

# corrosion protection by CHO inhibitors used in E.C.O.Film\* technology

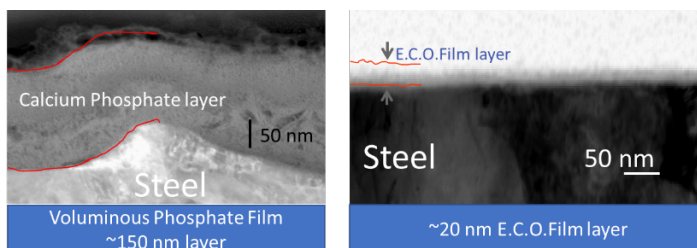
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## abstract

Industrial plants are facing increasingly restrictive phosphorus discharge limits, forcing them to reduce their use of phosphorus treatment to control corrosion in open recirculatory cooling systems. As a result, many operators have been required to significantly modify their traditional treatment programs. Other operators have successfully circumvented fouling by using phosphorus inhibitors. Surface analyses were used to identify passivation films that could render surfaces less susceptible to corrosion. Further efforts correlated the chemical composition of passivation films to respective treatment and water conditions, providing the knowledge to manipulate film chemistry for performance. Applying this combined knowledge led to the development of Engineered Carboxylate Oxide Films (E.C.O.Film) technology for non-phosphorous<sup>1</sup> cooling applications. A part of E.C.O.Film technology uses carbon-hydrogen-oxygen (CHO) inhibitors, which facilitate the construction of passivation films under non-phosphorous conditions. Their use will be discussed from a surface analysis perspective.

## introduction

Phosphate has been the main ingredient used in corrosion control programs for industrial cooling programs since transitioning away from chromate, beginning in the 1970s. When the correct ratio of calcium and phosphate are achieved in an industrial cooling program, a calcium/phosphate passivation film will form on the surface of iron-based metals, rendering those surfaces less susceptible to corrosion. This passivation film provides the necessary protection against corrosive factors such as oxygen, chloride, sulfate, and inorganic oxidizers (bleach, bromine, peroxides, chlorine dioxide, etc.). The performance provided by adding ortho-phosphate to industrial cooling systems led to decades of developing various calcium/phosphate salt inhibitor and dispersant polymers. These polymers feature a wide variety of monomers used in co-, ter-, and quad-polymers, where one monomer contains a sulfonic acid group. The advancement of calcium/phosphate dispersant polymers allowed for the use of phosphate throughout the pH range of industrial cooling—from pH 6.8 to 9.5.



**Figure 1. Transmission Electron Microscopy (TEM) cross-section comparing passivation films of typical alkaline program with  $\text{o-PO}_4$  (left) versus no added phosphorus program (right).**

Despite many successful applications of phosphate-based corrosion programs over three decades, risks associated with the addition of phosphorus remain. These include environmental concerns related to algae and microbial growth from phosphorus discharge to lakes, rivers, and other water bodies; and fouling due to either deposited calcium phosphate or precipitation of phosphorus-containing salt inhibitors. As a necessary micronutrient, phosphorus can accelerate algae and microbial growth. The main source of

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<sup>1</sup>May contain trace amounts

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elevated environmental phosphorous is agricultural runoff. Regardless, regulations target the points of industrial effluent: specifically, direct discharge cooling systems and water treatment facilities. Regulations regarding allowable phosphorus discharge date back to the 1980s and remain highly regional in their restrictions. The reduction of phosphate in industrial cooling corrosion programs has never fully come to fruition due to the small market segment that directly discharges cooling tower blowdown into natural bodies of water.

Combining the use of surface analytical techniques (X-ray Photoelectron Spectroscopy, XPS; Time of Flight Secondary Ion Mass Spectroscopy, ToF-SIMS; Infrared Spectroscopy, IR, etc.), chemical treatments, and knowledge of water characteristics, the concept of engineered passivation films was developed to enhance corrosion protection in industrial cooling applications. Analytical techniques identify the chemical composition of various layers within a passivation film. This combined with knowledge of water chemistry and applied chemical treatments, permits a desired film composition and thickness to be constructed for a given water environment. This approach has already shown removing phosphate from a cooling program will lead to increased corrosion rates due to thinning of the calcium phosphate layer. Figure 1 highlights TEM (Transmission Electron Microscopy) images taken from previously reported coupon samples that show the drastic change in passivation film thickness between a non-phosphorus and a traditional alkaline corrosion program. Engineered passivation films have led to the development of new yellow metal corrosion inhibitors as well as low phosphate or no added phosphorus cooling programs.

The use of saturation modeling is an invaluable tool when designing recirculating deposit and corrosion control programs. Even though low phosphate or no added phosphorus programs have an inherent reduced fouling tendency, it is still prudent to evaluate the saturation values of all potential salts other than calcium/phosphate species. A prerequisite for many low phosphate and no added phosphorus programs is that the pH set point be within the alkaline range (pH greater than 7.8). Within this pH range, there is still potential for calcium carbonate scale. Under standard alkaline conditions (4-6 ppm ortho-phosphate) a minimal amount of ortho-phosphate is available to influence the calculated saturation value of calcium carbonate. Thus, when a low phosphate or no added phosphorus program is designed, minimal change to the calcium carbonate saturation value will occur. However, the low ortho-phosphate quantity is enough to effect changes in the induction time (the time delay before the first crystallization aggregates form). Laboratory tests thus far have found calcium carbonate precipitating under 4-6 ppm ortho-phosphate conditions where no calcium carbonate scaling was observed by acid testing metal surfaces. A more detailed study is required to fully address potential changes in calcium carbonate induction time under low phosphate or no added phosphorus conditions. A successful CHO inhibitor must aid in the engineering of surface passivation films and calcite scale inhibition.

## methods and materials

Samples were acquired under laboratory conditions using a recirculating testing rig or from customer sites using a no added phosphorus corrosion control program. Samples were sent to a testing facility for surface chemistry analysis. Standard analysis uses XPS (x-ray photoelectron spectroscopy) to acquire semi-quantitative information of the elemental composition of the top 10 nm of a surface film. Additionally, ToF-SIMS (time of flight secondary ion mass spectroscopy) can be used to identify the mass spectra of the top 10 nm of a surface film or to perform a depth analysis to identify the composition, including how the passivation film forms. This technique is significantly more sensitive than XPS.

## CHO inhibitors

In efforts to mitigate fouling associated with organic phosphonate chemistry, polycarboxylic acid salt inhibitors were developed as a no added phosphorus chemical treatment for industrial systems. Polycarboxylic acid salt inhibitors are known to improve Calcium tolerance levels and do not add any phosphorus to a cooling application. Some polycarboxylic acid salt inhibitors can act as corrosion inhibitors depending on their concentration and hardness levels. Most polycarboxylic acid inhibitors are included within the CHO nomenclature. However, not all can be used as part of a low phosphorous corrosion control program. Using surface analysis in conjunction with performance criteria a select number of CHO inhibitors have been selected for use in E.C.O.Film applications. These CHO inhibitors are efficient in constructing the passivation films. The performance of CHO inhibitors depends on many factors such as molecular weight, anionic charge, molecular sterics, metal binding constants, and water

chemistry (salt concentrations, pH, etc.). While nitrogen-containing species can be incorporated in the molecular design, these species may contribute to biofilm growth or unnecessary oxidizer demand. Still, the lone pair of electrons on a nitrogen atom present an ideal ligand construct for binding to iron surfaces.

CHO inhibitors play certain roles in constructing passivation films and aiding in corrosion protection: (i) firstly, they possess the ability to interact with calcium ions or colloids in solution to inhibit crystal growth or precipitation; (ii) secondly, they aid in the engineering of passivation films by acting as transporters for colloidal species that become part of the cathodic matrix which prevents electron transfer at the metal interface; (iii) and thirdly, they act as surface buffering species that alter the rate of the anodic reaction's production of hydroxide anions. The selection of specific CHO inhibitors depends on specific water conditions as well as customer-driving forces and assets.

## field examples of using CHO inhibitors to engineer surface films

### East Coast power plant

The first study focuses on an East Coast power plant that sources make-up water from a reservoir. To directly discharge its cooling tower effluent, the power plant was required to use a no added phosphorus program. A water analysis of the reservoir revealed little or no presence of available ortho-phosphate that could be cycled up to achieve optimal corrosion protection.

**Table 1: East coast power plant make up water**

	Target
pH	7.8 – 8.0
M-alkalinity as CaCO <sub>3</sub>	100
Ca as CaCO <sub>3</sub>	56
Mg as CaCO <sub>3</sub>	48
Cl	40
SO <sub>4</sub>	46
SiO <sub>2</sub>	70 – 125
o-PO <sub>4</sub>	0 – 0.5
Hypochlorite - residual	0.3 – 1.0

Due to conductivity limits, only four cycles of concentration could be targeted for the application. Cycled up water in an evaporating recirculating system achieved an oscillating pH between 7.8-8.0. Table 1 summarizes the water characteristics of the cycled-up water, which contained ortho-phosphate levels between 0 and 0.5 ppm. Initial screening of various CHO inhibitors was conducted in beakers to select the best available to engineer a passivation film. CHO-2 and CHO-3 were selected based on beaker performance. CHO-9 worked complementary with CHO-2 and CHO-3.

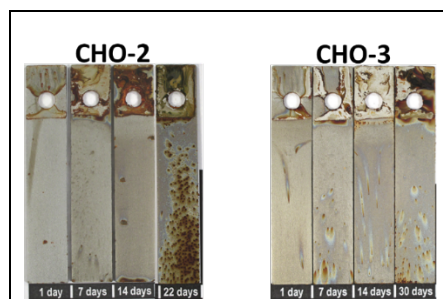
Site water was used as make-up water and cycled using an evaporating recirculating cooling test. Each product was dosed at 60 ppm for CHO-2 and CHO-3 with enough dispersant to handle suspended solids. Comparing the two CHO inhibitors, CHO-3 outperformed CHO-2 with instantaneous corrosion rates below the key performance indicator mark of 3 mpy. CHO-3 achieves a much steadier corrosion rate that oscillates in response to blow down and oxidizer feed increases the level of noise in the data set.

Figure 2 compares the coupons at various days throughout the 30-day testing duration. As can be seen, CHO-2 and CHO-3 are similar in appearance at seven and 14 days. However,

after 22 days CHO-2 is unable to maintain the passivation film under low hardness, phosphate, and pH conditions. Besides some low-pit density on the coupon around the surface edge, CHO-3 demonstrates a successful treatment program. Average pit depth was also significantly less for CHO-3 versus CHO-2 under the cycled-up reservoir conditions.

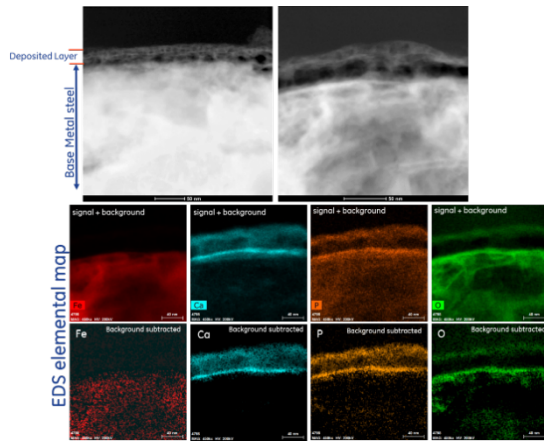
### South American chemical plant

A second study looks at a South American chemical plant's 30-day corrosion coupon, which was evaluated to understand the use of CHO-1 inhibitor in a low phosphate corrosion program. The chemical plant had switched from a traditional alkaline program to a low phosphate program to meet phosphorous regulations. The site operates with an ortho-phosphate upper



**Figure 2. Coupon results comparing CHO-2 and CHO-3 for East Coast power application using cycled up reservoir water. Average corrosion rates for CHO-2 were 2.0 mpy (143 micron, average measurable pit depth); average corrosion rates for CHO-3 were 1.30 mpy (43 micron, average measurable pit depth).**

limit of 3 ppm, while the corrosion program targets ~2.5 ppm. Corrosion rate targets are less than 1.0 mpy and are consistently met with this low phosphate program using CHO-1. TEM analyses of the coupon (Figure 3) revealed features like previously reported low phosphate experiments. The engineered passivation film is roughly 40-50 nm thick after a 30-day exposure, which is consistent with previous laboratory studies.



**Figure 3. TEM images of the CHO-1 engineered passivation matrix from a 30-day LCS field coupon. The engineered passivation matrix is roughly 40-50 nm thick and consists of a fully covered surface with significant percentage of Ca, P, and O. Carbon is present and is often not shown due to contamination.**

passivation films that enrich the metal oxide interface and form a dynamic Calcium-matrix capping layer utilizing the water chemistry present at cycles of concentration. Corrosion targets of less than 2 mpy can readily be achieved with E.C.O.Film technology.

Cross-sectional Energy Dispersive X-ray Spectroscopy, EDS, mapping highlights the ability of CHO-1 to properly transport water components into close interaction with the metal interface to form a passivation matrix consisting of calcium, phosphorus, and oxygen. Carbon also contributes a significant amount to the matrix and is often removed from analysis due to a large amount of interstitial contamination. It is even harder to accurately conclude the origins of carbon in surface analysis testing due to the presence of the carbonate anion and a large amount of carboxylic acid contribution from CHO-1 and/or the dispersant polymer. Biological contributions of carbon cannot also be ruled out under field conditions.

## conclusions

Effective corrosion protection can be achieved under a no added phosphorus program, including no ortho-phosphate or pyro phosphate added for low carbon steel protection and no phosphorus in the chemical treatments. CHO inhibitors have been developed that are able to facilitate several roles as a scale and corrosion inhibitor. SUEZ's E.C.O.Film technology provides