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## **25 YEARS OF BROMINE CHEMISTRY IN INDUSTRIAL WATER SYSTEMS: A REVIEW**

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### **ABSTRACT**

Bromine chemistry is used to great advantage in nature for fouling control by a number of sessile marine organisms such as sponges, seaweeds, and bryozoans. Such organisms produce small quantities of brominated organic compounds that effectively help keep their surfaces clean of problem bacteria, fungi, and algae. For over two decades, bromine chemistry has been used to similar advantage in the treatment of industrial water systems. The past several years in particular has seen the development of several diverse bromine product forms – one-drum stabilized bromine liquids, all-bromine hydantoin solids, and pumpable gels. The purpose of this paper is to review the development of bromine chemistry in industrial water treatment, discuss characteristics of the new product forms, and speculate on future developments.

**Keywords:** Oxidizing biocide, bleach, bromine, bromine chemistry, sodium hypobromite, activated sodium bromide, Bromochlorodimethylhydantoin, Bromochloromethylethylhydantoin, Dibromodimethylhydantoin,, BCDMH, BCMEH, DBDMH, stabilized bromine chloride, stabilized hypobromite

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## INTRODUCTION

Sessile marine organisms generate metabolites to ward off predators and deter attachment of potential micro- and macrofoulers. Sponges, algae, and bryozoans for example, produce a rich variety of bromine-containing compounds that exhibit antifouling properties (Fig. 1).<sup>1,2,3</sup> Scientists are actively studying these organisms to understand how they maintain surfaces that are relatively clean and slime-free.<sup>4</sup> Brominated furanones isolated from the red algae *Delisea pulchra*, for example, have been found to interfere with the chemical signals (acylated homoserine lactones) that bacteria use to communicate with one another to produce biofilms.<sup>5,6</sup> This work may eventually lead to more effective control of microorganisms in a number of industries such as industrial water treatment, oil and gas production, health care, etc. The control of microbiological fouling and the maintenance of clean heat transfer surfaces are, of course, very important in industrial water treatment.

In light of this modern-day research activity, it is interesting to note that a marine organism played a prominent role in the discovery of bromine itself. The French chemist Antoine-Jérôme Balard treated the brown seaweed *Fucus* with chlorine water and starch and isolated elemental bromine via distillation.<sup>7</sup> He published his results in 1826.<sup>8</sup> The original sample of bromine still exists today and is on display at the Royal College of Science, Imperial College (London, UK).<sup>9</sup>

Elemental bromine does not occur naturally but its bromide salt precursors are distributed in trace quantities throughout the earth. Seawater, for example, has a bromide content of 65 ppm. Note that this is much less than the chloride content of seawater at 2%. Although bromine can (and still is) produced from seawater, certain bodies of water and underground formations contain much higher concentrations of bromide and serve as the major source for the bromine and bromine-based products manufactured today (Fig. 2).<sup>10</sup> The Smackover formation in the south central US (Arkansas) has a bromide content about 70 times that of seawater (4000 – 4600 ppm). Other sources of bromide include deep wells in the Great Lakes region of the US and the Dead Sea in the Middle East. The Dead Sea is a particularly rich source with concentrations ranging from 5000 – 6500 ppm.<sup>11</sup> In the 1950s bromine production commenced in both Arkansas (US) and Israel to take advantage of these abundant sources of bromide.

The production of bromine requires oxidation of the bromide-containing brine. This can be accomplished by a number of methods. Commercial quantities of bromine were first produced in the US in 1846 and in Germany in 1865 using a combination of manganese dioxide and sulfuric acid. In 1890, Herbert M. Dow built a small plant in Canton, OH that produced bromine by an electrolytic process. Today, however, the only oxidant of any commercial importance is chlorine gas.<sup>12</sup> According to the Arkansas Geological commission, US bromine production in 2001 was 212,000 metric tons with Arkansas' output accounting for 97% of US production and about 40% of that worldwide.<sup>13</sup>

Although bromine was discovered almost two hundred years ago, it is only within the last 25 years that bromine-based biocide technologies have achieved commercial use in industrial water systems. Elemental bromine itself has not been employed commercially to any significant extent for control of microorganisms, apparently due to handling issues (it is a corrosive, fuming liquid). The non-use of the elemental form has not posed a detriment to innovation but rather has led to the development of a wide variety of innovative bromine-based delivery chemistries.

Today the water treatment community has many bromine-based biocide technologies to choose from – liquid two-component systems such as activated sodium bromide (effectively, *in-situ* generation of bromine), solid hydantoin-based technologies, and single-feed, liquid products such as stabilized hypobromite and stabilized bromine chloride. Still more recent innovations include all-bromine hydantoin solids, and pumpable gels. The purpose of this paper is to highlight some of the significant developments that gave rise to this family of oxidizing biocide products. A few years ago, Bartholomew

reviewed the use of bromine chemistry in cooling water systems and the present paper should be considered as a complement to this work.<sup>14</sup>

## DISCUSSION

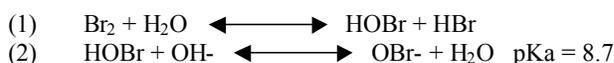
### Bromine Chemistry in Water Treatment – Early Studies and Fundamental Principles

Bromine is more expensive than chlorine and therefore its use in water treatment must necessarily be based upon microbiological performance, cost-effectiveness, and other attributes. Let's consider some of the performance attributes of elemental bromine and – by extension – other bromine technologies as well.

Although elemental bromine itself finds little application in water treatment, its use was suggested as far back as 70 years ago. In 1935, Henderson patented a process for treating water with bromine "...to destroy any pathogenic organisms that may be present."<sup>15</sup> Henderson's data showed that the performance of just 0.25-0.5 ppm bromine in a *Bacillus coli*-contaminated water was equivalent to 1.5 – 2.0 ppm chlorine. Henderson went on to say "In the amounts of bromine I use [ $<5$  ppm], the elemental bromine will all disappear from the water because of the action of the organic matter present and there is no necessity for...an after treatment of any kind." Concepts contained in the patent - improved effectiveness and rapid residual decay – still contribute to use of bromine chemistry today.

Subsequent laboratory studies of bromine confirmed a broad range of activity over many types of microorganisms. Reports of its ability to deactivate *Escherichia coli*, sterilize water, and kill spore-forming bacteria, yeasts and molds appeared in the 1930s and 40s.<sup>16-21</sup>

The addition of bromine to water generates hypobromous acid and hydrobromic acid (Eq 1). Depending on the pH, hypobromous acid can further convert to hypobromite (Eq 2). In 1938, Shilov and Gladchikova correctly measured a pKa value of 8.7 for the hypobromous acid – hypobromite conversion.<sup>21</sup>



A few years earlier, Ingham and Morrison accurately determined the pKa for the analogous chlorine system as 7.5 (Eqs. 3 and 4).<sup>22</sup>



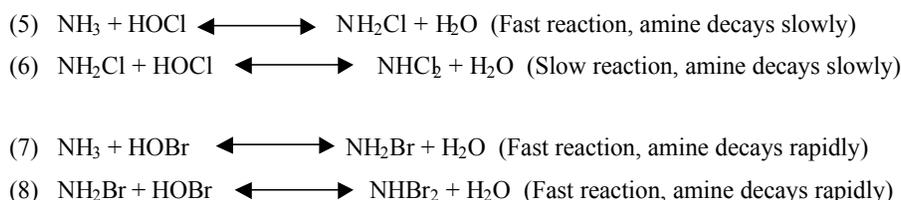
The relative amounts of the two hypohalous acids thus vary with system pH. Above pH 7.5, the relative concentration of HOCl declines rapidly while this decline does not occur until above pH 8.7 with HOBr (Fig. 3). Fair, et al. back in 1948 attributed the microbiological activity of chlorine solutions to HOCl where "its small molecular size and electrical neutrality...allow it to readily pass through the cell membrane."<sup>23</sup> Increased amounts of electroneutral HOBr at high pH would eventually contribute to the use of bromine chemistry for biocidal control in modern alkaline treatment programs.

The impact of pH on the effectiveness of chlorine had actually been known for many years. Workers as far back as 1921 noted that high pH decreased the microbiological activity of hypochlorite.<sup>24,25</sup> A striking example of this is the work by Rudolph, et al. on spores of *Bacillus metiens*.<sup>26</sup> Times to produce a 99% kill with 25 ppm available chlorine varied from 2.5 minutes at pH 6 to 131 minutes at pH 10 (Fig. 4). Note in particular the dramatic change in performance from pH 8 to pH 9, a pH range at which a majority of the water treatment programs run at today. The authors concluded that the rate of kill of chlorine was directly related to the concentration of HOCl which decreases rapidly at high pH. Many other studies over the years have pointed to a reduction in performance with chlorine at elevated pH levels.<sup>27</sup>

Other workers would discover that the addition of bromide improved the activity of chlorine-containing solutions.<sup>28</sup> Kristofferson, for example, showed that bromide added to sodium hypochlorite solutions boosted efficacy up to 1000 fold at pH 11 against a wide range of bacteria.<sup>29</sup> This was an indication that *in situ* generation of hypobromous acid could be effective in the alkaline systems used in modern industrial water treatment [see *Activated Sodium Bromide*].

Additional studies pointed to improved performance of chlorine and bromine mixtures in the presence of ammonia and other nitrogenous-containing materials.<sup>30-32</sup> The chemistry of chlorine and bromine differ significantly in the presence of excess ammonia. Chlorine forms predominately monochloramine which is a relatively ineffective biocide – some 50 to 100 times less active than free chlorine itself.<sup>33</sup> Bromine, in contrast, produces a mixture of bromamines in rapid equilibrium (mainly mono- and dibromamine at pH 7 to 9) which are relatively effective biocides. Dibromamine, for example, is said to have the same activity as hypobromous acid itself.<sup>34</sup> At pH 8.2 and a mole ratio of NH<sub>3</sub> to Br<sub>2</sub> of 10 (i.e., 1.1 ppm NH<sub>3</sub> to 1.0 ppm Br<sub>2</sub>) the mixture consists of a 50:50 mixture of mono- and dibromamine.<sup>35</sup> Johannesson demonstrated the improved microbiological effectiveness of bromamines vs. chloramines against an *E. coli* wild strain at pH 8.2 (Fig. 5).<sup>36</sup>

Another feature of bromamines is that they typically decay faster in the environment than chloramines.<sup>35</sup> The following equations summarize the chemistry of the haloamines as formed from chlorine or bromine in excess ammonia.



#### Early Applications of Elemental Bromine

The late 1930s saw a limited deployment of bromine in water systems. For example, the use of bromine for treatment of swimming pools and other recreational purposes was reported in the late 1930s.<sup>37,38</sup> A review of some of the aspects of bromine chemistry in swimming pools appeared in 1960.<sup>34</sup>

In 1948, Albright reported one of the first industrial applications of bromine chemistry in a cooling tower.<sup>39</sup> Use of liquid bromine removed “A troublesome and obstinate growth of algae which had infested the 10,000 gpm cooling tower...” Liquid bromine applied at 10 lbs. per day (slug fed to 2 ppm residual over a 15 minute period) replaced 30 lbs. of chlorine gas with apparently better

performance. Kott later showed that application of bromine applied to a large lake-fed water system (1.4 ppm residual for 9 hours) provided effective control of various forms of algae such as *Chroococcus*, *Chlorella*, and *Cosmarium*.<sup>40</sup> The latter species in particular was noted to be resistant to normal applications of chlorine. Kott went on to write, “Bactericidal action of bromine is very well known; however it is thought that bromine has not previously been used on such a large scale.” This field study confirmed previous lab work showing the relative effectiveness of bromine towards various types of algae.<sup>41,42</sup> Still by the late 1960s, applications of bromine chemistry in industrial water treatment were virtually non-existent.

#### The Growth of Bromine Chemistry in Water Treatment

Chlorine and chlorine-based chemistries proved to be effective microbiological control agents in the early days of industrial water treatment. However, in the 1960s and early 1970s several events would place greater demands on industrial water treatment programs and spawn the search for more effective biocide programs. These events included a new environmental awareness that led to the phase-out of chromate-based corrosion programs, the institution of water reuse practices, and the development of energy conservation measures. Technical advances such as better techniques for monitoring oxidant residuals and the introduction of cost effective bromine delivery systems such as bromine chloride, and bromochlorodimethylhydantoin helped bromine chemistry make a lasting impact on water treatment practices.

Environmental concerns caused the shift from acid feed with chromate to acid feed with chromate/zinc and finally to alkaline-based water treatment programs.<sup>43</sup> These alkaline based programs relied upon polyphosphates and, later, phosphonates and copolymers for corrosion and scale control.<sup>44</sup> Soon it was realized that the chlorine-based technologies often didn’t work as well in the new higher-pH environment that was now typically more like 8 and vs. the 6.0 – 7.0 employed with chromate-based programs. From the previous discussion, it is not surprising that problems developed with chlorine application under the new, higher pH conditions. The added phosphate and polymer nutrient loads did not help the situation and contributed to algae problems as well.

Environmental concerns created another issue with chlorine chemistry – persistent residuals. In many systems the residuals resulting from chlorination would tend to linger longer than desired. This made it difficult to discharge according to regulations without further treatment operations. The culprit here was combined chlorine, specifically chloramine. In 1973, Brungs recommended a residual discharge level of 0.002 mg/L or less “...because of the lethality of higher concentrations to trout, salmon and sensitive life stages of other fish.”<sup>45</sup> The development of the DPD test into a field-friendly technique made it particularly convenient to track chloramines and other combined forms of chlorine.<sup>46</sup> Investigations into the aqueous chemistry of bromine showed that combined forms of bromine such as bromamines were still effective biocidal agents and not as persistent.<sup>35,47</sup>

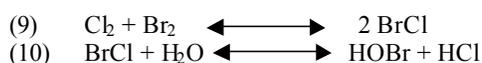
Increased energy costs and water reuse measures also spurred the search for newer, more cost effective technologies. It was realized that if system surfaces could be maintained under cleaner conditions energy savings could outweigh the increased costs of biocidal treatment. High performance film fill designs to maximize cooling tower efficiency placed further demands on industrial water treatment practices.<sup>48</sup> These events led to much research development on alternate disinfectants for once-through marine water, wastewater, and other aqueous systems. Field studies of bromine chemistry commenced in earnest.

As indicated above, there has been little interest in elemental bromine itself as an industrial biocide. This may be due to the fact that early on researchers recognized that bromine was significantly

more expensive than chlorine – at least 2 ½ times as much - and so sought ways to develop less expensive bromine-delivery systems. One such system was bromine chloride.

#### Bromine Chloride

Bromine chloride can be easily prepared by mixing chlorine and bromine in equimolar amounts according to equation 9. It was confirmed as a discrete compound in 1929 by comparing absorption spectra in carbon tetrachloride.<sup>49,50</sup> The addition of bromine chloride to water generates hypobromous acid and HCl (Eq. 10).<sup>51</sup> Bromine chloride is thus an economical way of introducing bromine chemistry into water since none of the bromine value is initially wasted due to conversion to the inactive bromide form.



In 1953, J. Kamlet patented the use of bromine chloride in a process to treat and disinfect water and disclosed data indicating good activity against *B. coli* compared to chlorine and bromine.<sup>32</sup> By the early 1970s, commercial quantities of bromine chloride became available and it was promoted as a biocide for both industrial water and wastewater.<sup>52</sup> In 1973, Wackenhuth performed a field study of bromine chloride for biofouling control in a utility condenser system.<sup>53</sup> His stated purpose was to identify a "...method for keeping circulating water systems free of biological fouling with minimum chemical consumption costs, and yet having a discharge which would be acceptable to regulatory agencies." The field data in side-by-side tests showed that both bromine chloride and chlorine provided acceptable biofouling control when dosed to 0.5 ppm free residual. However, both free and total halogen residuals at the outfall were desirably lower with bromine chloride (Table 1).

TABLE 1  
HALOGEN RESIDUALS AT UTILITY CONDENSER OUTLET AND OUTFALL SAMPLE POINTS

	BrCl	Cl <sub>2</sub>
Condenser		
Mean Free Residual, mg/L	0.49	0.49
Mean Total Residual, mg/L	0.70	0.97
Outfall		
Mean Free Residual, mg/L	0.01	0.08
Mean Total Residual, mg/L	0.09	0.25

In 1977, bromine chloride was extensively evaluated as an alternative to chlorine for fouling control in a once-through utility condenser employing a low salinity (7 ppt) estuarine water.<sup>54</sup> The EPA-sponsored report concluded that "...bromine chloride is an effective fouling control agent when applied on a continuous basis at a level of 0.5 ppm or less." The report went on to say, "Examination of the decay characteristics of bromine chloride and chlorine confirmed earlier reports that bromine-chloride-induced oxidants dissipate faster from estuarine water than do chlorine-induced oxidants."

In work related to control of enteric bacteria and viruses, Keswick performed extensive laboratory studies of the effectiveness of bromine chloride and chlorine against poliovirus and confirmed some of the performance characteristics of bromine chemistry.<sup>55</sup> This work showed that lower relative levels of bromine chloride compared to chlorine were needed for complete virus deactivation (log reduction >4, Fig. 6). This work further demonstrated that bromine chloride dosed to 0.15 mg/L was effective over a wide pH range (6-10, Fig. 7) and was more effective than chlorine in the

presence of glycine, a simple amino acid that may be considered representative of organic amine contamination in cooling systems (Fig. 8).

Additional reports of the use of bromine chloride for biofouling control were published in the 1980s.<sup>56,57</sup> After this initial level of activity, interest in use of bromine chloride declined no doubt due to handling issues related to its corrosive and acidic nature. A solution of bromine chloride in water was patented in 1993 and a field study of its use appeared several years later.<sup>58,59</sup> This solution was corrosive and required special handling procedures. In the late 1990s interest in bromine chloride would be renewed with the introduction of a stabilized form of the material with desirable handling properties [see *Stabilized Bromine Chloride and Stabilized Hypobromite*].

#### Bromochlorodimethylhydantoin.

Hydantoin molecules have been used industrially for a number of years. Dichlorodimethylhydantoin (DCDMH), for example, was employed as a bleaching agent for industrial laundries back in the 1930s.<sup>60</sup> In 1957, Paterson obtained composition of matter patent covering the brominated hydantoin of current use in water treatment.<sup>61</sup> The patent discloses preparations of both bromochlorodimethylhydantoin (BCDMH) as well as bromochloromethylethylhydantoin (BCMEH). In 1968, Paterson obtained additional patent coverage for the use of such N-halogenated compounds as a cohesive mass or agglomerate as a method of treating and disinfecting water.<sup>62</sup> The initial process used to manufacture the solid agglomerates appears somewhat primitive today – a product slurry was extruded onto a continuous tray dryer, chopped into 3” sticks, and dried using a bakery oven. A major bromine chemical supplier would eventually write a multimillion-dollar check to Paterson for the rights to the technology in 1978. The check remained in a sweater pocket for several months before she was gently reminded to cash the check in order to consummate the deal.<sup>63</sup>

One of the first applications of BCDMH to an industrial cooling system occurred in the late 1970s in a chemical plant located in El Dorado, AR.<sup>64</sup> In the 1980s, several patents issued relating to the use of BCDMH in cooling systems.<sup>65,66</sup>

Zhang did a thorough study of the disinfection effectiveness of BCDMH.<sup>67</sup> His data showed that BCDMH was more effective than chlorine at pH 8.5 when dosed to the same residual against all organisms tested – *E. coli*, *E. aerogenes*, *P. aeruginosa*, and polybacteria. Results of one study are shown in Fig. 9. Zhang also showed that BCDMH and other bromine biocides were effective in the presence of ammonia (Fig. 10). Many studies have subsequently demonstrated that the effectiveness of BCDMH in the laboratory carries over to the field.

Peterson found that a combination of BCDMH and glutaraldehyde provided effective microbiological control of an air washer system in a nylon fiber plant.<sup>68</sup> The previous biocide of tin-quat-diamine led to excessive slime build up. A petrochemical plant with 90/10 copper/nickel alloy heat exchangers converted from gaseous chlorine to BCDMH.<sup>69</sup> The conversion resulted in lower overall biocide usage, consistent pH control, lower consumption of corrosion inhibitor (tolyltriazole), and overall lower corrosion rates on copper alloy (Table 2).

A one-year field study in a refinery cooling system indicated that BCDMH use led to similar results with better control of both sessile and bulk water bacteria counts and lower corrosion rates on yellow metal compared to gaseous chlorine.<sup>70</sup>

TABLE 2  
COMPARISON OF CHLORINE AND BCDMH IN A PETROCHEMICAL PLANT

	Chlorine Gas	BCDMH
pH Range	5.5-7.0	7.0-7.5
Tolyltriazole Feed, relative	1	0.5
Corrosion rate, mpy	0.35	0.05
Biocide Usage, Kg/ day	182	34
Microbiological Counts, CFU/L	0-300	200-350

Smith, et al published case studies in 1993 comparing the performance of BCDMH to chlorine gas in utility recirculating cooling systems.<sup>71</sup> In one system, BCDMH dosed to 0.04 ppm free residual (20' feed time, once per day) provided improved microbiological control compared to the chlorine treatment regime (0.5 ppm free residual for 30 minutes per day). Bulk bacteria counts ranged from  $10^5$  –  $10^7$  CFU/mL under the chlorine/ non-oxidizing biocide program compared with  $<10^3$  CFU/mL under the BCDMH program. In addition, corrosion rates on 90/10 copper/nickel alloy decreased from 0.8 mpy (chlorine) to 0.1-0.4 mpy (BCDMH).

Field studies demonstrating the successful use of BCDMH in other industrial applications such as brewery pasteurizers and the similar molecule, BCMEH, in pulp and paper began appearing by the early 1990s and continue to the present day.<sup>72-74</sup> Benefits cited in brewery pasteurizers include less corrosion, better odor control, improved pasteurizer efficiency while those in pulp and paper include enhanced slime control, improved cost performance, and low environmental impact.

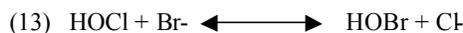
Zhang studied the hydrolysis chemistry of BCDMH and showed that it could be described as a facile release of HOBr followed by a slow release of HOCl according to equations 11 and 12.<sup>67</sup>



Indeed, analysis of BCDMH in demand free waters by the free and total DPD methods indicate that about half of the oxidant value analyzes as free halogen (i.e., free HOBr) with the other half analyzing as combined halogen (i.e., combined chlorine as HCDMH).<sup>75</sup> Excess bromide ion and warm water temperatures apparently aid the hydrolysis of the chlorine atom with generation of hypobromous acid via reaction 13 (next section). For example, it is common practice to preload a hot tub or spa on a BCDMH disinfection program with sodium bromide.<sup>76</sup> This discussion indicates that under certain biocide application regimens, i.e., shock dosing with short biocide residence time, both of the halogens on BCDMH may not be fully utilized for microbiological control purposes.<sup>14</sup>

#### Activated Sodium Bromide

Workers back in 1909 found that hypobromous acid could be generated from an equimolar combination of sodium bromide and chlorine according to equation 13.<sup>77,78</sup>



The reaction depends upon the concentration of HOCl in solution and thus the rate decreases at higher pH.<sup>79</sup> Due to the instability of hypobromite, the solution must be used immediately.

Houghton found that the effectiveness of small doses of chlorine in waters containing ammonia could be enhanced by addition of small amounts of bromide (Table 3).<sup>30</sup> Similar results were obtained in the absence of ammonia.

TABLE 3  
EFFECT OF BROMIDE ON ERADICATION OF *BACT. COLI* WITH 0.05 PPM CHLORINE  
(PH 7.6–8.0; 7–16 °C)

NH <sub>3</sub> , ppm	Br <sup>-</sup> , ppm	Bacteria, CFU		
		Initial	10 Minutes	30 Minutes
0.17	0	2200	570	203
	1.0		43	0
0.30	0	6800	2400	406
	2.0		20	3
0.33	0	3200	1750	496
	0.5		828	0
0.60	0	1530	1130	105
	1.0		870	1

Note: Studies performed using distilled water, contains 300 ppm NaHCO<sub>3</sub> (equivalent to about 150 ppm alkalinity as CaCO<sub>3</sub>).

In the 1970s, it was realized that one could introduce sodium bromide and chlorine into a water system and thus generate bromine species *in situ*.<sup>52</sup> Proper mixing of bromide and oxidant is essential, however, particularly in the presence of ammonia and other sources of contamination (Table 4).<sup>80</sup> Note that method C, in which hypochlorite and bromide is prereacted before addition to the ammonia-containing solution, provided the most activity against *E. coli*.

Reports of the use of activated sodium bromide in industrial cooling systems began to appear in the 1980s. A comparison of activated sodium bromide to chlorine gas was performed in a large utility cooling system (50,000 gpm) using river water make up.<sup>81</sup> Activated sodium bromide provided equivalent condenser biofouling control while reducing total oxidant discharge by over 60%.

Several patents later appeared citing improved control of macrofoulants such as Asiatic Clams, barnacles, and slimes using activated sodium bromide in combination with a nonionic surfactant.<sup>82,83</sup> The technology was also extended to control of Zebra Mussels.<sup>84</sup>

TABLE 4  
MIXTURES OF HYPOCHLORITE AND BROMIDE IN THE PRESENCE OF AMMONIA:  
EFFECT OF METHOD OF PREPARATION ON ACTIVITY

Contact Time	[NH <sub>3</sub> -N] = [Cl <sub>2</sub> ] = 1.0 mg/L		[NH <sub>3</sub> -N] = [Cl <sub>2</sub> ] = 2.0 mg/L	
	1 minute	5 minutes	1 minute	5 minutes
Method A	2	63	12	88
Method B, run 1	56	90	71	98
Method B, run 2	85	98	94	99
Method C	>99.99	>99.99	>99.99	>99.99

Notes: Test organism is *E. coli*; CFU/mL = 7.5 – 8.8 x 10<sup>6</sup>; pH = 7.0; temperature = 21 °C  
 Method A: mix hypochlorite and ammonia first; then add bromide  
 Method B: mix bromide and ammonia first; then add chlorine  
 Method C: mix hypochlorite and bromide first; then add to ammonia-containing solution

Moore et al. replaced a combination of chlorine gas and non-oxidizing biocide with activated sodium bromide in 8 chemical plant cooling towers.<sup>85</sup> The activated sodium bromide program provided effective biocontrol at low continuous residuals of 0.1 ppm (Table 5) and led to overall reductions mild steel corrosion in 5 of the 8 towers in the study. In addition, the cooling tower discharge proved compatible with artificial marsh post-treatment, significantly reducing the amount of water disposed of using injection wells.

TABLE 5  
COMPARISON OF CHORINE AND BROMINE IN CHEMICAL PLANT COOLING TOWER  
SYSTEMS (PH = 8.7 – 9.1)

Tower	Chlorine + Organic Biocide		Activated Sodium Bromide	
	Free Cl <sub>2</sub> , ppm	Bacteria, CFUs/mL	Free Cl <sub>2</sub> , ppm	Bacteria, CFUs/mL
A1	0.3-2.0	10 <sup>2</sup> -10 <sup>4</sup>	0.1	10 <sup>2</sup> -10 <sup>3</sup>
B1	0.2-1.5	10 <sup>3</sup> -10 <sup>4</sup>	0.1-0.2	10 <sup>1</sup> -10 <sup>3</sup>
N1	No data	10 <sup>2</sup> -10 <sup>5</sup>	0.1	10 <sup>2</sup> -10 <sup>4</sup>
N2	No data	10 <sup>3</sup> -10 <sup>4</sup>	0.1	10 <sup>3</sup>
T1	0.1-0.5	10 <sup>3</sup> -10 <sup>4</sup>	0.1	10 <sup>3</sup>
S1	0.1-3.0	10 <sup>2</sup> -10 <sup>5</sup>	0.1	10 <sup>2</sup>
S2	0.2-2.5	10 <sup>3</sup> -10 <sup>6</sup>	0.1-0.6	10 <sup>0</sup> -10 <sup>3</sup>

Nalepa, et al. compared activated sodium bromide to both high-dose and low-dose chlorine treatment regimens in an industrial cooling system operating between pH 8.2-8.4 using well water for make-up.<sup>86</sup> Activated sodium bromide, fed continuously to an average residual of 0.11 free and 0.15 total (as Cl<sub>2</sub>), provided effective microbiological control and led to a substantial decrease in general and pitting corrosion on mild steel. This was said to be due to the combination of chemical (less attack on passivated surfaces) and biological factors (better control of heterotrophic and sessile bacteria).

The reaction of chlorine compounds with bromide still remains a popular method of achieving the benefits of bromine chemistry in industrial water systems. Activated sodium bromide is often the method of choice in systems containing high levels of ammonia other nitrogen compounds such as once-

through systems, ammonia and urea (fertilizer) plants and ammonia chiller systems. Methods based on other oxidation methods such as ozone and electrolysis have also been described but have not received wide acceptance.<sup>87-89</sup>

Research continues on improvements to activated sodium bromide technology. Use of a proprietary anionic biodegreaser (linear alkylbenzenesulfonate, applied at 5 ppm) together with normal activated sodium bromide treatment gradually removed deposits on film fill surfaces (Table 6).<sup>90</sup> This treatment also restored cooling tower operating efficiency which gradually eroded under the previous biodegreaser program.

TABLE 6  
AVERAGE DEPOSIT WEIGHT CHANGES IN FIVE SECTIONS OF FILM FILL AT A  
GEOHERMAL POWER PLANT

Date	Avg. Deposit Weight, lbs.	Average Weight Loss, %
1/16/97	48.4	---
2/5/97	42.7	11.8
2/27/97	37.4	22.7

An improved biodegreaser has been developed which consists of an alkyl polyglycoside (APG) containing C<sub>8</sub> to C<sub>16</sub> alkyl groups.<sup>91</sup> The product is said to possess "...both dispersancy (dispersing aggregates) in the bulk water and detergency (removing biofilm matrix) in the solid/ liquid interphase." A field study in a coal-fired power plant indicated that daily slug doses of 20 ppm APG with activated sodium bromide (0.5 ppm free residual) provided immediate increases in levels of protein and ATP in the bulk water and dramatic improvements in cooling tower thermal efficiency relative to the activated bromide-only treatment (Fig. 11).

#### Dry Bromide/ Isocyanurate Mixtures

Dry solid bromide/ hypochlorite-releasing mixtures were patented back in 1958.<sup>92</sup> The patent contains data showing enhanced effectiveness of the bromide-containing compositions towards *M. Pyogenes* var. *aureus*. Additional patents related to combinations of isocyanurates and bromide salts as disinfectants for scouring cleansers and bleaching aids appeared in the 70s and 80s.<sup>93-96</sup>

Commercial products for water treatment were introduced about 10 years ago.<sup>97,98</sup> These products use a combination of dichloroisocyanurate or trichloroisocyanuric acid with sodium bromide to generate hypobromous acid *in situ* in the water system. The mole ratio of sodium bromide to chloroxidant is less than one. This takes advantage of bromide buildup in recirculating water systems and promotes more efficient utilization of bromine values to optimize product economics.<sup>99</sup> Field studies indicate effective microbiological control at reduced consumption rates relative to other halogen donor systems such as BCDMH and trichloroisocyanuric acid (Fig. 12, Table 7).

TABLE 7  
RELATIVE USAGE RATES FOR BROMIDE/ TRICHLOROISOCYANURIC ACID MIXTURE (7:93  
BY WT) VS. OTHER BIOCIDES IN COMFORT AND INDUSTRIAL COOLING SYSTEMS

System	Volume, kgals	Type	Feeder	pH	Comparative Biocide	Relative Use, Predicted, %	Actual Use, %
1	25	Comfort	Erosion	8.4	BCDMH	65	56
2	25	Comfort	Basket	8.5	BCDMH Trichlor	65 111	48 45
3	9	Industrial	Erosion	7.8	BCMEH	74	76
4	90	Comfort	Erosion	8.4	BCDMH	65	--
5	60	Comfort	Erosion	8.7	BCMEH	85	75
6	240	Industrial	Erosion	8.0	BCDMH	65	45
7	350	Industrial	Erosion	8.0	BCDMH	65	67

Predicted relative use was determined by taking the ratio of available halogen contents.

Technology for producing tablets of good integrity for controlled release into water systems was patented by Kuechler and Rakestraw in 1997.<sup>100</sup> Certain combinations of bromide/ chloroisocyanurate and dichlorooctylisothiazolin have been reported to exhibit synergistic properties towards slime-forming microorganisms such as *Pseudomonas aeruginosa*.<sup>101</sup>

#### Stabilized Bromine Chloride and Stabilized Hypobromite

Although bromine chemistry in its various forms has been shown to be highly effective for control of bacteria and algae in industrial water systems, methods of delivering the active biocide can be somewhat cumbersome. Elemental bromine and bromine chloride are both very corrosive and present handling challenges that limit their widespread commercial use. Activated sodium bromide is an effective method of delivering the benefits of bromine chemistry to a water system but the method requires two separate feed systems and proper metering and mixing equipment to achieve effective results. BCDMH, BCMEH, and bromide/ trichlor mixtures represent solid products that have achieved widespread acceptance in a number of application areas. However, their use in industrial water treatment often requires the use of in-line erosion feeders. The erosion feed method is not without problems as tablets and granules can clump or bridge restricting water flow and product delivery can vary depending upon water temperature, bed height, and flow rate. It is apparent that a need existed for a stable, easy-to-feed, bromine delivery system.

As indicated previously, activated sodium bromide can be generated from the reaction of bromide with an oxidant such as bleach or chlorine gas. The resulting solution is unstable, however, and must be used immediately. Goodenough, et. al reported the preparation of formulations with improved stability by combining elemental bromine with nitrogen compounds such as urea or sulfamic acid.<sup>102</sup> The formulations showed good activity against sulfate-reducing bacteria. This technology was apparently not pursued further, perhaps due to the relatively low activity of the solutions (1%).

More cost effective forms of stabilized bromine of higher activity were patented and subsequently commercialized in the late 1990s.<sup>103,104</sup> W.F. McCoy, et al. reported several advantages of a stabilized hypobromite formulation relative to traditional chlorine and bromine biocide technologies.<sup>105</sup> The advantages cited included: ten times more stable than bleach (NaOCl), less aggressive to water treatment chemicals such as scale and corrosion inhibitors (Table 8), and an improved environmental toxicity profile (Table 9).

TABLE 8  
COMPATIBILITY OF WATER TREATMENT CHEMICALS WITH HALOGEN BIOCIDES

Biocide	AMP Reversion, %	Tolyltriazole Degradation, %
None (Control)	0.9 ± 1.3	0 (normalized)
Chlorine	39 ± 2.8	18.1 ± 0.1
Bromine	20.7 ± 1.3	96.6 ± 1.3
Stabilized Hypobromite	4.1 ± 1.9	2.2 ± 4.6

Notes: 5 ppm total halogen residual (as Cl<sub>2</sub>), 1 hr contact, pH 8.2  
AMP is aminotrimethylene phosphonic acid

TABLE 9  
TOXICITY OF STABILIZED HYPOBROMITE TO UNSTABILIZED BROMINE

Aquatic Toxicity, LC50	Stabilized Hypobromite, ppm as Br <sub>2</sub>	Unstabilized Bromine, ppm as Br <sub>2</sub>
Rainbow Trout, 96 hr	0.60	0.23
Daphnia Magna, 48 hr	0.58	0.04
Sheepshead Minnow, 96 hr	2.30	0.19
Mysid Shrimp, 96 hr	3.65	0.17

LC50 is the lethal concentration for 50% of the test organisms after the indicated contact time.

Nalepa, et al. reported the development of a second generation stabilized bromine chloride product with excellent handling properties, efficacy, and performance.<sup>106,107</sup> Results of a four-month trial in a 14,000 gallon cooling system indicated good performance using a biocide application frequency of 3 times per week to a residual of 4.5 ppm total halogen residual as Cl<sub>2</sub>. Biocide dosing and residual decay remained consistent throughout the trial with no adjustments to the biocide feed system during the entire trial (Fig. 13). Corrosion rates on 60-day coupons were excellent with 0.28 mpy for mild steel (1010) and 0.11 mpy for copper (CDA 110).

Stabilized hypobromite provided good mitigation of microbiologically induced corrosion (MIC) based on measurements from an on-line localized corrosion monitor in pilot cooling system operating at pH 8.4.<sup>108</sup> Slug dosages of stabilized hypobromite (1 ppm total, residual, as Cl<sub>2</sub>) led to long-term reductions in the localized corrosion rate of more than 50%. This proved more effective than comparable dosages of bleach and activated sodium bromide.

#### Recent Bromine Biocide Developments – Dibromodimethylhydantoin; BCDMH Gel

A new solid biocide, dibromodimethylhydantoin (DBDMH), has recently been introduced into the marketplace.<sup>109</sup> The product is an effective bromine-delivery system with an active halogen content greater than elemental bromine itself (Eq 14).



Field trials indicate that the product effectively controls slimes, algae, and bacteria in industrial and building cooling systems when applied continuously (0.2 to 0.4 ppm free halogen residual, as Br<sub>2</sub>)

or slug dosed (to 0.3 to 0.8 ppm free residual, as Br<sub>2</sub>).<sup>110</sup> One feature of the product is the overall lower product consumption relative to other solid biocide products. In addition, saturated solutions of DBDMH typically remain near-neutral which minimizes the development of halogen vapors and corrosive conditions in flow-through erosion type feeders (Table 10).

TABLE 10  
SELECTED PROPERTIES OF SOLID OXIDIZING BIOCIDES

Biocide	Appearance	Solubility in Water, % (25° C)	pH (sat'd. solution)
Trichlor	White powder or tablets	1.2	2.8
BCDMH	White to off-white granules or tablets	0.2	3.5
BCMEH	White to off-white granules or tablets	0.2	3.5
DBDMH	White to off-white granules	0.1	6.6

Note: Trichlor = trichloroisocyanuric acid; BCMEH = bromochloromethylethylhydantoin

A pumpable, pourable gel based on a patented combination of BCDMH and clay was introduced just last year.<sup>111</sup> The product is thixotropic and can be fed using a flooded suction pump arrangement. BCDMH gel has good room temperature storage stability and exhibits microbiological activity similar to the parent BCDMH compound. For example, tests vs. *S. faecalis* and *E. coli* indicate complete kill of test organisms at application levels of 0.6 ppm as Cl<sub>2</sub>. Field trials indicate that BCDMH gel can improve biocide utilization relative to solid BCDMH and provide good control of algae compared to other bromine biocides.<sup>112</sup>

#### Current Trends in Industrial Water Treatment

##### Biofilm Control

The control of biofilms is of critical importance in industrial water chemistry since biofilms can reduce heat transfer, cause film fill fouling, and accelerate corrosion of cooling systems.<sup>113</sup> Biofilms consist of consortia of bacteria and other microorganisms attached to surfaces. Biofilms also contain by-products of microbial metabolism and entrained scale and debris.<sup>114</sup> It has been stated that over 99% of the bacteria in an industrial water system reside on the surfaces of the system.<sup>108</sup>

Work performed at Montana State University and by others indicates that biofilms do not represent an impenetrable barrier or fortress towards biocides as perhaps was once believed. The current view is that biofilms have a highly-ordered structure consisting of water channels, and groupings of bacteria in structures resembling mushrooms and towers.<sup>115</sup> This complex morphology is due to intracellular bacterial communication and enables the efficient transfer of nutrients and waste products into or out of the biofilm and between the various biota present in the diverse biofilm community.

Laboratory studies indicate that bromine chemistry can be effective against biofilm organisms. Ludensky and Himpler compared the performance of chlorine, bromine and BCMEH against biofilms of *Sphaerotilus natans*.<sup>116</sup> Dynamic tests using non-destructive biofilm monitoring techniques (heat transfer resistance and dissolved oxygen concentration) indicated biofilm control (but not eradication) at the following treatment levels: 10 ppm BCDMH, 15 ppm HOBr, and >20 ppm HOCl (i.e., chlorine did not control the biofilm at the maximum applied dose).

Recently a comparison of the efficacy of chlorine (NaOCl) and bromine (NaOBr) was performed at Montana State University.<sup>117</sup> The test employed a biocide contact time of 10 minutes on two-day *Pseudomonas aeruginosa* biofilms grown on polycarbonate disks. Average reductions in biofilm

populations were 0.9 logs for chlorine vs. 1.6 logs for bromine (Table 11). Surprisingly, a high dose of chlorine (50 ppm) did not improve effectiveness. These tests suggest a deeper penetration of bromine into the biofilm, perhaps due to reduced reactivity with the extracellular polysaccharide layer (EPS) produced by the bacteria.

TABLE 11  
LOG DENSITIES AND LOG REDUCTIONS FOR CONTROL AND TREATED REACTORS  
(48-HOUR BIOFILMS; 10-MINUTE CHALLENGE TIME)

Treatment	Control	Treated	Log Reduction
<i>Chlorine</i>			
5 ppm	5.84 ± 0.24	4.84 ± 0.25	1.04 ± 0.45
5 ppm	5.72 ± 0.33	4.94 ± 0.44	0.77 ± 0.42
50 ppm	5.32 ± 0.09	4.60 ± 0.24	0.72 ± 0.49
Avg.	5.63	4.79	0.84
<i>Bromine</i>			
3 ppm	5.67 ± 0.72	4.35 ± 0.32	1.32 ± 0.68
5 ppm	6.66 ± 0.52	4.26 ± 0.26	2.40 ± 0.59
7 ppm	5.04 ± 0.12	4.04 ± 0.37	1.00 ± 0.43
Avg.	5.79	4.22	1.57

Note: treatment concentrations determined using total DPD reagent and comparisons to chlorine and bromine standard solutions.

Further comparisons of the effectiveness of various bromine-based biocides against *Pseudomonas aeruginosa* biofilms were performed using a 96-well microplate technique. This work indicated that bromine biocides were more effective than chlorine-based ones against aged, 7-day biofilms.<sup>118</sup> For example, minimum biofilm eradication concentrations (MBEC) were as low as 5 ppm (total residual, as Cl<sub>2</sub>) for stabilized bromine chloride and dibromodimethylhydantoin vs. 20 ppm (free residual, as Cl<sub>2</sub>) for bleach or trichlor. Additional work indicates that stabilized hypobromite is more effective than chlorine and activated sodium bromide against MIC, based on localized corrosion measurements.<sup>108</sup>

TABLE 12  
EFFECT OF BIOCIDES ON BIOFILM POPULATIONS IN MODEL COOLING TOWERS  
AFTER SHORT, INTERMEDIATE, AND LONG CHALLENGE TIMES

Biocide	Dosage Level, ppm During Experiment	Log Reduction, Heterotrophic Biofilm (approx.)		
		Initial (~12 hrs)	24 Hours	4 Days
Chlorine	0 - 5 (variable)	4	3	4
Bromine	0 - 2 (variable)	3	3.5	3
Glutaraldehyde	30 - 24	2	1	1
DBNPA	9 - 7	1.5	0	> Control
Isothiazolone	9 - 7	1	0	> Control
Polymeric Quat	9 - 7	0	> Control	> Control
Ozone	0 - 0.2 (variable)	1.5	0	> Control

Control = Biofilm bacteria recovered to levels greater than the control (no biocide) system.

Note: Concentrations of non-oxidizing biocides slowly decreased during the experiment following the initial dose; oxidizing biocides were dosed several times at random intervals.

Thomas, et al., studied the effect of biocides on biofilms containing *Pseudomonas* species, *Legionella pneumophila*, and amoebae in pilot cooling towers.<sup>119</sup> This work showed that chlorine (0-5

ppm residual) and bromine (0-2 ppm residual) effectively controlled general biofilm bacteria over the 4-day duration of the experiment. Halogen residuals varied widely but never exceeded 5 ppm for chlorine and 2 ppm for bromine. Non-oxidizing biocides were not as effective in these tests (Table 12).

#### Legionnaires' Disease

Often scientific development is spurred on by tragic circumstances. For example, the arrival of bubonic plague to industrial Europe in the 1800s led to the development of effective water sanitation practices.<sup>120</sup> The famous outbreak of Legionnaires' disease in Philadelphia in 1976 added further momentum to the shift towards effective industrial biocontrol practices and bromine chemistry. A hotel comfort cooling system was implicated as the source of the outbreak. We now know that the disease was caused by the bacteria *Legionella pneumophila* and that specific serogroups such as 1 and 6 are particularly associated with outbreaks of the disease.<sup>121</sup> Conditions often present in man-made water systems such as warm water temperatures (30 – 40 C), dead-legs and other stagnant areas, and pockets of silt and debris, create conditions for *Legionella pneumophila* to develop and often thrive.

A number of trade organizations and government agencies have published recommended cooling system maintenance and treatment practices.<sup>121-127</sup> In addition to suggesting regular system inspections for system cleanliness and mitigation of stagnant flow areas, these organizations typically advocate the use of an oxidizing biocide, e.g. bromine, together with a non-oxidizing chemistry to minimize the risk associated with *Legionella* outbreaks. This treatment practice would appear to represent a good balance of varying the stressors placed on the microbial community, minimizing the problem of acquired microbial resistance, and mitigating corrosion induced by overly high levels of oxidizing biocides.

Many studies have demonstrated that bromine chemistry can be effective against both planktonic and surface-associated *Legionella pneumophila*. Thomas, et al., in a continuation of the biofilm work discussed above, identified several biocides, including chlorine and bromine, that were effective at controlling biofilm-associated *Legionella* (Table 13).<sup>119</sup>

TABLE 13  
EFFECT OF BIOCIDES ON BIOFILM-ASSOCIATED LEGIONELLA IN MODEL COOLING TOWERS AFTER SHORT, INTERMEDIATE, AND LONG CHALLENGE TIMES

Biocide	Dosage Level, ppm, During Experiment	Log Red'n, Biofilm-Associated <i>Legionella</i> (approx.)		
		Initial (~12 hrs)	24 Hours	4 Days
Chlorine	0 - 5 (variable)	ND	ND	ND
Bromine	0 - 2 (variable)	ND	ND	ND
Glutaraldehyde	30 - 24	ND	ND	ND
DBNPA	9 - 7	ND	ND	ND
Isothiazolone	9 - 7	1	0.5	0.5
Polymeric Quat	9 - 7	0	0	0
Ozone	0 - 0.2 (variable)	0	0	0

ND = none detected. Due to varying starting *Legionella* populations in the biofilm, this typically represents a 1 to 3 log reduction.

Stout, et al., constructed a laboratory model water system and used it to investigate the efficacy of several biocides on biofilms consisting of a consortium of *Legionella*, heterotrophic bacteria, and amoebae (Table 14).<sup>128</sup> The biofilms were grown for 14 days and the biocide contact time was 48 hours. This work showed that both chlorine and BCDMH could effectively control biofilm-associated *Legionella* bacteria.

TABLE 14  
EFFECTIVENESS OF BIOCIDES ON BIOFILM-ASSOCIATED LEGIONELLA IN A MODEL WATER SYSTEM AFTER SHORT, INTERMEDIATE, AND LONG CHALLENGE TIMES

Biocide	Dosage Level, ppm During Experiment	Log Reduction, Biofilm-Associated <i>Legionella</i>		
		3 Hours	12 Hours	2 Days
Chlorine	2	ND	ND	ND
	4	ND	ND	ND
BCDMH	10	0	1.5	ND
	100	ND	ND	ND
Glutaraldehyde	50	2.2	2.2	2.3
	100	3.8	3.6	3.6
Carbamate	4	1.1	1.1	1.2
	13	1.9	1.9	1.9
Polymeric Quat	5	0.1	0.0	0.0
	12	0.9	0.9	0.9

ND = none detected. Due to varying starting *Legionella* populations, this represents a 4.0 to 4.5 log reduction.

Additional work in the laboratory model system uncovered subtle differences in biocide performance amongst three different bromine-based biocides.<sup>129,130</sup> All proved effective against biofilm-associated *Legionella* with initial 3 to 3.9 log reductions in bacteria counts and also controlled planktonic *Legionella* with initial reductions of 3.6 to 4 log units (Table 15). In addition, both stabilized bromine chloride and DBDMH maintained long-lasting control of bacteria in both the biofilm and planktonic phases. At the conclusion of a 14-day recovery period (no biocide present in system during this time), biofilm-associated *Legionella* counts remained 1.5 to 1.8 log units lower than control values. Good long-term control of planktonic *Legionella* was also observed with these biocides (Table 16).

TABLE 15  
LABORATORY MODEL WATER SYSTEM EXPERIMENTS - LOG REDUCTION DATA

Biocide (1)	Residual, Max. as Cl <sub>2</sub>	Log Reduction, <i>Legionella</i> (2)		Log Reduction, HPC Bacteria (2)	
		Planktonic	Biofilm	Planktonic	Biofilm
SBC	4.1	3.9	3	2.2	2.2
DBDMH	1.9	3.6	3.6	3.6	2.7
Act. NaBr	1.7	4	3.8	3.4	3.7

1. SBC = stabilized bromine chloride; DBDMH = dibromodimethylhydantoin; Activated NaBr = NaOCl + NaBr.
2. Maximum log reductions; typically obtained at 2 - 12 hours after biocide application.

TABLE 16  
LABORATORY MODEL WATER SYSTEM EXPERIMENTS - 14-DAY RECOVERY DATA

Biocide	Log Reduction, <i>Legionella</i> (1)		Log Reduction, HPC Bacteria (1)	
	Planktonic	Biofilm	Planktonic	Biofilm
SBC	3.7	1.8	1.4	0.8
DBDMH	1.7	1.5	0.2	0.4
Act. NaBr	-0.1	0.1	0.2	0.3

1. Log reductions relative to control after the 14-day recovery period.

### Bromine Biocide Selection in Industrial Water Systems

As the preceding discussions indicate, bromine chemistry can represent an effective component of a modern industrial water treatment program. The selection of one particular product over another should be based on a number of economic and performance criteria and should be evaluated on a case-by-case basis.<sup>131,132</sup> For example, activated sodium bromide may be appropriate for a high-volume industrial application where the increased maintenance and testing requirements for this two-part system are compensated by the lower relative chemical cost of the system. Conversely, stabilized bromine biocide products are generally easy to feed and provide consistent product delivery so the higher chemical costs of these systems are in part compensated by reduced on-site testing and maintenance requirements. Automation, of course, plays an important and ever-increasing role on biocide application and ORP (oxidation/reduction potential) and other methods of biocide control often can be used to great advantage with the solid halogenated hydantoin products since precise manual biocide feed is often difficult with the erosion-type feeders generally employed with these products.

Water quality, the potential for contamination due to process leaks, and seasonal variations in water quality must also be considered when selecting an appropriate product for a particular application. UV exposure, water temperature, and other environmental factors also impact biocide consumption and should be taken into account. Bromine-based biocides differ in their general response to system impurities, UV exposure, and reaction to typical water treatment scale and deposit control technologies. Table 17 provides an overview and ranking of some of the properties of the biocides important for field applications.<sup>133</sup> This table is for general purposes and additional discussions with appropriate biocide suppliers is encouraged. For example, although stabilized liquid bromine products generally react slowly with typical system impurities (excellent impurity tolerance), all of the bromine-based biocides can be rendered essentially inactive in the presence of strong reducing agents such as hydrogen sulfide.

TABLE 17  
SELECTED PROPERTIES OF OXIDIZING BIOCIDES

Biocide	Appearance	Available Halogen, %	Water Solubility	pH (1% Solution)	UV Stability	Impurity Tolerance	Long-Term Activity
Industrial Bleach	Pale yellow liquid	12%, as Cl <sub>2</sub>	Complete	~12	P	P	P
Stabilized BrCl	Yellow to orange liquid	15% as Br <sub>2</sub> ; 7.0% as Cl <sub>2</sub>	Complete	11.9	G	E	E
Stabilized Hypobromite	Yellow to orange liquid	14% as Br <sub>2</sub> ; 6.4% as Cl <sub>2</sub>	Complete	12	G	E	E
Sodium Bromide (with oxidizer)	Water white liquid	NA	Complete	7	P	I	P
BCDMH	White, off-white gran, tab	58% as Cl <sub>2</sub>	0.2%	3.5 (Sat'd. solution)	G	G	G
BCMEH	White to off-white gran, tab	62% as Cl <sub>2</sub>	0.2%	3.5 (Sat'd. solution)	G	G	G
Dichlor/ NaBr	White to off-white gran, tab	57%, as Cl <sub>2</sub>	25%	6.0 (est.)	I	G	G
Trichlor/ NaBr	White to off-white gran, tab	83% as Cl <sub>2</sub>	1.2%	2.8 (est.)	I	G	G
DBDMH	White to off-white granules	111% as Br <sub>2</sub> ; 49% as Cl <sub>2</sub>	0.1%	6.6 (sat'd. solution)	G	G	G
BCDMH Gel	White to off-white gel	45% as Br <sub>2</sub> ; 20% as Cl <sub>2</sub>	>1%	3.5 (est.)	G	G	G

E = Excellent; G = good; I = Intermediate; P = Poor. Long-term activity refers to the long-term impact on microorganisms in the system after a slug dose.

## CONCLUSIONS

Today a number of bromine-containing oxidizing products are available to the industrial water treatment marketplace. The storage, economic, and handling issues associated with elemental bromine have given rise to a host of more user-friendly products that can deliver the benefits of bromine chemistry when applied to modern alkaline water treatment programs. Traditional biocides such as activated sodium bromide, BCDMH, and chloroisocyanurate/ bromide mixtures continue to be used effectively for microbiological control in industrial water systems. Newer products such as stabilized bromine chloride, stabilized hypobromite, dibromodimethylhydantoin, and BCDMH gel provide still more choices and feed options.

Trends such as the move to alkaline treatment programs, increased cycles of concentration, greater use of lower quality waters, and the demand for more effective control measures for microorganisms on surfaces and in the bulk water have led to increased interest in the use of bromine chemistry in industrial water treatment. Research into naturally-produced antifouling agents should provide the basis for future development and extension of bromine technology.

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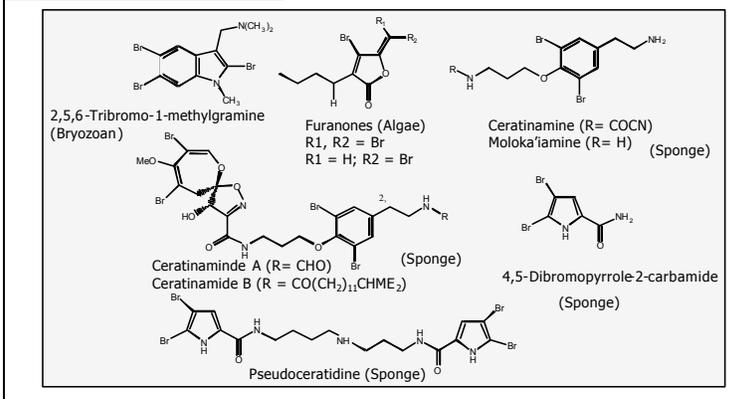
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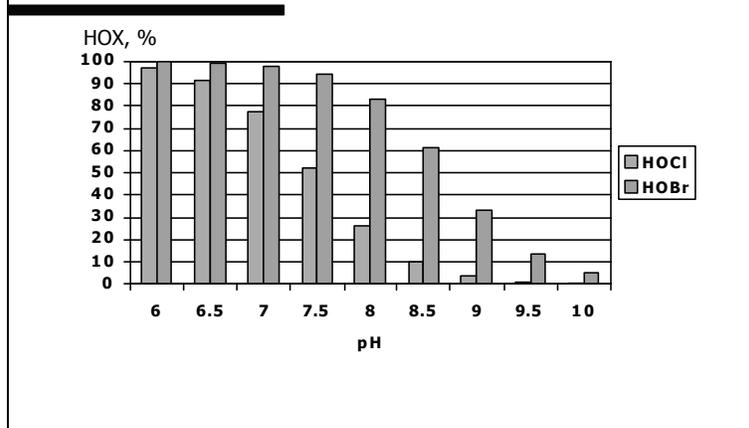
**Fig. 1: Naturally Occurring Bromine Compounds for Biofouling Prevention**



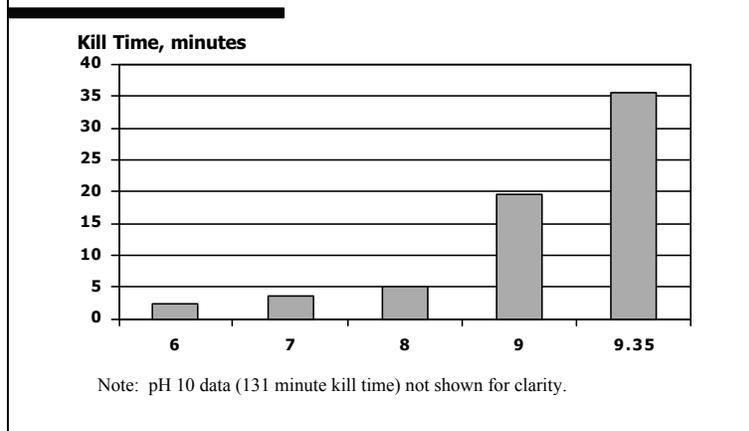
**Fig. 2: Sources of Bromine**



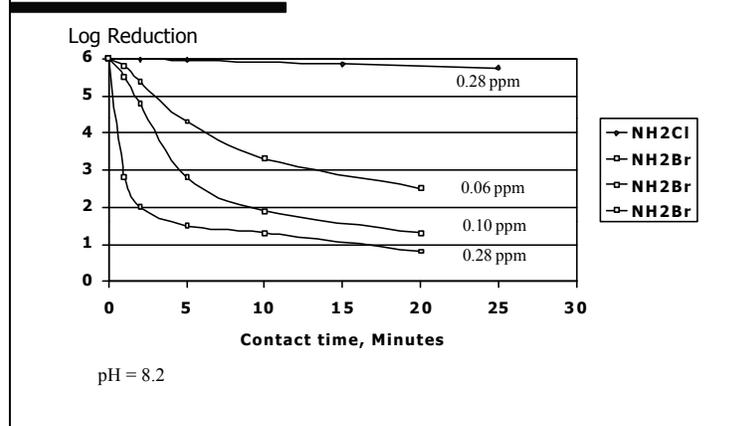
**Fig. 3: Effect of pH on Hypohalous Acid Dissociation**



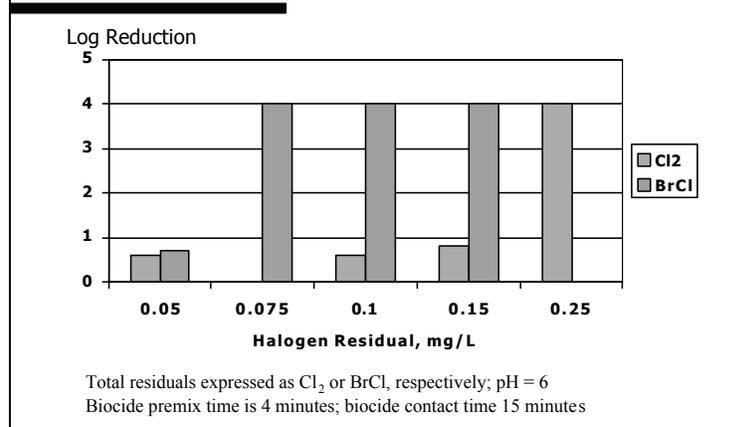
**Fig. 4: Effect of pH on Kill Times of *Bacillus metiens***



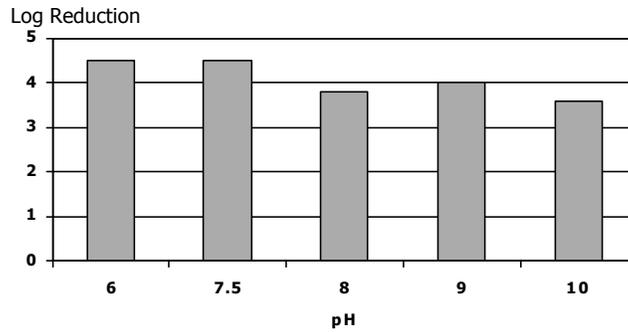
**Fig. 5: Activity of Chloramine vs. Bromamine towards *E. coli***



**Fig. 6: Effectiveness of BrCl and Chlorine towards Polio Virus type 1**

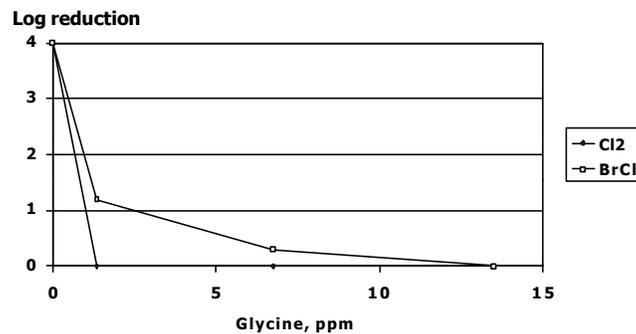


**Fig. 7: Effect of pH on BrCl  
Inactivation of Polio Virus type 1**



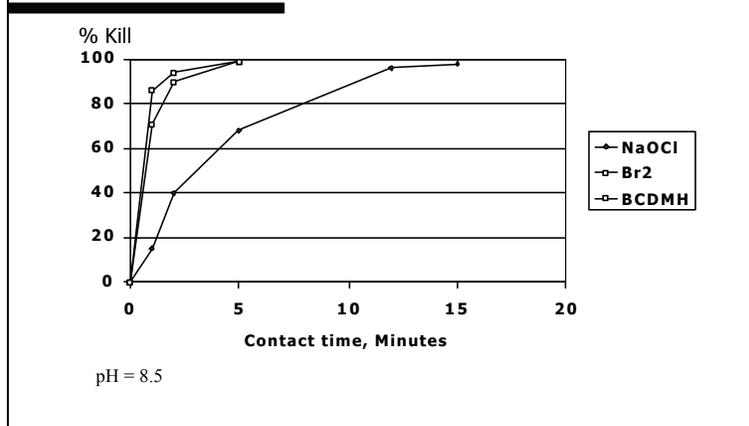
Total residuals expressed as BrCl.  
Biocide premix time is 4 minutes; biocide contact time 15 minutes

**Fig. 8: Inactivation of Poliovirus in  
Presence of Glycine**

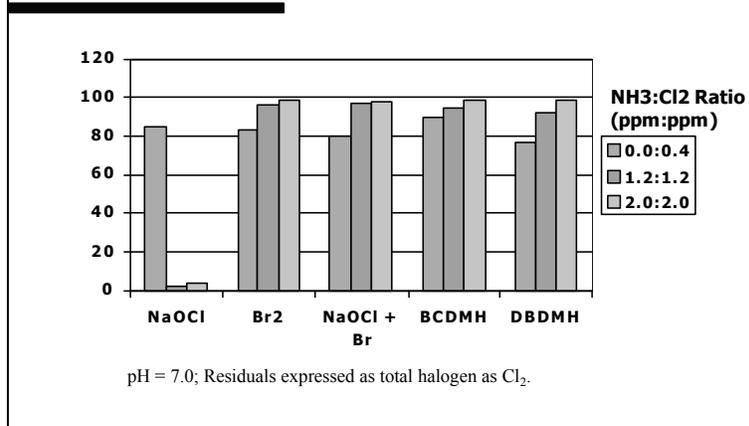


Total residuals added is 0.30 mg/L Cl<sub>2</sub> or 0.15 mg/L BrCl, respectively; pH = 7.5  
Biocide premix time is 4 minutes; biocide contact time is 15 minutes

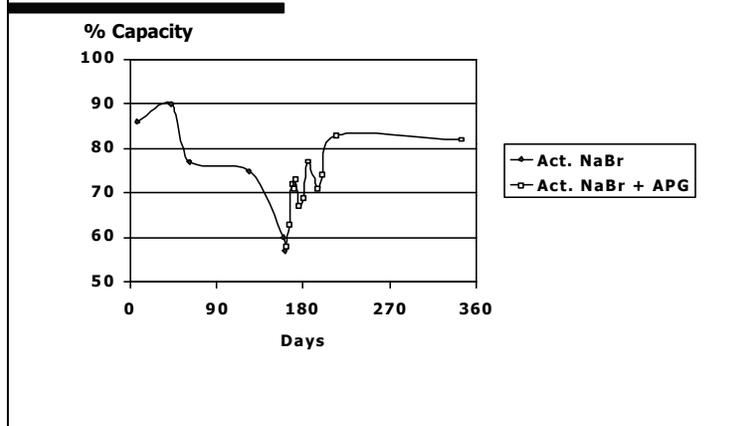
**Fig. 9: Activity of BCDMH, Bromine, and NaOCl on *P. aeruginosa***



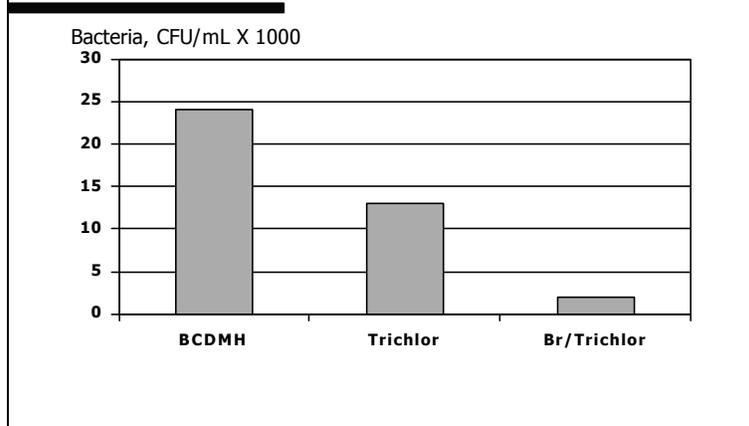
**Fig. 10: Effect of Ammonia on Halogen Activity vs. *P. aeruginosa***



**Fig. 11: Cooling Tower Thermal Efficiency in a Coal-Fired Power Plant**



**Fig. 12: Field Trial Efficacy Results of Halogen Donor Biocides**



**Fig. 13: Stabilized Bromine Chloride Slug Dose Comparison**

