



Beyond Laboratory Research on White Rust and Passivation

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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. Evapco designed and built small scale closed circuit coolers 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. Evapco conducted additional research focused on innovative pre-treatment technologies for the galvanized coils utilized in closed circuit coolers and evaporative condensers. Evapco's research efforts continue 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 1980's and early 1990's, 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 & 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."²

Several of the early articles^{1,2,3} on the subject refer to 'cooling towers' generically as an apparent catch all 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 (Figure 1).

As white rust became more prevalent in the mid 1980's, 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;

1. Hot dipped galvanized coils did not receive a chrome rinse, but experienced an increase in observed white rust along with mill galvanized components.
2. 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 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.
3. Not all mill galvanizers eliminated the use of hexavalent or trivalent chrome rinses. In the early 1990's, 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 “Because of the increasing restrictions on the use of chromate based corrosion inhibitors for use in cooling water, a general trend towards 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 1970’s and 1980’s. 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 1980’s, 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.

Evapco's 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 and so Evapco started a program to evaluate the parameters that are required to develop a good passivation layer.

Evapco's on-going 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 (Figure 2). On-going research and laboratory testing suggest the following aluminum content range for hot-dipped galvanized; 0.069 to 0.149%. 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 (Figure 3) named Tiny Cooler 1 and Tiny Cooler 2. These units provided the first test platform for side by side analysis to study the impact of immediate heat load on new galvanized coils.

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 non-oxidizing 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 (Figure 4). 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 hand held readings.

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

While informative, research using the Tiny Coolers alone was time consuming. The original testing took 4 to 6 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 twelve and

sixteen weeks limiting the speed of innovation. As research unfolded, more hypotheses and variables were uncovered worthy of additional study.

By 2012, AWT's updated guide paper on the subject maintained their 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, Evapco initiated bench-top tests 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 pre-treatment 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-PPM and alkalinity at 60-PPM (both as CaCO_3). Solutions were heated to 90 F, aerated, and changed out daily during the test. pH ranged between 7.2 – 7.8 reaching a maximum of 8.0 over the course of a day.

Twenty-eight separate jars (Figure 5) each containing two galvanized test strips (Figure 6) were utilized during the bench top testing. Six distinct inhibitor chemistries were tested across the 28 jars during the initial screening.

The bench-top testing conducted between March and July 2012, demonstrated the following:

- Comparing jars with the same temperature, aeration, water quality, inhibitor type and concentrations, factory applied pre-treated test strips exhibited less white rust potential than test strips which had not received pre-treatment (Figure 7).
- Bench-top galvanized strips tested with inhibitors used in previous Tiny Cooler testing exhibited less white rust formation compared to the Tiny Cooler coil results.
 - Galvanized test strips immersed in heated solutions do not appear to correlate well with reactions which 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 bench-tested samples and heated coils from the Tiny Coolers, the use of bench testing was minimized to refocus on tests utilizing heated coil sections.

Following bench-top screening, Evapco built additional research equipment 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' (Figure 8) holds up to four small coil sections which are exposed to identical operating conditions such as temperature, water quality, inhibitor dosage, etc.

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 (Figure 9). This study demonstrated that elevated sulfate (540-PPM) showed less potential to increase white rust compared to elevated chloride (200-PPM) (Figure 10). Further, comparing two coil sections exposed to elevated chloride (200-PPM), the coil section exposed to spray water containing an average of 66-PPM calcium developed more white rust versus one exposed to an average of 195-PPM calcium (Figure 11).

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, pre-treatment 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 which claim to passivate equipment starting with immediate heat load in as little as 24-hours, 48-hours, 1- week, or 2-weeks. A commercially available product advertised as a poly/ortho phosphate inhibitor which will 'prevent white rust' on galvanized in as little as 3 – 4 days or up to 2 weeks was tested in a Nano Cooler. Visually, the test showed promise during the first three weeks of feeding the product (Figure 12). As the test transitioned to alkaline treatment with pHs above 8.5, however, white rust quickly appeared (Figure 13). 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 12 & 13 is scheduled to be repeated with a longer passivation timeframe.

Evapco's investigation continues with a goal of optimizing a cost-effective, factory applied pre-treatment 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 pre-treated galvanizing develops less white rust than untreated hot dip galvanized in side-by-side testing under identical operating conditions (Figures 7 & 14).

Significant investment in the construction and on-going operation of Evapco's small scale test equipment (Figures 3 & 8) provides a platform to move beyond laboratory research relying on coupons or test strips. The ability to run controlled tests to evaluate the impact of heat load, water chemistry, inhibitor formulations, and factory applied pre-treatments 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.

References

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4. Johnson, K. M. and Mihelic, J. B. Cooling Tower Institute Technical Paper
Number TP-91-14. Update on White Rust Corrosion and Control.
5. Kunz, R. G. and Hines, D. W. (NACE Corrosion 90 Paper 348). Corrosion
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6. Busch, B. D. and Oldsburg, M. T. (The Analyst, Summer 2000). Advances
in the Inhibition of White Rust Corrosion.



Figure 1 – Photograph of Evaporative Condenser with White Rust



Figure 2 – Photograph of Galvanized Coil Samples from Tiny Coolers (SEM-EDXA)



Figure 3 – Photograph of Evapco's 'Tiny Coolers'

Analyte	Taneytown City			Blended Makeup		
	Avg.	Min.	Max.	Avg.	Min.	Max.
pH	7.6	7.35	7.83	7.7	7.6	7.9
Conductivity (mhos)	515	468	575	184	171	195
Calcium (as CaCO ₃)	152	119	178	45	36	50
Alkalinity	161	155	182	56	49	59
Chloride (ppm)	47	37	57	17	15	19
Sulfate (ppm)	22	19	27	7	6	8

Figure 4 – Early Tiny Cooler Tests - City & Blended Water Data



Figure 5 – Benchtop Testing Setup

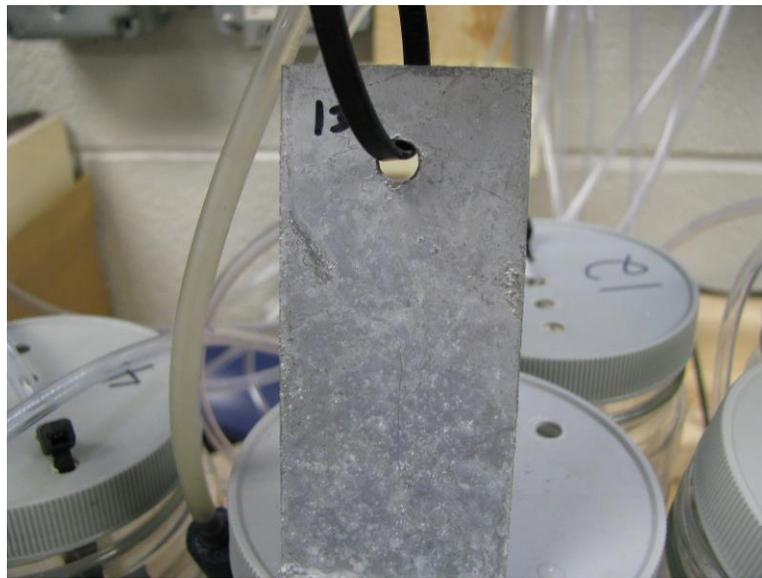


Figure 6 – Hot Dipped Galvanized Test Strip



Figure 7 –Test Strip with Factory Pre-treatment (L) Compared to Untreated Galvanized Strip (R)



Figure 8 – Photograph of Evapco's 'Nano Coolers'

NC1 will use water from the blended MU tank without any additions.							
	MU Target	Recirc Target	ppm as	by adding		mg/L in MU	mg/gal
NC2	33	100	Ca	Calcium Chloride (Cal-Plus) [solubility 745 g/L at 68F]	CaCl ₂	70	265
NC3	180	540	SO ₄	Sodium Sulfate, 99% [solubility 200 g/L at 68F]	Na ₂ SO ₄	264	999
NC4	67	200	Cl	Sodium Chloride [solubility 360 g/L at 68F]	NaCl	76	288

Figure 9 – Adjusting Makeup Water Quality to Individual Nano Coolers



Figure 10 – Photograph of Elevated Chloride (NC2) vs. Elevated Sulfate (NC3) Coil Sections

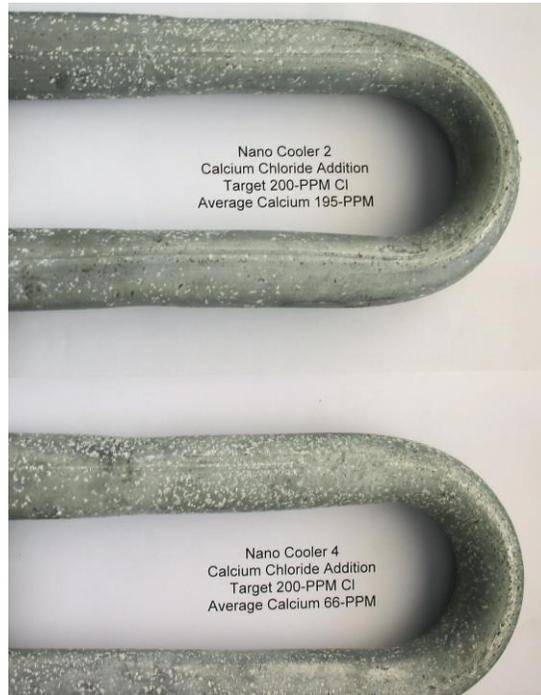


Figure 11 – Photograph of Higher Calcium (NC2) vs. Lower Calcium (NC4) Coil Sections



Figure 12 – Photograph from NC1 Following Third Week of Commercial Product Testing

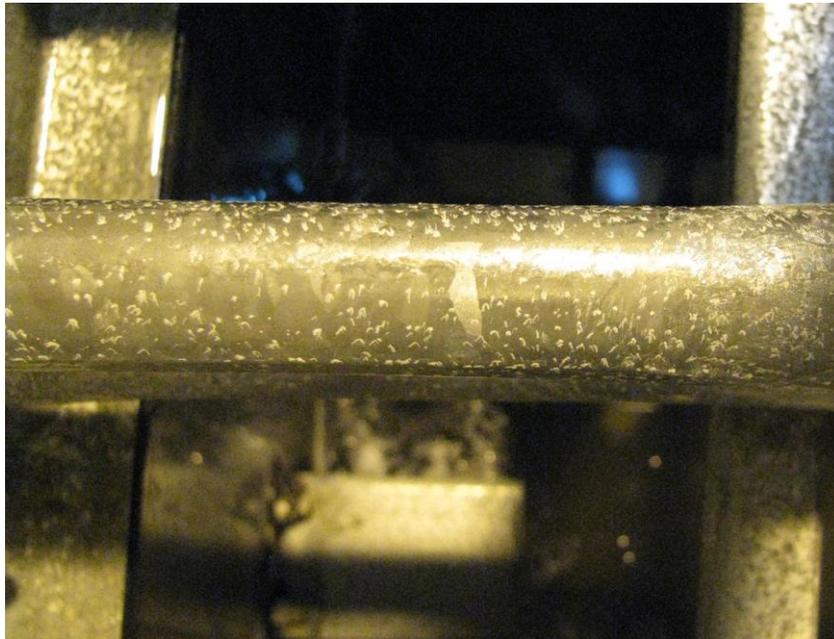


Figure 13 – Photograph of NC1 Coil Section after 1-day of Operation at 8.8 pH



Figure 14 – Photograph of Nano Cooler Coil Sections (from L to R)
Test 7 NC-Pre-Treat, NC-Galvanized, Test 8 NC-Pre-Treat, NC-Galvanized