The Impact of Mixing on the Chloramination Process

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ABSTRACT

Interest in chloramination treatment for potable water has increased in recent years with the advent of more stringent drinking water requirements as a result of chloramines ability to form stable chlorine residuals and minimal disinfection byproducts. However, many utilities which have switched to chloramination for secondary disinfection have reported problems upon the start-up of their new systems. It is believed that these issues may be the result of inadequate mixing.

A previous study by Jain (2007) identified an optimum mixing intensity for adequate chloramination by completing bench scale experiments on a standard jar test apparatus. This study was limited to three mixing speeds and further analysis was required to confirm Jain’s findings.

The purpose of this study was to continue Jain’s study and further investigate the impact of mixing on the chloramination process. A series of nine experiments were conducted at mixing speeds of 200 rpm and 300 rpm using a jar test apparatus. Ten dosing molar ratios of chlorine to ammonia were investigated in each experiment and sampling times of 15 and 45 minutes were utilized. Experimental conditions were set to correlate to those commonly present in drinking water treatment facilities and sodium bicarbonate was added to provide alkalinity. Experimental results were compared against model simulations produced by the Unified Plus Model system.

Experimentation indicated that monochloramine production approached the theoretical maximum at a mixing speed of 200 rpm \((G = 300 \text{ s}^{-1})\). Similar results were obtained when mixing speed was increased to 300 rpm \((G = 500 \text{ s}^{-1})\). As
such, the increase in mixing speed did not produce further benefits. Additionally, the breakpoint curve exhibited a left shift from the ideal breakpoint curve. As a result, further investigation was conducted into the application of carbonate to the experimental system. It was determined that the chloramination process was impacted by increasing the $C_t$. The mechanism for this impact is not completely known. Model comparisons with these results indicated that the system did not definitively exhibit the characteristics of either an open or closed system, but appeared to be closer to a closed system.
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1 INTRODUCTION

Safe drinking water is vital to all life on Earth. As such, many treatment practices have been developed to ensure that humans continue to have access to clean, fresh water supplies. Chlorination has long been the most popular method of disinfection utilized by the treatment facilities but has recently been plagued by problems associated with the formation of disinfection byproducts (DBPs). As a result, many treatment facilities in the United States have begun to shift to the use of chloramines in order to provide disinfectant residuals in response to the United States Environmental Protection Agency’s (USEPA) Stage 2 Disinfectants and Disinfection Byproducts Rule (Kirmeyer, Martel, Thompson, & Radder, 2004).

Chloramines are formed through a series of reactions that occur when aqueous chlorine and ammonia nitrogen are mixed at various dosing molar ratios ((Cl₂/N)₀). The three products of these reactions are monochloramine (NH₂Cl), dichloramine (NHCl₂), and trichloramine (NCl₃). Although all three species have disinfectant qualities, monochloramine is the most desirable for water treatment applications as it is the most stable and lacks any unpleasant taste or odor.

Within the proper range of environmental conditions, monochloramine will form with high efficiency if adequate mixing is provided to the reactants. However, adequate mixing can be more difficult to achieve than would be expected. According to a survey of water treatment plant operators utilizing chloramination for disinfection, 23% of respondents indicated that they had experienced problems related to poor mixing (Kirmeyer et al., 2004). These problems vary in scope. Studies indicate that lack of adequate mixing during chloramination can lead to nitrification within the distribution
system and may result in violations of the USEPA’s Surface Water Treatment Rule (Yang, Harrington, & Noguera, 2008). Additionally, insufficient mixing can result in a lower than required total chlorine residuals within the distribution system, potentially allowing bacterial infiltration that could adversely affect human health.

These problems indicate that mixing is of great importance to the chloramination process. As such, careful consideration must be taken during the design of these processes, with particular focus given to the intensity of mixing that will be provided. Until recently, very little information was available in regard to sufficient mixing intensities. In response to the poor survey results, Kirmeyer et al. (2004) suggested that a velocity gradient (G value) range of 300 s\(^{-1}\) to 1000 s\(^{-1}\) be utilized at treatment plants in order to obtain better mixing. Although this provides some guidance, the range is rather wide and could easily lead to a system being over or under designed. A recent study by Jain (2007) attempted to identify the optimum velocity gradient through bench scale experimentation. Although Jain (2007) examined a limited range of mixing intensities, the study concluded that a velocity gradient of 300 s\(^{-1}\) was capable of providing adequate mixing.

To further investigate the effect of mixing on the chloramination treatment process, a case study of a real-world water treatment facility was completed. The facility was designed with rapid mixing chambers capable of creating velocity gradients of 900 s\(^{-1}\), a baffled channel system, and chemical dispersion system for the reactants (CDM, 2002). The plant is currently achieving adequate mixing without the use of any of its rapid mixers, indicating a certain degree of over design in regard to the disinfectant processes. The information provided by all of these studies makes it clear that adequate mixing is essential to the production of proper total chlorine residuals by chloramine disinfection.
As such, this study aimed to provide further investigation into the optimum velocity gradient required for adequate chloramination treatment. Analyses of the resultant data lead to additional investigation into the impact of carbonate C\textsubscript{i} on the chloramination system. Results from all experiments were tested against speciation and pH predictions from the Unified Plus Model, a comprehensive model capable of simulating breakpoint curves.
2 CHLORAMINATION

2.1 Chloramine Utilization

Chlorine has long been the most common disinfectant utilized by drinking water treatment facilities because of its effectiveness, low cost, and its ability to maintain acceptable residual concentrations within a distribution system (Lee & Westerhoof, 2009). However, chlorine has come under increased scrutiny over the past several years due to its tendency to form disinfection byproducts (DBPs). These DBPs include trihalomethanes (THMs) and haloacetic acids (HAA₅), all of which have been identified as being potentially harmful to humans (Kirmeyer et al., 2004). To protect the public against exposure to these chemicals, the United States Environmental Protection Agency (USEPA) has established new treatment requirements over the past several years in order to regulate these compounds more stringently. In particular, the USEPA enacted the Stage 2 Disinfectants and Disinfection Byproducts Rule (Stage 2 DBP rule) in 2006 which greatly reduced the maximum concentrations of DBPs allowed in a potable water system (USEPA, 2009).

In response to these requirements, utilities have been forced to reevaluate their current treatment systems. Many of these facilities have started to shift their focus to using chloramines as disinfectants, as they produce much fewer DBPs than chlorine while still retaining similarly effective disinfection qualities. As of 1998, it was estimated that approximately 29% of large and medium sized water treatment plants utilized chloramines for disinfection (Rose, Rice, Hodges, Peterson & Arduino, 2007). In response to the increased governmental standards, some studies predict that the use of chloramines for disinfection could increase to approximately 65% of surface water...
treatment plants across the United States (Yang et al., 2008). Although these statistics show that chloramination has increased (and may continue to increase) in popularity as a treatment method over the past quarter century, it should not be mistaken as a new disinfection process. Chloramination has been utilized for drinking water treatment in the United States since the early 1900s and only fell out of favor due to the lack of available ammonia during World War II (Kirmeyer et al., 2004). As such, it is a time-tested method with many potential benefits for water treatment practices.

2.2 Chloramines

Chloramine is the collective name of a family of three chemicals formed by the reaction of aqueous chlorine with ammonia. These chemicals are monochloramine (NH₂Cl), dichloramine (NHCl₂), and trichloramine (NCl₃). The speciation of these chemicals is strongly dependent on the initial dosing molar ratio of Cl₂ to NH₃, pH, temperature, as well as other factors. While all three species have biocide qualities, monochloramine is the preferred species for disinfection as it is the most stable of the three compounds and has no undesirable taste or odor associated with it (Kirmeyer et al., 2004).

Although it provides a practical alternative to chlorination, chloramination is not fully exempt of problems. One major problem associated with chloramination is the proliferation of ammonia oxidizing bacteria (AOB) which can result in nitrification at the treatment plant (Yang et al., 2008). Surveys have shown that 63% of utilities using chloramination have experienced nitrification episodes (Yang et al., 2008). In addition, studies have shown that N-Nitrosodimethylamine (NDMA), a non-halogenated DBP, can be produced during the chloramination process (Charrois & Hrudey, 2007). Although a maximum contaminant level (MCL) has not yet been established by the USEPA, NDMA
is believed to be a cancer causing agent and as such it is undesirable in treated drinking water. Fortunately, studies have indicated that NDMA formation usually occurs below pH levels of 7.0, which is lower than the standard water pH at most drinking water utilities (Mitch, Oelker, Hawley, Deeb & Sedlak, 2005). Modeling evidence also suggests that residual concentrations of monochloramine may provide little benefit against the intrusion of rather “susceptible” bacteria such as *E. coli* into a distribution system (Betanzo, Hofmann, HU, Baribeau & Alam, 2008). Despite these issues, chloramination remains a preferred choice for disinfection, as it exhibits a far lower overall production of DBPs and is capable of maintaining a more stable residual within a distribution system than chlorine (Fisher, Sathasivan, Chuo, & Kastl, 2009).

### 2.3 Synthesis

As was mentioned in the previous section, chloramines are formed through a series of reactions between aqueous chlorine and ammonia. The reactants and the steps required for the production of chloramines species are detailed as follows.

#### 2.3.1 Aqueous Chlorine

Aqueous chlorine can be formed by the addition of hypochlorite salts, such as sodium hypochlorite (“bleach”), to water, or by bubbling chlorine gas into water. Upon addition to water, the chlorine quickly hydrolyzes to form hypochlorous acid (HOCl) as seen in Equation 2-1.

\[
\text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{HOCl} + \text{H}^+ + \text{Cl}^- \quad (2.1)
\]

In describing chloramine formation reactions, it is acceptable to use Cl₂ and HOCl interchangeably as they relate to each other on a one mole to one mole ratio as seen in this equation.
As a weak acid, hypochlorous acid may dissociate to form hypochlorite ion (OCl\(^{-}\)). Collectively, HOCl and OCl\(^{-}\) represent the available free chlorine of a solution.

### 2.3.2 Aqueous Ammonia

Ammonia (NH\(_3\)) is a common compound that dissolves readily in water. As a result of this solubility, forms of aqueous ammonia are found in many water bodies. Aqueous ammonia can also be produced synthetically by the addition of ammonium salts, such as ammonium chloride, to water.

### 2.3.3 Formation of Chloramines

Although it involves only two primary reactants, the formation of chloramines involves a complex system of competing reactions which are impacted by a number of variables, including pH, temperature, ratio of chlorine to ammonia nitrogen, and contact time (Li & Blatchley III, 2009). However, to simplify this system, the reactions can be depicted in a stepwise process, with the aqueous forms of chlorine and ammonia reacting to first form monochloramine (Equation 2.2).

\[
\text{NH}_3(\text{aq}) + \text{HOCl} \leftrightarrow \text{NH}_2\text{Cl} + \text{H}_2\text{O} \quad (2.2)
\]

Monochloramine will then react further in the presence of additional free chlorine to form dichloramine (Equation 2.3).

\[
\text{NH}_2\text{Cl} + \text{HOCl} \leftrightarrow \text{NHCl}_2 + \text{H}_2\text{O} \quad (2.3)
\]

And finally, dichloramine will react even further with available free chlorine to form trichloramine (Equation 2.4).

\[
\text{NHCl}_2 + \text{HOCl} \leftrightarrow \text{NCl}_3 + \text{H}_2\text{O} \quad (2.4)
\]
2.3.4 Chloramine Speciation

As competing reactions, the formation of the three chloramine species tends to be highly specific to a particular range of environmental conditions. In terms of disinfection, monochloramine is the most desirable end product of chloramine synthesis. Monochloramine formation is extremely rapid within a pH range of 6.5 to 9.0, a temperature of 25 °C, and at a chlorine to ammonia-nitrogen weight ratio of approximately 5:1 (equivalent to a molar ratio of 1:1) (Kirmeyer et al., 2004).

Dichloramine is much less stable than monochloramine and tends to be undesirable for disinfection due to its odor. Dichloramine formation is most efficient within a pH range of 4.0 to 6.0 and within a chlorine to ammonia-nitrogen weight ratio range of approximately 5:1 to 7.6:1 (equivalent to a molar ratio range of 1:1 to 1.5:1 respectively) (Kirmeyer et al., 2004). Outside of these conditions, the formation of dichloramine tends to be rather slow kinetically and it does not tend to form when contact times are very short. However, given enough contact time, some competition can be expected between the monochloramine and dichloramine species. Examples of the expected proportions of monochloramine and dichloramine speciation in terms of pH and temperature can be seen in Table 2.1.
Table 2.1: Proportions of monochloramine and dichloramine at differing pH and temperature conditions (NRC, 1994)

| pH | NH$_2$Cl | NHCl$_2$ | NH$_2$Cl | NHCl$_2$ | NH$_2$Cl | NHCl$_2$
|----|---------|---------|---------|---------|---------|---------
| 4  | 0       | 100     | 0       | 100     | 0       | 100     |
| 5  | 34      | 66      | 20      | 80      | 13      | 87      |
| 6  | 77      | 23      | 67      | 33      | 57      | 43      |
| 7  | 94      | 6       | 81      | 9       | 88      | 12      |
| 8  | 99      | 1       | 98      | 2       | 97      | 3       |
| 9  | 100     | 0       | 100     | 0       | 100     | 0       |

Trichloramine is the rarest of the three species in terms of production during water treatment practices. This is because the species normally only forms under acidic conditions where the pH is less than 4.4 and at high chlorine to ammonia-nitrogen weight ratios in excess of 7.6:1 (molar ratio of 1.5:1) (Kirmeyer et al., 2004). As these pH conditions are not within the operating ranges of drinking water treatment facilities, adverse water quality due to trichloramine production is not normally of concern.

2.4 Breakpoint Phenomenon

The reactions between aqueous chlorine and ammonia result in a unique phenomenon known as “breakpoint chlorination.” Upon the addition of the chemicals into water, chlorine will oxidize the ammonia that is present to form chloramines through the reactions outlined by Equations 2.2 to 2.4. As chloramines are produced, an initial rise in the concentration of total residual chlorine (primarily chloramine species) present in the water occurs. This rise continues up to a chlorine to ammonia-nitrogen dosing molar ratio of 1:1, where a peak in residual concentration is observed. This peak corresponds to
the optimum dosing for monochloramine production. As the molar ratio is increased further, the total residual begins to drop and approaches zero at a molar ratio of approximately 1.5:1 to 2:1 depending upon water conditions (Snoeyink & Jenkins, 1980). This minimum in total residual chlorine concentration is known as the breakpoint. The drop resulting in the breakpoint is caused by the breakpoint reaction, which is represented as

$$2\text{NH}_2\text{Cl} + \text{HOCl} \leftrightarrow \text{N}_2 + 3\text{H}^+ + 3\text{Cl}^- + \text{H}_2\text{O} \quad (2.5)$$

This equation helps explain the observed stoichiometry of the breakpoint phenomenon, as it requires 3 moles of chlorine for every 2 moles of ammonia (a ratio of 3:2 or 1.5:1). At molar ratios higher than the breakpoint, the total residual chlorine concentration again begins to increase. At this chlorine dose essentially all of the total chlorine residual will consist of excess free chlorine, as the available ammonia is already fully oxidized. However, trace concentrations of chloramine species may be observed.

The breakpoint phenomenon is depicted graphically by displaying the dosing molar ratio of chlorine to ammonia nitrogen along the x-axis and residual chlorine and the molar ratio of residual chlorine to initial ammonia nitrogen along the y-axis. This produces an easy to read plot that clearly displays the “hump-and-dip” form attributable to the breakpoint pattern described above (March & Gual, 2007). An example of an idealized plot of the breakpoint pattern can be seen in Figure 2.1.
Figure 2.1: Ideal breakpoint curve

In this idealized graph, the breakpoint can be observed at a molar ratio of 1.5:1. The preceding “hump” of residual chlorine depicts the combined chlorine region and the line after the breakpoint represents the free chlorine region. Throughout the course of this study, these plots will be referred to as “breakpoint curves.”
3 MIXING

Mixing is a very common operational procedure that has a broad range of applications. In general terms, mixing refers to the blending or combination of materials or chemicals for the purpose of creating a predominantly homogenous final system (Fair, 1968). As such, mixing which results in a perfectly homogenous final system is often referred to as uniform mixing.

Although it is a relatively simple process operationally, mixing is an essential step in numerous engineering systems, especially those important in drinking water treatment systems. Water treatment facilities utilize mixing in multiple phases of the treatment process, including but not limited to coagulation, flocculation, and disinfection. For such systems, the blending required for proper mixing can be produced by mechanical agitators such as paddles, pneumatic agitators, and baffle basins (Reynolds and Richards, 1996).

3.1 Velocity Gradient

Mixing is a physical process that requires a certain quantity of power to be imparted into a system in order to create the desired amount of blending. This holds true regardless of the mixing speed being utilized. It is therefore desirable to utilize a term known as the velocity gradient, or “G value,” to quantify the amount of power being input to a system in relation to the intensity of mixing achieved. As such, the computation of a system’s velocity gradient is an important aspect in the design and evaluation or a mixer. Velocity gradients of mechanical impeller systems without vertical baffles are calculated using the equation
where \( G \) is the velocity gradient \( (s^{-1}) \), \( P \) is the power dissipated \( (\text{ft-lb/s}) \), \( \mu \) is the absolute viscosity of water \( (\text{lb-s/ft}^2) \), and \( C \) is the total volume \( (\text{ft}^3) \) (Fair, 1968).

### 3.2 Applications for Chloramination

Mixing is a very important process for water treatment facilities, particularly in regard to disinfection. During disinfection, mixing is responsible for the dispersal of the chemical disinfectant or disinfectants throughout the water stream. At treatment facilities utilizing chloramination, mixing is also essential for the formation of chloramines from aqueous chlorine and ammonia. For chloramination to be an effective disinfection process, uniform mixing of chlorine and ammonia is required. A lack of uniform mixing can lead to incomplete reactions between chlorine and ammonia, and as a result, poor chlorine residuals. This is of great importance, as these poor chlorine residuals may result in non-compliance with applicable state and federal drinking water requirements.

A review of recent surveys and studies highlights the importance of adequate mixing during chloramination. A survey of water treatment plant operators indicated that 23% of respondents experienced problems with chloramine formation as a result of poor chemical mixing (Kirmeyer et al., 2004). Furthermore, bench scale analysis determined that the efficiency of monochloramine formation was greatly reduced by operating the mixers at too low of a velocity gradient (Jain, 2007). It has also been shown that excess concentrations of ammonia available during the chloramination process as a result of incomplete mixing, promote the growth of ammonia-oxidizing bacteria (Liu and Ducoste, 2006). In turn, these bacteria lead to nitrification problems that can also result in potential problems with regulatory compliance.
4 ALKALINITY

Drinking water treatment facilities rely upon a source water body for their individual water supplies. Each water body is different in regard to a number of variables, such as pH, temperature, and turbidity. In the design of these facilities, the source must be carefully considered to ensure that treated water will be a safe and desirable product for the end user. One of the most important variables that must be considered when reviewing the source water body is alkalinity. Alkalinity is a measure that reflects the ability of a water to neutralize acid and as such, alkalinity contributes to a water’s ability to maintain a relatively consistent pH level under differing conditions.

Measurement of source water alkalinity provides insight into the additional treatment systems that may be required beyond disinfection at a water treatment facility. Plant operators desire a water “end product” that maintains a consistent pH from the time it leaves the facility to the time it arrives at the consumer’s faucet. If a source water has a suitable alkalinity, no further systems may be required to treat the water. Source waters with low alkalinity will require chemical dosing to reduce the corrosive nature of the water. Otherwise, the water may leach heavy metals from piping in the distribution system and reduce disinfectant residuals, exposing the consumer to potential health risks (Vikesland and Valentine, 2002). Conversely, too high of an alkalinity can result in undesirable taste. Under such circumstances, a treatment plant may have to install a system to remove a percentage of alkalinity.

4.1 The Carbonate System

Alkalinity in natural waters is primarily attributable to bases such as carbonates (CO$_3^{2-}$), bicarbonates (HCO$_3^-$), and hydroxides (OH$^-$) (Snoeyink and Jenkins, 1980). As such,
alkalinity shares a close relation with the carbonate system. The carbonate system is an important acid-base system found in natural waters that involves the relationships between carbon dioxide (CO$_2$), carbonic acid (H$_2$CO$_3$), bicarbonate (HCO$_3^-$), carbonate (CO$_3^{2-}$), and carbonate containing solids (Snoeyink and Jenkins, 1980). Like alkalinity, the presence of carbonate species in a natural water source is primarily analyzed for the role it plays in regard to a systems pH. However, the total concentration of carbonate (referred to simply as C$_t$ in this study) in a water is dynamic due to the continuous reactions of water with atmospheric CO$_2$. This may result in slight changes to the buffering capacity of a water through the course of a day.

4.2 Chloramination Studies

During the current study, alkalinity was added into the experimental systems in the form of sodium bicarbonate in order to better represent the conditions found at real-world treatment facilities. Literature reviews did not uncover any information to indicate that such an addition would have any direct impacts on the chloramination process. However, secondary relationships were uncovered which indicated that C$_t$ could impact pH values and that any resultant pH changes may impact the speciation of chloramines. These relationships were discussed in Chapter 2 of this study.
5 EXPERIMENTAL SETUP

The measurements of free chlorine and chloramine species concentrations represent the critical experimental steps in this study. These measurements require a very high level of precision. Thus, great care had to be taken during the preparation of the experimental glassware and equipment in order to avoid any contamination that may adversely impact the results. Such care was also critical during the preparation of the chemical reagents. As such, the success of each experiment strongly hinged on the level of care taken during the experimental setup.

5.1 Glassware and Equipment

When circumstances allowed, all glassware and equipment utilized during this study was set aside and used specifically for this research alone in an attempt to reduce any possible sources of contamination. In preparation for an experiment, all glassware and equipment was thoroughly washed and then put through a chlorine soaking process. During this process, each item was soaked in a chlorine solution (approximately 15 mg/L Cl\textsubscript{2}) for 30 minutes to ensure that it would not exhibit any chlorine demand over the course of the experiment. Each item was then soaked in deionized (DI) water for approximately 15 minutes before being rinsed with DI water three additional times. Once dry, each item was ready for experimental use. This cleaning and soaking process was completed between each individual experiment to avoid any cross-contamination.

5.2 CDF Water

Just as was the case with the glassware and equipment, it was necessary to ensure that the water used in the experiment for the critical solutions was free of any chlorine demand.
Chlorine Demand Free (CDF) water was produced by dosing glass jars of reverse osmosis deionized (RODI) water with a low concentration of sodium hypochlorite in order to consume any chlorine demand that may be present. A concentration of 1.25 mg Cl$_2$/L was used in the early experiments but was later reduced to 0.50 mg Cl$_2$/L when this quantity was found to be sufficient to consume any demand. To remove the excess chlorine remaining in the CDF water, the jars were placed under UV light until DPD-FAS titration indicated that all chlorine had been degraded. This process took approximately one to two weeks depending upon the initial chlorine concentration and acted as a rate limiting step for the completion of this study. It should be noted that CDF water can be obtained more quickly by exposing the glass jar to direct sunlight. This method was not used during this study as most experiments were conducted during the fall and winter months.

5.3 Chemical Preparation

This study required the preparation of multiple chemical species for each experiment. The chemicals have been classified into three separate groups to clarify their use during the study. These groups are the critical solutions, titration solutions, and dry chemicals.

5.3.1 Critical Solutions

The critical solutions in this experiment are the chlorine stock solution and the ammonia stock solution. In order to accurately study the production of chloramines species, it is essential that these two solutions be produced carefully and to their exact specifications. As such, both solutions were made using CDF water. A detailed description of each solution’s preparation follows.
1) **Chlorine Stock Solution (1000 mg Cl\(_2\)/L):** The chlorine stock solution was prepared by diluting approximately 20 ml of reagent grade sodium hypochlorite (5% available free chlorine) to 1 L with CDF water. The 20 ml volume is an approximation due to the unstable nature of sodium hypochlorite, which causes the concentration of available free chlorine to decrease over time. Thus, the exact concentration of the sodium hypochlorite solution had to be determined prior to every experiment using DPD-FAS titration. This was done by first diluting 5 ml of the sodium hypochlorite to 250 ml using CDF water to create a solution with a concentration of about 1000 mg Cl\(_2\)/L. 5 ml of this solution was then further diluted to 1 L to produce a solution with a concentration of about 5 mg Cl\(_2\)/L. The exact concentration was determined by titrating three samples and taking the average of the readings. Using this exact concentration, the actual volume of sodium hypochlorite required to produce the 1000 Cl\(_2\)/L chlorine stock solution was calculated. The chlorine stock solution was then stored at 10 °C until its use.

2) **Ammonia Stock Solution (1000 mg NH\(_3\)-N/L):** The ammonia stock solution was prepared by dissolving exactly 1.91 g of reagent grade ammonium chloride (NH\(_4\)Cl) in a 500 ml volumetric flask using CDF water. The solution was then stored at 10 °C until its use.

### 5.3.2 Titration Solutions

The DPD-FAS titrimetric method for chlorine species determination requires the use of three different solutions.
1) **N-diethyl-p-phenylenediame (DPD) Solution**: DPD is used as an indicator for the presence of chlorine species, as it reacts with chlorine species to produce a distinctive red color. The presence of this coloration allows for the measurement of chlorine species concentrations. One liter of DPD solution was produced by dissolving 1 g of DPD oxalate in CDF water containing 8 ml of 9 N H$_2$SO$_4$ and 200 mg of disodium EDTA. The solution was then diluted to 1 L and stored in a brown glass bottle to avoid photodegradation.

2) **Ferrous Ammonium Sulfate (FAS) Titrant**: Once chlorine reacts with DPD to give a solution a distinct red color, the quantity of the chlorine species present can be measured using FAS titrant as 1.00 ml of FAS titrant will react with 100 $\mu$g of Cl$_2$. Thus, the concentration of the species in a 100 ml sample can be determined, with a 1.00 ml FAS titrant = 1 mg Cl$_2$/L. FAS titrant was produced by dissolving 1.106 g of ferrous ammonium sulfate hexahydrate in DI water containing 1 ml of 9 N H$_2$SO$_4$ and diluting to 1 L.

3) **Phosphate Buffer Solution**: Phosphate buffer is added to a sample prior to titration in an attempt to create/maintain optimum pH conditions for DPD-FAS titration. Phosphate buffer was produced by dissolving 24 g of anhydrous Na$_2$HPO$_4$ and 46 g of anhydrous KH$_2$PO$_4$ in DI water containing 800 mg of disodium EDTA. The solution was then diluted to 1 L and two drops of toluene were added to prevent mold growth.

### 5.3.3 Dry Chemicals

This study also required the use of two dry chemicals during the course of each experiment.
1) **Sodium Bicarbonate**: Sodium bicarbonate was added to each experimental reactor to establish a set carbonate $C_t$. Sodium bicarbonate was pre-weighed into 12 tins at the start of each experiment. The quantity of sodium bicarbonate was dependent upon the desired $C_t$.

2) **Potassium Iodide**: During DPD-FAS titration, the addition of FAS into a sample depletes the red color produced by free chlorine. The addition of potassium iodide then causes the chloramine species to produce color. Potassium iodide was preweighed prior to each experiment, with 24 tins containing 1 g of KI required for each experiment.

### 5.4 DPD-FAS Titrimetric Method Setup

The DPD-FAS method required a simple titration setup, including a titration stand, burette, and magnetic mixer. A 10-ml burette was utilized during the experiments to ensure that readings were taken with a high degree of accuracy. The use of pipettes for chemical addition was also required.

### 5.5 Temperature

This study aimed to recreate the conditions found in the Massachusetts Water Resources (MWRA) distribution system. As such, experiments were completed at a temperature of 10 °C, which was assumed to be the mean water temperature in the region during the course of a year. This was accomplished by storing all chemicals and conducting all phases of the experiment in a cold temperature room set at this temperature.
6 PROCEDURES

6.1 Experimental Design Process

This study was intended as a follow-up to the work completed by Jain (2007) which investigated the impact of different degrees of mixing on the chloramination process. As such, the initial experimental design had many commonalities shared with the experiments of Jain. However, new observations emerged during the course of this study which required several modifications to be made to the experimental procedure. This enabled the study to retain its original focus while also allowing for investigation into a newly discovered phenomenon.

6.2 Design Basis

The primary focus of this study was to investigate how different degrees of mixing impacted the chloramination treatment process through the use of bench scale experiments. During these experiments, chlorine was to be dosed prior to ammonia. Factors that had to be considered during the design phase included chlorine to ammonia nitrogen molar ratios, mixing speeds, reaction times, temperature, pH control, and the apparatus available for use. In addition, it was desirable to design the procedure in a method that would allow for the easy comparison of results with the most current computer model.

As was previously mentioned, the study aimed to recreate the water supply conditions of the MWRA system. As such, a temperature of 10 °C was utilized throughout the study. In order to recreate the alkalinity of the “real-world” treated water, pre-measured quantities of sodium bicarbonate were added to each experimental reactor to yield a C\textsubscript{t} of 10^{-3} M. Although this acted as a pH buffer to some degree, no further action was taken to
maintain a specific pH range. pH readings were taken during the course of the experiment to chronicle any changes.

Like Jain, bench scale experiments were completed with a *Phipps & Bird* jar test apparatus that was capable of providing mixing at a fixed impeller speed for six separate reactors. Velocity gradients were determined from impeller speeds using the “Laboratory G Curve for Flat Paddle in the Gator Jar” figure from the Manual of Water Supply Practices (2000). The jar test apparatus complete with reactors can be seen in Figure 6.1.

![Figure 6.1: Experimental jar test apparatus](image)

The impeller speeds that could be tested were limited to the apparatus’s maximum of 300 rpm. As a result, this study conducted experimental trials at Jain’s optimum mixing speed of 200 rpm (G value = 300 s\(^{-1}\)) and 300 rpm (G value = 500 s\(^{-1}\)) to determine if chloramination results would improve further at higher speeds.

A total of ten chlorine to ammonia nitrogen molar ratios were selected for use during the study in order to provide a broad overview of speciation throughout the breakpoint curve.
The molar ratios utilized were 0.50, 0.75, 1.00, 1.25, 1.50, 1.60, 1.75, 2.00, 3.00, and 4.00. Three molar ratios were selected between 1.50 and 1.75 to accurately identify the breakpoint. A “blank” reactor containing only chlorine was also tested to act as a check for the concentration of the chlorine stock solution. Given that the jar test apparatus can only mix six reactors at a given time, each experiment had to be conducted in two separate trials. Each trial investigated five molar ratios as well as one blank reactor.

Chlorine was to be dosed into each reactor prior to ammonia nitrogen. Sampling times of 15 minutes and 45 minutes were selected based on the kinetics of chloramine species formation. In order to spread out the large amount of work required during the sampling process, ammonia nitrogen was added into each reactor at set time intervals.

6.3 Experimental Procedure

The mixing speed to be tested (either 200 or 300 rpm) was determined prior to the start of each experiment. Based upon the specifications detailed in the previous section, the experiments were completed utilizing the procedure detailed below:

1. CDF water and all experimental reagents were allowed to acclimate to the cold room temperature (approximately 10 °C).

2. Jar test reactors were prepared with 2 L of CDF water.

3. Each reactor was dosed with predetermined volumes of chlorine stock solution. Five reactors plus a blank were dosed in each trial, with two trials for each experiment. Chlorine dosing specifications are given in Table 6.1.
<table>
<thead>
<tr>
<th>Reactor #</th>
<th>Molar Ratio (Cl₂:NH₃-N)</th>
<th>Add Z ml of 1000 mg Cl₂/L solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>-</td>
<td>10.00 (to 5 mg Cl₂/L)</td>
</tr>
<tr>
<td>1</td>
<td>0.5</td>
<td>5.06</td>
</tr>
<tr>
<td>2</td>
<td>0.75</td>
<td>7.59</td>
</tr>
<tr>
<td>3</td>
<td>1.0</td>
<td>10.12</td>
</tr>
<tr>
<td>4</td>
<td>1.25</td>
<td>12.65</td>
</tr>
<tr>
<td>5</td>
<td>1.5</td>
<td>15.18</td>
</tr>
<tr>
<td>6</td>
<td>1.60</td>
<td>16.19</td>
</tr>
<tr>
<td>Blank</td>
<td>-</td>
<td>10.00 (to 5 mg Cl₂/L)</td>
</tr>
<tr>
<td>7</td>
<td>1.75</td>
<td>17.71</td>
</tr>
<tr>
<td>8</td>
<td>2.0</td>
<td>20.24</td>
</tr>
<tr>
<td>9</td>
<td>3.0</td>
<td>30.36</td>
</tr>
<tr>
<td>10</td>
<td>4.0</td>
<td>40.48</td>
</tr>
</tbody>
</table>

**Table 6.1: Chlorine dosing requirements**

4. 168 mg of NaHCO₃ was added to each reactor to establish a Cᵢ = 10⁻³ M. The jar test apparatus was set to the desired mixing speed for one minute to ensure adequate dispersal of the chemicals. At this time, the initial pH of each reactor was measured and recorded.

5. The apparatus was again set to the desired mixing speed and the timer was started for the blank reactor. After a time of five minutes, 2 ml of 1000 mg/L NH₃-N solution was added to Reactor #1 to achieve a concentration of 1 mg/L NH₃-N. The addition of 2 ml of 1000 mg/L NH₃-N solution was then repeated for each Reactor at five minute intervals.

6. Sampling was completed at 15 minutes and 45 minutes. Free chlorine, monochloramine, and dichloramine concentrations were determined using the DPD Ferrous Titrmetric Method as outlined by Standard Method 4500-Cl F. (2005). Due to the lack of trichloramine found in past studies, trichloramine concentration was not measured during the course of this experiment. The procedure for DPD-FAS was completed as follows.
7. DPD-FAS method sampling:

a. pH was measured and recorded from each reactor at both the 15 minute and 45 minute sampling times.

b. A 100 ml sample was taken from each reactor using a graduated cylinder and transferred to a 250 ml beaker. 5 ml of phosphate buffer and 5 ml of DPD were subsequently added to the beaker.

c. The initial burette volume was recorded. Titration was then completed with FAS until the red color was discharged and the burette reading was recorded as Reading A. Free chlorine concentration was determined by subtracting Reading A from the initial reading.

d. A small KI crystal (about 0.5 mg) was added to the sample to reinvigorate the red color. The sample was titrated again until the red color was once again discharged. The burette reading was recorded as Reading B. Monochloramine concentration was determined by subtracting Reading A from Reading B.

e. 1 g of KI crystals was added to the sample to reinvigorate the red color for a third time. Titration was completed until the color was discharged. The burette reading was recorded as Reading C. Dichloramine concentration was determined by subtracting Reading B from Reading C.

6.4 Modified Experimental Procedure

As the experiments were completed during this study, a number of unexpected results began to be observed. These results will be discussed in great detail in the Results and
Analysis chapter. It was initially assumed that the patterns were the result of some unforeseen error. As such, a number of modifications were made to the procedure to improve areas of possible error. Further modifications were also made to increase the amount of information obtained during the course of the study. The modifications were as follows:

1. One area of concern was the standardization of the chlorine stock solution. Standardization was initially completed at room temperature while the remainder of the experiment was completed at 10 °C. To ensure that there was no discrepancy between the results found at these temperatures, the procedure was changed to ensure that all portions of the experiment, including standardizations, were completed in the cold temperature room.

2. The residence time of water in the rapid mix chamber of a real-world water treatment facility is very short. Thus, the 45 minutes of mixing utilized in this study was determined to be excessive. In order to better follow the practices of the utilities and to reduce any undesirable interaction with the atmosphere caused by excess mixing, mixing time was reduced to two minutes for each reactor. This practice was started in Experiment #5 and utilized for all experiments thereafter.

3. Based on the initial procedure, pH readings were measured following the initially dosing of chlorine and at the two sampling times. In order to better understand the dynamics of pH during the course of an experiment, a pH monitoring program was added to the procedure. This monitoring program involved the measurement of pH at approximately 30 to 60 second intervals.
throughout the course of the 45 minutes experimental time. Monitoring was conducted at chlorine to ammonia nitrogen molar ratios of 1.00 and 1.60 in an attempt to correlate with the total chlorine peak and the breakpoint. Monitoring was conducted starting with Experiment #3 and completed for all experiments thereafter.

4. During the course of this study, a possible relation between $C_t$ and chloramination was observed. As such, it became desirable to complete the experiments at differing $C_t$ values to see what impact this additional variable may have. A table of the new $C_t$ values and the mass of chemical to be added to each reactor is presented in Table 6.2. Note that all of these experiments were completed at 300 rpm.

<table>
<thead>
<tr>
<th>Desired $C_t$ (M)</th>
<th>NaHCO$_3$ Required (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$10^{-4}$</td>
<td>16.8</td>
</tr>
<tr>
<td>$10^{-3}$</td>
<td>168</td>
</tr>
<tr>
<td>$10^{-4}$</td>
<td>1680</td>
</tr>
</tbody>
</table>

**Table 6.2: Sodium Bicarbonate dosing requirements**

As part of these experiments, some of the molar ratios investigated were also changed to more clearly focus the results. For Experiments #5 through #9, the molar ratio of 4.00 was replaced by 0.25. Additionally, during Experiment #9, the molar ratio of 1.75 was also replaced by 0.85.
7 RESULTS AND ANALYSIS

A total of nine experiments were completed during the course of this study. The results from Experiments #2, #5, #6, #7, #8, and #9 are presented in a series of figures which portray variations in the breakpoint curve with respect to mixing speed and C_t values. Raw data for these experiments can be found in Appendix A. A breakdown of the experimental conditions for each of these experiments can be found in Table 7.1. Note that Experiment #6 is a retrial of Experiment #5. These figures include analysis of free chlorine, monochloramine, dichloramine, and total calculated chlorine. Due to a lack of observed trichloramine during this and previous studies, trichloramine data is not presented in these figures. It should also be noted that the results for Experiments #1, #3, and #4 are not presented due to errors that occurred during their preparation and implementation.

<table>
<thead>
<tr>
<th>Experiment #</th>
<th>Figure #</th>
<th>Mixing Speed (rpm)</th>
<th>C_t (M)</th>
<th>Reaction Time (min)</th>
<th>T °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>7.1</td>
<td>200</td>
<td>10^{-3}</td>
<td>45</td>
<td>10</td>
</tr>
<tr>
<td>5</td>
<td>7.2</td>
<td>300</td>
<td>10^{-3}</td>
<td>45</td>
<td>10</td>
</tr>
<tr>
<td>6</td>
<td>7.4</td>
<td>300</td>
<td>10^{-3}</td>
<td>45</td>
<td>10</td>
</tr>
<tr>
<td>7</td>
<td>7.6</td>
<td>300</td>
<td>0</td>
<td>45</td>
<td>10</td>
</tr>
<tr>
<td>8</td>
<td>7.7</td>
<td>300</td>
<td>10^{-2}</td>
<td>45</td>
<td>10</td>
</tr>
<tr>
<td>9</td>
<td>7.8</td>
<td>300</td>
<td>10^{-4}</td>
<td>45</td>
<td>10</td>
</tr>
</tbody>
</table>

Table 7.1: Summary of experimental conditions

7.1 Organization of the Figures

For the analysis of breakpoint curves, this study utilized the plotting method demonstrated by Jain (2007), in which the y-axis denotes the molar ratio of residual
chlorine to initial ammonia nitrogen (Cl\textsubscript{2}/N\textsubscript{o}) and the x-axis denotes the molar ratio of initial chlorine to initial ammonia nitrogen ((Cl\textsubscript{2}/N\textsubscript{o})\textsubscript{o}). For simplification throughout the discussion of results, the y-axis will be referred to as the “residual molar ratio and the x-axis will be referred to as the “dosing molar ratio.” This method of plotting differs from the more conventional method, which plots the y-axis in terms of chlorine concentration in milligrams per liter. The conventional method also utilizes the dosing molar ratio along the x-axis. Although the conventional method does provide an accurate representation of the reaction scheme, it is more difficult to quantify the results due to the lack of consistency between the two axes. For example, based upon theory, the monochloramine peak is expected to occur at a residual chlorine “height” of 5.06 mg/L and a dosing molar ration of 1:1 using the conventional method. To determine the efficiency of monochloramine production, this value must be known and a calculation must be completed using the experimentally determined height. If monochloramine production was expected to have an efficiency of 95%, the peak in this type of plot would be expected at a residual chlorine height of approximately 4.81 mg/L. In the method used in this study, the peak is expected to reach a height of 1.00 along the residual molar ratio axis at a dosing molar ratio of 1:1. This method allows for simple analysis of the efficiency of the experiment, as a height of 0.95 along the residual molar ratio axis would indicate that the mixing process was 95% efficient in the production of monochloramine. Thus, the clear readability of results directly from such plots makes them very effective tools for depicting breakpoint curves.
7.2 Effect of Mixing

The primary focus of this study is the effect of mixing on the chloramination process. Bench scale testing was conducted at mixing speeds of 200 (Experiment #2) and 300 rpm (Experiment #5) at 10°C to determine if monochloramine formation improved at a mixing speed greater than those tested by Jain (2007). The results of Experiments #2 and #5 can be found in Figures 7.1 to 7.2, respectively.

![Figure 7.1: Experiment #2 breakpoint curve](image-url)
Figure 7.1-1: Experiment #2 breakpoint curve corrected for free chlorine

Figure 7.1-2: Experiment #2 breakpoint curve corrected for free chlorine and dichloramine
Data from Figures 7.1 and 7.2 was collected into Table 7.2 found below.

<table>
<thead>
<tr>
<th>Reaction Time (minutes)</th>
<th>RPM</th>
<th>Figure #</th>
<th>Cl₂/N₀ @ Monochloramine Peak</th>
<th>(Cl₂/N₀)₀ @ Monochloramine Peak</th>
<th>Cl₂/N₀ @ Total Chlorine Peak</th>
<th>(Cl₂/N₀)₀ @ Total Chlorine Peak</th>
<th>(Cl₂/N₀)₀ @ Breakpoint</th>
</tr>
</thead>
<tbody>
<tr>
<td>45</td>
<td>200</td>
<td>7.1</td>
<td>0.68</td>
<td>1.00</td>
<td>0.99</td>
<td>1.15</td>
<td>1.50</td>
</tr>
<tr>
<td>45</td>
<td>300</td>
<td>7.2</td>
<td>0.94</td>
<td>0.75</td>
<td>0.94</td>
<td>0.75</td>
<td>1.25</td>
</tr>
</tbody>
</table>

Table 7.2: Breakpoint figure data at different mixing speeds

The data above shows that monochloramine was the predominant species of residual chlorine prior to the breakpoint under both mixing conditions, with a small jump of dichloramine observed just after the monochloramine peak. Based on our understanding of chloramine chemistry, the location of the dichloramine peak is logical as the species is formed as monochloramine is further oxidized.

Due to this small dichloramine peak as well as a small free chlorine peak, the location of the monochloramine peak and the total chlorine peak are offset by approximately 0.15 units along the x-axis (dosing molar ratio) in Experiment #2.  Free chlorine should not be
present prior to the breakpoint. It seems likely that some iodide ion may have been present during titration causing it to appear as if free chlorine was present. As such, it can be assumed that all of the free chlorine present prior to the breakpoint was actually monochloramine. A plot accounting for this change can be found in Figure 7.1-1. Furthermore, despite the location of the dichloramine peak being logical, it does not perfectly match the theoretical speciation expected along the breakpoint curve. According to theory, the monochloramine peak and total chlorine peak should be found at the same location (dosing molar ratio of 1:1) as all of the species are expected to be in the form of monochloramine prior to the monochloramine peak. As ideal conditions are difficult to reproduce, differences in variables such as solution pH or temperature may result in inconsistencies between observed data and theory. This appears to be the case in regard to the dichloramine peak observed in Experiments #2. If the presence of the dichloramine peak was in fact due to one or more of these conditions, it is possible that some monochloramine may have been incorrectly identified as dichloramine. Although it is not possible to determine the degree to which this occurred, Figure 7.1 was once again re-plotted. This corrected plot assumed that all free chlorine and dichloramine found prior to the breakpoint was misidentified and was actually monochloramine. The corrected plot can be found in Figure 7.1-2. It should be noted that further investigation would be required to determine if this assumption was feasible.

7.2.1 200 rpm vs. 300 rpm

The monochloramine and total chlorine results observed from Figures 7.1 and 7.2 were overlaid to produce Figure 7.3 found on the following page.
Figure 7.3: Breakpoint curves at 200 rpm and 300 rpm for 45 minutes at 10°C

Figure 7.3 presents a clear comparison of the bench scale results for 200 and 300 rpm. As was previously stated, a theoretical monochloramine yield of 100% (corresponding to both a monochloramine peak and a total chlorine peak of 1.00) would be expected at a dosing molar ratio of 1:1 under ideal mixing conditions. However, the experimental results for 200 rpm identified a monochloramine peak of 0.68 at a dosing molar ratio of 1:1 and a total chlorine peak of 0.99 located at 1.15:1. At 300 rpm, a monochloramine peak and total chlorine peak of 0.94 are observed at a dosing molar ratio of 0.75:1. These results show that there is some discrepancy between the monochloramine and total chlorine peaks at the two mixing speeds. While the monochloramine peak at 200 rpm (0.68) is lower than that at 300 rpm (0.94), the total chlorine peak for 200 rpm (0.99) is higher than at 300 rpm (0.94). Following theory, both the residual monochloramine and total chlorine yield should increase or remain steady as the mixing becomes more uniform as occurs when mixing speed increases.
This apparent discrepancy may have been caused by errors during the titration measurements of residual chlorine at 200 rpm. Experiment #2 was one of the earlier experiments completed in this study, and as such I had only limited experience with the DPD-FAS titration process. From Figure 7.1, it can be seen that small amounts of free chlorine were observed prior to the dosing molar ratio of 1:1. According to the chloramine reaction scheme, no free chlorine should be present during this time. It is possible that a small quantity of potassium iodide residue was present in the beakers used for these pre-breakpoint measurements, resulting in a false identification of some monochloramine as free chlorine. This would cause a lower than expected monochloramine peak. Furthermore, the measurement of dichloramine tends to be unsteady due to the nature of the reaction. Due to my lack of experience, it is possible that I may have over titrated during the dichloramine measurement resulting in an erroneously high total chlorine peak. This would bring the total chlorine peak closer to that which was observed at 300 rpm and indicate that there may be little additional benefit to increasing the mixing speed above 200 rpm.

In addition to the discrepancies discussed above, the results for 300 rpm show that both the monochloramine and total chlorine peaks occurred at a smaller dosing molar ratio (0.75:1) than is expected (1:1). As such, it seemed possible that the location of the monochloramine and total chlorine peaks in Experiment #5 may have been erroneous and a retrial, Experiment #6, was conducted. The results of Experiment #6 can be found in Figure 7.4.
As the results of Experiment #6 indicate, the monochloramine and total chlorine peaks once again occurred at smaller dosing ratios (0.6:1 and 0.75:1 respectively) than is expected. With the supporting data from Experiment #6, it was determined that the results of Experiment #5 were not erroneous but rather indicative of an as of yet unforeseen pattern. This observed “left shift” of the results along the y-axis will be discussed in further detail in Section 7.3.

7.2.2 Comparison with past studies

The study by Jain (2007) presented breakpoint curves for mixing speeds of 50, 150, and 200 rpm at 10ºC. Jain concluded in bench scale experiments, that a G value of 300 s⁻¹ (corresponding to 200 rpm) is the desirable velocity gradient for the formation of monochloramine through the mixing of ammonia and chlorine. The results of Jain’s experiment at 200 rpm can be seen below in Figure 7.5.
Figure 7.5: Breakpoint curve at 200 rpm for 45 minutes at 10°C (Jain, 2007)

The current study completed Experiment #2 at 200 rpm to determine if Jain’s results were reproducible. The residual total chlorine peak of 0.93 determined by Jain was very similar to the residual total chlorine peak of 0.96 found from Experiment #2 (see Figure 7.1 and Table 7.2). This indicates that the results of Jain’s study appear to be reproducible. However, some slight difference in speciation was observed, with Experiment #2 exhibiting a small free chlorine peak and a distinct dichloramine peak while Jain’s results depicted only a monochloramine peak. As free chlorine should not be present prior to the breakpoint, it is likely that all of the free chlorine found prior to the breakpoint in Experiment #2 was actually monochloramine. Applying this correction to the results of Experiment #2 allows for the two experiments to be directly compared. This comparison is depicted in Figure 7.5-1.
Figure 7.5-1: Comparison of Jain’s study with Experiment #2 results corrected for free chlorine

This figure shows a rather good fit between the results of both studies and further supports the reproducibility of Jain’s experiments. However, the results of Experiment #2 still differ slightly due to the presence of a prominent dichloramine peak. If the dichloramine peak was erroneous, further comparison can be made by assuming that the dichloramine present prior to the breakpoint was also monochloramine. The resulting plot can be found in Figure 7.5-2. This comparison shows an even closer match between the experimental results of both studies, with both the monochloramine and total chlorine peak heights and locations being found at similar molar ratios. Despite these results, it should be noted that further investigation would be necessary to determine if this assumption was feasible.
In addition to Experiment #2, the current study also included a series of experiments conducted at 300 rpm. The purpose of this increase was to determine if monochloramine formation improved significantly at a mixing speed greater than the 200 rpm tested by Jain. In Jain’s results, a residual monochloramine peak of 0.93 is located at a dosing molar ratio of 1:1. Both the monochloramine peak and total chlorine peak are the same as no dichloramine was observed. The height of the total chlorine peak in Jain’s study compares very favorably with the peak of 0.94 (see Figure 7.2 and Table 7.2) observed at a mixing speed of 300 rpm in Experiment #5 of the current study. The comparison of these two mixing speeds provides further support for Jain’s conclusion that a velocity gradient of 300 s\(^{-1}\) (200 rpm) is sufficient for the optimal formation of monochloramine through the mixing of ammonia and chlorine. Mixing at a velocity gradient greater than 300 s\(^{-1}\) would only reduce the energy efficiency and increase the operating costs of water treatment systems that use chloramination for disinfection.

Figure 7.5-2: Comparison of Jain’s study with Experiment #2 results corrected for free chlorine and dichloramine
It should be noted that despite the favorable comparison between the peak heights at mixing speeds of 200 rpm and 300 rpm, the location of the peaks in Experiment #5 vary greatly from those seen in Jain’s results. While Jain’s experiment showed a total chlorine peak at a dosing molar ratio of 1:1, the results of Experiment #5 show a peak at a dosing molar ratio of 0.75:1. A similar pattern was observed during the comparison of Experiment #2 and Experiment #5 in the previous section. This apparent “left shift” along the x-axis in Experiment #5, now observed for the second time, will be discussed in much greater detail in the following section.

7.3 Effect of Ct

As was briefly mentioned in Section 7.2, the results of Experiment #5 showed an unexpected pattern in regard to the location of the monochloramine and total chlorine peaks. Looking at Figure 7.3, it is clear that the monochloramine and total chlorine peaks for 300 rpm display a pronounced “left shift” along the x-axis when compared against the 200 rpm curves. These peaks occur well before the zero oxidation line indicating that the residual chlorine concentrations after mixing are greater than the original dosing concentrations. These results seemingly defy the fundamental law of conservation of mass.

As a result of this conflict, it was assumed that an error had occurred during Experiment #5 and all steps of the experimental procedure and trial were reviewed. Furthermore, the chlorine and ammonia stock solutions were thoroughly tested to ensure that their initial concentration values had been correct. This review process yielded no errors that would explain the observed phenomenon. A retrial was then completed, with the results of Experiment #6 once again showing the same pattern.
Having obtained reproducible results, the experimental procedure was then compared to the procedure use by Jain in her study. From this comparison, it was found that Jain did not add a set quantity of sodium bicarbonate to the reactors for the purpose of obtaining a predetermined $C_t$ value as was done in this experimental procedure, which called for $C_t = 10^{-3}$ M. As this was the only significant procedural difference noted and no major errors were identified, it was theorized that the $C_t$ may somehow be impacting the chloramination process. To test this, Experiment #7 was conducted using the same procedure as Experiments #5 and #6, but with no $C_t$ added to the reactors ($C_t = 0$). The results of Experiment #7 can be found in Figure 7.6.

![Figure 7.6: Experiment #7 breakpoint curve](image)

The results for Experiment #7 display some striking differences with those of Experiment #5 and #6. The lack of buffer in the form of $C_t$ caused the experiment to be completed under lower pH conditions which are more favorable to the formation of dichloramine. As a result, strong monochloramine and dichloramine peaks of almost equal height are
observed in Figure 7.6. Furthermore, the total chlorine peak was observed at the expected dosing molar ratio of 1:1, as opposed to a ratio of 0.75:1 as was observed in Experiment #6. Total chlorine values are once again observed to be higher than the theoretical values indicated by the zero oxidation line. However, the values are now much closer to the theoretical values than those observed for Experiment #6. It is possible this is the result of a slight over titration, as the “overshoots” at the dosing molar ratios of 0.25:1 and 0.50:1 correlate to approximately two drops of excess FAS titrant being added during the measurement. The slightly larger gap observed at dosing molar ratios of 0.75:1 and 1:1 likely are due to the difficulty in accurately determining the endpoint during dichloramine titration as was previously discussed.

The results of Experiment #7 indicate that C\textsubscript{t} may play a previously unidentified role in the chloramination process. To further test this hypothesis, the experiment was repeated twice more, utilizing differing C\textsubscript{t} values for each trial. For Experiment #8, the C\textsubscript{t} was increased to $10^{-2}$ M while in Experiment #9 a C\textsubscript{t} value of $10^{-4}$ M was utilized. The results of Experiments #8 and #9 can be found Figures 7.7 and 7.8, respectively.
Figure 7.7: Experiment #8 breakpoint curve

Figure 7.8: Experiment #9 breakpoint curve

The $C_t$ values and the corresponding peak locations for Experiments #5, #7, #8, and #9 are summarized in Table 7.3. The table is organized by increasing $C_t$ from 0 to $10^{-2}$ M.
<table>
<thead>
<tr>
<th>$C_t$ (M)</th>
<th>Experiment #</th>
<th>Figure #</th>
<th>$(\text{Cl}_2/\text{N})_o$ @ Total Monochloramine Peak</th>
<th>$(\text{Cl}_2/\text{N})_o$ @ Total Chlorine Peak</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>7</td>
<td>7.6</td>
<td>0.75</td>
<td>1.00</td>
</tr>
<tr>
<td>$10^{-4}$</td>
<td>9</td>
<td>7.8</td>
<td>0.75</td>
<td>0.85</td>
</tr>
<tr>
<td>$10^{-3}$</td>
<td>5</td>
<td>7.2</td>
<td>0.75</td>
<td>0.75</td>
</tr>
<tr>
<td>$10^{-4}$</td>
<td>6</td>
<td>7.4</td>
<td>0.65</td>
<td>0.75</td>
</tr>
<tr>
<td>$10^{-2}$</td>
<td>8</td>
<td>7.7</td>
<td>0.75</td>
<td>0.75</td>
</tr>
</tbody>
</table>

Table 7.3: Total chlorine peak data at varying $C_t$ values

From the data, it is clear that Experiments #8 and #9 both depict a “left shift” in the location of the monochloramine and total chlorine peaks as was observed in Experiments #5 and #6. When the $C_t$ was increased ten-fold from the $10^{-3}$ M used in Experiments #5 and #6 to $10^{-2}$ M for Experiment #8, the location of the total chlorine peak remained at a dosing molar ratio of 0.75:1. However, when the $C_t$ was decreased down to $10^{-4}$ M for Experiment #9, the location of the total chlorine peak only shifted to a dosing molar ratio of 0.85:1. This indicates that $C_t$ may react in the chloramination reaction scheme in a role similar to a catalyst. The addition of $C_t$ seems to initially cause a “left shift” in the production of monochloramine as it is increased from 0 M to $10^{-4}$ M and further to $10^{-3}$ M. At this point though, it seems that the addition of further $C_t$ from $10^{-3}$ M to $10^{-2}$ M has no further impact on the reaction.

7.3.1 Mechanism behind the “left shift”

As of now it is still not clear how the addition of $C_t$ has such an impact on the chloramination process but the reproducibility of this trend indicates to me that it is a real phenomenon. Therefore, the “left shift” that has been consistently observed in the experimental results poses two primary questions: how does $C_t$ cause this shift and how
are residual chlorine concentrations being measured at values higher than the dosing concentrations?

In this study, $C_t$ was initially added in the form of sodium bicarbonate to simply act as a buffer in the experimental system being tested. However, the carbonate system is also inclusive of gaseous carbon dioxide. Although the mixing time was reduced to two minutes to reduce the interaction between the experimental system and the atmosphere, it is likely that atmospheric carbon dioxide also interacted with the system. If the solutions are undersaturated at the time of mixing, carbon dioxide will enter the system and additional carbonate will be produced in the system following Equation 7.1:

$$\text{CO}_2^{(aq)} + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CO}_3$$  \hspace{1cm} (7.1)

It is possible that when excess $C_t$ is added to the system artificially or through the dissolution of carbon dioxide, it somehow disrupts the balance of the chlorine and ammonia stock solutions originally added to the system. Although I am not clear of what the mechanism of this interference may be, it could reduce the efficiency of the chloramine reactions resulting in the observed left shift of the monochloramine and total chlorine peaks. Further research would be required to identify the role of $C_t$ in this process.

Assessing the second question, the high residual chlorine concentrations observed in the results first lead to the assumption that the concentrations of the stock chlorine and ammonia solutions had to be incorrect. Thus, the stock chlorine concentration was checked multiple times for each experiment and found to be accurate. Furthermore, the ammonia solution was found to be accurate to within 5% of the expected concentration on each check with an ammonia probe. Experimental error could therefore reasonably be
expected to remain close to 5% rather than the approximate 20 to 30% error observed consistently in the results. The reason for this is not clear. Although a number of substances are known to interfere with DPD-FAS titration, bicarbonate and other forms of C_t have not been identified (Standard Methods, 2005). In addition, the high quality water used in the experiments makes it very unlikely that the other sources of interference would be present. However, Standard Methods (2005) does indicate that dissolved oxygen can react with DPD to produce some color when the pH of the solution increases above the optimum range of 6.2 to 6.5. Since all but Experiment #7 were completed at pH values higher than this range, it is possible that dissolved oxygen may have played some role in the residual chlorine concentrations being measured at values higher than the dosing concentrations.

For this explanation to be feasible, the pH of the experimental samples would have to remain above 6.5 after the addition of 5 ml of phosphate buffer as required by the DPD-FAS titration method. To test this, a solution with C_t = 10^{-2} M was produced by mixing sodium bicarbonate with DI water. 5 ml of phosphate buffer were then added to three 100 ml samples of the bicarbonate solution. The pH of each sample was measured before and after phosphate buffer addition. The average pH of the samples after phosphate buffer addition was 6.64, which is above the range specified by Standard Methods. Although this is not all that high, the Standard Methods procedure is very specific in describing the proper pH range, indicating the dissolved oxygen may be at least partially responsible for the high residual chlorine concentrations. However, further study would be needed to confirm that this effect also occurs when the sample has been dosed with chlorine and ammonia-nitrogen solutions. Further study would also be required to
determine whether $C_t$ or some other factor also contributed to the high residual chlorine concentrations.

7.4 Effect on pH

The addition of $C_t$ into the experimental reactors was initially included in the procedure in order to buffer the system and to retain conditions conducive to monochloramine formation. As such, a study was completed during the experimental trials to monitor pH changes. For each experiment, pH readings were taken every 30 seconds to two minutes throughout the course of the 45 minute experiment in reactors with a dosing molar ratio of 1:1 and 1.6:1. As the scope of this project expanded to investigate the impact of $C_t$ on the chloramination process, this study became particularly useful for analyzing the change in pH profiles with varying buffer concentrations. The pH profiles for Experiments #6 through #9 can be observed in Figures 7.9 to 7.16. Raw pH data can be found in Appendix B.

![Figure 7.9: Experiment #7 pH profile – Dosing MR = 1:1](image)
Figure 7.10: Experiment #7 pH profile – Dosing MR = 1.6:1

Figure 7.11: Experiment #9 pH profile – Dosing MR = 1:1
Figure 7.12: Experiment #9 pH profile – Dosing MR = 1.6:1

Figure 7.13: Experiment #5 pH profile – Dosing MR = 1:1
Figure 7.14: Experiment #5 pH profile – Dosing MR = 1.6:1

Figure 7.15: Experiment #6 pH profile – Dosing MR = 1:1
Figure 7.16: Experiment #6 pH profile – Dosing MR = 1.6:1

Figure 7.17: Experiment #8 pH profile – Dosing MR = 1:1
Figure 7.18: Experiment #8 pH profile – Dosing MR = 1.6:1

Data from Figures 7.9 to 7.18 was collected into Table 7.4. The table is organized by increasing $C_t$ from 0 to $10^{-2}$ M.

<table>
<thead>
<tr>
<th>$C_t$ (M)</th>
<th>Experiment #</th>
<th>Figure #</th>
<th>Dosing MR</th>
<th>Initial pH</th>
<th>Low pH</th>
<th>Change in pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>7</td>
<td>7.9</td>
<td>1:1</td>
<td>7.65</td>
<td>5.65</td>
<td>2.00</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7.10</td>
<td>1.6:1</td>
<td>8.15</td>
<td>5.22</td>
<td>2.93</td>
</tr>
<tr>
<td>10^{-4}</td>
<td>9</td>
<td>7.11</td>
<td>1:1</td>
<td>8.24</td>
<td>6.87</td>
<td>1.37</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7.12</td>
<td>1.6:1</td>
<td>8.34</td>
<td>6.59</td>
<td>1.75</td>
</tr>
<tr>
<td>10^{-3}</td>
<td>5</td>
<td>7.13</td>
<td>1:1</td>
<td>8.08</td>
<td>7.47</td>
<td>0.61</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7.14</td>
<td>1.6:1</td>
<td>8.16</td>
<td>7.53</td>
<td>0.63</td>
</tr>
<tr>
<td>10^{-2}</td>
<td>6</td>
<td>7.15</td>
<td>1:1</td>
<td>8.27</td>
<td>7.31</td>
<td>0.96</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7.16</td>
<td>1.6:1</td>
<td>8.47</td>
<td>7.47</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>7.17</td>
<td>1:1</td>
<td>8.40</td>
<td>8.17</td>
<td>0.23</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7.18</td>
<td>1.6:1</td>
<td>8.43</td>
<td>8.22</td>
<td>0.21</td>
</tr>
</tbody>
</table>

Table 7.4: Summary of experimental pH data
As was expected, the change in Ct buffer concentration used in the different experiments greatly impacted the pH profiles. Looking at the two extremes, the change in pH for Experiment #7 was 2.00 and 2.93 units for the dosing molar ratios of 1:1 and 1.6:1, while it was only 0.23 and 0.21 units respectively for Experiment #8.

7.4.1 Chloramine speciation at varying pH levels

The importance of this pH study lies not in the measured change of pH with differing Ct values but rather in the implications of these pH changes. As was previously discussed, chloramine reaction chemistry is impacted significantly by pH and temperature, with ideal monochloramine formation at 10 °C occurring at a pH of approximately 9.00 (NRC, 1994). As pH decreases, it is expected that the amount of dichloramine identified in a solution should increase, with proportions getting as high as 33% and 80% at pH levels of 6.00 and 5.00 respectively (ECAO, 1994).

Table 7.5 presents the height of the dichloramine peaks observed in the results of Experiments #5 through #9. The table is again organized by increasing Ct from 0 to $10^{-2}$ M.

<table>
<thead>
<tr>
<th>Ct (M)</th>
<th>Experiment #</th>
<th>Figure #</th>
<th>Dichloramine Peak Height ($\text{Cl}_2/\text{N}_0$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>7</td>
<td>7.6</td>
<td>0.66</td>
</tr>
<tr>
<td>$10^{-3}$</td>
<td>9</td>
<td>7.8</td>
<td>0.42</td>
</tr>
<tr>
<td>$10^{-3}$</td>
<td>5</td>
<td>7.2</td>
<td>0.17</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>7.4</td>
<td>0.20</td>
</tr>
<tr>
<td>$10^{-2}$</td>
<td>8</td>
<td>7.7</td>
<td>0.12</td>
</tr>
</tbody>
</table>

Table 7.5: Dichloramine peak data at varying Ct values
As expected according to theory, the dichloramine peak data clearly indicates that the levels of dichloramine present increased as overall solution pH decreased. The correlation between the pH data and the dichloramine data validate the appearance of these dichloramine peaks in the results. This validation indicates that under the experimental conditions, the monochloramine peak and the total chlorine peak should not be expected to always appear at the same location because of the observed levels of dichloramine. It should be noted that although the general trend regarding the increase of dichloramine peak height with decreased pH is supported by this pH study, it must again be noted that the exact heights of these peaks may be off due to the greater difficulty in accurately measuring dichloramine with the DPD-FAS titration method as opposed to measuring monochloramine.

7.5 Comparison with Unified Plus Model Predictions

The results of Experiments #5, #7, #8, and #9 were compared with computer simulations produced by the Unified Plus Model as presented by Huang (2008). The Unified Plus Model is the latest model geared towards simulating chlorination. This rather comprehensive model operates by utilizing the most up to date chlorination reaction scheme and is capable of simulating breakpoint curves under various initial conditions for both open and closed systems (Huang, 2008).

The experimental procedure calls for two minutes of rapid mixing in a jar test apparatus following the addition of ammonia-nitrogen. Under these conditions, the system can be considered “open” as the rapid mixing should increase the interaction between the solution and the atmosphere. After mixing ends, the system remains still for the remaining 43 minutes of each experiment and it is expected that there is very little
interaction between the solution and the atmosphere. Due to the limited interaction, the experiment is more apt to behave as a “closed” system despite the container still being open to the atmosphere. The “change” of the system from open in the first two minutes to closed for the final 43 minutes indicated that the experimental results may lie somewhere between those of the open and closed system. Thus, the results of Experiments #5 through #9 were compared with both the open and closed breakpoint simulations produced by the Unified Plus Model. These results can be observed in Figures 7.19 to 7.26. Note that a graphical comparison of Experiment #6 is not included within these figures as it nearly replicates that of Experiment #5 and provides little additional information.

![Figure 7.19: Experiment #7 comparison – Open system](image-url)
Figure 7.20: Experiment #7 comparison – Closed system

Figure 7.21: Experiment #9 comparison – Open system
Figure 7.22: Experiment #9 comparison – Closed system

Figure 7.23: Experiment #5 comparison – Open system
Figure 7.24: Experiment #5 comparison – Closed system

Figure 7.25: Experiment #8 comparison – Open system
The experimental and model simulation results for Experiments #5 through #9 are summarized in Table 7.6. Comparing the raw data found in this table and in the figures, it is clear that neither the open nor closed model simulations present perfect matches with the experimental results. This was further quantified by analyzing the data statistically.

Figure 7.26: Experiment #8 comparison – Closed system
<table>
<thead>
<tr>
<th>C&lt;sub&gt;t&lt;/sub&gt; (M)</th>
<th>Exp #</th>
<th>Figure #</th>
<th>System</th>
<th>Cl&lt;sub&gt;2&lt;/sub&gt;/N&lt;sub&gt;2&lt;/sub&gt; @ Monochloramine Peak</th>
<th>(Cl&lt;sub&gt;2&lt;/sub&gt;/N&lt;sub&gt;2&lt;/sub&gt;)@ Monochloramine Peak</th>
<th>Cl&lt;sub&gt;2&lt;/sub&gt;/N&lt;sub&gt;2&lt;/sub&gt; @ Dichloramine Peak</th>
<th>(Cl&lt;sub&gt;2&lt;/sub&gt;/N&lt;sub&gt;2&lt;/sub&gt;)@ Dichloramine Peak</th>
<th>Cl&lt;sub&gt;2&lt;/sub&gt;N&lt;sub&gt;2&lt;/sub&gt; @ Total Chlorine Peak</th>
<th>(Cl&lt;sub&gt;2&lt;/sub&gt;/N&lt;sub&gt;2&lt;/sub&gt;) @ Total Chlorine Peak</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>7</td>
<td></td>
<td>Open</td>
<td>0.07</td>
<td>0.75</td>
<td>90.67</td>
<td>0.25</td>
<td>0.75</td>
<td>66.67</td>
</tr>
<tr>
<td></td>
<td>7.20</td>
<td>Closed</td>
<td>0.12</td>
<td>84.00</td>
<td>0.75</td>
<td>66.67</td>
<td>0.72</td>
<td>0.72</td>
<td>9.09</td>
</tr>
<tr>
<td>10&lt;sup&gt;-4&lt;/sup&gt;</td>
<td>9</td>
<td></td>
<td>Open</td>
<td>0.60</td>
<td>0.83</td>
<td>10.07</td>
<td>0.95</td>
<td>0.75</td>
<td>26.67</td>
</tr>
<tr>
<td></td>
<td>7.22</td>
<td>Closed</td>
<td>0.81</td>
<td>2.41</td>
<td>1.00</td>
<td>33.33</td>
<td>0.50</td>
<td>0.50</td>
<td>19.05</td>
</tr>
<tr>
<td>10&lt;sup&gt;-3&lt;/sup&gt;</td>
<td>5</td>
<td></td>
<td>Open</td>
<td>0.97</td>
<td>0.94</td>
<td>3.19</td>
<td>1.00</td>
<td>0.75</td>
<td>33.33</td>
</tr>
<tr>
<td></td>
<td>7.24</td>
<td>Closed</td>
<td>0.94</td>
<td>0.00</td>
<td>1.00</td>
<td>33.33</td>
<td>0.05</td>
<td>0.05</td>
<td>70.59</td>
</tr>
<tr>
<td>10&lt;sup&gt;-2&lt;/sup&gt;</td>
<td>6</td>
<td></td>
<td>Open</td>
<td>0.97</td>
<td>0.90</td>
<td>21.25</td>
<td>1.00</td>
<td>0.60</td>
<td>66.67</td>
</tr>
<tr>
<td></td>
<td>7.26</td>
<td>Closed</td>
<td>0.97</td>
<td>17.50</td>
<td>1.00</td>
<td>66.67</td>
<td>0.05</td>
<td>0.05</td>
<td>75.00</td>
</tr>
<tr>
<td>N/A</td>
<td>No total chlorine peak found in model simulation</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 7.6: Summary of Experimental and Model Simulation Results
through the use of percent error, with the experimental data points utilized as the “accepted values” in the calculations. The percent errors for peak height and location for both the open and closed system simulations are also presented in Figures 7.27 and 7.28.

Figure 7.27: Percent error analysis - Open system

Figure 7.28: Percent error analysis – Closed system

The general trend in regard to residual chlorine concentrations indicates that increasing the levels of $C_t$ in the experimental system between 0 M to $10^{-3}$ M results in a better fit
between the model and the experimental data. Increasing the $C_t$ above $10^{-3}$ M appears to have little significant impact on the fit. Overall, Experiment #7 displayed the poorest fit, with percent errors of greater than 84% for the monochloramine peak height and no total chlorine peak observed at all. The only exception came in regard to the dichloramine peak heights, where Experiment #7 had the best results with percent errors of lower than 10%. However, the location of this peak was not close to the experimental results, with a percent error of 100%. This result suggests that the model may be capable of predicting dichloramine peak heights accurately at low $C_t$ values only. It is also possible that the high dichloramine peak height percent errors calculated for the other experiments is partially due to the difficulty in determining the dichloramine endpoint during titration as has previously been discussed. Experiment #5 displayed the best fit, with the lowest percent errors (all below 3.5%) for monochloramine and total chlorine peak heights in both the open and closed systems. Despite being tested at the same $C_t$ as Experiment #5, Experiment #6 showed slightly higher percent errors for monochloramine peak height and location but exhibited very similar results as Experiment #5 for dichloramine and total chlorine. It is not clear what caused the differing monochloramine results. As the $C_t$ was increased to $10^2$ M for Experiment #8, the fit remained strong, with the model and the experimental results differing most prominently in the predicted decay rate of monochloramine following the monochloramine peak. As is clearly depicted in Figures 7.25 and 7.26, monochloramine decayed faster than the model predicted.

The overall pattern regarding the percent errors found in Table 7.6 also indicated that the best fit between the experimental and simulated results occurred for the total chlorine peak heights ($\text{Cl}_2/\text{N}_0$). Percent errors were generally found to be in the low single digits
at all \( C_i \) values, except for Experiment #7, where no total chlorine peak was observed. Monochloramine peak height tended to be off slightly more, with higher percent errors observed. This indicates that the model was capable of inferring the overall pattern rather accurately even if some of the intermediate details were more skewed.

Despite the poor fit between the model and the experimental data for Experiment #7, one interesting observation was made during analysis. The experimental results portray large and distinct peaks of both monochloramine and dichloramine. However, the simulated results differ greatly, with a very small monochloramine peak noted at a low dosing molar ratio and dichloramine exhibiting a steady increase with no defined peak. Conversely, as was the case for the experimental results of Experiment #7, the simulated results for Experiment #9 both show large and distinct peaks of both monochloramine and dichloramine. In this way, the experimental results of Experiment #7 seem to fit more closely with the simulated results of Experiment #9. This fit can be shown quantitatively by comparing the percent errors that are obtained using the simulated results for Experiment #7 with those obtained using the simulated results of Experiment #9. As can be seen below in Table 7.7, the percent errors tended to drop significantly when the comparison was made with the simulated results for Experiment #9 rather than those of Experiment #7.

<table>
<thead>
<tr>
<th>Comparison</th>
<th>System</th>
<th>( \text{Cl}_2/N_0 ) @ Monochloramine Peak</th>
<th>( \text{Cl}_2/N_0 ) @ Monochloramine Peak</th>
<th>( \text{Cl}_2/N_0 ) @ Dichloramine Peak</th>
<th>( \text{Cl}_2/N_0 ) @ Dichloramine Peak</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Model</td>
<td>Exp</td>
<td>% Error</td>
<td>Model</td>
</tr>
<tr>
<td>Exp # 7 Data vs. Exp # 7 Model</td>
<td>Open</td>
<td>0.07</td>
<td>0.75</td>
<td>90.67</td>
<td>0.25</td>
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<tr>
<td></td>
<td>Closed</td>
<td>0.12</td>
<td>0.75</td>
<td>84.00</td>
<td>0.25</td>
</tr>
<tr>
<td>Exp # 7 Data vs. Exp # 9 Model</td>
<td>Open</td>
<td>0.68</td>
<td>0.75</td>
<td>9.33</td>
<td>0.95</td>
</tr>
<tr>
<td></td>
<td>Closed</td>
<td>0.81</td>
<td>1.00</td>
<td>8.00</td>
<td>1.00</td>
</tr>
</tbody>
</table>

Table 7.7: Percent error comparison
There are two possible explanations for this similarity. Although Experiment #7 is stated as definitively having a $C_t = 0$, this condition is very difficult to control and it is possible that a very low $C_t$ was present in the solution due to imperfections in any of the chemicals utilized. Even a minute $C_t$ could have produced experimental results similar to those predicted by the Experiment #9 simulation ($C_t = 10^{-4}$ M). It is also possible that the Unified Plus Model may not simulate breakpoint curves as accurately at lower $C_t$ values. Correspondence with Huang (personal communication, June 1, 2009) indicated that the discrepancies observed at the lower $C_t$ values may be related to the simulated pH and suggested that the experimental pH change data and the model’s simulations be compared. Graphical comparisons of the experimental pH data and the model simulations can be found in Figures 7.29 to 7.36.

![Figure 7.29: pH comparison – Experiment #7 MR = 1:1](image-url)
Figure 7.30: pH comparison – Experiment #7 MR = 1.6:1

Figure 7.31: pH comparison – Experiment #9 MR = 1:1
Figure 7.32: pH comparison – Experiment #9 MR = 1.6:1

Figure 7.33: pH comparison – Experiment #5 MR = 1:1
Figure 7.34: pH comparison – Experiment #5 MR = 1.6:1

Figure 7.35: pH comparison – Experiment #8 MR = 1:1
Figure 7.36: pH comparison – Experiment #8 MR = 1.6:1

The pH data from these graphs are summarized in Table 7.8. To compare the pH values, the difference between the final experimental pH and the final simulated pH was calculated. These differences are depicted in parentheses within Table 7.8 and are also presented in Figures 7.37 and 7.38.

### Table 7.8: Summary of experimental and model pH values

<table>
<thead>
<tr>
<th>C_t (M)</th>
<th>Experiment #</th>
<th>Dosing MR</th>
<th>Initial pH</th>
<th>(Difference from Experimental values)</th>
<th>Final pH</th>
</tr>
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<tbody>
<tr>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Closed Model</td>
</tr>
<tr>
<td>0</td>
<td>7</td>
<td>1:1</td>
<td>7.65</td>
<td>4.32 (-1.33)</td>
<td>4.43 (-1.22)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.6:1</td>
<td>8.15</td>
<td>4.22 (-1.00)</td>
<td>4.28 (-0.94)</td>
</tr>
<tr>
<td>10^{-4}</td>
<td>9</td>
<td>1:1</td>
<td>8.24</td>
<td>6.32 (-0.55)</td>
<td>6.70 (-0.17)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.6:1</td>
<td>8.34</td>
<td>5.90 (-0.69)</td>
<td>6.16 (-0.43)</td>
</tr>
<tr>
<td>10^{-3}</td>
<td>5</td>
<td>1:1</td>
<td>8.08</td>
<td>8.11 (+0.64)</td>
<td>7.79 (+0.32)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.6:1</td>
<td>8.16</td>
<td>7.38 (-0.15)</td>
<td>7.30 (-0.23)</td>
</tr>
<tr>
<td>10^{-2}</td>
<td>8</td>
<td>1:1</td>
<td>8.40</td>
<td>9.42 (+1.25)</td>
<td>8.38 (+0.21)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.6:1</td>
<td>8.43</td>
<td>9.41 (+1.19)</td>
<td>8.27 (+0.05)</td>
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</tbody>
</table>
As Huang suggested, a difference was observed between the experimental pH data and the simulated pH data for both the open and closed systems. The model predicted much lower pH values at a $C_t = 0$ M for both systems. According to the chloramine reaction chemistry, these lower pH values would favor greater formation of dichloramine and very little monochloramine as was observed in the simulated breakpoint curves for Experiment #7. In turn, the simulated pH data for Experiment #9 is slightly higher than the
experimental pH data for Experiment #7. This could have resulted in the model predicting more even monochloramine and dichloramine peaks and may explain why the experimental breakpoint curves for Experiment #7 seemed to fit better with the simulated breakpoint curves for Experiment #9.

Further analysis of the curves found in Figures 7.37 and 7.38 indicates that the pH differences tended to decrease as the C\textsubscript{t} levels increased during the closed system simulations. These simulations initially projected much lower pH values than were found experimentally and eventually approached a difference of close to zero, indicating a good fit. However, the open system simulations generally showed a steady rise along the y-axis, with simulations at a C\textsubscript{t} = 0 M projecting lower pH values than the experimental values and the simulations at a C\textsubscript{t} = 10\textsuperscript{-2} M projecting much higher values. The higher projected pH values may explain why monochloramine degradation occurred at a slower rate in the breakpoint curve simulations for Experiment #8 than was observed experimentally.

The dosing molar ratios that were selected for these comparisons were selected based upon the expected location of the total chlorine peaks and of the breakpoint. As has been described, the results of this study often found the peak to occur at a dosing molar ratio closer to 0.75:1 than 1:1. As such, it was useful to investigate how the model would compare to results at this dosing molar ratio. Despite having only three experimental data points, a model simulation was run for Experiment #5 at a dosing molar ratio of 0.75:1. A comparison of the model simulation and the data points can be found in Figure 7.39.
This pH comparison shows the closed system to be very close to the experimental data points while the open system predicted much higher pH values. These results are similar to those observed in Experiment #5 for a dosing molar ratio of 1:1, particularly in the location of the predicted pH values in the open system. It therefore seems feasible to assume that the trends discussed above should hold true for a dosing molar ratio of 0.75:1, as well as for 1:1 and 1.6:1.

7.5.1 The Left Shift

One of the main reasons for the use of the Unified Plus Model in this study was to determine if any of the simulations would show signs of the left shift that has consistently been observed in the experimental data. As such, it was particularly important to analyze the locations of the monochloramine peak and the total chlorine peak in the simulated results.

From Table 7.6, it is clear that almost every simulated monochloramine peak is found at the theoretical 1:1 dosing molar ratio. However, the open system simulation for
Experiment #9 showed a very slight left shift to a dosing molar ratio of 0.95:1. In addition, both the open and closed simulations for Experiment #7 show major shifts in the monochloramine peak to a dosing molar ratio of 0.25:1. As was discussed in the previous section, this major shift appears to be a result of the model’s inability to accurately predict pH when the system’s $C_t$ approaches zero. This in turn impacts the model’s ability to predict speciation at these low $C_t$ values. It therefore seems reasonable to conclude that the simulated monochloramine peak location results for Experiment #7 can be dismissed as being erroneous. As such, it seems that both the model and experimental results agree that little change should be expected in the location of the monochloramine peaks as the level of $C_t$ in the system is changed.

The location of the total chlorine peaks remained steady for Experiments #5, #6, and #8 at a dosing molar ratio of 1:1. However, when the $C_t$ is reduced for Experiment #9, the peak locations jump to dosing molar ratios of 1.30:1 and 1.20:1 in the open and closed simulations respectively, while no total chlorine peak was predicted in either of the simulations when the $C_t$ was further reduced for Experiment #7. Although the exact locations of the total chlorine peaks along the x-axis differ between the simulated and experimental results, this shows that the model also predicts that a left shift will occur as $C_t$ is increased from $10^{-4}$ M in Experiment #9 to $10^{-3}$ M in Experiments #5 and #6 as was observed with the experimental data.

7.5.2 Open System vs. Closed System Determination

Evaluation of the pH data indicated that the model’s pH simulations provided a better fit for the experimental data when the model was run under closed system conditions. However, this pattern did not carry over to the breakpoint curve simulations as there
tended to be little marked difference between the curves produced during both the open and closed simulations. Since pH, and indirectly C\textsubscript{i} due to its influence on pH, play such important roles in chloramine speciation, it seems feasible to suggest that the experimental system may more closely resemble a closed system. Further experimentation would be necessary before this could be stated definitively.
8 CONCLUSIONS

1) Confirming the conclusion of Jain (2007), for bench scale mixing experiments, a velocity gradient of 300 s\(^{-1}\) (corresponds to 200 rpm) provides adequate mixing of aqueous chlorine and ammonia nitrogen to form desirable concentrations of monochloramine. A higher velocity gradient of 500 s\(^{-1}\) (corresponds to 300 rpm) forms similar concentrations of monochloramine yet requires the expenditure of greater quantities of energy.

2) The experiments produced artificially high total chlorine residuals. This may have been caused by dissolved oxygen interference resulting from high pH levels (greater than pH = 6.5) during DPD-FAS titration.

3) Monochloramine and total residual chlorine peaks should not be expected to occur at the same dosing molar ratio due to the presence of dichloramine (Table 7.5).

4) The addition of carbonate C\(_t\) shifts the breakpoint curve to the left. The resulting peak dosing molar ratio may be up to 25% lower than the theoretical value (Table 7.3). The mechanism for this shift is not yet clear.

5) The Unified Plus Model simulated breakpoint chlorination curves and pH best at C\(_t\) = 10\(^{-3}\) M (Figures 7.27 and 7.28). The model does not accurately characterize chloramine speciation or pH as C\(_t\) approaches zero (Figures 7.27 and 7.28). Improvements to the model may be necessary to compensate for the observed discrepancies.

6) Overall, the Unified Plus Model was rather accurate in its ability to simulate total chlorine peak heights despite its inability to accurately predict these
values for the individual chloramine species (Table 7.6). Further improvements may be necessary to better correlate the overall pattern with individual speciation.

7) The Unified Plus Model simulates experimental pH profiles better when run under closed system conditions (Table 7.8). However, the model produced very similar breakpoint curve profiles when run under both the open and closed system conditions (Table 7.6). As such, it appears that the experimental system more closely exhibits the traits of a closed system. However, further experimentation is necessary before this can be stated definitively.
9 APPLICATIONS

The interesting results obtained during this study warranted further investigation to understand how these findings could be applied to the operation of actual water treatment facilities. As part of this investigation, the design of a real-world treatment plant was analyzed to determine if “passive mixing” was providing a high enough velocity gradient to warrant the shutdown of the rapid mixers. In addition, a survey of water treatment facility operators was reviewed to see if this study’s results may provide insight into some of the poor chloramination performance reviews that were obtained.

9.1 John J. Carroll Water Treatment Plant

The John J. Carroll Water Treatment Plant (formerly known as the Walnut Hill Water Treatment Plant) is the major water treatment plant of the Massachusetts Water Resources Authority’s distribution system. The plant has been active since July of 2005 and is capable of providing 405 million gallons per day for 41 Metropolitan Boston communities (MWRA, 2008).

The Carroll Water Treatment Plant utilizes chloramination for secondary disinfection. Following primary disinfection by ozonation, the plant utilizes a series of diffusers for the addition of free chlorine and ammonia nitrogen, allowing the chemicals to be dispersed throughout the treated water stream (CDM, 2006). This differs from the bench-scale experiments completed in this study, in which chlorine and ammonia were added to the reactors at one location only. Mixing of the chlorine and ammonia then occurs in four rapid mix chambers, which each create a velocity gradient of greater than 900 s⁻¹ (CDM, 2002). Following the rapid mix chambers, the water flows through a series of four over-and-under baffles before reaching the storage tanks (CDM, 2006).
This study determined that a $G$ value of 300 s$^{-1}$ provides adequate mixing of chlorine and ammonia for the formation of monochloramine. Although it is possible that the $G$ value would need to be increased when scaled up for use at an actual treatment plant, it seems likely that a $G$ value of over 900 s$^{-1}$ is much greater than would be required, indicating that the rapid mixers may have been over designed. In addition, during a conversation with David Coppes (personal communication, May 13, 2009), Director of Western Operations for the MWRA, he stated that the plant was obtaining adequate monochloramine formation with all four rapid mixers shut down. This indicates that the over-and-under baffles may be providing a high enough velocity gradient to provide adequate mixing.

Based on this information, the design plans of the plant were analyzed to determine if the velocity gradient produced by the passive mixing of the over-and-under baffles is in fact sufficient for monochloramine formation. The velocity gradient of the channel was calculated using Equation 3.1. Although this equation is stated to be for mechanical impeller systems, it can also be utilized to determine the velocity gradient produced passively by the flow of water through a baffled channel. To apply this equation to a baffled channel, power has to be calculated from the total head loss throughout the system (Fair, 1968). Additionally, the volume of the entire baffled channel system and not just an individual channel is considered. The number of baffles and channels, the volume of each of the baffles and channels, and design flow rates were obtained from the plants Design Report (CDM, 2002) and the Final Design Plans (CDM, 2006) respectively. Example calculations can be found in Appendix C.
Calculations completed for the current average flow rate of 200 MGD indicated that the velocity gradient produced by the over-and-under baffle was much lower than the 300 s\(^{-1}\) determined to be necessary by this study. The calculated velocity gradient ranged from a low of 26 s\(^{-1}\) at 32 °F to 38 s\(^{-1}\) at 80 °F. These temperatures correlate to the range of water temperature expected to flow through the plant over the course of a given year. These results make it clear that the over-and-under baffle system alone does not provide adequate levels of mixing for the production of monochloramine. Since the rapid mixers are not currently in operation, it seems likely that the use of diffusers for chemical addition is responsible for the adequate monochloramine formation found at the plant. Both the chlorine and ammonia diffusers utilized by the plant span the entire top-length of a baffle. Water first passes over a baffle which bubbles sodium hypochlorite and then passes over a second baffle which bubbles aqueous ammonia. By placing the diffusers at the top of these baffles, it appears that the design engineers ensured that the chemicals would be added at the locations of lowest water depth, allowing for the chemical to be uniformly distributed throughout the water stream. As such, lateral mixing is all that is required after dosing. This is much more effective than a single-point chemical injection (as was utilized in this study) which requires three-dimensional mixing to occur throughout the mixing chamber. With chlorine already distributed uniformly throughout the water, it seems that the further addition of a uniform column of ammonia is all that is necessary for uniform production of monochloramine at the John J. Carroll Water Treatment Plant.
9.2 Chloramination at Water Treatment Plants

In addition to the analysis of the John J. Carroll Water Treatment Plant described above, this research detailed a number of findings that are applicable to all water treatment plants that make use of the chloramination process. In particular, the study uncovered evidence to support optimum velocity gradients for mixing and insights to improve chemical dosing. Review of a 2003 survey of water treatment plant operators utilizing chloramination indicates that over 90% of respondents encountered some type of problem with their chloramination system (Kirmeyer et al., 2004). Applying the findings of this research may help solve some of the problems encountered by these operators.

According to the survey, 23% of respondents indicated that they were having difficulty obtaining acceptable mixing results (Kirmeyer et al., 2004). This could simply be the result of inadequate mixing resulting from an under designed system. As a result, the creators of the survey suggested that mixing should be performed at a velocity gradient between 300 and 1000 $s^{-1}$ in order to obtain desirable mixing (Kirmeyer et al., 2004). However, with such a broad range it is natural that many treatment plants would be designed with mixing systems that run closer to 1000 $s^{-1}$ in order to ensure that adequate mixing occurred. Conversely, this study indicates that rapid mix chambers should be designed to create velocity gradients closer to 300 $s^{-1}$. Lowering the $G$ value in this way will increase the overall energy efficiency of the system and decrease operating costs. Furthermore, engineers should carefully analyze chloramination system designs and pay particular attention to the mixing caused by baffled channels, piping, and even chemical injection systems. As was the case with the Carroll Water Treatment Plant, it is possible
that rapid mixers may not even be necessary for adequate monochloramine production. This could further reduce budgetary costs if a plant is still in the design phase.

Although chemical mixing is an essential step in the chloramination process, it is not the only area of importance. The chemical dosing process may be just as, if not more important than mixing, as inadequate concentrations of one chemical or another will cause undesirable results regardless of the quality of the mixing. Over 50% of the treatment plants surveyed indicated that they had experienced problems obtaining and maintaining a proper chloramine concentration in their water (Kirmeyer et al., 2004). Although some of these results may be attributed to operational error, this high percentage indicates that the chloramine chemistry itself may be impacted by some unidentified chemical or mechanism. This study suggests that the unknown mechanism may involve interactions between chloramines and the carbonate system. Although the mechanism is not yet clear, monochloramine formation was consistently impacted by the addition of varying concentrations of bicarbonate into the experimental system, with optimum monochloramine formation occurring at a dosing molar ratio of approximately 3.75:1 at a \( C_t = 10^{-2} \) M and 5.06:1 at a \( C_t = 0 \) M. As carbonate \( C_t \) will naturally vary from one water supply (and thus one treatment plant) to the next, it is not possible to make one specific suggestion that will improve all of these systems. Based on these results, I can only recommend that the system operators conduct their own bench scale experiments to determine the role that \( C_t \) plays on their own treatment systems. Doing this should allow the operators to evaluate the dosing requirements of their treatment system more accurately, which should hopefully eliminate some of the poor performance results described in the survey. It should be noted that due to the ever-changing nature of water
conditions, particularly in surface waters, it might be necessary to complete such experiments seasonally to ensure optimum performance year round.
10 RECOMMENDATIONS FOR FURTHER RESEARCH

1) The results indicated that carbonate C\textsubscript{t} caused a left shift to occur in the breakpoint curve. The mechanism responsible for these results is not completely known. Additional research could be conducted to uncover this mechanism and further the understanding of chloramine chemistry.

2) Artificially high chlorine residuals were observed in this study’s results. A simple experiment indicated that high pH during DPD-FAS titration may have been the cause. More extensive experimentation inclusive of chlorine and ammonia dosing and at differing C\textsubscript{t} values could provide additional support for this reasoning.

3) The case study of the John J. Carroll Water Treatment Plant determined that a novel chemical dispersion system likely provides adequate mixing during the chloramination process to eliminate the need for any mechanical mixing. Further study into the applications of such systems for other treatment process, such as coagulation, may yield similar results, resulting in increased energy and cost savings for utilities.
11 REFERENCES


Appendix A

Raw Experimental Breakpoint Curve Data
### Experiment #2:

<table>
<thead>
<tr>
<th>Molar Ratio</th>
<th>Initial pH</th>
<th>pH 15 Minutes</th>
<th>pH 45 Minutes</th>
<th>Initial pH A</th>
<th>Initial pH B</th>
<th>Initial pH C</th>
<th>pH A 15 Minutes</th>
<th>pH B 15 Minutes</th>
<th>pH C 15 Minutes</th>
</tr>
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## A3
Appendix B

Raw Experimental pH Data
Note: pH data was NOT collected for Experiment #2

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**MR = 1.6**

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<th>pH</th>
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| 1890 | 31.50 | 6.88 |  | 2700 | 45.00 | 6.59  
| 1980 | 33.00 | 6.88 |  |      |      |  
| 2070 | 34.50 | 6.87 |  |      |      |  
| 2160 | 36.00 | 6.86 |  |      |      |  
| 2310 | 38.50 | 6.88 |  |      |      |  
| 2430 | 40.50 | 6.88 |  |      |      |  
| 2550 | 42.50 | 6.88 |  |      |      |  
| 2700 | 45.00 | 6.87 |  |      |      |  

B6
Appendix C

Velocity Gradient Calculations
G Value Calculations for the John J. Carroll Water Treatment Plant

Calculations are based off the current average operating parameters at the plant (200 MGD). Values may differ slightly under different conditions.

Plant consists of two treatment trains, each of which handles half of the daily flow (currently 100 MDGD). As such, velocity gradients are measured for each train. These values should be equal as they handle equal flow.

Following ammonia addition for each train, the stream runs through a series of four over and under baffles. Water heights were obtained from the "Walnut Hill Water Treatment Plant Hydraulic Profile." Baffle dimensions were obtained from "Walnut Hill Water Treatment Plant WHCP-4 Drawing No. M-4 and M-5." These values were utilized to complete the G Value calculations as follows.

From the dimensions, volume (C) was first determined.

\[ C := 24327.7 \text{ ft}^3 \]

Flow rate was then converted from MGD to ft\(^3\)/s.

\[ Q := 154.73 \text{ ft}^3/\text{s} \]

Average areas were determined of the three baffles and the four channels in order to estimate the velocities at these areas. A1 and v1 correspond to the channels while A2 and v2 correspond to the baffles.

\[ A1 := 260.62 \text{ ft}^2 \quad A2 := 163.90 \text{ ft}^2 \]
\[ v1 := \frac{Q}{A1} \quad v2 := \frac{Q}{A2} \]
\[ v1 := 0.594 \text{ ft/s} \quad v2 := 0.944 \text{ ft/s} \]

Head loss (h) throughout the system is calculated using the velocities. h accounts for the number of baffles and channels in the system.

\[ h := 4 \left( \frac{v1^2}{2 \cdot 32.17 \frac{\text{ft}}{\text{s}^2}} \right) + 3 \left( \frac{v2^2}{2 \cdot 32.17 \frac{\text{ft}}{\text{s}^2}} \right) \]

\[ h := .063 \text{ ft} \]
The power of the system is then calculated.

\[ P := Q \cdot h \cdot 62.4 \frac{\text{lb}}{\text{ft}^3} \]

\[ P := 608.275 \frac{\text{lb}}{\text{s}} \]

Using the absolute viscosity (\(\mu\)) of water, \(G\) can then be calculated at any temp:

**For Zero Degrees C:**

\[ \mu := 3.7 \times 10^{-5} \frac{\text{lb} \cdot \text{s}}{\text{ft}^2} \]

\[ G := \sqrt{\frac{P}{\mu \cdot C}} \]

\[ G := 25.99 \text{s}^{-1} \]

**For 10 Degrees C:**

\[ \mu := 2.73 \times 10^{-5} \frac{\text{lb} \cdot \text{s}}{\text{ft}^2} \]

\[ G := \sqrt{\frac{P}{\mu \cdot C}} \]

\[ G := 30.26 \text{s}^{-1} \]

**For 26.7 Degrees C (80 Degrees F):**

\[ \mu := 1.79 \times 10^{-5} \frac{\text{lb} \cdot \text{s}}{\text{ft}^2} \]

\[ G := \sqrt{\frac{P}{\mu \cdot C}} \]

\[ G := 37.36 \text{s}^{-1} \]