

BREAKPOINT CHLORINATION FOR THE
CONTROL OF AMMONIA NITROGEN

BY

HO-SIK YOO

Bachelor of Science in Civil Engineering

Sung Kyun Kwan University

Seoul, Korea

1980

Submitted to the Faculty of the
Graduate College of the
Oklahoma State University
in partial fulfillment of
the requirements for
the Degree of
MASTER OF SCIENCE
DECEMBER, 1987



BREAKPOINT CHLORINATION FOR THE
CONTROL OF AMMONIA NITROGEN

Thesis Approved:

Don F. Kneannon
Thesis Advisor

John W. Venette

William F. McKinney

Norman H. Durham
Dean of the Graduate College

ACKNOWLEDGEMENTS

I wish to express my sincere appreciation to my major adviser, Dr. D. F. Kincannon, for his valuable guidance, advice, assistance, and friendship throughout the course of this investigation and my graduate studies. I would also like to thank Dr. McTernan and Dr. Veenstra for their valuable instruction and serving as committee members.

Finally, I would like to give my special recognition to my parents for their continued love, encouragement, and support throughout these studies.

TABLE OF CONTENTS

Chapter	Page
I. INTRODUCTION	1
II. LITERATURE REVIEW	3
Chemistry of Breakpoint Chlorination . . .	3
Obtainable Ammonia-N Reduction	5
Effluent Nitrate-N Concentration	5
Effect of Pretreatment	6
Reaction Rate	6
Effect of pH and Temperature	8
Shape of Breakpoint Chlorination Curve . .	8
III. METHODS AND MATERIALS	9
Process Description	9
Determination of Ammonia-N Concentration .	10
Determination of Nitrate-N Concentration .	11
Determination of Chlorine Residual (Total).	11
Determination of Temperature and pH	11
Preparation of Chlorine Solution	11
IV. RESULTS AND DISCUSSION	13
General Observations	13
Obtainable Ammonia-N Reduction	25
Effect of Pretreatment and Nitrification on Chlorine Dosage	25
Effect of Contact Time	27
Effect of pH	28
Nitrate Formation during Chlorination . . .	28
V. APPLICATION TO ACTUAL DESIGN	30
Required Cl:Ammonia-N Weight Ratio	31
Required Ca(OCl) ₂	35
VI. CONCLUSIONS	36
SELECTED BIBLIOGRAPHY	38

LIST OF TABLES

Table	Page
I. Reaction Rate to Monochloramine	7
II. Obtainable Ammonia-N Concentration	21
III. Chlorine:Ammonia-N Weight Ratio at Breakpoint .	22
IV. Effect of pH	23
V. Nitrate Formation during Chlorination	24
VI. Effluent Ammonia-N from Stillwater Plant . . .	34

LIST OF FIGURES

Figure	Page
1. Breakpoint Chlorination Curve of Grit Chamber Effluent (Stillwater)	15
2. Breakpoint Chlorination Curve of Primary Clarifier Effluent (Stillwater)	16
3. Breakpoint Chlorination Curve of Biological Tower Effluent (Stillwater)	17
4. Breakpoint Chlorination Curve of Final Clarifier Effluent (Stillwater)	18
5. Breakpoint Chlorination Curve of Final Clarifier Effluent (Okmulgee)	19
6. Effect of Contact Time	20
7. Effluent Ammonia-N (1985-1987)	32
8. Flow Rate (1985-1987)	33

CHAPTER I

INTRODUCTION

Nitrogen, in its various forms, has many effects on the environment. It causes dissolved oxygen depletion, toxicity to fish, eutrophication, and others. So, increasing concerns and interests have been being focused on the control of nitrogen. Nitrogen exists in several forms. Ammonia is the most abundant form that is encountered in wastewaters, and major problems associated with nitrogen also come from ammonia form.

The element nitrogen can neither be destroyed nor be created. The only thing an engineer can do is to transform the trouble making form of nitrogen to a less objectionable form. Currently, several techniques for ammonia control are available. Those are biological nitrification with or without denitrification, ion exchange, ammonia stripping and breakpoint chlorination. Nitrification is preferred in many case from an economical standpoint. It is a biological transformation of ammonia-N to nitrate-N by nitrifying bacteria. However nitrate, the end product of nitrification still has undesirable effects. For example, nitrate can be used as a nutrient of undesirable plants. Some states have established the discharge limit on nitrate nitrogen, and the

others may do so in the future. Since nitrification is a biological process, high sensitivity of nitrifying bacteria to temperature, pH, and toxic materials may contribute to a total failure of treatment plant. Therefore local conditions could force the design engineer to choose one of the latter methods as the major or polishing step of ammonia nitrogen control in spite of its relatively high operating cost. Breakpoint chlorination has some advantages and disadvantages over other methods. Particularly it does not require expensive capital cost while it can maintain effluent ammonia concentration to near zero. Since some states are establishing strict standards (less than 1 mg/L of ammonia nitrogen) that traditional biological process can not easily meet consistently, breakpoint chlorination should be studied more.

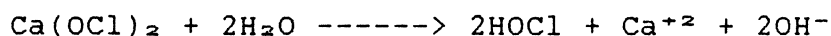
Breakpoint chlorination is well documented in many references while there are many things to be studied more such as achievable effluent concentration of ammonia, reaction rate, and nitrate formation in the breakpoint chlorination. The main purpose of this study is the determination of the achievable reduction of ammonia concentration by breakpoint chlorination and pretreatment effect on chlorine dosage. This study is intended to make it possible to consider breakpoint chlorination as a design alternative when strict discharge-limitation on ammonia nitrogen is forced by authorities.

CHAPTER II

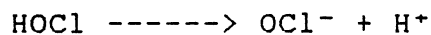
LITERATURE REVIEW

Chemistry of Breakpoint Chlorination

The chemistry of breakpoint chlorination is available in many references (1, 2, 3, 4). The following is a brief summary. When calcium hypochlorite is dissolved in water, the following reaction occurs to produce hypochlorous acid (1).

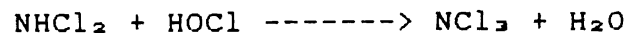
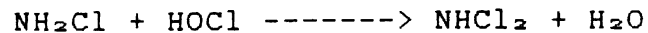
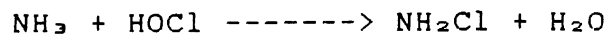


The active forms of chlorine in solution are hypochlorous acid and its dissociation product, hypochlorite ion (2).

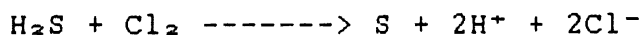
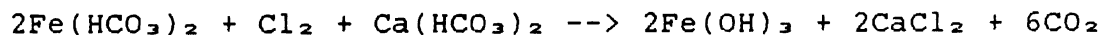


The term, free available chlorine residual, refers to the sum of hypochlorous acid and hypochlorite ion. This term will be used as the chlorine dosage in this study.

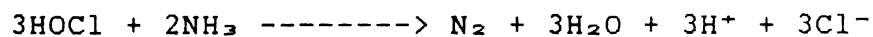
The addition of a sufficient amount of chlorine to a wastewater may convert the ammonia nitrogen in the wastewater to predominantly nitrogen gas. The step wise reaction includes the formations of mono-chloramine, di-chloramine, tri-chloride, and nitrogen gas (1, 2, 3, 4).



There are extra reactions such as followings that eventually result in chlorine demand (4).



The overall reaction of nitrogen gas production is shown below (2).



3 parts of Cl are required to react with 2 parts of N.

$$3 (35.45 \text{ g}) / 2 (14 \text{ g}) = 3.80 \text{ g of Cl} / 1 \text{ g of NH}_3\text{-N}$$

In practice, approximately 5 mg/L of free chlorine (or 10 mg/L of Cl_2) is required for every 1 mg/L of ammonia-N. In addition, acidity produced by the reaction must be neutralized by the addition of caustic soda or lime (2). Therefore breakpoint chlorination requires the addition of a lot of chemicals resulting in increased total dissolved solids. This complexity compels the design engineer to study thoroughly the effect of breakpoint chlorination on the individual condition before he decides a design

alternative.

Obtainable Ammonia-N Reduction

Tests on municipal wastewater and wastewater treatment plant effluent at Blue Plains pilot plant indicated that 95 to 99 percent of the ammonia nitrogen in solution was converted to nitrogen gas (5, 6). That is, ammonia-N concentrations in the samples following breakpoint were found to be consistently in the range of 0.2 mg/L or less.

Effluent Nitrate-N Concentration

Nitrate and nitrogen trichloride account for the remaining fractions of nitrogen at breakpoint. The studies at the Blue Plain plant have shown that the total concentration of these residuals seldom exceeds 10 percent of the influent ammonia nitrogen concentration (5). Pretreatment had no effect on effluent nitrate concentration (5, 7). Nitrate production following breakpoint chlorination of lime clarified filtered secondary effluent (breakpoint at $\text{Cl}_2:\text{NH}_4^+-\text{N}$ of 8:1) showed a linear increase in concentration at increased chlorine dosages (2). Temperatures of 5 to 40°C did not affect the final distribution of nitrogenous residuals in the effluent at Blue Plains (5). Nitrate formation was found to be slightly affected by pH at the breakpoint (2). The determination of effluent nitrate concentration is important since nitrate is an undesirable form of nitrogen too.

Effect of Pretreatment

Laboratory and pilot plant studies of breakpoint chlorination at the Blue Plains pilot plant (5, 7) and at Sunnyvale (8) have shown that increasing levels of pretreatment decrease the amount of chlorine required to achieve breakpoint. If those studies are compared to chlorine-disinfection study, interesting results can be seen. Gausser (9), Venosa (10), and Dhaliwal and Baker (11) reported the protective effect of ammonia on chlorine disinfection. Gordon (12) said "Facilities that produce a highly nitrified effluent seem to suffer an excessive chlorine demand because of the near absence of ammonia. The addition of a small amount of ammonia may substantially reduce this demand and still provide equivalent disinfection, probably by formation of less reactive chloramines." This is in contrast with the former breakpoint chlorination study since nitrification itself can be considered as a pretreatment. This study will be looking for the chlorine requirement of nitrified sample to reach breakpoint, since the effluent from Stillwater wastewater treatment plant is a highly nitrified one.

Reaction Rate

Almost nothing has been known about the speed of chlorine-nitrogen reactions. However, Morris (13, 14) has shown that the formation of monochloramine is second order

and very rapid in pure solution. 99 percent conversion of ammonia to monochloramine occurred at 25°C, pH 7, and with a molar ratio of 0.2×10^{-3} mol/L HOCl and 1.0×10^{-3} mol/L NH_3 . Table I is the results established by Morris. This is unique information about reaction rate. The other reactions in the breakpoint chlorination such as the formations of dichloramine and nitrogen trichloride should be guessed from this table.

TABLE I
REACTION RATE
TO MONOCHLORAMINE

pH	Seconds
2	421
4	147
7	0.2
8.3	0.069
12	33.2

The optimum pH was shown to be pH 8.3. Laboratory studies (2) have shown that the breakpoint reaction was

found to proceed to completion in less than 15 seconds at pH levels between 6 and 7. This rapid rate over the pH range of 6-7 leads to the design recommendation that a breakpoint chlorination contact period of one minute is sufficient for plant-scale application (2).

Effect of pH and Temperature

The studies at Blue Plains showed an optimum pH for breakpoint in the range of 6 to 7 (5, 7). There has been no report regarding temperature effect on chlorine dosage.

Shape of Breakpoint Chlorination Curve

Investigations (15) found that the presence of organic nitrogen may greatly alter the shape of the breakpoint curve. Organic nitrogen may obscure the classic form of hump and dip. The reaction of chlorine with compounds of organic nitrogen forms organic chloramines. The organic chloramines make up chlorine residual. The irreducible chlorine residual at breakpoint is the magnitude of chlorine residual including both chloramines (ammonia chloramine and organic chloramine). The magnitude is much greater when organic nitrogen is involved.

CHAPTER III

METHODS AND MATERIALS

Process Description

Samples from the Stillwater and Okmulgee wastewater treatment plants were used in this study. Collected samples were grab sample. For the purpose of the investigation of relationship between pretreatment and chlorine demand, four kinds of samples from the Stillwater plant were used. Those were the effluents from the grit chamber, primary clarifier, biological tower, and final clarifier. The temperatures and pH's of samples were relatively constant throughout all the treatment units (24°C, pH 6.5-7.0).

This study was conducted with a laboratory scale batch reactor. At first, all the necessary characteristics of the raw samples were determined. These characteristics include temperature, pH, ammonia-N, nitrate-N, and chlorine residual. Next, a 100 ml sample was introduced to 1 L beaker. Individual dosage of calcium hypochlorite solution was added through 1 ml, 5 ml, and 20 ml pipets. Two minutes of gentle mixing was provided. Two minutes was arbitrarily selected for a balance between poor and too much mixing since poor mixing does not provide enough chance for

reactants while prolonged mixing may cause dissipation of free chlorine residual. Then the beaker was allowed to set under non-mixing conditions for various contact times. As soon as the designed contact time had passed, four kinds of concentrations were determined. Those were ammonia-N, nitrate-N, free chlorine residual, and total chlorine residual. Later, the determination of free chlorine residual was stopped due to the interferences from monochloramine. Tests were generally conducted for one hour contact time and neutral pH (6.5-7.0). Tests were also conducted for different contact times and pH's to determine the effects of contact time and pH. A 5.2 N solution of sulfuric acid was used to lower pH.

Determination of Ammonia-N Concentration

The Nessler method was used to determine ammonia-N concentration (16). Removal of residual chlorine by sample pretreatment is needed to avoid the interferences from the formation of chloramine. Since the samples from both wastewater treatment plant did not contain any chlorine residual, a dechlorination step was not needed. For sample preservation, the pH of sample should be between 1.5 and 2, and the temperature should be 4°C (16). However fresh sample was used for the tests. Commercially manufactured reagent (HACH Nessler Reagent) and the colorimetric method was used.

Determination of Nitrate-N Concentration

The Cadmium Reduction method with powdered cadmium was used to determine nitrate-N concentration. For sample preservation, the pH of sample should be below 2, and the temperature should be 4°C (16). However fresh sample was used for the tests. Commercially prepackaged reagent (HACH Nitra Ver 5 Reagent Powder Pillow) and the colorimetric method was used.

Determination of Chlorine Residual (Total)

The DPD colorimetric method was used to determine chlorine residual. Commercially prepackaged reagent (HACH DPD Total Chlorine Reagent Powder Pillow) and colorimetric method was used.

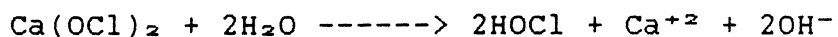
Determination of Temperature and pH

Temperature and pH was determined using digital pH/milivolt meter manufactured by Orion Research.

Preparation of Chlorine Solution

The common chlorine compounds used in wastewater-treatment plants are chlorine gas (Cl_2), calcium hypochlorite [$\text{Ca}(\text{OCl})_2$], sodium hypochlorite (NaOCl), and chlorine dioxide (ClO_2). Calcium and sodium hypochlorite are often used in small treatment plants where simplicity and safety are important (2). Chlorine in the form of a gas

is most commonly used due to its relatively low price. In this study, however, calcium hypochlorite was used for the reason of safety. The pertinent reaction is as follow:



As can be seen in this equation, calcium hypochlorites tend to increase the pH.

A concentrated chlorine solution was prepared by dissolving calcium hypochlorite in distilled water. A shaker was used for mixing. The chlorine residual in the concentrated solution was determined. Usually this would be around 1,000 mg/L as Cl. This value (mg/L as Cl) was used to get the weight ratio. The volume corrections was applied for the results of total chlorine residual, residual ammonia, and residual nitrate according to the following equation.

The corrected values = measured values * (sample V + chlorine solution V)/sample V

CHAPTER IV

RESULTS AND DISCUSSION

General Observations

Figures 1, 2, 3, and 4 show the relationship between ammonia-N concentration and chlorine dosage for the Stillwater plant. The chlorine dosage was expressed as Cl:ammonia-N weight ratio. The ammonia-N concentration of grit chamber effluent was about 30 mg/L. This decreased to about 1 mg/L in the plant effluent due to nitrification that had been occurring throughout all the units. The majority of the nitrification was occurring in the biological tower. This assumption comes from fluctuation of nitrate-N level depending upon treatment level. Table V shows nitrate-N concentration, and it is seen that the nitrate-N increased in the biological tower.

Free available chlorine was dosed according to initial ammonia-N concentration. Total chlorine residual increased gradually up to maximum point. The locations of maximum chlorine residual as well as breakpoint are different depending upon treatment level. This will be discussed in detail later. Chlorine residual decreased down to breakpoint, and then increased infinitely while plotting

typical hump and dip curve. The ammonia-N concentration did not show considerable change at first. Then ammonia-N started decreasing at just before the hump. Almost all the ammonia-N disappeared by the breakpoint. The sample from Okmulgee plant did not show a breakpoint (Figure 5). The reason is supposed to be characteristic of sample including organic-N content. One hour contact time and neutral pH (6.5-7.0) were used for the data in Figure 1, 2, 3, 4, and 5.

Figure 6 shows effect of contact time. Tables 2, 3, 4, and 5 show obtainable $\text{NH}_3\text{-N}$ reduction, chlorine: $\text{NH}_3\text{-N}$ weight ratio at breakpoint, effect of pH, and nitrate formation during chlorination respectively. Details will be discussed in order.

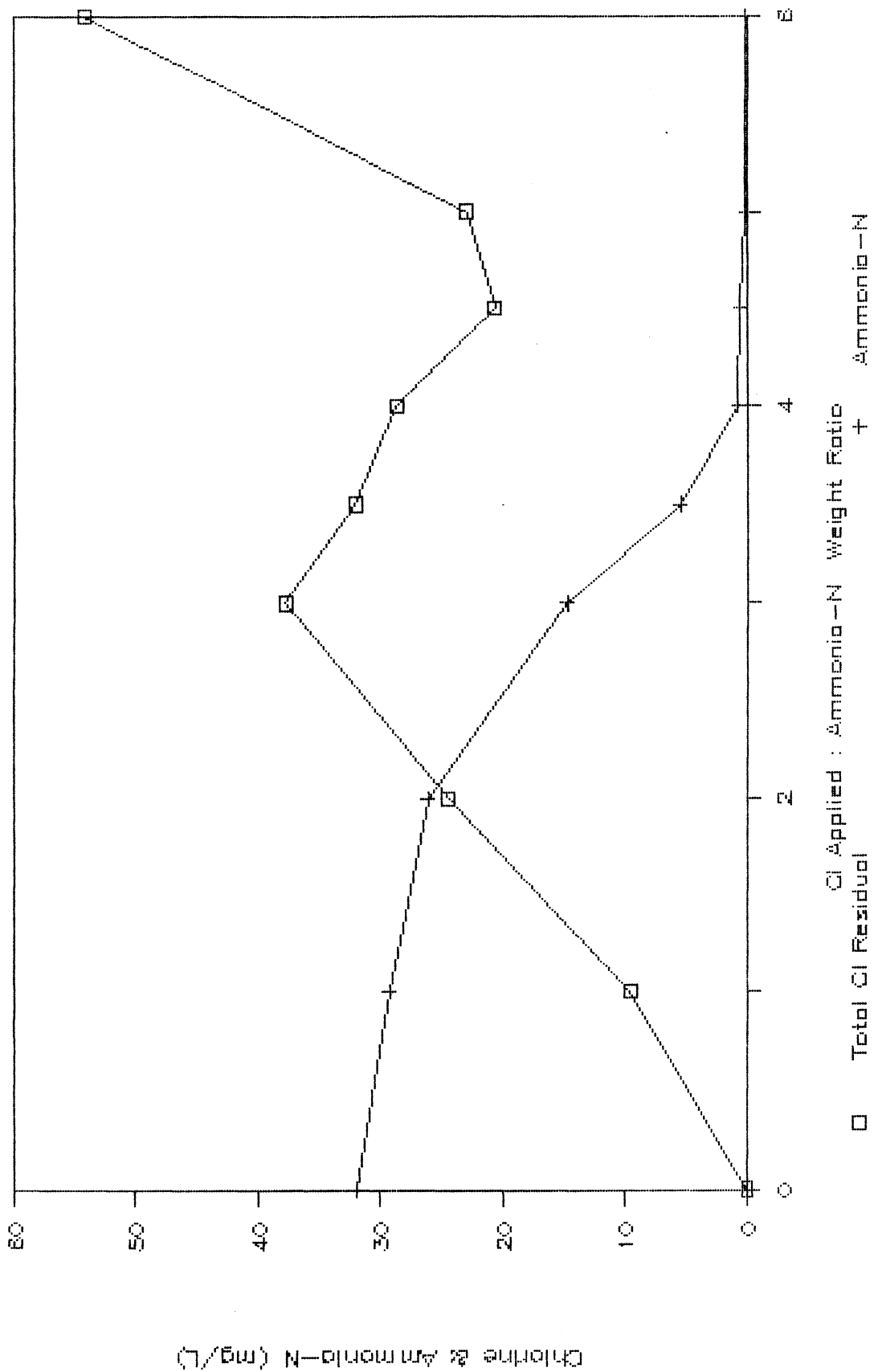


Figure 1. Grit Chamber Effluent (Stillwater)

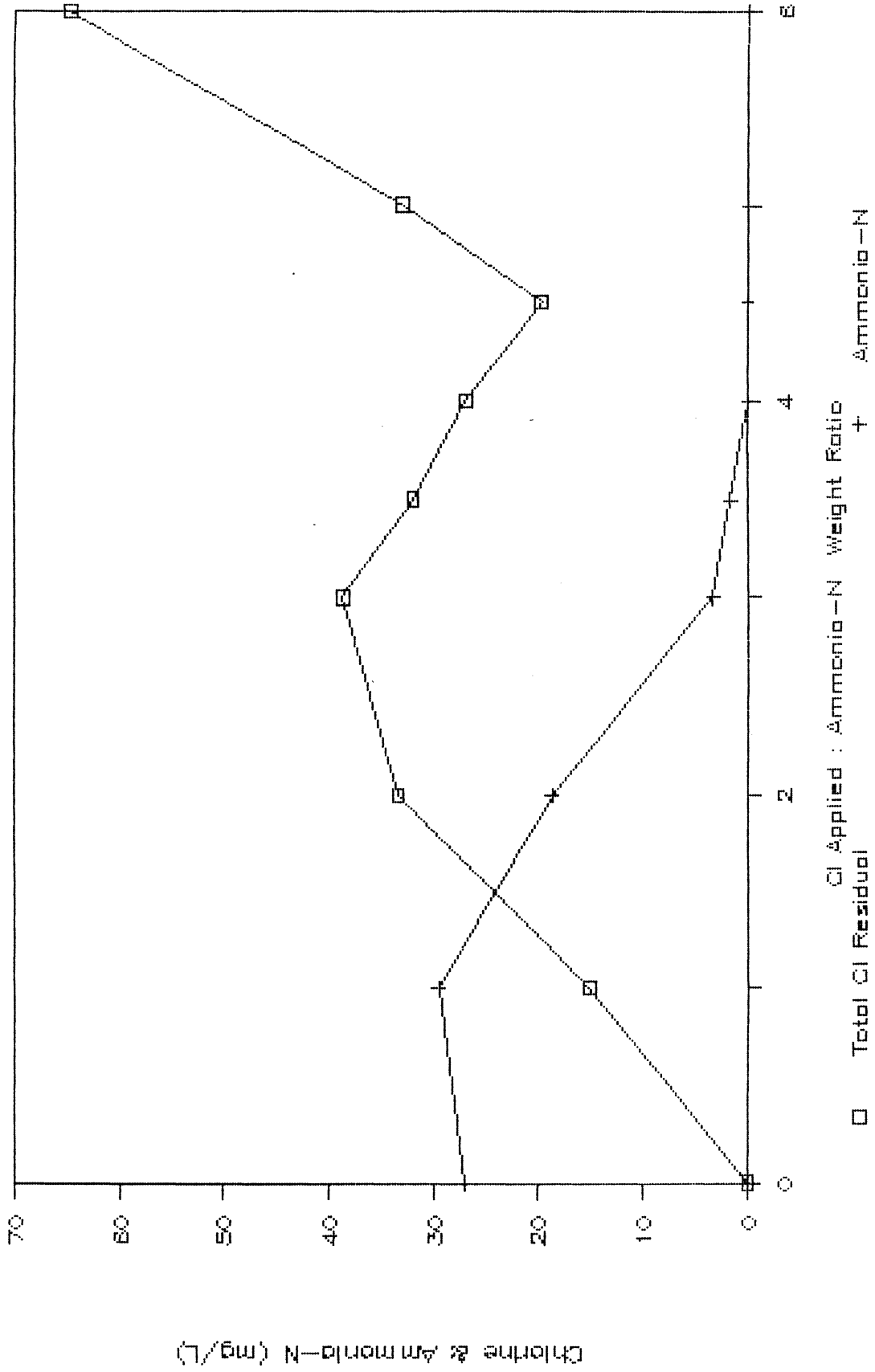


Figure 2. Primary Clarifier Effluent (Stillwater)

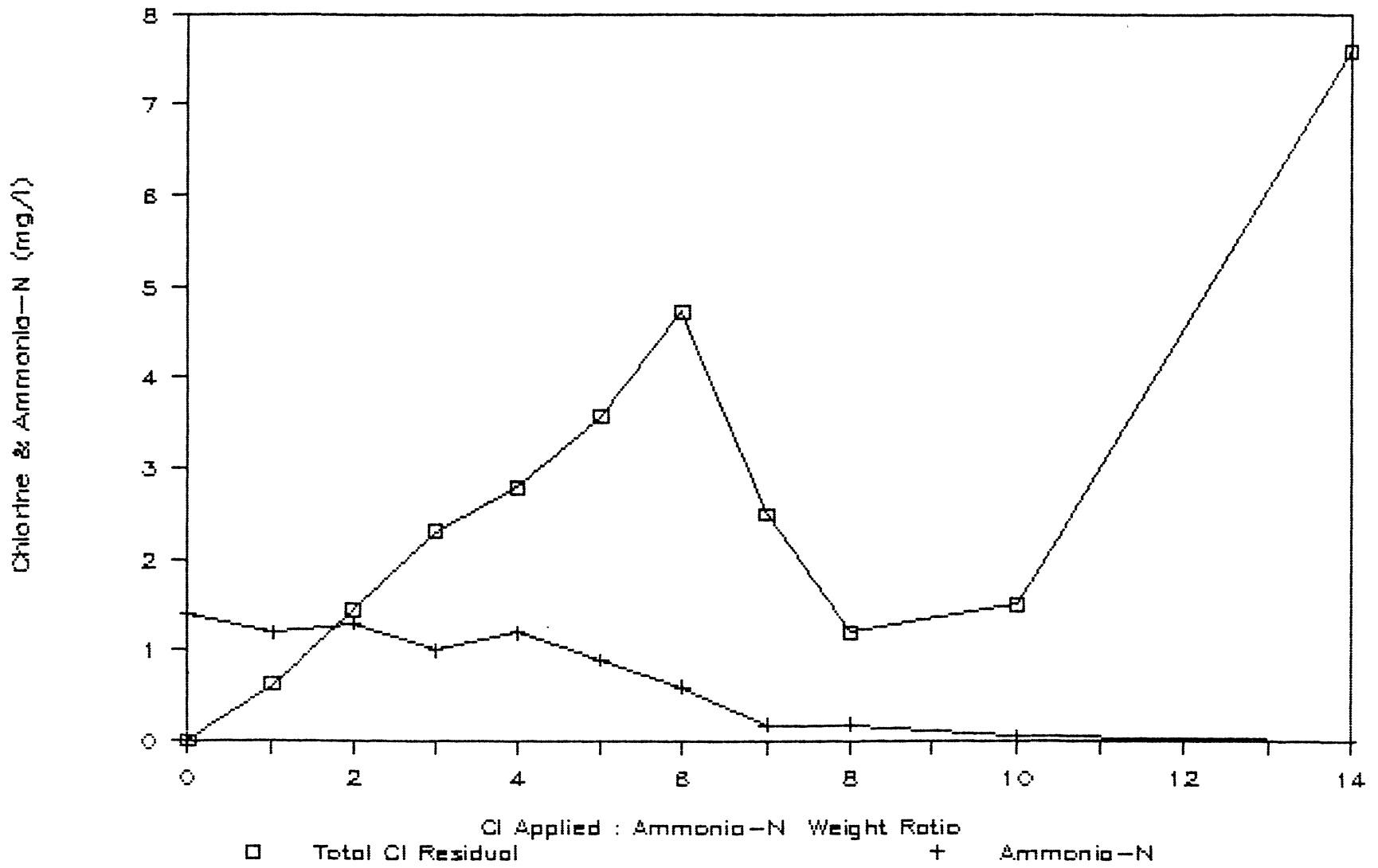


Figure 3. Biological Tower Effluent (Stillwater)

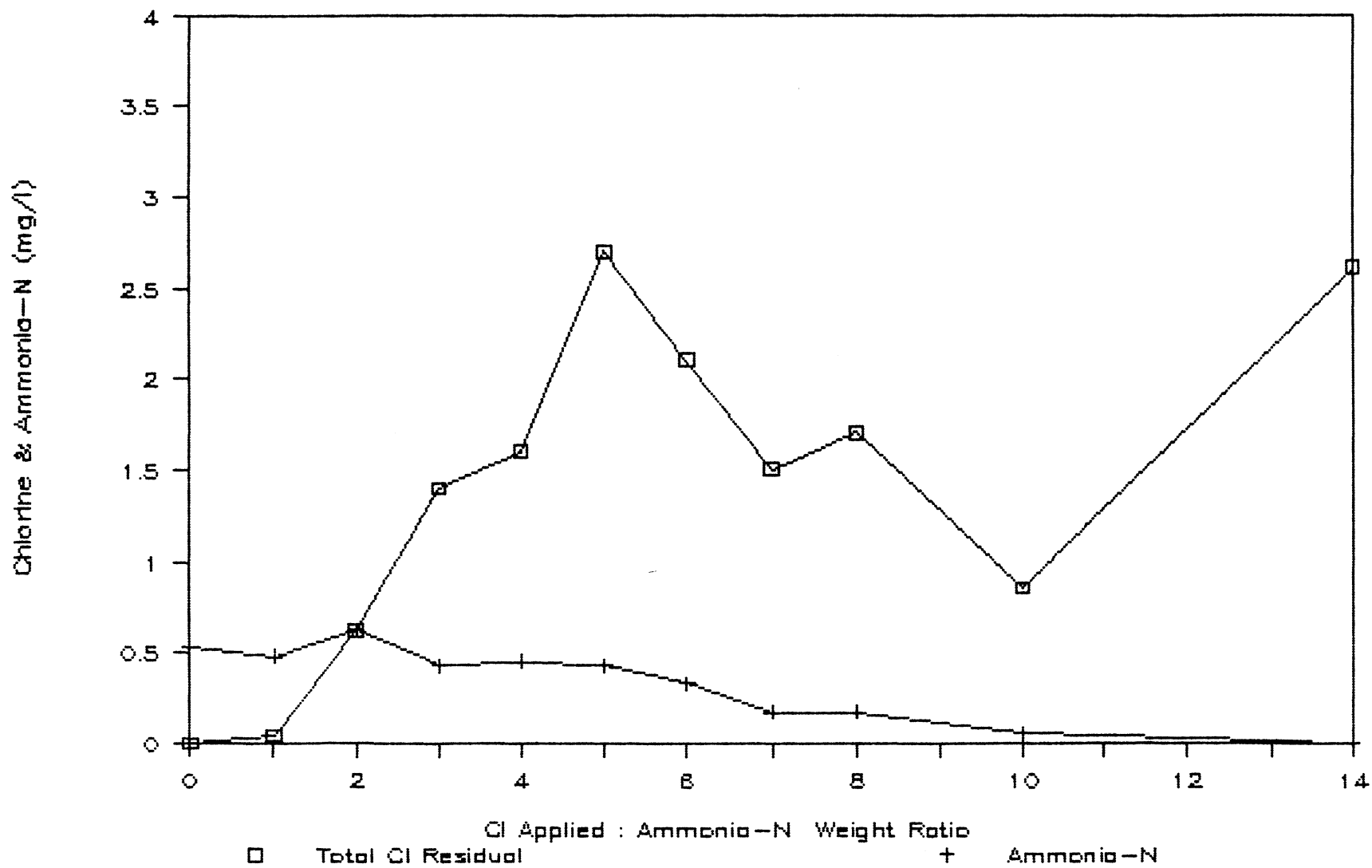


Figure 4. Final Clarifier Effluent (Stillwater)

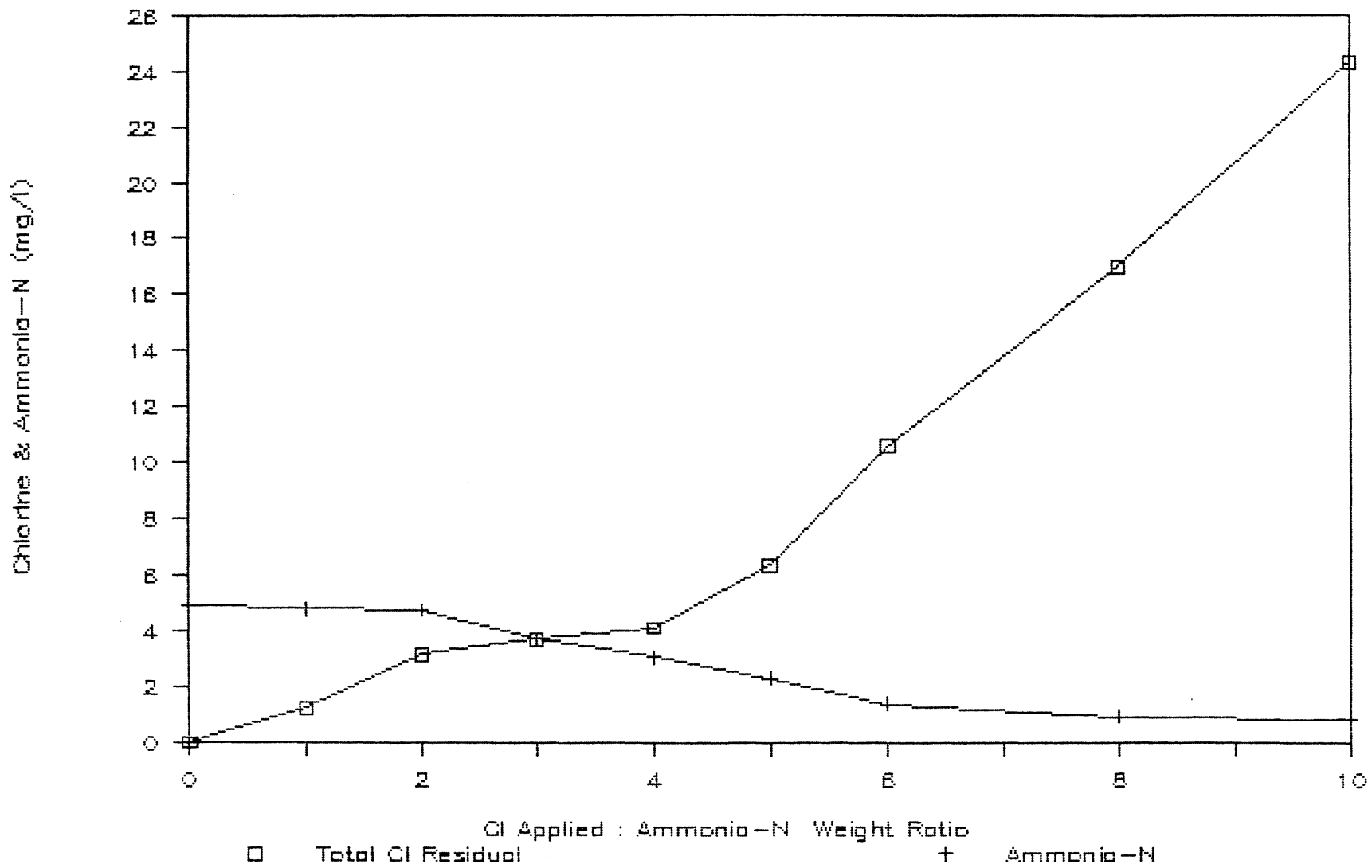


Figure 5. Final Effluent (Okmulgee)

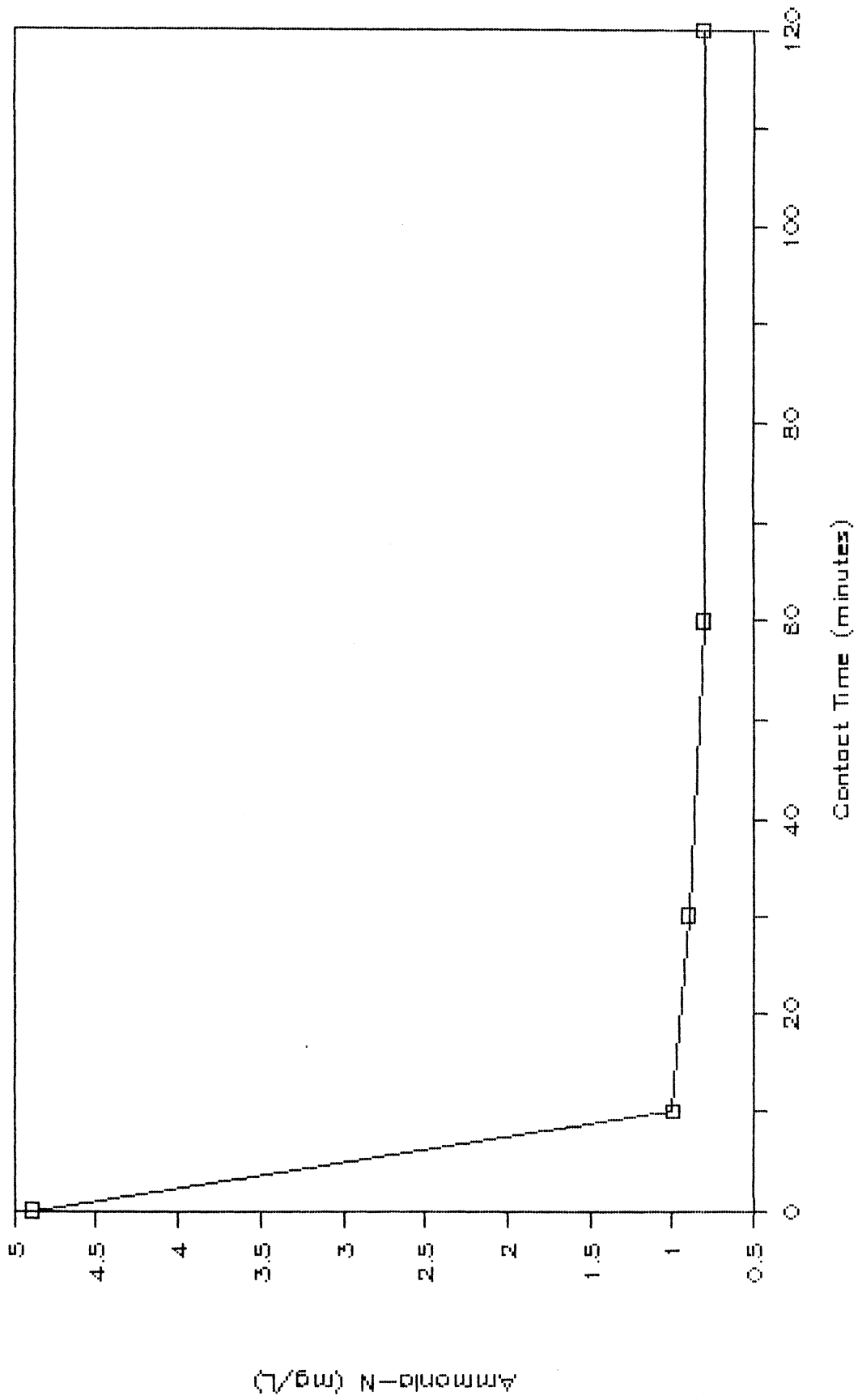


Figure 6. Effect of Contact Time (Okmulgee)

TABLE II
OBTAINABLE AMMONIA-N CONCENTRATION

Sample (effluent)	pH	Chlorine Dose Cl:NH ₃ -N ratio	NH ₃ -N (mg/L)	
			Initial	Final

From Stillwater Plant				
Grit chamber	6.5	5:1	32.0	0.2
Primary clarifier	6.7	4:1	27.1	0.0
Biological tower	6.8	10:1	1.4	0.0
Final clarifier	6.9	14:1	0.5	0.0
From Okmulgee Plant				
Final clarifier	6.6	15:1	4.9	0.8

* Contact time: 1 hour

* pH: 6.5 - 7.0

TABLE III

CHLORINE:NH₃-N WEIGHT RATIO AT BREAKPOINT

Sample (effluent)	Chlorine Dose (Cl:NH ₃ -N ratio)

From Stillwater Plant	
Grit chamber	4.5:1 - 5:1
Primary clarifier	4.5:1
Biological tower	8:1 - 9:1
Final clarifier	10:1
From Okmulgee Plant	
Final effluent	6:1

* Contact time: 1 hour

* pH: 6.5 - 7.0

TABLE IV
EFFECT OF pH

pH	Contact Time (min)	Ammonia-N (mg/L)
6.6	10	0.0
2.3	10	0.6
2.3	120	0.2

* Sample: Final effluent from Stillwater Plant

* Initial ammonia nitrogen concentration: 0.9 mg/L

* Applied chlorine-ammonia nitrogen weight ratio: 10:1

TABLE V
NITRATE FORMATION DURING CHLORINATION

Chlorine Dose Cl:NH ₃ ratio	Grit Ch.	Prim. C.	NO ₃ -N (mg/L)	
			Bio. Tower	Final Eff.
Initial	3.8	3.1	8.9	8.3
1:1	3.2	2.8	9.7	8.1
2:1	4.2	3.7	9.6	8.2
3:1	3.4	2.7	9.1	9.0
3.5:1	3.5	2.9		
4:1	3.8	3.1	9.1	8.3
4.5:1	3.6 B.P.	3.3 B.P.		
5:1	7.8	6.5	9.2	8.6
6:1	15.7	9.6	9.8	8.1
7:1			8.2	8.2
8:1			8.4 B.P.	8.4
10:1			10.5	8.0 B.P.
14:1			11.3	9.2
20:1			12.7	9.7
30:1			15.6	11.6

* Sample: From Stillwater Plant

* B.P.: Breakpoint

* Contact time: 1 hour

* pH: 6.5 - 7.0

Obtainable Ammonia-N Reduction

Results from Stillwater-sample (first four samples of table II) show obvious ammonia-N reduction down to zero mg/L except grit chamber effluent. The initial concentration might have nothing to do with final concentration in this case. In real application we are not supposed to get 0.0 mg/L of ammonia-N necessarily. Chlorine should be dosed according to the local limitations of ammonia-N discharge.

Result from Okmulgee-sample shows a refractory concentration of 0.8 mg/L, in spite of having increased the weight ratio up to 50:1. Here, attention should be paid to the characteristics of the samples. The Stillwater plant treats a municipal wastewater while the Okmulgee plant treats a combined wastewater (municipal and industrial). However it would be a hasty conclusion to say that the treatabilities of municipal and combined wastewaters are different, with only these two sets of samples. The ammonia-N concentrations of sufficiently chlorinated samples are shown in Table II.

Effects of Pretreatment and Nitrification on Chlorine Dosage

The results from this studies have shown that there is a rough relationship between pretreatment and chlorine-ammonia nitrogen weight ratio. Figure 1, 2, 3, and 4 show breakpoint chlorination curves of each unit of Stillwater

wastewater treatment plant, and Table III shows chlorine-ammonia nitrogen weight ratio required to reach breakpoint. The sample from the primary clarifier requires a little bit lower ratio than that from the grit chamber. This may be due to the reduction of substances exerting chlorine demand by increasing the levels of pretreatment. There are lot of substances which are capable of reacting with chlorine in a wastewater. The reduction of the materials which are more readily reactable with chlorine residual than ammonium ion in the wastewater can reduce the weight ratio, since all the reactions are competing with each other.

Next, an editorial thing can be found from the results. The samples from the biological tower and final clarifier requires much higher chlorine-ammonia weight ratio than those from the grit chamber and primary clarifier. This is contrary to the first observation. Here, attention should be paid to the dosage of the applied chlorine residual. The chlorine residual is dosed depending upon the ammonia-N concentration. Currently, the biological tower of the Stillwater plant is removing a large amount of ammonia-N by nitrification. Even though the ammonia-N in the wastewater is reduced considerably by nitrification, the wastewater would still have the majority of chlorine-reactable substances of the initial wastewater. That is why the chlorine-ammonia weight ratio of nitrified samples (from biological tower and final clarifier) was so high. This can be verified by samples from final effluent of Okmulgee

wastewater treatment plant. The sample did not show high concentration of nitrate nitrogen. The concentration was less than 1 mg/L. This means that there was no nitrification at all. It can be assumed that the characteristic of Okmulgee-wastewater were not favorable to nitrifying bacteria. So, the final effluent of Okmulgee plant showed fairly high concentration of ammonia-N (4.9 mg/L). Figure 5 shows breakpoint chlorination curves of the effluent of Okmulgee wastewater treatment plant. Even though it is not clear, it can be assumed that breakpoint will be less than 6:1 in that maximum ammonia-N reduction was obtained at 6:1. The breakpoint of the same stage of Stillwater plant was 10:1. This difference is assumed to be caused by the ammonia-N concentration. Finally, it can be concluded that nitrification can reduce ammonia-N concentration but it can not reduce the substances exerting chlorine demand at the same rate. So, a wastewater containing a low concentration of ammonia-N primarily due to nitrification will require a high chlorine-ammonia nitrogen weight ratio to reach breakpoint.

Effect of Contact Time

This experiment was conducted on the final effluent of Okmulgee wastewater treatment plant. The result is shown in Figure 6. The pH was maintained in neutral range (6.5-7). The initial ammonia-N concentration was 4.9 mg/L. Sufficient chlorine residual was dosed (8:1 of weight

ratio). So, 39.2 mg/L as Cl of free available chlorine was applied to the sample at contact time of 10, 30, 60, and 120 minutes. Figure 6 shows all the reactions were completed in 10 minutes. The residual ammonia-N concentration is considered as the irreducible portion caused by characteristic of the wastewater.

Effect of pH

The effect of pH was tested on a sample from the final clarifier effluent of Stillwater plant. Table IV shows a definite pH effect on breakpoint chlorination. The acidified sample could not reach the desired ammonia-N concentration even after two hours while the sample at optimum pH could do so in 10 minutes. This result agree with that of references (5, 7).

Nitrate Formation during Chlorination

Nitrate formation was not observed until breakpoint. The initial concentration of nitrate nitrogen was maintained until breakpoint. A gradual increase could be seen after breakpoint. Table V shows the results. However, The Cadmium Reduction method seems to be subjected to the interferences from free chlorine residual. Tests carried out with distilled water containing only free chlorine residual showed definite color development that could be read as nitrate in colorimetric method. Therefore the increase in nitrate nitrogen following breakpoint

chlorination is not reliable. However, this is not important in breakpoint chlorination since we do not need to go further beyond the breakpoint.

CHAPTER V

APPLICATION TO ACTUAL DESIGN

Breakpoint chlorination may work on the entire or partial flow of a wastewater treatment plant to meet the required effluent ammonia-N limitation. It also may work intermittently to treat unusual loading. Due to the low investment cost and flexibility of breakpoint chlorination, it may be considered as an alternative of a polishing step for an existing plant. It also has some more advantages associated with other treatment units. The chlorine residual of breakpoint chlorination effluent may serve for disinfection and grease removal. The disinfection with chlorine does not require any additional comment on that. Grease removal through chlorination has been used and well documented (17). The breakpoint chlorination incorporated with those units may be a very efficient unit on an economical standpoint.

Recently, NPDES permit limitations have been set for 2 mg/L of ammonia-nitrogen in the effluent of Stillwater wastewater treatment plant. The Stillwater wastewater treatment plant was not originally designed to remove ammonia-nitrogen since ammonia-nitrogen was not of concern

when the plant was designed. Interestingly, nitrification has been occurring in the existing facilities (14). Owing to nitrification, effluent ammonia-N concentration is around 1 mg/L in the summer with some variations from time to time. However, biological nitrification is greatly influenced by temperature. High concentration of ammonia-N was monitored in the winter. Figure 7 shows the variations in recent years (18). So, an additional facility for nitrification is under construction. Figure 8 shows flow rate in recent years (18).

The following is a rough estimation of chlorine requirement for the year 1986 if breakpoint chlorination had been used instead of biological nitrification.

Required Cl:NH₃-N Weight Ratio

The weight ratio should be determined according to the NH₃-N concentration. Table VI shows the fluctuation of NH₃-N concentration in the year 1986. The average of 7 mg/L means that a sufficient amount of ammonia had been nitrified already. As discussed in Chapter IV, a nitrified sample will require a relatively high Cl:NH₃-N weight ratio. So, a weight ratio of 6:1 will be used. This value was approximated from Figure 1, 2, 3, and 4.

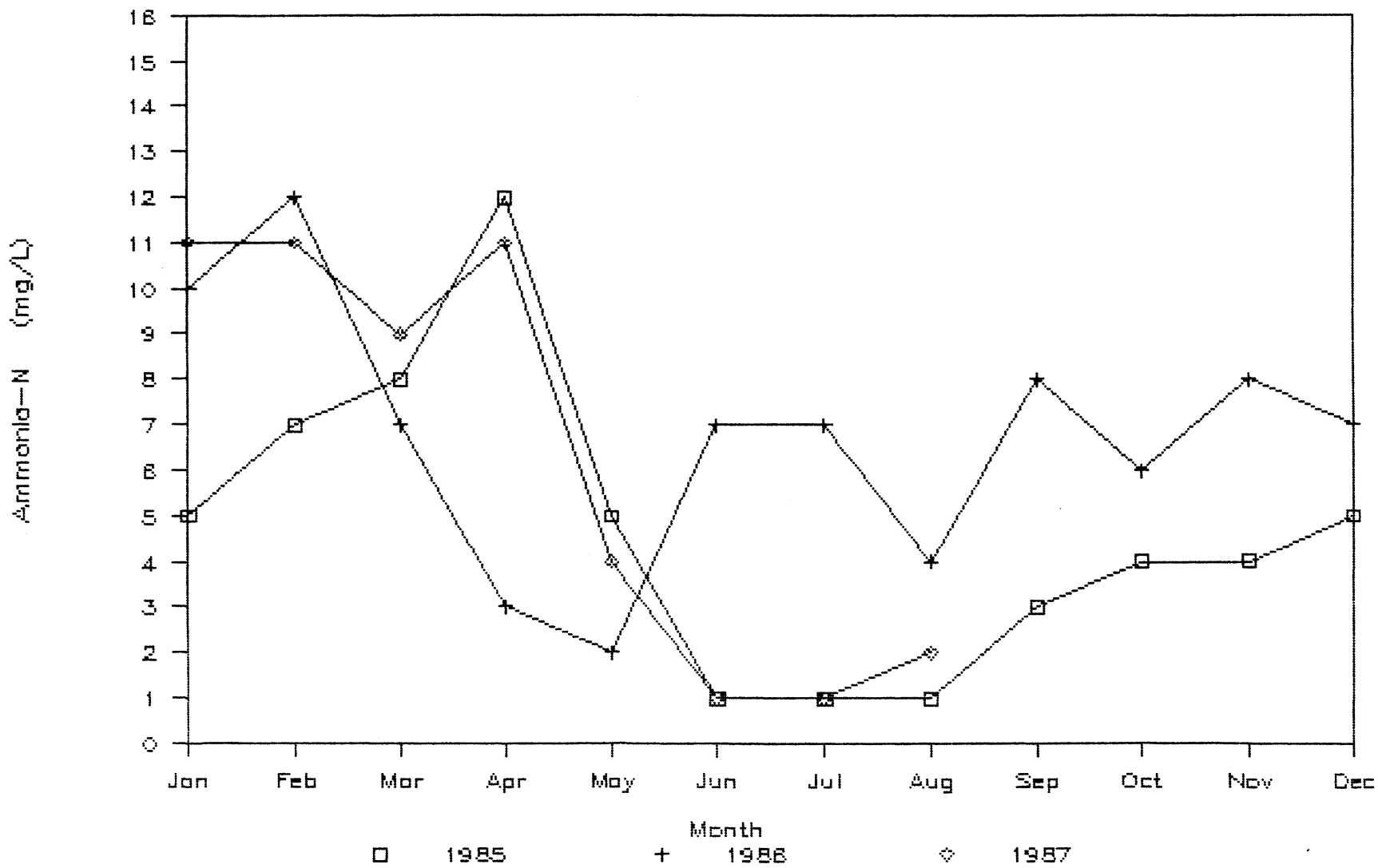


Figure 7. Effluent Ammonia-N, 1985-1987 (Stillwater)

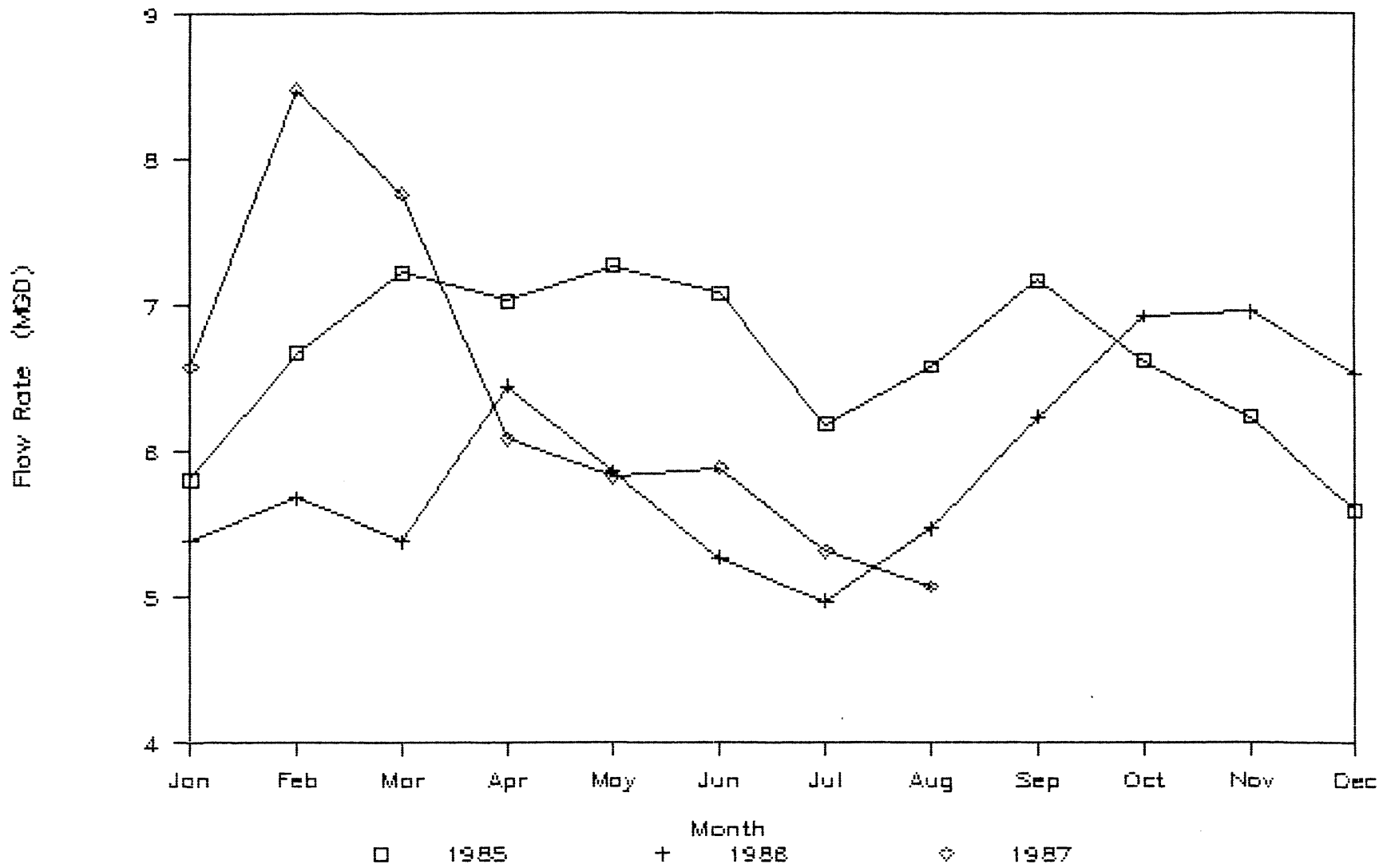


Figure 8. Flow Rate, 1985-1987 (Stillwater)

TABLE VI
EFFLUENT AMMONIA-N FROM STILLWATER PLANT
DAILY AVERAGE, 1986

	Flow Rate (MGD)	NH ₃ -N (mg/L)	8.34*MGD*mg/L (lbs/day)
Jan	5.38	10	449
Feb	5.68	12	568
Mar	5.38	7	314
Apr	6.44	3	161
May	5.86	2	98
Jun	5.27	7	308
Jul	4.97	7	290
Aug	5.47	4	182
Sep	6.23	8	416
Oct	6.93	6	347
Nov	6.96	8	464
Dec	6.52	7	381
Avg	5.92	7	331

* pH range: 6.9 - 7.4

Required $\text{Ca}(\text{OCl})_2$

Required available chlorine residual as Cl

$$= 331 \text{ lbs/day} * 6 = 1,986 \text{ lbs/day}$$

Required $\text{Ca}(\text{OCl})_2$ (Assume the efficiency: 65 %)

$$= 1,986 * \frac{143}{35.5*2} * \frac{1}{0.65} = 6,154 \text{ lbs/day}$$

CHAPTER VI

CONCLUSIONS

The following conclusions may be drawn from the observations made in this study:

1. In the majority of cases, ammonia-N can be reduced to zero mg/L by breakpoint chlorination. In some case, there could be a refractory portion of ammonia-N depending upon individual wastewater.
2. The initial concentration of ammonia-N has nothing to do with achievable final concentration.
3. The wastewater containing low concentration of ammonia-N primarily due to nitrification will require high chlorine-ammonia nitrogen weight ratio to reach breakpoint since the chlorine reactable substances are not reduced at so high rate as ammonia-N.
4. Almost all the reactions were completed in 10 minutes. Precise determination would be necessary for a real design of contact basin.
5. Samples out of the optimum pH range require much more contact time than those in the optimum pH range.

6. There is no significant amount of nitrate formation until breakpoint.

SELECTED BIBLIOGRAPHY

1. Sawyer/McCarty, Chemistry for Environmental Engineering, Third Edition.
2. EPA, Process Design Manual for Nitrogen Control, October, 1975.
3. Metcalf & Eddy Inc, Wastewater Engineering: Treatment/Disposal/Reuse, 2nd Edition.
4. Saunier, B.M. and Selleck, R.E., Kinetics of Breakpoint Chlorination in Continuous Flow Systems, Paper presented at 96th Annual Conference AWWA, New Orleans, Lo. June, 1976.
5. Pressley, T.A., Bishop, D.F., Pinto, A.P., and A.F.Cassel, Ammonia-Nitrogen Removal By Breakpoint Chlorination, Report prepared for the EPA, February, 1973.
6. Pressley, T.A., et al., Ammonia Removal By Breakpoint Chlorination, Environmental Science and Technology, July, 1972.
7. Pressley, T.A., Bishop, D.F., and S.G. Roan, Nitrogen Removal By Breakpoint Chlorination, Report prepared for the EPA, September, 1970.
8. Stone, R.W., Parker, D.S., and J.A. Cotteral, Upgrading Lagoon Effluent to Meet Best Practicable Treatment. Presented at the 47th Annual Conference of the WPCF, 1974.
9. Gasser, J.A., Disinfection of Nitrified Effluent, J. WPCF, 56, 1984.
10. Venosa, A.D., Current State of the Art Wastewater Disinfection, J. WPCF, 55, 1983.
11. Dhaliwal, B.S., and Baker, R.A., Role of Ammonia-N in Secondary effluent chlorination, J. WPCF, 55, 1983.
12. Gordon, J.H., The Effect of Ammonia in Effluent

Chlorination, J. WPCF, 57, 1985.

13. Morris, J.C., Kinetic Reactions between Aqueous Chlorine and Nitrogen Compounds, Fourth Rudolphs Research Conf., Rutgers Univ., June 15-18, 1965.
14. Kincannon, D.F., Paper presented at 4th Annual Joint Conference, Pollution Control Association of Oklahoma & AWWA, Oklahoma, April, 1987.
15. White, G.C., Handbook of Chlorination, 1972.
16. APHA, AWWA, WPCF, Standard Methods for The Examination of Water and Wastewater, 16th Edition.
17. Mahlie, W.S., Oil and Grease in Sewage, Sewage Works Journal, Vol. 12, No. 3, 1940.
18. Environmental Engineering Consultants, Monthly Operations Report for Stillwater Water Pollution Control Plant, 1985-1987.

VITA

HO-SIK YOO

Candidate for the Degree of

Master of Science

Thesis: BREAKPOINT CHLORINATION FOR THE CONTROL OF AMMONIA
NITROGEN

Major Field: Environmental Engineering

Biographical:

Personal Data: Born in Seoul, Korea, June 20, 1958,
the son of K. H. and S. D. Yoo.

Education: Graduated from Pai Chai High School, Seoul,
Korea, in February, 1976; received the Bachelor of
Science Degree in Civil Engineering from Sung Kyun
Kwan University in February, 1980; completed
requirements for the Master of Science Degree at
Oklahoma State University in December, 1987.

Professional Experience: Army Officer in Charge of
Site Survey, Korea, March 1980 to June 1982; Civil
Engineer, Dae Woo Co., Seoul, Korea, July 1982 to
October 1985.