

Bromine

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Brought to you by the APSP Recreational Water Quality Committee (RWQC)

I. INTRODUCTION

This fact sheet provides technical information on bromine sanitization used in swimming pools, spas and hot tubs. Bromine has a long history of use in sanitizing recreational water. It is in the same chemical family as chlorine and functions in much the same way. Bromine, like chlorine, is a U.S. Environmental Protection Agency (EPA) registered sanitizer that provides a residual in the water which kills bacteria and algae. Like chlorine, bromine is also an oxidizer which destroys organic contaminants.

II. General Description

Bromine can be introduced into water via tablets, granular distribution, or as part of a salt/oxidizer system. Bromine tablets are commercially available in several forms and chemistries with varying halogen and alkyl groups differentiating them. These differences can affect the performance of the tablets for the consumer. Bromine systems are also available which blend a salt (sodium bromide) with an oxidizer (typically chlorine or potassium peroxymonosulfate, also known as potassium monopersulfate) to generate bromine in the water. Bromine can also be generated *in situ* via electrolytic halogen generators.

It is important to keep in mind that no matter which system is employed, whether bromine is dissolved or produced in water, hypobromous acid (HOBr) and hypobromite ion (OBr⁻) are produced. The biocidal properties of bromine are primarily due to HOBr. Even in tablets where chlorine is a component, or in systems that employ sodium bromide and chlorine together, HOBr is still the primary sanitizer present in the water. This occurs since hypochlorous acid (HOCl) readily reacts with bromide ions in solution to make a new molecule of HOBr and a chloride ion (Cl⁻)¹. Bromine will combine with organic contaminants in the water to form combined bromine (bromamines). But unlike combined chlorine which is a slow acting sanitizer, bromamines are still very efficient².

Bromine has a low odor and is effective over a wide pH range. In the recommended pH range for swimming pools of 7.2-7.8, HOBr formation remains over 90%. At pH of 8.0, HOBr formation is still 83% compared to HOCl formation from chlorine at 23%. For this

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reason, in systems where pH may drift upward for short periods of time (i.e., hot tubs and spas) bromine is a popular choice.

Sunlight degrades both HOBr and HOCl. The stabilizer used for chlorine-treated pools (cyanuric acid) is not effective with bromine treated pools. Dimethylhydantoin (DMH), a chemical incorporated into bromine tablets provides some minor protection to HOBr against sunlight degradation.^{4,5}

According to ANSI/APSP/ICC-11 *Standard for Water Quality in Public Pools*, the ideal range for bromine is 3.0-4.0 ppm for pools and 4.0-6.0 for spas. Always consult and follow the directions for use on all labels for products that are being used.

The preferred method for testing bromine is to use a test kit designed for measuring bromine. Note that when testing for bromine with a chlorine test kit, the reading should be multiplied by 2.25 to obtain the bromine concentration. Additionally, Oxidation-Reduction Potential (ORP) may be used to test bromine-treated water; however, the reading will be lower than that obtained for chlorine.

Once bromine is used in a pool then it will remain a bromine pool, even if bromine is discontinued and chlorine is used. A popular misconception is that the pool must be drained to switch to chlorine. While that is the quickest method of converting a pool to chlorine, a pool with bromine or bromide ions can switch back to a chlorine pool over time. The greater the amount of oxidation and the greater the amount of sunlight present the shorter that conversion time. Keep in mind that during the conversion process, chlorine demand will remain high.

III. Bromine Tablets

Bromine tablets are white solids that are typically sold as compressed tablets or as capsule-shaped briquettes. The most prevalent forms of bromine tablets are 1-bromo-3-chloro-5, 5-dimethylhydantoin (BCDMH) and a tablet composed of a mixture of three chemicals: BCDMH, 1,3-dichloro-5, 5-dimethylhydantoin (DCDMH), and 1,3-dichloro-5-ethyl-5-methylhydantoin (DCEMH).

Bromine tablets are typically fed into the water via either a floater or a bromine feeder. Care should be taken when selecting the appropriate delivery system since the two predominant types of bromine tablets dissolve at different rates. Typically, BCDMH will dissolve more slowly than the blended BCDMH, DCDMH, DCEMH tablets.

When added to water, bromine tablets dissolve and react to produce HOBr, HOCl and dimethylhydantoin (DMH) residue. HOBr becomes the primary sanitizer in this system. As the HOBr reacts and generates bromide ions, in the presence of chlorine and other oxidizers, HOBr will be regenerated as the predominant sanitizer. Thus, even with chlorine present in the bromine tablets, bromine is the predominant sanitizer in the water.

Bromine tablets generally have a pH around 4.0, therefore, pH adjustment to the water will be necessary to maintain proper water balance. Even though bromine is effective over a wide pH range, it is important that the ANSI/APSP/ICC-11 recommended pH range of 7.2-7.8 and alkalinity range of 60-180 ppm be maintained.

As with chlorine sanitizers, it is recommended to periodically shock oxidize the water when using bromine tablets. Product label directions should be consulted to identify the type and frequency of supplemental oxidation treatments.

IV. TWO-PART BROMINE SYSTEMS

Bromine can be generated on site with a two-part system. The first part is sodium bromide. This typically is introduced as a granular or a liquid solution directly into the pool or spa. The sodium bromide creates bromide ions in the water, often referred to as a “bromide bank.” The sodium bromide alone is not a sanitizer. The second part of the system is an oxidizer, typically potassium monopersulfate, but can also be chlorine. When the oxidizer is added to the water, the bromide ions are oxidized into HOBr which is the active sanitizer in the system. As the HOBr is used in sanitization, it reduces back into bromide ions which can then be converted back into bromine with additional oxidizer. Sodium bromide only needs to be added periodically to maintain the system.

V. GRANULAR BROMINE

There are two types of granular bromine. One is bromo-chloro hydantoin similar to those used in bromine tablets. This granular form performs in the same way as the bromine tablets. The second is a mixture of sodium bromide and dichlor (packaged as a single product). This operates in a similar fashion as the two-part bromine systems described above. Granular products are introduced into the pool or spa through manual dispersion onto the water.

VI. BROMINE AS AN ALGAEICIDE

Bromine is an effective algaecide, particularly against difficult to control mustard and black algae, and its algaecidal properties are well known.⁶

Sodium bromide, as a source of bromine, has been EPA registered as an algaecide. However, sodium bromide alone will not kill algae. To be effective, it must be used in conjunction with an oxidizer, typically chlorine. If using sodium bromide as an algaecide, ensure that the product is EPA registered for that purpose and follow all label directions.

VII. TESTING CONSIDERATIONS

Current test kits and test strips will not distinguish between free and combined bromine. Both will test as free. Consequently, while combined chlorine readings in chlorinated pools and spas serve as a reminder of the need for oxidation of contaminants, there is no such indication in brominated pools and spas. The need for oxidation is often overlooked as irritating contaminants, such as brominated disinfection byproducts, accumulate in the

water. This could lead to a higher incidence of dermatitis associated with the use of bromine than chlorine.

VIII. SAFETY PRECAUTIONS

To ensure safe use and handling, all individuals involved in the manufacture, distribution, sale, or end-use of bromine must be properly trained and aware of product label sections that address the “Precautionary Statement, Environmental Hazards, and Physical and Chemical Hazards.” A Safety Data Sheet (SDS) should be read and understood by all individuals involved in the use of these products.

Bromine tablets, granular bromine, and bromine systems are oxidizers and must be handled properly. Avoid contact between bromine tablets or bromine compounds and easily oxidizable materials such as ammonia, urea, nitrogen-containing compounds, strong reducing agents, and other oxidizers regardless of their structure. Never place bromine tablets or compounds in any chemical feeder or floater with any other chemical, including chlorine. Store products in a cool, dry, well-ventilated area away from heat, open flames, organic material, and direct sunlight. Always store in original container and avoid getting the product wet in storage.

The use of ozone in conjunction with bromine as a primary sanitizer is not recommended due to the increased formation of the carcinogen bromate.

VIII. REFERENCES

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