Originally appeared in:
October 2020, pgs 37-39.
Used with permission.
HYDROCARBON PROCESSING®

HP Special Focus | Plant Safety and Environment

R. RUITENBERG, Nalco Water, an Ecolab company, Sugar Land, Texas

Protect your assets and our environment

Process cooling usually comprises the largest part of the water footprint of a refinery or petrochemical plant. Typically, most treatment programs contain phosphate (PO_4) and zinc (Zn) as key components in corrosion control to protect assets. These inorganic phosphates-based programs raise concerns of eutrophication in sensitive water bodies receiving the cooling water blowdown. Although surface run-off and sewage disposal are the main sources of eutrophication,[1] legislation on discharge of nutrients is tightening. Similarly, the use of zinc is restricted in some regions, and industrial producers have begun to seek more environmentally friendly treatment solutions to comply with the changing legislations.

This article describes a series of innovations tailored to regionally specific water qualities and discharge limits developed by the author's company to deliver on both the environmental and performance goals. Examples in industrial cooling systems are given to highlight that environmental protection and cost control are not necessarily mutually exclusive.

Traditional Zn- and PO_4-based cooling water treatment. Common examples of Zn- and phosphate-containing chemistries in cooling treatment have become the industry standard after chromates were phased out due to their toxicity. These standards include:

- Zn as cationic corrosion inhibitor component
- Ortho-phosphates, or poly-phosphates as key anodic corrosion inhibition actives
- Phosphonates in all-organic programs, degrading to phosphate.

Global legislation has tightened significantly to protect sensitive water bodies and drinking water resources. The main challenges associated with phosphate are not only eutrophication and associated algal blooms, but (tricalcium) phosphate scaling potential at high heat flux and control issues from variable background in the makeup. The high variability is sometimes seasonal or can come from recycled wastewater.

Traditional, organic-based, non-phosphorous (P)/low-P treatment programs have limitations, particularly if process control is not stringent.[2] Mild steel corrosion protection is challenging in high-stress water containing high chlorides and sulfates, and soft water with low hardness to aid inhibition mechanisms and low buffering. The long holding time index (HTI) at high cycles can increase the risk of tricalcium phosphate scaling.

Low-P, low-Zn (< 1 ppm limit each) cooling treatment of RO desalinated seawater. Reverse osmosis (RO) desalinated seawater is extremely corrosive due to a lack of buffer capacity and protective calcium ions, while the concentration of the aggressive chloride ion is relatively high. Localized corrosion can lead to process leaks and elevated maintenance costs if the water chemistry is not controlled carefully in the operating window.

A large petrochemical complex in Saudi Arabia suffered from severe localized corrosion and fouling due to lime deposition in the cooling system running on desalinated water (**FIG. 1**). This led to frequent shutdowns for re-tubing and reduced heat exchanger lifespan. The annualized cost of corrosion is estimated at $2.6 MM in maintenance alone. These systems were being treated by a competitor using calcium remineralization through lime addition and a Zn phosphate program. This treatment was not meeting the effluent limits on zinc and total phosphorous.

The author's company has established the optimal treatment window for RO desalinated water via bench-top and pilot cooling tower testing,[3] using dual cathodic inhibition utilizing the synergies between low levels of Zn and a proprietary, phosphorous-based inhibitor (phosphoric oligomer).[a] Additional research was conducted to arrive at the required low-P, low-Zn solution for this specific customer. Corrosion inhibition chemistry, as well as the operating window, is controlled to permit limit through a proprietary and advanced water performance system.[b]

The synergistic effects of low Zn and PSO dual-cathodic inhibitor (DCI), combined with best-in-class dispersancy under tag polymer control, ensured maximal availability of the inhibitor chemistry (**TABLE 1**). It provided excellent protection against general and pitting corrosion in desalinated water without the need for calcium re-mineralization. Target (general) mild steel (MS) corrosion rates of 4 mpy (mils/yr) were

FIG. 1. Fouling and under-deposit corrosion leading to premature bundle replacement.

achieved throughout (**FIG. 2**), while in full-scale optimization the average corrosion rate was below 2 mpy.

Suspended solids and turbidity values have dropped dramatically, as lime slurry was no longer dosed. The improved pH control and resulting drop in turbidity (15 ppm TTS down to below 2 ppm) voids the need to invest in side-stream filtration ($400,000).

The total Zn limit in the blowdown was consistently < 1 ppm. However, the tagged polymer, designed to maintain phosphate in solution, was re-dissolving the calcium phosphate deposits that had been built up in the system. The program was adjusted accordingly so that the effluent limit was reached over time.

The benefits of moving away from breaching effluent limits without achieving corrosion targets are significantly reduced maintenance cost, less production loss due to maintenance, and lower compliance costs, as shown in **TABLE 2.** The frequency of re-tubing and re-bundling was excessively high, with heat exchanger lifespan being much lower than the benchmark, incurring $1.7 MM in excessive maintenance costs.[4]

TABLE 1. Before and after: Competitor treatment vs. DCI program

KPI	Before	Target/limit	Author's company
pH control	Poor	Tight	Tight
TSS	15 mg/l	15 mg/l	< 1.5 mg/l
MS corrosion	6.6 mpy	4 mpy	1.8 mpy
Pitting corrosion	Severe	Low	Low
Free chlorine	0 mg/l	0.2 mg/l	0.2 mg/l
Bacterial counts	10^5 TVC/ml	10^3 TVC/ml	10^3 TVC/ml
Chloride	60 mg/l	40 mg/l	40 mg/l
Dissolved iron	2 mg/l	3.5 mg/l	0.1 mg/l
Effluent P	2.6 mg/l	1.0 mg/l	< 1 mg/l
Effluent Zn	1.8 mg/l	1.0 mg/l	< 1 mg/l

TABLE 2. Benefits of tailored treatment

Result	Impact
Pitting stopped, corrosion halved	$1.7 MM/yr maintenance cost savings
pH control lowering TSS discharge	Avoided $400,000 investment in side-stream filtration
Meet Zn and P limits, reduce analyticals	Avoided $500,000 in fines and analytical costs

TABLE 3. Water characteristics

Cooling water	Value
Effluent P-limit	< 0.5 ppm P
Chlorides	300 ppm Cl
MU Ca hardness	20–25 ppm $CaCO_3$
Low alkalinity in MU	30–35 ppm $CaCO_3$
Silica scaling risk	115 ppm SiO_2
Holding time index	> 200 hr
Alternating source	Fluctuations

TABLE 4. Novel no-PO_4, no-zinc treatment results

Characteristics	Remarks/results
Makeup source	City water, dissolved Al
Inorganic phosphate	84% reduction
MS coupon corrosion	70% reduction; ~1 mpy
Tower fill and tube replacement	Back to normal intervals (5 yr–7 yr)
Asset protection	Improved heat transfer and production security

No-P, low-Zn in soft cooling water.

A major petrochemical and refining corporation in China sought to improve its cooling water treatment both to comply with the Total P legislation (< 0.5 ppm P as total phosphate) and achieve better corrosion results. With the makeup source alternating between river water and soft ground water with high chlorides, the corrosion rates were causing lower lifespan of assets and high maintenance costs (**TABLE 3**). A low-P treatment program had been used since the plant commenced operation. The high

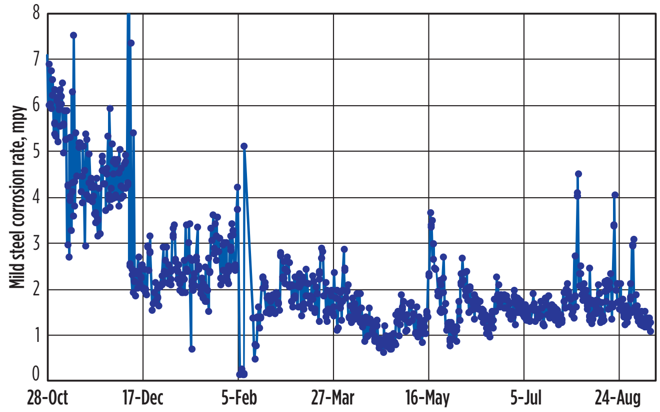

FIG. 2. Mild steel corrosion rate improvement with new program, with a target of < 4 mpy.

FIG. 3. MS coupons before (top) and after.

chlorides and high HTI compromised the robustness of this treatment program. The novel non-P program addresses these challenges through:[5]

- Scale inhibition and dispersion
- Corrosion protection and inhibitor stabilization.

The synergistic effect incorporates improved corrosion control, extending the application window to more corrosive water matrices, such as soft water and high-chloride/high-sulfate water. Since beginning the new non-P program, the mild steel corrosion rates have been much improved in corrosion coupons (**FIG. 3**). Online probe readings on the controller fell from 1.9 mpy to 0.6 mpy.

With the new, non-phosphorus treatment program, the plant:

- Lowered maintenance costs and extended asset life
- Reduced wastewater treatment cost by $480,000
- Complied fully with the total phosphorus discharge limits.

No PO_4, no Zn in city water cooling tower. Cooling systems running on city water experienced severe scaling due to high dissolved aluminum from algae control. Aluminium phosphate was formed, depleting the corrosion inhibitor and causing high mild steel corrosion rates of > 3 mpy. With Zn prohibited onsite, removing the ortho-phosphate from the treatment program required an alternative cathodic corrosion inhibitor. Pilot cooling tower testing was conducted to tailor a treatment program without inorganic phosphate to the challenging water chemistry. The resulting innovative, no-PO4, no-Zn cooling water treatment program significantly reduced scaling and discharge of phosphate, lowering corrosion and protecting both the operating assets and the environment, as shown in **TABLE 4.**

Takeaway. Innovations tailoring the corrosion control treatment to local regulatory requirements have led to a large improvement in both corrosion control and effluent quality, showing that protecting the environment can coincide with reductions in total cost of operation. Besides chemical innovation, control and data management are key to deliver these results. HP

NOTES

[a] Nalco Water Research's PSO
[b] 3D TRASAR™ technology

LITERATURE CITED

1. Chislock, M. F., *et al.*, "Eutrophication: Causes, consequences and controls in aquatic ecosystems," *Nature Education Knowledge,* 2013.
2. Townsend, G., *et al.*, "Corrosion challenges of desalinated water as cooling tower make-up under control with dual cathodic inhibition," MECC Bahrain, February 8–11, 2016.
3. Gilbert-Oriol, G, *et al.*, "Wastewater reuse for industrial applications in cooling towers," EMCHIE 2015, Tarragona, Spain, June 10–12, 2015.
4. Private communication with plant maintenance manager.
5. Xie, Y., *et al.*, "A novel non-phosphorous cooling water treatment program with robust scaling and corrosion control," NACE Corrosion 2019, Nashville, Tennessee, March 24–28, 2019.

RENATE RUITENBERG is a Senior Marketing Manager with Nalco Water focusing on global water treatment innovation for the refinery and petrochemical industries. Ms. Ruitenberg received her MSc degree in engineering from the Delft University of Technology in The Netherlands. After 20 yr in industrial water treatment, she drives innovations with passion and vision.