EFFECT OF MIXING ON MONOCHLORAMINE FORMATION THROUGH IN-LINE INJECTION OF CHEMCIALS IN WATER DISINFECTION PROCESS

by

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DISSERTATION

Submitted in partial fulfillment of the requirements
for the degree of Doctor of Philosophy in Civil Engineering at
The University of Texas at Arlington
August 2019

Arlington, Texas

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ACKNOWLEDGEMENTS

I am extremely grateful to my advisor Dr. Andrew Kruzic for his support and invaluable contribution during my PhD Study. I would also like to express my appreciation to my dissertation committee: Dr Ahmari, Dr Choi, Dr Prabakar and Dr Schug.

I am deeply indebted to my family. My parents for their wise counsel and positive thoughts and my sister who kept me motivated and offered me endless support. I would also like to extend my gratitude to my dear husband who stood by me every day through my study and helped me with his insightful suggestions.

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ABSTRACT

EFFECT OF MIXING ON MONOCHLRAMINE FORMATION THROUGH IN-LINE INJECTION OF CHEMCIALS IN WATER DISINFECTION PROCESS

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Addition of chlorine and ammonia to water for monochloramine formation in the secondary disinfection process in treatment plants has some challenges. Monochloramine formation as the only desirable product of the chloramination process is affected by several factors. These factors are pH, chlorine to nitrogen ratio and chemical mixing. In this study an investigation was conducted to measure the effect of mixing on monochloramine formation through direct injection of chemicals in a pipeline when keeping the other factors constant.

In this study two sets of experiments were conducted. In the first study a tracer salt testing was used to find a measure for mixing in the pipeline and that measure was used to discover a point/section in the pipeline where complete mixing was achieved in the cross section of the pipe. For measuring physical mixing in the pipeline, tracer salt was injected into two injection locations, that were chosen to be upper wall and centerline of the pipe. Samples were collected into 50 cylinders at 6 different distances from the injection point using a pitot tube. The conductivity of the samples was measured immediately and COV of the conductivities were calculated as a

measure of mixing. At each of the sampling points, 50 samples were collected in 5 points across the pipeline to have a representative value for salt conductivity in the cross section of the pipe. The results showed that centerline injection of tracer salt led to complete mixing 52 ft after injection point in the downstream of the straight pipeline at all velocities. In each step, velocity of water in the pipeline was increased to improve turbulence and reduce retention time in the pipeline. This change, improved COV values, resulting in better mixing of the tracer salt over a shorter time.

After assessing the effect of increase in flow velocity on mixing by tracer salt study in a straight section of pipeline, bends were added to the pipeline for tracer salt study. It was expected to see better mixing in shorter distance and less travel time, because of the addition of bends to the mainstream pathway. The results were in accordance with the expectations and bends improved physical mixing of the secondary flow with the main flow. Complete mixing was achieved in the order of seconds after salt injection.

In the next phase the result from first phase were used for chemical sampling. The section in which complete mixing was achieved in the downstream of the pipeline, was chosen as a sampling location for chloramination study and samples were collected even further down from that point to compensate for any errors in the experiments. Chlorine and ammonia solutions were injected into the upstream of the pipeline. Two sources of chlorine were used to asses effect of dilution ratio on monochloramine formation. Water samples were also collected in amber bottles for manual chemical addition and mixing to imitate well mixed condition as batch tests. The results showed that there was a difference in monochloramine values from batch test and pipeline samples in all four flow velocities. The batch test led to formation of higher concentration of monochloramine, because better mixing was achieved within a few seconds after the chemicals were added to the bottle which was provided immediately by shaking the bottles manually.

Effect of addition of bends on the chemical mixing process was also examined by adding bends to the path of chemicals that were being injected into the pipe. It was observed that despite improvements in providing a better physical mixing in a shorter time, monochloramine recovery did not enhance through bends.

Chapter 1

INTRODUCTION

Chlorination used to be the first choice of treatment plants as a secondary disinfection method for years, however from the time that it was found it produces disinfection by products (DBPs) and has less stability compared to chloramination, chloramines became one of the most common alternatives, used as secondary disinfectants in water treatment plants. There are three different kinds of chloramines (Mono-, Di, and Tri-chloramines) that do not show the same health impact and disinfection efficiency. Monochloramines (MCls) are stronger disinfectants compared to the other two chloramines and the only chloramine that is used for disinfection.

Kinetics and mechanisms of chloramine formation have been addressed in many studies, as well as the impact of environmental conditions including pH and Cl_2:N ratios, but fewer studies have investigated the effect of mixing and feeding conditions on chloramine formations and recoveries.

Treatment plants are using variety of methods in forming MCls but there is still a need for guidelines on how to form MCl in treatment plants because of the high decays and poor MCl recoveries observed in chloramination processes. According to a survey from water treatment plant operators utilizing chloramination for disinfection, 23% of respondents indicated that they had experienced problems related to poor mixing. In small pipes or tanks, it is easier to get good mixing and guarantee monochloramine formations but when trying to get optimum MCls in pipelines, high MCl formation and recovery is much harder to achieve.

1.1. Problem Statement

Optimum amount of monochloramines will form through adequate initial mixing providing that environmental conditions are fulfilled properly. However, what is an adequate mixing and how it can be achieved is largely unknown.

The hypothesis for this research is that faster and better mixing and feeding conditions of ammonia and chlorine to water stream are important to maximize MCl recovery and minimize MCl decay. The focus of this research is to try to completely mix chlorine and ammonia in the pipeline, as fast as possible, to assure monochloramine formation and prevent wasting chemicals as a result of adding random amounts of chemicals to the stream.

Kinetics of chloramine formation are known to be fast and the more time is required to get to complete mixing, the more possibility of imbalance in concentrations of Cl_2 and N for MCl production will occur. On the other hand, the chloramination reaction is competitive which affects the products of the reaction. Meaning that, inadequate concentration of chlorine or ammonia or insufficient contact time between them, will lead to formation of other undesired chemical compounds.

When injecting Cl_2 and N into the pipeline, it is important to have them in the same plume with proper concentrations as they enter the pipeline. An attempt must be made to keep Cl_2 and N in the same plume for a specific time so that they can react and form MCls. If Cl_2 and N are injected into the water, but their concentrations are not balanced fast, or if they are directed into two different plumes, it will potentially lead to poorer MCl recovery due to formation of dichloramine and trichloramines and eventually causes rapid decay.

As a result, in the experiments batch tests and MCl measurements after 30 minutes and 24 hours were performed.

The terms mentioned above, are explained in more details as follows:

Recovery is defined as the difference between the theoretical amounts of MCl that could be formed in case of 100% reaction and the actual monochloramine that forms after some initial time considering the time required for monochloramines to form. In current experiment, MCl recovery is measured after collecting water samples from pipeline and measuring monochloramine values after 30 minutes.

Demand is defined as the difference between the amount of chlorine added to water and the amount of residual chlorine remaining after a given contact time. In this study, batch test that is conducted manually by adding chlorine and ammonia to water and shaking the bottle vigorously, is used to measure water demand.

Decay is defined as the decrease in concentration of MCl in water as a result of various factors, such as autocatalysis, reaction with other compounds in water and nitrification within a specific time frame. In this study decay is measured by collecting water samples from the pipeline and measuring their MCl after 24 hours.

1.2. Research Objectives

The overall objectives of this study were to:

- Develop a method to measure mixing in a pipeline.
- To assess factors affecting mixing such as velocity of water in a pipeline, addition of bends to pipeline, injection location of chemicals and injection velocity of chemicals.
- To measure efficiency of monochloramine recoveries and decay under various conditions.
- To determine DCl and evaluate effect of imperfect mixing on DCl formation.
- To investigation of the impact of dilution ratio on MCl recovery.

1.3. Scope of the Research

The scope of the current study was to investigate degree of mixing and time to get complete mixing condition, through tracer study and examine effect of initial mixing on monochloramine formation in a 4-inch pipeline which was built in the water resources lab. The tests were conducted for a straight pipeline and pipeline with bends. Bends were added to evaluate effect of improvement in initial mixing condition. If they could enhance mixing in the pipeline, utilizing them for mixing chlorine and ammonia could be an easy and feasible recommendation for treatment plants. A thorough study was done on the effect of inline injection of tracer salt into a pipeline in which tap water was flowing with different velocities to investigate effect of turbulence in the pipeline. The study consisted of injection and sampling at different locations inside the pipe and at different distances throughout the pipeline using two measures of coefficient of variation.

In the second set of experiments, water was chloraminated by injecting chlorine and ammonia into the pipeline. Complete investigation was done on chlorine and ammonia residuals, downstream of the chemical injection points and the focus was mostly on MCl recovery as the main product for water disinfection.

Chapter 2

LITERATURE REVIEW

2.1. Water Disinfection

Drinking water disinfection in the US typically consists of primary disinfection and secondary disinfection. Primary disinfection inactivates bacteria, prevents infectious diseases and is done based on the CT concept. In this concept, C is disinfectant residual at the end of a proper contact time and T represents the contact time when at least 90% of the water has been exposed to the residual C (EPA, 1989). Secondary disinfection requires the presence of a disinfectant throughout the water distribution system to inactivate new introduced contamination and prevent regrowth of bacteria, viruses and protozoa.

Chemical disinfectants in drinking water treatment usually are strong oxidants, such as ozone, chlorine, chlorine dioxide and chloramine (U.S. EPA, 1999; EPA, 2001; Khiari, 2016). Chlorination was one of the first and most important disinfection methods in early 1900s, but overtime it was determined that chlorination produces many disinfection byproducts, some known to be carcinogenic such as trihalomethanes (THMs) and haloacetic acids (HAAs) (Gray, 2014). While free chlorine is still used in many distribution systems in the US as secondary disinfectant, chloramination is widely used as an alternative secondary disinfection agent because chloramines are more persistence, less reactive and produce less disinfection by-products in distribution systems (NHMRC, 2011).

2.2. What Are Chloramines

There are two types of chloramines in water systems: organic chloramines and inorganic chloramines. Organic chloramine are products of the reaction of dissolved organic nitrogen or dissolved organic carbon with free chlorine or inorganic chloramines similar to its reaction with ammonia. Organic chloramines are also referred to any organic halogen compounds measured as combined chlorine (Harp, 2002; How *et al.*, 2017). The family of organic compounds have the formula of R_2NCl and $RNCl_2$ (R is an organic group). Inorganic chloramines are products of the reaction between chlorine and ammonia and are the focus of current study. Organic chloramines are weaker disinfectants than inorganic monochloramine and are indistinguishable by the common analytical methods (Amy *et al.*, 2000). They have been used as disinfectants in USA in 30s and 40s (U.S. EPA, 1999). Further usage of this compound showed less production of health threatening disinfection byproducts and this made them even more common especially as secondary disinfectants since they lack the strength required to kill the viruses and bacteria in the first place. Chloramines are alternative disinfectants in treatment facilities because they last longer in distribution systems (DS), penetrate biofilms, produce less trihalomethanes, halo-acetic acids and other disinfection by products (Kirmeyer, 2004).

The reactions of chlorine and ammonia can lead to formation of three inorganic chloramine species: monochloramine (MCl), dichloramine (DCl) and nitrogen trichloride. The product of the reaction and its stability depends on several factors such as pH, chlorine to nitrogen ratio and mixing condition.

Monochloramine is the only desired product from the reaction between ammonia and chlorine as a disinfectant for water, because dichloramine is not as strong a disinfectant as monochloramine and nitrogen trichloride affects water quality by causing taste and odor problems in water. Additionally, both dichloramines and nitrogen tri-chlorides decay quickly in distribution systems (Black & Veatch Corporation, 2011; Prabakar, Samadi and Kruzic, 2017).

If any of the conditions such as pH or Cl_2:N ratio changes, monochloramine will be converted to di-, or tri-chloramine through the following competitive reactions:

$NH_2Cl + HOCl \leftrightarrow NHCl_2 + H_2O$ *Reaction 2-1* (Bone, 1999)

$NHCl_2 + HOCl \leftrightarrow NCl_3 + H_2O$ *Reaction 2-2* (Bone, 1999)

It is worth to mention that temperature is also an effective factor in MCl formation, but it only affects rate of reaction. Monochloramines are not stable and will be degraded over time in distribution systems. Monochloramine decay mechanism includes 4 different pathways (Sung, Huang and Wei, 2005). Auto decomposition pathway of chloramines is either hydrolysis of monochloramine to dichloramine.

$NH_2Cl + H_2O \rightarrow HOCl + NH_3$ *Reaction 2-3* (Bone, 1999)

$HOCl + NH_2Cl \rightarrow NHCl_2 + H_2O$ *Reaction 2-4* (Bone, 1999)

or acid catalyzed disproportionation of monochloramine to dichloramine.

$NH_2Cl + NH_2Cl \rightarrow NHCl_2 + NH_3$ *Reaction 2-5* (Bone, 1999)

The former Reaction 2-3 is not favorable because the equilibrium of Reaction 2-13 is to the right, and that's the reverse reaction of Reaction 2-3. So what increases dichloramine formation is lower pH values and higher Cl_2:N ratios (Black & Veatch Corporation, 2011). The other pathways are reactions with natural organic matters (NOMs) and irons. The kinetics of MCl decay is described by second-order equation for both autocatalytic reaction (Vikesland, Ozekin and Valentine, 1998) and the reaction with natural organic matters (Harrington *et al.*, 1999). Accordingly, there is a high chance that MCls are converted to DCls in distribution systems. Furthermore, the decay of chloramine release nitrogen to the environment which can lead to pH change and nitrification in distribution system (Bone, 1999).

In addition to impairing disinfection efficiencies, dichloramine can be precursors for other DBP. One of these DBPs is called Nitrosodimethylamine (NDMA). NDMA is produced through the sequence of the reactions as shown below.

$$HOCl + NH4+ \rightarrow ClNH2 \leftrightarrow NHCl2 + R-N-(CH3)2O2 \rightarrow O=N-N(CH3)2$$

Reaction 2-6 (Bone, 1999)

Hypochlorite + Ammonium → Monochloramine ↔ Dichloramine + Dimethylamine → N-Nitrosodimethylamine (NDMA)

To reduce the precursors, it is required to remove nitrosamines from water. One of the main substances in the reaction of nitrosamines was dimethylamine (DMA) and the other one is dichloramine. Therefore, by controlling dichloramine formation or in other way by optimizing monochloramine formation, maximum monochloramine formation and recovery in a system could be achieved and eventually reduce active and free substances that could form NDMAs.

2.3. Kinetics of Chloramine Formation

In monochloramine formation complete immediate mixing is necessary to ensure that the chemicals that are added to water are having enough contact with the flow stream and the platform is set for the required reactions to go forward because in slow reactions the kinetic of the chemicals determines the rate of reaction but fast and competitive reactions are affected by the mixing rate. Lack of enough mixing affects the selectivity and yield of the reaction and reduces the yield of the product specifically MCl recovery (EPA, 2001; Men *et al.*, 2007; Black & Veatch Corporation, 2011).

It is important to figure out enough time to produce complete chemical mixing in the before any unwanted chemicals or adverse reactions start. In order to be able to control the reactions the possible reactions and the conditions under which they may happen, must be explained. Reaction 2-7 to Reaction 2-11 presented below are possible reactions that will produce chlorine species:

$Cl_2(gas) + H_2O \leftrightarrow HOCl + HCl$ *Reaction 2-7* (EPA, 2001)

$HOCl \leftrightarrow H^+ + OCl^-$ Pk_a=7.6 @ 25° *Reaction 2-8* (EPA, 2001)

$OCl^- + H_2O \leftrightarrow HOCl + OH^-$ *Reaction 2-9* (Habchi et al., 2011)

$NaOCl \leftrightarrow Na^+ + OCl^-$ *Reaction 2-10* (Bone, 1999)

$NaOCl + H_2O \leftrightarrow HOCl + Na^+ + OH^-$ *Reaction 2-11* (EPA, 1999)

$NH_4^+ \leftrightarrow H^+ + NH_3$ Pk_a=9.3 @ 25° *Reaction 2-12* (Bone, 1999)

$NH_3 + HOCl \leftrightarrow NH_2Cl + H_2O$ *Reaction 2-13* (Bone, 1999)

Now, by addition of ammonia to water, reaction will happen between NH_3 and HOCl, not between NH_4^+ and OCl^- and monochloramine is formed through a second order reaction, if the solution is at proper pH (8.3). At pH values between 7 to 8 dichloramines form slower compared to monochloramines (in the order of minutes to hours), which shows the importance of immediate mixing rather than leaving it to the flow stream to do it in further distances downstream the injection point. Also, nitrogen tri-chloramines are formed even slower than dichloramines (Black & Veatch Corporation, 2011; Engelhardt and Malkov, 2015). At pH lower than 8.3, and more than 8.3, concentration of NH will increase and concentration of HOCl will decrease, which leads to reduction in the reaction rate.

In case of complete mix, monochloramine formation takes 0.07 to 3 seconds and that immediately eliminates free chlorine and reduces DBP formation potential under suitable conditions (pH=8.3, Cl_2:N, T= 25°C) (Bone, 1999), therefore in the current context it is very important to achieve mixing instantaneously. White proposes that based on the existing mixing devices, achieving complete mixing within 3 seconds would be rated as adequate, however none of his case studies are for mixing between chlorine and ammonia, but for chlorine mixing with the water stream (Black & Veatch Corporation, 2011).

Stoichiometrically, monochloramine is formed through Reaction 2-13 which is 1.0 mol of HOCl reacting with 1.0 mol of ammonia-nitrogen (NH_3-N). On a weight basis, this is equal to Cl_2:N ratio of 70.906/14 = 5.06, which is often rounded by 5:1. However, the ideal condition to form MCl equal to the stoichiometric amount often does not occur in many water treatment plants.

Although some studies mention mixing as an important issue and refer to poor mixing or well mixed terms in their articles for chloramine formation (Ger and Holley, 1976; Mitch, Gerecke and Sedlak, 2003), still sources lack a guide on the extent to which chlorine and ammonia must be mixed to guarantee an optimum monochloramine concentration.

2.4. How to Measure Chloramines

As it is shown in Reaction 2-7 to Reaction 2-11, chloramine can be measured from the amount of chlorine and ammonia present in the water. Inorganic chloramines are also called combined chloramines. They can be calculated by measuring total chlorine and free chlorine in water and subtracting their values.

Total chlorine = free chlorine + combined chlorine

There are several analytical methods for measuring chlorine and chloramine that are suggested depending on the water that is being tested, the error of the experiment, level of simplicity and skill required to do the tests (Engelhardt and Malkov, 2015). These methods include the iodometric method, the amperometric titration method, the DPD colorimetric method and the DPD ferrous titrimetric method (known as FAS method) suggested by Standard Methods for Examination of Water and Wastewater (Eaton *et al.*, 2005) and membrane introduction mass spectrometric (MIMS), headspace gas chromatography/mass spectrometry (GC-MS) for dichloramine measurement (Shang and Blatchley, 1999; Kosaka *et al.*, 2010), but it is recommended that for tap water and under the existing condition, the best method is FAS titration (Black & Veatch

Corporation, 2011; Engelhardt and Malkov, 2015). The procedure and logic behind all these methods are the same.

2.5. Dechlorination

In this study, the water that is being used is a treated water collected from tap water. Considering the goal of the current research which was to assess effect of mixing of chlorine and ammonia in pipeline and eventually the concentration of chloramine is going to be examined in a pipeline, the water should not contain any trace of chlorine and ammonia in it. As a result, the water, before addition of any chemicals to it, must be used. The tap water which is a treated water, already contains chlorine and ammonia.

Various methods exist for nitrogen removal from water such as selective ion exchange, air stripping, biological nitrification and denitrification. Dissolved organics are also used for removing organic nitrogen from wastewater. Ammonia-nitrogen can also be oxidized in chlorination at high residual chlorine levels by the process known as breakpoint chlorination. It is stated by Pressley (Pressley, Bishop and Roan, 1972) that breakpoint chlorination provides additional physical-chemical means to remove ammonia from wastewater. Therefore, to get rid of excess chlorine and ammonia in water, “breakpoint” chlorination was conducted because any other methods would have left us with potential either ammonia or chlorine in the water.

2.6. Factors Controlling Chloramine Formation

There are various factors that attribute to efficient formation of chloramine.

2.7.1 pH

pH value plays an important role, because HOCl is a weak acid and NH_3 is a weak base. As shown in Reaction 2-8, pK_a is 7.6 and as presented in Reaction 2-12, the pK_a for NH_4^+ is 9.3. as a result, if pH is less than 7.6, HOCl is predominant and if pH is more than 9.3, NH_3 is predominant. There is no single pH value in which they both are dominant. In Reaction 2-13, it is shown that the reaction between NH_3 and HOCl is first order with respect to each species, therefore they will be maximum at the pH value that is half of the summation of each pK_a which is equal to 8.45. Best pH range is between 7.5 and 9; with 8.3 being known as the best pH requiring minimum time for conversion of 99 percent of chlorine to monochloramine at 25°C. However, this number is for high concentration of chlorine (14.2 mg/l as Cl2) which is assumed to be a value added to non-nitrified wastewaters for disinfection purposes and then the chlorine reacting with a large amount of ammonia-nitrogen (U.S. EPA, 1999; Hankin, 2001). pH values around 7 will cause dichloramine formation, and trichlorides will be formed at pH values less than 4 (Bone, 1999).

2.7.3 Chlorine : ammonia nitrogen (Cl_2:N) ratio

The Cl_2:N ratio in chloramine formation, reaction determines type of chloramine that is being produced. If the ratio is in the range between 3-5:1 by weight, monochloramines will be formed. If the ratio is between 5-7:1 and ratios above 7.6:1 dichloramines and nitrogen trichlorides are more likely to be produced, respectively. Lower Cl_2:N ratio may also lead to releasing excess ammonia to water as a result of biofilm growth or nitrification, therefore, chlorine is needed to prevent biological activities (U.S. EPA, 1999). Ammonium ion concentration at effluent must be between 0-0.8 mg/L, thus decreasing chlorine concentration will cause releasing NH_4^+ more than 0.8 mg/L. It is recommended to use molar ratios less than 1:1, because at ratios 1:1, 1.5:1 and 2:1, nitrate, nitrogen gas and nitrogen chloride will be produced, total chlorine residuals will reach zero which is chlorination breakpoint, and without residuals disinfection will be impossible (Bone, 1999).

$$2NH_2Cl + HOCl = N_2 + H_2O + 3H^+ + 3Cl^-$$ *Reaction 2-14* (Bone, 1999)

However, in our experiment getting to that point is very unlikely hence excess ammonia will be provided to guarantee that the ratio is not a problem in formation of monochloramines.

2.7.4 Mixing

Mixing is another factor that that is known to have a great impact on chloramine formation during chlorine reaction with ammonia and many other negative impacts on the treatment process. Studies show that incomplete mixing can lead to nitrification within the distribution (Bone, 1999) system and may cause increase in the amount of ammonia more than EPA standards. Deficient mixing will lead to decline in required total chlorine residuals in distribution system that will allow bacterial activity and affect human health. However, despite other factors mentioned before, there is no single mixing rate and mixing method for ammonium and chloride that defines a proper mixing for all cases.

2.7. Mixing

Mixing has three steps: macro-, meso-, and micro-mixing. Macro-mixing is what defines the homogeneity at a bigger scale and can be improved by introducing more longitudinal velocity. It is mostly defined by the configuration of reactor and residence-time distribution (RTD).

Meso-mixing happens in intermediate structures that are the turbulent cascade vortices and are defined by turbulent kinetic energy and Re number strain-rate.

Micro-mixing takes place in turbulent flows in molecular scale, also known as Kolmogorov scale. Dissipation rate of kinetic energy in a flow determines the Kolmogorov scale and selectivity of the chemicals (Habchi *et al.*, 2011).

2.8. Turbulent Flow

Turbulent mixing encompasses a range of macro-mixing to micro-mixing. Macro-mixing is done to a great percent by turbulence but micro-mixing with the aim of reaction happening, requires some external assistance; such as addition of static mixers, baffles, bends or some hindrance in flow path.

2.8.1. What Is a Turbulent Flow?

If the Reynolds number of a flow is higher than 4000 (Tennekes, Lumley and Lumley, 1972) (Tennekes & Lumley, 1972), the flow is known as turbulent.

$$Re = \frac{vD}{\vartheta}$$

Equation 2-1 (Tennekes, Lumley and Lumley, 1972)

For Reynolds number less than 4000 and more than 2500 the flow is called transitional, and below 2500 is laminar flow.

When the inertia and viscosity interact with each other in momentum equations, the flow is considered turbulent, but there are also many other characteristics that makes the flow a turbulent one. For example, in a turbulent flow collision causes rapid mixing and raises rates of momentum, heat, and mass transfer. Also, a turbulent flow is dissipative, meaning that the kinetic energy of fluid changes into heat as a result of the contact between flow layers, which is called viscos shear stresses. Hence, turbulent flows lessen without continuous energy being provided. Turbulent flows have eddies of different sizes. Larger eddies are unstable and break up to smaller ones while transferring energy to them up to a point that the Reynolds number is small that makes the eddies stable. This process only happens in fine structures that are responsible for change of energy resulting from conversion of turbulence to heat. Thus, within these structures, chemicals will be mixed at molecular scale. Therefore, they provide a platform for non-uniformly distributed reactants. In turbulent flow, kinetic energy of turbulence is produced as a result of contact between mean flow and bigger eddies but kinetic energy dissipation into heat is in molecular scale and small structures (Magnussen, 1981).

The speed of a turbulent flow changes over time in direction and magnitude, therefore it has infinite degrees of freedom. However, the reverse of these sentences is not true. Meaning that, not all the chaotic or random flows are turbulent. It is worth to bear in mind that spreading velocity and fluctuations in all directions plays an important role (Luschik, Pavel'Ev and Yakubenko, 1994).

Toor in his book defined mixing the result of three different types of diffusions: molecular, eddy and bulk diffusions. He asserts that it depends on the fluid that is going to be dealt with, to choose on which of these three diffusions must invest (Toor, 1969). For example, in some fluids like polymers molecular diffusion is very slow. If molecular diffusion is fast enough, then it is possible for the system to be sub-microscopically mixed as soon as bulk diffusion has happened. Therefore, he states turbulent is not enough, because the smallest scale of turbulence is still large compared to molecular size, and the smallest eddy contains millions of molecules. Turbulence is only able to reduce the size to the smallest eddy. But in order to make sure the molecules of the chemicals meet each other; molecular diffusion is needed and at this point it can be said that chemical reaction is happening. This is called the interaction between molecular diffusion and turbulence (Brodkey, 1975). An increase in interfacial surface area maximizes the gradient of the species concentration, and the more concentration gradient the more the chemicals want to move toward each other to reach equilibrium (Hessel, V; Noel, 2012).

2.10 Various Turbulent Models

To solve the complex turbulent equations in three dimensions and being able to consider terms involved in a fluid's turbulence, several models are suggested and modified over time due to their usage. There is no single model for turbulence, and it must be chosen due to the problem and its limitations.

- Algebraic (zero equation) models: mixing length (first order model)
- One equation models: k-model, μt-model (first order model)
- Two equation models: k-ε, k-kl, k-ω2, low Re k-ε (first order model)
- Algebraic stress models: ASM (second order model)
- Reynolds stress models: RSM (second order model)

Each of these models consists of several complex equations that are solved based on Navier-Stokes equation and Newton's second law of motion (F=ma). Solving the Navier-Stokes equations for a turbulent flow is almost impossible and needs computer programming because the equations are non-linear and encompass terms for pressure, velocity, temperature, viscosity, buoyancy and so many other internal and external forces (Homicz, 2004; Karthik and Durst, 2011).

First order models are based on the analogy between laminar and turbulent flow. They are also called Eddy Viscosity Models (EVM) and it is assumed that the average turbulent flow field is similar to the corresponding laminar flow.

Second order models are to compensate the limitations of first order models in dealing with the isotropy of turbulence and the extra strains. There are two second order models.

Since models are not very reliable, first experiments must be conducted and in later steps models can be developed. By comparison between a model and experiments in the same scale it will be understood if the model is working well or not, and if so then it can be developed for larger scales.

2.11 Effect of Bends on Flow Stream

Fluid flowing in a pipe bend, produces a secondary flow as a result of centrifugal force. This flow is superimposed on the primary flow of the pipeline and increases the velocity of fluid at the outer core of the bend. The secondary flow is mostly dependent on parameters such as the curvature ratio, which is the ratio of pipe diameter to bend radius of curvature, Reynolds number, Dean number, inlet flow distributions condition of the entrance flow for example laminar or turbulent (Lai, So and Zhang, 1991).

The complicity of analyzing turbulent flow especially at swirling flows and bends necessitates using the turbulent models. The behavior of fluid is modeled using the k-Ɛ turbulent model as the most common model for simulating a flow in pipe bends and is presented in several studies (Kim, Yadav and Kim, 2014).

The results from turbulent simulation using the turbulent models, stated that movement of fluid toward the outlet of a bend, produces centrifugal force towards the outer wall of the pipe which is caused by curvature of the bend. A 90-degree bend produces centrifugal and boundary layers forming identical eddies (Sudo, Sumida and Hibara, 1998; Dutta, Saha and Nandi, 2015). Centrifugal forces push the flow toward the outer core of the pipe wall and if the curve is strong enough the adverse pressure gradient near the outer and inner walls of the bend will lead to flow separation, developing a secondary flow that later would be combined to the main flow and a spiral flow will be formed in the cross section of the bend. If the curve is not strong, fluid at the center of the pipe, passes towards the outside and returns to the center of the pipe. When injecting chemicals on bends, as the flow rate increases, the centrifugal and buoyance forces will increase and break the main stream and produce two layers (Sakakibara and Machida, 2012; Dutta *et al.*, 2016).

2.12 Mixing Measurement

Despite the fact that many plants all over the US are using chloramines, there have been a very few studies to completely look at the dynamic nature of these reactions. The implications for disinfection in real world situations where mixing is not instantaneous and the distribution of chlorine species is not constant over time and space and can vary to a great extent depending on the before mentioned conditions, such as pH and Cl_2:N. The theory of mixing in pipes and the many criteria affecting it, are still unknown.

Kinetics of chloramine formation are known to be fast if chlorine and ammonia are completely mixed, however, the competing reactions affect the resulting products (Bone, 1999; White, 2009).

If monochloramine is formed with dichloramines still in the system, auto-decomposition of monochloramine is probable to happen as well (Vikesland, Ozekin and Valentine, 1998). In addition, as stated by Kolmogorov (Kolmogorov, 1941), in order to have a progress in chemical reaction, mixing of reactants on a molecular extent is necessary (Bothe, 2010). Therefore, addition of chlorine and ammonia at a proper mixing rate, Cl_2:N ratio and pH, with enough contact time would have a significant impact on monochloramine formation and prevent any potential misuse of the chemicals (Jain and Wei, 2009; Samadi, Kruzic and Prabakar, 2018).

In 1969 different reaction conditions were studied by (Toor, 1969) and it was concluded that for the fast, competitive reaction between chlorine and ammonia to form monochloramines, mixing can play more important role on the target reaction than the time of blending. Impact of mixing on chloramintaion process was examined by (Jain and Wei, 2009) in a jar test area and velocity gradients were introduced as a measure of mixing. However, (Camp and Stein, 1943) have previously stated that the value of velocity gradient is a good indicator of turbulence inside a system, but it measures the energy that is imparted to water. The same amount of energy can be easily imparted by using larger blades but in slower rates.

There are two types of mixing: agitation and blending. Main focus is on the latter in this study, since blending is combination of several liquid streams to achieve uniformity. The goal is to know how much ammonia and chlorine are required and how far they must be mixed so the solution can be called a well-mixed mixture, and how far mixing needs to go on to have a homogenous solution.

At the very first steps towards defining a sufficient mixing, intensity of segregation Equation 2-2 was presented by Danckwert's (1952) (Danckwerts, 1952) to measure uniformity of blending and to show a better decline of concentration fluctuation intensity. Intensity of segregation is the effect of molecular diffusion on mixing and measures concentration changes near the targeted packets of fluid (Luschik, Pavel'Ev and Yakubenko, 1994).

$$I_s = (\frac{\sigma_m}{\sigma_u})^2 \quad \text{Equation 2-2}$$

In which:

I_s is Danckwert's intensity of segregation and is 1 when chemicals are unmixed and is 0 when they are totally mixed.

σ_m = standard deviation of concentration in blended flow which is presented in Equation 2-9

σ_u = standard deviation of two flows that are not mixed that is calculated based on the relative flow rates of the streams as follows (Danckwerts, 1952):

$$\bar{X}_A = \frac{Q_A}{Q_w + Q_A} \quad \text{Equation 2-3}$$

$$\bar{X}_w = 1 - \bar{X}_A \quad \text{Equation 2-4}$$

In this equation $\bar{X}_A$is volume fraction of stream that has unblended chemical A

Chemical A is the compound being added to water stream.

Q_A = flow rate of solution stream of chemical A, (m^3/s)

Q_w = flow rate of water stream being treated, (m^3/s)

$\bar{X}_w$ = volume fraction of water in unblended condition

For a large number of random samples from two streams, the standard deviation of concentration before blending is presented as:

$$\sigma_u \cong \sqrt{\bar{X}_A(1-\bar{X}_{A)}}$$

Equation 2-5

And since concentration values are much easier to be found in experiments with chemical dosing, the following reaction can be used instead:

$$\bar{X}_A = \frac{C_{dose}}{C_A + C_{dose}}$$

Equation 2-6

$$\frac{Q_A}{Q_w} = \frac{C_{dose}}{C_A}$$

Equation 2-7

And C_A = concentration of chemical A in feed stream, (kg/m^3)

C_{dose} = dose of chemical A to be applied to water stream, (kg/m^3)

Moreover, several researches have been conducted to measure micro-mixing and define this concept regarding homogeneity and time to achieve a homogenous solution. An investigation was done by Hiby to find a proper definition of mixing and time related to that in liquid mixtures (Hiby, 1981). Several methods were examined such as using conductivity probes, tracer tests, reaction decolorization and change in temperature as a result of a reaction and the results were compared showing that due to their condition, methods are different. One can use concentration change measurements over time and space for physical homogenization, while for chemical reactions intensity of segregation has to be measured.

Furthermore, coefficient of variation (COV) has been defined by Myers (Myers, Bakker and Ryan, 1997) to measure degree of homogeneity, which is the ratio of standard deviation of a factor assuming concentration to mean value of concentration. COV being zero implies that the saline aquifer is homogeneous, and a high COV implies a high degree of heterogeneity. For most of cases

COV less than 0.01-0.05 is considered as an acceptable level of blending (Myers, Bakker and Ryan, 1997; Chen, Zeng and Shi, 2013).

$$COV = \left(\frac{\sigma_m}{\bar{C} \text{ or } \bar{X}_A}\right) \times 100\% \qquad \textit{Equation 2-8}$$

$$\sigma_m = \sqrt{\frac{\sum_{i=1}^{n}(x_i - \bar{x})^2}{n-1}} \qquad \textit{Equation 2-9}$$

Where:

σ = standard deviation

n = number of data points

$\bar{x}$ = mean of x_i

x_i = values of the data

Brodkey (Lee and Brodkey, 1964) measured turbulent motion and mixing in the pipe. In his research concentration, velocity mean and concentration fluctuation intensity were measured. To measure concentration fluctuation as a result of mixing, Gentian violet tracer that has low molecular diffusivity was used which helped their experiment to be a good representative of mixing time.

In 1969 different reaction conditions were compared by Toor (Toor, 1969) and it was concluded that for simple, reversible reaction, with no competitive side reactions outcome will be the same regardless of the velocity of blending. However, fast, competitive, consecutive, poorly reversible reaction is affected by the time of blending. It was also understood that time characteristics of blending changes with the characteristic of water stream being treated. Since chlorine and ammonia undergo fast, competitive reactions to form monochloramines, this motivated us to focus more on effect of mixing on the target reactions. Toor also mentioned the fact that if the macromixing is achieved in a solution then it can be said that micro-mixing is also going to happen; while the reverse condition is not true.

There are lots of competing reactions involved in chemical addition to water that tracking the progress of each and the species formed and lost can be done only by using a complicated computer model. Recently Ducoste benefited from computational fluid mechanic (CFD) program and chose a turbulent model out of several two equation models that explains characteristic of chemical mixing in water treatment process, the best (Ducoste and Ortiz, 2002). Then he compared the results of an experimental approach with various turbulence models in different reactor geometries that created a variety of mixing conditions for fluids. He used a square duct with the length of 39.0 cm and area of 3.72 cm^2 which is very small, compared to the work suggested in this experiment (81.0 cm^2), and divided it to two parts, one for feeding and another for regular water stream. Next geometry used by him was a square duct with the same area but divided into three parts and the feeding part was the middle one. He also used a jet mixing tube and the outer tube's diameter was 3.1 cm. In all cases the samples were taken from centerline, immediately after injection, after mixers and at some distances from mixers.

In 2003, Zughbi investigated the effect of mixing in pipelines with single tees and double tees located on opposite sides of the pipe wall, both numerically and experimentally and stated that centerline jet injection resulted in production of the most homogenous mixture (Zughbi, Khokhar and Sharma, 2003). Ger Ahmet presented data from three single point injections: centerline, wall and jets injections. It was declared that better mixing is obtained at jet injections perpendicular to the wall. They proposed that for a straight pipe, injection on the wall requires a distance equal to 200 pipe diameter and the mixing distance decreases with jet injection (Ger and Holley, 1976). Fitzgerald, tested jets locating on the pipe wall and injecting chemicals at different angles to a galvanized steel pipe with 6.0-inch internal diameter. They calculated COV of the conductivity of the tracer salt (NaCl) in 13 points on the four radii spaced 90° apart, samples were taken at r values equal to 1.44", 2.20", and 2.76" and one sample was taken at the center of the pipe. They took into account the effect of non-uniformity in velocity in their calculations when measuring COV values. A 1/8" I.D brass tube was used for sampling and injection. Jet injections ranging from 90° (cross flow) to 120°, 135° and 150° relative to the ambient flow direction were located on the pipe wall. It was reported that 150° jet showed the least mixing distance and was recommended as the best choice. They also evaluated the effect of dual jet injection with a 90° jet on the opposite walls of the pipe and stated that double jet injection produces maximum mixing in the pipeline (Fitzgerald and Holley, 1979).

There has been some work focusing specifically on chloramine formation measuring G-value and intensity of mixing relating to that to optimize chloramine formation (Jain and Wei, 2009). G-value value is a good indicator of turbulence, but since it is the energy that is imparted to water, it cannot be a good representative of an adequate mixing, because you can easily impart the same amount of energy slowly with one large blade as well as some small blades with faster rates.

Chapter 3

MATERIALS AND METHODS

To achieve the objectives of the project two sets of experiments were designed. A tracer salt study and chloramination process in a straight pipeline and in pipeline with bends. For this purpose, a pipeline with the following features was designed and built in water resources laboratory at the University of Texas at Arlington.

3.1 Experimental Facilities for Tracer Salt Study

The pipeline was a polyvinyl chloride (PVC) pipe with 4.026 in I.D. It had 60 ft straight section and after that it was built in way to send the water to the drainage tank through another 60 ft straight section and these two straight pipes were connected to each other with 90-degree bends. A tank with capacity of 18,000 gallons was located beneath the laboratory and was filled with tap water. The mainstream of the tap water was then pumped from the tank into the 4.0-inch pipeline, using a centrifugal pump with 7.5 horsepower. A signet 2551 magmeter flow meter and sensor was located before the discharge from the pipeline to monitor the flow and a valve was installed in the downstream of the pipeline, 3 ft after the flow meter to control the flow of the mainstream running through the 4.0-inch pipeline. The flow meter and valve are shown in Figure 3-1 with the yellow and red color, respectively. The velocity of the water was chosen to be 1, 2, 4 and 8 fps. A Master-flex pump with the tube size of 13, 14 and 15 (Cole-Parmer n.d.) were chosen according to the injection flow velocities and were calibrated and used to inject the salt into the stream. For chemical and salt injection, stainless steel tubes with inside diameters of 0.152 in and 0.084 in and with adjustable ends were used. For sampling stainless steel pitot tubes with the same internal diameter as the injection tubes were used. They had adjustable ends and could move inside the pipeline to provide different sampling conditions. The Injection points were embedded at the upstream of the pipeline for injection of the secondary stream into the pipe. The schematic diagram of the pipeline is presented in Figure 3-1.

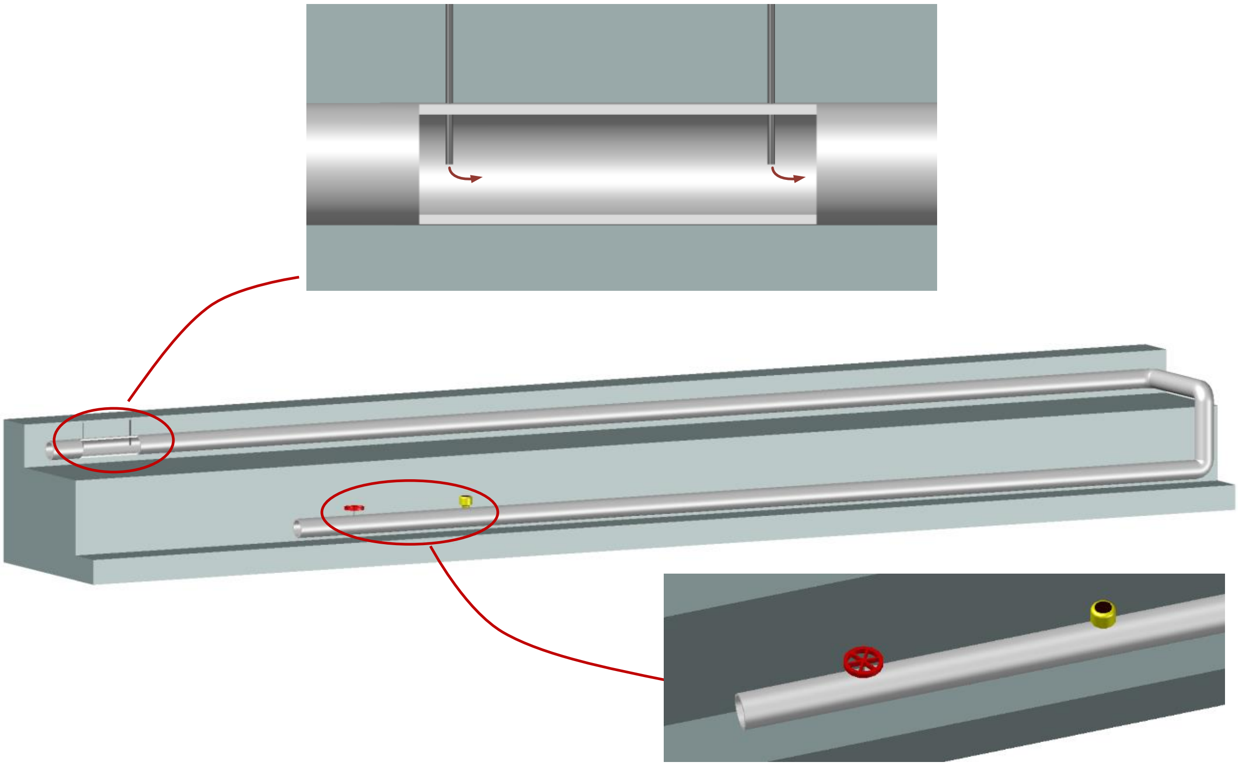

Figure 3-1. Schematic diagram of the pipeline with injection points

The minimum speed in the pipeline was chosen to be 1 fps, producing a transient flow in the pipeline. The velocity of the flow was increased in later steps of the experiment in order to produce turbulent flow in the pipeline and investigate effect of change in the flow rate and turbulent on COV values and mixing results.

The Reynolds number corresponding to the velocity of main flow is calculated and provided in Table 3-1.

Table 3-1. Reynolds number for different main flow velocities

V (fps)	Re
1.0	3.14×10^4
2.0	6.27×10^4
4.0	1.26×10^5
8.0	2.51×10^5

In Table 3-1, kinematic viscosity of water is 1.052×10^{-5} ft^2/s for 20° C and diameter of pipeline is 0.33 ft.

50 graduated glass measuring cylinders were used for sampling. A HACH HQ30-CDC401 conductivity meter and probe were used to measure the conductivity of water as NaCl was being injected into the water continuously, as a tracer salt.

Flanges were used in the upstream of the pipeline to be able to change the straight section of the pipe with bends. The removable sections of the pipe are shown in Figure 3-2.

Figure 3-2. Removable sections of the 4.0-inch pipeline

3.2 Tracer Study Procedure for COV Measurement

The tracer salt study was conducted in straight pipeline and in pipeline with bends to define a measure for mixing in the pipeline and assign a point in the downstream of the pipe for sampling for the next set of experiments, where complete mixing is achieved in the cross section of the pipeline within a short period of time.

3.2.1 Choosing a tracer salt

To choose a salt for secondary stream, three different salt solutions were prepared with various conductivities. Ammonium nitrate (NH_3NO_3) was chosen because it is an ionic compound and a strong electrolyte which means it completely dissociates into its ions in aqueous solutions. Another salt that was used was $MgCl_2$, which is a strong ionic compound as well, but has less conductivity compared to NH_3NO_3 because of the ions with less charges that are released to aqueous solutions. The last compound was sodium chloride (NaCl) which has the lowest conductivity compared to the previous compounds.

Although NH_3NO_3 and $MgCl_2$ gave better conductivity in the prepared solutions, because they were being diluted to a great extent as they were injected into the mainstream, a very little to no difference was observed between NaCl and the more conductive chemicals. As a result, NaCl was chosen to be injected as secondary stream. Among the tracers used mostly in distribution systems in the United States, such as sodium chloride, fluoride and lithium chloride, NaCl was chosen because it was cheap, less sensitive to temperature changes (Dey, Dipa., Herzog, Amanda., Srinivasan, 2007; Karamouz, Moridi and Nazif, 2010).

A fresh super saturated NaCl solution was prepared in each step and the target conductivity was measured and recorded. Although temperature changes had some influences on the solubility of NaCl, the tests were conducted in ambient temperature; and the changes in temperature were recorded for further investigations. The solubility of NaCl in water is approximately 35g per 100ml at 20℃. To prepare the fresh salt solution, 50 g of salt was added per 100 mL of milli-q water. The solution was prepared in 1-2 L of milli-q water and was used as secondary flow.

3.2.2 Straight Pipeline

In straight pipeline, tracer salt was injected into the pipeline at the upstream of the pipeline. Samples were collected from different locations, downstream of the injection points.

The first flow velocity that was examined was 1.0 fps. The saltwater was injected with the flow rate of 6.98 mL/min to the centerline of the pipe and samples were collected at 5 points through cross section of the pipe. The same procedure was followed for all experiments. However, for the last set of experiments, which was to increase the velocity of mainstream to 8.0 fps, the sampling points were reduced to 5 and 4 locations for centerline and upper wall injection, respectively. Station 4 was removed for centerline injection and stations 3 and 4 were removed for upper wall injection condition. The sampling stations were reduced because of the limited time for the experiments. The number of samples collected and measured each time were high and by measuring at the 1st and 2nd station as well as 5th and 6th station a pattern for mixing could be achieved. Moreover, 1.0 and 2.0 fps velocities were able to give enough data to have a mixing profile throughout the pipeline, and the middle stations did not make a great difference in our understanding of the mixing conditions inside the pipe. The results for centerline injection are presented in Figure 4-13 and Figure 4-14. The sampling points have reduced to 4 locations and stations 3 and 4 were removed for the 8.0 fps velocity. The procedure for 8.0 fps was the same as the previous velocities.

The details about sampling and injection procedure are delineated in the following sections.

3.2.2.1 Injection Procedure for Tracer Study

A secondary stream of NaCl was injected into the 4.0-inch pipeline using stainless steel tubes. Injection tubes had diameter of 0.152-inch for 1 and 2 fps flow velocities, and the dimeter was reduced to 0.082-inch for 4 and 8 fps main flow velocities. The diameter of the pitot tubes was changed to provide faster sampling time which will be explained in part 3.3 and the diameter of the injection stainless steel tubes were changed to be the same as diameter of pitot tubes.

The tubes for secondary stream had an adjustable end so that the location of the injection tube end could change across the pipe. Injection was done at the upstream of the flow and the injection points were at the upper wall and centerline of the pipe.

3.2.2.2 Determination of Injection Velocity for Tracer Study

In this study two sources of chlorine and one source for ammonia are injected to water to form chloramines. The sources for chlorine are onsite generated hypochlorite (OSGH) with concentration of 6,500 mg/L and high strength hypochlorite (HSH) with concentration of 86,000 mg/L and the source for ammonia is liquid ammonium sulfate (LAS) with the strength of 125,000 mg/L. For the tracer study, the tracer salt streams were injected into pipeline, imitating the treatment plants source strengths and target concentration, which is 4.0 mg/L for chlorine and the goal is to reach MCl values as high as TCl and is 1.0 mg/L for NH_3.

Chlorine to nitrogen ratio was 5:1 mass ratio. Proper ratio that results in maximum MCl is 5:1 and the proper pH is 8.3 which is suggested by EPA. In our experiments a set of solutions with different chlorine to ammonia ratio were prepared and the MCl recoveries were measure after 30 min and the 5:1 chlorine to nitrogen ratio was chosen for the experiment. The milli-q water was collected in amber bottles, 1-2 mols of sodium bicarbonate was added to water and then chlorine was added first, mixed well immediately and then ammonia was added to water within less than 2 seconds.

In all experiments pH was adjusted to 8.3 by using sodium hydroxide (NaOH) to increase pH and hydrochloric acid (HCl) to reduce pH. After 30 minutes the chlorine residuals were measured using HACH DR-890 colorimeter and according to the procedures provided in standard method for the examination of water and wastewater, section 4500-Cl (Chlorine Residuals). The residuals that were measured using the HACH DR-890 colorimeter were TCl, MCl and NH_3-N. Free chlorine, MCl and DCl were measured using the standard method section “F” which is ferrous ammonium sulfate titration method (FAS) (APHA, 2005).

The MCl recoveries are shown in Table 3-2.

Table 3-2. Chlorine and ammonia residuals for different chlorine to nitrogen ratios prepared with milli-q water

	Cl_2:N Ratio	4:1	5:1	5.5:1
	pH	8.67	8.76	8.64
DR 890	TCl	3.7	3.7	3.7
	MCl	3.26	3.55	3.43
	NH_3-N	0.1	0.08	0.02
FAS titration	TCl	3.75	3.8	3.65
	Free	0.4	0.3	0.2
	MCl	3.2	3.5	3.37
	DCl	0.1	0.05	0.07

Afterwards; using the chemical ratios, the injection concentrations are measured and presented in Table 3-3. Sample calculation for injection velocities are provided in Appendix A.

Table 3-3. Injection flow rates and flow velocities for different chemicals as secondary stream

v (fps)	Flow rate in the main pipe (L/min)	LAS 10% flow rate (mL/min)	HSH flow rate (mL/min)	OSGH flow rate (mL/min)
1	150.14	1.20	6.98	92.4
2	300.28	2.40	13.97	184.8
4	600.56	4.80	27.937	369.6
8	1201.1	9.61	55.87	739.1

It can be seen in Table 3-3, that injection velocities for HSH is not as low as LAS and not as high as OSGH. Therefore, the corresponding HSH velocities were used for salt injection.

3.2.2.3 Sampling Procedure for Tracer Salt Study

Six collection points were chosen at different distances from the injection point along the pipeline. Schematic of the pipeline with injection and sampling tubes located in the centerline is shown in Figure 3-3.

Since the results were sensitive to the speed of sample collection, the diameters of the sampling tubes were chosen in a way that they could provide less than a second collection time. Calculations are presented in Appendix A. The internal diameters of sampling tubes were 0.152 and 0.084 in for 1-2 fps and 4 -8 fps flow velocity, respectively.

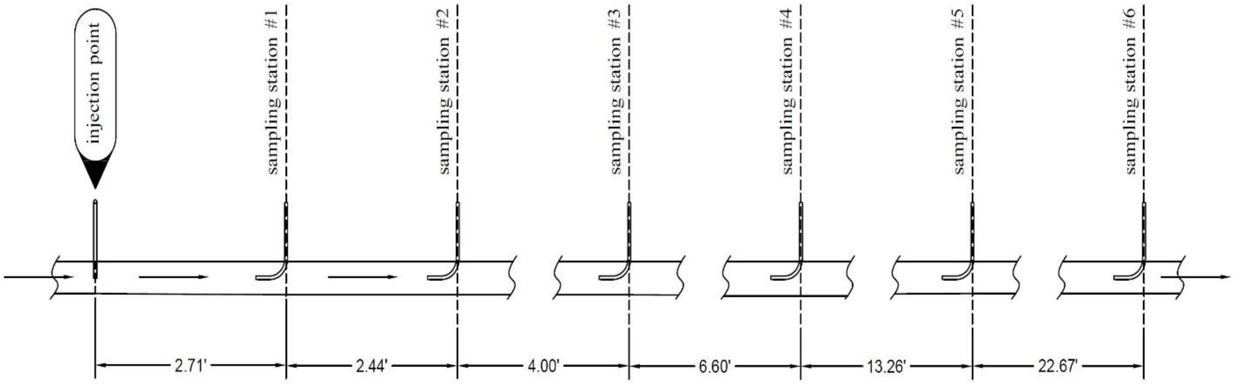

Figure 3-3. Schematic of the experiment pipeline

Samples were then collected in 50 discrete measuring cylinders as shown in Figure 3-4, in order to prevent any undesirable disturbance in the flow by the sampling equipment. Stainless-steel pitot tubes were mounted at the sampling points to collect samples.

Figure 3-4. Measuring cylinders and sampling tubes

The tubes were located in a way that they could be moved in radial direction of the pipe. As can be seen in Figure 3-3, samples were collected at different distances from injection point along the pipeline. Six sampling stations were chosen and fifty grab samples were taken from each sampling point. For all the six sampling stations, 5 points across the pipe were selected for sample collection. The five locations consisted of upper wall (UW), the point between the centerline and upper wall (MU), the center line (C), the point between the centerline and lower wall (ML) and lower wall (L). Conditions of centerline injection and upper wall sampling (CU) and centerline sampling (CC) are shown in Figure 3-5 to show how the tubes were moved radially. The conductivity of tracer salt was measured and presented as mg/L of Total Dissolved Solids (TDS) and coefficient of variation was calculated using Equation 3-1.

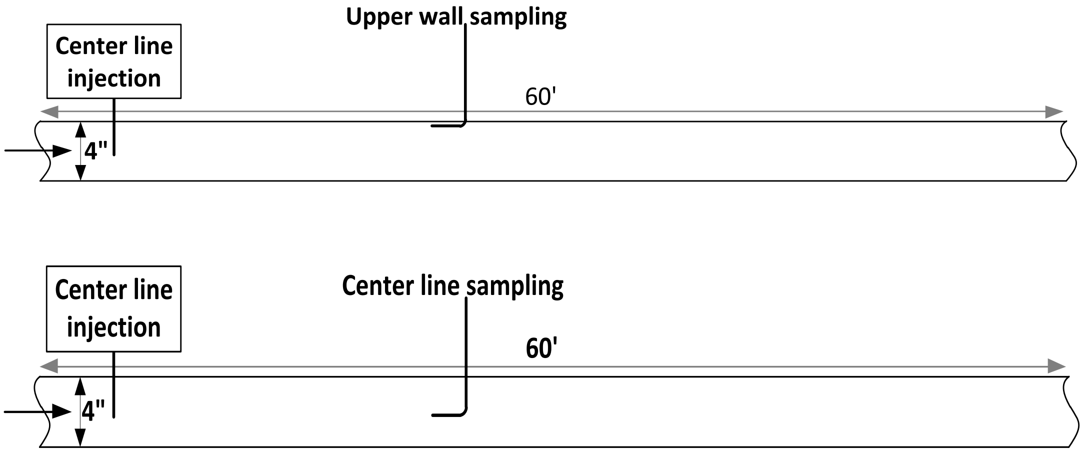

Figure 3-5. Examples of the position of the injection and sampling tubes for tracer salt study

Overall the experiments for trace salt tests consisted of two locations of injection, that were upper wall and centerline injection. Each were done for 4 different flowrates. Six sampling station were chosen along the pipeline in different distances from injection point and each time samples were collected in 50 measuring cylinders. Moreover, at every station the end of the pitot tube was located in 5 locations in the cross section of the pipeline that referred to as U, MU, C, ML and L. So that the COVs can provide a comprehensive information about the proper distance, time and sampling location required to gain complete mixing of salt with water.

3.2.3 Pipeline with Bends

To assess effect of bends on formation of turbulence in the pipeline and improve mixing, bends were added to the pipeline. As shown in Figure 3-6 and Figure 3-7 four 90-degree bends were added in the path of injection point. After addition of bends to the pipeline, two positions were chosen for salt injection. The first one was to put the injection tube after the first 90-degree bend, which gave the water path three 90-degree bends before getting into the straight section of the pipe and in this study will be referred to as “Point A” and the second location was after the third 90-

degree bend, after which there was only one 90-degree bend and will be known as “Point B”. points A and B are shown in Figure 3-6.

Figure 3-6. Injection points after addition of bends to the pipeline

A detailed figure of the bends and their detail distance are shown in Figure 3-7.

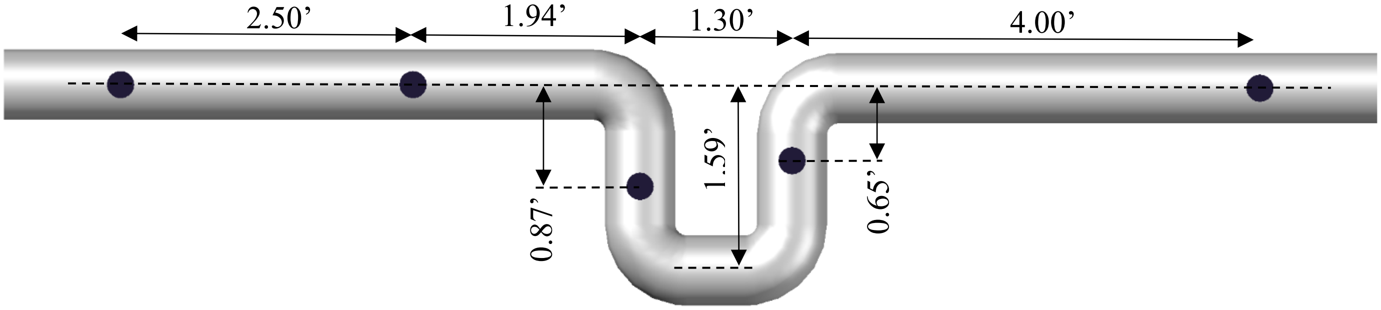

Figure 3-7. Dimension of 90-degree bends added to the pipeline

The tracer salt experiment was conducted for both locations of injection. Only centerline injection was studied, because shorter distance was achieved through centerline injection to get the complete mixing in the pipe. Samples were collected from two stations: station 3 which was located in a 4.0 ft distance after the bend and station 5 that was 25 ft from the bends. The sampling procedure was the same as the straight pipeline and the only difference was the number of stations from which the samples were taken.

3.3 Physical testing

As presented in Equation 3-2, chemical concentration measurement was required to calculate the COV and I_s values. For this purpose, a secondary stream of salt was injected into the pipeline. The measurements for conductivity of the salt were required to be fast because the flow of water in the pipe was causing mixing as the water traveled downstream. If the time to collect and measure samples was not short enough, the measured conductivities could not be a good representative of actual conductivity fluctuations in the pipeline. The available instruments for inline measurements of either conductivity or concentration, required at least half a minute measuring time and could not show characteristics of conductivity changes in the pipeline. The available inline conductivity sensors were not able to capture small variations, but for the purpose of the current experiments, discrete samples in both space and time were required. Moreover, if the sampling equipment or sensors were inside the pipeline, they could add more disturbance. As a result, the method that was chosen to give the fastest measurement, was to inject a secondary stream into the pipeline and measure the conductivity of the samples one by one by collecting samples outside the pipeline. The HACH HQ30-CDC401 conductivity meter and probe provided 10-15 seconds measurement time for each sample. It was recommended in the meter specifications to use a glassware that is only 1-2 mm larger in diameter compared to the diameter of the probe for more accurate sensor readings. For this purpose, measuring cylinders were used that had larger diameters than the probe. The conductivity is presented as mg/L of TDS. The base temperature was set to be 25ºC and any difference in temperature from the base temperature was corrected using a non-linear correction factor by the conductivity meter.

When measuring conductivity of the grab samples, the conductivity probe was rinsed with milli-q water and dried with a lint free cloth in between of each measurement.

The range of TDS measured by the instrument is 0-50,000 mg/L for NaCl and the temperature range is -10 to 110 ºC. The accuracy of the reading are ±0.5% of readings. A conductivity profile of saltwater was developed for the cross section of the pipe at each sampling station. In each set of experiments, background levels of TDS were determined in triplicates before salt injection. The conductivity of each sample was then subtracted from the background level. The target conductivity was measured from the stock solution.

Moreover, to make the sampling process faster, for 1 and 2 fps main flow velocities, 0.152-inch pitot tubes were used for sampling. However, when the velocity in pipeline increased to 4 and 8 fps, the diameter was reduced to 0.082 inch. The smaller diameter was used for pitot tubes to compensate for the lower pressure inside the pipeline and to provide faster sampling process. Because if more time was required for sample collection, the conductivity fluctuations could decrease before the samples were collected and inappropriately low COV values could be obtained.

3.4 Experimental Facilities for Water Chloramination

In second step of the project the same pipeline with the straight section and with bends addition was used. Tap water was collected in the same 18,000 gallons tank. The initial characteristics of tap water was measured and are presented in Table 3-4.

Table 3-4. Chlorine and ammonia residual of tap water

TCl (mg/L as Cl_2)	Free Chlorine (mg/L as Cl_2)	MCl (mg/L as Cl_2)	DCl (mg/L as Cl_2)	NH_3-N (mg/L)	pH
3.4	3.12	3.12	0.20	0.16	7.96

In addition to all the facilities used for tracer salt study, another master-flex pump was used for injection of the second chemical. Hach DR-890 colorimeter was used to measure TCl, MCl and NH_3-N. Amber bottles were used for collecting samples for manual addition of chlorine and ammonia to produce well mixed condition.

3.5 Chloramination Procedure

Effect of mixing on chloramination process was examined in a straight pipeline and pipeline with bends. The details about the experiments and procedures are provided in this section.

3.5.1 Water Dechlorination

To see effect of mixing of chlorine and ammonia it was required to dechlorinate water before flowing the mainstream from the tank to the 4.0 in pipeline. Sodium thiosulfate ($Na_2S_2O_3$) is a commonly used reagent for water dechlorination. However, addition of sodium thiosulfate to tap water leads to formation of high concentration of ammonia. Sodium thiosulfate when added to water will react with chlorine and if ammonia is available in water the chlorine molecules that were bonded to ammonia, will react with sodium thiosulfate and nitrogen will be released into water. As a result, nitrogen concentration would increase after water dechlorination. In this study it is required to reduce concentration of chlorine and ammonia at the same time or use water that is not chlorinated.

A solution to remove ammonia from water that has been studied in several studies is to add chlorine to water up to the point that it gets to break point described in “Chapter 2” (Pressley, Bishop and Roan, 1972; Jeong et al., 2014). In this study the same process was replicated. The chlorine to nitrogen ratio was increased with 0.5 increments from 5:1 to 9:1 mass ratio. The results are presented in Table 3-5.

It can be seen that concentration of chlorine and ammonia decreases with increase in Cl_2:N ratio up to ratio of 7.1:1. This amount is recommended to be about 7.6:1 and even up to 10:1 in other studies (Pressley, Bishop and Roan, 1972), but it can be seen that after 7.1:1, the residual values increase.

Table 3-5. Residual and ammonia chlorine with increase in Cl_2 :N ratio

Cl_2:N	TCl (mg/L)	Added Cl_2/fixed N (mg/L)
4.2:1	3.8	0.8
4.3:1	3.8	0.9
4.4:1	3.7	1
4.5:1	3.6	1.1
4.6:1	3.4	1.2
4.7:1	3.2	1.3
4.9:1	3.6	1.5
5.1:1	2.9	1.7
5.3:1	2.7	1.9
5.7:1	2.2	2.3
6.4:1	1.7	3
6.9:1	1.3	3.5
7:1	0.3	3.6
7.1:1	0.4	3.7
7.4:1	1.4	4
7.6:1	2.1	4.2
7.9:1	3.5	4.5

The minimum point on the graph is our target as it reduces both chlorine and ammonia concentration in tap water before being injected into the pipeline. The trend is also shown in Figure 3-8. It can be seen that the trend shown in Figure 3-8 matches the break point curve.

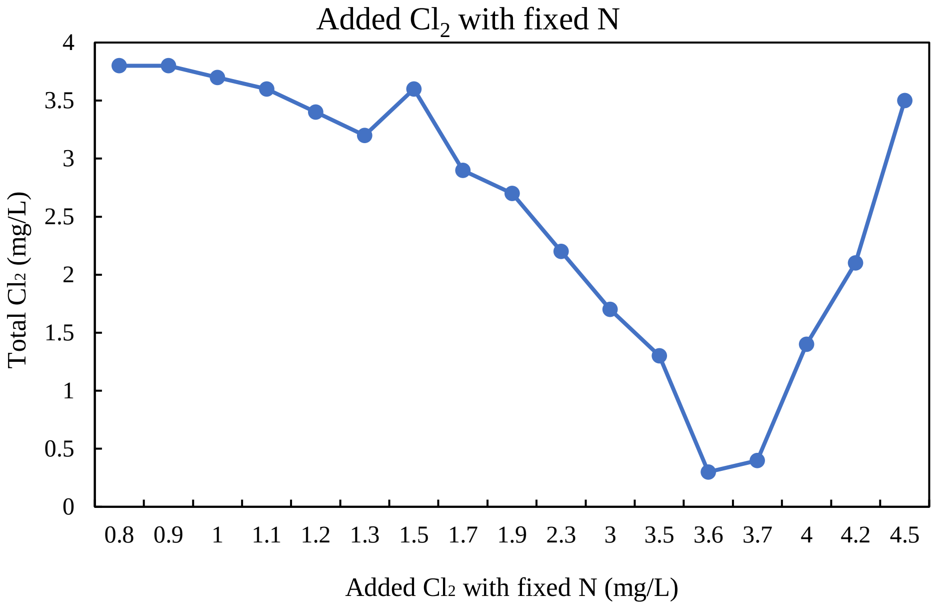

Figure 3-8. Total chlorine vs added chlorine for Cl_2 and N concentration reduction

The ratio gained for break point was then used for dechlorination of tank water. A master-flex pump was calibrated based on the ratio and chlorine source concentration for injection of chlorine into the pipe. Chlorine solution with concentration of 50,000 mg/L was injected into the pipeline through stainless steel tubes while tap water was passing through a 4inch PVC pipeline and the water was then discharged into the tank from the pipe. After 24 hrs of contact time, chlorine residual of the tank water was measured. If the concentration of TCl was in the range of 0.1-0.3 mg/L and concentration of NH_3-N was between 0.0-0.04 mg/L, the tank water could be used for the test.

3.5.2 Dilution Ratio

It is shown in previous section in Table 3-3, that two different sources for chlorine was used. The reason for variation in chlorine concentration was used to measure the effect of various dilution ratios on monochloramine formation rate. Dilution ratio in this study is defined as concentration of the compound in the stock solution to the target concentration. For OSGH, dilution ratio is equal to 1625, and for HSH is 21500. In theory a decrease in dilution ratio leads to better initial mixing, as it is injecting a diluted solution with higher injection velocity to the mainstream. Therefore, concentration difference between the mainstream and the secondary stream declines and mixing will be easier and faster. Thus, it is expected that the OSGH solution with better initial mixing, produces higher monochloramine recovery. In Table 3-6, injection flow velocities are presented, that are calculated from flow rates provided in Table 3-3 and the surface area of the pipeline.

Table 3-6. Flow velocities of secondary streams

Flow velocity of the main pipe (fps)	Injection velocity of LAS (fps)	Ratio of injection velocity of LAS to mainstream velocity	Injection velocity of HSH (fps)	Ratio of injection velocity of HSH to mainstream velocity	Injection velocity of OSGH (fps)	Ratio of injection velocity of OSGH to mainstream velocity
1.0	0.0056	0.0056	0.033	0.033	0.432	0.432
2.0	0.011		0.065		0.864	
4.0	0.074	0.0184	0.427	0.107	5.66	1.41
8.0	0.147		0.855		11.31	

It is shown in Table 3-6 that the injection velocity is low with lower flow rates. LAS that has the highest source concentration and lowest velocity ratio of 0.0056. As the velocity of main flow increases the velocity of the secondary stream rises and at its maximum gets to 1.4 times higher than the main flow velocity for case of OSGH. Since the water is injected with higher velocity, there will be more chance of chemical penetration into the pipeline and improvement in mixing of chemicals with the water as they are injected into the stream. Schematic of this process is shown in Figure 3-9.

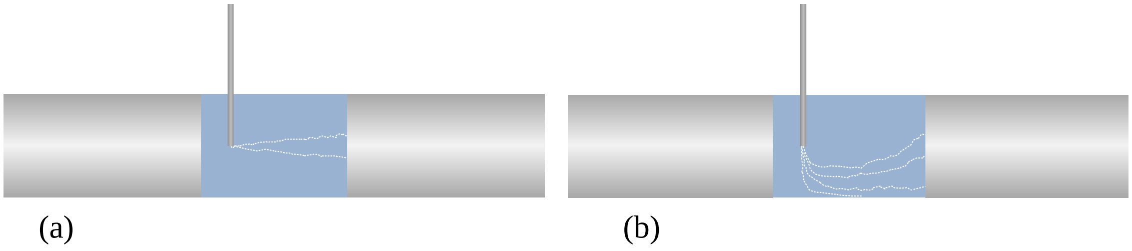

Figure 3-9. Effect of injection velocity on chemical mixing (a) Low injection velocity, (b) High injection velocity

3.5.3 Well Mixed Condition

At each step, before starting the chemical injection pumps, water samples were collected from the same sampling point in amber bottles. Later, chlorine was added first and mixed well and immediately ammonia solution was added. The mixture was blended well by shaking the amber bottles vigorously. Chlorine and chloramine residuals were measured after 30 min and 24 hrs after addition of chemicals. The measurements for well mixed condition are presented in Appendix C for the corresponding condition.

Moreover, well mixed condition was done for different Cl_2:N ratios on a regular tap water to see the effect of change in ratios on the chlorine residuals. The results are presented in a tabular format in Appendix C.

3.5.4 Order of Chemical Injection and Chemical Contact Time

To choose between the order of injection of chemicals into the pipeline and distance between them, there was some challenges.

It is recommended by TCEQ staff guidance (TCEQ, 2014) to add chlorine first, mix the chemical with water for five minutes and then ammonia must be added to water. In several treatment plants it was observed that they added ammonia first and then chlorine to water, with no mixing in between.

Another challenge was the distance between to chemicals. In some plants, chemicals are added at the same time, in some others there is a distance between the injection points of chlorine and ammonia. Since the issue of mixing these two chemicals was not assessed before and it was not possible to examine all cases some decisions were made.

First of all, the Cl_2:N ratio plays an important role in formation maximum MCl which is also shown in Table 3-2. If chlorine and nitrogen are not mixed at the concentration, the MCl production will be affected. Moreover, as mentioned in previous chapter, addition of chlorine to water produces DBPs. Since chlorine is an active reagent, if it is added first and mixed with the water, it causes DBPs formation, and reacts with other compounds in aqueous environment and its concentration when meeting ammonia would be unknown. Therefore, if the TCEQ recommendation is followed, it is necessary to have a sampling point at the location of ammonia injection to measure chlorine residuals and use that as base concentration for the concentration of ammonia that must be added to water. In the next chapter, the results from pipeline with bends for chloramination process, would confirm this statement.

The distance between chemicals was chosen based on several features. The goal was to add chlorine to water, try to mix it with water, but not give enough contact time to allow DBPs to be produced. The same procedure was performed for well mixed condition as explained in before.

Moreover, if the chemicals are injected at the same time, there is possibility that they spread across the pipeline in different pathways. But if chlorine is injected first, there is more chance that by the time that mainstream flow gets to the ammonia injection station, a wider area of water contains chlorine. A schematic of possible paths of secondary stream under current injection condition, is shown in Figure 3-10. As a result, in the tests, distance between injection points is 2.5 ft which is less than a second for the lowest flow velocity.

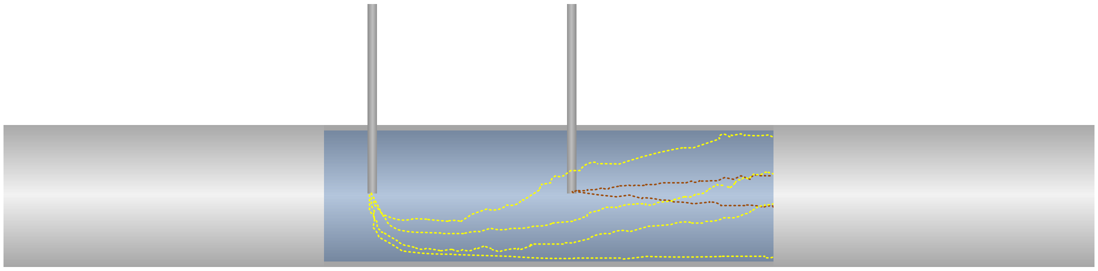

Figure 3-10. Possible pathway for the secondary streams under current injection condition

Considering the disagreements on the order of chemical addition, two order of addition were examined. First ammonia was injected at the upstream of the pipeline and after that chlorine was added to water at 2.5 ft downstream of the ammonia injection point. The same order of addition was conducted in 1.0 L amber bottles to assess well-mixed condition. The results are presented in Table 3-7.

Table 3-7. Chlorine and nitrogen residuals with the order of ammonia injection 1st and chlorine injection 2nd

Q (L/min)	q ammonia (1st) (mL/min)	q chlorine (2nd) (mL/min)	Target Cl (mg/L)
150.14	92.39	1.20	4.0
TCl = 0.2 mg/L	MCl = 0.18 mg/L	NH3-N = 0.0 mg/L	center-center injection

	pH	**Pipeline samples**	
30 min	8.10	Total	1.4
		Free	0.05
		Mono	0.97
		Di-	0.21
		NH3-N	0.01
24 hours	8.0	Total	0.7
		Free	0.1
		Mono	0.4
		Di-	0.12
		NH_3-N	0.04

	pH	**well mixed**	
30 min	7.92	Total	3.3
		Free	0.15
		Mono	2.99
		Di-	0.15
		NH3-N	0.2
24 hours	7.90	Total	2.3
		Free	0.2
		Mono	1.94
		Di-	0.14
		NH_3-N	0.29

Afterwards, the order was changed by injecting chlorine first and adding ammonia 2.5 ft after chlorine injection station. Well-mixed condition was repeated for this condition as well. The results are presented in Table 3-8.

Table 3-8. Chlorine and nitrogen residuals with the order of chlorine injection 1st and ammonia injection 2nd

Q (L/min)	q chlorine (1st) (mL/min)	q ammonia (2nd) (mL/min)	Target Cl (mg/L)
150.14	92.39	1.20	4.0
TCl = 0.2 mg/L	MCl = 0.18 mg/L	NH3-N = 0.0 mg/L	center-center injection

	pH	**Pipeline samples**	
30 min	8.21	Total	2.6
		Free	0.15
		Mono	2.1
		Di-	0.19
		NH3-N	0
24 hours	8.09	Total	1.4
		Free	0.1
		Mono	1.1
		Di-	0.15
		NH3-N	0.05

	pH	**well mixed**	
30 min	8.15	Total	4.0
		Free	0.15
		Mono	3.74
		Di-	0.12
		NH3-N	0.01
24 hours	8.10	Total	2.8
		Free	0.2
		Mono	2.47
		Di-	0.1
		NH3-N	0.1

Comparing the results between two tables shows that, dichloramine formation was not different. TCl and MCl formation was lower when ammonia was added first. It was also observed that NH_3-N residual was higher in the first scenario. Therefore, the second order was chosen for experiments. In all steps, chlorine was added first and ammonia was injected after that.

3.5.5 Straight Pipeline

3.5.5.1 Injection Procedure for Chloramination

At an upstream point in the straight pipeline, chlorine and ammonia were injected at the centerline of the pipe. Chlorine was injected first and ammonia was injected at 2.5 ft distance downstream from chlorine, which resulted in a range of 0.33 to 2.5 seconds interval between the two injections depending on the flow velocity in the pipe. The pipeline with straight section and the injection points is shown in Figure 3-11. A schematic figure of the whole pipeline is drawn in Figure 3-12.

Figure 3-11. Straight section of the pipeline with two injection points

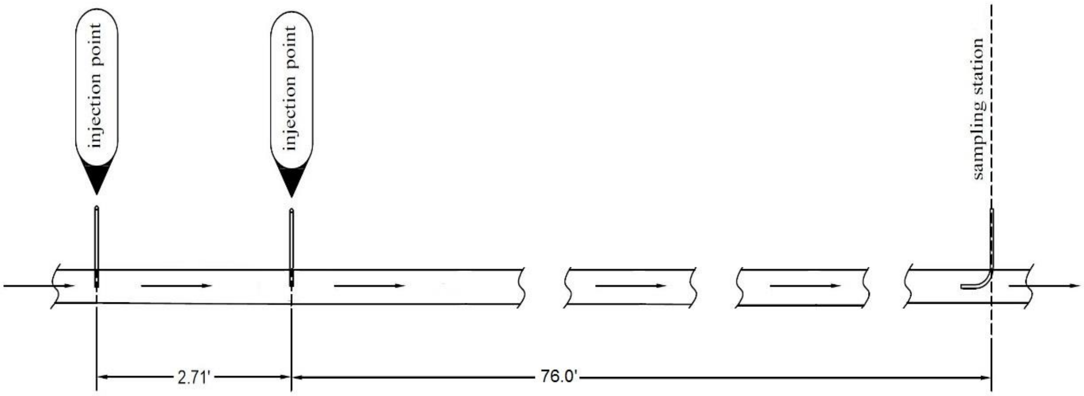

Figure 3-12. Schematic of the straight pipeline with chlorine and ammonia injection

The ammonia source was liquid ammonium sulfate (LAS) with a concentration of 125,000 mg/L. The concentration of chlorine solution was 6500 mg/L as Cl_2 obtained from a water treatment plant generating onsite generated sodium hypochlorite (OSGH) for one set of experiments and then it was increased to 86000 mg/L to simulate high strength sodium hypochlorite (HSH). As the flowrate of mainstream increased, the injection velocities increased. The ammonia and chlorine solution concentrations are the most common ones typically used in water treatment plants. To keep the target monochloramine concentration constant as the concentration of chlorine increased, the chlorine injection flow rate was decreased proportionally. First, LAS and OSGH were injected, afterwards in a different set of experiments LAS and HSH were injected into the pipeline. The secondary flow injection flowrates were equal to the ones mentioned in Table 3-2 for each primary flow stream.

3.5.5.2 Sampling Procedure for Chloramination

Once chemicals were injected, samples were collected in amber bottles from a point that complete mixing was achieved with tracer salt. Mixing was complete within 60 ft of the injection points, but to assure proper mixing across the pipeline, samples were taken even further down. Sampling point was located at 76 ft distance from the injection stations. This distance is chosen regarding the results from tracer study which will be explained in detail in “Chapter 4”.

3.5.6 Pipeline with Bends

To address the effect of bends on MCl formation in a pipeline, the straight section of the pipe was replaced with the section with bends.

3.5.6.1 Injection Procedure for Pipeline with Bends in Chloramination Process

For the second set of experiments, two different types of injection were examined.

First, the injection points did not change and bends were added to the pipeline downstream of the injection points. All the conditions were the same as straight pipeline, only bends were added on the path of water to the sampling points. This condition is referred to as “Before Bend” condition. Chlorine was injected first, after 2.5 ft LAS was injected into the pipeline. The distance between the second injection point and the first 90-degree bend was 1.94 ft. water goes through four 90-degree bends and after 76 ft from the injection points, samples are collected. The experiments are done for OSGH and HSH to evaluate effect of dilution ratio.

For the second part, chemicals were injected on the bends. Chlorine solution was injected first and after one 90-degree bend, LAS was injected. This condition is called "On-Bend" condition and the injection points with injection tubes and pumps in place are shown in Figure 3-13.

Figure 3-13. Injection points for on-bend condition

For this step samples were collected at the same sampling point as the straight pipeline.

3.5.7 Chemical analysis

For measuring recovery of chlorine, chlorine and ammonia residuals were measured. Each of the measurement methods are explained in the following sections.

3.5.7.1 Determination of Chlorine Residual and Ammonia

NH_3-N measurement was conducted using manual for HACH DR-890. To calculate precision of NH_3-N test, a solution containing 1.80 mg/L Cl_2 and 0.20 mg/L NH_3–N was used and standard deviation of ± 0.01 mg/L N was gained. The estimated detection limit for this method is 0.02 mg/L N.

Chlorine residuals could be measured using either HACH DR-890 or standard method, however, the instrument could not measure dichloramine values. As a result, both HACH DR-890 and standard method for the examination of water and wastewater, section 4500-Cl-F was used to measure chlorine residuals (APHA, 2005).

The method for TCl measurement using HACH DR-890, was DPD ultra high range with ability to measure between 0-10 mg/L of Cl_2. Precision of this method was examined, using a chlorine standard solution of 5.05 mg/L Cl_2 and representative lots of reagent and standard deviation of ± 0.05 mg/L Cl_2 was obtained. Additionally, the estimated detection limit for this method is 0.05 mg/L Cl_2.

The range of measurement for ammonia and MCl using DR-890 is 0-0.5 mg/L NH_3-N and 0–4.50 mg/L Cl_2, respectively. Precision for MCl test, MCl standard solution of 2.10 mg/L Cl_2 was used and had a standard deviation of ± 0.12 mg/L Cl_2. Estimated detection limit for this method is 0.05 mg/L Cl_2.

Procedures from the standard method were followed without any modifications. The test is very sensitive and prone to errors, and a few tips must be taken into consideration that are mentioned in throughout the process that are not mentioned in the standard method. For example, the order of phosphate buffer, DPD indicator and 100mL of sample addition to the flask is important. If the sample is added first, there is a high chance that unstable colorless amine is produced which affects the magenta color of the solution.

3.5.7.2 Equipment and Reagents needed

Safety glasses/goggles

Gloves

Lab Glassware

Phosphate Buffer; DPD Indicator Solution; Ferrous Ammonium Sulfate (FAS) Titrant;

Potassium Iodide crystals; Potassium Iodide Solution

3.5.7.3 Method characteristics

Maximum TCl measurement with this method is 5 mg/L Cl_2. Minimum detectable concentration with this method is 18 µg Cl as Cl_2/L, however normal working detections are higher.

Volume of sample required is equal to 100 mL.

3.5.7.4 Procedure

Free Chlorine

1. Place 5.0 mL of phosphate buffer reagent and 5.0 mL of DPD indicator in a beaker and mix.
2. Add 100 mL of sample and mix.
3. Titrate rapidly with FAS until the red color disappears.
4. Record the reading (A).

Monochloramine

1. Add 2 drops of Potassium Iodide (KI) solution and mix in the same beaker.
2. Continue to titrate until the red color has disappeared again.
3. Record the reading (B).

Darker colors indicate higher values of chlorine species. By addition of titrator gradually, the color will change into pale pink. As shown below.

Dichloramine

1. Add 1 gram of Potassium Iodide (KI) crystals and MIX to dissolve in the same beaker. Turn OFF stirrer plate OR remove beaker from stirrer plate.
2. Let stand for 2 minutes, turn ON stirrer plate and then continue titrating until the red color disappears.
3. Record the reading (C).
4. Add Readings A, B and C for Total Chlorine Residual in mg/L.

Total Chlorine (Simplified procedure)

To obtain the total Chlorine in one reading, add 1 gram of KI crystals at the start together with the specified amount of Buffer and DPD indicator.

Let stand 2 minutes.

Turn on stirrer plate. Titrate with standard FAS until clear.

Chapter 4

RESULTS AND DISCUSSION

Experiments were done in a pipeline with either straight section or addition of bends and the results are presented in this section. Detailed results for tracer salt study and water chloramination are presented in Tables in Appendix B and C, respectively.

4.1 Tracer Study for COV Measurements

The tracer salt study in the straight section of the pipeline and in pipeline with bends were conducted to investigate the proper condition in the pipeline to achieve a fast, complete mixing through inline injection of secondary flow. Explanations and discussions of the results for each study are provided in this chapter.

4.1.1 Straight Pipeline

The first flow velocity that was examined was 1.0 fps. The saltwater was injected with the flow rate of 6.98 mL/min into the centerline of the pipe and samples were collected at 5 points through cross section of the pipe. The conductivities presented in figures with the title “Average vs Station” such as Figure 4-1 are normalized by dividing average conductivity of 50 discrete samples by the target conductivity, for each mixing and sampling condition. As a result, the target conductivity would be dimensionless and equal to 1.0 in all the corresponding figures. The goal is to reach 1.0 within a short period of time after NaCl injection. The COV values are measured using equation 1-1 and the calculated COV values are presented in Figure 4-2.

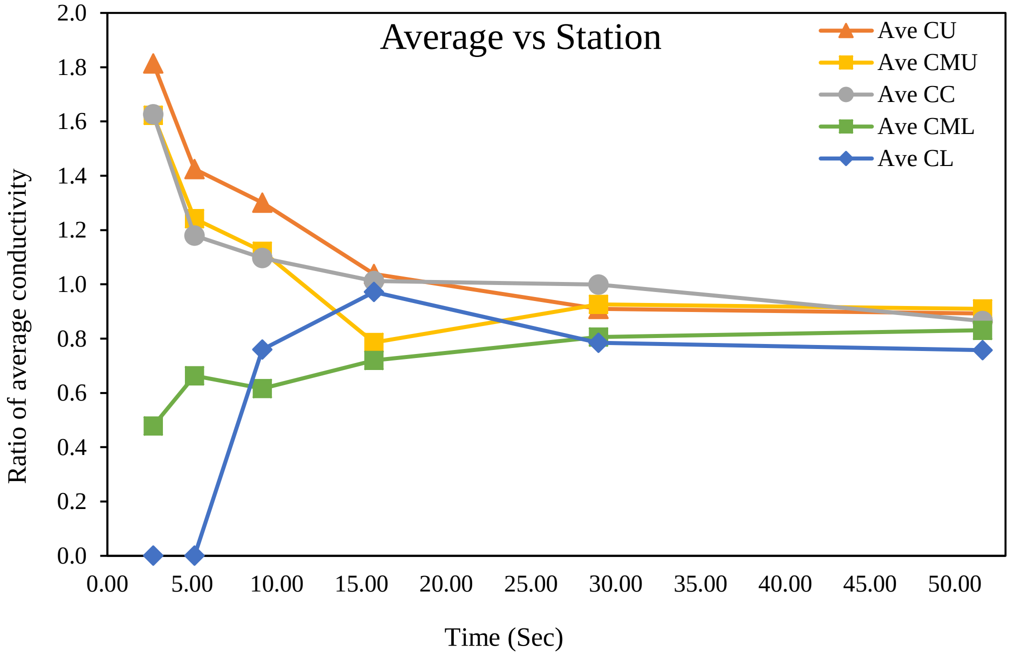

Figure 4-1. Average vs Station for centerline injection, Q=150 L/min, v=1.0 fps

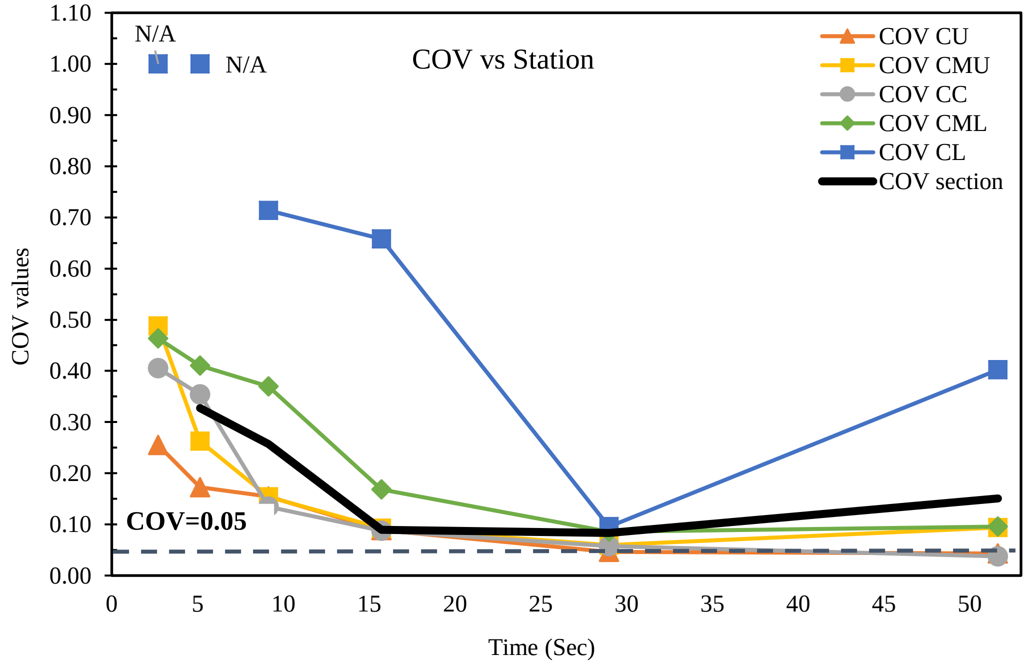

Figure 4-2. COV values for centerline injection, Q=150 L/min, v=1.0 fps

It can be seen in Figure 4-1 that the average values tend to get to 1.0 after 30 seconds. In Figure 4-2, in all steps, decrease in the COV values was observed as a result of more retention time in the pipeline. However, despite what the Figure 4-1 implies, it is observed in Figure 4-2 that complete mixing is not achieved in the pipeline. Therefore, it is concluded that COV is a better representative of mixing condition in the pipeline than the average values. It is seen that as the water travels down the pipeline and stays in the pipe for a longer time, the secondary flow has more time to mix with the mainstream and the COV values tend to decrease and get closer to the 0.05 line. This is an indication of achieving a better mixing which occurs after 52 seconds after the injection.

Moreover, when the injection is at the centerline and the sampling is from lower wall, the measured conductivity was the same as for tap water for the first station. This shows that no salt was caught by the sampling tubes up to 5.0 seconds after the injection.

In Figure 4-2, the black line that is referred to as COV section, is the COV values of the conductivity of the 250 samples, that were collected and measured in each section of the pipeline at each sampling station.

The I_s values were calculated using Equation 2-2 and are provided in Table 4-1, for 1.0 fps flow velocity. The I_s along with COV values for all other experiments are presented in a tabular form in Appendix B. Sample calculations for measuring I_s values are presented in Appendix A.

Table 4-1. I_s values for centerline injection, Q=150 L/min, v=1.0 fps

Sampling Station	Distance from Injection (ft)	I_s, CU	I_s, CMU	I_s, CC	I_s, CML	I_s, CL
Stat 1	2.71	3.021×10^{-6}	1.106×10^{-5}	7.632×10^{-6}	9.992×10^{-6}	4.651×10^{-5}
Stat 2	5.15	1.385×10^{-6}	3.203×10^{-6}	5.831×10^{-6}	7.838×10^{-6}	4.651×10^{-5}
Stat 3	9.15	1.101×10^{-6}	1.099×10^{-6}	8.419×10^{-7}	6.347×10^{-6}	2.368×10^{-5}
Stat 4	15.73	3.689×10^{-7}	4.001×10^{-7}	3.539×10^{-7}	1.317×10^{-6}	2.014×10^{-5}
Stat 5	28.99	9.851×10^{-8}	1.652×10^{-7}	1.523×10^{-7}	3.414×10^{-7}	4.233×10^{-7}
Stat 6	51.66	8.635×10^{-8}	4.097×10^{-7}	6.543×10^{-8}	4.242×10^{-7}	7.524×10^{-6}

As can be seen in Table 4-1, the I_s values have the same trend as COVs. They decrease as the water travels through the pipeline and get closer to zero in the last two points which are 29 seconds and 52 seconds after the injection. However, I_s values are not providing any additional information compared to the COV values.

As it was shown in Equation 2-2, I_s value captures effect of dilution ratio. Therefore, it requires different concentration of stock solutions as well as enough data, to calculate standard deviation of the concentrations. In tracer salt study only one concentration of salt solution was used. Ideally, to measure I_s values, it is required to change the concentration of the secondary solution. In later steps that chemicals were injected into the pipeline, two different concentration of chlorine solutions were used, however, because of the limited number of samples in which MCl recovery values that were measured, enough data was not available for standard deviation measurements. As a result, only COV values are presented and analyzed as a measure for mixing in this study.

In the next step, injection tube was moved upward for upper wall injection condition. The results for injection at upper-wall of the pipe for velocity of 1.0 fps are shown in Figure 4-3 and Figure 4-4. In Figure 4-4 the black line is the COV of the measured conductivities from 250 samples in the cross section of the pipeline.

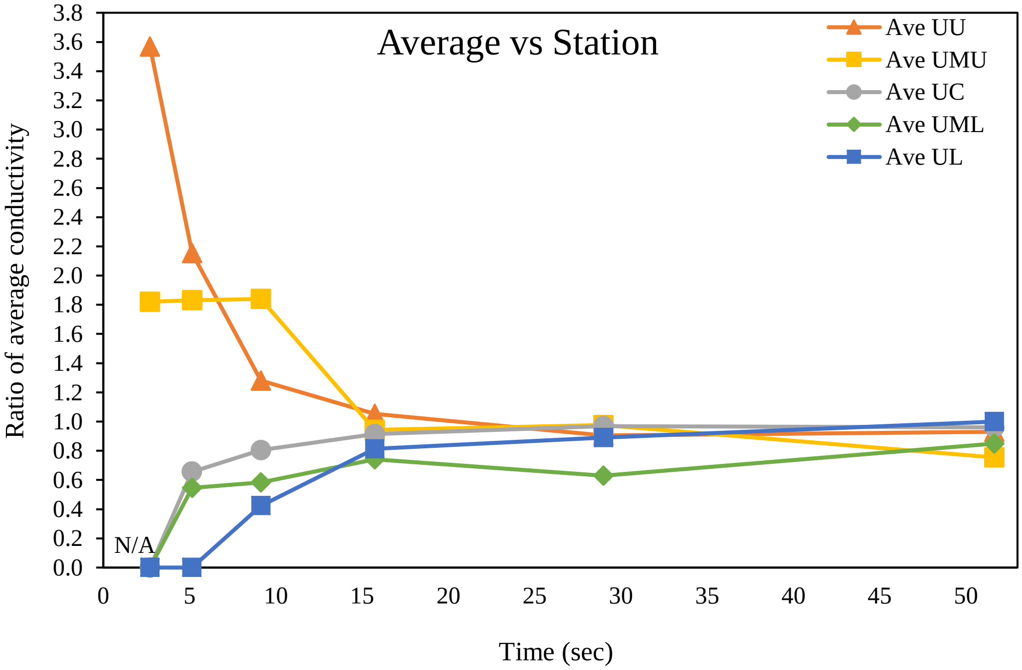

Figure 4-3. Average vs Station for upper wall injection, Q=150 L/min, v=1.0 fps

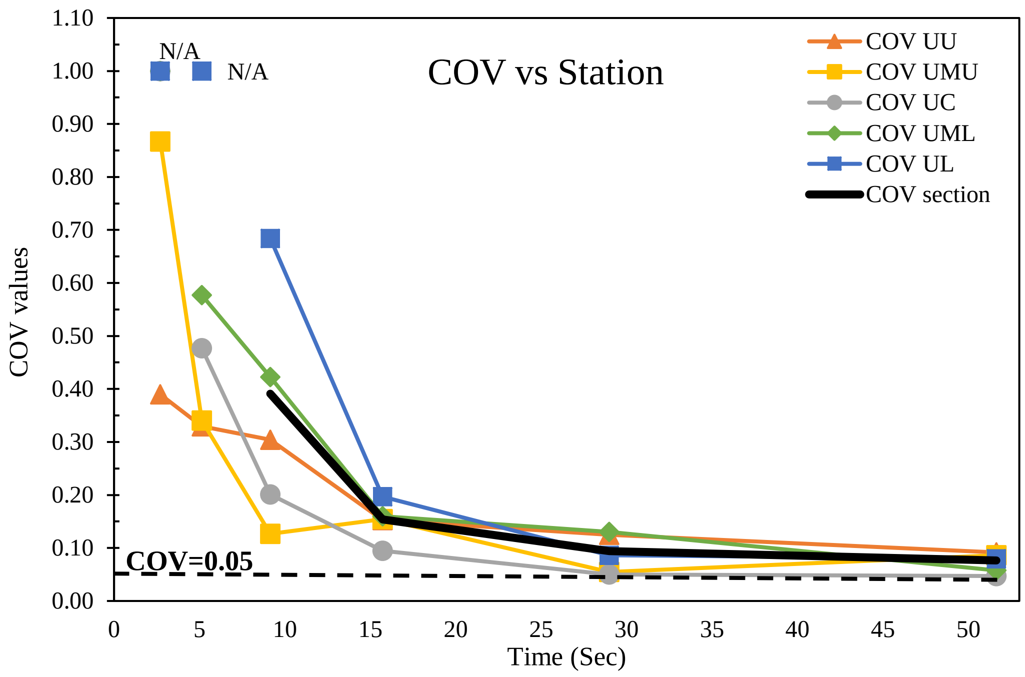

Figure 4-4. COV values for upper wall injection, Q=150 L/min, v=1.0 fps

Considering the results presented in Figure 4-4, it can also be seen that producing a homogeneous mixture requires higher flow velocity, if the injection and sampling are at the upper-wall, than the situation where injection is at upper-wall and samples are collected from the bottom of the pipe. The results in Figure 4-4 shows that in all conditions but one condition, (UC), all stations have COVs higher than 0.05 and the UC condition reaches complete mixing. However, the COV of the section shows that mixing is not complete under upper wall injection for 1.0 fps flow velocity.

The procedure for 2.0 fps was the same as 1.0 fps, however, increase in the flow velocity was causing more turbulence in the pipeline. The flow range of the mainstream varied between 297.5-306.0 L/min in all steps. The saltwater was being injected with the flow rate of 13.97 mL/min to the pipe. The results are presented in Figure 4-5 and Figure 4-6.

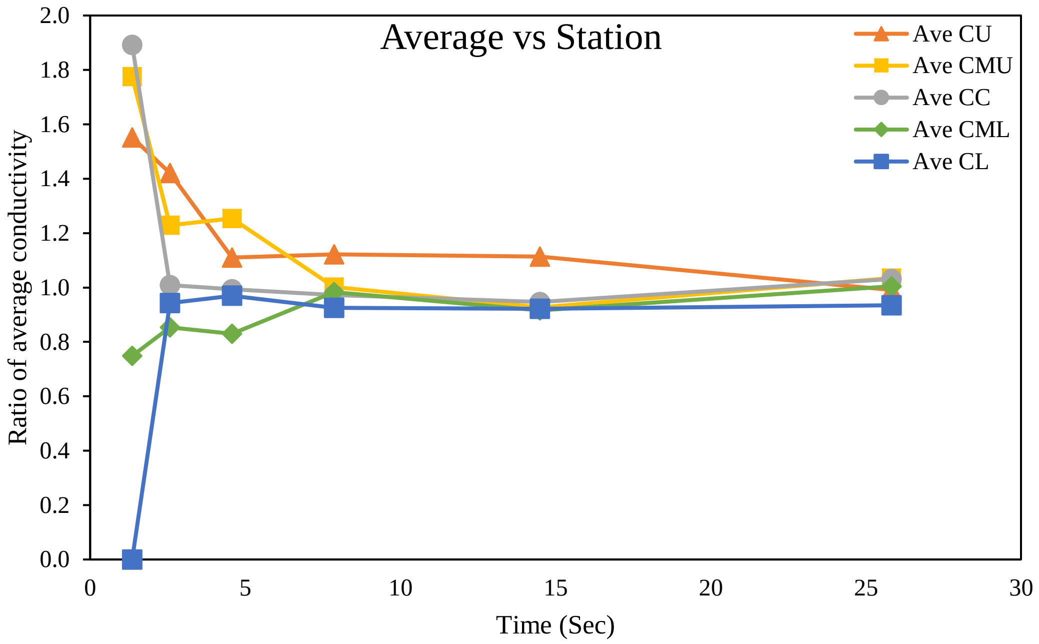

Figure 4-5. Average vs Station for centerline injection, Q=300 L/min, v=2.0 fps

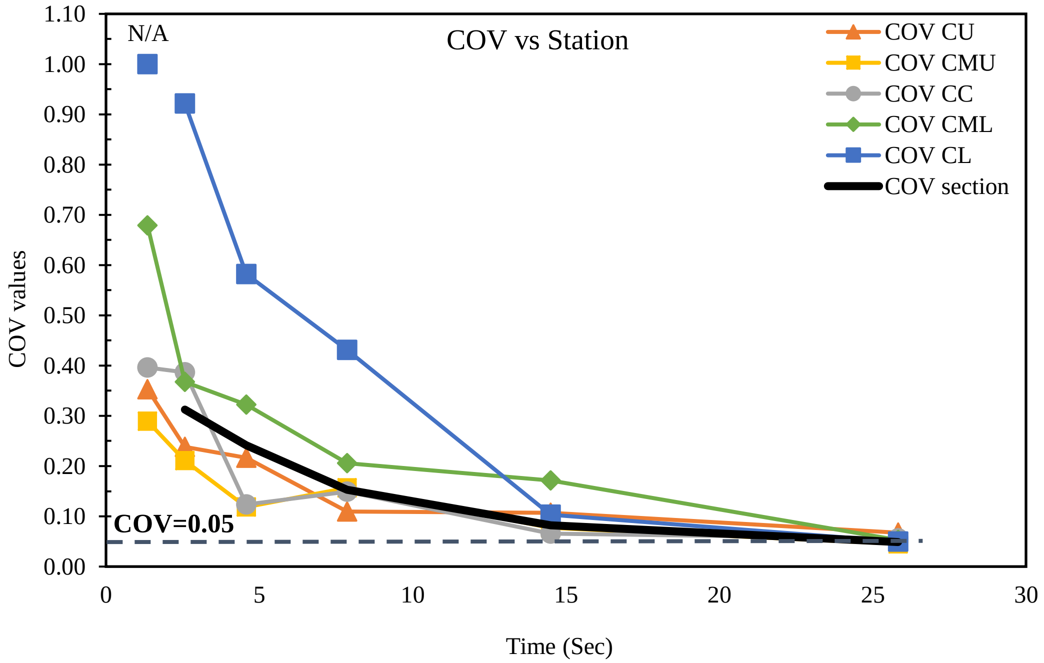

Figure 4-6. COV values for centerline injection, Q=300 L/min, v=2.0 fps

By comparing the results from Figure 4-2 and Figure 4-6 it can be seen that higher turbulence, reduces the required time to its half in order to get almost the same COV values. With increase in velocity, all points get close to 0.05 at the 6th station and only one condition (CU) results in COV equal to 0.067.

The results for injection at upper-wall of the pipe for flow rate equal to 300 mL/min and 2.0 fps flow velocity are shown in Figure 4-7 and Figure 4-8.

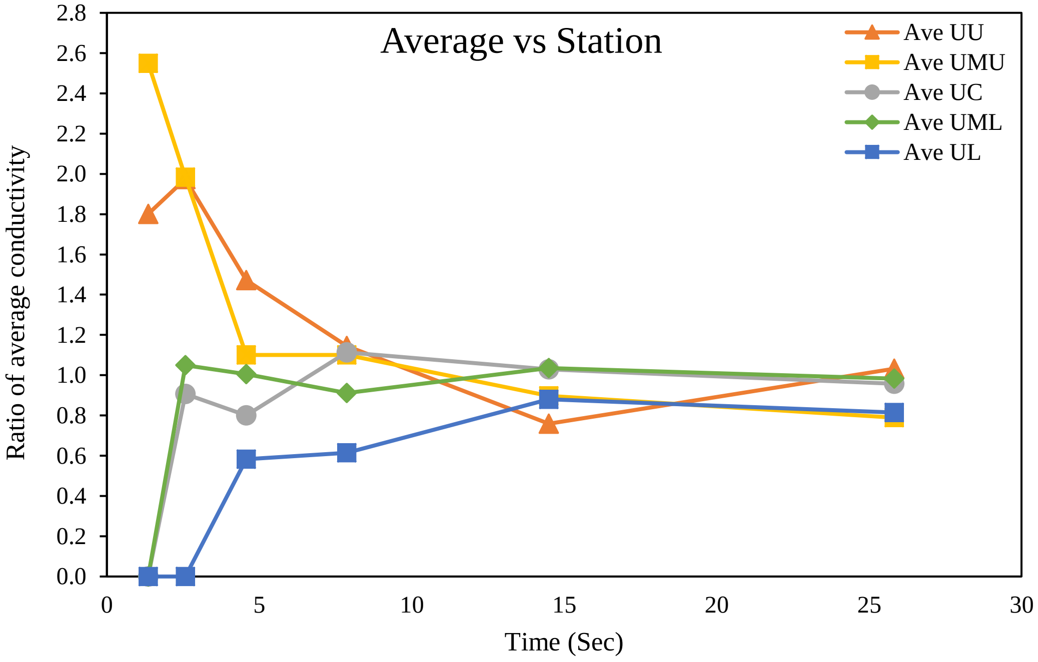

Figure 4-7. Average vs Station for upper wall injection, Q=300 L/min, v=2.0 fps

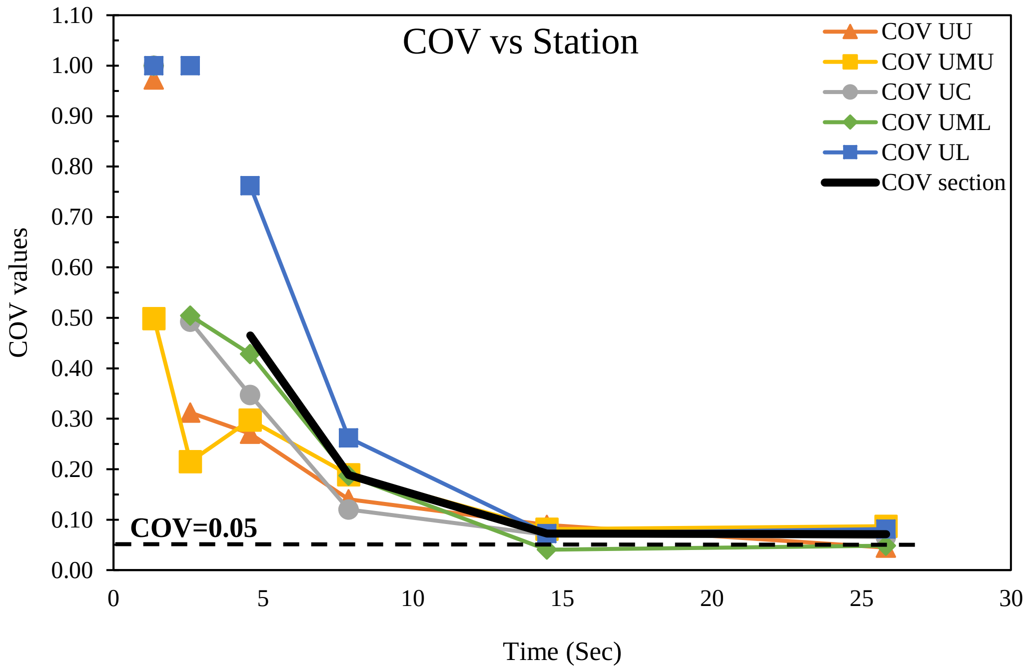

Figure 4-8. COV values for upper wall injection, Q=300 L/min, v=2.0 fps

As shown in Figure 4-8, there is no salt right after the salt injection when samples are collected from lower wall. Also, there is no mixing when samples were collected from upper wall. By passing through the pipeline, mixing condition boosts when the secondary flow spends more time in the pipeline, and it is observed that COVs continue to reduce. Although, the section COV line is higher than the 5% line, this station shows a great improvement compared to other stations.

To evaluate effect of turbulence on the required time for the salt to be mixed with water, the velocity was increased to 4.0 fps and the same experiments were conducted. The results are presented in Figure 4-9 and Figure 4-10. The flow range of the mainstream changed between 598-606 L/min in all steps. The saltwater was being injected with the flow rate of 27.93 mL/min to the pipe.

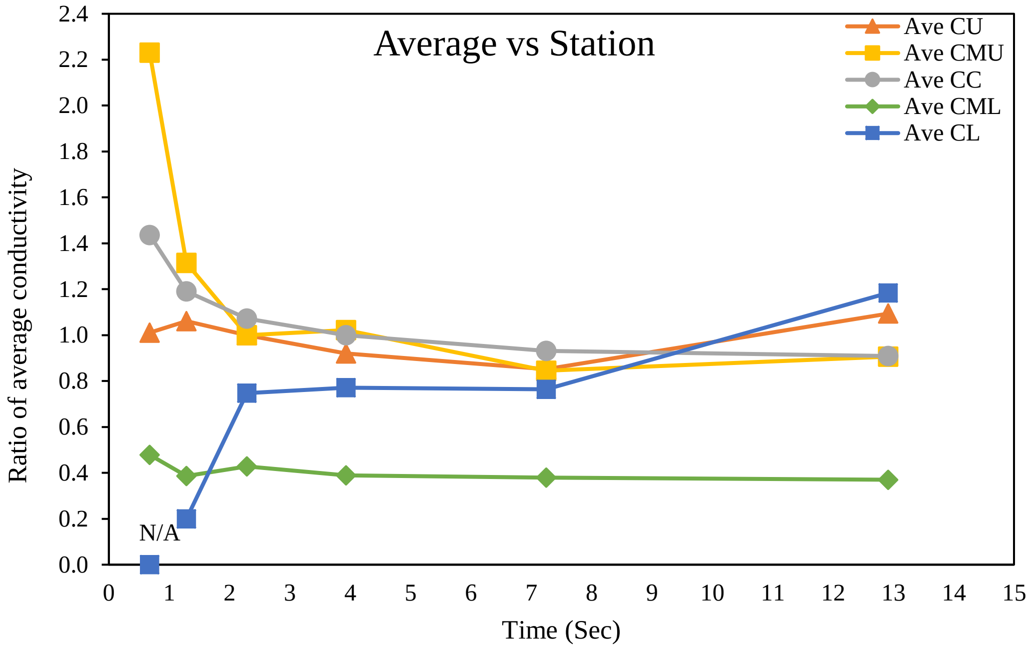

Figure 4-9. Average vs Station for centerline injection, Q=600 L/min, v=4.0 fps

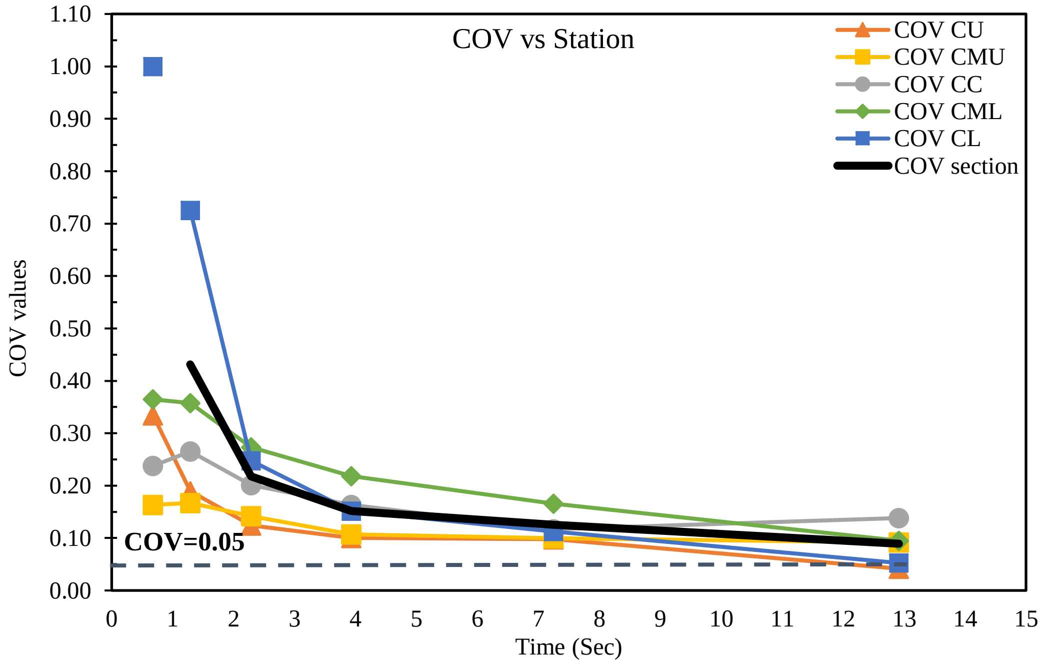

Figure 4-10. COV values for centerline injection, Q=600 L/min, v=4.0 fps

More uniform flow and uniform results are observed in Figure 4-9 and Figure 4-10, as the velocity is increased to 4.0 fps. The whole graph in Figure 4-10 is shifting downward and the COVs are getting closer to zero.

The results for upper wall injections at 4.0 fps are shown in Figure 4-11 and Figure 4-12.

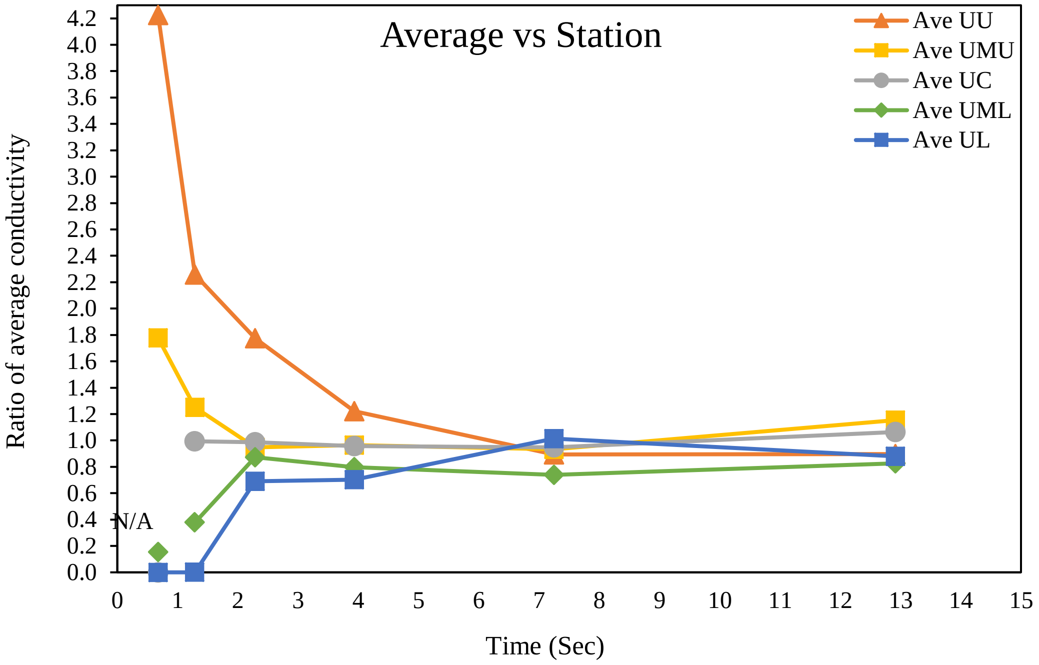

Figure 4-11. Average vs Station for upper wall injection, Q=600 L/min, v=4.0 fps

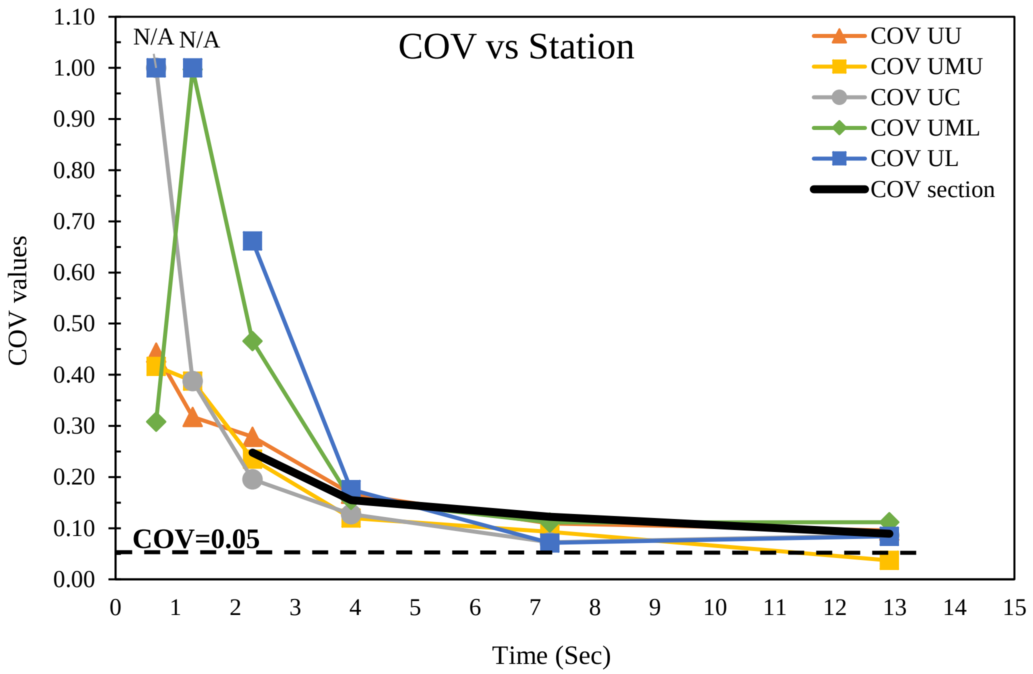

Figure 4-12. COV values for upper wall injection, Q=600 L/min, v=4.0 fps

It is shown in Figure 4-11 and Figure 4-12 that the number of samples with no salt at the upstream of the pipeline decreases, but there are still a few samples with no salt in them. After 13 seconds which is when samples were collected at the 6th station, mixing is not improved compared to previous experiments and more fluctuation in the COV values is seen. This may be because of the increase in the flowrate. Higher velocity must be examined to understand whether the increase in turbulence is causing the fluctuations or not.

For the last set of experiments for tracer study, the velocity of mainstream increased to 8.0 fps. The results for centerline injection are presented in Figure 4-13 and Figure 4-14. As explained in methodology, the sampling points have reduced to 5 locations for centerline injection and station 4 was removed. For upper wall injection sampling stations were reduced to 4 locations, and stations 3 and 4 were removed for the 8.0 fps velocity. The flow of the mainstream varied between 1200-

1212 L/min in all steps. The saltwater was being injected with the flow rate of 55.9 mL/min to the pipe.

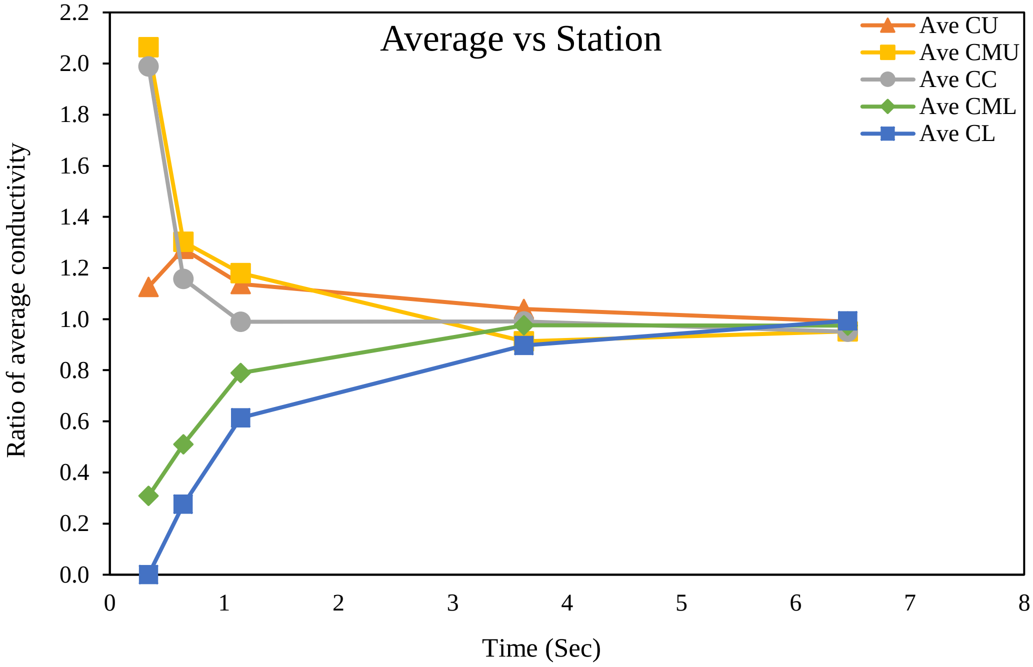

Figure 4-13. Average vs Station for centerline injection, Q=1200 L/min, v=8.0 fps

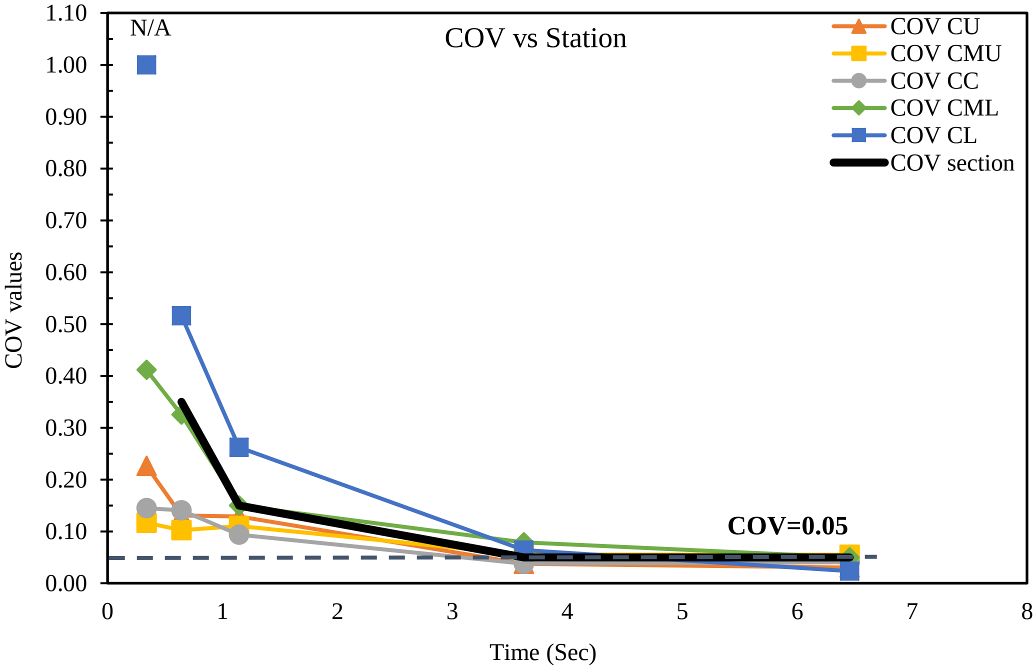

Figure 4-14. COV values for centerline injection, Q=1200 L/min, v=8.0 fps

It can be seen in Figure 4-13 that the trend of average values is convergence and all points are reaching 1.0 which was the target value. Moreover, at the 6th station in Figure 4-1, for 1.0 fps velocity, the standard deviation of the average values was equal to 0.06 and is decreased to 0.021 for 8.0 fps velocity. This shows that there is less fluctuation in the target average with increase in turbulence and shows a more uniform mixture. At 8.0 fps, the average values are not scattered even at 28 ft from the injection point which is within 3.7 seconds after salt injection. It is presented in Figure 4-14 that at the 6th station which is 3.7 seconds after the injection, all the COVs are close to 0.05 and not more than 0.055.

The results for upper wall injection for 8.0 fps are presented in Figure 4-15 and Figure 4-16.

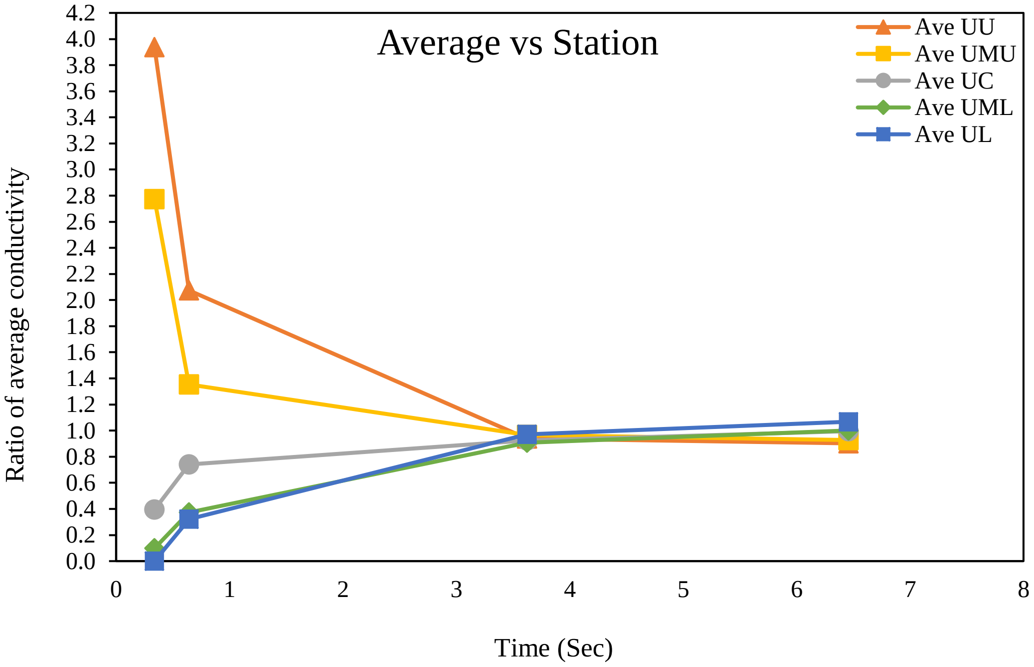

Figure 4-15. Average vs Station for upper wall injection, Q=1200 L/min, v=8.0 fps

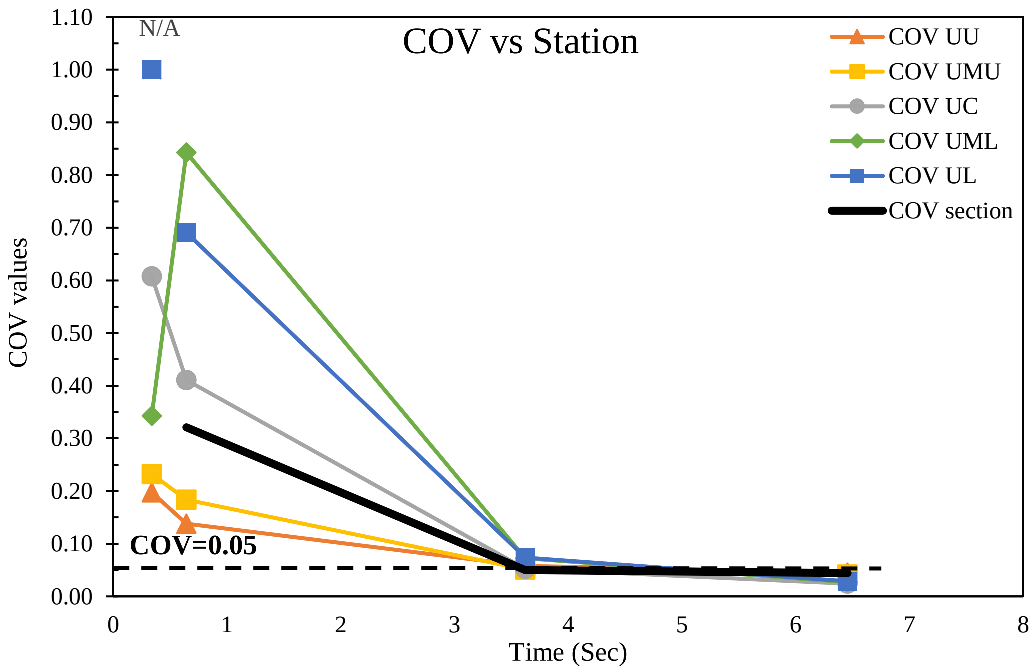

Figure 4-16. COV values for upper wall injection, Q=1200 L/min, v=8.0 fps

It can be seen in Figure 4-16, that when velocity increases, less time is required to obtain complete mixing. Considering the section COV line, complete mixing is achieved after 3.7 second after the injection. However, for retention time less than 3.7, the COV values are higher than the centerline injection.

4.1.1.1 The effect of velocity on mixing distance

The conductivity values at each station of the pipeline, in the cross section of the pipe were recorded and COV values of the 250 samples for each section of the pipe were calculated and are referred to as section values and are presented in Figure 4-17.

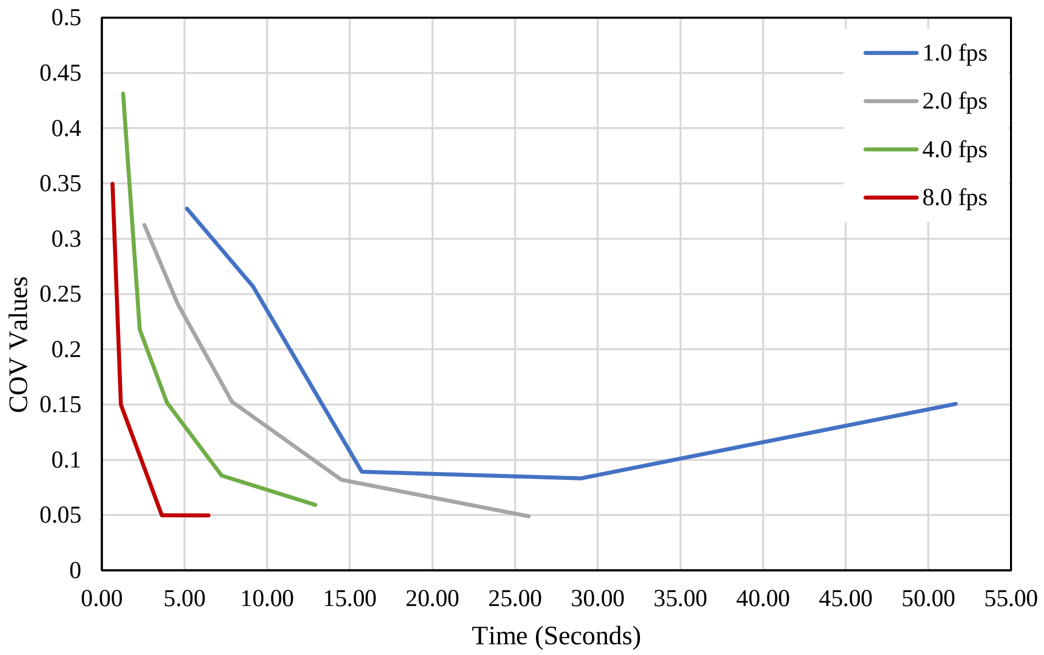

Figure 4-17. COV values at each station at different flow velocities in the pipeline vs time

The effect of increase in flow velocity on mixing measurement is shown in Figure 4-17. It is demonstrated that for centerline injection at 1.0 fps flow velocity, the required retention time to get to COVs less than 10%, was 29 seconds and it decreased to 25.8 seconds and 12.9 seconds for 2 fps and 4 fps, respectively. Finally, the least amount of time which was 3.63 seconds to achieve complete mixing (COV<0.05) was gained by increasing the velocity to 8 fps, which provides fastest initial mixing that is required for the chemicals to be mixed with each other.

Additionally, comparing Figure 4-14 and Figure 4-16, it can be seen that COV values after 6th station for both upper wall and centerline injection condition were less than 5%, meaning that complete mixing was achieved within 3.63 seconds, which was after the last station in both cases. However, under centerline injections conductivity fluctuations decreased within a shorter amount of time, as a result of growth in flow velocity and it is observed in standard deviation of target average from Figure 4-15 that there is more fluctuation in target conductivity compared to centerline injection at 6.5 seconds after the injection. Overall, the time for average values to get to 1.0 was shorter for centerline injections. Furthermore, as mentioned before, it is hypothesized that to get high monochloramine recovery, mixing is required instantly as the chemicals are injected into the pipeline, which was not achieved under upper wall injection. It is possible that when injection is at upper wall, poor mixing at the earlier stations leads to low monochloramine recoveries and higher decays. Therefore, centerline injection was chosen for the chloramination process.

For 8.0 fps flow velocity, under centerline injection condition, all the COV values were less than 0.05 which represents adequate mixing. Therefore, for chloramination process samples were taken even further down in the pipeline, to assure that complete mixing was achieved.

For these experiments, there were two factors that could affect mixing condition in the pipeline. One was increase in the fluid turbulence by increasing the flow velocity and the second one was retention of the secondary flow in the turbulent field. It was expected for the COV values to decrease as the distance from the injection point increased. The overall trend matches the expectation, but not for all the injection points in the cross section of the pipe. Increase is turbulence led to better mixing and complete mixing was achieved as the two criteria were met at the same time.

It was stated by (Lee and Brodkey, 1964; Shih, 2013) that the velocity profile for a cross sectional area in a pipeline for turbulent flow is axisymmetric around the center line of the pipe. According to the average conductivity values from tracer study as presented in Figure 4-1 to Figure 4-16, the mixing condition and velocity profile are not symmetrical in relevance to the horizontal line along the pipe. In the increased velocity, the concentration distribution was nearly symmetrical about the horizontal diameter only in the last station.

4.1.2 Pipeline with Bends

Tracer salt injections on bends was done for two points and samples were collected from 4.0 ft and 25 ft distance ft after the injection points. All 4 flow velocities were examined and the results are presented as follows:

Results for injection with three bends in the path of water presented in Table 4-2 and Table 4-3.

Table 4-2. Average values for NaCl injection on point A with three 90-degree bends after injection point

1st Injection	ft from injection	Ave CU	Ave CMU	Ave CC	Ave CML	Ave CL
		Q = 150 L/min				
Stat 3	7.50	0.5724	0.8604	0.7498	0.9439	0.7559
Stat 5	27.50	0.2852	0.9617	1.1800	1.3275	1.1870
		Q = 300 L/min				
Stat 3	7.50	0.9549	0.9962	1.1759	0.9155	1.2366
Stat 5	27.50	0.9219	1.0436	0.7664	0.9983	0.3291
		Q = 600 L/min				
Stat 3	7.50	0.9138	1.0429	0.9480	1.0259	0.9328
Stat 5	27.50	0.7604	0.7056	0.7431	0.7800	0.7695
		Q = 1200 L/min				
Stat 3	7.50	0.9888	0.9445	0.9101	0.8511	0.8717
Stat 5	27.50	0.8529	0.7405	0.8893	0.8442	0.8747

Table 4-3. COV values for NaCl injection on point A with three 90-degree bends after injection point

1st Injection	ft from injection	COV CU	COV CMU	COV CC	COV CML	COV CL
		Q = 150 L/min				
Stat 3	7.50	0.2329	0.1901	0.1239	0.0897	0.1176
Stat 5	27.50	0.2630	0.1160	0.0565	0.0613	0.0644
		Q = 300 L/min				
Stat 3	7.50	0.1308	0.0927	0.0879	0.2788	0.1985
Stat 5	27.50	0.1056	0.0824	0.0587	0.0622	0.0540
		Q = 600 L/min				
Stat 3	7.50	0.1	0.0536	0.0502	0.0472	0.0667
Stat 5	27.50	0.0417	0.0479	0.0437	0.0424	0.0550
		Q = 1200 L/min				
Stat 3	7.50	0.01863	0.01996	0.03907	0.04712	0.05353
Stat 5	27.50	0.03871	0.04973	0.03312	0.07822	0.12553

Comparing the results from COV values in Table 4-3 and COVs from centerline injection into the straight pipeline presented earlier, it can be seen that injection at point A with three 90-degree bends after injection point, resulted in better mixing and in the 5th station with higher flow velocity, COV values less than 0.05 were gained. At station 3, although the COVs do not show complete mixing, it is observed that the values enhance compared to the straight pipeline.

Results for point B with one 90-degree bends after injection point are given in Table 4-4 and Table 4-5.

Table 4-4. Average values for NaCl injection on point B with one 90-degree bend after injection

1st Injection	ft from injection	Ave CU	Ave CMU	Ave CC	Ave CML	Ave CL
		Q = 150 L/min				
Stat 3	4.60	0.6839	1.1964	0.9642	1.0319	0.8823
Stat 5	24.60	1.0930	1.1089	1.2492	1.2786	1.3007
		Q = 300 L/min				
Stat 3	4.60	0.7018	0.8392	0.9861	0.8400	1.0727
Stat 5	24.60	1.0848	1.1386	0.8359	1.0189	0.9657
		Q = 600 L/min				
Stat 3	4.60	0.8879	0.9214	0.9147	0.7924	0.7890
Stat 5	24.60	0.9705	0.9345	0.8993	0.8885	0.9360
		Q = 1200 L/min				
Stat 3	4.60	0.8475	0.8938	0.8069	0.8035	0.8732
Stat 5	24.60	0.9619	0.9660	0.8423	0.8577	0.8169

Table 4-5. COV values for NaCl injection on point B with one 90-degree bend after injection

1st Injection	ft from injection	COV CU	COV CMU	COV CC	COV CML	COV CL
		Q = 150 L/min				
Stat 3	4.60	0.1835	0.1413	0.1254	0.1286	0.3363
Stat 5	24.60	0.0622	0.0415	0.0510	0.0860	0.0505
		Q = 300 L/min				
Stat 3	4.60	0.3258	0.2476	0.1025	0.1703	0.1076
Stat 5	24.60	0.0760	0.0616	0.0775	0.0768	0.0768
		Q = 600 L/min				
Stat 3	4.60	0.0569	0.1005	0.0516	0.0801	0.0671
Stat 5	24.60	0.0497	0.0512	0.0419	0.0378	0.0451
		Q = 1200 L/min				
Stat 3	4.60	0.0674	0.0700	0.0563	0.0874	0.0546
Stat 5	24.60	0.0298	0.0499	0.0431	0.0711	0.0698

The results in Table 4-4 and Table 4-5 show that by addition of one 90-degree bend to the pipeline, mixing condition improved to a great extent. Comparison between the values in Table 4-3 and Table 4-5 for injection with three 90-degree bends after injection point and point B with one 90-

degree bends after injection point, showed almost same results and sometimes even better mixing with one 90-degree bend.

To have a better comparison, the COV values of the whole section at station 3 and station 5 for straight pipeline versus addition of one bend to the path of water, are compared in Figure 4-18.

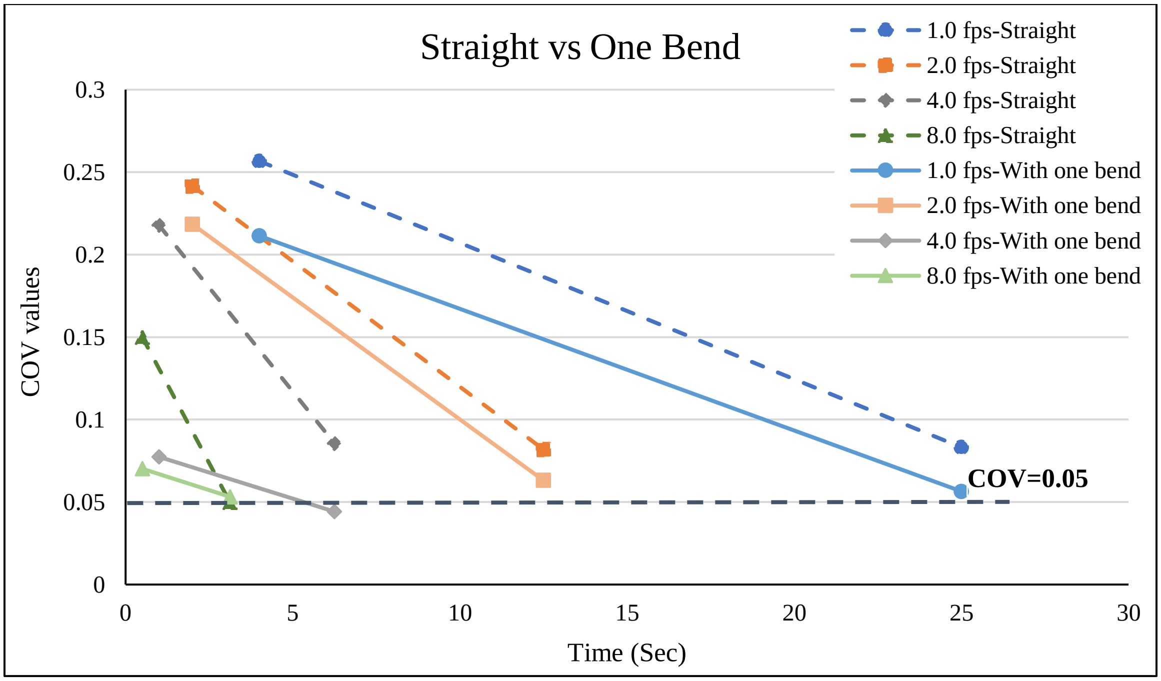

Figure 4-18. Section COV values for injection into straight pipeline vs pipe with bends

It is observed in Figure 4-18 that when there is one bend in the path of water for 1.0 fps which is the lowest velocity, there is a slight improvement in the COV values at the same time period. The same result is observed for 2.0 fps. Addition of one bend slightly improves COV values compared to straight pipeline. When the velocity of water increases to 4.0 fps, it takes 6 seconds to achieve complete mixing with one bend in the path of water compared to straight pipeline in which complete mixing was not gained with 4.0 fps at all. In Figure 4-18, the first point is representative of the 3rd station and the second point is located at the 5th station. With addition of bends to the pipeline, to get to a complete mixing, there was no need to have the last station, because complete mixing was gained at the 5th station. For 8.0 fps, there was a considerable improvement in mixing by adding bends. It is observed that COV value is 0.15 for straight pipeline at 0.5 seconds while with addition of one bend, it is reduced to 0.06.

In Figure 4-19, injection with three 90-degree bends after injection point and injection into straight pipeline is shown.

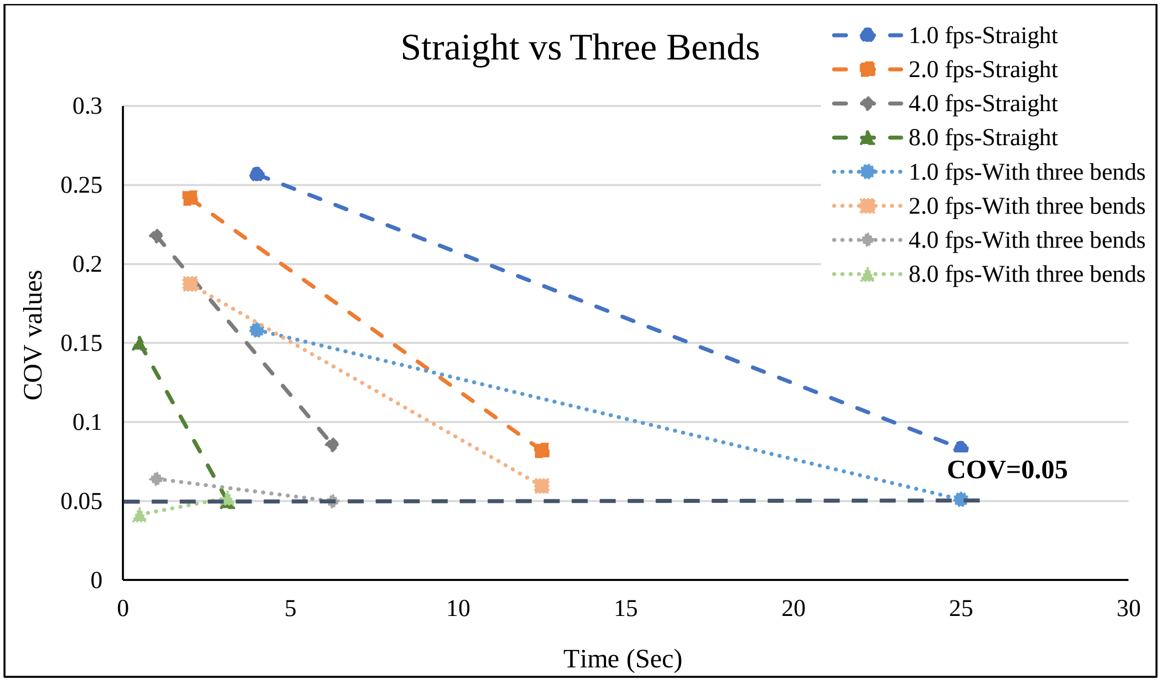

Figure 4-19. Section COV for injections into straight pipeline and pipe with three bends

It can be seen from Figure 4-19 that having 3 bends in the pathway of water reduces COV values and improves mixing to a noticeable amount. With increasing the velocity to 8.0 fps, the time to get complete mixing in the pipeline was reduced from 3.63 seconds to 0.5 seconds with addition of three 90-degree bend to the pipeline. The COVs for injection at point A which had three 90-degree bends after injection point, have the lowest values and injection into the straight pipeline has the highest COVs.

In Figure 4-18 and Figure 4-19 it is observed that section COVs for straight pipeline is more than section COVs for injection at point B with one bend after injection and point A with three bends after injection. It is seen that with injection at points A and B, COV decreases with increasing the retention time of the secondary flow in turbulence filed, which is in accordance with the expectations.

In the next graph addition of one bend to the path of water is compared with addition of three bends to the path of eater.

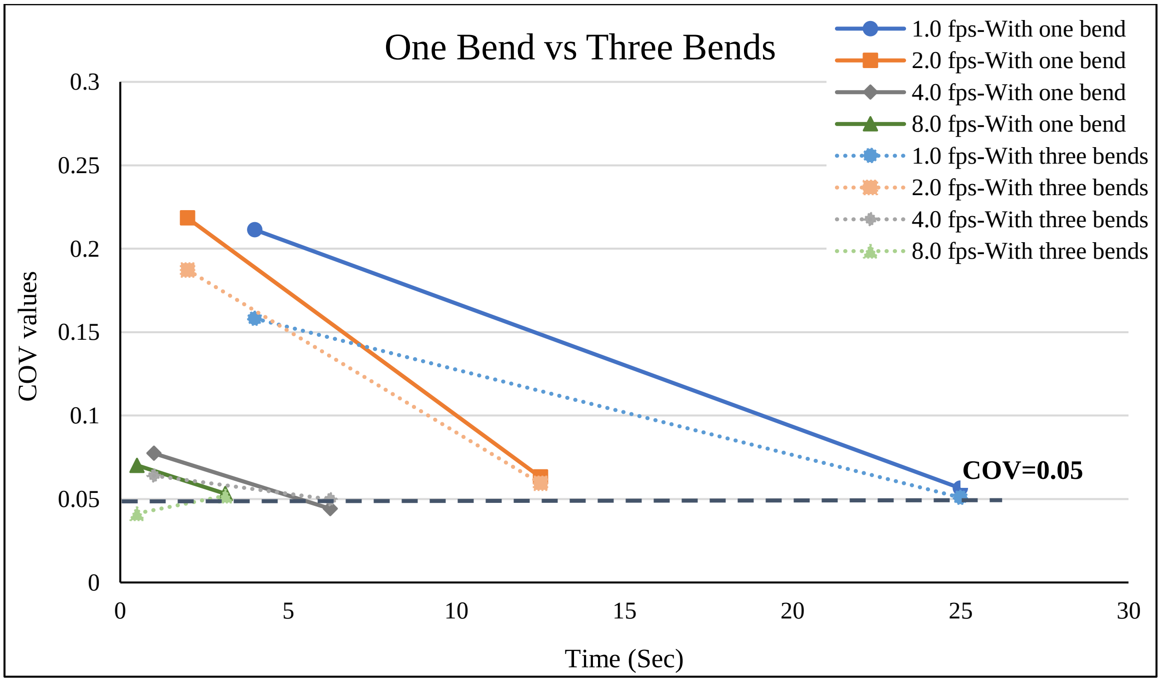

Figure 4-20. Section COV for injection into pipeline with one bend vs pipeline with three bends in the path of water

It was observed in Figure 4-20 that the COV values and the time to reach them were almost the same, however in all cases COVs for three bends in the path of water are less than COVs for one-bend condition in both stations. When the flow velocity was increased to 8.0 fps, complete mixing was achieved within 0.5 seconds with three bends in the path of water which was the shortest time to reach complete mixing in tracer salt study.

Overall, it can be concluded that addition of three 90-degree bends to the pipeline, led to improvement in degree of mixing compared to straight pipeline and compared to the injection location with one 90-degree bend. Also it was understood that addition of one bend leads to a complete and faster mixing in the pipeline compared to the straight pipeline and it can be advised that for the purpose of physical mixing, addition of even one 90-degree bends would suffice and create better homogeneity compared to straight pipeline.

4.2 Water Chloramination

Chloramination studies were conducted to investigate effect of mixing condition on MCl formation and recovery. In these experiments, results from previous steps were used for sampling procedure. Ammonia and chlorine residuals were monitored throughout the study and all the results and discussions are included in this section.

4.2.1 Straight Pipeline

As mentioned in chapter 2. the information from tracer salt experiments were used for sampling point for monochloramine recovery measurements which was chosen to be at the 76 ft. distance from the injection point. This length is more than the mixing distance achieved in the tracer study of the current experiment, therefore, any point in the cross section of the pipe is representative of the average concentration and it is enough to make only one measurement across the pipe. The goal of this study was to assess impact of mixing on monochloramine formation, therefore, colleting a sample from a point closer to injection location, where complete mixing was not achieved could not provide any helpful information. It is worth to mention that chlorine was injected first and then ammonia was injected into the pipeline.

Tables containing TCl, MCl, DCl and NH_3-N for each experiment including OSGH and HSH and before-bend and on-bend conditions are provided in Appendix C.

The results for water chloramination with OSGH in the straight pipeline are presented in Figure 4-21. The measured chlorine residuals for well mixed condition are also shown in Figure 4-21.

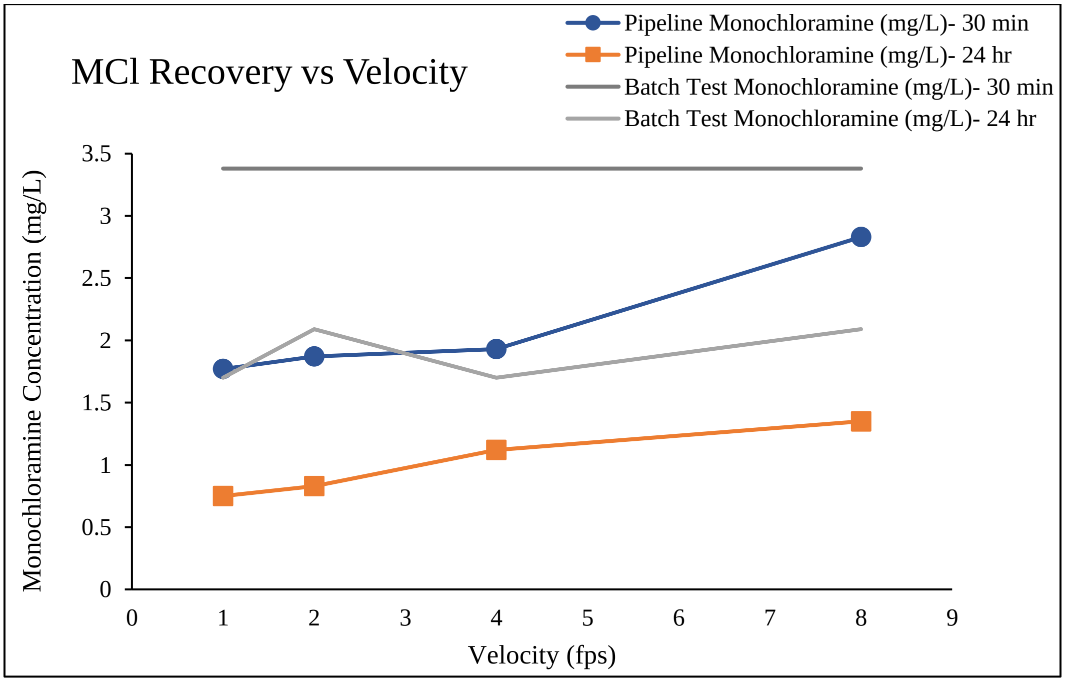

Figure 4-21. MCl recovery for OSGH injection into the straight pipeline

It was expected from the tracer salt study that increase in the velocity of the mainstream, reduce the mixing time and lead to faster formation of monochloramine and eventually produce higher MCl and lower MCl decay. It can be seen in Figure 4-21 that monochloramine concentration is highest when water flow velocity increases to 8.0 fps and the shortest time is required to get to low COV values, which is in accordance with the expectations. The monochloramine recovery is the best for both 30 minutes and 24 hours from well mixed condition in the batch test. The only difference between these experiments was mixing condition. As a result, it could be concluded that better mixing of the chemicals in the batch test was the reason for higher MCl formation and recovery. It was observed that monochloramine formation was quick under well mixed condition and the results after 30 minutes were as good as the instant measurements as presented in Table 4-6. However, in the pipeline, although the monochloramine formation was quick, monochloramine recoveries were lower than the well mixed condition. To evaluate effect of inline chemical addition and its impact on mixing, other factors affecting MCl recovery such as pH and Cl_2 to N ratio, were kept at the values suggested by EPA, throughout the experiment (EPA, 2001).

Table 4-6. Chlorine and ammonia residual for batch test

Wait time	TCl (mg/L as Cl_2)	MCl (mg/L as Cl_2)	NH_3-N (mg/L)
2.0 minutes	3.8	3.33	0.01
30 minutes	3.7	3.27	0.10

In the next step the HSH and LAS solutions were injected in a straight pipeline, and the results are presented in Figure 4-22.

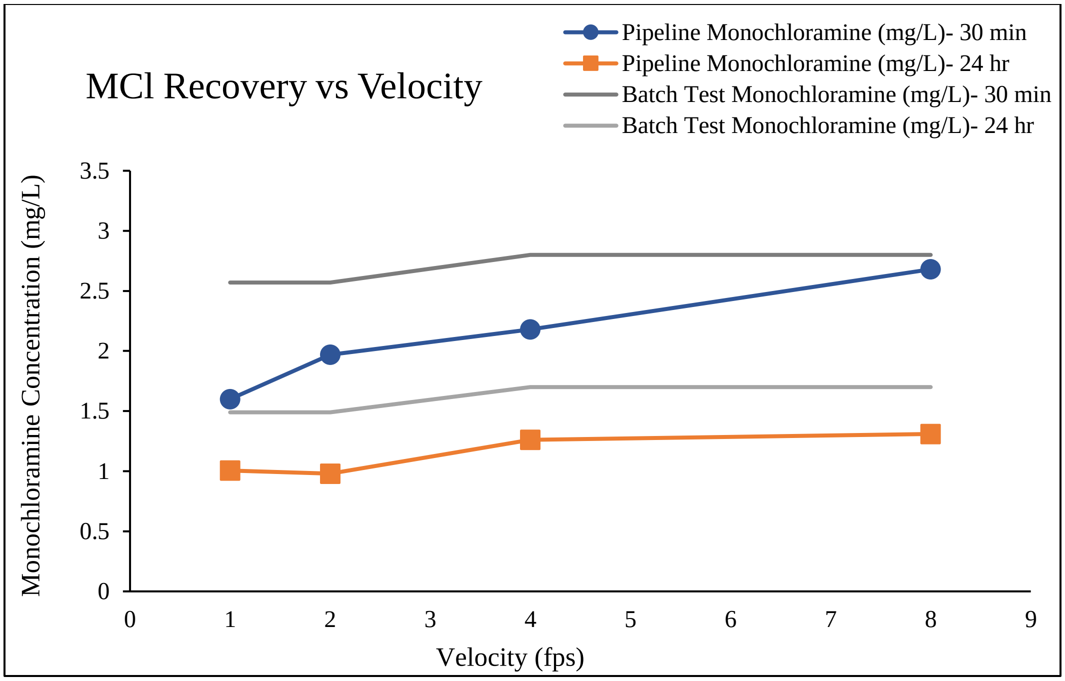

Figure 4-22. MCl recovery for HSH injection to the straight pipeline

As can be seen in Figure 4-22, MCl recovery grows with increase in turbulence that shows impact of better mixing on MCl values. Comparing the results from Figure 4-21 and Figure 4-22 with 8.0 fps, the MCl recovery is closer to the well mixed condition for HSH. The target chlorine for batch test is 4.0 mg/L as cl_2 and if the MCl recovery for batch test is equal to 3.4-3.5 it is considered a good recovery as observed in Figure 4-21. However, in Figure 4-22 the recovery for batch test is between 2.6-2.8 which is lower than the expectations. In all steps of the experiments lower recovery was attained with HSH solution. One explanation could be that with higher concentration of stock solution, more time was required for the chlorine and ammonia to be stabilized and form MCl.

Considering the trend of COV for tracer salt experiments, it was observed that COV decreased with increase in turbulence in the pipeline and it was mentioned in previous sections that lower values of COV (<0.05) are an indication of complete mixing. If the assumption that proper and faster mixing affects MCl recovery is correct, then better MCl recovery must be achieved with increase in flow velocity in each step. A relation between COV and MCl values are shown in Figure 4-23.

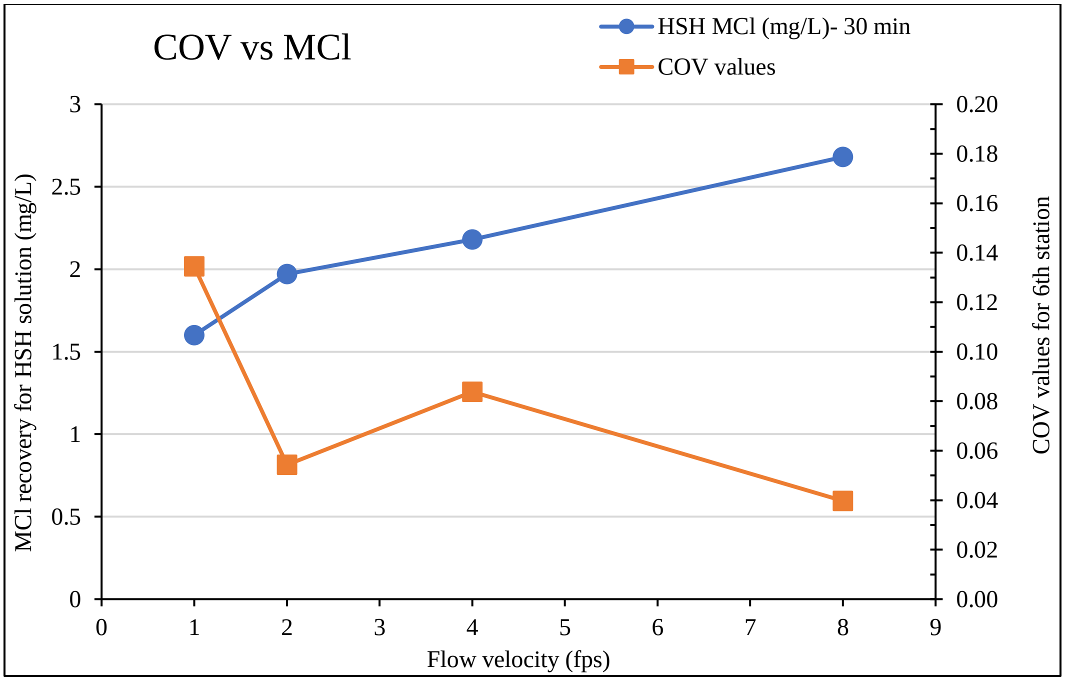

Figure 4-23. MCl recovery vs COV values with increase in flow velocity

It was expected to observe improvements in MCl recovery with growth in the flow velocity because as it was explained before, increase in flow velocity leads to decrease in mixing time and provides complete mixing within a shorter time frame. It is demonstrated in Figure 4-23 that with increase in flow velocity, as COV decreases, MCl recovery improves. Therefore, it can be concluded that the MCl recovery is affected by poor mixing in a straight pipeline.

4.2.2 Pipeline with Bends

In the next step, injection points were kept the same and a straight section of the pipe after injection points were replaced with bends and the process of chemical injection were repeated with both OSGH and HSH solutions.

The results for injection of OSGH and LAS into the pipe are presented in Figure 4-24. This condition is referred to as “Before-Bend” condition.

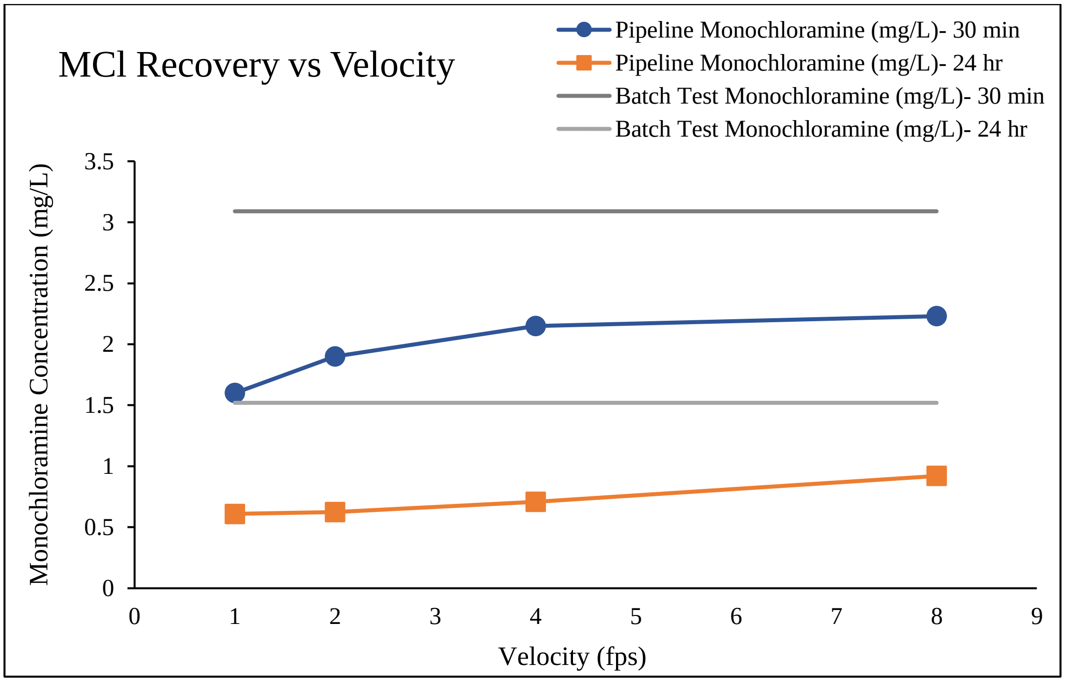

Figure 4-24. MCl recovery for OSGH injection into the pipeline for before-bend condition

It can be seen in Figure 4-24 that MCl recovery after 30 minutes increases when velocity increases form 1.0 fps to 2.0 fps, but after that increase in the flow velocity, has no impact on MCl recovery. Moreover, the effect of flow velocity on the decay of MCl was not considerable.

The results for injection of HSH and LAS into the pipe before-bend are presented in Figure 4-25.

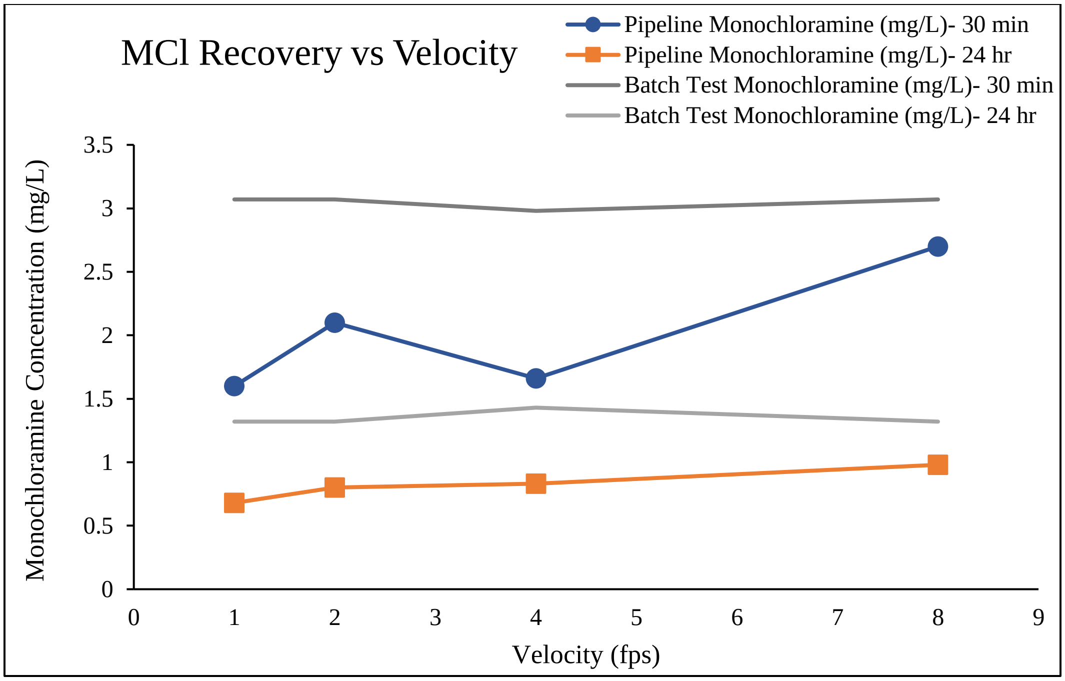

Figure 4-25. MCl recovery for HSH injection into the pipeline for before-bend condition

It can be seen in Figure 4-25 that the trend of MCl recovery is the same as straight pipeline for 30 minutes, but the MCl decay does not change with increase in flow velocity. It is observed that the decay of MCl for OSGH and HSH are almost the same for before bend condition. A possible explanation for lower MCl recoveries for before-bend injection condition compared to straight pipeline could be the short distance between the injection points and the bends. In this case, chlorine is injected first and after 2.5 ft ammonia is injected, and when the chemicals are injected the flow passes through bends after 2 ft. In 90-degree bends, plumes move together but in different layers and do not break as they pass the pipe curves. If the chemicals are not mixed with each other before reaching the bends, layers of water containing uneven chlorine to ammonia ratios would be formed. Since bends do not break water layers, their effect on water flow would be pushing the unevenly produced layers toward the downstream of the pipeline. therefore, if there is an imbalance between concentrations of chlorine and ammonia, they will get exaggerated by bends rather than being improved.

In the next step, the chemicals were injected on-bend and the results are provided in Figure 4-26 and Figure 4-27 for OSGH and HSH solution, respectively.

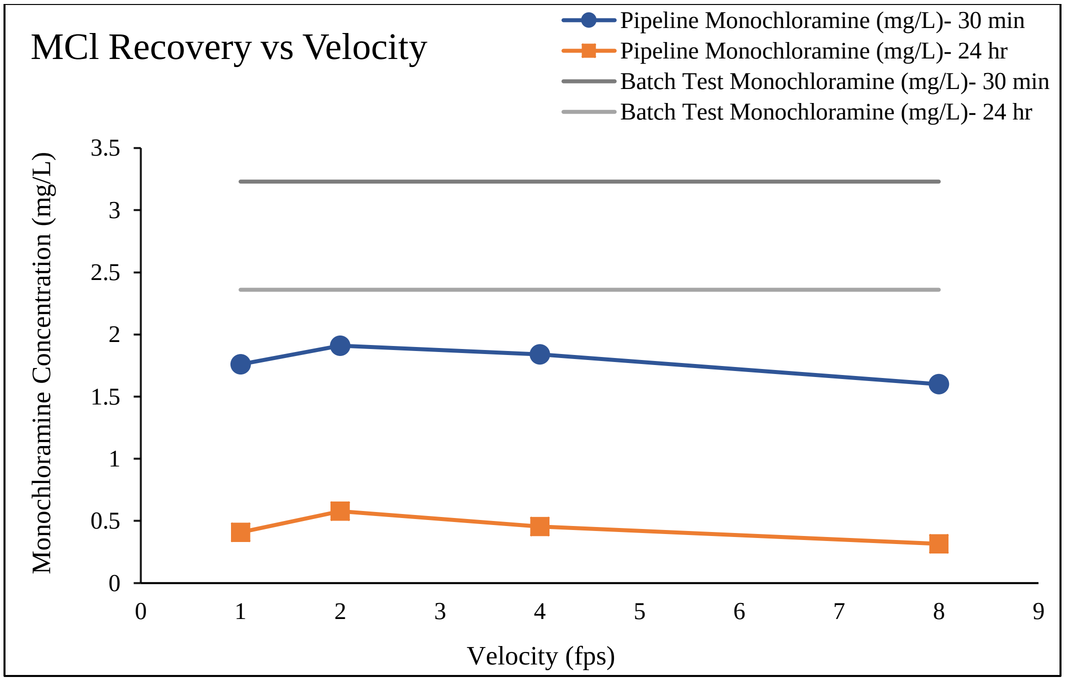

Figure 4-26. MCl recovery for OSGH injection into the pipeline for on-bend condition

In Figure 4-26 it is shown that for on-bend injection, MCl recovery increases from 1.0 fps to 2.0 fps and after that the recovery diminishes with growth in water flow rate. However, regarding the experiment error mentioned in chapter 3, it is likely that the MCl changes fall within the experimental errors.

It was expected to observe an increase in MCl recovery, with increase in the flow velocity because of faster mixing that is provided by increasing the turbulence, but for the on-bend injection condition for OSGH results did not match the expectations.

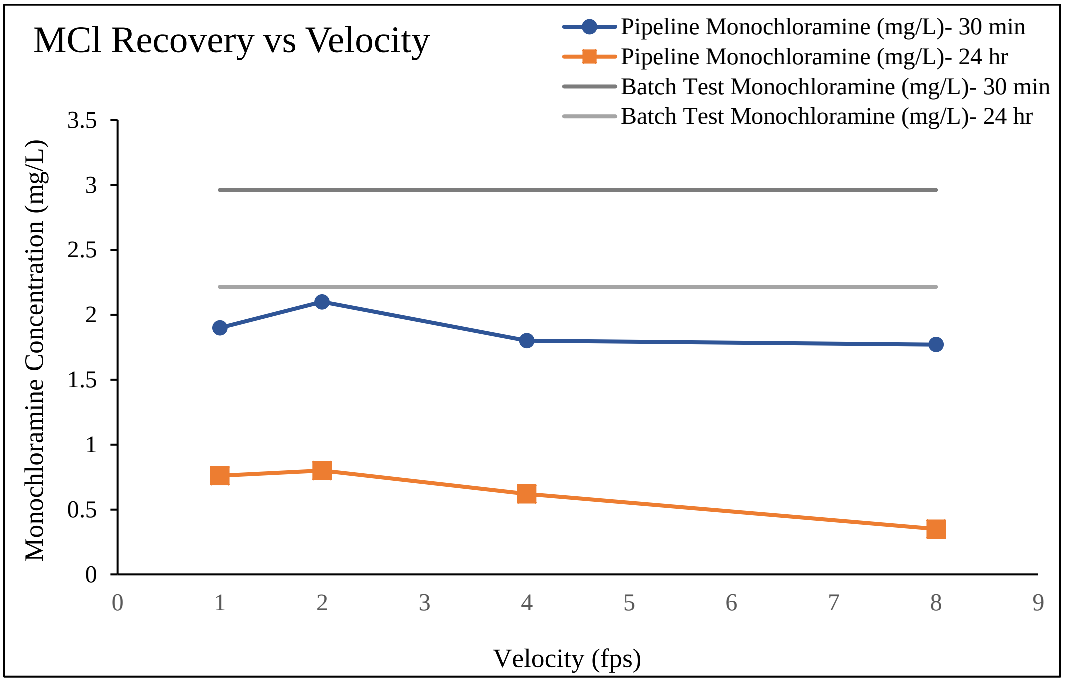

Figure 4-27. MCl recovery for HSH injection into the pipeline for on-bend condition

The same pattern as OSGH was seen with high strength chlorine solution in Figure 4-27 for on-bend injection. According to the observations seen in Figure 4-26 and Figure 4-27, the outcome from monochloramine recoveries was not the same as results from tracer salt with bends. In tracer salt tests it was noticed that addition of 90-degree bends and increase in the flow rate resulted in achieving COV values less than 0.05 for more cases across the pipe, creating adequate mixing condition, but addition of bends did not improve chemical mixing condition even at points were improvement in COV values were attained.

Obtaining low MCl recoveries when injecting chemicals on-bends could be justified by the fact that chlorine is a strong oxidant and as a result of passing through two bends, chlorine reacts with other chemicals in water and its concentration is affected before it gets to ammonia. Moreover, there is no guarantee that the remaining chlorine that is entering the mainstream is at the same direction and location that ammonia is, by the time that the chemicals pass through two 90-degree bends. The goal for addition of the bends to the pipeline was to benefit from the turbulence produced by bends. The location of the maximum velocity of the water stream passing through bends changes and it is not necessarily in the centerline of a pipeline, but the injection location of current study was at the centerline, which is highly possible that lacked maximum velocity of the water flow. As a result, there was no benefit in injecting the chemicals outside the area in which turbulence was produced inside the bends.

On the other hand, as mentioned before, it was expected for the MCl recoveries to improve with increase in flow velocity but it was not achieved for on-bend condition. This could be explained by the fact that when injecting chemicals on bends, as the flow rate increases, the centrifugal and buoyance forces will increase and break the mainstream and produce two separate layers with different flows containing eddies. The separate swirls of flows could cause imbalance in the concentration of chlorine and ammonia and reduce the chance for the chemicals to contact with each other which reduces the MCl recovery with increase in water flow. If there was an opportunity to inject the chemicals with the right concentrations in each of these eddies, then we could increase the possibility of forming higher monochloramines through bends.

The results for chloramination process for straight pipeline, before-bend condition and on-bend condition and for OSGH solution are provided in Figure 4-28.

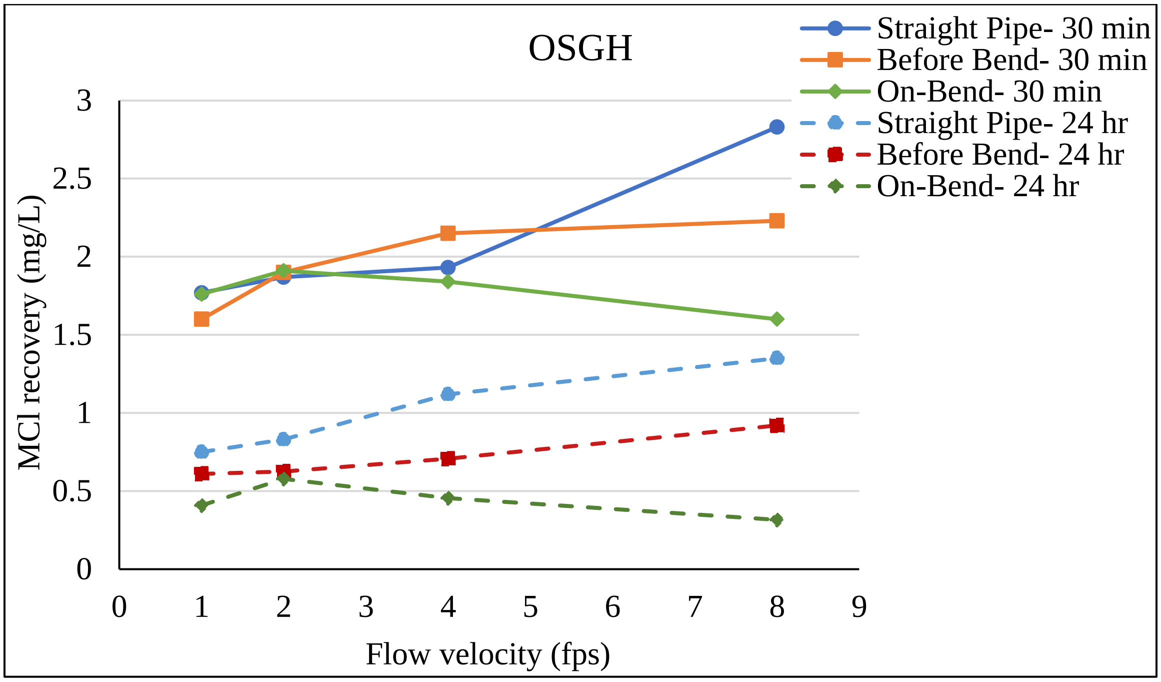

Figure 4-28. Monochloramine values for straight pipeline vs before-bend vs on-bend condition for OSGH solution

As mentioned before, it can be seen in Figure 4-28 that MCl recoveries for straight pipeline compared to before bend condition and for lower velocities are almost the same, but when the flow velocity increases, MCl recovery grows for straight pipeline which was expected to happen in all pipeline conditions after 30 minutes and 24 hours. For on-bend condition for lower velocities, MCl recovery is the same as the other two conditions, but the MCl recovery does not improve with faster mixing of the chemicals which was supposed to be provided by higher flow velocities.

After 24 hours, the MCl decays are discrete and it can be seen that straight pipeline had higher MCl values than the before bend condition and before bend resulted in better MCl values than the on-bend condition which were different from the expectations.

The results for chloramination process for straight pipeline, before-bend condition and on-bend condition and for HSH solution are provided in Figure 4-29.

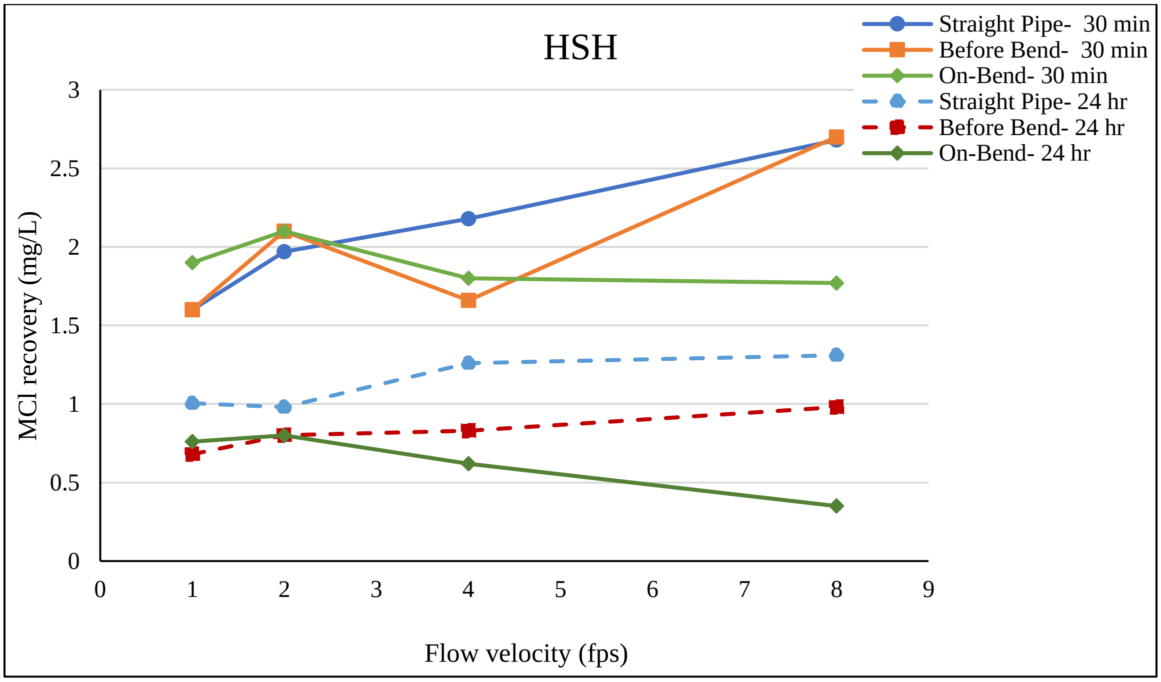

Figure 4-29. Monochloramine values for straight pipeline vs before-bend vs on-bend condition for HSH solution

It is observed in Figure 4-29, that MCl recoveries for straight pipeline, before bend condition and on-bend condition is almost the same and there no considerable difference between their recoveries. With increase in flow velocity it was expected to see improvement in all MCl recoveries. However, MCl recovery for only straight pipeline and before bend condition enhanced with increase in flow velocity and better initial mixing of chemicals and no improvement in MCl for on-bend condition was obtained.

As it was explained before, the results from tracer salt study showed that higher velocities provide better mixing in the pipeline and mixing improves even more with addition of bends. Also, it was expected that better MCl recoveries, lead to less MCl decay. If this was true, the MCl decays for straight pipeline must have been more than MCl decay than before bend and on-bend. However, regarding Figure 4-29, after 24 hours, the MCl decays for straight pipeline were less and MCl values are higher than the before bend condition and before bend had more MCl values than the on-bend condition which were different from the expectations.

4.2.3 Effect of Dilution Ratio

The effect of dilution ratio was examined by using two sources of chlorine with different concentrations. In the figures below the results are presented for three injection conditions. The tables that contain more details regarding the following figures, are presented in Appendix C.

First is injection into the straight pipeline.

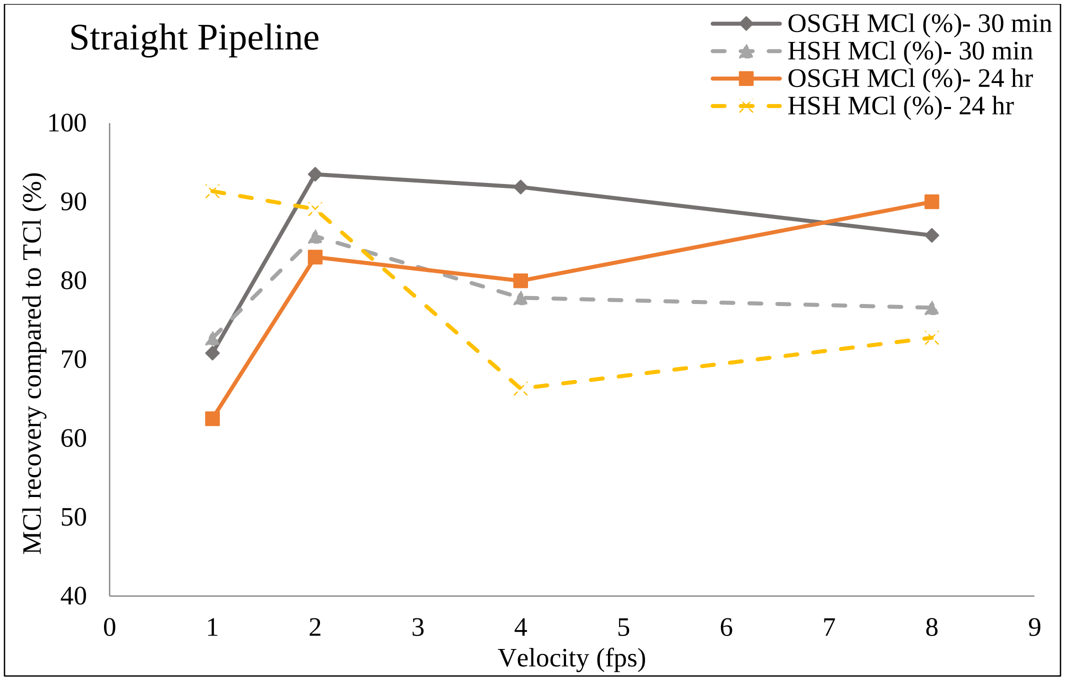

Figure 4-30. Percentage of MCl recovered compared to TCL from OSGH and HSH solutions in straight pipeline after 30 min and 24 hrs

As presented in Figure 4-30 it is illustrated that overall MCl recovery in OSGH is higher than HSH solution in the straight pipeline. At the velocity of 1.0 fps, MCL recovery for OSGH solution is low compared to HSH, but for 2.0, 4.0 and 8.0 fps the OSGH showed better results than MCl recoveries for HSH in 30 minutes and 24 hours. The results from Figure 4-30 are in accordance with the expectations from dilution ratio concept. It was expected that higher injection velocities and lower dilution ratios lead to improvement in MCL recovery. It is also observed that chlorine decay reduces when flow increases from 4.0 fps to 8.0 fps which could be because of better initial mixing of the chemicals with increase in the velocity of water. Better stability was achieved because of quicker mixing at higher velocities.

The same outcome was gained for before-bend and on-bend injection condition. They are explained in more details as follows:

Results for next figure presents the before-bend injection condition.

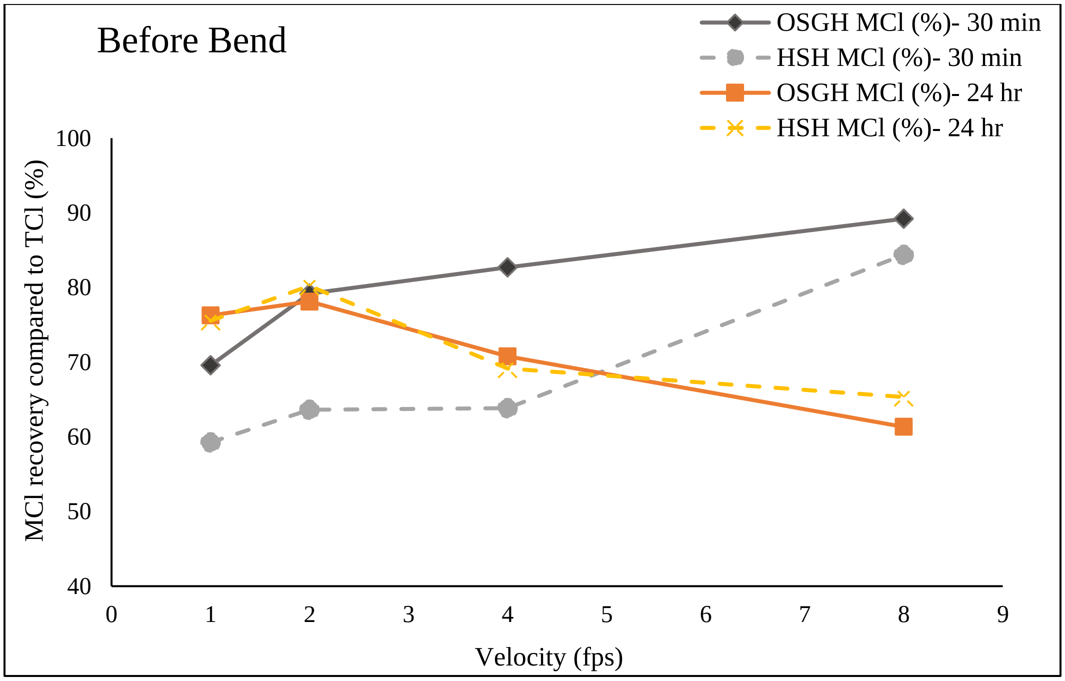

Figure 4-31. Percentage of MCl recovered compared to TCL from OSGH and HSH solutions in before-bend injection after 30 min and 24 hrs

It is observed in Figure 4-31 that OSGH resulted in better MCl recoveries compared to HSH, after 30 minutes. However, after 24 hrs, MCl decays were almost the same for both dilution ratios and OSGH solution did not lead to a better MCl recovery than the HSH. It was observed in MCl recoveries for before bend condition that bends deteriorated mixing of the chemicals and led to lower MCl formation and recovery. Lower decays of MCl could be the result of the worse mixing condition compared to the straight pipeline.

The result for on-bend injection is presented in Figure 4-32.

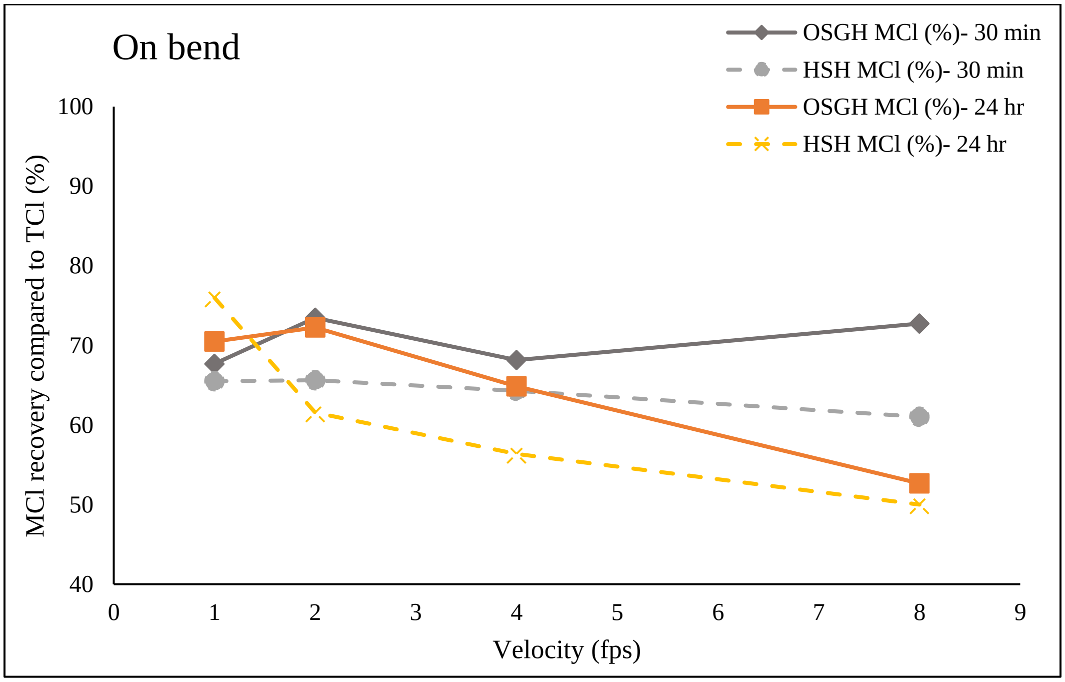

Figure 4-32. Percentage of MCl recovered compared to TCL from OSGH and HSH solutions in on-bend injection after 30 min and 24 hrs

It was seen that for 30 min the MCl recoveries for OSGH were better than HSH and after 24 hrs lower dilution ratio led to better MCl except for the velocity of 1 fps. It is observed that on-bend condition not much improvement in recovery and decay was attained regardless of the concentration of the stock solution. The poor recovery and greater decay of the monochloramine for on-bend condition could be the result of inappropriate injection location and providing a bad initial mixing condition for the chemicals passing through bends.

4.2.4 Dichloramines

Dichloramine values for each experiment were measured and the results are presented in this section.

The DCl residuals from well mixed condition are provided in Table 4-7.

Table 4-7. Dichloramine for batch test

DCl (mg/L)	OSGH	HSH
30 minutes	0195	0.265
24 hours	0.165	0.135

In Table 4-8, DCl values for different velocities, for a straight pipeline are presented.

Table 4-8. Monochloramine and dichloramine values for straight pipeline

	Straight-OSGH				Straight-HSH			
fps	MCl (mg/L)-30 min	DCl (mg/L)-30 min	MCl (mg/L)-24 hrs	DCl (mg/L)-24 hrs	MCl (mg/L)-30 min	DCl (mg/L)-30 min	MCL (mg/L)-24 hrs	DCl (mg/L)-24 hrs
1	1.77	0.25	0.75	0.09	1.6	0.29	1.005	0.17
2	1.87	0.25	0.83	0.2	1.97	0.25	0.98	0.2
4	1.93	0.29	1.12	0.295	2.18	0.41	1.26	0.21
8	2.83	0.32	1.35	0.18	2.68	0.545	1.31	0.325

Ideally high MCl formation and recovery reduces the chance of DCl formation, because addition of correct concentrations of chlorine and ammonia according to the 5:1 mass ratio, and complete mixing at a right pH must result in optimum formation of MCl. Therefore, it was expected to see lowest DCl from the batch test. However, considering MCl values in Table 4-7, the results did not match the expectations and the lowest DCl was obtained in straight pipeline, with 1.0 fps flow velocity after 24 hrs which was 0.09 mg/L as Cl_2 according to the results presented in Table 4-7 and Table 4-8.

Dichloramines at neutral pH tend to form slower and on the other hand their decay is faster than monochloramines. It was expected to see less dichloramine values after 24 hours but as presented in Table 4-8, the trend of dichloramine changes was not the same as expectation. The explanation for that might be because dichloramine was still forming after the 30-minute measurement, but we did not measure its values. If dichloramine formation rate was faster than its decay rate, then DCl after 24 hrs can be more than the 30 minutes.

In the next step the DCl values for different velocities, for the before bend condition are presented in Table 4-9.

Table 4-9. Monochloramine and dichloramine values for before-bend condition

	Before Bend-OSGH				Before Bend-HSH			
fps	MCl (mg/L)-30 min	DCl (mg/L)-30 min	MCl (mg/L)-24 hrs	DCl (mg/L)-24 hrs	MCl (mg/L)-30 min	DCl (mg/L)-30 min	MCL (mg/L)-24 hrs	DCl (mg/L)-24 hrs
1	1.6	0.225	0.61	0.106	1.6	0.23	0.68	0.19
2	1.9	0.2	0.625	0.14	2.1	0.249	0.802	0.23
4	2.15	0.265	0.708	0.31	1.66	0.385	0.83	0.265
8	2.23	0.315	0.92	0.21	2.7	0.395	0.98	0.28

The results from chloramination tests, do not match the expectations for OSGH as explained before and after 24 hours DCl values do not show a specific trend. However, for HSH, DCl values decrease after 24 hours which is in accordance with the expectation.

On the other hand, based on the MCl recoveries from the experiments, the DCl formation in straight pipeline was expected to be less than DCl from the before-bend condition. Comparing the DCl from Table 4-8 and Table 4-9, DCl values decreased when bends were used instead of straight pipeline which is not what was expected form the experiments.

DCl values for different velocities, for the on-bend condition are presented in Table 4-10.

Table 4-10. Dichloramine values for on-bend condition

	On Bend-OSGH				On Bend-HSH			
fps	MCl (mg/L)- 30 min	DCl (mg/L)- 30 min	MCl (mg/L)- 24 hrs	DCl (mg/L)- 24 hrs	MCl (mg/L)- 30 min	DCl (mg/L)- 30 min	MCL (mg/L)- 24 hrs	DCl (mg/L)- 24 hrs
1	1.76	0.301	0.423	0.109	1.9	0.365	0.76	0.256
2	1.91	0.34	0.578	0.15	2.1	0.38	0.8	0.35
4	1.84	0.25	0.454	0.18	1.8	0.38	0.62	0.31
8	1.6	0.35	0.316	0.14	1.77	0.23	0.35	0.29

It is seen in Table 4-10, that dichloramine values are higher than the expectation. It was expected to attain lower DCl formation in straight pipeline compared to DCl from the before-bend condition and both cases must have had less DCl than the on-bend condition. However, the DCl values did not have a trend and did not follow the expectations. Therefore, a correlation between better mixing, higher MCl recovery and DCl values could not be found.

The DCl and TCl values were measured after each experiment and the percent ratios of DCl to TCl are presented in Table 4-11 and Table 4-12 below. The actual values are presented in Appendix C.

Table 4-11. The percent ratio of DCl to TCl for OSGH

Main flow velocity (fps)	DCl/TCl-Straight-30 min (%)	DCl/TCl-Straight-24 hrs (%)	DCl/TCl-Before-bend- 30 min (%)	DCl/TCl-Before-bend- 24 hrs (%)	DCl/TCl-On-bend-30 min (%)	DCl/TCl-On-bend-24 hrs (%)
1	10	7.50	9.78	13.25	11.58	18.17
2	12.5	20	8.33	17.5	13.10	18.75
4	13.81	21.07	10.20	31	9.26	25.71
8	9.70	11.33	12.60	14	15.91	23.33

It is observed in Table 4-11 that the lowest ratio was achieved for straight pipeline and with OSGH solution after 24 hrs.

Table 4-12. The percent ratio of DCl to TCl for HSH

Main flow velocity (fps)	DCl/TCl-Straight-30 min (%)	DCl/TCl-Straight-24 hrs (%)	DCl/TCl-Before-bend- 30 min (%)	DCl/TCl-Before-bend- 24 hrs (%)	DCl/TCl-On-bend-30 min (%)	DCl/TCl-On-bend-24 hrs (%)
1	13.18	15.45	8.52	21.11	12.59	25.60
2	10.87	18.18	7.54	23	11.88	26.92
4	14.64	11.05	14.81	22.08	13.57	28.18
8	15.57	18.06	12.34	18.67	7.93	41.43

Highest DCl ratio in Table 4-12 was detected for HSH for on-bend condition at 8fps after 24hrs, which corresponds to the low MCl recovery and poor mixing condition of chemicals produced as a result of the 90-degree bends.

The values in Table 4-11 and Table 4-12 also show that dichloramine measurements were more than expected values, even for high MCl recoveries in the pipeline. The high values of dichloramine indicate that there is a platform for auto-decomposition in the pipeline which can later cause faster decay rate of monochloramine. One explanation for these results is that dechlorination of tank water affected water quality and resulted in high DCl formation in the pipeline.

On the other hand, it was observed in Figure 4-21 through Figure 4-27 that MCl recoveries within 24 hours show more decay in MCl concentration from pipeline compared to well mixed conditions. These results illustrate that inadequate mixing in the pipeline can be another reason for formation of relatively high concentrations of DCl which could be the main reason causing rapid decay rate of MCl. As a result, well mixed condition was repeated with tank water and filter effluent water which is water sample before any chemical addition to it so that the water would not require dechlorination. The comparison between two types pf water sample is presented in Table 4-13. In this table, the chlorine to ammonia mass ratio is 5:1. Target chlorine concentration is 4.0 mg/L and ammonia target concentration is 1.0 mg/L.

Table 4-13. Chlorine residual comparison for two water samples

Measurement time		**pH**	**Chlorine residuals for tank water (mg/L)**	**pH**	**Chlorine residuals for filter effluent (mg/L)**
30 min	Total	8.0	3.6	8.38	3.9
	Mono		3.23		3.73
	Di-		0.29		0.155
24 hours	Total	8.12	2.6	8.42	3.1
	Mono		2.36		2.9
	Di-		0.165		0.1

It can be seen in Table 4-13 that TCl and MCl values for filter effluent water samples are more in line with what were expected. It is observed that even after 24 hrs, the MCl decay rate in well mixed condition for tank water was more than filter effluent water. Although still well mixed condition for tank water led to formation of lower values of DCl and higher MCl recoveries which are better results compared to pipeline recoveries, to prevent any inaccuracy in results while measuring MCl and DCl, utilizing water samples from filter effluent is recommended.

Chapter 5

CONCLUSIONS

The goal of this study was to quantify the role of mixing and time in chloramine recovery and decay. A 4-inch PVC pipeline was built and tracer salt was injected into it. The velocity of water and velocity of secondary stream were changed throughout the experiment, as well as the injection and sampling locations. To measure mixing in pipeline COV values were calculated using conductivities of samples collected from numerous points in the pipeline and this study is referred to as tracer salt study. It was concluded for tracer salt study in straight pipeline that, centerline injection provides the lowest COV values within a shortest amount of time, that were indication of complete mixing in the pipeline. An increase in the velocity of the mainstream helped to achieve complete mixing in the pipeline in a shorter time. It was understood from the upper wall injection of tracer salt, that upper wall injection does not provide fast initial mixing, even with increase in the flow velocity. Therefore, for the purpose of chemical formation, upper wall injection could not be recommended. One 90-degree bend and three 90-degree bends were added to the pipeline and tracer salt study was conducted for each condition. It was observed that addition of one bend reduced the time required to complete mixing condition compared to straight pipeline and three bends reduced mixing time compared to the condition in which one bend was in the path of water. It was concluded that addition of one bend can improve mixing condition and reduce the time to complete mixing, however, if the aim of an experiment is to provide a rapid initial mixing, addition of three bends to the path of water will result in the fastest mixing time compared to the other conditions.

In the second set of experiments, chlorine and ammonia were injected into the pipeline. Tap water was dechlorinated and was pumped into the pipeline as a mainstream. MCl recovery was measured in the downstream of the pipeline where complete mixing was gained in the tracer salt study. The results proved that faster mixing leads to better recovery of MCl in a straight pipeline. It was expected to achieve better MCl recovery and less decay with the addition of bends, because bends provided faster mixing compared to straight pipeline in the tracer study. The actual results did not follow the expectations and the addition of bends did not improve recovery and decay of MCl. Moreover, in the pipeline with bends, higher velocities did not lead to any improvement in MCl recoveries and MCl values were less than the straight pipeline. It was concluded that faster mixing does not guarantee better MCl recoveries which was one of the most important observations in this study.

The effect of dilution ratio was examined by using chlorine stock solutions with different concentrations. The source solution with lower concentration required higher injection velocities. It was expected to see better MCl recoveries with increase in injection velocities because the chemicals were being injected into more depth and had better opportunity to mix with the main flow in a shorter time. The results matched the expectations and it was concluded that faster mixing of chemicals could be achieved through increasing the injection velocity of the secondary stream.

Dichloramines were measured in the chloramination process. It was observed in tracer salt study that lower velocity of the mainstream led to poor mixing of chemicals. With poor mixing between chlorine and ammonia it was expected to form less MCl and higher DCl with lower velocities and observe lower DCl with higher velocity. DCl to TCl ratios were calculated. It was concluded that in straight pipeline in which higher MCl recoveries were obtained, lowest DCl to TCl ratio was achieved. Implying that better mixing led to higher MCl recovery and formation of less DCl. However, for pipeline with bends the same trend was not observed and the DCl values were unexpected and no conclusion could be drawn based on DCl values and their relationship with MCls. Moreover, it was expected to see decrease in DCl values after 24 hrs as a result of dichloramine decay, but the DCl values after 24 hrs did not decrease for all cases.

The measured DCl values were high for all experiments which could be affected by two factors. Poor mixing in the pipeline could cause high DCl or the water quality that was used for the experiments. DCl values from the pipeline were higher than DCl values for batch test and it could be concluded that higher DCl values could be the result of inadequate mixing in the pipeline. However, the DCl values for batch test which provided completer mixing were high for all the experiments. As a result, filter effluent water was examined during a batch test and the results were compared to the batch test which was conducted with tanks water. Lower DCl formation was seen with filter effluent than DCl values form tank water ant it was concluded that lower DCl could be formed, if filter effluent was used for the experiments instead of dechlorinated tap water.

Chapter 6

SUGGESTIONS AND FUTURE WORK

The results from this research suggest that additional work and considerations can be done to find a method to achieve complete initial chemical mixing in a pipeline and produce highest concentration of monochloramine. The suggestions can be:

- To add mixers to a pipeline. Static mixers may be able to increase monochloramine formation with no addition of external energy, since they are capable of breaking the flow.
- To decrease the distance between two injection streams or inject them at the same time and assess the MCl recoveries if the chemicals are injected at the same time or closer than the current tests. The goal is to try to have right amount of chemicals in the same stream as soon as they enter the main flow and mix them immediately.
- If there is a considerable distance between the chlorine and ammonia injection, for example, if chlorine is injected first and after some time ammonia is added, concentration of chlorine when meeting ammonia would be unknown. Therefore, chlorine residuals at the location of ammonia injection must be measured and ammonia concentration must be calculated for the proper ratio using the new measured chlorine residuals.
- To measure MCl and pH at locations closer to injection points. The high concentration of chlorine solution increases the pH of the water. As a result, it is expected to see higher pH values near the injection points and then pH will decrease when the HSH is mixed with water at the current sampling point. At lower pH, DCl formation will increase and MCl

will decrease. It is recommended to keep track of such changes by collecting samples at several distances from the chemical injection points.

- To study bends in further detail. The movement of flow particles in bends must be tracked. It is recommended to inject chemicals on the pathway of water flow, when injecting chemicals on the bends. One chemical can be injected on one side on the wall and the second chemical can be injected on the other side of the wall to induce better mixing, depending on various studies conducted on flow through bends.
- According to the results from before bend condition, it is suggested to move the bend further down from the injection points and allow chlorine and ammonia to have more contact time after they are injected into the water to improve initial mixing of the chemicals and afterwards, pass the water through the bends.

APPENDIX A

SAMPLE CALCULATIONS

Sample Calculation for Choosing a Proper Size for Sampling Tube

The required volume set by conductivity probe to read the conductivity was 0.004 L. Assuming to be filled in 1 second the flow rate is calculated as follows:

$Q = {}^{V}\!/_{t} = 1.41 \times 10^{-4}$

For $v = 1.0,\ Q = A \times v$

$A = {}^{Q}\!/_{v} = 1.41 \times 10^{-4}$

$d = \sqrt{4A/\pi} = 0.161$

Where Q = Flow rate (cfs)

V = Volume (L)

t = Time (Sec)

A = Surface area (ft^2)

v = Flow velocity (m/s)

d = injection and sampling tube diameter (in)

Following the same procedure, the diameter for different velocities is presented in Table A-1.

Table A-1. Sampling tube sizing

Flow Velocity (fps)	Calculated diameter (in)	Chosen diameter (in)
1	0.161	0.152
2	0.114	
4	0.081	0.080
8	0.057	

Flow rate for injection of OSGH and the velocity of 1 fps are calculated as follows:

The source concentration (C_1) is equal to 6500 mg/L and the target concentration for chlorine is 4.0 mg/L.

$Q_1C_1 = Q_2C_2$

$$v_1 = 1.0\ fps, A_1 = \frac{\pi}{4}(\frac{4.026}{12})^2 = 0.088\ (ft^2)$$

$$Q_1 = Av = 0.088 \times 1 = 0.088\ (cfs) = 150.14\ \text{(L/min)}$$

$$Q_2 = \frac{150.14 \times 4.0 \times 1000}{86000} = 6.98\ mL/min$$

Sample Calculation for Measurement of I_s Value

Sample calculation for measuring one Is value for centerline injection, centerline sampling, for 1st station and for 1.0 fps velocity (150 L/min) is provided below:

$$Q_A = 150.14\ {}^{L}/_{min} = 2.5 \times 10^{-3}\ {}^{m^3}/_{s}$$

$$Q_w = 6.98\ {}^{mL}/_{min} = 1.16 \times 10^{-7}\ {}^{m^3}/_{s}$$

$$\bar{X}_A = \frac{Q_A}{Q_w + Q_A} = 4.65 \times 10^{-5}$$

$$\bar{X}_w = 1 - \bar{X}_A = 0.999953$$

$$\sigma_u \cong \sqrt{\bar{X}_A(1 - \bar{X}_{A)}} = 6.82 \times 10^{-3}$$

$$\sigma_m = \sqrt{\frac{\sum_{i=1}^{n}(x_i - \bar{x})^2}{n - 1}} = 1.88 \times 10^{-5}$$

$$I_s = (\frac{\sigma_m}{\sigma_u})^2 = 7.63 \times 10^{-6}$$

APPENDIX B

DATA FOR TRACER SALT STUDY

Injection into Centerline at Q = 150 L/min

Table A-2. Normalized average values for centerline injection, Q=150 L/min

Sampling Station	ft from injection	Ave CU, Q=150 L/min	Ave CMU, Q=150 L/min	Ave CC, Q=150 L/min	Ave CML, Q=150 L/min	Ave CL, Q=150 L/min
Stat 1	2.71	1.814	1.623	1.626	0.479	0.000
Stat 2	5.15	1.425	1.242	1.179	0.663	0.000
Stat 3	9.15	1.301	1.122	1.097	0.616	0.760
Stat 4	15.73	1.038	0.786	1.013	0.719	0.972
Stat 5	28.99	0.909	0.926	0.999	0.806	0.785
Stat 6	51.66	0.893	0.910	0.865	0.831	0.758

Table A-3. COV values for centerline injection, Q=150 L/min

Sampling Station	ft from injection	COV CU, Q=150 L/min	COV CMU, Q=150 L/min	COV CC, Q=150 L/min	COV CML, Q=150 L/min	COV CL, Q=150 L/min
Stat 1	2.71	0.255	0.488	0.405	0.464	1.00
Stat 2	5.15	0.173	0.262	0.354	0.411	1.00
Stat 3	9.15	0.155	0.154	0.135	0.369	0.714
Stat 4	15.73	0.089	0.093	0.087	0.168	0.658
Stat 5	28.99	0.046	0.059	0.057	0.086	0.095
Stat 6	51.66	0.043	0.094	0.038	0.096	0.402

Table A-4. I_s values for centerline injection, Q=150 L/min

Sampling Station	ft from injection	I_s CU, Q=150 L/min	I_s CMU, Q=150 L/min	I_s CC, Q=150 L/min	I_s CML, Q=150 L/min	I_s CL, Q=150 L/min
Stat 1	2.71	3.02×10^{-6}	1.11×10^{-5}	7.63×10^{-6}	9.99×10^{-6}	4.65×10^{-5}
Stat 2	5.15	1.39×10^{-6}	3.20×10^{-6}	5.83×10^{-6}	7.84×10^{-6}	4.65×10^{-5}
Stat 3	9.15	1.10×10^{-6}	1.10×10^{-6}	8.42×10^{-7}	6.35×10^{-6}	2.37×10^{-5}
Stat 4	15.73	3.69×10^{-7}	4.00×10^{-7}	3.54×10^{-7}	1.32×10^{-6}	2.01×10^{-5}
Stat 5	28.99	9.85×10^{-8}	1.65×10^{-7}	1.52×10^{-7}	3.41×10^{-7}	4.23×10^{-7}
Stat 6	51.66	8.64×10^{-8}	4.10×10^{-7}	6.54×10^{-8}	4.24×10^{-7}	7.52×10^{-6}

Injection into Centerline at Q = 300 L/min

Table A-5. Normalized average values for centerline injection, Q=300 L/min

Sampling Station	ft from injection	Ave CU, Q=300 L/min	Ave CMU, Q=300 L/min	Ave CC, Q=300 L/min	Ave CML, Q=300 L/min	Ave CL, Q=300 L/min
Stat 1	2.71	1.552	1.775	1.892	0.748	0.000
Stat 2	5.15	1.421	1.229	1.009	0.853	0.943
Stat 3	9.15	1.110	1.254	0.993	0.830	0.969
Stat 4	15.73	1.122	1.001	0.972	0.983	0.925
Stat 5	28.99	1.114	0.927	0.947	0.916	0.922
Stat 6	51.66	0.991	1.034	1.031	1.005	0.935

Table A-6. COV values for centerline injection, Q=300 L/min

Sampling Station	ft from injection	COV CU, Q=300 L/min	COV CMU, Q=300 L/min	COV CC, Q=300 L/min	COV CML, Q=300 L/min	COV CL, Q=300 L/min
Stat 1	2.71	0.353	0.289	0.396	0.679	1.000
Stat 2	5.15	0.238	0.211	0.387	0.367	0.922
Stat 3	9.15	0.216	0.118	0.124	0.322	0.582
Stat 4	15.73	0.110	0.157	0.149	0.206	0.431
Stat 5	28.99	0.107	0.077	0.066	0.171	0.103
Stat 6	51.66	0.067	0.045	0.056	0.053	0.050

Table A-7. I_s values for centerline injection, Q=300 L/min

Sampling Station	ft from injection	I_s CU, Q=300 L/min	I_s CMU, Q=300 L/min	I_s CC, Q=300 L/min	I_s CML, Q=300 L/min	I_s CL, Q=300 L/min
Stat 1	2.71	5.80×10^{-6}	3.90×10^{-6}	7.30×10^{-6}	2.15×10^{-5}	4.65×10^{-5}
Stat 2	5.15	2.63×10^{-6}	2.06×10^{-6}	6.95×10^{-6}	6.27×10^{-6}	3.95×10^{-5}
Stat 3	9.15	2.18×10^{-6}	6.51×10^{-7}	7.11×10^{-7}	4.83×10^{-6}	1.58×10^{-5}
Stat 4	15.73	5.58×10^{-7}	1.15×10^{-6}	1.04×10^{-6}	1.97×10^{-6}	8.65×10^{-6}
Stat 5	28.99	5.32×10^{-7}	2.77×10^{-7}	2.01×10^{-7}	1.36×10^{-6}	4.92×10^{-7}
Stat 6	51.66	2.11×10^{-7}	9.6×10^{-8}	1.46×10^{-7}	1.30×10^{-7}	1.15×10^{-7}

Injection into Centerline at Q = 600 L/min

Table A-8. Normalized average values for centerline injection, Q=600 L/min

Sampling Station	ft from injection	Ave CU, Q=600 L/min	Ave CMU, Q=600 L/min	Ave CC, Q=600 L/min	Ave CML, Q=600 L/min	Ave CL, Q=600 L/min
Stat 1	2.71	1.010	2.231	1.436	0.479	0.000
Stat 2	5.15	1.061	1.314	1.191	0.387	0.199
Stat 3	9.15	0.999	1.000	1.073	0.428	0.747
Stat 4	15.73	0.920	1.023	1.000	0.389	0.771
Stat 5	28.99	0.852	0.845	0.931	0.380	0.764
Stat 6	51.66	1.094	0.906	0.909	0.370	1.184

Table A-9. COV values for centerline injection, Q=600 L/min

Sampling Station	ft from injection	COV CU, Q=600 L/min	COV CMU, Q=600 L/min	COV CC, Q=600 L/min	COV CML, Q=600 L/min	COV CL, Q=600 L/min
Stat 1	2.71	0.334	0.163	0.238	0.365	1.000
Stat 2	5.15	0.190	0.167	0.265	0.357	0.726
Stat 3	9.15	0.124	0.142	0.201	0.273	0.248
Stat 4	15.73	0.100	0.107	0.163	0.218	0.152
Stat 5	28.99	0.098	0.100	0.117	0.166	0.113
Stat 6	51.66	0.042	0.092	0.138	0.095	0.052

Table A-10. I_s values for centerline injection, Q=600 L/min

Sampling Station	ft from injection	I_s CU, Q=600 L/min	I_s CMU, Q=600 L/min	I_s CC, Q=600 L/min	I_s CML, Q=600 L/min	I_s CL, Q=600 L/min
Stat 1	2.71	5.20×10^{-6}	1.24×10^{-6}	2.62×10^{-6}	6.19×10^{-6}	4.65×10^{-5}
Stat 2	5.15	1.67×10^{-6}	1.30×10^{-6}	3.27×10^{-6}	5.94×10^{-6}	2.45×10^{-5}
Stat 3	9.15	7.15×10^{-7}	9.38×10^{-7}	1.88×10^{-6}	3.47×10^{-6}	2.86×10^{-6}
Stat 4	15.73	4.65×10^{-7}	5.33×10^{-7}	1.24×10^{-6}	2.21×10^{-6}	1.07×10^{-6}
Stat 5	28.99	4.47×10^{-7}	4.62×10^{-7}	6.36×10^{-7}	1.28×10^{-6}	5.91×10^{-7}
Stat 6	51.66	8.04×10^{-8}	3.91×10^{-7}	8.89×10^{-7}	4.20×10^{-7}	1.28×10^{-7}

Injection into Centerline at Q = 1200 L/min

Table A-11. Normalized average values for centerline injection, Q=1200 L/min

Sampling Station	ft from injection	Ave CU, Q=1200 L/min	Ave CMU, Q=1200 L/min	Ave CC, Q=1200 L/min	Ave CML, Q=1200 L/min	Ave CL, Q=1200 L/min
Stat 1	2.71	1.127	2.064	1.989	0.308	0.000
Stat 2	5.15	1.275	1.303	1.157	0.510	0.275
Stat 3	9.15	1.138	1.180	0.990	0.789	0.614
Stat 5	28.99	1.039	0.913	0.991	0.976	0.897
Stat 6	51.66	0.991	0.952	0.951	0.975	0.994

Table A-12. COV values for centerline injection, Q=1200 L/min

Sampling Station	ft from injection	COV CU, Q=1200 L/min	COV CMU, Q=1200 L/min	COV CC, Q=1200 L/min	COV CML, Q=1200 L/min	COV CL, Q=1200 L/min
Stat 1	2.71	0.226	0.117	0.145	0.411	1.000
Stat 2	5.15	0.131	0.102	0.140	0.325	0.516
Stat 3	9.15	0.129	0.110	0.094	0.150	0.262
Stat 5	28.99	0.038	0.056	0.038	0.079	0.064
Stat 6	51.66	0.030	0.055	0.040	0.050	0.023

Table A-13. I_s values for centerline injection, Q=1200 L/min

Sampling Station	ft from injection	I_s CU, Q=1200 L/min	I_s CMU, Q=1200 L/min	I_s CC, Q=1200 L/min	I_s CML, Q=1200 L/min	I_s CL, Q=1200 L/min
Stat 1	2.71	2.38×10^{-6}	6.33×10^{-7}	9.74×10^{-7}	7.88×10^{-6}	$4.65E\times10^{-5}$
Stat 2	5.15	7.95×10^{-7}	4.84×10^{-7}	9.15×10^{-7}	4.92×10^{-6}	1.24×10^{-5}
Stat 3	9.15	7.74×10^{-7}	5.63×10^{-7}	4.09×10^{-7}	1.05×10^{-6}	3.19×10^{-6}
Stat 5	28.99	6.57×10^{-8}	1.44×10^{-7}	6.59×10^{-8}	2.87×10^{-7}	1.91×10^{-7}
Stat 6	51.66	4.26×10^{-8}	1.40×10^{-7}	7.51×10^{-8}	1.16×10^{-7}	2.53×10^{-8}

Injection into Upper Wall at Q = 150 L/min

Table A-14. Normalized average values for upper wall injection, Q=150 L/min

Sampling Station	ft from injection	Ave UU, Q=150 L/min	Ave UMU, Q=150 L/min	Ave UC, Q=150 L/min	Ave UML, Q=150 L/min	Ave UL, Q=150 L/min
Stat 1	2.71	3.568	1.820	0.000	0.000	0.000
Stat 2	5.15	2.154	1.831	0.656	0.547	0.000
Stat 3	9.15	1.281	1.839	0.804	0.582	0.424
Stat 4	15.73	1.053	0.942	0.913	0.741	0.813
Stat 5	28.99	0.905	0.977	0.968	0.629	0.891
Stat 6	51.66	0.930	0.754	0.961	0.849	1.000

Table A-15. COV values for upper wall injection, Q=150 L/min

Sampling Station	ft from injection	COV UU, Q=150 L/min	COV UMU, Q=150 L/min	COV UC, Q=150 L/min	COV UML, Q=150 L/min	COV UL, Q=150 L/min
Stat 1	2.71	0.390	0.867	1.000	1.000	1.000
Stat 2	5.15	0.329	0.340	0.477	0.577	1.000
Stat 3	9.15	0.304	0.127	0.201	0.422	0.684
Stat 4	15.73	0.153	0.154	0.095	0.160	0.197
Stat 5	28.99	0.125	0.055	0.050	0.130	0.086
Stat 6	51.66	0.092	0.086	0.047	0.058	0.080

Table A-16. I_s *values for upper wall injection, Q=150 L/min*

Sampling Station	ft from injection	I_s UU, Q=150 L/min	I_s UMU, Q=150 L/min	I_s UC, Q=150 L/min	I_s UML, Q=150 L/min	I_s UL, Q=150 L/min
Stat 1	2.71	7.06×10^{-6}	3.50×10^{-5}	4.65×10^{-5}	4.65×10^{-5}	4.65×10^{-5}
Stat 2	5.15	5.04×10^{-6}	5.39×10^{-6}	1.06×10^{-5}	1.55×10^{-5}	4.65×10^{-5}
Stat 3	9.15	4.30×10^{-6}	7.46×10^{-7}	1.88×10^{-6}	8.29×10^{-6}	2.18×10^{-5}
Stat 4	15.73	1.09×10^{-6}	1.11×10^{-6}	4.18E-07	1.19×10^{-6}	1.80×10^{-6}
Stat 5	28.99	7.25×10^{-7}	1.39×10^{-7}	1.15E-07	7.91×10^{-7}	3.45×10^{-7}
Stat 6	51.66	3.90×10^{-7}	3.47×10^{-7}	1.03E-07	1.54×10^{-7}	2.96×10^{-7}

Injection into Upper Wall at Q = 300 L/min

Table A-17. Normalized average values for upper wall injection, Q=300 L/min

Sampling Station	ft from injection	Ave UU, Q=300 L/min	Ave UMU, Q=300 L/min	Ave UC, Q=300 L/min	Ave UML, Q=300 L/min	Ave UL, Q=300 L/min
Stat 1	2.71	1.801	2.550	0.000	0.000	0.000
Stat 2	5.15	1.975	1.983	0.907	1.049	0.000
Stat 3	9.15	1.472	1.101	0.800	1.005	0.583
Stat 4	15.73	1.146	1.101	1.113	0.912	0.614
Stat 5	28.99	0.759	0.897	1.029	1.036	0.880
Stat 6	51.66	1.033	0.789	0.958	0.983	0.815

Table A-18. COV values for upper wall injection, Q=300 L/min

Sampling Station	ft from injection	COV UMU, Q=300 L/min	COV UC, Q=300 L/min	COV UML, Q=300 L/min	COV UL, Q=300 L/min	COV UMU, Q=300 L/min
Stat 1	2.71	0.972	0.499	1.000	1.000	1.000
Stat 2	5.15	0.312	0.216	0.493	0.504	1.000
Stat 3	9.15	0.271	0.298	0.347	0.428	0.762
Stat 4	15.73	0.141	0.189	0.120	0.187	0.262
Stat 5	28.99	0.090	0.081	0.070	0.040	0.073
Stat 6	51.66	0.045	0.087	0.065	0.049	0.082

Table A-19. I_s values for upper wall injection, Q=300 L/min

Sampling Station	ft from injection	I_s UU, Q=300 L/min	I_s UMU, Q=300 L/min	I_s UC, Q=300 L/min	I_s UML, Q=300 L/min	I_s UL, Q=300 L/min
Stat 1	2.71	4.40×10^{-5}	1.16×10^{-5}	4.65×10^{-5}	4.65×10^{-5}	4.65×10^{-5}
Stat 2	5.15	4.53×10^{-6}	2.16×10^{-6}	1.13×10^{-5}	1.18×10^{-5}	4.65×10^{-5}
Stat 3	9.15	3.40×10^{-6}	4.13×10^{-6}	5.62×10^{-6}	8.52×10^{-6}	2.70×10^{-5}
Stat 4	15.73	9.19×10^{-7}	1.67×10^{-6}	6.68×10^{-7}	1.63×10^{-6}	3.20×10^{-6}
Stat 5	28.99	3.73×10^{-7}	3.07×10^{-7}	2.27×10^{-7}	7.62×10^{-8}	2.46×10^{-7}
Stat 6	51.66	9.22×10^{-8}	3.54×10^{-7}	1.99×10^{-7}	1.10×10^{-7}	3.10×10^{-7}

Injection into Upper Wall at Q = 600 L/min

Table A-20. Normalized average values for upper wall injection, Q=600 L/min

Sampling Station	ft from injection	Ave UU, Q=600 L/min	Ave UMU, Q=600 L/min	Ave UC, Q=600 L/min	Ave UML, Q=600 L/min	Ave UL, Q=600 L/min
Stat 1	2.71	4.226	1.777	0.000	0.155	0.000
Stat 2	5.15	2.257	1.252	0.993	0.378	0.000
Stat 3	9.15	1.775	0.947	0.986	0.873	0.689
Stat 4	15.73	1.222	0.964	0.958	0.796	0.703
Stat 5	28.99	0.894	0.933	0.949	0.738	1.014
Stat 6	51.66	0.897	1.153	1.064	0.826	0.879

Table A-21. COV values for upper wall injection, Q=600 L/min

Sampling Station	ft from injection	COV UU, Q=600 L/min	COV UMU, Q=600 L/min	COV UC, Q=600 L/min	COV UML, Q=600 L/min	COV UL, Q=600 L/min
Stat 1	2.71	0.443	0.417	1.000	0.308	1.000
Stat 2	5.15	0.317	0.388	0.388	0.997	1.000
Stat 3	9.15	0.279	0.235	0.196	0.466	0.662
Stat 4	15.73	0.167	0.120	0.127	0.156	0.175
Stat 5	28.99	0.109	0.093	0.072	0.111	0.071
Stat 6	51.66	0.096	0.037	0.086	0.112	0.084

Table A-22. I_s values for upper wall injection, Q=600 L/min

Sampling Station	ft from injection	I_s UU, Q=600 L/min	I_s UMU, Q=600 L/min	I_s UC, Q=600 L/min	I_s UML, Q=600 L/min	I_s UL, Q=600 L/min
Stat 1	2.71	9.13×10^{-6}	8.07×10^{-6}	4.65×10^{-5}	4.41×10^{-6}	4.65×10^{-5}
Stat 2	5.15	4.68×10^{-6}	6.98×10^{-6}	6.98×10^{-6}	4.63×10^{-5}	4.65×10^{-5}
Stat 3	9.15	3.61×10^{-6}	2.57×10^{-6}	1.78×10^{-6}	1.01×10^{-5}	2.04×10^{-5}
Stat 4	15.73	1.30×10^{-6}	6.68×10^{-7}	7.53×10^{-7}	1.13×10^{-6}	1.43×10^{-6}
Stat 5	28.99	5.55×10^{-7}	4.02×10^{-7}	2.44×10^{-7}	5.76×10^{-7}	2.36×10^{-7}
Stat 6	51.66	4.26×10^{-7}	6.36×10^{-8}	3.43×10^{-7}	5.82×10^{-7}	3.31×10^{-7}

Injection into Upper Wall at Q = 1200 L/min

Table A-23. Normalized average values for upper wall injection, Q=1200 L/min

Sampling Station	ft from injection	Ave UU, Q=1200 L/min	Ave UMU, Q=1200 L/min	Ave UC, Q=1200 L/min	Ave UML, Q=1200 L/min	Ave UL, Q=1200 L/min
Stat 1	2.71	3.937	2.774	0.395	0.098	0.000
Stat 2	5.15	2.074	1.354	0.740	0.372	0.321
Stat 5	9.15	0.940	0.967	0.925	0.906	0.970
Stat 6	15.73	0.902	0.928	0.996	1.001	1.068

Table A-24. COV values for upper wall injection, Q=1200 L/min

Sampling Station	ft from injection	COV UU, Q=1200 L/min	COV UMU, Q=1200 L/min	COV UC, Q=1200 L/min	COV UML, Q=1200 L/min	COV UL, Q=1200 L/min
Stat 1	2.71	0.198	0.232	0.608	0.343	1.000
Stat 2	5.15	0.138	0.183	0.411	0.843	0.691
Stat 5	9.15	0.058	0.051	0.052	0.072	0.074
Stat 6	15.73	0.045	0.042	0.024	0.027	0.029

Table A-25. I_s values for upper wall injection, Q=1200 L/min

Sampling Station	ft from injection	I_s UU, Q=1200 L/min	I_s UMU, Q=1200 L/min	I_s UC, Q=1200 L/min	I_s UML, Q=1200 L/min	I_s UL, Q=1200 L/min
Stat 1	2.71	1.82×10^{-6}	2.51×10^{-6}	1.72×10^{-5}	5.46×10^{-6}	4.65×10^{-5}
Stat 2	5.15	8.86×10^{-7}	1.57×10^{-6}	7.85×10^{-6}	3.30×10^{-5}	2.22×10^{-5}
Stat 5	9.15	1.55×10^{-7}	1.23×10^{-7}	1.28×10^{-7}	2.43×10^{-7}	2.53×10^{-7}
Stat 6	15.73	9.55×10^{-8}	8.06×10^{-8}	2.72×10^{-8}	3.44×10^{-8}	3.82×10^{-8}

APPENDIX C

DATA FOR CHLORAMINATION PROCESS

Table C-1. Chlorine residuals and ammonia for 4:1 ratio of Cl_2: N under well mixed condition for regular tap water

	TCl	MCl	DCl	Free	NH_3-N	pH
Tap water	2.4	1.95	0.075	0	0.18	7.8
Dechlorinated Tap water	0.2	0.19	0.035	0	0.01	7.84

4:1 → Cl_2:N			
sampling time		**pH**	**Chlorine Residuals**
30 min	Total	7.88	3.3
	Free		0.05
	Mono		2.9
	Di-		0.23
	NH3-N		0.22
2.5 hours	Total	7.88	3.1
	Free		0.02
	Mono		2.75
	Di-		0.29
	NH3-N		0.12
4.5 hours	Total	7.91	3
	Free		0
	Mono		2.59
	Di-		0.21
	NH3-N		0.14
24 hours	Total	7.9	2.8
	Free		0

	Mono		2.48
	Di-		0.298
	NH3-N		0.13

Table C-2. Chlorine residuals and ammonia for 4.5:1 ratio of Cl_2: N under well mixed condition for regular tap water

4.5:1 → Cl_2:N			
sampling time		**pH**	**Chlorine Residuals**
30 min	Total	7.9	3.4
	Free		0.1
	Mono		3.03
	Di-		0.22
	NH3-N		0.17
2.5 hours	Total	7.89	3.3
	Free		0.03
	Mono		2.93
	Di-		0.275
	NH3-N		0.13
4.5 hours	Total	7.91	3
	Free		0
	Mono		2.63
	Di-		0.241
	NH3-N		0.12
24 hours	Total	8	2.8
	Free		0
	Mono		2.6
	Di-		0.22
	NH3-N		0.09

Table C-3. Chlorine residuals and ammonia for 5:1 ratio of Cl_2: N under well mixed condition for regular tap water

5:1 → Cl_2:N			
sampling time		**pH**	**Chlorine Residuals**
30 min	Total	8	3.5
	Free		0.14
	Mono		3.2
	Di-		0.2
	NH3-N		0.2
2.5 hours	Total	7.89	3.2
	Free		0.05
	Mono		2.84
	Di-		0.265
	NH3-N		0.15
4.5 hours	Total	7.94	3.1
	Free		0
	Mono		2.8
	Di-		0.239
	NH3-N		0.1
24 hours	Total	8.1	2.9
	Free		0
	Mono		2.76
	Di-		0.201
	NH3-N		0.07

OSGH- Straight Pipeline

Table C-4. Chlorine residual for straight pipeline and OSGH solution Q=150 L/min

Q (L/min)	q chlorine (1st) (mL/min)	q ammonia (2nd) (mL/min)	Target Cl (mg/L)
150.14	92.39	1.20	4.0
TCl = 0.1 mg/L	MCl = 0.09 mg/L	NH3-N = 0.0 mg/L	center-center injection

Pipeline samples		**pH**		**pH**	
30 min	Total	8.13	2.5	8.5	2.7
	Free		0.2		0.15
	Mono		1.77		1.74
	Di-		0.25		0.2
	NH3-N		0		0
24 hours	Total	7.99	1.2	8.31	1.2
	Free		0.15		<0.1
	Mono		0.75		1
	Di-		0.09		0.19
	NH3-N		0.13		0.12

well mixed		**pH**	
30 min	Total	8.21	3.9
	Free		0.25
	Mono		3.38
	Di-		0.195
	NH3-N		0.01
24 hours	Total	8.06	1.9
	Free		0
	Mono		1.7
	Di-		0.185
	NH3-N		0.04

Table C-5. Chlorine residual for straight pipeline and OSGH solution, Q= 300 L/min

Q (L/min)	q chlorine (1st) (mL/min)	q ammonia (2nd) (mL/min)	Target Cl (mg/L)
300.28	184.79	2.40	4.0
TCl = 0.1 mg/L	MCl = 0.09 mg/L	NH3-N = 0.0 mg/L	center-center injection

Pipeline samples			**8min**	**pH**	
30 min	Total	8.03	2	8.5	2.3
	Free		<0.1		0.15
	Mono		1.87		2.15
	Di-		0.25		0.2
	NH3-N		0		0
24 hours	Total	8	1	8.45	1.4
	Free		<0.1		<0.1
	Mono		0.83		1.29
	Di-		0.2		0.19
	NH3-N		0.04		0.02

well mixed		**pH**	
30 min	Total	8.5	3.9
	Free		0.15
	Mono		3.38
	Di-		0.195
	NH3-N		0.09
24 hours	Total	7.89	2.3
	Free		<0.1
	Mono		2.09
	Di-		0.145
	NH3-N		0.1

Table C-6. Chlorine residual for straight pipeline and OSGH solution, Q= 600 L/min

Q (L/min)	q chlorine (1st) (mL/min)	q ammonia (2nd) (mL/min)	Target Cl (mg/L)
600.56	369.6	4.80	4.0
TCl = 0.2 mg/L	MCl = 0.13 mg/L	NH3-N = 0.0 mg/L	center-center injection

Pipeline samples		**pH**		**pH**	
30 min	Total	7.93	2.1	8.4	2.1
	Free		<0.1		<0.1
	Mono		1.93		2.3
	Di-		0.29		0.175
	NH3-N		0		0
24 hours	Total	8.02	1.4	8.44	1.6
	Free		0		0
	Mono		1.12		1.418
	Di-		0.295		0.115
	NH3-N		0.03		0.01

well mixed		**pH**	
30 min	Total	8.21	3.9
	Free		0.25
	Mono		3.38
	Di-		0.195
	NH3-N		0.01
24 hours	Total	8.06	1.9
	Free		0
	Mono		1.7
	Di-		0.185
	NH3-N		0.04

Table C-7. Chlorine residual for straight pipeline and OSGH solution, Q= 1200 L/min

Q (L/min)	q chlorine (1st) (mL/min)	q ammonia (2nd) (mL/min)	Target Cl (mg/L)
1201	739.2	9.61	4.0
TCl = 0.1 mg/L	MCl = 0.09 mg/L	NH3-N = 0.0 mg/L	center-center injection

Pipeline samples		**pH**		**pH**	
30 min	Total	8.08	3.5	8.5	3.4
	Free		0.11		0.15
	Mono		2.83		3.03
	Di-		0.32		0.205
	NH3-N		0.1		0
24 hours	Total	8.06	1.5	8.33	1.6
	Free		<0.1		0
	Mono		1.35		1.5
	Di-		0.18		0.23
	NH3-N		0.06		0.09

well mixed		**pH**	
30 min	Total	8.5	3.9
	Free		0.15
	Mono		3.38
	Di-		0.195
	NH3-N		0.09
24 hours	Total	7.89	2.3
	Free		<0.1
	Mono		2.09
	Di-		0.145
	NH3-N		0.1

HSH- Straight Pipeline

Table C-8. Chlorine residual for straight pipeline and HSH solution, Q= 150 L/min

Q (L/min)	q chlorine (1st) (mL/min)	q ammonia (2nd) (mL/min)	Target Cl (mg/L)
150.14	6.99	1.20	4.0
TCl = 0.1 mg/L	MCl = 0.09 mg/L	NH3-N = 0.0 mg/L	center-center injection

Pipeline samples		**pH**		**pH**	
30 min	Total	8.03	2.2	8.68	2.4
	Free		<0.1		0.17
	Mono		1.61		1.97
	Di-		0.29		0.187
	NH3-N		0.02		0
24 hours	Total	8.02	1.1	8.73	1.7
	Free		0		0
	Mono		1.005		1.515
	Di-		0.17		0.165
	NH3-N		0.02		0.03

well mixed		**pH**	
30 min	Total	8.01	3.4
	Free		0.1
	Mono		2.565
	Di-		0.285
	NH3-N		0.02
24 hours	Total	8.01	1.7
	Free		0
	Mono		1.485
	Di-		0.15
	NH3-N		0.08

Table C-9. Chlorine residual for straight pipeline and HSH solution, Q= 300 L/min

Q (L/min)	q chlorine (1st) (mL/min)	q ammonia (2nd) (mL/min)	Target Cl (mg/L)
150.14	13.97	2.40	4.0
TCl = 0.1 mg/L	MCl = 0.1 mg/L	NH3-N = 0.02 mg/L	center-center injection

Pipeline samples		**pH**		**pH**	
30 min	Total	8.13	2.3	8.65	2.5
	Free		0.1		<0.1
	Mono		1.97		2.15
	Di-		0.25		0.18
	NH3-N		0		0
24 hours	Total	8.1	1.1	8.68	1.9
	Free		<0.1		<0.1
	Mono		0.98		1.69
	Di-		0.2		0.17
	NH3-N		0.04		0.04

well mixed		**pH**	
30 min	Total	8.01	3.4
	Free		0.1
	Mono		2.565
	Di-		0.285
	NH3-N		0.02
24 hours	Total	8.01	1.7
	Free		0
	Mono		1.485
	Di-		0.15
	NH3-N		0.08

Table C-10. Chlorine residual for straight pipeline and HSH solution, Q= 600 L/min

Q (L/min)	q chlorine (1st) (mL/min)	q ammonia (2nd) (mL/min)	Target Cl (mg/L)
600.56	27.93	4.80	4.0
TCl = 0.2 mg/L	MCl = 0.1 mg/L	NH3-N = 0.03 mg/L	center-center injection

Pipeline samples		**pH**		**pH**	
30 min	Total	8.03	2.8	8.73	3
	Free		0.1		0.168
	Mono		2.18		2.44
	Di-		0.41		0.216
	NH3-N		0.06		0.05
24 hours	Total	8.09	1.9	8.72	2
	Free		0		0
	Mono		1.261		1.519
	Di-		0.21		0.145
	NH3-N		0.11		0.12

well mixed		**pH**	
30 min	Total	8.21	3.8
	Free		0.3
	Mono		2.795
	Di-		0.245
	NH3-N		0.09
24 hours	Total	8.04	1.9
	Free		0<0.1
	Mono		1.65
	Di-		0.12
	NH3-N		0.17

Table C-11. Chlorine residual for straight pipeline and HSH solution, Q= 1200 L/min

Q (L/min)	q chlorine (1st) (mL/min)	q ammonia (2nd) (mL/min)	Target Cl (mg/L)
1201	55.87	9.61	4.0
TCl = 0.1 mg/L	MCl = 0.09 mg/L	NH3-N = 0.03 mg/L	center-center injection

Pipeline samples		**pH**		**pH**	
30 min	Total	8.15	3.5	8.9	3.9
	Free		0.182		0
	Mono		2.678		2.76
	Di-		0.545		0.31
	NH3-N		0.05		0.07
24 hours	Total	8.03	1.8	8.79	1.7
	Free		<0.1		0
	Mono		1.31		1.63
	Di-		0.325		0.25
	NH3-N		0.13		0.14

well mixed		**pH**	
30 min	Total	8.21	3.8
	Free		0.3
	Mono		2.795
	Di-		0.245
	NH3-N		0.09
24 hours	Total	8.04	1.9
	Free		0<0.1
	Mono		1.65
	Di-		0.12
	NH3-N		0.17

OSGH- Before Bend

Table C-12. Chlorine residual for before bend condition and OSGH solution, Q= 150 L/min

Q (L/min)	q chlorine (1st) (mL/min)	q ammonia (2nd) (mL/min)	Target Cl (mg/L)
150.14	92.39	1.20	4.0
TCl = 0.2 mg/L	MCl = 0.14 mg/L	NH3-N = 0.03 mg/L	center-center injection

Pipeline samples		**pH**		**pH**	
30 min	Total	8.29	2.3	8.69	2.5
	Free		0.5		0.2
	Mono		1.6		1.76
	Di-		0.225		0.26
	NH3-N		0.07		0.03
24 hours	Total	8.19	0.8	8.49	0.5
	Free		0.05		0
	Mono		0.61		0.285
	Di-		0.106		0.14
	NH3-N		0.13		0.11

well mixed		**pH**	
30 min	Total	8.12	3.5
	Free		0.02
	Mono		3.09
	Di-		0.29
	NH3-N		0
24 hours	Total	8.12	1.8
	Free		0.05
	Mono		1.52
	Di-		0.3
	NH3-N		0.12

Table C-13. Chlorine residual for before bend condition and OSGH solution, Q= 300 L/min

Q (L/min)	q chlorine (1st) (mL/min)	q ammonia (2nd) (mL/min)	Target Cl (mg/L)
300.28	184.79	2.40	4.0
TCl = 0.2 mg/L	MCl = 0.14 mg/L	NH3-N = 0.03 mg/L	center-center injection

Pipeline samples		**pH**		**pH**	
30 min	Total	8.5	2.4	8.74	3
	Free		0.05		0.09
	Mono		1.9		2.01
	Di-		0.2		0.245
	NH3-N		0.06		0.02
24 hours	Total	8.28	0.8	8.48	0.8
	Free		0		0
	Mono		0.625		0.42
	Di-		0.14		0.2
	NH3-N		0.18		0.19

well mixed		**pH**	
30 min	Total	8.12	3.5
	Free		0.02
	Mono		3.09
	Di-		0.29
	NH3-N		0
24 hours	Total	8.12	1.8
	Free		0.05
	Mono		1.52
	Di-		0.3
	NH3-N		0.12

Table C-14. Chlorine residual for before bend condition and OSGH solution, Q= 600 L/min

Q (L/min)	q chlorine (1st) (mL/min)	q ammonia (2nd) (mL/min)	Target Cl (mg/L)
600.56	369.6	4.80	4.0
TCl = 0.2 mg/L	MCl = 0.14 mg/L	NH3-N = 0.03 mg/L	center-center injection

Pipeline samples		**pH**		**pH**	
30 min	Total	8.25	2.6	8.95	3.1
	Free		0.21		0.34
	Mono		2.15		2.6
	Di-		0.265		0.17
	NH3-N		0.14		0.03
24 hours	Total	8.16	1	8.97	1.4
	Free		0		0
	Mono		0.708		1.3
	Di-		0.31		0.11
	NH3-N		0.12		0.06

well mixed		**pH**	
30 min	Total	8.12	3.5
	Free		0.02
	Mono		3.09
	Di-		0.29
	NH3-N		0
24 hours	Total	8.12	1.8
	Free		0.05
	Mono		1.52
	Di-		0.3
	NH3-N		0.12

Table C-15. Chlorine residual for before bend condition and OSGH solution, Q= 1200 L/min

Q (L/min)	q chlorine (1st) (mL/min)	q ammonia (2nd) (mL/min)	Target Cl (mg/L)
1201	739.2	9.60	4.0
TCl = 0.2 mg/L	MCl = 0.14 mg/L	NH3-N = 0.03 mg/L	center-center injection

Pipeline samples		**pH**		**pH**	
30 min	Total	8.19	2.5	8.72	2.9
	Free		0		0.13
	Mono		2.23		2.74
	Di-		0.315		0.18
	NH3-N		0		0.01
24 hours	Total	8	1.2	8.48	1.4
	Free		0		0
	Mono		0.92		1.18
	Di-		0.21		0.2
	NH3-N		0.1		0.09

well mixed		**pH**	
30 min	Total	8.12	3.5
	Free		0.02
	Mono		3.09
	Di-		0.29
	NH3-N		0
24 hours	Total	8.12	1.8
	Free		0.05
	Mono		1.52
	Di-		0.3
	NH3-N		0.12

HSH- Before Bend

Table C-16. Chlorine residual for before bend condition and HSH solution, Q= 150 L/min

Q (L/min)	q chlorine (1st) (mL/min)	q ammonia (2nd) (mL/min)	Target Cl (mg/L)
150.14	6.99	1.20	4.0
TCl = 0.1 mg/L	MCl = 0.07 mg/L	NH3-N = 0.0 mg/L	center-center injection

Pipeline samples		**pH**		**pH**	
30 min	Total	8.36	2.7	8.66	3.0
	Free		0.85		0.88
	Mono		1.6		1.86
	Di-		0.23		0.211
	NH3-N		0.05		0.06
24 hours	Total	8.29	0.9	8.48	1
	Free		0		0.1
	Mono		0.68		0.88
	Di-		0.19		0.178
	NH3-N		0.22		0.23

well mixed		**pH**	
30 min	Total	8.18	3.5
	Free		0.1
	Mono		3.07
	Di-		0.305
	NH3-N		0
24 hours	Total	8.11	1.5
	Free		0
	Mono		1.32
	Di-		0.165
	NH3-N		0.09

Table C-17. Chlorine residual for before bend condition and HSH solution, Q= 300 L/min

Q (L/min)	q chlorine (1st) (mL/min)	q ammonia (2nd) (mL/min)	Target Cl (mg/L)
300.28	13.97	2.40	4.0
TCl = 0.1 mg/L	MCl = 0.09 mg/L	NH3-N = 0.0 mg/L	center-center injection

Pipeline samples		**pH**		**pH**	
30 min	Total	8.64	3.3	8.86	3.2
	Free		0.95		0.9
	Mono		2.1		2.17
	Di-		0.249		0.23
	NH3-N		0.08		0.06
24 hours	Total	8.37	1.0	8.59	1.0
	Free		0.07		0.11
	Mono		0.802		0.81
	Di-		0.23		0.2
	NH3-N		0.27		0.28

well mixed		**pH**	
30 min	Total	8.18	3.5
	Free		0.1
	Mono		3.07
	Di-		0.305
	NH3-N		0
24 hours	Total	8.11	1.5
	Free		0
	Mono		1.32
	Di-		0.165
	NH3-N		0.09

Table C-18. Chlorine residual for before bend condition and HSH solution, Q= 600 L/min

Q (L/min)	q chlorine (1st) (mL/min)	q ammonia (2nd) (mL/min)	Target Cl (mg/L)
600.56	27.93	4.80	4.0
TCl = 0.1 mg/L	MCl = 0.14 mg/L	NH3-N = 0.03 mg/L	center-center injection

Pipeline samples		**pH**		**pH**	
30 min	Total	8.24	2.6	8.49	2.4
	Free		0.36		0.29
	Mono		1.66		1.77
	Di-		0.385		0.35
	NH3-N		0		0
24 hours	Total	8.29	1.2	8.52	1.2
	Free		0		0
	Mono		0.83		0.9
	Di-		0.265		0.22
	NH3-N		0.11		0.1

well mixed		**pH**	
30 min	Total	8.48	3.2
	Free		0.225
	Mono		2.98
	Di-		0.3
	NH3-N		0.01
24 hours	Total	8.22	1.9
	Free		0.15
	Mono		1.43
	Di-		0.17
	NH3-N		0.13

Table C-19. Chlorine residual for before bend condition and HSH solution, Q= 1200 L/min

Q (L/min)	q chlorine (1st) (mL/min)	q ammonia (2nd) (mL/min)	Target Cl (mg/L)
1201	55.87	9.61	4.0
TCl = 0.1 mg/L	MCl = 0.07 mg/L	NH3-N = 0.01 mg/L	center-center injection

Pipeline samples		**pH**		**pH**	
30 min	Total	8.25	3.2	8.63	3.5
	Free		0		0
	Mono		2.7		3.0
	Di-		0.395		0.28
	NH3-N		0		0
24 hours	Total	8.08	1.5	8.43	1.7
	Free		0.215		0
	Mono		0.98		1.155
	Di-		0.28		0.22
	NH3-N		0.08		0.11

well mixed		**pH**	
30 min	Total	8.18	3.5
	Free		0.1
	Mono		3.07
	Di-		0.305
	NH3-N		0
24 hours	Total	8.11	1.5
	Free		0
	Mono		1.32
	Di-		0.165
	NH3-N		0.09

OSGH- On Bend

Table C-20. Chlorine residual for on bend condition and OSGH solution, Q= 150 L/min

Q (L/min)	q chlorine (1st) (mL/min)	q ammonia (2nd) (mL/min)	Target Cl (mg/L)
150.14	92.39	1.20	4.0
TCl = 0.2 mg/L	MCl = 0.08 mg/L	NH3-N = 0.02 mg/L	center-center injection

Pipeline samples		**pH**		**pH**	
30 min	Total	8.28	2.6	8.53	2.4
	Free		0.217		0.285
	Mono		1.76		1.82
	Di-		0.301		0.229
	NH3-N		0.01		0.01
24 hours	Total	8.21	0.6	8.49	0.4
	Free		0		0
	Mono		0.408		0.165
	Di-		0.109		0.118
	NH3-N		0.17		0.19

well mixed		**pH**	
30 min	Total	8.24	3.8
	Free		0.14
	Mono		3.23
	Di-		0.412
	NH3-N		0
24 hours	Total	8.33	2.7
	Free		0.18
	Mono		2.36
	Di-		0.145
	NH3-N		0.18

Table C-21. Chlorine residual for on bend condition and OSGH solution, Q= 300 L/min

Q (L/min)	q chlorine (1st) (mL/min)	q ammonia (2nd) (mL/min)	Target Cl (mg/L)
300.28	184.79	2.40	4.0
TCl = 0.2 mg/L	MCl = 0.08 mg/L	NH3-N = 0.02 mg/L	center-center injection

Pipeline samples		**pH**		**pH**	
30 min	Total	8.31	2.6	8.68	2.5
	Free		0.3		0.245
	Mono		1.91		2.1
	Di-		0.34		0.25
	NH3-N		0.02		0
24 hours	Total	8.2	0.8	8.61	0.3
	Free		0.105		0
	Mono		0.578		0.165
	Di-		0.15		0.118
	NH3-N		0.21		0.19

well mixed		**pH**	
30 min	Total	8.24	3.8
	Free		0.14
	Mono		3.23
	Di-		0.412
	NH3-N		0
24 hours	Total	8.33	2.7
	Free		0.18
	Mono		2.36
	Di-		0.145
	NH3-N		0.18

Table C-22. Chlorine residual for on bend condition and OSGH solution, Q= 600 L/min

Q (L/min)	q chlorine (1st) (mL/min)	q ammonia (2nd) (mL/min)	Target Cl (mg/L)
600.56	369.6	4.80448	4.0
TCl = 0.2 mg/L	MCl = 0.08 mg/L	NH3-N = 0.02 mg/L	center-center injection

Pipeline samples		**pH**	**6min**	**pH**	**6 min**
30 min	Total	8.29	2.7	8.63	2.7
	Free		0.09		0.15
	Mono		1.835		1.84
	Di-		0.25		0.215
	NH3-N		0		0
24 hours	Total	8.2	0.7	8.58	0.4
	Free		0		0
	Mono		0.454		0.24
	Di-		0.18		0.11
	NH3-N		0.12		0.06

well mixed		**pH**	
30 min	Total	8.24	3.8
	Free		0.14
	Mono		3.23
	Di-		0.412
	NH3-N		0
24 hours	Total	8.33	2.7
	Free		0.18
	Mono		2.36
	Di-		0.145
	NH3-N		0.18

Table C-23. Chlorine residual for on bend condition and OSGH solution, Q= 1200 L/min

Q (L/min)	q chlorine (1st) (mL/min)	q ammonia (2nd) (mL/min)	Target Cl (mg/L)
1201	739.2	9.60	4.0
TCl = 0.2 mg/L	MCl = 0.08 mg/L	NH3-N = 0.02 mg/L	center-center injection

Pipeline samples		**pH**		**pH**	
30 min	Total	8.19	2.2	8.72	2.6
	Free		0.09		0.195
	Mono		1.59		1.56
	Di-		0.35		0.325
	NH3-N		0.01		0
24 hours	Total	8	0.6	8.48	0.2
	Free		0.1		0
	Mono		0.316		0.135
	Di-		0.14		0.075
	NH3-N		0.16		0.11

well mixed		**pH**	
30 min	Total	8.24	3.8
	Free		0.14
	Mono		3.23
	Di-		0.412
	NH3-N		0
24 hours	Total	8.33	2.7
	Free		0.18
	Mono		2.36
	Di-		0.145
	NH3-N		0.18

HSH- On Bend

Table C-24. Chlorine residual for on bend condition and HSH solution, Q= 150 L/min

Q (L/min)	q chlorine (1st) (mL/min)	q ammonia (2nd) (mL/min)	Target Cl (mg/L)
150.14	6.99	1.20	4.0
TCl = 0.2 mg/L	MCl = 0.07 mg/L	NH3-N = 0.01 mg/L	center-center injection

Pipeline samples		**pH**		**pH**	
30 min	Total	8.22	2.9	8.56	3.1
	Free		0.6		0.61
	Mono		1.9		2
	Di-		0.365		0.314
	NH3-N		0		0
24 hours	Total	8.12	1.0	8.43	1.1
	Free		0.1		0.09
	Mono		0.76		0.82
	Di-		0.256		0.201
	NH3-N		0.12		0.14

well mixed		**pH**	
30 min	Total	8.48	3.6
	Free		0.225
	Mono		2.96
	Di-		0.44
	NH3-N		0.01
24 hours	Total	8.22	2.7
	Free		0.15
	Mono		2.215
	Di-		0.27
	NH3-N		0.13

Table C-25. Chlorine residual for on bend condition and HSH solution, Q= 300 L/min

Q (L/min)	q chlorine (1st) (mL/min)	q ammonia (2nd) (mL/min)	Target Cl (mg/L)
300.28	13.97	2.40	4.0
TCl = 0.2 mg/L	MCl = 0.07 mg/L	NH3-N = 0.01 mg/L	center-center injection

Pipeline samples		**pH**		**pH**	
30 min	Total	8.22	3.2	8.6	3.5
	Free		0.75		0.6
	Mono		2.1		2.08
	Di-		0.38		0.28
	NH3-N		0		0
24 hours	Total	8.16	1.3	8.47	1.3
	Free		0.135		0.12
	Mono		0.8		0.966
	Di-		0.35		0.2
	NH3-N		0.15		0.14

well mixed		**pH**	
30 min	Total	8.48	3.6
	Free		0.225
	Mono		2.96
	Di-		0.44
	NH3-N		0.01
24 hours	Total	8.22	2.7
	Free		0.15
	Mono		2.215
	Di-		0.27
	NH3-N		0.13

Table C-26. Chlorine residual for on bend condition and HSH solution, Q= 600 L/min

Q (L/min)	q chlorine (1st) (mL/min)	q ammonia (2nd) (mL/min)	Target Cl (mg/L)
600.56	27.93	4.80	4.0
TCl = 0.2 mg/L	MCl = 0.07 mg/L	NH3-N = 0.01 mg/L	center-center injection

Pipeline samples		**pH**		**pH**	
30 min	Total	8.27	2.8	8.52	2.5
	Free		0.155		0.125
	Mono		1.8		1.75
	Di-		0.38		0.3
	NH3-N		0		0
24 hours	Total	8.29	1.1	8.55	1.2
	Free		0.08		0.07
	Mono		0.62		0.785
	Di-		0.31		0.165
	NH3-N		0.09		0.11

well mixed		**pH**	
30 min	Total	8.48	3.6
	Free		0.225
	Mono		2.96
	Di-		0.44
	NH3-N		0.01
24 hours	Total	8.22	2.7
	Free		0.15
	Mono		2.215
	Di-		0.27
	NH3-N		0.13

Table C-27. Chlorine residual for on bend condition and HSH solution, Q= 1200 L/min

Q (L/min)	q chlorine (1st) (mL/min)	q ammonia (2nd) (mL/min)	Target Cl (mg/L)
1201	55.87	9.60	4.0
TCl = 0.2 mg/L	MCl = 0.07 mg/L	NH3-N = 0.01 mg/L	center-center injection

Pipeline samples		**pH**		**pH**	
30 min	Total	8.2	2.9	8.3	2.8
	Free		0.325		0.28
	Mono		1.77		1.69
	Di-		0.23		0.33
	NH3-N		0.01		0.02
24 hours	Total	8.22	0.7	8.4	0.6
	Free		0.05		0
	Mono		0.35		0.38
	Di-		0.29		0.125
	NH3-N		0.14		0.15

well mixed		**pH**	
30 min	Total	8.2	3.6
	Free		0.225
	Mono		2.96
	Di-		0.44
	NH3-N		0.01
24 hours	Total	8.21	2.7
	Free		0.15
	Mono		2.215
	Di-		0.27
	NH3-N		0.13

Effect of Dilution Ratio on MCl Recovery for Injection into Straight Pipeline

Table C-28. Percentage of MCl recovered compared to TCl from OSGH and HSH solutions in straight pipeline after 30 min and 24 hrs

fps	OSGH MCl (%)- 30 min	OSGH MCl (%)- 24 hrs	HSH MCl (%)- 30 min	HSH MCl (%)- 24 hrs
1	70.8	62.5	72.7	91.4
2	93.5	83	85.6	89.1
4	91.9	80	77.8	66.3
8	85.8	90	76.6	72.8

Effect of Dilution Ratio on MCl Recovery under Injection Before Bend Condition

Table C-29. Percentage of MCl recovered compared to TCl from OSGH and HSH solutions for before bend injection condition after 30 min and 24 hrs

fps	OSGH MCl (%)- 30 min	OSGH MCl (%)- 24 hrs	HSH MCl (%)- 30 min	HSH MCl (%)- 24 hrs
1	69.6	76.3	59.3	75.6
2	79.2	78.1	63.6	80.2
4	82.7	70.8	63.8	69.2
8	89.2	61.3	84.4	65.3

Effect of Dilution Ratio on MCl Recovery under Injection On Bend Condition

Table C-30. Percentage of MCl recovered compared to TCl from OSGH and HSH solutions for on bend injection condition after 30 min and 24 hrs

fps	OSGH MCl (%)- 30 min	OSGH MCl (%)- 24 hrs	HSH MCl (%)- 30 min	HSH MCl (%)- 24 hrs
1	67.7	70.5	65.5	76
2	73.5	72.3	65.6	61.5
4	68.1	64.8	64.3	56.4
8	72.7	52.7	61.0	50

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