SOMETHING IN THE WATER

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Water conservation is becoming a higher priority in virtually every geographical region due to scarcity or competing demands. This competition for water means that lower quality water sources are frequently being used in industrial applications. Water conservation had been restricted to high volume process users (pulp and paper mills, etc.), but is now affecting more moderate consumers, such as cooling systems.

Water quality can be impacted by the amount of total organic carbon (TOC) or nutrients, such as nitrogen (N) or phosphorus (P), present. Typically, carbon is not the limiting nutrient. Cooling systems can be thought of as low efficiency bio-reactors and the growth of microbes will be constrained by whichever nutrient is rate limiting.

In wastewater treatment plants, where the goal is to grow microbes, the target ratio is 100:5:1 (C:N:P). Nitrite, nitrate or ammonia are all readily bio-available. Phosphorus, as orthophosphate (PO_4), from either the cooling water program or the plant environment, completes the conditions. Fertilizer plants are particularly

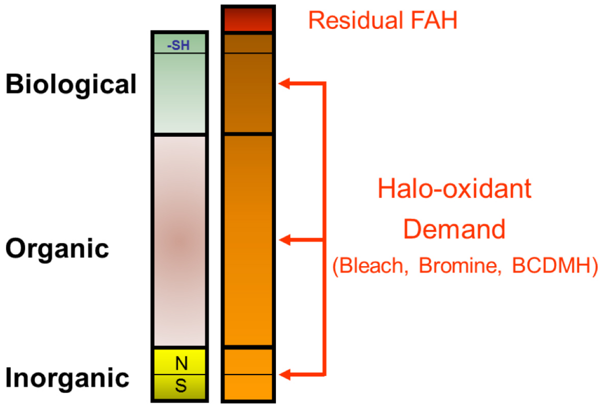

Figure 1. Before a residual is established, it is necessary to react with all the demands.

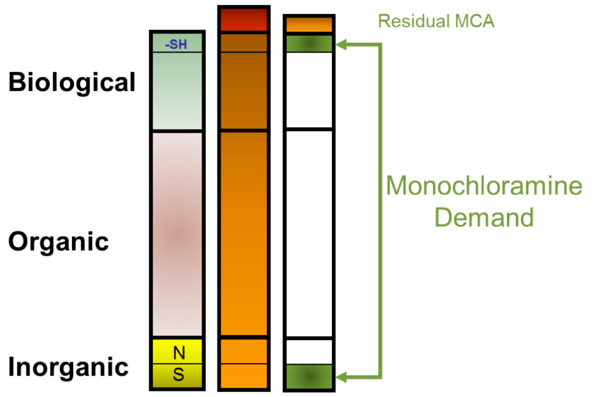

Figure 2. With MCA, the lower demand reduces the consumption of the biocide.

Figure 3. Cooling tower before Oxamine dosing showing slime and algal deposits.

Figure 4. After less than a week, the majority of the slime has been removed.

susceptible to elevated microbial activity for these reasons.

Higher microbial loading can lead to the following:

- Microbiologically induced corrosion (MIC) – this can override even the best cooling water treatment program and lead to localised corrosion.
- Fouling/deposition – in warmer climates, controlling algae can be a problem and its presence promotes pathogenic bacteria.
- Legionella – one of the risk factors for elevated levels of Legionella organisms is a higher level of general microbial activity.

Biocides

An oxidising biocide such as chlorine gas or sodium hypochlorite, alone or combined with non-oxidising biocides or bromine, is the conventional biocide treatment approach. While effective, the disadvantage of a strong oxidiser is its potential to react with a number of materials:

- Organics – whether from the source water or biofilm, these can represent 75% of the biocide demand. Process leaks can increase them further.
- Ammonia or sulfide – both of these will preferentially react with chlorine.
- Microbes – this is the intended target, but normally these account for <25% of the oxidiser used.

The general use of alkaline cooling chemistry means that chlorine is not as effective as in the past. Above a pH of 8.5, the amount of HOCl present is minor. While the OCl^- anion is biocidal, it is less effective compared to HOCl.

Using bromine chemistry is one way to overcome this effect. A much higher level of the uncharged HOBr at a given pH, compared to chlorine, makes it a better choice for alkaline cooling waters. In addition, bromamines have the same toxicity as HOBr, making them well suited for fertilizer plants.

Another option, chlorine dioxide, has seen limited use due to issues surrounding its generation and safety. As ClO_2 is more costly to use (stripping and oxidative demand) and more hazardous (chlorite and chlorate precursors are extreme fire hazards), it is not surprising that its use is limited.

It is also common practice to use some type of non-oxidising biocide or biodispersant (bio-detergent) to enhance the performance of oxidising biocides. These are employed to offset the protection that biofilm offers microbes, especially with chlorine and ClO_2. While the use of a supplemental non-oxidising biocide is generally beneficial, it adds cost and raises the environmental footprint of the treatment program.

Oxamine®, Buckman's monochloramine (MCA) based program, is a relatively recent addition to industrial biocides. However, MCA has been used to maintain microbial control in potable water systems for decades. MCA is a weak oxidant that is selective and preferentially reacts with sulfur bonds. Biological control is achieved by selectively reacting with sulfur bonds within microbial proteins.

This selectively means that MCA does not interact with the mass of biological material in a system and this targeted action allows for a lower overall biocide demand, whilst providing effective control. Figures 1 and 2 illustrate the 'sinks' that contribute to the system demand for oxidants.

The result is that in order to establish a monochloramine residual, less than 10% of what would be required for chlorine or bromine is used. A water with 2 – 5 ppm of Cl_2 demand will typically need only 0.1 – 0.5 ppm of MCA to meet the demand and only slightly more to provide a residual. This dramatic lowering of oxidant demand makes MCA an attractive biocide for high demand cooling water applications.

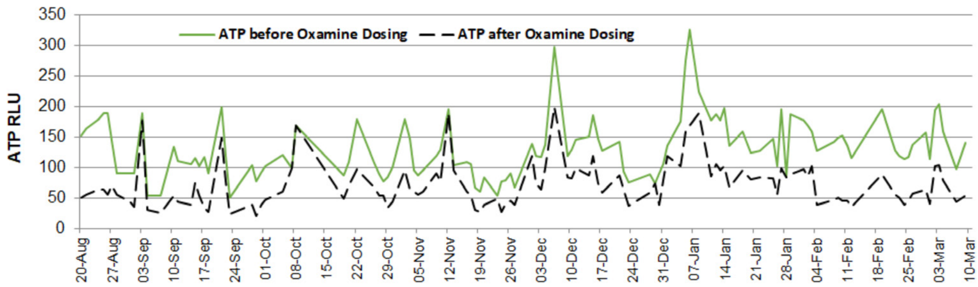

Figure 5. The drop in ATP after the dosing of Oxamine is indicative of biocidal effect.

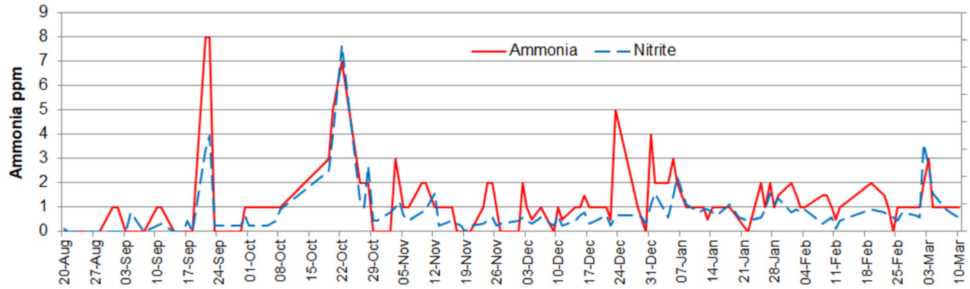

Figure 6. Oxamine shows good control at moderate levels of ammonia ingress.

A second benefit of using MCA is that it can readily penetrate biofilm and kill organisms embedded in it allowing it to degrade. Applications in paper mills, raw water clarifiers and other applications have shown rapid biofilm removal once monochloramine is started. This 'cleaning' action is rapid with it being apparent in just a few days after its application is started.

Figures 3 and 4 show the effects of using Buckman's Oxamine program on a paper mill cooling tower. After only a few days of exposure, the slime that had been chronically present (Figure 3) was removed (Figure 4).

The performance of the program as a general biocide has been well documented in over 300 installations globally. Figure 5 shows the effect on adenosine triphosphate (ATP – a marker for microbial activity) in a fertilizer plant.

Regulations are increasingly limiting adsorbable organic halogens (AOX)/trihalomethane (THM) in plant outfalls. Since MCA minimises their formation, it provides a more sustainable environmental benefit.

Coping with high ammonia environments

Contamination of the cooling water with nitrogen and phosphorus makes microbial control more challenging in fertilizer plants:

- Ammonia ingress – ensures that this nutrient is present.
- Oxidising bacteria – both ammonia and nitrite oxidisers will convert ammonia to nitrous or nitric acid, which can depress the cooling water pH.
- Phosphate – in integrated plants, phosphate and/or phosphate rock dust can get into the cooling system in addition to phosphate from the cooling water treatment.
- Metallurgy – the extensive use of lower grades of stainless steel in heat exchangers means there are restrictions on the level of chlorides that can be tolerated.
- Irrigation – cooling water bleed-off is frequently used for irrigation and there are limits on the amount of sodium and chloride that can be contained in this water. Sodium hypochlorite is a significant contributor.

Ammonia contamination can vary from trace amounts to hundreds of ppm. While ammonia ingress does increase general microbial activity, it is the pH depression of cooling water due to its conversion to nitric/nitrous acids that is the concern. Nitrosomonas (NH_3 to NO_2) and the nitrobacter genus (NO_2 to NO_3) are responsible. While the general cooling water bacterial population may be 10^3 colony forming units/mL (CFU/mL) or higher, it is rare for either of these groups to be higher than 10^1 CFU/mL. Given the difficulty culturing/measuring ammonia oxidising bacteria (AOB) or nitrite oxidising bacteria (NOB), their presence is normally monitored by trending nitrite/nitrate levels, acid consumption or cooling water alkalinity.

The standard treatment is targeted bromination, with the bromine:chlorine ratio increasing as the potential for AOB/NOB activity rises. While this treatment is effective, it does have the drawback of increasing the chlorides in the cooling water, which can work against water conservation efforts. Non-oxidising biocides can provide temporary relief, but they are seldom practical for longer-term control. Consequently, non-oxidising biocides are used in a secondary role.

Buckman's Oxamine chemistry is an excellent general microbicide and biofilm control agent, but its efficacy on AOB/NOB is not as strong as bromine. In Figure 6, one

Table 1. Each biocide type has limitations, meaning that each is not perfect in all circumstances			
Biocide	**Oxidising potential (mV)**	**Relative volatility (compared to HOCl)**	**Comments**
Chlorine dioxide	+1.71	788	Vapours more corrosive compared to chlorine. Precursors are highly dangerous and cost is high
Chlorine gas	+1.49 (HOCl)	1 (HOCl)	Risk of gas release has resulted in changeover to hypo. High dosage rates can depress the system pH
Chlorine + bromine	+1.33	0.4 (HOBr)	The standard for industry with ammonia and alkaline cooling water
Hypochlorite	+0.90 (OCl^-)	<1 (OCl^-)	Seldom used on its own, but normally combined with bromine
Monochloramine	0.75	7	Low usage rate and excellent for water conservation. Able to control microbes in moderate levels of ammonia ingress
Non-oxidisers	Not applicable	Not applicable	High cost and risk of immunity limits their use to upset conditions or for limited periods of time

Table 2. Comparison of biocide options for industrial applications										
Biocide	**Reactivity organics**	**NH_3 reactivity**	**H_2S reactivty**	**NH_3 bacteria control**	**Microbial tolerance**	**Biofilm removal**	**Stripping losses**	**Vapour phase corrosion**	**Chloride contribution**	**Hazard level**	**Use cost**
Chlorine dioxide	H	N	H	M	L	M	H	H	M	H	H
Chlorine gas	H	H	H	P	L	P	M	M	H	H	L
Chlorine + bromine	M	N	H	E	L	M	L	L	H	L	M
Hypochlorite	M	H	H	P	L	P	L	M	H	L	L
Monochloramine	L	N	H	M	L	E	M	L	L	L	M
Non-oxidisers	L	V	V	V	M	V	N	N	N	M	H
Legend	L = low; M = moderate; H = high; V = variable; N = nil; P = poor; E = excellent										

can see that when there are peaks in the cooling water ammonia, control of AOB is not complete.

At ammonia levels below 2 ppm, good control is provided by Oxamine. However, at high nutrient levels or excessive ammonia, supplemental microbial control is required. Use of non-oxidising biocides is one option, but field trials show that the persistence after a dosage is 5 – 10 days. This is an effective approach if the upset is of short duration (days to a few weeks). When the ammonia ingress is going to be elevated for longer periods (weeks to months) or occurs periodically, a combination program (oxamine and bromine) offers a number of benefits:

- Water conservation/chloride reduction – MCA will lower the cooling water chlorides by 50 – 70%. This will lower bleed-off and provide water savings of 10 – 20%.
- Lowered hypo consumption – this reduces shipping costs and the logistics of ensuring inventory.
- Lower biofilm levels – using MCA to remove biofilm keeps surfaces clean without the need for other biocides or chemicals.
- Minimises and in some cases eliminates non-oxidiser usage – by combining these two technologies, it is possible to have the advantages of both and non-oxidisers will be rarely needed.

Oxamine is formed in a proprietary generator that can be easily integrated into an existing hypo/bromine dosing system. The generator is designed to control the reaction conditions so that only MCA is generated. If hypochlorite and ammonia are reacted in a poorly controlled manner, one will get a mixture of different chloramines. The monochloramine is most efficient; the formation of other chloramines represents wasted hypochlorite. Strict control of the ratio of reactants and reaction conditions results in >95% conversion to MCA in the generator.

The installation of the Oxamine generator allows a plant to change between Oxamine and targeted bromination either manually or via an integrated suite of software controls. This allows for system optimisation across all key performance indicators (KPIs) locally or by remote control.

Summary

Microbial control in a high ammonia environment can be challenging, but by understanding the biocide options, it is possible to design a program that best suits a plant's needs. A blended MCA/bromine program builds upon the best attributes of both biocides to conserve water and protect the environment. WF