

A LABORATORY INVESTIGATION OF CHLORINE STABILITY IN WATER AT VARIOUS PH VALUES

Thesis for the Degree of B.S. MICHIGAN STATE COLLEGE Marshall Hines 1947

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A Laboratory Investigation of Chlorine Stability in

Water at Various pH Values

A Thesis Submitted to

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CONTROL TO TOTATO SOLINO

By

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Gandidate for the Degree of

Eschelor of Science

June 1947

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Acknowledgement

The suther wishes to express his a preciation to "r. Z. F. Eldridge under whose guidance and direction this investigation was corried out.

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HISTORICAL

Chlorine is one of the most widely distributed elements known, but it is never found in the free condition. It exists in enormous quantities in combination with potassium, calcium, end magnesium, end particularly with sodium as sodium chloride or common salt.

Chlorine was discovered in 1774 by the Swedish chemist Scheele, who named it dephlogisticated muriatic acid. About 1785 Berthollet, because of the method used in the preparation of chlorine, considered it a compound of hydrochloric acid and oxygen and called it oxygenated muriatic acid. This term had previously been used by Lavoisier to describe chlorine. In 1810 Sir Humphrey Davy proved that chlorine was an element and gave it the name it bears today. The word chlorine is from the Greek word meaning green.

Probably the first use to which chlorine was put was as a bleach. James Watt first noticed that chlorine had bleaching properties. His attempt to produce chlorine for this propose ended in failure because the chlorine had a destructive effect on fibers. This difficulty was overcome when Henry succeeded in preparing a combination with lime that could be reduced to a dry powder. The manufacture of chloride of lime was taken up by Charles Tennant in 1799 in Scotland,¹

As a disinfectant, chlorine was first used about 1800 by de Morieau, in France, and by Criukshank, in England. These men didn't know what took place in disinfecting a substance. Until

the middle of the 19th century disinfection was regarded as a process that arrested putrefaction. Micro-organisms were not associated with the process.

In 1839 Theodor Schwann, who is regarded as the founder of the school of anticeptics reported that "Permentation is arrested by any influence capable of killing fungi; especially by heat, potassium arsenate, etc----".² His results were not generally accepted because of the belief in the theory of spontaneous generation. This theory was finally refu§ed by Fasteur in 1862, who proved the possibility of preparing sterile culture medic.

One of the corliect chlorine preparations used in conitary work was an electrolyzed sea water known as Mormite Fluid. This was introduced by M. Hermite in 1809 and was employed for domestic purposes and for fluching sewers and latrines. During electrolysis of sea water the magnesium chloride is partially converted into hypochlorite which dissociates into magnesium hydrate and hypochlorous acid.

Leter strong selt solutions were substituted for sea water and the product was commercially known as "Electrozore". In 1893 a plant was installed at Brewster, N, Y. for chlorinating savage from a small group of houses with "Electrozore". The savage was discharged into a small creek which polluted Croton Lake. The application of "Electrozone" proved successful. This was the first occasion on which the specific object of chlornation was the destruction of hacteria.¹

The first occasion on which chlorine compounds were used

for the disinfection of water is not definitely known. As early as 1850 wells were treated with bleach, but these treatments were made without definite knowledge of the destruction of bacteria.

The credit for the first sytematic use of chlorire in water disinfection is due to A. C. Houston of England. His work was performed at Lincoln in 1004-1905. Owing to flood conditions the reservors, filters and distribution system became infected with typhoid bucilli which caused a severe epidemic. The storage and purification works were treated with sodium hypochlorite containing 10% available chlorine. The dosage was one part per million of chlorine. The results were very satisfactory.¹

At the Royal Testing Station in Berlin, numerous experiments in severe chlorination were made by Kranejuhl and Furrjuivut. The results were judged by the B. coli content which was taken as the index of pathogenicity because this harmless intestinal bacillus were found to be more frequent and less viable than the majority of pathogenic organisms. B. coli is easy to test for and the B. coli index is still used in bacterial analysis of water.¹

It was common European practice to use large doses of chlorine, several parts per million, and then remove the excess after a predetermined contact period. Sodium bisulfite was used to remove the excess chlorine. Today water supplies are dosed to about 0.5 p.p.m. or less.

The first big ettempt to chlorinate on a larger scale in this country was in Chicago. In 1908 the Union Stock Yards Co. were proceeded against by the City of Chicago regarding the effluent

of the Fubbly Creek filter plant. Copper sulfate had been used in the filters but stock shippers complained that the water had a deleterious effect upon the animals consuming it. The copper treatment was eliminated and bleach substituted. The results were very satisfactory.¹

About the same time Jersey City water was treated with chlorine. The ability of this process to purify water adequately was contested in court. The judge held that from all evidence the chlorine had a beneficial affect on the water and that it left no deleterious substance in the water.

The increase in the use of chlorine was tremendous the first few years of its use. In 1908 some 50,000,000 gallons were treated a day; in 1911 over 800,000,000 gallons per day. Today the majority of plants treat with chlorine and practically all plants are equipped to do so in case of danger of pollution. Where surface water is the source of supply, chlorination is used almost without exception.

Today most plants chlorinate with pure chlorine rather than bleach as formerly. Chlorination usually requires complicated mechanisms which need the attention of skilled operators to avoid breakdown or incorrect dosage. The dangers from the interruptions of service are so great they must be avoided by every means possible. In 1916 an attendant at the water works in Milwaukee stopped the operation of the chlorinator for 8 hours. The water was badly polluted that day, and there resulted over 50,000 cases of enteritis, over 400 cases of typhoid, and 40-50 deaths.³

The graph below shows the typhoid fever cases in Philadelphia and the effect of chlorination of the public water supply on the typhoid rate.



Typhoid fever cases per 100,000 pop. from 1890, Philadelphia⁴

During the years 1909-10-11, when practically the whole of the city supply was filtered the average typhoid rate was 90 cases per 100,000 population, but when the water was also chlorinated, in 1914-15-16, the rate was only 35, a reduction of 61%.

When two substances, A and B, react with each other and there is no further change in the relative masses of the two substances, equilibrium has been reached. When the reaction products, C and D, can react with each other to form A and B, the reaction is said to be reversible and is generally written in the form:

A + B ≠ C + D

When equilibrium has been reached the velocity of the reaction between A and B is equal to that between C and D. The speed of the reactions is expressed by the Law of Mass Action, first stated by the Norwegians Guldberg and Waage in 1079: "The rate of reaction between any two substances in a mixture is proportional to the product of the active masses of these substances in the mixture."⁵

In line with common practice (A) will be used to represent the concentration of the substance A in moles per liter. Denote the velocity of the reaction from left to right by $\mathbf{v} \rightarrow \mathbf{,}$ then

 $\mathbf{v} \longrightarrow \boldsymbol{\alpha}$ (A) X (B), therefore $\mathbf{v} \longrightarrow = F_1(A) \times (D)$ where K_1 is a proportionality factor or number, Similarly

 $\mathbf{v} \leftarrow \mathbf{C}$ (C) \mathbf{x} (D), therefore $\mathbf{v} \leftarrow = F_2(C) \mathbf{x}$ (D) F_2 will be a different number from K.

Exfore any A and B have reacted, the concentration of these are at the highest values, i.e., $\mathbf{v} \rightarrow \mathbf{i} \mathbf{s}$ a maximium at the beginning of the reaction. No C or D are present at the start, therefore $\mathbf{v} \leftarrow = \mathbf{C}$ at the start. As A and B react to produce C and D, the

concentrations of A and D decrease and consequently $\mathbf{v} \longrightarrow \mathbf{d}\mathbf{c}\mathbf{c}\mathbf{r}\mathbf{e}\mathbf{s}\mathbf{e}\mathbf{s}\mathbf{e}\mathbf{s}$. On the other hand, $\mathbf{v} \longrightarrow \mathbf{s}\mathbf{t}\mathbf{r}\mathbf{r}\mathbf{t}\mathbf{s}$ at zero and increases as the concentrations of C and D become greater and greater. Finally a point of equilibrium is reached where the two velocities are equal, i.e., $\mathbf{v} \longrightarrow = \mathbf{v} \longrightarrow \mathbf{c}$. At this point

 $Y_1(A) \times (B) = Y_2(C) \times (D)$

or transposing,

$$\frac{(0) \times (0)}{(0) \times (0)} = \frac{k^{2}}{k^{2}} = k$$

K is simply a number or constant. It is the quotient of the two numbers F_1 and F_2 . K is called the mass action constant.

This general algebraic expression will be found vary useful in studying reversible reactions. For example consider the ionization of a substance like acetic acid in squeeus solution. This ionization is a reversible reaction as indicated by the equation

$$H(C_2H_3O_2) \Longrightarrow H^{\bullet} + C_2H_3O_2^{-}$$

Since this is a reversible reaction it is governed by the law of mass action, so the following ionic relations will be true:

$$\frac{(\mathbf{h}^{+}) \times (\mathbf{C}_{2}\mathbf{H}_{3}\mathbf{C}_{2}^{-})}{[\mathbf{H}(\mathbf{C}_{2}\mathbf{H}_{3}\mathbf{C}_{2})]} = \mathbf{K}$$

This expression states that the constant F is equal to the hydrogen ion concentration in moles per liter, (1^+) , times the acetate ion concentration in moles per liter, $(C_2H_3C_2^-)$, divided by the un-ionized acetic sold in moles per liter, $[H(C_2H_3C_2)]$.

The respective quantities of the three substances will always

be such that the above indicated quotient will always have a value numerically equal to K. The constant K which represents the above relation between the concentrations of the ions and the unionized substance is called the ionization constant.

Instead of four substances - A, B, C and D - we have only three, namely, H^{+} , $C_2H_3O_2^{-}$ and $H(C_2H_3O_2)$. This does not alter the situation: it makes a simple relation with three factors instead of four.

Fure water is ionized to a very small extent according to the ionic equation

Applying the Lew of Mass Action

$$\frac{(\mathrm{H}^{+}) \times (\mathrm{OH}^{-})}{(\mathrm{H}_{2}\mathrm{O})} = \mathrm{K}$$

On account of its slight dissociation, any change in (H^*) or (OH^-) will have only a slight effect on the value for (H_2O) In fact, (H_2O) mey be considered as a constant. If the value (H_2O) is designated as K_1 , then

$$\frac{(H^{+}) \times (OH^{-})}{K_{1}} \neq K \text{ or } (H^{+}) \times (OH^{-}) = K_{1} \times K = K_{H_{2}O}$$

 $K_{\rm H_{2}O}$ equals the ion product for water. By experiment the numerical value for $K_{\rm H_{2}O} = 1 \times 10^{-14}$. If (H⁺) is made small then (OH⁻) will be correspondingly larger and vice versa.

In pure water, the value for $(H^{+}) = (OH^{-}) = 1 \times 10^{-7} \text{ m}./1$. Since water is a neutral substance, it is possible to define a neutral solution as one which has a value for (H^{+}) or $(OH^{-}) =$ $1 \times 10^{-7} \text{ m}./1$. Assume a slightly acid solution, the (H^+) of which has been determined to be 1×10^{-6} m./l. Applying the equation

$$(H^{+}) \times (OH^{-}) = 1 \times 10^{-14}$$
$$(OH^{-}) = \frac{1 \times 10^{-14}}{1 \times 10^{-6}} = 1 \times 10^{-8} \text{ m}_{\bullet}/1.$$

It follows that a solution in which $(H^{+}) > 10^{-7}$ or the $(OH^{-}) < 10^{-7}$ is an acid solution or gives an acid reaction. Also, a solution in which $(H^{+}) < 10^{-7}$ or the $(CH^{-}) > 10^{-7}$ is an alkaline solution or gives a basic reaction.

It is customary, now, to use the system of expressing the acidity or alkelinity of a solution in terms of the logarithm of the reciprocol of the (H^{+}) and this is known as the "pH" value. Then

pH =
$$\log \frac{1}{(H^{+})}$$

Suppose the (H⁺) of a solution is 1 × 10⁻³ m./1., then
pH = $\log \frac{1}{10^{-3}} = \log 10^{+3} = 3$

The following table shows the relationship between the (H^+) and the pH values.

		Neut ral						
(H+)	10-0	⁵ 10 ⁻	.1 10-2	² 10 ⁻³	10-4	10-5	10-6	10-7
рН	0.5	1	2	3	4	5	6	7
			Alke	line				
(H+)	10- ⁸	10-9	10-10	10-11	10-13	2 10-3	13 10-	-14
рH	8	9	10	11	12	13	14	

Thus, an acid solution is one in which $(H^{+}) > 10^{-7}$ or pH < 7.

A neutral solution is one in which $(H^*) = 10^{-7}$ or pH = 7An alkaline solution is one in which $(H^*) < 10^{-7}$ or pH > 7See bibliography note 6 for source of information on mass action and pH.

The pH of a solution can be determined by figuring the concentration of the reacting substances, but in water and sewage analysis there are two other methods in common use, namely the colorimetric and electrometric methods.

Colorimetric methods make use of the changes in color which certain dyes undergo under various changes in hygrogen-ion concentration. This change in color is not complete with a very small change in pH but extends over a comparatively wide range of pH. Indicators have certain definite pH ranges for color change and the indicator selected should be governed by the pH of the sample tested. The accuraccy of the indicator is greatest near the center of its range and decreases as the limits are approached. The sample under test is compared with color standards. The following are some indicators and the pH ranges covered by them.⁷

Indicator	pН	Rai	1g e
Benzo yellow	2.4	to	4.0
Bromphenol blue	3.0	to	4.6
Bromcresol green	3.8	to	5.4
Chlorphenol red	5•2	to	6.8
Bromthymol blue	6.0	to	7.6

Phenol	red	6.8	to	8.4
Cresol	red	7.2	to	8.8
Thymol	blue	8.0	to	9.6
Tol yl 1	red	10.0	to	11.6

There are several types of electrometric pH meters. They make use of standard cells and a Wheststone bridge. Class electrodes are commonly used. A Beckman electrometric pH meter was used in the control work for this thesis. The problem of chlorine stability is a direct result of observations of swimming pools which formerly used hard water and more recently softened water. A few case histories are cited to give an overall picture of the problem.⁸

Prior to 1931 the Michigan State College pool was supplied with a pool water of 500 p.p.m. hardness and a pH of about 7.6. Liquid chlorine was added for disinfection and residuals of 0.3 to 0.5 p.p.m. were maintained. In the fall of 1931 the pool was supplied with zeolite-softened water. After several weeks of operation the pH dropped to 5.5 and chlorine residuals were zero. The pool water was badly contaminated. The pool was emptied and refilled with hard water. The pool operated satisfactorily as previously.

In the summer of 1940, when the Moore's Park outdoor pool in Lansing was opened, a lime-soda treated water was used and a similar experience resulted. Formerly a well water of 500 p.p.m. was used. The pool was operated at a pH of 7.2 to 7.4, with a chlorine residual of 0.3 to 0.5 p.p.m. In 1940 the pool was supplied with lime-soda softened water with a hardness of 85 p.p.m. and a pH of 7.6 to 8.6. With bright sunlight the pH fell to a range of 5.5 to 3.5. To correct the pH, about 175 pounds of sode ash were added during the course of two weeks. The pH would reach 7.1 at night but drop to 5.5 during the day.

A similar situation existed at the outdoor pool at Midland.

It was found that by adding lime the pH would remain up and chlorine residuals could be maintained.

Following this experience, the Moore's Park pool was treated with 15 to 20 pounds of lime during the course of two days. The pH was raised from 5.5 to 7.6. The chlorine consumption dropped from a maximum of 12 lb. to 6 lb. per day and chlorine residuals of 0.3 to 0.5 p.p.m. were maintained throughout the day.

The Richmond Park pool at Grand Rapids was examined. The water is a softened river water with a hardness of 100 p.p.m. and a pH range of 9.0 to 10.0. No difficulty is experienced in maintaining chlorine residuals in bright sunlight. The stability of the chlorine in this pool as contrasted to the other pools cited is probably due to two factors - (1) the high pH and (2) the relatively higher calcium and magnesium carbonate content of the soft water.

In this investigation an attempt to duplicate this condition in the laboratory was made. It is also desired to find out the effect of pH on chlorine stability.

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Each series tested in the laboratory consisted of ten oneliter samples, each of different pH. Ten one-liter volumetric flasks were filled with the sample water. The pH of each was adjusted so that the pH values ranged from about 3.0 to 12.0. The pH value below that of the sample was adjusted with sulfuric sold. The pH above that of the sample was adjusted with solium hydroxide and lime. No attempt was made to adjust the pH to a certain value, but rather to adjust for values within the range 3 to 12. The pH values were determined with a Beckman electrometric pH meter.

Small quantities of different types of organic matter were added to each sample in equal emounts. Organic matter used included settled sewage, peptone, activated sludge and urea. Chlorine in the liquid form was added in equal amounts to each sample.

The same quantity of chlorine as was added to the samples was added to a liter of distilled water. This was tested for residual chlorine and this value used as the initial chlorine. The indivudual samples were tested at 15 minutes, 4 hours and 24 hours.

The starch-iodide method as outlined below was used to test for chlorine residuel.

 Pleced 100 ml. of the sample in an Erlenneyer flask.
 Added 1 ml. of concentrated hydrochloric acid (This test must be carried out in an acid medium because free iodine

forms compounds in an elkaline solution)

3. Added a small crystal of potessium iodide.

4. Added 1 ml. of starch indicator solution.

5. Titrated with 0.005N sodium thiosulfate solution.

The reactions that take place are as follows:

 $2KI + Cl_2 = 2I + 2KCl$

$$2I + 2Na_2S_2O_3 = Na_2S_4O_6 + 2NaI$$

Calculations:

M1. 0.005N thiosulfate x 1.773 = p.p.m. Chlorine The factor 1.773 is obtained as follows; Equivalent weight of $Na_2S_2O_3 = 158.11$ Equivalent weight of I = 126.92 Equivalent weight of Cl = 35.457

- B. One milliliter of 0.005N Na₂S₂O₃ contains 0.005 × 158.11/1000 = 0.00079055 gm. or 0.79055 mg. of Na₂S₂O₃.
- b. 0.79055 mg. Na₂S₂O₃ is equivalent to 126.92/158.11 × 0.79055 = 0.6342 mg. iodine.
- c. 0.6342 mg. of iodine is equivalent to 35.457/126.92 * 0.6342 =
 0.1773 mg. chlorine.

Of the 1-liter sample under test, 100 ml. was used for the chlorine determination (Step 1 above). Then

 $0.1773 \times 1000/100 = 1.773$ mg. of Cl₂ per liter per ml. of 0.005N sodium thiosulfate or 1.773 p.p.m. per milliliter

of 0.005N sodium thiosulfate used.

Therefore, ml. thiosulfate (Step 5) \times 1.773 = p.p.m. Cl₂.

The chlorine residual thus found in each sample was subtracted from the initial chlorine to find the loss in chlorine.

EXPERIMENTAL DATA AND CURVES

On the following pages are recorded all the results of the 29 experimental series run in the laboratory.

The curves are plotted with chlorine loss as ordinate and pH as abscissa.

The different types of water tested include college tap water, zeolite and lime-soda softened waters, distilled water and college tap lime softened.

Approximately 900 titrations were preformed in this investigation.

The first few series were tested only once or twice during the 24 hour run. As the investigation proceeded it was believed advantageous to compile data three times for each series.

The term stability is taken to mean the degree to which chlorine remains available in the solution for bactericidal purposes.



No Organic Matter Added

NaOH ---- $Ca(OH)_2$ ----

	on one our	Desage	рн	CI	Chlorine	Loss in p	
		p.p.m.		p.p.m.	20 hrs.		
Distilled	none		6.1	9.58	1.96		
Dist.50%	11		7.3	8.87	1.78		
Dist. 25% Tap 75%	19			"	2.03		
Tap				"	2.65		
"	NaCH	40	8.9		2.31		
	10	80	10.6		2.49		
	$Ca(OH)_2$	37	8.1		2.49		
"	11	74	8.7	"	2.31		
							-
	Distilled Dist.50% Tap 50% Dist. 25% Tap 75% Tap " "	Distilled none Dist.50% " Tap 50% " Dist.25% " Tap 75% " Tap 75% " M NaOH " Ca(OH)2 " " " U " Ca(OH)2 " "	Distilled none Dist.50% " Tap 50% " Dist.25% " Tap 75% " Tap 75% " M NaCH M 80 " Ca(OH)2 37 " M " M 1 M 1 M 74	Distilled none 6.1 Dist.50% " 7.3 Tap 50% " " Dist.25% " " Tap 75% " " Tap 75% " " M NaOH 40 8.9 " " 80 10.6 " Ca(OH)2 37 8.1 " " 74 8.7	Distilled none 6.1 9.58 Dist.50% " 7.3 8.87 Tap 50% " " " Dist.25% " " " Tap 75% " " " "Tap 75% " " " "Tap 75% " " " "Tap 75% " " " "NaOH 40 8.9 " " NaOH 40 8.9 " " Ca(OH) ₂ 37 8.1 " " " 74 8.7 " "	Distilled none 6.1 9.58 1.96 Dist.50 " 7.3 8.87 1.78 Tap 50% " " " 2.03 Dist. 25% " " " 2.65 Tap 75% " " " 2.65 " NaOH 40 8.9 " 2.31 " NaOH 40 8.9 " 2.49 " Ca(OH)2 37 8.1 " 2.49 " " 74 8.7 " 2.31	Distilled none 6.1 9.58 1.96 Dist.50 " 7.3 8.87 1.78 Tap 50% " " " 2.03 Dist. 25% " " " 2.65 Tap 75% " " " 2.65 " NaOH 40 8.9 " 2.31 " NaOH 40 8.9 " 2.49 " Ca(OH)2 37 8.1 " 2.49 " • 74 8.7 " 2.31 " • 10.6 " 2.49 " • 6.1 9.53 1 • • • 1 1 1 • • • • • 1 • • • • • • • • • • • • • • • • • • • • • • • •

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College Tap Water (350 p.p.m. Hardness) No Organic Matter Added

V

NaOH -----Ca(OH)2 -----

No.	Chemical	Dosage	pН	Cl	Chlori	ne Loss in	p.p.m.
		p.p.m.		p.p.m.	24 hrs.		
1	H ₂ SO ₄	300	4.9	8.87	2.65		
2	"	200	6.1		2.13		
3	10	100	6.6	"	1.6		
4	none		7.3	"	2.49		
5	NaOH	100	9.5		2.65		
6		200	10.9	"	3.02		
7		30 0	11.1	"	2.65		
8	Ca(OH)2	100	7.9	"	3.19		
9	11	200	8.1	"	3.37		
10	"	300	9.4	"	3.54		

Series 2

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No.	Chemical	Dosage	рH	C1	Chlori	ne Lossi in	p.p.m.
		p.p.m.		p.p.m.	4hrs.	24 hrs.	
1	Peptone	0	7.2	8.16	1:07	2.49	
2	W	2	H	**	1.96	4.61	
3.	W	10	**	10	4.44	6.92	
4	W	20	w	*	4.61	6.56	



College Tap Water (350 p.p.m. Hardness) 5 p.p.m. Peptone

l

NaOH Ca(OH)2

No.	Chemical	Dosage	pH	C1	Chlor	ine Loss in p.p.m.	
		p.p.m.		p.p.m.	3 hrs.	24 hrs.	
1	H2SO4	300	5.0	8.16	1.6	3.55	
2		200	6.1		1.78	4.26	
3		100	6.6		1.78	5.33	
4	none		7.3	10	3.12	6.74	
5	NaOH	100	9.4		3.55	7.1	
6	**	200	10.8	n	2.84	6.74	
7	*	30 0	11.4		1,95	6.03	
8	Ca(OH) ₂	100	7.9		3.12	5.22	
9	"	200	8.4	"	3.2	5.39	
10		300	9.4		3.2	5.22	

Series 5



pH College Tap Water (350 p.p.m. Hardness) No Organic Matter Added

NaOH ----Ca(OH)2 ----

...

No.	Chemical	Dosage	pH	Cl	Chlorine Loss in p.p.m.
		D.D.M.		p.p.m.	24 hrs.
1	H2504	300	4.9	8.4	2.63
2		200	6.1		1.66
3		100	6.6		1.84
4	none		7.3		2.2
5	NaOH	100	9.4		2.55
6		200	10.9		2.55
7		300	11.6		2.47
8	Ca(OH)	150	8.2	**	2.63
9	"	275	9.4		2.63
10		400	11.3	"	2.2

Series 6



College Tap Water (350 p.p.m. Hardness) 5 p.p.m. Peptone

NaOH Ca(OH)2

No.	Chemical	Dosage	pH	Cl	Chlori	ine Loss in	p.p.m.
		p.p.m.		p.p.m.	24 hrs.		
1	H2 SO4	300	3.9	8.41	4.33		
2		200	6.0		4.86		
3		100	6.6	"	6.28		
4	none		7.3		7.17		
5	NaOH	100	9.5		7.35		
6		200	10.9		7.51		
7	"	300	11.7	"	6.28		
8	$Ca(OH)_2$	150	8.2	"	6.81		
9		275	10.7	"	6.81		
10		400	11.6	*	6.46	2	



Distilled Water

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NaOH -----Ca(OH)2 -----

No.	Chemical	Dosage	pH	C1	Chloripe Loss in p.p.m.		
		D.D.M.		p.p.m.	24 hrs.		
1	H_SO4	50	3.2	8.4	3.08		
2	"	10	3.9	n	3.08		
3	none		6.0	H	2.9		
4	NaOH	5	7.5		3.44		
5		10	9.5		4.5		
6		50	10.5		6.1		
7	Ca(OH) 2	20	8.5		5.85		
8		24	10.2	11	7.34		
9		50	10.8		6.63		

Series 8



Mixtures of College Tap and Distilled Water No Organic Matter Added

No.	Water	Percent	pН	Cl	Chlorine Loss in p.p.m.		
				p.p.m.	24 hrs.		
1	Dist. Tap	100	6.1	8.4	4.14		
2	Dist. Tap	80 20	7.1		6.45		
3	Dist. Tap	60 40	7.2		6.84		
4	Dist. Tap	40 60	7.3		6.98		
5	Dist. Tap	20 80	7.4	"	7.16		
6	Dist. Tap	100	7.4		7.16		

Series 9

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College Tap Water (350 p.p.m. Hardness) 5 p.p.m. Peptone

NaOH -----Ca(OH)2

No.	Chemical	Dosage	pH	C1	Chlorine Loss in p.p.m.		
		p.p.m.		D.D.M.	30 min.	4 hrs.	24 hrs.
1	H2 504	300	4.7	7.36	1.24	2.84	4.79
2		200	6.1		1.51	2.93	5.14
3	10	100	5.6		1.86	3.37	6.2
4	none		7.3		2.04	4.88	6.65
5	NaOH	100	9.4	"	2.48	5.85	6.83
6		200	10.8	"	0.88	4.52	6.48
7	10	300	11.5		0.88	3.64	6.21
8	Ca(OH)2	150	8.2	"	2.66	5.5	6.56
9	W	275	10.7		1.33	4.88	6.65
10	11	400	11.4		1.24	2.48	6.22

Series 10

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Distilled Water 5 p.p.m. Peptone

No.	Chemical	Dosage	pH	C1	Chlori	ne Loss in	p.p.m.
		p.p.m.		p.p.m.	15 min.	4 hrs.	24 hrs.
1	H2 204	50	3.2	8.9	1.55	216	4.56
2		10	3.9		1.35	2.87	4.73
3		2	4.7		1.45	4.47	4.47
4	nöne		6.1		1.25	2.78	5.0
5	$Ca(OH)_2$	2	7.5	"	1.45	2.42	4.29
6		4	8.4		1.6	2.96	4.29
7	"	10	9.4	"	2.9	3.94	6 .06
8		15	9.9		2.6	5.35	7.75
9		25	10.5		1.55	3.67	7.75
10		50	11.4	"	1.45	3.58	7.13

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College Tap Water (350 p.p.m. Hardness) 20 ml. Activated Sludge NaOH -----Ca(OH)₂ -----

No.	Chemical	Dosage	pH	C1	Chlorin	de Loss in j	p.p.m.
		р.р.ш.		p.p.m.	15 min.	4 hrs.	21 hrs.
1	H2SO4	300	5.1	6.3	0.15	2.66	3.81
2	11	200	6.1		0.92	2.58	3.29
3		100	6.7		1.51	2.58	3.73
4	none		7.4	10	1.34	3.11	4.0
5	NaOH	100	9.4	"	1.42	2.93	4.17
6		200	10.8				4.0
7		300	11.1	"	0.1	1.25	3.73
8	Ca(OH)2	150	8.3	H	1.69	2.84	4.35
9	**	275	9.4	11	1.51	3.46	4.35
10	11	400	11.1		0.1	1.15	3.82

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College Tap Water (350p.p.m. Hardness) 20 ml. Activated Sludge NaOH -----Ca(OH)2----

No.	Chemical	Dosage	pH	C1	Chlor	ine Loss in	p.p.m.
		p.p.m.		p.p.m.	15 min.	4 hrs.	21 hrs.
1	H2 SO4	300	5.0	5.96	0.19	2.32	4.18
2	20	200	6.1	"	1.67	2.85	3.84
3	**	100	6.6		.01	3.03	4.09
4	none		7.2	н	1.34	3.38	4.53
5	NaOH	100	10.3	"	1.69	3.65	4.62
6	"	200	10.7		0.36	3.38	4.80
7	"	300	11.2	"	0.48	1.51	3.91
8	Ca(OH)2	150	7.9	н	2.49	3.38	4.98
9		275	10.1		2.85	2.41	4.98
10	"	400	11.1		0.19	4.18	4.27

Series 13



College Tap Water (350 p.p.m. Hardness) 20 ml. Settled sewage NaOH Ca(OH)₂

No	Chemical	Dosage	pH	Cl	Chlor	ine Loss in	p.p.m.
		p.p.m.		p.p.m.	15 min.	4 hrs.	21 hrs.
1	H ₂ SO ₄	300	5.0	5.7	5 0	2.48	3.53
2	"	200	6.1	"	0.44	3.28	3.81
3	"	100	6.6		1.95	3.46	4.34
4	none		7.3	"	2.3	3.63	4.52
5	NaOH	20	7.9	"	2.74	4.08	4.88
6	"	200	10.8	"	0.74	3.19	4.51
7	"	300	11.2	"	. 0.05	1.51	3.74
8	$Ca(OH)_2$	150	8.0	"	2.48	3.81	4.70
9		275	10.5	"	1.06	4.08	4.70
10	10	400	11.3		0.26	1.51	2.92

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College Tap Water 20 ml. setteled sewage

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NaOH ------CA(OH)₂ -----

No.	Chemical	Dosage	pH	Cl	Chlori	ne Loss in	p.p.m.
		p.p.m.		p.p.m.	15 min.	5 hrs.	24 hrs.
1	H ₂ SO ₄	300	4.9	5.4	0	2.39	4.16
2		200	6.0	"	0.52	4.16	4.60
3	"	100	6.6	"	2.48	4.43	4.78
4	none		7.3	"	3.36	4.43	4.95
5	NaOH	20	7.9	11	3.27	4.29	4.95
6		200	10.8		- 0.35	3.54	4.69
7		300	11.2		0.08	1.42	3.10
8	Ca(OH)2	150	8.1	"	3.54	4.60	5.13
9	"	275	10.4		2.21	4.6	5.13
10	"	400	11.1	"	0.08	1.68	3.10

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No	Chemical	Dosage	pН	Cl	Chlori	ne Loss in	p.p.m.
		p.p.m.		p.p.m.	15 min	3 hrs.	
1	H2804	300	2.9	3.4	1.54	2.78	
2		150	4.0		1.41	2.69	
3		100	6.0		0.6	2.34	
4	none		7.3		1.45	2.90	
5	NaOH	10	8.4	"	1.27	3.01	
6	"	80	9.3		0.65	3.10	
7		150	11.2		0.48	2.48	
8	Ca(OH)2	100	8.7		1.18	2.90	
9	"	150	9.4		0.65	2.51	
10	"	300	11.5		0.04	2.16	

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Red Cedar River Water

NaOH -----Ca(OH)2

No	Chemical	Dosage	pH	C1	Chlori	ne Loss in	p.p.m.
1.1		p.p.m.		p.p.m.	15 min.	4 hrs.	21 hrs.
1	H2504	200	3.1	9.75	4.05	9.04	9.45
2		150	4.6		4.05	8.95	9.43
3	**	100	5.9	"	8.75	8.55	9.31
4	none		7.2	"	4.15	8.65	9.34
5	NaOH	10	8.3	"	4.25	8.69	9.36
6	**	80	9.3		4.45	8.60	9.40
7	17	150	11.2		3.75	8.10	9.25
8	Ca(OH)2	50	8.5		4.65	8.75	9.45
9	"	150	9.5		4.15	8.15	9.4
10	**	300	11.4	"	3.65	7.15	9.22

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Red Cedar River Water

NaOH Ca(OH)₂

No	Chemical	Dosage	pН	Cl	Chaorin	ne Loss in p	D.p.m.
		p.p.m.		p.p.m.	15 min.	3 hrs.	20 hrs.
1	H ₂ SO ₄	200	3.3	10.6	5.1	9.0	10.07
2	"	150	5.0		4.4	8.83	9.89
3	10	100	6.2	"	4.2	7.94	9.98
4	none		7.3	"	5.0	8.74	10.12
5	NaOH	10	8.3	"	5.0	8.65	10.19
6		80	9.1	"	5.2	8.92	10.16
7	18	150	11.1	"	4.84	8.04	10.16
8	Ca(OH)2	30	8.7	"	5.55	9.1	10.12
9		150	9.4		5.8	9.1	10.25
10		200	10.9		4.84	8.12	10.05

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Red Cedar River Water

NaCH -----Ca(OH)2

No	Chemical	Dosage	Cl	pН	Chlor	Chlorine Loss in p.p.r	
		p.p.m.	p.p.m.		15 min,	3 hrs.	21 hrs.
1	H ₂ SO4	200	10.0	2.8	4.7	9.12	9.65
2	Ħ	150		4.6	4. 86	9.08	9.65
3	W	100		5.5	4.68	8.62	9.65
4	none		Ħ	6.9	4.65	7.38	9.29
5	NaCH	20	Ħ	8.1	4.9	8.6	9.5
6	Ħ	120	Ħ	9.3	4.77	8 .48	9.34
7	W	30 0		10.2	4.7	6.28	9.47
8	$Ca(OH)_{2}$	50	*	7.9	5.22	9.24	9.65
9	W	250		9.2	5.04	8.64	9.65
10	H	4 00	H	10.2	4.33	7.64	9.47

Series 19

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Red Cedar River Water

NaOH -----Ca(OH)₂ -----

No	Chemical	Dosage	pH	C1	Chlor	ine Loss in	p.p.m.
		p.p.m.		p.p.m.	15 min	3 hrs.	23 hrs.
1	H2504	200	3.8	15.3	3.4	10.1	11.9
2	H	150	5.6		3.4	8.68	13.7
3		100	6.3		2.8	9.4	13.35
4	none		7.4	"	3.9	9.98	14.01
5	NaOH	30	8.8		4.15	10.6	14.29
6		150	9.8	W	3.1	8.68	13.35
7	H	300	11.1	n	2.7	8.27	12.55
8	Ca(OH)2	50	8.7	Ħ	3.97	9.45	14.24
9		250	9.7	H	3.8	9.34	13.53
10		400	10.8		3.1	8.02	13.08

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College Tap (350 p.p.m. hardness) 25 ml. Settled Sewage NaOH -----Ca(OH)2 -----

No	Chemical	Dosage	pН	C1	Chlorine	Loss in p.r	• T •
Aster In		p.p.m.		p.p.m	15 min.	3 hrs.	23 hrs.
1	H2 SO4	300	2.7	11.7	0	1.1	4.15
2	*	200	5.4		0.1	2.6	4.88
3	none		7.3		1.95	3.55	6.03
4	H2 SO4	100	6.3		2.0	3.65	5.5
5	NaOH	30	8.4		2.85	4.45	6.38
6	19	100	9.4	11	1.95	4.53	5.65
7	10	200	10.1		0.4	4.1	5.7
8	Ca(OH)2	75	8.2		2.05	4.44	6.38
9	"	250	9.0	11	3.1	4.61	6.62
10	14	500	10.1		1.08	3.38	6.38

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Zeolite softened (Zero hardness) 25 ml. settled sewage

NaOH -----Ca(OH)₂

No	Chemical	Dosage	Cl	pH	Chlorine Loss in p.p.m.		
		p.p.m.	D.D.M.		15 min.	4 hrs.	21 hrs.
1	H ₂ SO ₄	300	7.0	3.9	0.1	2.3	4.6
2	11	200		5.9	1.5	4.29	5.23
3	"	100		6.5	3.06	4.75	5.58
4	none			7.6	3.67	4.93	5.67
5	NaOH	20		8.7	3.72	5.0	5.76
6	"	50	н	9.3	2.12	5.05	5.76
7	. 11	150		10.3	0.16	2.65	4.7
8	Ca(OH),	50	**	8.6	3.64	5.14	5.58
9	"	150	19	9.2	2.3	5.23	6.06
10		550	10	10.3	0.88	2.3	3.86

Series 22

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Zeolite softened (Zero hardness) 25 ml. settled sewage

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NaOH -----Ca(OH)₂ -----

No	Chemical	Dosage	C1	pH	Chlori	Chlorine Loss in p.p.m.	
		p.p.m.	p.p.m		15 min.	5 hrs.	23 hrs.
1	H2SO4	300	71	3.8	0.4	3.06	4.62
2		200		5.8	2.8	4.94	5.27
3		100		6.4	3.4	5.08	5.56
4	none			7.8	3.7	5.01	5.86
5	NaOH	20		8.8	3.74	5.3	6.13
6		50		9.3	1.9	5.15	6.04
7		150		10.1	.93	4.26	5.21
8	Ca(OH)	50		8.5	4.07	5.42	6.21
9	7	150		9.1	3.0	5.77	6.48
10		550		10.0	1.16	3.15	5.06

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Lime-Soda Softened (Lansing Plant) (85 p.p.m. Hardness) NaOH --Settled Sewage Ca(OH)2-

No	Chemical	Dosage	C1	pН	Chlorine Loss in p.p.m.		
		p.p.m.	p.p.m.		15 min.	4 hrs.	23 hrs.
1	H2 SO4	100	8.47	2.8	0.27	1.73	4.06
2	**	50		3.5	0.43	1.73	4.22
3	**	20	"	6.5	0.67	2.45	4.75
4	none			9.3	1.57	3.24	4.93
5	NaOH	10	"	10.1	0.43	3.24	4.22
6	"	20		10.3	0.67	2.80	4.67
7	"	50		10.8	0.13	1.92	4.29
8	Ca(OH)2	25		10.1	0.41	3.24	4.67
9	19	50		10.2	0.57	3.07	4.83
10		100		10.6	0.4	2.45	4.75

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Lime-Soda Softened (Lansing Plant) (85 p.p.m. Hardness) NaOH -----Settled Sewage Ca(OH)2

No	Chemical	Chemical Dosage Cl pH		Chlorig	e Loss in p.	.p.m.	
		p.p.m.	p.p.	n	15 min.	4 hrs.	23 hrs.
1	H2S64	60	7.26	3.25	0	2.66	4.41
2	"	40		4.3	0	2.83	4.46
3	11	15		7.3	0.79	3.45	4.66
4	none			9.5	0.59	3.54	4.42
5	NaOH	5	"	9.8	0.38	3.8	4.6
6	**	20		10.5	0.06	1.66	4.78
7	"	60		10.9	0	1.5	3.54
8	Ca(OH)2	15		9.9	0.71	3.72	4.6
9	"	70		10.5	0.53	2.11	4.25
10	**	150		10.9	0.16	1.14	3.36

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College Tap Water (Lime-Softened to 110 p.p.m.) 25 ml. Settled Sewage

NaOH -----Ca(OH)2 -----

No.	Chemical	Dosage	pH	C1	Chlorin	ne Loss in :	p.p.m.
		p.p.m.		p.p.m.	15 min.	4 hrs.	22 hrs.
1	H ₂ SO ₄	100	3.5	6.2	0.17	1.95	3.27
2	"	70	6.3	"	2.39	4.96	5.4
3	"	65	6.7	"	3.19	5.32	5.56
4	"	50	8.8		4.16	5.58	5.76
5	"	25	9.9		0.44	3.19	4.25
6	none		10.5		0	1.33	3.9
7	NaOH	30	10.8	"	0	1.59	3.72
8	"	100	11.1	"	0.25	1.24	3.1
9	Ca(OH) 2	100	10.9		0.7	1.5	2.66
10		300	11.1		0.53	1.68	3.37

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NaOH ---Ca(OH)2 -----

No.	Chemical	Dosage	pH	C1	Chlorin	e Loss in p	.p.m.
		p.p.m.	-	p.p.m.	15 min.	3 hrs.	24 hrs.
1	H2504	30 0	3.4	7.62	0.08	0.62	1.23
2	"	200	5.7		0.17	3.45	6.82
3		100	6.3		0.36	5.76	7.09
4	none		7.1		0.44	2.12	4.52
5	NaOH	30	8.1		0.97	3.9	6.11
6		100	9.1		0.97	3.01	5.04
7		200	9.8		0.52	2.3	4.52
8	$Ca(OH)_2$	75	8.4		0.97	3.01	5.22
9		350	9.3		1.06	2.39	4.52
10	"	500	10.6	**	0.35	1.6	3.9

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Zeolite Softened (O Hardness) 5 p.p.m. Urea

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NaOH ------Ca(OH) 2

	No.	Chemical	Dosage	pH	C1	Chlorin	ne Loss in	p.p.m.
			p.p.m.		p.p.m.	15 min.	4 hrs.	21 hrs.
	1	^H 2 ^{SO} 4	300	4.6	7.1	0	1.17	2.75
	2		200	5.6		0	4 . 8 8	6.83
	3	H	100	6.3	"	0	6.39	6.83
	4	none		7.3		0.1	3.02	4.62
	5	NaOH	20	8.3		1.5	4.62	5.86
	6	11	100	9.2	"	1.6	4.79	6.12
* ***	7	19	200	10.0	"	1.78	3.38	5.06
	8	Ca(OH)2	50	8.5		0.9	3.2	5.06
	9	**	200	9.4		0.2	1.78	3.83
	10		600	10.4		0	1.6	3.91

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5 p.p.m. Urea

NaOH -----Ca(OH)2

No.	Chemical	Dosage	рH	Cl	Chlorin	Chlorine Loss in p.p.m.			
		p.p.m.		p.p.m.	15 min.	4 hrs.	23 hrs.		
1	H2SO4	50	3.1	8.5	0.35	1.4	2.92		
2	"	15	6.7	"	0	3.98	7.7		
3	••	8	8.1		0.26	3.62	7.79		
4	none		9.3		0.26	2.1	5.04		
5	NaOH	10	9.9		1.15	3.54	5.84		
6		20	10.2		1.05	2.82	5.66		
7	**	50	10.6		0.35	1.76	4.24		
8	Ca(OH)2	20	10.0		1.15	2.92	5.84		
9		50	10.4	**	1.05	2.73	4.95		
10		150	10.9		1.67	2.3	4.69		

Series 29
CONCLUSION

An interpretation of each series will be presented and then a general conclusion.

Series 1 - Tap water - No organic matter added.

The curve is fairly straight; there are no marked changes.

Series 2 - Tap water - No organic matter added. The greatest stability is at pH 6.6. Chlorine activity increases until pH 10 where it drops off. Lime causes greater chlorine loss than NaOH.

Series 3 - Omitted because pH's were not checked.

Series 4 - Peptone in tap water without adjustment of pH. Indicates that with increase of organic matter there is an increase in chlorine loss.

Series 5,6,7 - Tap water- Peptone edded.

The chlorine is more stable at low pH and is successively less stable as the pH increases until about pH 9 to 10, after which a greater residual is maintained. Lime solution offers greater chlorine stability than NaOH.

Series 8 - Distilled water

Chlorine stability decreases as the pH increases up to pH 10.2 at which point stability increases. Series 9 - Mixtures of tap and distilled.

As in series 8, there is increasing chlorine loss with increase in pH.

Series 10 - Tap water and peptone

In this series chlorine residuals were run three times during the 24-hour period. Chlorine loss increases as the pH increases up to pH 9.4, after which a decrease is noted. The greatest chlorine loss in the 15-minute run was at pH 7.3.

Series 11 - Distilled water and peptone

Chlorine activity is low at low pH and increases with greater pH up to pH 9.9 after which point the chlorine becomes more stable.

Series 12,13 - Tap water and activated sludge

Chlorine loss increases as the pH increases up to about pH 9.4. The critical point was not located in series 13 because no sample was adjusted to a pH between 8 and 10. Chlorine stability is about equal in lime and NaOH solutions.

Series 14,15,21 - Tap water and settled sewage

As with peptone chlorine stability decreases as pH increases to a pH of about 9, after which chlorine becomes more stable. The critical point was not reached in 14 and 15, but in series 21 there were several pH values near the critical point. Lime and NaOH solutions follow similar patterns. The greatest chlorine loss occurs in the 15 minutes.

Series 16,17,18,19,20 - Red Cedar River vater

There is not quite the marked change in river water as in other samples. Chlorine loss was considerable over the whole pH range. Ethility did increase between pH 6 and 7, and then egain at velues greater than 8.5.

Series 22,23 - Zeolite-softened and settled sevage

This water shows marked changes, with good chlorine stability at low pH and decreasing stability with increasing pH up to 9 to 9.5. The critical point is at pH 8.5 for the 15 minute runs.

- Series 24,25 Lime-soda softened water and settled sewage This water shows successively less chlorine stability with increasing pH up to pH 9.5 to 10.0 after which greater stability is indicated. The curve is not so marked as college tap and zeolite softened. There is considerable loss in the lower pH range.
- Series 26 Tap water, lime-softened and settled sevage There is a marked change here with increasing chlorine loss of the pH increases up to pH 8.8 after which the loss drops very rapidly.

Series 27 - Tap water and urea

Series 28 - Zeolite softened and urea

Series 29 - Lime-soda softened and urea

These three samples show increasing chlorine loss up

to pH 6.5 at which point there is less loss up to 7.0 - 7.5 in 27 and 28, and 9.3 in 29. Then the curves swing up as in all previous samples until pH 8 to 9 in 27 and 28, and 10.0 in 29, after which stability increases. Little loss is experienced in 15 minutes.

General Conclusions;

In all samples tested (except those with usea where two critical points occured) chlorine is increasingly less stable until pH 8.5 to 10 after which stability increases. Not much difference was noted between lime and NaOH solutions as concerns chlorine stability.

The animonia radical in the different organic matter used is probably responsible for the loss of chlorine. Chlorine combines with animonia to form chloramines. The test results indicate that these combinations take place more readily at certain pH's. Some chemical combinations take place within a very narrow pH range, but whether this is true in this case is not known.

The action of chlorine in swimming pools was not duplicated in the laboratory. Both hard and soft waters showed similar tendencies in the laboratory as concerns chlorine stability. The use of lime in swimming pools to increase chlorine stability did increase stability in the test samples, but the pH was higher in the test samples then in the pools.

Suggested further study:

In any future investigation of this type it would be well to

work within narrower pH limits, i.e., 6.5 to 10.0. Tests for ammonia should be made since indications are that ammonia is a big factor. Also, pH values should be checked at time of test to determine if there is a drop in pH.

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