

Advancements in Cleaning and Passivation of Cooling Water Systems

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Abstract

Newly installed piping and heat exchangers should be pre-cleaned to remove surface rust and passivated to protect against initial corrosion prior to entering service. Traditionally, high levels of polyphosphate [1], organic phosphate [2], ortho phosphate, and combinations have been used to both pre-clean and passivate in one step. Both polyphosphate and organic phosphate have good iron sequestering and rust removal properties. Chromate and zinc are effective at forming a protective film, but have fallen out of favor due to environmental restrictions. Nitrite is an effective passivator in closed cooling loops, but promotes microbiological activity in open cooling tower systems and does not become incorporated into a durable, protective film. High levels of molybdate are also used for pretreatment, but molybdate is expensive for large systems and increasingly subject to environmental restrictions.

Periodically it may also be necessary to clean equipment to remove accumulated corrosion products and deposits in order to restore thermal performance. Traditional cleaning methods include mechanical brushes and scrapers, acid cleaning, or neutral pH cleaning using high levels of sequestrants or chelants. Regardless of whether a mechanical or chemical cleaning method is used, the freshly cleaned steel surfaces should also be passivated immediately following cleaning to protect against flash rust until the normal treatment program is established. Proper initial passivation has been reported to approximately double the life expectancy of mild steel heat exchangers [3].

This paper describes the development and application of a new non-phosphate pre-treatment chemistry that forms a truly passive film on steel surfaces. This passivation treatment can be used in combination with either mildly acidic or neutral pH solutions to provide a one-step cleaning and passivation. The use of electrochemical techniques in the development and evaluation of the chemistry, including cyclic polarization and electrochemical impedance spectroscopy, are discussed. A case history is provided to illustrate the effectiveness of this technology for cleaning and passivation as part of a comprehensive program for protecting industrial cooling systems from corrosion.

Introduction

Industrial cooling systems rapidly form iron oxide deposits which reduce their heat transfer efficiency. It is common to mechanically clean these systems when the iron oxide deposits become excessive. Mechanical means such as scraping, brushing, sand blasting, and high pressure water washing are few of the well-known mechanical cleaning methods. Mechanical cleaning, while effective in many cases, is time-consuming, laborious and expensive. Also, it is not always possible for the physical removal methods to access



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all the areas of the system where the deposits are located. Chemical cleaning is more versatile in being able to reach all areas of the system and more effective in terms of removing all traces of rust and deposition.

Traditional methods employed for chemically removing corrosion products relied upon strong acids and required special precautionary measures for handling and application. Additionally, the extreme pH risked excessive loss of the base metal, particularly in systems with mixed metallurgy.

More recently, considerably safer neutral pH cleaning programs for rust removal were introduced.

These formulations essentially consist of (1) a strong reducing agent to reduce ferric (Fe^{3+}) iron oxide deposits into a soluble ferrous (Fe^{2+}) form, and (2) an organic phosphate chelant to complex the dissolved iron. The system is thoroughly flushed after this process to remove the dissolved iron. Though safer to handle, neutral pH cleaners still can be very aggressive to carbon steel base metal. Provided that the final pH of the solution is greater than approximately 6.0, these neutral pH cleaners can provide some degree of passivation.

Regardless of whether the cleaning is performed mechanically or chemically, freshly cleaned steel surfaces are extremely vulnerable to flash rust. A separate passivation step is required after the cleaning process to protect the bare metal from flash rust and to protect against the high initial corrosion rate that occurs when the equipment is initially placed into service.

To achieve a one-step cleaning and passivation, there exists a need for a strong corrosion inhibitor chemistry that protects the steel surfaces from the aggressive cleaning chemistry and provides a strong passive film to protect the surfaces as they are placed into service. The starting point for corrosion inhibitor development was an inhibitor chemistry originally developed to comply with emerging restrictions on phosphorus discharge. The development and application of this corrosion inhibitor for use in cooling towers under normal operation has been described in earlier publications [4] [5]. This corrosion inhibitor chemistry was selected because it interacts directly with metal surfaces to form a reactive polyhydroxy complex (RPC) that is independent of calcium, pH, or other water chemistry constituents. It also possesses many of the other desired attributes including an excellent aquatic effects profile. The ability of the RPC chemistry to protect and passivate the base metal during preoperational cleaning is the focus of this study. Efficacy of the RPC chemistry was compared to traditional polyphosphate and organic phosphate cleaning and passivation chemistries.

Laboratory Studies

Most metallic corrosion occurs via electrochemical reactions at the interface between the metal and an electrolyte solution. Since corrosion phenomena are electrochemical in nature, they are governed by the measurement of equilibrium corrosion potential (E_{corr}) of

the metal surface. During the late '70s and early '80s, corrosion specialists began to discover that electrochemical instruments and techniques could be valuable tools for mechanistic understanding and problem solving. Electrochemical methods can be very helpful in rapidly evaluating the persistence of a passive layer formed on a metallic specimen in the presence of inhibitor when that specimen is transferred into a second solution not containing a corrosion inhibitor.

Electrochemical Experimental

The passivation chemistries selected for laboratory evaluation were two well-established phosphate chemistries and the RPC chemistry, which were compared to untreated blank water samples for their ability to form a persistent protective film. The organic phosphate (HEDPA) was evaluated at a concentration of 1,250 mg/L as $\text{PO}_4^{=}$, the polyphosphate (TKPP) was evaluated at a concentration of 320 mg/L as $\text{PO}_4^{=}$, and the RPC was evaluated at a concentration of 12 mg/L. The blank water contained 150 mg/L Ca as CaCO_3 , 100 mg/L Mg as CaCO_3 , 100 mg/L M-Alkalinity as CaCO_3 , 50 mg/L chloride as Cl⁻, 10 mg/L silica as SiO_2 , at pH 8.0.

Working electrodes were made from cylindrical shaped carbon steel electrochemical coupons. Corrosion resistance performance of different passivation chemistries was evaluated using electrochemical techniques including open circuit potential (OCP), cyclic polarization (CP), and electrochemical impedance spectroscopy (EIS) measurements. Carbon steel coupons were passivated for 8 hours in baths containing the passivation chemistries. After passivation, the electrochemical coupons were rinsed with RO water and placed in the blank water. The pH of the blank solution was maintained at 8.0-8.2 using caustic soda. Electrochemical measurements were performed in a three electrode cell consisting of a graphite counter electrode, an Ag/AgCl reference electrode, and the carbon steel coupon. Electrochemical impedance spectroscopy (EIS) measurements were performed using the excitation signal of 10 mV sinusoidal potential through a frequency domain from 100 kHz down to 10 mHz. The impedance diagrams were recorded at the equilibrium OCP, while polarization scans were traced at a rate of 0.5 mV s⁻¹. Unless otherwise stated, each experiment was conducted in at least triplicate using freshly prepared solution in each case and with the average of the reliable data reported. Figure 1 shows the electrochemical testing apparatus used for the experimental work.



Figure 1. Potentiostat arrangement used for electrochemical studies

Open Circuit Potential (OCP) Evaluation – Open circuit potential measurements were made in blank water with bare mild steel (MS) coupons and also on the coupons passivated as described above using the organic phosphate, polyphosphate, and RPC chemistries. OCP measurements were taken at 5 minute intervals for an extended period of 36 hours. Comparing the OCP profiles obtained for these electrodes indicate that after the electrode surface was passivated using RPC, the OCP is >200 mV more positive than that the MS coupons passivated with polyphosphate and organic phosphate chemistries. These results indicate that the RPC passive film is thermodynamically more stable than phosphate and is very effective in reducing corrosion. Moreover, the passive film retained its effectiveness in the untreated blank water, with the OCP decreasing <100 mV during the 36-hour exposure. In the cases of the polyphosphate and organic phosphate passivations, the OCP values quickly become more negative, indicating rapid dissolution of the passive film by diffusion of aggressive ions and subsequent increase in corrosion rates.

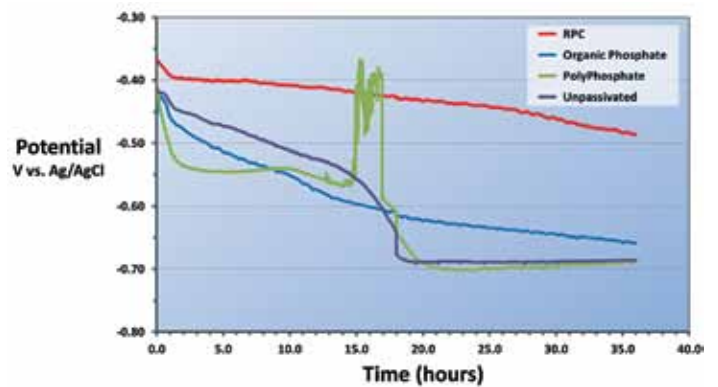


Figure 2. Open circuit potential after passivated coupon is placed in untreated water

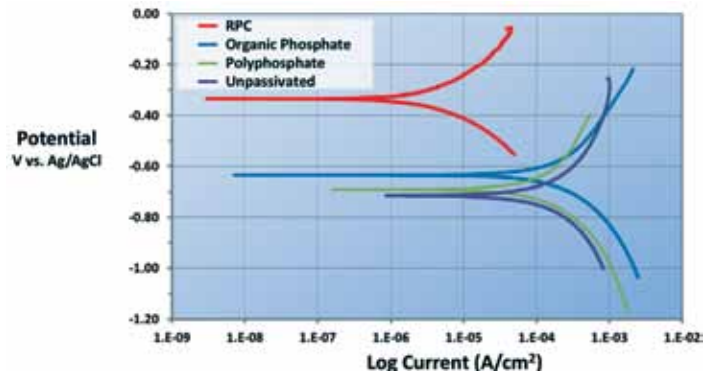


Figure 3. Cyclic polarization after passivated coupon is placed in untreated blank water

From the cyclic polarization curves, some electrochemical corrosion kinetic parameters can be obtained, such as the corrosion potential (E_{corr}), Tafel slopes, corrosion current density (I_{corr}), and corrosion rates in Table 1.

Type of Passivation	E_{corr} (mV)	Beta (mV/dec)	I_{corr} ($\mu\text{A}/\text{cm}^2$)	Corrosion Rate (mpy)	% Inhibition
Blank	-705	110.8	9.28	5.2	
Non-Phosphate	-417	176.4	1.61	0.7	83%
Polyphosphate	-690	134.8	8.73	3.99	6%
Organic Phosphate	-634	113.7	3.68	0.95	60%

Table 1. Cyclic polarization data of various passivation treatments

An immediate observation from comparing the E_{corr} (Figure 3 & Table 1) and OCP (Figure 2) is that both the electrochemical techniques are in good agreement. Small differences could be attributed to the effect of polarization. It is clearly seen from Fig. 3 that the coupon passivated with RPC chemistry has lower passivation current and lower currents at all applied potential values. The corrosion resistance of different passivation treatments was calculated using Stern-Geary Equation:

$$I_{corr} = b_a b_c / (b_a + b_c) 2.303 R_p \quad (1)$$

From the graph and the table, it is clear that the corrosion current for different passivation treatments increases in the order:

$$(I_{corr})_{RPC} < (I_{corr})_{Organic\ phosphate} < (I_{corr})_{Polyphosphate} \quad (2)$$

Inhibition efficiency (% Inh) of various passivation treatment programs has been calculated using the formula:

$$\% Inh = (I_{corr})_{blank} - (I_{corr})_{treatment} / (I_{corr})_{blank} * 100 \quad (3)$$

It is clear from Table 1 that higher inhibition efficiency was obtained by the RPC passivation treatment than the polyphosphate and organic phosphate chemistries, indicating the stability and persistent nature of the RPC non-phosphate passive film.

Electrochemical Impedance Spectroscopy Measurements – The long-term corrosion behavior of the three passivation treatments on the surface of carbon steel electrodes was probed by electrochemical impedance spectroscopy (EIS). Electrical resistance is a well-known parameter for characterization of the ability of a circuit element to resist the flow of electrical current. Similar to resistance, impedance is also a measure of the ability of a circuit to resist the flow of electrical current. However, unlike resistance, impedance is not limited by the simplifying properties of a single resistor. Electrochemical impedance is usually measured by applying an AC potential to an electrochemical cell and then measuring the AC current response through the cell. EIS is one of the most useful techniques to discern the corrosion mechanism, evaluate protective films on metals in aggressive solutions, and analyze film formation at the metal-electrolyte interface. When a metal surface is covered (passivated) with a protective layer, the corrosion is controlled by the transport of the species in the protective film through diffusion channels resulting from passive film breakdown or micro cracks. The response can be represented as the relationship between the imaginary and real components of impedance, referred to as a Nyquist plot. Figure 4 presents the Nyquist impedance diagram recorded at OCP for various passivation treatments.

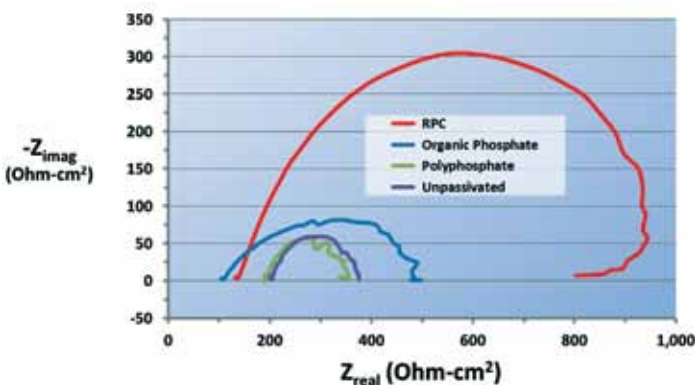


Figure 4. Nyquist plots for different passivated coupons in untreated water

It is clear that the semicircle diameter increases in the order:

Polyphosphate \leq Unpassivated $<$ Organic phosphate \ll RPC

Since the diameter of the capacitive semicircle represents the resistance of the coating, an increase in diameter represents increased resistance. Figure 4 illustrates that the corrosion resistance of RPC passive film is much greater than other traditional organic phosphate and polyphosphate passivation treatments, consistent with OCP and CP measurements in Figures 2 and 3. The EIS results also confirmed that RPC passivation forms a highly protective film on mild steel in the test water, significantly outperforming the polyphosphate and organic phosphate passivation chemistries.

Comparison with Nitrite and Molybdate Passivation

Carbon steel coupons were passivated for 6 hours in baths containing the treatment solutions of interest in blank water (described above). Baths 1 and 2 contained the RPC corrosion inhibitor at 12 mg/L and 6 mg/L respectively, bath 3 contained 100 mg/L of molybdate (as $MoO_4^{=}$), and bath 4 contained 1,200 mg/L of nitrite (as NO_2^-). Following the 6-hour passivation period, the coupons were rinsed in DI water and placed into untreated blank water for a period of 3 days to evaluate the persistence of the passive film. After exposure, the coupons were removed and photographed. Average corrosion rate was determined by weight loss. The coupon appearance and corrosion rate are shown in Table 2.

Bath	Treatment	Corrosion Rate	Coupon After 3 Days in Untreated Blank Water
1	RPC, 12 mg/L	2.7 mpy	
2	RPC, 6 mg/L	2.9 mpy	
3	$MoO_4^{=}$, 100 mg/L	7.2 mpy	
4	NO_2^- , 1,200 mg/L	14.5 mpy	

Table 2. Corrosion rate and coupon appearance after 6-hour passivation and 3-day exposure to untreated blank water.

Preoperational Cleaning Passivation OCP Evaluation

One of the major needs for passivation chemistry is during preoperational cleaning when the freshly cleaned surfaces are most vulnerable to flash rust just prior to the equipment entering service. To simulate the condition of new steel heat exchangers subject to environmental rusting during the construction period, a new steel heat exchanger tube was first allowed to rust outdoors for several days, then cut into sections approximately 3 in (7.5 cm) long. One rusted tube section was placed into a beaker containing a neutral pH, precleaning and passivation solution containing organic phosphate, reducing agent, and surfactant. A second section from the same tube was placed into another beaker containing the same chemistry with the addition of the RPC passivating chemistry. The solutions were stirred for 6 hours until the both specimens were substantially free of rust. The pH of the cleaning solutions remained in the 6.5-6.7 range during the 6-hour exposure. Figure 5 and 6 show the specimens in the beakers before and after cleaning.



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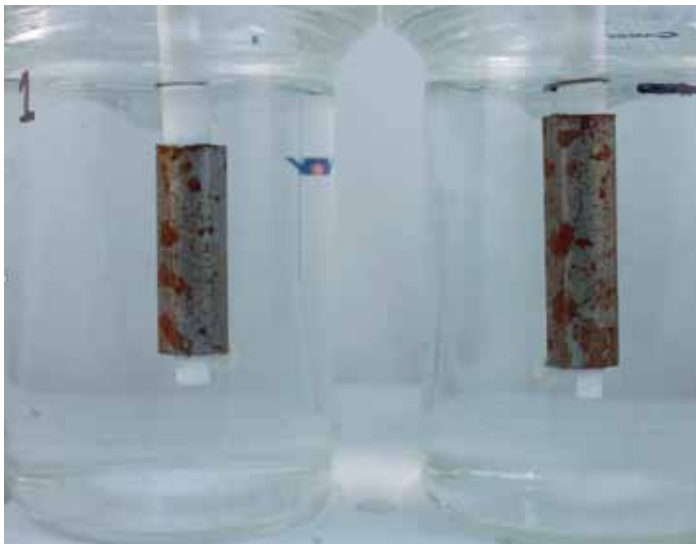


Figure 5. Precleaning and passivation study at start of 6-hour exposure. Specimen on right contains the RPC passivation chemistry.

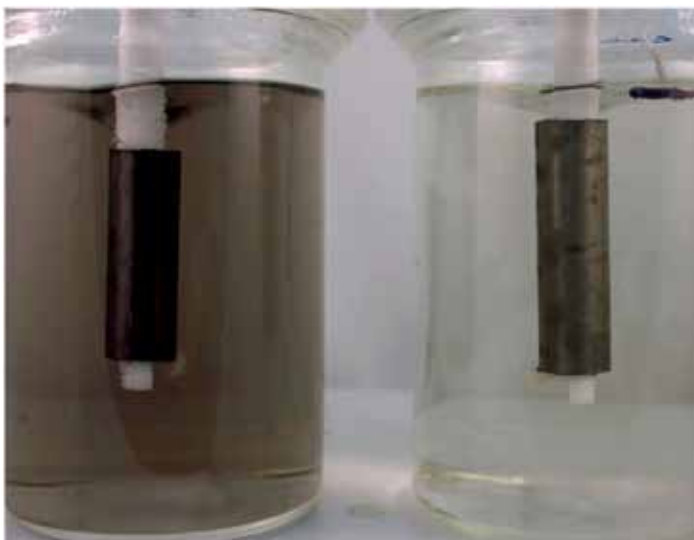


Figure 6. Precleaning and passivation study at completion of 6-hour exposure. Specimen on right contains the RPC passivation chemistry.

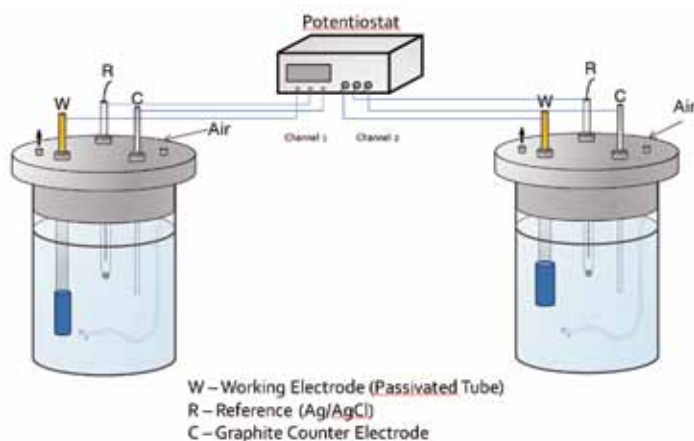


Figure 7. OCP measurement of cleaned tube specimens

As shown in Figure 6, after 6 hours, the cleaning solution without the RPC passivation chemistry is noticeably darker than the solution with RPC chemistry due to additional corrosion of the base

metal. Following the cleaning, both specimens were placed in baths of untreated blank water for 24 hours to evaluate their ability to resist corrosion using open circuit potential as illustrated in Figure 7.

In this test, the precleaning solution containing the RPC chemistry exhibited an open circuit potential more than 200 mV higher than the solution without RPC (Figure 8).

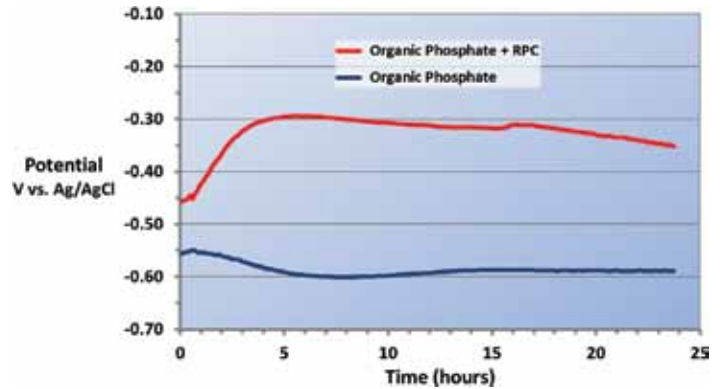


Figure 8. OCP of cleaned specimens over 24 hours in untreated water, with and without RPC passivation chemistry

Figures 9 and 10 show the two specimens after the 24-hour exposure to the untreated blank water. The steel tube section that was exposed to the cleaning solution containing the RPC passivation chemistry clearly resisted rusting, while the specimen not exposed to RPC readily rusted after cleaning.



Figure 9. Tube section cleaned and passivated with RPC, organic phosphate, and reducing agent after 24-hour exposure to untreated blank water.



Figure 10. Tube section cleaned with organic phosphate and reducing agent after 24-hour exposure to untreated blank water.

Copper Sulfate Verification Test

A simple, visual test for passivation is to expose steel or stainless steel specimens to a copper sulfate solution. Immersion in a copper sulfate solution is one of the verification tests described in the ASTM A967 standard specification for chemical passivation treatments [6]. Copper ions in solution act as electron acceptors at the cathode of the corrosion cell and readily electroplate onto unpassivated or weakly passivated surfaces, producing a very pronounced copper discoloration to the steel surface (Figure 11). The test can be performed in the field as an acceptance test

criteria for equipment passivation procedures. A well passivated steel coupon will exhibit considerable resistance to copper plating even when exposed to a solution containing a high concentration of copper ions.

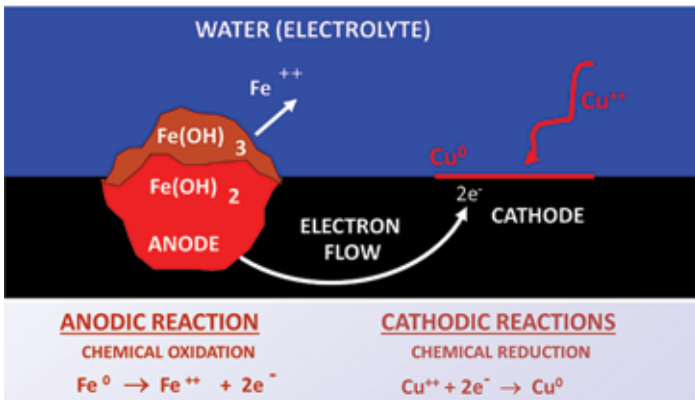


Figure 11. Mechanism of copper electroplating onto steel surfaces

Exposure to a copper sulfate solution was used to evaluate the effectiveness of RPC passivation chemistry compared to established organic phosphate and polyphosphate passivation chemistries. Mild steel coupons were treated for 6 hours in passivation solutions and then exposed to a 15% copper sulfate solution for 20 seconds. Following exposure, the coupons were rinsed with deionized water, dried, and visually inspected for copper plating as an indication of passivation effectiveness. A relatively high concentration of copper sulfate was used in order to produce severe test conditions that would discriminate among the passivation chemistries. As shown in Figure 12, the RPC passivation chemistry clearly demonstrated effectiveness superior to organic phosphate and polyphosphate in the copper sulfate exposure test, and at significantly lower treatment concentrations.

Organic phosphate passivation

640 mg/L as PO₄³⁻ for 6 hours
Surface is copper plated.
Passive film failed.

Polyphosphate passivation

320 mg/L as PO₄³⁻, 6 hours
Surface is copper plated.
Passive film failed.

RPC passivation

3.8 mg/L as RPC, 6 hours
Steel resisted copper plating, indicating a strong passive film.



Figure 12. Passivated coupons after 20 sec. exposure to 15% CuSO₄ solution

Preoperational Cleaning Application

A Midwest manufacturing plant resumed operation after being idle for 18 months. Prior to resuming operation, the cooling system was cleaned using an acidic cleaning solution with surfactant and dispersants recirculated at a target pH of 3.0. The cleaning solution was inhibited using a triazole together with the RPC passivation chemistry. Mild steel coupons were installed to evaluate base metal loss and passivation effectiveness. The steel coupons were removed for after 2 days showed a dull grey passivated surface (Figures 13 and 14). The presence of RPC on the coupon was confirmed by surface analytical methods.



Figure 13. Passivated steel coupon after 2 day exposure to pH 3 cleaning solution containing RPC



Figure 14. Coupon surface magnified 40x

Carbon steel coupons exposed during the cleaning process were further evaluated to determine the corrosion resistance of the passive RPC film. The copper sulfate verification test described earlier was performed on the exposed coupon shown in Figure 13 and compared to a new, carbon steel coupon. The lower half of each coupon was exposed to a 15% copper sulfate solution for 20 seconds. As shown in Figure 15, the new coupon is copper plated on its lower half, while the coupon passivated during the acidic chemical cleaning effectively resisted copper plating.



Figure 15. New coupon (top) and coupon passivated with RPC during the acidic chemical cleaning (bottom) after half-exposure to a 15% copper sulfate solution for 20 seconds. Note the copper plating on the new coupon as compared to the absence of copper plating on the RPC-passivated coupon.

A second carbon steel coupon that was exposed during the chemical cleaning process was evaluated for passivation by placing it in untreated blank water and comparing its OCP to a new coupon over time as described in the Experimental section. The RPC passivated coupon maintains its potential for several days in untreated water (Figure 16).

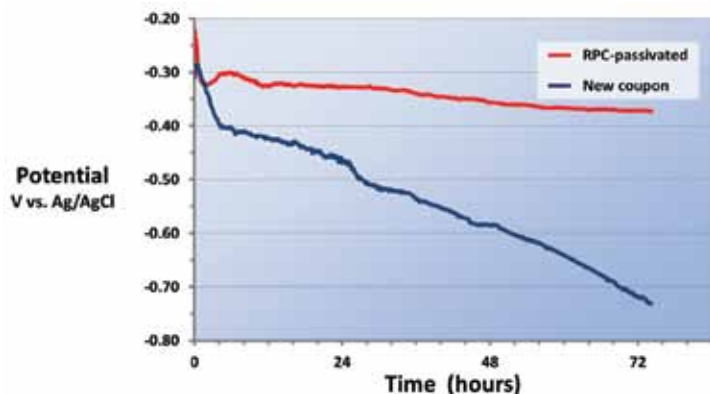


Figure 16. OCP measurement over time on carbon steel coupon passivated with RPC during chemical cleaning compared to a new carbon steel coupon.

As further visual evidence of passivation, the untreated OCP test baths were photographed after 3 days. Figure 17 shows the rust-colored solution containing the new coupon on the left and the clear solution containing the RPC-passivated coupon on the right.

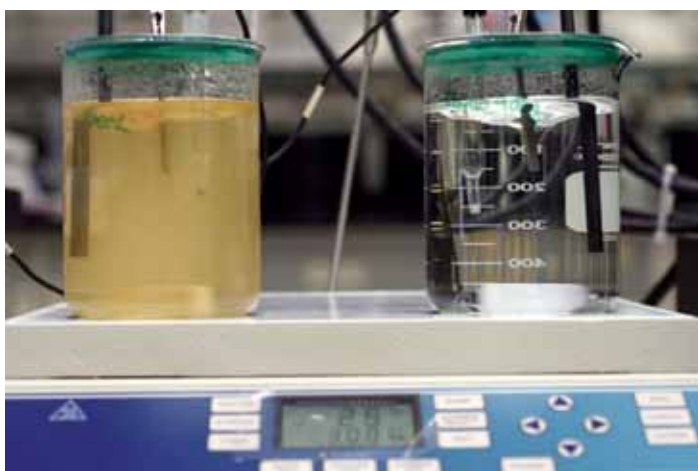


Figure 17. OCP test baths after 3 days showing the rust-colored solution containing the new coupon on the left and the clear solution containing the RPC-passivated solution on the right.

Neutral pH Cleaning Formulations With RPC

Neutral pH formulations containing various levels of RPC were studied for their effectiveness in cleaning rusted coupons and were also evaluated for corrosion rate on fresh coupons.

Cleaning solutions were prepared according to Table 3 and applied at a dosage of 10%.

Ingredient	Standard Neutral pH Cleaner	Formulation #1 With RPC	Formulation #2 With RPC	Formulation #3 With RPC
Water	71.10%	78.41%	78.51%	79.34%
HEDPA	7.20%	7.20%	7.20%	7.20%
Erythorbic	1.20%	1.20%	0.60%	
NaBZT		0.50%	0.50%	0.50%
PMA		0.12%	0.12%	0.12%
Polymer 1	4.00%	0.06%	0.06%	0.06%
Polymer 2	1.00%			
Surfactant	0.20%			
RPC		0.50%	1.50%	1.50%
NaOH		7.21%	7.21%	6.98%
KOH	10.50%			

Table 3. Table showing neutral pH cleaning solution chemistries used to clean coupons in Figure 18.

Figure 18 shows the coupon appearance before and after cleaning in the neutral pH formulations with and without RPC.

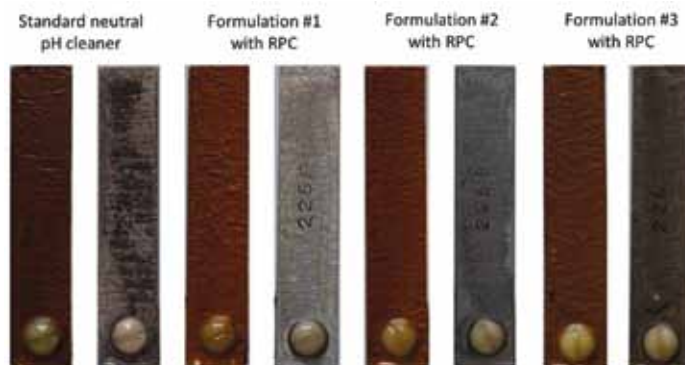


Figure 18. Before and after cleaning photos of the corroded coupons in standard neutral pH cleaners with and without RPC. Cleaning duration was 6 hours for all.

Formulations #1, #2, and #3 with RPC cleaned more effectively and left the coupons with a dull grey finish consistent with passivation. A fresh corrosion coupon was inserted into each of the cleaning bath to study the effect of the cleaner product on the base metal. Corrosion rates were measured by weight loss. The cleaning solutions containing RPC also exhibited a ~60-70% reduction in corrosion rate as compared to the standard neutral pH cleaner.

Conclusions

Effective cleaning and passivation of heat exchangers and piping is required during initial start-up and periodically during the operational life of the system. Using advanced electrochemical techniques, a powerful new passivation chemistry has been developed that protects the base metal during the cleaning process and provides a persistent passive film that resists corrosion for several days as the system is placed back in service. The new Reactive Polyhydroxy Complex (RPC) based chemistry was found to be superior to traditional polyphosphate and organic phosphate based treatments in terms of forming a stable and persistent passive film. The RPC chemistry can be used in conjunction with either acidic or neutral pH cleaners to achieve simultaneous cleaning and passivation, eliminating the need for a separate passivation step.

Acknowledgements

The authors gratefully acknowledge DeAnn Wills-Guy of Chem-Treat for conducting the electrochemical studies.

Nomenclature

b_a	Anodic Tafel slope, Eq. (1)
b_c	Cathodic Tafel slope, Eq. (1)
Beta	Anodic Tafel slope, mV/decade, Table 2
cfu	Colony forming units
CP	Cyclic polarization
E_{corr}	Corrosion potential at equilibrium, mV or V
EIS	Electrochemical impedance spectroscopy
HEDPA	1-Hydroxyethylidene-1,1-diphosphonic acid
I_{corr}	Corrosion current at equilibrium, mA or A