

June 1976

Report No. Env. E. 53-76-2

A Kinetic Analysis of Ammonia Removal By Chloramine Conversion On Activated Carbon

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6/76 2

Report to the Division of Water Pollution Control

Massachusetts Water Resources Commission

Contract Number 73-07-(1)



ENVIRONMENTAL ENGINEERING
DEPARTMENT OF CIVIL ENGINEERING
UNIVERSITY OF MASSACHUSETTS
AMHERST, MASSACHUSETTS

A KINETIC ANALYSIS OF AMMONIA REMOVAL BY CHLORAMINE
CONVERSIONS ON ACTIVATED CARBON

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Contract Number MDWPC 73-07(1)

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June 1976

ACKNOWLEDGEMENTS

This research represents the results of a Ph.D. Dissertation by Alfred B. Scaramelli. Members of the Dissertation Committee were Dr. Francis A. DiGiano (Chairman), Dr. Tsuan Hua Feng (Civil Engineering) and Dr. James R. Kittrell (Chemical Engineering). The assistance of C. James Martel (Research Associate), Robert Pariseau (Chemist) and David Friedman (M.S. Graduate student) is also sincerely appreciated. This research was supported by the Massachusetts Division of Water Pollution Control, Contract Number 73-07(1).

ABSTRACT

The stoichiometry and kinetics of chloramine-activated carbon reactions were examined to establish design criteria for achieving effective ammonia removal from wastewater. Continuous flow operation of a carbon reactor verified that both mono- and dichloramine were converted by surface reactions to nitrogen gas. While monochloramine reacted by a parallel pathway to form both ammonia and nitrogen gas, steady-state reaction conditions did not correspond to stoichiometric conversions. Rather, interference from basic compounds, i.e buffer and/or hydroxide ions, was implicated in reducing the conversion rate of monochloramine to ammonia until a steady-state rate was achieved.

Dichloramine reacted by a single pathway to produce nitrogen gas with no ammonia production. This pathway offers the potential for 100 percent ammonia removal. However, accumulation of surface oxides, a by-product of the reaction, resulted in a poisoning of the carbon surface after 6 g dichloramine had been applied per g of carbon.

Kinetic analysis revealed that the overall conversion of monochloramine could be described by a first-order, irreversible model. Moreover, the parallel reactions to ammonia and nitrogen gas were also first-order.

The rate of nitrogen gas production decreased with increased pH. This implied an acid catalyzed nitrogen reaction. However, for any given pH, the rate constant associated with nitrogen production did not measurably increase with time suggesting that the surface oxides

produced by conversion of monochloramine to ammonia are not necessarily utilized for nitrogen production. Rather, these oxides may be unstable and lost from the surface before conversion to nitrogen gas can occur. Another possibility for lack of oxide utilization is that the virgin carbon surface already contains the required oxide complexes to promote the nitrogen gas reaction.

The dichloramine-carbon reaction also followed first-order, irreversible kinetics. Poisoning of the reaction due to surface oxide build-up was adequately described by a modified first-order model. Because of the difficulty of measuring surface oxides, this model included the amount of dichloramine applied to the reactor as a measure of surface oxide accumulation.

By varying carbon particle size, diffusional mass transfer was shown to have little effect on the rate of monochloramine reaction but a very significant effect on that of dichloramine. Moreover, for the same particle diameter, the overall reaction rate of dichloramine was 20 times that of monochloramine, suggesting the dichloramine surface reaction rate to be much greater than that of monochloramine.

Addition of selected organics - methylene blue, dodecylbenzene-sulfonate and dinitrophenol - reduced the rate of mono- and dichloramine conversion on the carbon surface; however, an even greater reduction was noted when alum clarified, raw wastewater was used. Despite organic interference, the dichloramine reaction rate was at least an order of magnitude greater than that of monochloramine. From a design standpoint, this research has demonstrated that the reaction of dichloramine

with the surface of activated carbon can provide an effective means of nitrogen removal from wastewater. Moreover, because only a few minutes are required for completion of the reaction, this process could be directly incorporated with organic adsorption to simplify design of physical-chemical treatment plants.

Total cost (operation and amortized capital) for a 10 mgd physical-chemical treatment plant employing lime clarification, filtration and chlorination-carbon contact and sludge handling by gravity thickening, centrifugation and recalcination was estimated to be \$748/MG. The proposed system will achieve greater than 90 percent removal of BOD, suspended solids, phosphorus and ammonia.

ENGINEERING RELEVANCE

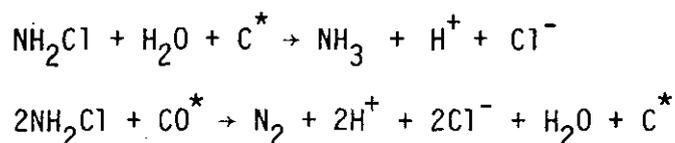
This research has considered the design criteria and costs associated with either of the following physical-chemical processes incorporating chloramine-carbon reactions for removal of ammonia:

- (1) Formation of Monochloramine from Ammonia and Chlorine Followed by Conversion to Nitrogen Gas on Activated Carbon

and

- (2) Formation of Dichloramine from Ammonia and Chlorine Followed by Conversion to Nitrogen Gas on Activated Carbon

Continuous flow, carbon contactors were used to verify that monochloramine reacts on the carbon surface by two pathways such that:

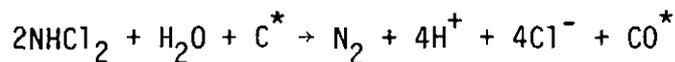


In these stoichiometric equations, C^* represents a carbon surface site and CO^* a site at which an oxide is produced.

This process cannot produce 100 percent removal of ammonia because some monochloramine is actually re-converted to ammonia. Theoretically, if all ammonia is initially reacted to form monochloramine, then only 67 percent ammonia removal can be achieved in a given reactor. Our studies have also shown that the presence of organics in alum, clarified wastewater interferes with these chloramine surface reactions such that only 25 percent removal of ammonia is possible in a given stage.

Obviously, in multiple staging, ammonia produced by the surface reaction can be chlorinated to form more monochloramine which can then be reacted on a follow-up carbon column. This alternative for achieving high percent removal of ammonia seems impractical. Another possibility for optimizing the process would be to insure removal of organics before the chlorination step. This may be practical because contact time for conversion of monochloramine on the carbon surface is only about 8 minutes in the absence of organics. Without removing organics, our studies indicate that required contact time increases to 16 minutes.

A better alternative for nitrogen removal appears to be dichloramine formation followed by conversion to nitrogen gas on activated carbon. However, the reaction to form di- rather than monochloramine, requires that pH be decreased to 4.3. Our laboratory studies have confirmed the subsequent reaction pathway of dichloramine to be:



In contrast to monochloramine conversion, this reaction produces only nitrogen gas. Thus, 100 percent removal of nitrogen is possible. However, a somewhat greater ratio of NH_3/Cl_2 is required to initially form NHCl_2 rather than NH_2Cl . This reaction pathway is also more favorable from a kinetics standpoint. While monochloramine conversion required 16 minutes with a wastewater feed, dichloramine conversion required only 1 minute. Organics were again noted to interfere; in their absence, conversion was accomplished in only 15 seconds. However, despite this interference, the dichloramine reaction pathway is still much faster.

Our research has examined in detail the kinetics of these conversion processes. A first-order model accounting for approach to a steady-state conversion rate was developed. In addition, the importance of pore diffusion on rate control was established. Our results indicate that dichloramine conversion is limited by pore diffusion while monochloramine is not. This suggests that the smallest possible fraction of carbon particle sizes be used to enhance the rate of dichloramine reaction.

An important point to be clearly understood is that conversion of dichloramine to nitrogen gas should continue at a steady-state rate for a very long time. This is in contrast to adsorption of organics; here, the adsorptive capacity is exhausted with time. For dichloramine conversion, our studies indicate that surface poisoning, which retards the reaction rate, does not occur until 6 g of NHCl_2/g carbon have been applied. Assuming that 20 mg/l of ammonia is completely reacted to form dichloramine, the carbon "usage" rate would be 115 lbs/MG of wastewater treated. This is far less than the "exhaustion" rate of carbon (500-1000 lbs/MG) based on organic removal capacity. Thus, in a carbon column intended for both adsorption of organics and nitrogen removal, regeneration would be required long before surface poisoning was significant.

The total cost (operating and capital amortized at 6 percent for 20 years) of physical-chemical treatment to provide 95 percent removal of phosphorus, BOD, suspended solids and nitrogen, as well as excellent disinfection, is estimated as \$0.75 per 1000 gallons. Treatment includes

chemical clarification with lime; multi-media filtration; chlorine contact (dosage of 120 mg/l as Cl_2); carbon contact; and sludge handling by gravity thickening, centrifugation and recalcination. This cost is quite competitive with nitrification-denitrification and affords the opportunity of better process control and enhanced removal of both organics and harmful bacteria.

It is also important to recognize the difference between chloramine-carbon reactions and breakpoint chlorination, another alternative nitrogen control scheme. In breakpoint chlorination, the chlorine dosage is intentionally increased to avoid formation of mono- and dichloramine. However, process control is difficult because of the varying strength of wastewater and as a result, under and over dosing occur; under dosing causes release of potential toxic chloramines while over dosing is expensive and may produce toxic nitrogen trichloride. In contrast to breakpoint chlorination, chloramines initially formed are removed on the carbon surface. This feature assures reliable performance even if ammonia concentration varies. Moreover, this process offers the advantage of controlling the extent of nitrogen removal by adjusting the chlorine dosage to provide for conversion of only a fraction of the total ammonia to chloramines.

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NOMENCLATURE

C	Chloramine concentration (ML^{-3})
C_B	Surface concentration of adsorbed basic compound (ML^{-3})
C_S	Chloramine concentration at carbon surface (ML^{-3})
C_O	Influent chloramine concentration (ML^{-3})
C^*	Carbon surface site
CO^*	Oxidized carbon surface site
D	Bulk diffusivity (L^2t^{-1})
D_e	Effective diffusivity (L^2t^{-1})
D_p	Particle diameter (L)
E	Fraction of available reaction sites remaining on the carbon surface
k	Global rate constant for chloramine conversion ($\text{L}^3\text{t}^{-1}\text{M}^{-1}$)
k_1	Global rate constant for ammonia production ($\text{L}^3\text{t}^{-1}\text{M}^{-1}$)
k_2	Global rate constant for nitrogen gas production ($\text{L}^3\text{t}^{-1}\text{M}^{-1}$)
$k_T \text{NH}_2\text{Cl}$	Global rate constant for monochloramine conversion ($\text{L}^3\text{t}^{-1}\text{M}^{-1}$)
$k_T \text{NHCl}_2$	Global rate constant for dichloramine conversion ($\text{L}^3\text{t}^{-1}\text{M}^{-1}$)
k_B	Intrinsic rate constant for adsorption of basic compound ($\text{L}^3\text{t}^{-1}\text{M}^{-1}$)
k^*	Intrinsic rate constant for chloramine conversion ($\text{L}^3\text{t}^{-1}\text{M}^{-1}$)
\bar{k}^*	Experimentally determined intrinsic rate constant for chloramine conversion ($\text{L}^3\text{t}^{-1}\text{M}^{-1}$)
m_p	Mass of carbon particle (M)
N_c	Chloramine flux ($\text{ML}^{-2}\text{t}^{-1}$)

Q	Volumetric flowrate (L^3t^{-1})
R	Carbon particle radius (L)
R_c	Rate of chloramine reaction ($ML^{-3}t^{-1}$)
r	Distance from center of carbon particle (L)
r_p	Reaction rate of carbon particle ($ML^{-3}t^{-1}$)
r_s	Reaction rate of carbon particle at outer surface conditions ($ML^{-3}t^{-1}$)
r_{N_2}	Rate of nitrogen gas production ($ML^{-3}t^{-1}$)
r_{NH_3}	Rate of ammonia production ($ML^{-3}t^{-1}$)
$r_{T NH_2Cl}$	Rate of monochloramine conversion ($ML^{-3}t^{-1}$)
$r_{T NHCl_2}$	Rate of dichloramine conversion ($ML^{-3}t^{-1}$)
t	Operating time (t)
W	Weight of carbon particle (M)
X	Fractional chloramine conversion
α	Constant relating dichloramine conversion to surface site consumption (MM^{-1})
ϵ	Carbon particle porosity
δ	Tortuosity factor
η	Effectiveness factor
ϕ_s	Thiele Modulus
ρ	Carbon particle density (ML^{-3})
τ	Space time (MtL^{-3})

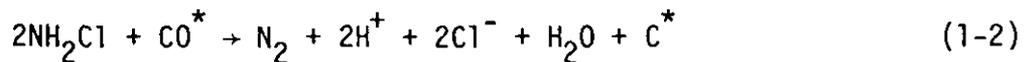
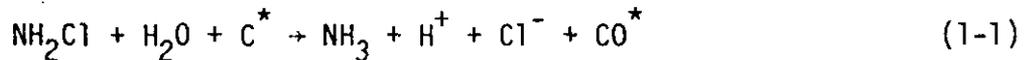
CHAPTER I

INTRODUCTION

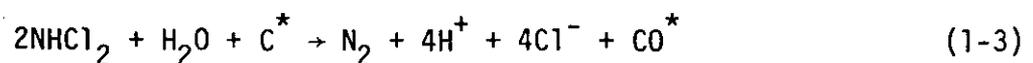
Biological processes for ammonia removal are often inadequate due to industrial waste toxicity, shock loading and low temperatures. Moreover, biological nitrification may reduce oxygen demand but does not eliminate the algal nutrient sources (NO_3^-). Biological denitrification requires strict operation control and is easily upset. Temporary failure in the biological system results in immediate and possibly prolonged damage to receiving streams.

While several physical-chemical processes are currently available for ammonia removal each suffer limitations. Ammonia stripping at high pH is unattractive in cold climates due to tower freezing problems; in addition, formation of CaCO_3 scale presents cleaning problems. Ion exchange, using clinoptilolite, also requires stripping of a concentrated ammonia waste. Breakpoint chlorination, used for many years in treatment of potable water, requires high chlorine dosage for wastewater treatment and produces toxic chloramines which may pass into the receiving stream. Because of these limitations, the potential application of chlorination followed by activated carbon contact for ammonia removal has recently been examined. This process can readily treat industrial wastes and shock loads and is unaffected by cold weather conditions. In contrast to breakpoint chlorination, less chlorine is required, toxic chloramines are eliminated and the degree of ammonia removal can be controlled.

Laboratory and pilot plant studies indicate that chloramines, formed by the reaction of chlorine with ammonia, react on the carbon surface to produce nitrogen gas (Bauer and Snoeyink, 1973; Stasiuk et al., 1973; Atkins et al., 1973). While the stoichiometry of the reaction of ammonia with chlorine to form mono- and dichloramine is well established (Weil and Morris, 1949), the subsequent chloramine-carbon reactions have only recently been investigated by Bauer and Snoeyink (1973). From their research on reaction stoichiometry the following parallel reaction pathway for monochloramine conversion was proposed:



Here CO^* represents an active carbon site containing an acidic surface oxide and C^* indicates a site with no surface oxide. It is important to note that the monochloramine reactions (Equations 1-1 and 1-2) cannot produce 100 percent removal of nitrogen because a fraction of the monochloramine is converted back to ammonia (Equation 1-1). For every three moles of monochloramine reacting, two are converted to nitrogen gas, thus giving a theoretical steady-state conversion of about 67 percent. In contrast, the proposed dichloramine reaction offers the potential for 100 percent removal of ammonia:



By this pathway, dichloramine reacts with an active surface site to produce nitrogen gas and a surface oxide. Oxides are not removed from the surface by this reaction and continually accumulate.

While the role of surface oxides in this surface reaction process has been inferred from batch laboratory studies (Bauer and Snoeyink, 1973), the reaction mechanisms described by Equations 1-1, 1-2 and 1-3 have not been verified. In addition to reaction stoichiometry, the rate of chloramine conversion is also important from a process design standpoint because this determines the required carbon contact time. To date, limited pilot plant studies have shown a carbon contact time of 10 minutes to be sufficient for chloramine conversion. However, optimization of process design by examination of reaction kinetics is lacking.

The obvious application of chloramine-carbon reactions for nitrogen removal is in combination with carbon contact for removal of organics. Toward this goal, a two-stage treatment system has been proposed by Atkins et al. (1973). However, the possible poisoning of the second-stage chloramine conversion process by escape of organics from the first-stage adsorbers has yet to be investigated in detail. Another interesting design possibility exists should there be minimal interference of organics on chloramine-carbon reactions. In this case, a combined unit process could be used for simultaneous removal of organics and nitrogen. Either of these possibilities will alter process design in physical-chemical plants. To optimize process design of the physical-chemical nitrogen removal process described, this research was directed towards:

- (1) investigation of the stoichiometry and kinetics of the mono- and dichloramine-carbon reactions and
- (2) the interaction of organic adsorption with the chloramine-carbon reactions.

CHAPTER I I BACKGROUND DEVELOPMENT

Ammonia Discharge Effects

Ammonia nitrogen discharged from wastewater treatment facilities imposes an oxygen demand on receiving waters from biological oxidation of ammonia to nitrate. In addition, ammonia may accelerate eutrophication and cause fish toxicity. Although much greater attention has been given to phosphorus as the limiting nutrient for algal growth, nitrogen may also be limiting in specific instances (Gerloff and Skoog, 1957). Fish toxicity results from the molecular form of ammonia (NH_3) and the combined form (NH_2Cl and NHCl_2). Although most natural waters have a pH far enough below the pK_a (9.3 at 20°C) of NH_4^+ , increases in pH can produce a significant fraction of NH_3 . More importantly, chlorination of ammonia containing wastewaters produces chloramines which are toxic to fish. Katz and Cohen (1975) examined toxicity of monochloramine on mosquito fish and found that monochloramine dissipated more slowly than free chlorine and caused acute toxicity.

Ammonia Removal Processes

Biological nitrification-denitrification is the most common method of removing ammonia nitrogen from wastewater. Barth (1966, 1968) and Balakrishnan and Eckenfelder (1970) were among several authors to examine ammonia removal by this process. Ammonia is oxidized to nitrate (nitrification) which is then reduced to nitrogen gas (denitrification). Because this is a biological process, waste toxicity, shock loading and

low temperature must all be considered as detrimental. While toxicity and shock loading are quite system specific, the growth rate of nitrifying bacteria has been shown by Knowles, et al. (1965) to be severely retarded below 5°C. In the denitrification process, NO_3^- serves as the electron donor instead of oxygen. However, to promote the need for an electron donor, biological growth must be artificially induced by addition of a supplemental carbon source. Although methanol has been found to be most economical for this purpose, dosage must be closely regulated to prevent excess additions which can cause unwanted reduction of sulfates to hydrogen sulfide and can contribute BOD to the process effluent. As can be expected for any biological process, Dawson and Murphy (1973) found denitrification to be ineffective below 5°C. Moreover, the rate of denitrification was significantly depressed below pH 6.0 and above pH 8.0 such that pH control may be needed.

Several physical-chemical methods for ammonia removal are currently available. Although these processes are amenable to treatment of industrial wastes and shock loads, some limitations are inherent. Air stripping of ammonia is accomplished by elevating pH to 10-11 and passing the wastewater through a stripping tower. Under these conditions, ammonia is in the molecular form and escapes to the atmosphere as a gas as shown by Equation 2-1:



The principal problems associated with ammonia stripping are inefficiency

in cold weather, required shutdown during freezing conditions and formation of calcium carbonate scale in the stripping tower. Mulbarger et al. (1968) reported that ammonia stripping tower performance was severely affected by ambient temperature conditions and therefore the tower must be heated during winter operation. Roesler et al. (1971) examined two major problems of ammonia stripping: absorption of CO_2 from the air with subsequent precipitation of carbonates and the biological oxidation of ammonia to nitrates in the aerobic tower. Carbonate scale forms readily on the packed tower media and must be removed frequently by acid washing or mechanical scrubbing. In cold weather, ice forms on the tower packing thereby reducing gas transfer efficiency and creating possible tower damage. McKinney (1971) also stated that ammonia released to the atmosphere by this process is readily soluble in water and will be quickly returned to the environment.

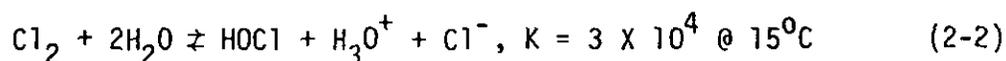
The use of clinoptilolite, a natural zeolite, for removal of ammonia has been examined by several researchers. Eliassen and Tchobanaglou (1968) reported that 80-90 percent ammonia removal efficiency could be achieved. However, organic molecules fouled the resin by selective adsorption onto the particles. Koon and Kaufman (1975) also examined the use of clinoptilolite with specific emphasis of optimization of the resin regeneration process. Although regeneration at pH 12.5 with NaCl and NaOH was most effective, severe attrition of the resin resulted from excessive caustic conditions. Regeneration of the exchange resin also results in a concentrated ammonia brine which must be disposed. Ammonia

stripping of the concentrated waste is one possibility for ultimate elimination from the water cycle. However, the problems associated with this process, as discussed earlier, can severely limit applications. Although ammonia will be removed by ion exchange at the new Upper Occoquan Treatment Plant, Virginia (Nitrogen Control, EPA, 1975), further reduction of total nitrogen by breakpoint chlorination will be necessary.

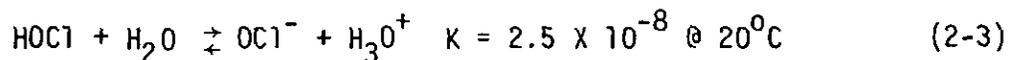
Breakpoint chlorination for the removal of ammonia has been used for many years in the treatment of drinking water. As early as 1939 Griffin (1939) established that breakpoint chlorination was a practical and valuable means for ammonia removal. Although this process has long been accepted in water treatment it was not until recently that it was considered for wastewater treatment. Pressley et al. (1972) examined this process for treatment of raw, secondary and lime-clarified municipal wastewaters and found that ammonia removal could be regulated by varying chlorine dosage. However, a large chlorine requirement was necessary for complete conversion of ammonia to end products; any ratio below this level would result in toxic chloramines in the process effluent. Because of this limitation, the potential application of chlorination followed by active carbon contact for ammonia removal has recently been examined. This process can readily treat industrial wastes and shock loads. In contrast to breakpoint chlorination, less chlorine is required, toxic chloramines are eliminated and the level of ammonia removal can be controlled. Laboratory and pilot plant studies indicate that chloramines, formed by the reaction of chlorine with ammonia, react on the carbon surface to produce nitrogen gas (Bauer and Snoeyink, 1973; Atkins et al., 1973; Stasiuk et al., 1973).

Chloramine Chemistry

Aspects of Chlorination. Chlorine has been used for many years in water and wastewater treatment for the elimination of pathogens and for the oxidation of both organic and inorganic compounds. When added to water, chlorine gas hydrolyzes to yield:



Because of this large disproportionation constant, free chlorine molecules (Cl_2) are virtually absent above pH 3.0. The active chlorine species are thus hypochlorous acid and its dissociation product, hypochlorite ion (Weber, 1972) as given by:



Both species comprise free available chlorine residual with an oxidation state of $\text{Cl}^{(+1)}$.

Chlorine can also be applied as hypochlorite salts which dissociate completely in water to yield hypochlorite ion:



Subsequent equilibration also gives hypochlorous acid as given by Equation (2-3). Addition of hypochlorite salts will tend to raise pH while chlorine gas will lower pH.

Chloramine Formation. Ammonia is present in wastewater as a result of degradation of proteins, urea and other organo-nitrogen compounds.

In aqueous solution oxidized chlorine (HOCl) reacts with ammonia to form chloramines. Berliner (1931) established the following stoichiometry for mono- and dichloramine formation:



Under low pH conditions nitrogen trichloride may be formed:



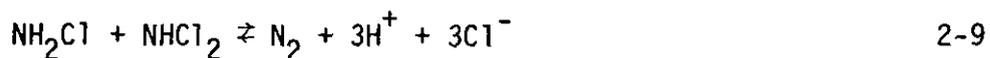
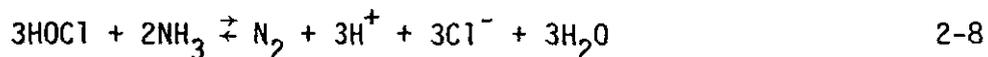
Weil and Morris (1949) have examined the kinetics of chloramine formation. The rate of monochloramine formation was found to be second order with respect to NH_3 and HOCl; at pH 8.3, a maximum rate constant of 5.1×10^6 l/mol-min was measured. Therefore, at this pH a solution containing 10^{-3} M HOCl and NH_3 will require 0.02 minutes for 99 percent conversion to monochloramine. Dichloramine formation occurs at lower pH and was found to be second order with respect to NH_2Cl and HOCl. However, rate of formation was considerably slower than monochloramine with a rate constant of 3.4×10^2 l/mol-min.

Chloramine-pH Relationships. Both the rate of chloramine formation and the ratio of NH_2Cl to NHCl_2 produced depend mainly on pH and the ratio of $\text{Cl}_2:\text{NH}_3$. Chapin (1931) indicated that above pH 8.5 only monochloramine exists, that between pH 4-5 dichloramine predominates and between pH 5-8.5 a varying mixture results. Below pH 4, nitrogen trichloride begins to appear. Palin (1950) determined the distribution

of mono- and dichloramine as a function of pH at a $\text{Cl}_2:\text{NH}_3$ mole ratio of 1:1. As shown in Figure 1, maximum monochloramine formation occurred above pH 8.0 while pH 4.2 was optimum for dichloramine formation.

Breakpoint Chlorination Reactions. Breakpoint chlorination occurs when sufficient chlorine has been applied to a water sample to cause chemical oxidation of ammonia to nitrogen gas and other end products. As illustrated in Figure 2, formation of mono- and dichloramine between points A and B produces a linear increase in chlorine residual. At point B, the $\text{Cl}_2:\text{NH}_3$ mole ratio is 1:1 and maximum formation of monochloramine occurs according to Equation 2-5. Beyond this point, combined chlorine residual declines due to oxidation of chloramines to nitrogen gas. However, complete oxidation of the combined residual is never achieved in wastewater chlorination (Pressley et al., 1972). The term breakpoint applies to description of point C where the $\text{Cl}_2:\text{NH}_3$ mole ratio is 1.5:1 (Pressley et al., 1972; Bauer and Snoeyink, 1973). Chlorine addition beyond the breakpoint yields a free chlorine residual.

According to Pressley et al. (1972), Bauer and Snoeyink, (1973) and Wei and Morris (1973), the overall breakpoint reactions can generally be described as:



These equations indicate a $\text{Cl}_2:\text{NH}_3$ mole ratio of 3:2 (1.5:1) for complete conversion of ammonia to nitrogen gas. However, other researchers have speculated that breakpoint requires a $\text{Cl}_2:\text{NH}_3$ mole ratio of 2:1 and

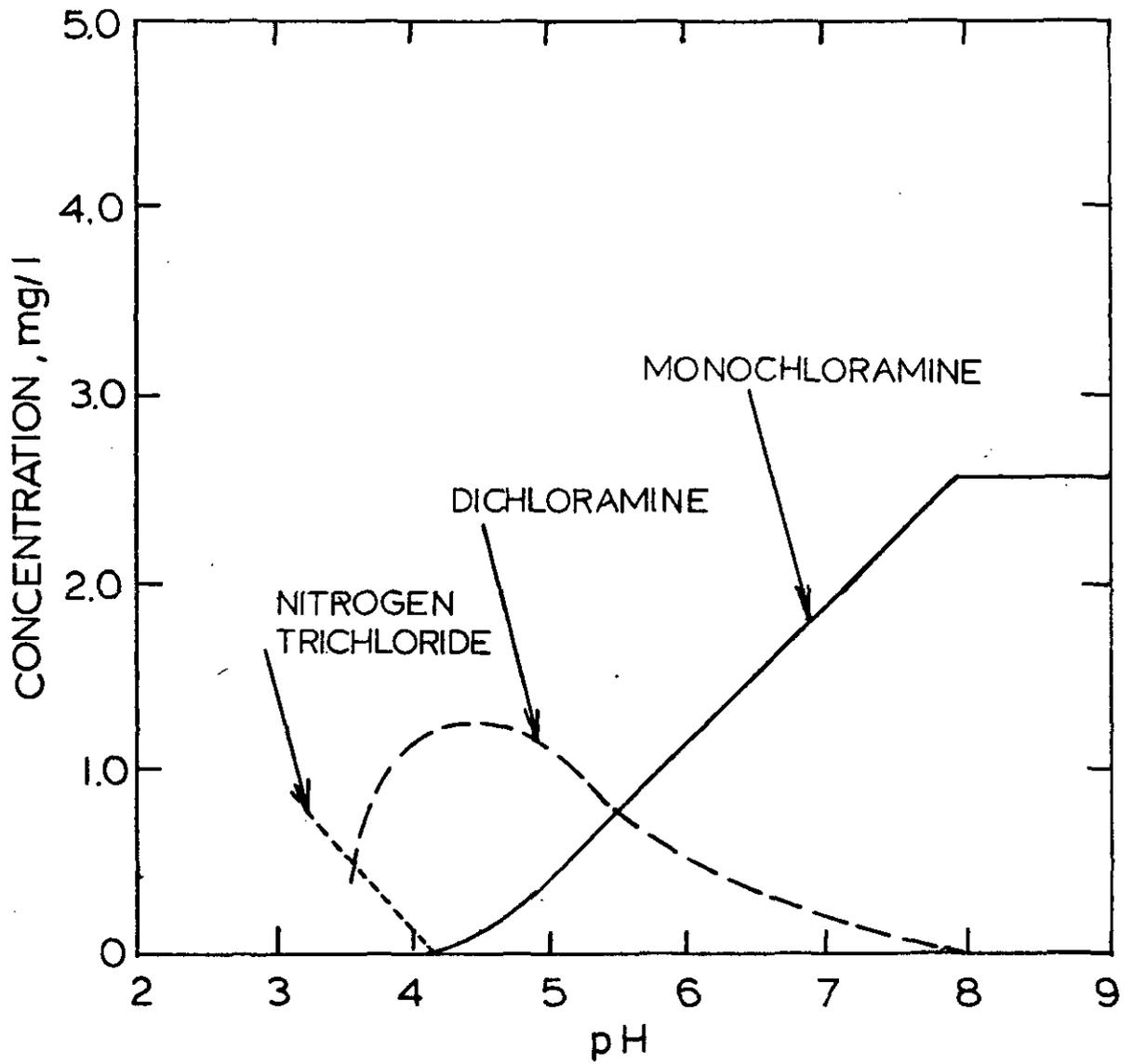


Figure 1. Chloramine species distribution. Initial chlorine and ammonia dosage of 2.5 and 0.5 mg/l, respectively (Palin, 1950).

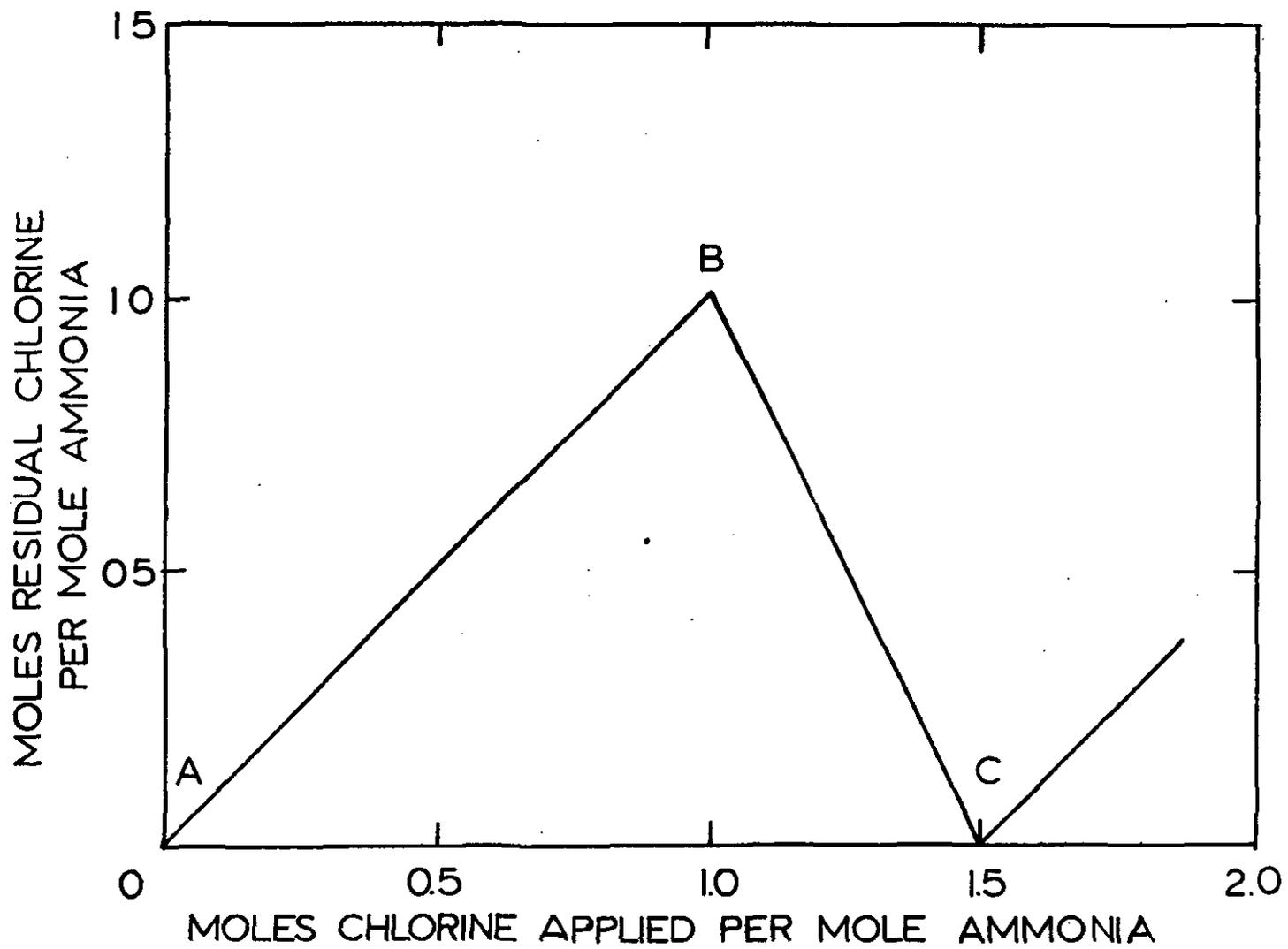


Figure 2. Theoretical breakpoint chlorination curve.

produces N_2O and NO as gaseous end products. This postulation is refuted by experimental evidence of only N_2 gas production (Pressley et al., 1972 and D'Agostaro, 1972).

Control of pH in breakpoint chlorination is important such that formation of NO_3^- and NCl_3 can be prevented. Pressley et al. (1972) have shown that these end products are minimized at pH 6.4. The concentration of NO_3^- increased with increasing pH while that of NCl_3 increased with decreasing pH. Neither species was present in significant amounts until chlorine dosage exceeded breakpoint. Thus, their presence can be due to overdosing (Palin, 1950) which should be avoided solely from economic aspects. In addition, NCl_3 is particularly undesirable because of its toxicity and obnoxious odor.

As should be expected, the presence of other chlorine demanding substances in wastewater will cause the chlorine requirement for breakpoint chlorination to exceed the theoretical $Cl_2:NH_3$ mole ratio of 3:2. After achieving breakpoint chlorination in the pH range of 6.5-7.5, Pressley et al. (1972) reported 95-99 percent ammonia removal for initial ammonia concentrations of 8-15 mg/l. Removal of organics significantly reduced the breakpoint dosage. For example, lime clarified, secondary effluent required a $Cl_2:NH_3$ mole ratio of 1.6:1 while raw wastewater required 2:1. In another study, chemical clarification of raw wastewater with ferric chloride followed by carbon adsorption indicated a breakpoint requirement of 1.64:1 (Stearns and Wheeler, 1973).

Chloramine-Carbon Reactions

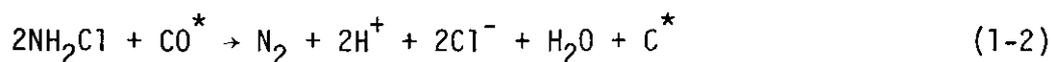
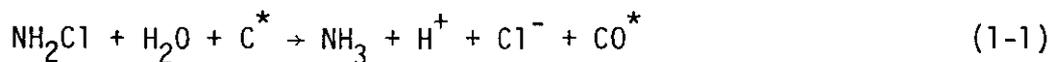
Successful operation of the breakpoint chlorination process requires chlorine dosages in excess or equal to breakpoint requirements. Lower dosages result in only partial oxidation of chloramines to nitrogen gas thereby introducing the problem of potential toxicity to fish and other aquatic life if discharged untreated. Increased chlorine costs together with the need for precise control of the breakpoint process have resulted in research on a technique for reducing chlorine demand while eliminating chloramines. The key feature of this process is the conversion of chloramines to N_2 by activated carbon. Hager and Flentje (1965) noted the removal of chloramines from aqueous solution by activated carbon. More research has followed suggesting that the chloramine-carbon reactions are a heterogeneous oxidation reaction.

Lawrence et al. (1970) observed that chloramines were destroyed by activated carbon but that some chloramines were converted back to ammonia. Dichloramine was destroyed more readily than monochloramine and a gaseous end product was noted. These researchers concluded that adsorption was not responsible for chloramine removal. D'Agostaro (1972) also observed that a fraction of the chloramines reacted were converted back to ammonia and that nitrogen gas production was the pathway for nitrogen removal. A maximum nitrogen removal of 20 percent occurred at pH 8 at a $Cl_2:NH_3$ mole ratio of 1:1.

In laboratory-scale column studies, Stasiuk et al. (1973) were able to control chloramine-carbon ammonia removal by regulation of pH

and $\text{Cl}_2:\text{NH}_3$ ratio. At pH 7.0 and a $\text{Cl}_2:\text{NH}_3$ mole ratio of 1.6:1, both breakpoint reactions and chloramine reactions on the carbon surface yielded nearly 100 percent NH_3 removal. Analysis of the data indicates that dichloramine reacted faster with the carbon than monochloramine. A contact time of 10 minutes was sufficient to reduce chloramines below 1 mg/l in the column effluent. Limited data on startup of the column system indicates that an acclimation period was required before nitrogen removal began to occur.

The only postulation of stoichiometry for the chloramine-carbon reactions was given by Bauer and Snoeyink (1973). Batch reactor studies indicated that chlorine dosages below the breakpoint requirement could be used to oxidize ammonia if chlorination was followed by carbon contact. From their research the following parallel reaction pathway for monochloramine conversion was proposed:



Batch reactor data indicated that monochloramine conversion proceeded according to Equation 1-1 until surface oxides had accumulated to such a level to allow the reaction given by Equation 1-2. Thus, total nitrogen concentration remained constant for a period of time and then gradually decreased. This data implied that an initial acclimation period was necessary for build-up of surface oxides before any nitrogen removal could be achieved. However, the presence of surface oxide was only postulated and not measured. Because ammonia is an end product of the monochloramine-

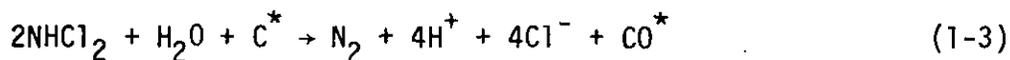
carbon reactions (Equation 1-1), 100 percent nitrogen yield cannot be achieved. If these oxidation-reduction reactions occur repeatedly on the carbon surface a dynamic equilibrium will result where two of every three moles of monochloramine reacting will form nitrogen gas resulting in 67 percent theoretical nitrogen yield.

Bauer and Snoeyink (1973) pretreated the carbon surface with free chlorine to examine the effect of the presence of surface oxides on the initial acclimation period of the monochloramine-carbon reactions. As noted by Magee (1956), the reaction of free chlorine with active carbon results in the production of surface oxides:



Results indicated an immediate decrease in total nitrogen following chlorine pretreatment. This observation was consistent with the hypothesis that some minimum level of surface oxides is required for conversion of monochloramine to nitrogen gas.

Bauer and Snoeyink (1973) also investigated the dichloramine-carbon reaction and found an immediate destruction of both dichloramine and total nitrogen; the primary end product was nitrogen gas. They did not observe an acclimation period for the dichloramine reaction nor any production of ammonia. From this information, the dichloramine-carbon reaction was presented as:



Nitrogen gas was proposed as the sole nitrogen end product of the reaction, thus permitting the potential for 100 percent nitrogen yield. The role of surface oxides in chloramine-carbon conversion was only inferred by Bauer and Snoeyink (1973) and the reaction pathways have yet to be verified.

Atkins et al. (1973) conducted a pilot-scale study of ammonia removal from wastewater by chlorination followed by carbon contact. In this physical-chemical system, lime clarification and carbon adsorption prior to chlorination provided for removal of organics. Carbon contactors for chloramine conversion were operated in upflow mode to enable escape of nitrogen gas. A contact time of 10 minutes was found sufficient to completely convert chloramines by surface reactions. Results indicated that complete ammonia removal from wastewater could be achieved at a $\text{Cl}_2:\text{NH}_3$ mole ratio of 1.8:1, while 50 percent removal required a mole ratio of 0.8:1. Application of chlorine gas to the lime clarified effluent reduced pH from 9.0 to 6.0 and resulted in a distribution of both monochloramine and dichloramine entering the carbon contactor. Subsequent reaction of chloramines with the carbon surface caused further pH depression to 3.5 as a result of hydrogen ion production according to Equations 1-1, 1-2 and 1-3. This pH depression favors dichloramine rather than monochloramine formation. Thus, reaction time could be reduced if, as observed by Lawrence et al. (1970) and Bauer and Snoeyink (1973), dichloramine reacts with the carbon surface more rapidly than monochloramine.

The study by Atkins et al. (1973) produced results which were somewhat inconsistent with those of Bauer and Snoeyink (1973). Effluent ammonia concentration from the carbon contactor was in excess of influent monochloramine concentration for a fresh carbon bed and approximately equal to influent monochloramine for carbon that had been used for several days for nitrogen removal. Influent ammonia to the carbon contactor was not measured. Thus, the discrepancy with the findings of Bauer and Snoeyink (1973) may be attributed to the presence of some unreacted ammonia entering the carbon contactor. Additionally, system pH was not controlled thus preventing isolation of chloramine species. This prevented any comparison with the stoichiometry proposed by Bauer and Snoeyink (1973).

Role of Surface Oxides. According to Bauer and Snoeyink (1973), surface oxides play an important role in the chloramine-carbon reactions. The reaction of chloramines with carbon results in oxidation of the carbon surface by formation of surface complexes termed surface oxides. Snoeyink and Weber (1972), Boehm (1966) and Puri (1970) have reviewed the characteristics of oxides on carbon surfaces following reaction with oxidizing agents. A primary characteristic of these oxides is that they are acidic in nature. Boehm (1966) has developed a titration procedure which permits categorization of these oxides into selected groups.

Surface complexes formed by the chloramine-carbon reactions have not been examined to date. However, insight into their mechanism of formation and subsequent role in surface reactions can be gained from examination of the chlorine-carbon reaction as given by:



Magee (1956) noted that the reaction of free chlorine with carbon resulted in the reduction of chlorine to chloride with oxidation of the carbon surface by formation of a surface oxide. A gradual reduction in dechlorination efficiency was noted and attributed to a poisoning of the carbon surface by oxides. In addition, the release of CO and CO₂ from the surface suggested a degree of surface oxide instability. This evolution of oxides may delay poisoning of the surface by exposing additional active sites.

The dichloramine-carbon reaction is analogous to the chlorine-carbon reaction in that the carbon surface is continually oxidized. From this analogy, it is anticipated that the rate of dichloramine conversion will gradually diminish as the surface becomes poisoned by oxides. Again, as was noted for the chlorine-carbon reaction, the possible evolution of oxides from the carbon surface as CO or CO₂ could delay this poisoning effect. In contrast to the dichloramine-carbon reaction, the monochloramine-carbon reactions proposed by Bauer and Snoeyink (1973) do not allow for poisoning of the surface. That is, according to Equations 1-1 and 1-2, at steady-state a dynamic condition should exist where oxides are repeatedly formed and consumed by monochloramine reaction on the carbon surface. However, should oxides evolve from the surface, it is possible for nitrogen gas production to be reduced.

Although some oxides are evolved from the surface, significant amounts still accumulate and thus cause surface poisoning. Snoeyink et al. (1973) studied the accumulation of surface oxides on carbon as a function of the amount of free chlorine reacted. As shown in Figure 3, the concentration of surface oxides increased to a plateau indicating a finite limit to oxide accumulation on the surface of carbon. Many of the oxides were volatile and could be removed by drying at 105°C.

Snoeyink et al. (1973) observed that only a fraction of oxides produced on the carbon surface are measured by the titration procedure of Boehm (1966). A stoichiometric relationship between oxides produced and chlorine reacted could not be obtained. Some oxides were evolved while others were not titratable with NaOH. Therefore, it appears that surface oxide data can only be used to establish a general trend in chloramine-carbon reactions and cannot be used to quantitatively evaluate stoichiometry.

Organic Adsorption and Chloramine-Carbon Reactions. The obvious application of the chloramine-carbon reactions for ammonia removal is in combination with carbon adsorption for organic removal. Atkins et al. (1973) have tested a two-stage treatment system in which organic removal occurs in the first-stage carbon contactors followed by chlorination and chloramine-carbon ammonia removal in the second-stage contactors. Limited operational data indicates successful operation of the second-stage ammonia removal process without any interference from organics. However, the possible poisoning of the chloramine-carbon reactions (second-stage) by escape of organics from the first-stage adsorbers has yet to be examined

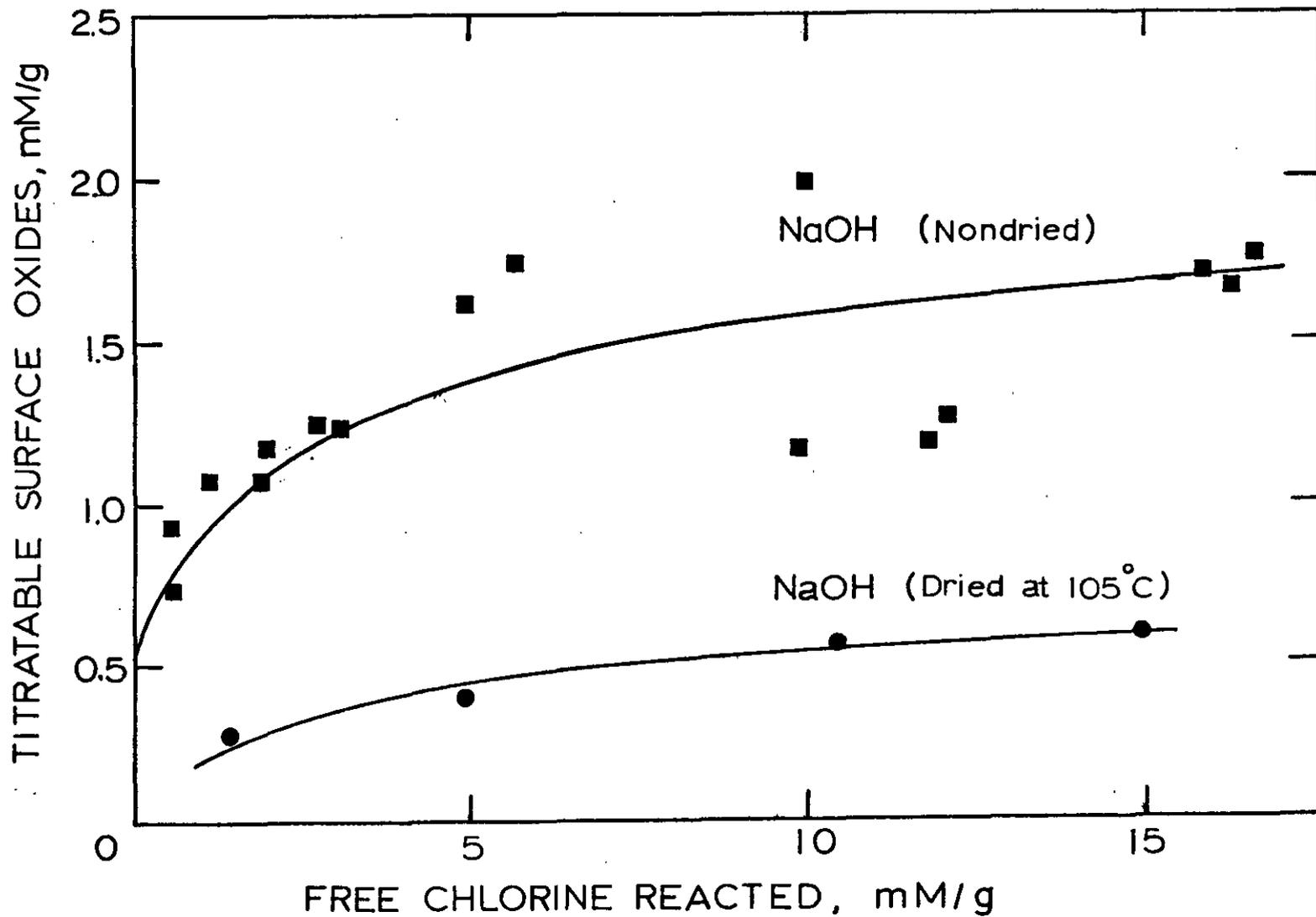


Figure 3. NaOH titratable surface oxides produced by chlorine-carbon reaction (Snoeyink, *et al.*, 1973).

in detail. Alternatively, if organics do not interfere with the chloramine-carbon reactions, then a combined unit process for simultaneous removal of ammonia and organics may be feasible. Both of these possibilities must be thoroughly explored to efficiently utilize the organic and ammonia removal potential of activated carbon.

The production of surface oxides from the chloramine-carbon reactions is important not only for nitrogen removal but for organic adsorption as well. In equilibrium experiments, Coughlin and Erza (1968) and Coughlin and Tan (1968) demonstrated that the presence of surface oxides on activated carbon greatly reduced adsorptive capacity for phenol, nitrobenzene and benzenesulfonate. An increase in surface acidity and a decrease in surface area due to micropore blockage by oxides were both considered factors in reducing adsorption. Snoeyink et al. (1973) showed a decrease in capacity of carbon for p-nitrophenol as surface oxide concentration increased. They proposed that oxides were either destroying the carbonyl functional groups or blocking pores. Mattson et al. (1969) also observed a decrease in adsorption of aromatics as carbon surface acidity increased. Gasser and Kippling (1960) reported that increased oxygen content on the surface also decreased hydrophobicity while increasing polarity. As a result, the carbon became more selective for adsorption of polar compounds. Based on this finding, simultaneous chloramine-carbon reaction and organic adsorption could enhance removal of polar organics due to the increased surface polarity from surface oxide accumulation.

The decrease in adsorptive capacity with formation of oxides is considered to be a reversible interaction based upon experiments in

which original sorptive capacity was restored when oxides were removed. This result is particularly noteworthy with regard to thermal regeneration in a combined ammonia-organic removal process. That is, if, as noted by Boehm (1966) and Puri (1970), all oxides are removed by heating to 1000⁰C, then thermal regeneration will minimize oxide interference with organic adsorption. Moreover, the removal of oxides by regeneration will eliminate the poisoning effect associated with removal of nitrogen by the dichloramine-carbon reaction (Equation 1-3). On the other hand, oxide formation may be desirable for monochloramine conversion to nitrogen (Equation 1-2). Here, removal of oxides by thermal regeneration will result in reduced nitrogen gas production when the carbon is placed back in-line.

The implication of surface oxide-organic adsorption research presented is that organic adsorption capacity may be reduced by chloramine-carbon reaction in a combined process of organic and ammonia removal. However, much more data is needed to confirm this postulation. Bishop *et al.* (1973), in a wastewater pilot plant study, observed that chloramine-carbon contact reduced organic adsorption capacity. In the absence of chloramines, carbon loading reached 0.30 gTOC/g with an effluent TOC of 8.0 mg/l; in the presence of chloramines (1-10 mg/l as Cl₂), carbon loading was reduced to 0.24 g TOC/g at a comparable effluent TOC. However, it is important to note that this reduction in adsorption capacity was attributed only to a lack of biological activity in the chlorinated column and not to formation of oxides.

While little information is available on the reduction of organic sorptive capacity by chloramine-carbon reactions, there is even less on the effect of sorbed organics on conversion of chloramines to nitrogen gas.

Sorbed organics may interfere with chloramine reactions on the carbon surface by either blocking or competing for available reaction sites. Interference may result in a reduced rate of chloramine conversion, suppressed nitrogen gas production, or both. This possibility must be explored for optimum process design.

Kinetic Considerations. To date, limited pilot plant studies by Atkins et al. (1973) have shown a carbon contact time of 10 minutes to be sufficient for 95 percent chloramine conversion. However, a kinetic interpretation of the role of organics and surface oxides in the chloramine-carbon reactions is lacking. This must be accomplished for optimum design of the ammonia-organic removal system.

Although the chloramine-carbon reactions have not been examined from a kinetic viewpoint, a similar application of carbon for the reduction of aqueous free chlorine may provide some insight into their behavior. Suidan and Snoeyink (1975) found that the carbon surface was oxidized in the form of surface oxides by the conversion of free chlorine to chloride and that the rate of conversion decreased as the amount of chlorine reacted. These findings are analogous to results expected for the dichloramine-carbon reaction in which the increase in surface oxides with dichloramine loading should result in a reduction in reaction rate due to surface poisoning. Additionally, these authors developed a surface rate expression to describe the chlorine-carbon reaction and incorporated this into a pore diffusion model to predict the performance of a carbon dechlorination bed. Pore diffusion had a significant effect on the rate of chlorine

reaction. Because chloramines also react on the carbon surface, it may be expected from these studies that pore diffusion is rate controlling and must therefore be examined to optimize process design.

C H A P T E R I I I

APPROACH TO THE INVESTIGATION OF CHLORAMINE-CARBON KINETICS

The most direct and practical approach to evaluation of the rates of conversion of mono- and dichloramine on the carbon surface is by conduct of fixed-bed reactor experiments. The choice of modeling the bed as a differential or integral reactor depends upon the magnitude of the reaction rate and the extent of analytical capabilities in measuring incremental changes in reactant and product concentrations. Because of the difficulty inherent in exact analysis of chloramine species, an integral reactor model is the more logical choice. That is, by allowing large variation in concentration through the bed, slight errors in analyses would not be critical in data interpretation. Since the rate of reaction is a function of concentration, it varies from location to location, and any measured rate is an integrated average of all point rates in the column. Analysis of data to obtain a rate expression describing chloramine-carbon reaction was performed by integration of an assumed rate equation and comparison with observed results.

The simplest kinetic model to account for a decreasing rate of conversion with reaction time in the bed, as observed in preliminary laboratory studies, is a first-order irreversible expression given by:

$$r = \frac{-d C}{d \tau} = k C \quad (3-1)$$

For Equation 3-1, C is the concentration of mono- or dichloramine, τ the space time or reaction time in the column and k, the global first-order rate constant. To relate the reaction rate directly to the mass

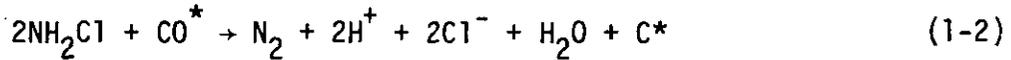
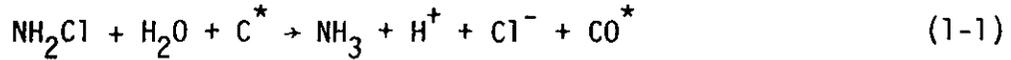
of carbon in the bed, it is appropriate to consider space time as

$$\tau = W/Q \quad (3-2)$$

where W is the mass of carbon (g) in the given bed length and Q the volumetric flowrate (l/hr). Thus, the reaction rate constant has the units of l/hr-g.

In this research, kinetic analysis is to include the approach to a steady state conversion rate measured on a time-scale of hours. A pseudo steady-state analysis of kinetic data is quite appropriate for a plug flow reactor having a short space time (e.g. on the order of minutes). In this case, the increase in process operating time as the reactants move down the bed is minimal in relationship to the time required for ultimate steady-state to be reached. Thus, at any given operating time, a pseudo-steady state condition exists in the reactor where a rate constant can be obtained from the reactant concentration profile along the reactor length defined by the total space time selected. It should be noted that as the chloramine-carbon reactions approach true steady-state, concentration of products formed in the reactor will vary thus causing a change in the rate constant with operating time. The rate constant measured will be referred to as the global rate constant. As such, it includes both the intrinsic rate of chloramine conversion on the carbon surface and the diffusional rate of mass transfer to a reaction site. While both an intrinsic and diffusional rate are included, a first-order interpretation is justified because of the first-order description of pore diffusion.

According to Equations 1-1 and 1-2, the monochloramine-carbon reactions proceeded by an irreversible, parallel pathway given by:



The overall rate of monochloramine conversion ($r_{\text{T NH}_2\text{Cl}}$) is the sum of both the rate of ammonia production (r_{NH_3}) and the rate of nitrogen gas production (r_{N_2}):

$$r_{\text{T NH}_2\text{Cl}} = r_{\text{NH}_3} + r_{\text{N}_2} \quad (3-3)$$

Assuming a first-order irreversible reaction, overall monochloramine conversion in the reactor can be expressed as:

$$\begin{aligned} -r_{\text{T NH}_2\text{Cl}} &= \frac{-d[\text{NH}_2\text{Cl}]}{d\tau} = k_1 [\text{NH}_2\text{Cl}] + k_2 [\text{NH}_2\text{Cl}] \\ &= k_{\text{T NH}_2\text{Cl}} [\text{NH}_2\text{Cl}] \end{aligned} \quad (3-4)$$

$$\text{where } k_{\text{T NH}_2\text{Cl}} = k_1 + k_2 \quad (3-5)$$

Integrating Equation 3-4 with the following initial condition

$$[\text{NH}_2\text{Cl}] = [\text{NH}_2\text{Cl}]_0 \text{ at } \tau = 0$$

yields:

$$\ln \frac{[\text{NH}_2\text{Cl}]}{[\text{NH}_2\text{Cl}]_0} = -k_{\text{T NH}_2\text{Cl}} \tau \quad (3-6)$$

Thus, a plot of $\ln[\text{NH}_2\text{Cl}]/[\text{NH}_2\text{Cl}]_0$ versus τ , should be linear for verification of a first-order reaction. Such data must be collected at various operating times in order to measure the approach to a final, steady-state conversion rate.

Rate constants for ammonia (k_1) and nitrogen gas production (k_2) can also be evaluated. Assuming first-order formation of these end products gives:

$$r_{\text{NH}_3} = \frac{d[\text{NH}_3]}{d\tau} = k_1[\text{NH}_2\text{Cl}] \quad (3-7)$$

$$r_{\text{N}_2} = \frac{d[\text{N}_2]}{d\tau} = k_2[\text{NH}_2\text{Cl}] \quad (3-8)$$

The ratio of these conversion rates is thus

$$\frac{r_{\text{NH}_3}}{r_{\text{N}_2}} = \frac{d[\text{NH}_3]}{d[\text{N}_2]} = \frac{k_1}{k_2} \quad (3-9)$$

which when integrated becomes:

$$\frac{[\text{NH}_3] - [\text{NH}_3]_0}{[\text{N}_2] - [\text{N}_2]_0} = \frac{k_1}{k_2} \quad (3-10)$$

By plotting ammonia versus nitrogen gas production within the reactor space time, τ , the ratio k_1/k_2 can be obtained. Thus, with k_1/k_2 and $k_T \text{NH}_2\text{Cl}$ (Equation 3-5) known, the values of k_1 and k_2 follow directly.

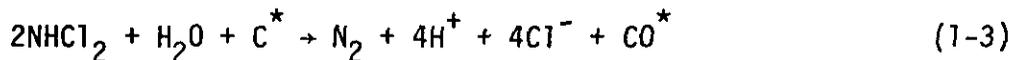
Again, these rate constants must be evaluated at various operating times to measure the approach to final, steady state conversion rates.

Although nitrogen gas production is difficult to measure directly, measurements of monochloramine conversion and ammonia production can be used to obtain a calculated value. That is, at any operating time, the change in monochloramine concentration in the reactor must be accounted for in either ammonia or nitrogen gas production as given below:

$$\Delta[\text{NH}_2\text{Cl}] = \Delta[\text{NH}_3] + \Delta[\text{N}_2] \quad (3-11)$$

This balance is necessarily correct if no other pathways for nitrogen transformations are available. Experimental evidence to date has confirmed this assumption.

Unlike monochloramine-carbon reactions, the lack of surface oxide regeneration in the dichloramine-carbon reaction forces consideration of a poisoning effect on reaction rate. According to Bauer and Snoeyink (1973), the dichloramine-carbon reaction proceeds by only the following pathway:



Thus, as dichloramine reacts with the carbon surface, active sites are consumed while surface oxides are formed (Equation 1-3). The accumulation of oxides results in a poisoning of the surface which will reduce the rate of dichloramine conversion. As operating time increases, this poisoning effect should continually decrease reaction rate because the number of available C^* sites is reduced. As the reaction rate slows, dichloramine concentration leaving the reactor will increase. In this sense, the poisoning effect will produce a reactor response analogous to

that observed for exhaustion of a fixed bed in which organics are adsorbed.

Assuming first-order, irreversible kinetics, the rate of dichloramine conversion at a specific operating time is

$$r_{\text{NHCl}_2} = \frac{d [\text{NHCl}_2]}{d\tau} = -k_T \text{NHCl}_2 [E] \quad (3-12)$$

where $k_T \text{NHCl}_2$ represents the global, first-order dichloramine rate constant and E the fraction of available C^* sites remaining on the surface at any given time. Therefore, at initial startup of the reactor, E is unity because the carbon is fresh and not poisoned by the surface reaction. As the amount of dichloramine reacted increases, E decreases due to the reduction in available C^* sites; E approaches zero as the carbon surface becomes totally oxidized.

The decrease in E with operating time is directly related to the number of available C^* sites on the surface. However, direct measurement of C^* is very difficult and another parameter related to E must be used. Dichloramine loading, i.e. g dichloramine reacted/g carbon is directly related to E as given by:

$$E = 1 - \alpha \left(\frac{Q [\text{NHCl}_2]_0}{W} \right) X t \quad (3-13)$$

where Q = volumetric flow rate, l/hr

W = carbon weight, g

$[\text{NHCl}_2]_0$ = influent NHCl_2 , mM

X = fractional dichloramine conversion, $\frac{[\text{NHCl}_2]_0 - [\text{NHCl}_2]}{[\text{NHCl}_2]_0}$

α = constant relating dichloramine conversion to surface site consumption, M/g

In this simple approach to examine poisoning of the carbon surface, it is assumed that C^* sites are continually consumed as dichloramine reacts and that regeneration of C^* sites by evolution of oxides does not occur.

Substituting for E in Equation 3-12 yields:

$$\frac{d[NHCl_2]}{d\tau} = -k_T NHCl_2 [NHCl_2] \frac{[1 - \alpha Q [NHCl_2]_0 Xt]}{W} \quad (3-14)$$

After finding $k_T NHCl_2$ and α , the breakthrough of dichloramine with time can be predicted. For relatively short column reaction time, operating time only changes slightly and can be considered constant as a dichloramine slug passes through the reactor. Therefore, for a small change in τ , Equation 3-14 can be integrated to give

$$\int_{[NHCl_2]_0}^{[NHCl_2]} \frac{d[NHCl_2]}{[NHCl_2]} = -k_T NHCl_2 \frac{[1 - \alpha Q [NHCl_2]_0 Xt]}{W} \int_0^\tau d\tau \quad (3-15)$$

or,

$$-\ln \frac{[NHCl_2]}{[NHCl_2]_0} = -\frac{\alpha Q [NHCl_2]_0}{W} k_T NHCl_2^\tau [Xt] + k_T NHCl_2^\tau \quad (3-16)$$

Thus, a plot of $-\ln [NHCl_2]/[NHCl_2]_0$ versus $[Xt]$ yields a straight line with $k_T NHCl_2$ obtained from the intercept and α from the slope for known values of Q and τ . From the definition of fractional conversion, X, Equation 3-16 can be rearranged to give

$$- \ln \frac{[\text{NHCl}_2]}{[\text{NHCl}_2]_0} = \frac{-\alpha Q [\text{NHCl}_2]_0}{W} k_T \text{NHCl}_2^\tau \left(1 - \frac{[\text{NHCl}_2]}{[\text{NHCl}_2]_0}\right) + k_T \text{NHCl}_2^\tau \quad (3-17)$$

where effluent dichloramine can be predicted with time for various conditions of τ , (W/Q) and $[\text{NHCl}_2]_0$.

Evaluating the Importance of Pore Diffusion Control. The kinetics of the heterogeneous reaction of chloramines with a porous carbon surface requires consideration of molecular diffusion. This diffusion occurs through a stagnant film around the carbon particle and then within the internal pore structure. Global reaction rates are based upon the observed changes in bulk solution concentrations. Thus, reaction kinetics incorporate both film and pore resistances in addition to the rate of the intrinsic surface reaction. The magnitude of these transport resistances on the chloramine-carbon reaction must be established from a process design standpoint. More specifically, large pore diffusion resistance relative to intrinsic surface reaction may require use of a small carbon particle size to achieve a relatively rapid reaction rate.

Smith (1970) stated that in fixed bed catalytic reactors, external resistances are small for normal operating conditions. However, internal resistances may be rate controlling. For a first-order monochloramine reaction, pore diffusion can severely retard the rate of chloramine conversion on the carbon surface by limiting the arrival rate of chloramine at available reaction sites.

Diffusion and subsequent reaction of chloramines on the carbon surface can be described mathematically such that the importance of pore diffusion control can be evaluated. For a spherical particle of radius R , a mass balance on chloramine, C , for a spherical-shell volume of thickness, Δr , at steady-state conditions yields,

$$\begin{aligned} \text{MASS IN} & \quad - \text{MASS OUT} & \quad - \text{REACTION RATE} = 0 \\ 4\pi r^2 N_c \Big|_r & \quad - 4\pi r^2 N_c \Big|_{r + \Delta r} & \quad - 4\pi r^2 \Delta r R_c = 0 \end{aligned} \quad (3-18)$$

where N_c (M/L^2-t) is the flux of C across the spherical shell and R_c (M/L^3-t) the rate of chloramine reaction. Dividing Equation 3-18 by $4\pi\Delta r$ and letting $\Delta r \rightarrow 0$ gives:

$$\frac{d}{dr} (r^2 N_c) = r^2 R_c \quad (3-19)$$

Assuming only diffusive transport inside the carbon particle, the flux N_c is

$$N_c = - D_e \frac{dC}{dr} \quad (3-20)$$

where D_e represents the effective diffusivity of chloramine in the carbon particle. A first-order, irreversible reaction of chloramine on the carbon surface can be described by

$$R_c = - k^* \rho_p C \quad (3-21)$$

where k^* is the intrinsic rate constant ($L^3/t-W$) and ρ_p is the carbon particle density (W/L^3). For this first-order reaction with simultaneous

diffusion, Equation 3-19 can be written as

$$\frac{d^2C}{dr^2} + \frac{2}{r} \frac{dC}{dr} - \frac{k^* \rho_p C}{D_e} = 0 \quad (3-22)$$

with the following boundary conditions:

$$\frac{dC}{dr} = 0 \quad \text{at } r = 0 \quad (3-23)$$

$$C = C_s \quad \text{at } r = R \quad (3-24)$$

It may be noted that the concentration of chloramine on the carbon surface, C_s , is assumed constant. The solution to this linear differential equation is given by:

$$\frac{C}{C_s} = \frac{R}{r} \frac{\sinh r\sqrt{k^* \rho_p / D_e}}{\sinh R\sqrt{k^* \rho_p / D_e}} \quad (3-25)$$

Substitution of the dimensionless group (Thiele Modulus)

$$\phi_s = \frac{R}{3} \left(\frac{k^* \rho_p}{D_e} \right)^{1/2} \quad (3-26)$$

into Equation 3-25 yields:

$$\frac{C}{C_s} = \frac{R}{r} \frac{\sinh (3\phi_s r/R)}{\sinh 3\phi_s} \quad (3-27)$$

Equation 3-27 describes the concentration profile of chloramine in the carbon particle with respect to distance (r) into the carbon pore. However, the form of Equation 3-27 is of little use in examining pore

diffusion effects on the chloramine reactions. Rather, from a reaction kinetics viewpoint, it would be more desirable to predict the removal of chloramine from the bulk solution. The rate of disappearance of chloramine per unit weight of particle, m_p , is given by:

$$r_p = \frac{-1}{m_p} 4\pi R^2 D_e \left. \frac{dC}{dr} \right|_{r=R} \quad (3-28)$$

Simplifying Equation 3-28 by substituting

$$m_p = \frac{4}{3} \pi R^3 \cdot \rho_p \quad (3-29)$$

yields

$$r_p = - \frac{3 D_e}{R \rho_p} \left. \frac{dC}{dr} \right|_{r=R} \quad (3-30)$$

The term dC/dr , in Equation 3-30, is obtained by first differentiating Equation 3-25 with respect to r and then evaluating the derivative at $r=R$. Thus, the disappearance rate, r_p , of chloramine at the carbon surface, i.e. from bulk solution, due to surface reaction and diffusion is described by:

$$r_p = \frac{-3 D_e C_s}{R \rho_p} \left[\sqrt{k^* \rho_p / D_e} \coth (\sqrt{k^* \rho_p / D_e} R) - \frac{1}{R} \right] \quad (3-31)$$

If the entire, active carbon surface were exposed to the bulk phase concentration, then diffusion of chloramine through the carbon pores to a reaction site would be eliminated. For this case, the rate

of chloramine conversion would be given by

$$r_s = - k^* C_s \quad (3-32)$$

where r_s is the surface reaction rate with no pore diffusion resistance and k^* the intrinsic rate constant.

The importance of pore diffusion on the chloramine-carbon reactions can be determined by comparing the actual reaction rate of a carbon particle (r_p) to the rate in the absence of pore diffusion (r_s). Because it is often difficult to obtain a diffusion free particle, r_s is not readily evaluated. However, pore diffusion may still be examined quantitatively by defining an effectiveness factor (Thiele, 1939) as the ratio of the actual rate of the particle, r_p , to the rate of a diffusion free particle, r_s

$$\eta = \frac{r_p}{r_s} = \frac{k C_s}{k^* C_s} = \frac{k}{k^*} \quad (3-33)$$

where k represents the observed or global rate constant. As such, η varies from 0 to 1, with lower values indicating strong pore diffusion resistance.

Combining Equations 3-31 and 3-33, the effectiveness factor for a first-order reaction in a spherical particle can also be expressed as:

$$\eta = \frac{r_p}{r_s} = \frac{3 D_e}{k^* \rho_p R} \left[\sqrt{k^* \rho_p / D_e} \coth \left(\sqrt{k^* \rho_p / D_e} R \right) - \frac{1}{R} \right] \quad (3-34)$$

Substitution of ϕ_s , the Thiele Modulus (Eq. 3-26), further simplifies this relationship to:

$$\eta = \frac{1}{\phi_s} \left[\frac{1}{\tanh 3\phi_s} - \frac{1}{3\phi_s} \right] \quad (3-35)$$

The relative importance of diffusion and surface reaction is evident from a plot of Equation 3-35 as given in Figure 4. Small values of ϕ_s correspond to large values of η . Thus in this region, intraparticle mass transport has no effect on the rate and the surface reaction controls. From Equation 3-26, small values of ϕ_s correspond to small particle diameters, large diffusivities and slow intrinsic reaction rates. In contrast, for $\eta \ll 1$ and large ϕ_s , intraparticle transport may control reaction rate. Therefore, large particle diameters, low diffusivities and large intrinsic rates characterize pore diffusion control.

Use of the effectiveness factor, to determine diffusional resistance, requires values for D_e and k^* . While D_e can be estimated from a calculation of bulk diffusivity, k^* cannot be readily evaluated. Therefore, it is necessary to relate this intrinsic rate constant to a measurable kinetic parameter. From Equation 3-33,

$$k^* = \frac{k}{\eta} \quad (3-36)$$

where k , the global rate constant, is a measurable quantity. Substitution of Equation 3-36 into Equation 3-26 gives:

$$\phi_s = \frac{R}{3} \left(\frac{k \rho_p}{\eta D_e} \right)^{1/2} \quad (3-37)$$

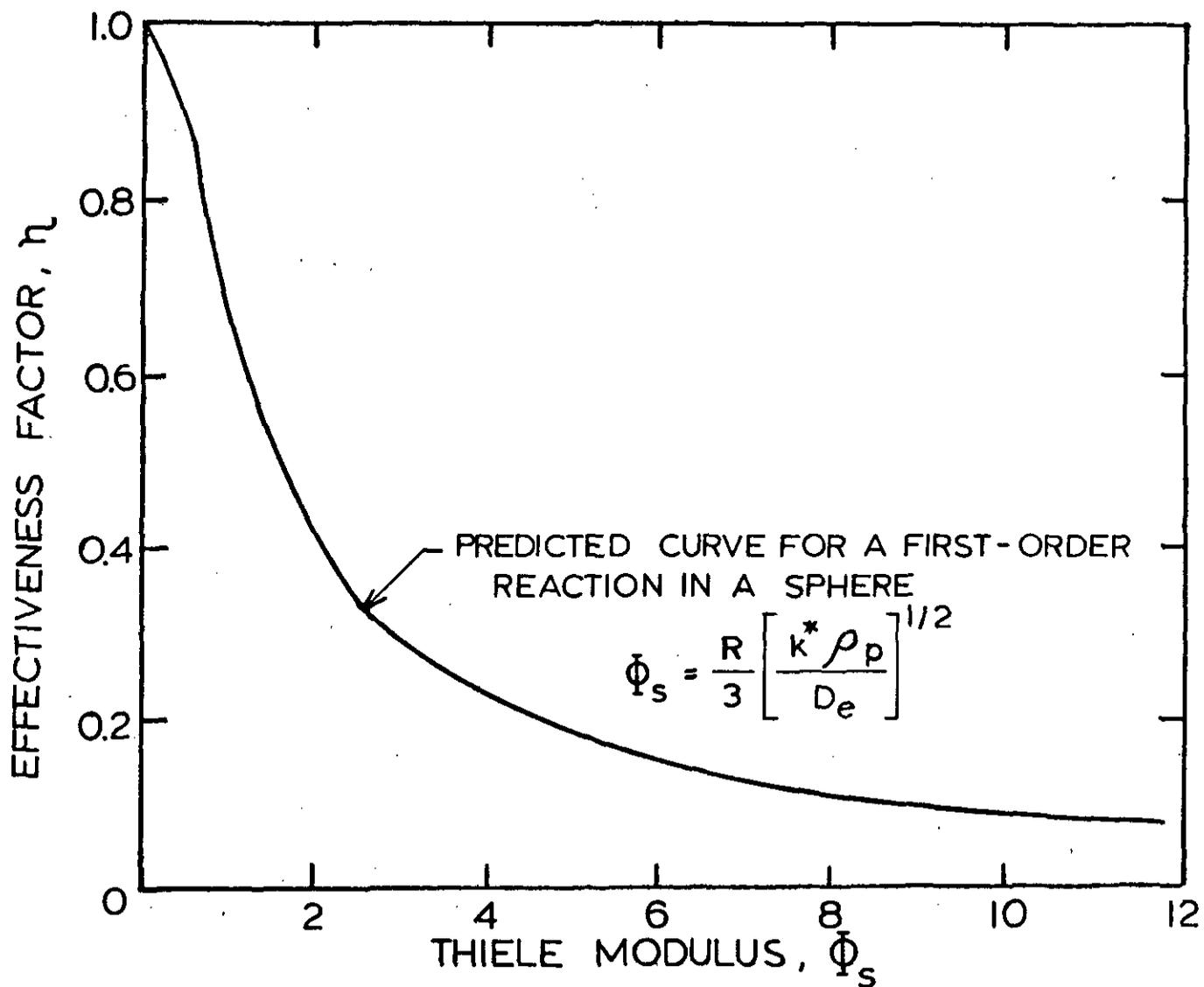


Figure 4. Predicted curve of η and ϕ_s for a first-order reaction in a sphere.

Knowing values of R , k , ρ_p and D_e , simultaneous solution of Equations 3-35 and 3-37 gives the value of η and ϕ_s for a specific carbon particle size. The value of η obtained for a particular particle size indicates the significance of pore diffusion. Additionally, a decrease in particle size should result in an increase in η if the reaction is affected by diffusional resistance.

The preceding diffusion-surface reaction model has been based on the assumption of first-order, irreversible kinetics. For a series of experiments in which carbon particle size is the only variable, the intrinsic rate constant, k^* , can be easily calculated from Equation 36. Although k^* should be constant for all particle diameters, experimental error will undoubtedly cause some variation. To provide a more direct comparison of this experimental data to results predicted theoretically by the first-order reaction-diffusion model, it is possible to calculate a single k^* which provides the best fit to all the data. To obtain the "best" value of k^* , designated as \bar{k}^* , a simple trial and error procedure in which the sum of the squared differences between the observed k_i^* values for each experiment and the selected \bar{k}^* is minimized. That is,

$$\sum_{i=1}^n (\bar{k}^* - k_i^*)^2 = \text{minimum} \quad (3-38)$$

where

$$k_i^* = \frac{k_i}{\eta_i} \quad (3-39)$$

Having determined the value of \bar{k}^* , ϕ_{s_i} can be calculated for each experimental result from

$$\phi_{s_i} = \frac{R_i}{3} \left[\frac{\bar{k}^* \rho_p}{D_e} \right]^{1/2} \quad (3-40)$$

and η_i from:

$$\eta_i = \frac{k_i}{\bar{k}^*} \quad (3-41)$$

The coordinate points (ϕ_{s_i}, η_i) thus experimentally obtained can be compared for "goodness of fit" to the theoretical relationship given by Equation 3-35 and plotted as Figure 4.

C H A P T E R I V
EXPERIMENTAL MATERIALS AND METHODS

Apparatus

A schematic diagram of the laboratory-scale system is presented in Figure 5. The free chlorine solution was prepared from sodium hypochlorite. The ammonia solution consisted of *ammonium chloride* and a buffer for pH control. Both solutions were prepared using chlorine free water in 55 gal (208 l) polyethylene tanks and withdrawn in equal volumes for feed to a clear acrylic mixing reactor. In appropriate experiments, the ammonia feed tank was also used to supply test organics to the carbon contactor. The mixing reactor provided complete formation of chloramines prior to entering the column. In monochloramine studies a two minute residence time was found to be sufficient while 15 minutes was required for dichloramine studies (after Weil and Morris, 1949).

After mixing, test solutions were pumped by a Masterflex pump (Cole-Parmer Corporation, Chicago, Illinois) to a 1.5 inch I.D. clear acrylic column for chloramine-carbon reaction. The column was packed with carbon of the desired particle size range. A sufficiently large ratio of column diameter to particle diameter was used to avoid wall effects. This ratio varied from 31 to 175 for the particle size ranges studied. To insure an equal distribution of flow across the bed, a minimum depth of 10 column diameters of Ottawa sand was packed ahead of the carbon. The sand was the same particle size as the carbon and

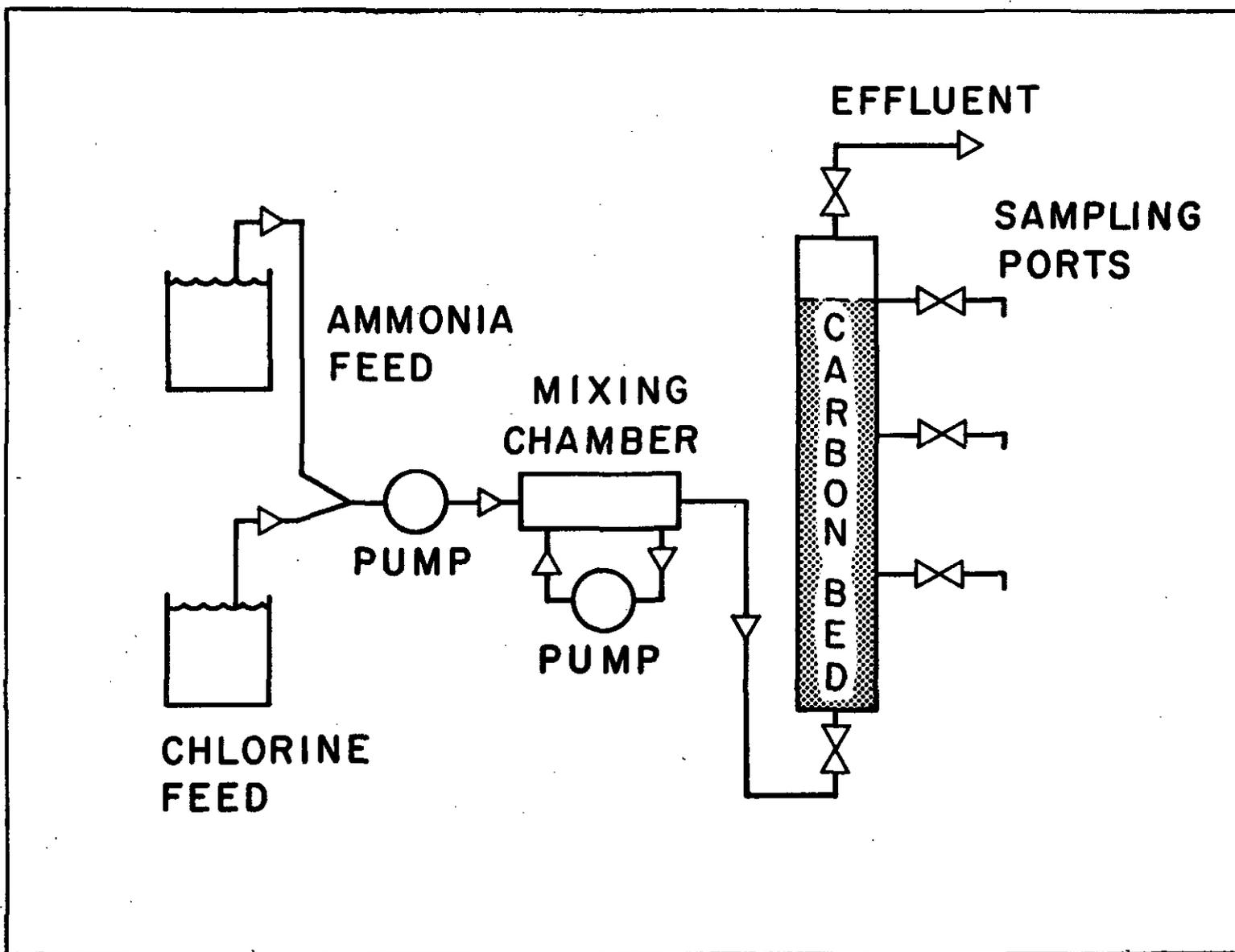


Figure 5. Schematic diagram of laboratory-scale system for formation of chloramine and reaction with activated carbon.

was inert to chloramines. A stainless steel screen (0.01 cm mesh) was emplaced above the carbon to maintain packed bed conditions and while allowing the escape of nitrogen gas. Column application rate was 8.6 gpm/sq ft (350 l/min/sq m) in monochloramine studies and 10.0 gpm/sq ft (407 l/min/sq m) in dichloramine studies; these rates were determined sufficient to minimize film diffusion effects. Upflow operation of the carbon column was essential for escape of nitrogen gas produced by the chloramine-carbon reactions. Ports along the column provided for liquid and carbon sampling and established conversion as a function of space time (W/Q). A gas trap was installed in the effluent stream of the column which provided for periodic gas collection and analysis.

Chloramine Formation

Mono- and dichloramine were formed by the reaction of ammonia with free chlorine (Equations 2-5 and 2-6.) Ammonia and free chlorine solutions were continuously withdrawn from feed tanks and fed to a mixing chamber for chloramine formation. Monochloramine stoichiometry and kinetics were examined at $\text{Cl}_2:\text{NH}_3$ mole ratios of 1:1 and 0.5:1 each with an initial ammonia concentration of 1 mM (2 mM in ammonia feed tank). Mole ratios less than 1:1 will not provide complete ammonia conversion to monochloramine and thus unreacted ammonia will enter the column. At ratios exceeding 1:1, breakpoint reactions occurred resulting in a decrease in influent monochloramine concentration (see Figure 3). Studies were conducted at pH 7.7, 8.3 and 9.1. A phosphate buffer (2.83×10^{-2} M Na_2HPO_4 and 0.17×10^{-2} M KH_2PO_4) was used for studies

at pH 7.7 and 8.3 while a borate buffer (2×10^{-2} M $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10 \text{H}_2\text{O}$) was used at pH 9.1. The pH of the buffered ammonia and free chlorine solutions was adjusted to desired initial pH using H_2SO_4 or NaOH.

Dichloramine-carbon stoichiometry was examined using a column influent concentration of 0.98 mM NHCl_2 . This solution was maintained by operating at a $\text{Cl}_2:\text{NH}_3$ mole ratio of 1.4:1 with an initial ammonia concentration of 2 mM. Kinetics of the dichloramine-carbon reaction were examined at a $\text{Cl}_2:\text{NH}_3$ mole ratio of 1:1 with an initial ammonia concentration of 1 mM prior to chlorination. Dichloramine studies were conducted at pH 4.2 using a phosphate buffer (2.86×10^{-2} M KH_2PO_4) in the ammonia feed tank. Initial pH of the buffered ammonia and chlorine solution were adjusted by addition of H_2SO_4 . It should be noted that dichloramine formation was unstable and breakpoint reactions occurred at mole ratios less than 1:1.

Selection of Test Organics

Dodecylbenzenesulfonate (ABS), 2,4-dinitrophenol (DNP) and methylene blue (MB) were selected as model organic compounds for determining the effect of organics on the chloramine-carbon reactions. ABS (mol wt 348) is representative of linear anionic detergents which comprise a significant fraction of organics in wastewater (Rebhun and Manka, 1971). MB (mol wt 347) is a basic organic dye with a molecular weight similar to ABS but containing three benzene rings. DNP (mol wt 184), a breakdown product of phenolic pesticides, was selected for its large dipole moment (3.3 debyes @ 20°C benzene) to determine if removal of

polar organic compounds could be enhanced by the presence of acidic surface oxides on the carbon. That is, according to Equations 1-2 and 1-3 an increase in surface oxide level accompanies conversion of chloramine to nitrogen gas and as a result, surface polarity should also increase which may enhance removal of polar organics. Concentration of test organics was 20 mg/l in all experiments with the exception of MB (30 mg/l) in the monochloramine study.

The reactivity of the test organics with free chlorine was determined in simple, batch kinetic experiments. All three organics did not react with chlorine (1.0 mM) above pH 7.7 after 10 minutes of contact. At pH 4.2, a slight reaction was observed for MB and DNP. A decrease in chlorine and organic concentration of 5 percent was observed for DNP after a reaction time of 10 minutes, while an 8 percent decrease was noted for MB.

Alum clarified, raw wastewater from the University of Massachusetts pilot plant was fed to the contactor to determine the effect of a mixture of organic compounds on the chloramine-carbon reactions. Parallel column studies were conducted using chlorinated and non-chlorinated wastewater feeds. From measurements of COD and TOC, there was no detectable oxidation of organics by free chlorine in the chloramine mixing reactor. However, the formation of chlorinated organics and their subsequent removal by carbon contact was not determined. Jolley (1975) examined chlorination of primary effluent and found that about 1 percent of the original chlorine dosage was associated with formation of stable chlorine-containing organic compounds.

Analytical Materials and Methods

Activated Carbon. The activated carbon used in this study was coal base, Filtrasorb 400 (Calgon Corporation, Pittsburgh, Pennsylvania). This carbon was mechanically sieved to obtain a range of particle sizes. Carbon was then washed and dried at 105°C prior to use in all experiments. Specifications on the carbon are listed in the manufacturer's bulletin (Calgon Corporation, Pittsburgh, Pennsylvania, 1969).

Analytical Methods. The DPD Ferrous Titrimetric Method (Standard Methods, 1971) was used to determine concentrations of free chlorine, mono- and dichloramine and nitrogen trichloride. A recent comprehensive study (Public Health Service, 1969) on nine analytical methods of determining free and combined chlorine residuals rate the DPD method as the most accurate and precise. Wei and Morris (1973) examined the method in detail and concluded that dichloramine could be determined within a 2.0 percent error while the error in monochloramine determination was 6.5 percent. All samples were analyzed immediately after being taken.

Ammonia and chloride concentrations were determined by specific ion electrodes (Orion Research Electrodes, Orion Research, Cambridge, Massachusetts). The "known addition" method of analysis was employed for both determinations. Use of the electrodes provided for rapid and accurate measurements. Error in ammonia analysis was 4.0 percent with a lower limit of detection of 0.017 mg/l NH₃, while a 2.0 percent error was incurred in chloride analysis with a lower detection limit of 1.5 mg/l Cl⁻. There was no interference of chloramines or organic compounds on electrode measurements.

Nitrate formation was determined by the Chromatropic Acid Method (Standard Methods, 1971). This method was selected over other available methods because chlorides, oxidants and organic matter do not interfere with the analysis. Relative error for the analysis was 3.0 percent. For pH measurements, a Radiometer Dual Electrode pH meter (Radiometer, Copenhagen, Denmark) was employed.

Acidic surface oxides were determined by titration with an aqueous solution of NaOH (after Boehm, 1966). Small quantities of carbon were periodically withdrawn from the column and dried at 105°C. A known volume of base (25 ml of 0.02 N NaOH) was then added to a bottle containing 0.2 g of dried carbon. Following 48 hours of agitation, a 20 ml aliquot of supernatant was withdrawn and back-titrated with acid (0.02N HCl) to a pH 8.3 endpoint to determine the concentration of unreacted base. Acidic surface oxide concentration is the amount of base consumed per gram of carbon, me/g, and can be calculated as:

$$\text{Surface Oxide Concentration} = \frac{[0.5 \text{ me base added} - 1.25^*(\text{ml acid titrated})]}{X [0.02 \text{ me acid/ml}]} \times \frac{1}{0.2 \text{ g carbon}} \quad (4.1)$$

me/g

Surface oxide data obtained in the research can only be used as a general trend in examining chloramine-carbon reactions due to the quantitative inaccuracy of the procedure. This is supported by recent research by Snoeyink et al. (1973), in which only a fraction of the surface oxides produced by the chlorine-carbon reaction were measured

* To calculate the amount of unreacted base remaining in the original 25 ml sample, the quantity of acid back-titrated with the 20 ml aliquot is multiplied by 1.25.

by this same titration procedure. Therefore, it can be inferred that surface oxide data will not give a direct stoichiometric relationship between chloramines reacted and oxides produced. However, a general increase in surface oxide concentration should be observed as chloramine-carbon reactions proceed.

This research has also shown that the buffer systems used to maintain system pH will prevent direct measurement of surface oxides by titration. Figure 6 presents surface oxide data for experiments in which monochloramine (pH 8.3) and dichloramine (pH 4.2) were reacted with the carbon surface. Without examining the effect of the buffer on the titrant volume used, it would appear that more surface oxides were produced by the dichloramine reaction. However, as also shown in Figure 6, the buffer solution-carbon system alone at pH 4.2 required significantly less volume of back titrant to be used than the buffer-carbon system at pH 8.3. Both experiments confirm the fact that buffers are adsorbed into the carbon pores and are not removed by surface washing and drying. These adsorbed buffers then react with NaOH and produce the same effect as a surface oxide site. The results given in Figure 6 indicate that the base requirement of adsorbed buffer at pH 4.2 was greater than that at pH 8.3. This can be explained by the extra amount of base required to raise the pH from 4.2 to 8.3, the eventual endpoint of back titration with strong acid. Beyond pH 8.3, base consumption for both buffer-carbons systems would be the same because concentrations were equal. Thus, with the added equivalents of OH^- ion being equal for both systems,

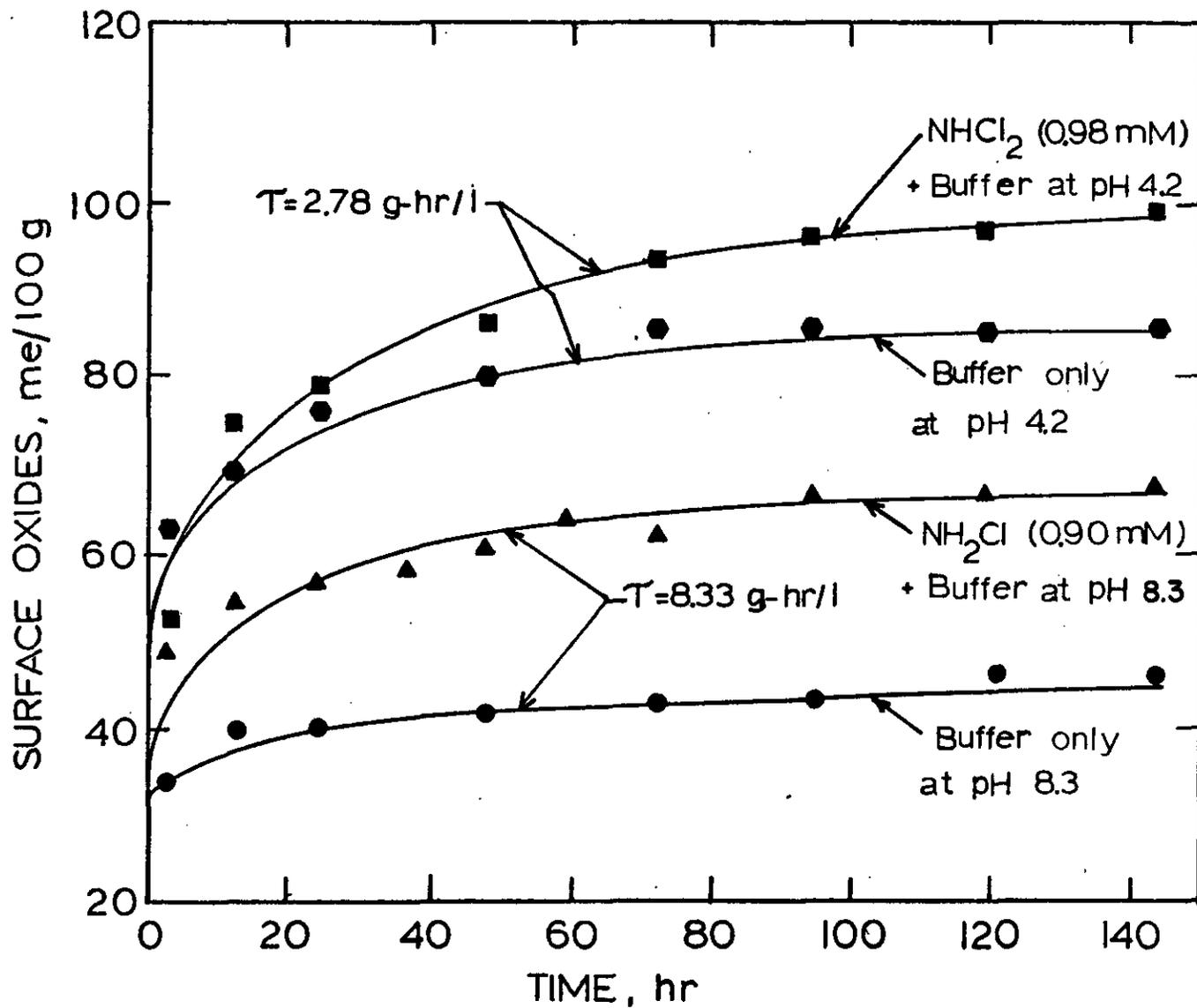


Figure 6. Interaction of buffer on surface oxide titration at pH 4.2 and 8.3.

less OH^- ions will be left in the original pH 4.2 system. This buffer effect will then prevent direct comparison of surface oxides in mono- and dichloramine experiments.

Selected test organics were identified spectrophotometrically using a Perkin Elmer-Coleman 111 Spectrophotometer (Perkin Elmer Corporation, Norwalk, Connecticut). Wavelengths for maximum absorbance of ABS, MB and DNP were 224, 668 and 360 nm, respectively. In wastewater studies, organics were measured by TOC or COD. A Beckman Total Organic Carbon Analyzer (Beckman Instruments, Fullerton, California) was used to monitor TOC while COD was determined according to the procedure given by Standard Methods (1971).

Gaseous end products produced by the chloramine-carbon reactions were periodically captured and analyzed on a Varian Aerograph 2760 gas chromatograph (Varian Aerograph, Walnut Creek, California). Based on studies by D'Agostaro (1972), Stasuik et al. (1973) and Pressley et al. (1972), effluent gases were analyzed for N_2 , CO, CO_2 , O_2 and H_2O . Gas chromatographic operating specifications were as follows:

Detector	Thermal Conductivity
Carrier gas	Helium
Column	Carbonsieve-B
Packing	140 x 170 mesh
Length	2 meters
Flowrate	42 ml/min
Temperature Program	Hold 37°C for 4 minutes, increase $40^\circ/\text{minute}$ to 180°C .

Experimental Program

Research on the chloramine-carbon reactions examined stoichiometry, kinetics and the effect of adsorption of organics on process performance. A continuous flow, packed bed reactor was operated at room temperature for all experimentation (20-23°C).

Monochloramine-Carbon Studies. Stoichiometry and kinetics were examined at pH 7.7, 8.3 and 9.1 using $\text{Cl}_2:\text{NH}_3$ mole ratios of 1:1 and 0.5:1. The ammonia concentration was 1 mM prior to chlorination in each experiment. After reaction with chlorine, the feed concentration of monochloramine to the packed bed was 0.90 mM in experiments with an initial $\text{Cl}_2:\text{NH}_3$ ratio of 1:1 and 0.50 mM with a ratio of 0.5:1. Both free chlorine and dichloramine were absent. Monochloramine solution was passed upflow through 600 g of activated carbon at an application rate of 8.6 gpm/sq ft.

Operating the carbon bed as an integral reactor, three ports were located along its length to provide for liquid and carbon sampling. Samples were withdrawn from the column in order of largest to smallest space time. For a given operating time, the feed solution was sampled last. To minimize upset of bed hydraulics, the rate of liquid sample withdrawal was kept below 10 percent of the upflow rate. Following liquid sample withdrawal, approximately 1 g of carbon was removed at each space time to measure surface oxides. In each experiment, analyses consisted of free chlorine, mono- and dichloramine, ammonia, chloride, nitrate, surface oxide concentration and pH. With the exception of surface oxide measurement, all analyses were conducted immediately after withdrawal of samples. Concentration profiles with respect to distance within the reactor (i.e. space time) and reactor operating time were of interest.

Using a 12 x 20 U.S. Standard mesh carbon, the average particle diameter was 0.12 cm. Space times (W/Q) at the sampling ports were 8.33, 16.66 and 25 g-hr/l. These correspond to empty bed contact times of 1.3, 2.6 and 3.9 minutes. In kinetic studies, another particle size range (30 x 40 mesh), yielding an average diameter of 0.05 cm, was used for comparative analysis of rate control by pore diffusion; here space times were 8.53, 17.75 and 23.75 g-hr/l or 1.33, 2.8 and 3.7 minutes of empty bed contact.

The reactor was operated continuously until a pseudo, steady-state condition was reached when no detectable change occurred in monochloramine conversion and ammonia production for 48 hours. This approach to pseudo steady-state usually required approximately 140 hours of operation. In one experiment, operation was extended to 250 hours to determine if any further slow change in conversion would occur.

The gaseous end product of monochloramine-carbon stoichiometry was measured from gas samples collected after 140 hours of reactor operation. About 5 hours were required to obtain 800 cc of gas for further analysis. In these experiments, no organic compounds were present.

Dichloramine-Carbon Studies. In all experiments, phosphate buffer was added to control pH at 4.2, where maximum formation of dichloramine occurs. However, at a $\text{Cl}_2:\text{NH}_3$ ratio of 1.4:1, dichloramine could not be totally isolated; instead, the feed stream contained 0.98 mM dichloramine, 0.035 mM free chlorine, 0.07 mM nitrogen trichloride and 0.35 mM of unreacted ammonia. Because of the much faster conversion rate of dichloramine than monochloramine, bed mass was reduced from 600 g to 80 g of 12 x 20 mesh carbon. The

application rate was 10 gpm/sq ft. In comparison with the reactor used in monochloramine-carbon studies, space time was greatly reduced such that samples were only taken from the feed and exit streams. Although a phosphate buffer was used, the buffer capacity was slightly exceeded by production of hydrogen ions from the dichloramine-carbon reaction (Equation 1-3) such that pH dropped from 4.2 to 3.8 through the reactor length. This reactor was operated for 1000 hours to observe the poisoning effect caused by build-up of surface oxides.

A lower $\text{Cl}_2:\text{NH}_3$ mole ratio of 1:1 was used in another series of experiments. This ratio produced a feed stream containing 0.37 mM dichloramine, 0.02 mM free chlorine, 0.03 mM nitrogen trichloride and 0.41 mM of unreacted ammonia. To obtain kinetic data of dichloramine conversion as a function of space time, the carbon mass in the reactor was varied while holding feed concentration and flowrate constant. This procedure was required because the conversion rate was too fast to allow accurate measurements at sampling ports along the reactor length. To determine the importance of pore diffusion control, the following different particle size fractions were used in a series of experiments: 12 x 20 mesh ($D_{\text{avg}} = 0.120$ cm); 30 x 40 mesh ($D_{\text{avg}} = 0.050$ cm); 50 x 60 mesh ($D_{\text{avg}} = 0.027$ cm) and 60 x 80 mesh ($D_{\text{avg}} = 0.021$ cm).

Interaction of Adsorption and Chloramine-Carbon Conversions. The interaction of adsorption of organics with the chloramine-carbon reactions was investigated by applying specific test organics and either mono- or dichloramine simultaneously to a fresh carbon bed (600 g).

Monochloramine studies were performed at pH 8.3 at a $\text{Cl}_2:\text{NH}_3$ mole ratio of 1:1. The feed to the carbon bed contained 0.90 mM monochloramine, 0.02 mM unreacted ammonia and one of the following specific test organics: ABS (20 mg/l), MB (30 mg/l) or DNP (20 mg/l). Operation of the reactor was continued until total breakthrough of the test organic occurred. The effect of organics on the rate of monochloramine conversion and nitrogen production was determined by comparative analysis of experimental data taken with and without the addition of these test organics. Similarly, the effect of monochloramine-carbon reactions on organic adsorptive capacity was measured by comparing results of experiments in which the feed solution contained only the test organic and the phosphate buffer with those in which monochloramine was also added. In another series of experiments, alum clarified, raw wastewater, containing an average ammonia concentration of 16 mg/l as NH_3 , was chlorinated and fed to the carbon bed reactor. A sodium hypochlorite dosage of 66 mg/l as Cl_2 produced a $\text{Cl}_2:\text{NH}_3$ mole ratio of 1:1. System pH was maintained at 8.3 using a phosphate buffer. Because of the varying composition of wastewater, feed concentrations of monochloramine ranged from 0.56 to 0.77 mM and unreacted ammonia from 0.01 to 0.05 mM; additionally feed TOC ranged from 20 to 25 mg/l. Operation of the reactor was continued until an apparent steady-state condition was reached where monochloramine conversion remained constant for 48 hours.

In studies of simultaneous organic adsorption and dichloramine conversion, the test organics were MB (20 mg/l) and DNP (20 mg/l). Their presence sufficiently reduced the rate of dichloramine reaction such that

column profiles of concentration within the reactor could be obtained. All other experimental conditions of dichloramine feed were identical to those described previously for kinetic experiments.

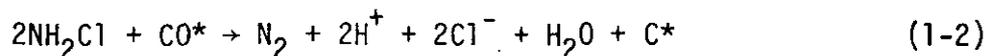
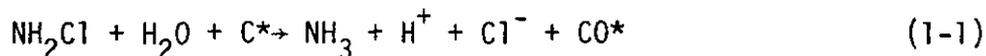
Additionally, chlorinated and non-chlorinated wastewaters were fed in parallel to two different carbon reactors. Each reactor contained 1000 g of carbon (12 x 20 mesh). At a $\text{Cl}_2:\text{NH}_3$ mole ratio of 1:1 and pH 4.2, the feed concentration of dichloramine ranged from 0.28 to 0.35 mM and unreacted ammonia from 0.35 to 0.40 mM; additionally feed COD ranged from 40 to 70 mg/l. Insufficient buffer capacity of the chlorinated feed solution caused pH to decrease from 4.2 to 3.8 within the reactor.

C H A P T E R V

RESULTS AND DISCUSSION - MONOCHLORAMINE-CARBON REACTIONS

Monochloramine Stoichiometry

A parallel pathway for monochloramine-carbon reaction was proposed by Bauer and Snoeyink (1973):



The nitrogen gas yield from the reactions is given by

$$\% \text{ N yield} = \frac{(\Delta\text{NH}_2\text{Cl}) - (\Delta\text{NH}_3)}{(\Delta\text{NH}_2\text{Cl})} \times 100 \quad (5-1)$$

where $\Delta\text{NH}_2\text{Cl}$ represents the overall decrease in monochloramine according to Equations 1-1 and 1-2, and ΔNH_3 the increase in ammonia according to Equation 1-1. Thus the fraction of monochloramine reacting to produce ammonia can be subtracted from the total reacted to calculate percent nitrogen gas production, i.e. % N yield.

Approach to Apparent Steady-State Conversion. The approach to apparent steady-state conditions of nitrogen gas (N) yield, surface oxide level and unreacted monochloramine are shown in Figure 7 for a typical monochloramine-carbon experiment. This data was obtained at a space time (W/Q) of 25 g-hr/l which corresponded to an empty bed contact time of 4.0 minutes. After 1.5 hours of column operation, feed monochloramine was predominantly converted to ammonia with some nitrogen gas production; nitrogen yield was 8 percent at this operating time. Thus, nitrogen gas was initially produced without significant surface oxide formation from ammonia production. This suggests that an acclimation period was not required for nitrogen gas formation to occur. Additionally, the data indicates that virgin carbon contains a significant quantity of titratable

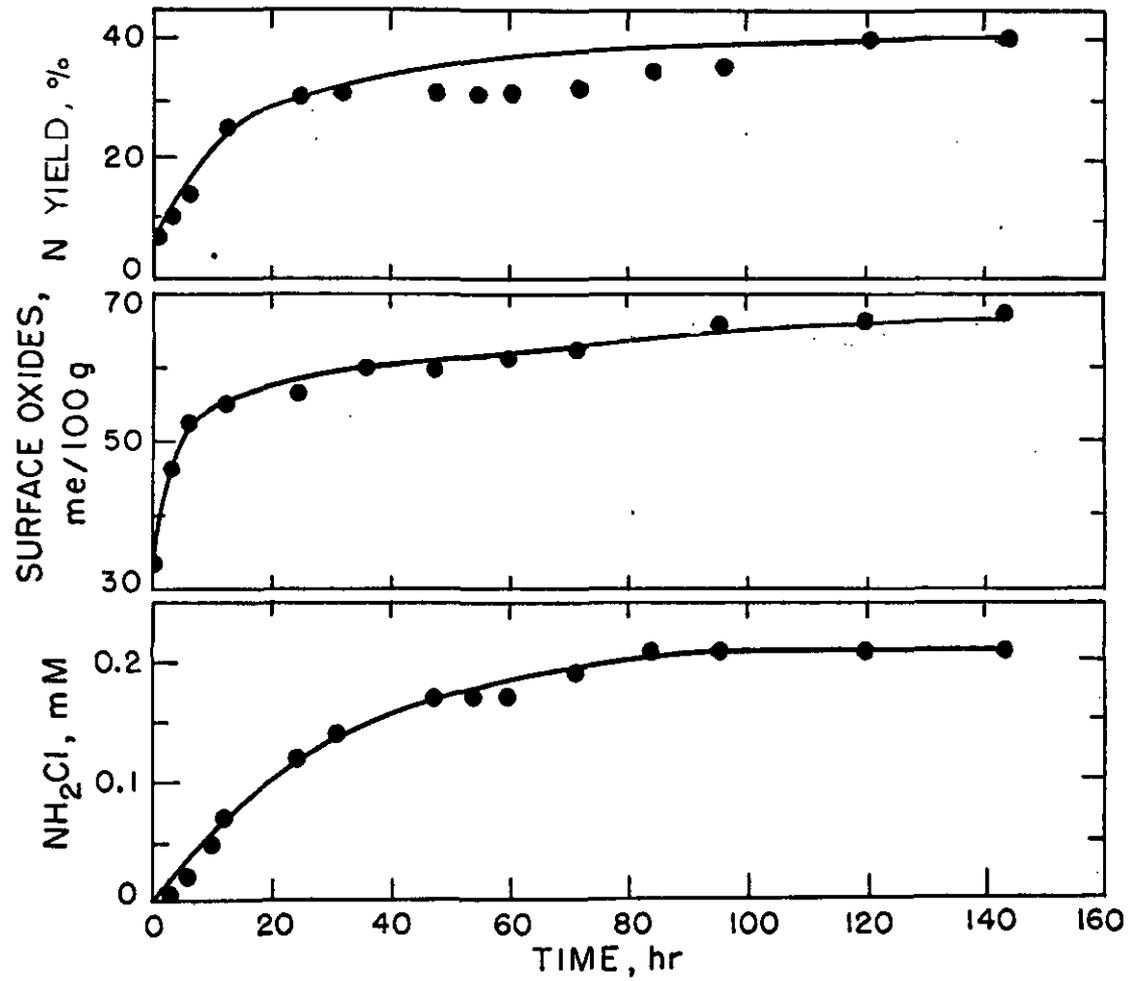


Figure 7. Nitrogen yield, surface oxide level and effluent monochloramine concentration with operating time for influent $\text{NH}_2\text{Cl}=0.90\text{mM}$, $D_p=0.12\text{cm}$ and $W/Q=25\text{g-hr/l}$ at pH 8.3.

surface complexes. It is quite possible that some of these complexes are of the proper form to promote the reaction of monochloramine to nitrogen gas.

The relationship between the monochloramine reacted ($\Delta\text{NH}_2\text{Cl}$) and nitrogen yield deserves closer attention. Figure 7 indicates that as reactor operation continued, less monochloramine was converted; i.e. exit NH_2Cl concentration increased. This could alter production of either ammonia or nitrogen gas. By rewriting Equation 5-1 as,

$$\% \text{ N yield} = \left[1 - \frac{\Delta\text{NH}_3}{\Delta\text{NH}_2\text{Cl}} \right] \times 100 \quad (5-2)$$

it is apparent that a decrease in $\Delta\text{NH}_2\text{Cl}$ was accompanied by a much larger decrease in ΔNH_3 in order for % N yield to increase with operating time. Thus, of the two pathways for monochloramine conversion, a shift to greater nitrogen gas and less ammonia production occurred at longer operating times.

The monochloramine-carbon reactions were non steady-state as indicated by the increase in monochloramine concentration leaving the reactor with time; however, after 140 hours of column operation, an apparent steady-state condition was reached corresponding to 42 percent nitrogen yield. Continued operation for 250 hours did not increase yield. However, according to the reaction mechanisms given by Equations 1-1 and 1-2 as proposed by Bauer and Snoeyink (1973), 67 percent nitrogen yield should be attained at true equilibrium. Although it is impossible to state that equilibrium had been achieved in the experiment described above, there is also reason to question the elementary mechanism proposed

by Bauer and Snoeyink. In this regard, two experimental observations are noteworthy. First, the initial formation of nitrogen gas suggests that the reaction may depend upon the surface properties of the virgin carbon and secondly, the rapid decrease in ammonia production with time indicates an interference with the surface reaction given by Equation 1-1. Further exploration of alternative mechanistic explanations for monochloramine conversion will follow in a later section.

Chloride Balance. A chloride mass balance was performed to further verify the surface reaction pathway for monochloramine conversion with subsequent release of chloride. Results presented in Table 1 indicate that the chloride produced by the reactions was stoichiometrically equal to the monochloramine reacted; the maximum discrepancy was 2.5 percent. This result is in agreement with Equations 1-1 and 1-2. Furthermore, there was no initial uptake of Cl-containing species again indicating that adsorption of monochloramine without subsequent surface reaction does not occur. Mass balances on Cl-species were performed in all monochloramine studies with very reproducible results.

By-Product Gas Analysis. After 140 hours of reactor operation, apparent steady-state conditions had been reached where nitrogen gas production seemed constant. The resulting composition of gas leaving the reactor after this time is given in Table 2. As shown, nitrogen comprised 92.9 percent of the gas collected. This very large percentage of nitrogen gas found, supports the general pathway of monochloramine conversion proposed by Bauer and Snoeyink (1973) and confirms previous gas analyses performed by D'Agostaro (1972) and Stasiuk et al. (1973).

Table 1

Chloride Balance - Monochloramine-Carbon Reactions

time hr	NH ₂ Cl reacted mM	Chlorides produced mM
3	0.95	0.93
6	0.93	0.93
8	0.88	0.90
12	0.88	0.87
24	0.77	0.76
48	0.70	0.70
72	0.67	0.63
96	0.70	0.70
120	0.70	0.70
144	0.70	0.70

Table 2

Monochloramine-Carbon By-Product Gas Analysis
at Apparent Steady-State

N_2	92.9 %
CO	0.9 %
CO ₂	0.5 %
O ₂	4.8 %
H ₂ O	1.0 %

The small fractions of CO and CO₂ present could have resulted from decomposition of surface oxides, while oxygen may have been produced by decomposition of oxides or by release of dissolved oxygen from the liquid stream.

The fact that surface oxides evolve from the carbon may account for the less than theoretical nitrogen yield. Surface oxides, formed from ammonia production, may be unstable and would rapidly be removed from the surface as CO and CO₂, thus not allowing sufficient reaction time necessary for nitrogen gas production.

Surface Oxides. As discussed in the Analytical Materials and Methods Section, acidic surface oxide data can only indicate a general trend in examining stoichiometry due to the quantitative inaccuracy of the procedure. Figure 8 shows the level of surface oxides with operating time at pH 8.3 for two reactor space times of 8.33 and 25 g-hr/l. Assuming the experimental reactor to operate in plug flow fashion, the highest concentration of oxides should be expected at the feed end of the reactor where the monochloramine concentration is highest. However, the data indicates no significant difference in apparent surface oxide level at the two reactor space times selected.

Because of the inaccuracy of the procedure for measuring surface oxides, it is difficult to interpret these results. Oxide titrations were performed after the carbon had been dried at 103⁰C. Snoeyink et al. (1973) (Figure 3) indicated that a large fraction of titratable surface oxides were lost on drying. Therefore, it is possible that drying the

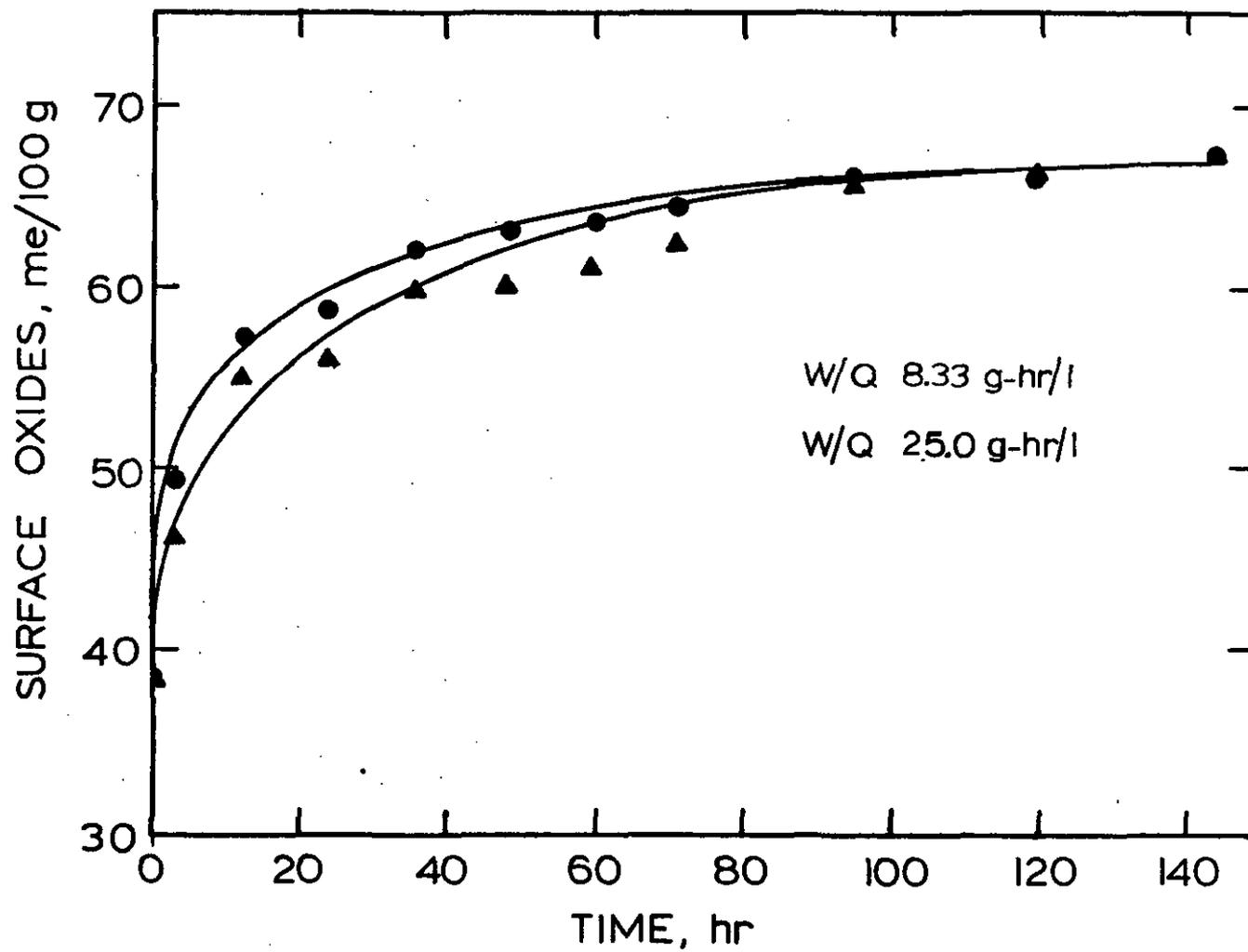


Figure 8. Surface oxide column profile with operating time.

carbon prior to titration may have had the overwhelming effect of reducing the oxide level at all sampling locations. Additionally, the buffer solution, used to maintain system pH, contributed significantly to the surface oxide titration. Because the concentration of buffer did not appreciably change throughout the column (approximately 10^{-2} M as PO_4^{-2}), a uniform buffer interference on oxide titration also resulted. This interference would then mask any significant difference in surface oxide level due to surface reaction.

Effect of pH on Monochloramine Conversion. If the monochloramine-carbon reactions proposed by Bauer and Snoeyink (1973) are controlled by stoichiometry, then a change in system pH should not alter steady-state monochloramine conversion or nitrogen gas yield. To test this hypothesis, the reactions were examined at pH 7.7, 8.3 and 9.1.

In Figure 9, the fractional monochloramine concentration ($\text{NH}_2\text{Cl}/\text{NH}_2\text{Cl}_0$) leaving the reactor is shown as a function of operating time for the three pH conditions studied. Initially, monochloramine was completely removed regardless of pH. However, as operation continued, a greater amount of unreacted monochloramine was found at higher pH. At higher pH, the apparent steady-state (140 hours) rate of overall monochloramine conversion was necessarily lower. This decrease in conversion with increasing pH suggests that basic compounds interfere with surface reaction sites which convert monochloramine to either ammonia or nitrogen gas. That is, basic compounds may compete with monochloramine for adsorption/reaction

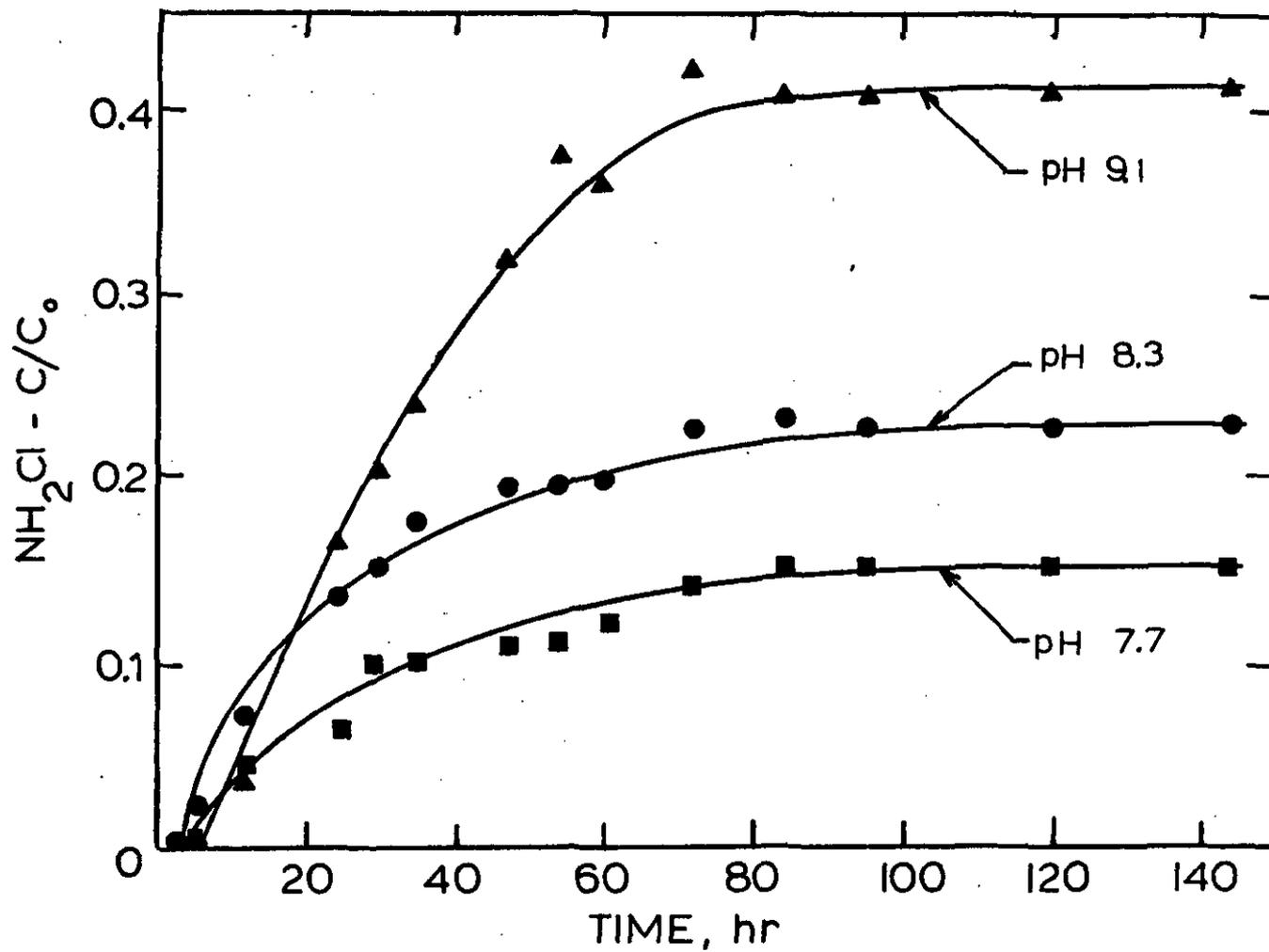


Figure 9. Effect of pH on monochloramine conversion for influent $\text{NH}_2\text{Cl}=0.90$ mM.

sites with the net effect being a reduced rate of monochloramine conversion as a result of inhibited ammonia and/or nitrogen gas production. It may further be reasoned that the approach to steady-state conversion is controlled by the adsorption kinetics of basic compounds present in the feed stream rather than the production of surface oxides as given by the stoichiometry of Equation 1-1. For this experimental reactor, the feed solution contained a phosphate buffer and hydroxide ions, both of which contribute to basicity.

Of the two pathways for monochloramine to react, Figure 10 clearly shows that conversion to nitrogen gas was significantly reduced at higher pH. After 140 hours of operation, an apparent steady-state condition was reached where nitrogen yield at pH 7.7, 8.3 and 9.1 was 47, 42 and 34 percent, respectively. Additionally, ΔNH_3 was decreased with increasing pH. For nitrogen yield to decrease at higher pH, Equation 5-2 shows that the ratio of $\Delta\text{NH}_3/\Delta\text{NH}_2\text{Cl}$ must increase:

$$\text{N yield, \%} = \left[1 - \frac{\Delta\text{NH}_3}{\Delta\text{NH}_2\text{Cl}} \right] \times 100 \quad (5-2)$$

For this ratio to increase, the decrease in $\Delta\text{NH}_2\text{Cl}$ must be greater than the decrease in ΔNH_3 . Therefore, decrease in $\Delta\text{NH}_2\text{Cl}$ is comprised of decreases in both ΔNH_3 and ΔN_2 . Thus, increased pH reduced both nitrogen yield and ammonia production. This experimental evidence is in support of interference caused by basicity.

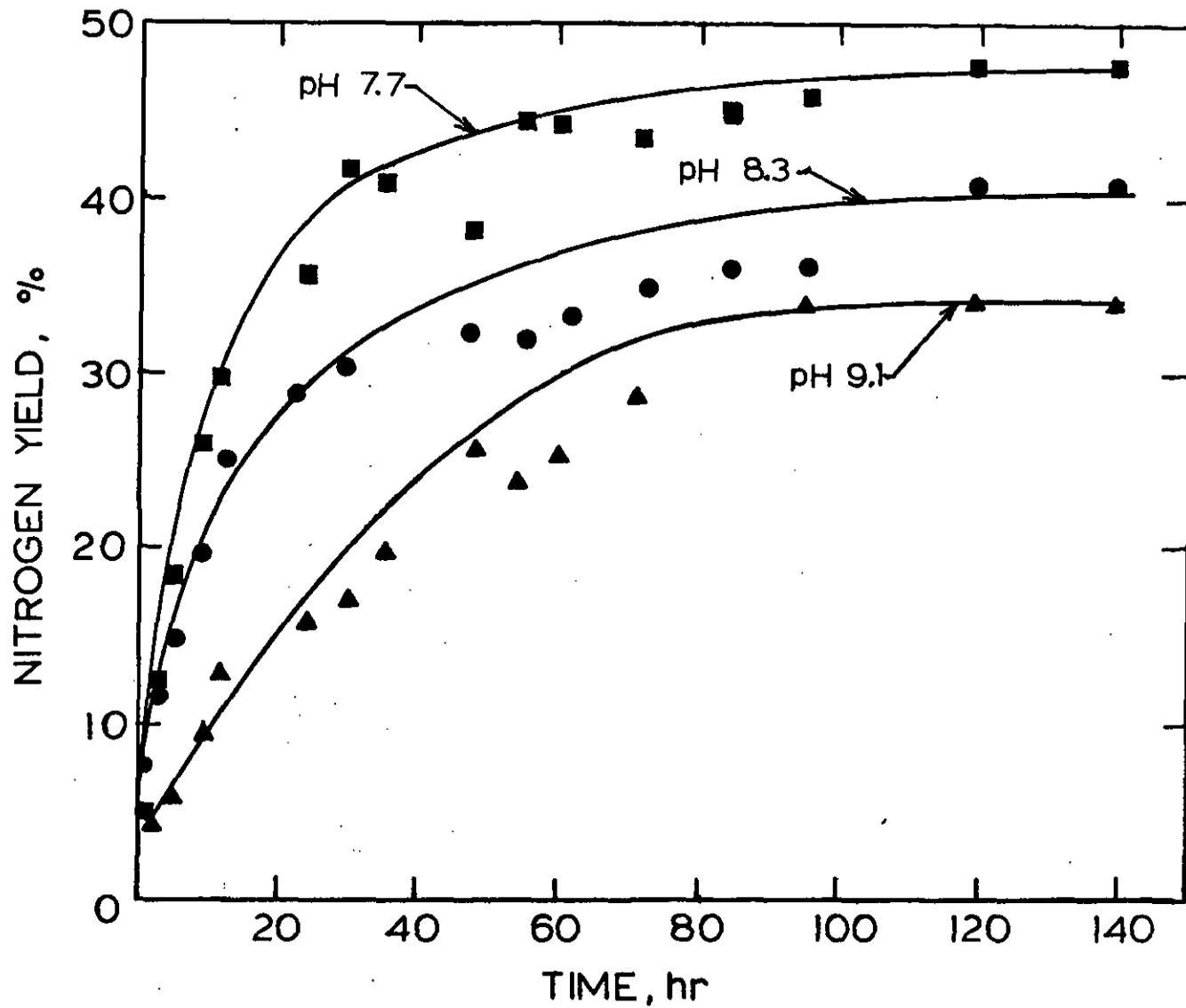


Figure 10. Effect of pH on nitrogen gas yield for influent $\text{NH}_2\text{Cl}=0.90$ mM.

Another explanation for the effect of pH on stoichiometry and rate is derived from considering local pH within the carbon pores. Although the feed solution was buffered, it is still possible for pH to be depressed in the carbon pores due to the production of hydrogen ions by monochloramine-carbon reactions. If this occurs, then dichloramine species could form (Figure 2) which would, according to Bauer and Snoeyink (1973), be converted to nitrogen gas. However, this explanation seems unlikely because ammonia production should also have been decreased at lower pH as a fraction of mono- was converted to dichloramine. The experimental results showed the opposite effect of pH on ammonia production.

Monochloramine Kinetics

Concentrations of monochloramine and ammonia were measured at various space times within the reactor to test the first-order kinetic model given by Equation 3-6 for pseudo steady-state conditions. The resulting semi-logarithmic plots of remaining monochloramine as a function of space time after different operating times is given in Figure 11. From this data, the assumption of a first-order, irreversible surface reaction provides a reasonable kinetic model. The fact that the global rate constant, $k_T \text{ NH}_2\text{Cl}$, decreased at longer operating times indicates a non-steady state condition. However, after 140 hours the rate of monochloramine conversion became constant and an apparent steady-state condition was reached. The decrease in the global rate constant with operating time is consistent with the observation of decreased monochloramine conversion as given in Figure 7. As noted earlier in Equation 3-3,

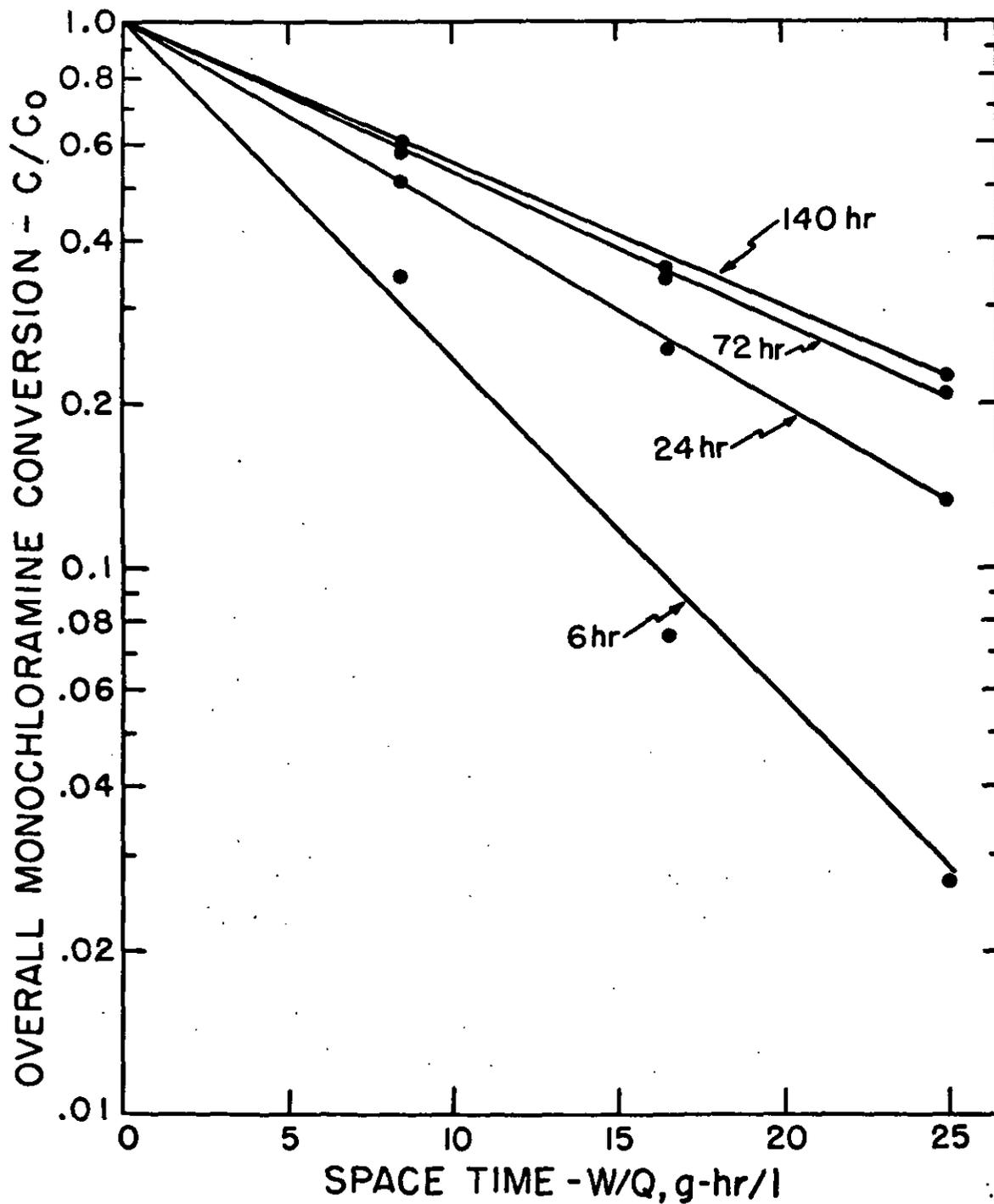


Figure 11. First-order conversion of monochloramine with reaction time (space time) in the carbon bed at various operating times for influent $NH_2Cl=0.90$ mM, $D_p=0.12$ cm and pH 8.3.

the overall rate of monochloramine conversion is the sum total of the rate of ammonia production (r_{NH_3}) and nitrogen gas production (r_{N_2}). These rates are changing with operating time such that the net effect is a reduced overall rate. However, without further data analysis, it is impossible to conclude whether or not both rates are reduced.

Figure 12 shows that the concentration profile of ammonia decreased as operating time increased suggesting a decreasing rate of ammonia production. After 140 hours of operation, the concentration profile of ammonia in the reactor remained constant and an apparent steady-state condition was reached.

From the observations of overall rate of monochloramine conversion (Figure 11) and ammonia production (Figure 12), the first-order rate constants for ammonia (k_1) and nitrogen gas (k_2) formation can be calculated according to the mathematical development given by Equations 3-7 to 3-10. Figure 13 shows the resulting plots of Equation 3-10 yielding k_1/k_2 at different operating times. The linearity of the data verifies the assumption of first-order formation. From k_1/k_2 and $k_T \text{NH}_2\text{Cl}$, the values of k_1 and k_2 can be calculated.

The shift in reaction rate constants as operation of the reactor continued can be examined by plotting k_1 , k_2 and $k_T \text{NH}_2\text{Cl}$ as shown in Figure 14. While k_2 decreased only slightly, k_1 decreased dramatically thus depressing the overall monochloramine rate constant, $k_T \text{NH}_2\text{Cl}$, because:

$$k_T \text{NH}_2\text{Cl} = k_1 + k_2 \quad (3-5)$$

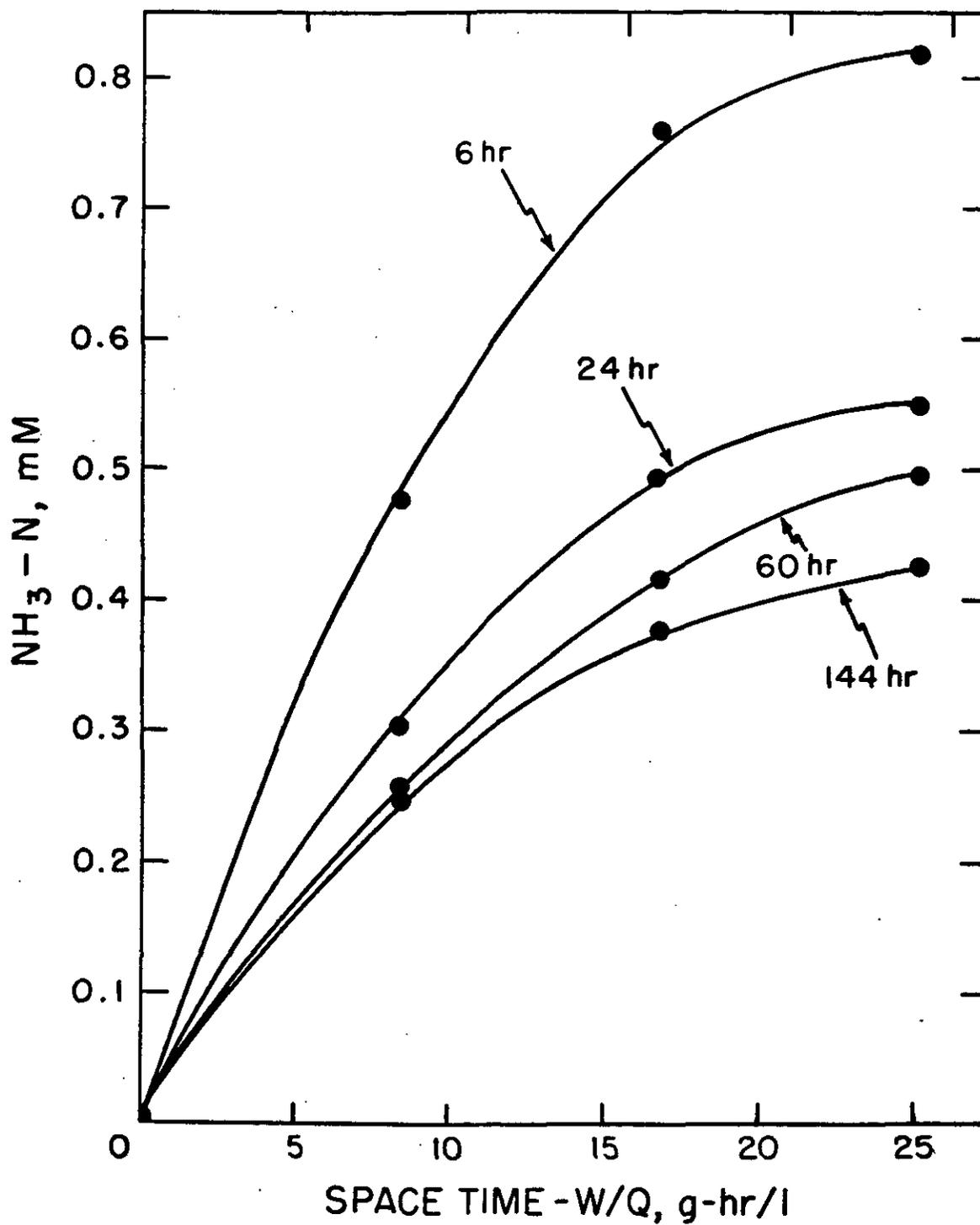


Figure 12. Ammonia production with reaction time (space time) in the carbon bed at various operating times.

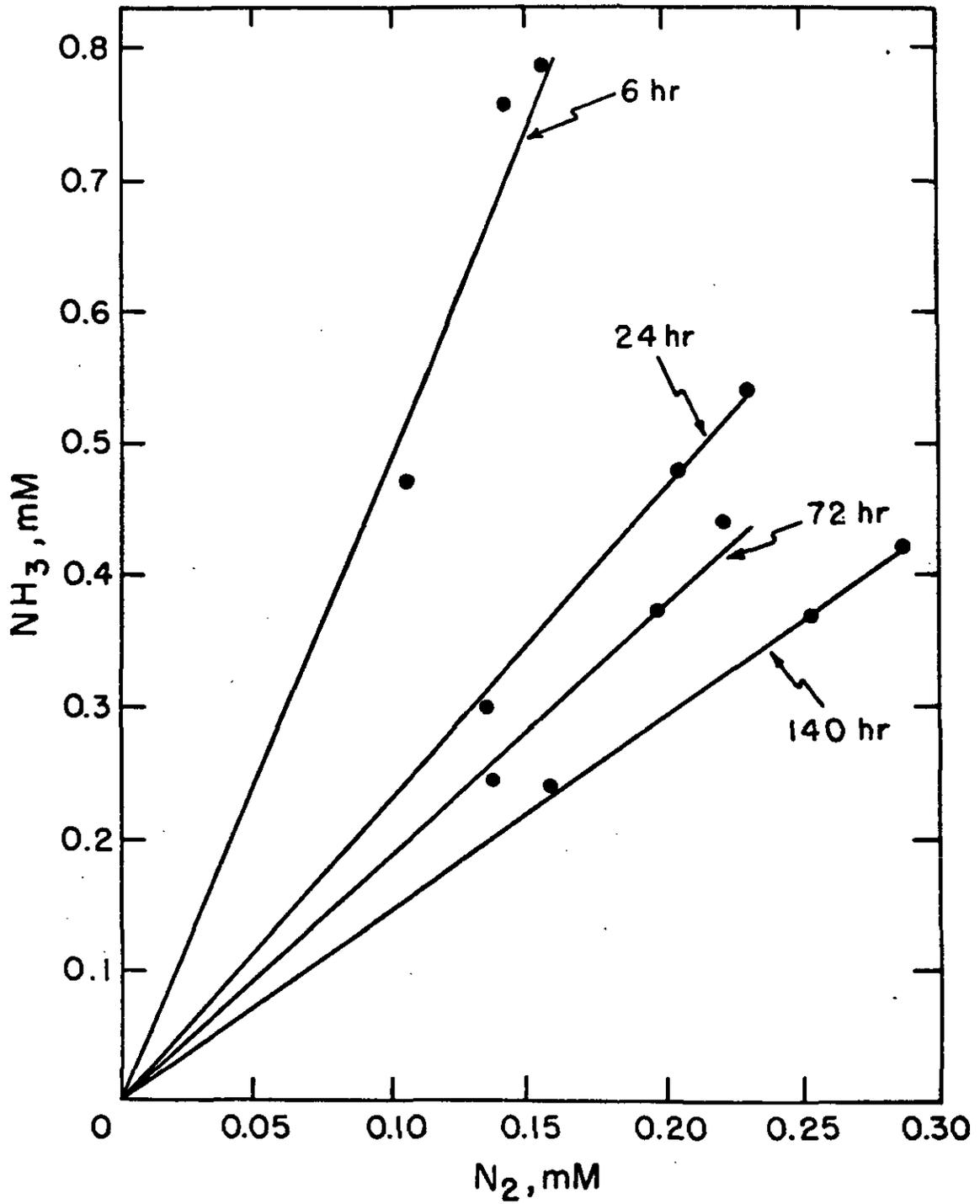


Figure 13. Determination of rate constant ratio, k_1/k_2 .

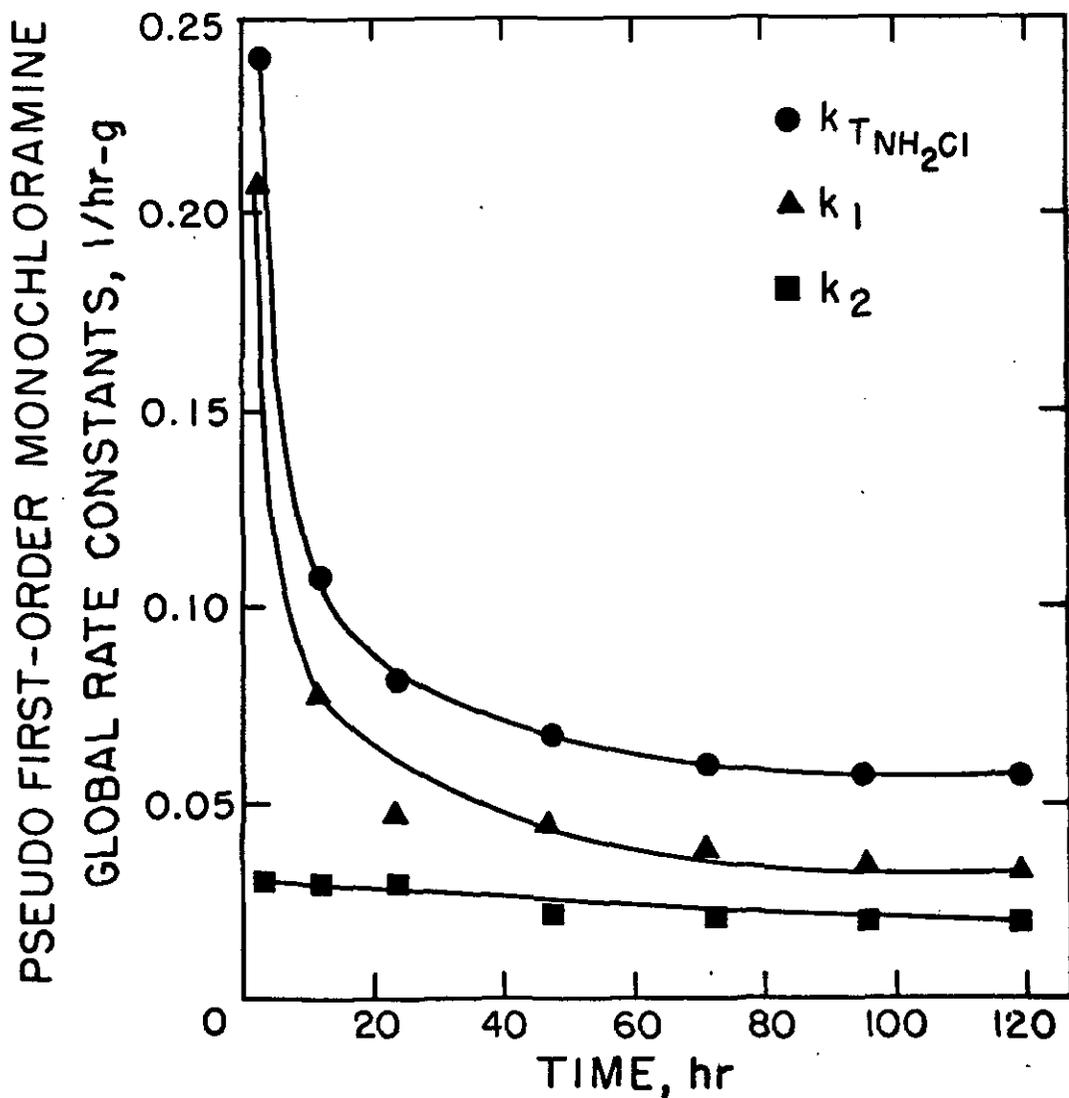


Figure 14. Decrease in pseudo first-order, global rate constants, $k_{T\text{NH}_2\text{Cl}}$, k_1 , and k_2 , with operating time.

Initially, the overall rate of monochloramine conversion was fast enough to prevent the escape of unreacted monochloramine as can be seen from Figure 7. During this period, most of the monochloramine was converted to ammonia because k_1 was much greater than k_2 . However, as k_1 decreased, more monochloramine was converted to nitrogen gas. Finally, after 140 hours, the rate constants shown in Figure 14 did not change appreciably. This lends support to the contention that steady-state conditions were thus achieved with a nitrogen conversion of about 42 percent rather than 67 percent as proposed by Bauer and Snoeyink (1973).

A decrease in the rate constant for ammonia production, k_1 , with operating time may be attributed to a reduction in available reaction sites. As discussed in an earlier section (see Effect of pH on Monochloramine Conversion), basic compounds may interfere by occupying otherwise available reaction sites. The buffer used to maintain system pH appears to be one such interfering basic compound. As earlier shown in Figure 6, a feed solution containing only phosphate buffer produced an increase with operating time in the amount of acid back-titrated for surface oxide determination. This suggested that the buffer was reacting with the surface in some manner. The continual decrease in k_1 could therefore be explained by preferential buffer-carbon interactions which limit the rate of monochloramine reaction. The approach to a steady-state value of k_1 could be then be due to final equilibration of the buffer with reactive sites. This possibility

is supported by noting that the time to reach a constant level of surface oxides with a feed of only the buffer solution (Figure 6) was about the same as required to reach an apparent steady-state for monochloramine conversion.

An explanation for the lack of increase in the rate constant k_2 with time is also in order. This result seems contrary to expectations if surface oxides produced by monochloramine conversion to ammonia were an important rate determining factor. That is, the reaction kinetics of monochloramine conversion to nitrogen gas could be considered as first-order with respect to both reactants, monochloramine and surface oxides, where

$$\frac{d N_2}{dt} = k_2' [CO^*] [NH_2Cl] \quad (5-3)$$

and

$$k_2 = k_2' [CO^*] \quad (5-4)$$

Thus, if k_2 did not increase, then the surface oxides produced do not participate in the nitrogen gas producing reaction. Although surface oxide sites are required, there may be sufficient sites on the virgin carbon to sustain the reaction for a long time. This seems plausible based on the experimental observation of gas production even during start-up of the reactor. It should also be noted that evolution of CO and CO₂ from the carbon surface as measured in gas analyses may be caused by rapid loss of oxides produced by conversion to ammonia. Thus, these oxides may be too unstable to serve as reactive sites for conversion to nitrogen gas.

Although the rate constant, k_2 , did not increase, there was an increase in nitrogen gas production. This is also consistent with the observation of first-order dependency on monochloramine and the decrease in the rate constant k_1 with time. As k_1 decreased, the rate of ammonia production decreased thus enabling a greater fraction of monochloramine to participate in the nitrogen gas producing reaction.

It should also be noted that the rate constants, k_1 and k_2 are difficult to determine precisely during the first 48 hours of reactor operation. That is, the relatively large rate constant for ammonia production prevents accurate evaluation of the smaller nitrogen gas rate constant. In fact, if k_2 is a function of available reaction sites, then a slight increase in k_2 with time may be expected as surface oxides are produced from ammonia formation. However, calculation of k_2 showed the opposite trend. The inaccuracy of the rate constant determination will be considered in subsequent data analysis.

pH Effect on Kinetics. Kinetic studies at pH 8.3 indicated that basic compounds possibly reduced the rate of ammonia production. It was proposed that as system basicity increased, interference with the ammonia production reaction would also increase. To test this hypothesis, monochloramine-carbon reactions were also investigated at pH 7.7 and 9.1.

Figure 15 shows the fraction of monochloramine remaining in solution (C/C_0) with space time at apparent steady-state conditions (140 hours) for the three pH conditions studied. First-order, irreversible kinetics were applicable with a decrease in $k_T \text{ NH}_2\text{Cl}$ noted as pH was

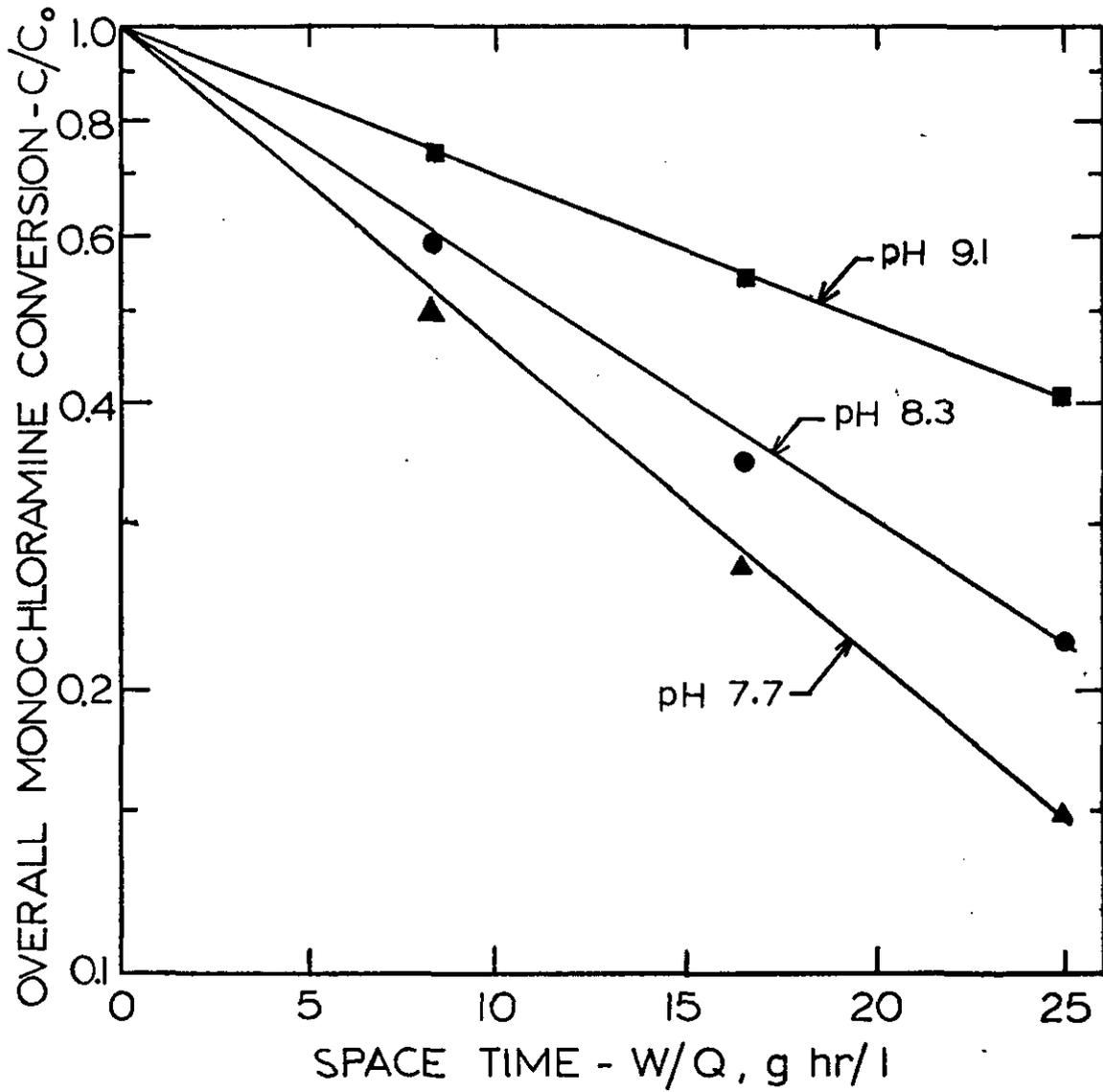


Figure 15. Effect of pH on first-order conversion of monochloramine at apparent steady-state column conditions.

increased. The approach of $k_T \text{NH}_2\text{Cl}$ to a steady-state value at each pH is given in Figure 16. As shown, $k_T \text{NH}_2\text{Cl}$ was consistently lower with increased pH at all operating times.

Using the same kinetic approach as presented in Figure 13, the individual rate constants k_1 and k_2 comprising $k_T \text{NH}_2\text{Cl}$ were also evaluated at pH 7.7 and 9.1. As seen by comparison of results given in Figure 17 an increase in system pH from 7.7 to 9.1 significantly reduced k_1 from 0.44 to 0.024 1/hr-g. The value obtained at pH 8.3 was 0.034 1/hr-g. These results supports the hypothesis that ammonia production is controlled by basicity. To explain these observations, a simple retardant rate model can be proposed as follows:

$$r_{\text{NH}_3} = \frac{1}{1 + k_B C_B} [\text{NH}_2\text{Cl}] \quad (5-5)$$

where $k_1 = \frac{k}{1 + k_B C_B} \quad (5-6)$

Here C_B represents the base concentration adsorbed on the carbon and k_B the rate constant associated with base-carbon site interactions. According to this model, k_1 decreases as basicity increases. Thus, if hydroxide ions interfere in the reaction, an increase in pH will decrease k_1 . Additionally, an increase in adsorbed buffer with time at any given pH will also reduce k_1 . A change in k_1 using a different buffer to maintain pH may also be expected because of different adsorptive capacities for surface reaction sites.

The results presented in Figure 17 also indicate that k_2 was reduced by increased system pH. However, an interference of basic compounds

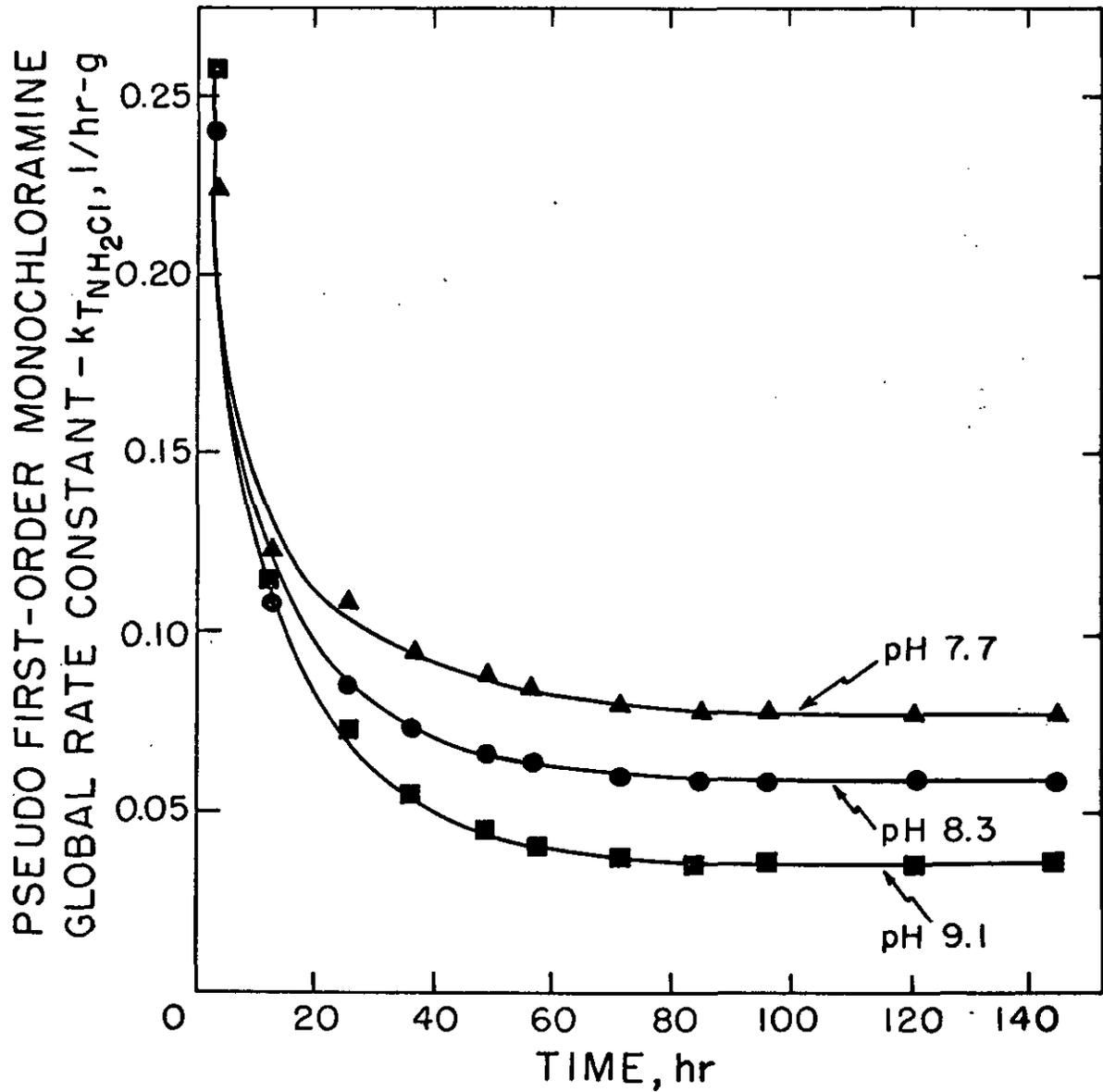


Figure 16. Effect of pH on pseudo first-order, global rate constant, k_{T, NH_2Cl} , with operating time.

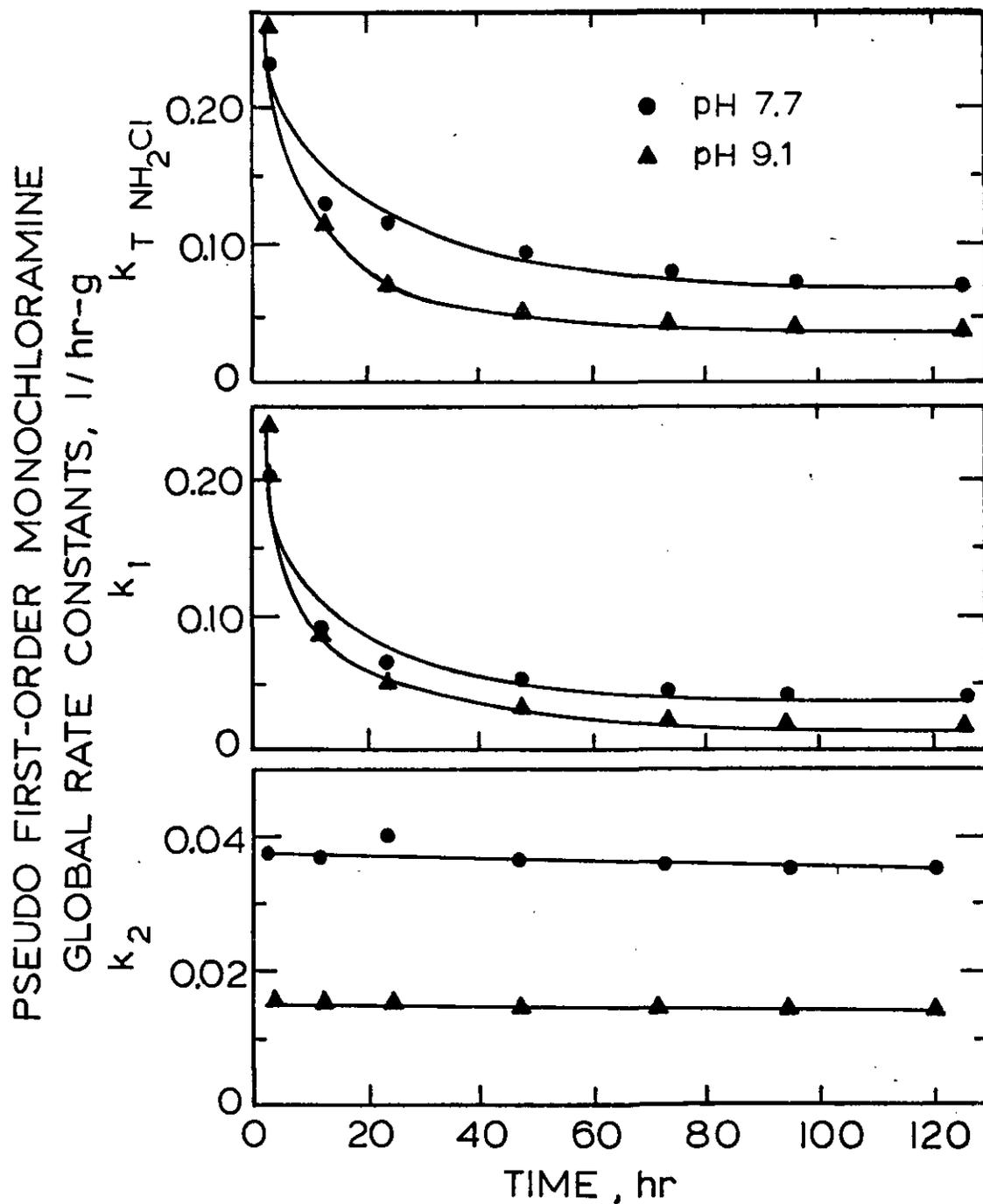


Figure 17. Comparative effect of pH on pseudo first-order, global rate constants, $k_T \text{ NH}_2\text{Cl}$, k_1 and k_2 with operating time.

with nitrogen gas reaction sites does not necessarily follow. This conclusion is apparent because k_2 did not decrease significantly at any given pH with operating time. Instead, it may be possible for the intrinsic rate of nitrogen gas production to be a function of pH. That is, this reaction may be acid catalyzed in which case reaction rate is more rapid at lower pH.

A summary of the kinetic data obtained at all three pH conditions is presented in Table 3. At apparent steady-state, the data indicates that the decrease in $k_T \text{ NH}_2\text{Cl}$ with increasing pH is a result of a decrease in both k_1 and k_2 .

Pre-chlorination of Carbon Bed. Results thus far indicate that surface oxides, either present on the virgin carbon or formed from ammonia production, are required for nitrogen gas formation. Thus, if the oxide sites can be increased prior to monochloramine reaction, a greater nitrogen yield should result. To examine this possibility, the carbon was pre-chlorinated to increase the surface oxide level according to the following reaction pathway proposed by Magee (1956):



Suidan and Snoeyink (1975) established that complete oxidation of the carbon surface occurred at a loading of 3-4 g Cl_2 reacted/g carbon. To insure significant surface oxidation, the carbon in this experiment was chlorinated in a batch reactor to a loading of 2 g Cl_2 reacted/g carbon.

Table 3

Apparent Steady-State, First-Order Monochloramine

Global Rate Constants

pH	k_1	k_2	$k_T \text{ NH}_2\text{Cl}, 1/\text{hr-g}$
7.7	0.044	0.033	0.078
8.3	0.034	0.023	0.058
9.1	0.024	0.012	0.036

Results presented in Figure 18 indicate that first-order reaction kinetics could still be used to describe monochloramine conversion in the pre-chlorinated carbon bed. Further kinetic analysis, as presented in Figure 19, indicated that the decrease in $k_T \text{ NH}_2\text{Cl}$ with operating time was the result of a decrease in k_1 and not k_2 .

Values of k_1 were significantly lower for pre-chlorinated carbon than for untreated carbon. This can be explained by oxidation of reaction sites on the carbon surface during pre-chlorination. Of the total sites oxidized, a significant portion were those required for ammonia production. Thus, the reduction in ammonia reaction sites lowers the frequency of monochloramine surface reaction and thus decreases k_1 .

Despite the initial high level of surface oxides produced from chlorination, k_2 did not increase but remained constant with operating time. This suggests that the surface oxides formed from chlorination do not contain the proper functional groups required for nitrogen gas production. Alternatively, while the oxides formed may have the potential to produce nitrogen gas, they may be extremely unstable and evolve as CO and CO₂. This instability would minimize any significant oxide buildup on the surface and would prevent increased nitrogen gas production.

Figure 20 indicates that pre-chlorination of the carbon significantly reduced the overall rate constant. Apparent steady-state values for untreated and chlorinated carbon were 0.058 and

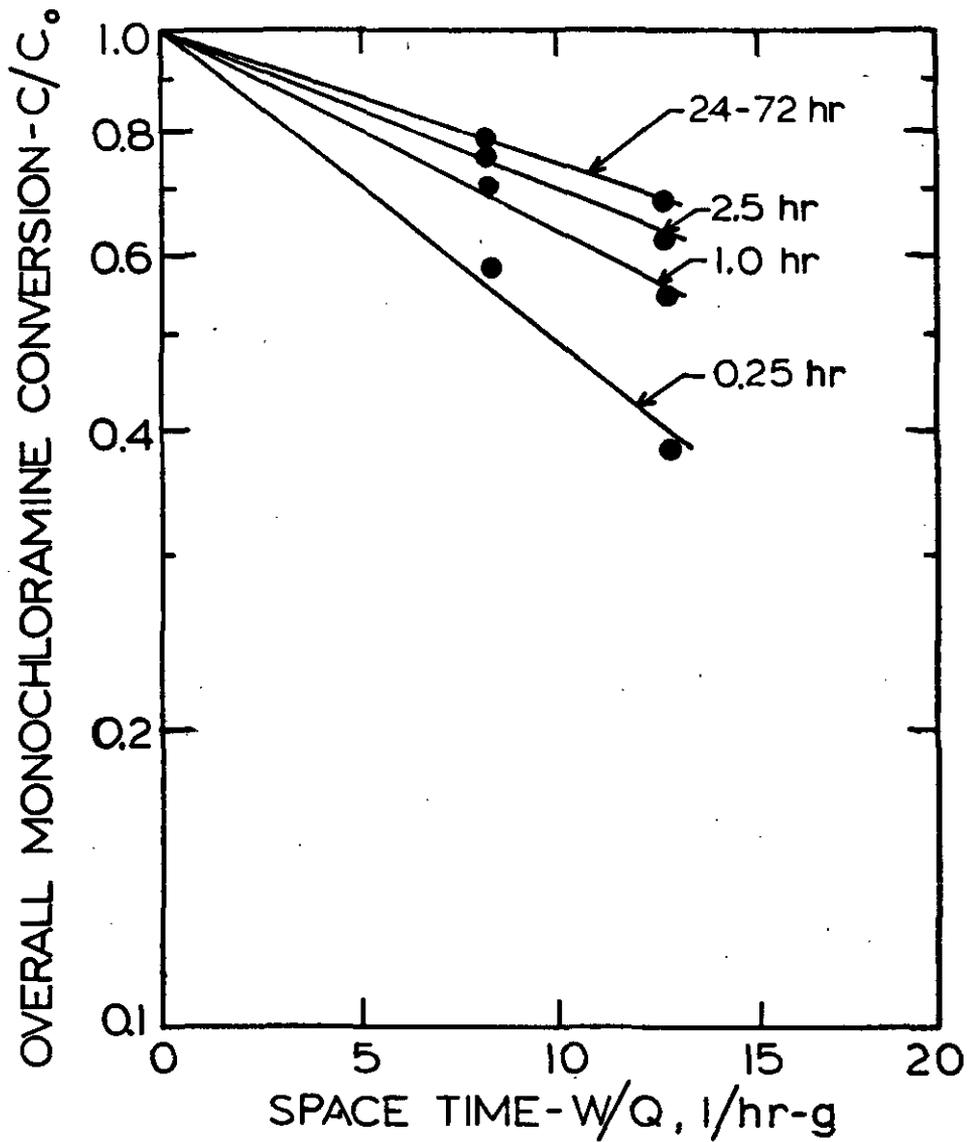


Figure 18. First-order conversion of monochloramine with space time at various operating times for pre-chlorinated carbon (2g Cl_2/g) with influent $NH_2Cl=0.90mM$ and pH 8.3.

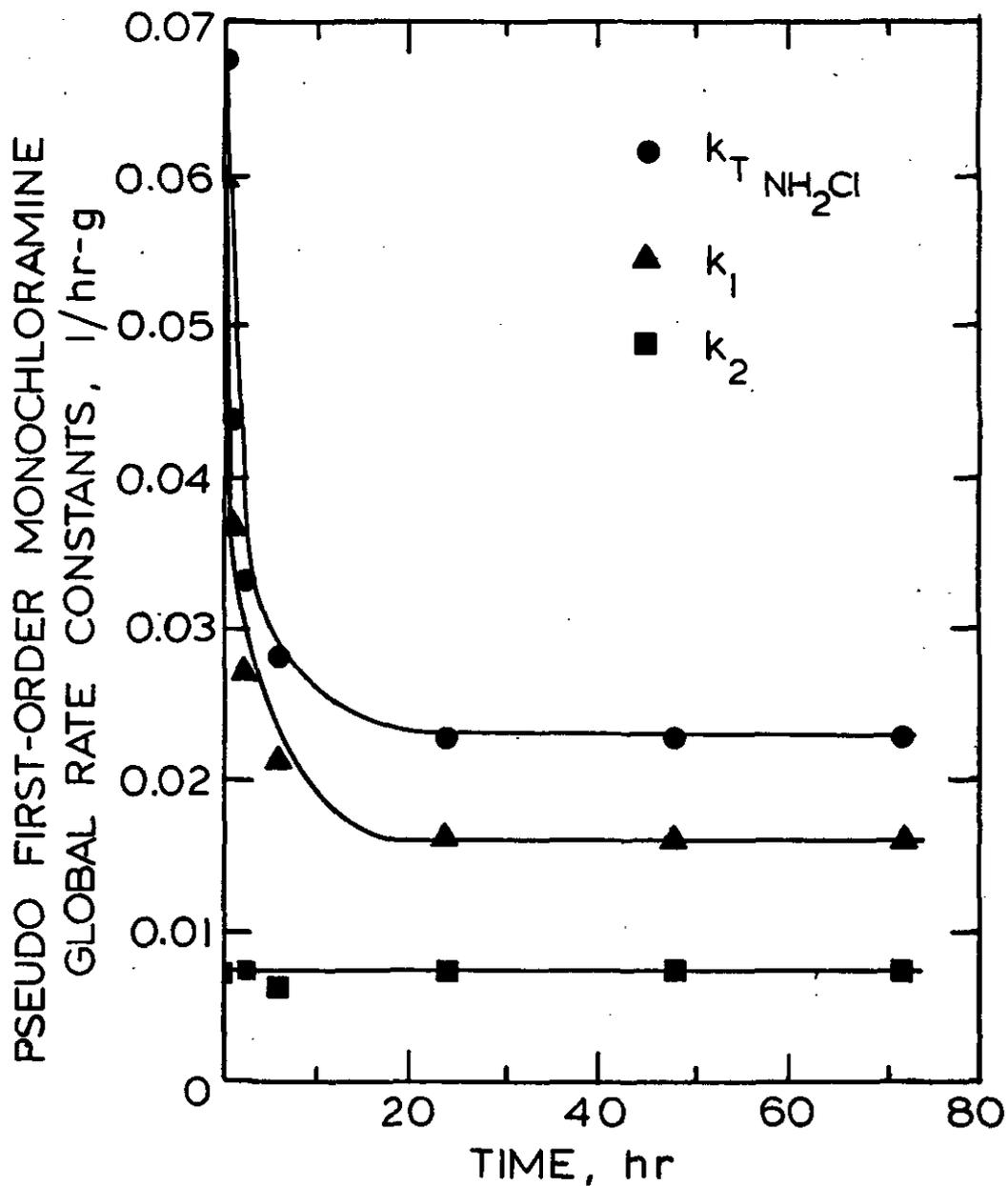


Figure 19. Depression in pseudo first-order, global rate constants, k_T NH_2Cl , k_1 and k_2 with operating time for pre-chlorinated carbon.

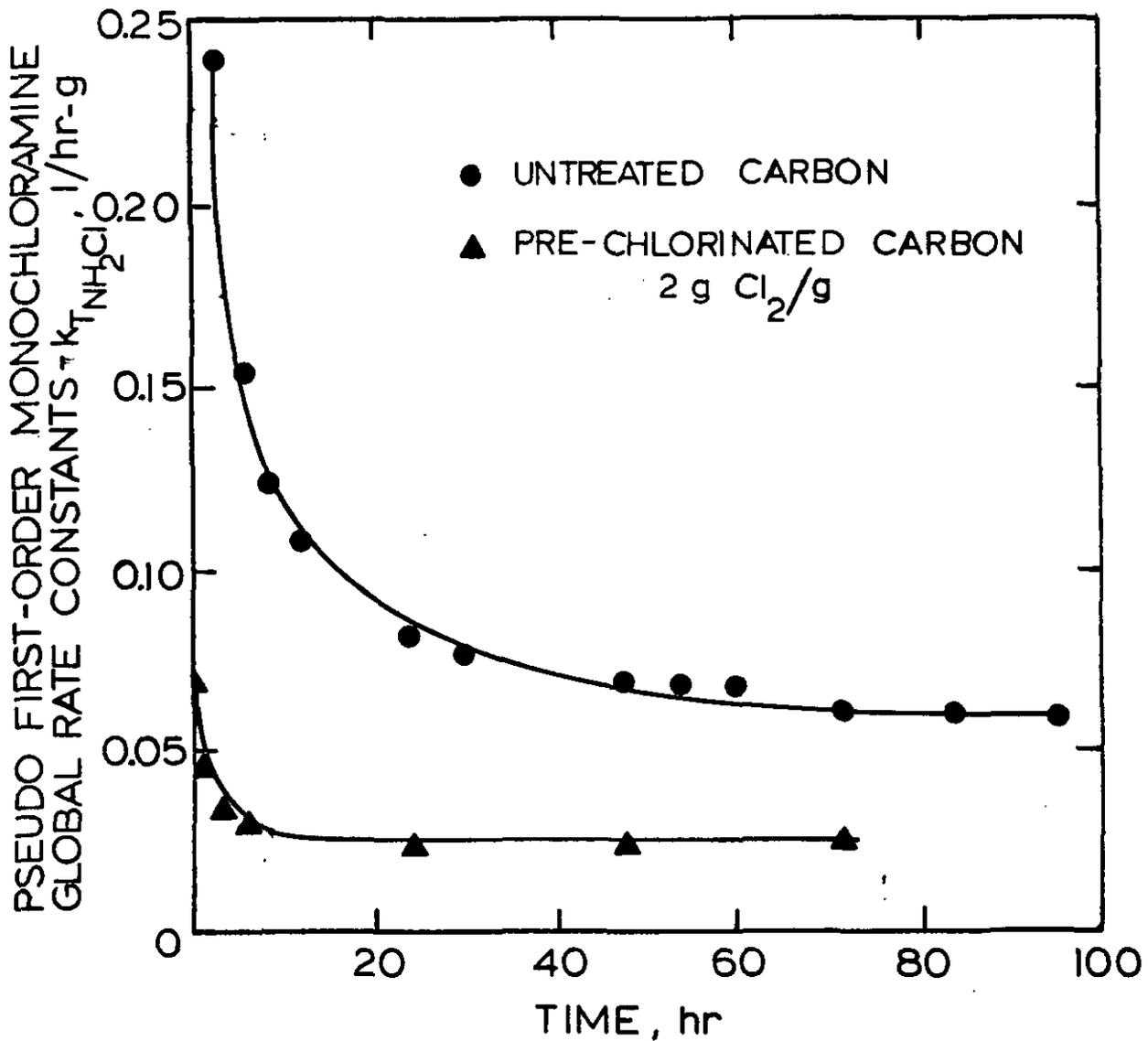


Figure 20. Comparison of $k_T \text{ NH}_2\text{Cl}$ with operating time for pre-chlorinated and untreated carbon.

0.023 1/hr-g, respectively. Bauer and Snoeyink (1973) also observed that the rate decreased as the degree of pre-chlorination increased. Destruction of the carbon surface by chlorine oxidation may be responsible for a reduction in total sites available for either monochloramine reaction pathway. This is supported by the observation that both k_1 and k_2 were reduced by pre-chlorination. It may also be possible for k_2 to be reduced if the oxides required for nitrogen formation are produced from the ammonia reaction. As shown, k_1 was decreased by pre-chlorination and thus less oxides will be formed.

Verification of First-Order Monochloramine Dependency. If the monochloramine reactions are indeed first-order, then the global rate constant should be independent of monochloramine concentration. To verify this, a different feed monochloramine concentration was used while maintaining flow rate and carbon weight constant. As expected, a first-order dependency was again observed. The resulting approach to an apparent steady-state value at both pH 7.7 and 8.3, given in Figure 21, supports the first-order model proposed. The higher value of $k_T \text{ NH}_2\text{Cl}$ at pH 7.7 also supports the basicity interference postulation discussed earlier.

Effect of Pore Diffusion Control. The effect of pore diffusion on the monochloramine-carbon reactions was examined by varying carbon particle size in the reactor and measuring overall monochloramine conversion. Influent monochloramine concentration and flow were maintained constant for all particle size studies. At the operational

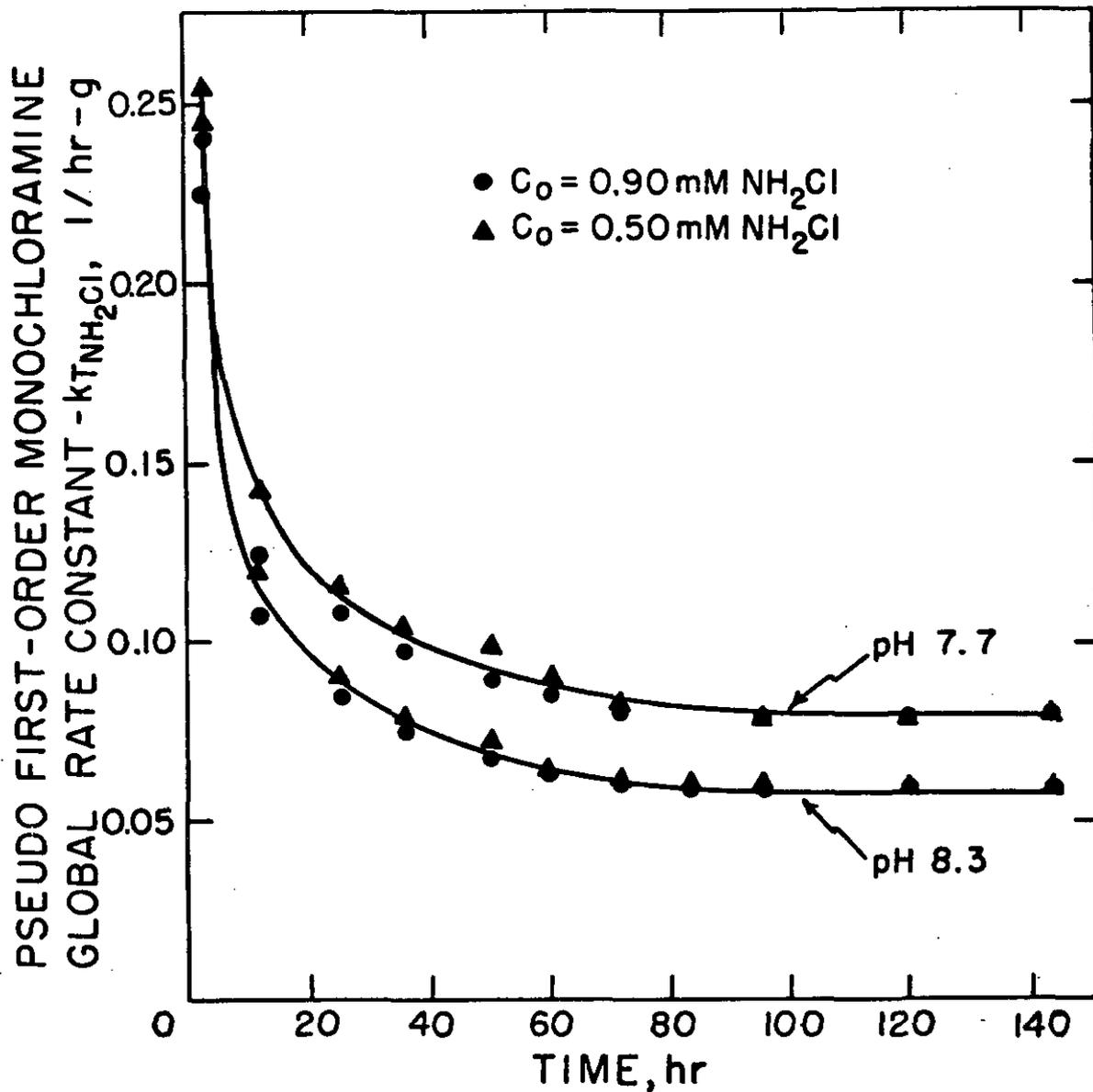


Figure 21. Influence of monochloramine influent concentration on pseudo first-order, global rate constant, $k_T \text{ NH}_2\text{Cl}$.

application rate of 8.6 gpm/sq ft, film diffusion resistance was negligible; an additional increase in flowrate of 40 percent did not affect monochloramine conversion. Figure 22 shows the rate constant, $k_T \text{ NH}_2\text{Cl}$, obtained at an apparent steady-state condition for the size fractions of 12 X 20 and 30 X 40 U.S. Standard mesh. The data indicates that the overall reaction rate is affected to some degree by pore diffusion; a decrease in arithmetic average particle size diameter of 60 percent ($d_{\text{avg}}=0.12$ cm vs $d_{\text{avg}}=0.050$ cm) increased $k_T \text{ NH}_2\text{Cl}$ from 0.058 to 0.089 1/hr-g.

The effectiveness factor, as developed in Equations 3-18 to 3-37 to determine the importance of pore diffusion control, requires calculation of an effective diffusivity, D_e , for the carbon particle. According to Wheeler (1955), the diffusivity within the porous structure can be given by:

$$D_e = \frac{\epsilon D}{\delta} \quad (5-8)$$

where D = bulk phase diffusivity, cm^2/sec
 ϵ = carbon particle porosity
 δ = tortuosity factor

Manufacturer specifications on Filtrasorb 400 carbon indicate a porosity of 0.66. Assuming a tortuosity factor of 2.0 for activated carbon (Wheeler, 1955) and using the Wilke-Chang equation (Wilke and Chang, 1955) for calculation of bulk diffusivity of monochloramine in water ($1.677 \times 10^{-5} \text{ cm}^2/\text{sec}$), the effective diffusivity for monochloramine was found to be $5.484 \times 10^{-6} \text{ cm}^2/\text{sec}$.

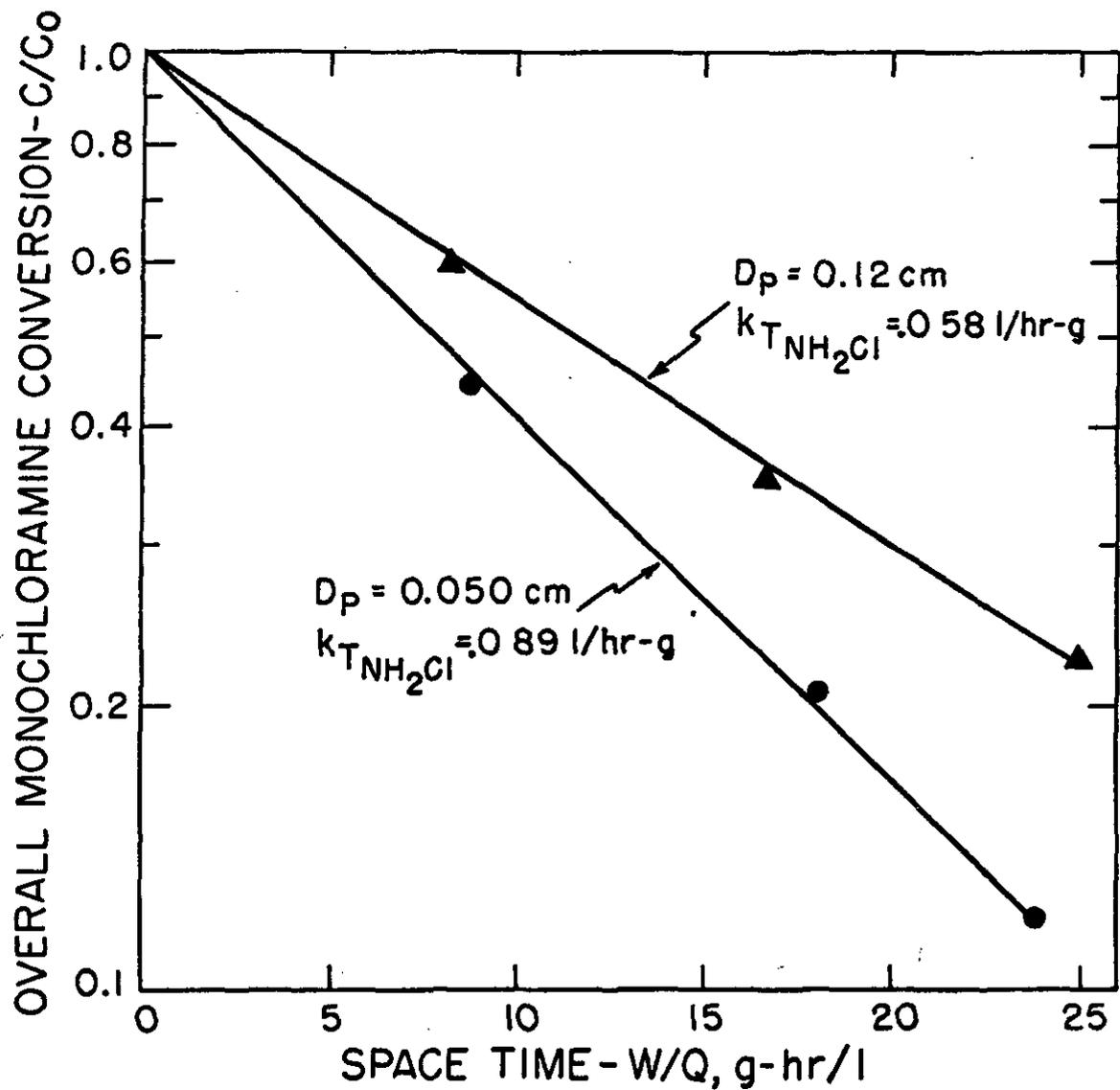


Figure 22. Effect of carbon particle size on k_{T, NH_2Cl} at apparent steady-state within the carbon bed for influent $NH_2Cl = 0.90$ mM and pH 8.3.

Table 4 presents values of η and ϕ_s for both average particle diameters of 0.12 and 0.050 cm at apparent steady-state. As expected, the effectiveness factor increases with decreasing particle size as pore diffusion effects become less significant. The high values of η indicate that the monochloramine-carbon reactions are not strongly controlled by pore diffusion for this particle size range.

Results in Table 4 can now be used to verify the assumption of first-order, irreversible kinetics for the monochloramine-carbon reactions by determining the quality of fit of these two coordinate points (η , ϕ_s) to the theoretical functional relationship given by Equation 3-35. But first, the intrinsic rate constant, k^* , must be calculated from the global rate constant and effectiveness factor by:

$$k^* = \frac{k_T \text{NH}_2\text{Cl}}{\eta} \quad (5-9)$$

Because k^* was found to vary slightly with particle size it was necessary to estimate its true value by the procedure outlined in Chapter 3. Results in Figure 23 indicate that the experimental data points (η_j , ϕ_j) are in close agreement with those predicted for a first-order reaction with pore diffusion. Therefore, a first-order kinetic description of the reactions is justified. Calculations from this data show that a relatively diffusion free particle, with an effectiveness factor of 0.95, can be achieved using a diameter of 0.015 cm.

Table 4

Effectiveness Factor and Thiele Modulus for Various
Carbon Diameters - Monochloramine Reactions

Particle Size	η	ϕ_s
12 X 20 mesh - $D_{avg} = 0.12$ cm	0.61	1.16
30 X 40 mesh - $D_{avg} = 0.050$ cm	0.87	0.51

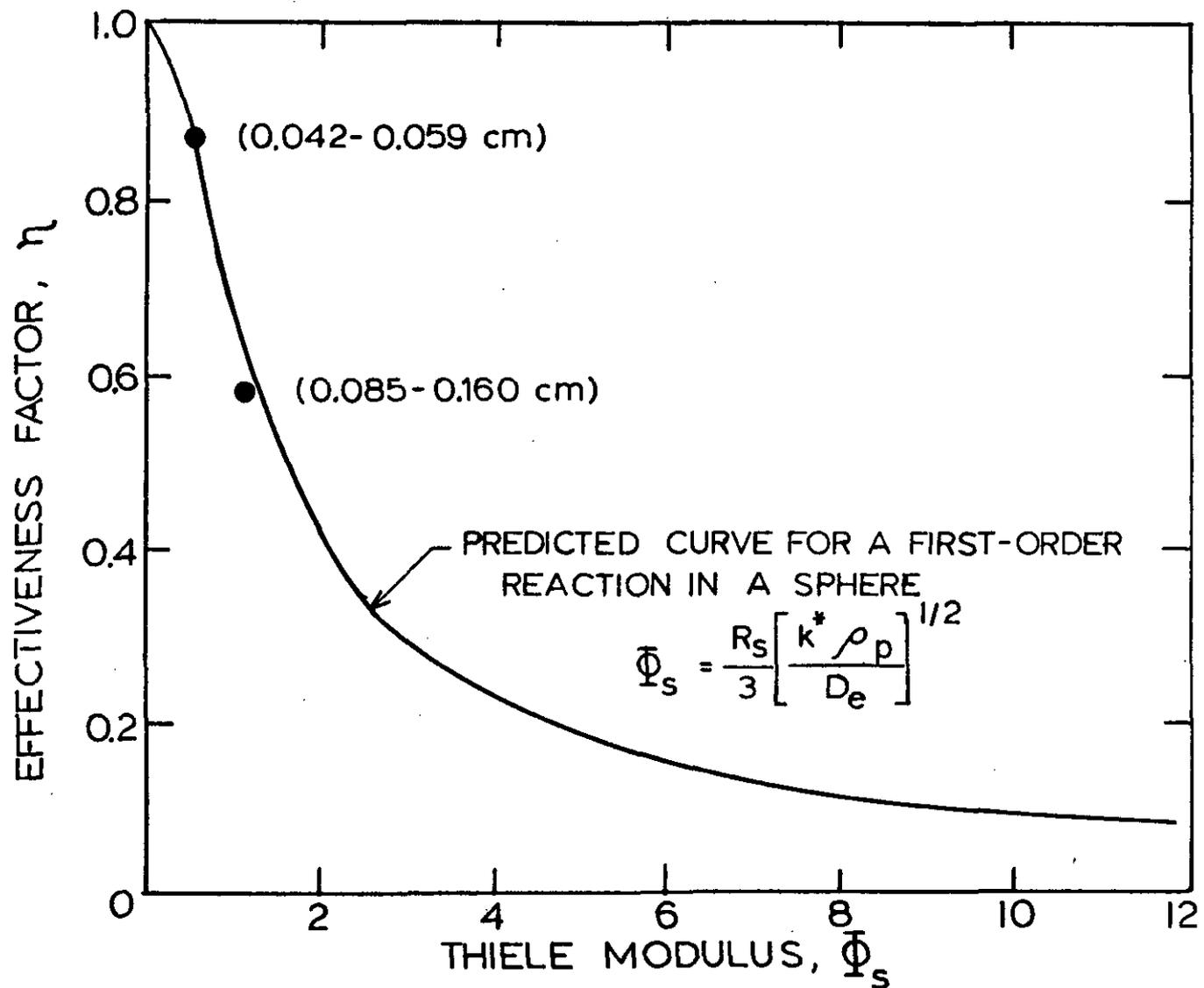


Figure 23. Experimental vs theoretical effectiveness factors for verification of first-order, irreversible monochloramine reaction kinetics.

Summary. The research has confirmed the parallel reaction pathway of monochloramine to produce both ammonia and nitrogen gas as first proposed by Bauer and Snoeyink (1973). However, the results of this research indicate that stoichiometric conversion of monochloramine to nitrogen gas was not achieved because of interference from basic compounds. These compounds compete with monochloramine for specific reaction sites and thus reduce conversion efficiency. Additionally, it was observed that the virgin carbon contained sufficient surface oxide groups to produce nitrogen gas. This suggests that the oxides formed from ammonia production may not be necessary for nitrogen gas formation.

The overall conversion rate of monochloramine was adequately described by a first-order, irreversible kinetic model. Using a pseudo steady-state analysis to account for the relatively slow change in reaction rate with time, a shift in rates of monochloramine conversion to ammonia and nitrogen gas was measured over 140 hours of operation. The ammonia production rate constant, k_1 , rapidly decreased with time while the nitrogen gas constant, k_2 remained relatively constant. This caused the overall monochloramine conversion rate constant, $k_T \text{ NH}_2\text{Cl}$, to decrease. Although the rate constant k_2 remained unchanged, the rate of nitrogen gas production increased slightly to a steady-state level because more monochloramine was available to react by this pathway as k_1 decreased.

Kinetic analysis of reactor operation at pH 7.7, 8.3 and 9.1 revealed that the rate constant k_1 decreased with increasing pH. This supported the hypothesis that ammonia production was reduced by the presence of basic compounds; i.e. phosphate buffer or hydroxide ions competed with monochloramine for specific ammonia surface reaction sites. At a given pH, the interaction of phosphate buffer with the surface, as indirectly evidenced by acid back titration for measurements of surface oxides, paralleled the decrease in ammonia production rate to a final steady-state where the buffer had equilibrated with the carbon surface.

The intrinsic reaction rate governing nitrogen gas production also decreased with increasing pH. This suggests the possibility of an acid catalyzed reaction. However, at a given pH, k_2 remained relatively constant with time. This result was unexpected because surface oxides, produced along with ammonia, were postulated to react with monochloramine to produce nitrogen gas by the parallel reaction pathway.

The fact that k_2 did not increase with time suggests that surface oxides produced by conversion to ammonia are either (1) too unstable to participate in subsequent reactions or (2) incapable of causing conversion to nitrogen gas. The latter possibility implies that the required oxide complexes for nitrogen production are available on the virgin carbon, and in sufficient quantity to sustain the nitrogen reaction for a considerable time. It should be noted, however, that because of the inaccuracy of determining k_2 at early operating times, the rate constant could have actually increased slightly with time. This would suggest

that, while impossible to measure, oxides formed by ammonia production could have increased the rate of nitrogen gas formation.

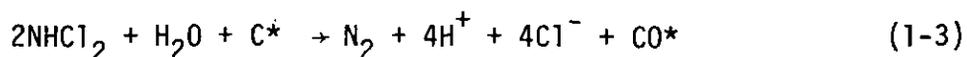
The importance of pore diffusion control on the rate of monochloramine conversion was determined by calculation of effectiveness factors from experimental data collected using two different particle size ranges. Surface reaction was shown to be slow in comparison with diffusion and thus rate controlling. Experimental results fit a model describing first-order, irreversible reaction and pore diffusion in a spherical particle.

C H A P T E R V I

RESULTS AND DISCUSSION - DICHLORAMINE-CARBON REACTIONS

Dichloramine Stoichiometry

Bauer and Snoeyink (1973) proposed that dichloramine reacts with the carbon surface by a single pathway to produce nitrogen gas with no production of ammonia:



In a typical experiment using dichloramine as feed to the carbon bed, Figure 24 shows that nitrogen yield reached 98 percent after 36 hours. This conversion is consistent with that expected from the reaction pathway given by Bauer and Snoeyink (1973). The small discrepancy between 100 percent theoretical yield and the observed steady-state value is attributed to experimental error inherent in the analyses.

While the phosphate buffer maintained a constant feed pH of 4.2, pH of the exit stream varied slightly with operating time. Following start-up, pH increased to 5.5 due to adsorption of hydrogen ions from bulk solution by the carbon. Then, pH gradually declined for 24 hours to a steady-state value of 3.8; this indicated that the buffer was insufficient to counter hydrogen ion production in the dichloramine reaction. Although formation of nitrogen trichloride from a shift in dichloramine equilibrium distribution could also have lowered pH, it seems unlikely due to the limited column reaction time of 15 seconds.

Chloride Balance. A mass balance on Cl-containing species was performed to verify stoichiometry and to determine if any removal of

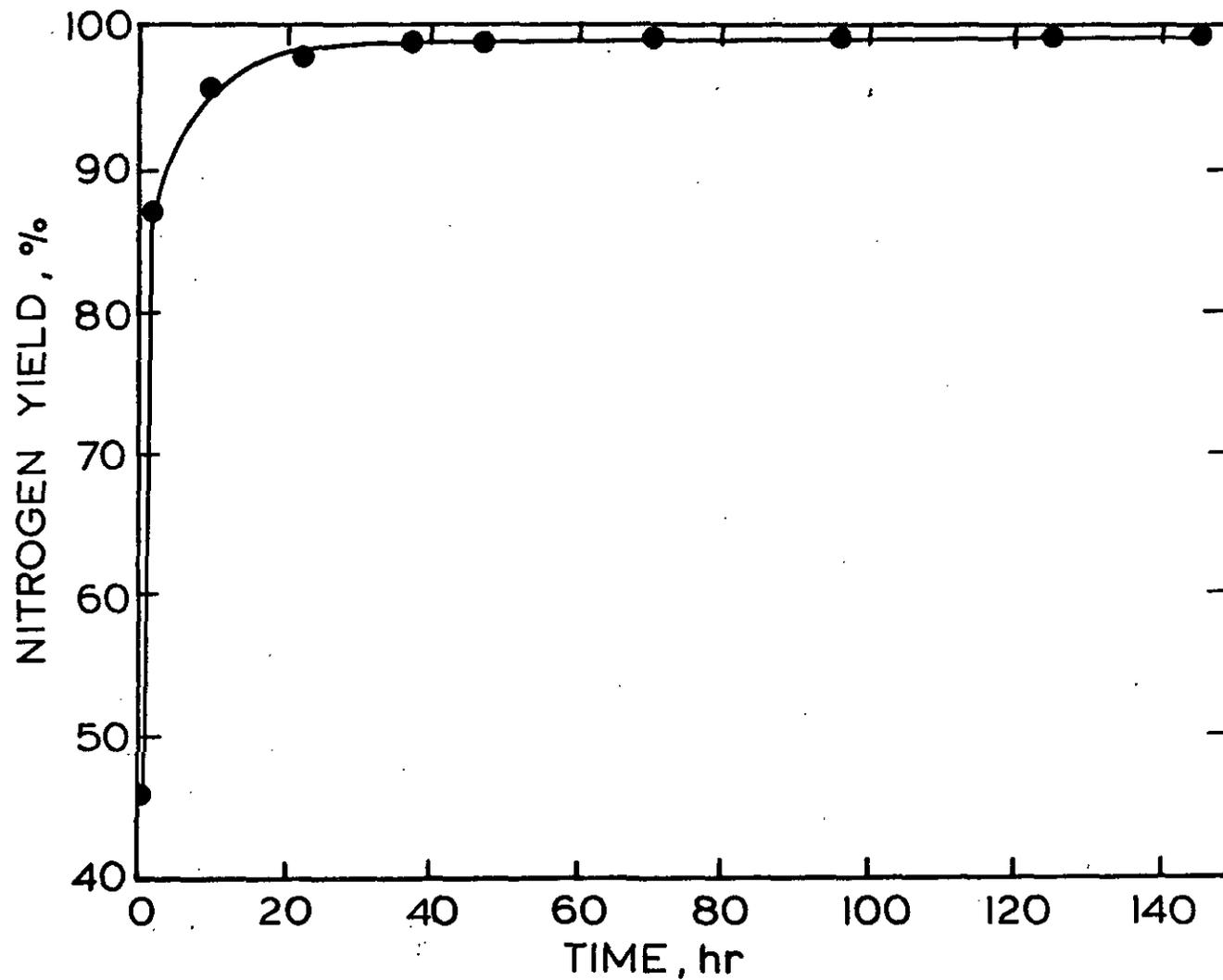


Figure 24. Nitrogen gas yield with operating time for influent $\text{NH}_2\text{Cl}=0.98$ mM, $D_p=0.12$ cm and $W/Q=2.78$ g-hr/l.

dichloramine is occurring by adsorption without subsequent reaction. According to the stoichiometry presented in Equation 1-3, for every mole of dichloramine reacted, two moles of chloride ions are produced. Results presented in Table 5 are in general agreement with stoichiometry. Initial uptake of chloride ions, as observed by Magee (1956) in the reaction of free chlorine with activated carbon, may be responsible for loss of chloride ions noted for the 24 hour sample.

By-product Gas Analysis. Table 6 presents results of gas analysis obtained after 140 hours of reactor operation at a space time of 2.78 g-hr/l (contact time of 25 seconds). Nitrogen comprised 90.3 percent of the gas collected and confirmed the final end product of dichloramine conversion proposed by others (Bauer and Snoeyink, 1973; D'Agostaro, 1972). The presence of small quantities of CO and CO₂ were probably due to evolution of oxides from the surface. Magee (1956) observed similar results in studies of chlorine-carbon reactions. The amounts of O₂ and H₂O were equal to those measured in gas analysis of monochloramine conversion. This indicates that O₂ and H₂O were not products of chloramine reactions, but rather derived from gas-liquid equilibration.

Gas analysis also indicated an increase in CO₂ from 0.5 percent, as produced in monochloramine conversion, to 3.6 percent in dichloramine conversion. This was attributed to a higher concentration of surface oxides formed in the dichloramine reaction resulting in a greater evolution of CO₂ from the oxidized carbon surface.

Table 5

Chloride Balance - Dichloramine-Carbon Reaction

time hr	NHCl_2 reacted mM	Chloride produced mM
24	0.87	1.61
48	0.98	1.97
72	0.96	1.83
96	0.96	1.97
120	0.96	1.97
140	0.96	1.97

Table 6

Dichloramine-Carbon By-Product Gas Analysis at
Apparent Steady-State

N ₂	90.3 %
CO	0.9 %
CO ₂	0.5 %
O ₂	4.8 %
H ₂ O	1.0 %

Surface Oxides. As noted in monochloramine conversion studies, acidic surface oxide data can only be used to show a trend in oxide levels. The results obtained in dichloramine studies were shown earlier in Figure 6. Buffer continually adsorbed into the carbon pores and added to the oxide titration with the effect being an additional increase in surface oxide level. Despite buffer interference, however, a gradual increase in surface oxide level due to dichloramine reaction was observed.

Surface Poisoning by Oxide Formation. According to Equation 1-3, dichloramine should continue to produce nitrogen gas provided that surface reaction sites (C^*) are available. However, as the reaction proceeds, C^* sites are consumed and CO^* sites are produced. This continual buildup of surface oxides should result in a poisoning of the dichloramine reaction. It must be noted that the symbol C^* represents a complex reaction site. Similarly, the dichloramine reaction may produce a variety of oxide complexes which, for lack of detailed information, are designated as CO^* .

As shown in Figure 25, the gradual increase of dichloramine in the exit stream with time indicated a poisoning effect. However, up to approximately 6 g $NHCl_2$ applied/g carbon (140 hours), the amount of dichloramine reacted remained relatively constant. Because reaction rate is a function of available sites, it was expected that conversion would begin to decrease immediately following column startup. However, short-circuiting through the column may have occurred at column startup resulting in a higher effluent concentration. Additionally,

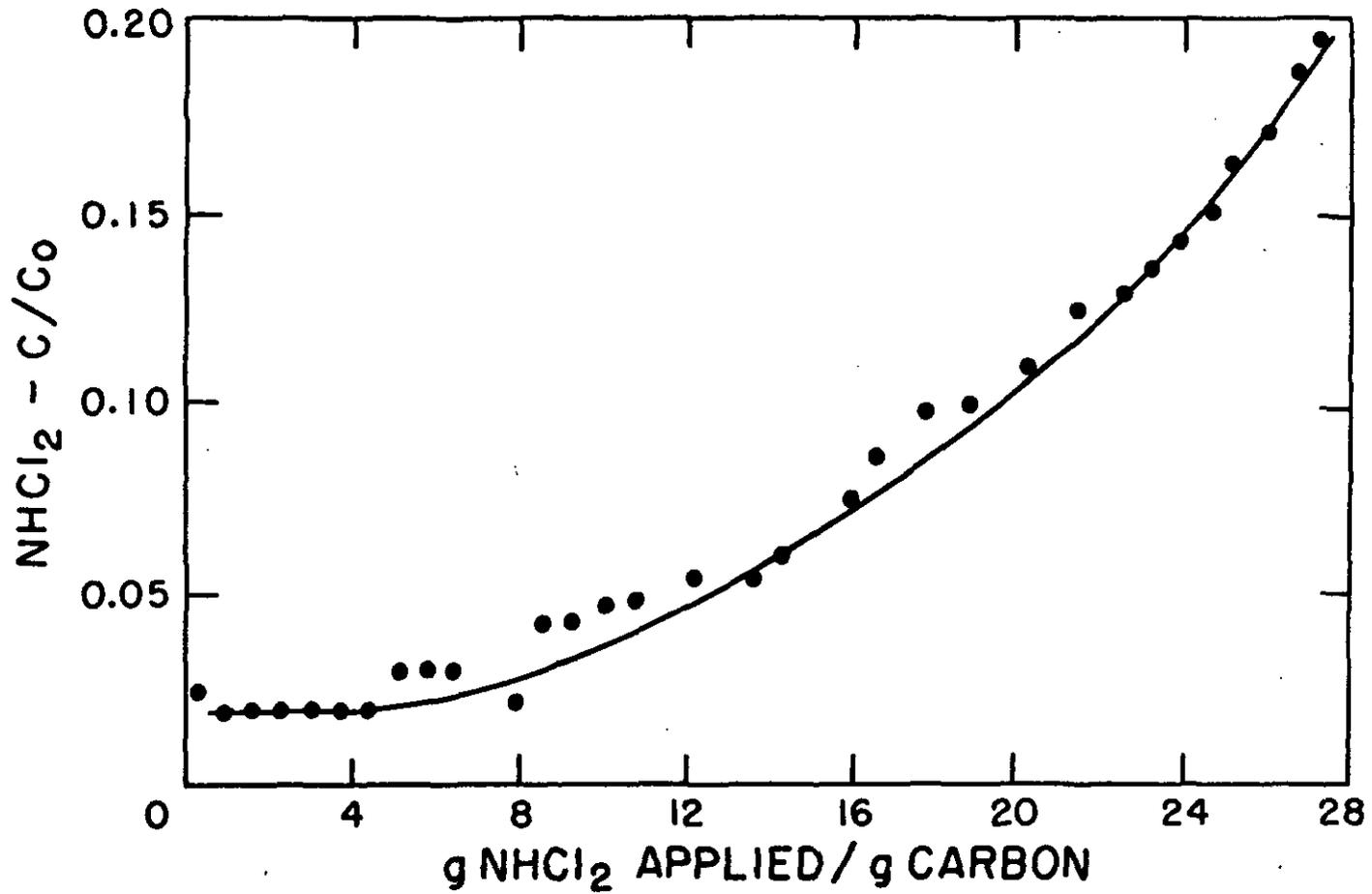


Figure 25. Deterioration of dichloramine conversion efficiency at extensive loadings for $W/Q=2.78$ g-hr/l and $D_p=0.12$ cm.

error in analytical technique may have given higher than actual conversions. Still another possibility may be that the virgin carbon surface contained such a large number of C* sites, that extensive surface reaction was required to reduce total site population to a rate limiting level.

It is important to note that the poisoning effect observed in this study will not occur in practical operation of a dichloramine-carbon system for ammonia removal. That is, 6 g NHCl_2 applied/ g carbon would only be achieved after treating a wastewater volume far in excess of that which exhausts the organic sorptive capacity of the bed. Additionally, thermal regeneration of the carbon will remove both sorbed organics and surface oxides, thus preventing any oxide accumulation over regeneration cycles.

Dichloramine-Carbon Kinetics

The viability of the dichloramine-carbon reaction for ammonia removal not only depends on nitrogen gas yield but also on reaction rate. That is, while the reaction produces only nitrogen gas, the required contact time for desired conversion must be known. As was the case for monochloramine conversion studies, the reaction order and extent of pore diffusion control associated with dichloramine conversion were of major interest. However, the effect of surface poisoning must also be included here. The necessary kinetic model to handle this case has been developed in Chapter 3 and given

again below:

$$-\ln \frac{[\text{NHCl}_2]}{[\text{NHCl}_2]_0} = -\frac{\alpha Q [\text{NHCl}_2]_0}{W} k_{\text{T NHCl}_2} \tau [Xt] + k_{\text{T NHCl}_2} \tau \quad (3-16)$$

The objective of collecting experimental kinetic data is to find the values of α (related to the poisoning effect) and $k_{\text{T NHCl}_2}$. For any given dichloramine reaction study, $[\text{NHCl}_2]_0$, the feed dichloramine concentration and W/Q , the flowrate to carbon mass ratio were held constant. Further, by measuring dichloramine conversion after a specified space time, τ , of 2.78 g-hr/l, a linear plot of

$$-\ln \frac{[\text{NHCl}_2]}{[\text{NHCl}_2]_0} \text{ vs } X t \quad (6-1)$$

should result if the model proposed appropriately describes the data. However, because a poisoning effect was not noted until 6 g of NHCl_2 were applied per g carbon, i.e. $Xt = 140$ hours, data points taken before this time were excluded in a test of the model.

As shown in Figure 26, a very good fit of experimental data was obtained to the model proposed. Values of $k_{\text{T NHCl}_2}$ and α were calculated to be 1.38 l/hr-g and 0.0027 moles/g, respectively. Figure 27 shows the predicted and experimental dichloramine conversion as a function of time using the model only after poisoning was observed, i.e. 6 g NHCl_2 applied/g carbon. Further verification of the model would entail operating the reactor at various space times and influent concentrations while maintaining the same particle size fraction. The constants, $k_{\text{T NHCl}_2}$ and α , obtained herein should apply equally well to other conditions.

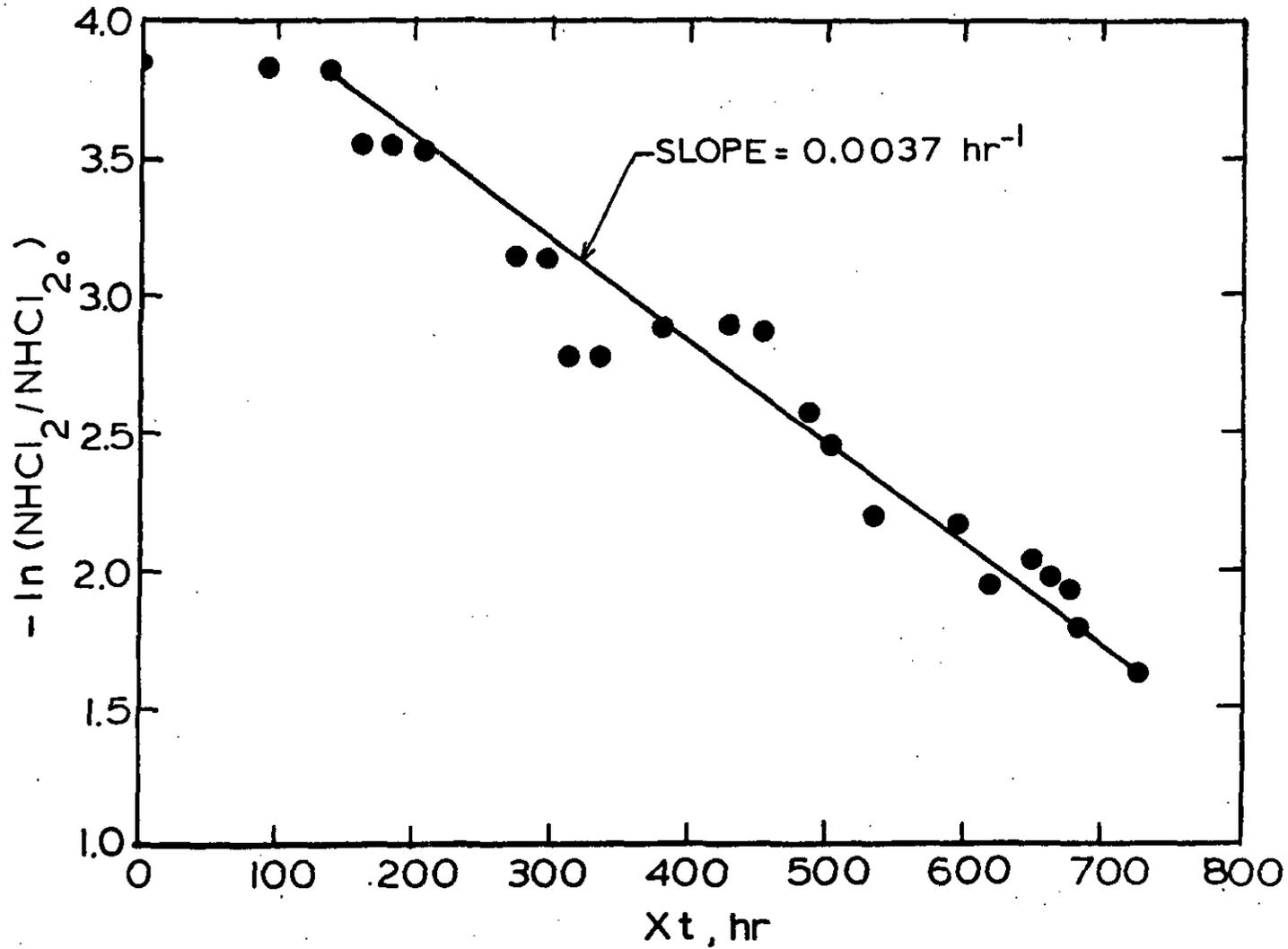


Figure 26. Determination of poisoning constant, α , from experimental data.

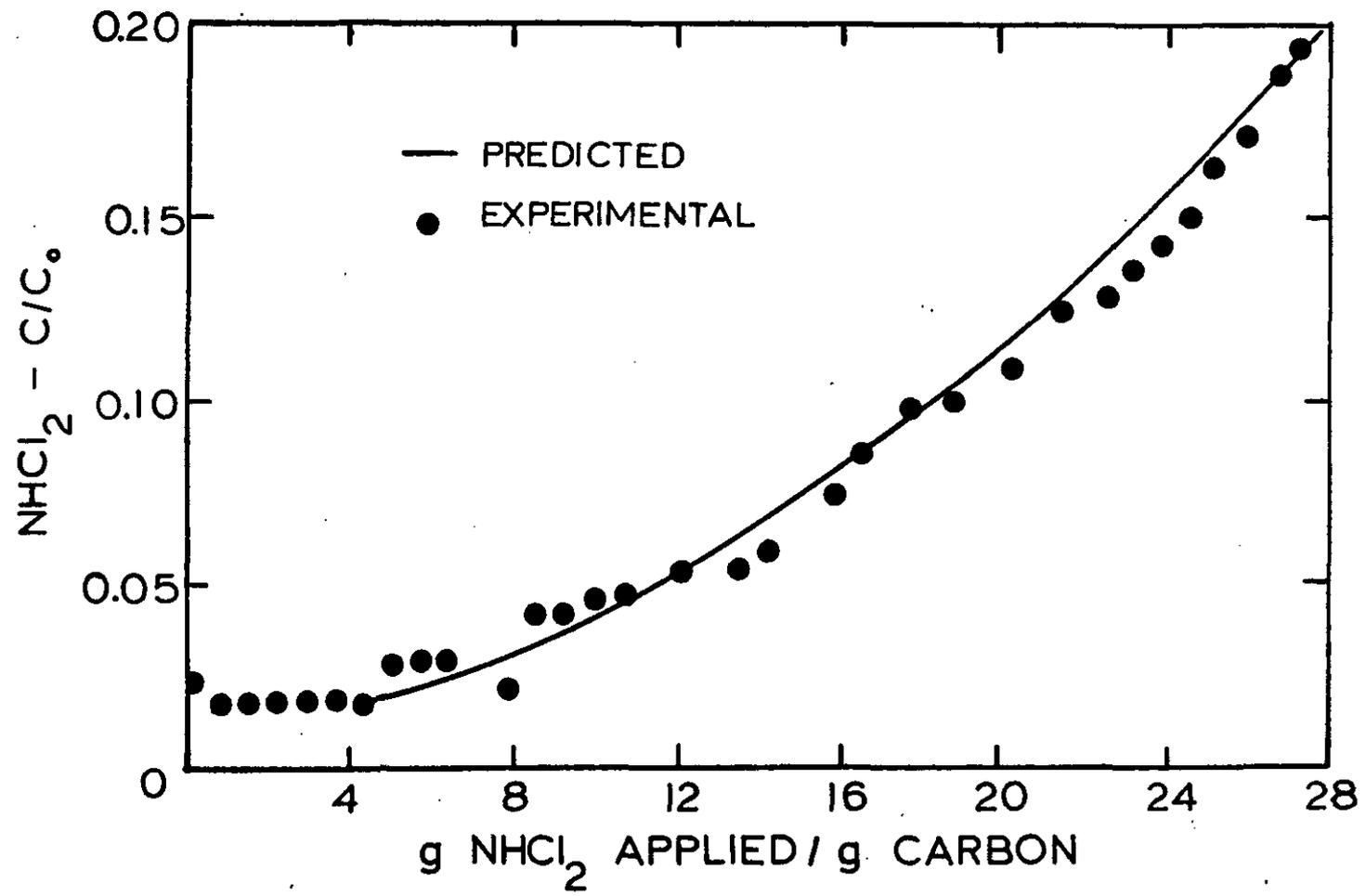


Figure 27. Prediction of dichloramine conversion with loading for surface poisoning model.

Effect of Pore Diffusion Control. The effect of pore diffusion on observed conversion rate of dichloramine was determined by measuring the change in the global rate constant with particle size. The rate constant, $k_T \text{ NHCl}_2$, is not considered to be a function of α and is based only on intrinsic reaction rate and pore diffusion resistance. From Figure 25, it may be concluded that reaction rate remained constant up to 6 g NHCl_2 applied/g carbon. Therefore, data taken during this constant rate period can be used to evaluate $k_T \text{ NHCl}_2$ from:

$$\ln \frac{[\text{NHCl}_2]}{[\text{NHCl}_2]_0} = - k_T \text{ NHCl}_2 \tau \quad (6-2)$$

The validity of the first-order kinetic model describing dichloramine conversion to nitrogen gas is shown by the data presented in Figure 28 for particle size fractions ranging from 12 X 20 U.S. Standard mesh ($d_{\text{avg}}=0.12$ cm) to 60 X 80 U.S. Standard mesh ($d_{\text{avg}}=0.021$ cm). Strong pore diffusion control is indicated by the decrease in rate constant with increase in particle size. Further, for the same size fraction, dichloramine rate constants are about 20 times greater than monochloramine rate constants (see Figure 22).

These results indicate that the intrinsic surface reaction rate for dichloramine conversion must be much faster than that of monochloramine because both molecules have approximately equal diffusivities. Additionally, because the rate of dichloramine reaction is so much faster, pore diffusion is a more significant rate controlling factor. That is, with a high rate of reaction, only the exterior of the carbon pores would be utilized, resulting in a significant concentration decrease inside the particle.

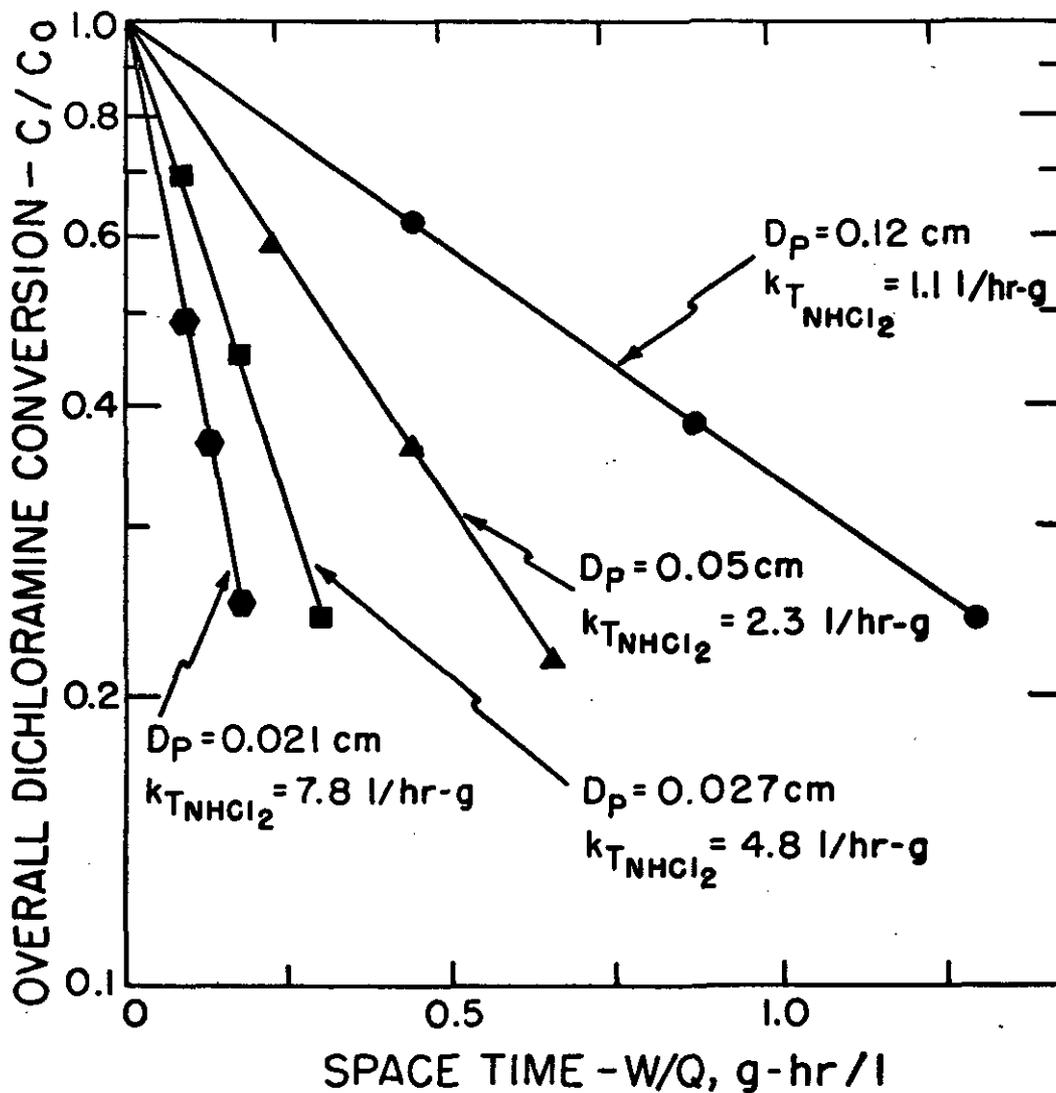


Figure 28. Effect of carbon particle size on $k_{T \text{ NHCl}_2}$ at apparent steady-state within the carbon bed for influent $\text{NHCl}_2 = 0.37 \text{ mM}$.

These results indicated pore diffusion to exhibit a significant effect on rate control. To more quantitatively define the importance of pore diffusion, the effectiveness factor, η , as applied to monochloramine conversion rate data was again used. This analysis required the same information for calculation of effective diffusivity (Equation 5-8) as previously discussed. While a different value for bulk diffusivity ($1.33 \times 10^{-5} \text{ cm}^2/\text{sec}$) was needed, the other two system constants, ϵ and δ , were the same. The resulting effective diffusivity was thus calculated to be $4.376 \times 10^{-6} \text{ cm}^2/\text{sec}$.

The values of η and ϕ_s obtained from the procedure outlined in Chapter 3 are presented in Table 7 for experiments conducted with particle size fractions ranging from 12 X 20 ($d_{\text{avg}} = 0.12 \text{ cm}$) to 60 X 80 ($d_{\text{avg}} = 0.021 \text{ cm}$) U.S. Standard mesh. In contrast to the monochloramine conversion reactions, the dichloramine conversion reaction was strongly pore diffusion controlled as indicated by the low effectiveness factors obtained for all particle sizes. This result confirms the fact that the intrinsic rate of dichloramine is much faster than that of monochloramine.

The data presented in Table 7 can now be used for further verification of the first-order kinetic model. The same calculation procedure as described for monochloramine kinetics, and as outlined in Chapter 3, allows calculation of the intrinsic rate constant, k^* , from the global rate constant, $k_T \text{ NHCl}_2$, obtained for each particle

Table 7

Effectiveness Factor and Thiele Modulus for Various
Carbon Diameters - Dichloramine Reaction

Particle Size	η	ϕ_s
12 X 20 mesh - $D_{avg} = 0.12$ cm	0.050	19.70
30 X 40 mesh - $D_{avg} = 0.050$ cm	0.124	7.70
50 X 60 mesh - $D_{avg} = 0.027$ cm	0.194	4.79
60 X 80 mesh - $D_{avg} = 0.021$ cm	0.220	4.18

size fraction:

$$k^* = \frac{k_T \text{NHCl}_2}{\eta} \quad (6-3)$$

As expected, due to experimental error, the value of k^* varied somewhat. Again as was presented for monochloramine conversion kinetics, the true value of k^* was estimated by minimizing the sum of the squared differences between the observed and estimated true value of k^* (see Chapter 3).

Experimental results of η_i , ϕ_{s_i} shown in Figure 29 are in close agreement with those given by the model describing first-order reaction with diffusion. Calculations show that a particle diameter of 0.0008 cm is required to yield a diffusion free ($\eta = 0.95$) carbon particle for the dichloramine conversion reaction while a much larger particle diameter (0.015 cm) was required for monochloramine. This further indicates the importance of pore diffusion on dichloramine conversion.

Summary. These results obtained adequately supported the reaction stoichiometry proposed by Bauer and Snoeyink (1973) in which dichloramine reacts by a single pathway to produce nitrogen gas. A chloride balance showed that two moles of chlorides were produced for every mole of dichloramine reacted and thus agreed with proposed stoichiometry. Due to the quantitative inaccuracy of the surface oxide titration, a direct relationship between dichloramine conversion and oxide production could not be established. However, the data indicated a general trend of increasing surface oxide level

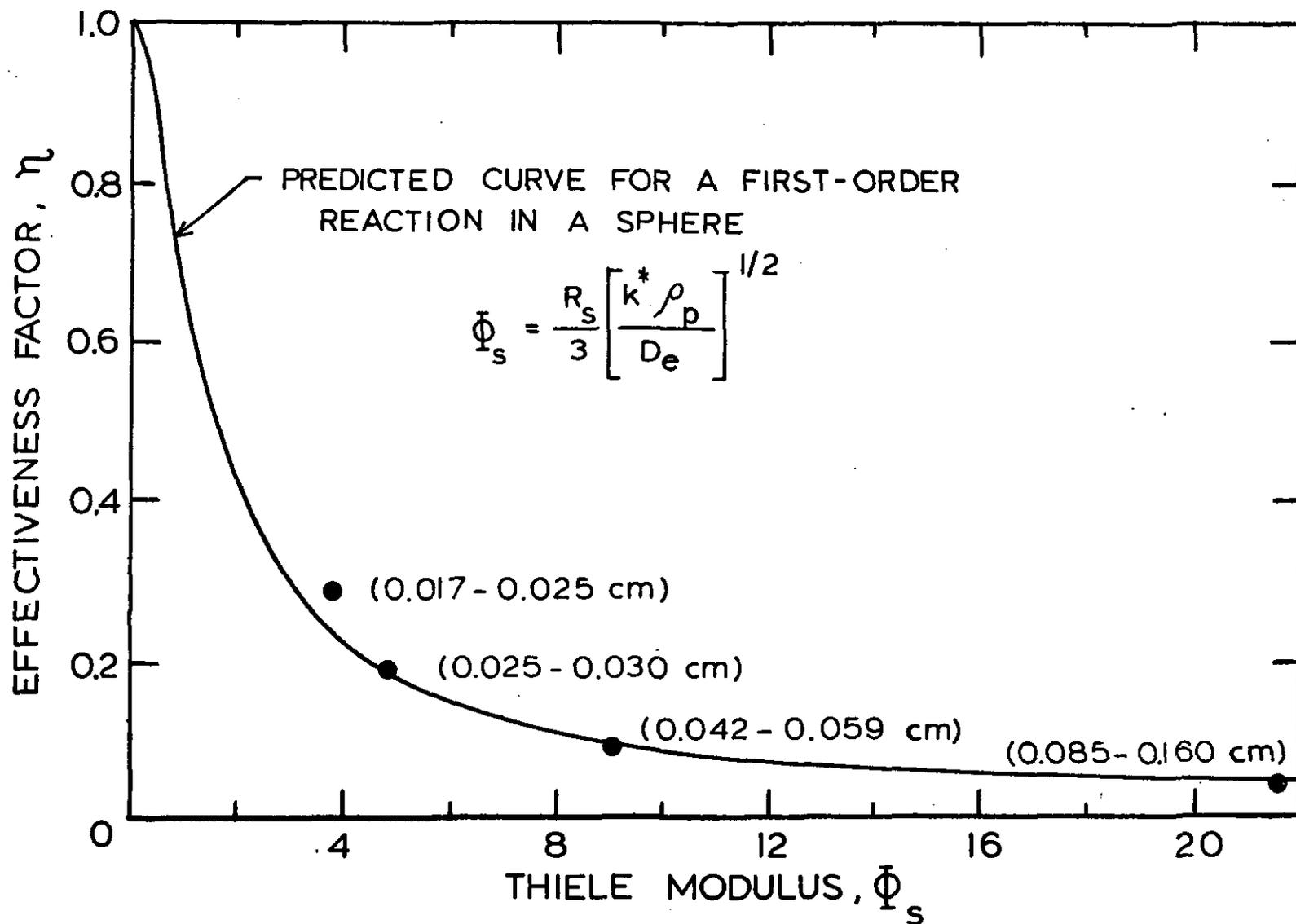


Figure 29. Experimental vs theoretical effectiveness factors for verification of first-order dichloramine reaction kinetics.

with dichloramine reacted. The increase in surface oxides eventually poisoned the carbon surface and thus reduced the rate of dichloramine reaction.

Because dichloramine produces only nitrogen gas as an end product, this reaction is more favorable than monochloramine conversion from a process design viewpoint. That is, by providing sufficient contact time, all of the ammonia can be converted to dichloramine which in turn will react to produce nitrogen gas.

To describe the decreasing rate of dichloramine conversion, a modified first-order kinetic model was developed and tested. Although surface oxide accumulation could not be directly measured, the poisoning effect was indirectly described in terms of the dichloramine applied per g carbon. The experimental data agreed quite well with the proposed model in which both a poisoning factor, α , and the global rate constant, $k_T \text{ NHCl}_2$, were obtained.

Particle size studies showed that the rate of dichloramine conversion is far more dependent upon pore diffusion than monochloramine. This result could be expected because the global rate constant for dichloramine conversion was about 20 times greater than that for monochloramine. This faster reaction rate also results in a shorter carbon contact time for dichloramine conversion. Calculation of the effectiveness factor, η , also confirmed the importance of pore diffusion control and supported the use of a model for first-order reaction with diffusion.

CHAPTER VI

RESULTS AND DISCUSSION - SIMULTANEOUS ADSORPTION OF ORGANICS AND CONVERSION OF CHLORAMINES ON THE CARBON SURFACE

To effectively apply either mono- or dichloramine conversion processes for removal of ammonia, possible interferences caused by adsorption of organics must be investigated. That is, if interference is minimal, then a combined unit process involving chlorination followed by carbon contact can be used for removal of both ammonia and sorbable organics. This is more economical than design of separate processes which would otherwise be necessary for adsorption and ammonia removal. The extent of interference can be measured by reduction in $k_T \text{NH}_2\text{Cl}$, k_1 , k_2 and $k_T \text{NHCl}_2$. In these studies, the test organics, MB, ABS and DNP as well as alum clarified, raw wastewater, were fed simultaneously with chloramines to a fresh carbon bed.

Adsorption of Organics and Conversion of Monochloramine

Figures 30 and 31 indicate that the overall rate constant for monochloramine conversion was reduced to a lower steady-state value by the presence of MB, ABS and alum clarified, raw wastewater but not by DNP. The greatest depression of the rate constant was produced by wastewater. In this system, the apparent steady-state, global rate constant was reduced from 0.058 (NH_2Cl only) to 0.030 1/hr-g. It should also be noted that a constant chlorine dosage was applied to the wastewater feed; therefore, the feed monochloramine concentration ranged from 0.56 to 0.77 mM. The concentration of organics, as measured by total organic carbon (TOC), was about 20 mg/l.

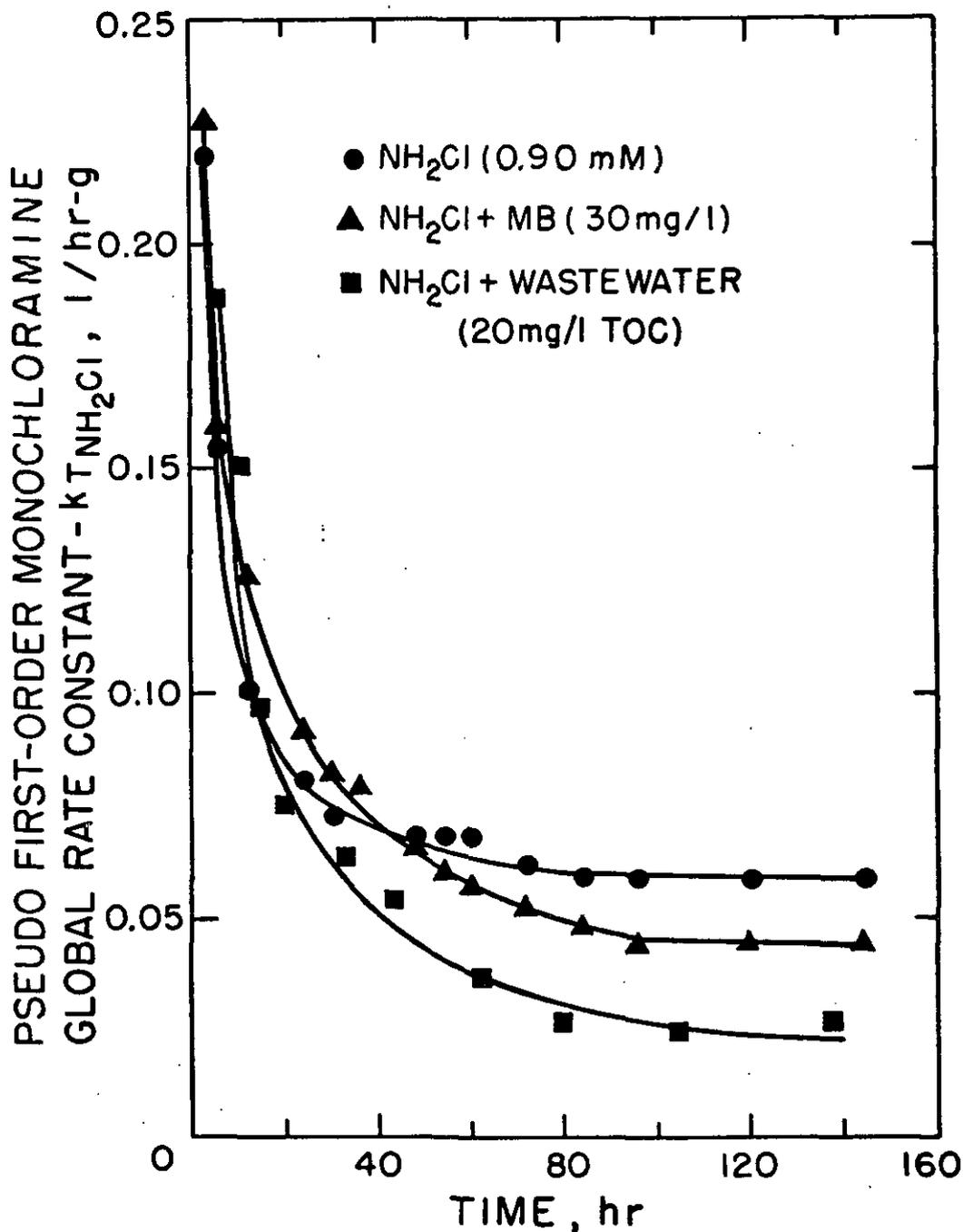


Figure 30. Depression of $k_T \text{NH}_2\text{Cl}$ by the addition of MB and alum clarified, raw wastewater for pH 8.3 and $D_p = 0.12$ cm.

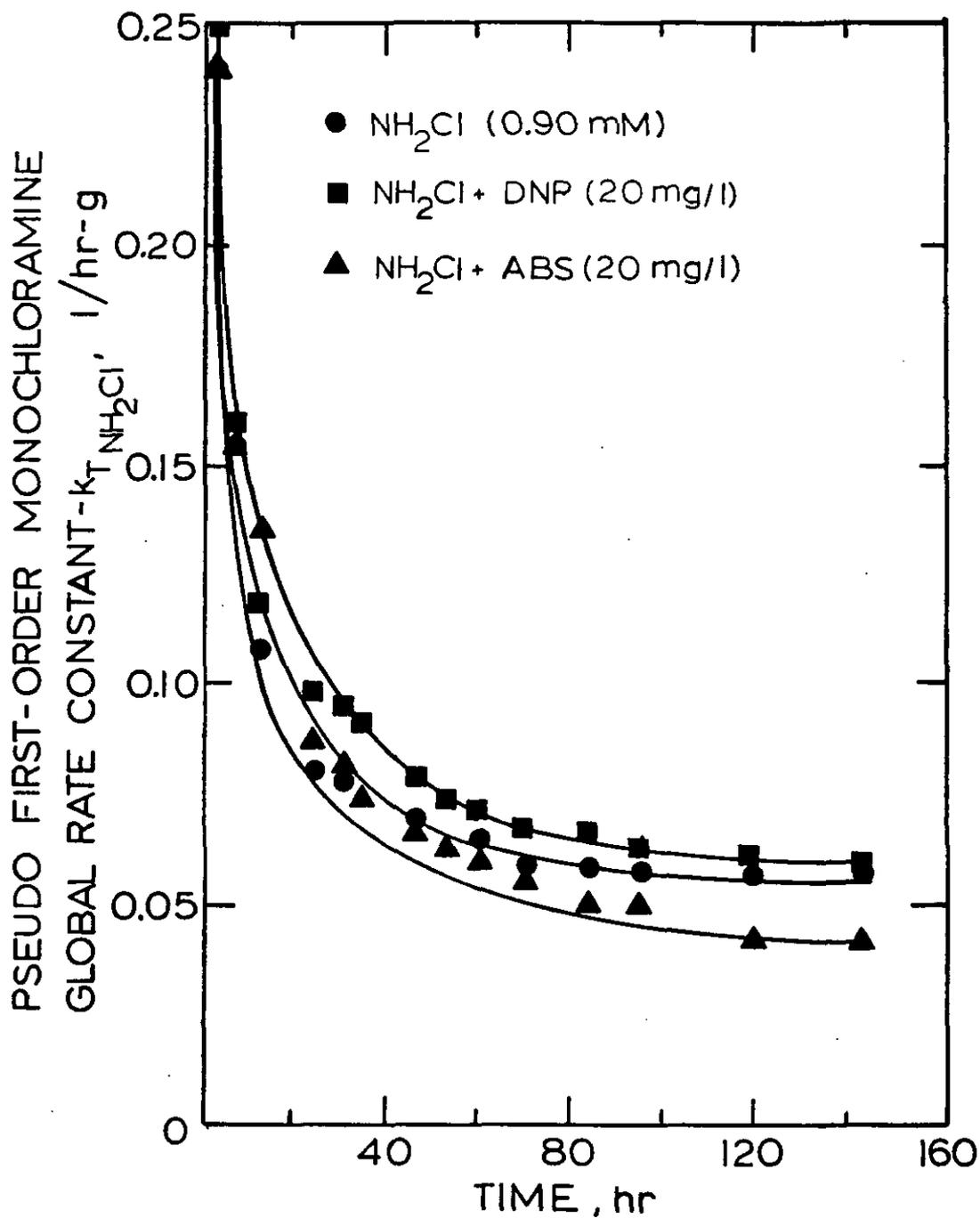


Figure 31. Depression of $k_{T \text{ NH}_2\text{Cl}}$ by the addition of ABS and DNP.

The results given in Figures 30 and 31 indicate a range of interference behavior with the monochloramine-carbon reactions. For a reduction in $k_T \text{NH}_2\text{Cl}$ to be observed, either ammonia and/or nitrogen gas production were reduced, i.e. this interference should be reflected by decreases in k_1 and/or k_2 . As shown in Figure 32, the presence of wastewater and ABS reduced both k_1 and k_2 . Thus, partial blockage of both the ammonia and nitrogen gas reactions is indicated. However, it appears that the presence of MB produced little interference with ammonia production, k_1 , but instead, only depressed the nitrogen gas production rate. Obviously, because DNP did not decrease $k_T \text{NH}_2\text{Cl}$, there was no measured reduction of either k_1 or k_2 .

To explain the extent of interference caused by adsorption of organics, the concept of site competition must be considered. In Chapter 5, investigation of phosphate buffer interaction and pH implied that basicity may be an important factor controlling the kinetics of monochloramine conversion. Although the specific organic compounds MB, ABS and DNP used were of different basicities, (MB the greatest, DNP the least), there was no trend of increased depression of k_1 with increased basicity. However, it is probable that this effect was masked by the much higher concentration of phosphate buffer (3×10^{-2} M vs approximately 10^{-4} M for the test organic). MB, ABS and wastewater significantly reduced k_2 with time corresponding to increased extent of adsorption. This indicates that these organics partially occupied reaction sites required for nitrogen gas production. Again, there was no correlation of basicity of the organic and greater reduction of k_2 .

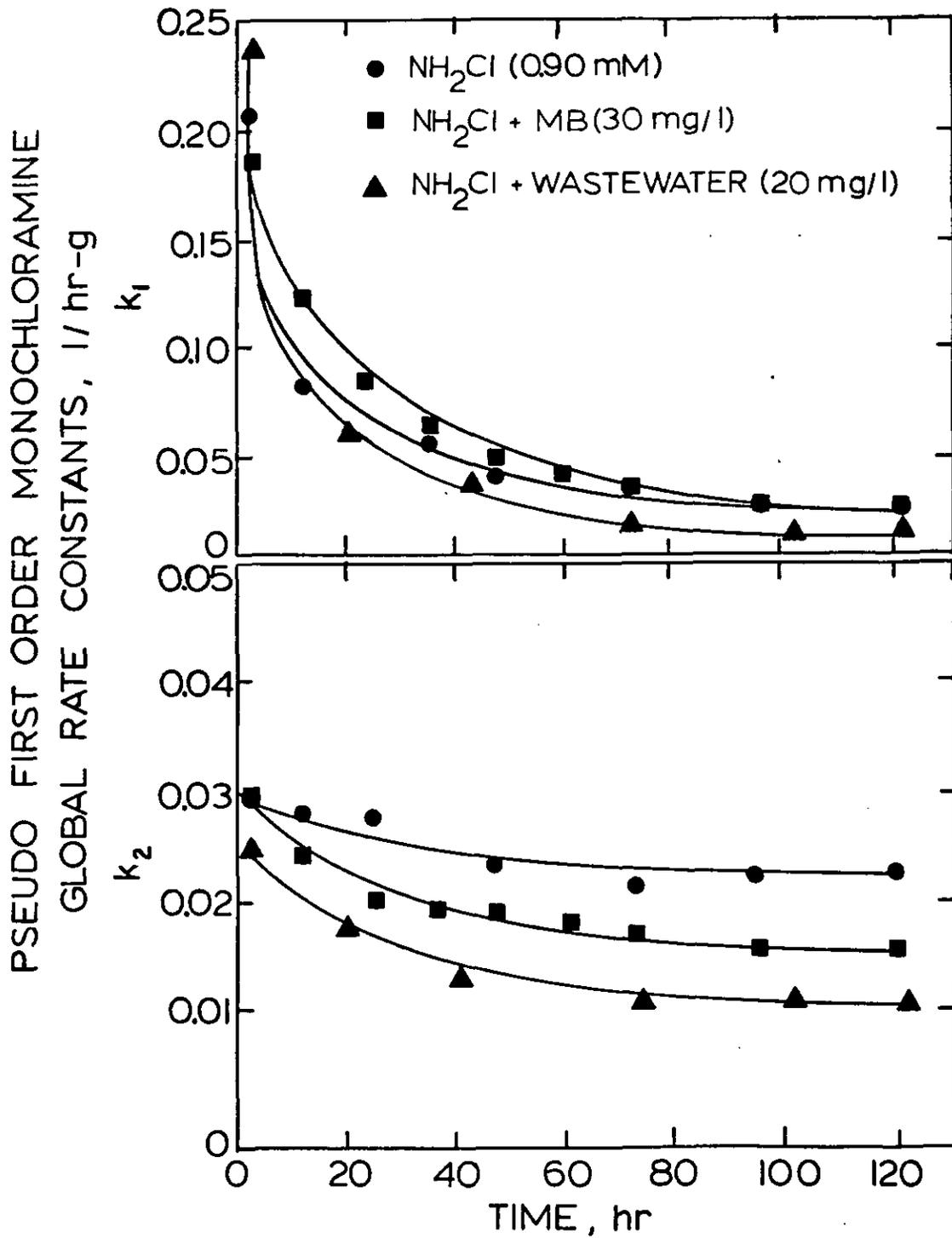


Figure 32. Comparison of pseudo first-order, global rate constants, k_1 and k_2 , by addition of selected organics.

The rate constants k_1 , k_2 and $k_T \text{NH}_2\text{Cl}$, at apparent steady-state are presented in Table 5 for all systems studied. The practical implication of the almost 50 percent reduction of $k_T \text{NH}_2\text{Cl}$ in the presence of wastewater is that reaction time will correspondingly need to be doubled to achieve the same ammonia removal.

Thus far, the reduction in rate constants caused by adsorption of organics has been presented. However, it is important to realize that nitrogen gas yield, and thus net removal of ammonia, is also reduced. This can be seen by examination of Figure 33; MB and wastewater reduced nitrogen gas production from 42 percent (without organics) to 24 percent. ABS reduced steady-state yield to 36 percent, while no effect was observed for DNP. The decrease in yield indicates that for a given amount of monochloramine reacted, the presence of organics caused less monochloramine conversion to nitrogen gas, and more to ammonia (See Equation 5-2).

Further insight into the interaction caused by organic adsorption can be gained by examining the breakthrough pattern of MB, ABS and DNP in the presence of monochloramine. As shown in Figures 34 and 35 the sorptive capacity for MB and ABS was somewhat reduced when monochloramine was present. This suggests that adsorption sites were preferentially occupied by either monochloramine prior to surface reaction or by surface oxides subsequently produced. This finding supports the competition theory proposed to explain suppression of the rate constants by certain organic molecules. Further verification is given by noting from Figure 36 that the adsorption capacity of DNP was not affected by the monochloramine-carbon reactions. This organic also did not suppress the rate of

Table 8

Apparent Steady-State Monochloramine Rate Constants - pH 8.3

Influent Composition	k_1	k_2	k_T NH_2Cl (1/hr-g)
NH_2Cl (0.90 mM)	0.034	0.024	0.058
Wastewater (20 mg/l TOC) + NH_2Cl	0.021	0.009	0.030
MB (30 mg/l) + NH_2Cl	0.033	0.010	0.043
ABS (20 mg/l) + NH_2Cl	0.027	0.016	0.043
DNP (20 mg/l) + NH_2Cl	0.034	0.025	0.059

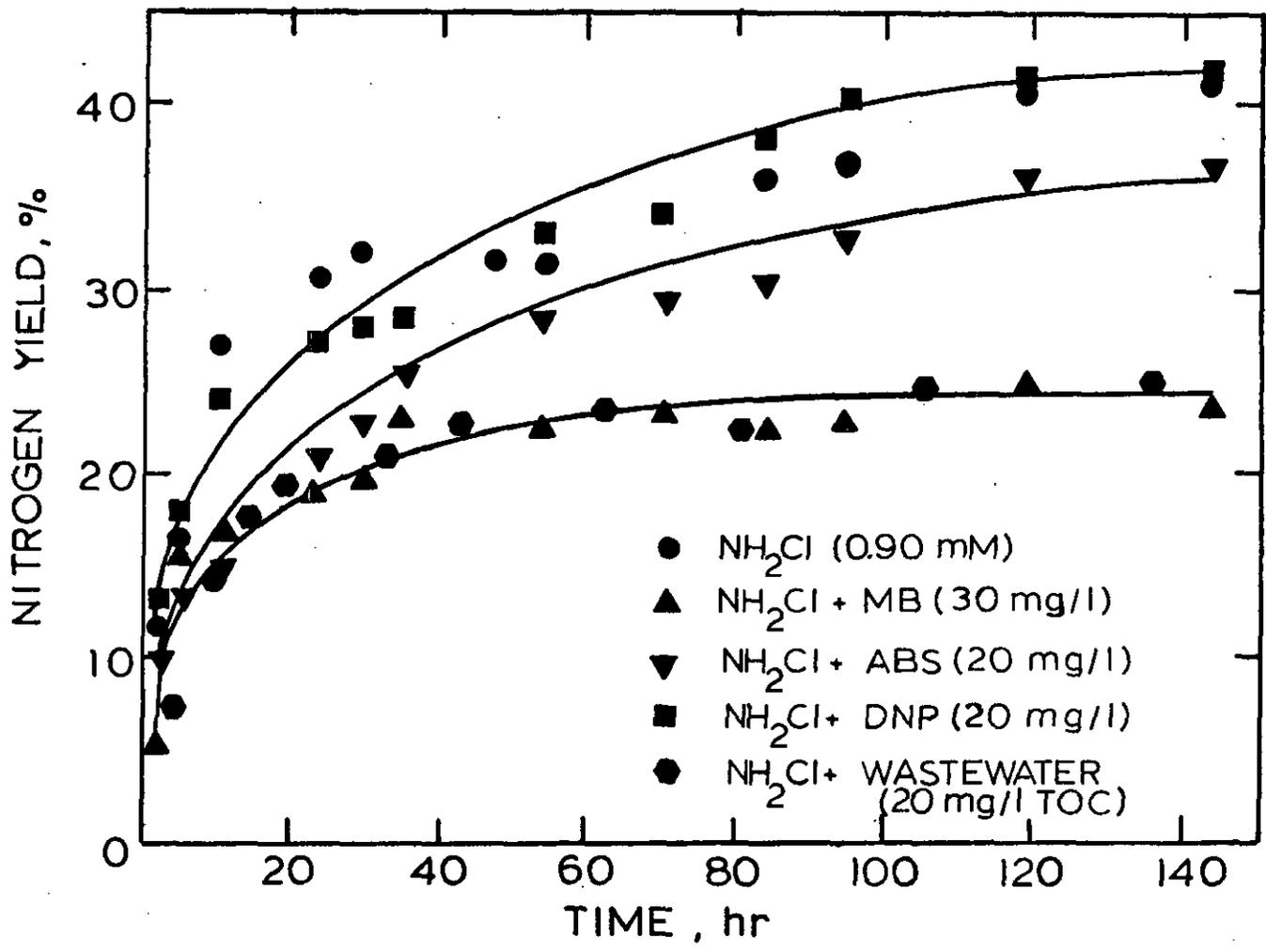


Figure 33. Depression of nitrogen gas yield by addition of selected organics.

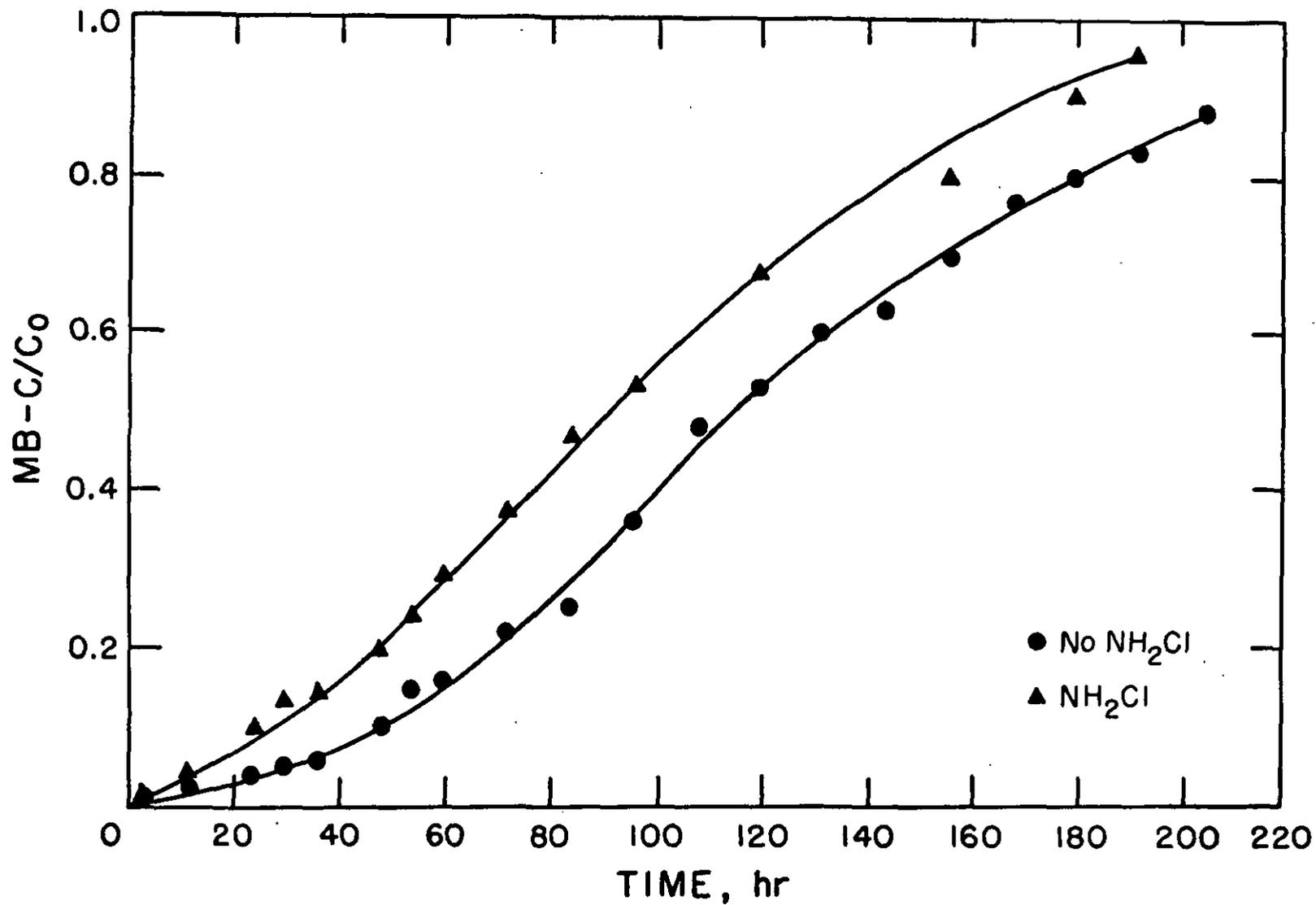


Figure 34. Effect of monochloramine-carbon reactions on the adsorptive behavior of MB at $W/Q=8.33$ g-hr/l.

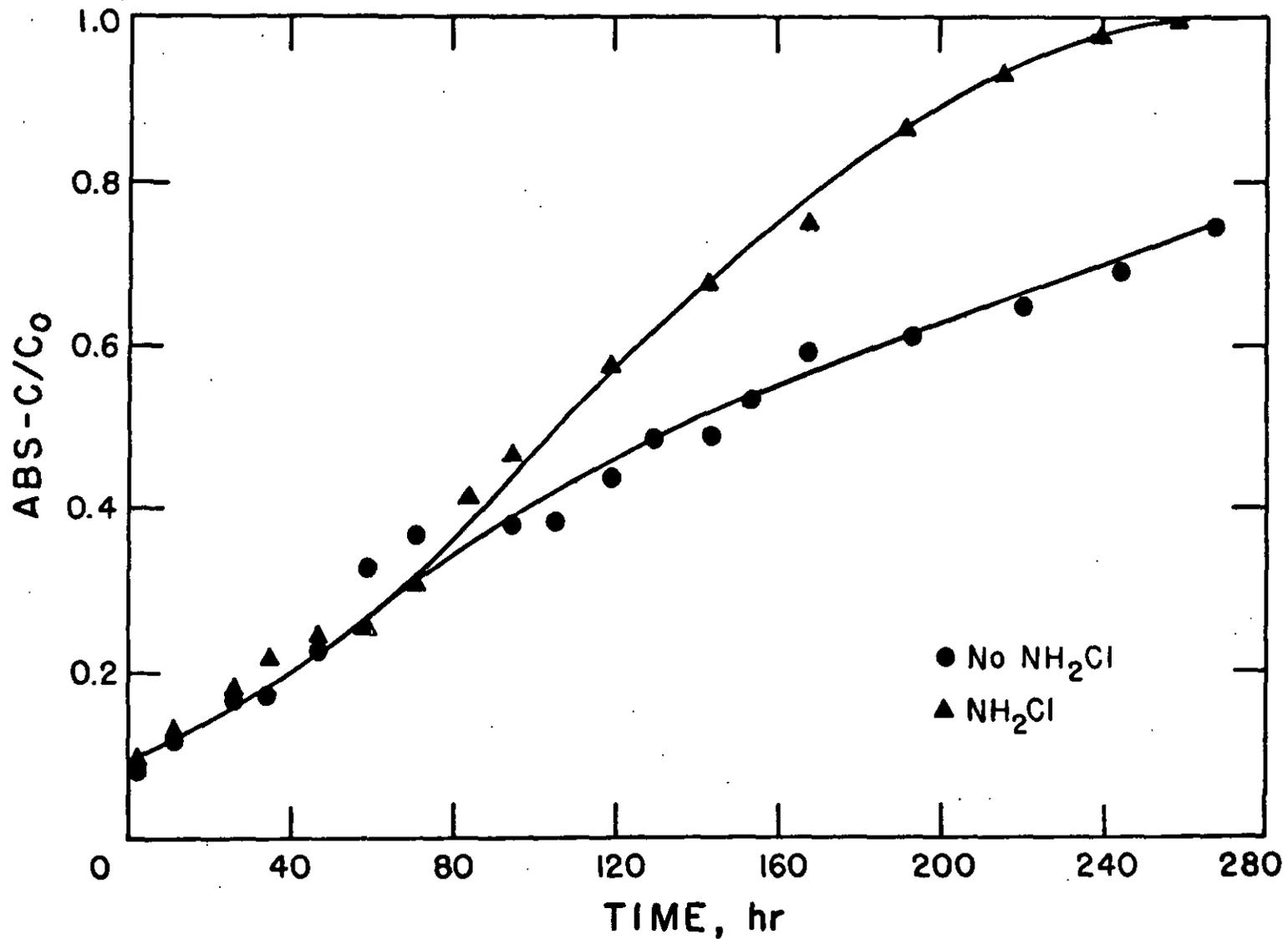


Figure 35. Effect of monochloramine-carbon reactions on the adsorptive behavior of ABS at $W/Q=25.0$ g-hr/l.

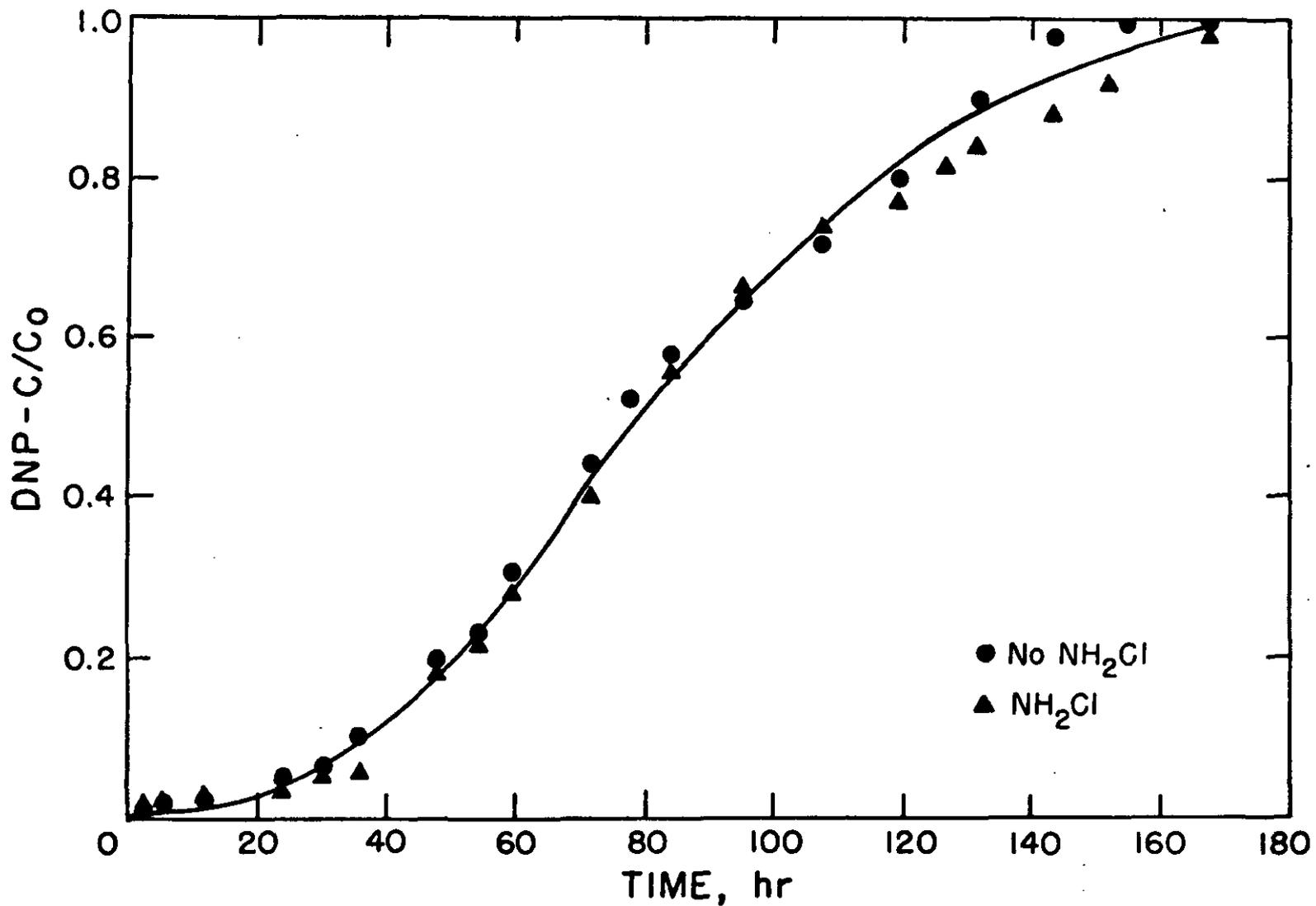


Figure 36. Effect of monochloramine-carbon reactions on the adsorptive behavior of DNP at $W/Q=8.33$ g-hr/l.

monochloramine conversion. The original intent of selecting DNP for study was to test the hypothesis that an increase in carbon surface polarity caused by oxide buildup would enhance the removal of more polar compounds. The fact that DNP neither interfered with monochloramine conversion nor was removed to a greater extent implies that surface reaction sites needed for DNP adsorption and monochloramine conversion are mutually exclusive.

Adsorption of Organics and Conversion of Dichloramine

Dichloramine reacts with activated carbon by a single pathway to produce nitrogen gas as the only nitrogen end product. Therefore, interaction of organic compounds with the reaction should not affect nitrogen gas yield, but may alter reaction rate. That is, all dichloramine reacted has to be converted to nitrogen gas in contrast to monochloramine, which can form either ammonia or nitrogen gas. Nitrogen gas yield with operating time is presented in Figure 37 for the systems investigated. Steady-state nitrogen yield was greater than 95 percent in each system. However, yield was less than 100 percent because small amounts of monochloramine were being converted to ammonia. The presence of monochloramine may be due to initial adsorption of hydrogen ions which caused pH to increase such that the dichloramine equilibrium was shifted towards monochloramine. As dichloramine conversion proceeded, hydrogen ion production caused pH to gradually decrease to a steady-state value of about 3.8; the time required was usually 24 to 48 hours. Once pH became constant, nitrogen yield also became constant.

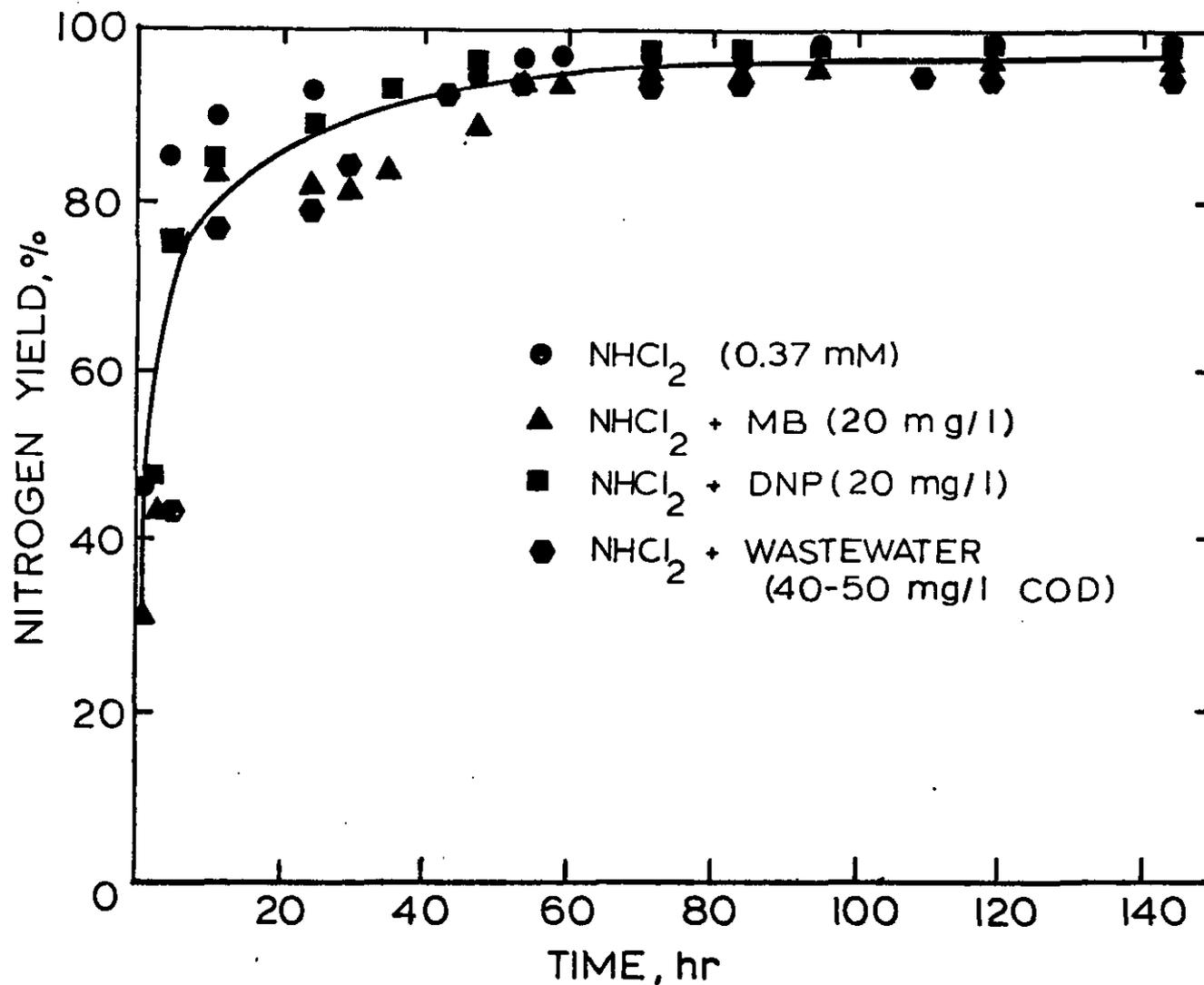


Figure 37. Nitrogen gas yield with addition of selected organics.

Figure 38 indicates that while nitrogen gas yield was unaffected, reaction rate was significantly reduced by the presence of organics. In fact, the reduction in rate constant seemed parallel to the extent of adsorption of organics. That is, the greatest reduction in rate was noted initially when adsorption was also most actively occurring. An apparent steady-state rate constant was obtained when the carbon was exhausted. For a feed solution of only dichloramine (0.37 mM), reaction rate remained constant for 140 hours of operation corresponding to a loading of 2 g NHCl_2 reacted/g carbon.* For feed of alum clarified wastewater, organic sorptive capacity was reached after 160 hours of operation; dichloramine loading for this time period was approximately 0.1 g NHCl_2 reacted/g carbon. Both MB and DNP reached sorptive capacity after a dichloramine loading of approximately 0.5 g reacted/g carbon. A loading of 5 g/g was previously required to observe a surface poisoning effect; however, loadings for all studies incorporating organic feed were far below this level. This indicates that in systems containing organics, the decrease in the global rate constant was due only to site competition and not to surface oxide poisoning.

Clearly, these results indicate that organic compounds compete with dichloramine for adsorption/reaction sites. Once occupied by an organic, a site is no longer available for dichloramine reaction. As in monochloramine conversion studies, alum clarified wastewater had the greatest effect on the global rate constant. It is interesting to note that DNP reduced the dichloramine rate constant but not the monochloramine rate

* The amount reacted rather than the amount applied is used in this case to determine concentration on the carbon surface.

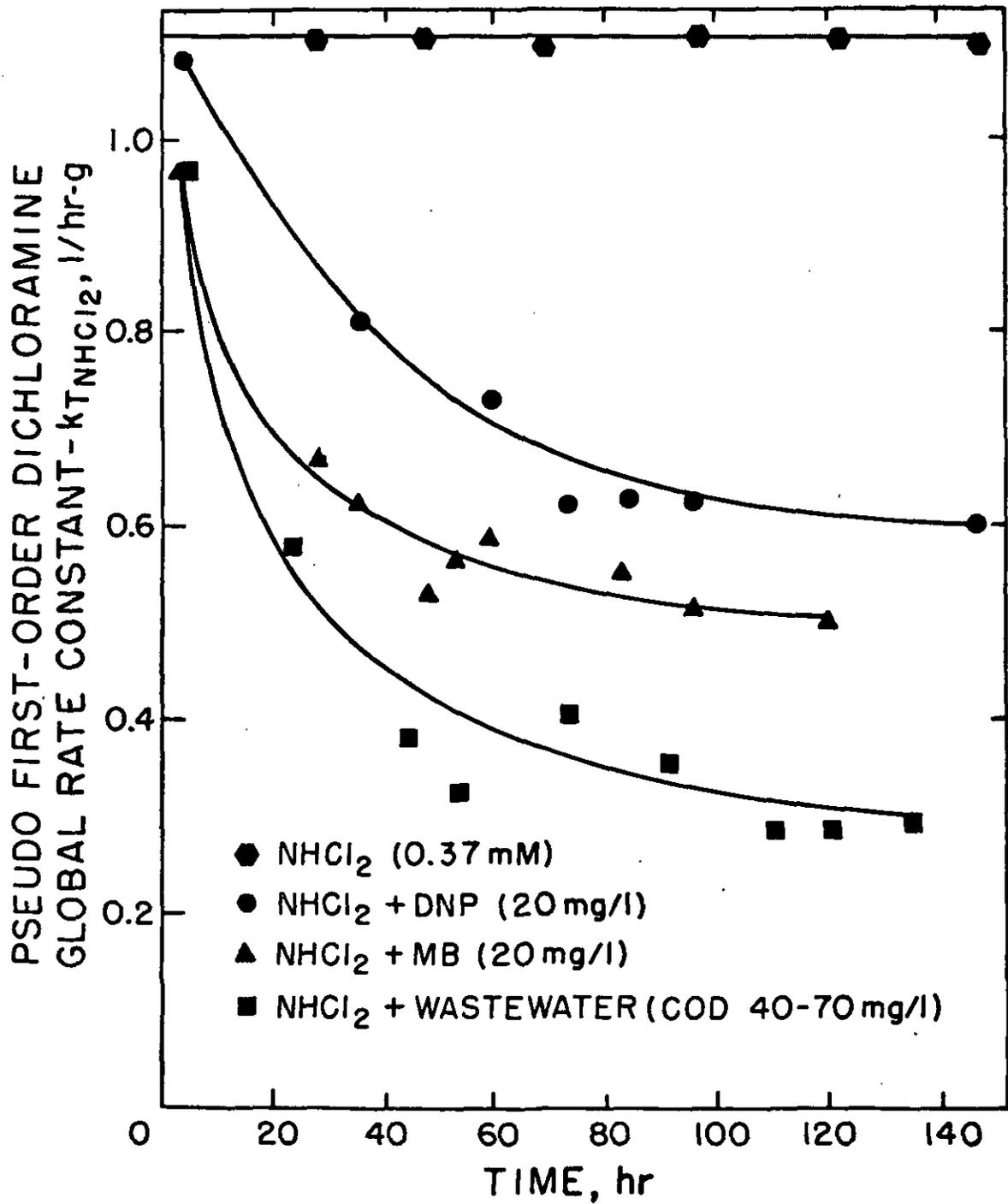


Figure 38. Depression of $k_{T \text{ NHCl}_2}$ by the addition of DNP, MB and alum clarified, raw wastewater.

constant. This suggests that dichloramine may react on different surface sites than monochloramine. Additionally, the decrease in system pH from 8.3 to 4.2-3.8 may change surface functional groups such that sites required for organic adsorption and/or dichloramine reaction are altered.

Despite organic interference, the rate constant for the dichloramine reaction was considerably larger than that for monochloramine. Rate constants at apparent steady-state with a feed of chlorinated wastewater were 0.30 l/hr-g for dichloramine and 0.03 l/hr-g for monochloramine. Thus, the dichloramine reaction is still a factor of ten faster than that of monochloramine.

Figure 39 presents COD breakthrough curves for wastewater with and without the presence of dichloramine. Operated in parallel, feed COD to the two reactors ranged from 40 to 70 mg/l. As shown, sorptive capacity was reduced. Expressed in terms of loading, 0.12 g COD/g carbon was reached in the reactor without a chlorinated feed and only 0.07 g COD/g carbon in that with chlorination. It should also be noted that the immediate breakthrough of TOC in both reactors was due to the short contact time of six minutes. While this contact time enabled complete nitrogen removal, it is far less than required for adsorption. Parallel operation of these two reactors has thus indicated the importance of biological activity on the carbon surface. After 160 hours of operation, removal of organics had ceased in the reactor receiving chlorinated feed; however, removal continued at a low steady-state (30 percent reduction in TOC) in the reactor being fed without addition of chlorine. This residual removal seems directly attributable to biological

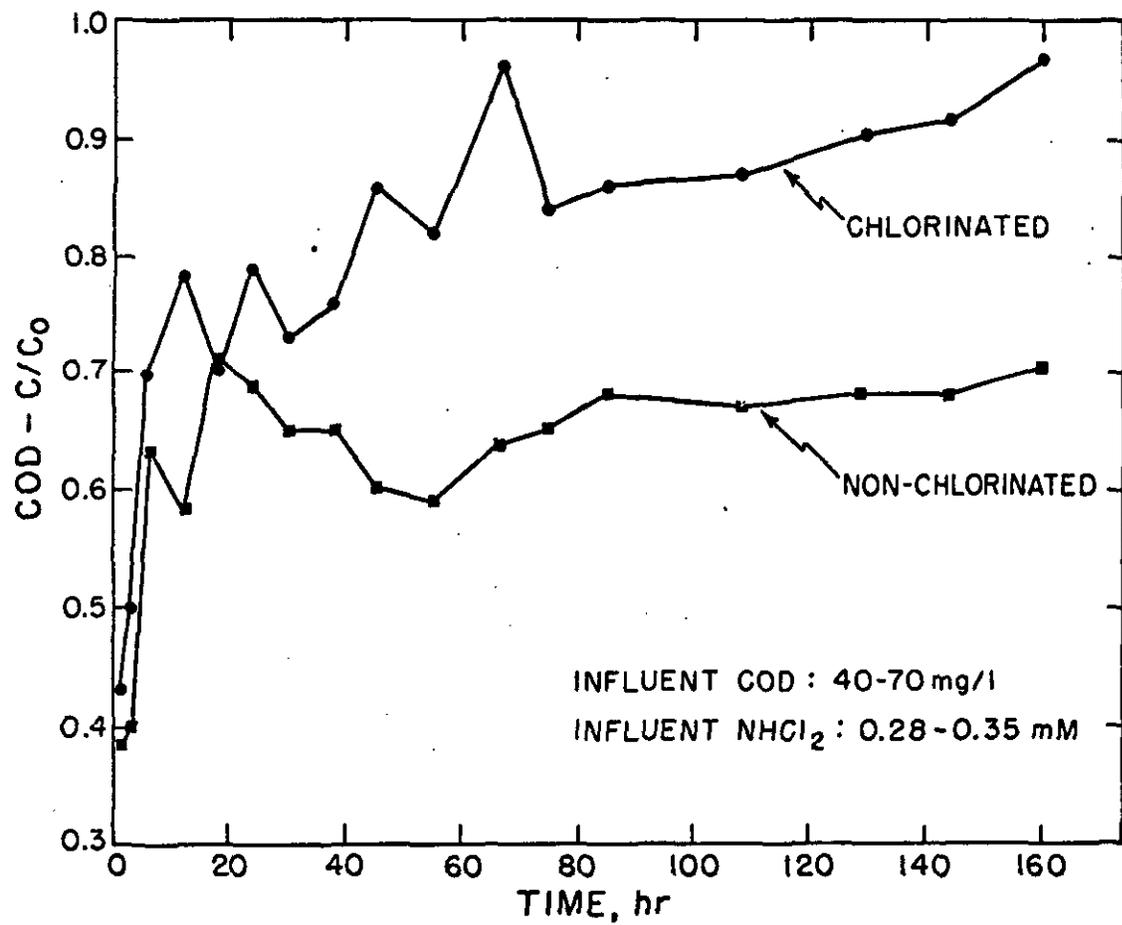


Figure 39. Comparative removals of COD in carbon beds supplied with chlorinated and non-chlorinated wastewater at W/Q=38 g-hr/l (contact time 6 minutes).

activity rather than adsorption. The absence of such biological activity is to be expected in the reactor receiving chlorinated wastewater feed (66 mg/l as Cl_2) thus explaining the lack of continued organic removal. Although less likely, it is also possible that competition between organics and dichloramine for surface sites accounted for this reduced removal of organics.

Summary

Organic compounds competed with monochloramine for specific adsorption/reaction sites and reduced monochloramine conversion. This competitive behavior may inhibit ammonia and/or nitrogen gas production depending on the characteristics of the specific organic. Of the systems tested, alum clarified, raw wastewater had the greatest effect on both the rate of monochloramine conversion and nitrogen gas production while DNP had the least. From a practical point of view, the presence of organics in the wastewater feed would double the reactor contact time required (from 8 minutes to 16 minutes for 95 percent conversion) and reduce the nitrogen removal from 47 to 24 percent.

In addition, the monochloramine-carbon reactions reduced the adsorptive capacity of MB and ABS but did not affect DNP. These results support the organic-monochloramine site competition theory.

Organics also competed with dichloramine for specific adsorption/reaction sites. Because dichloramine reacts by only a single pathway to produce nitrogen gas it was impossible for organics to affect nitrogen

yield. However, the reaction rate of dichloramine was significantly reduced. Organic interference varied, with alum clarified wastewater exhibiting the greatest effect. Despite this interference, in comparison to monochloramine the dichloramine reaction rate was quite rapid; with a wastewater feed, the rate of dichloramine reaction is still 10 times faster than that of monochloramine.

Thus, these results have shown that conversion of ammonia to nitrogen gas and adsorption of residual organics can be accomplished in the same carbon bed. The formation of dichloramine at pH 4.2 rather than monochloramine at pH 8.3 has the advantages of (1) nitrogen gas being the only nitrogen end product, thereby yielding the potential for 100 percent nitrogen yield and (2) carbon contact time being shorter due to the faster rate of dichloramine reaction, even in the presence of organics.

Figure 38 implies that organic sorptive capacity was reached far before poisoning of the carbon by dichloramine reaction was observed. From a practical design standpoint, a loading of 6 g NHCl_2 applied/g carbon, that required for poisoning to be observed, would only be achieved after treating a wastewater volume far in excess of the carbon organic sorptive capacity. Therefore, use of a combined ammonia and organic removal process would necessitate thermal regeneration for removal of sorbed organics prior to any significant surface poisoning. Regeneration not only removes organics but surface oxides as well, thus minimizing oxide interference with organic adsorption when the carbon is placed back in line. Moreover, regeneration is most compatible with the dichloramine reaction because it prevents

accumulation of oxides which would result in poisoning. In contrast, regeneration is undesirable for the monochloramine reaction because oxide removal will result in more ammonia production and therefore less nitrogen yield.

C H A P T E R V I I I
P R O C E S S D E S I G N A N D C O S T C O N S I D E R A T I O N S

Process Design

This research has shown that both mono- and dichloramine formed from ammonia react on the carbon surface to produce nitrogen gas. However, from a design standpoint it is important to recognize the possible process alternatives for ammonia removal that derive from consideration of these reactions.

The conversion of monochloramine on the carbon surface has been shown to be capable of producing a maximum "net" ammonia removal of 42 percent. This is a result of formation of a fraction of monochloramine to ammonia. Moreover, in the presence of alum clarified wastewater, only 25 percent ammonia removal was achieved. Ammonia removal could be increased to a more desirable level by multiple staging of chlorine addition. That is, rather than allow re-formed ammonia to escape, more monochloramine could be formed and then reacted on the carbon surface in a follow-up reactor. This process alternative seems very impractical because of the very low net ammonia removal (25 percent of feed ammonia) achieved at each stage. Another possibility for utilizing the monochloramine reaction is to remove organics in a separate carbon bed prior to chlorination. While this alternative would increase ammonia removal to 42 percent, multiple staging of chlorine addition would still be required and again appears impractical.

A better alternative for nitrogen removal appears to be dichloramine formation followed by conversion to nitrogen gas on activated carbon.

However, the reaction to form di- rather than monochloramine, requires that pH be decreased to 4.2. In contrast to monochloramine conversion, this reaction produces only nitrogen gas. Thus, 100 percent removal of nitrogen is possible. In addition to achieving greater nitrogen removal, this process also requires far less reaction time than conversion of monochloramine. In this research, only one minute was needed to obtain maximum nitrogen removal in the presence of alum clarified wastewater; this compares to 16 minutes required for monochloramine conversion.

Because both breakpoint chlorination and dichloramine carbon conversion remove almost all ammonia, it is also important to compare the dosage requirements for these two processes. To achieve breakpoint chlorination of chemically clarified wastewater, Bishop, et al. (1972) have shown that a molar $\text{Cl}_2:\text{NH}_3$ ratio of 1.6:1 was required at pH 6.5-7.5. In this research, Figure 40 shows that with alum clarified wastewater a higher molar $\text{Cl}_2:\text{NH}_3$ ratio of 2:1 was required to obtain an overall ammonia removal of 90 percent by breakpoint reactions and dichloramine conversion on the carbon surface at pH 4.2. However, as seen in Figure 40 the dosage to achieve 90 percent removal was disproportionately greater than that required for 70 percent removal. A savings in total chlorine dosage can be achieved by two stage addition. That is, in the first stage a molar $\text{Cl}_2:\text{NH}_3$ ratio of 1.2:1 would result in 70 percent overall removal of ammonia. In the second stage, with only 30 percent of the ammonia remaining, a molar $\text{Cl}_2:\text{NH}_3$ ratio of 1.2:1 would yield an additional 70 percent removal

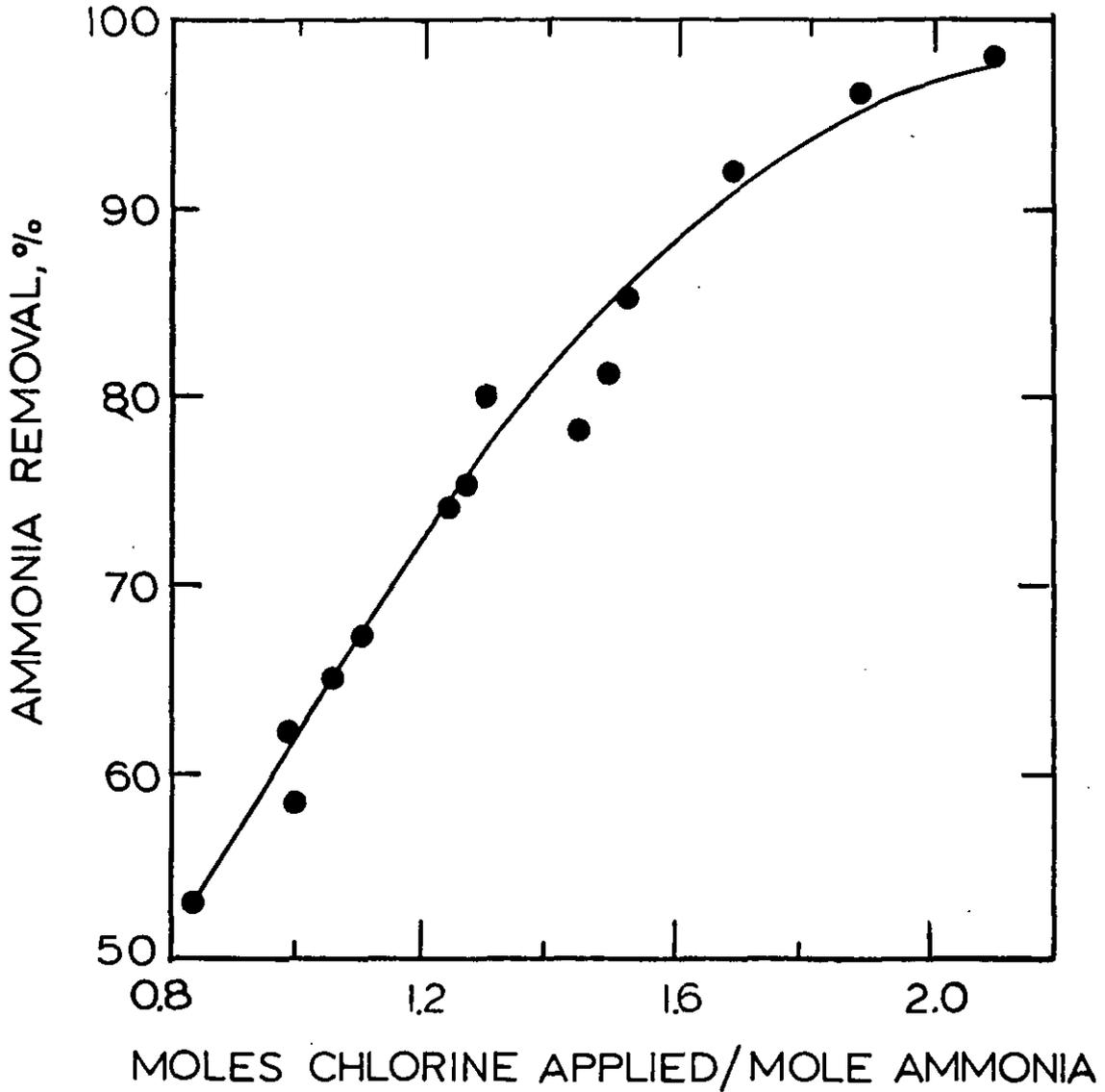


Figure 40. Overall ammonia removal vs chlorine dosage for alum clarified, raw wastewater containing 20 mg/l ammonia at influent pH 4.2.

of the remaining ammonia fraction. Thus, the total ammonia removal through both stages would be 70% + .70 (30%) or 91% and the molar ratio required 1.2:1 + 0.3 (1.2:1) or 1.6:1. Therefore, both breakpoint chlorination and dichloramine-carbon conversion will require the same molar ratios of $\text{Cl}_2:\text{NH}_3$.

Although the chlorine dosage requirement has been shown to be equivalent, it is important to recognize the process control drawbacks of breakpoint chlorination as compared to dichloramine-carbon conversion. In breakpoint chlorination, the chlorine dosage is intentionally increased to avoid formation of monochloramine and dichloramine. However, process control is difficult because of the varying strength of wastewater and as a result, under and over dosing occur; under dosing causes release of potential toxic chloramines while over dosing is expensive and may produce toxic nitrogen trichloride. In contrast to breakpoint chlorination, chloramines initially formed are removed on the carbon surface. This feature assures reliable performance even if ammonia concentration varies. Moreover, this process offers the advantage of controlling the extent of nitrogen removal by adjusting the chlorine dosage to provide for conversion of only a fraction of the total ammonia to chloramines.

The only major disadvantage of dichloramine-carbon conversion therefore appears to be the need for pH adjustment, i.e. pH must be reduced to 4.2 for dichloramine formation. However, the possibility of selective formation of small fractions of monochloramine in the mixing reactor could be considered to lessen pH adjustment. Maintaining pH at 5-6 in the feed to the carbon bed would favor dichloramine formation while still allowing

for some monochloramine formation. Although both surface reactions produce hydrogen ions, a higher effluent pH would result from a combined mono- and dichloramine feed. This would also reduce the upward pH adjustment required after carbon contact thereby providing a savings in operating cost; however, ammonia removal efficiency would also be slightly reduced due to partial monochloramine conversion back to ammonia.

Another process alternative is to consider breakpoint chlorination, without pH adjustment, followed by carbon contact. For example, Pressley, et al. (1972) found that breakpoint could be obtained at a $Cl_2:NH_3$ molar ratio of 1.6:1 at pH 6.5-7.5; however, chloramines remained. Thus, in the proposed process, carbon contact following breakpoint chlorination would enable conversion of residual chloramines and produce complete ammonia removal. This would also eliminate the process control problems associated with matching chlorine dosage to ammonia feed concentration.

Description of Proposed Treatment Scheme. Process costs were estimated for a 10 mgd physical-chemical treatment plant incorporating coagulation, filtration and chlorination-carbon contact. The goal of the treatment scheme was to remove BOD, phosphorus, ammonia and suspended solids to a high degree. A schematic flow diagram of the proposed system is presented in Figure 41. Chemical coagulation with either alum (180 mg/l) or lime (360 mg/l as $CaOH_2$) was selected to meet the requirement of 95 percent phosphorus removal; this process can remove 75 percent of the BOD (Martel, et al., 1975). Two-stage recarbonation of lime-clarified wastewater is provided.

Following chemical clarification, the wastewater is passed through dual-media filters at an application rate of 5 gpm/sq ft. Effluent from the filters will contain less than 1 mg/l suspended solids.

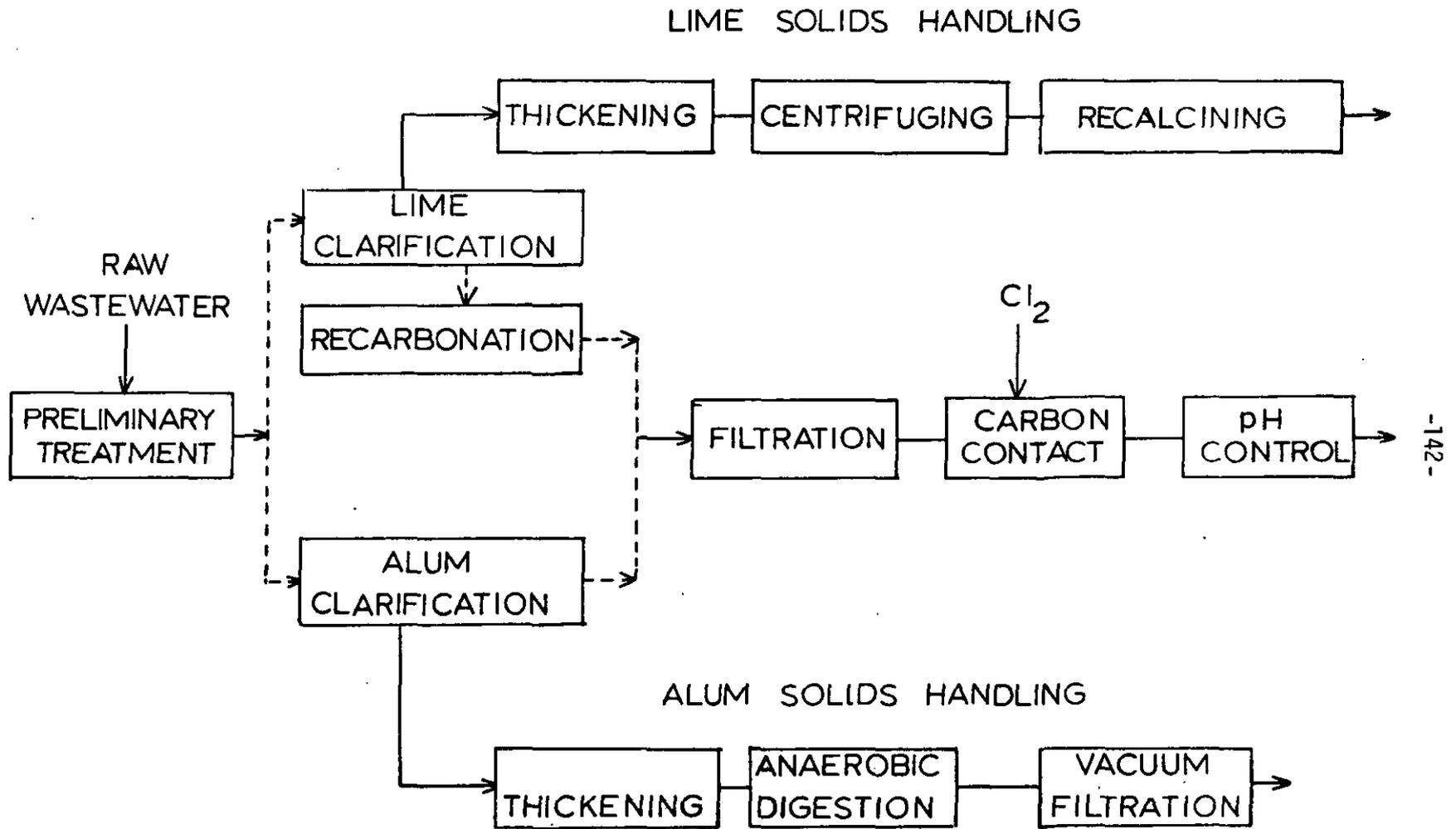


Figure 41. Flow diagram of alternative physical-chemical treatment systems.

Dissolved organics and ammonia are subsequently removed by a combined unit process consisting of chlorination and activated carbon contact. At this stage of treatment the wastewater is assumed to contain 20 mg/l TOC and 20 mg/l of ammonia.

Chlorination of the ammonia produces chloramines which are converted to nitrogen gas by the carbon. As was indicated in Figure 40, the $\text{Cl}_2:\text{NH}_3$ mole ratio dictates the degree of ammonia removal. Two-stage chlorination is used to provide a desired 90 percent ammonia removal. In the first-stage, 70 percent of the influent ammonia (20 mg/l) is removed with a chlorine dosage of 5700 lb/day (91 mg/l). The remaining ammonia fraction of approximately 6 mg/l is then chlorinated in a second-stage to achieve an overall removal of 90 percent; dosage for the second-stage is 1670 lb/day (27 mg/l). Total chlorine requirement for the two-stage system is 7370 lb/day (118 mg/l). In contrast, a single-stage chlorine addition would require 8670 lb/day Cl_2 (139 mg/l) to achieve equivalent ammonia removal.

Solids handling from alum treatment includes gravity thickening, anaerobic digestion, vacuum filtration and landfill disposal. Economics of lime treatment dictate the recovery and reuse of CaO from the lime-sludge by gravity dewatering, centrifuging and recalcining. It is assumed that the recalcining process will recover 60 percent of the required lime (Evans and Wilson, 1972). Ash, remaining after recalcining, is disposed of by landfill. The CO_2 produced as a by-product of recalcining is recovered and use as the acid source for recarbonation.

The carbon contactors not only remove ammonia, in the form of chloramines, but also adsorb dissolved organics. Therefore, an integrated process design must provide for both reactions to occur.

Results of this research indicate that chloramine-carbon reactions are quite rapid and require only a few minutes of carbon contact for complete conversion. However, organic adsorption requires considerably more carbon contact time to achieve acceptable removals. Thus, the reaction which controls the contact time requirement is adsorption. Four columns, each containing 4500 ft³ of carbon, provide a 20 minute contact time. The columns are operated in upflow mode at an application rate of 6 gpm/sq ft. For a carbon capacity of 0.2 lb TOC/lb carbon, the organic exhaustion rate is 835 lb carbon/MG.

The location of chlorine addition to the carbon contact system is an important factor in process design. Chloramines retard biological activity on the carbon surface and reduce overall organic removal. Therefore, it is proposed to apply first-stage chlorination between the second and third carbon column; this would provide approximately five minutes of non-chlorinated wastewater-carbon contact and allow for partial biological oxidation of organics. In addition, because biological activity will produce a steady-state organic removal of about 30 percent, it is recommended that these first two columns not be regenerated but rather be used as biological slime reactors for continual removal of biodegradable organics.

Production of hydrogen ions by the chloramine-carbon reactions will require an upward adjustment of pH to meet effluent discharge guidelines. For this purpose, the choice of lime instead of alum, for chemical clarification, offers a distinct economic advantage. That is, a higher effluent pH would result from chlorination of a lime-clarified, recarbonated wastewater rather than an alum-clarified

wastewater. This would reduce chemical requirements for pH control and thereby provide a savings in operating costs. However, choice of the lime system may slightly reduce ammonia removal efficiency. Chlorination of the lime-clarified wastewater would reduce pH to 4.5-5.5. This pH range would favor dichloramine formation but also allow for some monochloramine formation. The reduced removal efficiency is a result of partial conversion of the monochloramine back to ammonia.

Process Costs. Capital costs (\$/MG) include equipment, construction and design. All costs were amortized for 20 years at 6 percent interest; no federal assistance was assumed. Economic capital costs indicators, obtained from Engineering News Record (1976), were used to update costs for chemical clarification and filtration which were presented by Evans and Wilson (1972) for South Lake Tahoe. The indicators were also used for computing cost of the carbon contact-regeneration system which was designed according to the EPA Carbon Adsorption Design Manual (1973).

Cost for lime treatment includes coagulation, recarbonation, recalcination and solids handling while alum treatment provides for coagulation and solids handling. An 8500 pounds per day evaporator and chlorinator is used for chlorine gas feed with one unit on standby.

The unit operating costs shown in Table 9 represent current prices in the Northeastern United States. Three individuals per shift are required to operate the plant. Labor costs were updated using an Hourly Earnings Index Ratio (Chemical Engineering, 1976). Oil is used as a fuel source primarily for lime recalcination and carbon regeneration. Only 60 percent of the required lime is recovered by recalcination; thus,

Table 9

Unit Operating Costs Based on May 1976 Available Prices

Labor	
Operating	\$9.32/hr
Maintenance	\$7.72/hr
Electricity	\$30/1000 kwh
Fuel Oil	\$0.35/gal (1.33 therm/gal)
Chemicals	
Lime - Ca(OH)_2	\$0.03/lb
Alum	\$0.02/lb (49% dry alum)
Chlorine gas	\$0.16/lb
Carbon	\$0.44/lb

make-up lime is required. Regeneration of the spent carbon results in an 8 percent carbon loss per cycle.

Operating costs for effluent pH control assume use of lime for chemical clarification. Using this treatment scheme, effluent pH from the chloramine-carbon contactors will be approximately 3.5. To raise pH such that effluent requirements are satisfied (pH 7), a lime dosage of 37 mg/l as $\text{Ca}(\text{OH})_2$ will be required to offset hydrogen ion production from dichloramine conversion.

Table 10 presents total costs for the physical-chemical treatment system. Capital and operating costs to achieve greater than 90 percent removal of BOD, phosphorus and ammonia are \$186/MG and \$562/MG, respectively for lime clarification and \$218/MG and \$534/MG, respectively for alum clarification. Total treatment costs are \$748/MG and \$753/MG for lime clarification and alum clarification, respectively. This compared to about \$680/MG for an alternative conventional nitrification/denitrification system employed at Central Contra Costa Sanitary District Water Reclamation Plant, California (Nitrogen Control Design Manual, 1975).

Table 10

Total Costs for Physical-Chemical Treatment

Based on May 1976 Prices

Unit Process	Capital Cost \$/MG	Operating Cost \$/MG	Total Cost \$/MG
Preliminary Treatment	2.44	11.22	13.66
Chemical Clarification			
with Lime	70.28	169.57	239.85
with Alum	102.54	141.30	243.84
Filtration	44.87	24.80	69.67
Chlorination-Carbon Contact	48.46	252.00	300.46
Regeneration	17.85	95.00	112.85
pH Control	<u>2.54</u>	<u>9.25</u>	<u>11.79</u>
Total Cost			
with Lime Clarification	186.00	562.00	748.00
with Alum Clarification	218.00	535.00	753.00

C H A P T E R I X

CONCLUSIONS

Continuous flow operation of a carbon reactor verified that both mono- and dichloramine were converted by surface reactions to nitrogen gas. While monochloramine reacted by a parallel pathway to form both ammonia and nitrogen gas, the stoichiometry proposed by Bauer and Snoeyink (1972) did not appear to control equilibrium reaction conditions. Rather, interference from basic compounds was implicated in reducing the conversion rate of monochloramine to ammonia. This was verified from kinetic analysis conducted at pH 7.7, 8.3 and 9.1. Rate of conversion decreased with increased pH. In addition, the phosphate buffer ($3 \times 10^{-2}M$) used to control pH adsorbed onto monochloramine reaction sites. The extent of buffer interaction with the surface seemed to decrease with reactor operating time and paralleled the pattern observed for the decrease in monochloramine conversion rate.

Dichloramine reacted by a single pathway to produce nitrogen gas with no ammonia production. Thus, formation and subsequent reaction of dichloramine offers the potential for 100 percent nitrogen removal. However, accumulation of surface oxides, a by-product of the reaction, resulted in a poisoning of the carbon surface. This poisoning effect was observed after 6 g $NHCl_2/g$ carbon had been applied. Beyond this loading, dichloramine conversion efficiency began to decrease at an increasing rate.

Kinetic analysis revealed that the overall conversion of monochloramine could be described by a first-order, irreversible model. Moreover, the parallel reactions to ammonia and nitrogen gas were also first-order. These reactions could be described by a pseudo steady-state model because the approach to steady-state conversion was very slow. The decrease in overall conversion rate to an apparent steady-state after 140 hours could be explained primarily by a decrease in the ammonia production rate constant.

The intrinsic rate of nitrogen gas production given by the rate constant, k_2 , decreased with increased pH. This implies an acid catalyzed reaction. However, for any given pH, k_2 did not measurably increase with time as may have been expected if production of surface oxides was an important factor. This result suggested that the surface oxides produced by conversion of monochloramine to ammonia cannot be utilized for nitrogen production. Rather, these oxides may be unstable and lost from the surface before conversion to nitrogen gas can occur. Alternatively, the virgin carbon surface may contain the required oxide complexes to promote the nitrogen gas reaction. The initial formation of nitrogen gas, without significant oxide formation from ammonia production, supports this hypothesis.

The dichloramine-carbon reaction also followed first-order, irreversible kinetics. Poisoning of the reaction due to surface oxide buildup was adequately described by a modified first-order model. Because of the difficulty of measuring surface oxides, this model included the amount of dichloramine applied to the reactor as a measure of surface oxide accumulation.

By varying particle diameter, the monochloramine reaction was shown to be strongly controlled by surface reaction with little influence of pore diffusion. In contrast, the rate of dichloramine conversion was shown to be strongly controlled by pore diffusion. Moreover, for the same particle diameter, the overall reaction rate was 20 times that of monochloramine, suggesting the dichloramine surface reaction rate to be much greater than that of monochloramine. Simultaneous feed of MB, ABS, DNP or alum clarified, raw wastewater produced varying degrees of inhibition of monochloramine reactions. The greatest effect was noted for wastewater (nitrogen yield was reduced from 42 to 25 percent) while no effect was noted for DNP. Competition for reaction/adsorption sites was also indicated by the reduced adsorption capacity of MB and ABS.

While simultaneous adsorption of organics also reduced the rate of dichloramine conversion, the resulting rate was still far greater than observed for monochloramine. Extended parallel operation of carbon columns receiving chlorinated and non-chlorinated wastewater (alum clarified) showed that dichloramine produced nearly 100 percent conversion to nitrogen gas. However, biological activity was prevented such that organics were removed by only adsorption in contrast to the non-chlorinated system in which biological activity extended removals.

Total cost for a 10 mgd physical-chemical treatment plant employing lime clarification, filtration and chlorination-carbon contact is estimated to be \$748/MG. The system is designed to remove greater than 90 percent BOD, suspended solids, phosphorus and ammonia.

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APPENDIX

Table A-1

Results of Monochloramine Experiments at pH 7.7 and $D_p=0.12$ cm.

time hr	$\tau=0$ g-hr/l		$\tau=8.33$ g-hr/l		$\tau=16.66$ g-hr/l		$\tau=25.0$ g-hr/l	
	NH ₂ Cl mM	NH ₃ mM						
1.5	0.775	0.010	--	--	--	--	0.0	0.765
3	0.775	0.010	0.183	0.494	0.027	0.677	0.003	0.706
6	0.761	0.010	0.282	0.394	0.068	0.565	0.007	0.647
12	0.761	0.007	0.275	0.329	0.106	0.488	0.035	0.547
24	0.704	0.008	0.268	0.276	0.113	0.365	0.046	0.447
30	0.761	0.008	0.324	0.271	0.148	0.377	0.078	0.429
36	0.732	0.009	0.317	0.247	0.134	0.376	0.074	0.424
48	0.704	0.008	0.310	0.224	0.162	0.329	0.078	0.406
54	0.704	0.008	0.296	0.206	0.148	0.312	0.078	0.365
60	0.704	0.008	0.310	0.206	0.155	0.312	0.085	0.365
72	0.704	0.008	0.310	0.200	0.169	0.294	0.099	0.353
84	0.704	0.008	0.338	0.176	0.183	0.288	0.106	0.353
96	0.704	0.008	0.352	0.200	0.183	0.294	0.106	0.353
120	0.704	0.008	0.352	0.200	0.190	0.282	0.106	0.341
144	0.704	0.008	0.352	0.200	0.190	0.282	0.106	0.341

Table A-2

Results of Monochloramine Experiments at pH 8.3 and $D_p = 0.12$ cm

time hr	$\tau=0$ g-hr/l		$\tau=8.33$ g-hr/l		$\tau=16.66$ g-hr/l		$\tau=25.0$ g-hr/l	
	NH ₂ Cl mM	NH ₃ mM						
1.5	0.958	0.009	--	--	--	--	0.00	0.882
3	0.958	0.010	0.289	0.582	0.023	0.824	0.003	0.853
12	0.958	0.010	0.451	0.371	0.155	0.588	0.070	0.659
24	0.901	0.000	0.465	0.300	0.211	0.482	0.124	0.541
30	0.930	0.000	0.465	0.300	0.218	0.482	0.141	0.535
48	0.873	0.007	0.479	0.259	0.254	0.429	0.169	0.494
54	0.873	0.000	0.479	0.259	0.254	0.429	0.169	0.494
60	0.873	0.000	0.479	0.259	0.254	0.429	0.169	0.494
72	0.873	0.009	0.507	0.229	0.296	0.382	0.197	0.459
84	0.901	0.017	0.507	0.247	0.296	0.400	0.209	0.459
96	0.901	0.013	0.521	0.247	0.310	0.400	0.203	0.459
120	0.901	0.013	0.528	0.247	0.310	0.372	0.203	0.423
144	0.901	0.013	0.528	0.247	0.310	0.327	0.203	0.423

Table A-3

Results of Monochloramine Experiments at pH 9.1 and $D_p=0.12$ cm.

time hr	$\tau=0$ g-hr/l		$\tau=8.33$ g-hr/l		$\tau=16.66$ g-hr/l		$\tau=25.0$ g-hr/l	
	NH ₂ Cl mM	NH ₃ mM						
1.5	0.901	0.000	--	--	--	--	0.000	0.859
3	0.901	0.000	0.220	0.647	0.009	0.859	0.000	0.859
6	0.901	0.000	0.310	0.571	0.032	0.841	0.003	0.859
12	0.930	0.000	0.493	0.365	0.130	0.694	0.035	0.777
24	0.930	0.000	0.535	0.329	0.282	0.553	0.155	0.671
36	0.930	0.000	0.578	0.271	0.338	0.471	0.218	0.571
48	0.930	0.000	0.662	0.194	0.422	0.376	0.296	0.471
54	0.901	0.000	0.662	0.182	0.451	0.347	0.338	0.435
60	0.901	0.000	0.662	0.176	0.465	0.324	0.324	0.429
72	0.901	0.000	0.662	0.153	0.507	0.271	0.380	0.371
84	0.901	0.000	0.662	0.159	0.493	0.271	0.366	0.353
96	0.901	0.000	0.662	0.159	0.493	0.271	0.366	0.353
120	0.901	0.000	0.662	0.159	0.493	0.271	0.366	0.353
144	0.901	0.000	0.662	0.159	0.493	0.271	0.366	0.353

Table A-4

Results of Monochloramine Experiments at pH 8.3 and $D_p=0.050$ cm.

time hr	$\tau=0$ g-hr/l		$\tau=8.70$ g-hr/l		$\tau=18.10$ g-hr/l		$\tau=23.75$ g-hr/l	
	NH ₂ Cl mM	NH ₃ mM						
1	0.958	0.027	0.073	0.765	0.001	0.829	0.000	0.829
3	0.958	0.028	0.183	0.624	0.002	0.765	0.000	0.765
6	0.958	0.027	0.268	0.518	0.038	0.700	0.008	0.735
12	0.958	0.019	0.353	0.440	0.056	0.647	0.011	0.682
24	0.958	0.028	0.366	0.430	0.085	0.635	0.025	0.675
48	0.958	0.031	0.409	0.380	0.141	0.547	0.068	0.595
60	0.958	0.028	0.437	0.350	0.197	0.506	0.076	0.589
72	0.958	0.033	0.437	0.350	0.197	0.506	0.090	0.580
96	0.958	0.052	0.048	0.390	0.208	0.510	0.106	0.570
120	0.958	0.044	0.048	0.385	0.208	0.506	0.106	0.564
144	0.958	0.044	0.048	0.358	0.208	0.506	0.106	0.564

Table A-5

Results of Monochloramine Experiments with MB (30 mg/l) at pH 8.3.

time hr	$\tau=0$ g-hr/l		$\tau=8.33$ g-hr/l		$\tau=16.66$ g-hr/l		$\tau=25.0$ g-hr/l	
	NH ₂ Cl mM	NH ₃ mM						
1.5	0.817	0.010	--	--	--	--	0.000	0.782
3	0.845	0.010	0.183	0.588	0.009	0.741	0.000	0.741
6	0.845	0.012	0.254	0.529	0.035	0.706	0.004	0.724
12	0.845	0.010	0.380	0.382	0.090	0.636	0.021	0.694
24	0.817	0.014	0.465	0.312	0.183	0.529	0.070	0.618
36	0.817	0.010	0.479	0.282	0.239	0.471	0.107	0.565
48	0.817	0.009	0.521	0.235	0.310	0.371	0.152	0.506
60	0.817	0.010	0.535	0.235	0.352	0.400	0.176	0.529
72	0.817	0.016	0.578	0.206	0.394	0.341	0.225	0.471
84	0.845	0.010	0.606	0.200	0.437	0.330	0.282	0.447
96	0.845	0.010	0.606	0.200	0.437	0.329	0.282	0.447
120	0.817	0.010	0.592	0.177	0.423	0.312	0.282	0.412
144	0.845	0.010	0.606	0.200	0.437	0.329	0.282	0.447

Table A-6

Results of Monochloramine Experiments with ABS (20 mg/l) at pH 8.3

time hr	$\tau=0$ g-hr/l		$\tau=8.33$ g-hr/l		$\tau=16.66$ g-hr/l		$\tau=25.0$ g-hr/l	
	NH ₂ Cl mM	NH ₃ mM						
1.5	0.901	0.000	--	--	--	--	0.000	0.812
3	0.901	0.000	0.261	0.588	0.017	0.812	0.001	0.812
6	0.901	0.000	0.366	0.471	0.076	0.724	0.007	0.782
12	0.901	0.000	0.437	0.400	0.141	0.662	0.031	0.753
24	0.901	0.010	0.507	0.312	0.254	0.518	0.099	0.647
36	0.901	0.000	0.507	0.283	0.245	0.459	0.141	0.565
48	0.930	0.000	0.578	0.253	0.331	0.424	0.180	0.529
60	0.930	0.000	0.952	0.241	0.366	0.400	0.204	0.506
72	0.930	0.010	0.620	0.221	0.409	0.371	0.247	0.494
84	0.901	0.010	0.620	0.212	0.409	0.365	0.254	0.477
96	0.930	0.000	0.634	0.194	0.423	0.341	0.261	0.453
120	0.901	0.000	0.634	0.165	0.451	0.282	0.303	0.382
144	0.930	0.010	0.620	0.200	0.465	0.300	0.324	0.394

Table A-7

Results of Monochloramine Experiments with DNP (20 mg/l) at pH 8.3.

time hr	$\tau=0$ g-hr/l		$\tau=8.33$ g-hr/l		$\tau=16.66$ g-hr/l		$\tau=25.0$ g-hr/l	
	NH ₂ Cl mM	NH ₃ mM						
1.5	0.845	0.006	--	--	--	--	0.000	0.765
3	0.873	0.009	0.197	0.582	0.014	0.747	0.001	0.765
6	0.901	0.012	0.296	0.506	0.478	0.706	0.008	0.741
12	0.901	0.012	0.352	0.429	0.107	0.635	0.028	0.694
24	0.873	0.013	0.366	0.394	0.155	0.553	0.073	0.618
36	0.873	0.011	0.380	0.365	0.176	0.517	0.085	0.588
48	0.901	0.010	0.380	0.365	0.208	0.482	0.113	0.547
60	0.873	0.011	0.422	0.324	0.239	0.447	0.135	0.518
72	0.845	0.014	0.423	0.294	0.261	0.400	0.163	0.465
84	0.873	0.014	0.451	0.271	0.254	0.388	0.158	0.447
96	0.845	0.012	0.437	0.253	0.254	0.365	0.158	0.434
120	0.845	0.015	0.437	0.247	0.261	0.353	0.169	0.412
144	0.930	0.014	0.535	0.229	0.338	0.341	0.242	0.400

Table A-8

Results of Monochloramine Experiments with

Wastewater (20 mg/l TOC) at pH 8.3.

time hr	$\tau=0$ g-hr/l		$\tau=5.55$ g-hr/l		$\tau=11.1$ g-hr/l		$\tau=22.2$ g-hr/l	
	NH ₂ Cl mM	NH ₃ mM						
3	0.901	0.271	0.282	0.822	--	--	0.003	1.070
6	0.873	0.136	0.507	0.429	--	--	0.056	0.857
19	0.929	0.157	0.578	0.429	--	--	0.141	0.786
28	0.916	0.157	0.606	0.400	--	--	0.169	0.750
40	0.845	0.179	0.619	0.350	--	--	0.239	0.643
48	0.732	0.041	0.619	0.121	--	--	0.268	0.386
62	0.535	0.250	0.465	0.300	--	--	0.225	0.500
72	0.676	0.161	0.563	0.236	--	--	0.310	0.429
86	0.704	0.043	0.605	0.114	--	--	0.366	0.286
96	0.648	0.157	0.563	0.207	--	--	0.338	0.379
109	0.704	0.100	0.634	0.150	0.535	0.221	0.366	0.343
120	0.817	0.540	0.732	0.114	0.634	0.186	0.423	0.366
132	0.802	0.066	0.732	0.114	0.634	0.186	0.423	0.329
142	0.845	0.059	0.788	0.100	0.676	0.178	0.450	0.336

Table A-9

Results of Dichloramine Experiments with
Wastewater (30-40 mg/l COD) at pH 4.4.

time hr	$\tau=0$ g-hr/l				$\tau=4.0$ g-hr/l				$\tau=16.0$ g-hr/l			
	NH ₂ Cl mM	NHCl ₂ mM	NCI ₃ mM	NH ₃ mM	NH ₂ Cl mM	NHCl ₂ mM	NCI ₃ mM	NH ₃ mM	NH ₂ Cl mM	NHCl ₂ mM	NCI ₃ mM	NH ₃ mM
5	0.014	0.408	0.014	0.457	0.001	0.008	0.000	0.679	0.000	0.001	0.000	0.714
24	0.000	0.268	0.038	1.035	0.005	0.021	0.005	1.107	0.006	0.001	0.002	1.107
30	0.014	0.253	0.036	0.914	0.000	0.049	0.014	0.964	0.000	0.002	0.004	0.964
45	0.028	0.296	0.000	1.000	0.007	0.053	0.028	1.036	0.003	0.002	0.000	1.036
54	0.028	0.268	0.000	0.750	0.014	0.070	0.000	0.786	0.001	0.003	0.000	0.786
74	0.028	0.380	0.019	0.914	0.014	0.070	0.000	0.964	0.001	0.005	0.003	0.964
86	0.000	0.310	0.028	0.750	0.000	0.070	0.018	0.786	0.003	0.005	0.006	0.786
110	0.000	0.253	0.028	0.786	0.007	0.076	0.014	0.821	0.001	0.004	0.006	0.821
120	0.028	0.289	0.000	1.143	0.028	0.084	0.000	1.178	0.011	0.005	0.009	1.178
135	0.028	0.253	0.000	1.257	0.028	0.092	0.000	1.293	0.003	0.004	0.007	1.293
160	0.028	0.253	0.019	1.214	0.056	0.088	0.009	1.257	0.002	0.004	0.008	1.257