UNIVERSITY OF CALIFORNIA

LOS ANGELES

Modeling of Chlorination Breakpoint

A thesis submitted in partial satisfaction of the requirements for the degree Master of Science in Civil Engineering

by

Linling Shen

2014

UMI Number: 1560931

UMI

Dissertation Publishing

UMI 1560931

ProQuest®

ABSTRACT OF THE THESIS

Modeling of Chlorination Breakpoint

by

Linling Shen

Master of Science in Civil Engineering

University of California, Los Angeles, 2014

Professor Michael K. Stenstrom, Chair

The dynamics of breakpoint chlorination has been widely studied by a number of investigators. In this thesis four previously developed chlorination reaction schemes and simulation models were reviewed and discussed. The approach by Stenstrom & Tran was best fit. In order to have quantitative results of the breakpoint reactions, a mathematical model consisting of eight simultaneous ordinary differential equations (ODE) was examined. The eight ODEs are simultaneously solved with ode23s function in MATLAB, which is based on second and fourth-order Runge-Kutta formulas. The reaction rate coefficients were estimated through an optimization technique, which

sought the minima of the sum of squares of the difference between the predicted and

observed values. Results illustrated an agreement between the predicted values and the

experimental observations based on Wei's data.

The thesis of Linling Shen is approved.

Keith D. Stolzenbach

Jennifer A. Jay

Michael K. Stenstrom, Committee Chair

University of California, Los Angeles

2014

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

ACKNOWLEDGEMENTS

I will forever grateful to my advisor Dr. Michael K. Stenstrom, not only for his guidance and assistance in completing this thesis, but for his patience and encouragement. His encyclopedic knowledge motivated me to conduct the study and finish the thesis.

I would also like to thank the rest members of my thesis committee: Professor. Keith D. Stolzenbach and Professor. Jennifer A. Jay. The comments made by the committee greatly improve my understanding of this study, and I really appreciate their kind help.

Finally, without my parents Jiming Shen and Lijun Zhou, my boyfriend's irreplaceable love, I may not be able to finish this thesis. I wish to express my gratitude to them.

1 Introduction

Disinfection, a key component of water treatment, is used to ensure that water is free of microbial pathogens for safe consumption. One of the most important disinfectants is chlorine. Chlorine has traditionally been used for disinfection and because of its cost-effectiveness and broad ability for inactivating pathogenic microorganisms, it continues to play a crucial role in disinfecting drinking water and wastewater in the U.S. In addition, chlorine has widespread use in controlling odors and removing color from drinking water, removal of iron, manganese via redox reactions, as well as reducing bio-fouling in power plant condensers. Chlorine can also be employed to eliminate ammonia nitrogen from drinking water and wastewater through oxidation reactions, and the process is generally referred to as breakpoint chlorination. When added to water, chlorine rapidly hydrolyzes to form aqueous free chlorine, which reacts with any ammonia to have different products. Monochloramine, dichloramine and nitrogen trichloride are produced by the substitution reactions while redox reactions result in nitrogen gas, nitrate, and the chloride ion. For disinfection purposes, monochloramine is often regarded as the most desirable species due to its stable chemical characteristics and biocidal property.

In the early 1970's, it was discovered that chlorination could create undesirable byproducts if not well controlled, producing chlorinated organic compounds,

particularly the carcinogenic trihalomethanes (THM's), which are harmful to humans and aquatic life (Rook 1974). This can be problematic, leading to unstable disinfectant residuals, higher coliform counts, and nitrification issues. Better process control can weaken these problems, and reduce chlorine dosage, which in turn decreases the operating cost. Moreover, formation of chloramine and maintenance of good disinfection effect requires careful control and management. A dynamic mathematic model, which can practically predict the performance of the process, is a useful tool for process control. Ideally, having an understanding of the chlorine ammonia reaction system can be conducive to maximizing the effectiveness of chlorination processes while minimizing undesirable impacts.

The primary goal in this thesis is to develop a better understanding of the breakpoint chlorination mechanism using a kinetic simulation model of such process based on experimental observations with the aim to provide a rational basis for process control and operation. Wei's (1974) data was selected as the most useful from five data sets.

The specific objectives of this thesis are:

1. Better understand the chlorine-ammonia reaction scheme.

2. Develop a mathematical model for the breakpoint chlorination reactions based on Wei's experimental data.

3. Improve estimation technique for kinetic parameters by adoption of an optimization strategy.

4. Evaluate effects of pH and temperature on the phenomena

5. Discuss different trends of parameters under various kinds of conditions.

2 Literature review

Chlorine was first discovered in Sweden in 1744. At that time, people believed that odors from water could transmit diseases and they used chlorine to remove odors from the water. The initial use of water chlorination dated back to 1846 when Semmelweis added chlorine to water as a germicide at the Vienna General hospital. Since then chlorine was found to be an effective tool for destruction of many microorganisms associated with waterborne diseases, such as typhoid, cholera, dysentery, and gastro-enteritis. People who died from these diseases exceed the people killed during all wars in history. With this new discovery, chlorination began to be adopted in Belgium (1903) and Great Britain (1905) as a potable water disinfectant. In the U.S., the first attempt to use chlorine to disinfect drinking water supplies took place in 1908 at the Boonton Reservoir in New Jersey (McGuire 2013) and later spread to Canada in 1917. Its use has grown each year and the trend has continued until recently. Undoubtedly, chlorine and its derivatives are the most commonly used disinfectants and their discovery has been one of the most significant advances in public health. A better understanding of chlorine chemistry can help improve current chlorination processes.

2.1 Basics of chlorination chemistry

Chlorine is a strong oxidant and can undergo considerable reactions when in contact

with water and other compounds.

2.1.1 Hydrolysis reaction

Gaseous chlorine, when injected into water, dissolves according to Henry's law and rapidly reacts with water to form hypochlorous acid and hydrochloric acid as follows:

$$Cl_2(g) + H_2O \rightleftharpoons HOCl + H^+ + Cl^- \tag{1}$$

The hydrolysis constant has been widely studied and was defined as follows:

$$K_{HYD} = \frac{[HOCl][H^+][Cl^-]}{[Cl_2]}$$

Where: [] stands for the molar concentration

Connick and Chia (1959) presented hydrolysis constants of reaction of molecular chlorine with water as shown in Table 2-1. Later in 1978, the reaction rate of K_{HYD} was reevaluated by Margernm and Gray (1978) and the forward reaction rate constant was equal to 28.6 s^{-1}, which indicates that hydrolysis reaction is quite rapid, reaching equilibrium in a few tenths of a second.

Table 2-1 Chlorine hydrolysis constants at different temperatures

Temperature dependency of pK$_{HYD}$ for chlorine					
Temperature	0	15	25	35	45

(°C)					
pK$_{HYD}$	3.8356	3.5513	3.4045	3.2924	3.2182

From Connick and Chia, 1959

Hypochlorous acid is a weak acid and dissociates according to the following equation:

$$HOCl \rightarrow H^+ + OCl^-$$ (2)

The dissociation constant is defined as:

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} \quad K_a = \frac{[H^+][OCl^-]}{[HOCl]}$$

The value of K$_a$ is also temperature dependent. The hydrolysis dissociation constant was published by Morris (1966), is shown in Table 2-2 and has generally considered as reliable estimates.

Table 2-2 HOCl hydrolysis constants at different temperatures (Morris, 1966)

Temperature dependency of pK$_a$ for HOCl								
Temperature (°C)	0	5	10	15	20	25	30	35
pK$_a$	7.825	7.754	7.690	7.633	7.582	7.537	7.497	7.463

Distributions of various aqueous chlorine species over wide ranges of temperatures and pH levels are shown in Figure 2-1 (Deborde & von Gunten 2008), where the allocation of Cl$_2$, HOCl and ClO$^-$ is pH and temperature dependent. Over a pH range from 6 to 9,

which is typical in water treatment, hypochlorous acid and hypochlorite dominate. Cl_2 hydrolysis is almost complete at pH 4 as indicated in Figure 2-1. Therefore, Cl_2 can usually be ignored during water and wastewater treatment. As seen in this figure, the distribution of hypochlorous acid and hypochlorite acid is strongly impacted by pH values. It is well established that HOCl is a more rapid germicidal agent compared to the other chlorine species.
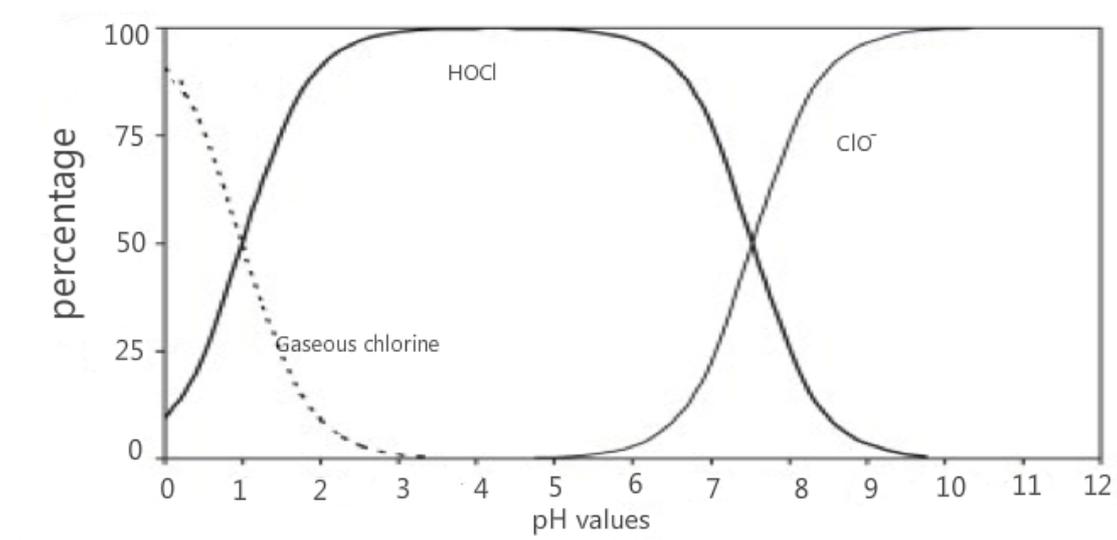
Figure 2-1 Relative distribution of main aqueous chlorine species as a function of pH at 25°C and for a chloride concentration of 5×10^{-3}M.

2.1.2 Chlorine reactions with Ammonia

2.1.2.1 Ammonia reaction with water

There are many sources of ammonia. In natural waters, it can be produced from the

decomposition of organic nitrogen compounds derived from plants and animals. In polluted waters, ammonia can originate from sewage effluent, agricultural runoff, decomposition of organic nitrogen compounds, and rainwater. In neutral pH water, ammonia is mainly present as the ammonium ion (NH_4^+). The hydrolysis reaction of NH_3 is described as follows:

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^-$$ (3)

The hydrolysis constant is defined as:

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

The value of K_b is temperature-dependent and excellent data of the ammonia dissociation constant by Bates and Pinching (1950) is reported in the Table 2-3.

Table 2-3 Ammonia hydrolysis constants at different temperatures (Bates and Pinching, 1950)

Temperature dependency of pK$_b$ for ammonia							
Temperature (°C)	0	5	10	15	20	25	30	35
pK$_b$	10.081	9.903	9.730	9.564	9.401	9.264	9.093	8.947

2.1.2.2 Monochloramine formation and hydrolysis reactions

Reaction (4) shows the formation of monochloramine and its hydrolysis reaction:

$$HOCl + NH_3 \rightleftharpoons NH_2Cl + H_2O$$ (4)

It was widely analyzed by Chapin (1929), Wei and Morris (1949), and Margerum and Gray (1978). In Morris' study, the forward reaction rate was estimated as 6.05×10^6 M^{-1} min^{-1} at 25°C. Margerum and Gray measured the same rate constant as 2.8×10^5 M^{-1} s^{-1} at 25°C in 0.1 M NaClO$_4$. Granstrom (1954) first proposed a reverse reaction which was reevaluated by Isaac and Morris (1983) with a rate of 2.1×10^{-5} s^{-1} at 25°C. The rate of monochloramine hydrolysis was also determined, which was found to be 1.9×10^{-5} s^{-1}.

2.1.2.3 Dichloramine formation and hydrolysis reactions

Two main pathways occur to form dichloramine. When free chlorine exists, it is produced directly from the reaction of monochloramine with free chlorine, as show below:

$$HOCl + NH_2Cl \rightleftarrows NHCl_2 + H_2O \tag{5}$$

Morris et al. (1951) reported the forward reaction rate constant to be a linear function of pH and equal to 24120 M^{-1} min^{-1} at 25°C and pH=7. Margerum and Gray (1978) estimated the forward constant to be equal to 150 $M^{-1}s^{-1}$ in 0.5 M NaClO$_4$ at 25°C and the reverse reaction constant to be 6.5×10^{-7} s^{-1} under the same conditions. Isaac and Morris (1983) experimentally found the forward and reverse reaction rates to be 350 M^{-1} s^{-1} and 7.6×10^{-7} s^{-1} respectively, at 25°C. However, it should be noted that the hydrolysis reaction is experimentally difficult to measure.

Another pathway to derive dichloramine is through disproportionation reaction of monochloramine, as shown below:

$$NH_2Cl + NH_2Cl \rightleftharpoons NHCl_2 + NH_3 \tag{6}$$

Granstrom (1954) was the first researcher to quantitatively study the disproportionation of monochloramine which produced dichloramine. A two-term expression was used to describe the reaction, as shown below.

$$d[NHCl_2]/dt = k_1[NH_2Cl] + k_2[NH_2Cl]^2$$

He also experimentally evaluated the rate constants and found them to be

$$k_1 = 5.2 \times 10^9 e^{(-17080/RT)} \, \text{min}^{-1}.$$

$$k_2 = k_{2a} + k_{2b}[H^+] + k_{2c}[HAC]$$
$$k_{2a} = 4.75 \times 10^3 e^{4310/RT} M^{-1} \, \text{min}^{-1}$$
$$k_{2b} = 6.3 \times 10^8 e^{4310/RT} M^{-2} \, \text{min}^{-1}$$
$$k_{2c} = 1.68 \times 10^5 e^{4310/RT} M^{-2} \, \text{min}^{-1}$$

Granstrom also made semi-qualitative observations on the effects of ionic strength and chloride ion catalysis. Neither reaction varied significantly due to the ionic strength effect.

2.1.2.4   Nitrogen Trichloride formation and decomposition reactions

The pathway of the formation of nitrogen trichloride was experimentally studied by Saguinsin and Morris (1975) over the pH range from 2.3 to 4.5 and confirmed the following two reactions:

$$HOCl + NHCl \rightarrow NCl_3 + H_2O \tag{7}$$

$$Cl_2 + NHCl_2 \rightarrow NCl_3 + H^+ + Cl^- \tag{8}$$

They found that reaction (8) only crucial when the pH is low (< 4). This was because dichloramine was unstable when free chlorine was present. It was impossible to isolate this reaction; therefore no particular pH-dependent relationship can be drawn from their data. Morris and Isaac (1983) deduced the rate constant of the reaction (7) at 2.1 M^{-1} s^{-1} at 25°C in order to match the observed data.

Saguinsin and Morris (1975) discovered that the hydrolysis of NCl_3 was pH dependent and the reaction rate to be $3.2 \times 10^{-5}(1 + 5.88 \times 10^5 [OH^-])$ s^{-1}.

$$NCl_3 + H_2O \rightarrow HOCl + NHCl_2 \tag{9}$$

The decomposition reaction of nitrogen trichloride was found to be strongly related to ammonia concentration and was assumed to be reduced by the reaction of NCl_3 and NH_3 as presented below:

$$NCl_3 + NH_3 \rightarrow NHCl_2 + NH_2Cl \tag{10}$$

11

2.2 Oxidation Stoichiometry

The stoichiometric ratio P is defined as the ratio of the moles of chlorine reduced to the moles of ammonia nitrogen oxidized. The moles of chlorine reduced could be calculated by subtracting the total chlorine residual from the initial molar dose of gaseous chlorine. The moles of ammonia nitrogen oxidized are equal to the sum of the nitrogenous final redox products. The ratio in aqueous solution of ammonia and chlorine should be calculated as follows:

$$P = \frac{C_1 - r}{n_1 - q}$$

Where:

C_1: initial molar dose of Cl_2

n_1: initial molar concentration of ammonia

r: total chlorine residual (molar concentration)

q: total ammonia nitrogen residual (molar concentration)

the terms r and q may represent the sums of the following:

r=C+M+2D+3E

q=N+M+D+E

Where C, N, M, D and E are molar concentrations of free chlorine, free ammonia, monochloramine, dichloramine, and nitrogen trichloride, respectively.

Table 2-4 shows various possible redox reaction end products for nitrogen and the corresponding stoichiometric ratio based on the assumption that the ammonia is oxidized entirely by the corresponding compounds indicated. If nitrogen were the only nitrogenous redox product, the P ratio would be 1.5 at breakpoint. Likewise, if the ammonia was entirely oxidized to nitrate, the ratio would be P=4.0.

Table 2-4 Stoichiometric ratio P for various possible products of ammonia

nitrogen and chlorine

Product	P ratio
N_2H_4	0.5
NH_2OH	1.0
N_2	1.5
N_2O	2.0
NO	2.5
NO_2^-	3.0

N_2O_4	3.5
NO_3^-	4.0

Palin (1949) proposed that nitrogen and small amounts of nitrate were the primary nitrogenous oxidation products formed in the breakpoint region. In his study, the P ratio was nearly 1.7, somewhat larger than the theoretical value of 1.5, which would be obtained if the nitrogen gas were the only product according to the following reaction:

$$2NH_3 + HOCl \rightarrow N_2 + 3Cl^- + 3H^+ + 3H_2O \tag{11}$$
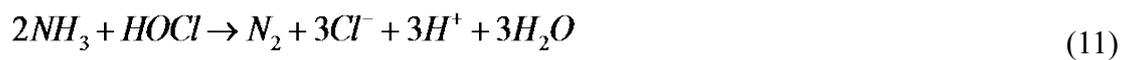
The amount of nitrate was found to rise when the pH and initial chlorine to ammonia ratio increased.

In Wei's data, the P ratio increased rapidly during the first 7 min or so and continued to surge for contact time greater than 20 min. It also boosted with the increasing initial chlorine to ammonia ratio. However, nitrogen trichloride was not determined in the study of Wei and Morris (1974).

2.3 Chemistry of chloramines in water

Chloramines are referred to as the group of monochloramine, dichloramine and nitrogen trichloride compounds. The process of forming these three chlorine species is

identified as chloramination, during which both chlorine and ammonia are added to water. For disinfection purposes, monochloramine is the most desirable species among these three due to its chemical stability and biocidal properties. The first utilization of chloramination as a drinking water disinfection process occurred in the 1920's . Later in the 1940's, the discovery of breakpoint chlorine reactions allowed operators to remove ammonia in order to obtain disinfection by the residual free chlorine . Chloramination, regarded as a secondary disinfectantion process produces monochloramine, which is less reactive and consequently results in fewer disinfection byproducts than free chlorine.

In the early 1920's, Houston (1925 and 1926) observed that chlorine used in excess could remove tastes and odors. In the following years, many operators adopted this process of super chlorination and by the mid 1930's many of them noticed that in some water when chlorine dose was raised, the residual would increase. However, as more chlorine was added, the residual would instead decrease, sometimes disappearing altogether. Choosing a chlorine dose beyond this point would create a new residual, which was very nearly proportional to the dosage. This phenomenon gave rise to the term of breakpoint chlorine dose-residual curve.

Griffin (1940) was the first investigator to study the reactions of chlorine and ammonia in an aqueous solution; he put forward the empirical breakpoint chlorination reactions:

$$NH_3 + HOCl \rightarrow NH_2Cl + H_2O \tag{12}$$

$$NH_2Cl + HOCl \rightarrow NHCl_2 + H_2O \tag{13}$$

$$NHCl_2 + HOCl \rightarrow NCl_3 + H_2O \tag{14}$$
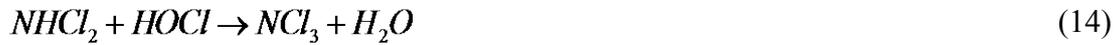
Where: NH_2Cl is monochloramine

$NHCl_2$ is dichloramine

$NHCl_3$ is nitrogen trichloride

These empirical equations were derived from the valences of nitrogen and chlorine, and only qualitatively describe breakpoint stoichiometry.

The kinetics and equilibrium concentrations of these reactions are related to temperatures and pH. The free chlorine residual is the total concentration of hypochlorous acid and the hypochlorite ion while the sum of monochloramine, dichloramine, and nitrogen trichloride compose the combined chlorine residual. The total chlorine residual is the sum of combined residual and free chlorine residual.

Figure 2-2 partially illustrates the reactions of these three compounds and their behaviors in three zones. As shown in zone 1, the total chlorine residual approximately increases proportional to the amount of chlorine added until the molar ratio reaches 1. Beyond a molar ratio of 1, the total chlorine residual decreases with the addition of chlorine, as depicted in zone 2. This is due to the oxidation of chloramine species by chlorine. Eventually, all the chloramines are oxidized and this point is called the

breakpoint, and is the beginning of zone 3. After passing the breakpoint, the free

chlorine residual increases proportionally to the amount of chlorine added. When water

contains other reducing contaminants (such as H_2S, Fe^{2+}, Mn^{7+} etc.), all three zones will

be shifted to the right. According to Palin and Johnson's study, in zone 1, the only

chloramine species is monochloramine at pH 8, while at pH 6, dichloramine exists

(Palin & Johnson 1975). In zone 2, ammonia can be oxidized to nitrogen gas and nitrate

by hypochlorous acid, leading to the reduction of chlorine residual. In Zone 2 the

residual mainly consists of monochloramine, dichloramine, and some free chlorine. At

low pH, traces of trichloramine may be present. The end products are a function of pH,

temperature, and initial chlorine concentration relative to initial ammonia nitrogen

concentration.
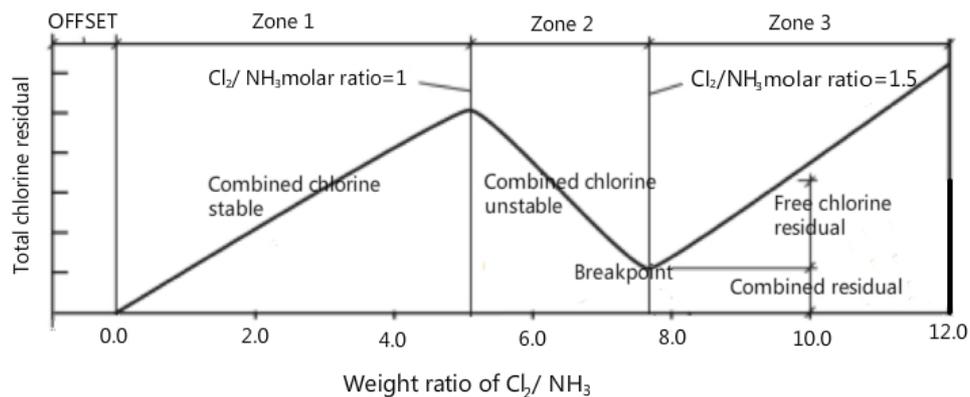
Figure 2-2 Chlorine reactions with ammonia nitrogen

2.4 Breakpoint kinetics and mechanisms

The mechanisms of breakpoint reactions have been widely analyzed by a number of researchers.

Chapin (1931) was the first researcher to study the conditions that affected the allocation and formation of the three chloramines. The results of his work revealed that at short reaction times, before the breakpoint:

1. Only monochloramine existed when pH was higher than 8.5

2. At pH range of 4.5 to 5, dichloramine predominated

3. At pH less than 4.4, in high concentrations of nitrogen trichloride were observed

4. At pH 7, the amount of monochloramine and dichloramine were approximately the same

However, due to the fact that these experiments were conducted in batch reactors with a high chlorine dose and at excessive ammonia concentration, his results did not reflect the practical conditions in the real waters or wastewaters. Chapin also performed experiments with different chlorine to ammonia molar ratios and observed the following overall reaction at pH=5 with a molar ratio of approximately 1.5:

$$3Cl_2 + 2NH_3 \rightarrow N_2 + 6HCl \tag{15}$$

Griffin (1940) was the first person to use the term "breakpoint" to describe the reactions between the chlorine and ammonia in an aqueous solution. In his experiments, the ammonia concentration was low and the pH was set to different values. The breakpoint occurred at molar ratio of chlorine to ammonia around 2.0 and the rate of the breakpoint reaction was observed to be the fastest at pH of 7 and 8.

Palin (1950) made a significantly large contribution to chlorination research. He developed both NOT-FAS and DFS-FAS analytical methods in order to perform the experiments at low ammonia concentrations, at different pH and chlorine dosages in the batch reactors. It was observed that at pH greater than 7.5, monochloramine was the predominant species. At pH greater than 8, the amount of dichloramine and nitrogen trichloride were insignificant. The reaction below indicated the loss of monochloramine:

$$2NH_2Cl + HOCl \rightarrow N_2 + 3HCl + H_20 \qquad (16)$$

Dichloramine was unstable and could be easily decomposed, which led to a loss of the total chlorine residual. The following two reactions suggested the mechanism for decomposition:

$$2NHCl_2 + H_2O \rightarrow N_2 + HOCl + 3HCl \qquad (17)$$

$$NHCl_2 + NH_2Cl \rightarrow N_2 + 3HCl \qquad (18)$$

Nitrogen trichloride and hypochlorous acid coexisted at the final stage and they were fairly stable:

$$NHCl_2 + HOCl \rightarrow NCl_3 + H_2O \tag{19}$$

Palin also proved that N_2 and NO_3^- were the two major nitrogen end products.

2.5 Comprehensive reaction models

Several models were proposed and developed by researchers to investigate the chloramine systems and test the postulated set of reactions occurring under the breakpoint region and combined conditions.

2.5.1 Model of Morris and Wei

Based on the previous studies, Wei and Morris (1974) were the first to propose an overall breakpoint reaction mechanism. They performed extensive kinetic experiments in batch laboratory reactors at three different pH values (6.7, 7.0 and 7.2), fixed chlorine to ammonia molar ratio of 1.8, over four temperatures to calibrate the proposed model. Table 2-5 summarizes the reaction scheme for the chlorination mechanism.

The initial steps represented by reaction R-1 and R-2 were well established and both reaction coefficients were estimated. Reaction R-3 accounted for the formation of nitrogen trichloride in acid and neutral solutions for chlorine doses in excess of the

breakpoint. Reaction R-4 was the reverse reaction of R-3. Both of these two reactions explained the presence of nitrogen trichloride as an intermediate. Reaction R-4 was quite slow; hence, NCl_3 often occurred at the end of the reaction system.

In their research, reactions R-2 and R-5 were the rate-limiting steps among the whole reaction system. Formed in reaction R-5, nitroxyl radical (NOH) was chosen as the key intermediate, which accounted for the loss of chlorine and ammonia, although it was acknowledged that other compounds might also be possible. Reactions of R-6, R-7 and R-8 were all hypothetical at that time. NOH was involved in all these three reactions, reacting with NH_2Cl, $NHCl_2$, and HOCl, respectively. It seemed logical to assume that if these reactions were more rapid compared to reaction 5, their absolute reaction rates would be of little concern. Only the competitive and simultaneous production of N_2 and NO_3^- were important. The combination of reactions R5 and R6 described the interaction of $NHCl_2$ and NH_2Cl, which was assumed to be the major reaction producing the breakpoint. Reaction R-7 showed the regeneration of hypochlorous acid. Nitrogen gas (N_2), nitrate (NO_3^-), and chloride ion (Cl^-) were the three end products of this reaction system.

They also tried to determine the orders of all these reactions. Orders of reactions R-1 and R-2 were known with a high certainty. Morris and Wei determined the rate of decomposition of dichloramine to be first-order with respect to dichloramine concentration and proportional to hydroxyl ion activity, which was observed from their

21

experiments. However, no indications were available for the orders of the other reactions. Uisng computer modeling, Morris and Wei made progress to overcome these hurdles. Comparisons between the modeled and observed data helped them revise the reaction orders improve data fit. They assumed overall second-order, and first-order for each reactants in R-6, R-7 and R-8. They hypothesized a second-order reaction for R-3 and a first-order reaction for R-4 improve fit between the data and model results.

Table 2-5 Breakpoint reaction mechanisms after Wei and Morris (1974)

Reaction	Rate Coefficient	
$HOCl + NH_3 \rightarrow NH_2Cl + H_2O$	k_1	R-1
$HOCl + NH_2Cl \rightarrow NHCl_2 + H_2O$	k_2	R-2
$HOCl + NHCl_2 \rightarrow NCl_3 + H_2O$	k_3	R-3
$NCl_3 + H_2O \rightarrow NHCl_2 + HOCl$	k_4	R-4
$NHCl_2 + H_2O \rightarrow NOH + 2H^+ + 2Cl^-$	k_5	R-5
$NOH + NH_2Cl \rightarrow N_2 + H_2O + H^+ + Cl^-$	k_6	R-6
$NOH + NHCl_2 \rightarrow N_2 + HOCl + H^+ + Cl^-$	k_7	R-7
$NOH + 2HOCl \rightarrow NO_3^- + 3H^+ + 2Cl^-$	k_8	R-8

The final reaction rate coefficients are summarized in Table 2-6. The kinetic parameter k_{10} was previously evaluated by Morris (1967), while parameters of k_{30} and k_{40} were selected by trial and error to improve data fit; k_{60}, k_{70}, k_{80} were chosen so that the overall model fit the stoichiometry observed in their data.

When estimating the observed rate coefficient k_{20}, Wei conducted the experiment at different pHs values ranging from 6.7 to 7.2 with temperatures from 5°C to 20°C. According to the experimental conditions, several simplifying assumptions were made: R-1 occured instantaneously and R-6 was negligible. Hence, the concentration of NH_2Cl was only dependent on the reaction 2.

$$\frac{d[NH_2Cl]}{dt} = -k_2[NH_2Cl]([HOCl]+[OCl^-]) = -k_{20}[NH_2Cl][HOCl]$$

Both theoretical and observed rate coefficients could be determined from the experimental data. By averaging the k_{20} value, the activation energy and Arrhenius coefficient were obtained and are shown on Table 2-6.

According to this proposed model, computations of the breakpoint reactions made the use of the differential rate equations for each of the reactions from 1 through 8 with specific rate parameter values based on the selected pH and initial concentrations of hypochlorite. However, the range of pH studied was narrow, so more pH values are needed for application to water supplies.

Table 2-6 Breakpoint chlorination rate coefficients (after Wei and Morris)

Observed Rate Coefficients	Theoretical Rate Coefficients
$k_{10} = 9.7 \times 10^8 e^{(-3000/RT)}$	$k_1 = \dfrac{k_{10}}{\left(1 + \dfrac{K_a}{[H^+]}\right)\left(1 + \dfrac{K_b[H^+]}{K_w}\right)}$
$k_{20} = 2.43 \times 10^4 e^{(-2400/RT)}$	$k_2 = \dfrac{k_{20}}{\left(1 + \dfrac{K_a}{[H^+]}\right)}$
$k_{30} = 8.75 \times 10^{10} e^{(-3800/RT)}$	$k_3 = \dfrac{k_{30}[H^+]}{\left(1 + \dfrac{K_a}{[H^+]}\right)}$
$k_{40} = 6.32 \times 10^{11} e^{(-13000/RT)}$	$k_4 = k_{40}[H^+]$
$k_{50} = 2.11 \times 10^{10} e^{(-7200/RT)}$	$k_5 = k_{50}[OH^-]$
$k_{60} = 5.53 \times 10^7 e^{(-6000/RT)}$	$k_6 = k_{60}$
$k_{70} = 6.02 \times 10^8 e^{(-6000/RT)}$	$k_7 = k_{70}$
$k_{80} = 7.18 \times 10^7 e^{(-6000/RT)}$	$k_8 = \dfrac{k_{80}}{\left(1 + \dfrac{K_a}{[H^+]}\right)}$

Notes:
1. Concentration in moles/liter
2. Activation energies in cal/g mole
3. R=1.987 cal/g mole °K
4. Time in seconds

5. k_4 and k_5 are in seconds, all the others are in liter/mole-sec

2.5.2 Model of Saunier

Most of previous research was performed in batch reactors. Saunier (1976) conducted a series of experiments in several types of reactors: batch, plug flow, continuous flow stirred tank reactor (CSTR) and a non-ideal tubular reactor. They collected data mainly from the plug flow reactor and assumed ideal plug flow. They also adopted the DPD-FAS technique to measure free chlorine, monochloramine, dichloramine and nitrogen trichloride. When comparing the predicted values obtained from Wei and Morris 's model and data collected from the plug flow reactor, several disparities occurred. The disappearance of monochloramine was much faster than that predicted by the model. The critical concentration of free chlorine was much lower and there was a large difference between the predicted and observed nitrogen trichloride concentrations.

Saunier also discovered that P ratio was dependent on molar dose ratio and contact time. It was found that P ratio varied from less than 1 early in the reaction and increased to at least 1.5 with at long contact time. The observation of P ratio less than 1.5 led Saunier to develop a new mechanism, with NH_2OH proposed as an intermediate. He also observed that the rate of redox reaction increased in a pattern proportional to the initial ammonia concentration. In his study, the concentration of nitrite was also incorporated

into the mechanism, which appeared to be significant when the molar ratio was
sufficient to produce nitrate. The revised model is presented in Table 2-7.

Table 2-7 Breakpoint reaction mechanism after Saunier (1976)

Reaction	
$NH_3 + HOCl \rightarrow NH_2Cl + H_2O$	R-1
$NH_2Cl + HOCl \rightarrow NHCl_2 + H_2O$	R-2
$NHCl_2 + HOCl \rightarrow NCl_3 + H_2O$	R-3
$NCl_3 + H_2O \rightarrow NHCl_2 + HOCl$	R-4
$NHCl_2 + 2H_2O \rightarrow NH_2OH + HOCl + HCl$	R-5
$NH_2OH + HOCl \rightarrow NOH + HCl + H_2O$	R-6
$NHCl_2 + H_2O \rightarrow NH_2OH + HCl$	R-7
$NOH + NH_2Cl \rightarrow N_2 + HCl + H_2O$	R-8
$NOH + NHCl_2 \rightarrow N_2 + HCl + HOCl$	R-9
$NOH + HOCl \rightarrow NO_2^- + H^+ + HCl$	R-10
$NO_2^- + HOCl \rightarrow NO_3^- + HCl$	R-11

Table 2-8 summarizes the Saunier's revised rate coefficients. Since there was an excellent agreement between the study of Anbar and Yagil (1962) and the study of Morris (1967) on the kinetics of the formation of monochloramine, Saunier did not reevaluate the value of k_1. For the dichloramine formation parameter, they were proposed to the following relationship:

$k_{20}=1.99\times10^4 e^{(-2400/RT)}$

Saunier adopted the values of k_3 and k_4 proposed by Saguinsin and Morris (1975) as follows:

$$k_3 = 3.43\times10^5 e^{-7000/RT}(1+10^{-pK_a+1.4})(1+\frac{K_a}{[H^+]})^{-1}$$
$$k_4 = 8.56\times10^8 e^{--18000/RT}(1+5.88\times10^5[OH^-])(1+\frac{K_a}{[H^+]})^{-1}$$

The results of the experiments revealed that parameter k_5 was proportional to [OH⁻] concentration when pH ranged from 6 to 8 and initial ammonia concentration was approximately 1 mg/l. Moreover, when pH was above 8, the k_5 decreased with increasing pH. Hence, the value of k_5 was proportional to the initial ammonia concentration. The final relationship of k_{50} was as follows:

$$k_{50} = 2.03\times10^{14} e^{-7200/RT}$$
$$k_5 = N_0 k_{50}[OH^-]$$

Where N_0 is the initial free ammonia concentration

Values of parameter k_6 and k_7 were chosen in order to provide a good fit between the

observed and predicted stoichiometry. As for the k_8, they used an empirical function.

Table 2-8 Breakpoint chlorination rate coefficients (after Saunier)

Observed Rate Coefficients	Theoretical Rate Coefficients
$k_{10} = 9.7 \times 10^8 e^{(-3000/RT)}$	$k_1 = \dfrac{k_{10}}{\left(1 + \dfrac{K_a}{[H^+]}\right)\left(1 + \dfrac{K_b[H^+]}{K_w}\right)}$
$k_{20} = 1.99 \times 10^4 e^{(-2400/RT)}$	$k_2 = \dfrac{k_{20}}{\left(1 + \dfrac{K_a}{[H^+]}\right)}$
$k_{30} = 3.43 \times 10^5 e^{(-7000/RT)}$	$k_3 = \dfrac{k_{30}[H^+]}{\left(1 + \dfrac{K_a}{[H^+]}\right)}$
$k_{40} = 8.56 \times 10^8 e^{(-18000/RT)}$	$k_4 = k_{40} \dfrac{1 + 5.88 \times 10^5 [OH^-]}{1+}$
$k_{50} = 2.03 \times 10^{14} e^{(-7200/RT)}$	$k_5 = N_0 k_{50}[OH^-]$
$k_{60} = 1.0 \times 10^8 e^{(-6000/RT)}$	$k_6 = k_{60}$
$k_{70} = 1.3 \times 10^9 e^{(-6000/RT)}$	$k_7 = k_{70}$

$$k_{80} = 1.0 \times 10^7 e^{\left(-6000/RT\right)}$$	$$k_8 = \dfrac{k_{80}}{\left(1 + \dfrac{K_a}{[H^+]}\right)}$$

Saunier used the revised kinetic model to predict the behavior of the different chlorine species as follows:

1. The observed concentration of monochloramine matched well to the predicted value at normal pH range. However, at high pH or high initial ammonia concentration, the agreement was still very poor.

2. The predicted concentration of dichloramine was lower than what was measured.

3. The agreement between the predicted nitrogen trichloride concentration and the observed one was still very poor.

4. The revised model could predict the concentration of free chlorine residual very well.

2.5.3 Stenstrom and Tran's contribution (Stenstrom & Tran 1983)

In their study, they conducted the chlorination experiments in three pilot reactors consisting of one plug flow with 0.5 inch diameter, and 2 dispersed flow reactors, with 2.0 inch diameter and 3.0 inch diameter, respectively. A total of 23 sub experiments were implemented over a pH range from 4.0 to 8.4 and at chlorine to ammonia molar ratio of 1.2 to 2.2. They used Wei and Morris's breakpoint mechanism for the study, but

modified the kinetic parameters except for k_1 using an estimation technique, in order to

improve the fit between the experimental data. The initial trial reaction rate coefficients

were selected from below and Table 2-9 shows the different rate coefficients.

k_1 was selected from Morris's evaluation (Morris 1967)

k_2 was selected from Wei's evaluation (Wei 1972)

k3 was selected from Saguinsin's evaluation (Saguinsin & Morris 1975)

k4 was selected based on Saguinsin's data

k5 was selected from Saunier's evaluation (Saunier 1976)

k6, k7, k8 were estimated form the parameter estimation procedure.

Table 2-9 Initial trial values for reaction rate coefficients in Stenstrom and Tran's

study

Observed Rate Coefficients	Theoretical Rate Coefficients
$k_{10} = 9.7 \times 10^8 e^{(-3000/RT)}$	$k_1 = \dfrac{k_{10}}{\left(1 + \dfrac{K_a}{[H^+]}\right)\left(1 + \dfrac{K_b[H^+]}{K_w}\right)}$
$k_{20} = 2.43 \times 10^4 e^{(-2400/RT)}$	$k_2 = \dfrac{k_{20}}{\left(1 + \dfrac{K_a}{[H^+]}\right)}$

$k_{30} = 3.43 \times 10^5 e^{(-7000/RT)}$	$k_3 = k_{30}[\dfrac{1+10^{-pK_a+1.4}}{(1+\dfrac{k_a}{H^+})^2}]$
$k_{40} = 3 \times 10^{10} e^{(-20000/RT)}$	$k_4 = k_{40} \dfrac{1+5.88 \times 10^5 [OH^-]}{1+}$
$k_{50} = 2.03 \times 10^{14} e^{(-7200/RT)}$	$k_5 = N_0 k_{50}[OH^-]$
$k_{60} = 5.0 \times 10^7 e^{(-6000/RT)}$	$k_6 = k_{60}$
$k_{70} = 6 \times 10^8 e^{(-6000/RT)}$	$k_7 = k_{70}$
$k_{80} = 5.0 \times 10^7 e^{(-6000/RT)}$	$k_8 = \dfrac{k_{80}}{\left(1+\dfrac{K_a}{[H^+]}\right)}$

Notes:

1. concentrations in g mole/liter
2. activation energy in cal/g mole
3. R=1.987 cal/g mole $^{\circ}$K
4. Time is seconds

Since the rate parameter k_1 was precisely estimated and well matched by different authors, they accepted the results of the earlier authors, but used a parameter estimate technique proposed by Becker and Yeh (1972) to identify the other parameters. The parameter estimation algorithm includes sequential estimation and linearization of the objective function around an initial set of parameter values.

The results of the experiments were summarized as follows:

1. Free chlorine did not exist at any time when chlorine concentration was below the breakpoint dosage. Hence, disinfection of water and wastewater below the breakpoint does not benefit from free chlorine.

2. Monochloramine was always present at a higher concentration than dichloramine during the first 15 seconds. But when pH was near 7, monochloramine decreased to the same concentration as dichloramine. At pH value greater than 7.5, monochloramine was always higher in concentration than dichloramine.

3. Dichloramine became the major component when pH was below 6.5.

4. Nitrogen trichloride always existed at low concentrations. But high chlorine to ammonia ratio could produce more nitrogen trichloride than low ratio.

5. At around pH of 4, chlorine residual was approximately 90 percent of the initial dose. At pH from 6 to 6.5, total chlorine residual was about 65 percent of the initial dose and residual percentage decreased to approximately 35% of the initial dose when the pH value was between7.5 to 8.4.

2.5.4 The work of Jafvert and Valentine

Typically, chlorine-ammonia systems are categorized into three types with respect to different chlorine to ammonia molar ratios. At molar ratios less than 1.0, the measurable chlorine species are chloramines, and the region is the combined region. In the breakpoint region, the applied molar ratio is greater than 1.5. The transition region

is between these two regions where molar ratios ranges from 1 to 1.5.

In the previous three investigations, only the breakpoint region was studied. Jafvert and Valentine (1992) studied all three regions and developed a unified model suitable for all chlorine to ammonia ratios. Due to the discrepancies among different investigators regarding the chlorination model, Jafvert and Valentine reexamined the reactions and mechanisms in their research. Table 2-10 illustrates reaction schemes of their study. R-1 to R-4 elucidated monochloramine's formation and hydrolysis reactions. R-5 was the disproportionation of monochloramine. R-6, the reverse reaction of monochloramine disproportionation was of little significance. R-7 accurately predicted residuals in combined region. They adopted Hand and Margerum's mechanism for the decay of dichloramine when HOCl was in excess, shown as R-8 and R-13. R-9, R-10, and R-11 explained the decay of dichloramine in the presence of excess ammonia. R-12 and R-14 provided formation of nitrate and nitrogen gas, respectively.

Jafvert and Valentine conducted a series of experiments to validate the proposed model. Initially, they performed experiments in breakpoint and transition regions with initial chlorine to ammonia molar ratios of 1.25, 1.5, 1.75, and 2.0. All of these experiments were executed at pH values of either of 6, 7, or 8 with initial ammonia concentration of either 0.107mM or 0.214mM in batch reactors. The slowly decaying process in combined chlorine region was monitored for about 170 hours with the initial chlorine

concentration of 0.7mM. Later,   experiments with initial chlorine to ammonia ratio of either of 0.25, 0.5, or 0.75 were performed at pH values of 6.5, 7.0, or 7.5.

From the study, they clarified that the disproportionation of monochloramine was catalyzed in acid solutions, while the decomposition of dichloramine was base-catalyzed when no free chlorine existed. The proposed model could be used to predict transient concentrations of all these chlorine species over a wide range of chlorine to ammonia molar ratios over the pH range of 6 to 8. The model was validated by data only from batch reactors.

Table 2-10 Breakpoint reaction mechanisms after Jafvert and Valentine (1992)

Reaction	
$HOCl + NH_3 \rightarrow NH_2Cl + H_2O$	R-1
$NH_2Cl + H_2O \rightarrow HOCl + NH_3$	R-2
$HOCl + NH_2Cl \rightarrow NHCl_2 + H_2O$	R-3
$NHCl_2 + H_2O \rightarrow HOCl + NH_2Cl$	R-4
$NH_2Cl + NH_2Cl \rightarrow NHCl_2 + NH_3$	R-5
$NHCl_2 + NH_3 \rightarrow NH_2Cl + NH_2Cl$	R-6

$NHCl_2 + NH_2Cl \rightarrow N_2 + 3H^+ + 3Cl^-$	R-7
$NHCl_2 + HOCl \rightarrow NCl_3 + H_2O$	R-8
$NHCl_2 + H_2O \rightarrow NOH + 2HCl$	R-9
$NOH + NHCl_2 \rightarrow N_2 + HOCl + HCl$	R-10
$NOH + NH_2Cl \rightarrow N_2 + H_2O + HCl$	R-11
$NHCl_2 + 2HOCl + H_2O \rightarrow NO_3^- + H^+ + 4HCl$	R-12
$2H_2O + NHCl_2 + NCl_3 \rightarrow N_2 + 2HOCl + 3HCl$	R-13
$H_2O + NH_2Cl + NCl_3 \rightarrow N_2 + HOCl + 3HCl$	R-14

2.5.5 Summary on the breakpoint simulation model

This section summarizes and compares the four breakpoint models. Wei and Morris

proposed the first completed model for breakpoint chlorination and evaluated

parameters of k_1, k_2, k_3, k_4, and k_5 one by one in batch reactors. The schematic diagram

for their model is shown in Figure 2-3. They tried to create test conditions to favor

certain reactions to facilitate kinetic analysis. They made an excellent initial effort to

understand chlorination reaction mechanisms and their contribution was valuable.

However, this process was complex. Kinetic parameters obtained based on

experimental conditions may not be able to predict the species in practical ranges of pH and temperature.
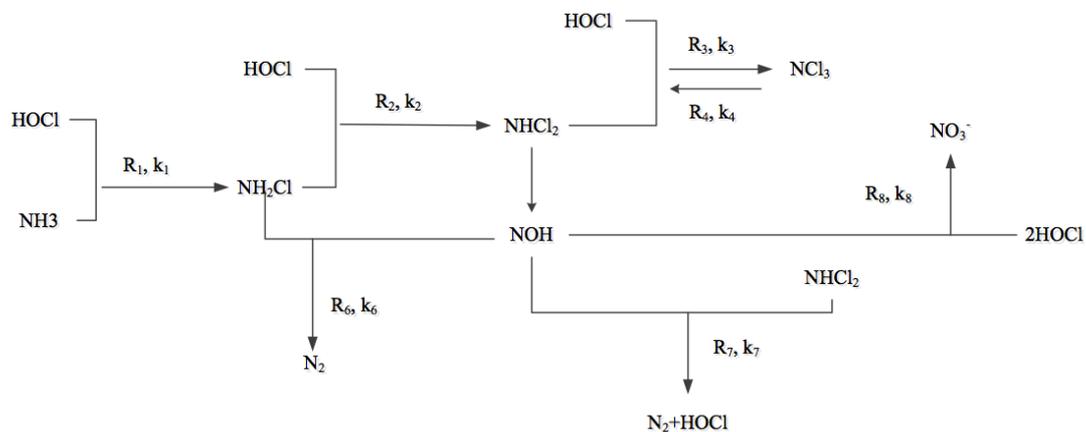
Figure 2-3 Schematic diagram in Wei and Morris' research for breakpoint reactions

In Saunier's research, plug flow reactors were used to estimate the kinetic parameters. He employed trial and error technique to estimate parameters to achieve good agreement between the observations and calculated concentrations. As a consequence, they proposed modifications to Morris and Wei's model, which showed some improvement agreement between model results and data. However, predictions still reflected some significant errors. Their model suffered due to the assumption of an ideal plug flow reactor, which is not practical for many situations. The reaction scheme in Saunier's study was different from that of Wei and Morris', as illustrated in Figure 2-4.
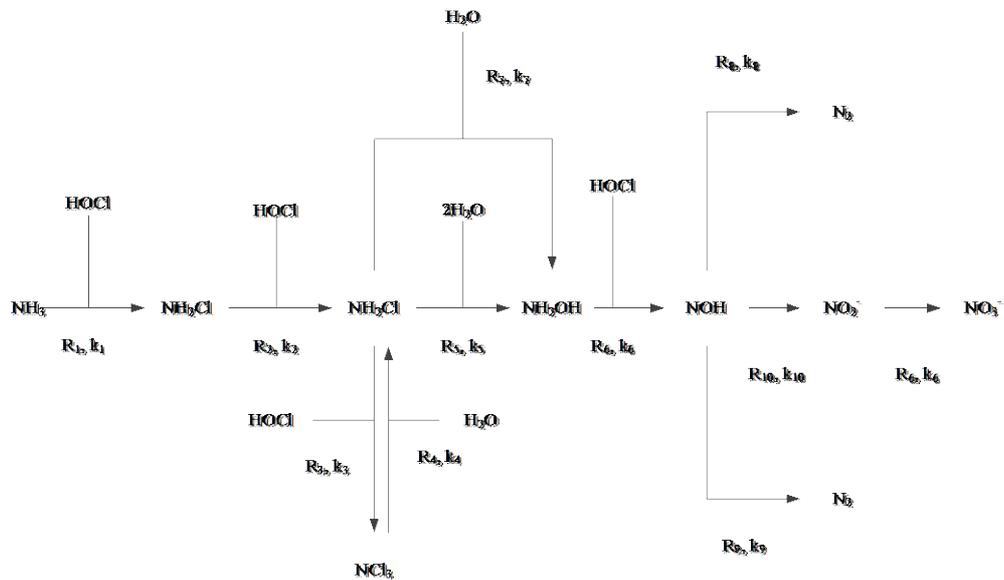
Figure 2-4 Schematic diagram in Saunier's research for breakpoint reactions

Dynamic dispersion model presented by Stenstrom and Tran was a significant step forward from the models presented by Wei & Morris and Saunier. Their model included various mixing conditions and could predict various chlorine species with fewer errors. The parameter estimation method used in the study could be employed to characterize the kinetic parameters of the various reactions involved in the breakpoint chlorination at pragmatic conditions. Nevertheless, future work was still needed to have a complete improvement on the chlorination breakpoint model.

Unlike previous proposed reaction schemes, the model proposed by Jafvert and Valentine was not constrained by Cl/N ratios, and is shown in Figure 2-5. Prediction of

the speciation and fate of chlorine species could be accomplished with any molar ratio at pH value ranging from 6 to 8. However, a considerable amount of critical information was still lacking. Additional research is required to characterize the unknown products formed when dichloramine decayed with excessive ammonia. More accurate analysis was needed so that the kinetics of nitrogen trichloride and nitrite/nitrate can be precisely examined. Temperature dependencies should also be taken into account. More experiments at lower pH or higher pH should also be conducted.
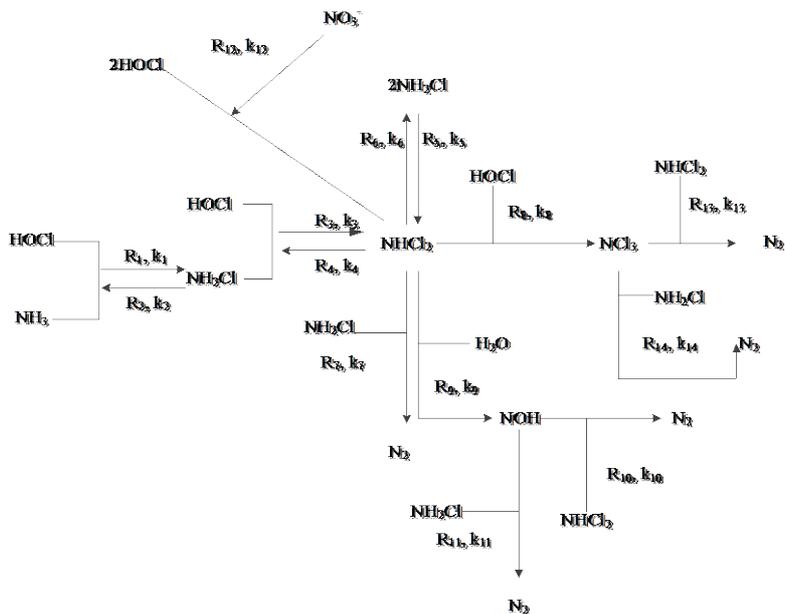
Figure 2-5 Schematic diagram in Jafvert and Valentine's research for breakpoint reactions.

38

3 Breakpoint Chlorination Mathematical Modeling

3.1 Reaction mechanisms

In this thesis, model from Morris &Wei was adopted to describe the various reactions with ammonia and chlorine as shown in Figure 2-3. The major difference between Wei-Morris and Saunier models was the decomposition reaction of dichloramine. In Wei-Morris' model, the decomposition of dichloramine was experimentally observed to be first-order in relation to dichloramine concentration and proportional to hydroxyl ion activity. The proposed mechanism was shown below:

$$NHCl_2 \rightarrow H^+ + NCl_2^-$$
$$NCl_2^- + H_2O \rightarrow NCl(OH)^- + Cl^- + H^+$$
$$NCl(OH)^- \rightarrow NOH + Cl^-$$
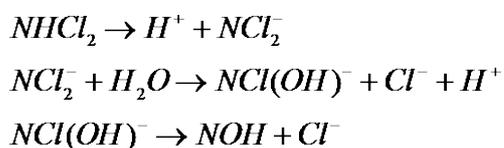
Mechanism indicated that R-5 in the Wei & Morris's model was not an elementary reaction. They also postulated NOH to be the intermediate in the reaction system. However, Saunier proposed another mechanism that NH_2OH is the intermediate and that R-5 is not an elementary reaction for the following reasons:

1. Dichloramine decomposition should follow a more complex pattern since R-5 in Wei and Morris's model is not elementary.

2. McCoy (1954) and Anbar (1962) found very little concentration of NH_2OH during the reaction of chlorine with ammonia.

3. When P ratio was less than 1.5, Wei-Morris's model is not applicable..

The breakpoint mechanism presented by Saunier still has a problem of predicting end product (N_2, NO_3^-) concentration at P ratio less than 1.5 due to the non-elementary R-5. The value of k_5 used in this model was determined by a parameter identification method.

Based on the previous reasons, the Wei-Morris model was used in this study. The reaction rate coefficient parameters were modified in order to best fit with the observations using the parameter estimation technique.

Table 3-1 List of symbols

n_1	Initial ammonia nitrogen concentration (NH_3 + NH_4^+) in molar concentration, mole/l
C	Molar ratio of free chlorine (OCl^-+$HOCl$) to n_1
C_1	Molar ratio of initial chlorine concentration to n_1
N	Molar ratio of total nitrogen (NH_3 + NH_4^+) to n_1

M	Molar ratio of monochloramine to n_1
D	Molar ratio of dichloramine to n_1
E	Molar ration of nitrogen trichloride to n_1
G	Molar ratio of nitrogen gas to n_1
S	Molar ratio of nitroxyl radical to n_1
I	Molar ratio of nitrate nitrogen to n_1

Based on the reaction scheme, rate expressions for these reactions were shown as follows:

$$r_1 = k_1[HOCl][NH_3] = k_1 CN$$
$$r_2 = k_2[HOCl][NH_2Cl] = k_2 CM$$
$$r_3 = k_3[HOCl][NHCl_2] = k_3 CD$$
$$r_4 = k_4[NCl_3] = k_4 E$$
$$r_5 = k_5[HOCl][NHCl_2] = k_5 CD$$
$$r_6 = k_6[NH_2Cl][NOH] = k_6 MS$$
$$r_7 = k_7[NHCl_2][NOH] = k_7 DS$$
$$r_8 = k_8[HOCl][NOH] = k_8 CS$$

Where: [] = Denotes molar concentration

HOCl= unionized hypochlorite acid

NH₃= unionized ammonia

Table 3-2 shows how each species is involved in each reaction.

Table 3-2 Species consist different reactions

	r1	r2	r 3	r 4	r 5	r 6	r 7	r 8
C	-	-	-	+	-		+	-
N	-							
M	+	-				-		
D		+	-	+	-		-	
E			+	-				
S					+	-	-	-
G						+	+	
I								+

Where: - means consumption of the species; + means production of the species; blank: means not involved in the reaction.

3.1.1 Basic concept

Both in batch reactor and plug flow reactor, the continuity equation was as follows:

$$\frac{dc}{dt} = r$$

Where: c= solute molar concentration

r=reaction rate

(r > 0, for rate of formation; r < 0, for rate of consumption)

3.1.2 The mathematical model

The continuity equation was associated with chlorination reactions (R-1 through R-8) to produce a set of eight ordinary-differential equations, shown below, which are capable of predicting the various chlorine species generated in the batch and plug flow reactors during breakpoint chlorination. All reaction rates were presented with symbols and the ionized species were involved.

$$\frac{dC}{dt} = -k_1 n_1 CN - k_2 n_1 CM - k_3 n_1 CD + k_4 E + k_7 n_1 SD - 2k_8 n_1 CS$$

$$\frac{dN}{dt} = -k_1 n_1 CN$$

$$\frac{dM}{dt} = k_1 n_1 CN - k_2 n_1 CM - k_6 n_1 SM$$

$$\frac{dD}{dt} = k_2 n_1 CM - k_3 n_1 CD + k_4 E - k_5 D - k_7 n_1 SD$$

$$\frac{dE}{dt} = k_3 n_1 CD - k_4 E$$

$$\frac{dS}{dt} = k_5 D - k_6 n_1 SM - k_7 n_1 SD - k_8 n_1 CS$$

$$\frac{dG}{dt} = k_6 n_1 SM + k_7 n_1 SD$$

$$\frac{dI}{dt} = k_8 n_1 CS$$

43

3.2 Available experimental data from literature

Since there have been extensive studies conducted on aqueous chlorine and ammonia reactions, data from the literature were reviewed and used in this study. Consistent with the goal of this study, the typical ranges of parameters used in the drinking water treatment processes were used as criteria for data selection from the literature. The initial chlorine concentration was less than 10 mg/L, pH 6.7 to 7.2, temperature 5ºC to 35ºC.

In the study of Wei and Morris (1974), they performed a series of batch experiments in the breakpoint region. Three pH values, 6.7, 7.0, 7.2, were selected for experiments since studies of kinetic patterns near these pH values were considered to be especially significant, where the characteristic features of the breakpoint process occur within this period. Temperatures in the reactor were controlled at 5ºC, 10ºC, 15ºC and 20ºC respectively by a water bath. This range of temperature was chosen to cover seasonal variations of water temperature in water treatment plants and to provide more complicated results of the phenomena occurring in breakpoint chlorination. 400 ml of ammonium chloride solution was added to the reactor and a phosphate buffer was used to maintain the pH at a constant level. The ratio of chlorine to ammonia was fixed at 1.81 mg/L using 1 mg/L of ammonia nitrogen. The analytical method DPD-FAS was used in all experiments to accurately and precisely determine the concentration of each

species. The observed data from Wei-Morris's experiments were employed in this study.

Saunier (1976) also studied the breakpoint reactions using a plug flow reactor and tap water. However, due to different mixing conditions and other constituents involved with the tap water, their observed data was not adopted here. In 1983, Stenstrom and Tran (1983) conducted the experiments in plug flow reactors with three different sizes ranging from 0.5 inch to 3 inches at pH values from 4.0 to 8.4. In 1992, Jafvert and Valentine (1992) conducted numerous experiments in combined, transition, and breakpoint regions.

The observations in Wei & Morris's experiments interpreted from the figures in their papers and are listed in Appendix A.

3.3 Parameter estimation technique

Since the rate coefficient k_1 was precisely estimated by Wei and Morris, we therefore did not need to focus on the estimation of kinetics of the formation of monochloramine in this thesis. Only the rate coefficients of k_2, k_3, k_4, k_5, k_6, k_7 and k_8 were evaluated.

To perform the parameter estimation, the "FMINCON" function technique in MATLAB was employed. The "FMINCON" function can be used to obtain a constrained minimum value of a scalar function of several variables with an initial

estimate included. Its process was based on the minimization of the sum of square of

three concentration differences between the experimental data and the predicted values

to identify the best-fit values for the seven model parameters. The least square criterion

was used as an objective function as follows:

$$S = \sum_i (\alpha_i)^2 + \sum_i (\beta_i)^2 + \sum_i (\delta_i)^2$$

over k_2, k_3, k_4, k_5, k_6, k_7, k_8

where:
$$\alpha_i = C_i - C_i^*$$
$$\beta_i = M_i - M_i^*$$
$$\delta_i = D_i - D_i^*$$
i is the observation time

C_i^*, M_i^*, D_i^* were the measured values and C_i, M_i, D_i were the expected values

(simulated results).

The algorithm uses sequential estimation and linearization of the objective function

based on an initial set of parameter estimations. The parameters are then sequentially

and the effect of the parameters on the objective function are observed, leading to a new

set of parameters that minimizes the sum of the squares error of the linearized model.

Using the new set of parameters, the model reevaluated and a new set of perturbations

made. The process terminates when no improvement in the objective function is

possible.

4　Modeling results and discussion

4.1 Reaction Rate Coefficients

Figures 4-1 through Figure 4-7 show estimated rate coefficients for three pH values and four temperatures. Reaction rate k_2 was found to increase with increasing temperature, which is in agreement with the results of the previous study (Wei & Morris 1974; Saunier 1976). Under the same temperature, the value of k_2 at pH 7 was always larger than the other two estimates, which showed that the k_2 value was related to pH and would have a peak value during this pH range. For the parameter k_3, the trend was different from the results predicted by Wei & Morris' model. In their model, at the same pH, as the temperature increased, and the k values rose correspondingly, which contradicted the results here. It may be due to the exclusion of nitrogen trichloride for the speciation of the chlorine species, which in turn affected the estimation of the parameter values. For parameter k_4, it seemed to have no pattern in relation to temperature and pH. Parameter k_5 showed a good agreement with We-Morris' model. With the increasing temperature, the k_5 values enhanced; as the pH increased from 6.7 to 7.2, the reaction rate accelerated as well. Reaction rates of k_6 and k_7 are both pH independent, as shown in Figure 4-6 and Figure 4-7, which are also in accordance with the previous study. Similarly, they increased when the temperatures increased. For reaction rate k_8, the values were higher at pH 6.7 than at 7.2, increasing as the temperature increased.

Figure 4-1 Reaction rate coefficient k$_2$

Figure 4-2 Reaction rate coefficient k$_3$

Figure 4-3 Reaction rate coefficient k₄
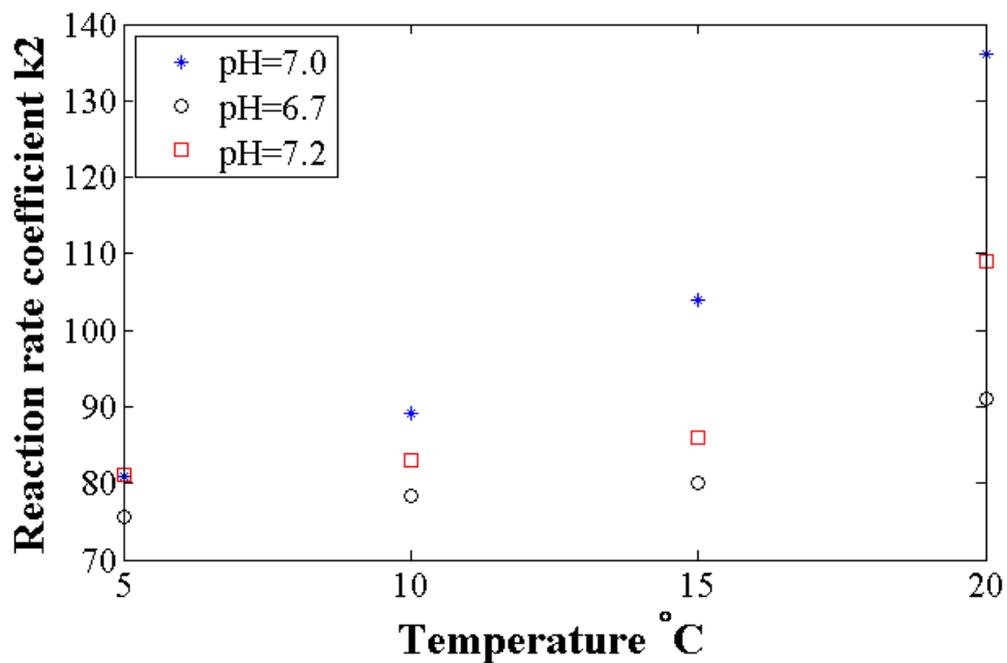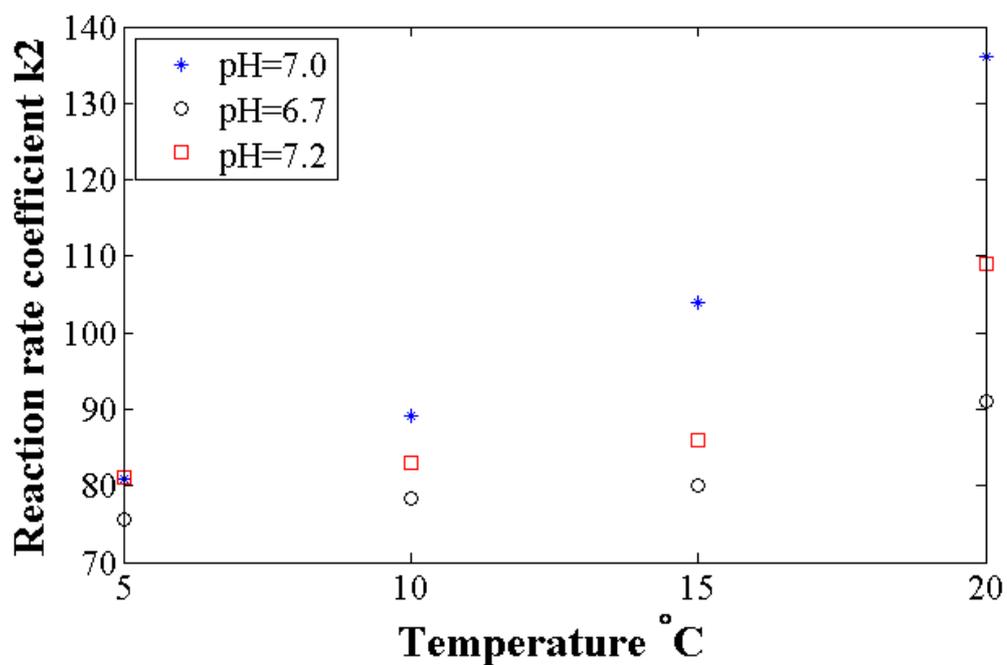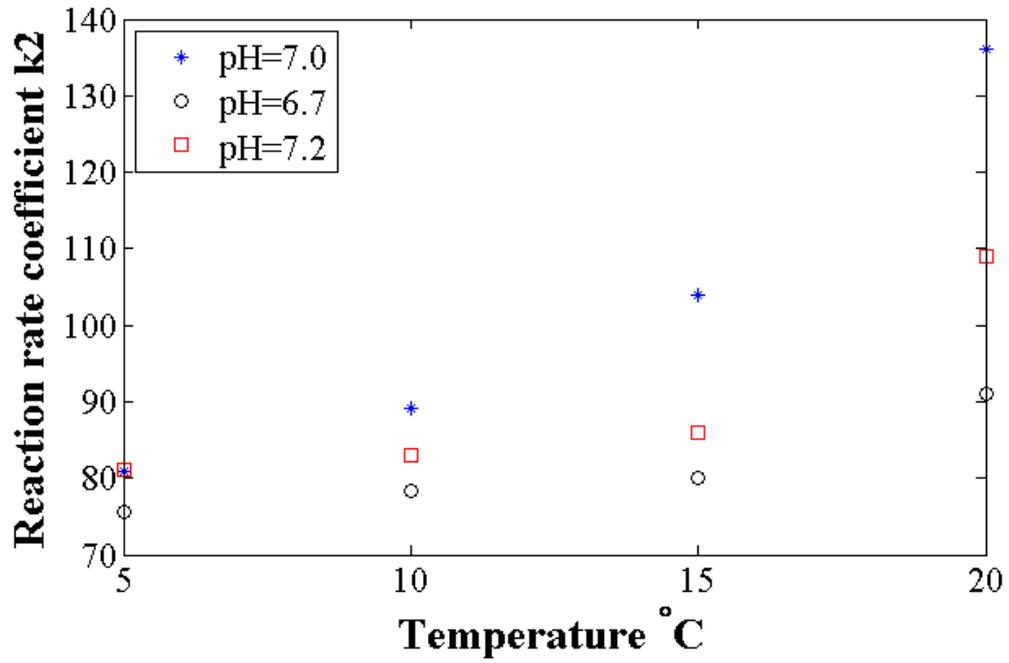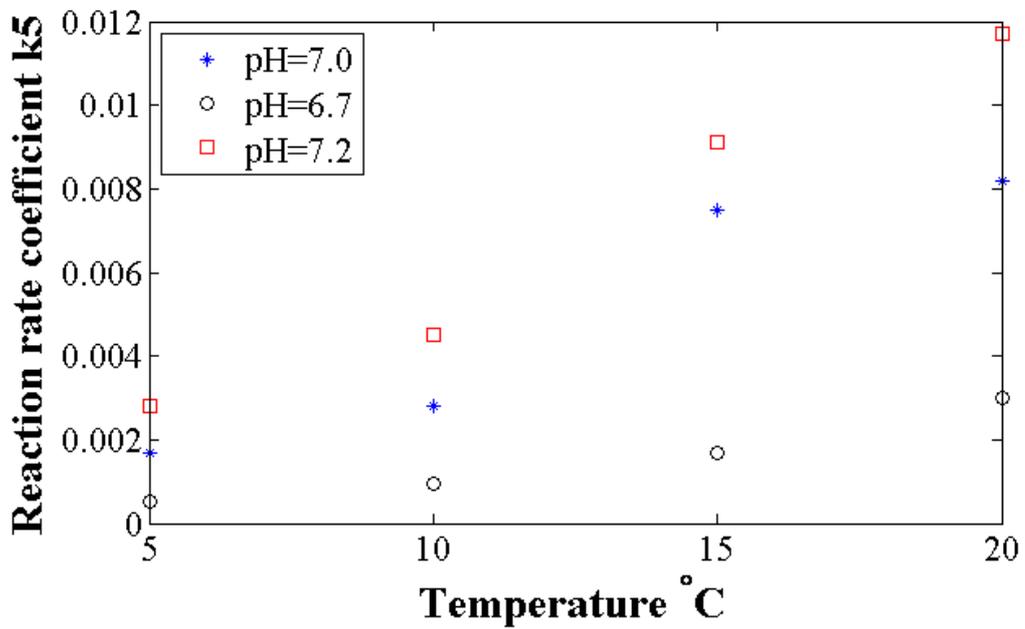

Figure 4-4 Reaction rate coefficient k₅
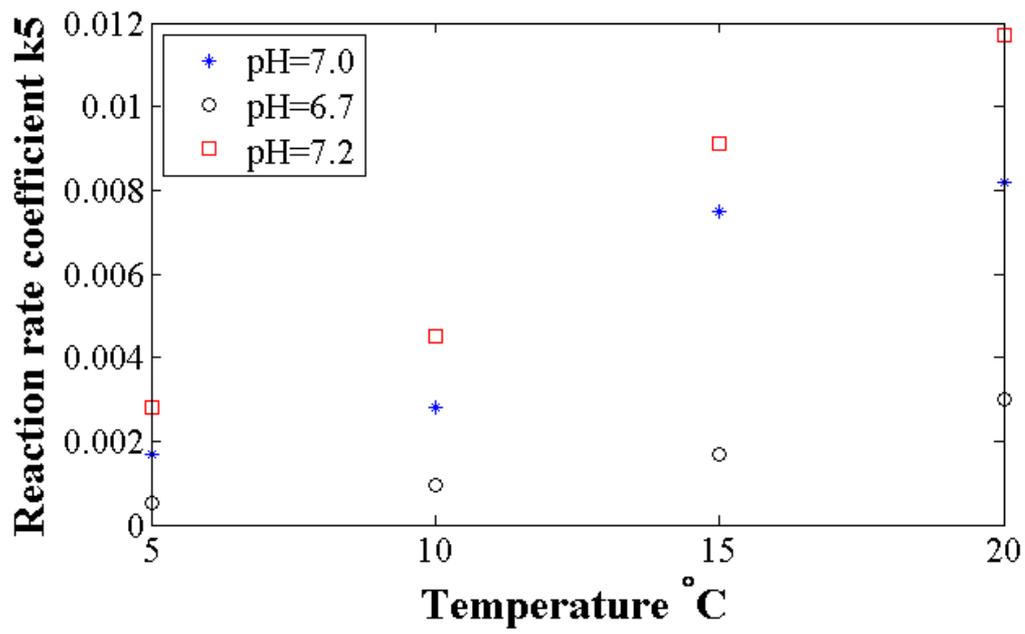
Figure 4-5 Reaction rate coefficient k$_6$
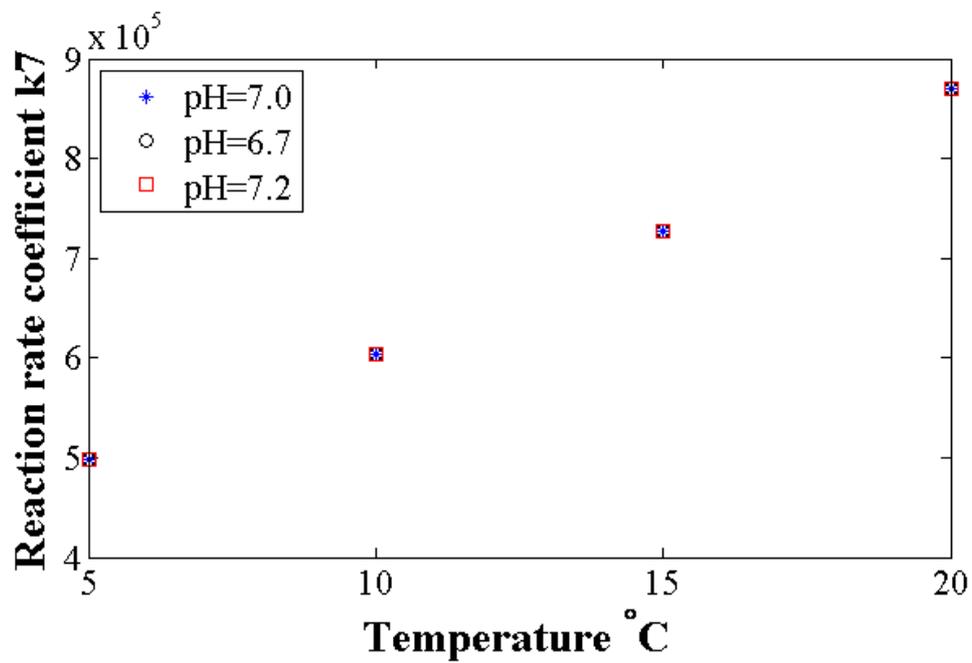
Figure 4-6 Reaction rate coefficient k$_7$
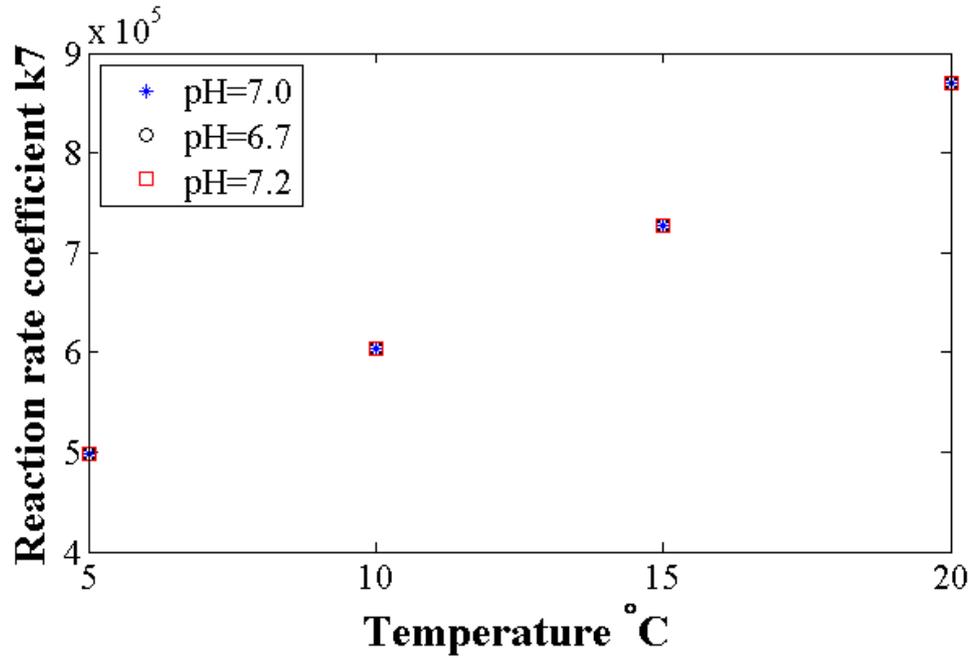
Figure 4-7 Reaction rate coefficient k_8

4.2 Experimental and simulation results

Figure 4-8 through Figure 4-19 compare Wei's experimental data and predicted results using the rate coefficients obtained using the estimation technique. A solid line in the figures referred as the model outputs and the observed concentrations were represented as individual data points. To facilitate the reaction stoichiometry and kinetic characteristics, the concentration of each species was expressed as molar ratio to initial ammonia concentration, which implied the initial point of total chlorine in the system was 1.8. The experimental data are included in Appendix A.

Figure 4-8 Experimental data and simulation results in batch reactor at pH=7, T=20°C, Cl/N=1.8

Figure 4-9 Experimental data and simulation results in batch reactor at pH=7, T=15°C, Cl/N=1.8

Figure 4-10 Experimental data and simulation results in batch reactor at pH=7,

T=10°C, Cl/N=1.8

Figure 4-11 Experimental data and simulation results in batch reactor at pH=7,

T=5°C, Cl/N=1.8

Figure 4-12 Experimental data and simulation results in batch reactor at pH=7.2,

T=20°C, Cl/N=1.8

Figure 4-13 Experimental data and simulation results in batch reactor at pH=7.2,

T=15°C, Cl/N=1.8
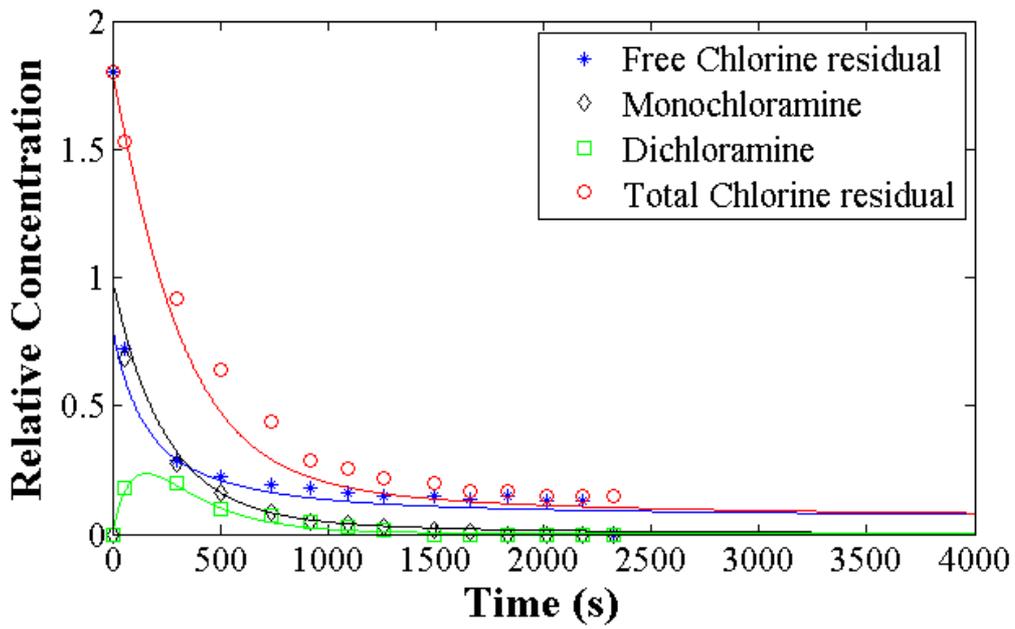
Figure 4-14 Experimental data and simulation results in batch reactor at pH=7.2, T=10°C, Cl/N=1.8
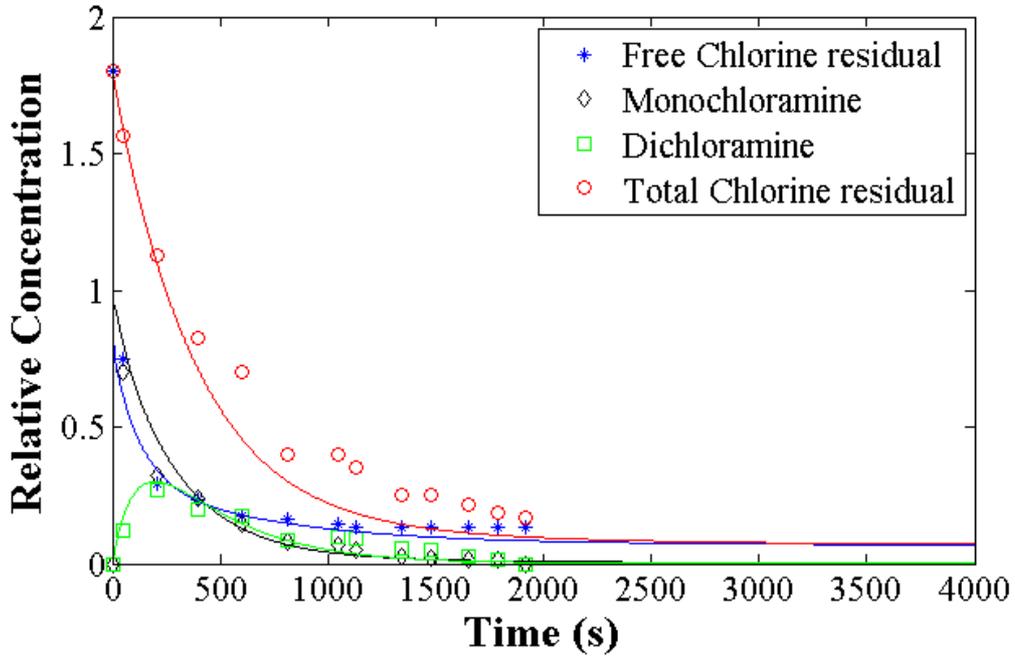
Figure 4-15 Experimental data and simulation results in batch reactor at pH=7.2, T=5°C, Cl/N=1.8
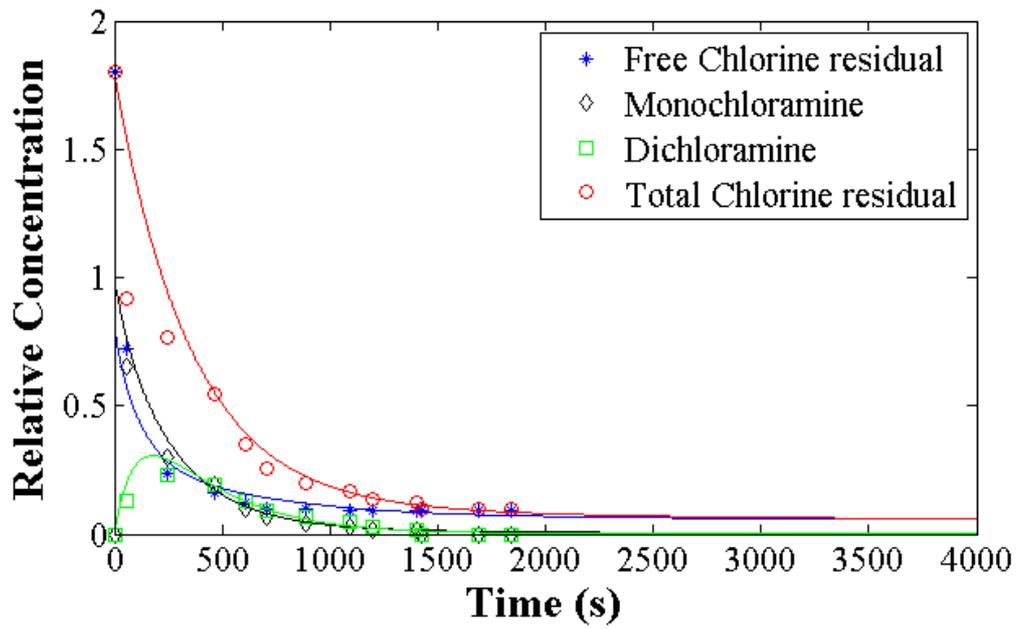
Figure 4-16 Experimental data and simulation results in batch reactor at pH=6.7,

T=20°C, Cl/N=1.8
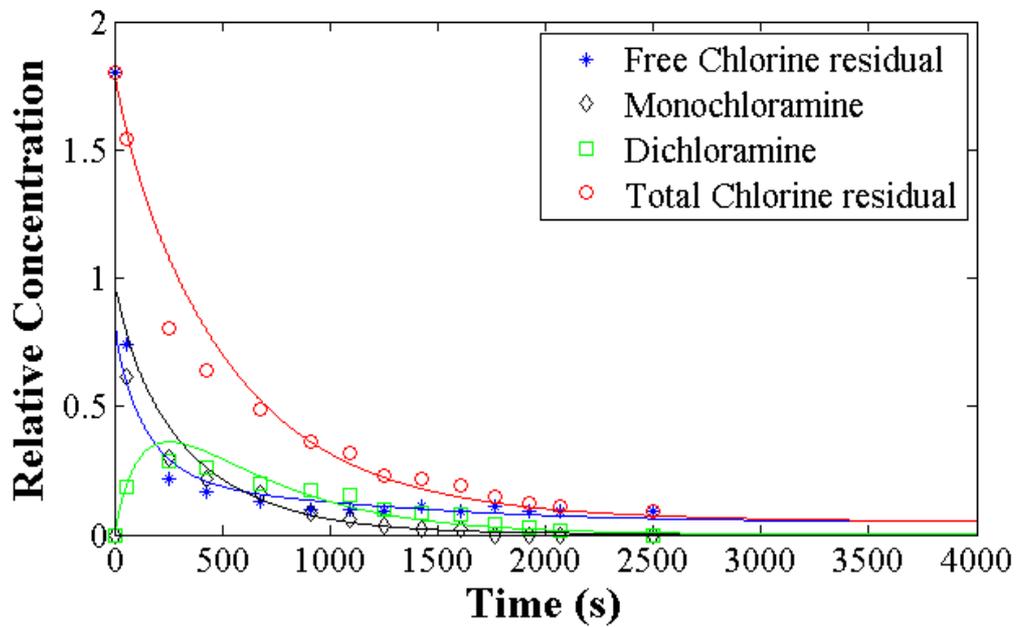
Figure 4-17 Experimental data and simulation results in batch reactor at pH=6.7,
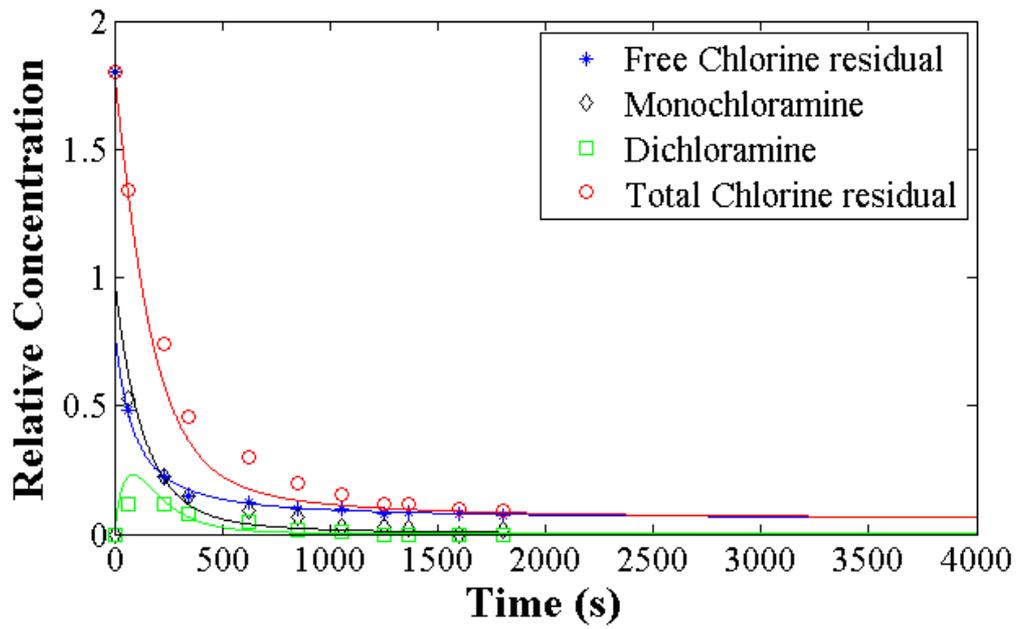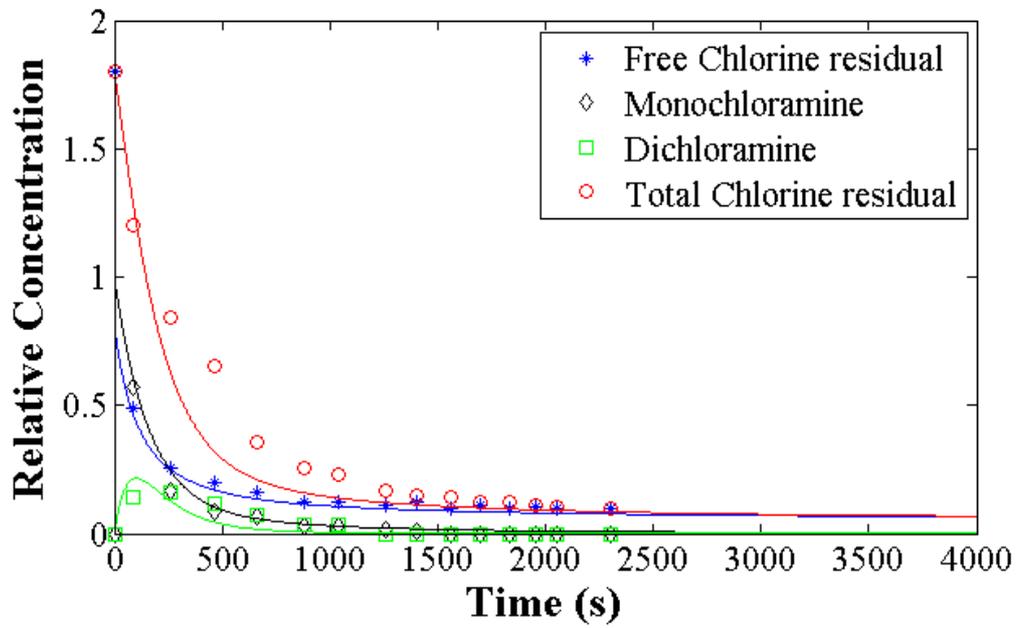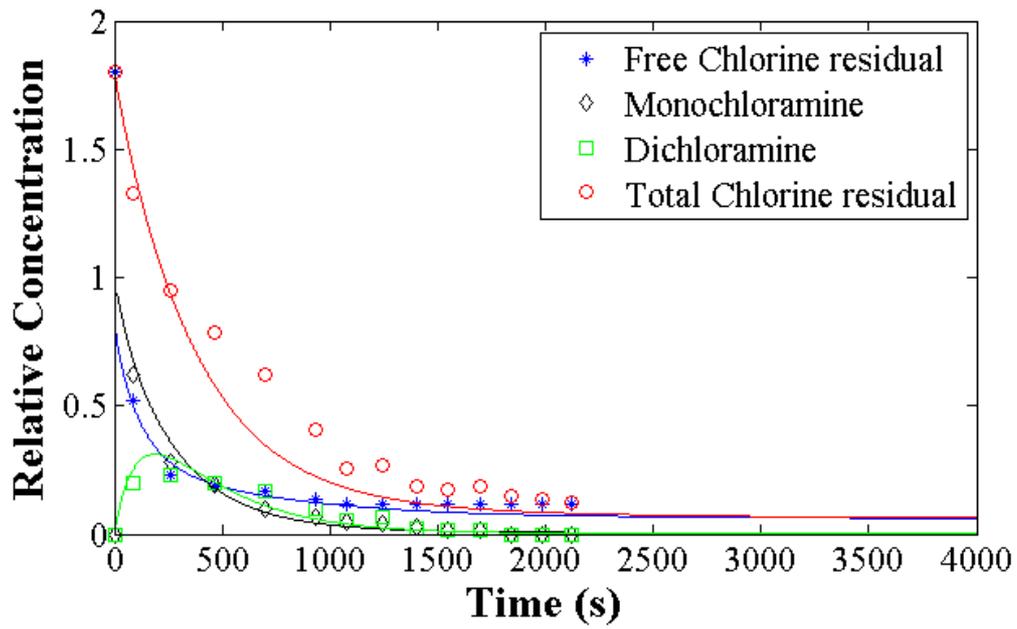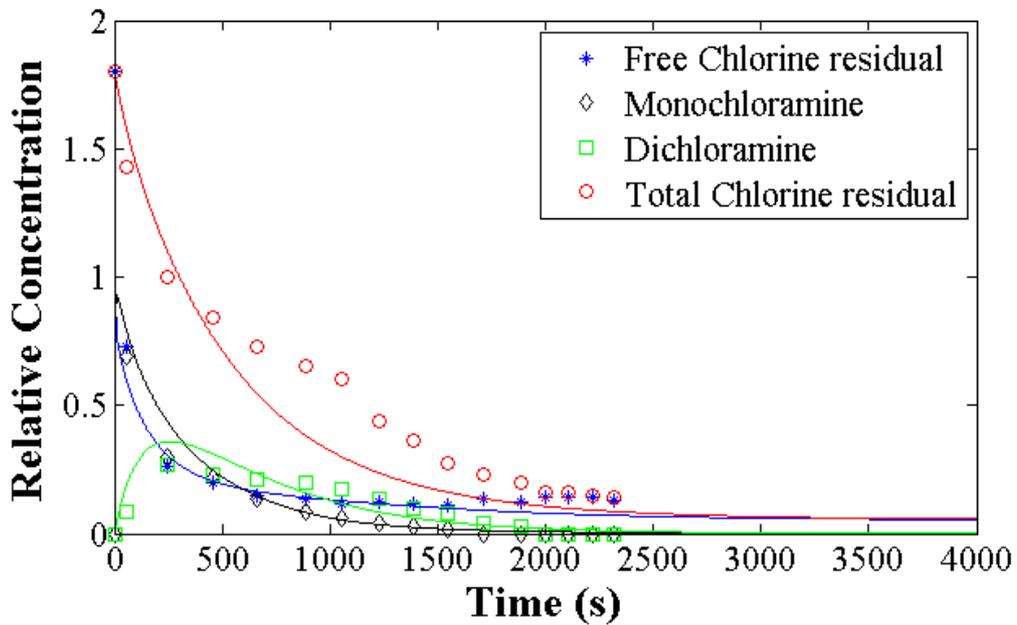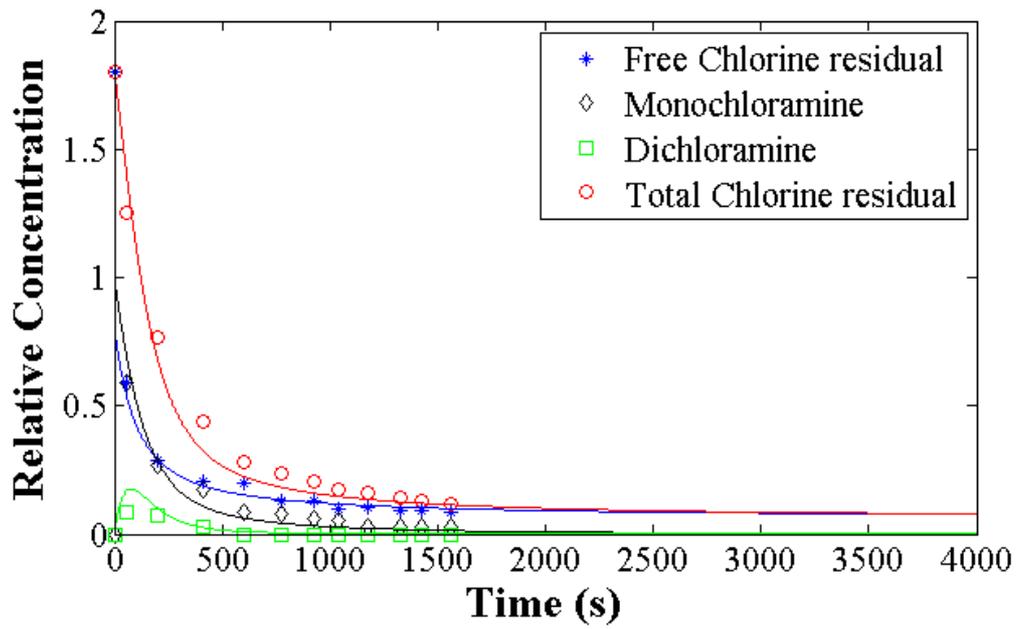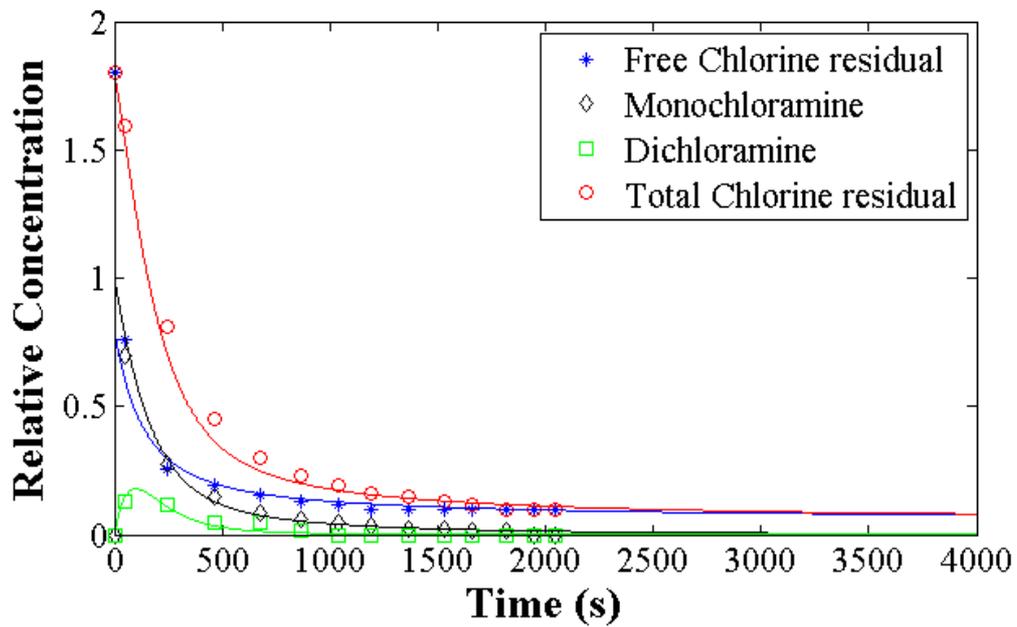
T=15°C, Cl/N=1.8
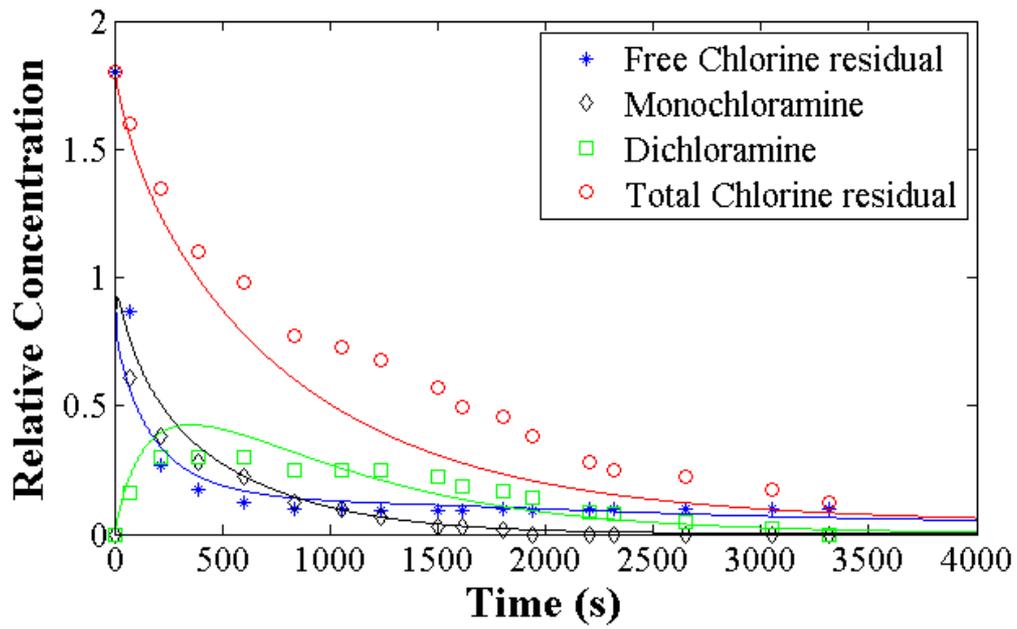
Figure 4-18 Experimental data and simulation results in batch reactor at pH=6.7,

T=10°C, Cl/N=1.8
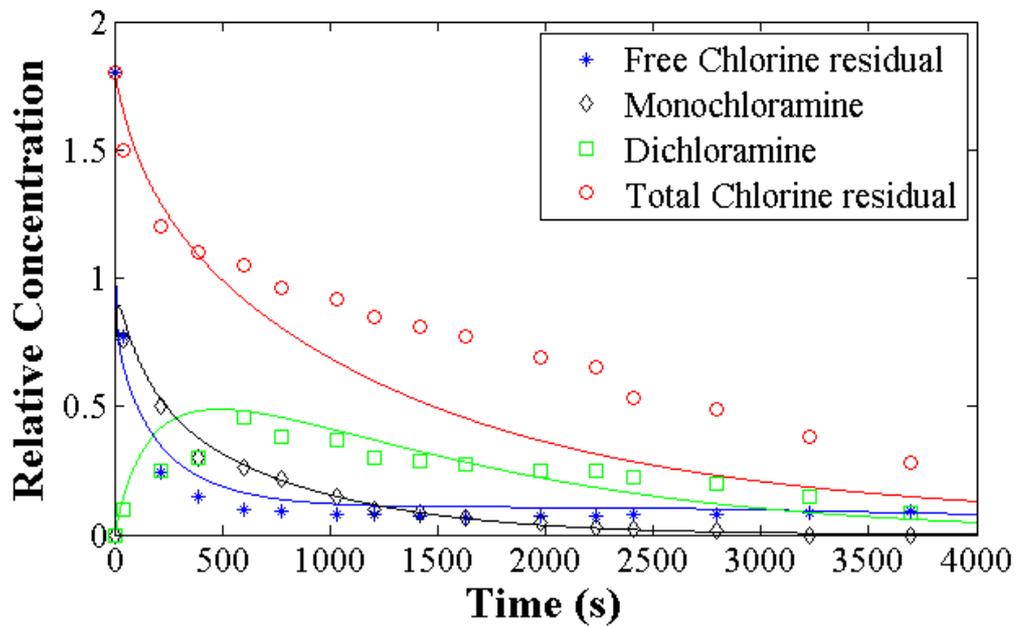
Figure 4-19 Experimental data and simulation results in batch reactor at pH=6.7,

T=5°C, Cl/N=1.8

4.2.1P ratio

If chlorine is applied in a molar ratio larger than the stoichiometric ratio, the excess chlorine will remain in the form of free chlorine after the reaction is complete. Thus, the stoichiometric ratio can be calculated by subtracting the remaining free chlorine from the initial chlorine dosage, both as a molar ratio to the initial ammonia. In the experiments of Wei and Morris, the molar ratio was fixed at 1.8. The free chlorine after completion was about 0.1. The stoichiometric ratio therefore was calculated as nearly 1.7.

4.2.2 Monochloramine

At 1 mg/L NH_3-N concentration, the agreement between the predicted and measured monochloramine is excellent at three different pH values and four temperatures (Se Figure 4-8 through Figure 4-19). Since the chlorine to ammonia ratio was fixed at 1.8, all the monochloramine reacted to nearly zero at the end of the reaction. During the first several minutes of contact time, monochloramine was always present at a higher concentration than free chlorine, as shown in Figure 4-8 though Figure 4-19. In all these 12 conditions, the formation of monochloramine was very rapid and the maximum concentration of monochloramine occurred at the beginning of the experiment, which agreed with Wei and Morris's predictions. After its formation, monochloramine exhibited a rather rapid decrease.

4.2.3 Dichloramine

The computed dichloramine concentration matched well with experimental data at all three pH values with four temperatures. A maximum dichloramine concentration was detected in the initial stage of each experiment, in accordance with the forecast by Morris and Wei. Though the exact position and each maximum in dichloramine were different, dichloramine in each figure followed a definite and consistent pattern under 12 different conditions. Under the same pH, the maximum value of dichloramine increased as the temperature decreased (see Figure 4-8 through Figure 4-11, Figure 4-12 through Figure 4-15, Figure 4-16 through Figure 4-19). Under the same temperature, the maximum value of the dichloramine decreased as the pH increased. Dichloramine at lower pH composed a larger portion of the total chlorine species. At pH 6.7, dichloramine became the predominant species in the residual chlorine for a certain period after reaching the peak, except for the condition of temperature of 20°C. There was an important effect of pH on the transient concentration of dichloramine. As the pH decreased from 7.2 to 6.7, the maximum concentration of dichloramine increased, the time of occurrence of the maximum concentration was delayed, and the persistence of dichloramine also increased.

4.2.4 Free chlorine

The final simulated and measured concentrations of free chlorine are compared in Figure 4-8 through Figure 4-19. In general, the agreement was excellent for most situations. In some cases, the computed free chlorine concentration was slightly higher than the observed free chlorine. Free chlorine concentrations dropped very quickly during the first five minutes as HOCl reacted to form chloramines. After that brief period, free chlorine concentration stayed relatively constant for a protracted period. In all these cases, the final free chlorine concentration was about 20% of the initial chlorine dosage. Free chlorine regenerated in the constant stages, as observed from the measured data. This was not predicted by the model. This resurgence was generally more distinct under the low pH and temperatures than at higher pH and temperatures values.

4.2.5 Total chlorine

The measured total chlorine was calculated as the aggregation of free chlorine, monochloramine and dichloramine. Nitrogen trichloride is usually included in the total residual, but was not in this case since it was not measured in the experiments. Figure 4-8 through Figure 4-19 compare the predicted and observed total residual chlorine. Generally, the predicted total chlorine was higher than the data. However, theoretically the predicted values of total chlorine should be larger than the experimental data due to the involvement of nitrogen trichloride. As the temperature declined, the rate of

reaction decreased. At lower pH values, the deviation between the predicted and observed concentration was larger than that at higher pH. Similarly, it tended to have a better fit at higher temperatures.

5 Recommendations

Though we can obtain the different parameters for a good agreement between the observed data and simulated values, additional work is needed to have to develop an improved model of the Wei and Morris breakpoint chlorination model:

1. Establish an Arrhenius function for each observed rate coefficient.

2. Collect sufficient data at different temperatures, pH, Cl/N ratios, and initial ammonia concentrations so that we can estimate all kinetic coefficients and find a more precise relationship between observed rated coefficients and theoretical rate coefficients. The more data that are included, the more accurate the model will be.

3. Use regression method to find the function f(pH) that can help relate k_i with k_{io}, as shown below:

    $k_i = k_{io} * f(pH)$

4. The breakpoint chlorination model should be validated in natural waters containing carbonate, sulfate, and other species.

6 Appendix A

Table 7-1 Wei's laboratory results in batch reactor at pH=7, T=20ºC, Cl/N=1.8

Time (second)	Free chlorine (mole/L)	Monochloramine (mole/L)	Dichloramine (mole/L)
0	1.8	0	0
61.2	0.48	0.527	0.118
227.4	0.225	0.225	0.118
347.4	0.147	0.147	0.0808
627.0	0.124	0.0918	0.0464
852.0	0.0958	0.0653	0.0153
1056.1	0.1	0.0303	0.0118
1254.4	0.0808	0.029	0
1362.0	0.0843	0.0198	0
1602.0	0.0774	0	0
1800.0	0.071	0.014	0

Table 7-2 Wei's laboratory results in batch reactor at pH=7, T=15ºC, Cl/N=1.8

Time (second)	Free chlorine (mole/L)	Monochloramine (mole/L)	Dichloramine (mole/L)
0	1.8	0	0
86.7	0.488	0.57	0.142
260.2	0.258	0.17	0.16
462.7	0.2	0.084	0.117
665.1	0.16	0.064	0.072
881.9	0.12	0.03	0.035
1040.9	0.12	0.027	0.035
1257.8	0.108	0.0133	0
1402.5	0.12	0.0086	0
1561.3	0.1	0	0
1694.5	0.108	0	0
1836.1	0.1	0	0
1951.8	0.104	0	0
2053.1	0.1	0	0
2298.8	0.1	0	0

Table 7-3 Wei's laboratory results in batch reactor at pH=7, T=10ºC, Cl/N=1.8

Time (second)	Free chlorine (mole/L)	Monochloramine (mole/L)	Dichloramine (mole/L)
0	1.8	0	0
87.7	0.52	0.623	0.2
263	0.233	0.283	0.233
467.5	0.183	0.19	0.2
701.3	0.167	0.095	0.17
935.1	0.133	0.068	0.095
1081.2	0.117	0.046	0.052
1241.9	0.117	0.041	0.065
1402.6	0.116	0.027	0.02
1548.7	0.116	0.0183	0.017
1694.8	0.116	0.0133	0.0183
1840.9	0.116	0	0
1987	0.116	0	0
2118.5	0.116	0	0

Table 7-4 Wei's laboratory results in batch reactor at pH=7, T=5ºC, Cl/N=1.8

Time (second)	Free chlorine (mole/L)	Monochloramine (mole/L)	Dichloramine (mole/L)
0	1.8	0	0
57.1	0.73	0.69	0.086
242.9	0.26	0.3	0.27
457.14	0.2	0.217	0.233
662.9	0.15	0.133	0.21
885.7	0.133	0.084	0.2
1057.1	0.117	0.061	0.175
1228.6	0.125	0.041	0.133
1385.7	0.117	0.03	0.097
1545.5	0.1125	0.016	0.079
1714.3	0.133	0	0.043
1885.7	0.125	0	0.026
2000	0.142	0	0
2105.7	0.142	0	0
2217.1	0.14	0	0
2320	0.13	0	0

Table 7-5 Wei's laboratory results in batch reactor at pH=7.2, T=20ºC, Cl/N=1.8

Time (second)	Free chlorine (mole/L)	Monochloramine (mole/L)	Dichloramine (mole/L)
0	1.8	0	0
60	0.59	0.59	0.086
198	0.2846	0.2692	0.072
412.5	0.2037	0.1741	0.0294
600	0.2007	0.0853	0
772.5	0.1296	0.0813	0
925	0.13	0.058	0
1037.4	0.0953	0.053	0
1175	0.102	0.03	0
1325	0.0907	0.0314	0
1425	0.0927	0.0269	0
1563	0.0877	0.0253	0

Table 7-6 Wei's laboratory results in batch reactor at pH=7.2, T=15ºC, Cl/N=1.8

Time (second)	Free chlorine (mole/L)	Monochloramine (mole/L)	Dichloramine (mole/L)
0	1.8	0	0
51.9	0.76	0.7	0.131
246.3	0.254	0.277	0.115
466.7	0.192	0.146	0.049
674.1	0.154	0.086	0.049
868.5	0.13	0.058	0.0177
1037	0.115	0.049	0
1192.6	0.1	0.037	0
1361.1	0.1	0.025	0
1529.6	0.097	0.0207	0
1659.3	0.098	0.0177	0
1814.8	0.096	0.01307	0
1944.4	0.096	0	0
2048.1	0.096	0	0

Table 7-7 Wei's laboratory results in batch reactor at pH=7.2, T=10ºC, Cl/N=1.8

Time (second)	Free chlorine (mole/L)	Monochloramine (mole/L)	Dichloramine (mole/L)
0	1.8	0	0
60	0.72	0.686	0.1769
296.3	0.285	0.277	0.2
503.7	0.223	0.162	0.1
740.7	0.1923	0.083	0.0734
918.5	0.177	0.047	0.0469
1096.4	0.162	0.0397	0.0254
1259.3	0.146	0.0269	0.01308
1496.3	0.146	0.0177	0
1659.3	0.138	0.01	0
1837	0.146	0	0
2014.8	0.1307	0	0
2177.8	0.1307	0	0
2325.9	0	0	0

Table 7-8 Wei's laboratory results in batch reactor at pH=7.2, T=5ºC, Cl/N=1.8

Time (second)	Free chlorine (mole/L)	Monochloramine (mole/L)	Dichloramine (mole/L)
0	1.8	0	0
52.2	0.75	0.7	0.123
210	0.295	0.325	0.269
393.75	0.231	0.238	0.2
603.8	0.177	0.146	0.1769
813.8	0.1615	0.08	0.085
1050	0.146	0.0675	0.1
1128.75	0.131	0.05	0.09
1338.75	0.131	0.0254	0.055
1476	0.131	0.0223	0.05
1653.75	0.131	0.0138	0.0269
1785	0.131	0.0162	0.0162
1916.25	0.131	0	0

Table 7-9 Wei's laboratory results in batch reactor at pH=6.7, T=20ºC, Cl/N=1.8

Time (second)	Free chlorine (mole/L)	Monochloramine (mole/L)	Dichloramine (mole/L)
0	1.8	0	0
54.5	0.725	0.65	0.1306
245.5	0.2385	0.3	0.2304
463	0.1615	0.1923	0.1923
607	0.123	0.095	0.1306
709	0.1	0.065	0.09
886.4	0.095	0.041	0.065
1091	0.089	0.03	0.05
1200	0.09	0.0186	0.03
1404.5	0.089	0.0146	0.017
1427.3	0.09	0	0
1690	0.09	0	0
1840.9	0.09	0	0

Table 7-10 Wei's laboratory results in batch reactor at pH=6.7, T=15ºC, Cl/N=1.8

Time (second)	Free chlorine (mole/L)	Monochloramine (mole/L)	Dichloramine (mole/L)
0	1.8	0	0
53	0.74	0.6182	0.183
250	0.22	0.3	0.2845
428.5	0.167	0.22	0.261
678	0.13	0.16	0.2
910.5	0.1	0.087	0.173
1089.5	0.096	0.063	0.157
1250.4	0.093	0.037	0.1
1428	0.108	0.024	0.083
1607	0.092	0.02	0.08
1767	0.11	0	0.043
1928	0.092	0	0.03
2071	0.092	0	0.016
2500	0.093	0	0

Table 7-11 Wei's laboratory results in batch reactor at pH=6.7, T=10ºC, Cl/N=1.8

Time (second)	Free chlorine (mole/L)	Monochloramine (mole/L)	Dichloramine (mole/L)
0	1.8	0	0
73	0.87	0.61	0.164
219	0.27	0.38	0.3
386.7	0.175	0.28	0.3
601	0.125	0.225	0.3
833.5	0.1	0.125	0.25
1056.9	0.098	0.096	0.25
1233	0.089	0.069	0.25
1503.7	0.089	0.03	0.225
1611.1	0.092	0.0275	0.1875
1804.4	0.1	0.015	0.17
1941.9	0.092	0	0.14
2204	0.1	0	0.088
2320	0.096	0	0.077
2650.1	0.1	0	0.049
3050.4	0.1	0	0.02375
3316.7	0.1	0	0

Table 7-12 Wei's laboratory results in batch reactor at pH=6.7, T=5ºC, Cl/N=1.8

Time (second)	Free chlorine (mole/L)	Monochloramine (mole/L)	Dichloramine (mole/L)
0	1.8	0	0
43	0.77	0.76	0.1
214.8	0.24	0.5	0.25
386.6	0.15	0.3	0.3
601.4	0.1	0.26	0.46
773.2	0.092	0.22	0.38
1030.9	0.081	0.15	0.37
1202.7	0.077	0.1	0.3
1417.5	0.072	0.084	0.29
1632.3	0.069	0.069	0.275
1975.9	0.072	0.046	0.25
2233.6	0.072	0.028	0.25
2405.5	0.077	0.022	0.225

7 Reference

Anbar M. and Yagil G. (1962). The hydrolysis of chloramine in alkaline solution. *Journal of the American Chemical Society* **84**(10), 1790-6.

Bates R. G. and Pinching G. D. (1950). Dissociation Constant of Aqueous Ammonia at 0 to 50-Degrees from Emf Studies of the Ammonium Salt of a Weak Acid. *Journal of the American Chemical Society* **72**(3), 1393-6.

Becker L. and Yeh W. W. G. (1972). Identification of Parameters in Unsteady Open Channel Flows. *Water Resources Research* **8**(4), 956-&.

Chapin R. M. (1929). Dichloro-amine. *Journal of the American Chemical Society* **51**(7), 2112-7.

Chapin R. M. (1931). The influence of pH upon the formation and decomposition of the chloro derivatives of ammonia. *Journal of the American Chemical Society* **53**(3), 912-20.

Connick R. E. and Chia Y. T. (1959). The Hydrolysis of Chlorine and Its Variation with Temperature. *Journal of the American Chemical Society* **81**(6), 1280-4.

Deborde M. and von Gunten U. (2008). Reactions of chlorine with inorganic and organic compounds during water treatment - Kinetics and mechanisms: A critical review. *Water Research* **42**(1-2), 13-51.

Granstrom M. L. (1954). The disproportionation of monochloramine.

Griffin A. (1940). Observations on break-point chlorination. *Journal (American Water Works Association)* **32**(7), 1187-90.

Houston S. A. C. (1925 and 1926). 19th and 20th Annual Reports of Metropolotan Water Board.

Isaac R. A. and Morris J. C. (1983). Transfer of active chlorine from chloramine to nitrogenous organic compounds. 1. Kinetics. *Environmental Science & Technology* **17**(12), 738-42.

Jafvert C. T. and Valentine R. L. (1992). Reaction Scheme for the Chlorination of Ammoniacal Water. *Environmental Science & Technology* **26**(3), 577-86.

Margerum D. W. and Gray E. T. (1978). Chlorination and Formation of N-Chloro Compounds in Water Treatment. *Abstracts of Papers of the American Chemical Society* **175**(Mar), 158-.

McCoy R. E. (1954). Evidence for the presence of hydroxylamine as an intermediate in the decomposition of chloramine by hydroxide. *Journal of the American Chemical Society* **76**(5), 1447-8.

McGuire M. J. (2013). *The chlorine revolution: water disinfection and the fight to save lives*. American Water Works Association.

Morris J., Weil I. and Culver H. (1951). Kinetic Studies on the Breakpoint with Ammonia and Glycine. *Photocopied paper obtained from author*.

Morris J. C. (1966). Acid Ionization Constant of Hocl from 5 to 35 Degrees. *Journal of Physical Chemistry* **70**(12), 3798-&.

Morris J. C. (1967). *Kinetics of reactions between aqueous chlorine and nitrogen compounds.* John Wiley & Sons, New York, NY.

Palin A. (1950). A Study of the Chloro Derivatives of Ammonia and Related Compounds. *Inst. Wtr. Engrs* **4**, 151-89.

Palin A. and Johnson J. D. (1975). Water disinfection: chemical aspects and analytical control.

Palin A. T. (1949). *Study of the chloro derivatives of ammonia and related compounds, with special reference to their formation in the chlorination of natural and polluted waters.* University of London.

Rook J. J. (1974). Formation of haloforms during chlorination of natural waters. *Water Treatment and Examination* **23**, 234-43.

Saguinsin J. and Morris J. (1975). The chemistry of aqueous nitrogen chloride. *Disinfection Water and Wastewater, Ann Arbor Science Publishers, Inc, Ann Arbor, MI.*

Saunier B. M. (1976). Kinetics of Breakpoint Chlorination and Disinfection. *Ph. D. Dissertation.*

Stenstrom M. and Tran H. (1983). A Theoretical and Experimental Investigation of the Dynamics of Breakpoint Chlorination in Dispersed Flow Reactors.

Wei I. and Morris J. (1974). Dynamics of Breakpoint Chlorination. Chemistry of Water Supply, Treatment and Distribution (AJ. Rubin, editor). *Ann Arbor Science Publ., Ann Arbor, Mich.*

Wei I. W.-t. (1972). Chlorine-ammonia breakpoint reactions: kinetics and mechanism.

Weil I. and Morris C. (1949). Kinetic Studies on the Chloramines .1. The Rates of Formation of Monochloramine, N-Chlormethylamine and N-Chlordimethylamine. *Journal of the American Chemical Society* **71**(5), 1664-71.

Yagil G. and Anbar M. (1962). The kinetics of hydrazine formation from chloramine and ammonia. *Journal of the American Chemical Society* **84**(10), 1797-803.