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Alternative chemistry for cooling water formulation

Colin Hogan and **Peter DeMartine** of **BWA Water Additives** discuss new multi-functional chemistry to reduce cooling water treatment costs

The industrial water treatment industry consists of formulators and service companies working together to meet the needs of end users. Formulators typically offer customised speciality chemicals to service companies to help them address a variety of industrial cooling waters and operating conditions encountered across the very different end markets of commercial and institutional buildings or light manufacturing (the middle market) and heavy industries, like steel manufacturing or power generation.

Service companies often develop a myriad of complex formulations to meet each unique cooling water treatment (CWT) scenario. Factors such as the hardness, alkalinity and pH of the cooling water drive decisions on what type of CWT formulation should be developed and applied.

The typical CWT regime uses a biocide programme for microbiological control that is dosed separately from the combined corrosion and/or scale inhibitor programme. The latter is often a complex formulation based on multiple components, such as phosphates or another corrosion control chemistry, as well as sulfonated and non-sulfonated polymers and/or phosphonates for scale inhibition.

CWT challenges

Maintaining many highly customised complex CWT formulations in a service company's product line presents challenges. Inventorying a multitude of components can increase working capital. Managing many different SKUs of the formulations also adds cost and works against classic best practices in product rationalisation. Service companies saddled with such costs and complexity often have difficulty keeping up with evolving customer needs.

For example, many end users have become more concerned with or even required to minimise the environmental impact of their facility's wastewater discharges. One culprit here is often cooling tower blow-down, which carries with it CWT chemicals that commonly contain phosphorus and nitrogen. When these nutrients are added in excess to natural waters, it can stimulate eutrophication, or the depletion of oxygen levels in water, which negatively impacts aquatic plant and animal life.

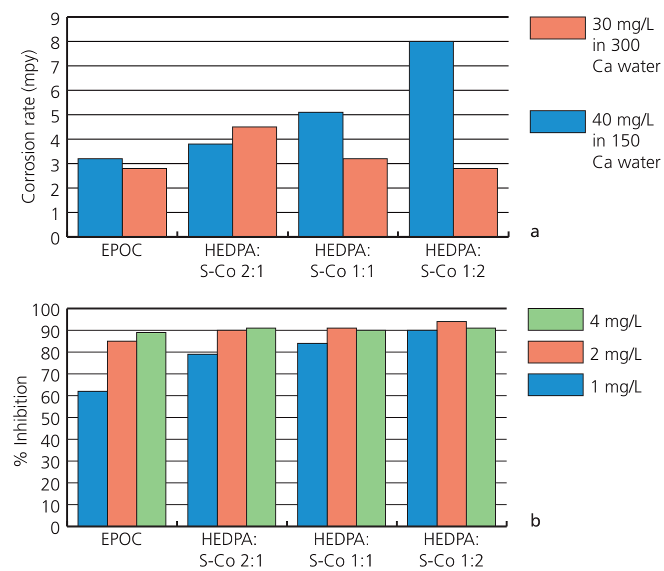


Figure 2 - Corrosion inhibitor (a) & calcium carbonates inhibition (b) comparison: EPOC v. HEDPA/S-Co Formulations

BWA Water Additives saw this challenge as an opportunity. R&D chemists at the company's technology centre in Manchester, UK, collaborated on ideas to develop multi-functional chemistries that could reduce CWT formulation costs, while simultaneously improving corrosion control and scale inhibition performance. Such chemistries should also ideally be free of both phosphorus and nitrogen, thus satisfying the environmental concerns of many end users.

The resulting product, Belcor 585, is an enhanced phosphonocarboxylate (EPOC) with inherent multi-functional behaviours. It is a robust corrosion control chemistry that also has strong scale inhibition tendencies, a dual behaviour that is uncommon to typical corrosion control chemistries.

The EPOC chemistry is very effective on waters with Langelier Saturation Indices (LSIs) in the 1.2-2.0 range, which are usually classified as 'medium to hard' and thus tend to be treated with more complex, costly formulations. (The LSI is a calculated number used to predict the calcium carbonate stability of water; it indicates whether the water will precipitate, dissolve or be in equilibrium with calcium carbonate.) The average savings of switching from the typical formulation to an EPOC-based formulation in these waters is 20%.

Corrosion inhibition

Tests were conducted to demonstrate how EPOC scale and corrosion inhibition performance compares with widely used additives like hydroxyphosphono acetic acid (HPA), 1-hydroxyethylidene-1,1-diphosphonic acid (HEDPA) and phosphono polymaleic acid (PPMA).

In a rotating coupon test, a direct comparison of EPOC with PPMA and HPA was made using mill-finished, pre-cleaned and weighed mild steel coupons, rotated in aerated synthetic water for 42 hours. Performance comparison with formulated HEDPA and sulfonated copolymer (S-Co) were conducted with beaded finished coupons, using the same testing process and water chemistries.

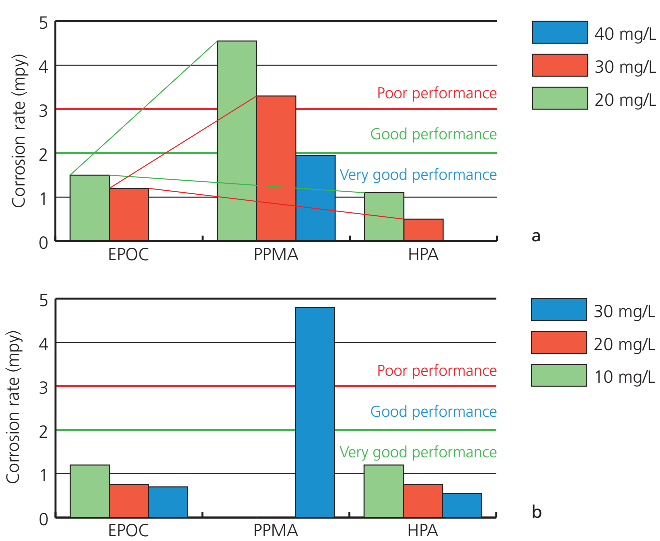


Figure 1 - Corrosion tests in 150 (a) & 300 mg/litre water, comparing EPOC, PPMA & HPA

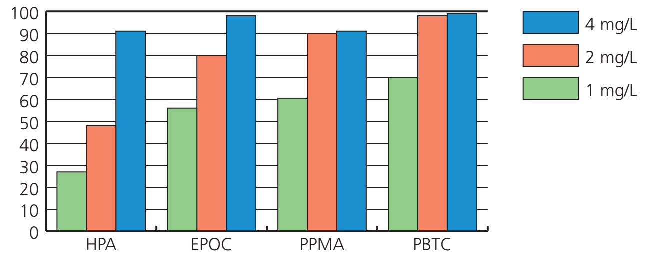


Figure 3 - Calcium carbonate inhibition of HPA, EPOC, PPMA & PBTC

To demonstrate the corrosion inhibition performance of EPOC, it was evaluated in both 150 and 300 mg/litre calcium waters at 10, 20 and 30 mg/litre solids. Blank corrosion rates for these two waters were 1.78 mm/y (70 mpy) and 0.53 mm/y (21 mpy) respectively. EPOC gave good corrosion rates at each dose level.

In 300 mg/litre calcium water, rates were 1.17 mpy (0.0297 mm/y), 0.75 mpy (0.019 mm/y) and 0.69 mpy (0.017 mm/y) at dose levels of 10, 20 and 30 mg/litre solids respectively. The results in the 150 mg/litre calcium water were particularly significant, given the corrosive nature of this water. Corrosion rates of 0.037 mm/y (1.46 mpy) and 0.0292 mm/y (1.15 mpy) were achieved at 20 and 30 mg/litre solids, respectively.

Figure 1 compares the performance of EPOC with PPMA and HPA. In 150 mg/litre calcium water, PPMA only achieved a good rating at the 40 mg/litre solids dose level, whereas both EPOC and HPA provided equivalent results at 20 mg/litre. This clearly demonstrates that EPOC can outperform PPMA. In 300 mg/litre calcium water, EPOC and HPA achieved equivalent corrosion inhibition, but PPMA demonstrated unacceptable performance even when dosed at high levels (30 mg/litre solids).

Figure 2 compares the performance of EPOC versus formulations of HEDPA and S-Co, again in both 150 and 300 mg/litre calcium waters. These tests used beaded finish coupons, for which blank corrosion rates were measured at 0.874 mm/yr (34.4 mpy) and 0.523 mm/yr (20.58 mpy) respectively.

The increasing corrosion rate with decreasing HEDPA formulation component in the more aggressive 150 mg/litre calcium water was expected, given the corrosivity of this water. The opposite trend was apparent in the higher calcium water, where an increasing polymer formulation component favours a lower corrosion rate. Corrosion rates with EPOC were significantly better with all three formulations in both waters.

Scale inhibition

The calcium carbonate jar test, which represents a cooling water situation under high temperature conditions that would be similar to a heat exchanger, is used to measure an additive's ability to inhibit the precipitation of calcium carbonate. Air bubbling is used to facilitate CO_2 loss, which moves the equilibrium towards carbonate formation, thereby increasing the test severity. The higher the amount of calcium retained in solution, the greater the scale inhibition properties of the additive.

In this accelerated test, phosphono butane tricarboxylic acid (PBTC), a commonly used scale inhibitor, was included as a benchmark to assess the other additives. PPMA was found to provide adequate scale inhibition, but at a dose of 4 mg/litre solids it performs poorly compared to either PBTC or EPOC.

It is well-known that, whilst HPA is an excellent corrosion inhibitor, it is only a mediocre scale inhibitor, barely reaching 90% inhibition at 4 mg/litre at best. By contrast (Figure 3), EPOC showed improved performance, giving 100% inhibition at 4 mg/litre, which clearly demonstrated its multi-functionality as both a scale and a corrosion inhibitor. It effectively matched the performance of PBTC.

Figure 2b compares the performance of EPOC versus formulations of HEDPA and S-Co in the same test. At the lowest dose level of 1 mg/litre, EPOC calcite inhibition performance was recorded at a modest 60% compared to the HEDP and S-Co formulations. However, at ≥2 mg/litre, EPOC exhibited equivalent performance compared to all three formulation types. This again demonstrates its dual scale and corrosion inhibition functionality.

Chlorine stability

In a CWT formulation, chlorine stability is an important factor in the selection of an additive. It is essential for the formulator to know that the chemistry will withstand oxidising biocides. The chlorine stability test provides the amount of chloride consumption of the additive, which is expressed as a percentage of the blank.

In the chlorine stability test, PPMA was clearly the most resistant to halogen attack, with 94% chlorine remaining after the five-hour test period. HPA was the least tolerant, with only 79% left. By contrast, with EPOC an intermediate amount of halogen, 89%, was left. Therefore, EPOC halogen stability is not an issue for the same reason that allows HPA to be used in conjunction with oxidising biocides.

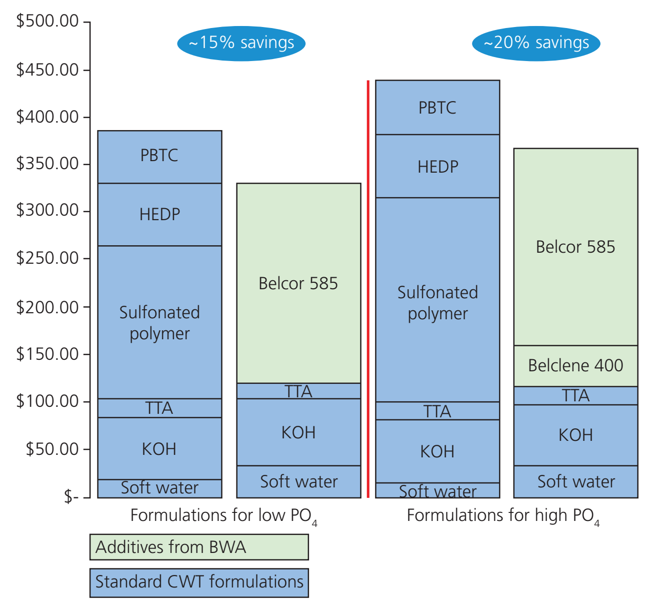
Although HPA can be degraded in the bulk cooling water by halogen-releasing biocides, the degree of breakdown is mediated by variables like the amount of halogen in the water, the residence (contact) time, water temperature and amount of transition metals present. However, once HPA reacts with either calcium or iron at the metal surface and forms a corrosion-inhibiting film, it is significantly more resistant to halogen oxidation.

In other words, once HPA forms a film on the metal surface, it is not particularly susceptible to either chlorine or bromine. This is why when HPA is used, even in systems that employ oxidising biocides, improved corrosion rates are noted.

Although the work has not been completed with EPOC, it is expected that the same performance would be observed. Since HPA can be effectively used in systems that employ oxidising biocides and has already found widespread adoption in cooling waters, EPOC is expected to be a much improved additive.

Cost reduction

The components of a cooling water formulation can be assembled in many combinations, based on the knowledge and experience of the water treater. In a low phosphorus application, replacing PBTC, HEDP and sulfonated polymer with Belcor 585 can reduce finished product costs by 15%. In a high phosphorus application, Belcor 585, along with Belclene 400, replaces the PBTC, HEDP and sulfonated polymer to provide approximately 20% reduction in finished product costs (Figure 4).



Note - TTA = tolyltriazole, KOH = potassium hydroxide

Figure 4 - Finished product cost comparison of traditional CWT formulations vs formulations simplified with additives from BWA

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