An Investigation of the Alternatives for Wastewater Disinfection: Economic, Social, and Technical -- A Theoretical and Experimental Investigation of the Dynamics of Breakpoint Chlorination in Dispersed Flow Reactors

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AN INVESTIGATION OF THE ALTERNATIVES FOR WASTEWATER DISINFECTION: ECONOMIC, SOCIAL, AND TECHNICAL

A THEORETICAL AND EXPERIMENTAL INVESTIGATION OF THE DYNAMICS OF BREAKPOINT CHLORINATION IN DISPERSED FLOW REACTORS

by

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ABSTRACT

The dynamics of breakpoint chlorination were examined in three continuous dispersed flow reactors. The reactors were comprised of ½, 2 and 3 inch PVC pipe, which where 730, 41, and 23 feet long, respectively. Chlorination of ammonia a various chlorine to ammonia ratios were investigated over the pH range of 6.5 to 7.5.

Seventeen experiments were performed in the three reactors over the course of the experimental investigations. Chlorine residuals, including free, monochloramine, dichloramine, and nitrogen trichloride, and ammonia were analyzed simultaneously.

To quantitatively characterize the breakpoint reactions, a mathematical model, consisting of eight simultaneous, quasi-linear, partial differential equations was developed. The model was solved using an implicit finite difference technique. The reaction rate coefficients were treated as parameters, and were estimated using a search technique to minimize the sum of squares of the difference between the expected and measured values.

The model can now be used to simulated continuous flow chlorination processes in order to develop process operating strategies to maximize or minimize any given experimental objective.

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1. INTRODUCTION

In 1846 at the Vienna General Hospital, Semmelweis added chlorine to water as a germicide. He was the first to use this powerful disinfectant. Unfortunately it was not until the 20th century that chlorine found widespread use as a disinfectant. Belgium (1903), Britain (1905) and the United States (1908) quickly adopted chlorine as a potable water disinfectant. Undoubtly chlorination of water supplies was one of the most significant advances in public health of this century.

It is surprising to note that the fundamental mechanisms of chlorination, disinfection, and chlorine chemistry are not well known, although much has been learned in the past 30 years. The kinetics of disinfection and the reactions of chlorine with ammonia and other reduced compounds, especially the reactions which form the higher chloramines, are not fully understood.

In addition to chlorine's use as a disinfectant, it has found widespread uses in treatment plants. In water treatment chlorine is used to control odors, taste, and color, remove iron, manganese, and hydrogen sulfide. It is used as control technique to retard the growth of pressure increasing slimes in water transmission systems, and to prevent clogging of filters. In wastewater treatment plants, chlorine is used to oxidize ammonia and organic matter, inactivate iron-fixing and slime producing bacteria, control activated sludge bulking, and prevent the generation of hydrogen sulfide.

Despite the wide spread acceptance of chlorine as a water and wastewater disinfectant, better and less expensive methods of disinfection are being actively sought. The desire to find alternate disinfectants has resulted from undesirable side effects of the chlorination process. The production of chlorinated organic compounds, particularly trihalomethanes (THM's), has become a particularly bothersome aspect of chlorination. Various methods of THM control are being developed, including the development of alternate disinfectants and improved methods of chlorination. An original goal of this research project was to evaluate alternative disinfection processes. An early and obvious finding was that a host of alternative processes exist, such as ozonation and disinfection with other halogens, and that a useful and through evaluation of alternative methods could only be accomplished through extensive experimental evaluations. Therefore the scope of the project was reduced to evaluate the second objective, which was an evaluation of chlorine kinetics, which will hopefully result in better chlorination practices.

The goal of this research project became the development of an improved understanding of chlorination kinetics in non-ideal or dispersed flow reactors, which are commonly found in water and wastewater treatment plants. An experimental program was conducted to evaluation chlorination in the presence of ammonia in several reactors, ranging from nearly perfect plug flow mixing regimes to complete-mixing reactors. Three dispersed flow reactors were used: a 5/8 inch reactor, 770 feet long, a 2 inch reactor 40 feet long, and a 3 in reactor 24 feet long. From experiments in these reactors a more fundamental understanding of chlorination dynamics was developed.

The specific technical goals and accomplishments of this work are as follows:

1. Development of a mathematical model describing the break-point chlorination reactions.

2. Generation of experimental data for the verification of the mathematical model.

3. Improvement in numerical techniques for implementing the Danckwerts or flux entrance boundary condition.

4. Improvement in methods for estimating dispersion coefficients from retention time distribution curves.

5. Refinement of analytical methods for measuring chlorine and chloramines in the presence of ammonia.

6. Development of a unique numerical solution method for a coupled, non-linear system of several parabolic partial differential equations.

7. Evaluation of the effects of dispersion on chlorination.

8. Improved estimation of kinetic parameters estimated by Wei and Morris (1972) and Saunier and Selleck (1975).

9. Development of practical concepts for improved chlorination from the new kinetic information.

2. LITERATURE REVIEW

BASICS OF CHLORINATION CHEMISTRY

Chlorine is a strong oxidant and undergoes numerous reactions when it contacts water and other substances. Over the past 40 years an understanding of chlorine chemistry has developed, and most of the elementary reactions with water, ammonia and some organic substances are known.

Hydrolysis Reaction

Chlorine gas when dissolved in water undergoes very fast hydrolysis reactions to form hypochlorous acid and hydrochloric acid, as follows:

$$Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^- \tag{2.1}$$

The hydrolysis of chlorine has been studied extensively. and is defined as follows:

$$K_c = \frac{[\ H^+\ ]\ [\ Cl^-\ ]\ [\ HOCl\ ]}{[\ Cl_2\ ]} \tag{2.2}$$

where [ ] denotes molar concentration.

The value of K_c varies with temperature and various reported values are shown in Table 2.1. The hydrolysis reaction is quite rapid, going to completion in a matter of a few tenths of a second (Shilov and Solodusenkov, 1936, 1947). The equilibrium described by equation 2.1 is such that only insignificant amounts of chlorine exits in the gaseous form at neutral pH's in the range of concentrations of interest in water and wastewater treatment (White, 1972).

Table 2.1 Hydrolysis Constants

pH	Value (moles/liter)	Temperature Deg. C.	Reference
(1)	(2)	(3)	(4)
6.7	1.2 x 10	25	Morris(1967)
7.2	1.4 x 10	26	Chia(1901)
5.5	1.6 x 10	20	Hammer(1902)

When sodium and calcium hypochlorites are used for chlorination in lieu of gaseous chlorine, the hydrolysis reaction tends to increase solution pH, as follows:

$$\mathrm{NaOH} + \mathrm{H_2O} \rightarrow \mathrm{HOCl} + \mathrm{Na^+} + \mathrm{OH^-} \qquad (2.3)$$

or

$$\mathrm{Ca(OCl)_2} + 2\mathrm{H_2O} \rightarrow 2\mathrm{HOCl} + \mathrm{Ca(OH)_2} \qquad (2.4)$$

Otherwise the reactions are the same as with gaseous chlorine.

Ionization Reaction

Hypochlorous acid is a weak acid and undergoes the following dissociation reaction:

$$\mathrm{HOCl} \rightarrow \mathrm{OCl^-} + \mathrm{H^+} \qquad (2.5)$$

The dissociation constant (proton reaction constant) is defined as

$$K_a = \frac{[\ H^+\ ]\ [\ OCl^-\ ]}{[\ HOCl\ ]} \qquad (2.6)$$

The value of K_a is also temperature dependent and values for the pK_a are shown in Table 2.2. The precent distribution of hypochlorous acid and hypochlorite ion is strongly influenced by pH. Relative distributions of these two species as well as chlorine gas are shown in Figure 2.1. It is well established that the distribution between HOCl and OCl^- has profound effects on disinfection efficiency (Butterfield, 1943; More, 1951, and Fair, 1958).

Chlorine Reactions with Ammonia

Ammonia Reactions with Water

Chlorine reacts with both organic and inorganic nitrogen compounds in water, and these reactions strongly influence disinfection efficiency. Most surface water supplies contain small quantities of ammonia which result from the decomposition of plant and animal protein by saprophylic bacteria under both anaerobic and aerobic conditions. The end product of these reactions is ammonia which is present in neutral pH waters primarily as the ammonium ion (NH_4^+). The distribution between ammonia and the ammonium ion is described as follows:

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^- \qquad (2.7)$$

where:

$$K_b = \frac{[\ NH_4^+\ ]\ [\ OH^-\ ]}{[\ NH_3\ ]} \qquad (2.8)$$

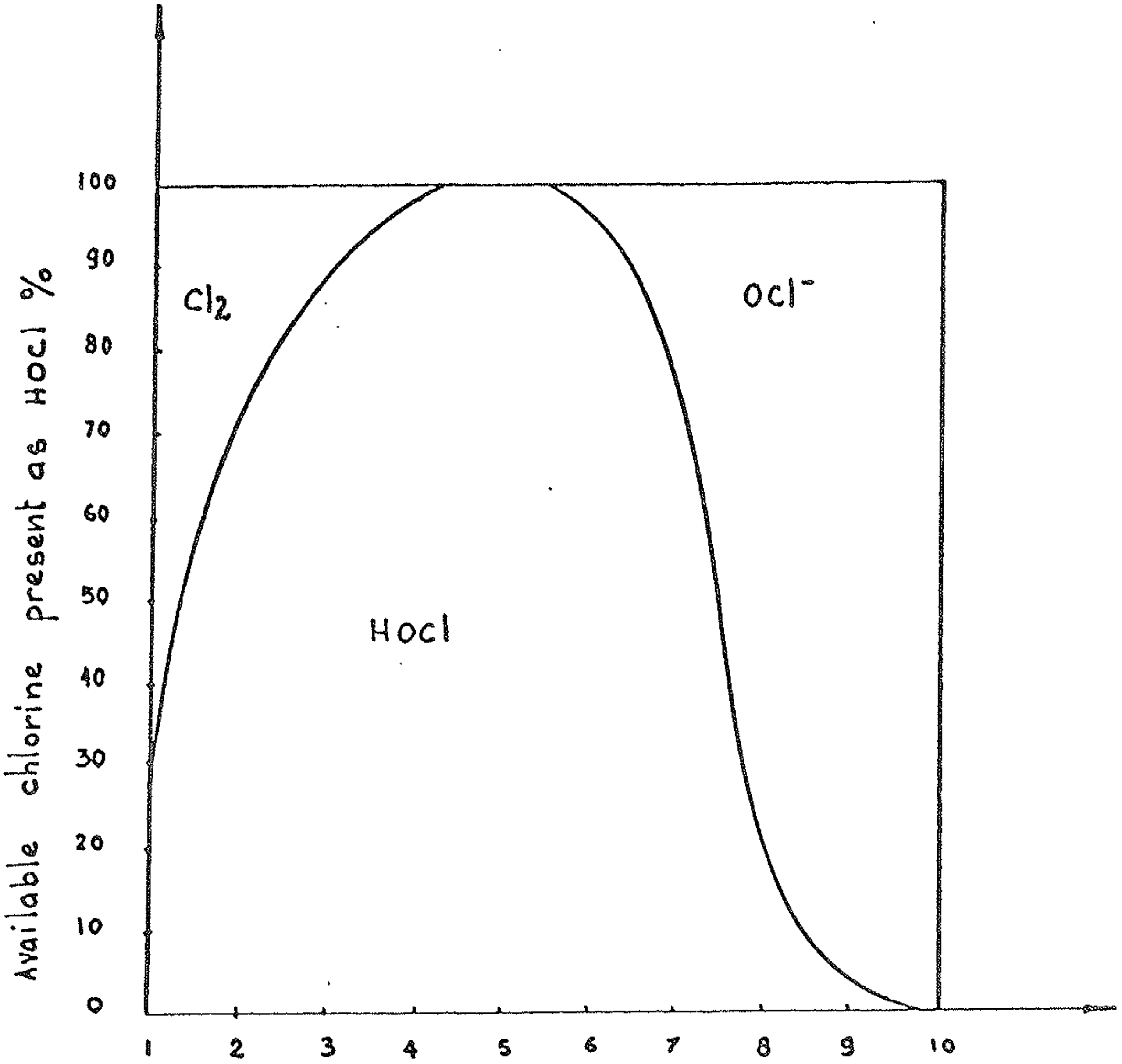


Figure 2-1: Relative Distributions of Gaseous Chlorine, HOCl, and OCl

The value of K_b is well known and several values are reported in Table 2-2

Table 2-2 Dissociation Constants and Hydrolysis Constants for Chlorine and Ammonia.

Temp, ° C (1)	Constants		
	pK_a [1] (2)	pK_b [2] (3)	pK_c [3] (4)
0	7.825	10.081	3.836
5	7.754	9.903	–
10	7.690	9.730	–
15	7.633	9.564	3.551
20	7.582	9.401	–
25	7.537	9.246	3.404
30	7.497	9.093	–
35	7.463	8.947	3.292

[1] Morris (1946)
[2] Bates and Pinching (1950)
[3] Connick and Chia (1959)

Breakpoint Chlorination

The reaction of chlorine and ammonia in aqueous solution were investigated first by Griffin (1940, 1941); he proposed the empirical breakpoint chlorination reaction as follows:

$$HOCl + NH_3 \longrightarrow NH_2Cl + H_2O \qquad (2\text{-}9)$$

$$HOCl + NH_2Cl \longrightarrow NHCl_2 + H_2O \tag{2-10}$$

$$HOCl + NHCl_2 \longrightarrow NCl_3 + H_2O \tag{2-11}$$

where:

NH_2Cl: Monochloramine

$NHCl_2$: Dichloramine

NCl_3: Nitrogen Trichloride

The empirical equations proposed by Griffin (1941, 1942) follow from the valences of nitrogen and chlorine, but only qualitatively describe the true breakpoint stoichiometry.

The distribution of these species are summarized in Figure 2-2. The total concentration of hypochlorous acid and hypochlorite ion are called free chlorine residual, and the total concentration of monochloramine, dichloramine and nitrogen trichloride is the combined chlorine residual. When water does not contain any ammonia and other reducing agents (such as H_2S, Fe^{++}, Mn^{++}, etc.), the concentration of chlorine residual will be virtually the same as the chlorine added to aqueous solution, as shown by the straight line in the Figure 2-2.

If water contains ammonia, a series of breakpoint reactions occur. The first combined chlorine residual is monochloramine, and predominantly exists when the initial Cl/N ratio is less than 4. As the ratio of chlorine dose to initial ammonia concentration exceeds 5, dichloramine is formed either by reaction between monochloramine and free chlorine, or by disproportionation reaction of monochloramine (Granstrom, 1954). In the next step of the break-

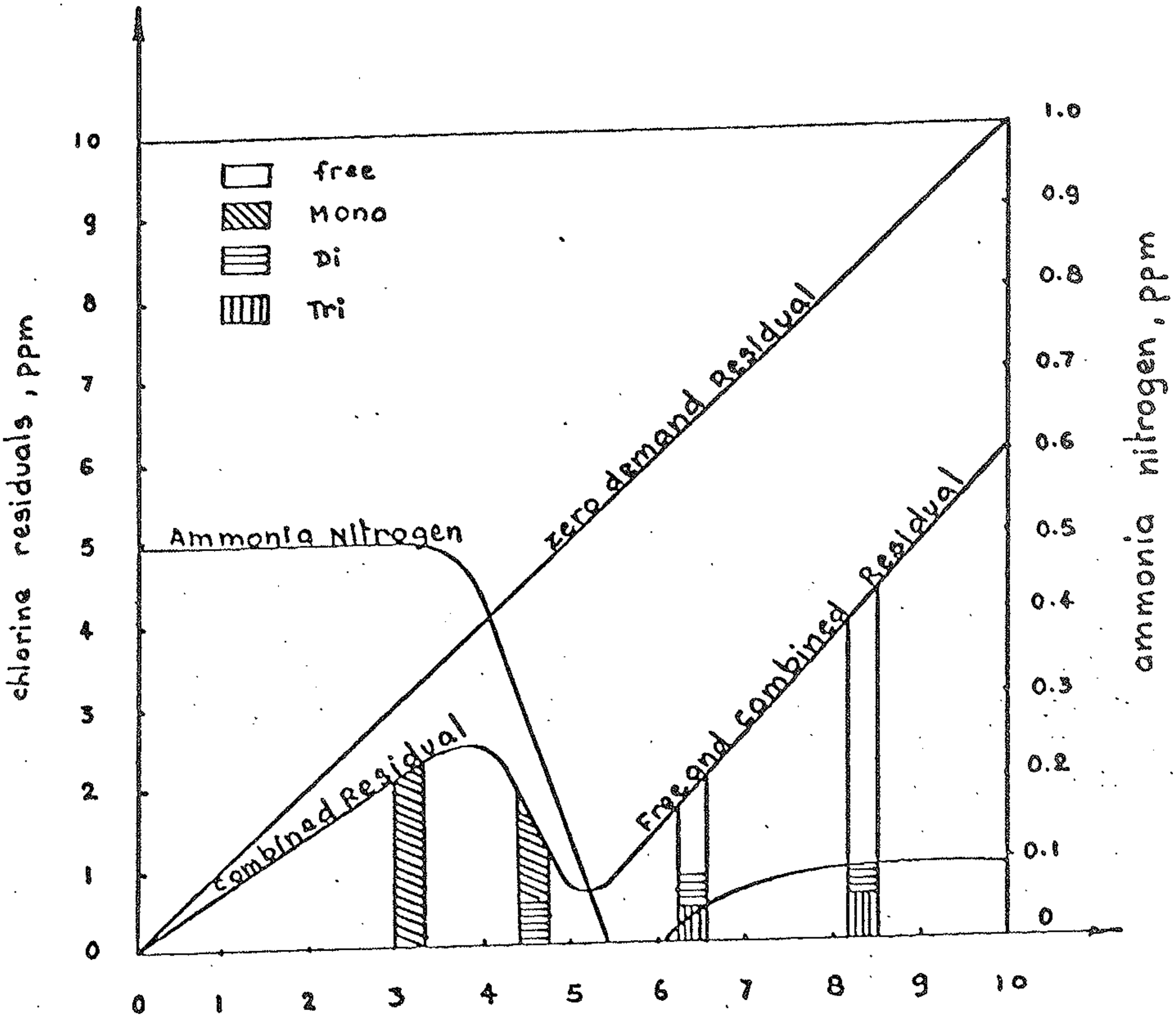


Figure 2-2: Distribution of Species During Breakpoint Chlorination

point reaction, several reactions are involved in the decomposition of dichloramine and the oxidation of ammonia which will be discussed later.

As additional chlorine is added dichloramine is formed which reacts further to from nitrogen trichloride, nitrate, or nitrogen gas. The final distribution of these end products is qualitatively understood, and was investigated earlier by several pioneering researchers.

Calvert (1940) reported that the breakpoint appears at the chlorine to ammonia ratio by weight of 7.5 to 1.0, while White (1972) proposed a much higher ratio of 10 to 1.0. Palin investigated the development of breakpoint chlorination at different pH's and different chlorine to ammonia-nitrogen ratios. His results are shown in Figures 2-3 to 2-5, and represent our current understanding of the breakpoint reactions.

Mode of Disinfection by Chlorine

There is some disagreement among researchers investigating the mode of action of Chlorine on bacterial cells. Green (1946) postulated that chlorine reacts irreversibly with the enzymatic system of bacteria, oxidizing the sulfhydril groups and abolishing the enzyme triosephosphate dehydrogenase. Wyss (1962) concluded that chlorine destroys a part of the enzyme system of the cell, which causes an imbalanced metabolism, thus resulting in death since the cell cannot repair itself. Friberg (1956) performed his experiment on the reaction of radioactive chlorine with bacteria in water, and showed that chlorine penetrates into bacterial cells. This penetration was reported by Rudolphs (1936) as much faster in living cells than in dead cells.

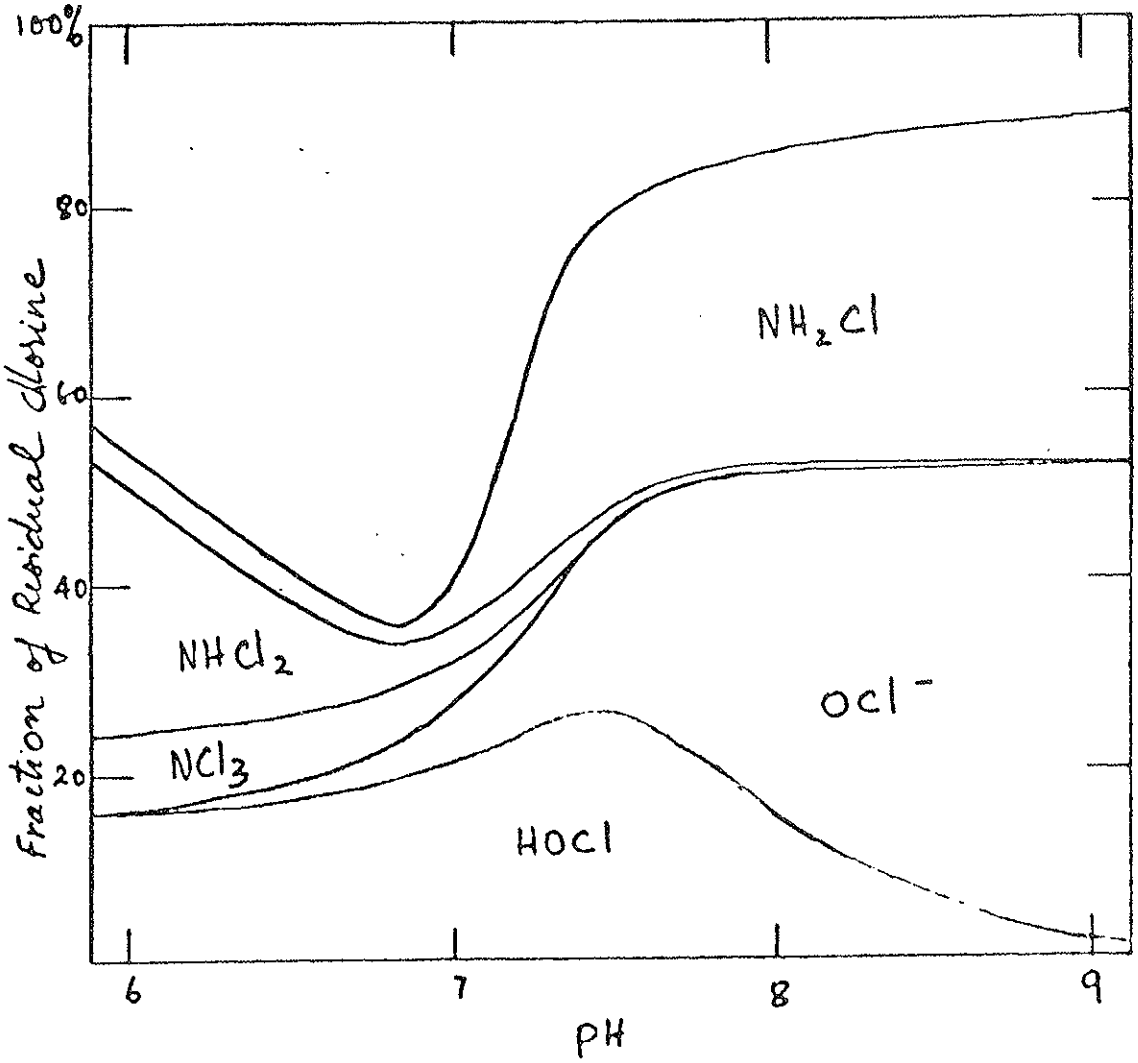


Figure 2-3: Variation of Chlorine Residual with pH after 10 Minute Contact Time for Cl/N Ratio of 2.37 ....

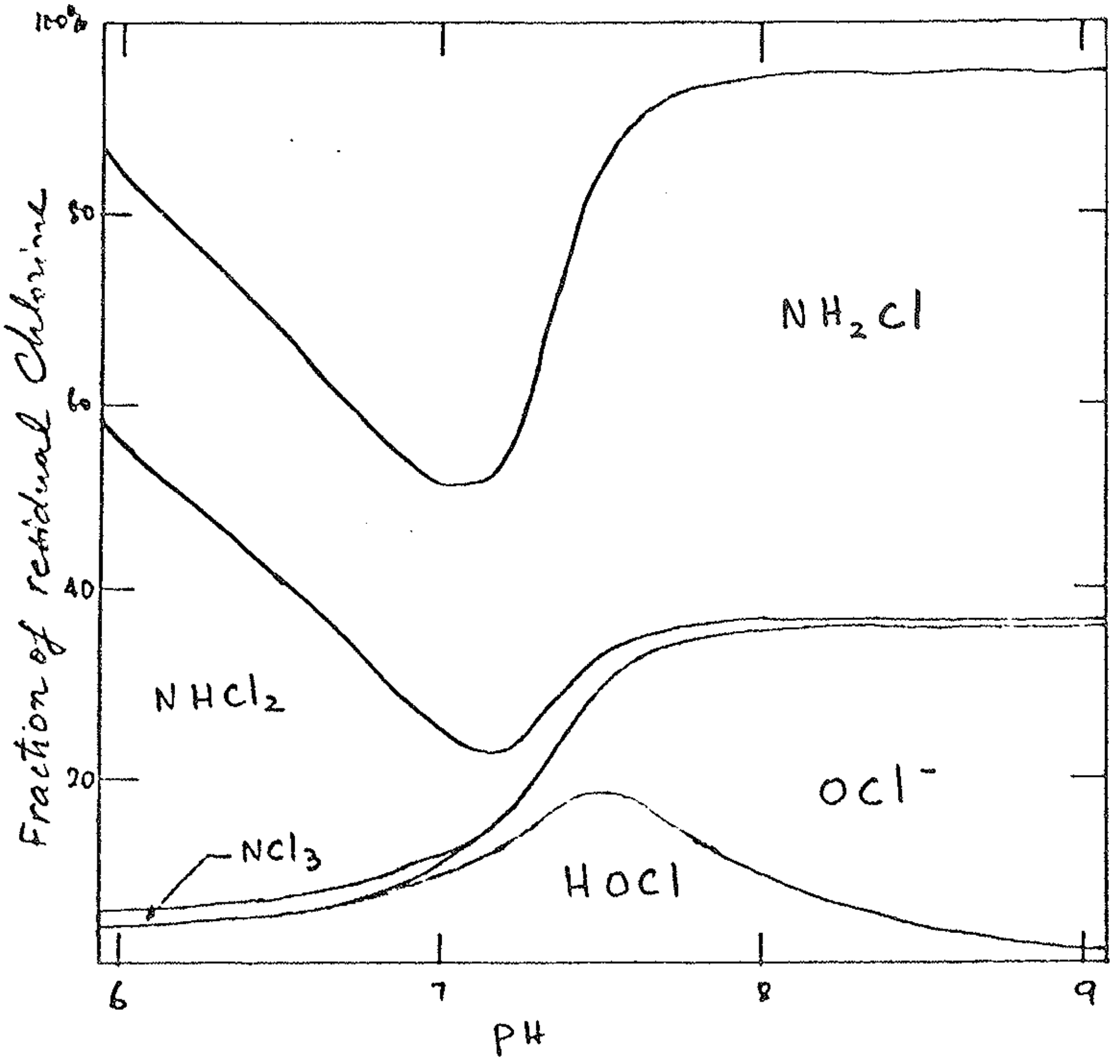


Figure 2-4: Variation of Chlorine Residual with pH after 10 Minute Contact Time for Cl/N Ratio of 1.82 ....

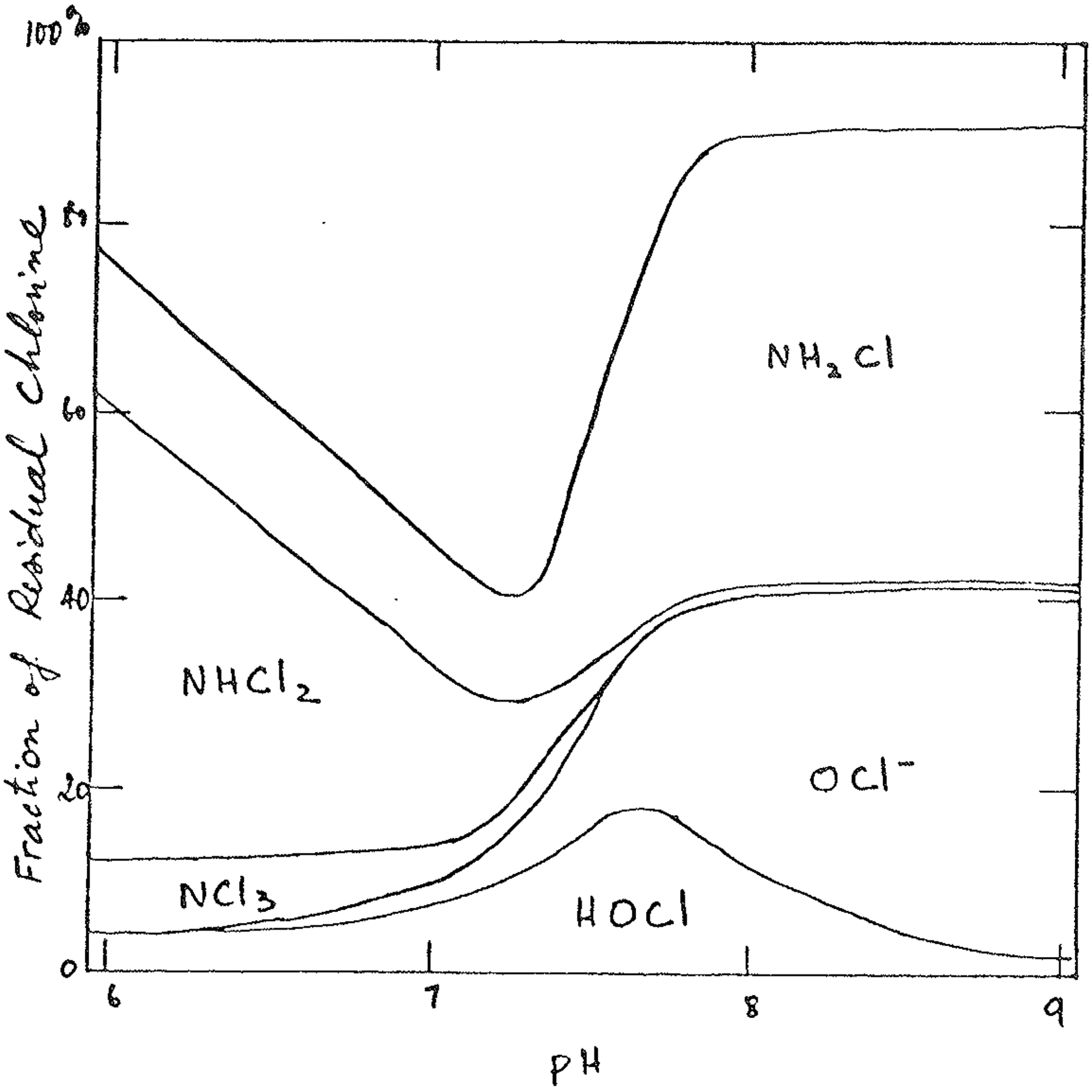


Figure 2-5: Variation of Chlorine Residual with pH after 10 Minute Contact Time for Cl/N Ratio of 1.62 ....

Other investigators have proposed that direct oxidation of hypochlorous acid on the cell membrane is the main mechanism of disinfection. The exact disinfection mode remains a subject of controversy and interest.

The Disinfectant Qualities of Different Chlorine Residuals

Butterfield et al. (1943) conducted experimental studies on the deactivation of *Escherichia Coli* with free chlorine. His results showed that one hundred times higher chlorine residual is required to inactivate with the hypochlorite ion than with hypochlorous acid. Fair et al. (1947) using Cysts of *Entamoeba Histolytica*, found that dichloramine has about 60 percent and monochloramine about 20 percent of the potential germicide of hypochlorous acid. Nitrogen trichloride has unknown disinfecting properties. Saunier and Selleck (1976) used the Gard (1957) model to simulate the disinfection in a plug flow and compete-mix continuous flow reactors. Their results show that hypochlorous acid is approximately 30 times more germicidal than the hypochlorite ion. Dichloramine was found to have disinfecting properties approximately equal to hypochlorous acid which was concurred with Fairs, et. al. (1947) results.

Byproduct Formation from Breakpoint Chlorination

Nitrogen Trichloride

Nitrogen trichloride (NCl_3)is an undesirable nuisance residual produced from the reaction between HOCl and $NHCl_2$. The presence of a small concentration of NCl_3 as low as 0.05 mg/l in potable water can cause objectionable taste and odor. If the concentration exceeds 0.1 ppm, NCl_3 can irritate the muscosa layer in stomach and intestines Fortunately during the breakpoint chlorination process, NCl_3 is usually present in relatively low concentrations. Also it is an unstable compound with very low solubility in water, and is quickly destroyed by sunlight.

Chlorophenols

Phenols are frequently found in surface waters as a result of industrial pollution, especially pollution from oil refineries. During chlorination chlorophenols are formed which have important taste and odor problems as well as health effects. Chlorophenol, di-chlorophenol, and trichlorophenol can be formed. Generally chlorophenols have more toxic biological properties than phenols. The reaction between chlorine and phenol is summarized as follows in Figure 2-6.

According to Lee (1967), the odor threshold odor concentration of 2-chlorophenol and 2,6 or 2,4-dichlorophenol is from 2 to 3 µg/l, while the odor threshold concentration of 2,4,6-trichlorophenol is more than 1 mg/l. Furthermore trichlorophenol is readily oxidized by additional hypochlorous acid to form a mixture of non-phenolic compounds.

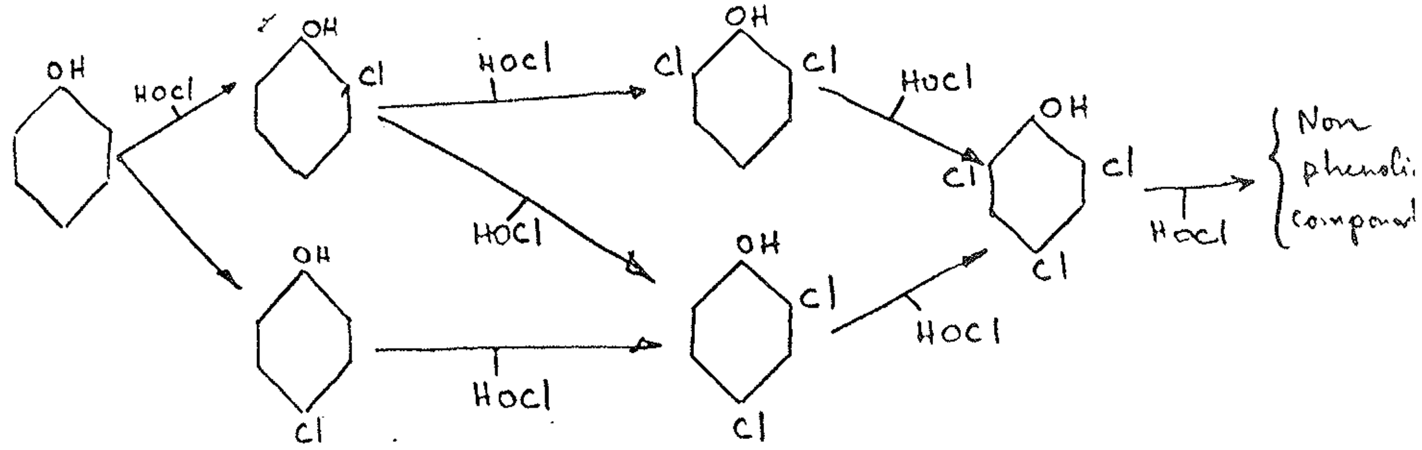


Figure 2-6: Reactions of Chlorine Species and Phenol.

Chloramines also can react with phenol to produce chlorophenol. However, this reaction is much slower than the reactions between free chlorine and phenol; therefore the taste and odor of chlorophenols produced from chloramines may appear in the distribution system very far from the treatment plant, but not at the treatment plant itself.

In water supply practice, the chlorination of phenol is usually performed by super chlorination followed by a dechlorination. A large amount of free chlorine is added to insure the complete oxidation of phenol to trichlorophenol then to non-phenolic compounds.

Trihalomethanes

Trihalomethanes can be produced from a series of reactions of chlorine and precursor substances (humic materials, acetyl derivatives, etc.). The US Environmental Protection Agency (EPA) is specially interest in the following six halogenated substances because of their potential health effects.: chloroform, bromodichloromethane, dibromochloromethane, bromoform, carbon tetrachloride and 1,2-dichoroethane. Stevens and Symons (1975) indicated that carbon tetrachloride is not formed in chlorination. The health significance of trihalomethanes is not well defined but they are considered unwanted compounds to be avoided if possible.

The elimination of trihalomethane in drinking water can be done by two ways:

- Removal of organic precursors
- Removal of trihalomethane itself

The processes for used for trihalomethane removal usually also eliminate chlorine residual and are therefore impracticable in water supply. Removal of precursors is a alternate approach which can be partially accomplished by alum coagulation followed by filtration and sedimentation. Activated carbon adsorption is more effective but more expensive.

Carcinogenics

Out of the list of 235 organic compounds identified in drinking water, twenty-one were classified as having carcinogenic activity and four are confirmed as carcinogenic as shown in Table 2-3. The presence of these carcinogens in drinking water is usually not from the chlorination, but from raw water sources. The Environmental Protection Agency, found chloroform in water supplies from 80 different locations.

Table 2-3: Organic Carcinogenic Chemicals in Drinking Water*

Chemical	Concentration (μg/l)
Aldrin	-
Benzene	50
Benzo(a)pyrene+	0.0002-0.002
Bis-2-chloroethyl ether	0.07-0.16
Bis-chloromethyl ether+	-
BHC (Lindane)	-
Carbon tetrachloride+	5.
Chloradane	-
Chloroform	0.1-311.
1,2-Dibromoethane (EDB)	-
1,1-Dichloroethane (EDC)	-
Dieldrin	0.05-0.09
DDT	-
DDE	-
Endrin	-
Heptachlor	-
1,1,2-Trichloroethane	0.35-0.45
Trichloroethylene	-
Tetrachloroethane	10.
Tetrachloroethylene	0.4-0.5
Vinyl chloride+	-

* After Kraybill (1975).

Most of the current research is focussed on carbon tetrachloride and chloroform, which can be generated from the reaction between chlorine and aromatic organic compounds. Even though carbon tetrachloride and chloroform are present in water in parts-per- billion range, Kraybill (1975) still believes that they have serious health effects since the exposure is continuous.

Since the some halogenated organic compounds found in water have potential health effects, some researchers have suggested using ozonation in lieu of chlorination in drinking water treatment processes. Ozonation can produce ozonides and epoxides which are highly suspected themselves of being carcinogens. Alternatives to chlorination have not been proven to be safer and more effective than chlorination.

Dechlorination

The total amount of chlorine used in North America in 1975 was estimated at 10.5 million tons (recorded by Chlorine Institute). Approximately 80 percent of this amount was consumed by chemical industries, 16 percent by Pulp and Paper Industries. The remaining 4 percent was for sanitary purposes, which include water and wastewater treatment, cooling water treatment, swimming pool disinfection and house hold use. The increased use of disinfection by chlorination makes the dechlorination process much more important in both industrial wastewater and drinking water treatment.

Aeration is the simplest method for dechlorination, but it is slow and its effect is very moderate. Other methods include treatment with sulfur dioxide, hydrogen peroxide, ferrous sulfate, and activated carbon.

Dechlorination by Sulfur Dioxide

Sulfur dioxide (SO_2) is used wastewater due to its low cost and convenience. It has a high solubility in water and the hydrolysis reaction of is

$$SO_2 + H_2O \longrightarrow H_2SO_3$$

(2-13)

SO_2 reacts with free chlorine and chloramines as follows:

$$SO_2 + H_2O + HOCl \longrightarrow 3H^+ + SO_4^= + Cl^- \quad (2\text{-}14)$$

$$SO_2 + 2H_2O + NH_2Cl \longrightarrow NH_4^+ + 2H^+ + SO_4^= + Cl^- \quad (2\text{-}15)$$

Approximately 0.9 mg of SO_2 is required to remove 1 mg of chlorine residual as Cl_2, and about 2.1 mg of alkalinity as $CaCO_3$ is required to neutralize the H^+ ion produced by dechlorination reaction.

Dechlorination by SO_2 is very rapid resulting in very low capital cost for a reaction facility, but the material costs can be quite high. Dean (1974) estimated that the cost of chlorination followed by dechlorination with SO_2 is about 1.3 times of the cost of chlorination itself.

Sodium bisulfite ($NaHSO_3$), sodium sulfite (Na_2SO_3), and sodium thiosulfate ($Na_2S_2O_3$) can also be used for dechlorination, but they are more expensive than SO_2 gas.

Dechlorination by Hydrogen Peroxide

According to Mischenko (1961), hydrogen peroxide reacts with hypochlorous acid to produce oxygen and the chloride ion as follows:

$$H_2O_2 + HOCl \longrightarrow O_2 + H^+ + Cl^- + H_2O \quad (2\text{-}16)$$

The equilibrium constant is

$$K_{eq} = e^{-\Delta G^{o}/RT}$$

where

$$\Delta G^{o} = -36.3$$

The kinetics of dechlorination by hydrogen peroxide are not well defined; however, reaction rates as indicated are slow. Therefore this method is not very useful in dechlorination practice.

Dechlorination by Activated Carbon

Activated carbon is an excellent dechlorinating agent. According to Bauer (1973), the initial step of reaction between chlorine and activated carbon (C*) can be summarized as follows:

C* reaction with free chlorine:

$$C^* + HOCl \longrightarrow CO^* + H^+ + Cl^- \tag{2-17}$$

C* reaction with monochloramine:

$$C^* + H_2O + NH_2Cl \longrightarrow NH_3 + H^+ + Cl^- + CO^* \tag{2-18}$$

C* reaction with dichloramine:

$$C^* + H_2O + 2NHCl_2 \longrightarrow N_2 + 4H^+ + 4Cl^- + CO^* \tag{2-19}$$

According to US EPA Technology Transfer information (Oct - 1975), the surface oxide of carbon (CO*) will be emitted as CO_2 gas. Thus, the total reaction is:

$$C^* + 2HOCl \longrightarrow CO_2 + 2H^+ + 2Cl^- \qquad (2\text{-}20)$$

$$C^* + 2NH_2Cl + 2H_2O \longrightarrow CO_2 + 2NH_4^+ + 2Cl^- \qquad (2\text{-}21)$$

$$C^* + 4NHCl_2 + 2H_2O \longrightarrow CO_2 + 2N_2 + 8H^+ + 8Cl^- \qquad (2\text{-}22)$$

In summary carbon dioxide is formed as a final product, dichloramine is decomposed to nitrogen gas and monochloramine is destroyed to produce ammonia and the chloride ion. following reaction on activated carbon (C^*). Bauer (1973) indicated that contrary to the above model that after reaction 2-17 proceeds to a certain degree, the surface oxide on carbon can oxidize monochloramine and release nitrogen gas as an end product.

$$CO^* + 2NH_2Cl \longrightarrow H_2O + 2H^+ + 2Cl^- + N_2 + C^* \qquad (2\text{-}23)$$

The dechlorination process is required in many cases to remove the potential toxic byproducts from chlorination. Additionally it can be used to remove ammonia in wastewater chlorination by dechlorinating after oxidizing the ammonia or converting it to dichloramine. Dechlorination with activated carbon will remove the dichloramine, resulting in ammonia removal with less that the breakpoint chlorine dosage requirement. (Stasiuk et al. (1974)). Dechlorination with sulfur dioxide (SO_2) is not practicable in this case, because chloramine would be converted back to ammonia.

BREAKPOINT KINETICS AND MECHANISMS

Early Investigations in the Breakpoint Mechanisms

Chapin (1929) is the first person who investigated the conditions that limit the formation of the three chloramines in aqueous solution. Chapin indicated that at pH greater than 8.5, only monochloramine is formed, at pH less than 5, dichloramine is the predominant species, at pH less than 4.4, nitrogen trichloride is formed at a significant level. He also observed that at pH 7, monochloramine and dichloramine are produced at the same amount. However, this experiment was performed in a batch reactor, with ammonia concentration in excess, and high chlorine dose (2000 ppm). Thus, Chapin's results do not reflect correct image of the practical water or wastewater chlorination. Chapin (1931) also studied the chlorination reactions at different chlorine to ammonia molar ratios. He observed that at pH 5, the molar ratio at the breakpoint is 1.5, and the total reaction is:

$$3Cl_2 + 2NH_3 \longrightarrow N_2 + 6HCl \qquad (2\text{-}24)$$

Berliner (1931) stated that the physical and chemical properties of aqueous chlorine are highly dependent on the range of its concentration. He concludes that research in chlorination has to be performed at a realistic ranges of concentration. A few mg/l of chlorine is the range of interested in water treatment.

Griffin (1940) is the first person to use the term "breakpoint" to describe the reaction between chlorine and ammonia in aqueous solution. His experiments were conducted at low ammonia concentrations (0.5 mg/l) and at different pH's. He indicated that the breakpoint occurred at the molar ratio of chlorine to ammonia of about 2.0. The rate of breakpoint reaction was observed to be fastest at a pH between 7 and 8.

Palin`s Contribution

Palin's work in chlorination research is concentrated in two areas: analytical methods for chlorine determination, and elucidation of reaction mechanism. He developed the NOT-FAS method (1949, 1954) and DPD-FAS method (1957, 1967, 1968). Using the NOT-FAS method, Palin (1950) performed his chlorination experiments with low ammonia concentration (0.5 mg/l), at different pH and chlorine dose. His results can be summarized as follows:

a. Monochloramine was the dominant species at pH greater than 7.5. At pH greater than 8, the formation of dichloramine and nitrogen trichloride is insignificant. He explained the loss of monochloramine by the following reaction:

$$2NH_2Cl + HOCl \longrightarrow N_2 + 3HCl + H_2O \qquad (2\text{-}25)$$

b. Dichloramine was unstable and its decomposition resulted in a loss of total chlorine residual. However, at a certain period in the reaction, an increase in free chlorine concentration was observed. The mechanism for decomposition of dichloramine was suggested as follows:

$$2NHCl_2 + H_2O \longrightarrow N_2 + HOCl + 3HCl \qquad (2\text{-}26)$$

and

$$NHCl_2 + NH_2Cl \longrightarrow N_2 + 3HCl \qquad (2\text{-}27)$$

c. Nitrogen trichloride and free chlorine coexisted at final stage and they were fairly stable:

$$HOCl + NHCl_2 \longleftrightarrow NCl_3 + H_2O \qquad (2\text{-}28)$$

Palin performed his experiments in batch reactor with contact times of 10 minutes, 2 hours, and 24 hours, which where too long for the development of a kinetic model. Reactions (2-25), (2-26), and (2-27) are non-elementary reactions, they cannot be incorporated in a mechanistic model. However, they can be used to explain the loss of chlorine residual and the production of nitrogen gas (N_2) and nitrate (NO_3^-) during breakpoint chlorination. Palin proved that N_2 and NO_3^- were the major end products, described as follows:

Let:

$$P = \Sigma P_i X_i \qquad (2\text{-}28)$$

where:

P = molar ratio of Cl_2 reduced to NH_3 - N oxidized in the total chlorination reaction.

P_i = stoichiometric ratio of Cl_2 to NH_3 - N required to produce the i th species.

X_i = mole fraction of NH_3 - N oxidized to produce the i th species.

Let:

i = 1 for N_2

i = 2 for NO_3^-

If N_2 and NO_3^- are the only end products from the breakpoint chlorination, then:

$$2NH_3 + 3HOCl \longrightarrow N_2 + 3H_2O + 3HCl \qquad (2\text{-}29)$$

and

$$NH_3 + 4HOCl \longrightarrow NO_3^- + H_2O + 5H^+ + 4Cl^- \qquad (2\text{-}30)$$

Thus:

$$P_1 = 1.5 \text{ and } P_2 = 4.0$$

$$\Sigma X_i = X_1 + X_2 = 1 \qquad (2\text{-}31)$$

$$P = 1.5X_1 + 4X_2 \qquad (2\text{-}32)$$

By substituting equation 2-31 into equation 2-32 the following result is obtained:

$$P = 1.5 - 2.5X_2 \qquad (2\text{-}33)$$

where:

$$X_2 = \frac{[NO_3^-]}{[\text{ammonia oxidized}]}$$

Therefore:

$$[NO_3^-] = \frac{P - 1.5}{2.5} \cdot [\text{ammonia oxidized}] \qquad (2\text{-}34)$$

The nitrate concentrations calculated from Equation (2-34) match very closely to Palin's results.

The Work of Morris and Co-Workers

The work of Morris and co-workers was concentrated on the development breakpoint reaction mechanism and the accompanying kinetic parameters.

Morris and Weil (1949, 1950)

In order to overcome the experimental difficulties of observing the extremely rapid breakpoint reactions, Morris and Weil (1949, 1950) performed their experiments at low concentration (in the order of 10^{-5}M). They used the orthotolidine method for determination of the different chlorine residual components. The study was done in a pH range of 4.5 to 6.0. The reactions between free chlorine and ammonia were expressed as:

$$NH_4^+ + OCl^- \longrightarrow NH_2Cl + H_2O \qquad (2\text{-}35)$$

and

$$NH_3 + HOCl \longrightarrow NH_2Cl + H_2O \qquad (2\text{-}36)$$

If either reaction 2-35 or 2-36 is an elementary reaction, the rate of formation of NH_2Cl in diluted water solution is:

$$\frac{d[NH_2Cl]}{dt} = k_1[NH_3][HOCl] \qquad (2\text{-}37)$$

where k_1 is theoretical rate coefficient. Morris showed that the changes in ionic strength will have the same influence which ever mechanism (Equation (2-35) or Equation (2-36)) is operative. Thus, total rate of formation of monochloramine (NH_2Cl) can be expressed as a function of pH as follows:

$$\frac{d[NH_2Cl]}{dt} = \frac{k_1([NH_3] + [NH_4^+])([HOCl] + [OCl^-])}{\left(1 + \frac{K_a K_b}{K_w} + \frac{K_a}{[H^+]} + \frac{K_b[H^+]}{K_w}\right)} \tag{2-38}$$

Letting :

$$k_{10} = \frac{k_1}{1 + \frac{K_a K_b}{K_w} + \frac{K_a}{[H^+]} + \frac{K_b}{K_w}[H^+]} \tag{2-39}$$

equation 2-38 can be simplified to

$$\frac{d[NH_2Cl]}{dt} = k_{10}([NH_3] + [NH_4^+])([HOCl] + [OCl^-]) \tag{2-40}$$

where ($[NH_3] + [NH_4^+]$) and ($[HOCl] + [OCl^-]$) are the observed concentrations of ammonia and free chlorine, respectively. pH dependence of this rate coefficient is shown on Figure 2-7. Morris and Weil also experimentally defined the theoretical rate coefficient k_1 as

$$k_1 = 2.5 \cdot 10^{10}\ e^{-2500/RT} \tag{2-41}$$

Morris (1967) revised his work in (1950) and proposed:

$$k_1 = 9.7 \cdot 10^{8}\ e^{-3000/RT} \tag{2-42}$$

and

$$k_2 = 7.6 \cdot 10^{7}\ e^{-7300/RT} \tag{2-43}$$

for the theoretical rate of formation of dichloramine, a second order reaction between monochloramine and hypochlorous acid.

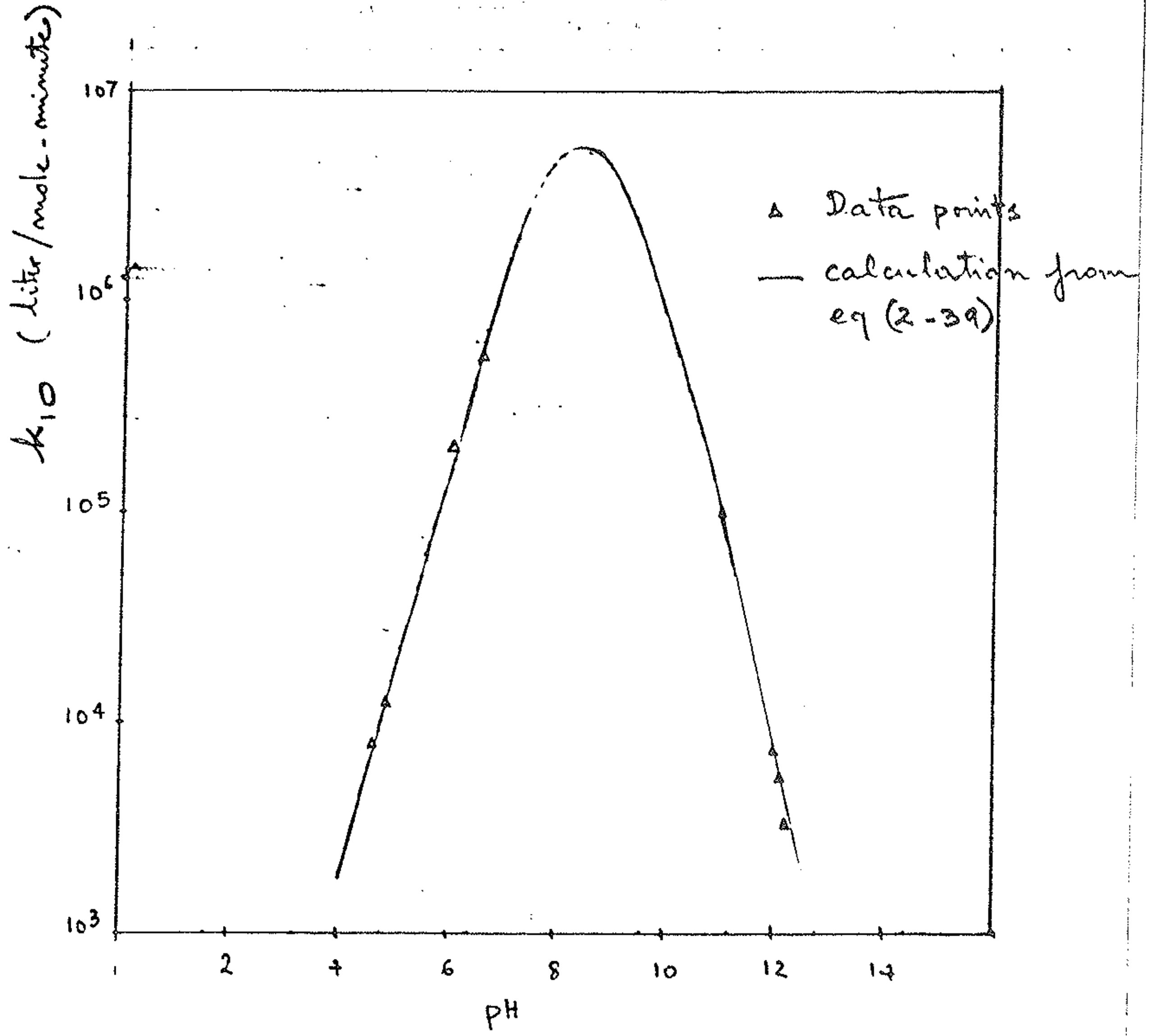


Figure 2-7: pH Dependence of the Rate of Formation of Monochloramine

Morris and Granstrom (1954)

Morris and Granstrom (1954) investigated the disproportionation reactions which tend to shift the relative concentration of monochloramine and dichloramine into opposite directions. Their study showed that there are two parallel processes involving in the disproportionation of monochloramine. One of them is first-order reaction and he other is second-order. However, they are acting independently. The overall rate of disproportionation reaction was described as[a]:

$$\frac{d[NH_2Cl]}{dt} = k_{11}[NH_2Cl] + k_{12}[NH_2Cl]^2 \qquad (2\text{-}44)$$

where:

k_{11} = rate constant of the first-order process

k_{12} = rate constant of the second-order process

k_{11} and k_{12} were extrapolated from experimental data:

$$k_{12} = 5.21 \,.\, 10^9 e^{-17.0/RT_K} \qquad (2\text{-}45)$$

$$k_2 = \left\{4.75 \,.\, 10^3 + 6.3 \,.\, 10^8[H^+] + 1.68 \,.\, 10^5[HAC]\right\} e^{-43.1/RT_K} \qquad (2\text{-}46)$$

---

[a] The kinetic coefficient used in this equation are the same as shown in Granstrom work (1954), which is different from the lists of symbols shown in the nomenclature section.

Morris (1966)

Following his work in 1946, Morris continued to investigate the variation of HOCl hydrolysis constant K_a with respect to temperature. The result from this study showed that the rate of change could be described as follows:

$$pK_a = \frac{300}{T_K} - 10.0686 + 0.0253\ T_K \tag{2-47}$$

BREAKPOINT SIMULATION MODEL BY MORRIS AND WEI (1972)

Morris and Wei`s contributions on the development of breakpoint chlorination can be classified by three phases as follows:

Development of a mechanistic model

Evaluation of kinetics parameter

Breakpoint simulation.

The Mechanistic Model

Based on the works of Chapin (1929, 1931), Griffin (1940, 1941), Palin (1950) and Morris and Weil (1949, 1950, 1952, 1967), Wei (1972) developed the first complete model for breakpoint chlorination. This model can be summarized as shown in Table 2-4.

Reactions R-1, R-2 and R-3 are similar to the mechanism proposed by Griffin (1940, 1941). Reactions R-3 and R-4 explain the presence of nitrogen trichloride (NCl_3) as an intermediate product. Reaction R-4 is very slow;

therefore, usually NCl_3 is present in the last phase of breakpoint reaction.

Table 2-4. Breakpoint Reaction Mechanism.

$HOCl + NH_3 \longrightarrow NH_2Cl + H_2O$ (R-1)

$HOCl + NH_2Cl \longrightarrow NHCl_2 + H_2O$ (R-2)

$HOCl + NHCl_2 \longrightarrow NCl_3 + H_2O$ (R-3)

$NCl_3 + H_2O \longrightarrow NHCl_2 + H_2O$ (R-4)

$NHCl_2 + H_2O \longrightarrow NOH + 2H^+ + 2Cl^-$ (R-5)

$NOH + NH_2Cl \longrightarrow N_2 + H_2O + H^+ + Cl^-$ (R-6)

$NOH + NHCl_2 \longrightarrow N_2 + HOCl + H^+ + Cl^-$ (R-7)

$NOH + 2HOCl \longrightarrow NO_3^- + 3H^+ + 2Cl^-$ (R-8)

After Morris and Wei (1972)

Reaction R-5 is the rate limiting step of the entire mechanism. Nitroxyl radical (NOH) is produced in this step and it is the key mechanism for the loss of chlorine and ammonia nitrogen during breakpoint chlorination. Reaction R-6, R-7 and R-8 show the reaction between NOH and NH_2Cl, $NHCl_2$ and HOCl, respectively. Nitrogen gas (N_2), nitrate (NO_3^-) and the chloride ion

(Cl^-) are the final products of the combined reaction. The regeneration of hypochlorous acid (HOCl) is explained through reaction R-7.

Evaluation of Kinetic Parameters

The kinetic parameters used by Wei (1972) are summarized in Table 2-5. k_{10} was evaluated by Morris (1967); k_{30} and k_{40} were selected by trial and error to approach Palin's data (1950); k_{60}, k_{70}, and k_{80} were selected to fit the stoichiometry calculated from experimental data. Wei evaluated k_{20} and k_{50} by using laboratory batch experiments.

Table 2-5. Breakpoint Chlorination Rate Coefficients.

Observed Rate Coefficients	Theoretical Rate Coefficient
$k_{10} = 9.7 \cdot 10^{8}\, e^{(-3.0/RT)}$	$k_1 = \dfrac{k_{10}}{\left(1 + \dfrac{K_a}{[H^+]}\right)}\left(1 + \dfrac{K_b[H^+]}{K_w}\right)$
$k_{20} = 2.43 \cdot 10^{4}\, e^{(-2.4/RT)}$	$k_2 = \dfrac{k_{20}}{\left(1 + \dfrac{K_a}{[H^+]}\right)}$
$k_{30} = 8.75 \cdot 10^{10}\, e^{(-3.8/RT)}$	$k_3 = \dfrac{k_{30}\,[H^+]}{\left(1 + \dfrac{K_a}{[H^+]}\right)}$
$k_{40} = 6.32 \cdot 10^{11}\, e^{(-13./RT)}$	$k_4 = k_{40}\,[H^+]$
$k_{50} = 2.11 \cdot 10^{10}\, e^{(-7.2/RT)}$	$k_5 = k_{50}\,[OH^-]$
$k_{60} = 5.53 \cdot 10^{7}\, e^{(-6.0/RT)}$	$k_6 = k_{60}$
$k_{70} = 6.02 \cdot 10^{8}\, e^{(-6.0/RT)}$	$k_7 = k_{70}$
$k_{80} = 7.18 \cdot 10^{7}\, e^{(-6.0/RT)}$	$k_8 = \dfrac{k_{80}}{1 + \dfrac{K_a}{[H^+]}}$

Wei's assumptions and formulations can be summarized as follows:

Estimation of the Dichloramine Formation Parameter

For the estimation of the dichloramine formation parameter, k_{20}, Wei performed his experiment at pH's ranging from 6.7 to 7.2; temperatures varied from 5°C to 20°C. According to this test conditions, the following assumptions were made:

- Reaction 1 takes place instantaneously.
- Reaction 6 is negligible.

Therefore, the changes in concentration of NH_2Cl were only dependent on reaction R-2 as follows:

$$-\frac{dM}{dt} = k_2 MC = k_{20} M[HOCl] \qquad (2\text{-}48)$$

where

$M = [NH_2Cl]$

$C = [HOCl] + [OCl^-]$

k_2 = observation rate coefficient of reaction 2-48.

k_{20} = theoretical rate coefficient of reaction 2 -48.

Letting

$R_m = M/N_o$ and $R_f = C/N_o$ and letting

N_o = initial molar concentration of ammonia

Equation (2-47) can now be written as

$$k_2 = -\frac{d\ (\mathrm{lr}\ (R_m))}{dt}\left(\frac{1}{R_f N_o}\right) \qquad (2\text{-}49)$$

N_o is known, R_m and R_f were evaluated from experiments; therefore, k_2 and k_{20} were determined from experimental data.

Average values of k_{20} at each temperature were used for the determination of activation energy and Arrhenius coefficient of k_{20}. Results from this analysis are shown on Table 2-5.

Estimation of the Nitrogen Radical Parameter

To estimate the nitrogen radical formation parameter, k_{50}, Wei performed an experiment at pH's ranging from 6.7 to 7.2, initial ammonia concentrations varying from 0.25 to 1.5 mg/l, and temperatures were controlled at 5°C, 15°C and 20°C.

The following assumptions were made:

- Reaction 6, 3 and 8 were negligible.
- No change in NOH concentration (steady state).
- Reaction 1 was instantaneous.

Therefore only the three following reactions were considered in the breakpoint mechanism:

$$NH_2Cl + HOCl \xrightarrow{k_2} NHCl_2 + H_2O \qquad \text{(R-2)}$$

$$NHCl_2 + H_2O \xrightarrow{k_5} NOH + 2H^+ + 2Cl^- \qquad \text{(R-5)}$$

$$NOH + NHCl_2 \xrightarrow{k_7} N_2 + HOCl + H^+ + Cl^- \qquad \text{(R-7)}$$

Letting:

$N = [NH_3] + [NH_4^-]$

$N_o = N$ at $t = 0$

T = molar concentration of total chlorine residual

$T_o = T$ at $t = 0$

C = molar concentration of free chlorine residual ($[HOCl] + [OCl^-]$)

$M = [NH_2Cl]$

$D = [NHCl_2]$

According to the above assumptions [NOH], $[NO_3^-]$, and $[NCl_3]$ were negligible. Consequently, the mass balance of nitrogen was written as

$$N_o = M + D + \frac{2}{3}(T_o - T) \tag{2-50}$$

Since N_o was constant, it followed that:

$$\frac{dT}{dt} = \frac{3}{2}\left(\frac{dD}{dt} + \frac{dM}{dt}\right) \tag{2-51}$$

Assuming reactions 2, 5, and 7 to be elementary reactions, the following equations were established:

$$-\frac{dD}{dt} = k_5 D + k_7 D(NOH) - k_2 MC \tag{2-52}$$

and

$$-\frac{dM}{dt} = k_2 MC \tag{2-53}$$

Substitution of equations (2-52) and (2-53) into equation (2-51), yielded:

$$-\frac{dT}{dt} = \frac{3}{2}\left\{k_5 D + k_7 D[NOH]\right\} \tag{2-54}$$

Steady state assumption for NOH:

$$\frac{d[NOH]}{dt} = 0 = k_5D - k_7D[NOH]$$

or:

$$k_7D[NOH] = k_5D \tag{2-55}$$

Substituting equation 2-55 into equation 2-54 yields:

$$\frac{dT}{dt} = 3k_5D \tag{2-56}$$

For the evaluation of k_5, Wei converted equation 2-56 to a logarithmic form as follows:

$$\frac{3}{2.303} k_5 = \left(\frac{T}{N_o}\right) \left(\frac{D}{N_o}\right)^{-1} \left(- \frac{d\ (\log T)}{dt}\right) \tag{2-57}$$

This equation was used to evaluate k_5 and k_{50}, where K_5 is equal to $k_5[OH^-]$. Values of k_{50} were plotted against temperature to determinate the Arrhenius coefficient and activation energy, which were shown previously in Table 2-5.

Experimental Procedures

Wei performed his experiments in a batch reactor by first adding 400 ml of ammonium chloride water using a phosphate buffer to maintain pH at a constant level between 6.7 and 7.2. Temperature was controlled by a water bath at 10° C, 15°C and 20°C. Sampling times were fixed at 2 minutes to 6 minutes. A concentration of 1 mg/l of ammonia nitrogen was used in most of his experiments. The chlorine to ammonia molar ratio was fixed at 1.8. The DPD-FAS method was chosen for the determining free chlorine, monochloramine and dichloramine concentrations.

Since the experiments were performed in a batch reactor, Wei derived a set of eight ordinary differential equations to predict each chlorine species involved in his mechanistic model.

Conclusion and Summary of the Morris-Wei Model The areas of Wei's work which require further development or additional work are:

- The experiments were done in a narrow range of pH (6.7 to 7.2); therefore, no significant dependence of P ratio (chlorine reduced to ammonia oxidized) with pH was observed.
- No analysis for NCl_3 was made during the experiments; consequently, P ratios predicted from the mathematical model were always greater than the experimental values.
- The mathematical model overestimated the NCl_3 concentrations, which was probably because k_3 was too high and k_4 was too low.
- At low temperatures, the half life computation were always larger than the his experimental results; therefore the value ofk_5 is probably in error at low temperatures.
- The maximum concentration of $NHCl_2$ could not be evaluated with any great precision in batch experiments, because the sampling time for analysis had to be spaced at least two minutes apart.
- Wei performed his experiments in a batch reactor in which 400 ml of chlorine solution was added to 400 ml of ammonia water. Although, the resulting solution was thoroughly mixed, a period of time is required for such a mixture to reach homogeneity at the molecular level. Consequently, their experiments were affected by a large initial degree of segregation. According to Danckwerts (1957), these effects would result

in different different reaction rates than those resulting in a truly homogeneous mixture.

CONTRIBUTION OF SELLECK AND SAUNIER (1976, 1979)

Selleck and Saunier (1976, 1979) performed a large series of experiments in several types of reactors, which are described in Table 2-6. The majority of their data were collected in a dispersed flow reactor, which they assumed was no different than a plug flow reactor:

- 22 sets of data with low NH_3 - N (approximately 1 mg/l) in clean water
- 9 sets of data with high NH_3 - N (3 to 20 ppm) in clean water
- 6 sets of data for a tertiary effluent obtained from a municipal treatment plant.

Since the detention time of their plug flow reactor was only five minutes, the samples collected from the last point were kept in a beaker for a fixed period of time in order to simulate longer detention times.

For their batch reactor, only four sets of data were completed with clean water at low ammonia concentration, while no completed sets of data were generated from the continuous flow stirred tank reactor or dispersed flow reactor.

Table 2-6. Selleck and Saunier's Chlorination Pilot Plant (1976)

characteristics reactor type	diameter (in)	length (ft)	volume (gal)	flow rate (GPM)	detention time (minutes)	Reynolds Number	Sampling Points
non-ideal plug flow reactor	.75	433.0	—	2.0	5.0	8.28×10^3	6
dispersed flow reactor	4.0	91.10	—	2.0	32.0	1.59×10^3	6
continuous stirred tank reactor	27.75	—	90	2.0	29.72	$>10^4$	1

DPD-FAS method was used to differentiate free chlorine, monochloramine, dichloramine, and nitrogen trichloride. However, the determination of NCl_3 lacked of consistency.

The work of Selleck and Saunier was concentrated on the two following aspects:

- Revising the kinetic parameters provided by Morris and co-workers.
- Revising the Morris and Wei`s mechanistic model.

Revising Morris and Wei`s Kinetic Parameters

The comparisons between predicted values from Morris and Wei's model and data collected from the plug flow reactor showed several shortcomings of Wei's model, summarized as follows:

- The disappearance of monochloramine was much faster than predicted from the model.
- The critical concentrations of free chlorine were much lower than the predicted.
- There was very little agreement between predicted and observed nitrogen trichloride concentrations.

Consequently, Selleck and Saunier decided to revise the kinetic parameters provided by Wei and Morris. Their revised rate coefficient are summarized on Table 2-7.

Table 2-7. Breakpoint Chlorination Rate Coefficients.

Observed Rate Coefficients	Theoretical Rate Coefficient
$k_{10} = 9.7 \cdot 10^{8}\, e^{(-3.0/RT_K)}$	$k_1 = \dfrac{k_{10}}{\left(1 + \dfrac{K_a}{[H^+]}\right)}\left(1 + \dfrac{K_b[H^+]}{K_w}\right)$
$k_{20} = 1.99 \cdot 10^{4}\, e^{(-2.4/RT_K)}$	$k_2 = \dfrac{k_{20}}{\left(1 + \dfrac{K_a}{[H^+]}\right)}$
$k_{30} = 3.43 \cdot 10^{5}\, e^{(-7.0/RT_K)}$	$k_3 = \dfrac{k_{30}\left(1 + 10^{-pK_a + 1.4}\right)}{\left(1 + \dfrac{K_a}{[H^+]}\right)}$
$k_{40} = 8.56 \cdot 10^{8}\, e^{(-18.0/RT_K)}$	$k_4 = k_{40}\dfrac{1 + 5.88 \times 10^{5}[OH^-]}{\left(1 + \dfrac{K_a}{[H^+]}\right)}$
$k_{50} = 2.03 \cdot 10^{14}\, e^{(-7.2/RT_K)}$	$k_5 = k_{50}N_o[OH^-]$
$k_{60} = 1.0 \cdot 10^{8}\, e^{(-6.0/RT_K)}$	$k_6 = k_{60}$
$k_{70} = 1.3 \cdot 10^{9}\, e^{(-6.0/RT_K)}$	$k_7 = k_{70}$
$k_{80} = 1.0 \cdot 10^{7}\, e^{(-6.0/RT_K)}$	$k_8 = \dfrac{k_{80}}{1 + \dfrac{K_a}{[H^+]}}$

After Selleck and Saunier (1976)

Note: N_o = initial ammonia nitrogen concentration.

Confirmation of Morris` k_1:

Since there are excellent agreement between the study of Morris (1967) and the study of Anbar and Yagil (1962) on the kinetics of the formation of monochloramine, Selleck and Saunier did not revise the value of k_1.

Estimation of Dichloramine Formation Parameter

The basic assumptions were similar to the two assumptions made by Wei:

- Reaction 1 is very fast
- Reaction 6 is slow.

The rate coefficient k_2 was estimated in plug flow reactor and continuous stirred tank reactor separately. Results from these experiments showed the following relationship:

$$k_{20} = 1.99 \; . \; 10^4 e^{-2.4/RT_K} \qquad (2\text{-}58)$$

Estimation of Nitrogen Radical Parameter

Again, the basic assumptions were the same as Wei and Morris assumptions; however, Selleck Saunier's experiments were performed in plug flow reactor and CSTR with tap water and tertiary effluent. Their results showed that k_5 was proportional to $[OH^-]$ concentration when pH ranged from 6 to 8 and initial ammonia concentration was approximately 1 mg/l. When pH was above 8, k_5 decreased as the pH was increased. Therefore the value of k_5 also appeared to be proportional to the initial ammonia concentration. To accommodate these dependencies Selleck and Saunier proposed the following equation:

$$k_{50} = 2.03 \times 10^{14} e^{-7.2/RT_K} \tag{2-59}$$

and

$$k_5 = n_0 k_{50} [OH^-] \tag{2-60}$$

Estimation of Nitrogen Trichloride Parameters

The values of k_3 and k_4 proposed by Sanguinsin and Morris (1975) were using in Selleck and Saunier's study as follows:

$$K_3 = 3.43 \cdot 10^5 e^{-7.0/RT_K} (1 + 10^{-pK_a + 1.4}) (1 + \frac{K_a}{[H^+]})^{-1} \tag{2-61}$$

and

$$K_4 = 8.56 \times 10^8 e^{-18/RT_K} (1 + 5.88 \times 10^5 [OH^-]) (1 + \frac{K_a}{[H^+]})^{-1} \tag{2.62}$$

Estimation of the Remaining Parameters

An empirical function was assumed for k_8 as follows:

$$k_8 = 10^7 \; e^{-6/RT_K} \left(1 + \frac{K_a}{[H^+]}\right)^{-1} \tag{2-63}$$

The following relationships for k_6 and k_7 were selected to provide a good fit between observed and predicted stoichiometry:

$$k_6 = 1 \cdot 10^8 \; e^{-6.0/RT_K} \tag{2-64}$$

and

$$k_7 = 1.3 \cdot 10^9 e^{-6.0/RT_K}. \qquad (2\text{-}65)$$

The reaction mechanisms for nitrite and nitrate formation were added to account for nitrate production. Lister's (1962) value of k_{82} was used, as follows:

$$k_{82} = 3.82 \cdot 10^5 e^{-6.45/RT_K} \qquad (2\text{-}66)$$

Summary of the Revisions of the Morris and Wei Model

Selleck and Saunier's additions and revisions to Morris and Wei's model can be summarized as follows:

- The agreement between predicted and observed monochloramine concentrations was improved; but, at high pH or high initial ammonia concentration this agreement was still poor.
- The predicted dichloramine concentrations were lower than observed values.
- The observed nitrogen trichloride concentrations fluctuated greatly and the agreement between predicted and observed values was still poor.
- The revised model predicted free chlorine residual well.

Selleck and Saunier proposed two mechanistic modifications to Morris and Wei's model, summarized as follows:

- Hydroxyamine (NH_2OH) is the key intermediate in the breakpoint chlorination mechanism.
- Nitrite (NO_2^-) is an intermediate species which appears in significant concentrations when the chlorine to ammonia ratio is sufficient to pro-

duce nitrate (NO_3^-).

Their revised model is summarized in Figure 2-8. Since the nitroxyl radical (NOH) and hydroxyamine (NH_2OH) can not be measured at a relatively precise level the values of k_{52} and k_{53} can not be directly evaluated. Therefore Selleck and Saunier can not directly verify their model with experimental data.

3. EXPERIMENTAL PROCEDURE AND METHODS

ANALYTICAL METHODS OF THE DETERMINATION OF CHLORINE RESIDUALS

Primary Evaluations

Iodometric Titration

At pH less than 8, free and combined chlorine residuals oxidize potassium iodine (KI) to liberate free iodine. Starch can be used to detect the presence of free iodine, since it will change color from clear to dark blue. Chlorine residual can be measured quantitatively by a titration of free iodine released with standard solution sodium thiosulfate ($Na_2S_2O_3$) after adjusting the pH to 3-4. The end-point is determined by the change in color from blue to clear. CH_3 COOH is used as a catalyst.

The chemical reactions can be summarized as follows:

$$Cl_2 + 2I^- \longrightarrow I_2 + 2Cl^- \qquad (3-1)$$

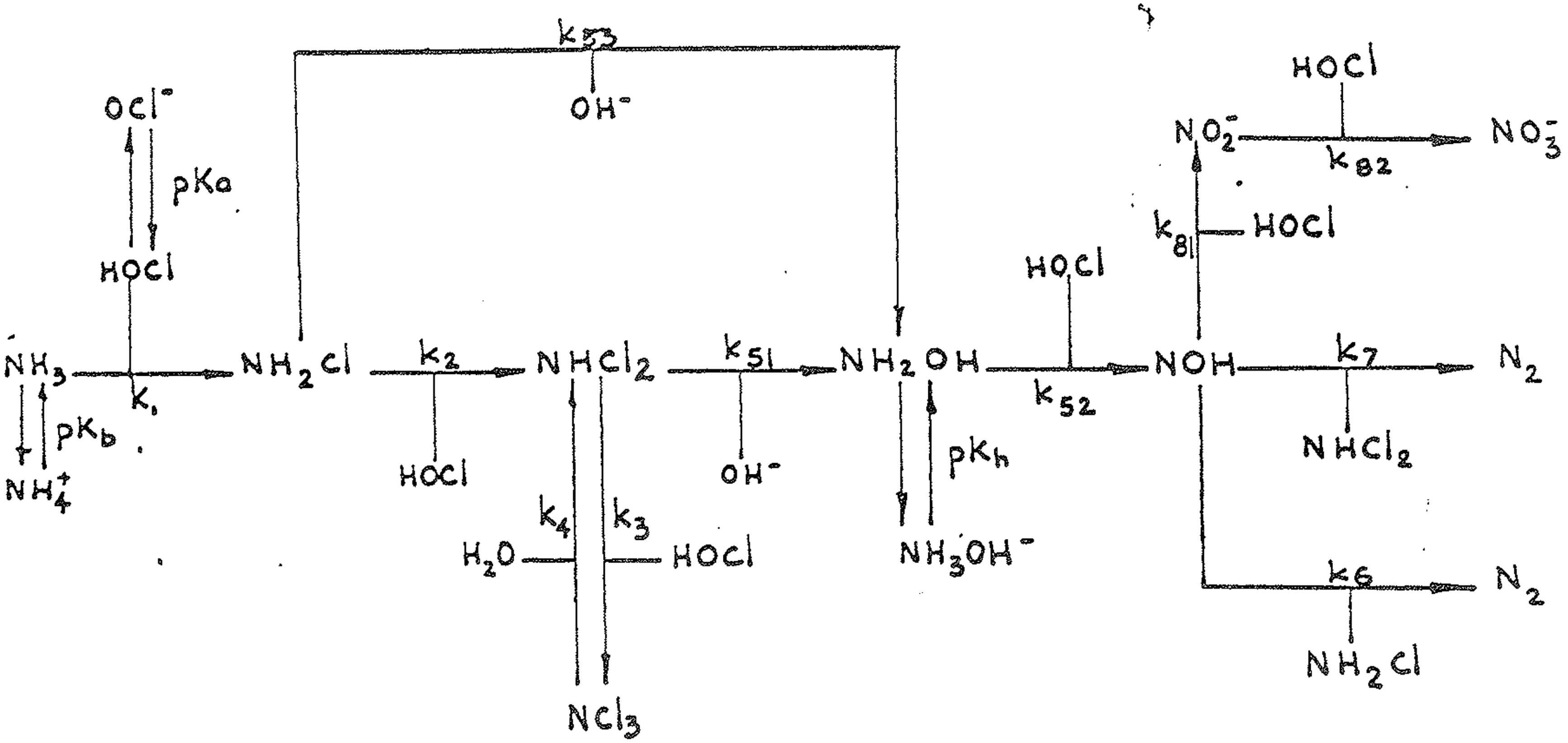


Figure 2-8: Breakpoint Model of Saunier and Selleck (1976).

$$I_2 + \text{starch} \longrightarrow \text{blue color} \quad (3\text{-}2)$$

$$I_2 + 2Na_2S_2O_3 \longrightarrow Na_2S_4O_6 + 2NaI \quad (3\text{-}3)$$

The reactions are dependent upon pH and the end point is not very sharp which reduces precision. A large sample is required for the titration and the range of sensitivity is low as 0.2 mg/l (White (1972)).

Acid-Orthotolidine-Arsenite Method (OTA)

Orthotolidine is an aromatic organic compound existing in solution at pH of 1.3 or lower (Palin (1980)). Orthotolidine is oxidized by chlorine and chloramine to produce a yellow holoquinone. It takes 5 minutes for the reaction to reach to completion. Since the color development is directly proportional to the amount of chlorine reacted, a color comparator or spectrophotometer can be used to evaluate the total chlorine residual concentration. The reaction is shown in Figure 3-1.

The reaction between orthotolidine and free chlorine is much faster than with combined chlorine residual; therefore, free chlorine can be differentiated from chloramine if the reactions are stopped after a brief period. Five seconds after orthotolidine is added to the sample, arsenite can be added to remove combined chlorine, and the color developed is assumed to caused by free chlorine only.

This method has the disadvantage in that it always indicates higher free chlorine concentration than is present in the sample (Sawyer (1967).

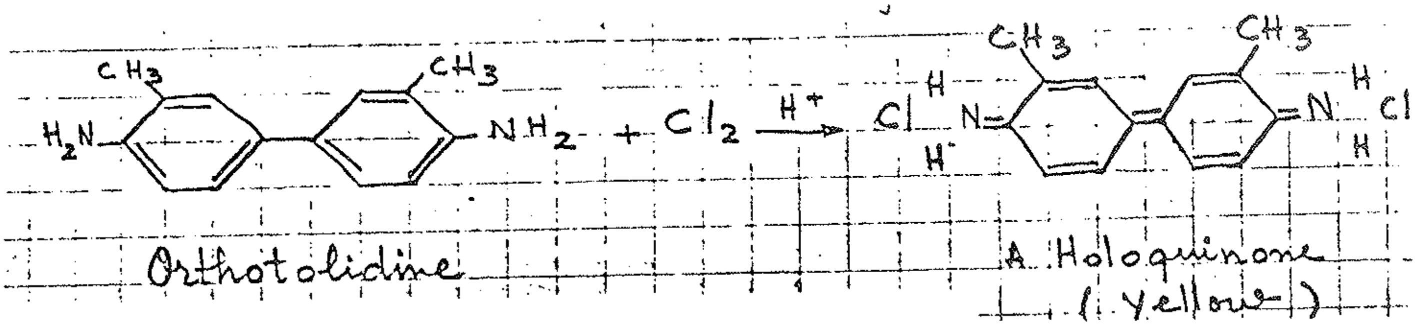


Figure 3-1: Reaction between Orthotolidine and Chlorine

Stabilized Neutral-Orthotolidine Method (SNORT)

Palin (1949) developed the neutral orthotolidine titration method as an improvement over the orthotolidine method. In neutral solution, orthotolidine reacts with chlorine and produces meriquinones. When hexametaphosphate is applied to the solution as stabilizer, meriquinone appears with pure blue color. Ferrous ammonium sulfate can then be used to titrate the resulting meriquinones. Johnson (1969) further developed the procedure using aerosol orthotolidine (aerosol AT) as a stabilizer, producing the stabilized neutral orthotolidine (SNORT) method. The analysis can be performed at pH 7 which reduces the interference of monochloramine on free chlorine. Unfortunately the color is stable for only a brief period and the analysis must be completed within within 2 minutes. To analyze for monochloramine, potassium iodine (KI) is added to neutral solution, and the developed color is proportional to both the free chlorine and monochloramine concentrations. If the sample is in acid solution, the resulting color is proportional to total chlorine residual concentration.

One half of the nitrogen trichloride (NCl_3) reacts with orthotolidine as free chlorine; therefore, SNORT usually gives a higher free chlorine residual than really exists.

Amperometric Titration Method

This method is an application of the polarographic principle. It can be used to determine free chlorine as well as combined residual through the free iodine released from the reaction between combined chlorine and potassium iodide.

Phenylarsene oxide (C_6H_5AsO) is used as titrant. The chemical reactions between phenylarsene oxide and free chlorine residual or free iodine are as follows:

$$C_6H_5AsO + HOCl + H_2O \longrightarrow C_6H_5AsO(OH)_2 + HCl \quad (3\text{-}4)$$

$$C_6H_5AsO + I_2 + 2H_2O \longrightarrow C_6H_5AsO(OH)_2 + 2HI \quad (3\text{-}5)$$

Free chlorine residual is determined at neutral pH range by adjusting with a phosphate buffer. The addition of small amount of potassium iodide (KI) will release the free iodine if combined residual measurement is desired. When potassium iodide is added in excess with acetate buffer as catalyst, the reaction of dichloramine and KI becomes very rapid, which can be used to determinate dichloramine concentration by difference.

The equipment required to perform an amperometric titration consist of dual platinum electrodes, a mercury battery, and a microammeter. When the electrodes are immersed in a sample, the mercury battery impresses an appropriate voltage across the electrodes, and the current is proportional to the reducible species (hypochlorite ion or iodine).

As phenylarsene oxide (reducing agent) is added, the concentration of reducible species decreases, causing the cell to become more and more polarized, reducing the microammeter reading. The end-point is detected when further addition of phenylarsene oxide fails to reduce cell current.

This method can overcome the interferences caused by color and turbidity; however, nitrogen trichloride appears in part as free chlorine and partly as dichloramine, which causes errors and corrections in both fractions.

Chlorine Electrode

The chemical principle of this method is similar to the iodometric titration method. When iodide was added in an acidic solution, the concentration of free iodine released is equal to the total chlorine residual concentration. Free Iodine concentration is measured by the chlorine electrode. The electrode contains a reduction and a reference element. The reduction element develops a potential which depends upon the relative concentration of iodine (I_2) and iodide ion (I^-), as follows:

$$E_1 = E_o + \frac{S}{2} \log \frac{[I_2]}{I^-]}. \qquad (3\text{-}6)$$

where:

E_1 = potential developed by reduction element

E_o = a constant

S = Electrode slope (approximately 58 mv/decade @ 20^C)

The reference element develops a potential that depends on iodide-ion concentration as follows:

$$E_2 = E_o' - S \log [I^-] \tag{3-7}$$

E_2 = potential developed by reference element

E_o' = a constant

The difference in potential between two electrode elements is:

$$E_1 - E_2 = E_o - E_o' + \frac{S}{2} \log [I_2] \tag{3-8}$$

A high impedance voltmeter or pH meter can be used to measure the difference in potential which is then correlated to iodine concentration.

This method provides the total chlorine residual concentration of a sample at the same precision and sensitivity as iodometric titration method, but is faster since a titration is not required.

FAS-DPD Method

In 1957, Palin developed a new method of for residual determination using Diethyl -p- Phenylene Diamine (DPD) instead of Orthotolidine. The color produced is quite stable, and ferrous ammonium sulfate $[F_e(NH_4)_2 (SO_4)_2]$ is used as titrant. The decolorization is spontaneous and the end point is sharp.

In describing the procedure it is necessary to know that in the absence of iodine ion (Isub-), free chlorine reacts instantly with DPD indicator to produce a red color as shown in the Figure 3-2: If a small amount of potassium

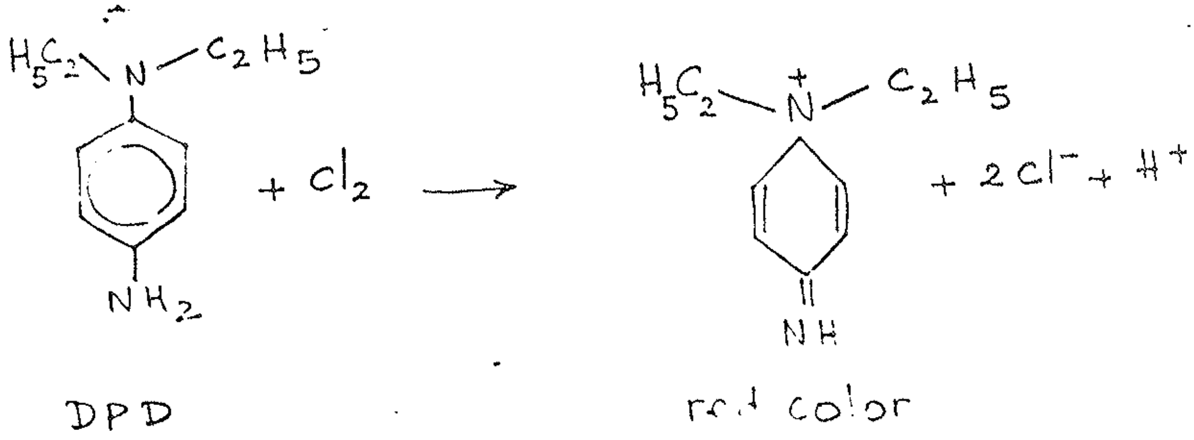


Figure 3-2: Reaction of DPD Indicator with Free Chlorine

iodide (KI) is added as catalyst, monochloramine will react to produce a red color. When KI is added in excess, Dichloramine and a portion of nitrogen trichloride will also react to produce a red color. Palin (1967) suggested adding a small crystal of KI before adding the DPD indicator if nitrogen trichloride analysis is desired in order to activate and improve the response.

Adoption of DPD-FAS method

The quality of experimental data is largely dependent upon the precision of the analytical methods used. For the purpose of this study, the analytical method for chlorine residual is required to have the following characteristics:

- It must be able to separate chlorine residual types (free chlorine, mono-chloramine, dichloramine, nitrogen trichloride).
- Since the analysis must always be performed before the breakpoint reactions are complete (non-steady state), the time interval for each analysis must be short and consistent, and the pH has to be maintained constant during the analysis.
- End points have to be sharp and consistent.
- High accuracy and precision is required at low residual concentrations (0.1 mg/l).
- The analyses must be free from interferences when tap water and chlorine/ammonia solutions are analyzed.

In an effort to select the best analytical methods, the previously described procedures were all evaluated experimentally. Table 3-1 was developed from this experience and the information and recommendations provided by White (1972, 1978), Stock (1967), Palin (1975, 1968, 1967, 1977, 1957), and Standard Methods (1975).

Table 3-1: Summary of Analytical Methods for Chlorine Residuals

Method	Components	pH	Accuracy & Precision	Time (min)	Interferences	Disadvantages
Iodometric Titration	Total residual	3.5	Applicable high concentration	2.	Ferric & manganese ions	poor endpoint large sample
OTA	Free & combined	1.5	Low accuracy for free residual	0.5	Turbidity,color manganese ions	lengthy procedure
SNORT	Free,mono, and di	7 or 2	over indicates free residual	4.	Turbidity,color manganese	NCl_3 interferes at high concentration
Amperometric titration	Free, mono, di & tri	7 or	very precise	2.	temperature, copper & silver	NCl_3 correction required
chlorine electrode	total residual	4.	less than iodometric at high concentrations	1.	strong oxidizing agents	drifts
DPD-FAS	Free, mono, di & tri	7	high accuracy for low concentration	3.	oxidized manganese	reduced accuracy for NCl_3

The DPD-FAS method appears to be well suited for the purpose of this investigation. The results for free chlorine are very consistent and reliable. Since the measurements must be performed while breakpoint reactions are not in equilibrium, short and consistent time intervals for sample collection times and analysis are required. At the end point, all free chlorine residuals are reacted with ferrous ammonium sulfate, formation reactions of monochloramine and dichloramine are stopped,

and their rate of destruction are relatively slow; therefore, at this step the titration times are not very critical.

The DPD-FAS method has some problems in the evaluation of nitrogen trichloride. A portion of nitrogen trichloride appears as dichloramine, and has to be evaluated and removed from dichloramine analysis by calculation. *Standard Methods* (1975) describes the titration procedure as follows:

> For free available chlorine: Place 5 ml of phosphate buffer and 5 ml of DPD indicator solution in a flask, mix, add 100 ml of sample, and titrate rapidly with standard FAS solution until the red color disappears (reading A).
>
> Monochloramine: Add 0.1 ml of KI solution, mix, and titrate until the red color is again disappears (reading B).
>
> Dichloramine: Add about 1 mg of KI, mix until dissolved. Let stand for 2 minutes, and continue the titration until the red color disappears (reading C).
>
> Nitrogen trichloride: Place a small crystal of KI in a titration flask, add 100 ml of sample, mix, add 5 ml of buffer and 5 ml of DPD indicator.

Titrate rapidly until the red color disappears (reading D). The calculation procedures are shown in Table 3-2.

Table 3-2: Calculation Procedure

Reading	Species
A	free Cl_2
B - A	NH_2Cl
C - B	$NHCl_2+\frac{1}{2}NCl_3$
2(D - A)	NCl_3
C - D	$NHCl_2$

Standard Methods (1975) states "should monochloramine be present with nitrogen trichloride, which is unlikely, it will be included in reading D, in which case nitrogen trichloride is from 2(D - B)."

For the determination of nitrogen trichloride, this method appears to be suitable at neutral pH and at low monochloramine concentration. At low pH, an addition of a small crystal of KI before buffering the solution can make a portion of dichloramine appear in reading D. Palin (1957) suggested adding samples and reagents in the following order: phosphate buffer, a small crystal of KI, sample, and DPD indicator. This procedure compensates for potential interference at low pH.

In this study, the breakpoint reactions are observed in a dynamic condition; monochloramine and nitrogen trichloride usually will coexist, which is different than typical case for treatment plant operation. Monochloramine can be considered as an interference in the evaluation of nitrogen trichloride. The reading "D" is not consistent when monochloramine is present at high concentration. To overcome this problem Palin (1967) suggested using two methods, DPD-FAS and neutral- orthotolidine. One half of the nitrogen trichloride will appear in the free chlorine analysis by the neutral orthotolidine method. Therefore, two times of the difference in the two analysis for free chlorine should represent the nitrogen trichloride concentration. This method is good for the analysis of a sample with high nitrogen trichloride concentration. At low concentration and especially when the titrations have to be done while the breakpoint reactions are not in equilibrium, it is extremely difficult to get an accurate result from two different analytical methods.

Chapin (1931) used carbon tetrachoride (CCl_4) extraction to remove nitrogen trichloride from solution to avoid interferences. This procedure is useful but time consuming to determinate the nitrogen trichloride concentration. The titration for dichloramine after nitrogen trichloride is removed by extraction gives reading (E). Nitrogen trichloride is determined as follows:

$$[\ NCl_3\ ] = 2\ [\ (D-B) - E\ ] \qquad (3\text{-}9)$$

Palin (1968) indicated that the efficiency of extraction of nitrogen trichloride with carbon tetrachloride depends upon the age of the nitrogen trichloride solution. However, this is not a problem in this research, since all solution ages are maintained constant.

The extraction of nitrogen trichloride by carbon tetrachloride can be done in a separatory funnel. The loss of NH_2Cl can be compensated by applying a correction factor given by Chapin (1931); however it was determined in this research that the compensation was negligible. Results from this method and amperometric titration method show a good agreement on total residual as shown in Table 3-3.

draft

Table 3-3: Comparison of DPD-FAS and Amperometric Methods for Chlorine Residual Determination[+].

Cl_2	NH_3-N	Temp	pH	Contact Time (sec)	Residuals				Total Residual	
					Free	NH_2Cl	$NHCl_2$	NCl_3	DPD-FAS	Amp-Tit.
9.30	0.96	20	6.00	130.	1.64	1.70	4.72	0.22	8.28	8.25
9.30	0.96	20	6.00	330	1.02	0.74	5.04	0.28	7.00	7.04
9.15	0.90	18.5	6.75	150	1.72	1.84	3.72	0.12	7.40	7.37
9.15	0.90	18.5	6.75	630	1.06	0.16	2.32	0.26	3.80	3.78
9.00	0.96	20.5	7.00	90	1.94	2.06	2.54	0.04	6.58	6.57
9.35	1.00	20.5	8.15	120	3.78	3.10	0.36	0.0	7.24	7.25
9.35	1.00	20.5	8.15	400	2.54	1.36	0.14	0.10	4.14	4.12

[+] all concentrations in mg/l.

ANALYTICAL METHODS FOR AMMONIA NITROGEN

There are four methods available for the determination of ammonia nitrogen (NH_3-N):

Two colorimetric methods: Nesslerization and Phenate.

One titration method: Acidimetric.

One electrochmemical method: gas sensitive electrode.

Primary evaluations

Nesslerization method

The Nesslerization method can be directly or following distillation. The Nessler reagent is a strong alkaline solution of potassium mercuric iodide (K_2HgI_4) or ($2KIHgI_2$). This reagent reacts with ammonia nitrogen and produces an yellowish- brown color. The intensity of this color is proportional to ammonia-nitrogen concentration; therefore, photometric methods can be used to evaluate ammonia nitrogen concentration. The major chemical reaction involves in this method is:

$$2\ K_2HgI_4 + NH_3 + 3KOH \rightarrow + 7KI + 2H_2O \qquad (3\text{-}10)$$

According to Standard Methods (1975), the US EPA recommended methods (1974) and Jenkins (1977), the precision of direct Nesslerization method is usually very poor. Pretreatment of samples to remove interfering substances is usually required. Standard Methods (1977) suggests using distillation for pretreatment of samples. The relative error of Nesslerization following distillation ranges from four to ten percent; however, data provided by US EPA Methods (1974) show that at low ammonia concentration (<200 mg/l) there is a lack of precision. Zadorojny (1973) also showed the low precision of Nesslerization method. Table 3-4 shows this low precision.

Table 3-4 Precision and Accuracy of the Distillation and Nesslerization Procedure for Ammonia Analysis+

Ammonia Nitrogen Increment (μg/l)	Coefficient of Variation (percent)
210	58
260	27
1710	14
1920	14.5

+ From US EPA Recommended Methods (1974).

Indophenol Method (Phenate)

Ammonia is oxidized to nitrite (NO_2) by hypochlorite in a strongly basic solution. The reaction between nitrite and sodium phenate forms a dark blue color (Berthelot (1859)). The color intensity is proportional to nitrite concentration and can be evaluated by spectrophotometry.

Rossum (1963) used manganese sulfate ($MnSO_4H_2O$) as a catalyst to improve the sensitivity of indophenol method. This procedure has been adopted by

Standard Methods (1975).

Color, turbidity, high alkalinity (over 500 mg/l) and high acidity (above 100 mg/l) interfere with this analysis. Distillation is usually recommended as a pretreatment method to improve the precision and accuracy of the indophenol method. Standard Methods (1975) indicated the sensitivity range of Indophenol method is from 10 to 500 mg/l of ammonia nitrogen. The US EPA recommended methods (1974) suggest using sodium nitroprusside as catalyst, increasing the range of measurement to up to 2000 mg/l of ammonia nitrogen.

Acidimetric method

This method is used only on distilled samples. Ammonia is titrated directly with standard .02 Normal sulfuric acid. At the end point, the mixed indicator (methylene blue and methyl red) turns a pale lavender color. The end point of this method is not very sharp. Standard Methods (1977) recommends using the acidimetric method only on samples with high ammonia-nitrogen concentration (above 5 mg/l).

Gas Electrode method

The Electrode consists of a reference element, a sensing element and a hydrophobic-gas permeable membrane which separates the sample from the internal filling solution. At high pH, the ammonium ion (NH_4^+) is converted to ammonia gas (NH_3). The gas diffuses through the probe membrane until the partial pressures of ammonia on both sides of the membrane are equivalent. From to Henry's law, this partial pressure is proportional to ammonia concentration. After diffusing through the membrane, ammonia reacts with water in the filling solution, releasing the hydroxide and ammonium ions. The the concentration of ammonium ion existing in filling solution is unchanged due to high background concentration. Thus:

$$[OH^-] = [NH_3] \text{ x coeficient.} \tag{3-11}$$

The potential of electrode sensing element varies with the change in hydroxide ion concentration, while the potential of the electrode reference element is proportional to concentration of chloride ion in filling solution, which is constant. The response of electrode to ammonia concentration is determined according to the Nerst equation as follows:

$$E = E_o - S \log[OH^-] \tag{3-12}$$

or

$$E = E_o' - S \log[NH_3] \tag{3-13}$$

where:

E = sensing element potential

E_o = reference potential

S = electrode slope

Volatile amines interfere with electrode measurements and changes in temperature will affect the calibration curve slope. The ionic strength can change the solubility of ammonia gas, but this is not a concern in the concentration ranges used in this research. Saunier (1976) and Jenkins (1977) reported the precision of the electrode between 2 and 4 percent, which is the same as indophenol method.

Adoption of Gas-Electrode

This research used ammonia concentration from 100 to 1500 µg/l. Acidimetric method is not valuable in this concentration range. Nesslerization was also eliminated because of its low precision. The indophenol method after distillation and the gas-electrode were more promising. Indophenol following distillation requires much more time, more advanced laboratory technique, while gas-electrode is quite simple and one measurement can be done in about three minutes. Therefore the gas-electrode method was selected.

EXPERIMENTAL TECHNIQUES

Pilot Plant Design

General Description of the Breakpoint Chlorination Pilot Plant

A pilot plant was designed and built in UCLA Water Quality Control Laboratory during the year of 1979. This pilot plant was composed of the following items:

- A plug flow reactor 730 feet long with 0.5 inch diameter (nominal) and

18 sample points.

- One dispersed flow reactor 41 feet long with 2.0 inch diameter (nominal) and 12 sample points.

- One dispersed flow reactor 23 feet long with 3.0 inches diameter (nominal) and 12 sample points.

The process and instrumentation diagram is shown in Figure 3-3.

Engineering Design

Ammonium Water Reservoir

An electric motor driven propeller was used to mix ammonium chloride (NH_4Cl) with water in a 360 gallon tank. The power requirement was determinated as follows:

$$Re = \frac{d^2 n \rho}{\mu} \tag{3-14}$$

where:

μ = dynamic viscosity, lb-sec-ft^2 (N-Sec/m^2)

μ = 2.05 x 10 sup -5 lb-sec-/ft^2 at 20°C

e = mass density of liquid, slug/ft^3 (Kg/m^3)

e = 1.936 slug/ft^3 at 20°C

n = spinning speed, RPS

Using n = 1760 RPM (standard RPM for a single phase AC motor)

then ≃ 30 RPS

d = diameter of propeller

Using an existing propeller 4 inches in diameter.

Thus the Reynolds number can be computed as follows:

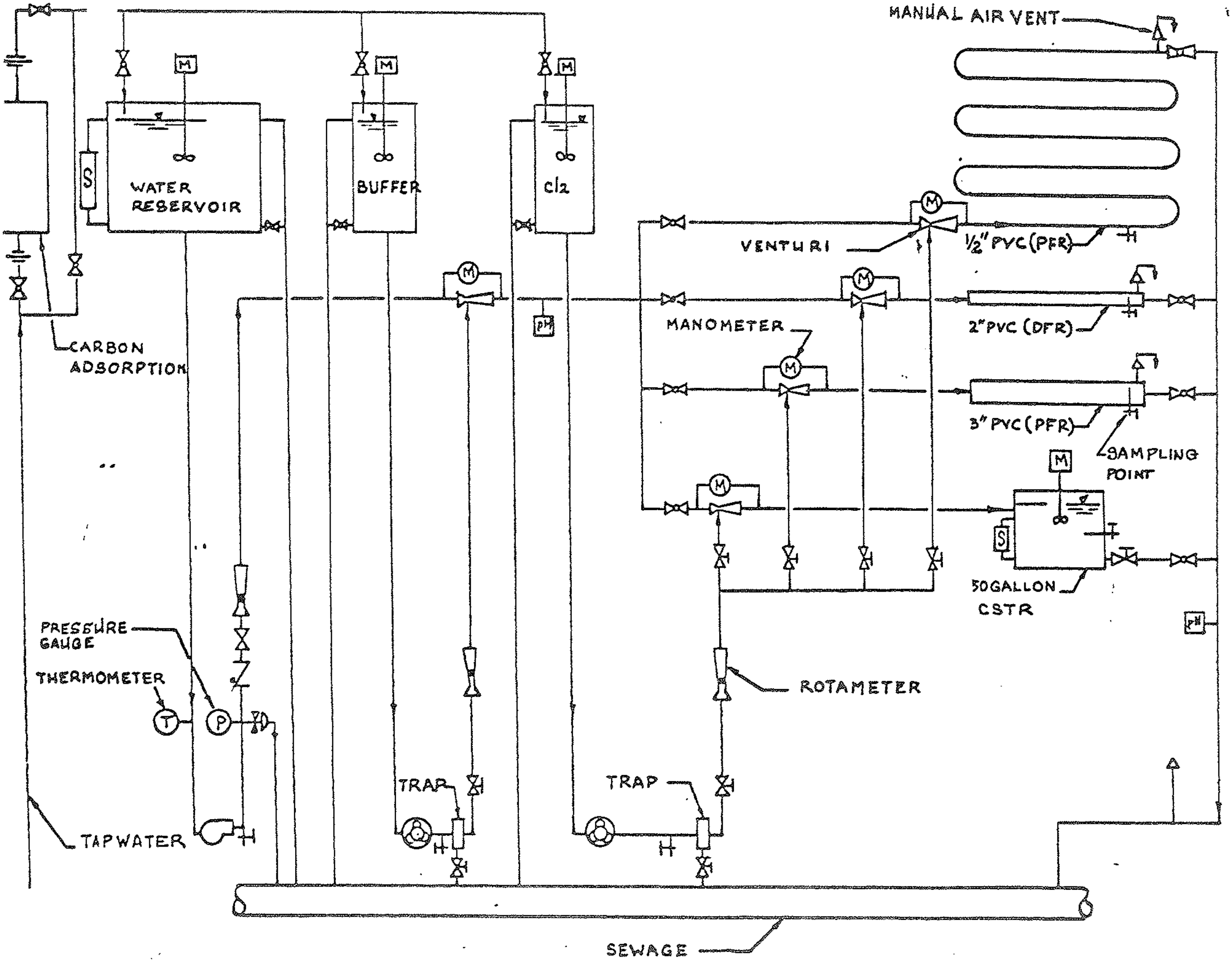


Figure 3-3: Process Flow and Instrumentation Diagram for the Pilot Plant.

$$Re = 3.15 \times 10^{5} \qquad (3\text{-}15)$$

Using Rushton's (1952) relationship for power requirement in turbulent conditions (Re > 10,000):

$$P = k \rho n^{3} d^{5} \qquad (3\text{-}16)$$

Using k = 1.0 for three a blade marine type propeller (in S.I. units).

$$P = 70 \text{ watt} = 51.63 \text{ ft} \qquad (3\text{-}17)$$

(3-17)

Using a motor driven at 0.25 BHP and 1750 RPM. Checking the mean velocity gradient as follows:

$$G = \left(\frac{P}{\mu V} \right)^{1/2} \qquad (3\text{-}18)$$

where:

G = mean velocity gradient, sec^{-1}

V = fluid volume, ft^{3} (m^{3})

V = 360 gallons = 48.13 ft^{3}

P = 51.63 ft lb_f/sec.

$\mu = 2.05 \times 10^{-5}$ lb-sec/ft^{2}

therefore: G = 229 sec.^{-1} To calculate the perfect mixing time, the relationship between discharge rate, revolution and diameter of propeller is:

$$\frac{Q}{nd^{3}} = N_Q \qquad (3\text{-}19)$$

where:

N_Q = constant, depend upon the type of propeller

Q_R = discharge rate of propeller (circulation rate).

Rase (1977) suggested using $N_Q = 0.5$ for

$$G = \left(\frac{P}{\mu V} \right)^{1/2} \tag{3-20}$$

where:

$V = 360$ gallons $= 1.363\ m^3$ Thus:

$$G = 227\ \text{sec.}^{-1}$$

Calculating the perfect mixing time, form the the previous relationship between discharge rate, revolution and diameter of propeller can be written as follows:

$$\frac{Q_R}{nD^3} = N_{QR} \tag{3-21}$$

where:

N_{QR} = constant, depend upon the type of propeller

Q_R = discharge rate of propeller (circulation rate).

Using $N_{QR} = 0.5$ for a three blade propeller (Rase (1977)).

$$Q_R = .0066\ m^3/\text{sec.} \tag{3-22}$$

Therefore the perfect mixing time for batch reactor:

$$t = \frac{V}{Q_R}$$

$$t = 207\text{sec.}$$

Chlorine Injector Chlorine was injected to ammonia water through a venturi mixing device as shown in Figure 3-4.

For this device at a total flow rate of 1 GPM, the head loss, as measured by the mercury manometer was 2 inches Hg. The degree of mixing can be expressed in term of mean velocity gradient G

$$G = \left(\frac{P}{\mu V} \right)^{1/2} \tag{3-23}$$

where:

$$P = \gamma Q H_L$$

$$P = 62.4 \times \frac{1}{450} \times \frac{2 \times 13.7}{12}$$

$$P = 0.32 \text{ft lb}/\text{sec.}$$

and

V = capacity of mixing device, ft^3

$V \simeq .0004\ ft^3$

Thus:

$$G = 6148\ sec^{-1}$$

Because of the mean velocity gradient was so high, the solution could be considered as instantaneously homogeneous in radial direction

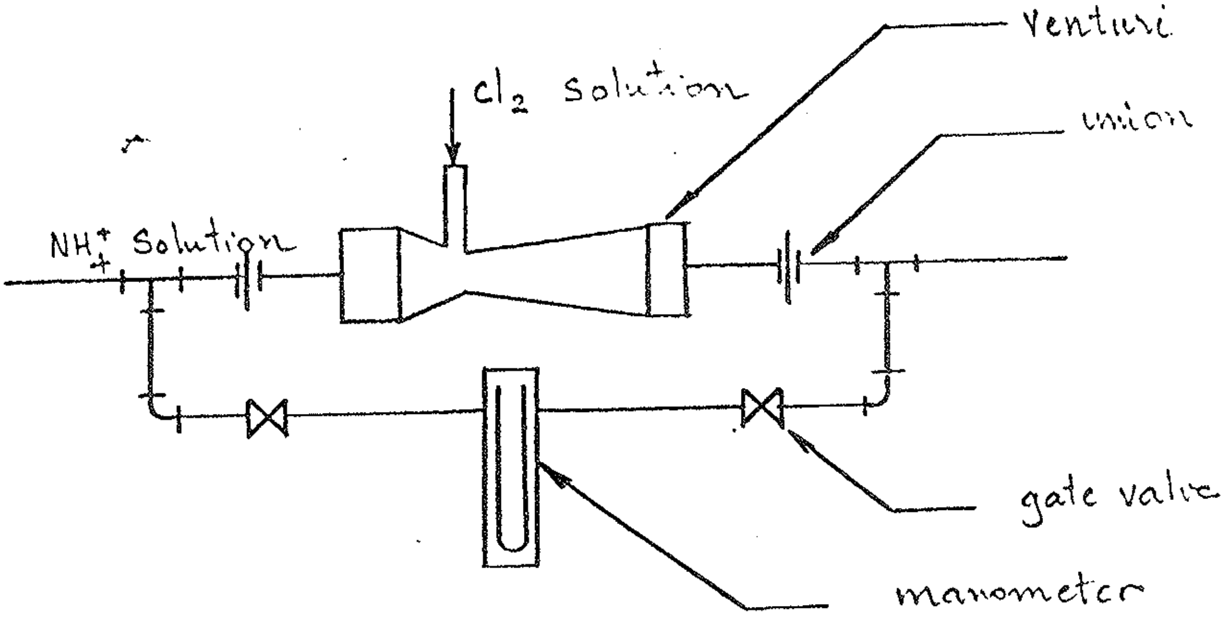


Figure 3-4: Chlorine Injector

Water pump

The water pump was sized for the most critical flow conditions, summarized as follows :

- Sized for the plug flow reactor.
- Flow rate at 1.0 gallon per minute.

The energy requirement was calculate as follows:

$$H_T = H_f + H_B + H_V + H_I + H_o + \Delta H \qquad (3\text{-}24)$$

where:

H_T = total head requirement

H_f = head loss by friction

H_B = head loss through bends

H_V = head loss through venturi

H_I = head loss caused by inlet suction

H_o = head loss caused by outlet discharge

ΔH = difference in head between two energy end points (water surface elevation at outlet - water surface elevation at reservoir).

Using the Hazen-Williams formula:

$$H_f = 10.393 \times \frac{Q^{1.852} \times L}{C^{1.852} \times D^{4.87}} \qquad (3\text{-}25)$$

where:

Q = 1.0 GPM

D = .60 in

C = 140 (for small PVC pipe)

L = 730 ft.

$H_f = 9.68$ ft. water

and considering head losses at the elbows and side outlet as follows:

$$H_B = C\frac{V^2}{2g} \times n \tag{3-26}$$

where:

$V = 1.13$ fps

$g = 32.2$

$C = .9$ (for short radius elbow)

$C = 1.8$ (for side outlet)

$n = 18$ (number of side outlets)

$n = 20$ (number of elbows)

Summing head losses for elbows and side outlets as follows:

$$H_B = 20\left(.9 \times \frac{(1.13)^2}{62.4}\right) + 18\left(1.8 \times \frac{(1.13)^2}{62.4}\right) \tag{3-27}$$

$H_B = 1.0$ ft. water

Assuming a head loss through venturi:

$$H_V = 2 \text{ in Hg} = 2.26\text{ft. water} \tag{3-28}$$

Inlet head losses were calculated as follows:

$$H_I = 1.0 \times \frac{V^2}{2g} \tag{3-29}$$

$H_I = 0.02$ ft. water

Head losses at the outlet were calculate from the following:

$$H_o = 1.0 \times \frac{V^2}{2g} \tag{3-30}$$

$$H_o = 0.02 \text{ ft. water}$$

The hydrostatic difference in elevation between two energy end points is zero for the most critical condition.

Therefore:

$$\Delta H = 0$$

Summing all losses yields:

$$H_T = 13 \text{ ft water}$$

Therefore the theoretical power requirement was:

$$P = \gamma Q H_T \tag{3-31}$$

$$P = 2 \text{ ft.lb./sec.}$$

In order to maintain the most precise experimental conditions flow should be maintained at constant rate during all phases of the experiment. In order to provide constant flow while the water level in ammonia nitrogen water feed reservoir was dropping, a positive displacement pump useed. A positive displacement pump has the flattest flow versus head characteristic curve. A Flotex positive displacement pump with flexible vane, direct couple motor driven, $\frac{1}{8}$BHP was used to pump ammonia water from reservoir to reactors.

Chlorine and Buffer Pumps Masterflex pumps (positive displacement peristaltic) serial N^{o}7018 were used to pump chlorine solution and buffer to the venturi injectors. The range of possible flow rates was 60 ml per minute to 240 milliliters per minute. Since the flow was pulsating, a trap was installed in discharge line to eliminate flow variations, as shown in Figure 3-5.

Reactors

The basic characteristic of reactor are summarized on Table 3-5

Table 3-5: Summary of Reactor Characteristics*

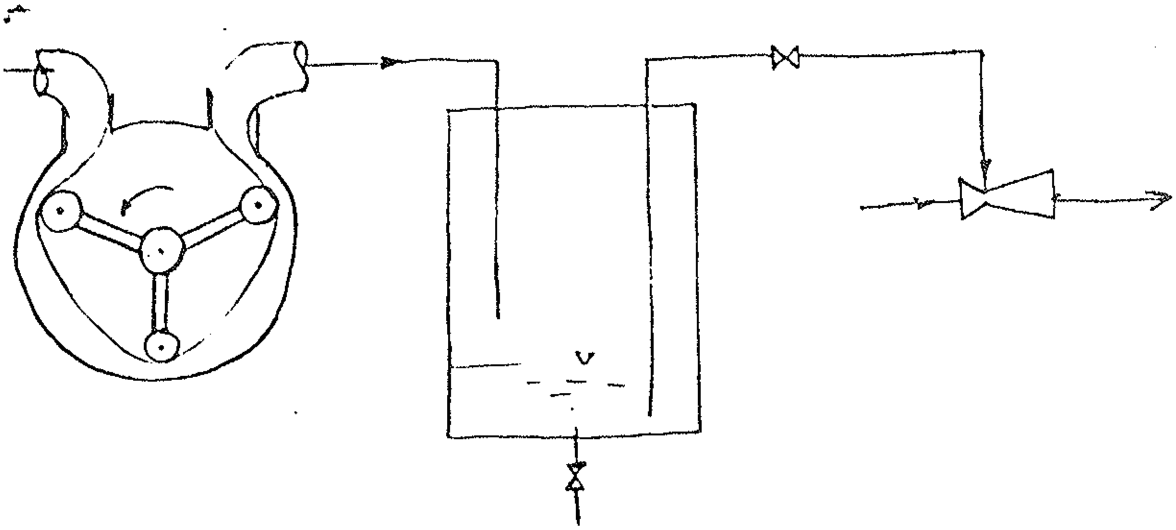


Figure 3-5: Pulsation Dampener

Reactor	Pipe Material	Diameter (in)	Flowrate[a] (GPM)	Reynolds Number	Flow Required
Plug flow	PVC	0.5	1.0	6000	Turbulent
Dispersed Flow #1	PVC	2.0	1.0	1700	Laminar
Dispersed Flow #2	PVC	3.0	1.0	1130	Laminar

[a] Flow rate was varied from 1.5 GPM to 0.6 GPM.

The sampling devices for each reactor were connected to the reactor's shell at different locations and also were used to drain the reactors. For the dispersed flow reactors the flow regime was laminar; therefore the sampling device was attached to a perforated capillary tube running from the reactor's shell to its central axis. In this manner it was assured that the collected samples would be representative of the reactor's average concentration at the sampling point.

Pilot Plant Operation

The operation of pilot plant for a single experiment can be briefly described as follows:

- Rinse the reactor with chlorine free water (dechlorinated with granular activated carbon adsorbers), and shut off the inlet and outlet valves to isolate the reactor from the entire system. Open the bypass valve to the laboratory drains.
- Fill the reservoir with chlorine free water and add ammonium chloride

(NH_4Cl) to get the desired ammonia nitrogen concentration.

- Use NaOH or H_2SO_4 to adjust the pH to a desired value, but the pH was always maintained at 7.5 or less to prevent the loss of ammonia during the experiment due to volatilization.
- Fill the chlorine solution tank with chlorine free water and add sodium hypochlorite (NaOCl) solution to get the desired chlorine concentration.
- Make up the buffer solution as required for each experiment (NaOH, phosphate buffer, or acetate buffer).
- Empty the air traps and rinse them.
- Turn on the chlorine and buffer pumps to build up pressure inside air traps. When both reagents reach the injector/venturi, the ammonia water pump was turned on.
- Adjust the flow rates of ammonia, chlorine, and buffer solution to the desired values.
- Turn on the inlet valve, shut off the outlet valve, open the air relief valve, and shut off the bypass valve of the reactor.
- When the reactor is filled with water as indicated by water flowing from air relief valve, the outlet valve is opened slightly so that water flows out under slight pressure but not under suction.
- Close the air relief valve.
- Check and adjust the flow rates as necessary.
- Record temperature, pH, flow rates, pressure, and headloss through mixing devices.
- Operate the system for approximately one-half hour to reach steady-state flow conditions.

Samples were collected from the sample connections located closest to the effluent end of the reactor and analyzed immediately. Sampling progressed until all samples were taken. Sampling was always performed first at the effluent end of the reactor to avoid disturbing the upstream flow regime. Samples were taken with out reducing the system pressure.

4. EXPERIMENTAL RESULTS

TRACER STUDY

Objective

The objective of this part of study was to determine the dispersion coefficient "$\hat{D}$" of chlorine residuals in different reactors at different flow rates.

Theoretically, the dispersion of chlorine residuals is a multicomponent diffusion phenomena; however, in dilute solution it can be considered as binary diffusion without any significant error. The longitudinal dispersion coefficient has two components:

$$D_{AB} = D_m + D_h \tag{3-32}$$

where:

D_{AB}: Binary virtual diffusion coefficient (dispersion coefficient) of solute A into solvent B.

D_m: Molecular diffusion coefficient (diffusivity) of A into B.

D_h: Hydrodynamic diffusion coefficient of A into B.

Diffusivities of chlorine and chlorine derivatives in dilute solution are in the range of 1.5×10^{-5} cm^2/sec which is much smaller than the hydrodynamic diffusion coefficient in longitudinal direction; therefore, it is possible to introduce a generalized longitudinal dispersion coefficient D for all chlorine derivatives used in this study. The longitudinal dispersion coefficient is results primarily from convective transport and radial diffusion

(Taylor Diffusion). For the purpose of this study, the mean concentration over a cross section area of the reactor is the most interesting factor. Therefore, coefficient D was defined as the mean value of longitudinal dispersion coefficient over a cross sectional area of a dispersion reactor. Coefficient D was also considered as a constant along the reactor, but not at inlet and outlet boundary.

Theory for Dispersion Coefficient Calculation

The transport of solutes in solvents flowing through tubes became an interesting subject for engineers and physiologists in the early of this century. This concept has been used to measure the flow rates in water mains by Allen (1923) and in blood vessels by White (1947), among other topics.

Taylor (1953, 1954) developed two approximation formulas to calculate D. His basic assumption were:

- The method is only valid after a long dispersion time, when the process has come to steady-state.
- No dispersing material is added to the flow.
- Geometries are within the following limits:

$$\frac{4L}{a} \gg \frac{ua}{D} \gg 6.9 \qquad (4\text{-}1)$$

where:

L = Length over which appreciable change in concentration occurs For laminar flow D was determined as

$$D = \frac{a^2 \bar{u}^2}{48D} \tag{4-2}$$

For turbulent flow the following relationship was obtained:

$$D = 10.1\ a\ v_* \tag{4-3}$$

where:

a = radius of tubular reactor

$\bar{u}$ = mean velocity of flow

u = velocity relative to axis which moves with the mean flow

D = diffusivity

$v_* = \left(\frac{\tau_o}{\rho}\right)^{1/2}$

τ_o = friction stress exerted on the pipe wall

ρ = fluid density

Since $\frac{\bar{u}}{v_*}$ depends only on the Reynolds number, D can be calculated based only on the Reynolds number.

The need for precise estimation of D is required for the solution of the non-steady transport equation, in which Danckwerts (1953) introduced the flux boundary condition to solve the steady state dispersion equation. The flux boundary condition will be presented and discussed further in later chapter.

Mathematical solution for the transient dispersion equation can be obtained after making some logical assumptions.

Considering the problem in one dimension the following equation is obtained:

$$\frac{\delta c}{\delta t} = D\frac{\delta^2 c}{\delta x^2} - u\frac{\delta c}{\delta x} \tag{4-4}$$

where:

$$C = C(x,t) \tag{4-5}$$

Subject to the initial condition:

$$C = 0 \quad @ \quad 0 \leq x \leq \infty \tag{4-6}$$

and subject to the boundary condition:

$$uC(0^-) - D(0^-)\frac{\delta C(0^-)}{\delta x} = uC(0^+) - D(0^+)\frac{\delta C(0^+)}{\delta x} \tag{4-7}$$

$$\lim_{x \to \infty} C = 0 \tag{4-8}$$

The physical configuration for the inlet conditions is shown in Figure 4.1.

Assuming from $x = 0^-$ to $x = 0^+$ the flow is extremely turbulent, the solution is homogeneous. Consequently, the diffusion effect is reduced to zero.

$$D(0^-) = D(0^+) \simeq 0$$

Equation 4-6 can be written as

$$C(0^-) = C(0^+) = C_o \tag{4-9}$$

where:

C_o = constant for a step function input. Letting :

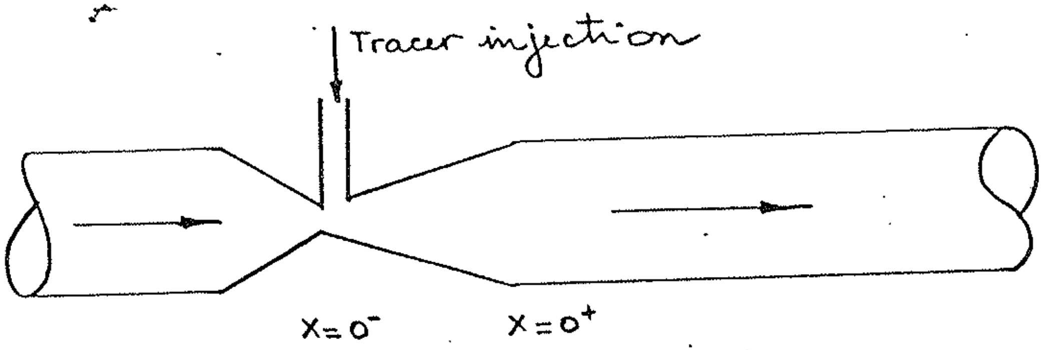


Figure 4-1 Physical Configuration of the Inlet Boundary Condition

$$\overline{C}(x,S) = L[C(x,t)] \tag{4-10}$$

Appling the Laplace transform on equation (4-4):

$$S\overline{C} = D\frac{d^2\overline{C}}{dx^2} - u\frac{d\overline{C}}{dx} \tag{4-11}$$

Or:

$$\frac{d^2\overline{C}}{dx^2} - \frac{u}{D}\frac{d\overline{C}}{dx} - \frac{S}{D}\overline{C} = 0 \tag{4-12}$$

Letting m_1 and m_2 be the roots of equation (4-12)

$$m^2 - \frac{u}{D}m + \frac{S}{D} = 0$$

Thus:

$$m_1 = \frac{u}{2D} + \frac{1}{\sqrt{D}}\sqrt{\frac{u^2}{4D} + S} \tag{4-13}$$

$$m_2 = \frac{u}{2D} - \frac{1}{\sqrt{D}}\sqrt{\frac{u^2}{4D} + S} \tag{4-14}$$

and

$$\overline{C} = A_{(S)}\, e^{\left[\frac{ux}{2D} + \frac{x}{\sqrt{D}}\sqrt{\frac{u^2}{4D} + S}\right]} + B_{(S)}\, e^{\left[\frac{ux}{2D} - \frac{x}{\sqrt{D}}\sqrt{\frac{u^2}{4D} + S}\right]} \tag{4-15}$$

Apply the following boundary conditions:

$$C = 0 \quad @ \quad x \rightarrow \infty \tag{4-16}$$

$$\overline{C} = 0 \quad @ \quad x \to \infty \qquad (4\text{-}17)$$

$$A = 0 \qquad (4\text{-}18)$$

$$C = C_o \quad @ \quad x = 0 \qquad (4\text{-}19)$$

$$\overline{C} = \frac{C_o}{S} \quad @ \quad x = 0 \qquad (4\text{-}20)$$

$$B = \frac{C_o}{S} \qquad (4\text{-}21)$$

Equation 4-15 becomes:

$$\overline{C} = \frac{C_o}{S}\, e^{\left[\frac{ux}{2D} - \frac{x}{\sqrt{D}}\sqrt{\frac{u^2}{4D} + S}\right]} \qquad (4\text{-}21)$$

$$L^{-1}(\,\overline{C}\,) = C_o\, e^{\left(\frac{ux}{2D}\right)}\, L^{-1}\left[\frac{1}{S}\, e^{\left(-\frac{x}{\sqrt{D}}\sqrt{\frac{u^2}{2D} + S}\right)}\right] \qquad (4\text{-}22)$$

$$C(x,t) = L^{-1}\left[\overline{C}(x,S)\right] \qquad (4\text{-}23)$$

$$C(x,t) = C_o\, e^{\left(\frac{ux}{2D}\right)}\, L^{-1}\left[\frac{1}{S}\, e^{\left(-\frac{x}{\sqrt{D}}\sqrt{\frac{u^2}{2D} + S}\right)}\right] \qquad (4\text{-}24)$$

Letting:

$$\alpha = \frac{x}{\sqrt{D}} \quad \text{and} \quad \beta = \frac{u}{2\sqrt{D}} \qquad (4\text{-}25)$$

and through the following steps:

$$L^{-1}\left[\frac{1}{S}\, e^{\left(-\frac{x}{\sqrt{D}}\sqrt{\frac{u^2}{2D}+S}\right)}\right] = L^{-1}\left[\frac{1}{S}\, e^{\left(-\alpha\sqrt{\beta^2+S}\right)}\right] \tag{4-26}$$

$$L^{-1}\left[\, e^{\left(-\alpha\sqrt{\beta^2+S}\right)}\right] = \frac{\alpha}{2\sqrt{\pi t^3}}\, e^{\left(-\frac{\alpha^2}{4t}\right)}\, e^{\left(-\beta^2 t\right)} \tag{4-27}$$

and

$$L\left[\int_0^t f(\tau)d\tau\right] = \frac{F(S)}{S} \tag{4-28}$$

We obtain:

$$L^{-1}\left[\frac{1}{S}\, e^{\left(-\alpha\sqrt{\beta^2+S}\right)}\right] = \int_0^t \frac{\alpha}{2\sqrt{\pi t^3}}\, e^{\left(-\frac{\alpha^2}{4\tau}+\beta^2\tau\right)} d\tau \tag{4-29}$$

$$= e^{-\alpha\beta}\int_0^t \left[\frac{\alpha+2\beta\tau}{4\sqrt{\pi t^3}}\right] e^{\left[-\frac{(\alpha-2\beta\tau)^2}{4\tau}\right]} d\tau$$

$$= e^{-\alpha\beta}\int_0^t \frac{\alpha+2\beta\tau}{4\sqrt{\pi t^3}}\, e^{\left[-\frac{(\alpha-2\beta\tau)^2}{4\tau}\right]} d\tau$$

$$+ e^{\alpha\beta}\int_0^t \frac{\alpha-2\beta\tau}{4\sqrt{\pi t^3}}\, e^{\left[-\frac{\alpha+2\beta\tau}{4\tau}\right]} d\tau \tag{4-29}$$

In right hand side of Equation 4-29 let:

$$\eta = -\frac{\alpha - 2\beta\tau}{\sqrt{4\tau}} \quad \text{in first term}$$

$$\eta = \frac{\alpha + 2\beta\tau}{\sqrt{4\tau}} \quad \text{in second term}$$

After performing the integral separately for each term, equation 4-29 becomes:

$$L^{-1}\left[\frac{1}{S}\, e^{\left(-\alpha\sqrt{\beta^2 + S}\right)}\right] = \frac{e^{-\alpha\beta}}{2} \operatorname{erfc}\left(\frac{\alpha - 2r\,\beta\, t}{2\sqrt{t}}\right) \tag{4-30}$$

$$+ \frac{e^{\alpha\beta}}{2} \operatorname{erfc}\left(\frac{\alpha + 2\,\beta\, t}{2\sqrt{t}}\right) \tag{4-31}$$

Substituting the value of α and β in Equation 4-31:

$$L^{-1}\left[\frac{1}{S}\, e^{\left(-\frac{x}{\sqrt{D}}\sqrt{\frac{u}{4D} + S}\right)}\right] = \frac{1}{2}\, e^{\left[-\frac{ux}{2D} \operatorname{erfc}\left(\frac{x - ut}{2\sqrt{Dt}}\right)\right]} \tag{4-32}$$

$$+ \frac{1}{2}\, e^{\left[\frac{ux}{2D} \operatorname{erfc}\left(\frac{x + ut}{2\sqrt{Dt}}\right)\right]} \tag{4-33}$$

Substitute Equation (4-33) in Equation (4-28):

$$C(x,t) = \frac{C_o}{2}\left\{ \operatorname{erfc}\left(\frac{x - ut}{2\sqrt{Dt}}\right) + e^{\left(\frac{ux}{D}\right)} \operatorname{erfc}\left(\frac{x + ut}{2\sqrt{Dt}}\right)\right\}$$

Or:

$$\frac{C}{C_o} = \frac{1}{2} \operatorname{erfc}\left(\frac{x - ut}{2\sqrt{Dt}}\right) + e^{\left(\frac{ux}{D}\right)} \operatorname{erfc}\left(\frac{x + ut}{2\sqrt{Dt}}\right) \tag{4-34}$$

Equation 4-4 is linear, thus:

$$\frac{C - C_i}{C_o - C_i} = \frac{1}{2}\,\mathrm{erfc}\left(\frac{x - ut}{2\sqrt{Dt}}\right) + e^{\left(\frac{ux}{D}\right)}\,\mathrm{erfc}\left(\frac{x + ut}{2\sqrt{Dt}}\right) \qquad (4\text{-}35)$$

where: C_i = background concentration of flowing fluid.

C_o, C_i, x and u are given, the curve F = C(t) is provided from experiment; therefore, D can be identified. When the input function is a Dirac delta function, and if the reactor is a closed vessel, the output function (C = C(t)) can be converted to F curve as follows:

$$F = \int_0^t C\,dt \quad \text{or} \quad C = \frac{dF}{dt} \qquad (4\text{-}36)$$

Van Der Laan (1957) developed a method to calculate the dispersion coefficient D without solving the dispersion equation. Assuming the input is a Dirac delta function, he set up a set of three partial differential equations which are similar to the work of Wehner (1956)

$$\left(\frac{\partial}{\partial\theta} + \frac{\partial}{\partial z} - \frac{1}{Pe_a}\frac{\partial^2}{\partial z^2}\right)R_a = 0 \qquad z \leq 0 \qquad (4\text{-}37)$$

$$\left(\frac{\partial}{\partial\theta} + \frac{\partial}{\partial z} - \frac{1}{Pe_a}\frac{\partial^2}{\partial z^2}\right)R = \delta(\theta)\delta(z - z_o) \qquad 0 \leq z \leq z_1 \qquad (4\text{-}38)$$

$$\left(\frac{\partial}{\partial\theta} + \frac{\partial}{\partial z} - \frac{1}{Pe_b}\frac{\partial^2}{\partial z^2}\right)R_b = 0 \qquad z \geq z_1 \qquad (4\text{-}39)$$

If the reactor is stretched from $-\infty$ to $+\infty$ where:

$\theta = \frac{vt}{V}$

v = volumetric flow rate

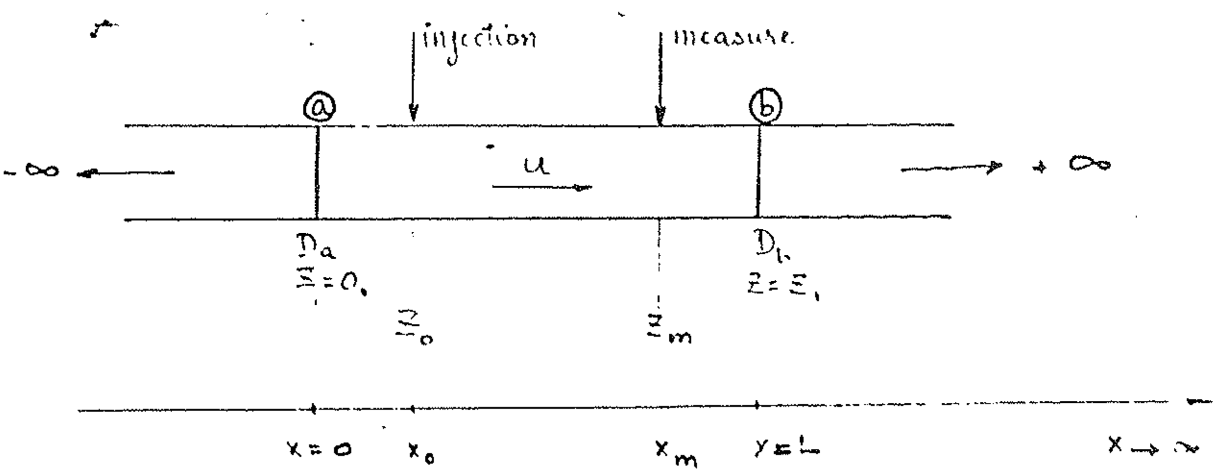


Figure 4.2: Hypothetical Reactor

v = volume of reactor from x_o to x_m where: $\Theta = \frac{vt}{V}$

V = volume of reactor from x_o to x_m

$Z = \frac{x}{x_m - x_o}$

$R = \frac{CV}{q}$

q = Actual amount of tracer injected

= Volume of tracer of Unit concentration

P_e = Peclet number

$= \frac{UL}{D}$

δ = Dirac Delta function

Initial condition:

$$R_a = R_b = R = 0 \text{ @ } \Theta < 0 \tag{4-40}$$

Boundary condition

$$R_a(-\infty) = \text{finite} \tag{4-41}$$

$$R_b(+\infty) = \text{finite} \tag{4-42}$$

$$R_a(0^-) = R(0^+) \tag{4-43}$$

$$R(Z_1^-) = R_b(Z_1^+) \tag{4-44}$$

Flux Boundary condition:

$$R_a(0^-) - \frac{1}{Pe_a}\frac{dR_a(0^-)}{dZ} = R(0^+) - \frac{1}{Pe}\frac{dR(0^+)}{dZ} \qquad (4\text{-}45)$$

$$R(Z_1^-) - \frac{1}{Pe}\frac{dR(Z_1^-)}{dZ} = R_b(Z_1^+) - \frac{1}{Pe_b}\frac{dR(Z_1^+)}{dZ} \qquad (4\text{-}46)$$

Letting $\bar{R} = L\ R\ (\Theta)$

Taking Laplace transform of the above partial differential equations, and solving the set of three ordinary differential equations for $\bar{R}$, $\bar{R}a$ and $\bar{R}b$ yields:

$$\bar{R}a = A\ e^{\left[(q_a + \frac{1}{2})Pe_a Z\right]} \quad @\ Z \leq 0 \qquad (4\text{-}47)$$

$$\bar{R} = \frac{A}{2q}\left\{(q + q_a)\ e^{\left[(q + \frac{1}{2})PeZ\right]} + (q - q_a)\ e^{\left[-(q - \frac{1}{2})PeZ\right]}\right\}$$

$$- \frac{U\ (Z - Z_o)}{2q}\ e^{\left[(q + \frac{1}{2})\ Pe(Z - Z_o)\right]}$$

$$\frac{U\ (Z - Z_o)}{2q}\ e^{\left[-\ (q - \frac{1}{2})\ Pe(Z - Z_o)\right]}$$

(4.48)

$$0 \leq Z \leq Z_1$$

$$\bar{R}_b = B \exp\left[-(q_b - \tfrac{1}{2})\ Pe_b\ (Z - Z_1)\right] \tag{4-49}$$

$$@\ Z \geq Z_1$$

where:

$q = \sqrt{(s/Pe + \frac{1}{4})}$

s = parameter Laplace transform

U(Z) = step function

$B = \bar{R}\ @\ Z \rightarrow Z_1$

$A = e^{-\frac{1}{2}PeZ_o}$

$$\frac{(q + q_b)\ e^{[qPe(Z_1 - Z_o)]} + (q - q_b)\ e^{[-qPe(Z_1 - Z_o)]}}{(q + q_a)(q + q_b)\ e^{[q + PeZ_1]} - (q - q_a)\ (q - q_b)\ e^{[-qPeZ_1]}} \tag{4-50}$$

But:

$$\frac{d\bar{R}}{ds}_{s \rightarrow o} = \int_o^{\infty} \Theta\ R d\ \Theta = \bar{\Theta} \tag{4-51}$$

$$\frac{d^2\bar{R}}{ds^2}_{s \rightarrow o} - \left(\frac{d\bar{R}}{ds}\right)^2_{s \rightarrow o} = \int_o^{\infty} \Theta 2 R d\Theta - \bar{\Theta}^2 = \sigma^2 \tag{4-52}$$

The result of this calculation is tabulated as shown in Table 4-1.

$$\overline{R}_b = B \exp\left[-(q_b - \tfrac{1}{2})\ Pe_b\ (Z - Z_1)\right] \qquad (4\text{-}49)$$

$$@\ Z \geq Z_1$$

where:

$q = \sqrt{(s/Pe + \frac{1}{4})}$

s = parameter Laplace transform

U(Z) = step function

$B = \overline{R}\ @\ Z \rightarrow Z_1$

$A = e^{-\frac{1}{2}PeZ_o}$

$$\frac{(q + q_b)\ e^{[qPe(Z_1 - Z_o)]} + (q - q_b)\ e^{[-qPe(Z_1 - Z_o)]}}{(q + q_a)(q + q_b)\ e^{[q + PeZ_1]} - (q - q_a)\ (q - q_b)\ e^{[-qPeZ_1]}} \qquad (4\text{-}50)$$

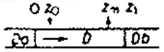
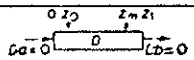
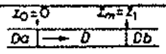
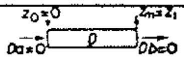
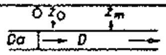
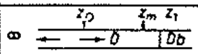
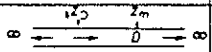
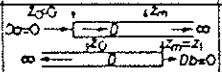
But:

$$\frac{d\overline{R}}{ds}_{s \rightarrow o} = \int_o^{oo} \Theta\ Rd\ \Theta = \overline{\Theta} \qquad (4\text{-}51)$$

$$\frac{d^2\overline{R}}{ds^2}_{s \rightarrow o} - \left(\frac{d\overline{R}}{ds}\right)^2_{s \rightarrow o} = \int_o^{oo} \Theta 2Rd\Theta - \overline{\Theta}^2 = \sigma^2 \qquad (4\text{-}52)$$

The result of this calculation is tabulated as shown in Table 4-1.

Table 4-1: Residence Time Distribution Calculations

		θ	σ^2
I		$1+\frac{1}{Pe}\left[2-(1-\alpha)e^{-Pez_0}-(1-\beta)e^{-Pe(z_1-z_m)}\right]$	$\frac{1}{Pe^2}\left[2Pe+8+2(1-\alpha)(1-\beta)e^{-Pez_1}-(1-\alpha)e^{-Pez_0}\left\{4z_0Pe+4(1+\alpha)+(1-\alpha)e^{-Pez_0}\right\}-(1-\beta)e^{-Pe(z_1-z_m)}\left\{4(z_1-z_m)Pe+4(1+\beta)+(1-\beta)e^{-Pe(z_1-z_m)}\right\}\right]$
II		$1+\frac{1}{Pe}\left[2-e^{-Pez_0}-e^{-Pe(z_1-z_m)}\right]$	$\frac{1}{Pe^2}\left[2Pe+8+2e^{-Pez_1}-e^{-Pez_0}\left\{4z_0Pe+4+e^{-Pez_0}\right\}-e^{-Pe(z_1-z_m)}\left\{4(z_1-z_m)Pe+4+e^{-Pe(z_1-z_m)}\right\}\right]$
III		$1+\frac{1}{Pe}\left[\alpha+\beta\right]$	$\frac{1}{Pe^2}\left[2Pe-2+2e^{-Pe}+2(\alpha+\beta)(1-e^{-Pe})+3(\alpha^2+\beta^2)+2\alpha\beta e^{-Pe}\right]$
IV		1	$\frac{2}{Pe^2}\left[Pe-1+e^{-Pe}\right]$
V		$1+\frac{1}{Pe}\left[2-(1-\alpha)e^{-Pez_0}\right]$	$\frac{1}{Pe^2}\left[2Pe+8-(1-\alpha)e^{-Pez_0}\left\{4z_0Pe+4(1+\alpha)+(1-\alpha)e^{-Pez_0}\right\}\right]$
VI		$1+\frac{1}{Pe}\left[2-(1-\beta)e^{-Pe(z_1-z_m)}\right]$	$\frac{1}{Pe^2}\left[2Pe+8-(1-\beta)e^{-Pe(z_1-z_m)}\left\{4(z_1-z_m)Pe+4(1+\beta)+(1-\alpha)e^{-Pe(z_1-z_m)}\right\}\right]$
VII		$1+\frac{2}{Pe}$	$\frac{1}{Pe^2}\left[2Pe+8\right]$
VIII		$1+\frac{1}{Pe}$	$\frac{1}{Pe^2}\left[2Pe+3\right]$

$Pe = \frac{u(x_m - x_0)}{D}$ $\alpha = \frac{Da}{D}$

$z = \frac{x}{x_m - x_0}$ $\beta = \frac{Db}{D}$

After Van Der Laan (1958)

Let:

t = time, measured time of injection.

$\bar{t}$ = mean residence time.

Thus:

$$\bar{t} = \frac{\int_0^\infty t\ c dt}{\int_0^\infty c dt} \qquad (4\text{-}53)$$

$$\bar{\theta} = \bar{t}\ \frac{v}{V} \qquad (4\text{-}54)$$

Let:

S = variance of tracer curve

Thus:

$$S^2 = \frac{\int_0^\infty c t^2 dt}{\int_0^\infty c dt} - \left\{\frac{\int_0^\infty c\ t dt}{\int_0^\infty c\ dt}\right\}^2 \qquad (4\text{-}55)$$

$$\sigma^2 = \frac{S^2}{(V/v)^2} \qquad (4\text{-}56)$$

If a "C" curve is obtained from the experiment, the Peclet number can be calculated from the results shown in Table 4-1 and from equations 4-34 or 4-36.

Tracer Experimental Techniques

The experimental equipment was assembled as shown in Figure 4-3. Sodium chloride (NaCl) was selected as injection tracer because of the Diffusivity of NaCl in aqueous solution is closed to be the same as Diffusivity of chlorine in water. According to CRC Handbook of Chemistry and Physics (1983), the diffusivity of sodium chloride in aqueous solution at 25^{o} C is 1.5×10^{-5} cm^2/sec.

The flow was set at the desired rate, the background concentration was recorded. At time t = o, a known concentration of NaCl in solution was injected into the venturi mixer and the recorder was turned on simultaneously. As the salt flowed downstream by convection and dispersion, the recorder traced a curve of conductivity versus time. When the flow was laminar, samples were collected at different times, measured, and plotted versus time.

From a calibration experiment as shown in Figure 4-3, it was found that the conductivity - concentration relationship is linear at low salt concentration (less than 1500 ppm of NaCl).Therefore the recorder output can be used as a "C" curve (Levenspiel 1957, 1962) in the calculation of the dispersion coefficient D.

Tracer Calculations and Results

Using the relationships for a closed vessel, $\bar{\Theta}$ and σ can be calculated as follows:

$$\bar{\Theta} = \frac{\bar{t}}{V/Q} = 1 + \frac{1}{Pe} \qquad (4\text{-}57)$$

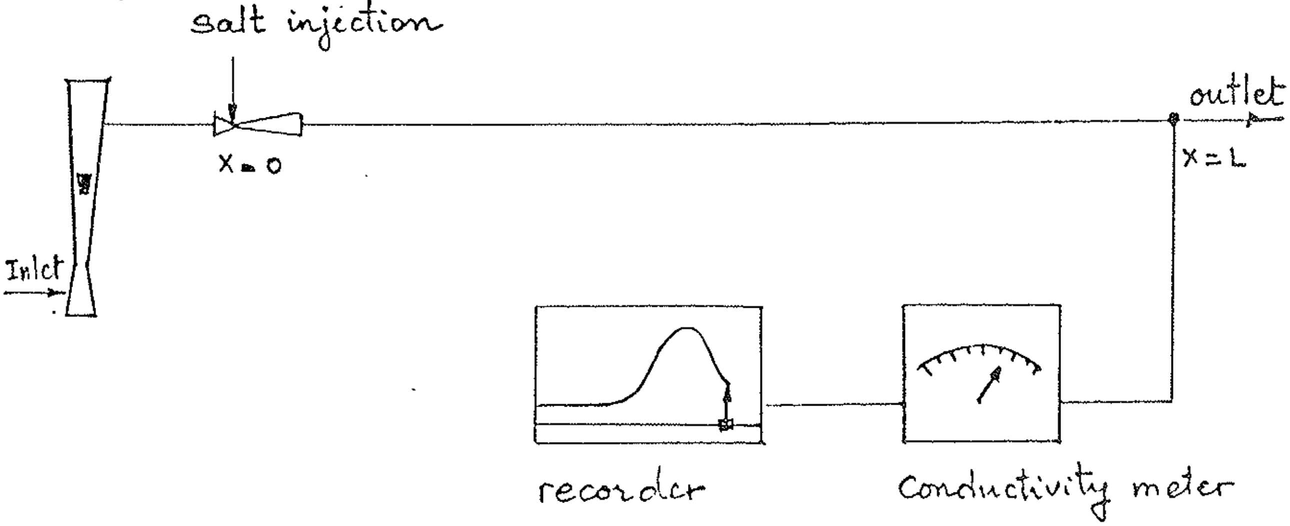


Figure 4-3: Tracer Experimental Arrangement

and

$$\sigma^2 = \frac{S^2}{(V/Q)^2} = \frac{1}{Pe}\,(2Pe + 3) \tag{4-58}$$

Sine the measurement of V and Q were made with some experimental error, equation 4-58 can not be used directly to calculate the Peclet number. Let us consider V/Q as and unknown, so equations 4-57 and 4-58 lead to:

$$\frac{\bar{\theta}^2}{\sigma^2} = \frac{\bar{t}^2}{S^2} = \frac{\left(1 + \frac{1}{Pe}\right)^2}{(2Pe + 3)\frac{1}{Pe^2}} \tag{4-59}$$

or:

$$\frac{\bar{t}^2}{S^2} = \frac{(Pe + 1)^2}{2Pe + 3} \tag{4-60}$$

Simpson's rule can be used to compute $\bar{t}$ and $\bar{S}^2$. From equation 4-60 solve for Pe, then for D. For verification of the solution, the Peclet number will be substituted into equation 4-58 to check for V/Q.

Figures 4-4 to 4-9 show the results of six tracer experiments for the three reactors at two different flow rates. The results from the previously described calculations were used to determine the value of the dispersion

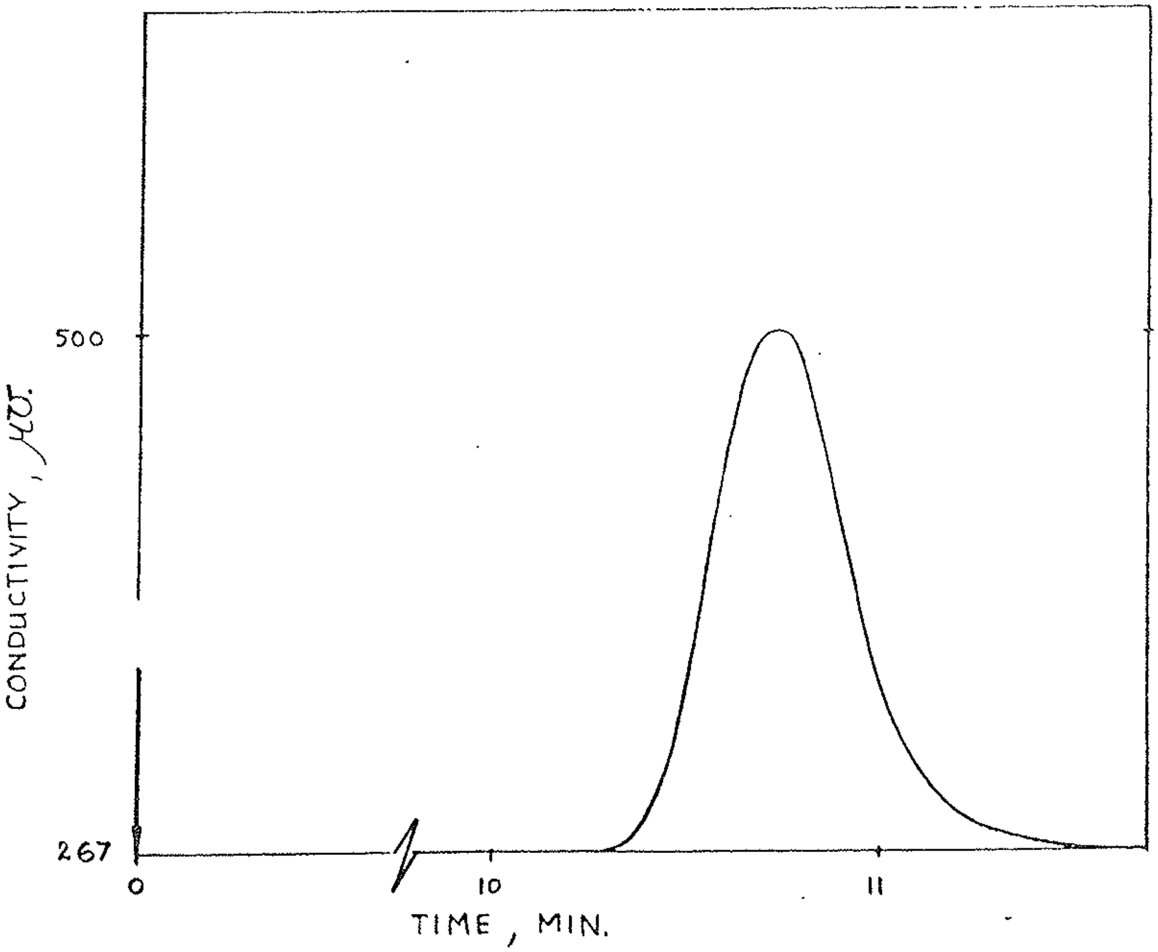


Figure 4-4 Tracer Experiment for the Plug Flow Reactor at 0.6 GPM

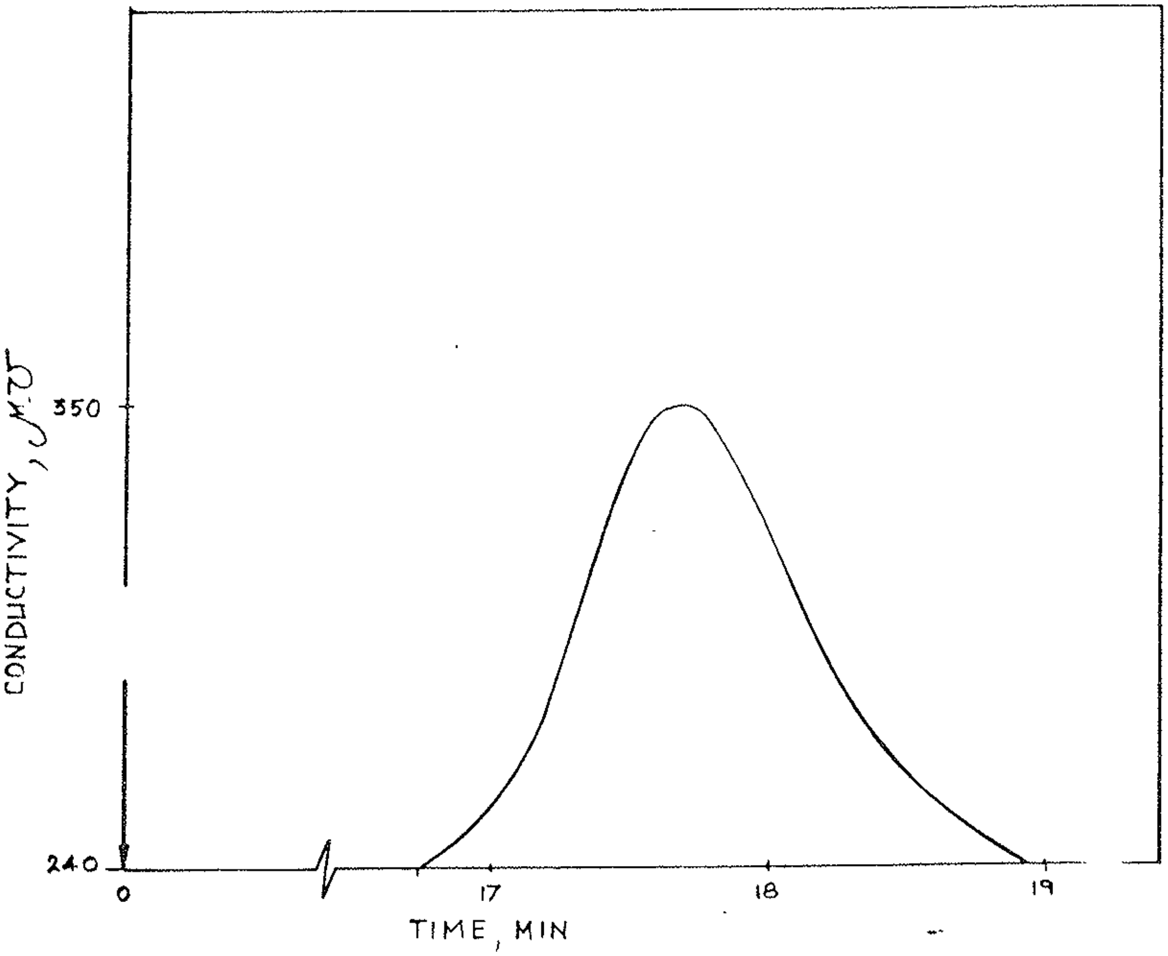


Figure 4-5 Tracer Experiment for the Plug Flow Reactor at 1.0 GPM

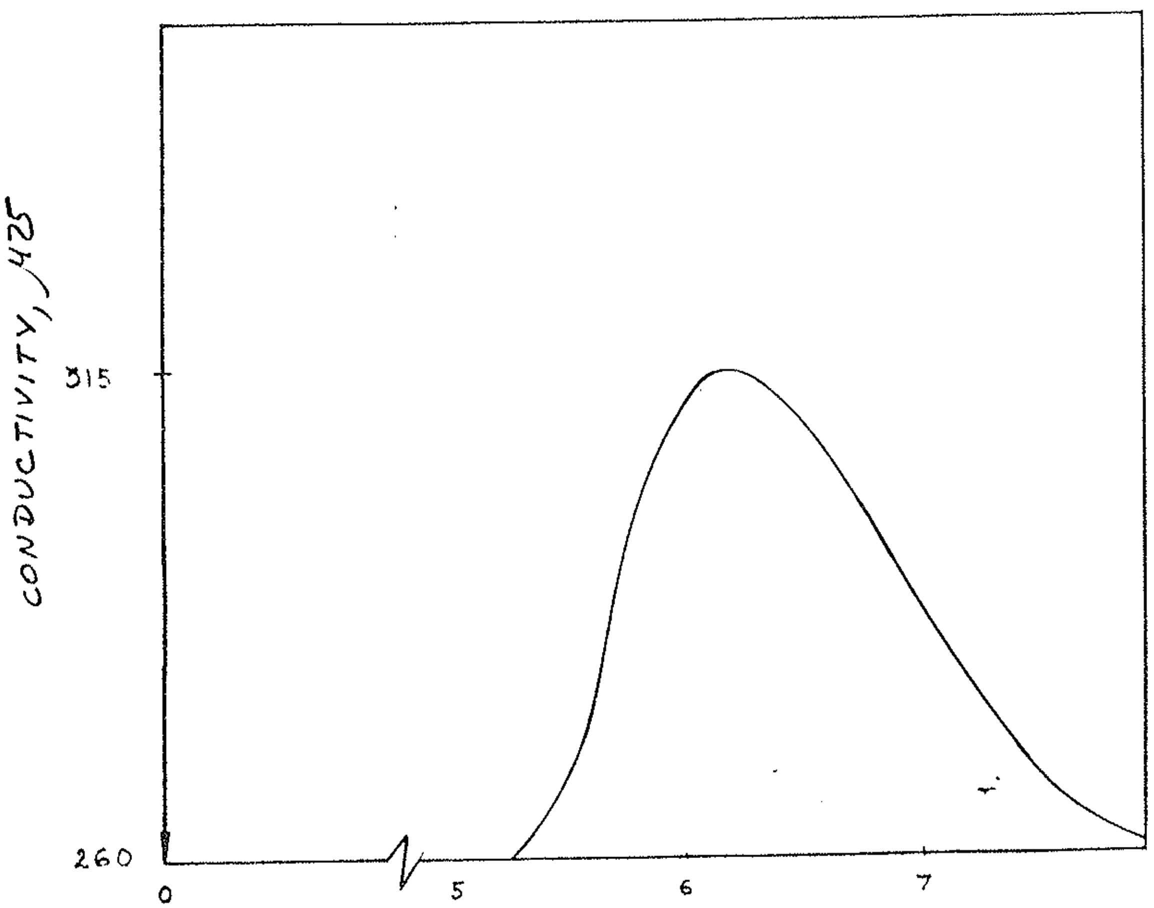


Figure 4-6 Tracer Experiment for the Dispersed Flow Reactor (2 inch) at 0.6 GPM ....

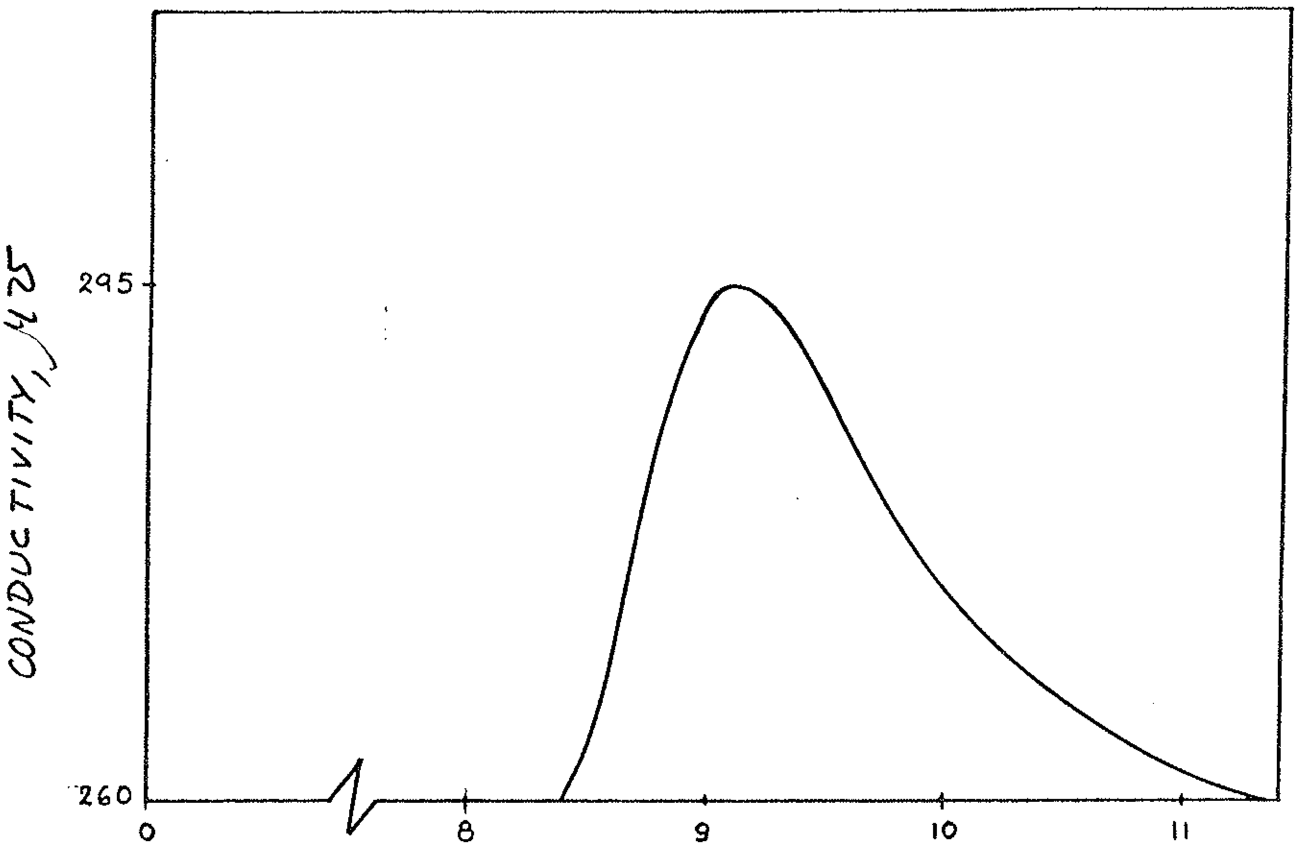


Figure 4-7 Tracer Experiment for the Dispersed Flow Reactor (2 inch) at 1.0 GPM ....

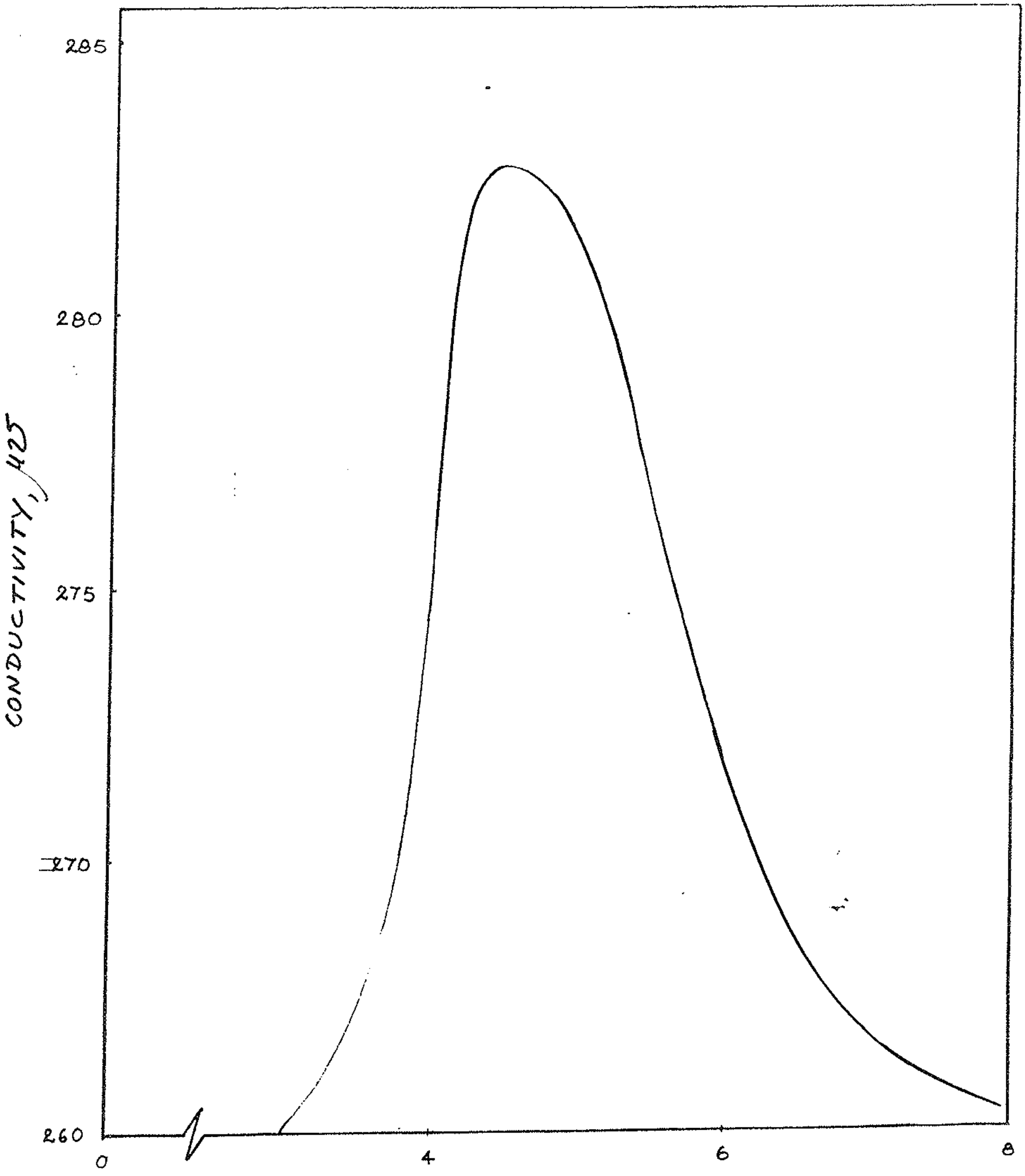


Figure 4-8 Tracer Experiment for the Dispersed Flow Reactor (3 inch) at 0.6 GPM

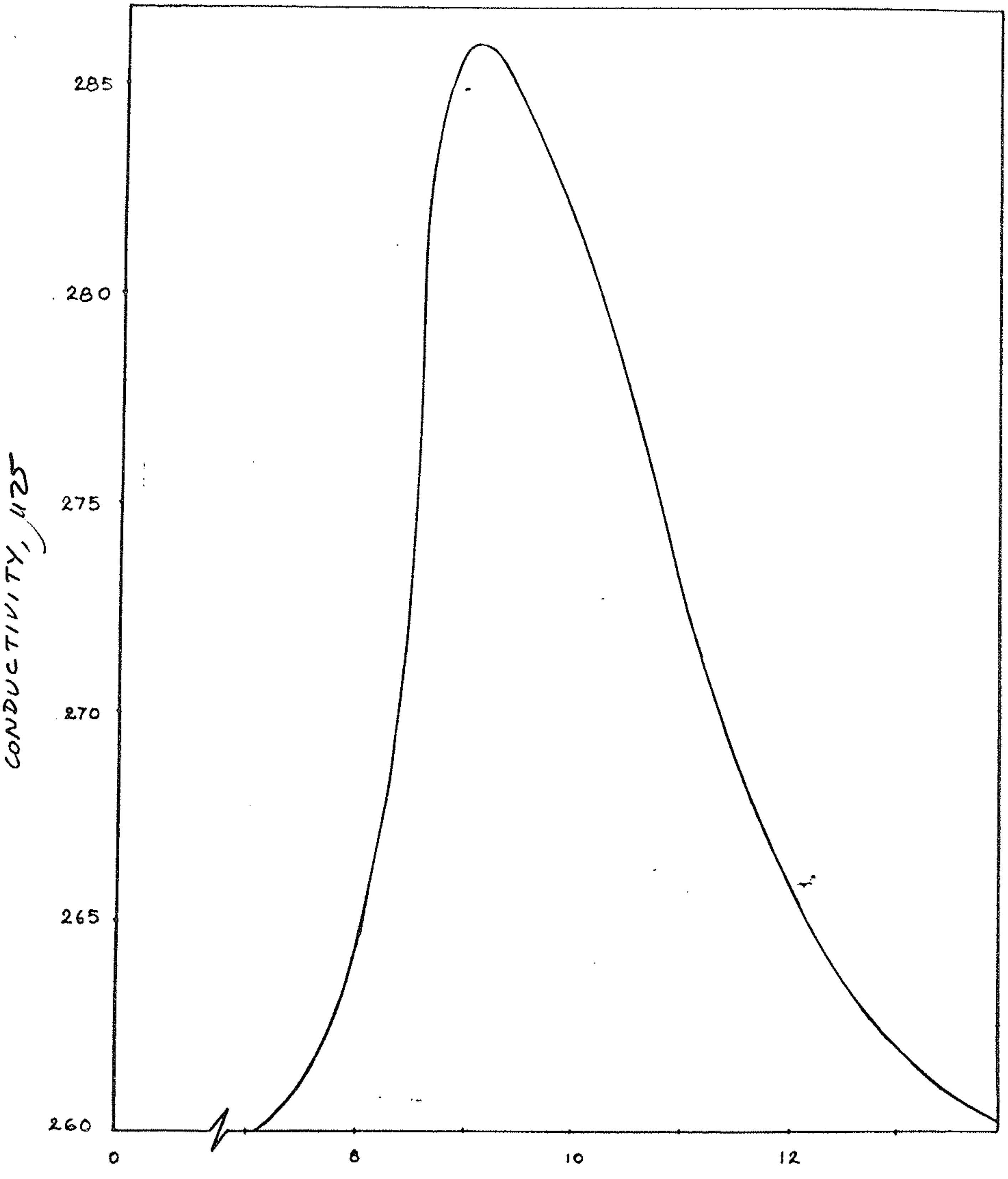


Figure 4-9 Tracer Experiment for the Dispersed Flow Reactor (3 inch)at 1.0 GPM ....

coefficient and are listed in Table 4-2.

Table 4-2 Summary of Dispersion Coefficients

Reactor	Flow rate (GPM)	Dispersion Coefficient (ft^2/min)
Plug Flow	1.0	8.188
	0.6	5.732
Dispersed Flow (2 inch)	1.0	2.945
	1.0	0.762
Dispersed Flow (3 inch)	1.0	0.762
	0.6	0.322

CHLORINATION RESULTS

A total of 17 experiments were performed in the three pilot plants over a pH range of 6.5 to 7.5 and a chlorine to ammonia molar ratio of 0.8 to 1.8. Table 4-3 summarizes the experiments and the various conditions for each experiments. Figures 4-10, 4-11, and 4-12 show the results of similar experiments in each reactor. The effect of dispersion can be visually observed. The remaining experiments and the data tabulation are in the appendix.

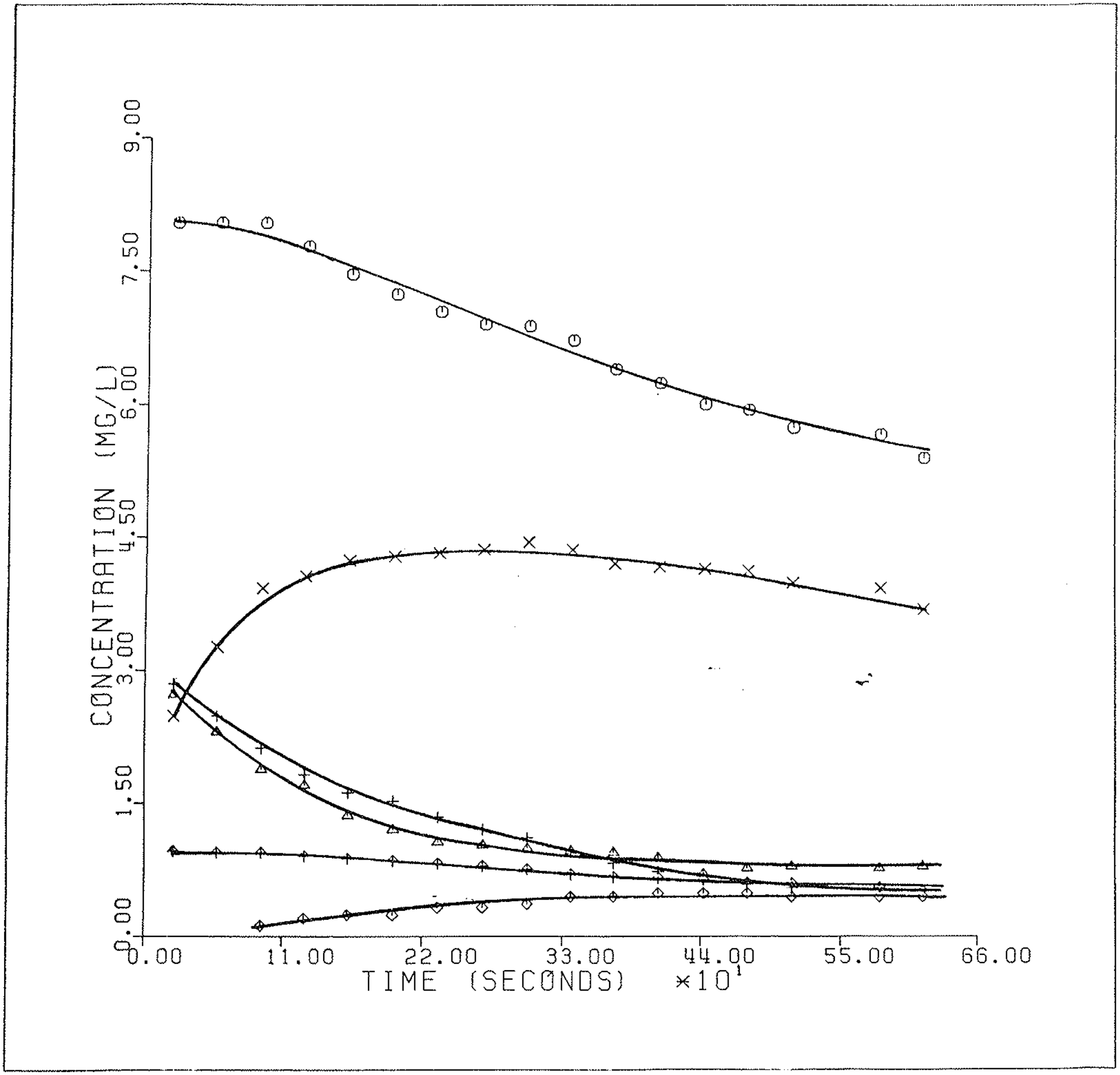
Table 4-3: Summary of Breakpoint Experimental Conditions

Reactor (inch)	Flow Rate (GPM)	Temperature (deg C)	Detention Time (sec)
0.5	0.6 to 1.0	18 to 24	700
2.0	0.6 to 1.0	18 to 24	500
3.0	0.6 to 1.0	18 to 24	500

*Nominal Pipe Size

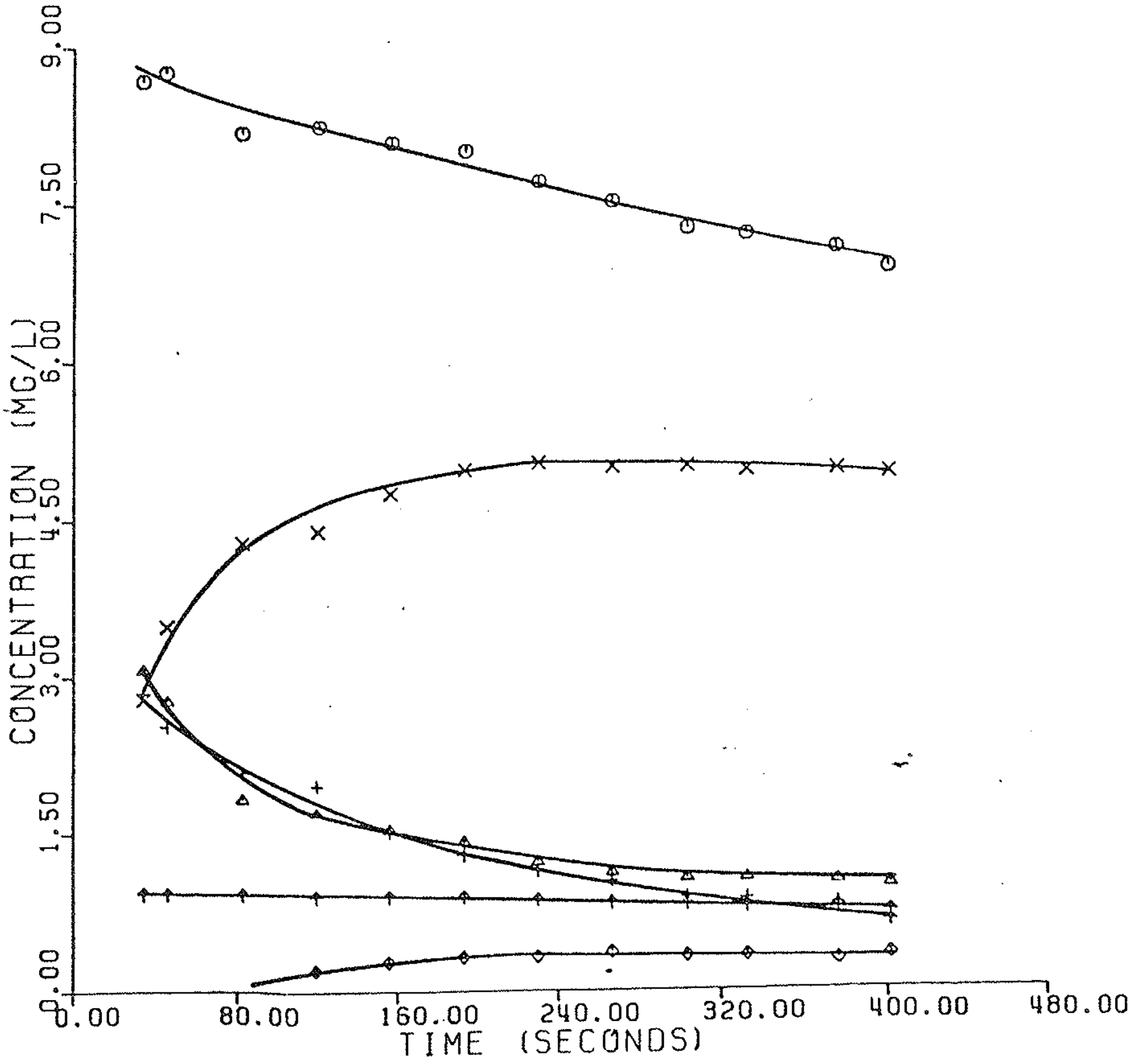
CONCENTRATION (MG/L) VS. TIME(SEC)

Figure 4.10: Sample Experimental Result of the 0.5 inch Reactor. (Temp=24.5 deg C, pH=6.1, Amm=0.95 mg/l, Cl=8.89 mg/l, Q= 1.0GPM)



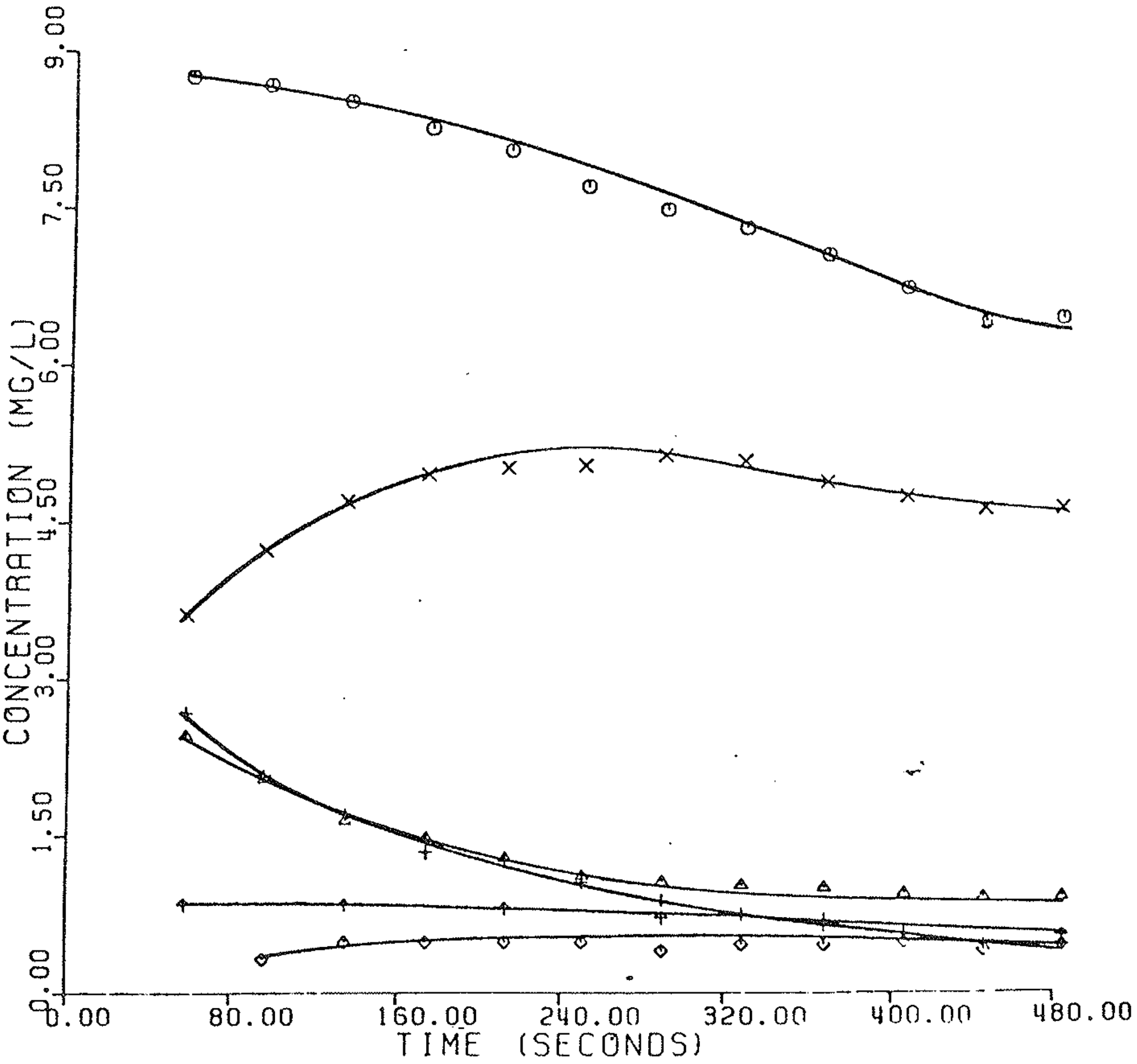
CONCENTRATION (MG/L) VS. TIME(SEC)

Figure 4.11: Sample Experimental Result of the 2.0 inch Reactor. (Temp=20.0 deg C, pH=6.14, Amm=0.95 mg/l, Cl=9.00 mg/l, Q= 1.0GPM)



CONCENTRATION (MG/L) VS. TIME (SEC)

Figure 4.12: Sample Experimental Result of the 3.0 inch Reactor. (Temp=20. deg C, pH=6.05, Amm=0.95 mg/l, Cl=9.27 mg/l, Q= 1.0GPM)



5. BREAKPOINT CHLORINATION MODEL FOR A DISPERSED FLOW REACTOR

ADOPTION OF THE MORRIS AND WEI MECHANISM

The decomposition of Dichloramine is the major difference between Morris-Wei and Selleck-Saunier models. Morris and Weil (1949) observed from their experiments that the rate of decomposition of dichloramine is first order with respect to dichloramine concentration and proportional to hydroxyl ion activity. They proposed the following mechanisms:

$$NHCl_2 \rightarrow H^+ + NCl_2^- \tag{5-1}$$

$$NCl_2^- \xrightarrow{(OH)} NCl + Cl^- \quad (slow) \tag{5-2}$$

$$NCl + OH^- \rightarrow NOH + Cl^- \quad (fast) \tag{5-3}$$

or

$$NCl_2^- + H_2O \text{ or } (OH) \rightarrow NCl(OH)^- + Cl^- + H^+ \tag{5-4}$$

$$NCl(OH)^- \rightarrow NOH + Cl^- \tag{5-5}$$

These mechanisms show that the reaction R-5 in Morris-Wei model is not an elementary reaction. According to Wei, the nitroxyl radical was used as a representation for an intermediate, and other possible species would serve equally well without effect on model computations. However, Saunier and Selleck disagreed on this point. Based on the previous research performed by McCoy (1954) and Anbar (1962), Saunier proposed using hydroxylamine (NH_2OH)

as an intermediate for three main reasons:

- Reaction R-5 in Morris-Wei model is not an elementary reaction, and the dichloramine decomposes according to a more complex pattern.

- McCoy (1954) and Anbar (1962) found hydroxylamine (NH_2OH) in minute concentration during the reaction of chlorine with ammonia.

- The Morris-Wei model cannot predict the P ratio (moles of chlorine reduced divided by the moles of ammonia oxidized) when it is less than 1.5.

According to Palin (1950) and Morris (1952), for initial chlorine to ammonia ratios below the break point, the decomposition of dichloramine can appear at P ratio of less than 1.5; however, the rate was very slow, and it could be observed only after several hours of contact time. For the purpose of this study, this result is considered insignificant and will be neglected. Additionally it is unnecessary to include some intermediate species in the breakpoint mechanism if analytical methods for these intermediate species are not available.

The breakpoint mechanism proposed by Saunier shown previously in Figure 2-8 also cannot predict any end produce (N_2 and NO_3^-) at a P ratio of less than 1.5. Because reaction R-5 was found as nonelementary reaction, an experimental rate coefficient will be used for k_5 and was determined by the parameter identification method.

From these reasons the Morris-Wei mechanism was adopted for this study. The parameter estimates however, except for k_1, were modified for the best fit with experimental data using the parameter estimation technique.

$$\frac{\delta c}{\delta t} = \frac{\delta}{\delta x} \left(D \frac{\delta c}{\delta x} \right) - V \frac{\delta c}{\delta x} + r$$

Reaction Mechanisms

The reaction mechanism which is used in this study are summarized as shown in Figure 5-1. The initial trial values for rate coefficients were selected as shown in Table 5-1, from the following sources:

k_1 was evaluated by Morris (1967)

k_2 was evaluated by Wei (1972)

k_3 was evaluated by Sanguinsin (1975)

k_4 was evaluated based on Sanguinsin's data (1975)

k_5 was evaluated by Saunier (1975)

k_6, k_7 and k_8 - Trial value

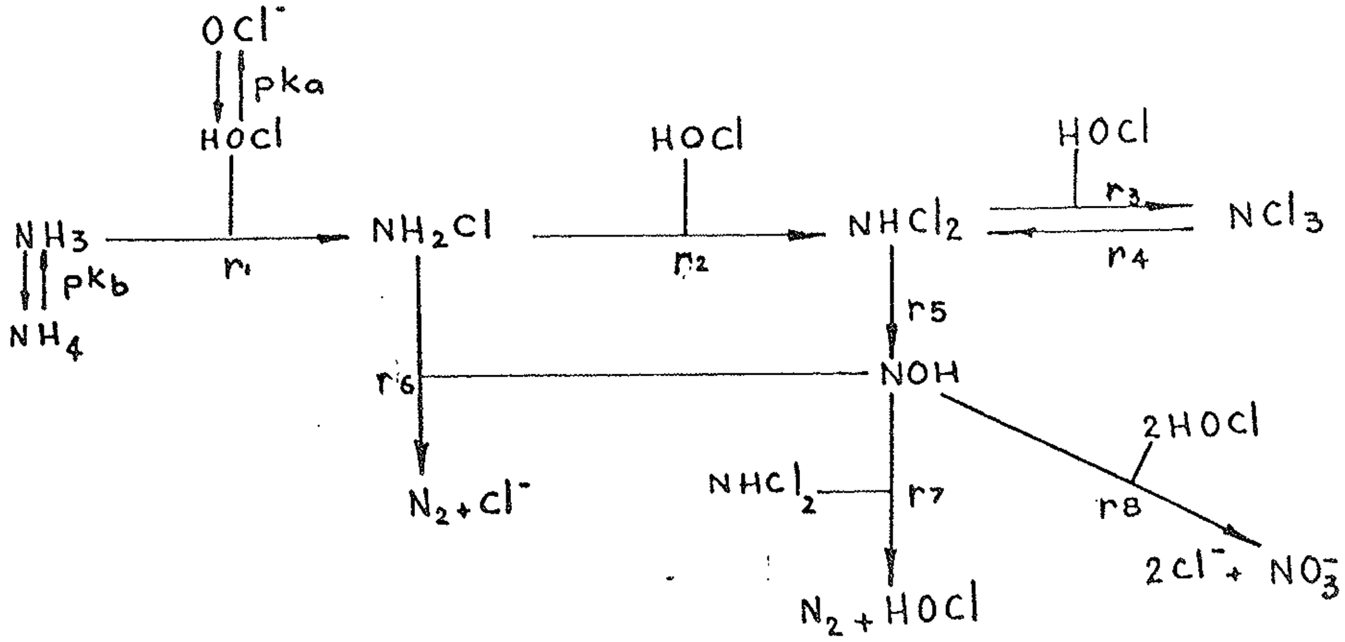


Figure 5-1: Breakpoint Mechanisms of Morris and Wei

MATHEMATICAL MODELING

Basic Concepts

In considering a binary mixture with constant total density, the continuity equation becomes:

$$\frac{\partial C_A}{\partial t} = \underline{\Delta}(D_{AB}\,\underline{\Delta}C_A) - \underline{V}\underline{\Delta}C_A + r \qquad (5\text{-}6)$$

where:

$\underline{\Delta}$ = Gradient operator

A = subscript for solute

B = subscript for solvent (water)

C_A = solute molar concentration

D_{AB} = binary virtual diffusion coefficient (dispersion coefficient)

V = mass average velocity

r = rate of reactions

$r > 0$ for rate of formation

$r < 0$ for rate of consumption

For the case of dispersed flow reactors it is only necessary to consider one dimensional flow as follows:

$$\frac{\partial CA}{\partial t} = \frac{\partial}{\partial x}\left(D_{AB}\frac{\partial CA}{\partial x}\right) - V\frac{\partial CA}{\partial x} + r \qquad (5\text{-}7)$$

As previously indicated on chapter 4, D_{AB} can be replaced by D for all chemical component without making any significant error. Thus the continuity equation can be written as: as follows: {partial-c} over {partial t} = {partial} over {partial x} (D {partial c} over {partial x}) - V {partial c} over

Table 5-1: Initial Trial Values of Rate Coefficients

Observed Rate Coefficients	Theoretical Rate Coefficients
$K_{10} = 9.7 \times 10^{8}\ e^{\left(\frac{-3000}{RT}\right)}$	$k_{1} = \dfrac{k_{10}}{\left[1 + \frac{K_a}{H^+}\right]\left[1 + \frac{K_b\,[H^+]}{K_w}\right]}$
$k_{20} = 2.43 \times 10^{4}\ e^{\left(\frac{-2400}{RT}\right)}$	$k_{2} = \dfrac{k_{20}}{\left(1 + \frac{K_a}{[H^+]}\right)}$
$k_{30} = 3.43 \times 10^{5}\ e^{\left(\frac{-7000}{RT}\right)}$	$k_{3} = k_{30}\left[\dfrac{1. + 10^{-pK_a + 1.4}}{\left(1. + \frac{K_a}{[H^+]^2}\right)}\right]$
$k_{40} = 3 \times 10^{10}\ e^{\left(\frac{-20,000}{RT}\right)}$	$k_{4} = k_{40}\left[\dfrac{1 + 5.88 \times 10^{5}\,[OH]}{\left(1. + \frac{K_a}{[H^+]}\right)}\right]$
$k_{50} = 2.03 \times 10^{14}\ e^{\left(\frac{-7200}{RT}\right)}$	$k_{5} = k_{50}\,N_o\,[OH^-]$
$k_{60} = 10^{7}\ e^{\left(\frac{-6000}{RT}\right)}$	$k_{6} = k_{60}$
$k_{70} = 10^{8}\ e^{\left(\frac{-6000}{RT}\right)}$	$k_{7} = k_{70}$
$k_{80} = 5 \times 10^{7}\ e^{\left(\frac{-6000}{RT}\right)}$	$k_{8} = \dfrac{k_{80}}{\left(1 + \frac{K_a}{[H^+]}\right)}$

The Mathematical Model

Based on the concepts developed by Stenstrom (1975, 1977), the continuity equation shown previously (eq 5-8) was combined with the breakpoint shown in Figure 5-1, to produce set of eight non-linear partial differential equations. These equations can predict the concentration of all major chlorine species generated in a dispersed flow reactor during the breakpoint chlorination process. They are summarized as follows:

$$\frac{\partial c}{\delta t} = \frac{\partial}{\delta x}(D\frac{\partial c}{\delta x}) - V\frac{\partial c}{\delta x} - r_1 - r_2 - r_3 + r_4 - r_7 - 2r_8 \tag{5.9}$$

$$\frac{\partial N}{\delta t} = \frac{\partial}{\delta x}(D\,\frac{\partial N}{\delta x}) - V\,\frac{\partial N}{\delta x} - r_1 \tag{5-10}$$

$$\frac{\partial M}{\delta t} = \frac{\partial}{\delta x}\,(D\frac{\partial M}{\delta x}) - V\,\frac{\partial M}{\delta x} + r_1 - r_2 - r_6 \tag{5-11}$$

$$\frac{\partial D}{\delta t} = \frac{\partial}{\delta x}\,(D\,\frac{\partial D}{\delta x}) - V\frac{\partial D}{\delta x} + r_2 - r_3 + r_4 - r_5 - r_7 \tag{5-12}$$

$$\frac{\partial S}{\delta t} = \frac{\partial}{\delta x}\,(D\,\frac{\partial S}{\delta x}) - V\frac{\partial S}{\delta x} + r_5 - r_6 - r_7 - r_8 \tag{5-13}$$

$$\frac{\partial G}{\delta t} = \frac{\partial}{\delta x}\,(D\,\frac{\partial G}{\delta x}) - V\,\frac{\partial G}{\delta x} + r_6 + r_7 \tag{5-14}$$

$$\frac{\partial I}{\delta t} = \frac{\partial}{\delta x}\,(D\frac{\partial I}{\delta x}) - V\frac{\partial I}{\delta x} + r_8 \tag{5-15}$$

$$\frac{\partial E}{\delta t} = \frac{\partial}{\delta x}\,(D\frac{\partial E}{\delta t}) - V\frac{\partial E}{\delta x} + r_3 - r_4 \tag{5-16}$$

Initial conditions and Boundary Conditions

at t = 0

$c = 0$ $\qquad 0 <= x <= L$

$N = 1$ $\qquad 0 <= x <= L$

$M = D = S = G = I = E = 0 \qquad 0 <= x <- L$

Entrance boundary condition:

at $x = 0$

$M = D = S = G = I = E = 0$

Exit boundary condition:

$$\frac{\partial Q}{\partial x} = 0. \qquad @ \ x = L \tag{5-17}$$

where Q represents each species

Modified Entrance Boundary Condition The "Danckwerts" flux boundary condition (Danckwerts, 1953) must be used for c and N, since the rate at which ammonia and chlorine are fed into the reactor is fixed and must equal equal the rate at which it passes through the cross sectional entrance area by convection and diffusion (at x = 0). The entrance boundary condition for c and N is expressed as follows:

$$\text{flux of chlorine} = \dot{V}C^{*} = VC - D\frac{\partial c}{\partial x} \tag{5-18}$$

$$\text{flux of ammonia nitrogen} = \dot{V}N^{*} = VN - D\frac{\partial n}{\partial x} \tag{5-19}$$

where:

C^{*} = concentration of chlorine in the entering stream (at x = 0-)

Vdo = flow of chlorine solution per unit cross section area of dispersed flow reactor (at x = 0-)

N^* = concentration of ammonia nitrogen in the entering stream (at x = 0 -)

$\ddot{V}$ = flow of ammonia solution per unit cross section area of dispersed flow reactor (at x = 0-)

$V = \dot{V} + \ddot{V}$ = total flow per unit cross section area of dispersed flow reactor.

c = concentration of chlorine (at x = 0+)

N = concentration of ammonia nitrogen (at x = 0+)

Wehner (1956) and Pearson (1959) in attempting to make improvements for the Danckwerts entrance boundary conditions disagreed with Danckwerts about the difference between two concentrations at x = 0+ and x = 0-. Pearson asserted that the discontinuity of dispersion coefficient at x = 0 is not a realistic assumption. He observed that the discontinuity in concentration at either x = 0 or x = L is necessarily a consequence of the imposed discontinuities in D. Pearson replaced the constant dispersion coefficient used by Danckwerts with another form which can be described graphically as follows:

When x varies from 0 to $\frac{1}{a}$, D equals $D_{oa}x$. When x varies from $\frac{1}{a}$ to $L - \frac{1}{a}$, D equals D_o. When x varies from $L - \frac{1}{a}$ to L, D equals $D_{oa}(L - x)$. From these assumptions, Pearson established three sets of partial differential equation and asserted that their solution are matched together at A and B. However, Pearson's assumption creates a discontinuity condition in the gradient of the dispersion coefficient at A and at B.

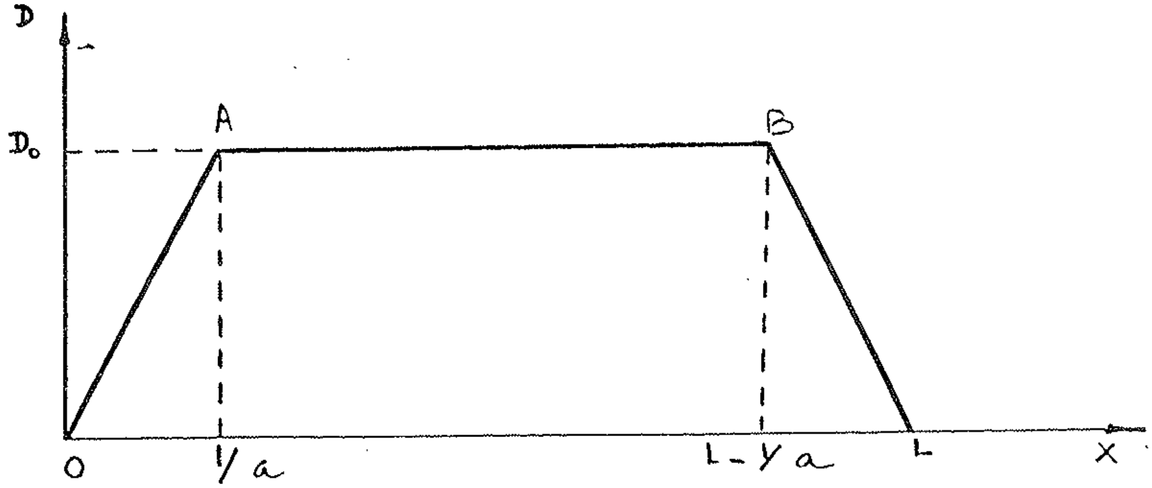


Figure 5-2: Pearson`s Boundary Treatment

In this study a new entrance boundary value for D is proposed as follows:

$$D = \frac{D_o x}{a + x} \qquad (5\text{-}20)$$

where "a" is an arbitrary value chosen for the best fit with the data collected. In equation 5-20, D increases continuously from zero to D_o as x increases; consequently there is no discontinuity of concentration at inlet boundary.

Exit Boundary Condition

Let U be the generalized molar concentration ratio of the species question and initial ammonia concentration. For a long dispersed flow reactor, Danckwerts suggested the following exit boundary condition:

$$\frac{\partial U}{\partial x} = 0 \qquad @\ x = L \qquad (5\text{-}21)$$

where L is the length of dispersed flow reactor. Therefore a zero gradient condition exists at x = L. This implies that the flux across the exit boundary is due to convective transport alone. This assumption appears to be realistic for a long tubular reactor and it is useful for numerical solution techniques.

NUMERICAL ANALYSIS

The generalized partial differential equation can be written in linearized form as follows:

$$\frac{\delta U}{\delta t} = \frac{\delta}{\delta x}\left(D\frac{\delta U}{\delta x}\right) - V\frac{\delta U}{\delta x} + KUU^{*} + HQ \tag{5-22}$$

where:

K and H are constants,

U represents any species.

All nonlinear terms (reactions rates) can be separated into two classes: those which are functions of the dependent variable U, and those which are not. The terms which are functions of U can be factored into the product of U and some function of U, called U*. The non-linear terms which are not functions of U are called Q. Rearranging equation 5-22 and using the chain rule for the second partial gives:

$$\frac{\delta U}{\delta t} = D\frac{\delta^2 U}{\delta x^2} + \left(\frac{\delta D}{\delta x} - V\right)\frac{\delta U}{\delta x} + KUU^{*} + HQ \tag{5-23}$$

The partial derivative of D with respect to x at the center of the characteristic average computational grid can be determined analytically as follows:

$$\frac{\delta D}{\delta x}\bigg|_{i-\frac{1}{2},j+\frac{1}{2}} = \frac{AD_o}{(x + A)^2} \tag{5-24}$$

Substituting equation 5-24 into equation 5-23 gives:

$$\frac{\partial U}{\partial t} = D\frac{\partial^2 U}{\partial x^2} + \left(\frac{AD_o}{(x + A)^2} - V\right)\frac{\partial U}{\partial x} + KUU^* + HQ \tag{5-25}$$

Letting

$$\frac{AD_o}{(x + A)^2} - V = Z \tag{5-26}$$

Then:

$$\frac{\partial U}{\partial t} = D\,\frac{\partial^2 U}{\partial x^2} + Z\frac{\partial U}{\partial x} + KUU^* + HQ \tag{5-27}$$

<u>Characteristic</u> <u>average</u> <u>method</u>

If we consider the above partial differential equation with respect to the entrance boundary condition we see that as x approaches zero the dispersion D also approaches zero. Therefore at the entrance boundary the equation is a hyperbolic differential equation which must be solved by a suitable numerical such as the centered difference method (Von Rosenberg, 1969). As D becomes large the differential equation is strongly parabolic and must be solved by parabolic method, such as Crank-Nicolson (Von Rosenberg, 1969). The characteristics averaging method (Melsheimer and Adler, 1973) was chosen to solve this equation because it can handle both cases, when either D is large or when D is zero.

Finite Difference Analogs

There are six nodal points involved in the characteristic average computational grid and is described graphically in Figure 5-3. On the characteristic average method, the finite difference analog for different terms which are involved in equation can be written as follows:

$$\frac{\delta U}{\delta t} = \tfrac{1}{2}\left[\frac{U_{i-1,j+1} - U_{i-1,j}}{\Delta t} + \frac{U_{i,j+1} - U_{i,j}}{\Delta t}\right] \qquad (5\text{-}28)$$

$$\frac{\delta U}{\delta x} = \tfrac{1}{2}\left[\frac{U_{i,j} - U_{i-1,j}}{\Delta x} + \frac{U_{i,j+1} - U_{i-1,j+1}}{\Delta x}\right] \qquad (5\text{-}29)$$

$$\frac{\delta^2 U}{\delta x^2} = \tfrac{1}{2}\frac{[\, U_{i,j} - 2\, U_{j-1,j} + U_{i-2,j} \,]}{(\Delta x)^2} +$$

$$\tfrac{1}{2}[\, U_{i+1,j+1} - -2U_{i,j+1} + U_{i-1,j+1}\frac{]}{(\Delta x)^2} \qquad (5\text{-}30)$$

$$U_{i-\frac{1}{2},j-\frac{1}{2}} = \frac{1}{4}[U_{i,j} + U_{i,j+1} + U_{i-1,j} + U_{i-1,j+1}\,] \qquad (5\text{-}31)$$

$$D = \tfrac{1}{2}[D_{i-1,j} + D_{i,j}\,] \qquad (5\text{-}31)$$

The Finite Difference Equations

After substitution of the previously described analogs, the finite difference equation for interior points can be written as:

$$U_{i-1,j+1}\left[\frac{1}{2\Delta t}\ \frac{1}{4(\Delta x)^2}(D_{i-1} + D_i\,) + s\frac{Z}{2\Delta x} - \frac{KU^*}{4}\,\right] + U_{i,j+1}$$

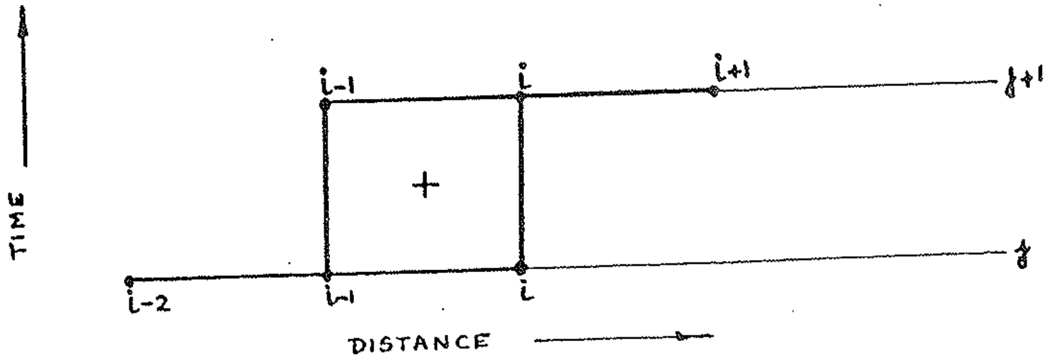


Figure 5-3: Characteristics Averaging Analogs

$$[\frac{1}{2\Delta t} + \frac{1}{2(\Delta x)^2}(D_{i-1} + D_i) - \frac{Z}{2\Delta x} - \frac{KU^*}{4}] +$$

$$U_{i+1,j+1}\ [\frac{1}{4(\Delta x)^2}(D_{i-1} + D_i)] =$$

$$U_{i-2,j}\ [\frac{1}{4(\Delta x)^2}(D_{i-1} + D_i)] + U_{i-1,j}\ [\frac{1}{2\Delta t} - \frac{1}{2(\Delta x)^2}(D_{i-1} + D_i)$$

$$- \frac{Z}{2\Delta x} + \frac{KU^*}{4}] + U_{i,j}\ [\frac{1}{2\Delta t} + \frac{1}{4(\Delta x)^2}(D_{i-1} + D_i) + \frac{Z}{2\Delta x} + \frac{KU^*}{4}] + HQ \quad (5\text{-}32)$$

where:

$U_o >$ 0 for free chlorine and ammonia nitrogen.

$U_o =$ 0 for other chlorine derivatives.

The finite difference equation at exit boundary:

$$\frac{\delta U}{\delta x} = 0 \text{ at } x = L \text{ or:} \quad (5\text{-}33)$$

$$U_{i-1,j+1} = U_{i+1,j+1} \quad (5\text{-}34)$$

and

$$U_{i-1,j} = U_{i+1,j} \quad (5\text{-}35)$$

Substituting into the interior equation yields;

$$U_{i-1,j+1}\ [\frac{1}{\Delta t} + \frac{1}{4(\Delta x)^2}(D_{i-1} + D_i) - \frac{KU^*}{2}] +$$

$$U_{i+2,J+2} - [\frac{1}{4(\Delta x)^2}(D_{i-2} + D_i)] =$$

$$U_{i-2,j}\left[\frac{1}{4(\Delta x)^2}(D_{i-1}+D_i)\right]+$$

$$U_{i-1,j}\left[\frac{1}{\Delta t}-\frac{1}{4(\Delta x)^2}(D_{i-1}+D_i)+\frac{KU^*}{2}\right]+HQ \qquad (5\text{-}36)$$

Solution Technique

The entrance boundary equation, the exit boundary equation and a set of equations for interior point can be rearranged into the following form:

$$[B]U = F \qquad (5\text{-}37)$$

where [B] is a tridiagonal matrix, {U} is a column matrix for unknown values, {F} is a column matrix for known values. This equation can be solved by the Thomas Algorithm as described by Von Rosenberg (1969). The non-linear terms, U* and Q, must be solved by a trial and error technique, such as direct iteration, or a projection method. These techniques are also described by Von Rosenberg 1969).

The problem becomes one of solving the eight simultaneous equations equations which are all similar to equation 5-36 and 5-37. The iteration methods available to solve this set of eight equations are direct iteration, forward projection, backward projection, weighted iteration, and iteration using a root finding technique such as Newton-Rapson or Regula-Falsi. Backward projection appeared to be the most efficient method.

PARAMETER ESTIMATION

The rate coefficient k_1 was estimated precisely by Weil and Morris (1949) and it was not necessary to rework on the kinetics of formation of monochloramine in this study. The remaining parameters to be estimated are k_2, k_3, k_4, k_5, k_6, k_7, and k_8.

To perform the parameter estimation the technique proposed by Yeh (1974, 1975) was used. The weighted least squares criterion was used as the objective function as follows:

$$\text{Min } J = W_C\Sigma_i\Sigma_j\ (\alpha_i^j)^2 + W_M\Sigma_i\Sigma_j\ (\beta_i^j)^2 + W_D\Sigma_i\Sigma_j\ (\delta_i^j)^2 +$$

$$W_E\Sigma_i\Sigma_j\ (\xi_i^j)^2 = +W_N\Sigma_i\Sigma_j\ (\mu_i^j)^2 + W^P\Sigma_i\Sigma j\ (\eta_i^j)^2 \qquad (5\text{-}38)$$

Over

$$k_2, k_3, k_5, k_6, k_7, k_8$$

where:

$$\alpha_i^j = C_i^j - C_i^{*j} \qquad (5\text{-}39)$$

$$\beta_i^j = M_i^j - M_i^{*j} \qquad (5\text{-}40)$$

$$\delta_i^j = D_i^j - D_i^{*j} \qquad (5\text{-}41)$$

$$\xi_i^j = E_i^j - E_i^{*j} \qquad (5\text{-}42)$$

$$\mu_i^j = N_i^j - N_i^{*j} \tag{5-43}$$

$$\eta_i^j = P_i^j - P_i^{*j} \tag{5-44}$$

i is the sample location number, and j is the observation time.

$$C_i^{*j}, M_i^{*j}, D_i^{*j}, E_i^{*j}, N_i^{*j} \text{ are the measured values, and} \tag{5-45}$$

$C_i^j, M_i^j \cdot D_i^j \cdot E_i^j, N_i^j$ are the expected values (simulation results).

at time = j, andx = j.

and

P = molar ratio of chlorine reduced ammonia oxidized.

$$P_i^j = \frac{C\text{ initial} - (C_i^j + M_i^j + D_i^j + E_i^j)}{N\text{ initial} - N_i^j} \tag{5-46}$$

$$P_i^{*j} = \frac{C\text{ initial} - (C_i^{*j} + M_i^{*j} + E_i^{*j})}{N\text{ initial} - N_i^{*j}} \tag{5-47}$$

Parameter Estimation Algorithm

The parameter estimation algorithm requires the sequential estimation and linearization of the objective function around an initial set of parameter estimates. By perturbing the parameters are observing the effect on the objective function, a new set of parameter estimates can be obtained which reduces the objective function. This procedure is followed until further perturbations provide no improvement in the objective function. The following step-by-step description is provided to demonstrate the procedure.

Step 1. Select initial value k_2^o, k_3^o, k_4^o, k_5^o, k_6^o, k_7^o, and k_8^o. One possible starting set is shown in Table 5.2. (The superscript denotes trial number.) Solve the mathematical model for C, M, D, E, N and P for the given sampling point and time.

Step 2. Calculate initial errors $(\alpha_i^j)^o$ and J. If $J \leq$ minimum criteria, stop.

Step 3. Establish the influence coefficient matrix: perturb each parameter by an incremental value and recalculate the errors (α, β, δ, ξ, and μ). Calculate the influence coefficient as the ratio of the change in error to the change in parameter, i.e., $\frac{\Delta\alpha}{\Delta k_2}$. Repeat this calculation until all parameters are perturbed and the errors are determined at all different observation times. The influence coefficients calculated form the influence coefficient matrix.

Step 4. Make a Taylor series expansion of α, β, δ, ξ, and μ about their initial value, i.e.,

$$(\alpha_i^j)^1 = (\alpha_i^j)^o + (k_2^1 - k_2^o)\,\frac{\partial k_2}{\delta\alpha_i}\Big|^o + (k_3^1 - k_3^o)\,\frac{\partial k_3}{\delta\alpha_i}\Big|^o$$

$$+ (k_4^1 - k_4^o)\,\frac{\partial k_4}{\delta\alpha_i}\Big|^o + (k_5^1 - k_5^o)\,\frac{\partial k_5}{\delta\alpha_i}\Big|^o$$

$$+ (k_6^1 - k_6^o) \frac{\delta k_6}{\delta \alpha_i} |^o + (k_7^1 - k_7^o) \frac{\delta k_7}{\delta \alpha_i} |^o$$

$$+ (k_8^1 - k_8^o) \frac{\delta k_8}{\delta \alpha_i} |^o + \text{high order terms.} \tag{5-48}$$

Similar equations are developed for $(\beta_i^j)^1$, $(\delta_i^j)^1$, $(\xi_i^j)^1$, and $(\mu_i^j)^1$. The new parameter estimates k_2^1, k_3^1, k_4^1, k_5^1, k_6^1, k_7^1 and k_8^1 are determined to minimize the objective function. The initial values for α, β, δ, ξ and μ were dêtermined in step 2. The partial derivatives of k_2, k_3, k_4, k_5, k_6, k_7 and k_8 with respect to each parameter are the terms in the the influence coefficient matrix, and can be calculate since the perturbation in the parameters are know as well as the new error terms.

Step 5. Calculate the objective function from $(\alpha_i^j)^1$, (β_i^j), $(\delta_i^j)^1$, (ξ_i^j) and $(\mu_i^j)^1$. Next the optimization technique must determine a set of new parameters which minimizes the objective function. It has been shown that the objective function will be quadratic in form and therefore a quadratic programming technique can be used to determine the new parameter estimates. Quadratic program is convenient since it accommodates constraints for the parameter estimates, which are required since there are physical bounds for the parameters. These physical bounds were selected and are listed in Table 5.2. Alternately, any constrained optimization technique can be used to obtain the new parameter estimates.

Step 6. Replace k_2^o, k_3^o, k_4^o, k_5^o, k_6^o, k_7^o, k_8^o by k_2^1, k_3^1, k_4^1, k_5^1, k_6^1, k_7^1 and return to step 1. The procedure should terminate when the objective function is smaller than the minimum criteria, or no improvement is occurring with each iteration.

Table 5-2 Maximum and Minimum Values for Rate Coefficients

Rate Coefficients	Boundary Value[a,b]	
	Lower Bound	Upper Bound
k_2	10	1000
k_3	10^{-1}	10
k_4	10^{-7}	$5. \times 10^{-5}$
k_6	100	10^4
k_7	10^3	10^5
k_8	100	10^4

[a] using units of moles for concentration, liters for volume and seconds for time.

[b] Temperature from 10°C 30°C and pH from 5.5 to 9.0.

6. MODELING RESULTS AND DISCUSSION

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APPENDICES

Table A1: Experimental Results for the Chlorination Reactor (0.5"), at t=24.5 , deg C, pH=6.10, Cl=8.89, ammonia=0.95, Q=1.0 GPM)

POINT NO.	TIME (SEC)	FREE (MG/L)	MONO (MG/L)	DI (MG/L)	TRI (MG/L)	TOTAL (MG/L)	AM (MG/L)
1	23.	2.72	2.84	2.48	0.0	8.04	0.95
2	58.	2.30	2.48	3.26	0.0	8.04	0.94
3	93.	1.88	2.12	3.92	0.12	8.04	0.94
4	128.	1.70	1.82	4.06	0.20	7.78	0.90
5	163.	1.36	1.62	4.24	0.24	7.46	0.87
6	198.	1.20	1.52	4.28	0.24	7.24	0.85
7	232.	1.06	1.34	4.32	0.32	7.04	0.82
8	267.	1.02	1.20	4.36	0.32	6.90	0.79
9	302.	0.98	1.10	4.44	0.36	6.88	0.75
10	337.	0.96	0.96	4.36	0.44	6.72	0.70
11	372.	0.94	0.82	4.20	0.44	6.40	0.67
12	407.	0.88	0.72	4.16	0.48	6.24	0.65
13	442.	0.70	0.68	4.14	0.48	6.00	0.63
14	477.	0.76	0.58	4.12	0.48	5.94	0.60
15	512.	0.78	0.54	3.98	0.44	5.74	0.59
16	581.	0.76	0.54	3.92	0.44	5.66	0.55
17	616.	0.78	0.50	3.68	0.44	5.40	0.50

Table A2: Experimental Results for the Chlorination Reactor (0.5"), at t=24.0 deg C, pH=7.20, Cl=5.48, ammonia=0.90, Q=1.0 GPM)

POINT NO.	TIME (SEC)	FREE (MG/L)	MONO (MG/L)	DI (MG/L)	TRI (MG/L)	TOTAL (MG/L)	AM (MG/L)
1	53.	0.62	4.18	0.40	0.0	5.20	0.86
2	88.	0.54	4.06	0.48	0.0	5.08	0.84
3	123.	0.48	3.88	0.50	0.0	4.86	0.81
4	158.	0.44	3.86	0.52	0.0	4.82	0.79
5	193.	0.34	3.84	0.54	0.0	4.72	0.77
6	228.	0.28	3.84	0.56	0.0	4.68	0.75
7	262.	0.22	3.84	0.56	0.0	4.62	0.73
8	297.	0.18	3.80	0.56	0.0	4.54	0.73
9	332.	0.20	3.70	0.56	0.0	4.46	0.72
10	367.	0.18	3.64	0.56	0.0	4.38	0.70
11	402.	0.14	3.64	0.56	0.0	4.34	0.69
12	437.	0.12	3.64	0.54	0.0	4.30	0.68
13	472.	0.10	3.60	0.54	0.0	4.24	0.67
14	507.	0.06	3.60	0.54	0.0	4.20	0.66
15	542.	0.06	3.58	0.54	0.0	4.18	0.65
16	577.	0.02	3.58	0.54	0.0	4.14	0.65
17	611.	0.0	3.60	0.54	0.0	4.14	0.63
18	646.	0.0	3.58	0.54	0.0	4.12	0.62

Table A3: Experimental Results for the Chlorination Reactor (3.0"), at t=20.5 deg C, pH=6.04, Cl=9.31, ammonia=0.92, Q=1.0 GPM)

POINT NO.	TIME (SEC)	FREE (MG/L)	MONO (MG/L)	DI (MG/L)	TRI (MG/L)	TOTAL (MG/L)	AM (MG/L)
1	89.	2.42	2.42	3.36	0.0	8.20	0.85
2	148.	1.76	1.82	4.22	0.16	7.96	0.0
3	207.	1.36	1.48	4.58	0.32	7.74	0.82
4	267.	1.14	1.28	4.80	0.36	7.58	0.0
5	327.	0.92	0.94	4.88	0.40	7.14	0.76
6	386.	0.92	0.74	4.88	0.40	6.94	0.0
7	446.	0.88	0.58	4.84	0.36	6.66	0.72
8	506.	0.82	0.56	4.84	0.36	6.58	0.0
9	556.	0.82	0.46	4.84	0.40	6.52	0.64
10	625.	0.80	0.46	4.76	0.36	6.38	0.0
11	685.	0.78	0.38	4.70	0.36	6.22	0.58
12	745.	0.78	0.32	4.46	0.40	5.96	0.55

Table A4: Experimental Results for the Chlorination Reactor (3.0"), at t=20.0 deg C, pH=6.50, Cl=9.08, ammonia=0.97, Q=1.0 GPM)

POINT NO.	TIME (SEC)	FREE (MG/L)	MONO (MG/L)	DI (MG/L)	TRI (MG/L)	TOTAL (MG/L)	AM (MG/L)
1	75.	1.98	2.48	3.30	0.0	7.76	0.90
2	137.	1.48	1.88	3.88	0.16	7.40	0.0
3	199.	1.32	1.54	4.00	0.20	7.06	0.87
4	262.	1.10	1.30	4.18	0.24	6.82	0.0
5	325.	0.94	0.90	4.10	0.28	6.22	0.75
6	387.	0.88	0.84	4.00	0.24	5.96	0.0
7	450.	0.84	0.74	4.10	0.24	5.92	0.64
8	512.	0.78	0.58	3.76	0.28	5.40	0.0
9	576.	0.66	0.52	3.68	0.36	5.22	0.59
10	639.	0.64	0.46	3.50	0.36	4.96	0.0
11	702.	0.66	0.38	3.50	0.36	4.90	0.52
12	765.	0.66	0.30	3.38	0.32	4.66	0.0

Table A5: Experimental Results for the Chlorination Reactor (3.0"), at t=21.8 deg C, pH=7.15, Cl=9.30, ammonia=0.97, Q=0.6 GPM)

POINT NO.	TIME (SEC)	FREE (MG/L)	MONO (MG/L)	DI (MG/L)	TRI (MG/L)	TOTAL (MG/L)	AM (MG/L)
1	89.	3.56	3.16	0.48	0.0	7.20	0.73
2	148.	3.18	2.66	0.42	0.0	6.26	0.62
3	207.	2.94	2.26	0.36	0.16	5.72	0.53
4	267.	2.60	1.86	0.34	0.16	4.96	0.45
5	327.	2.38	1.46	0.28	0.20	4.32	0.39
6	386.	2.16	1.12	0.22	0.20	3.70	0.34
7	446.	1.96	1.08	0.18	0.24	3.46	0.30
8	506.	1.94	0.90	0.16	0.24	3.24	0.28
9	566.	1.84	0.84	0.16	0.24	3.08	0.25
10	625.	1.68	0.66	0.14	0.24	2.72	0.20
11	685.	1.68	0.54	0.12	0.24	2.58	0.16
12	745.	1.70	0.44	0.10	0.28	2.52	0.14

Table A6: Experimental Results for the Chlorination Reactor (2.0"), at t=20.0 deg C, pH=6.14, Cl=9.04, ammonia=0.95, Q=1.0 GPM)

POINT NO.	TIME (SEC)	FREE (MG/L)	MONO (MG/L)	DI (MG/L)	TRI (MG/L)	TOTAL (MG/L)	AM (MG/L)
1	35.	3.06	2.34	2.78	0.0	8.68	0.93
2	46.	2.76	2.52	3.48	0.0	8.76	0.92
3	83.	1.82	2.08	4.28	0.0	8.18	0.92
4	120.	1.70	1.96	4.40	0.20	8.26	0.91
5	156.	1.54	1.52	4.76	0.28	8.10	0.90
6	193.	1.42	1.30	4.98	0.32	8.02	0.89
7	230.	1.22	1.14	5.04	0.32	7.72	0.86
8	267.	1.12	1.04	5.00	0.36	7.52	0.83
9	304.	1.06	0.88	5.00	0.32	7.26	0.81
10	333.	1.06	0.86	4.96	0.32	7.20	0.79
11	377.	1.02	0.80	4.96	0.28	7.06	0.77
12	402.	0.98	0.64	4.92	0.32	6.86	0.73

Table A7: Experimental Results for the Chlorination Reactor (2.0"), at t=22.5 deg C, pH=6.80, Cl=9.13, ammonia=0.95, Q=1.0 GPM)

POINT NO.	TIME (SEC)	FREE (MG/L)	MONO (MG/L)	DI (MG/L)	TRI (MG/L)	TOTAL (MG/L)	AM (MG/L)
1	35.	3.08	3.02	2.22	0.0	8.32	0.87
2	46.	2.50	2.54	2.56	0.20	7.80	0.80
3	83.	1.94	1.96	2.64	0.28	6.82	0.75
4	120.	1.86	1.84	2.84	0.32	6.86	0.71
5	156.	1.76	1.58	2.74	0.32	6.40	0.65
6	193.	1.64	1.28	2.66	0.28	5.86	0.60
7	230.	1.52	0.80	2.24	0.28	4.84	0.49
8	267.	1.46	0.68	2.00	0.28	4.42	0.40
9	304.	1.44	0.54	1.88	0.32	4.18	0.37
10	333.	1.34	0.52	1.82	0.28	3.96	0.33
11	377.	1.34	0.42	1.72	0.32	3.80	0.29
12	402.	1.32	0.32	1.50	0.36	3.50	0.25

Table A8: Experimental Results for the Chlorination Reactor (3.0"), at t=18.3 deg C, pH=6.74, Cl=9.15, ammonia=0.90, Q=1.0 GPM)

POINT NO.	TIME (SEC)	FREE (MG/L)	MONO (MG/L)	DI (MG/L)	TRI (MG/L)	TOTAL (MG/L)	AM (MG/L)
1	89.	2.20	2.34	3.24	0.0	7.78	0.84
2	148.	1.72	1.84	3.72	0.12	7.40	0.79
3	207.	1.42	1.36	3.80	0.36	6.94	0.73
4	267.	1.26	1.00	3.78	0.40	6.44	0.66
5	327.	1.12	0.76	3.48	0.40	5.76	0.56
6	386.	1.12	0.58	3.16	0.40	5.26	0.49
7	446.	1.14	0.36	2.90	0.40	4.80	0.43
8	506.	1.18	0.24	2.58	0.44	4.44	0.41
9	566.	1.02	0.24	2.44	0.42	4.12	0.39
10	625.	1.06	0.16	2.32	0.42	3.96	0.36
11	685.	1.16	0.14	2.28	0.32	3.90	0.33
12	745.	1.18	0.10	2.08	0.32	3.68	0.28

Table A9: Experimental Results for the Chlorination Reactor (3.0"), at t=24.5 deg C, pH=7.15, Cl=9.15, ammonia=0.92, Q=0.6 GPM)

POINT NO.	TIME (SEC)	FREE (MG/L)	MONO (MG/L)	DI (MG/L)	TRI (MG/L)	TOTAL (MG/L)	AM (MG/L)
1	89.	2.36	2.24	1.58	0.0	6.18	0.70
2	148.	2.08	1.48	1.42	0.0	4.98	0.57
3	207.	1.84	1.18	1.16	0.0	4.18	0.46
4	267.	1.68	0.98	0.90	0.16	3.72	0.40
5	327.	1.64	0.52	0.62	0.24	3.02	0.31
6	386.	1.60	0.26	0.50	0.32	2.68	0.25
7	446.	1.44	0.24	0.32	0.32	2.32	0.15
8	506.	1.44	0.18	0.26	0.28	2.16	0.13
9	566.	1.42	0.16	0.24	0.24	2.06	0.11
10	625.	1.42	0.16	0.20	0.28	2.06	0.11
11	685.	1.32	0.14	0.16	0.28	1.90	0.11
12	745.	1.32	0.10	0.12	0.32	1.86	0.11

Table A10: Experimental Results for the Chlorination Reactor (3.0"), at t=20.0 deg C, pH=7.40, Cl=9.15, ammonia=0.92, Q=0.6 GPM)

POINT NO.	TIME (SEC)	FREE (MG/L)	MONO (MG/L)	DI (MG/L)	TRI (MG/L)	TOTAL (MG/L)	AM (MG/L)
1	89.	2.96	2.34	1.50	0.0	6.80	0.75
2	148.	2.32	1.48	1.42	0.0	5.22	0.53
3	207.	2.00	1.14	0.84	0.28	4.26	0.42
4	267.	1.86	0.68	0.74	0.30	3.58	0.37
5	327.	1.84	0.60	0.64	0.32	3.40	0.34
6	386.	1.78	0.48	0.56	0.34	3.16	0.25
7	446.	1.82	0.34	0.24	0.36	2.76	0.18
8	506.	1.64	0.30	0.24	0.34	2.52	0.15
9	566.	1.66	0.22	0.20	0.32	2.40	0.12
10	625.	1.64	0.14	0.14	0.34	2.26	0.11
11	685.	1.62	0.12	0.08	0.36	2.18	0.10
12	745.	1.62	0.10	0.02	0.32	2.06	0.10

Table A11: Experimental Results for the Chlorination Reactor (2.0"), at t=20.5 deg C, pH=7.03, Cl=9.00, ammonia=0.95, Q=1.0 GPM)

POINT NO.	TIME (SEC)	FREE (MG/L)	MONO (MG/L)	DI (MG/L)	TRI (MG/L)	TOTAL (MG/L)	AM (MG/L)
1	35.	2.96	3.20	2.12	0.0	8.28	0.0
2	46.	2.28	2.60	2.52	0.0	7.40	0.0
3	83.	1.94	2.06	2.54	0.0	6.54	0.0
4	120.	1.84	1.86	2.66	0.16	6.52	0.0
5	156.	1.74	1.50	2.48	0.24	5.96	0.0
6	193.	1.54	1.32	2.36	0.32	5.54	0.0
7	230.	1.38	0.82	1.94	0.32	4.46	0.0
8	267.	1.34	0.76	1.74	0.32	4.16	0.0
9	304.	1.36	0.58	1.54	0.28	3.76	0.0
10	333.	1.36	0.46	1.38	0.40	3.60	0.0
11	377.	1.34	0.32	1.32	0.40	3.38	0.0

Table A12: Experimental Results for the Chlorination Reactor (2.0"), at t=20.5 deg C, pH=8.15, Cl=9.36, ammonia=0.99, Q=1.0 GPM)

POINT NO.	TIME (SEC)	FREE (MG/L)	MONO (MG/L)	DI (MG/L)	TRI (MG/L)	TOTAL (MG/L)	AM (MG/L)
1	35.	4.68	3.78	0.42	0.0	8.88	0.90
2	46.	4.34	3.48	0.40	0.0	8.22	0.88
3	83.	3.98	3.24	0.38	0.0	7.60	0.82
4	120.	3.78	3.10	0.36	0.0	7.24	0.76
5	156.	3.70	2.94	0.30	0.08	7.02	0.71
6	193.	3.48	2.70	0.24	0.12	6.54	0.64
7	230.	3.10	2.24	0.22	0.16	5.72	0.59
8	267.	2.88	1.92	0.20	0.16	5.16	0.52
9	304.	2.82	1.80	0.20	0.16	4.98	0.47
10	333.	2.78	1.70	0.16	0.20	4.84	0.42
11	377.	2.66	1.56	0.16	0.20	4.58	0.37
12	402.	2.54	1.36	0.14	0.20	4.24	0.34

Table A13: Experimental Results for the Chlorination Reactor (3.0"), at t=20.0 deg C, pH=6.05, Cl=9.27, ammonia=0.99, Q=1.0 GPM)

POINT NO.	TIME (SEC)	FREE (MG/L)	MONO (MG/L)	DI (MG/L)	TRI (MG/L)	TOTAL (MG/L)	AM (MG/L)
1	58.	2.46	2.68	3.62	0.0	8.76	0.85
2	96.	2.04	2.08	4.24	0.32	8.68	0.0
3	135.	1.64	1.70	4.70	0.48	8.52	0.84
4	174.	1.48	1.34	4.96	0.48	8.26	0.0
5	213.	1.28	1.26	5.02	0.48	8.04	0.80
6	251.	1.12	1.06	5.04	0.48	7.70	0.0
7	290.	1.06	0.88	5.14	0.40	7.48	0.71
8	329.	1.02	0.74	5.08	0.46	7.30	0.0
9	368.	1.00	0.70	4.88	0.46	7.04	0.64
10	407.	0.94	0.56	4.74	0.48	6.72	0.0
11	446.	0.90	0.46	4.62	0.40	6.38	0.0
12	485.	0.90	0.46	4.62	0.44	6.42	0.53

Table A14: Experimental Results for the Chlorination Reactor (3.0"), at t=20.0 deg C, pH=7.00, Cl=9.27, ammonia=0.98 Q=1.0 GPM)

POINT NO.	TIME (SEC)	FREE (MG/L)	MONO (MG/L)	DI (MG/L)	TRI (MG/L)	TOTAL (MG/L)	AM (MG/L)
1	58.	2.74	3.08	1.68	0.0	7.50	0.85
2	96.	2.10	2.52	1.72	0.0	6.34	0.78
3	135.	1.86	2.18	1.58	0.04	5.66	0.70
4	174.	1.70	2.08	1.54	0.16	5.48	0.65
5	213.	1.62	1.72	1.38	0.20	4.92	0.59
6	251.	1.50	1.48	1.36	0.20	4.54	0.51
7	290.	1.44	1.38	1.28	0.16	4.26	0.46
8	329.	1.42	1.14	1.02	0.20	3.78	0.39
9	368.	1.38	0.90	0.94	0.20	3.42	0.33
10	407.	1.24	0.64	0.88	0.28	3.04	0.29
11	446.	1.26	0.60	0.74	0.28	2.88	0.25
12	485.	1.20	0.50	0.58	0.32	2.60	0.22

Table A15: Experimental Results for the Chlorination Reactor (3.0"), at t=20.5 deg C, pH=7.47, Cl=9.42, ammonia=0.90 Q=1.0 GPM)

POINT NO.	TIME (SEC)	FREE (MG/L)	MONO (MG/L)	DI (MG/L)	TRI (MG/L)	TOTAL (MG/L)	AM (MG/L)
1	58.	3.86	3.06	0.68	0.0	7.60	0.73
2	96.	3.40	2.82	0.52	0.20	6.94	0.62
3	135.	3.16	2.42	0.40	0.32	6.30	0.55
4	174.	3.00	2.08	0.36	0.32	5.76	0.50
5	213.	2.90	1.52	0.36	0.28	5.06	0.43
6	251.	2.62	1.40	0.34	0.28	4.64	0.36
7	290.	2.44	1.32	0.34	0.20	4.30	0.30
8	329.	2.36	0.98	0.30	0.28	3.92	0.27
9	368.	2.24	0.86	0.28	0.28	3.66	0.24
10	407.	2.10	0.76	0.26	0.28	3.40	0.22
11	446.	2.08	0.70	0.24	0.24	3.26	0.19
12	485.	1.98	0.60	0.20	0.28	3.06	0.17

Table A16: Experimental Results for the Chlorination Reactor (3.0"), at t=22.0 deg C, pH=7.70, Cl=9.51, ammonia=0.92 Q=1.0 GPM)

POINT NO.	TIME (SEC)	FREE (MG/L)	MONO (MG/L)	DI (MG/L)	TRI (MG/L)	TOTAL (MG/L)	AM (MG/L)
1	58.	3.96	2.90	0.58	0.0	7.44	0.74
2	96.	3.50	2.46	0.60	0.08	6.64	0.62
3	135.	3.10	2.04	0.60	0.16	5.90	0.52
4	174.	2.90	1.54	0.36	0.28	5.08	0.43
5	213.	2.76	1.32	0.26	0.32	4.66	0.35
6	251.	2.42	1.06	0.20	0.36	4.04	0.30
7	290.	2.34	0.86	0.14	0.40	3.74	0.25
8	329.	2.20	0.52	0.10	0.40	3.22	0.20
9	368.	2.30	0.44	0.10	0.28	3.12	0.17
10	407.	2.30	0.34	0.08	0.32	3.04	0.14
11	446.	2.10	0.34	0.10	0.32	2.86	0.12
12	485.	2.10	0.32	0.10	0.32	2.84	0.12