EnviroAqua CONSULTANTS INC.

Water Talk

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Bromine based Microbiocides

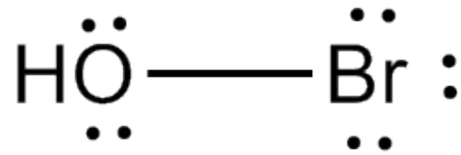
Bromine-based biocides provide effective protection against bacteria, fungi, and algae in commercial and industrial water systems. These biocides provide some advantages as microbiocides due to their low cost, quick kill rate, broad spectrum of effectiveness and very low occurrence of resistance.

CHEMISTRY

If bromine gas was added to water it would generate hypobromous acid and hydrogen bromide by the following reaction:

$$Br_2 + H_2O = HOBr + HBr$$

Unlike chlorine, bromine is not offered as a microbiocide. However it is available in various forms and delivery systems that provide access to hypobromous acid for industrial water treatment. Hypobromous acid is an effective general purpose biocide especially under alkaline pH conditions of 8 to 9+.



Hypobromous acid is in equilibrium with OBr^- which is pH dependent. OBr^- like OCl^- is less effective as a microbiocide then the HOBr or HOCl form. At pH 7.5 half the chlorine is present as OCl^- and as the pH increases the % of OCl^- increases and the effectiveness is reduced. The transition for bromine is at a pH of 8.5. As a result, bromine based chemicals are more effective under alkaline conditions than chlorine based chemicals.

IMPURITIES

Some of the same impurities that reduce chlorine effectiveness also reduce bromine effectiveness. These include unsaturated organics such as olefins or aromatics, ferrous iron. Manganese (Mn^{2+}) and sulfides.

Bromine, like chlorine, can also be degraded by heat and sunlight. Bromine has the advantage over chlorine in that it works well at elevated pH and also in the presence of amines and urea.

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Some of the common chemicals used as corrosion inhibitors and scale control agents in cooling water systems can be degraded by bromine, but typically less than with chlorine. These include AMP or NTMP, HEDP and the azole corrosion inhibitors.

BROMINE DEMAND

Any impurity like the ones mentioned above will remove the bromine residual necessary for good microbiological control. Additional bromine would need to be added to completely react with these impurities so that a free form of bromine residual can be established. The addition bromine necessary to react with the organics is referred to as the bromine demand.

When bromine reacts with many nitrogen containing impurities like amines, urea, proteins, amino acids they produce brominated amines that do have microbiological properties. As a result it is common to control bromine on the total bromine residual.

Bromine can also be lost from the system by evaporation or volatilization but to a lesser extent than chlorine because of its lower volatility

MEASUREMENT AND DOSAGE

It is common practice to regulate bromine dosage based on total halogen residual and not free as is commonly done with chlorine. This is because the combined forms of bromine such as the bromamines often retain effectiveness as microbiocides.

For continuous feed total bromine residuals between 0.1 to 0.5 mgs/l as chlorine are typically used. For intermittent use a total residual of 0.5 to 2.0 mgs/l as chlorine is normally recommended. If a stabilized bromine product is used, higher residuals are often used.

The DPD Method (N,N-diethyl phenylenediamine) is commonly used. Bromine can be expressed as chlorine or as bromine. To convert mgs/l as chlorine to mgs/l as bromine multiply by 2.25

PRODUCT FORMS

Sodium Bromide is a white, crystalline salt. It is typically used as a 40% active solution in water. Sodium bromide does not have microbiological control properties by itself, but must be used with an activating agent such as other forms or chlorine such as chlorine gas, bleach, calcium hypochlorite, organic chlorine compounds or ozone. The chlorine or ozone oxide the bromide ion to hypobromous acid by the following reaction (based on using bleach):

$$HOCl + NaBr = HOBr + NaCl$$

Sodium bromide can also be converted to bromine by electrically using DC current. The sodium bromide to oxidant ratio should be maintained in the range of 0.5:1.0 to 2.0:1.0 on a molar basis, based on label directions. There is little advantage feeding excess bromide, so NaBr to oxidant ratios <1.0 are common. The following table shows the ratio for various oxidants.

Mole Ratio NaBr 40%	**NaBr 40 lbs**	**Chlorine Gas, lbs**	**Bleach, lbs**	**Calcium Hypo, lbs**
0.5:1.0	**1.0**	**0.43**	**4.3**	**0.66**
1.0:1.0	**1.0**	**0.21**	**2.1**	**0.33**
2.0:1.0	**1.0**	**0.11**	**1.1**	**0.16**

One supplier has a tablet combination of sodium bromide and trichloro-s-triazinetrione which creates hypochlorous acid in solution which reacts with the bromide ion to produce hypobromous acid.

Stabilized Bromine liquid products are available for use as microbiocides. Because liquid sodium hypobromous acid is unstable in water it has to be stabilized usually with sulfamic acid. The products may say that it contains sodium hypochlorite and sodium bromide or bromine chloride(a gas at room temperatures) but the end product is a sodium hypobromite adduct with sulfamic acid. Each product may be made from a different raw material so it may say something different on the label.

The stabilized bromine products have good stability as long as they are in highly alkaline solution but should be packaged in UV protected containers with a vent on the container just like with bleach. If fed with a diaphragm pump, a degasifying head is necessary. Alternately a peristaltic pump can be used for feeding.

When stabilized bromine is added to water it releases hypobromite and there will be a combination of free and combined bromine in the system. Since the products are highly alkaline, they cause the precipitation of calcium carbonate, if fed into a bypass line of cooling tower water on an alkaline program. The product should be fed to the header where rapid dilution can occur.

Hydantoins are commonly used as tablets or granular forms in the treatment of cooling towers. The hydantoins are bromochlorohydantoins and one common chemical is 1-bromo-3chloro-5,5-dimethylhydantoin commonly called **BCDMH.** Some products have other hydantoins and are mixtures. These include dibromohydantoin (**DBDMH**) which has no chloride.

Hydantoins are sparingly soluble in water and require a feeder with high flow rates to make it soluble in the water. Often it is fed intermittently using a feeder with a reservoir of pellets and a control valve and meter to control the feed rate. Care should be taken to prevent pressure build-up when the flow stops (pressure release valve or no valve on the exit to maintain atmospheric pressure)

Whatever the source of bromine, it is an extremely effective microbiocide for cooling systems. As with any oxidizer care needs to be taken in the storage and handling of these products.

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