FATE OF BULK HYPOCHLORITE SOLUTIONS IN TWO WATER TREATMENT FACILITIES

by

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Abstract

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Measurement of oxyhalides in various strength hypochlorite solutions has been an issue of importance in the last decade, especially in view of the current aim of Homeland Security to reduce the usage of chlorine gas. Hypochlorite solutions have a potential of introducing disinfection by-products when used for water treatment. Previous works have shown the possibility of high levels of chlorate and perchlorate in high strength hypochlorite solutions. Perchlorate is an endocrine disruptor that inhibits iodide intake by the thyroid, thus reducing the production of essential thyroid hormones. Chlorate also has several adverse effects on the blood and thyroid systems. Perchlorate is regulated in the states of Massachusetts and California at the levels of 2 ppb and 6 ppb respectively, and is being considered for federal regulation at the level of 15 ppb. Chlorate has a health reference limit (HRL) of 210 ppb and a proposed action level of 200 ppb in California, with a current notification level of 800 ppb in California. Chlorate is also being considered for federal regulation with a level yet to be determined.

Chlorate and perchlorate measurement was done using ion chromatograph (IC) with carbonate eluent and conductivity detector. Due to the sensitivity limitations of the system, it was desired to measure some of the samples without dilution. This required the removal of free chlorine from the solution (quenching) to prevent destruction of system components, such as the column and the suppressor. Chlorine removal was achieved by addition of 20% excess hydrogen peroxide, based on molar ratio of 1:1 to chlorine and subsequent catalytic removal of residual hydrogen peroxide, which is also detrimental to IC equipment, using manganese dioxide. The process showed consistent and reproducible results.

One objective of this study was to investigate the degree to which hypochlorite solutions degrade, and the increase in chlorate and perchlorate levels in storage tanks. This was accomplished by comparing chlorine, chlorate and perchlorate levels in storage tanks to newly delivered solutions. Two facilities that had different suppliers were sampled. For both suppliers, variations in chlorine and chlorate levels were found in different hypochlorite deliveries. One of the suppliers generally had a much higher chlorate level in hypochlorite than the other supplier. Chlorine concentrations were equal or greater than the declared trade percent for both suppliers. Variations were also found in hypochlorite and chlorate concentrations stored at each facility. From a comparison between stored and newly delivered material it was found that significant hypochlorite degradation takes place. This results in increase of chlorate and perchlorate levels in the tanks.

Based on the results from tank samples and using an assumed chlorine dose of 5 mg/L, chlorate concentrations in the tanks are high enough that it would probably cause the concentrations in water to exceed the HRL. Nevertheless, despite perchlorate concentrations increasing during the storage, residual concentrations in finished water would probably be significantly below typical standards and therefore do not seem to be of a concern.

In previous studies, a model that predicts hypochlorite degradation and chlorate production has been generated based on laboratory results. In this study, field data of hypochlorite degradation and chlorate formation in storage tanks was compared to this model (available in AWWA website as Hypochlorite Assessment Model). Using the average of sample temperatures as an input to the model, most of the data points from this study were found to deviate from the values predicted by the model by less than 10%.

Dilution of high strength hypochlorite solutions with softened water and low strength hypochlorite was examined. The two dilution sources produced similar levels of hypochlorite degradation and chlorate formation. Most of the data in the dilution experiment was within 10% deviation from the values predicted by Hypochlorite Assessment Model. This study also confirmed the results from previous work that dilution decreases hypochlorite degradation and chlorate formation.

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Chapter 1

Background and Objectives

1.1 Transition from Chlorine Gas to Hypochlorite

Chlorine gas had been used for water disinfection since 1893. In 1974, following the Safe Drinking Water Act, all the public water supplies in US were required to disinfect water and provide a chlorine residual. However, chlorine gas can also be a deadly weapon. It was used as a chemical weapon in World War I, and recently in Iraq. In addition, accidents occurring because of chlorine gas can be very dangerous. In the US, several accidents associated with chorine gas occurred in last ten years. Due to these reasons, reducing the usage of chlorine gas became one of the aims of the Homeland Security Department (DHS). In 2007, the Department initiated Chemical Facility Anti-Terrorism Standards Program. The program required high-risk facilities to make improvements to decrease the risk, especially if the treatment plant is located in a highly populated area (DHS 2007, Desing 2008)

As a result, many water treatment facilities have switched to hypochlorite solution as an alternative to chlorine gas as a secondary disinfectant. Some facilities chose to install an onsite hypochlorite generation systems (OSG), which typically produce 0.8% hypochlorite solutions, and some use a high concentration hypochlorite provided by an external supplier, which is typically 10-12.5%. The focus of the current study was on the high concentration hypochlorite solutions.

Hypochlorite manufacture and quality can vary and it also degrades during storage, thus reducing chlorine concentration and producing chlorate and perchlorate, that are disinfection by-products. The loss of the chlorine means that more of the solution needs to be applied to achieve desirable chlorine residual, therefore longer periods of storage will lead to higher levels of chlorate and perchlorate in drinking water.

1.2 Scope of the Study

The interest of the current study was to investigate the storage of hypochlorite in real field conditions. There is a model in the literature that addresses the storage of hypochlorite, however, there is relatively little data from real hypochlorite storage systems. Therefore, the focus of the study was collection of real system information. There was a need to address the issue in Texas specifically and to gain understanding in processes taking place locally. There could be numerous applications of the study in addition to usage of hypochlorite for secondary disinfection, and one of them is usage of high strength hypochlorite for raw lake water application to control biofilm and zebra mussels.

1.3 Research Objectives

The research objectives of this study are:

- Investigate real local systems using hypochlorite in water treatment (in Dallas Ft-Worth Metroplex, Texas), primarily focusing on hypochlorite decomposition, chlorate and perchlorate formation.
- Compare chlorate and perchlorate levels against existing and proposed regulations.
- Come to a better understanding of real world conditions.
- Check how well the Hypochlorite Assessment model predicts the results from local water treatment facilities.
- Test for possible practical ways to decrease the generation of chlorate, such as dilution of high-strength hypochlorite with softened water produced by an industrial softening system and low strength on-site generated hypochlorite.
- To achieve the objectives of the research, it was first necessary to find an efficient way to quench the hypochlorite solution and to measure the analytes in ion chromatograph available in the laboratory.

Chapter 2

Literature Review

2.1 Hypochlorite Manufacture

2.1.1 Commercial Hypochlorite and its Decomposition

Most of the time, the strength of commercial hypochlorite is defined by the manufacturer using a trade percent:

$$Trade\ \% = \frac{Available\ chlorine\ \left({}^{g}\!/\!{}_{L}\ \ as\ Cl_2\right)}{10}$$

Other terms that can be used:

$$Weight\ \%\ available\ chlorine = \frac{Available\ chlorine\ \left({}^{g}\!/\!{}_{L}\ \ as\ Cl_2\right)}{10 \times specific\ gravity}$$

$$Weight\ \%\ sodium\ hypochlorite = Weight\ \%\ available\ chlorine \times \frac{MW_{NaOCl}}{MW_{Cl_2}} (=1.05)$$

(Odyssey 2012)

Once hypochlorite is added to water, the following reaction occurs:

$$NaOCl + H_2O \rightarrow HOCl + Na^+ + OH^-$$

Over time, hypochlorite solution decomposes, forming oxygen, chlorate and perchlorate. (Snyder 2009)

2.1.1.1 Chlorate formation mechanism:

The chlorate formation is a result of a slow reaction of two hypochlorite ions followed by a relatively fast reaction of the hypochlorite ion with chlorite:

$$OCl^- + OCl^- \rightarrow ClO_2^- + Cl^- \ (slow)$$

$$OCl^- + ClO_2^- \rightarrow ClO_3^- + Cl^- \ (fast)$$

At pH above 11 chlorate formation is a second order reaction:

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

$$rate = k_2[OCl^-]^2$$

At pH below 11 chlorate formation is a third order reaction:

$$2HOCl^- + OCl^- \rightarrow ClO_3^- + 2H^+ + 2Cl^-$$

$$rate = k_{obs}[HOCl^-]^2[OCl^-]$$

(Adam 1994, Adam 1999)

2.1.1.2 Perchlorate formation mechanism:

Perchlorate is formed as a result of hypochlorite ion reaction with chlorate:

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

$$rate = k[OCl^-]^1[OCl_3^-]^1$$

(Snyder 2009)

2.1.2 Influence of Hypochlorite Manufacture on Chlorate and Oxygen Formation

High strength sodium hypochlorite is typically produced by passing chlorine gas through the sodium hydroxide solution:

$$Cl_2 + 2NaOH \rightarrow NaOCl + NaCl + H_2O$$

(Snyder 2009, Odyssey 2012)

Sodium hypochlorite can be produced either in a batch or continuous production. Solutions that are manufactured in a batch production, will commonly produce high levels of chlorate due to the challenge in controlling the pH and the temperature in every part of the reactor. Even though the batch process originated during 1950's, and is not currently favored, it is still in use to some extent by many manufacturers to recover as much chlorine gas as possible from a tanker truck. If the pH is allowed to drop below 10 at any location in the reactor during the production, which can easily happen in a batch reaction, hypochlorous acid will form and lead to higher chlorate formation. Also, batch productions are likely to have temperature variations that can lead to high local temperatures, which will accelerate chlorate formation. Continuous manufacture provides better control over temperature and pH, which reduces chlorate formation. (Odyssey 2012)

The quality of produced hypochlorite as well as the amount of metals depends on the sodium hydroxide used in the process. High level of metals will catalyze the breakdown of hypochlorite during storage to oxygen and chloride:

$$OCl^- + OCl^- \rightarrow O_2 + 2Cl^- \ (very\ slow)$$

Usually this reaction is very slow, but it is facilitated by transition metal ions. They serve as a "catalyst" of the reaction and can facilitate the reaction even at very low concentrations. On the occasion that oxygen is produced, it can cause problems in pumps and piping, such as "oxygen lock", which will result in problems with the flow. (Adam 1994, Odyssey 2012)

The quality of hypochlorite will also depend on the quality of precursors used for its production.

2.1.3 Sodium Hydroxide and Chlorine Gas Manufacture

Commercial production of sodium hydroxide and chlorine gas utilizes electrolytic chlor-alkali cells and includes one of the three main types of processes: mercury cells, diaphragm cells, and membrane cells.

The overall reaction that takes place in the process:

$$2NaCl + 2H_2O \rightarrow Cl_2 + H_2 + 2NaOH$$

All the three processes use nearly saturated NaCl brine for the electrolysis reaction.

Chlorine gas is produced at the anode:

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

The reaction at the cathode is unique to each process.

2.1.3.1 Mercury cell

Sodium amalgam is produced at the cathode, then reacted with water in a decomposer, to produce hydrogen gas and caustic soda solution. Traces of heavy metals and magnesium need to be removed from the brine. Typically, evaporated salt is used. If mined salt is used it should be highly purified. The brine in the process must be relatively pure and this results in pure products.

However, due to the environment and safety considerations, this process had become less popular throughout the years.

Cathode reaction:

$$Na^+ + e^- + Hg_x \rightarrow NaHg_x$$

Followed by separation in a decomposer:

$$2NaHg_x + 2H_2O \rightarrow 2NaOH + H_{2(g)} + 2Hg_x$$

2.1.3.2 Diaphragm cell

The cathode cell is separated from the anode cell by a permeable, usually asbestos based diaphragm. Less expensive brine of mined salt can be used. The caustic solution that is produced at the cathode contains 11%wt sodium hydroxide and 18%wt sodium chloride. Sodium chloride concentration is reduced to 1% by evaporation and subsequent removal of sodium chloride salt. Chlorine gas contains oxygen and must be purified.

The reaction at the cathode is:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$

2.1.3.3 Membrane cell

Cathode cell is separated from the anode cell by a cation permeable membrane. Only sodium ions can pass through the membrane. The lifetime of this membrane depends on the purity of the brine. The caustic solution needs to be concentrated after it is produced. Similarly to the mercury process, chloride ions concentration in the caustic solution is relatively low. Chlorine gas contains some oxygen and needs to be purified. The brine also needs to contain low concentrations of calcium, magnesium, sulfite, and other divalent ions to avoid their build up on the membrane. To achieve this goal, calcium is precipitated as calcium carbonate, magnesium and iron as hydroxides. Use of evaporated salt can reduce the price of brine pre-treatment.

Hydrogen evolves at the cathode:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$

That results in the remaining sodium hydroxide solution.

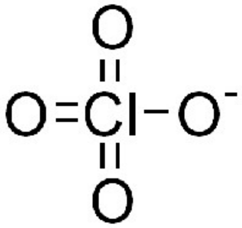
In conclusion, sodium hydroxide produced in the mercury cell process has the highest purity out of the three. Membrane cell sodium hydroxide is almost as high in purity as the mercury process. The diaphragm process provides the lowest purity of the product. However, the diaphragm process also

provides the least expensive product. Production of chlorine and sodium hydroxide other than in a chlor-alkali process exist, though is not as common.
(Schmittinger 2000, Adam 1994)

2.2 Health and Regulatory Aspects

2.2.1 Perchlorate

Perchlorate is an oxygen chlorine compound that consists of four oxygen atoms and one chlorine atom. In perchlorate ion, chlorine has an oxidation state of +7.



Perchlorate is an endocrine disruptor that inhibits iodide intake by the thyroid, thus reducing the production of essential thyroid hormones that are also very important for neurodevelopment (Kirk 2006). Perchlorate is a common contaminant in food and water. It can come from different sources, such as rocket fuel, fireworks and in Chilean nitrate used for agricultural purposes, where it occurs naturally (Greer 2002, Snyder 2011, USEPA 2002, USEPA 2011). In addition to other possible sources, usage of hypochlorite as a disinfectant has a potential of significantly increasing perchlorate levels in drinking water, depending on its concentration in the hypochlorite.

Even though perchlorate is not yet regulated on the federal level, it is regulated in the states of Massachusetts and California at the levels of 2 ppb and 6 ppb respectively. The value of the Massachusetts regulatory limit is based on a reference dose of 0.00003 mg/kg/day, which was derived from earlier animal toxicological studies. Reference dose of 0.00003 mg/kg/day will translate to the drinking water equivalent level (DWEL) of 1 μg/L. (USEPA 2002). In setting the MCL of perchlorate to

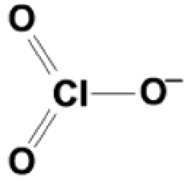
2 μg/L rather than 1 μg/L, the state of Massachusetts was seeking to retain safety for vulnerable populations, while also considering disinfection benefits. (MassDEP 2006).

Later, based on human toxicology studies (Greer 2002), the new EPA reference dose was established at 0.0007 mg/kg/day. It would imply a drinking water equivalent of 15 μg/L, calculated for an average weight of an adult person, which stands at 70kg. (USEPA 2008, USEPA 2011)

In 2004, the Office of Environmental Health Hazard Assessment (OEHHA) recommended to set the Public Health Goal (PHG) of perchlorate to 6 μg/L, based on the same human toxicology studies (Greer 2002), but made adjustments to the primary vulnerable population, which was defined as pregnant women and their fetuses. This value was a basis for perchlorate regulation in the state of California, which became effective in 2007. In 2012, OEHHA changed the PHG to 1 μg/L, now defining the primary vulnerable population as infants 0-6 month, with a goal to protect them from any decrease in iodide uptake by the thyroid as a result of perchlorate exposure (OEHHA 2012). However, California MCL was not yet changed to the new proposed PHG.

2.2.2 Chlorate

Chlorate is an oxygen chlorine compound that consists of three oxygen atoms and one chlorine atom. In chlorate ion, chlorine has an oxidation state of +5.



Chlorate is used in agriculture as an herbicide, and as a bleaching agent in the textile and paper industry. Chlorate is also a disinfection by-product that is introduced into the water during hypochlorite and chlorine dioxide usage. In addition, chlorate can occur in foods along with chlorine dioxide and chlorite, due to its use in flour treatment, as decolorizing and bleaching agent (Alfredo 2014). Chlorate is stable in the environment under aerobic conditions, but undergoes decomposition to chloride under anaerobic conditions (Borodinsky 2011).

Chlorate can be introduced via chlorine dioxide use as an antimicrobial agent in the processing of poultry, fruits, and vegetables (Borodinsky 2011). It can be also introduced indirectly, through the disinfection of surfaces and lines in the food industry. Studies also indicate that chlorate entering water supply as a result of hypochlorite application is equal to or exceeds the amount entering as a result of the chlorine dioxide application (Gordon 1997).

Intake of high levels of chlorate has resulted in kidney failure and hemolysis (breaking down of red blood cells) (USEPA 2014b). Animal studies prove that chronic and sub-chronic exposure to chlorate has an adverse effect on blood and thyroid (McCauley 1995, Hooth 2001, USEPA 2014b).
A study performed in Italy between years 2002-2005 showed that women exposed to chlorate levels exceeding 200 μg/L in drinking water had an elevated risk of having newborns with obstructive urinary defects, cleft palate and spina bifida. (Righi 2012)

Chlorate was published in the EPA CCL3 list, and has a health reference limit (HRL) of 210 μg/L (Alfredo 2014). EPA used a study of chronic exposure of rats to chlorate that was published by the National Toxicology Program (NTP) in 2005 (NTP 2005) to perform the Benchmark Dose Method (BDM), which constitutes an alternative to NOAEL approach for risk estimation of non-carcinogenic compounds. The method involves adapting a mathematical model to the data of the study with a special benchmark dose software package (Filipsson 2003). BMDL (lower 95% confidence limit of BMD) set by EPA corresponded to 0.9 mg/kg/day for rats. Afterwards, an uncertainty factor (UF) of 30 is applied. This is a common uncertainty factor that is applied to account for interspecies and intraspecies differences (usually 10 for interspecies differences and 3 for intraspecies). (Hardy 2009, ATSDR 2008). In this way, 0.03 mg/kg/day exposure limit for humans was derived, which resulted in HRL of 210 μg/L.

Though chlorate is not yet regulated on the national level, the state of California established the notification level of 800 μg/L, while the proposed action level is 200 μg/L in drinking water, as recommended by OEHHA. This recommendation is primarily established on no observed adverse health effect (NOAEL) in rats. This value is believed to protect humans from any adverse effects. (OEHHA 2002) When recommending a proposed action level of 200 µg/L, OEHHA used a Relative Source Contribution (RSC) factor of 0.2 for drinking water, as follows:

$$C = \frac{30\mu g / kg - day \times 70kg \times 0.2}{2L / day} = 210 \, {}^{\mu g}\!/_{L}$$

However, current RSC that is used by the California Department of Public Health (CDPH) is 0.8, resulting in the notification limit of 800 µg/L:

$$C = \frac{30\mu g / kg - day \times 70kg \times 0.8}{2L / day} = 840 \, {}^{\mu g}\!/_{L}$$

(EPA 2014, CEPA 2010, OEHHA 2015)

A complete EPA review of chlorate is expected to be published by the end of 2015, after consideration of chlorate and other unregulated disinfection by-products (DBP) together with reviewing currently existing microbial and DBP regulations. (USEPA, 2014). Also, it appears that new monitoring data has to be collected for a chlorate regulation decision. The existing monitoring data was collected at the time of the Information Collection Rule, in 1997-98. This data showed that 22/59 facilities using hypochlorite had chlorate levels that exceed HRL. (Robertson, 2012). Since then, hypochlorite had become more widely used and therefore reevaluation is required.

2.3 Hypochlorite Decay Model

Several studies were performed in the last two decades that allowed the development of the Hypochlorite Assessment Model. Currently, the model is available in the American Water Works Association (AWWA) website and incorporates the prediction of hypochlorite degradation, and chlorate and perchlorate formation.

2.3.1 Hypochlorite Decomposition and Chlorate Formation

Hypochlorite decay model was developed using mainly laboratory data, from which kinetics of the reactions was inferred. Initially, the model was developed to express hypochlorite decomposition and chlorate formation (Adam 1994, Adam 1999, Gordon 1997)

As shown earlier, the reaction rate of hypochlorite can be expressed as follows:

$$-\frac{d[OCl^{-1}]}{3dt} = k_2[OCl^-]^2$$

The model incorporates numerical calculations and describes the effect of the temperature and ionic strength on the decomposition of OCl^-.

$$\log k_2 = 0.149\mu + \log[2.083\times10^{10} T \exp(-1.018\times10^5 / RT)\exp(-56.5 / R)$$

μ - Ionic strength

T – Temperature

k_2 In the units of $\frac{1}{M\times\sec}$

Concentrations and temperatures for which the model was developed are reported in the referenced studies.

(Adam 1999, Adam 1994)

The model was developed using the Eyring equation that describes the variation of chemical reaction rate with temperature:

$$\log k_0 = \log[2.083\times10^{10} T \exp(-\Delta H^{\ddagger} / RT)\exp(\Delta S^{\ddagger} / R)$$

Plot of $\frac{k_0}{T}$ $vs.$ $\frac{1}{T}$ allows to determine $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$.

The observed rate constant includes two independent decomposition pathways of hypochlorite, chlorate pathway and oxygen pathway.

Values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were found for different hypochlorite solutions, and extrapolated to infinite dilution. Then, the ionic strength term was incorporated and numerical values were set for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ at infinite dilution. The agreement between the rate constant in tested solutions had an average error of 10 percent. As it can be seen, this model is based on a chemical description of the system. Kinetic information was used to develop chemical and thermodynamic equations that show hypochlorite break-down in pH 11-14 range. (Adam 1994, Gordon 1997)

The model was confirmed with one field study, where degradation in a storage tank was measured and compared to the model. The deviation between predicted and measured values was 13-24% (Gordon 1997). Based on these studies, a model software called *Bleach 2001* was developed.

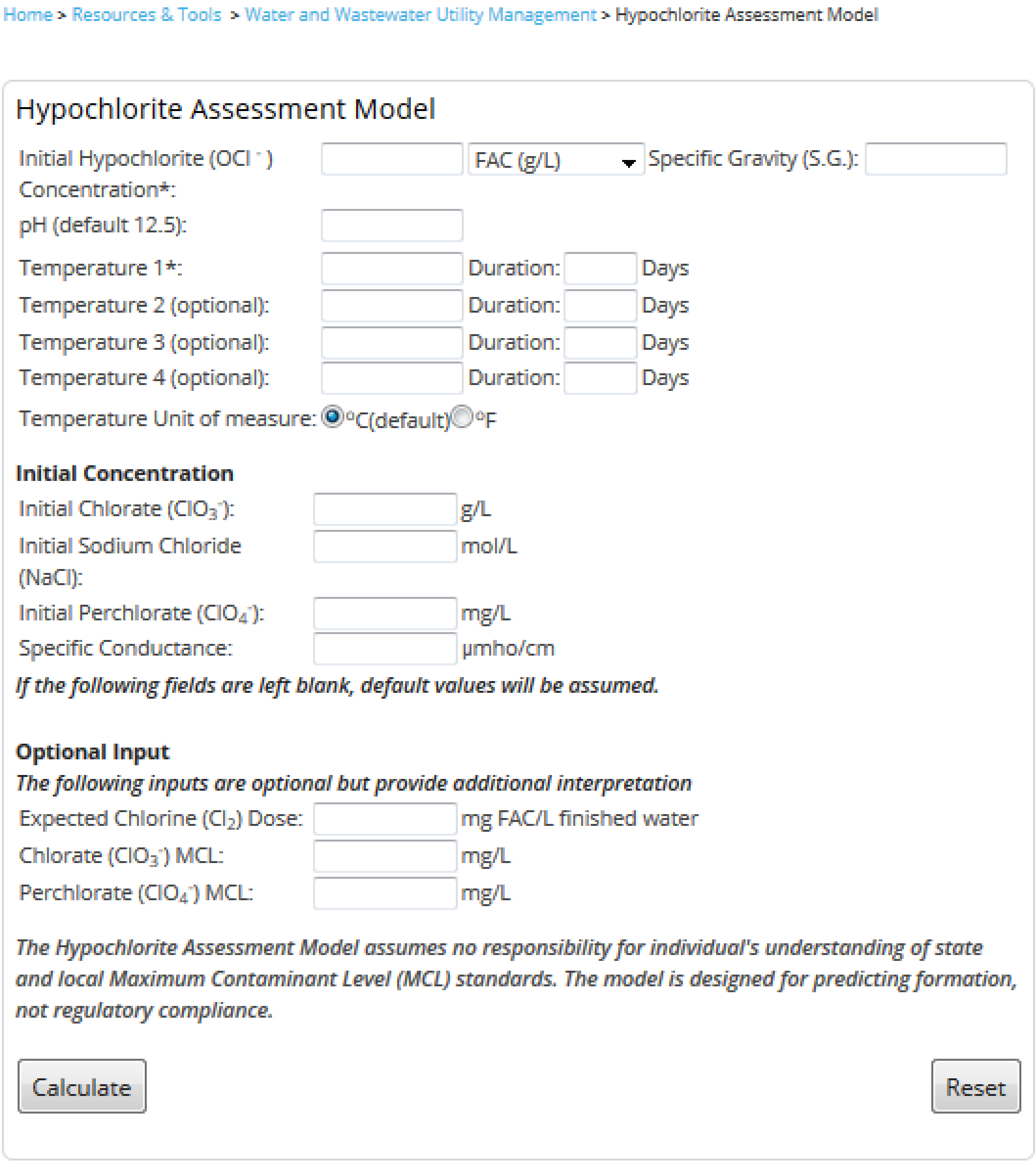
2.3.2 Perchlorate Formation

Later, the model was extended to predict perchlorate formation also. (Snyder 2009, Pisarenko 2009). The rate law used is as follows:

$$Rate = \frac{dClO_4}{dt} = k_{calc}\left[OCl^-\right]^1\left[ClO_3^-\right]^1$$

$$log\ k_{calc} = 0.0788(I) + log\ (2.084\times10^{10}\times T\times e^{\frac{-1.01\times10^5}{RT}}\times e^{\frac{-106}{R}})$$

- The agreement between the observed and measured perchlorate concentrations was 10% or better
- Perchlorate formation predicted by the model was not compared to real field studies
- Based on the study, the model software was upgraded, and currently is available as a tool in the AWWA website under the name of *Hypochlorite Assessment Model.*



Home > Resources & Tools > Water and Wastewater Utility Management > Hypochlorite Assessment Model

Hypochlorite Assessment Model

Initial Hypochlorite (OCl^-) Concentration*: FAC (g/L) Specific Gravity (S.G.):

pH (default 12.5):

Temperature 1*: Duration: Days

Temperature 2 (optional): Duration: Days

Temperature 3 (optional): Duration: Days

Temperature 4 (optional): Duration: Days

Temperature Unit of measure: ● °C(default) ○ °F

Initial Concentration

Initial Chlorate (ClO_3^-): g/L

Initial Sodium Chloride (NaCl): mol/L

Initial Perchlorate (ClO_4^-): mg/L

Specific Conductance: µmho/cm

If the following fields are left blank, default values will be assumed.

Optional Input

The following inputs are optional but provide additional interpretation

Expected Chlorine (Cl_2) Dose: mg FAC/L finished water

Chlorate (ClO_3^-) MCL: mg/L

Perchlorate (ClO_4^-) MCL: mg/L

The Hypochlorite Assessment Model assumes no responsibility for individual's understanding of state and local Maximum Contaminant Level (MCL) standards. The model is designed for predicting formation, not regulatory compliance.

Figure 2.1: AWWA Hypochlorite Assessment Model interface (Copyright AWWA 2011)

2.3.3 Limitations of the Model

Hypochlorite Assessment Model does not take into account the effect of transition metals that catalyze the breakdown of hypochlorite to chloride and oxygen. The model does not consider transition metals activity, because their role is complex. It is known that they serve as catalysts in the pathway of hypochlorite decomposition to oxygen. Decomposition of hypochlorite assignable to the metals depends on their concentrations, joint effect with other transition ions, and the exposure to UV light. (Gordon 1997, Adam 1994)

2.4 Summary of Factors Affecting Hypochlorite Decomposition

2.4.1 pH – decomposition of hypochlorite and chlorate formation are minimal in the pH range of 11.86-13. At pH higher than 13 the concentration of hydroxide ion contributes to the ionic strength of the solution. At pH levels lower than 10.5, the hypochlorous acid mechanism of decomposition, which is a third order reaction, is still very significant, which results in higher decomposition rates of hypochlorite and chlorate formation.

2.4.2 Ionic Strength - it had been shown that ionic strength contributes to hypochlorite decomposition. Increase in ionic strength will reduce the stability of the solution.

2.4.3 Dilution - dilution decreases the decomposition by decreasing the hypochlorite ion concentration and also by decreasing the ionic strength that contributes to decomposition. The decrease of the hypochlorite ion concentration by the factor of 2 should slow down the decomposition rate by the factor of 4 (second order reaction), but in fact the decomposition is reduced by more than the factor of 4. It can be explained by the fact that decrease in hypochlorite concentration also decreases ionic strength, which is another factor that decreases the decomposition.

2.4.4 Temperature – decomposition rates are derived from Eyring equation, which shows a strong dependence on the temperature. The higher the temperature, the higher hypochlorite decomposition rate and as a result, higher chlorate and perchlorate formation.

2.4.5 Effect of Matrix Ions – sulfate and carbonate at concentrations below 1 g/L did not influence decomposition rates at pH=13. At pH close to 11, presence of carbonate ion actually stabilizes the solution. Chloride - elevated concentrations of chloride ion increase decomposition as a result of increase in ionic strength.

2.2.6 Transition Metal Ions – facilitate the breakdown to oxygen and chloride as discussed earlier. (Adam 1994, Gordon 1997)

2.5 Previous Field Studies

Other studies that measured chlorate and perchlorate in water treatment facilities (in addition to Adam 1994, Gordon 1997, Adam 1999) are as follows:

- Assessment of chlorate concentrations in hypochlorite, finished and raw water at 7 different facilities, including bulk and OSG hypochlorite (Alfredo 2014)
- Chlorate, perchlorate and bromate concentrations measured in several OSG and bulk hypochlorite facilities (Stanford 2011)
- Chlorate, perchlorate and bromate concentrations in OSG systems (Stanford 2013)

Most of these studies found elevated chlorate levels (that would exceed HRL) at least in some of the facilities. Perchlorate levels were elevated occasionally only. Some of these studies also did laboratory experiments that confirmed degradation of hypochlorite dependence on the temperature and dilution. Results that were compared to the model showed deviation up to 10% from model prediction.

Studies in Florida showed that the investment in softening equipment and even bigger storage tanks are almost equivalent to the savings in sodium hypochlorite consumption that will result from its dilution and lower degradation. (Odyssey 2012)

2.6 Analytical Methods

Chlorate has been measured in drinking water with the use of ion chromatography for many years, and details of the measurement are described in EPA method 300.1 that was published in 1997. The analysis is done with conductivity detector and carbonate eluent. Perchlorate measurement is described in EPA method 314 from 1999. This method also uses a conductivity detector, however, using sodium hydroxide eluent and an appropriate column. Liquid chromatography-mass spectrometry (LCMS) and ion chromatography-mass spectrometry (ICMS) have been used more recently for chlorate and perchlorate measurement in drinking water.

Ion chromatography has been used for chlorate measurements in hypochlorite for about two decades. In the earlier studies, hypochlorite samples were analyzed directly by ion chromatography (Adam 1999). High dilution ratios have been used in these cases (Adam 1994). Innovate LCMS method was also developed for measurement of chlorate and perchlorate in hypochlorite (Pisarenko 2009). However, mass spectroscopy is not always an available or affordable option. Therefore, ion chromatography with conductivity detector remains the most feasible option for many laboratories.

2.6.1 Quenching Agents

In previous studies, the primary goal of hypochlorite ion removal (quenching) was to stop the formation of chlorate and perchlorate over time and preserve the sample for further analysis (Pisarenko 2010, Snyder 2009). However, analytical chemistry department advice for the current study was not to inject strong oxidizing agents with concentrations higher than 10 mg/L directly in ion chromatograph, as those will significantly reduce the performance of the analytical column by reacting with its components. Precautions should also be taken with the suppressor as it is also a very sensitive device. It was very important especially due to the fact that the goal was to measure hypochlorite without any dilution for perchlorate analysis (if it would be diluted, it would become undetectable due to sensitivity limitations).

Several quenching agents were tested in the past, and it was found that malonic acid is the best option for LCMS. On the other hand, it was causing peaks that interfere with analytes when used with ion chromatography and thus was not recommended for it. The most appropriate quenching agent for ion chromatography was found to be hydrogen peroxide (Stanford 2013). The ability of peroxide to quench chlorine is explained by the fact that the standard reduction potential of H_2O_2 $(E_0 = 1.77V)$ is higher than of OCl^- $(E_0 = 0.89V)$ (Liu 2003). However, there are reports of a problematic character of chlorine use for peroxide removal and vice versa (Liu 2003). This problematic character arises from mutual interference of those two chemicals in most of the tests.

Chapter 3

Materials and Methods

3.1 Materials and Water

- Chlorate and perchlorate 1000µg/ml standards were purchased from Sigma Aldrich (analytical grade).
- Hydrogen peroxide 30% wt. in water, ACS reagent, was obtained from Sigma Aldrich.
- Manganese dioxide (>99%) was also purchased from Sigma Aldrich
- Ag On-Guard II and H On-Guard II Cartridges were obtained from Thermo Scientific/Dionex
- Water used for eluent and standards preparation: Carbon-Free water, purified using APEC WATER Reverse Osmosis System coupled with MILLIPORE Milli-Q water system.

3.2 Samples Collection

Hypochlorite samples were collected into HDPE bottles and then directly taken to the laboratory using ice chest filled with ice and then were stored in refrigerator in the laboratory. In some cases, when the samples were collected by the plant staff, they were stored in the facility refrigerator before they were taken to the lab.

3.3 Chlorine and Hydrogen Peroxide Measurement

- Measurement of chlorine concentration in hypochlorite was performed by using Hach® digital titrator and hypochlorite titration kit, Model CN-HR (Hach® 2013)
- Hydrogen peroxide concentration was measured with the Hach® hydrogen peroxide kit, Model HYP-1 (Hach® 1991)
- Quenched hypochlorite samples were tested with the Hach® DPD colorimetric test (DR-890 Colorimeter), which is intended for residual total chlorine measurements (Method 10070, Hach 2009)

3.4 Chloride, pH and Conductivity Measurements for Model Inputs

- pH was measured with Accumet AP85 pH meter from Fisher Scientific, equipped with pH probe. The meter was pre-calibrated with pH standards before each set of measurements.
- Chloride concentration was measured by the sensION MM374 from Hach®, equipped with chloride specific electrode ISE Cl-9652C, which was also pre-calibrated before each set of measurements.
- There was an attempt of measuring conductivity with Accumet AP85 using a conductivity probe, which however, was encountered with several problems that require more investigation. Therefore, conductivity was not used as an input for the model in this case.

3.5 Quenching Agent Selection

Measurement of chlorate and perchlorate in hypochlorite solutions requires pre-treatment of the sample before the analysis in ion chromatography (IC). The chlorine needs to be removed prior to the measurement as it is damaging to IC columns. Quenching agents tested in the current study are presented in Table 3.1.

Table 3.1: Quenching agents

Quenching agent	**Quenching ability**	**Interferences in the IC**
Hydrogen peroxide	Good	Not detected
Acetic acid	Poor	Moderate
Malonic acid	Good	High
Methanosulfonic acid	Good	High

Conclusion: hydrogen peroxide as a quenching agent is the most appropriate solution for the analytical system used in the study – IC with conductivity detection.

However, several problems arose with peroxide quenching:

- Hydrogen peroxide is unstable over time and therefore its concentration decreases over time.
- Hydrogen peroxide and chlorine are mutual interferences in their measurements.
- High hydrogen peroxide residuals have the same harming effects on the system components as chlorine.
- Nearly impossible to determine whether hydrogen peroxide was under dosed or overdosed during the reaction.

Out of ten reactions with the same sample and the same amounts of hydrogen peroxide added, only about one gave a final result of less than 10 mg/L in the DPD Hach® test.

Figure 3.1: DPD Hach® kit

The solution was to overdose the hydrogen peroxide and then catalytically remove the residual with small amount of manganese dioxide. Manganese dioxide has been used for the removal of excess hydrogen peroxide remaining after the reaction in previous studies, but not in an application of chlorine removal (Shelor 2011, Shelor 2012)

3.6 Quenching Procedure

The quenching procedure was done in the following manner:

1. Hypochlorite solution concentration is measured by Hach® digital titration kit, Model CN-HR

Figure 3.2: Hach® hypochlorite titration kit

2. Hydrogen peroxide solution concentration is measured by Hach® hydrogen peroxide titration kit, Model HYP-1.

Hydrogen peroxide concentration does not have to be checked each time if it is stored in refrigerator. However, it would be a good practice to check it from time to time, at least once in a month. The concentrated hydrogen peroxide needs to be diluted by a factor of 10,000 prior to titration to achieve the suitable range for the test, because this test is intended for low peroxide concentrations. This was achieved by adding 5 μL with a 10 μL pipet into a 50ml volumetric flask and dilution with milli-q water.

Figure 3.3: Hach® hydrogen peroxide test kit

3. 10ml of the hypochlorite solution are placed in a 50ml beaker with a small magnetic stirrer
4. Hydrogen peroxide 30% wt. is added carefully in portions of 100 μL using 100 μL pipet. It is continued to be added to reach about 20% excess to the calculated amount, based on measured concentrations of hypochlorite and peroxide solutions. The reaction is vigorous and exothermic.

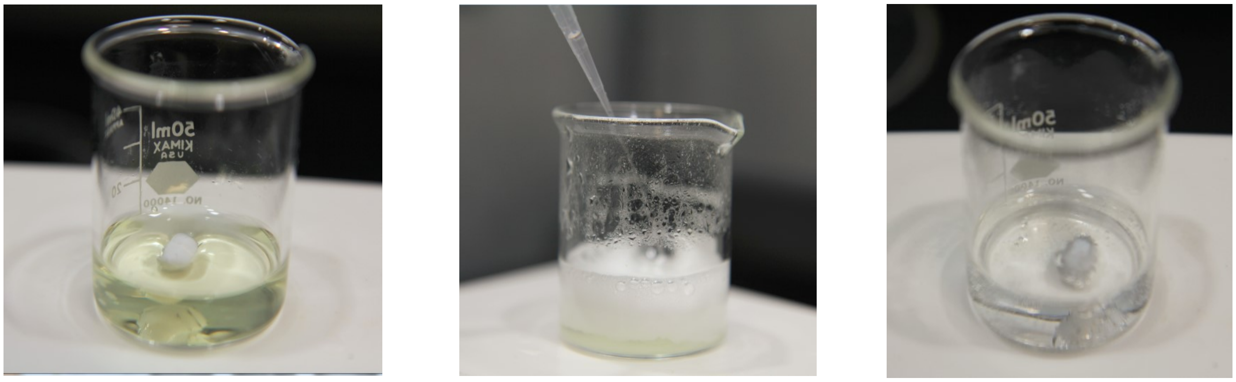


Figure 3.4: Reaction of hypochlorite with hydrogen peroxide: left-initial hypochlorite solution; middle-vigorous reaction with hydrogen peroxide that is added; right-clear solution after the reaction is over

If the hypochlorite samples that are tested have similar chlorine concentration, it is possible to skip the calculation step. The overdose can also be done visually by watching the reaction. Reaction of hydrogen peroxide with hypochlorite is vigorous, therefore when no more bubbles are noticed after addition of subsequent 100 μL peroxide, the reaction is over.

5. A small amount of manganese dioxide powder is added (about 1.5 mg for 10ml sample), as it removes the residual hydrogen peroxide. It is set on slow mixing overnight.

Figure 3.5: Addition of manganese dioxide

6. The contents of the beaker are transferred into a 10 mL volumetric flask and the volume is completed to the 10 ml mark, as some of the sample evaporates during the procedure. Prior to addition of the deionized water to the volumetric flask, it is used to wash the residual sample out of the reaction beaker.

7. If chloride concentrations in the sample are too high, On Guard II Ag and H cartridges can be used for its removal. However, in case of high chlorate concentration, 1:100 dilution is needed. Therefore, chloride peak does not interfere with chlorate peak. In a case of lower dilution ratios, it would be recommended to use the cartridges prior to the measurement in the ion chromatograph.

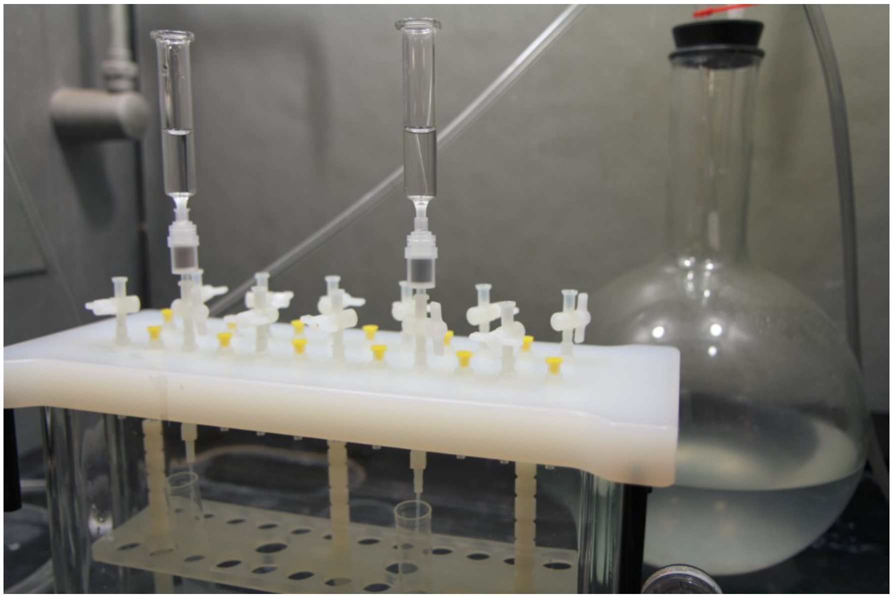


Figure 3.6: Chloride removal cartridges used with vacuum manifold

8. All the samples are filtered using 0.45μm syringe filter

3.7 Qualification and Quantification of the Analytes

Samples were analyzed using the following analytical system:

- DX500 Ion Chromatograph
- CD25 Conductivity Detector
- AS23 Analytical Column
- AG23 Guard Column
- ESRS 500 Suppressor
- Sample Loop: 25 μL
- Eluent: Carbonate

External standards were used for the qualification and quantification of the analytes. Each set that was analyzed contained at least five calibration points at the appropriate concentration ranges. In addition, a standard was injected between about each 10 samples of the same set. Most of the samples were prepared and ran in triplicates.

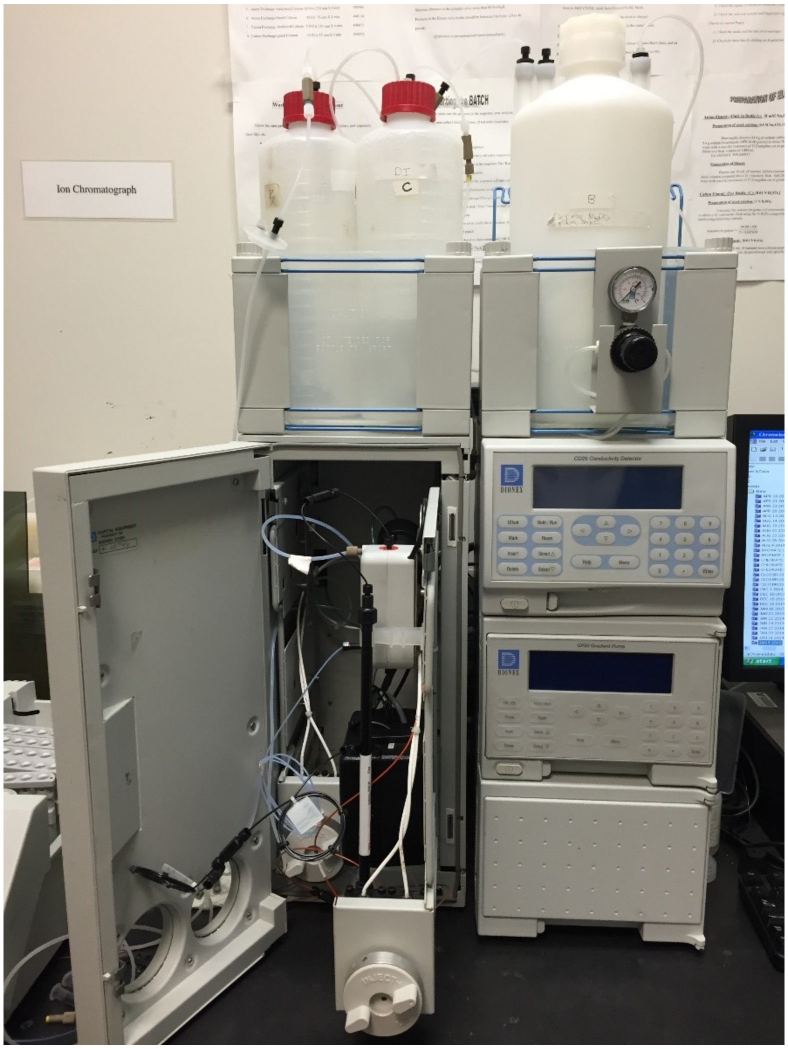


Figure 3.7: Ion chromatograph

Even though AS23 column and carbonate eluent are not intended for perchlorate measurement in water, it was possible to measure perchlorate in hypochlorite samples, due to relatively high concentrations. Samples measured for perchlorate were not diluted or passed through the cartridges, but analyzed following the quenching procedure. It was possible to detect perchlorate down to 0.25 ppm level in the treated hypochlorite samples, which was sufficient to meet the goals of the study.

3.8 Calibration Curves

Construction of calibration curve is usually done by injecting the known concentrations of standard solutions of the relevant compounds, and collecting the response that each concentration caused in the chromatograph. Typically, at least 5 points should be present to construct a calibration curve. Then, the concentration is plotted against the response and the linear regression line is fitted. The higher the linearity of the curve, the better precision can be achieved in the measurement. Afterwards, samples with unknown concentration are tested, and the concentration is found from the equation of the calibration curve. It is important that the concentrations of the samples stay within the calibration curve limits since the extrapolation can bring a large error. If the concentrations fall outside of the calibration curve, dilution should be done (for high concentrations) or new calibration curve constructed for the required concentration range.

Two main possibilities for construction of the calibration curve are:

I. Forcing the y-intercept to zero
II. Letting the regression model to have a non-zero y-intercept

Though both of these methods are widely used, Dylan et al gives some guidelines for making a decision which method to choose. For making the decision, the Standard Error of y-intercept (SEy) should be found. It can be found using the regression function in any statistical software. The following will apply:

$$\begin{aligned} &if\ y-intercept > SE_y \quad \Rightarrow b = y-intercept\ value \\ &if\ y-intercept \le SE_y \quad \Rightarrow b = 0 \end{aligned}$$

The proper choice of the method will reduce the error associated with the regression model.

(Dylan 2009a)

3.9 Limit of Detection (LOD)

LOD is the smallest concentration of the analyte at which it can be confidently stated that the analyte is present.

Three main methods exist to determine the LOD:

I. Visual evaluation

Visual evaluation is not a quantitative technique, and is based on the visual confidence of the analyst that the peak is present.

II. Signal-to-noise relation

Value of signal to noise (S/N) = 3 is usually used to determine LOD. This technique is also subject to analyst bias, due to manual measurement of the signal and the noise levels.

III. Standard deviation of the response and the slope

This technique relies on the overall performance of the calibration curve:

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

S': $x - variable\ slope$

σ: $estimated\ by\ SE_y$

The third method of standard deviation of the response and the slope seems to be the preferred method according to the author. (Dylan 2009b)

Chapter 4

Laboratory Results

4.1 Calibration Curves

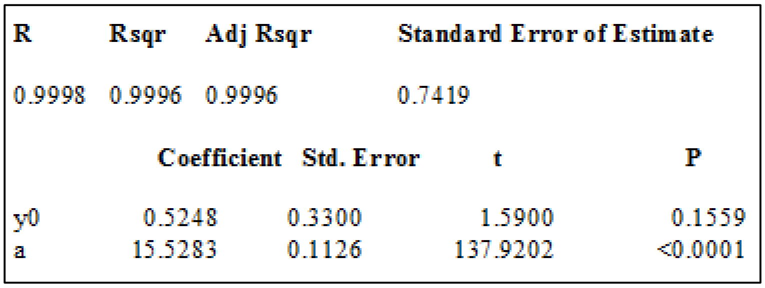
For preparation of each calibration curve, at least five points were used in an appropriate range, as mentioned earlier. To decide whether to set the intercept as zero for the calibration curve, the strategy recommended by Dylan et al. was performed, as described earlier.

4.1.1 Perchlorate

Table 4.1: Concentration vs. response of perchlorate

Concentration[ppm]	Response (peak area) [μS*t]
1	0.067
2.5	0.1437
5	0.2897
7.5	0.4385
10	0.5972
25	1.5155
50	3.1733
75	4.8858
100	6.3591

Table 4.2: Regression analysis performed for perchlorate data using statistical software (Sigma Plot 12.5)



R	Rsqr	Adj Rsqr	Standard Error of Estimate
0.9998	0.9996	0.9996	0.7419

	Coefficient	Std. Error	t	P
y0	0.5248	0.3300	1.5900	0.1559
a	15.5283	0.1126	137.9202	<0.0001

From the data given in Table X:

$$y - intercept = 0.5248$$

$$SE_y = 0.3300$$

$$y - intercept > SE_y \Rightarrow b = y - intercept\ value$$

$$0.5248 > 0.3300 \Rightarrow b = 0.5248$$

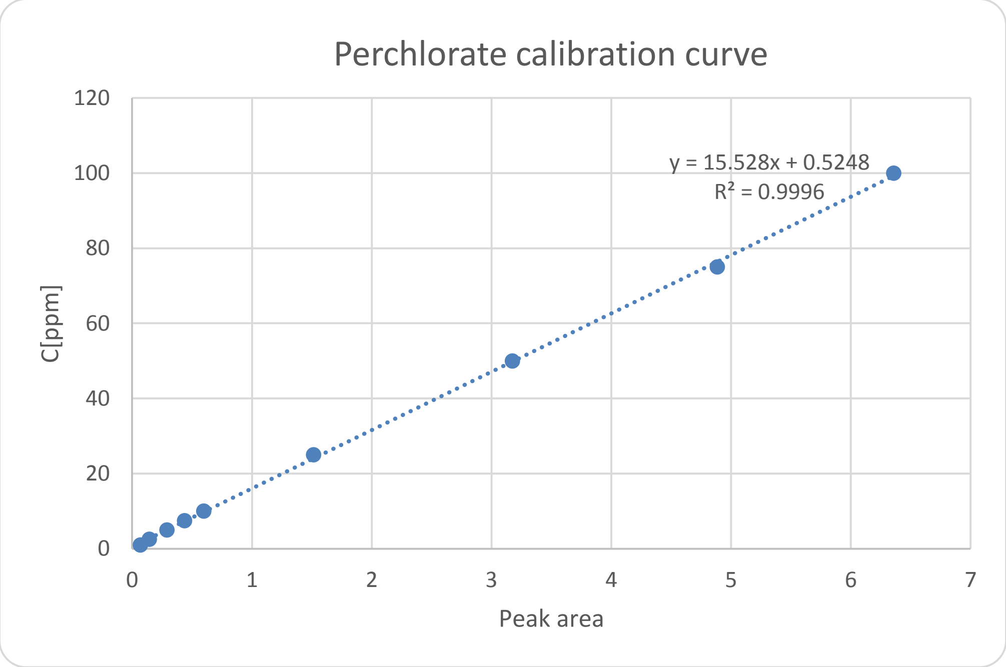


Figure 4.1: Sample perchlorate calibration curve

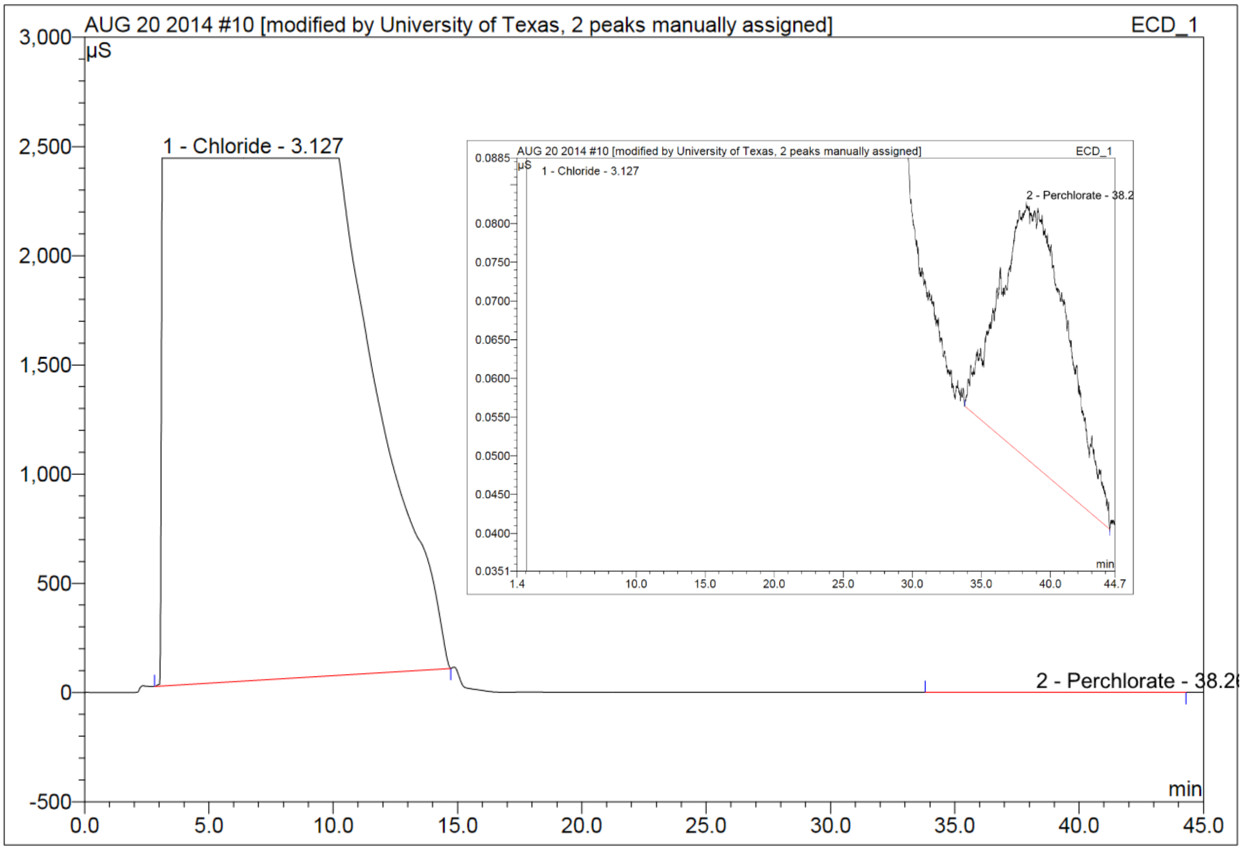


Figure 4.2: Perchlorate chromatogram

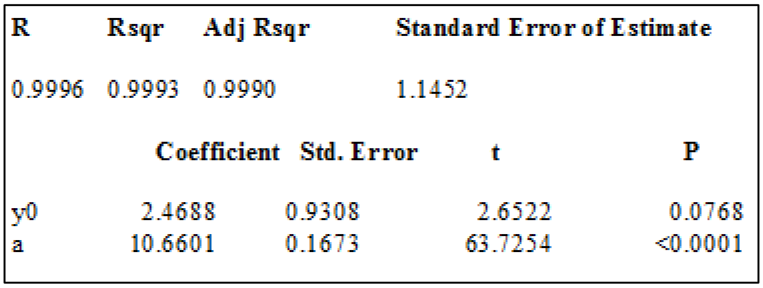
Retention time for perchlorate – 38min

4.1.2 Chlorate

Table 4.3: Concentration vs. response of chlorate

Concentration[ppm]	Response (peak area) [µS*t]
10	0.7976
25	2.0871
50	4.3934
75	6.7011
100	9.2529

Table 4.4: Regression analysis performed for chlorate data using statistical software



R	**Rsqr**	**Adj Rsqr**	**Standard Error of Estimate**
0.9996	0.9993	0.9990	1.1452

	Coefficient	**Std. Error**	**t**	**P**
y0	2.4688	0.9308	2.6522	0.0768
a	10.6601	0.1673	63.7254	<0.0001

$$y - intercept = 2.4688$$
$$SE_y = 0.9308$$

$$y - intercept > SE_y \;\; \Rightarrow b = y - intercept\ value$$
$$2.4688 > 0.9308 \;\; \Rightarrow b = 2.4688$$

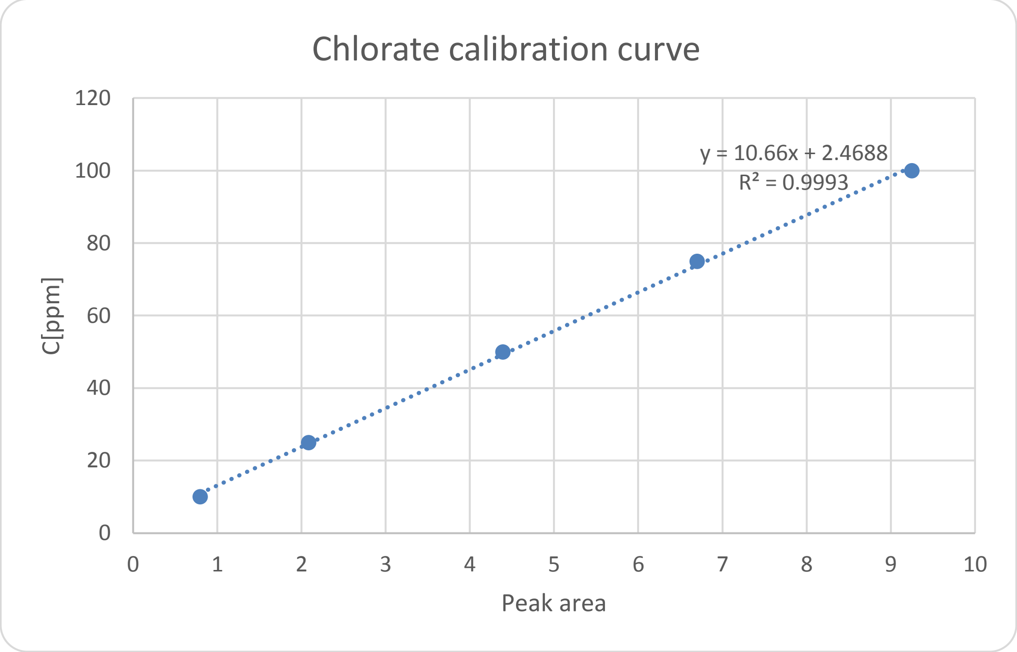


Figure 4.3: Sample chlorate calibration curve

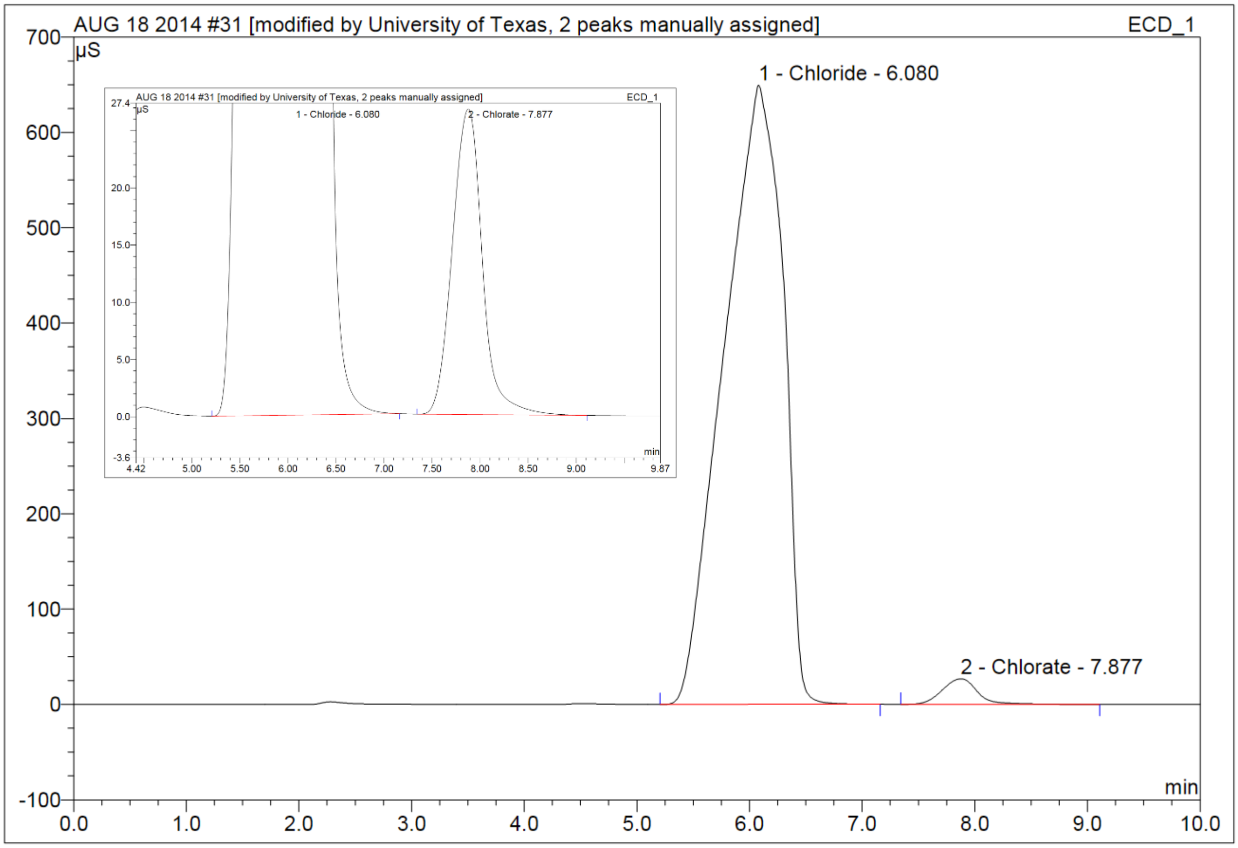


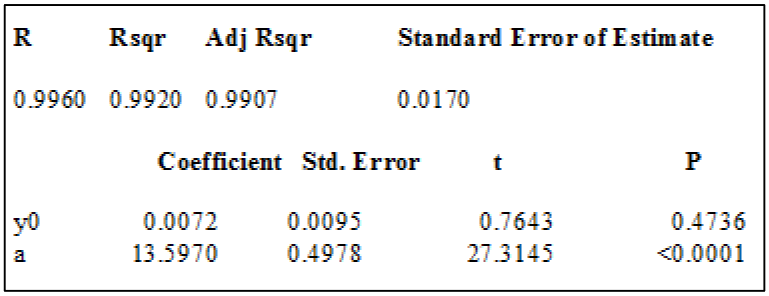
Figure 4.4: Chlorate chromatogram

Retention time for chlorate – 7.9min

In a similar manner, appropriate calibration curves were developed for other concentration ranges. For the majority of the curves, b could not be set at zero.

For the low chlorate concentrations calibration curve, which was intended for the measurement of the compound in finished water, the conditions for setting intercept as zero applied, as shown in Table 4.5.

Table 4.5: Regression analysis performed for low concentrations of chlorate



R	Rsqr	Adj Rsqr	Standard Error of Estimate
0.9960	0.9920	0.9907	0.0170

	Coefficient	Std. Error	t	P
y0	0.0072	0.0095	0.7643	0.4736
a	13.5970	0.4978	27.3145	<0.0001

$$y - intercept = 0.0072$$
$$SE_y = 0.0095$$

$$y - intercept \le SE_y \quad \Rightarrow b = 0$$
$$0.0072 < 0.0095 \quad \Rightarrow b = 0$$

Calibration curves for both chlorate and perchlorate had correlation coefficients (R^2) higher than 0.99. There was a slight difference between the regression equations at each run, but they stayed relatively close to each other. In addition, during the run of a set, a standard was injected in approximately each 10 samples (in accordance with EPA method 300.1). The deviation between peak areas of standards in the same set stayed within 5%.

4.2 Limit of Detection

As explained earlier, there are several methods for finding the limit of detection. Analytical chemistry experts at UTA have advised two of these methods: the visual evaluation and the standard deviation of the response and the slope. As a result, it was decided to check both and select the conservative result.

4.2.1 Perchlorate

Standard deviation of the response and the slope method:

$$LOD = \frac{3.3 \times \sigma}{S'} = \frac{3.3 \times 0.3300}{15.529} = 0.07\,ppm$$

S': $x - variable\ slope$

σ: $estimated\ by\ SE_y$

The values were taken from Table 4.2 for perchlorate regression analysis.

Visual evaluation:

Visual evaluation showed that the lowest concentration at which perchlorate peak could be recognized with the current system capability was 0.25ppm.

Therefore, 0.25ppm was the LOD value for perchlorate

4.2.2 Chlorate

- For the calibration curve intended for the measurement of chlorate in hypochlorite solutions (relatively high concentrations):

  Standard deviation of the response and the slope method:

  $$LOD = \frac{3.3 \times \sigma}{S'} = \frac{3.3 \times 0.9308}{10.66} = 0.288\,ppm$$

  The values were taken from Table 4.4

  Visual evaluation:

  Visual evaluation showed that the lowest concentration at which chlorate peak could be recognized with the current system capability was 0.03ppm.

Therefore, 0.3ppm (0.288ppm rounded up) was the LOD value for chlorate, when detecting its concentrations in hypochlorite solutions.

- For calibration curve intended for measurement of chlorate in water (relatively low concentrations):

$$LOD = \frac{3.3\times\sigma}{S'} = \frac{3.3\times 0.0095}{13.597} = 0.0023\,ppm$$

However, as mentioned, visual evaluation can recognize chlorate peak only at 0.03ppm.

Therefore, LOD for chlorate detection in water was 0.03ppm.

4.3 Spiking Experiments

Hypochlorite samples were spiked with standards to check the recoveries of the process and to validate the whole method. The results of the tests for perchlorate and chlorate recoveries from the spiked samples are presented in Tables 4.6 and 4.7. The samples were spiked with three different concentrations, in triplicates for each sample. As can be seen in these tables, spike recoveries were above 90%. These are very acceptable results and it was concluded that the method could be used in a subsequent testing of chlorate and perchlorate in hypochlorite samples from the field. Spike recoveries were calculated using the following formula, which accounts for volume corrections (needed when the volume of the added standard is significant):

$$\%recovery = \frac{spiked\ sample\ conc.(measured) - sample\ conc.\times volume\ fraction}{standard\ added\ conc.\times volume\ fraction}\times 100$$

Table 4.6: Hypochlorite samples spiked with perchlorate

Perchlorate (ppm)				
	not spiked	spiked 1	spiked 2	spiked 3
Duplicate 1	Not detectable	4.974	9.921	23.24
Duplicate 2	Not detectable	4.918	9.887	23.44
Duplicate 3	Not detectable	4.814	9.045	23.42
Average		4.902	9.617	23.37
SD		0.081	0.496	0.111
Average % recovery		98.0%	96.2%	93.5%
%RSD		1.66	5.16	0.48

Table 4.7: Hypochlorite samples spiked with chlorate (after dilution)

Chlorate (ppm)				
	not spiked	spiked 1	spiked 2	spiked 3
Duplicate 1	35.56	38.42	40.29	50.07
Duplicate 2	35.89	38.77	42.53	53.35
Duplicate 3	35.36	38.23	40.94	50.29
Average	35.60	38.48	41.25	51.24
SD	0.268	0.274	1.152	1.837
Average % recovery		93.1	92.1	98.1
%RSD	0.75	0.71	2.79	3.59

4.4 Incubation Experiment

4.4.1. Description and Results

Two practical ways for diluting high strength hypochlorite were tested and then compared to the Hypochlorite Assessment Model: dilution with softened water and low strength hypochlorite. Both solutions used for dilution were collected from an OSG water treatment plant. While it is more likely that softened water will be used for dilution, low strength hypochlorite was also tested to see if it yields better results. The use of low strength hypochlorite for dilution is possible only for plants that produce OSG hypochlorite, but desire to store bulk hypochlorite for emergency purposes. Therefore, the intention was to check the possibility of a bulk hypochlorite dilution with OSG hypochlorite for such a facility.

A sample of high strength was collected from a delivery truck at one of the facilities that uses high strength hypochlorite. Two samples were collected from a facility that is generating on-site low strength hypochlorite (0.8%) for the purposes of dilution. The facility generates low strength hypochlorite using a water softening system for the purpose of brine preparation. Both low strength hypochlorite (0.8%) and softened water were collected.

Hypochlorite samples at different dilution ratios were incubated to check the impact of dilution on the stored material. Five samples at different dilution ratios were incubated at temperature of 40ºC for 63 days:

- 100% High strength hypochlorite
- 50% High strength hypochlorite + 50% Softened water
- 50% High strength hypochlorite + 50% Low strength hypochlorite
- 25% High strength hypochlorite + 75% Softened water
- 25% High strength hypochlorite + 75% Low strength hypochlorite

Samples were placed into 2L HDPE bottles, and every 7 days a 100ml sample was collected from each bottle. All the samples were analyzed for chlorine and chlorate. High strength and some of the medium strength samples were analyzed for perchlorate.

It should be noted that in this experiment the samples were not analyzed in triplicates for chlorate and perchlorate due to the vast number of samples and laboratory limitations, and because the primary goal of this experiment was to determine the trends rather than exact concentrations. Due to this reason, standard deviation could not be calculated and added to the graphs.

Total chlorine measurements were done in triplicates. However, these measurements were done with the DPD Hach® kit because at that stage of the experiment, the digital titrator and cartridges were not available. The use of the DPD kit required very high dilutions (x 20,000), which can introduce an error into the results, especially when dealing with low concentrations. This could be a possible reason for several points with deviation from the trend, especially in the four fold dilution. Results from various dilution experiments are presented in Figures 4.5-4.7.

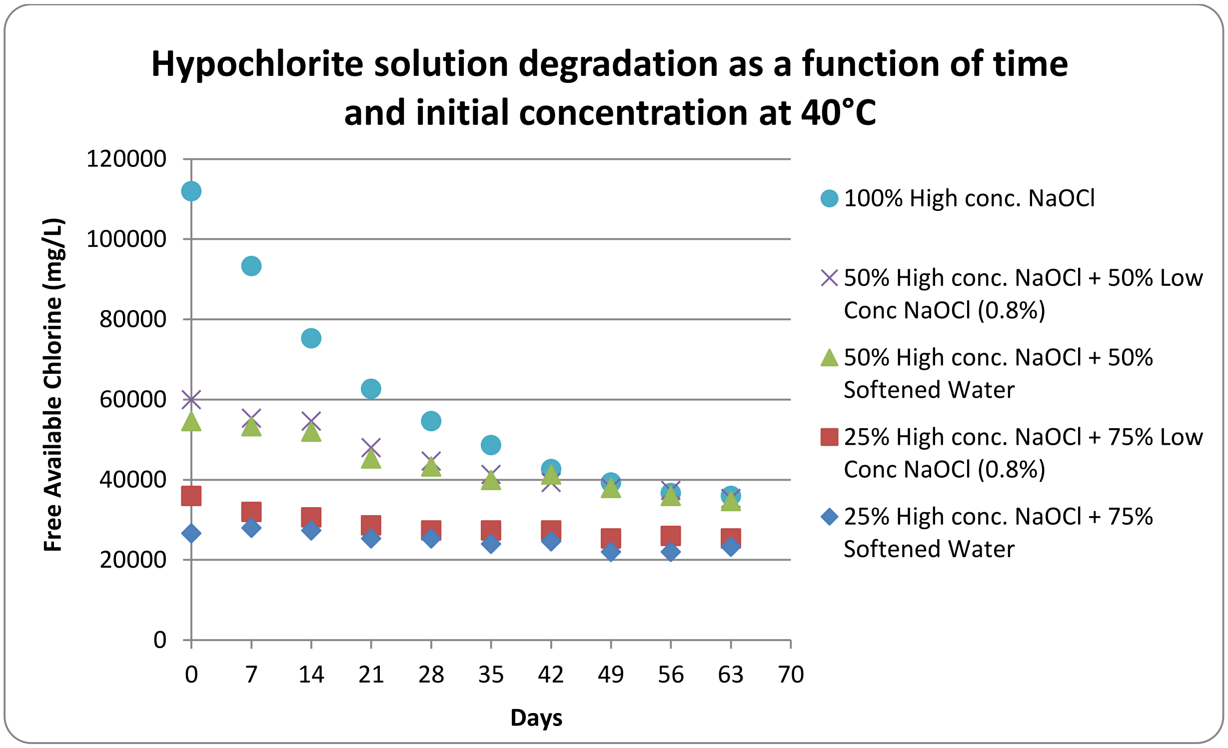


Figure 4.5: Hypochlorite solutions degradation as a function of time at 40ºC

It can be seen that the undiluted sample starts with relatively high chlorine concentration, and after 60 days degrades to about 1/3 of initial chlorine concentration. The degradation is much slower for solutions that were diluted with 1:1 dilution ratio, and slows down even more for solutions with 2:1 dilution ratio. This means that at high temperatures the decrease in chlorine strength will be higher for higher strength hypochlorite solutions, a fact that corresponds to the previous studies. Also, no significant difference can be seen in samples diluted with low strength hypochlorite (0.8%) and samples diluted with softened water at the same ratios.

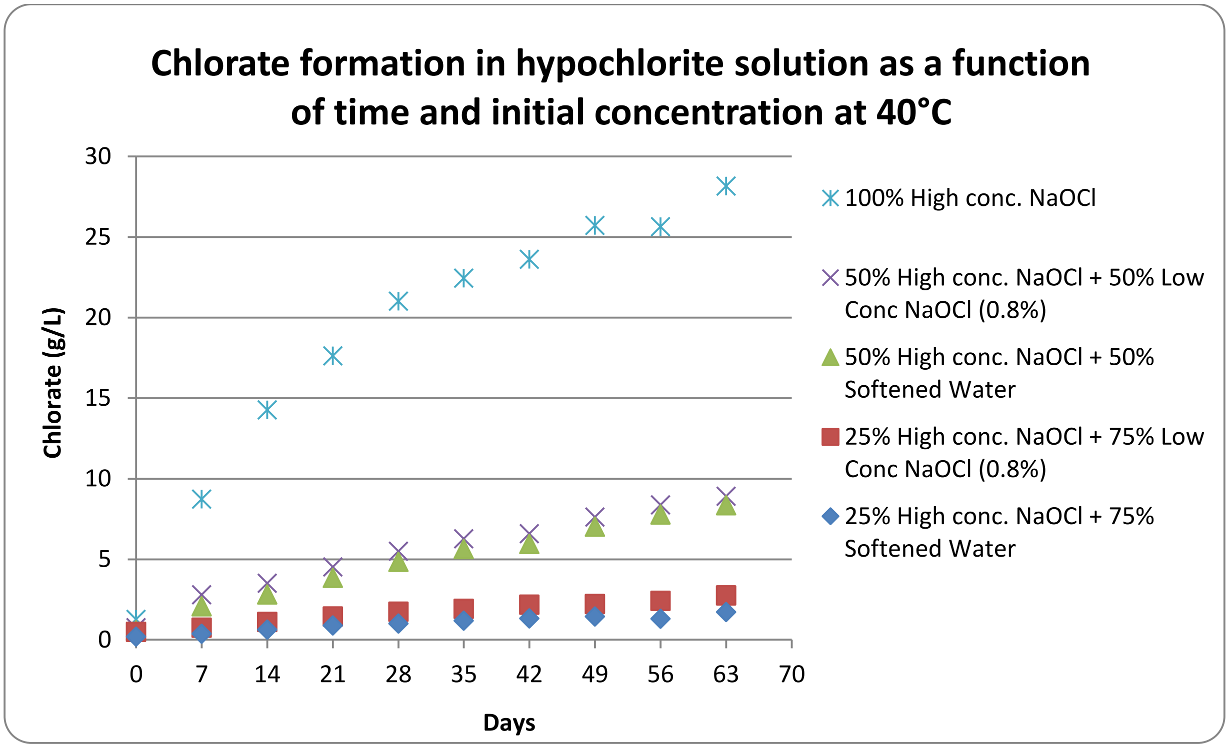


Figure 4.6: Chlorate formation in hypochlorite solutions as a function of time at 40ºC

Similarly to hypochlorite degradation, chlorate formation is much higher in high strength solutions. There is an about 30 fold increase in the chlorate concentration in the high strength solution relatively to the initial chlorate concentration. Chlorate formation slows down significantly at 1:1 dilution ratio, and even more at 2:1 dilution. Samples diluted with low strength hypochlorite (0.8%) and samples diluted with softened water at the same ratios have similar chlorate formation trends.

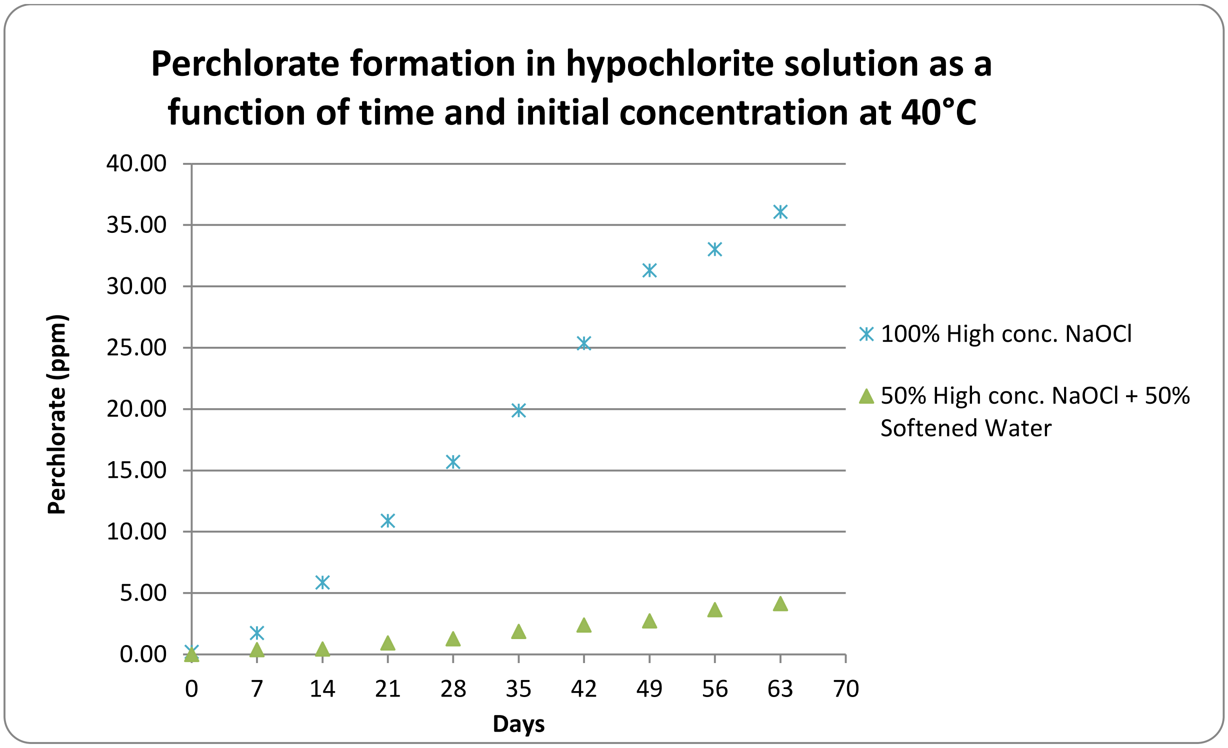


Figure 4.7: Perchlorate formation in hypochlorite solutions as a function of time at 40ºC

The formation of perchlorate in the high strength sample was compared to a sample diluted with softened water at 1:1 dilution ratio. Perchlorate comparison was limited to these two samples due to laboratory constraints. However, these two samples are sufficient to show that there is a significant decrease in perchlorate formation even at 1:1 dilution ratio.

4.4.2 Comparison to the Model

Incubation results were compared to the Hypochlorite Assessment Model available in AWWA website. Model calculations are based on predictive algorithms derived from earlier research on the subject and user-defined inputs, such as storage conditions. Other inputs that define the initial solution are recommended, such as pH, chloride concentration, conductivity and the initial chlorate and perchlorate concentrations. If some of the values are not inputted, model defaults will be used. However, the initial chlorine concentration and temperature are required inputs. Comparison of hypochlorite degradation and chlorate formation in each of the experiments to the model is shown in Figures 4.8-4.17.

In this experiment, chlorine, temperature, pH, chloride, chlorate concentrations were inputted. Inputs for each of the five initial samples are summarized in the following table:

Table 4.8: Hypochlorite model inputs for the incubation experiment

Description	100% High strength hypochlorite	50% High strength + 50% Low strength	50% High strength + 50% softened water	25% High strength + 75% Low strength	25% High strength + 75% softened water
Chlorine [g/L]	112.0	60.0	54.67	36.0	26.67
Temperature	40ºC	40ºC	40ºC	40ºC	40ºC
Chlorate [g/L]	0.906	0.578	0.412	0.452	0.155
pH	12.75	12.49	12.46	12.12	12.12
Chloride[M]	1.60	0.7941	0.6971	0.4292	0.2923

4.4.2.1 - 100% High strength hypochlorite

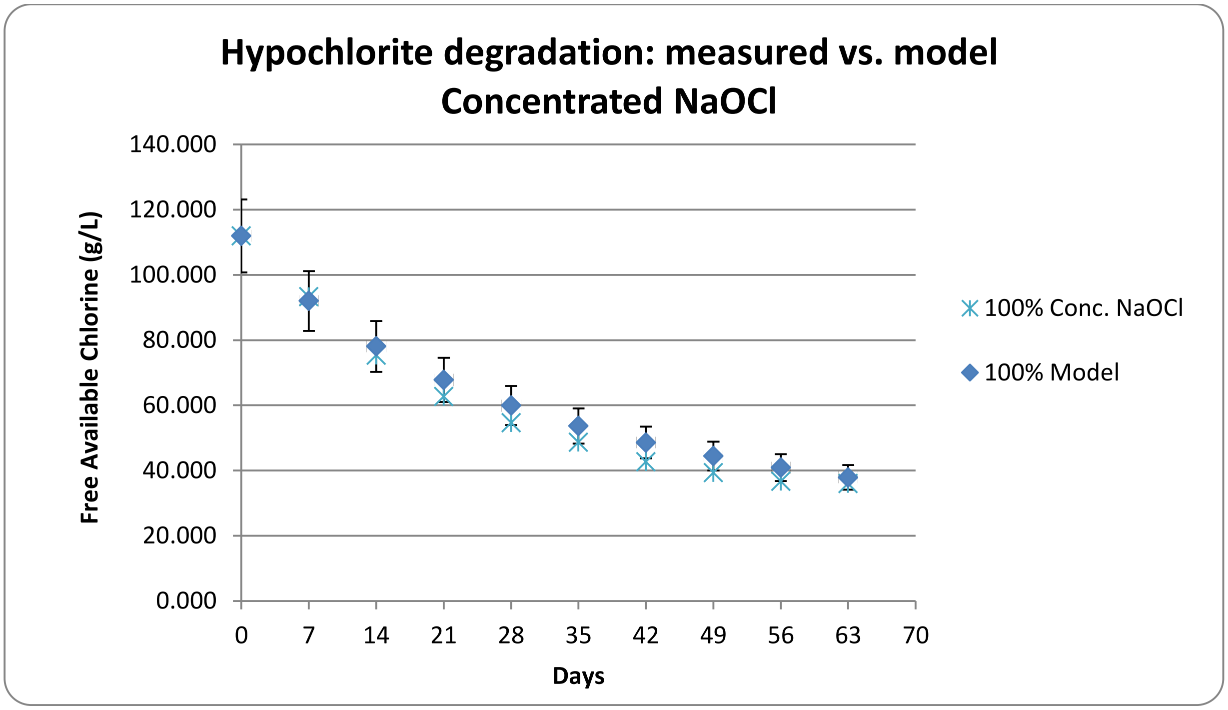


Figure 4.8: Hypochlorite degradation in concentrated hypochlorite incubated at 40ºC

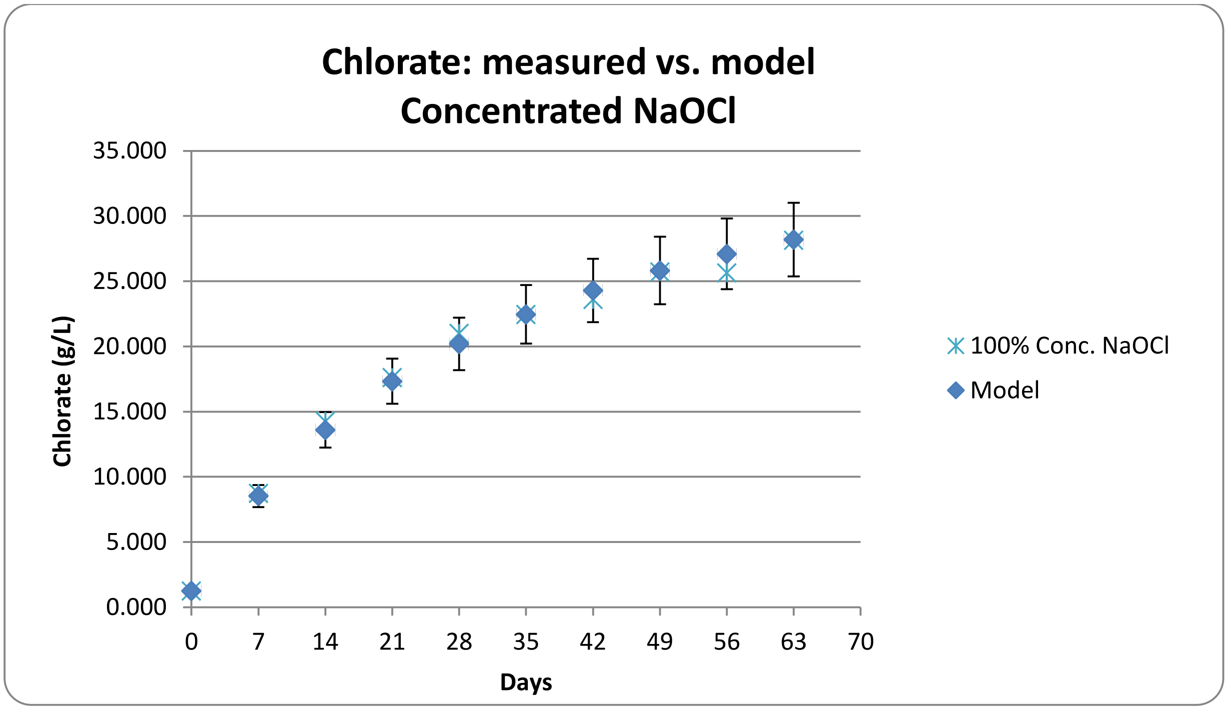


Figure 4.9: Chlorate formation in concentrated hypochlorite incubated at 40ºC

4.4.2.2 - 50% High strength hypochlorite + 50% Softened water

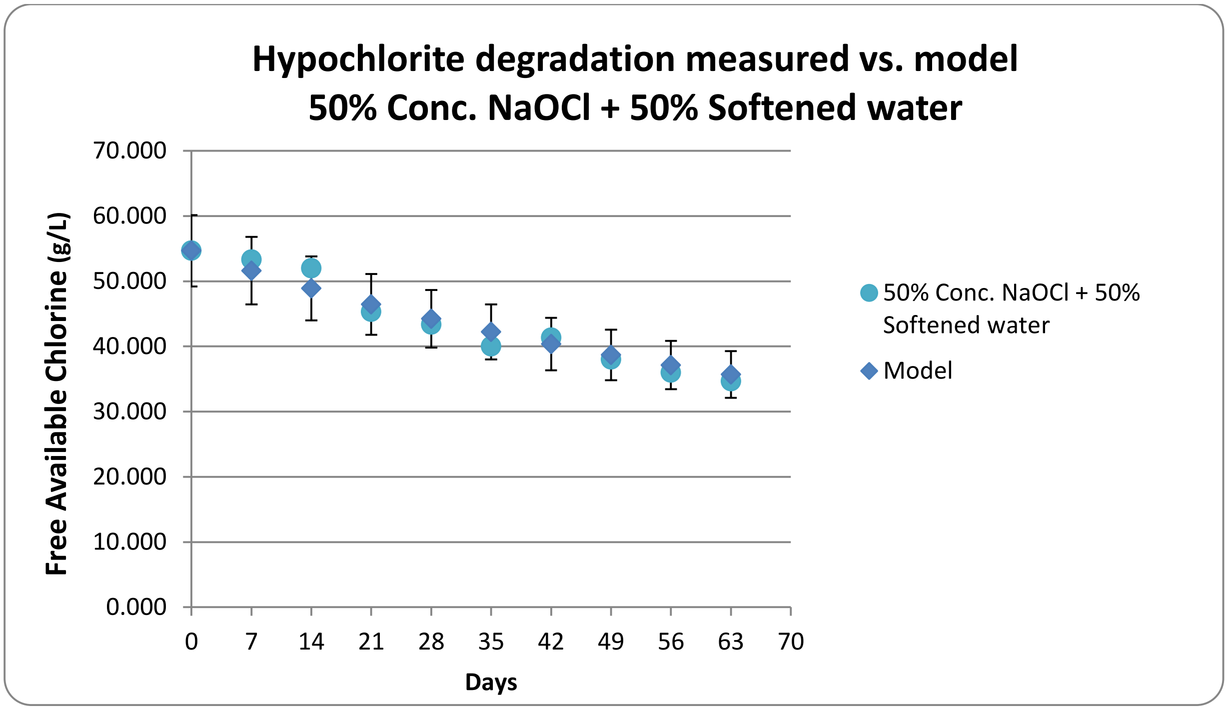


Figure 4.10: Hypochlorite degradation in high strength hypochlorite diluted 1:1 with softened water (used for OSG hypochlorite production), incubated at 40°C

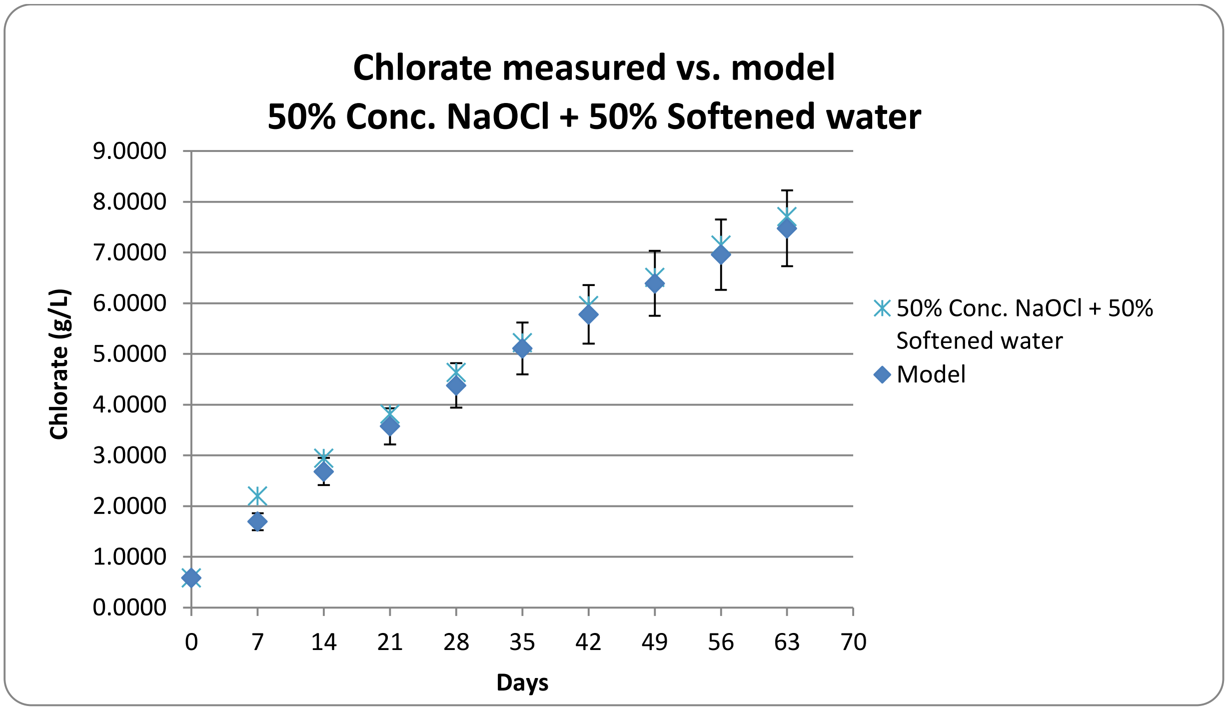


Figure 4.11: Chlorate formation in high strength hypochlorite diluted 1:1 with softened water (used for OSG hypochlorite production), incubated at 40°C

4.4.2.3 - 50% High strength hypochlorite + 50% Low strength hypochlorite

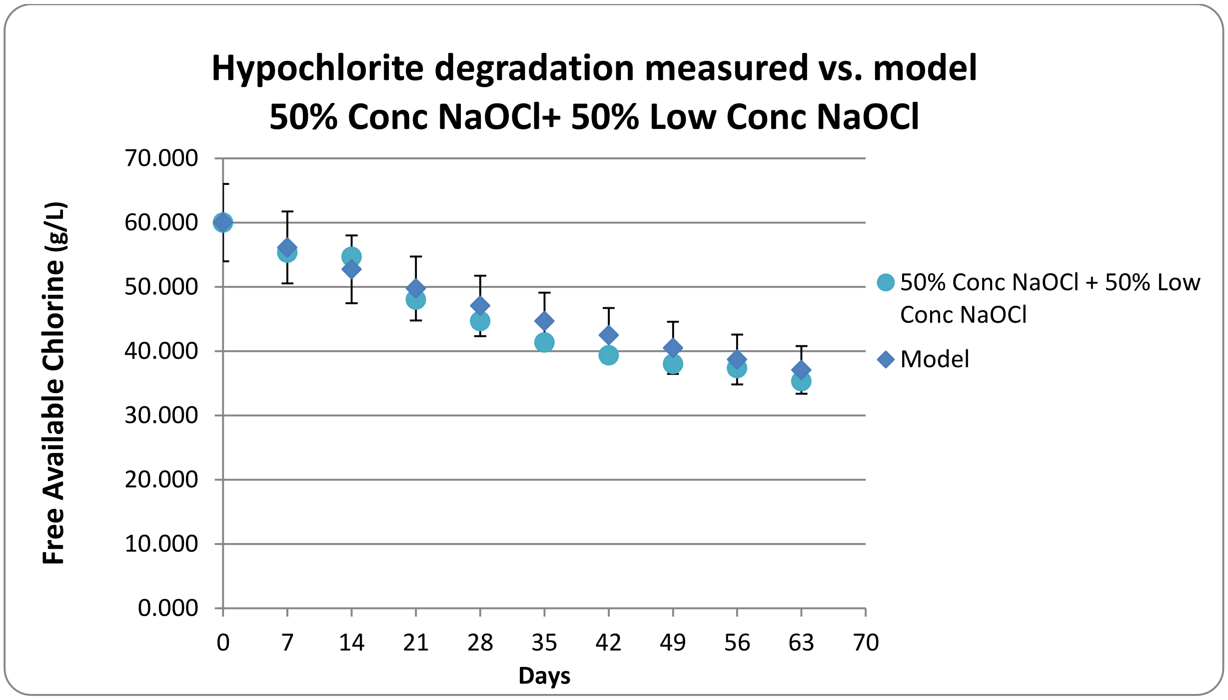


Figure 4.12: Hypochlorite degradation high strength hypochlorite diluted 1:1 with low strength (OSG) hypochlorite incubated at 40ºC

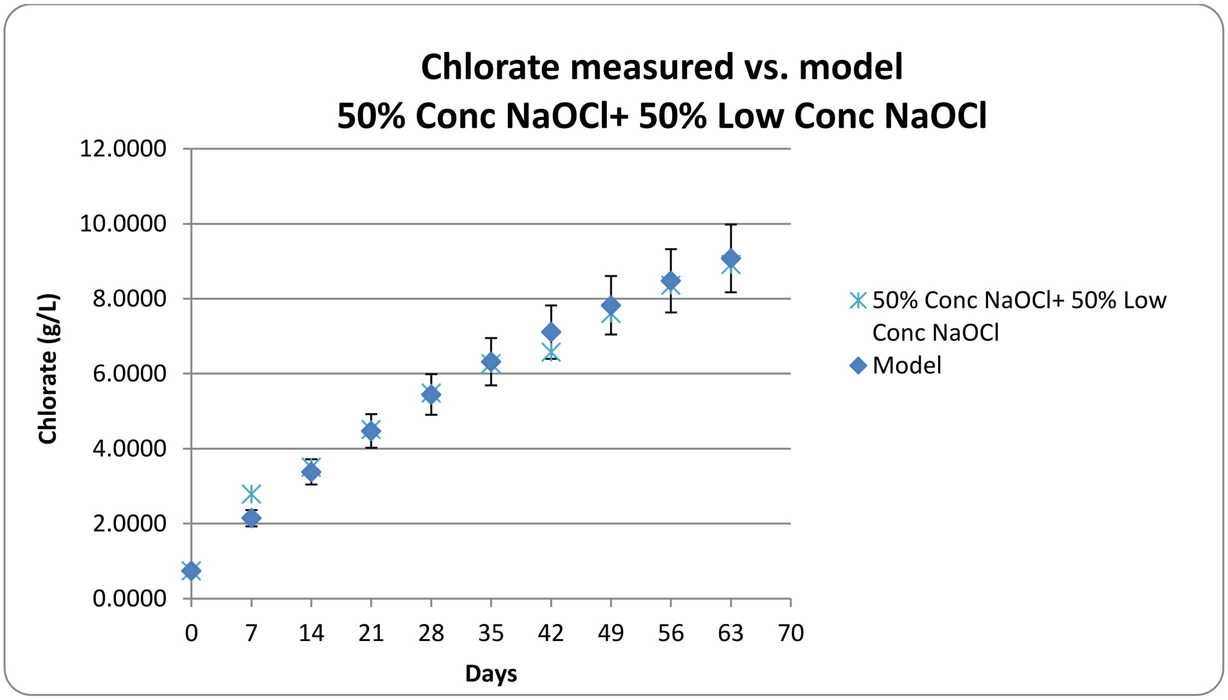


Figure 4.13: Chlorate formation in high strength hypochlorite diluted 1:1 with low strength (OSG) hypochlorite incubated at 40ºC

4.4.2.4 - 25% High strength hypochlorite + 75% Softened water

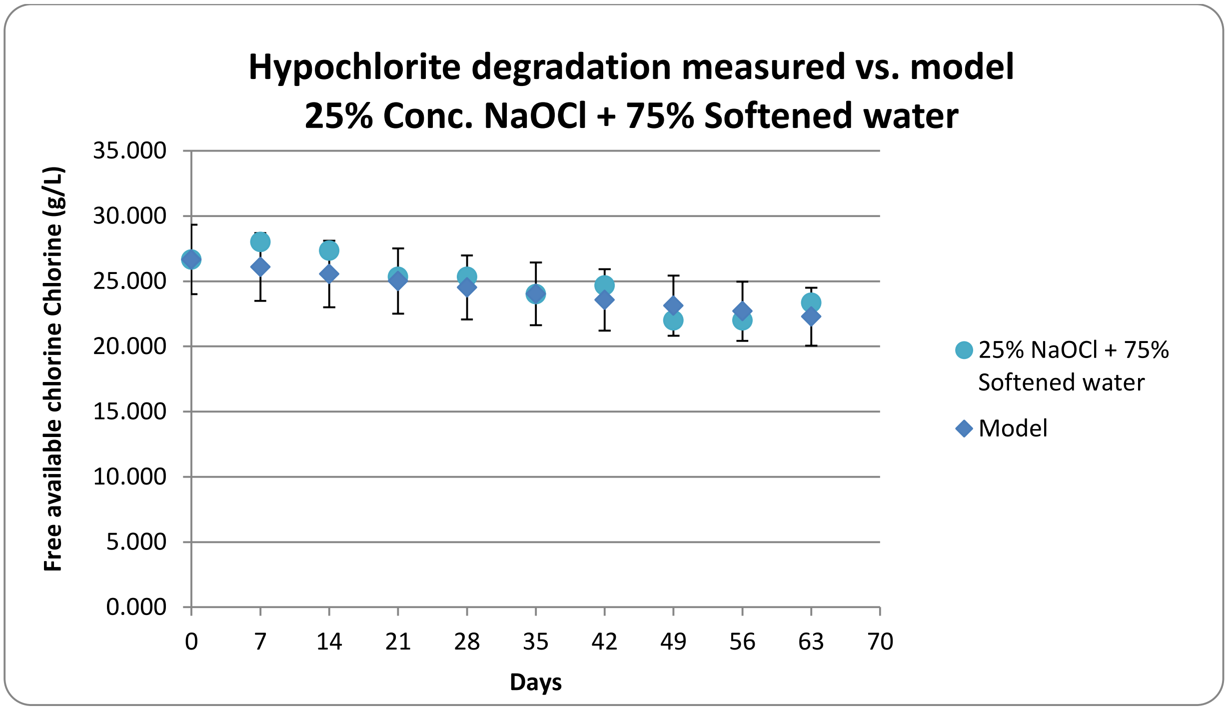


Figure 4.14: Hypochlorite degradation in high strength hypochlorite diluted 2:1 with softened water (used for OSG hypochlorite production), incubated at 40ºC

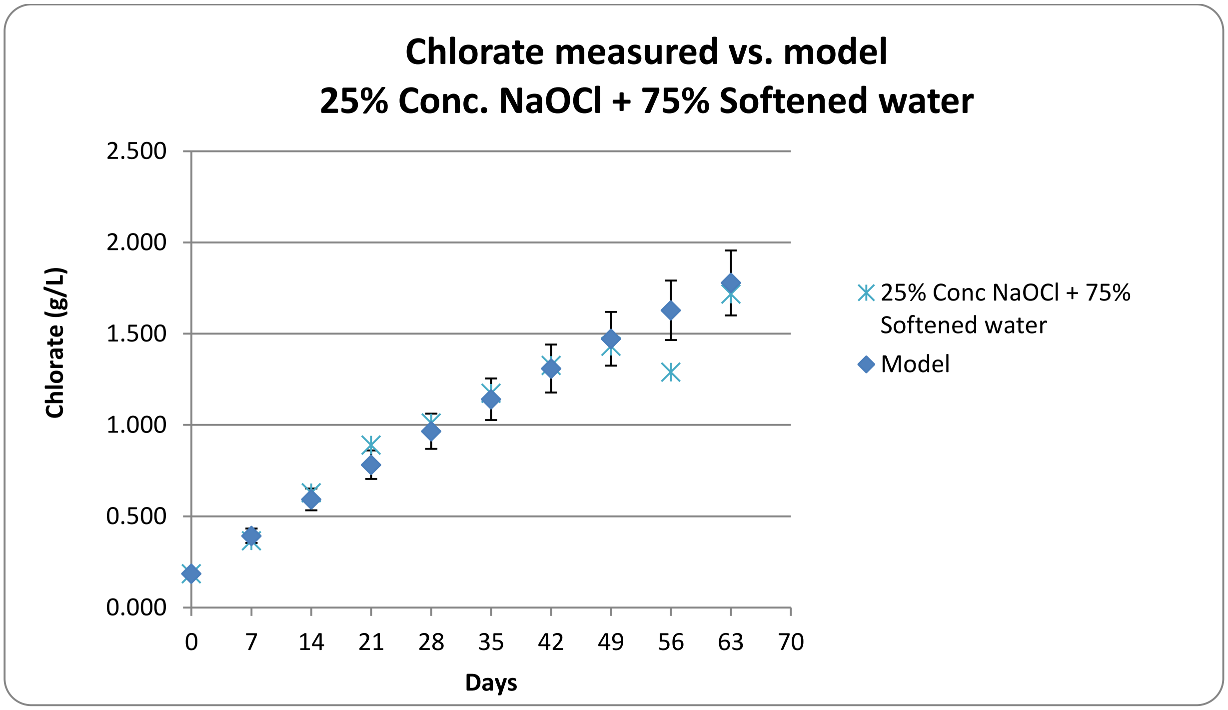


Figure 4.15: Chlorate formation in high strength hypochlorite diluted 2:1 with softened water (used for OSG hypochlorite production), incubated at 40ºC

The deviation from the model is within 10% for most of the data points for all the four experiments. Some of the points have higher deviation, which can be attributed to experimental error that can be more significant because incubation measurements were not done in triplicates (as a result of experiment constraints). The main goal of the experiment was to see the degradation trend in different concentrations of hypochlorite.

4.4.2.5 - 25% High strength hypochlorite + 75% Low strength hypochlorite

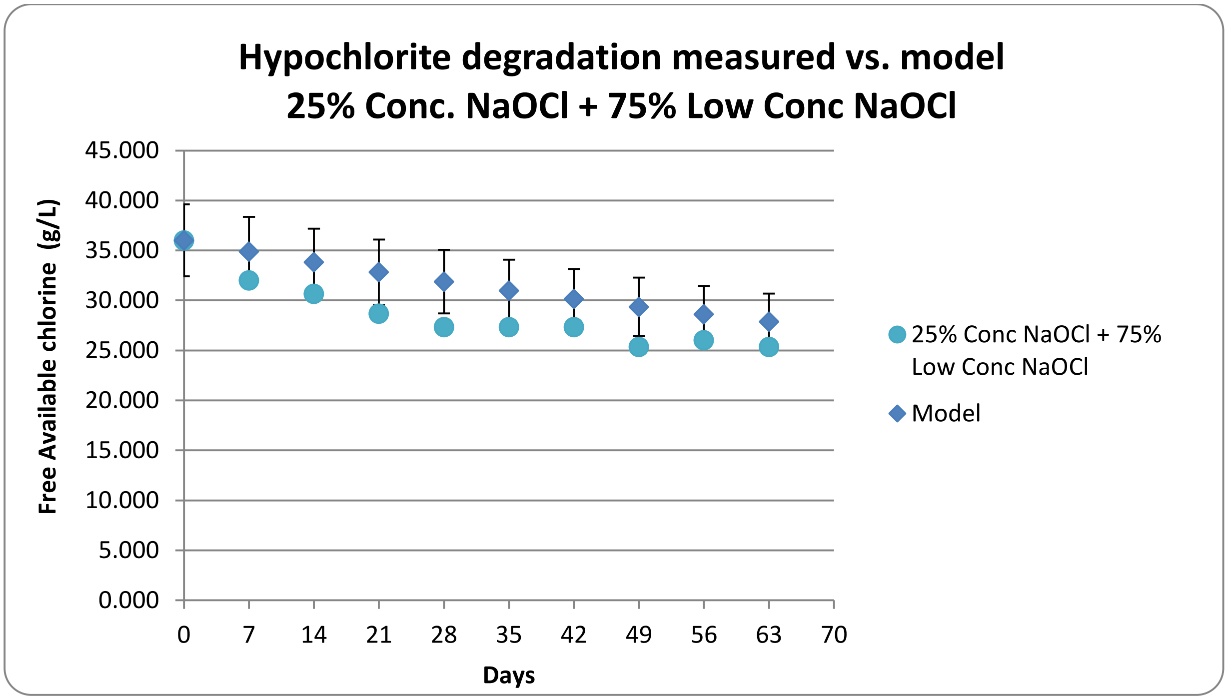


Figure 4.16: Hypochlorite degradation in high strength hypochlorite diluted 2:1 with low strength (OSG) hypochlorite incubated at 40ºC

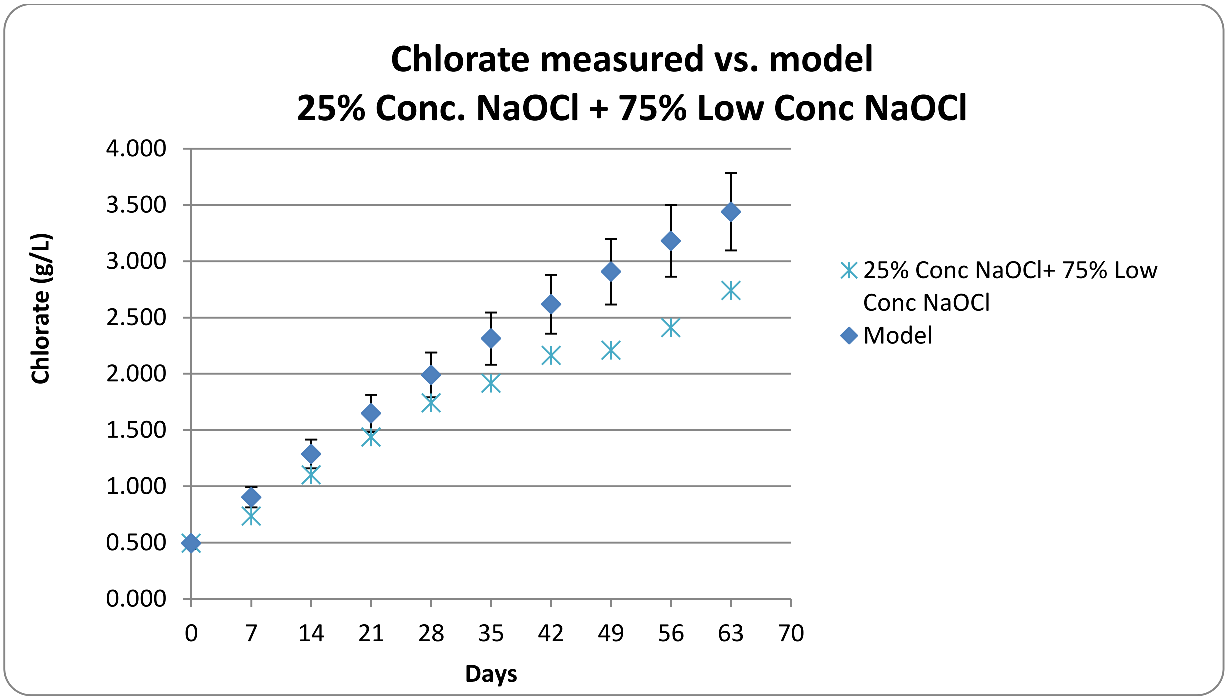


Figure 4.17: Chlorate formation in high strength hypochlorite diluted 2:1 with low strength (OSG) hypochlorite incubated at 40ºC

25% High strength hypochlorite + 75% Low strength hypochlorite experiment has the highest deviation from the model out of the five experiments. As can be seen in Figure 4.16, hypochlorite degradation seems to be higher than predicted. On the other side, as shown in Figure 4.17, chlorate formation is slower than predicted. Deviation from the model can be attributed to various factors:

- Low strength hypochlorite constitutes 75% of the solution and the model is not designed for on-site generated hypochlorite due to the pH range (the model is designed for pH 11-13). Even though that after the mixing with 25% of high strength hypochlorite the pH was in a range suitable for the model (12.12), it is possible that some elements in the low strength hypochlorite are slowing down the formation of chlorate. On the other hand, trace metals, for example, could cause higher hypochlorite degradation via oxygen pathway, without an increase in the formation of chlorate.
- No attempts in the literature to dilute high strength hypochlorite with low strength hypochlorite were found. Therefore, the outcome of such a dilution is not completely predicted.

4.4.2.6 - Conclusions from comparison to the model

1. For high strength hypochlorite, the incubation experiment data lays within 10% deviation from the Hypochlorite Assessment Model prediction. Therefore, the model can be considered as reliable for prediction of hypochlorite behavior at constant temperatures and the experiment can proceed to the next stage – comparison of real field data to the model prediction.
2. Most of the data in the incubation experiment was within 10% deviation from the Hypochlorite Assessment Model prediction, both for hypochlorite degradation and chlorate formation (except the solution that contained 75% of low strength hypochlorite). These results are satisfactory for the purpose of the experiment and show in an unambiguous way that the model can show the difference in degradation for various dilution ratios of hypochlorite. This will help with the assessment of the dilution impact in field storage conditions.
3. The data for the solution that contained 75% low strength hypochlorite (and 25% high strength hypochlorite) deviates from the model at a degree exceeding 10%. There could be various possible reasons for that, however, the exact cause is not known. In order to make a conclusion, reproducibility of the experiment has to be checked by repeating the experiment and comparing to the model again.

Chapter 5

Water Treatment Facilities

5.1 Facility #1 Details

5.1.1 Tank Properties

The hypochlorite storage tank at Facility I is made of fiberglass-reinforced plastic (FRP), with sidewall thickness of 0.210" and bottom thickness of 0.271". Hypochlorite height level can be measured up to about 14.5ft, however, maximum operating height is 14ft. If hypochlorite reaches a level higher than the maximum operating height, the “high” alarm will sound. The facility is equipped with two identical tanks.

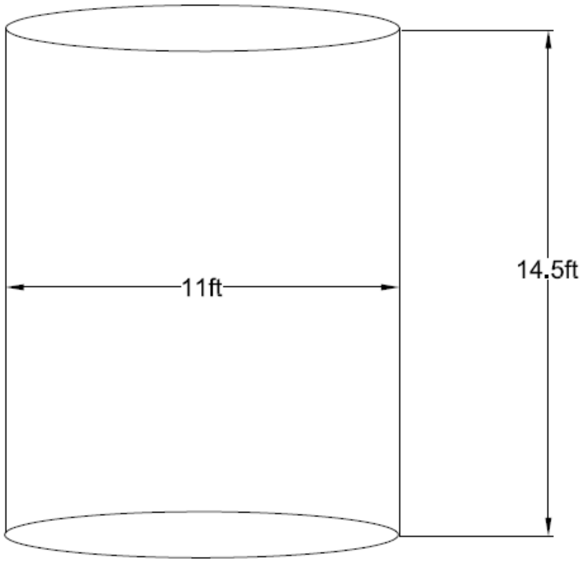


Figure 5.1: Tank dimensions at Facility I

5.1.2 Operation Details

- Hypochlorite deliveries are usually received in 10 days to 2 weeks periods.
- Hypochlorite is used as an only disinfectant at the facility, e.g. for contact time (CT) and for chorine residual. The facility switched from chlorine gas to hypochlorite about 10 years ago.
- The tanks are usually refilled once they reach about 3ft. One truck load will add about 3ft more to each tank. Next delivery is received once the operating tanks level (about 6ft) is emptied by half.
- This facility receives hypochlorite from Supplier I at a declared 10% (trade percent) available chlorine.
- Deliveries are usually made in the early mornings, at about 7am. Typically, the truck is filled a night before the delivery.
- There is a constant outflow from the tank. However, comparing to the size of the tank, it can be considered negligible (it will take a very long time to empty the tank) for the purposes of degradation measurements.
- Hypochlorite is pulled from 6’’ above the bottom point
- Hypochlorite flow rate: ~1000ml/min
- Hypochlorite is pulled out of both tanks simultaneously or from one tank at a time, depending on the operating personnel decision.
- Peristaltic pumps are used for supplying the hypochlorite from the tank to the application point.

Because the deliveries are not very frequent, most of the time this tank is operating close to a batch mode.

5.1.3 Sample Collection

The tank samples were collected from the pipeline that comes out of the tank, right after the pump. The truck samples were collected from the pipe that is used for filling the tank. No possibility of collecting from the top of the tank or truck was available.

5.2 Facility #2 Details

5.2.1 Tank Properties

The hypochlorite storage tank at the Facility II is made out of concrete, with wall thickness of 1’3”, and inner Teflon lining 4mm thick. Maximum operating height in the tank is 13ft. The tank has a square door at the top that can be opened by the operator, and is also equipped with a venting pipe at the top. The facility is equipped with two identical tanks.

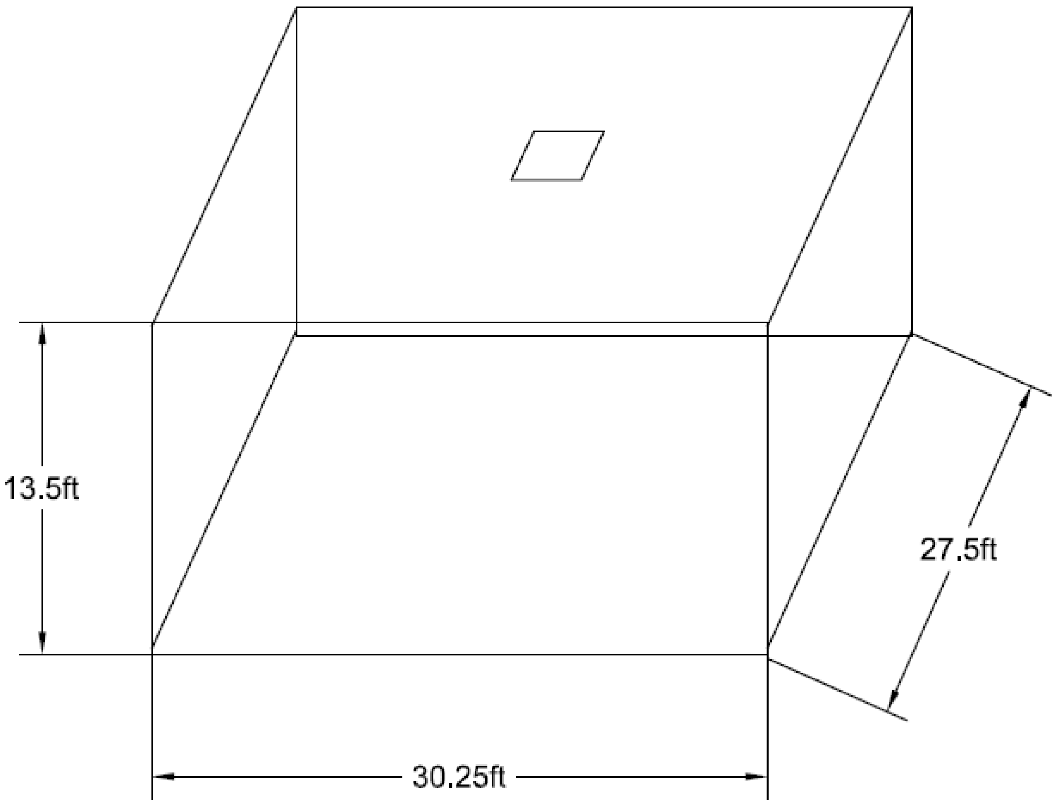


Figure 5.2: Tank dimensions at Facility II

5.2.2 Operation Details

- The “dead volume” is 3ft (the level in the tank has to be above 3ft for proper pumping). However, the goal is to keep the tank level around 6ft.
- The deliveries are usually received every other day (during the week) or at an interval of two days. Each truckload adds 1ft to hypochlorite level in the tank.
- This facility receives hypochlorite from Supplier II at the declared 12.5% (trade percent) available chlorine.
- Hypochlorite is used as a secondary disinfectant, only for chlorine residual, while ozone is the primary disinfectant at the facility. The facility switched from chlorine gas to ozone and hypochlorite about two years ago.
- Hypochlorite flow rate: ~1.5gal/min
- Deliveries can be done either during the first part of the day (anytime between 5am to noon) or afternoon (1pm to 5pm). If the delivery is in the afternoon, the truck is filled in the morning. For morning deliveries it was not confirmed when the truck is filled. However, it is reasonable to assume that it is filled a night before, similar to Facility I. The tank filling line is equipped with a filter for solids.
- Only one of the two tanks was filled with hypochlorite and was in use at the time of the experiment.
- Gear pumps are used for supplying the hypochlorite from the tank to the application point.

This facility can operate in a three modes:

1. Regular mode - operates in a manner that hypochlorite deliveries are ordered at the frequent (relatively constant) intervals, in order to keep hypochlorite level at the tank constant. Therefore, at the regular operation mode, the tank can be considered close to a CSTR (Continuously Stirred Tank Reactor).
2. Unexpected delay in deliveries mode - it happens that due to various reasons (such as truck that broke on the way) there might be no delivery for a period of time. At the periods when there are no deliveries, the tank can be considered close to a batch reactor, similar to Facility I.

3. Very frequent deliveries mode - when the period of no deliveries is over, the facility will receive very frequent deliveries to bring the tank to the desired level. At the times of very frequent deliveries, neither batch nor CSTR can be considered.

5.2.3 Sample Collection

Most of the tank samples were collected from the pipeline that comes out of the tank, right after the pump. Some samples (for comparison) were collected from the top of the tank through the top door, with the help of small bottle connected to a wire that was dipped into the tank. The truck samples were collected from the top of the truck, to avoid collecting crystallized material that might be in the filling pipe of the truck (offered by the driver).

5.3 Stored and Delivered Hypochlorite Measurements

5.3.1 Assumed chlorine application dose

Chlorine application dosage was assumed to be 5mg/L based on the data from the water treatment facilities. Facility I targets chlorine residual of about 3.5 mg/L leaving the plant, and 1.0-1.5mg/L goes toward chlorine demand at the plant. That brings the total chlorine application dose to about 5mg/L. Facility II targets a chlorine residual of 3.90 mg/L at the exit from the plant, and 1.10 mg/L is consumed for chlorine demand. That also brings the total chlorine application dose to 5mg/L. Based on the previous experience of the facilities, the targeted residual at the exit from the plants is required to keep the chloramine residual in the distribution system above 0.5mg/L, as required by Texas Commission of Environmental Quality (TCEQ 2007).

5.3.2 Measurement at Peak Temperatures

Samples from both facilities were measured in the month of August, a time when the temperatures usually reach the highest point. On average, in August 2014, for the Dallas Fort-Worth area, the high and the low temperatures were 34ºC and 24ºC respectively. Theoretical chlorate and perchlorate concentrations in drinking water were calculated based on the hypochlorite strength and the application of 5mg chlorine for a liter of water. At that point of study, no water samples were collected from the plants. Later, some of the hypochlorite samples were collected in conjunction with finished water samples. However, this was done during the months of September-November, when the temperatures are not as high. Table 5.1 presents the results from August 2014.

Expected chlorate concentration was calculated as follows:

$$Expected\ chlorate = \frac{Chlorate\ hypochlorite\ [mg/L]}{FAC\ hypochlorite\ [mg/L] \Big/ Application\ dose}$$

Expected perchlorate concentration was calculated in a similar way.

Table 5.1: Chlorine degradation and disinfection by-products formation in hypochlorite storage tanks in the month of August

Facility	Description	Chlorine	Chlorate	Perchlorate
Facility I	Delivered	108 g/L	947ppm	<250ppb
	Tank	96 g/L	6476ppm	486ppb
	Percent degradation/increase	11%	584%	>94%
	Concentration in water assuming 5mg/L FAC	5mg/L	338ppb*	0.025ppb**
Facility II	Delivered	133 g/L	1315ppm	<250ppb
	Tank	106 g/L	9900ppm	3237ppb
	Percent degradation/increase	21%	653%	>1195%
	Concentration in water assuming 5mg/L FAC	5mg/L	467ppb*	0.153ppb**

* California proposed action level for chlorate: 200ppb

** Currently regulated at MCL of 2ppb and 6ppb in Massachusetts and California respectively

Based on the results from the tank and the truck samples from August and considering chlorine dose of 5 mg/L, chlorate concentrations in the tanks are high enough that it would probably cause the concentrations in water to exceed the proposed action level.

Despite perchlorate concentrations rising during the storage, residual concentrations in finished water would probably be below the typical standards and therefore seem to be not of a concern.

5.3.3 Chlorate Measurement in Hypochlorite in Conjunction with Measurement in Finished Water

Table 5.2 presents calculated chlorate concentrations in finished water, based on the chlorine dosage of 5mg/L compared to measured concentrations in finished water. Water samples were collected right after the hypochlorite samples collection. However, the actual residence time can be up to a day before the concentration in finished water can be changed accordingly to the hypochlorite concentration. This fact can cause some deviations between the expected and measured concentrations. In addition, there was no possibility to collect raw water samples, because it would require the shut down of the system (in one of the facilities). Therefore, it was assumed that the concentration of chlorate in raw water is negligible in comparison to its increase in finished water as a result of hypochlorite application.

Table 5.2: Calculated chlorate concentration in finished water vs. measured concentrations in finished water.

Facility	Date	Chlorate measured [ppm]	Chlorate expected [ppm]
Facility I	9.29.14	0.203	0.287
	11.24.14	0.094	0.115
Facility II	9.26.14	0.468	0.536
	10.13.14	0.740	0.744
	10.20.14	0.340	0.360
	10.22.14	0.361	0.377
	10.27.14	0.442	0.451

It can be clearly seen from Table 5.2 that in most of the cases, the expected chlorate concentrations are close to the measured concentrations. Therefore, chlorate concentration in water can be assessed with reasonable accuracy by its measurement in hypochlorite and calculation based on free chlorine concentration and application dosage**.**

The differences between measured and expected concentrations can also be attributed to the fact that the amount of applied chlorine is sometimes a little less than 5mg/L, depending on the amount needed to achieve the desired residual.

5.3.4 Comparison Between Samples Collected From the Top and Bottom at Facility 2

To confirm the well-mixing assumption, several samples were collected from the bottom and the top of the tank at Facility II. There was no possibility to collect samples from the top of the tank at Facility I.

Chlorine measurements were done by titration in duplicates, as shown in the following table:

Table 5.3: Free chlorine in samples collected from the top and the bottom of the tank

Date	Location in tank	Measurement 1 Chlorine [g/L]	Measurement 2 Chlorine [g/L]	Average Chlorine [g/L]
10.13.14 noon	Bottom	99.5	99	99.2
	Top	98.5	99	98.8
10.13.14 evening	Bottom	103.5	103	103.3
	Top	97.5	97	97.3
10.15.14	Bottom	107.5	108.5	108
	Top	107.3	109	108.1
10.17.14	Bottom	112	114	113
	Top	112	113	112.5

Results presented in Table 5.3 confirm that the tanks can be considered well mixed for the purposes of the study. In other words, no significant difference was found between the samples collected from the top of the tank and from the bottom. The only exception can be the measurement that was done on 10.13.14 evening, which can be attributed to the fact that the sample was collected shortly after a delivery of the new material, and there was not enough time for the tank to reach good mixing.

5.3.5 Comparison Between Suppliers and the Composition of Hypochlorite

Most of the field samples were pre-treated and analyzed in triplicates.

Table 5.4: Comparison between freshly delivered hypochlorite from both suppliers

Facility	Date	Chlorine (FAC)		Chlorate	
		Average concentration [g/L]	%RSD	Average concentration [ppm]	%RSD
Supplier I	5.16.14	110.7±6.1*	5.5%	1202±24	2%
	8.1.14	108.1±1.7	1.5%	947**	N/A
	9.29.14	108.6±0.6	0.6%	1555±34	2.2%
	11.7.14	123.7±1.0	0.8%	1412±14	1.0%
	11.24.14	125.0±0.9	0.7%	808±16	1.9%
	Supplier I range	108-125	N/A	808-1555	N/A
	Mean	115.2		1185	
Supplier II	8.8.14	133.3±2.3	1.7%	1315**	N/A
	9.25.14	134.9±2.3	1.7%	1571±35	2.2%
	10.13.14	125.3±0.4	0.3%	4899±9	0.18
	10.15.14	129.0±1.4	1.1%	2985±74	2.5%
	10.17.14	137.0±2.1	1.5%	1410±12	0.82%
	Supplier II range	125-137	N/A	1315-4899	N/A
	Mean	131.9		2436	

%RSD – relative standard deviation

*Total chlorine was tested using Hach® DPD kit for this sample

**These samples were not done in triplicates, therefore SD could not be calculated

From the data presented in Table 5.4, it can be seen that chlorate concentrations in hypochlorite from Supplier II are generally higher than in hypochlorite from Supplier I. The difference can possibly be attributed to the processes of hypochlorite production and the quality of reactants used by the different suppliers.

Alterations in chlorate concentrations from the same supplier could also be attributed to the production process (there might be variation in the process conditions, especially if it is a batch process) and reactants. In addition to the process, the difference can be contributed by variations in storage times in the delivery truck, e.g. the time between the filling of the truck with hypochlorite and the delivery. For example, if the truck was loaded before the weekend and delivered only after the weekend, it could be exposed to high temperatures without proper isolation. It can cause degradation of hypochlorite and excessive formation of chlorate. The two highest values of chlorate in both suppliers support this assumption: both deliveries with the highest values were done on Monday: 10/13/14 and 9/29/14.

According to Odyssey Manufacturing (Odyssey 2012), delivered bleach typically has a limit of 1500ppm chlorate. Most of the Supplier I measured values stay below 1500ppm. However, this is not the case with Supplier II, which has several measurement significantly exceeding 1500ppm.

5.3.5 Comparison Between Hypochlorite Degradation in Both Facilities

It is known that at the higher levels of chlorine in the hypochlorite solutions, hypochlorite degradation rate increases (2^{nd} order), and chlorate formation too. It would be expected that a solution with a higher percent of hypochlorite would degrade faster. However, the operation of the facility is also a very meaningful factor. Comparison between samples collected from the tanks at both facilities is shown in Table 5.5.

Most of the field samples were pre-treated and analyzed in triplicates.

Table 5.5: Comparison between samples from the storage tanks at both facilities

Facility	Date/Description	Chlorine (FAC)		Chlorate	
		Average concentration [g/L]	%RSD	Average concentration [ppm]	%RSD
Facility I	5.16.14 Tank before delivery	102.4±8.4*	8.2%	4652±131	2.8%
	8.1.14 Before delivery	95.8±0.4	0.5%	6476**	
	8.1.14 After delivery	103.2±0.6	0.6%	3276**	
	9.29.14 Before delivery	97.5±1.0	1.0%	5596±35	0.63%
	10.29.14 After delivery	118.2±1.5	1.3%	2503±28	1.1%
	11.3.14	114.5±3.0	2.6%	2827±31	1.1%
	11.7.14 Before delivery	114.7±4.2	3.6%	3426±54	1.6%
	11.12.14	116.7±2.1	1.8%	2529±42	1.6%
	11.17.14	117.3±2.0	1.7%	2633±22	0.8%
	11.24.14	117.3±1.8	1.5%	2690±59	2.2%
	Facility I range	95-118		2503-6476	
	Mean	109.8		3792	
Facility II	8.8.14	105.9±0.9	0.9%	9900**	
	9.26.14	103.8±0.7	0.6%	11120±56	0.51%
	10.13.14	99.2±0.3	0.3%	14763±210	1.4%
	10.20.14	124.5±0.0	0%	8965±91	1.0%
	10.22.14	124.5±0.5	0.4%	9390±91	0.97%
	10.24.14	122.0±1.0	0.8%	10034±81	0.81%
	10.27.14	120.0±1.3	1.1%	10832±180	1.7%
	10.29.14	117.3±1.0	0.9%	12311±548	4.5%
	11.10.14	105.8±0.3	0.3%	13025±370	2.8%
	Facility II range	99-125		8965-14763	
	Mean	113.7		11149	

*Total chlorine was tested using Hach® DPD kit for this sample

**These samples were not done in triplicates, therefore SD could not be calculated

From the data presented in Table 5.5, it can be clearly seen that chlorate levels in Facility II are much higher than in Facility I. There are several possible reasons that can contribute to that:

1. Facility II stores higher strength hypochlorite, which degrades faster
2. There is a higher chlorate concentration in the material delivered to Facility II
3. Concrete has a two-orders higher thermal conductivity than fiberglass
4. Relatively long residence times of hypochlorite in the Facility II tank can contribute to the higher degradation ratios

5.4 Comparison to Hypochlorite Assessment Model

Field results that were collected in between the deliveries were compared to the results that the model would predict. In such periods storage tanks could be considered “batch reactors”. In Facility II it was possible only at the period before the plant shuts down for winter, because there were no deliveries of the new material at this time. The real field data collected at the beginning of such periods was entered into the assessment software as an initial condition. Temperatures of the samples and the ambient temperatures at the time of the collection were recorded.

To make the comparison to the model possible, storage temperatures had to be approximated. In the real world, outside temperatures are constantly changing. Temperatures in the tank will change accordingly, but at a much slower rate than the outside temperatures, depending, among other factors, on the thermal conductivity of the tank. Radiation is also a component that will influence the heating rate (e.g. If the tank is exposed to the sun, the heating of its contents will be faster). Another factor is the volume of the tank and level of solution in it (and the thermal conductivity of the solution itself). However, measurement of all these factors would require big resources. As a result, simplified approximation was required.

Initially, the average season temperatures were calculated using the “weather underground” (http://www.wunderground.com/history) website. However, no agreement between those temperatures and the sample temperatures was found. Therefore, it seemed that taking an average of the sample temperatures in different periods would be a better approximation.

Tables C.1 and C.2 in Appendix C summarize the temperatures during the measurement period. Figures 5.5-5.10 present the field results compared to the model. Facility II data is shown first because the measurements were done at a higher temperatures: middle of October to beginning of November. Facility I is shown next because the measurements were done during the month of November, when the temperatures were much lower.

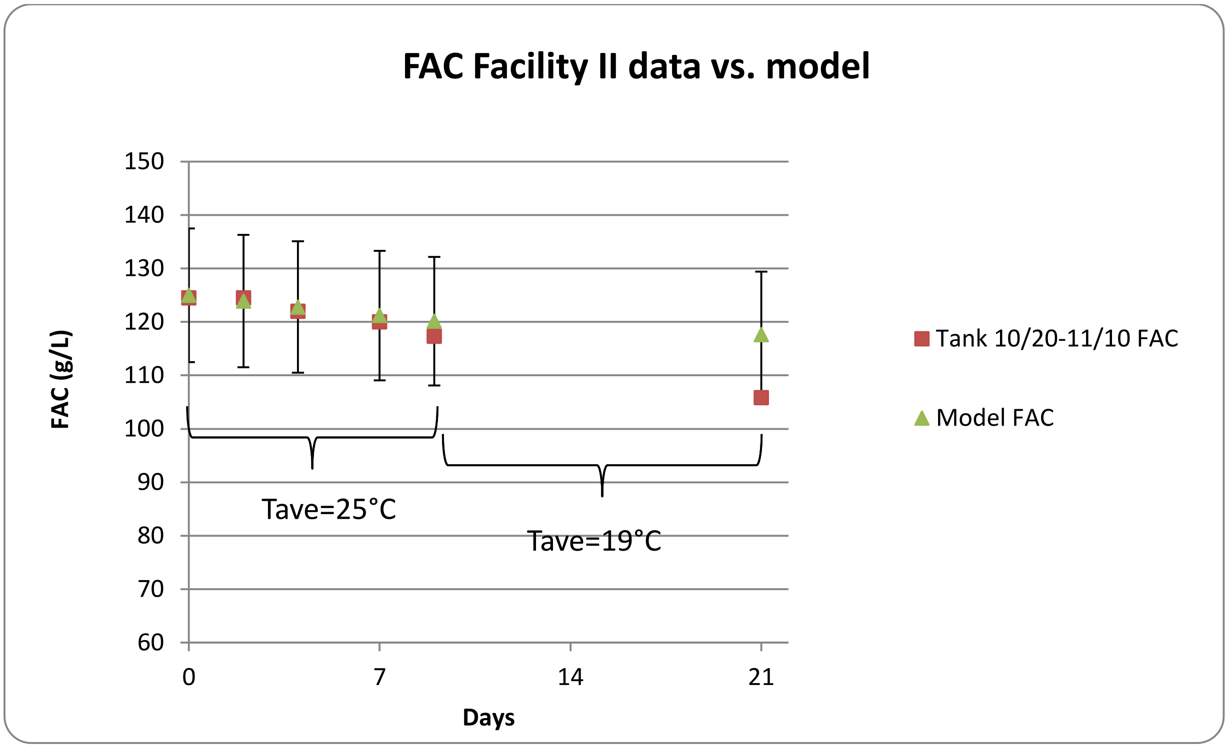


Figure 5.3: Comparison of predicted and measured FAC concentrations at Facility II

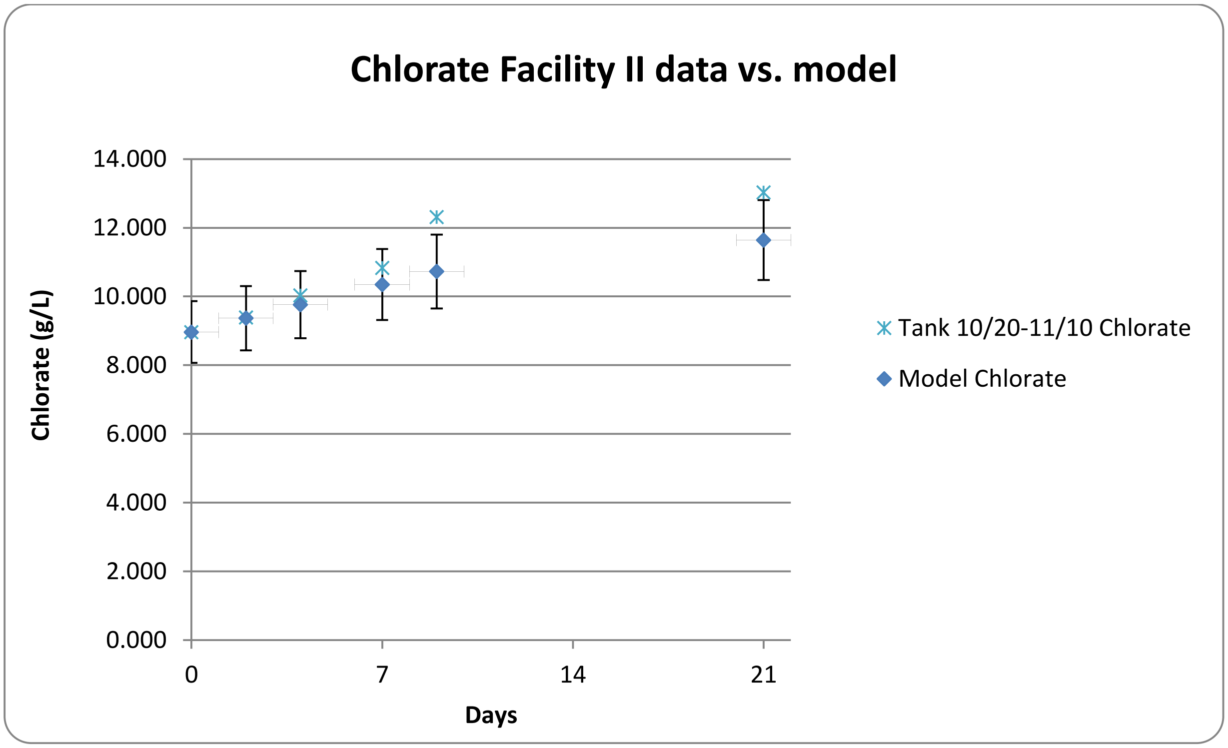


Figure 5.4: Comparison of predicted and measured chlorate concentrations at Facility II

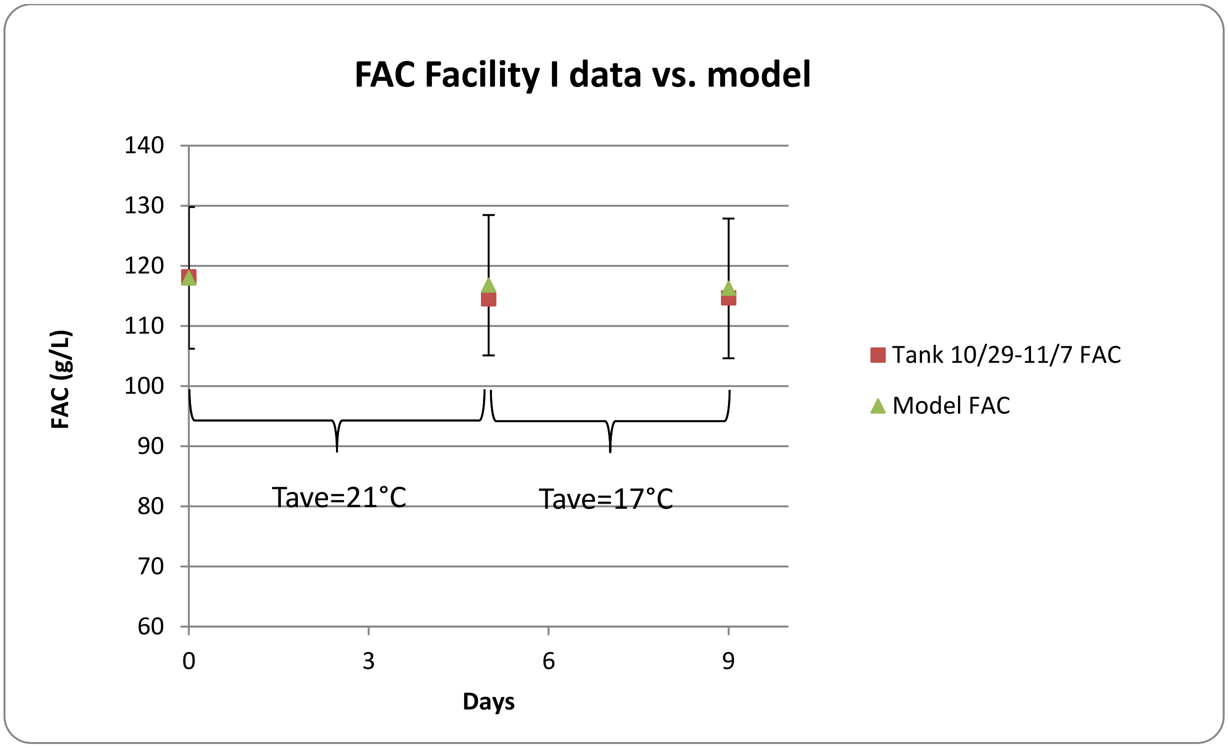


Figure 5.5: Comparison of predicted and measured FAC concentrations at Facility I during 10/29-11/7

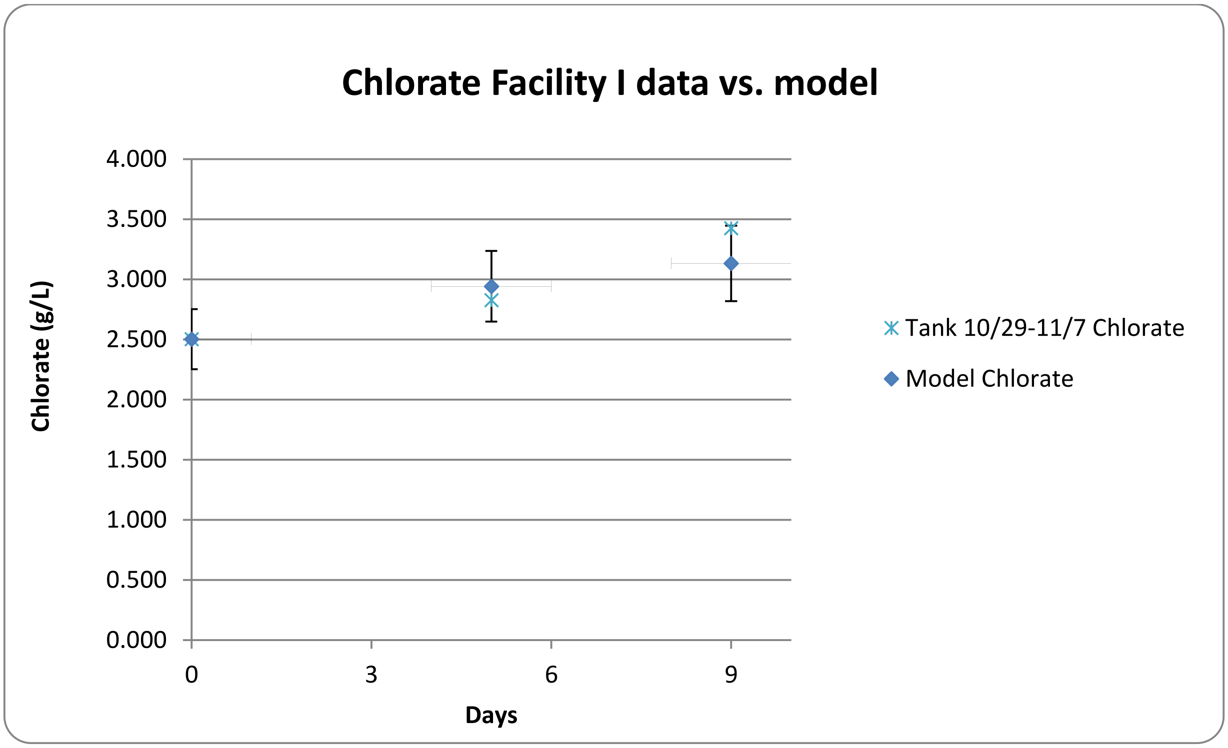


Figure 5.6: Comparison of predicted and measured chlorate concentrations at Facility I during 10/29-11/7

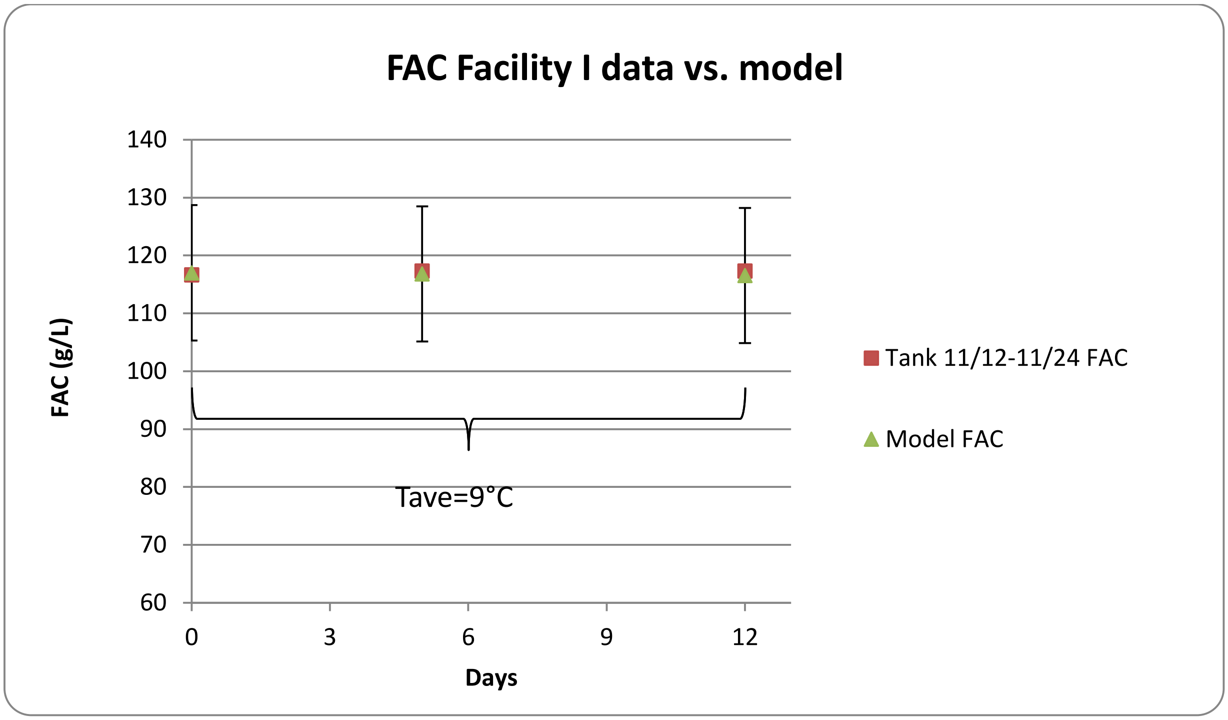


Figure 5.7: Comparison of predicted and measured FAC concentrations at Facility I during 11/12-11/24

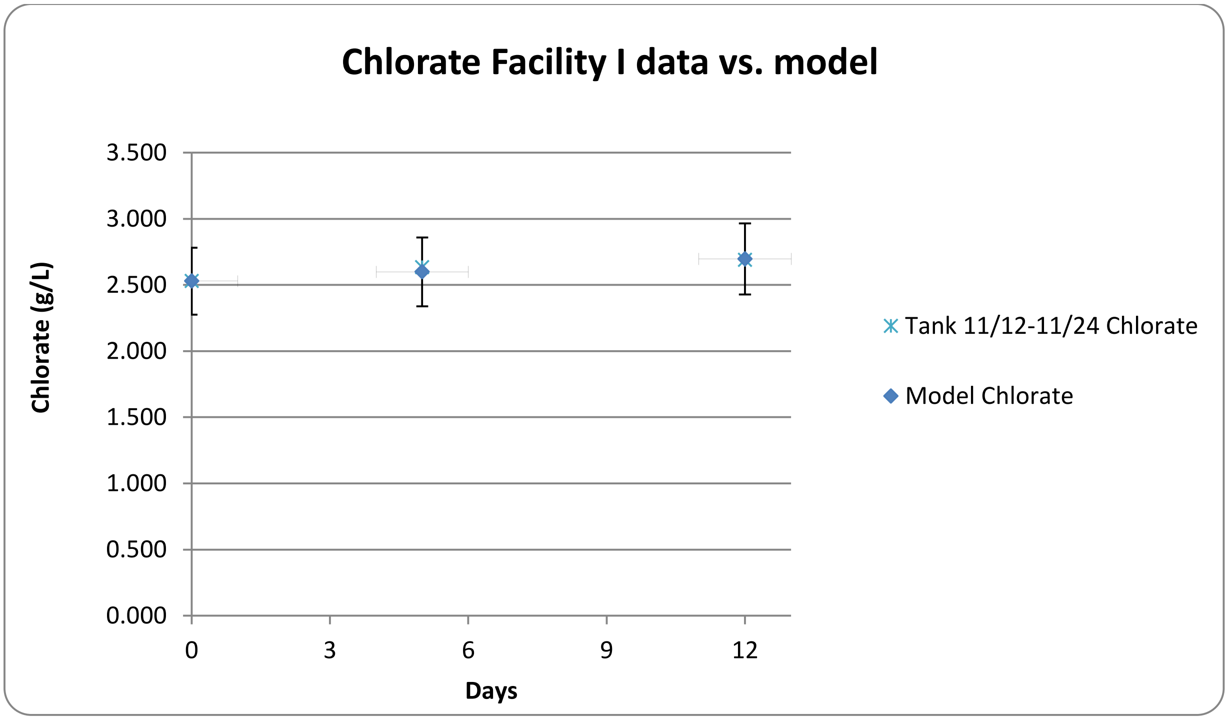


Figure 5.8: Comparison of predicted and measured chlorate at Facility I during 11/12-11/24

As can be seen from the comparison to the model, most of the data is within 10% variation from the values predicted by the model. Some of the points have larger deviation, yet it is still a reasonably good fit considering the simplifying assumptions for the storage temperatures. The comparison shows that the degradation trend for the real storage conditions can be approximated by the model prediction. However, as mentioned earlier, the model is limited to the periods in between the deliveries only. Also, knowing the solution temperatures over a period of time might be challenging. In addition, as mentioned earlier, the model does not take into account quality of hypochlorite, such as suspended solids and transition metals content.

Chapter 6

Summary and Conclusions

Many water treatment plants are abandoning chlorine gas and switching over to hypochlorite due to the safety concerns. Therefore, there is more need in assessment of hypochlorite degradation and by-products formation. Some facilities that consider hypochlorite as an alternative desire to know possible adverse effects before the transition, such as in the case of the current study. To estimate the effect of such a transition in Texas conditions, two water treatment plants that use bulk hypochlorite were studied. Samples were collected and measured for the chlorine and chlorate levels, and some of them were measured for perchlorate. However, in order to measure chlorate and perchlorate there was a need to develop a reliable procedure for the sample pre-treatment that would be suitable for the ion chromatograph that the laboratory is equipped with. The main conclusions of this study are summarized below.

6.1 Pre-treatment procedure

- Pre-treatment procedure with hydrogen peroxide and manganese dioxide allows a slight overdose of hydrogen peroxide and subsequent removal of the residual without changing the concentration of the analytes
- The procedure gives consistent and reproducible results

6.2 Dilution experiment and comparison to the Hypochlorite Assessment Model

- No significant differences in hypochlorite and chlorate can be seen in samples diluted with low strength hypochlorite and samples diluted with softened water at the same ratios
- Hypochlorite degradation, chlorate and perchlorate formation were significantly slower in the diluted solutions, which is in agreement to the previous work
- There is a significant decrease in perchlorate formation even with a dilution of 1:1

- There was a good agreement of the data with the Hypochlorite Assessment Model (only solution that contained 75% low strength hypochlorite and 25% high strength hypochlorite deviated from the model for over 10%)

6.3 Water treatment facilities

- Concentrations in the storage tank can be considered uniform for the purpose of the study (no high deviations in chlorine levels were found between the top and bottom of the tank)
- In the month of August:
  - The degradation of the hypochlorite solution was found to be 10-20% comparing to new delivered material
  - Considering a chlorine dose of 5 mg/L, chlorate concentrations in the tanks at both facilities would probably cause the concentrations in water to exceed the health reference limit of 210ppb
  - Perchlorate levels at both facilities seem to be not of a concern considering current regulation
- The chlorate concentration in finished water can be estimated with reasonable accuracy based on its concentration in storage tanks
- Chlorate levels in supplied hypochlorite can vary. One of the two suppliers had chlorate levels below the recommended level of 1500ppm, while another supplier sometimes had chlorate levels two times higher than 1500ppm
- Chlorate levels at Facility II were much higher than at Facility I, which could be the result of higher chlorate concentrations in the supplied material and also of the way the facility is operating.
- Chlorine content from both suppliers was equal or higher than a declared trade percent
- Not much difference was seen in chlorine content between the two facilities, even though hypochlorite delivered to Facility II has a higher strength
- Chlorate levels in the storage tanks increase as a function of time in the periods between the deliveries, whereas chlorine levels decrease as a function of storage time
- Comparison of the field data to the model:

- Ambient air temperatures cannot be considered representative of the hypochlorite temperature inside the tank
- Most of the field data was within 10% deviation of the values predicted by the model. Therefore, real storage conditions can be approximated by model prediction

Chapter 7

Recommendations for future research

The recommendations for future research are as follows:

- Develop a framework for understanding the impacts of the residual storage volume (a volume that is never drained) and the frequency of deliveries on chlorine decay, chlorine use and chlorate production. The goal is to help make future design decisions concerning the extent of residual storage volume needed. This includes the use of the model for prediction of various scenarios of the residual volume and frequency of deliveries. Preliminary part of this work is shown in Appendix B.
- Measure bromate concentrations in hypochlorite produced by local suppliers and its concentrations in storage tanks
- Measure chlorate in local facilities that use OSG systems
- Test how well the Hypochlorite Assessment Model predicts perchlorate formation for real field data

Appendix A

E-mail conversation with OEHHA representative concerning chlorate notification and action levels in California

Delson, Sam@OEHHA <Sam.Delson@oehha.ca.gov>
Thu 2/5/2015 1:10 PM

To: Breytus, Anna;
Cc: Leichty, Julian@OEHHA <Julian.Leichty@oehha.ca.gov>; Communications@EPA <CEPAComm@CALEPA.ca.gov>;

Anna,

Our technical staff looked into your question and provided this explanation that may be helpful:

OEHHA proposed an action level of 0.2 ppb using a Relative Source Contribution (RSC) of 0.2 but CDPH decided that an RSC of 0.8 would be more appropriate. So that ended up changing the notification level to 0.8.

OEHHA's calculation was: $C = \frac{30 \text{ mg/kg-day} \times 70 \text{ kg} \times 0.2}{1{,}000 \times 2 \text{ L/day}} = 210\ \mu\text{g/L}$

CDPH's calculation was: $C = \frac{30 \text{ mg/kg-day} \times 70 \text{ kg} \times 0.8}{1{,}000 \times 2 \text{ L/day}} = 840\ \mu\text{g/L}$

This is clarified in footnote #6 on pages 6 and 7 of this document: http://www.waterboards.ca.gov/drinking_water/certlic/drinkingwater/documents/notificationlevels/notificationlevels.pdf
It states, in part, " CDHS utilized OEHHA's risk assessment when developing the NL, but with RSC = 0.8, rather than OEHHA's RSC = 0.2. CDHS felt that this value reflected the greater contribution of drinking water to total chlorate exposures." (CDHS refers to the California Department of Health Services, which was split into two departments in 2007. The drinking water program then became part of the new California Department of Public Health (CDPH), and in 2014 the program was transferred to the State Water Resources Control Board.)

I hope this is helpful.

Sam Delson
Deputy Director for External and Legislative Affairs
California Office of Environmental Health Hazard Assessment (OEHHA)
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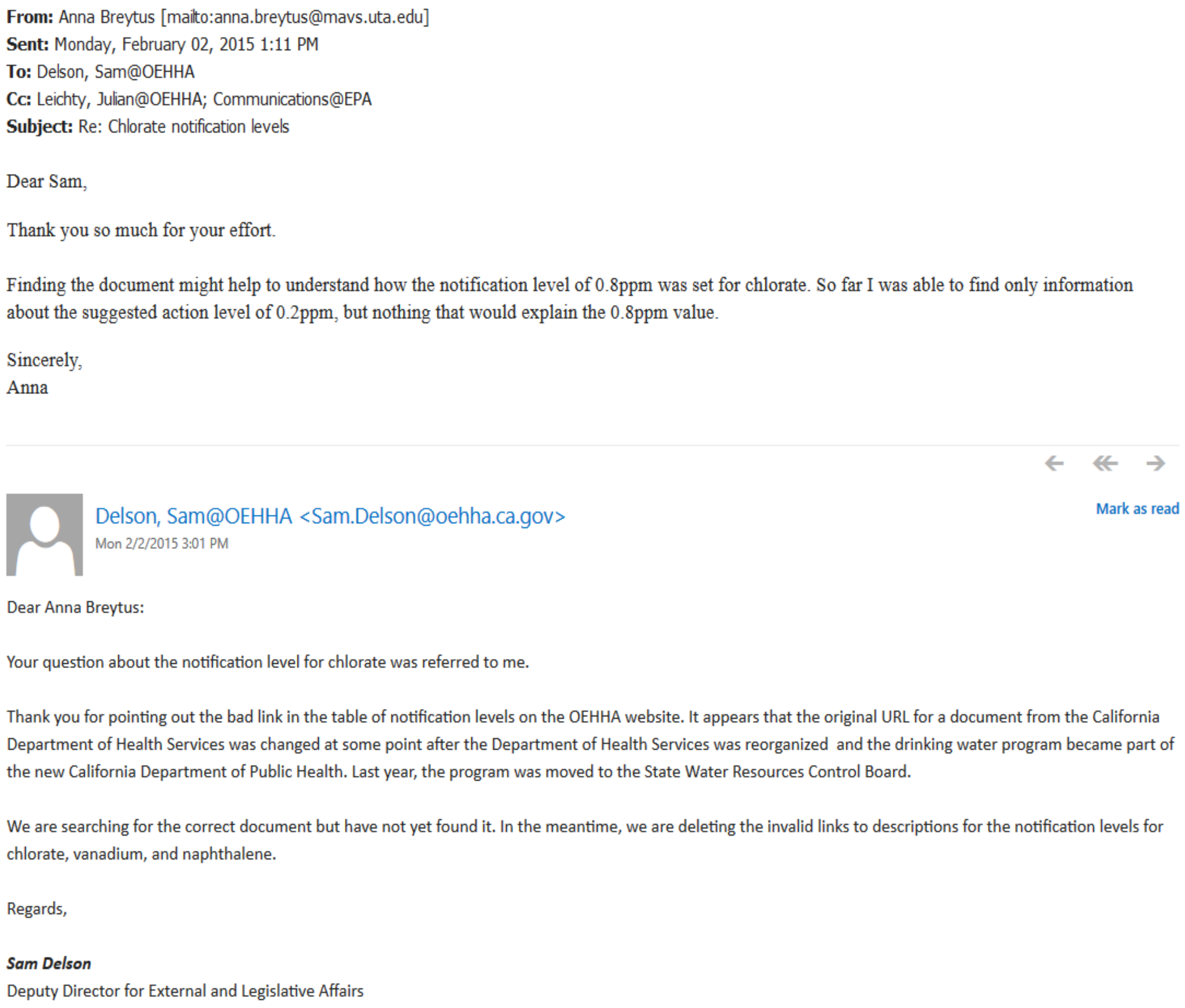

From: Anna Breytus [mailto:anna.breytus@mavs.uta.edu]
Sent: Monday, February 02, 2015 1:11 PM
To: Delson, Sam@OEHHA
Cc: Leichty, Julian@OEHHA; Communications@EPA
Subject: Re: Chlorate notification levels

Dear Sam,

Thank you so much for your effort.

Finding the document might help to understand how the notification level of 0.8ppm was set for chlorate. So far I was able to find only information about the suggested action level of 0.2ppm, but nothing that would explain the 0.8ppm value.

Sincerely,
Anna

Delson, Sam@OEHHA <Sam.Delson@oehha.ca.gov>
Mon 2/2/2015 3:01 PM

Dear Anna Breytus:

Your question about the notification level for chlorate was referred to me.

Thank you for pointing out the bad link in the table of notification levels on the OEHHA website. It appears that the original URL for a document from the California Department of Health Services was changed at some point after the Department of Health Services was reorganized and the drinking water program became part of the new California Department of Public Health. Last year, the program was moved to the State Water Resources Control Board.

We are searching for the correct document but have not yet found it. In the meantime, we are deleting the invalid links to descriptions for the notification levels for chlorate, vanadium, and naphthalene.

Regards,

Sam Delson
Deputy Director for External and Legislative Affairs

Appendix B

Simulation of hypothetical conditions with the use of the Hypochlorite Assessment Model

For the model simulation, trade percent of 12.5% available chlorine was considered.

Initial chlorate concentrations that were considered are 1.5g/L and 4 g/L. 1.5 g/L is a reasonable value based on the data from both plants (this value is slightly higher than average for Supplier I and close to lower values of Supplier II) and 4g/L as an average of the two highest values from Supplier II.

In addition, the dilution factors of 2:1 and 4:1 were considered for each scenario. It is assumed that the dilutions were done with softened water that does not contain analytes.

Scenarios 1 and 2 show the situation in the tank if no new material is added for a period of 30 days. In scenario 3, however, addition of new material on a regular basis is considered. In this case, the assumption was that ¼ of the tank is used at the end of each 5 days and then there is a delivery of new material that fills up ¼ of the tank volume to bring it to the initial volume. The value of 5 days was considered as it is an intermediate value between the two facilities (one facility receives deliveries every 10-14 days and another one every 1-2 days). Initial concentration was chosen as 125g/L chlorine and 1.5g/L chlorate. The assumption is that the newly delivered material has the same concentration each time, which is equal to the initial concentration.

In all the cases, the temperature of 30ºC was chosen as an average between the high and the low temperatures during the month of August in Dallas Fort-Worth Metroplex.

Table B.1: Hypochlorite model assessment considering initial chlorate concentration of 4 g/L

Scenario 1.1		Scenario 1.2		Scenario 1.3	
Temperature	30ºC	Temperature	30ºC	Temperature	30ºC
Time	30days	Time	30days	Time	30days
Dilution:	none	Dilution:	1:1	Dilution:	1:3
Initial chlorate	4 g/L	Initial chlorate	2 g/L	Initial chlorate	1 g/L
Initial FAC	125 g/L	Initial FAC	62.5 g/L	Initial FAC	31.25 g/L
Initial chlorate in water assuming 5 mg/L chlorine application	160ppb	Initial chlorate in water assuming 5 mg/L chlorine application	160ppb	Initial chlorate in water assuming 5 mg/L chlorine application	160ppb
Chlorate in water after 30 days assuming 5 mg/L chlorine application	776ppb	Chlorate in water after 30 days assuming 5 mg/L chlorine application	332ppb	Chlorate in water after 30 days assuming 5 mg/L chlorine application	223ppb

Table B.2: Hypochlorite model assessment considering initial chlorate concentration of 1.5 g/L

Scenario 2.1		Scenario 2.2		Scenario 2.3	
Temperature	30ºC	Temperature	30ºC	Temperature	30ºC
Time	30 days	Time	30 days	Time	30 days
Dilution:	none	Dilution:	1:1	Dilution:	1:3
Initial chlorate	1.5 g/L	Initial chlorate	0.75 g/L	Initial chlorate	0.375 g/L
Initial FAC	125 g/L	Initial FAC	62.5 g/L	Initial FAC	31.25 g/L
Initial chlorate in water assuming 5 mg/L chlorine application	60 ppb	Initial chlorate in water assuming 5 mg/L chlorine application	60 ppb	Initial chlorate in water assuming 5 mg/L chlorine application	60 ppb
Chlorate in water after 10 days assuming 5 mg/L chlorine application	255 ppb	Chlorate in water after 10 days assuming 5 mg/L chlorine application	87 ppb	Chlorate in water after 10 days assuming 5 mg/L chlorine application	70 ppb
Chlorate in water after 30 days assuming 5 mg/L chlorine application	646 ppb	Chlorate in water after 30 days assuming 5 mg/L chlorine application	220 ppb	Chlorate in water after 30 days assuming 5 mg/L chlorine application	119 ppb

Table B.3: Hypochlorite model assessment considering addition of new material every 5 days (at the degree of ¼ of the tank active volume) with initial chlorate concentration of 1.5 g/L

Scenario 3.1		Scenario 3.2		Scenario 3.3	
Temperature	30ºC	Temperature	30ºC	Temperature	30ºC
Time	30 days	Time	30 days	Time	30 days
Dilution:	none	Dilution:	1:1	Dilution:	1:3
Initial chlorate	1.5 g/L	Initial chlorate	0.75 g/L	Initial chlorate	0.375 g/L
Initial FAC	125 g/L	Initial FAC	62.5 g/L	Initial FAC	31.25 g/L
Initial chlorate in water assuming 5 mg/L chlorine application	60 ppb	Initial chlorate in water assuming 5 mg/L chlorine application	60 ppb	Initial chlorate in water assuming 5 mg/L chlorine application	60 ppb
Chlorate in water after 30 days assuming 5 mg/L chlorine application	351 ppb	Chlorate in water after 30 days assuming 5 mg/L chlorine application	146 ppb	Chlorate in water after 30 days assuming 5 mg/L chlorine application	92 ppb
Chlorate in water after 40 days assuming 5 mg/L chlorine application	370 ppb	Chlorate in water after 40 days assuming 5 mg/L chlorine application	N/A	Chlorate in water after 40 days assuming 5 mg/L chlorine application	N/A

From Tables B.1-B.3, the following can be concluded:

1. As seen in Table B.1, material delivered with 4g/L chlorate will result in 160ppb in water even if fed directly, a value that is not far from HRL of 210 ppb.
2. For hypochlorite delivered with 1.5 g/L of initial chlorate and stored for 30 days, fourfold dilution will keep the level of chlorate below 200ppb for 30 days. Without the dilution, chlorate levels will exceed

HRL after 10 days. In addition to the impact of the direct chlorate increase in hypochlorite, it is important to note that due to the degradation of hypochlorite, dilution factor required to achieve application of 5 mg/L of chlorine to water is reduced (larger volume of hypochlorite is needed), therefore chlorate levels in water will increase according to this factor.

3. From comparison of results in Tables B.2 and B.3 it is obvious that the addition of the new material on a regular basis will yield lower chlorate levels than storing for 30 days without addition of fresh material.
4. Storing hypochlorite only for emergencies has disadvantages and is likely to be a problem.
5. For Scenario 3.1, the system will reach a steady state after about 40 days, e.g. change in chlorine and chlorate concentrations will be less than 1% between the deliveries.
6. More simulations with different scenarios are needed for making conclusions.

Appendix C

Temperatures during field measurements period

Table C.1: reported high and low ambient temperatures and measured temperatures for Facility II

Date	High[C]	Low[C]	Taverage[C]	Tsample[C]	Tambient[C]	Tsample_average[C] (used for the model)
10/20/2014	27.8	15.6	21.7	**26.5**	24	25
10/21/2014	27.8	15.6				
10/22/2014	27.8	16.7	22.8	**25.8**		
10/23/2014	27.8	18.9				
10/24/2014	30.0	16.7	24.5	**25**	16.7	
10/25/2014	32.2	17.8				
10/26/2014	31.7	18.9				
10/27/2014	30.0	18.9	23.3	**25.4**		
10/28/2014	26.7	17.8				
10/29/2014	25.6	12.2	15.6	**20.9**		
10/30/2014	26.7	12.8				19
10/31/2014	20.0	10.0				
11/1/2014	17.2	3.9				
11/2/2014	20.6	8.9				
11/3/2014	23.9	13.9				
11/4/2014	22.2	11.7				
11/5/2014	13.9	10.6				
11/6/2014	22.2	7.8				
11/7/2014	21.1	7.2				
11/8/2014	22.2	10.0				
11/9/2014	23.9	6.1				
11/10/2014	27.2	12.8		**16.7**	20	

*Dates of samples collection are highlighted

Table 0.2: reported high and low ambient temperatures and measured temperatures for Facility I

Date	High[C]	Low[C]	Taverage[C]	Tsample[C]	Tambient[C]	Tsample_average[C] (for the period)
10/29/2014	25.0	13.9	15.7	**24**	21.5	21
10/30/2014	26.1	13.9				
10/31/2014	18.9	10.6				
11/1/2014	16.7	5.0				
11/2/2014	20.0	7.2				
11/3/2014	23.9	12.8	15.6	**18**	16	17
11/4/2014	21.1	12.2				
11/5/2014	13.9	11.1				
11/6/2014	22.2	7.2				
11/7/2014	20.0	6.1		**16**	8	
11/12/2014	3.9	0.0	2.2	**11.7**	3.3	9
11/13/2014	3.9	-1.1				
11/14/2014	3.9	-2.2				
11/15/2014	7.2	3.9				
11/16/2014	5.0	-2.2				
11/17/2014	6.7	-3.3	11.7	**6.1**	0.6	9
11/18/2014	12.8	-2.2				
11/19/2014	17.8	3.9				
11/20/2014	21.7	5.6				
11/21/2014	20.0	15.0				
11/22/2014	17.2	13.9				
11/23/2014	25.0	10.0				
11/24/2014	15.6	5.6		**11**	6	

*Dates of samples collection are highlighted

Appendix D

Attempt to measure bromate in hypochlorite

At the beginning of the study, there was an attempt to measure bromate in hypochlorite samples. However, no consistent results were reached due to the interference of bromate peak with chlorite peak at high chlorite concentrations, which are present in hypochlorite especially during the summer months. Though chlorite peak was not confirmed with a standard, based on the previous studies chlorite is the cause of such an interference and mass spectroscopy would provide the proper separation (DeBorba 2012, Pisarenko 2009, Stanford 2013).

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Weather underground website, temperatures in Dallas and Fort Worth during the months of October and November 2014, http://www.wunderground.com/history.

Biographical Information

Anna graduated cum laude with a bachelor degree in Chemical Engineering from the Technion – Israel Institute of Technology in 2008. Following her graduation, she worked in industry for a few different companies and gained some industrial valuable experience.

In 2013, Anna decided to continue into higher education in Environmental Engineering field, due to the desire to meet the need for clean water all over the world. She enrolled into Environmental Engineering program at University of Texas at Arlington. During her studies, Anna held a graduate research assistant position, and was involved in different projects in water quality field, with primary emphasis on disinfection by-products.

Anna is interested in working for improvement of drinking water quality in developed and developing countries.