DARRELL HARTWICK, BUCKMAN, CANADA, AND MAZHAR S. WARSI, KHURRAM SHAHZAD AND MUHAMMAD AKHTAR GURMANI, BUCKMAN, SINGAPORE, EXAMINE MONOCHLORAMINE AS A TOOL FOR WATER CONSERVATION.

CONTROLLING WATER CONSUMPTION

Industrial plants are typically sited in locations that meet a number of parameters, such as proximity to markets, cost of raw materials, market demand/pricing and a suitable workforce, but seldom is the availability of water a major factor in these decisions. In reality, industrial plants are only one of several water consumers and frequently compete for available water supplies alongside human consumption and agriculture. Areas with limited fresh water heighten this competition and force non-conventional approaches to water conservation.

Balancing the needs of different water consumers is not unique to any one geography and examples can be found in the US and elsewhere. Title 22 water, or reclaimed sewage water, is mandated for industrial use in areas of California. This water, while treated, is still of lesser quality than fresh water as it contains amounts of chloride, organics and P higher than would be considered normal.

Australia has most of its population in regions that are water deficient and this has resulted in reclaimed water (treated sewage water) being used for water features and for agricultural use. The market garden area around Melbourne largely relies on reclaimed water for irrigation purposes, since the surface water supplies are not sufficient. A similar situation exists in Pakistan, where heavy industry water users face water restrictions and rely on surface and bore water for their plants.

It is worth noting that these limitations are not only in regions with little or no water, even areas with abundant water supplies are facing restrictions. In northern Alberta, Canada, for example, there is sufficient fresh water but oil extraction plants are prohibited from using fresh water. Instead they are required to use reclaimed water (separated from the oil/water mixture from oil wells) and brackish well waters. When these limitations are combined with the general trend in industry to minimise discharge back to the environment, impurities in the water will be concentrated to higher levels than in the past.

Cooling systems typically have only minimal pretreatment, which is designed to remove suspended solids but does not change the soluble ions that are present. In fact, some pretreatment, such as chlorination, actually increases the ionic loading as the chlorine (which is used to control microbial activity) is converted to the corrosive chloride anion.

Table 1. Oxidising potential of different biocides

Oxidant	mV potential
Chlorine dioxide (ClO_2)	+1.71
Hypochlorous acid (HOCl)	+1.49
Hypobromous acid (HOBr)	+1.33
Hypochlorite (OCl^-)	+0.90
Monochloramine (H_2NCl)	+0.75

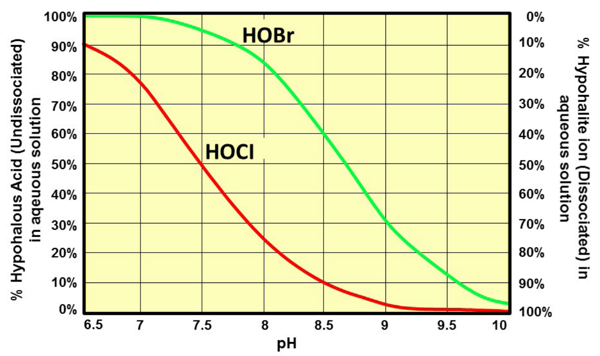

Figure 1. The disassociation of HOCl is more severely affected by pH than HOBr.[1]

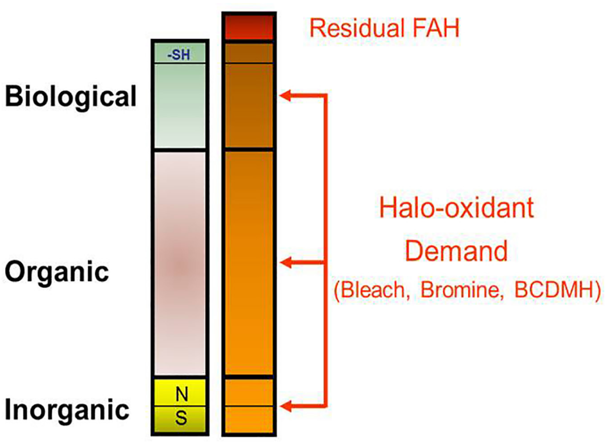

Figure 2. Before a residual can be established, it is necessary to satisfy all the demands that exist within the system.

Of particular importance is the presence of nutrients in the make-up water. Ions such as phosphate, nitrate and total organic carbon (TOC) will promote microbial activity and as conditions increasingly favour microbial activity, the greater the biocide demand will be.

Cooling systems share a lot of commonality with bioreactors, even though they are designed for very different functions. Though the fill in a cooling system is very similar to that found in bioreactors, the difference is that cooling water has lower levels of bioavailable carbon, which limits microbial activity. However, the lower bioavailable carbon may make fouling more severe since microbes respond by increasing the formation of extra-cellular polysaccharide (EPS) in an effort to trap more nutrients.

The equation shows the general process that occurs in any system where these conditions are met. Food is converted partially into carbon dioxide and new cells. What is not shown is the production of related organic material, EPS.

$$\text{Organic Carbon} + O_2 \xrightarrow[\text{Aerobic Bacteria}]{NH_3,\ PO_4} CO_2 + H_2O + \text{New Cells}$$

Carbonaceous bugs (oxidation)

Wastewater treatment plants target a ratio of 100:5:1 (C:N:P) and this provides a perspective on what can increase the potential for microbial activity in cooling systems. N can be in the form of nitrite (NO_2), nitrate (NO_3) or ammonia (NH_3), all of which are readily bioavailable for protein manufacture by microbes. Phosphorus in the form of orthophosphate (PO_4), whether it is from the cooling water programme or the make-up water, is the final component.

By having a system that is inherently similar to a bioreactor, deterioration of the water quality can lead to a higher microbial loading and this will result in:

- Corrosion: microbiologically influenced corrosion (MIC) can nullify even the best cooling water treatment programme.
- Fouling/deposition: in warmer, more tropical environments, controlling algae can be a problem both to prevent fouling and also since it can provide conditions that favour the development of pathogenic bacteria.
- Pathogenic organisms: it is well established that higher levels of general microbial activity can allow acceptable background levels of legionella to be amplified to quantities that pose a health risk.

Furthermore, as it becomes more difficult to maintain microbial control, the demand for oxidising and non-oxidising biocides increases. Non-oxidising biocides have both a cost and environmental footprint. Other impurities, such as chloride and sulfate, impact the inherent corrosivity of the water and make corrosion control more problematic. Chloride can come from the make-up water and from the use of chlorine or hypochlorite.

Consequently, lower quality waters and increased biocide demand, combined with plants wanting to operate for longer periods between turnaround, means that performance standards need to improve. All of these drivers are forcing innovation in cooling water treatment. Effective microbial control is, in effect, the cornerstone of cooling water treatment programmes as industrial plants respond to changes in their operating environment.

Microbial control

Biocide programmes typically employ chlorine or chlorine combined with bromine to provide broad spectrum microbial control. These biocides are nonspecific in terms of how they react, which allows them to kill bacteria, algae and fungi. However, the disadvantage of a strong oxidiser is its lack of specificity, meaning that its demand will be higher since it is consumed by a number of different substrates in cooling water, including:

- Microbes: these are the intended targets but in most systems they represent on the order of 10 – 20% of the total oxidant demand.
- Organics: this normally consumes 80% or more of the oxidant. These can be from the source water or biofilms that develop within the cooling system.
- Other: this captures contaminants such as ammonia (water or process leaks), sulfide (SRB bacteria or process leaks) or other process leaks.

Most cooling systems operate under alkaline pH conditions that degrade the efficacy of chlorine/hypochlorite. Regardless of whether a zinc/phosphate or an all-organic programme is used, the cooling water pH will be in the range of 8.0 – 8.9. At this pH, <20% of the chlorine will be present as the uncharged hypochlorous acid (HOCl) form (Figure 1).

While the OCl^- anion is able to damage the cell, its entry into the cell interior is inhibited by the net anionic charge on the cell wall. As a result, OCl^- is less effective compared to the uncharged HOCl. To offset this, sodium bromide is commonly used with chlorine in alkaline cooling waters.

The much higher level of the uncharged HOBr remains at a given pH, compared to chlorine, making it a better choice for alkaline cooling waters. Additionally, bromamines have effectively the same toxicity as HOBr, making this chemistry well-suited for use in fertilizer plants.

Chlorine dioxide (ClO_2) has been less successful due to issues surrounding its generation and its much higher stripping rate over cooling towers.[2] The net result is that ClO_2 is more costly to use (stripping and oxidative demand) and more hazardous (chlorite and chlorate precursors are extreme fire hazards). Consequently, ClO_2 does not occupy as significant a role as a microbicide in cooling systems. A further drawback with chlorine dioxide is its high oxidation potential, causing it to be less selective in its reactions.

To improve the performance of the oxidising biocide, some type of non-oxidising biocide or biodispersant is used. Chlorine will penetrate biofilm, but does so very ineffectively since it has a greater tendency to react with the biofilm before it has an opportunity to reach the microbes in the biofilm. The most effective are biodispersants that can disrupt biofilm and provide better contact of the oxidising biocide with bacteria in it. The more effective types of biodispersants are those that use alkyl dimethyl amides.

Buckman's Oxamine® chemistry is based upon monochloramine (MCA), and it is unique in that it does not suffer from many of the limitations of other oxidising biocides.

Being a weak oxidant, Oxamine requires more time to provide an acceptable kill; however, its persistence offsets the lower oxidative power. The unique aspect of monochloramine is its selectivity as an oxidant and how it preferentially reacts with selected regions of proteins. This selectivity is why system demand for Oxamine is dramatically

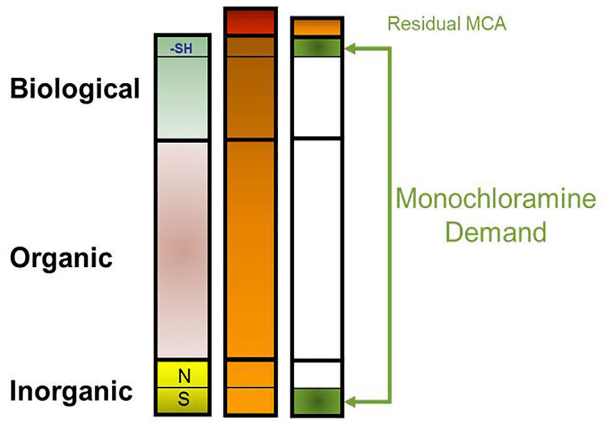

Figure 3. With Oxamine, the consumption of biocide is much less since there are fewer substrates that will react with it.

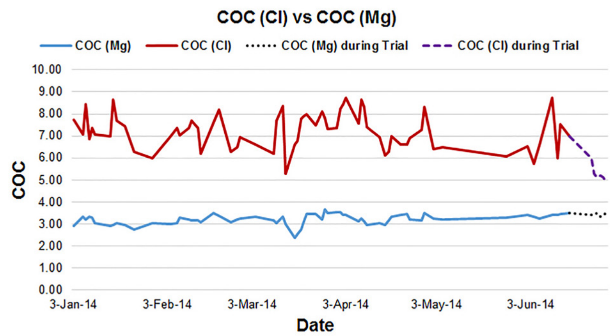

Figure 4. After the Oxamine feed was started, the chloride levels in the cooling water declined and more closely matched the cycles based upon magnesium.

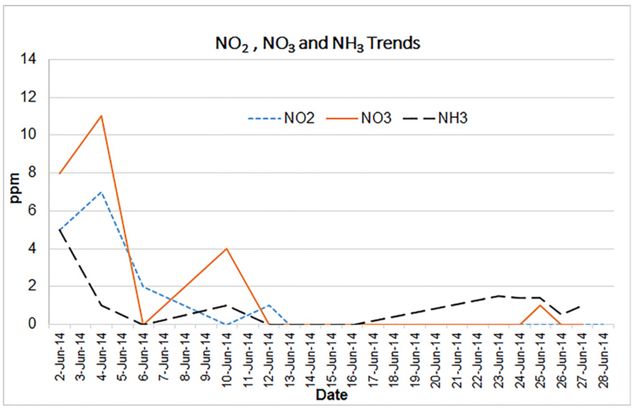

Figure 5. Microbial control was excellent with Oxamine.

less than for other oxidisers. In other words, MCA does not interact with the mass of biological material in a system. In effect, it damages proteins that allow a microbe to function, without being consumed by materials that do not affect cell viability. This targeted action allows for a lower overall biocide feedrate without sacrificing control.

This selectivity manifests itself in the lowered oxidant demand. Figures 2 and 3 illustrate the 'sinks' that contribute to the system demand for oxidants.

The overall effect 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 have a small positive residual. This dramatic lowering of oxidant demand makes monochloramine a very attractive biocide for high demand cooling water applications.

A major benefit of using Oxamine is that since it is an uncharged ion and a weak oxidiser, it has the potential to more readily penetrate biofilm and affect organisms embedded in it. Once these are killed the integrity of the biofilm is degraded and it strips from surfaces.

Increasingly plants are facing regulatory limits on the discharge of halogenated organics, such as adsorbable organic halogens (AOX) and trihalomethane (THM). Being a very weak oxidant, Oxamine will not form as many halogenated organics as chlorine and bromine. This is particularly beneficial in waters with high organic loadings. Since monochloramine may not generate as many chlorinated organics, it lessens the environmental impact.[3]

Fertilizer industry

Initially, Oxamine was used by Buckman in water treatment in the paper industry where the very high organic loadings made microbial control challenging with non-oxidising biocides and virtually impossible with oxidisers. As Oxamine is a weak oxidiser, it was able to selectively control microbes where other chemistries were not effective or were not cost-effective.

Water treatment in the fertilizer industry was a logical extension for this technology since Oxamine offers benefits that match plant needs. Ammonia/urea plants are relatively uniform in their design and consequently share similar limitations across different plants, including:

- Ingress of ammonia: either from the atmosphere or via exchanger leaks, results in ammonia being present in the cooling water on a regular basis.
- Oxidising bacteria: both ammonia oxidisers and nitrite oxidisers will convert the alkaline ammonia to nitrous or nitric acid. These acids can lower the cooling water pH to harmful levels.
- Orthophosphate: in integrated plants the migration of phosphate and/or phosphate rock dust into the cooling system will further enhance microbial activity. Cooling water treatment can also contribute phosphate.
- Metallurgy: the extensive use of SS304 in heat exchangers means that plants can be restricted on the level of chlorides that they can tolerate. This can lead to higher water consumption.
- 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 adds both and is a significant contributor.
- Supplemental non-oxidising biocides: use of these increases the environmental footprint of the plant and costs.

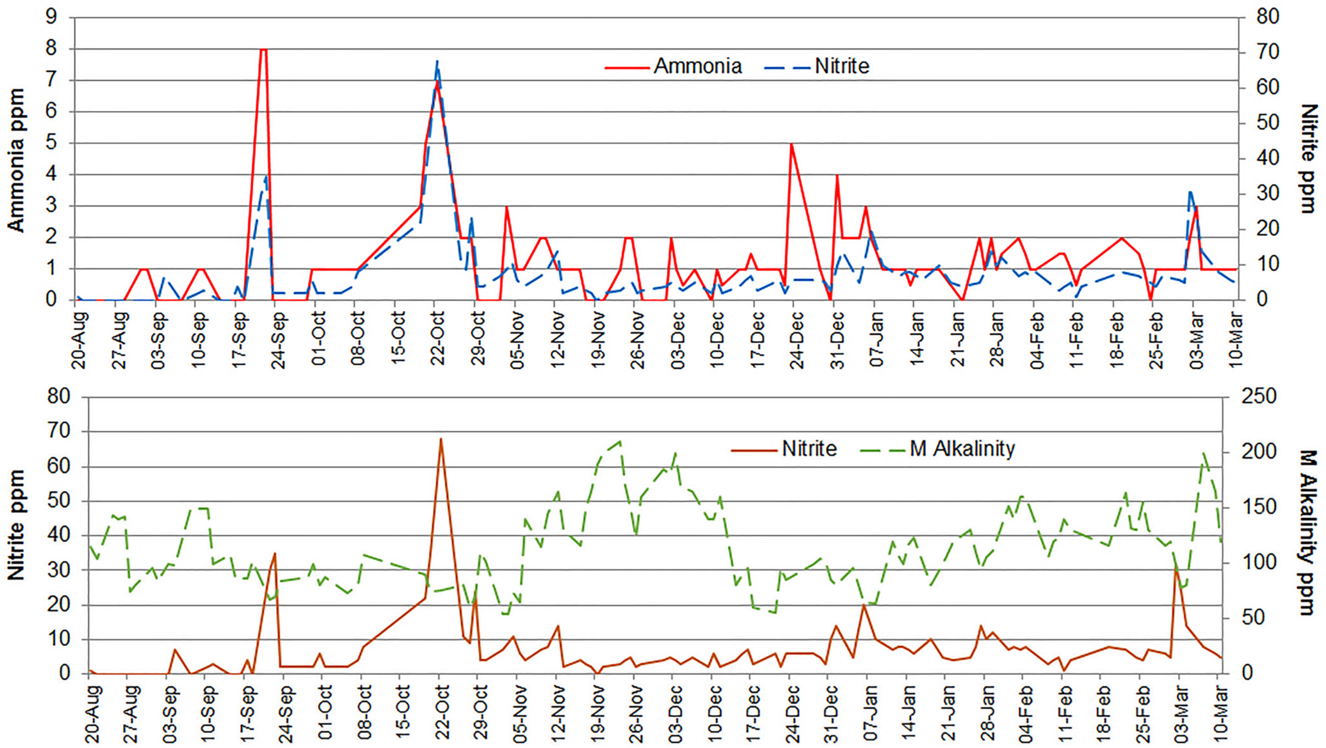

Figure 6. These results cover the time up to March 2016. They show that when there are peaks in ammonia, nitrite increases and then recovers quickly. In the top graph, the overall control of the M alkalinity has been good.

In addition to broad spectrum and cost-effective microbial control, Oxamine allows water conservation as it minimises the contribution of chloride.

Since most urea plants have large numbers of 304 grade (S30400) stainless steel tubed heat exchangers, the limits on cooling water chlorides are dictated by them. While there is variation in the limits that different plants use, the following are Buckman's recommended ranges to avoid stress corrosion cracking damage, (FAH = free available halogen):

- 304/304L – 175 – 200 ppm chloride (at 60°C) and FAH ‹0.5 ppm.
- 316/316L – 300 – 400 ppm chloride (at 60°C) and FAH ‹0.5 ppm.

Hypochlorite (or chlorine gas) will contribute at least 50% of the chloride found in the cooling water. As a result, the biocide has a major impact on the allowable cycles of concentration and, consequently, the water usage. Lowering the chloride level in the cooling water improves both water conservation and flexibility on water being used for irrigation.

Equipment

A proprietary Oxamine generator was installed to feed the cooling water system of a 1500 tpd ammonia/urea plant in central Pakistan. This system had a recirculation rate of 48 000 m^3/hr and a volume of 20 000 m^3, making it a good test site. The generator was unique in that it was designed to control the reaction conditions so that only monochloramine was generated. If hypochlorite and ammonia are reacted in a poorly controlled manner, a mixture of different chloramines is formed.

$HOCl + NH_3 \rightarrow NH_2Cl$ (monochloramine) + H_2O
$HOCl + NH_2Cl \rightarrow NHCl_2$ (dichloramine) + H_2O
$HOCl + NHCl_2 \rightarrow NCl_3$ (trichloramine) + H_2O

The strict control of the ratio of reactants and reaction conditions resulted in ›95% conversion to MCA in the generator and this minimised the wastage of the precursors. It was then carried to the cooling tower in dilution water, which moved it quickly to the application point and also ensured a consistent strength going to the tower.

The generation of MCA is exothermic and, without proper engineering safeguards built into the system, it is possible to damage the equipment and/or have an accidental release of fumes. The generator comes with an integrated suite of monitoring and reporting sensors. These sensors/controls serve to ensure that the precursors (sodium hypochlorite and ammonium donor solution) are mixed at the correct ratio, that the dilution water and pH values are correct and that safe temperature limits are not exceeded.

The Oxamine generator at this site was activated and has been in use for more than 20 months. The operating environment was very challenging with summer temperatures reaching the mid to high 40°C range. The unit was located outside, where it is exposed to the ambient conditions. Despite this, the generator has worked in temperatures ranging from 10°C to ›45°C and has proven reliable under these conditions.

Results and discussion

While Oxamine has been widely used on over 300 applications, the first major industrial application selected in Asia was a fertilizer plant cooling water system. There were three key performance indicators (KPIs) used to evaluate the technology:

- Chloride reduction: the plant was limited on cycles of concentration by the chloride level in the cooling water. The chloride comes both from the make-up water and also from the hypo fed as a biocide. The target was to lower the level of chloride in the cooling water by 60%, which would result in less bleed-off and save water.
- Microbial count: maintaining the current standard for microbial control without the need for additional biocides was a requirement. The target value was ‹104 CFU/mL.
- Ammonia converting bacteria: since this was an ammonia/urea fertilizer plant, there were always trace levels of ammonia in the cooling water. Nitrite and nitrate are markers that give an indication of microbial control. The target was to maintain the current metric of NO_2/NO_3 ‹10 ppm.

The biocide programme before Oxamine was a combination of sodium hypochlorite, sodium bromide and the periodic addition of a non-oxidising biocide.

While maintaining microbial control was critical so that there was no fouling of heat exchangers (HX), water conservation was the priority. The plant had a large number of HXs with 304 grade stainless steel tubes and their internal standard was to limit the cooling water chloride level to less

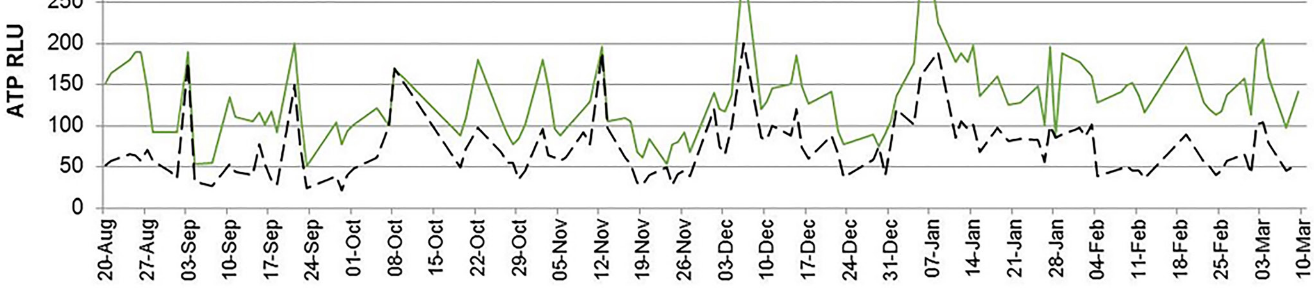

Figure 7. This graph covers the period up to March 2016 and shows the drop in ATP after the dosing of Oxamine.

than 200 ppm to prevent attack (SCC). This limit restricted the cycles of concentration to well below what it would be if normal control parameters were used.

Between 60 – 100 ppm of the chloride in the cooling water came from the hypochlorite feed. In order to minimise the amount of chloride, hypochlorite was only fed at night for six hours per day. In plants with continuous hypochlorite feed, the chloride contribution as a percentage of the total chloride content would be higher.

Using Oxamine caused the amount of chloride from the biocide to fall by more than 40% to 30 – 40 ppm in the cooling water. In Figure 4, the cycles based upon magnesium indicate what the actual cycles are and the ones using chloride gives a false high value due to the biocide contribution. As the amount of chloride from the biocide goes down, one would expect the two curves to converge, which is exactly what occurred with Oxamine. Figure 5 shows that the trend for nitrite/nitrate declined after the change to Oxamine which confirmed that microbial control has been good. Plate counts were consistently at $\leq 10^3$ CFU/mL.

This trial was initiated in 2014 and the results have continued to be quite consistent. Figure 6 shows more recent results and they are in line with the initial data. During periods when ammonia levels were moderately elevated in the cooling water, the dosage of Oxamine was not changed. Despite this, the biocide was able to rapidly re-establish control as soon as the ammonia fell. The pattern shown in Figure 6 is comparable to what was seen when using hypochlorite and bromide.

In Figure 7, the total ATP before and after dosing Oxamine confirms that there was a reduction in microbial activity. This graph actually understates the biocidal effect since it reports the total ATP and not just cellular ATP. A considerable portion of the ATP that is still present after the dosing is actually 'free' or non-cellular ATP that has not had time to degrade. It is not uncommon to see a lag of several hours before non-cellular ATP begins to degrade and disappear.

If only cellular ATP was reported, the spread between the two would be wider; however, even with this constraint it is clear that monochloramine reduces ATP values in the cooling water.

Conclusion

The initial trial of Oxamine at this ammonia/urea plant in Pakistan commenced in 2014 and the plant continues to use it in this cooling system. Based upon the trial results, the plant has permanently converted from hypochlorite/bromide to Oxamine on this cooling tower. After assessing the performance on the one cooling system, the plant operators decided to convert a second large open recirculating cooling loop to Oxamine. The benefits achieved using Oxamine chemistry at this plant were:

- Chloride reduction: by reducing the amount of chloride contributed to the cooling water (compared to sodium hypochlorite), the cycles of concentration can be increased without exceeding limits imposed by system metallurgy.
- Water conservation: the higher cycles of concentration resulted in a 16% reduction in water used by the cooling tower system. This was a dramatic saving for the plant.
- Microbial control: by providing a level of microbial control that was comparable to hypochlorite, the plant was able to minimise the use of other microbicides on a regular basis. This lowered the cost and helped lessen the environmental impact.
- Transportation costs: since the hypochlorite requirements dropped, this saved costs related to both buying it and shipping it to the site.
- Chemical savings: dosage rate for corrosion and scale inhibitors went down as the cycles of concentration increased. This provided an additional savings to the plant.

In addition to the obvious return on investment drivers, there are the less tangible return on environment advantages that accrue with using Oxamine. Cutting hypochlorite usage by 50% means that fewer truckloads are shipped to the plant and this lowers CO_2 emissions.

The hypochlorite savings experienced at this plant are not unique and have occurred at other locations. At a second Pakistani fertilizer plant that converted to Oxamine, the hypochlorite consumption fell from 3000 kg/day to only 500 kg/day. As one would expect, the chlorides added to the cooling water from the biocide went from 75 ppm to 15 ppm, which had a positive effect on water conservation.

While the reduction in hypochlorite will vary, it is large enough to have an impact on the overall economics, both from the water conservation perspective as well as the cost of the hypochlorite itself. Incremental savings related to the size of bulk storage for hypochlorite or improved ease of inventory management, while not large, are nonetheless positive outcomes.

As noted earlier, water supplies in this region have appreciable levels of organics, and trace amounts of chlorinated organics will be formed with conventional oxidising biocides. Oxamine can reduce the potential for forming chlorinated organics, which are harmful to the environment. This lowers the environmental footprint of the plant and improves the health of the environment, compared to chlorine.

The environmental conditions for the equipment at the Pakistani sites are much harsher than would be experienced in North America. In spite of that, the Oxamine generators have displayed excellent reliability. They have also shown a very high selectivity for producing only monochloramine and not di or trichloramine.

Buckman's Oxamine chemistry based on monochloramine is unique in offering a combination of improved biocidal effects, reduced environmental impact and favourable economics. Its production with a proprietary generator is efficient and highly selective. Oxamine can be fitted into large industrial cooling systems where there is a desire to lower water consumption or with waters that have appreciable amounts of organics present. WF

References

1. SERGENT, R. H., 'Enhanced Water Management Using Bromine Chemistry', CTI, Technical Paper Number TP-86-9 (1986).
2. MCCOY, W., BLATCHLEY, E., & JOHNSON, R., 'Hypohalous Acid and Haloamine Flashoff in Industrial Evaporative Cooling Systems', CTI, Technical Paper Number TP-90-09 (1990).
3. EMMERT, G., L, Department of Chemistry, The University of Memphis, Internal Report (2010).