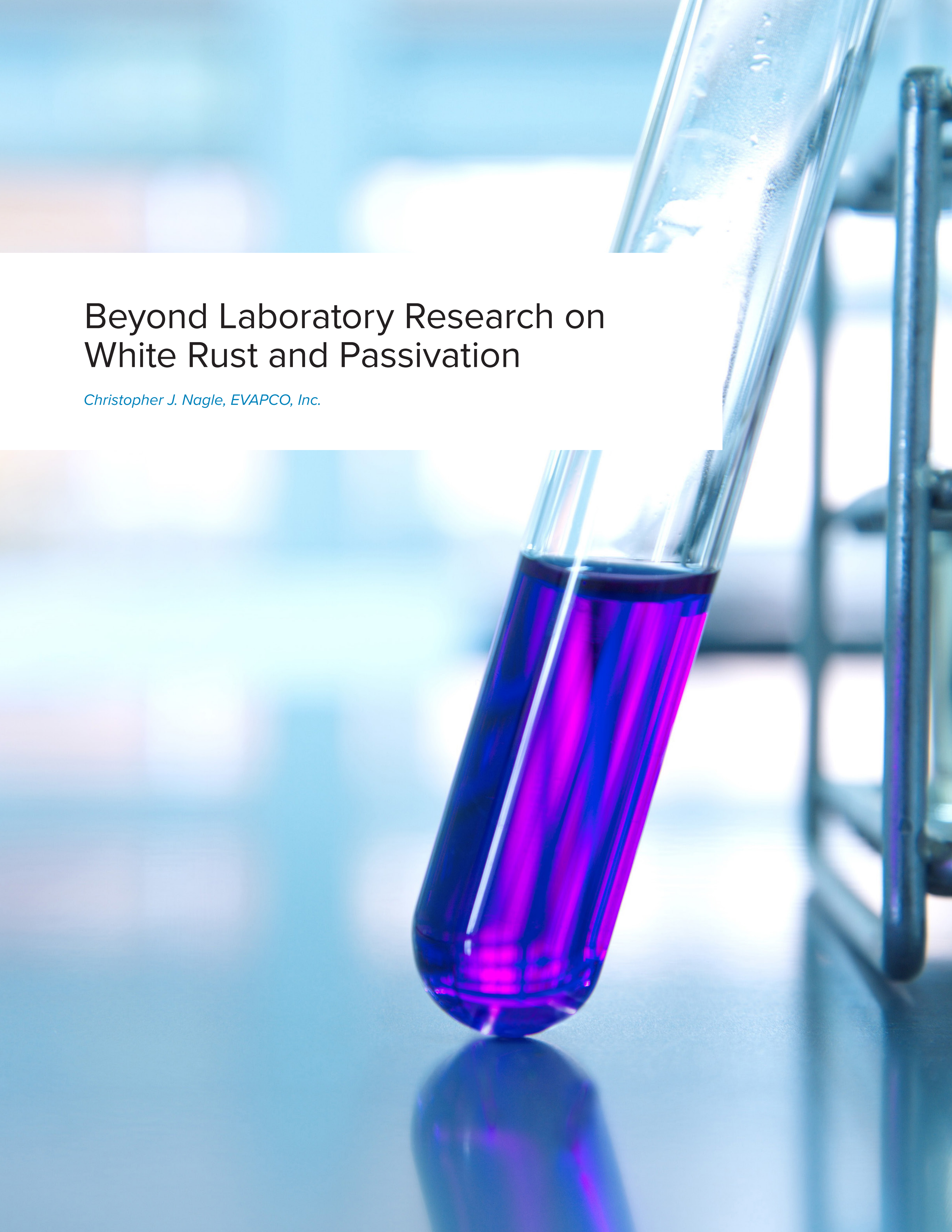
Beyond Laboratory Research on White Rust and Passivation

Christopher J. Nagle, EVAPCO, Inc.



Abstract

In support of customer requests for better outcomes for new equipment commissioned with immediate heat load, Evapco initiated an in-depth study to investigate the formation and control of white rust. This study, which began over three years ago, led to the development of industry leading research equipment specifically designed to evaluate white rust formation on evaporative heat transfer surfaces. A small-scale closed-circuit coolers was designed and built to replicate the dynamic conditions associated with evaporative cooling equipment commissioned with immediate heat load.

In addition to proprietary research, controlled testing was performed using commercially available products marketed as either white rust inhibitors or passivation aids for evaporative cooling systems containing galvanized materials of construction. The controlled testing included routine wet chemistry, visual inspections, and photography to determine how quickly white rust formed and the relative percentage of surface area impacted. Additional research was conducted to focus on innovative pre-treatment technologies for the galvanized coils utilized in closed-circuit coolers and evaporative condensers. This research effort continued with a goal of providing a factory applied pre-treatment capable of minimizing the formation of white rust in evaporative cooling equipment commissioned with immediate heat load across a wide variety of makeup water qualities and water treatment formulations.

A Brief History of White Rust in Evaporative Cooling

For over 50 years the evaporative cooling industry has relied on galvanized steel as a preferred material of construction due to its cost-effective combination of corrosion protection and long service life. The galvanizing process provides the underlying steel with a coating of superior hardness, ductility, and adherence unmatched by any coating or painting process.

In the late 1980s and early 1990s, articles began to surface noting an increased occurrence of premature corrosion of new galvanized steel referred to as white rust. A 1992 article in *The Analyst* noted, “The problem with white rust corrosion of cooling water towers was not widely observed until the mid-1980s.”[1]

The Cooling Tower Institute published *Guidelines for Treatment of Galvanized Cooling Towers to Prevent White Rust* (1994). The Association of Water Technologies published *White Rust: An Industry Update and Guide Paper* (2002 and 2012).

The 2002 version of AWT's guide paper stated, "The corrosion of galvanized steel cooling towers may be referred to as white rust and the consequence of white rust can be premature failure of galvanized steel components."

Several of the early articles[1-3] on the subject refer to "cooling towers" generically as an apparent catchall for the broader array of evaporative cooling equipment. When it comes to the topic of white rust and passivation, a distinction should be drawn between open cooling towers constructed of mill-galvanized steel for basins and casing as distinct and different from closed-circuit coolers and evaporative condensers constructed of both mill galvanized steel and hot-dipped galvanized steel coils. A chemical formulation used successfully to pre-clean and passivate an open cooling tower started without load may not be a good technical selection to passivate a closed-circuit cooler or evaporative condenser commissioned with immediate heat load, as shown in Figure 1.

Figure 1: Evaporative Condenser With White Rust

As white rust became more prevalent in the mid 1980s, customers, engineers, and water treatment professionals searched for explanations. Some of the early articles pondered what impact an increase in "aluminum content of the zinc alloy"[1] or "the elimination of chrome rinse by the galvanizers"[2] might have on the observed "increase in the incidence of white rust in cooling towers."[1]

For decades, it was well understood that "The chromate anion is extremely effective at minimizing the formation of white rust and at inhibiting corrosion at zinc surfaces."[4] Therefore, it would be logical to assume that the elimination of a chromate-based rinse from a mill galvanizing process might be a contributing factor to the observed increase in white rust. There are likely at least three reasons why this explanation should not be considered the sole root cause:

Hot dipped galvanized coils did not receive a chrome rinse but experienced an increase in observed white rust along with mill galvanized components.

The chrome rinse "helps prevent initial corrosion and staining until the steel is fabricated and placed into service."[4] It is unlikely that a chromate rinse applied to mill galvanized steel would provide long term protection against white rust on its own as it would "wash away" or "wear off" as water is circulated across a tower, cooler, or condenser.

Not all mill galvanizers eliminated the use of hexavalent or trivalent chrome rinses. In the early 1990s, Johnson and Mihelic noted "Traces of the chromate anion can be found on the surfaces of all 14 coupons utilized in this test, ..., and is still done by at least some manufacturers of mill galvanized steel."[4] To this day, the majority of mill galvanized steel used in the manufacture of evaporative cooling equipment in North America receives a hexavalent chrome wash.

As early as 1990, papers discussing white rust corrosion noted that "Because of the increasing restrictions on the use of chromate-based corrosion inhibitors for use in cooling water, a general trend toward alkaline cooling water treatment has become an industry standard."[4] The precise timelines will need to be left to the water treatment professionals who were practicing in the field during the 1970s and 1980s. The generation of water treatment professionals raised on alkaline treatment programs could view the decrease in usage of pH control associated with chromate and stabilized phosphate treatment programs, the ascent of alkaline treatment programs, and the increased incidence of white rust on newly commissioned galvanized equipment as one common timeline. In this transition from the dominance of pH control to alkaline treatment programs, it was observed "Higher pH levels combined with newer deposit control agents may minimize corrosion, scaling, and fouling in the coolers but can simultaneously cause premature failure of a cooling tower made of galvanized steel."[5]

Regardless of the possible or probable root causes for the uptick in observed white rust, which began in the mid 1980s, the problem persists for today's customers and their water treatment providers. In 2010, the International Institute of Ammonia Refrigeration held their 32nd annual conference in San Diego, California. Discussions with contractors and customers highlighted the challenges associated with passivating galvanized condensers for an industry facing shorter equipment lead times coupled with the near universal requirement for immediate heat load upon commissioning.

Investigation into Passivation

There have been continuing complaints from Evapco customers about galvanized steel developing white rust corrosion, resulting in shorter equipment life. These complaints are particularly prevalent on coil products that are placed under immediate load. It is well understood that the initial corrosion layer (passivation layer) is very important to equipment life, so a research program was started to evaluate the parameters that are required to develop a good passivation layer.

The ongoing research includes the use of scanning electron microscope-energy dispersive x-ray analysis (SEM-EDXA) to determine the elemental composition of white rusted areas and metal surfaces adjacent to the location of the corrosion product shown in Figure 2. Ongoing research and laboratory testing suggest the following aluminum content range for hot-dipped galvanized steel: 0.069 to 0.149%.

Figure 2: Galvanized Coil Samples From Tiny Coolers (SEM-EDXA)

The research conducted to date has not identified a correlation between aluminum content either within white rust deposits or on non-white-rusted galvanized areas near the corrosion product.

It should be noted that Evapco's current research is focused on hot-dipped galvanized coils as opposed to the "Galvanized Steel Surfaces"[1] detailed in Table 1 of the 1992 *Analyst* article, which likely were mill galvanized.

In support of customer requests for better commissioning outcomes, Evapco, Inc., initiated a study of the formation and control of white rust. This research focused on the formation of a passive layer capable of minimizing the formation of white rust in galvanized cooling equipment commissioned with immediate heat load.

Evapco designed two small-scale closed circuit coolers named Tiny Cooler 1 and Tiny Cooler 2, shown in Figure 3. These units provided the first test platform for side-by-side analysis to study the impact of immediate heat load on new galvanized coils.

Figure 3: Evapco's "Tiny Coolers"

Beginning in 2011, these side-by-side coolers provided an opportunity to study the effectiveness of pH control, orthophosphate-based treatments, and other variables on the potential for, and quantity of, white rust formation on new galvanized coils started with immediate heat load. The closed-loop water supplied to the inlet of the coil bundle was heated to approximately 100°F, with the systems operating five days per week for approximately 8 to 10 hours per day. Glutaraldehyde nonoxidizing biocide was manually dosed three times per week during operation, and sodium hypochlorite was manually dosed at the end of each week just prior to the idle weekend period.

The earliest series of tests provided makeup water "produced" by blending approximately 70% reverse osmosis (RO) permeate with approximately 30% Taneytown, Maryland, municipal water. Table 1 lists the water composition. Conductivity controllers automated the blowdown of the spray water to maintain cycles of concentration in the 2.0 to 2.5 range. Water temperature and pH data were tracked automatically with daily calibration, as required, based on handheld readings.

Table 1: Early Tiny Cooler Test-City and Blended Water Data

	Taneytown			Blended makeup		
Analyte	**Ave.**	**Min.**	**Max.**	**Ave.**	**Min.**	**Max.**
pH	7.2	7.35	7.83	7.7	7.6	7.9
Conductivity (mhos)	515	468	575	184	171	195
Calcium ($CaCO_3$)	152	119	178	45	36	50
Alkalinity	161	155	182	56	49	59
Chloride (mg/L)	47	155	182	17	15	19
Sulfate (mg/L)	22	19	27	7	6	8

Later testing reduced the percentage of RO permeate to study the impact of using a variety of different acids to trim alkalinity/pH.

For the earliest tests, the passivation phase of the trial lasted between four and six weeks with manual chemical feed and testing of inhibitor residuals, pH, and conductivity twice per day. Every Wednesday, makeup and recirculating water samples were collected for a complete laboratory analysis using atomic absorption spectroscopy and ion chromatography. At the end of the prescribed passivation period, a transition phase of approximately two to three weeks was initiated to move to an alkaline treatment program.

The Tiny Cooler testing in 2011 and early 2012 suggested the following for new galvanized equipment commissioned with immediate heat load:

Simply maintaining spray water pH below 8.3 during the passivation phase does not preclude white rust formation.

Commercially available orthophosphate based treatments suggested to control white rust in combination with pH control do not ensure a uniformly passivated surface.

Applying factory pre-treatment to the galvanized coil prior to shipment and startup can reduce the potential for subsequent white rust formation.

Although is was informative, research using the Tiny Coolers alone was time consuming. The original testing took four to six weeks, but due to the lack of satisfactory results, the passivation and transition times were increased, resulting in a significantly longer test cycle. Each test then took between 12 and 16 weeks, limiting the speed of innovation. As research unfolded, more hypotheses and variables were uncovered that were worthy of additional study.

By 2012, AWT's updated guide on the subject maintained its earlier reference to a survey amongst their membership, which found "white rust corrosion was identified as a serious and prevalent problem."[2]

In an effort to increase the pace of discovery, benchtop tests were initiated and designed to simulate equipment started with heat load. Previous *Analyst* articles reference the use of galvanized panels in conjunction with small-scale testing.[6]

A test matrix was established to evaluate hot dip galvanized test strips, mill galvanized test strips, and both varieties exposed to proprietary pretreatment processes. The test schedule incorporated six to eight weeks of simulated passivation followed by a two to three-week transition to an alkaline treatment program. All test panels were submerged by day and allowed to air dry overnight.

Immersion solutions were "manufactured" by blending Taneytown city water and RO permeate to achieve calcium hardness of 50 mg/L and alkalinity at 60 mg/L (both as CaCO3). Solutions were heated to 90°F, aerated, and changed out daily during the test. pH ranged between 7.2 and 7.8, reaching a maximum of 8.0 over the course of a day.

Twenty-eight separate jars, shown in Figure 4, each containing two galvanized test strips (Figure 5), were utilized during the benchtop testing. Six distinct inhibitor chemistries were tested across the 28 jars during the initial screening.

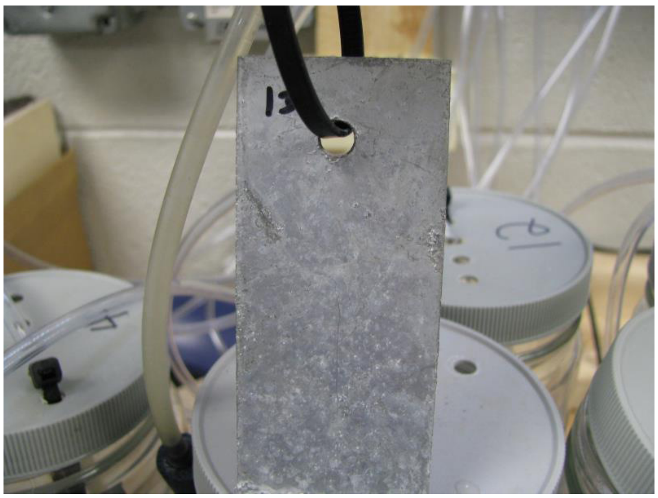
Figure 4: Benchtop Testing Setup

Figure 5: Hot-Dipped Galvanized Test Strip

The benchtop testing conducted between March and July 2012 demonstrated the following:

- Comparing jars with the same temperature, aeration, water quality, inhibitor type, and concentrations, the factory-applied pretreated test strips exhibited less white rust potential than test strips that had not received pretreatment, as shown in Figure 6.
- Benchtop galvanized strips tested with inhibitors used in previous Tiny Cooler testing exhibited less white rust formation compared to the Tiny Cooler coil results.

Figure 6: Test Strip With Factory Pretreatment (L) Compared to Untreated Galvanized Strip (R)



Galvanized test strips immersed in heated solutions do not appear to correlate well with reactions that occur when a heated coil is cooled by spray water. This suggests that heating the liquid (immersion bath) does not create the same increase in corrosion potential as heating the coil metallurgy (increasing skin temperature).

Because of the poor correlation between heated solution benchtested samples and heated coils from the Tiny Coolers, the use of benchtesting was minimized to enable refocusing on tests utilizing heated coil sections.

Following benchtop screening, additional research equipment was built to evaluate white rust formation on evaporative heat transfer surfaces. Four very small coolers were designed and built to provide faster testing of hypotheses and variables. Each new "Nano Cooler," shown in Figure 7, holds up to four small coil sections, which are exposed to identical operating conditions (e.g., temperature, water quality, inhibitor dosage).

Figure 7: Evapco's Nano Coolers

In conjunction with the two Tiny Coolers, the addition of the Nano Coolers provides an opportunity to study more variables side by side. One example of the increased flexibility available from the Nano Coolers was a test that studied the impact of varying calcium, chloride, and sulfate concentrations in the spray water on the galvanized coil sections shown in Figure 8.

Figure 8: Elevated Chloride (Nano Cooler 2) vs. Elevated Sulfate (Nano Cooler 3) Coil Sections

This study demonstrated that elevated sulfate (540 mg/L) showed less potential to increase white rust compared to elevated chloride (200 mg/L), as shown in Table 2. Further, comparing two coil sections exposed to elevated chloride (200 mg/l), the coil section exposed to spray water containing an average of 66 mg/L calcium developed more white rust versus one exposed to an average of 195 mg/L calcium, as shown in Figure 9.

Table 2: Water source

NC1 will use water from the blended MU tank without any additions

	MU Target	Rec Target	mg/L	By Adding	mg/L in MU	mg Per gallon
NC2	33	100	Ca	$CaCl_2$ (Cal-Plus) (Sol. 745 g/L @ $CaCl_2$ 68 °F)	70	265
NC3	180	540	SO_4	Na_2SO_4, 99% (Sol. 200 g/L @ Na_2SO_4 68 °F)	264	999
NC4	67	200	Cl	NaCl (Sol. 360 g/L @ NaCl 68 °F)	76	288

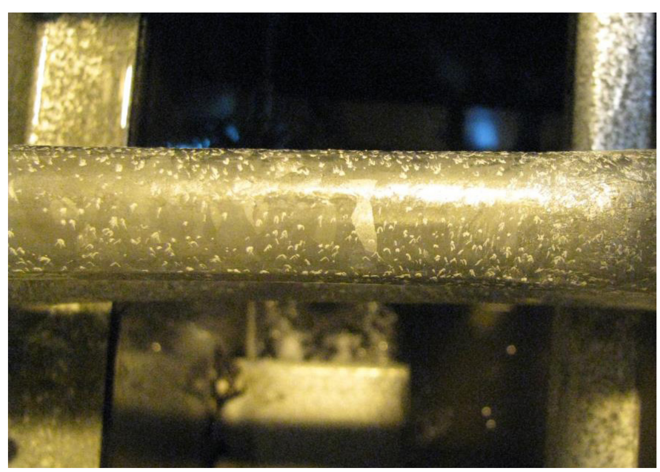
Figure 9: Higher Calcium (Nano Cooler 2) vs. Lower Calcium (Nano Cooler 4) Coil Sections

The impact of variables such as coil inlet temperature (85–100 °F), duration of passivation (2–10 weeks), transition from passivation to alkaline treatment (0–3 weeks), passivation chemistry, pretreatment techniques, wet operation (8–22 hours/day), and a variety of makeup water characteristics continue to be explored using both the Nano and Tiny Cooler systems.

Proprietary passivation formulations and commercially available treatment products have been tested. Testing to date suggests that vendors and their customers should be skeptical of products that claim to passivate equipment starting with immediate heat load in as little as 24 hours, 48 hours, one week, or two weeks. A commercially available product advertised as a poly/orthophosphate inhibitor that will "prevent white rust" on galvanized surfaces in as little as three or four days or up to two weeks was tested in a Nano Cooler. Visually, the test showed promise during the first three weeks of feeding the product (see Figure 10). As the test transitioned to alkaline treatment with pHs above 8.5, however, white rust quickly appeared, as shown in Figure 11. A subsequent Nano Cooler test sequence suggests that more than four weeks may be required to sufficiently passivate new galvanized surfaces before a successful transition to an alkaline treatment program is possible. With this insight, the test of a commercially available product, shown in Figures 10 and 11, is scheduled to be repeated with a longer passivation timeframe.

Figure 10: Nano Cooler 1 Following Third Week of Commercial Product Testing

Figure 11: Nano Cooler 1 Coil Section After One Day of Operation at pH 8.8



The investigation continued with a goal of optimizing a cost-effective, factory-applied pretreatment capable of minimizing the formation of white rust in evaporative cooling equipment commissioned with immediate heat load. Several years of bench, Nano Cooler, and Tiny Cooler testing have consistently shown that factory pretreated galvanizing develops less white rust than untreated hot-dip galvanization in side-by-side testing under identical operating conditions, as shown in Figures 5 and 11.

Significant investment in the construction and ongoing operation of the small-scale test equipment (see Figures 3 and 6) provides a platform to move beyond laboratory research relying on coupons or test strips. The ability to operate controlled tests to evaluate the impact of heat load, water chemistry, inhibitor formulations, and factory-applied pretreatments on galvanized surfaces will help to provide the data necessary for a better understanding of the control parameters necessary for successful passivation in the presence of heat load. These insights will make it easier to provide better commissioning outcomes with reduced occurrence of white rust, for customers and water treatment professionals alike.

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Christopher Nagle is vice president of Water Systems at Evapco. He can be reached at (410) 756-2600 or cnagle@evapco.com.