

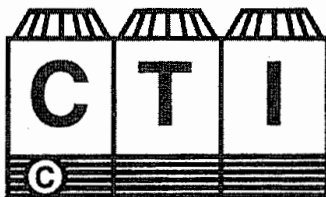
PAPER NO: TP86-09

CATEGORY: WOOD ATTACK

## COOLING TOWER INSTITUTE

### ENHANCED WATER MANAGEMENT USING BROMINE CHEMISTRY

RODNEY H. SERGENT  
GREAT LAKES CHEMICAL CORPORATION



The studies and conclusions reported in this paper are the results of the author's own work. The paper has been presented before, and reviewed by the Cooling Tower Institute, and approved as a valuable contribution to cooling tower literature.

Presented at the 1986 Cooling Tower Institute Annual Meeting  
Houston, Texas - January 27-29, 1986

ENHANCED WATER MANAGEMENT  
USING BROMINE CHEMISTRY

INTRODUCTION

In recent years, treatment programs used in cooling tower systems have undergone a metamorphosis. Tightening of EPA effluent discharge regulations, increased awareness of municipal and environmental safety factors, and the movement toward water reuse and reclamation underlie these changes. For example, in recirculated cooling water systems, non-heavy metal corrosion inhibitors, nonphenolic biodegradable biocides, increasing system pH values, and minimal chlorine discharge limits have replaced, to a large degree, acid chromate programs using continuous high-chlorine residuals and chlorinated phenolics for algae and micro-organism control. In addition, treated sewage and reclaimed water sources are now seriously considered for cooling tower make-up.

These current trends create some very real opportunities and, hence, some challenges for all of us involved in the business and science of water treatment. This paper will focus on bromine chemistry and some of its unique properties, with regard to providing solutions to the new and changing problems we face.

(1)

### Background

Elemental bromine ( $\text{Br}_2$ ) is a fuming red liquid at room temperature. Bromine appears between chlorine and iodine on the periodic table and has a molecular weight of 159.8. As a halogen, bromine exhibits the expected biocidal properties in water. Investigations concerning the use of bromine for the disinfection of water were reported in the 1930's (1,2).

Bromine is most often found in nature in the form of bromide salts. Sea water contains 65 ppm of bromide and surface water contains approximately 0.5 ppm of bromide. Bromine is produced commercially from natural brines. The Dead Sea is the richest deposit, containing 4000-6000 ppm bromide. In the United States, salt water formations in southern Arkansas, Michigan and Ohio contain 2000-4000 ppm bromide (3,6).

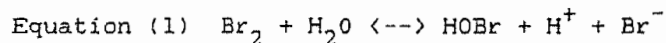
Bromine is manufactured in large, granite towers where the hot salt water is reacted with gaseous chlorine and steam. Bromine gas from this manufacturing step is then condensed and purified. Domestic production totalled 385 million lbs in 1984 (4). In constant dollars, the price of bromine relative to chlorine has dropped from a factor of 6.6 to a factor of 2.3 in the last two decades. The cost of bromine chemistry has come down to levels which permit its use in water treatment.

(2)

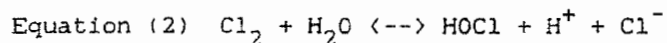
Bromine Chemistry in Water

The physical and chemical properties of bromine fall between those of chlorine and iodine. Bromine hydrolyzes in water to give hypobromous acid and hydrobromic acid analogous to the hydrolysis of chlorine ( Equations 1 & 2).

K1

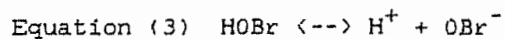


K1

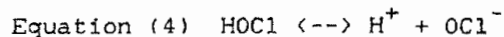


Hypobromous acid ionizes under alkaline conditions to form the hypobromite ion analogous to the ionization of hypochlorous acid (Equations 3 & 4).

K2



K2



Since the unhydrolyzed form of the halogen and the undissociated form of the hypohalous acid are the effective biocidal species for bromine and chlorine, it is important to identify the concentration of each species as a function of pH. Table I shows the hydrolysis and ionization constants for bromine and chlorine.

(3)

Table I

$K_2$	$K_1$	$K_2$	Reference
Cl <sub>2</sub>	.	3.3 X 10 <sup>-8</sup>	Moore (23)
Cl <sub>2</sub>	4.66 X 10 <sup>-4</sup>	3.2 X 10 <sup>-8</sup>	Latimer (24)
Br <sub>2</sub>	5.9 X 10 <sup>-9</sup>	1.0 X 10 <sup>-9</sup>	Wys & Stockton (2)
Br <sub>2</sub>	5.8 X 10 <sup>-9</sup>	2.06 X 10 <sup>-9</sup>	Latimer (24)

Figure 1 and Table II shows the relative concentrations of hypohalous acid as a function of pH using the equation:

$$K_2 = \frac{[H^+][OCl^-]}{[HOCl]}$$

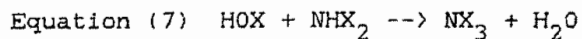
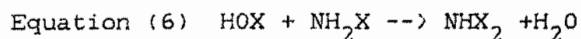
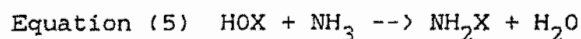
Table II

pH	% HOCl	% HOBr
6.0	97	100
7.0	76	98
7.5	50	94
8.0	24	83
8.5	9	60
9.0	3	33

Hypobromous acid shows little ionization until the pH approaches eight (8). This results in increasing disinfection rates for bromine relative to chlorine as the pH of a system increases above approximately 7.5.

(4)

Bromine and chlorine also differ in their reactions with nitrogen compounds. While both form haloamines, chloramines are very poor biocides relative to hypochlorous acid. Bromamines, on the other hand, are almost as effective as hypobromous acid (5). Equations 5-7 show the typical reactions with ammonia.



Monohaloamines and dihaloamines are the most prevalent species under typical disinfection conditions. The chloramines are much less reactive in solution than the bromamines. Table III shows the relative species in solution at a pH of 8.0 (6).

Table III

<u>Haloogen Species</u>	<u>% HOX</u>	<u>% OX</u>	<u>%NH<sub>2</sub>X</u>
HOCl	19	81	---
HOBr	90	10	---
NH <sub>2</sub> Cl	--	--	100
NH <sub>2</sub> Br	82	8	<10

The differences shown in Table III may explain the relative increased biocidal activity of bromamines versus chloramines.

(5)

Bromamines are also good virucides. Mills reports that under conditions typical of secondary treated sewage, Polio II virus was inactivated in less than five minutes by bromamines while an equivalent concentration of chloramines failed to kill all of the virus in 60 minutes (6). These finding may vary at different  $\text{NH}_3$  concentrations.

A measure of the chemical stability of haloamines is the relative degradation rates of the various species. In Figure II bromamines have a half-life of minutes compared with many hours for chloramines (21). A 2.5 ppm concentration of dibromamine has a half life of 64 minutes (22).

Studies done by Bongers, et al., indicate that brominated residuals decay much faster than chlorinated residuals. When bromine chloride and chlorine were applied at equal molar concentrations to ammonia-containing waters, the brominated system residuals were 1/2 to 2/3 the levels of the chlorinated system (7).

#### Toxicity

The toxicity of bromine residual is similar and in some cases not as severe as that of chlorine residual (8). Ward et al. demonstrated that bromine residuals produced by bromine chloride were less toxic than those of chlorine at approximately equal concentrations (9). The environmental persistence of organobromine compounds is also less. Mills states that bromobenzene photo-

(6)

degrades in 1/100 the time of chlorobenzene (10). A ground water study in California measured a half-life for bromoform of 15 days compared with 50 days for chloroform (11). More importantly, Bouwer et al. has shown a seeded, anaerobic culture with 160 ppb of brominated trihalomethane (THM) degraded to less than 0.1 ppb in less than two weeks (11). When 157 ppb of chlorinated THM was run using the same method, 117 ppb remained after two weeks. Clearly bromine chemistry is more environmentally acceptable than chlorine chemistry.

#### Bromine Chemistry in Water Treatment

Bromine chemistry offers significant performance advantages over chlorine in the disinfection of water. Summarizing these benefits:

1. Bromine chemistry is more effective than chlorine at pH's above 7.5.
2. Bromine chemistry is much more effective than chlorine in the presence of ammonia and nitrogenous materials.
3. Bromine is a much better virucide than chlorine.
4. Toxic oxidizing residuals are much lower with bromine chemistry than with chlorine chemistry.

(7)



5. Organo bromides degrade faster in the environment than the corresponding chlorine analogs.

6. Trihalomethane (THM) formation is about the same with bromine and chlorine disinfection. However, bromoform is much more rapidly degraded to non-toxic materials in the environment than is chloroform.

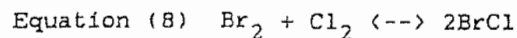
In spite of its many benefits, bromine does require some special handling considerations and procedures. Liquid, elemental bromine is very corrosive, especially when wet, and gives off a noxious, dark red vapor. It is not particularly soluble in water. Additionally, during hydrolysis, 50% of the bromine molecule forms HBr. This acid does not add to biocide performance. Fortunately, there are alternatives to using elemental bromine to obtain hypobromous acid in solution. These include:

- the use of the interhalogen species BrCl,
- the in-situ production of HOBr using a bromide salt and oxidizing agent, and
- the use of an N-Halo bromine donor compound.

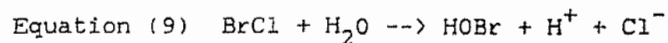
#### Bromine Chloride

Bromine chloride is an equilibrium product of an equimolar mixture of bromine and chlorine (Equation 8).

(8)



Like bromine, BrCl is handled as a liquid and must be kept at 20 psia to maintain a liquid physical state at ambient temperature. Bromine chloride is considerably more soluble in water than either bromine or chlorine and is less corrosive than bromine. The unique property of bromine chloride is that it hydrolyzes to form hypobromous acid and hydrochloric acid exclusively (equation 9).



Because chlorine is less expensive than bromine, bromine chloride is the least expensive source of hypobromous acid available (19). Once in solution, the performance of BrCl is virtually indistinguishable from elemental bromine.

While a substantial amount of work has been completed confirming the desirable bromine performance characteristics of BrCl, full scale testing has been punctuated with feeding equipment problems (7,9). Recently announced design improvements by one supplier suggest that a reliable feed system will soon be available (20). In contrast to conventional methods, this system will feed bromine chloride as a liquid rather than a gas.

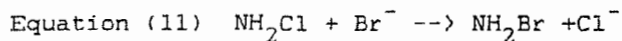
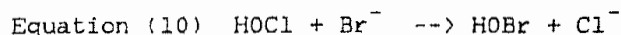
Bromine chloride should be considered for disinfection

(9)

of once-through cooling water and wastewater effluent. The excellent disinfection properties and rapid decay of oxidant residuals will reduce toxic effects seen with chlorinated effluents.

#### Bromide Salts

The use of bromide salts to enhance the disinfection of chlorine and other oxidants was begun in the early 50's. Hypochlorous acid will oxidize bromide ion to hypobromous acid (Equation 10). Similarly, chloramines will react with bromide ion to form bromamines (Equation 11). The reaction of hypochlorous acid with bromide is much faster than that between chloramine and bromide.



Like bromine chloride, bromide additions have been tested in both cooling water (17,18) and waste water applications. In both cases, the bromide ion is mixed with the oxidant immediately before injection into the water to be treated. The molar ratio of bromide to chlorine can drastically affect the amount of improvement afforded by bromide addition. Work done by Alleman and Gendron at Purdue University illustrates the effect of bromide on disinfection in the presence of nitrogen compounds

(10)

(Figure III). This laboratory data is further born out by a full scale trial at Tillsonburg, Ontario. The addition of sodium bromide, plus chlorine reduced bacterial populations greater than 99% (including a 50% reduction in a chlorine resistant Clostridium sp.) while reducing the total residual halogen by 90%. Bromine chemistry should play a key role in the use of treated sewage for cooling water make-up.

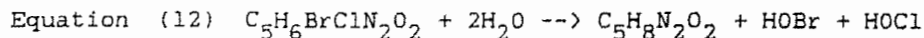
The use of bromide ion in a recirculating tower system offers further economy of scale. Bromide ion only needs to be fed at a level needed to maintain an effective concentration. This is usually 1/2 to 1/5 the amount that would be fed on a once-through system. The cycling-up of bromide ion greatly reduces the amount of bromide required on a daily basis.

A bromide salt addition system can easily be retrofitted to most chlorinated systems that use gaseous  $Cl_2$  or sodium hypochlorite. The system requires the addition of a storage tank and a metering pump. The simplicity of the system makes bromide addition an excellent solution to meeting halogen discharge requirements for most chlorinated systems.

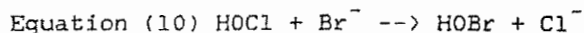
#### Bromochlorodimethylhydantoin

Bromochlorodimethylhydantoin (BCDMH) was first introduced to the CTI in January 1980 (12, 13) under the trademark BromiCide® (Figure IV). BCDMH is an N-Halo compound which

hydrolyzes in water to release hypobromous acid and hypochlorous acid (Equation 12).



If bromide ion is present in solution, hypochlorous acid will react quickly to form hypobromous acid (see Equation 10).



Because of the prevalence of bromide ion in most use situations, the disinfection chemistry of BCDMH is that of bromine. BCDMH offers several advantages over bromine in the areas of safety, convenience, and application technologies.

BCDMH is a solid, usually in stick, tablet or coarse granular form. The compound is only slightly soluble (1500 ppm) and therefore can be effectively fed in a sidestream feeder. Both shock dosage or continuous feeding of the material has been effective in controlling the biological growth in cooling water systems (12,13,14). Because the feed device or brominator is a simple plastic tank with a flow indicator, capital and maintenance costs for the feed system are quite low. BCDMH is a specialty chemical, and it is thus more expensive than gaseous chlorine or sodium hypochlorite on a cost per pound of halogen basis. However, on a use-cost basis, BCDMH compares much better, because of improved pH control and higher activity at pH's above

(12)

7.6. Compared to bleach, BCDMH is a stable, concentrated product form which is both safe to handle and easy to use. The simplicity of the system can reduce operator attention and improve control. BCDMH has been proven effective in systems where little, if any, residual can be measured using field methods. BCDMH has also shown greater compatibility than chlorine with tolyltriazole (26).

BCDMH is best used in systems where the performance of an oxidizing biocide can be coupled with the need for increased safety and reliability. BCDMH is especially cost-effective versus non-oxidizing biocides. Often, replacing one non-oxidizing biocide in an alternating, non-oxidizing biocide program can greatly enhance a system's biological control without increasing the cost. BCDMH's low toxicity (16) and ease in handling make it an attractive product for many systems. For these reasons, BCDMH use has spread rapidly especially among small to medium tower markets.

#### Summary

Bromine Chemistry offers many unique properties for enhancing a water management program. Regardless of the method used to generate a residual, hypobromous acid delivers faster kill rates than an equimolar concentration of hypochlorous acid at an elevated pH or in the presence of ammonia or nitrogenous materials. In addition, the faster degradation of most bromine

compounds relative to their chlorinated analogs increases the environmental acceptability of most brominated effluents relative to chlorination.

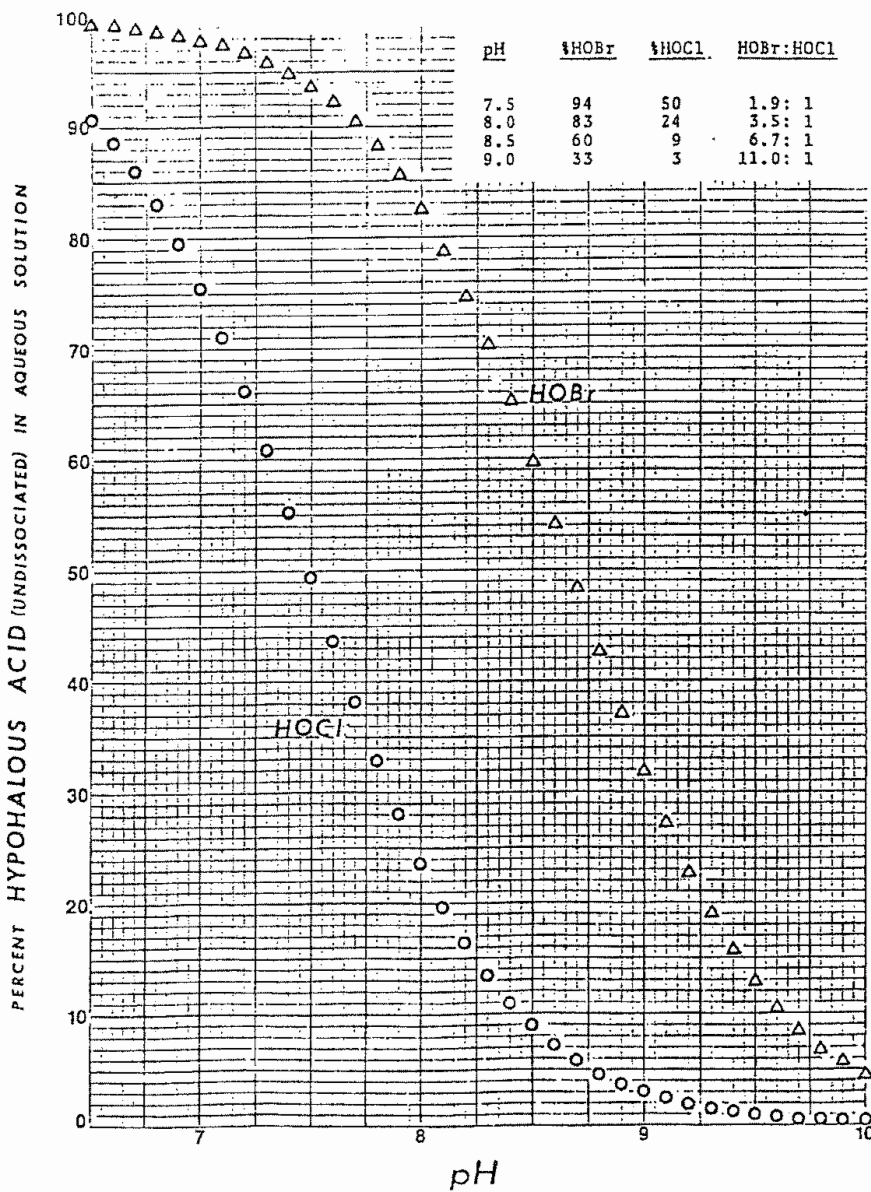
Based on these advantages, the application of bromine chemistry to water treatment requirements has moved out of the speculative research phase and has moved into the sphere of a practical, commercial reality.

1. Beckwith, T. D. and Moser, J. R.; "Germicidal Effectiveness of Chlorine, Bromine, and Iodine", Journal of the American Water Works Association, 25:367-374 (1933).
2. Tanner, F.W. and Pitner, G.; "Germicidal Action of Bromine", Proc. Soc. Exp. & Biol. Med. 4C (1939)
3. Jolles, Z.E. ed. Bromine and its Compounds, Academic Press, New York, 1966
4. Chemical Marketing Report, July 22, 1985: 53-54
5. Johannesson, J. K., "Anomalous Bactericidal Action of Bromamine", Nature 181:1799-1800 (1958)
6. Mills, J. F., "Interhalogens and Halogen Mixtures as Disinfectants" in Disinfection Water and Wastewater ed by Johnson, J. D., Ann Arbor Science Publishers (1975)
7. Bongers, L.H. and O'Connor, T.P., "Bromine Chloride - An Alternative to Chlorine for Fouling Control in Condenser Cooling Systems", EPA - 600/7-77-053 (May 1977)
8. Liden, L. H. et.al., "Effects of Chlorobrominated and Chlorinated Cooling Waters on Estuarine Organisms", Journal WPCF, 52,1:173-182 (1980)
9. Ward, R. W. et.al., "Disinfection Efficiency and Residual Toxicity of Several Wastewater Disinfectants Volume II - Wyoming, Michigan," EPA-600-77-203 (1977)
10. Groninger, G. D. and Mills, J. F., "Disinfection of Wastewater Plant Effluents Using Bromine Chloride Versus Chlorine and its Environmental Impact" in Water Chlorination Environmental Impact and Health Effects Vol. 3, 733-740 ed. by Jolley et.al., Ann Arbor Science (1980)
11. Bouwer, E. J. et.al., "Anaerobic Degradation of Halogenated 1- and 2- Carbon Organic Compounds", Environ. Sci. & Tech, 15(5):596-599 (1981)
12. BromiCide® A Biocide for cooling water systems Macchiarolo, Johnson, and Hornack, Cooling Tower Institute TP.219A January (1980) Houston, TX
13. Matson and Characklis, "Biofouling Control in Recycled Cooling Water with Bromochlorodimethylhydantoin", Cooling Tower Institute, TP 250A, February, 1982
14. Kozelski and Colturi, "Corrosion and Biofouling in a Cooling Tower System with Demineralized Water Make-up", Corrosion 83 paper #280, National Association of Corrosion Engineers, April 1983, Anaheim, California



15. Ellis, J. G., Dvorkovitz, V., "Stable Solid Disinfectant Compositions", United State Patent #2,815,311, dated December 3, 1957.
16. Wilde, E. W. et.al., "Acute Toxicity of Chlorine and Bromine to Fathead Minnows and Bluegills", Bull Environ., Contam. Toxicology 31:309-314 (1983).
17. Hester, Pierson and Klen, "Effective Chlorine Minimization on a High Chlorine Demand Water Sources", EPRI Condenser Biofouling Control Symposium State-of-the-Art 6-1985, Lake Buena Vista, Florida.
18. Lucas, J. A., "A Chlorine Reduction Program", EPRI Condenser Biofouling Control Symposium: the State-of-the-Art, 6/8/85, Lake Buena Vista, Florida.
19. Chiesa, R. and Geary, D., "Cost Comparison of Alternate Biocides for Condenser Biofouling Control", EPRI Condenser Biofouling Control Symposium: the State-of-the-Art, 6/85, Lake Buena Vista, Florida.
20. Slifer, G. and Royer, C., "Feeding Bromine Chloride: A New Concept", EPRI Condenser Biofouling Control Symposium: the State-of-the-Art, 6/85, Lake Buena Vista, Florida.
21. Greene, D., "Wastewater Disinfection with Bromine Chloride", The Chesapeake Water Pollution Control Association and the Water and Waste Operators Association of Maryland, Delaware and District of Columbia - Joint Meeting, Ocean City, Maryland, June 1979.
22. Johnson, J. D. and Overby, R., "Bromine and Bromamine Disinfection Chemistry", Journal of the Sanitary Engineering Division Proceedings of the American Society of Civil Engineers, October 1971.
23. Moore, E. W., "Fundamentals of Chlorination of Sewage and Waste", Water and Sewage Works Vol. 98:150-160 (1951)
24. Latimer, "The Oxidation States of the Elements and Their Potentials in Aqueous Solution", Prentice-Hall, Inc., New York, 1952
25. Wyss and Stoctom, "The Germicidal Action of Bromine", Arch. Biochem. Vol. 12:267-271, (1947)
26. Personal correspondence with Dr. Dan P. VanderPool, Mobay Chemical Corporation.

FIGURE I



(17)

FIGURE II  
RELATIVE DECAY RATIOS:

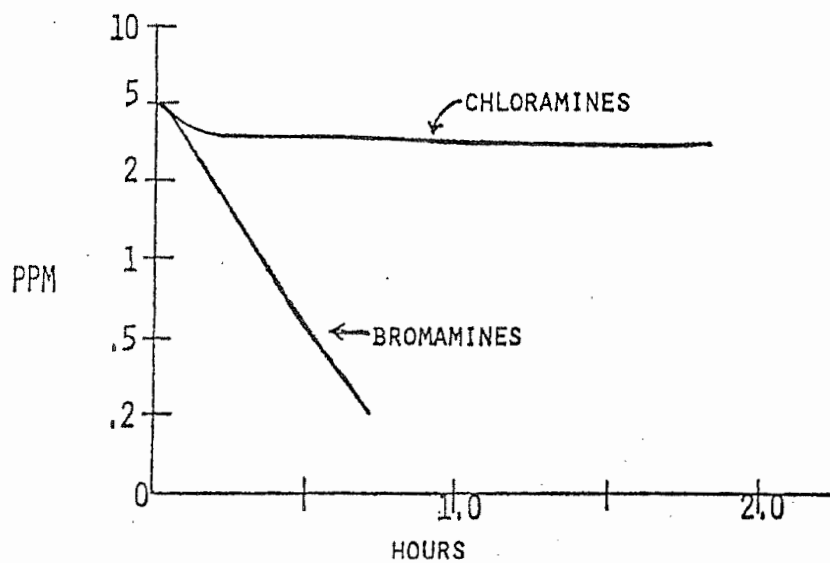
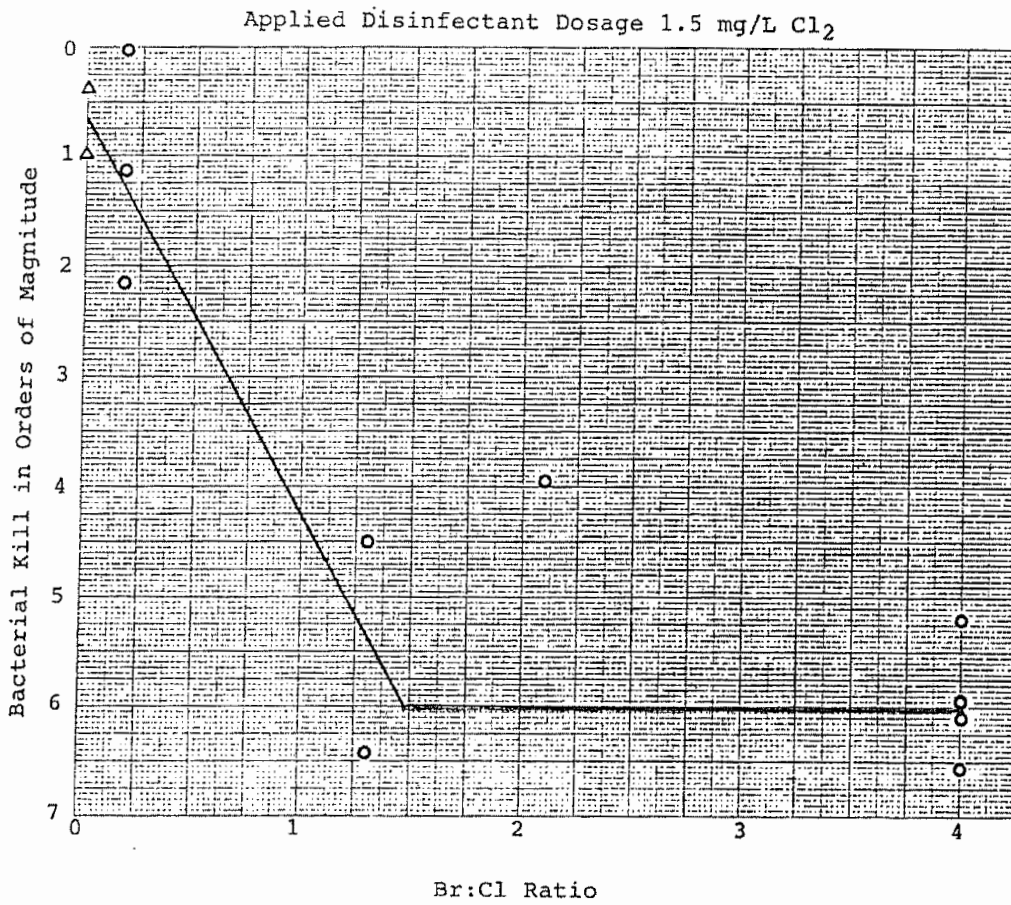
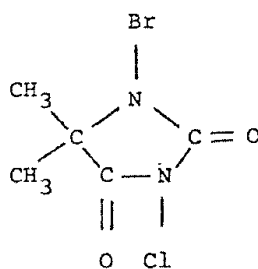


FIGURE III  
Effect of NaBr on Disinfection of 2° Wastewater



△ = chlorine only  
 ○ = bromine and chlorine

FIGURE IV



1-BROMO-3-CHLORO-5,5-DIMETHYLHYDANTOIN