AN ABSTRACT OF THE THESIS OF

C1	hing-lin Chang	for the	M. S.
(N	ame of student)		(Degree)
in Civ	il Engineering p	resented on	Nov 10 1967 (Date)
	(Major)		(Dáte)
Title:	Effect of Carbo	on Adsorption	on Chlorine Requirement of
	Treated Efflue	nt	
Abstra	act approved:	Redacted	for privacy
	$\overline{\overline{D}}$	onald C. Phi	llips

The chlorination curves of treated domestic wastewater were investigated both before and after carbon adsorption. The tertiary treatment processes employed in this study included coagulation, sedimentation, sand filtration and carbon adsorption. Ammonia nitrogen and total organic carbon were determined for the samples studied to evaluate their effect on the breakpoint chlorination.

Based on this study, the following conclusions were made:

- 1. The chlorination curve of the carbon column effluent which is the final effluent of the tertiary waste treatment is of similar shape to those reported for potable water supplies. The Cl:NH₃-N ratio for the carbon column effluent obtained in this study was about 5.0-6.0:1 at the humps and 7.4-8.8:1 at breakpoint. These values are also close to the values reported for the chlorination of potable waters.
- 2. The carbon adsorption significantly reduces the chlorine

requirement of the treated wastewater. However, the reduction of chlorine requirement has little correlation with the reduction of total organic carbon content in the carbon adsorption process.

- 3. The chlorination curve of the treated domestic wastewater without carbon adsorption appears in somewhat irregular shapes. In some cases, two humps and two breakpoints were obtained. Possibly this phenomenon is due to the effect of organic chloramines.
- 4. When the ammonia content in the treated wastewater is low, it is economically feasible to chlorinate the effluent beyond the breakpoint to achieve the dual objects--satisfactory disinfection and ammonia removal.

Effect of Carbon Adsorption on Chlorine Requirement of Treated Effluent

bу

Ching-lin Chang

A THESIS

submitted to

Oregon State University

in partial fulfillment of the requirements for the degree of

Master of Science

June 1968

APPROVED:

Redacted for privacy

Professor of Civil Engineering in charge of major

Redacted for privacy

Head of Department of Civil Engineering

Redacted for privacy

Dean of Graduate School

Date thesis is presented _	Nov	10.1967	
			
Tuned by Onal Grosenickla	us for	Ching-lin Chang	

ACKNOWLEDGMENTS

The author wishes to express his appreciation to Dr. Donald C. Phillips for his advice and direction in all phases of this work.

The author is also indebted to the faculty and staff of the Department of Civil Engineering for the preparation and use of the experimental facilities.

TABLE OF CONTENTS

INTRODUCTION	1
MECHANISM OF CHLORINE IN WATER	4
REACTION OF CHLORINE WITH AMMONIA	5
REACTION OF CHLORINE AND ORGANIC NITROGEN	6
BREAKPOINT CHLORINATION	8
GENERAL PROCEDURE OF THE EXPERIMENTS	11
Experimental Apparatus Experimental Procedure Analytical Methods	11 11 12
RESULTS	14
The Shape of Chlorination Curve The Cl:NH3-N Ratio The Change of Water Quality after Carbon Adsorption The Effect of Total Organic Carbon Content on the Chlorine Requirement Breakpoint Chlorination and Ammonia Removal	14 26 26 27 28
DISCUSSION	30
CONCLUSION	33
BIBLIOGRAPHY	34

LIST OF TABLE

<u>Table</u>		Page
1.	Analytical data for samples	17
	LIST OF FIGURES	
Figure		Page
1.	Chlorination curves of organic chloramines	10
2.	Flow diagram of the pilot plant.	15
3.	Chlorination curve for distilled water plus ammonia	15
4.	Chlorination curves, Test 1 and 2.	19
5.	Chlorination curves, Test 3 and 4.	20
6.	Chlorination curves, Test 5 and 6.	21
7.	Chlorination curves, Test 7 and 8.	22
8.	Chlorination curves, Test 9 and 10.	23
9.	Chlorination curves, Test 11.	24
10.	Comparison of chlorination curves before humps at various ammonia contents.	25
11.	Schematic diagram showing oxidation of ammonia by chlorine.	29

EFFECT OF CARBON ADSORPTION ON CHLORINE REQUIREMENT OF TREATED EFFLUENT

INTRODUCTION

It has been 60 years since the first plant scale application of sewage chlorination at Red Bank, N. J. Due to economical considerations, the general practice in sewage chlorination has been to maintain less than 2 ppm of residual chlorine after 15 or 30 minutes of contact time (8), in spite of the fact that there is no real assurance that the maintenance of this level of residual chlorine will correspond to the required colicidal effect (7). The high organic content in the effluent of secondary waste treatment makes it prohibitive to chlorinate the effluent to reach the breakpoint. The conditions, however, may be different for the chlorination of the effluent of the tertiary treatment because the organic content will be greatly reduced.

Activated carbon adsorption is one of the most effective processes in tertiary waste treatment as demonstrated at Lake Tahoe (2). Considerable research has been done on breakpoint chlorination of natural water and water supply but little has been reported on the breakpoint chlorination of treated sewage. The purpose of this study is to evaluate the effect of carbon adsorption on breakpoint chlorination.

MECHANISM OF CHLORINE IN WATER

When chlorine gas is added to water, the following equilibrium is established:

$$Cl_2 + H_2O \Longrightarrow HOC1 + C1^- + H^+$$
 (1)

$$K_{h} = \frac{[HOC1][C1^{-}][H^{+}]}{[C1_{2}]}$$
 (2)

The hydrolysis of chlorine gas is almost instantaneous and the K_h value is reported as 4.5×10^{-4} at $25\,^{\circ}$ C(3, p. 803). Based on this K_h value, pH from 5 to 9, and chlorine dosage of 100 mg/l, the [HOCl]/[Cl₂] ratio will range from 1.6×10^4 to 1.6×10^8 . Therefore, it can be said that, in the ordinary practice, the chlorine gas added to water is completely hydrolized.

The hypochlorous acid, HOCl, ionized partially as follows:

$$HOC1 \Longrightarrow H^{+} + OC1^{-} \tag{3}$$

$$K_i = \frac{[H^+][OC1]}{[HOC1]} = 2.7 \times 10^8 \text{ at } 25^{\circ}C$$
 (4)

The distribution of HOCl and OCl depends on pH and temperature.

The ratio of HOCl to OCl can be calculated from the relationship:

$$\frac{[\text{HOC1}]}{[\text{HOC1}] + [\text{OC1}]} = \frac{1}{1 + [\text{OC1}] / [\text{HOC1}]} = \frac{1}{1 + K_{i/[H^{+}]}}$$
(5)

The reaction of sodium or calcium hypochlorite in water is similar to that of chlorine gas:

$$NaOCl \rightarrow Na^{+} + OCl^{-}$$
 (6)

$$Ca(OC1)_2 \rightarrow Ca^{++} + 2 OC1^{-}$$
 (7)

The hypochlorite ions combine with H^{+} to establish the equilibrium as shown in Equation (3).

REACTION OF CHLORINE WITH AMMONIA

Ammonia is normally present in sewage in a significant amount.

Ammonia hydrolyzes in water as follows:

$$NH_3 + H_2O \implies NH_4^+ + OH^-$$
 (8)

$$\frac{[NH_4^+][OH^-]}{[NH_3]} = 1.8 \times 10^{-5} \text{ at } 25 \,^{\circ}\text{C}$$
 (9)

The ratio of $\mathrm{NH_4}^+$ to $\mathrm{NH_3}^-$ also depends on pH and may be calculated by the following equation:

$$\frac{[NH_4^+]}{[NH_4^+] + [NH_3]} = \frac{1}{1 + [NH_3] / [NH_4^+]} = \frac{1}{1 + [OH^-] / 1.8 \times 10^{-5}}$$
(10)

At pH 6.0, 99.95% of ammonia is in the form of NH_4^+ ; 99.45% at pH 7.0 and 94.77% at pH 8.0.

Hypochlorous acid reacts with ammonium ion in a stepwise process:

$$NH_4^+ + HOC1 \rightarrow H_2O + H^+ + NH_2C1$$
 (11)

$$NH_2Cl + HOCl \rightarrow H_2O + NHCl_2$$
 (12)

$$NHCl_2 + HOCl \rightarrow H_2O + NCl_3$$
 (13)

The ratio of monachloramine to dichloramine is dependent on dosage, and the resulting pH of the solution. The equilibrium of the ammonium ion with mono- and dichloramine is shown as:

$$2 NH_2Cl + H^+ \rightleftharpoons NH_4^+ + NHCl_2$$
 (14)

$$\frac{[NH_4^+][NHCl_2]}{[H^+][NH_2Cl]^2} = K = 6.7 \times 10^5 \text{ at } 25^{\circ}C$$
 (15)

Nitrogen trichloride does not exist in a significant amount above pH 4 unless an excess HOCl is present. Its mechanism and rate of formation are still not clear (10).

REACTION OF CHLORINE AND ORGANIC NITROGEN

According to Morris (10), the reaction of unipositive chlorine with organic nitrogen may be generalized as:

$$X-C1 + R_2NH \rightarrow C1NR_2 + H^+ + X^-$$
 (16)

In which X may represent either HO, NH₂ or NHCl and defines the reaction when either hypochlorous acid, monochloramine or dichloramine are involved. The reaction rates of several simple nitrogenous compounds have been determined by Morris. However, at present, there is no way to predict the mechanism of organic chloramines in sewage. Hypochlorous acid and monochloramine react with organic nitrogenous compounds to form various forms of chloramines.

Nusbaum (11) stated that when ammonia nitrogen is low compared with albuminoid nitrogen, protein chloramine formation is accelerated.

The organic chloramines have a much lower bactericidal effect than monochloramine. Rhines' experiment (12) showed a marked reduction in colicidal effect upon the addition of L-serine. According to Feng (4), many organic chloramines are titrated as available residual chlorine by the starch-iodide method but show little lethal activity, and many organic chloramines which do not react with orthotolidine have some lethal activities at certain pH levels.

This may be the reason of Heukelekian and Faust's finding that little correlation is found between the reduction of coliform bacteria and residual chlorine (7).

BREAKPOINT CHLORINATION

Nitrogen that exists in the form of NH₃ or NH₄⁺ is considered as ammonia nitrogen (NH₃-N). As shown in Equation (11) and (12), hypochlorous acid reacts with the ammonium ion to form mono- and dichloramine at neutral pH levels. When the molar ratio of Cl:NH₃-N is less than 1:1, or the weight ratio of 5.07:1 (ammonia is expressed as nitrogen), the monochloramine predominates and there is no significant change in ammonia concentration if dechlorinated before ammonia determination. When the molar ratio of Cl:NH₃-N exceeds 1:1, oxidation of ammonia and reduction of chlorine is noted and both the concentration of available chlorine and ammonia begin to decrease until the breakpoint, or zero point, is reached. At this point, neither residual chlorine nor ammonia is present. After the breakpoint, addition of chlorine produces hypochlorous acid.

The mechanism and endproduct of the breakpoint reaction are not fully understood. Formerly it was considered that dichloramine was oxidized to form nitrogen gas (6), (9):

$$NH_2Cl + NHCl_2 \rightarrow N_2 + 3H^+ + 3 Cl^-$$
 (16)

or
$$2 \text{ NH}_2 \text{Cl} + \text{HOCl} \rightarrow \text{N}_2 + \text{H}_2 \text{O} + 3 \text{ H}^+ + 3 \text{ Cl}^-$$
 (17)

Morris et al (9) suggested that the breakpoint reaction starts with the decomposition of dichloramine as:

$$NHC1_2 + H_2O \rightarrow NOH + 2 H^+ + 2 C1^-$$
 (18)

$$2 \text{ NOH} + \text{HOCl} \rightarrow 2 \text{ NO} + \text{H}_2\text{O} + \text{H}^+ + \text{Cl}^-$$
 (19)

And the NO formed would combine with dissolved oxygen to give NO₂ and finally be oxidized to nitrate.

Sawyer (13, p. 252) stated that nitrous oxide, nitrogen, and nitrogen trichloride had been identified among the gaseous products of the breakpoint reaction. Sawyer also suggested that the formation of nitrous oxide could be represented by:

$$NH_2Cl + NHCl_2 + HOCl \rightarrow N_2O + 4 HCl$$
 (20)

Equation (16 and 17) indicate that the weight ratio of Cl:NH₃-N at the breakpoint is about 7.6:1. Equation (18-19) show a ratio of 12.7:1, and Equation (20) shows a ratio of about 10:1. A survey of the literature shows that the ratio ranges mostly from 7.6-10:1, although some reported the ratio as high as 15-20:1 for natural waters. It seems that there might be two or more endproducts, or the endproduct depends on the concentrations of reactants involved in the breakpoint reaction, thus making the Cl:NH₃-N ratio quite variable with the experimental conditions.

The shapes of chlorination curve of organic chloramines depend on the nature of the organic substances (1), (5). They are shown schematically in Figure 1.

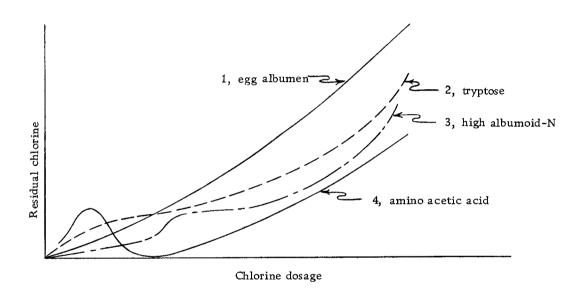


Figure 1. Chlorination curves of organic chloramines. (Curves 1, 2, and 4 after Calvert; curve 3, after Griffin and Chamberlin.)

GENERAL PROCEDURE OF THE EXPERIMENTS

Experimental Apparatus

The experiments were conducted at the Water Research Demonstration Laboratory at the Corvallis Sewage Treatment Plant. The plant treats about 5 MGD of domestic sewage utilizing the processes of primary sedimentation, high-rate trickling filtration, final sedimentation and chlorination.

The effluent of the high-rate trickling filter was pumped to the pilot plant in the laboratory. The processes in the pilot plant consisted of alum coagulation and sedimentation, followed by sand filtration and carbon adsorption. The sand filter was $5\frac{1}{2}$ inches in diameter and 36 inches deep. The effective size of the sand was 0.50 mm with a uniform coefficient of 1.55. The carbon column was $5\frac{1}{2}$ inches in diameter and 48 inches deep. The activated carbon used was Calgon Filtrasorb Type 300, 8×30 mesh. The flow diagram of the pilot plant is shown in Figure 2.

Experimental Procedure

The effluents of the sand filter and the carbon column were collected after more than one hour of continuous flow for each test series. The filtration rate was kept at 2.5 gpm per square foot.

After the samples were collected, the filters were shut down and backwashed with tap water. The coagulation and sedimentation units were in continuous operation most of the time.

A sodium hypochlorite solution with a concentration of about 3.0 to 3.5 mg/ml was used for the chlorination. The exact concentration of the hypochlorite solution was determined before the chlorination. The volume of each batch of samples was 900 ml. Increasing dosages of the hypochlorite solution were added to two series of samples. The dosage increments were varied from 0.5 to 2 ml so as to adequately define the chlorination curves. After 60 minutes of contact time, the residual chlorine was titrated using 250 ml to 400 ml of samples. Since the turbidity of the samples was low, the direct starch-iodide method as described in the Standard Methods (Water) was used for the determination of residual chlorine. During the titration, the pH of samples was buffered to pH 4.0 to minimize the interference by nitrite.

Analytical Methods

The following analyses were made for each test series: pH, alkalinity, turbidity, temperature, ammonia nitrogen, and total carbon.

The alkalinity was titrated potentiometrically with 0.02 N sulfuric acid solution to pH 4.5 or 4.0.

The turbidity was determined with Hach turbidimeter model 1860.

The direct nesslerization method was used for the determination of ammonia nitrogen with a Spectronic 20 at the wavelength 460 m μ and light path 10 mm.

The total carbon was determined by a Beckman infrared carbon analyzer. First the samples were injected to determine both inorganic and organic carbon. Then the samples were acidified with HCl to pH of about 2 and aerated with CO₂-free air for about five minutes. This process removed the inorganic carbon. The acidified and aerated samples were injected to the carbon analyzer again to determine the organic carbon.

RESULTS

The Shape of Chlorination Curve

When chlorine is applied to water containing ammonia, the ammonia will react with chlorine to form monochloramine. The concentration of monochloramine increases as the dosage of chlorine increases up to the point where all the ammonia is converted to monochloramine. This point is referred to as the 'hump'. After the hump, the oxidation of ammonia begins and the residual chlorine decreases. Theoretically, the breakpoint should be at the point where all the ammonia is oxidized and no residual chlorine exists. However, this exact point is difficult to attain. Furthermore, if nitrogen trichloride and organic chloramines are formed, they are titrated as residual chlorine by the starch-iodide method. humps and breakpoints in the following discussion are determined from the intersections of two slopes on the chlorination curves. This method is subject to some error, but it is not the purpose of this study to determine the exact locations of the humps and breakpoints. As discussed previously, the Cl:NH3-N ratio at the breakpoint varies with the nature of the water. The approximate location of the breakpoint is sufficient for the determination of the range of Cl:NH₃-N ratio.

Figure 3 shows the chlorination curve of distilled water containing 3.47 mg/l of ammonia nitrogen. The water was not buffered. The hypochlorite ions combine with hydrogen ions to form hypochlorous acid and cause the pH of water to rise according to Equations (6) and (3). Oxidation of ammonia releases hydrogen ions and lowers the pH value. After the breakpoint, the residual chlorine exists as HOCl thus the pH value rises again. The variation in pH values can be used as a check for the location of the hump at the breakpoint (Figure 3). In natural waters or sewage, the variation of pH value is slight due to the buffering action of bicarbonates.

The chlorination curve near the breakpoint, or usually called the "valley", in Figure 3 is flatter than for those reported in the literature in which the ammoniated distilled water is buffered.

Organic substances, especially nitrogenous compounds, complicated the shape of chlorination curves. Figures 4, 5, 6, 7, 8 and 9 show the chlorination curves of sand and carbon filter effluents at various ammonia nitrogen levels. The letters C and S of the samples refer to the effluent of carbon column and sand filter respectively. The numbers following the letters C and S identify the number of the test. No coagulant was added before filtration for samples C-1 to C-3 and S-1 to S-3. Other samples were coagulated before filtration. The analytical data of the samples are shown in Table 1.

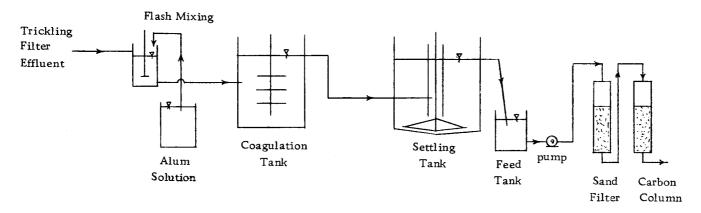


Figure 2. Flow diagram of the pilot plant.

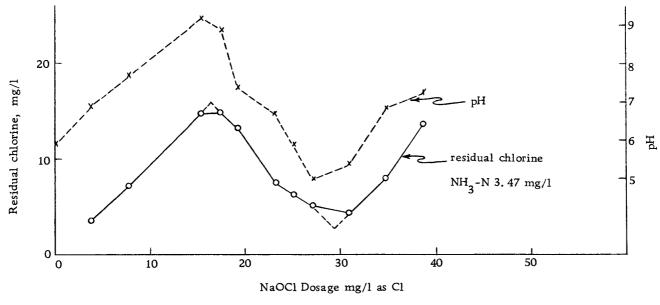


Figure 3. Chlorination curve for distilled water plus ammonia.

Table 1. Analytical data for samples

Sample	C-1	S-1	C-2	S-2	C-3	S-3	C-4	S-4	C-5	S-5	C-6	S-6
Water temperature ^O C	22~	22~	22,5~	22~	22~	22~	22~	22~	21~	21 ~	22~	22 ~
	23	23	24	23.5	23.5	23.5	23, 5	23.5	22	22	23.5	23.5
Turbidity, units	3.9	4.5	3.7	4.4	3,8	4.6	5, 2	6.2	7.5	8.8	1.4	3.3
Alkalinity, mg/l	83.7 ^a	74. 7 ^a	72.0^a	64.0 ^a	63.5	58.0	63.3	45.0	54.7	51.3	40.6	21.6
pН	7,68	7. 28	7, 50	7.23	7. 28	7.20	7.31	6.70	7.16	6.90	7. 10	6.31
Total Carbon, mg/l												
inorganic + organic	23	28.5	22	26	19.0	24. 5	17.5	22.5				
organic	4	11	3.0	7. 0	5.0	19.5	2.5	9. 5				
NH ₃ -N, mg/L	5.70	5. 70	3.50	4.04	4. 50	4.70	4. 50	5, 00	5.00	5.30	1. 93	2.50
Cl:NH3-N ratio												
hump	5.9	6.1	6.8	7.7	5. 8	6.6	5. 1	6, 2	5.0	5, 9	5. 6	8.3
breakpoint	8.7	9. 5	11.7	11.7	8, 8	9.9	8, 2	8, 9	8.2	9, 4	7.4	10. 4
Sample	C-7	S-7	C-8	S-8	C-9	S-9	C-10	S-10	C-11	S-11		
Water temperature ^O C	22~	22~	21~	21~	21~	21~	21.5~	21, 5~	21~	21 ~		
-	23	23	22.5	22,5	22	22	23	23	22.5	22.5		
Turbidity, units	3, 1	4, 3	12	13	4, 6	6.4	6, 2	8, 5	9, 8	13		
Alkalinity, mg/l	98. 2	36.4	52.7	48.3	69, 2	49. 1	53, 6	53, 3	57.0	56.0		
рH	7, 10	6.70	6,80	6.68	7, 18	6,60	7. 10	6.90	7.01	6.81		
Total Carbon					•							
inorganic + organic	27	17			17.5	21.5						
organic	1	6			2	6.5						
NH3-N, mg/l	4.10	4.80	6.24	6.60	6, 42	6. 58	5. 40	6.00	6.00	6.30		
Cl:NH ₃ -N ratio				- * · · ·	. •		•			- •		
hu mp	5. 5	6.8	5.9	5.9	5, 1	*	5 . 5	5. 9	6.0	*		
bre a kpoint	7.6	9. 4	7. 9	8.8	7.6	7.8	7. 7	8. 5	8.3	9, 2		

a Endpoint at pH 4.0. All other samples are at pH 4.5.

^{*} Two humps, ratio not calculated.

The chlorination curves for the effluent of the carbon column are all of similar shape. This indicates that the chlorination curve of the carbon column effluent is controlled predominantly by the concentration of ammonia nitrogen in water. The humps and valleys are steeper in the carbon column effluent than in the sand filter effluent. Before the humps, the chlorination curves are relatively close regardless of the ammonia concentration (Figure 10).

The chlorination curves of the sand filter effluent are consistently lower than those of carbon column. This is conceivable because the organic content of the sand filter effluent is higher than that of the carbon column effluent. The shapes of the curves for the sand filter effluent are somewhat irregular. In some cases two humps and two valleys are observed as shown in Figures 7, 8 and 9. Originally, it was suspected that there might be some experimental errors involved. After repeated experiments, however, it was found that the cause of irregular shapes might be due to some unknown organic substances or some reducing substances in water, which would be oxidized at the chlorine dosage of about 40 mg/l. The cases of double humps were observed in the sand filter effluent only, and were not experienced in the carbon column effluent. In those samples which showed two humps, a faint septic odor (but not of H₂S) was noticed. The sand filter effluent was slightly yellowish, and color decreased with the increasing chlorine dosage. The

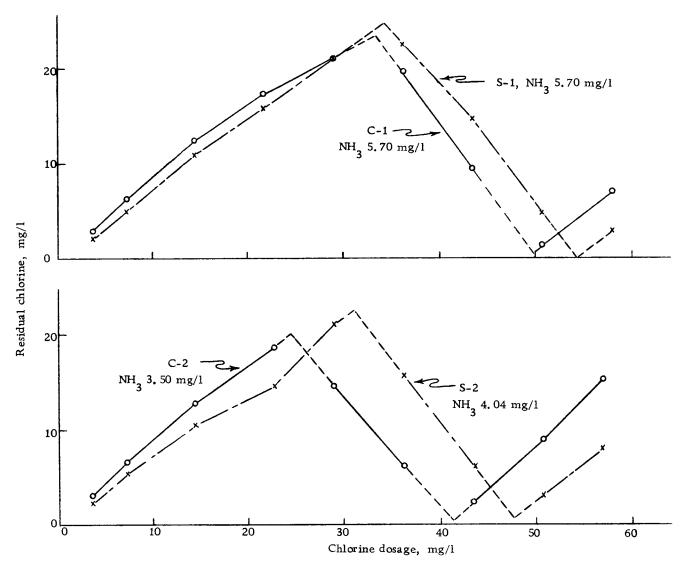


Figure 4. Chlorination curves, Test 1 and 2.

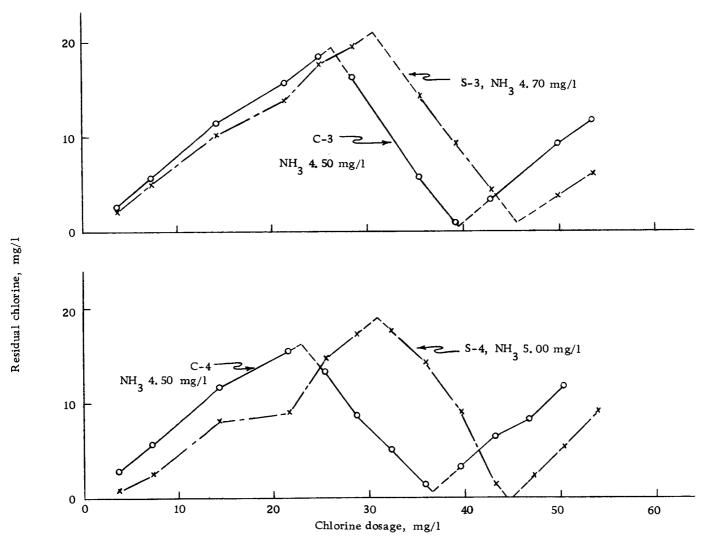


Figure 5. Chlorination Curves, Test 3 and 4.

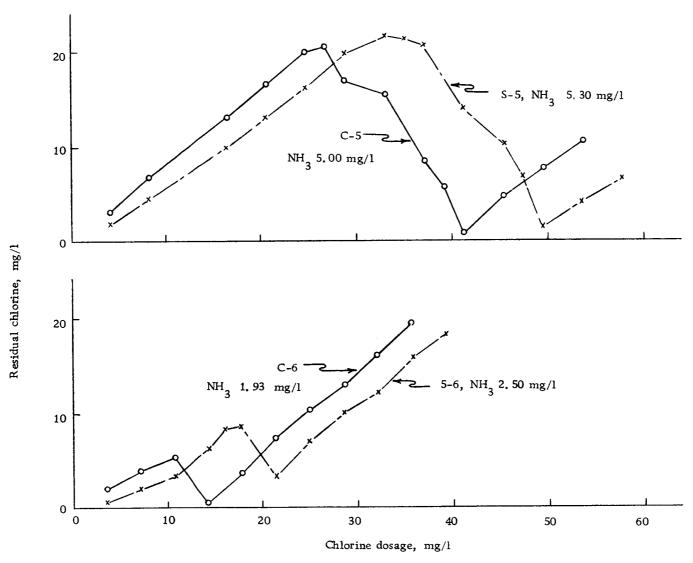


Figure 6. Chlorination curves, Test 5 and 6.

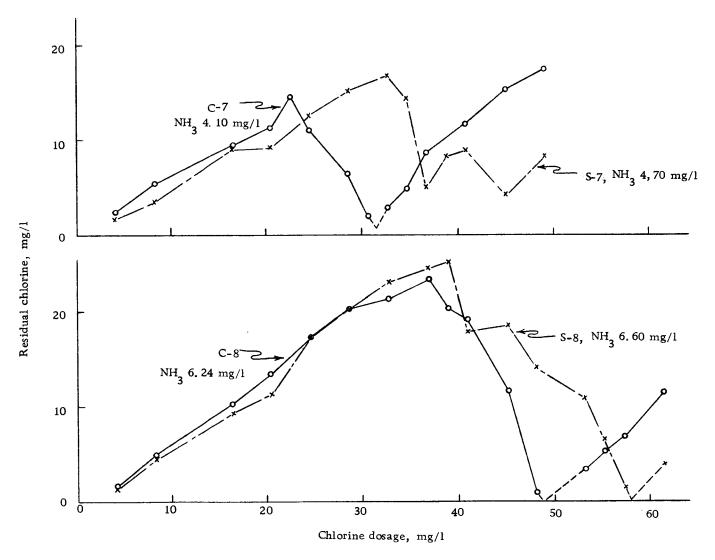


Figure 7. Chlorination curves, Test 7 and 8.

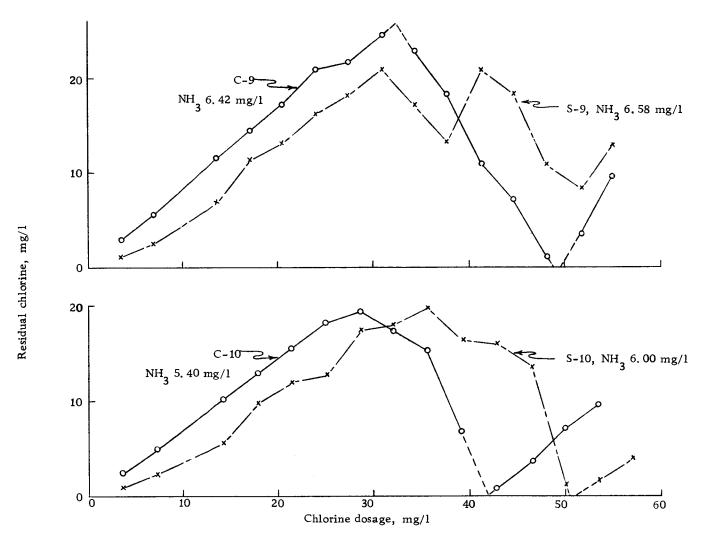


Figure 8. Chlorination curves, Test 9 and 10.

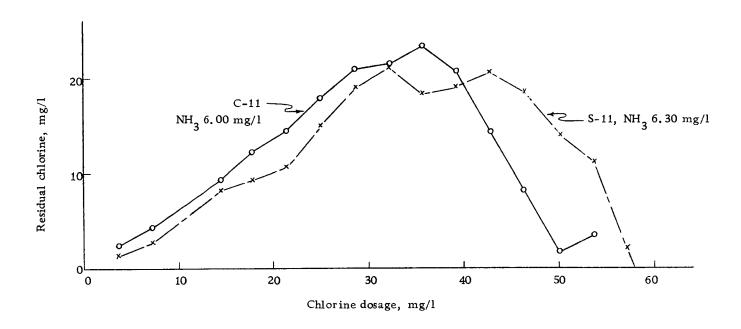


Figure 9. Chlorination curves, test 11.

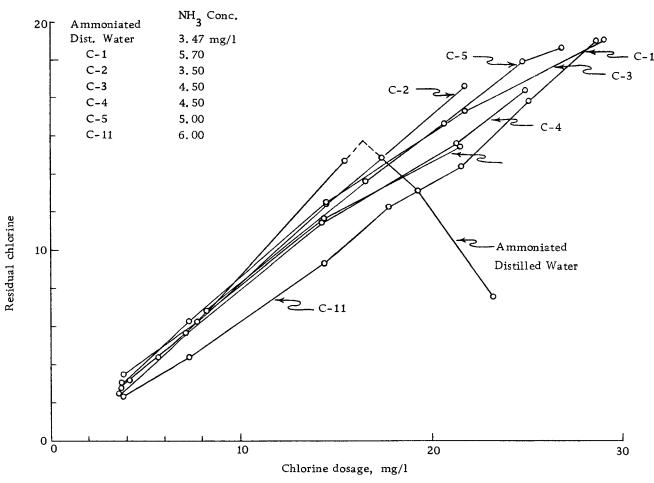


Figure 10. Comparison of chlorination curves before humps at various ammonia contents.

locations of breakpoints in these cases were judged from the chlorination curves and the complete decoloration of the samples.

The $Cl:NH_3-N$ Ratio

The Cl:NH₃-N ratio for carbon column effluent ranges from 5.0-6.0:1 at the humps and 7.4-8.8:1 at the breakpoint (C-2 has higher values) as listed in Table 1. For the sand filter effluent, most of the ratios fall in the range from 5.9-6.8:1 at humps and 8-10:1 at breakpoints.

From the results of the experiments, it appears that, at the same NH₃-N concentration, the chlorine dosage required to reach the hump for the carbon column effluent is about 15-20% less than for the sand filter effluent. To reach the breakpoint, the chlorine dosage required is about 10-15% less for the carbon column effluent than for the sand filter effluent.

All the C1:NH₃-N ratios fall in the range of 7.6-10:1 as reported in the literature for the natural waters. This indicates that other forms of nitrogenous compounds play only a minor role in the chlorination.

The Change of Water Quality After Carbon Adsorption

The effluent of the sand filter was slightly yellowish in color and, occasionally, had a faint septic sewage odor. The color and

odor were completely removed after carbon adsorption.

No pH adjustment was made in the coagulation process. Accordingly, the turbidity removal in the process was not very efficient. Addition of alum in the coagulation process depressed the pH of the influent from about 7.5 to less than 7.0. The pH and alkalinity increased after carbon adsorption. Probably, this was due to adsorption of organic acids by the activated carbon.

The amount of total organic carbon in the sand filter effluent was 6-11 mg/l, and 1-5 mg/l in the carbon column. It is difficult to evaluate the efficiency in terms of percent removal since the precision of the total carbon determination at 1 to 2 mg/l level was estimated to be approximately \pm 0.5 mg/l.

The Effect of Total Organic Carbon Content on the Chlorine Requirement

Since the organic chloramines affect the chlorination curve to a greater extent than the carbonaceous compounds, it would be more logical to use the organic nitrogen as a parameter for chlorine consumption instead of total organic carbon. Unfortunately, the kjeldahl method is very time consuming and requires a large amount of samples. The carbon analyzer takes only about two minutes to obtain a result with a fairly good precision. Since the chlorine requirement increases with the increase of COD and BOD, an attempt was made

to find what correlation could be obtained from the total organic carbon in the sample.

The results are shown in Table 1. Various approaches were used in attempting to correlate the amount of total organic carbon to the differences in the chlorine requirements, locations of humps and breakpoints, and the shape of the chlorination curves. No correlation was established. This is possibly due to:

- (a) The carbon content of organic nitrogeneous compounds is quite varied.
- (b) Some organic carbonaceous compounds do not consume chlorine.

Breakpoint Chlorination and Ammonia Removal

When the chlorine dosage is less than the amount required to reach the hump, there is little change in ammonia nitrogen. After the hump, the ammonia nitrogen is oxidized to some unknown end-product. After the breakpoint, there is definitely no ammonia nitrogen remaining.

The amount of ammonia nitrogen remaining after chlorination varies with the contact time. Due to the technical difficulties and time involved, the data obtained were only semiquantitative. The relation of ammonia nitrogen and chlorine dosage is shown schematically in Figure 11.

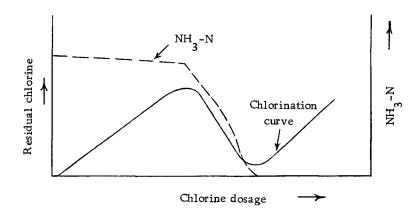


Figure 11. Schematic diagram showing oxidation of ammonia by chlorine.

DISCUSSION

It is generally recognized that the free residual chlorine has a much greater bactericidal activity than chloramines. The present practices of sewage chlorination are not sufficient to eliminate the water-borne pathogenes (8),(7). Since the primary objective of the tertiary treatment of sewage is the reuse of wastewater, it seems that chlorination beyond breakpoint is a proper solution for the safeguard to public health. In addition, if there is a trace amount of phenol remaining in the effluent, the odor resulting from chlorophenol is unacceptable for the use of water supply. Again, breakpoint chlorination will solve this problem.

Ammonia nitrogen cannot be removed by the coagulation and filtration processes. Breakpoint chlorination not only eliminates ammonia but also reduces total nitrogen in the treated effluent.

Based on the data obtained from this study, the following calculations show the amount and cost of chlorine required to obtain breakpoint chlorination:

When there is 7 mg/l of NH₃-N in the carbon column effluent, and Cl:NH₃-N ratio taken at 8.5, the chlorine dosage of

$$(7 \times 8.5) + 2 = 61.5 \text{ mg/l}$$

of chlorine is required to remove all the ammonia nitrogen

and to maintain 2 mg/l of free residual chlorine.

At \$125/ton of liquid chlorine, or 6.25¢/lb, the cost of chlorine will be $6.25 \times 61.5 \times 10^{-6} \times 1000 \times 8.34 = 3.2¢/1000$ gal.

This cost is reasonable considering satisfactory disinfection and ammonia removal are obtained. The cost of chlorine will be reduced to about 1.9¢/1000 gal when NH₃-N is at 4 mg/l. The prerequisite for using breakpoint chlorination for ammonia removal is that the ammonia content in the treated wastewater must be low, or less than 10 mg/l, otherwise the cost will be prohibitively high.

From the data obtained, it shows that, at low organic content (less than 10 mg/l as carbon), the total organic carbon is not suitable as a parameter for the chlorine requirement. Two humps and two valleys in the chlorination curves of sand filter effluent indicate that some organic chloramines can be oxidized by the chlorine.

These organic chloramines may affect the oxidation of the monochloramine. Unfortunately, the methods available at the present time cannot differentiate the mono- and dichloramine from the various forms of organic chloramines.

If the chlorine requirement is defined as that amount of chlorine which must be added to produce a specified amount of free residual chlorine beyond the breakpoint, the effect of carbon adsorption is obvious. To what extent the chlorine requirement will be reduced

is not predictable from the amount of total organic carbon present.

It seems that ammonia and total organic nitrogen are better parameters for the determination of the chlorine requirement. Until the mechanism of organic chloramines is understood, the chlorine requirement of the treated wastewater still must be determined for each individual wastewater.

CONCLUSION

- 1. The chlorination curve of the carbon column effluent, which is the final effluent of the tertiary waste treatment, is of similar shape to those reported for potable water supplies. The Cl:NH₃-N ratio for the carbon column effluent obtained in this study was about 5.0-6.0:1 at the humps and 7.4-8.8:1 at breakpoint. These values are also close to the values reported for the chlorination of potable waters.
- 2. The carbon adsorption significantly reduces the chlorine requirement of the treated wastewater. However, the reduction of chlorine requirement has little correlation with the reduction of total organic carbon content in the carbon adsorption process.
- The chlorination curve of the treated domestic wastewater without carbon adsorption appears in somewhat irregular shapes.
 In some cases, two humps and two breakpoints were obtained.
 Possibly this phenomenon is due to the effect of organic chloramines.
- 4. When the ammonia content in the treated wastewater is low, it is economically feasible to chlorinate the effluent beyond the breakpoint to achieve the dual objects--satisfactory disinfection and ammonia removal.

BIBLIOGRAPHY

- 1. Calvert, C. K. Treatment with copper sulfate, chlorine, and ammonia. Journal of the American Water Works Association 32:1155-1164, 1940.
- 2. Culp, G. and R. Culp. Reclamation of waste water at Lake Tahoe. Public Works 97(2):86-90. 1966.
- 3. Fair, G. M. and J. C. Geyer. Water supply and waste-water disposal. New York, Wiley, 1954. 973 p.
- 4. Feng, T. H. Behavior of organic chloramines in disinfection. Journal of the Water Pollution Control Federation 38:613-628.
- 5. Griffin, A. E. and N. S. Chamberlin. Some chemical aspects of breakpoint chlorination. Journal of the New England Water Works Association 55:371-383. 1941.
- 6. Harvill, C. R. et al. Practical application of ammonia-induced break-point chlorination. Journal of the American Water Works Association 34:275-287. 1942.
- 7. Heukelekian, H. and S. D. Faust. Compatibility of wastewater disinfection by chlorination. Journal of the Water Pollution Control Federation 33:932-942. 1961.
- 8. Laubusch, E. J. State practices in sewage disinfection. Journal of the Water Pollution Control Federation 30:1233-1240. 1958.
- 9. McKee, J. E. et al. Chemical and colicidal effects of halogens in sewage. Journal of the Water Pollution Control Federation 32:795-819. 1960.
- 10. Morris, J. C. Kinetics of reactions between aqueous chlorine and nitrogen compounds. In: Principles and applications of water chemistry, ed. by S. D. Faust and J. V. Hunter. New York, Wiley, 1967. p. 23-53.
- 11. Nusbaum, I. Sewage chlorination mechanism. Water and Sewage Works 99:295-297. 1952.

- 12. Rhines, C. E. The fundamental principles of sewage chlorination. Water and Sewage Works 113:97-101. 1966.
- 13. Sawyer, C. N. Chemistry for sanitary engineers. New York, McGraw-Hill. 1960. 367 p.