tank	296.38	5717	259.23
	OC1	202.20	6217	162.62
	OC2	302.73	5733	264.01
	OC3	191.56	7067	135.54

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

The two facilities studied in this investigation currently are producing chlorate at concentrations of concern, with 3 of 8 samples exceeding the most conservative maximum contaminant level of 200 μg/L. Due to the fact that perchlorate concentration was undetectable due to laboratory constraints, no conclusions can be made about the exact levels of perchlorate in the finished water. However, as it is known that the concentration of perchlorate is less than 1 ppm, it is doubtful that the levels of perchlorate in the finished water exceed the maximum recommended contaminant level.

Based on the results of this study, storage time does not appear to increase the chlorate concentration in the low-strength hypochlorite solutions. Though the chlorate concentration of the hypochlorite solution from the storage tank was high, there was not a significant difference between the chlorate concentrations collected from the hypochlorite generator and those from the storage tank. Based on the results of this study, altering the flow rates of the water and brine during hypochlorite generation affects the final chlorate condition to a greater degree than storage. However, as the data set is limited, further research is required to validate this claim.

Neither facility achieved the expected 0.8% chlorine concentration under the recommended flow rates given by the Operation and Maintenance when measured by the UTA environmental lab. Therefore, there are concerns that the facilities are not operating efficiently. When the facilities apply the hypochlorite solution to disinfect drinking water, they must apply a larger quantity to achieve the same residual chlorine level than if their systems were operating efficiently. This leads to concerns because if more hypochlorite solution is added to the drinking water, the concentrations of chlorate and perchlorate in the finished water also increase. Therefore, for water treatment facilities to reduce the residual levels of disinfectant byproducts in the finished drinking water, it is important that hypochlorite generators operate efficiently and produce hypochlorite solutions with optimum chlorine concentrations.

Though very few trends were observed relating chlorate concentration to operating conditions, the density of the final solution did appear to have a significant impact on chlorate concentration. Additionally, higher densities were correlated with higher chlorine concentrations in the finished hypochlorite solutions. Therefore, by increasing the density of the hypochlorite solutions by either increasing the flow of brine relative to the flow of water, or by increasing the concentration of the brine solutions in the onsite generation systems, operators may be able to boost chlorine content while limiting byproduct formation.

6.2 Recommendations for Future Research

To better understand how operating conditions affect the byproduct and chlorine concentration in finished hypochlorite solutions, hypochlorite generators from several manufacturers must be examined. This study focused on only one hypochlorite manufacturer and thus, conclusions from this study are limited. Additionally, for each manufacturer, more hypochlorite generators should be examined to ensure the results are representative. Finally, factors such as the cleanliness of the electrodes and the inlet water temperature were not evaluated for their effect on byproduct formation or chlorine concentration. In future studies, it would be beneficial to examine and quantify these factors and investigate if they affect the resulting concentrations of the byproducts and chlorine.

Additionally, to discover the source of the discrepancy in the chlorine concentration measured by the water treatment facility and the UTA environmental lab, it is recommended that each facility use their testing method to measure the chlorine concentration of a known standard. Based on these results, finding the source of error should be easier. Also, further investigation is required as to why the hypochlorite generators are not producing chlorine concentrations at the optimum levels when the recommended flow rates are applied. This information is important as it may increase the operation efficiency of the generators and thus, reduce the residual concentration of disinfection byproducts found in the finished drinking water.

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