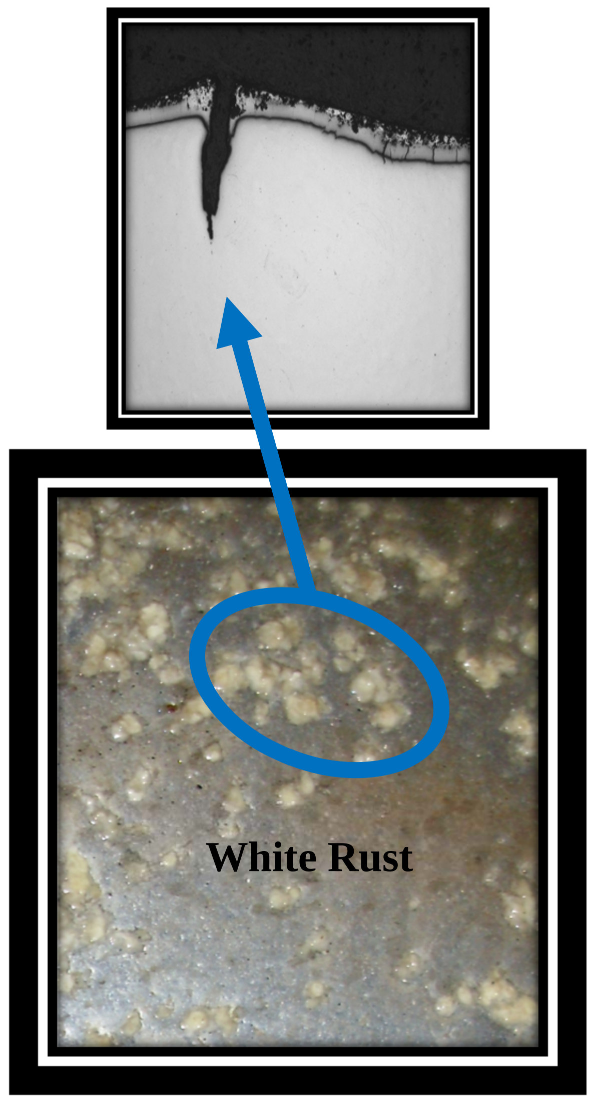
<u>White Rust Prevention</u>

An Industry Update and Guide Paper - 2012

Presented By:
Association of Water Technologies (AWT)



Special Acknowledgements

This is a revision of the original 2002 document version. A product of the White Rust Project team, this document has been updated by the Cooling Technical Committee and Special Projects Committee of AWT. Special thanks is given to the Technical Committee Chairs and AWT Board of Directors for their gracious contribution of time and knowledge toward the production and updating of this document.

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Forward

The Association of Water Technologies (AWT) is an international trade association founded to serve the interests of water treatment professionals and to advance the technologies of safe, sound and responsible water treatment practice. AWT is a non-profit organization providing education and training, public awareness, networking, research, industry standards and resource support. Association activities serve to benefit members, as well as advance the arts and sciences of the water treatment industry. Moreover, AWT makes a commitment to the public as a responsible steward of the environment.

The corrosion of galvanized steel components commonly used in HVAC-related applications, such as cooling towers and evaporative condensers, may be referred to as white rust and the consequence of white rust can be premature failure of galvanized steel components.

The on-going occurrence of white rust corrosion of cooling-related components led the AWT Technical Committee to create a White Rust Project team and conduct a survey amongst the AWT membership to assess the magnitude of concern for white rust corrosion. A brief overview of the survey results is as follows: white rust corrosion was identified as a serious and prevalent problem. It was identified that white rust corrosion occurs predominantly with newly constructed/installed galvanized steel towers and related cooling components. The predominant chemistry parameter known to aggravate white rust is high alkalinity/high pH, and is further aggravated by low hardness (softened water) and/or elevated chloride and sulfate concentration. It is known that water treatment professionals have various methods of prevention, but that these methods are not always successful when alkalinity/pH, chlorides, sulfates and/or hardness levels are not maintained within the prescribed ranges.

Furthermore, the conclusions of the survey offered the following: 1) white rust is a prevalent problem and 2) the AWT organization should prepare a topic update and guidelines to increase awareness and promote prevention of white rust corrosion of galvanized steel cooling components. The intention of this publication is to draw from and summarize published references and anecdotal experiences into one central document that will effectively present the topic of white rust corrosion and its prevention. The intended audiences for this document are water treatment professionals, cooling tower owners/operators, and architect/design and mechanical contracting firms involved in the specification and/or installation of cooling-related components. Prevention of white rust corrosion can be accomplished if all parties involved in specifying, manufacturing, operating and maintaining galvanized steel cooling components work together. Reference sources are provided for more detailed information on the causes, cures and prevention of white rust corrosion of galvanized steel cooling towers and related galvanized steel cooling equipment.

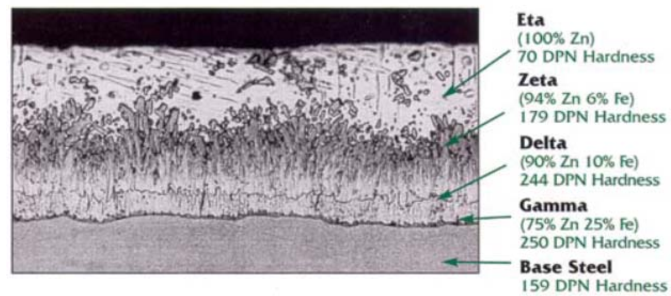
Section One - Introduction and Background

Since the 1950's, galvanized steel has remained the principal material of construction for factory assembled cooling towers and related components. This fact attests to the cost-effectiveness of galvanized steel, and when properly maintained this material can provide 20 years or more life expectancy in cooling applications. However, as noted in the Forward of this document, white rust corrosion continues to be a prevalent problem that has led to many towers requiring premature replacement. White rust corrosion can reduce life expectancy significantly, in some cases failure has occurred within a year or two of startup. This has led to a growing trend of using alternative materials of construction for factory assembled cooling towers such as fiberglass, plastic and stainless steel or hybrids of these two materials along with galvanized steel. None the less, galvanized steel cooling components still remain the most common choice especially when the decision is solely based on up-front cost for cooling component material. One objective for this document is to offer the reader some guidance in determining what materials of construction might be best based on the water chemistry, design, environmental and operational conditions existing or expected.

Many documents dedicated to the discussion of white rust corrosion have been published over the last 10-15 years. Some publications[8,11] have reported that changes to the galvanizing and finishing process has increased the potential for white rust, while other publications[2,5,7,12] refute this conclusion altogether and report that changes to the water treatment and related cooling water chemistry has increased the potential for white rust. Still other documents note that changes to both the galvanizing process and the water chemistry have increased the potential for white rust corrosion. There will be discussion of both these variables later, but briefly; there have been notable changes to the galvanizing process and the water treatment chemistry that have been driven in large part by environmental restrictions and regulations as well as cost-reduction initiatives. Also, the intent of this document is to identify these manufacturing and treatment changes and provide guidance for those who will consider purchasing and operating a new galvanized steel cooling component or have purchased and need to operate an existing galvanized cooling component.

<u>White Rust</u>

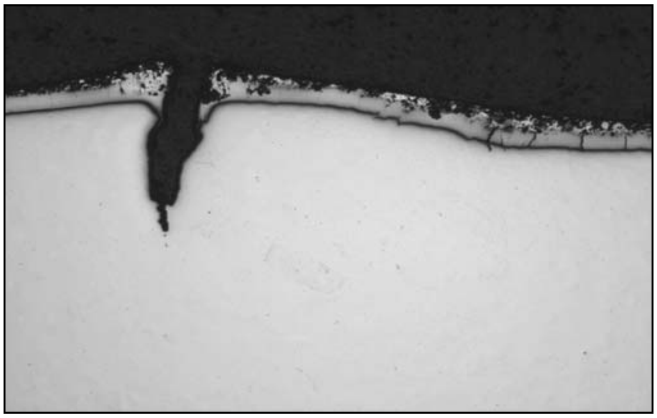
Galvanizing produces a coating of zinc-iron intermetallic alloy layers on steel with a relatively pure outer layer of zinc.



The zinc is anodic to steel and thus will provide cathodic or sacrificial protection to any small areas of steel that may be exposed (i.e., scratches, cut edges, etc.). Additionally, the zinc coating will oxidize and provide a physical barrier in protecting the bulk of the steel surface from any direct contact with the environment. Since the wear of galvanized steel in service is inevitable, it is fair to say that with all things being equal, a thicker (as measured by weight of zinc applied per surface area) and more durable zinc coating inherently will provide protection for a longer period of time.

White Rust may sometimes be interchanged with the term *Wet Storage Staining* since they have a similar corrosion mechanism. Wet storage staining is typically a pre-construction problem where new galvanized steel sheet or parts are exposed to a wet or moist environment because of improper storage. Post-construction white rust is a problem where the fresh galvanized surface is not able to form a protective, non-porous basic zinc oxide and typically the surface is partially wetted or completely submerged in water. In both cases, the deterioration begins when a localized corrosion cell is formed. The activity of such a corrosion cell/pit, results in rapid penetration through the zinc coating to the steel.

Under these corrosive conditions, the surrounding zinc coating may be unable to protect the base steel and consequently the corrosion will continue to penetrate through the base steel.



White rust corrosion is often identified by the white, gelatinous or waxy deposit that can be observed. This deposit is a zinc-rich oxide, reportedly $3Zn(OH)_2 \bullet ZnCO_3 \bullet H_2O$ and can be quite similar chemically to the protective zinc oxide typically identified as a dull-gray passive oxide. One critical difference between the two oxides is that the white rust oxide is porous and generally non-protective of the substrate, while the passive oxide is dense and non-porous effectively protecting the substrate from exposure to the environment. Corrosion control of galvanized steel, as with any metal, depends on forming and maintaining a stable and passive oxide layer.

If the oxide is disrupted, repair is crucial. If the oxide layer is constantly disrupted or removed, general corrosion potential will increase or in the case of galvanized steel, depletion of the zinc coating will eventually occur. And if pitting corrosion occurs and is not mitigated, the life expectancy of the component will be greatly reduced.

It is not the intention with this document to detail the specific reactions and chemistry of white rust. It is important to know that the specific mechanisms and causes of white rust can vary from system to system since there are a number of variables (with various combinations and permutations) that lead to white rust corrosion. One variable is the galvanizing process; several changes have been noted that have likely reduced the window of tolerance of the galvanized steel to white rust corrosion. Another variable is water treatment chemistry, which has changed significantly since the early 1980's.

The incidence of white rust corrosion can be heavily impacted by water chemistry, especially during the initial start-up operational period.

Having awareness as to how the galvanizing process and water chemistry can impact white rust potential is useful in obtaining a resolution or ideally an avoidance of the white rust corrosion.

<u>*Galvanizing Processes*</u>

Hot dip galvanizing is applied to a weight per square foot requirement, which can range from light to heavy. The amount of galvanizing applied may also be expressed in terms of thickness, which will correlate with weight, i.e., light/thin to heavy/thick. The hot dip coating actually alloys with the steel and forms an integral zinc-steel alloy bond between the base steel and outer pure zinc layer. The zinc oxide weight applied, the thickness applied to the working surface and interalloying are critical factors affecting galvanized steel performance. Components manufactured for cooling tower application may be manufactured using a post-fabricated hot dip process or a pre-fabricated hot dip process. Another consideration for the galvanized coating relative to performance is formability. Pre-fabricated hot-dip galvanizing must allow for cold working to be done without damage or fracturing of the coating. Some galvanized steel is not suitability for cooling water/HVAC applications. The tower manufacturer needs to ensure that the galvanized steel product purchased is suitable for these applications.

Up until the 1960's, the predominant method of galvanizing for manufacture of galvanized steel cooling towers and other cooling components was a post-fabrication hot dip process. This method of hot-dip galvanizing (HDG) is still used extensively for coating large structural parts (i.e., pre-fabricated cooling tower structural parts, evaporative condenser bundles, etc.) and for small miscellaneous parts. This zinc coating is rough and heavy (1.5 oz./ft^2) with an average thickness of 3 – 6 mils applied to the exposed surface (*per side*). The galvanizing process often will include a water-based quenching step where post-passivation is done, typically using chromate. The chromate passivation provides pre-operational protection of the galvanized coating. The governing specification for post-fabrication hot dip galvanizing is ASTM A123.

Three cooling tower OEMs and one trade publication[6] report that the more common galvanized steel product used today for cooling tower manufacture is the heavy mill galvanizing (HMG) process.

This is also a hot-dip process, but instead of post-fabrication & batch galvanizing, the raw, pre-fabricated rolled steel sheet is put through a continuous galvanizing process. The galvanized sheet roll still needs to be cold-worked by the tower OEM for fabrication of cooling towers; hence, this can be termed a pre-fabrication process. The governing specification for pre-fabricated hot-dip galvanizing is ASTM A653 (also, cooling tower components should meet a G210 HMG classification). The HMG process will produce a more uniform, thinner coating of zinc and zinc-steel interalloy (relative to the post-manufacture galvanizing process) with at least 3.0 mils thickness (2.1 oz./ft^2) *total* or 1.5 mils (1.05 oz./ft^2) on *each side*. Aluminum may be added primarily to enhance the corrosion resistance of this thinner coating. Quenching may be either an air-cooled or water-spray process. Chromate post-passivation may be done or some other form of pre-operational protection may be used.

Electrogalvanizing is a third galvanizing process where zinc is deposited on steel in a relatively thin layer by a process of electroplating. There is no interalloy layering with this process and the weight of zinc applied is thin compared to hot-dip galvanizing. Consequently, electrogalvanized steel product would have a fairly short life expectancy if used for the manufacture of wetted cooling tower parts.

Experience indicates that both HDG and HMG galvanized steel can provide reliable, long-term operating service in a cooling tower environment. However, as reported in at least two publications[8,11], there are notable differences between the HDG and HMG methods of galvanizing (and resulting product) that can directly impact the initial tolerance to white rust corrosion and generally impact the life expectancy of galvanized steel cooling components. It should not be assumed that all galvanized steel product has equal tolerance to white rust corrosion. For example, due to more stringent environmental regulation, some galvanized steel producers no longer use chromate passivation while others have reduced the concentration of chromate in their passivation step. Chromate is an excellent passivator of galvanized steel and the reduction or elimination, in some cases, of chromate is expected to increase the vulnerability of the galvanized steel to white rust.

Water Chemistry & Treatment

A typical water treatment program is designed to control scale, corrosion and microbiological related problems that may occur throughout the cooling cycle. The old standard of using chromate-based treatments and acid pH control along with a biocide provided excellent results. This treatment and pH chemistry regime were favorable to protecting and maintaining galvanized steel surfaces, but is long gone due to regulatory ban of chromates in the 1980's.

Today's cooling water treatment programs have been greatly influenced by several factors including environmental restrictions, energy and water conservation efforts, and the on-going focus on increasing facility safety. Some specific factors include:

- As noted, the USEPA ban of chromates in cooling systems - effectively implemented by the middle 1980's,
- A more recent and growing trend toward reducing the concentration of phosphate-based inhibitors,
- The use of acids has grown less popular due to safety and handling concerns,
- Efforts to conserve water and/or reduce operating costs have pushed many operations to increased cycling of the water chemistry,
- In many cases, the facility will modify the water source to achieve higher cycles or use poorer quality water sources, which are lower cost and/or more plentiful.

Consequently, water treatment professionals have adopted and supported these trends by modifying the water treatment program. Today, many treatments are using less anodic corrosion inhibitors and have compensated with a higher pH control range in order to provide effective corrosion control and avoid acid feed. Water softening has become a more common option to help maximize water conservation. Unfortunately, these trends have mostly been contrary to the needs of protecting and maintaining galvanized steel surfaces.

The following section will highlight the needs for the chemical treatment program and provide water chemistry guidelines that can help ensure reasonable life expectancy for all cooling system components, including galvanized steel components. The following section should also help a prospective buyer (of a cooling tower) to determine if galvanized steel is an appropriate material of construction choice.

Section Two - Prevention of White Rust

The discussion of white rust corrosion prevention is presented to address the responsibilities of the equipment OEM and that of the water treater separately. It is critical that the personnel specifying, purchasing and ultimately operating the cooling system be educated on what the requirements are for the prevention of white rust.

If these requirements cannot be achieved, an alternate cooling component material of construction should be considered (see Section Five).

<u>*Equipment Manufacturers' Perspective*</u>

Cooling equipment OEMs have the responsibility to manufacture a product that meets customer and industry specifications. To help ensure the product achieves life expectancy, cooling equipment manufacturers have developed chemistry and water treatment recommendations for cooling towers and related equipment. The seller, buyer and owner/operator needs to ensure that the intended or existing conditions will be able to achieve the manufacturer's recommendations. The information to follow is extracted from several cooling equipment manufacturer references. The specific manufacturers whose documents were reviewed are identified in the Table 1. Moreover, these recommended operating ranges are summarized in Figure 1 – Galvanized Towers Operating Ranges. This visually differentiates between initial and routine service.

Pre-Installation Handling Guidelines:

√ Abide by the American Galvanizers Association recommendation to store galvanized metals under dry conditions until it is placed in service to prevent "wet storage staining".

√ Tower manufacturer publications may or may not note if the galvanized steel is pre-passivated with chromate. The manufacturer's product should be pre-passivated with chromate or some suitable alternative should be utilized.

√ Several cooling tower OEMs note a need to consider alternative materials of construction (MOC) if system conditions are expected or known to be harsh relative to galvanized steel. The choice of cooling tower construction materials should consider corrosion resistance, structural integrity and durability, desired equipment life, and not just upfront cost. Stainless steel, plastic, fiberglass and epoxy coated galvanized are becoming common alternatives to galvanized steel, but at a higher upfront cost, to gain improved equipment life.

Post-Installation Handling Guidelines:

√ All OEM publications reviewed indicate that the potential for white rust corrosion is greatest when the tower is newly constructed, having a freshly exposed galvanized surface. All OEM companies referenced below recommend the tower be pre-passivated prior to putting any heat load on the tower.

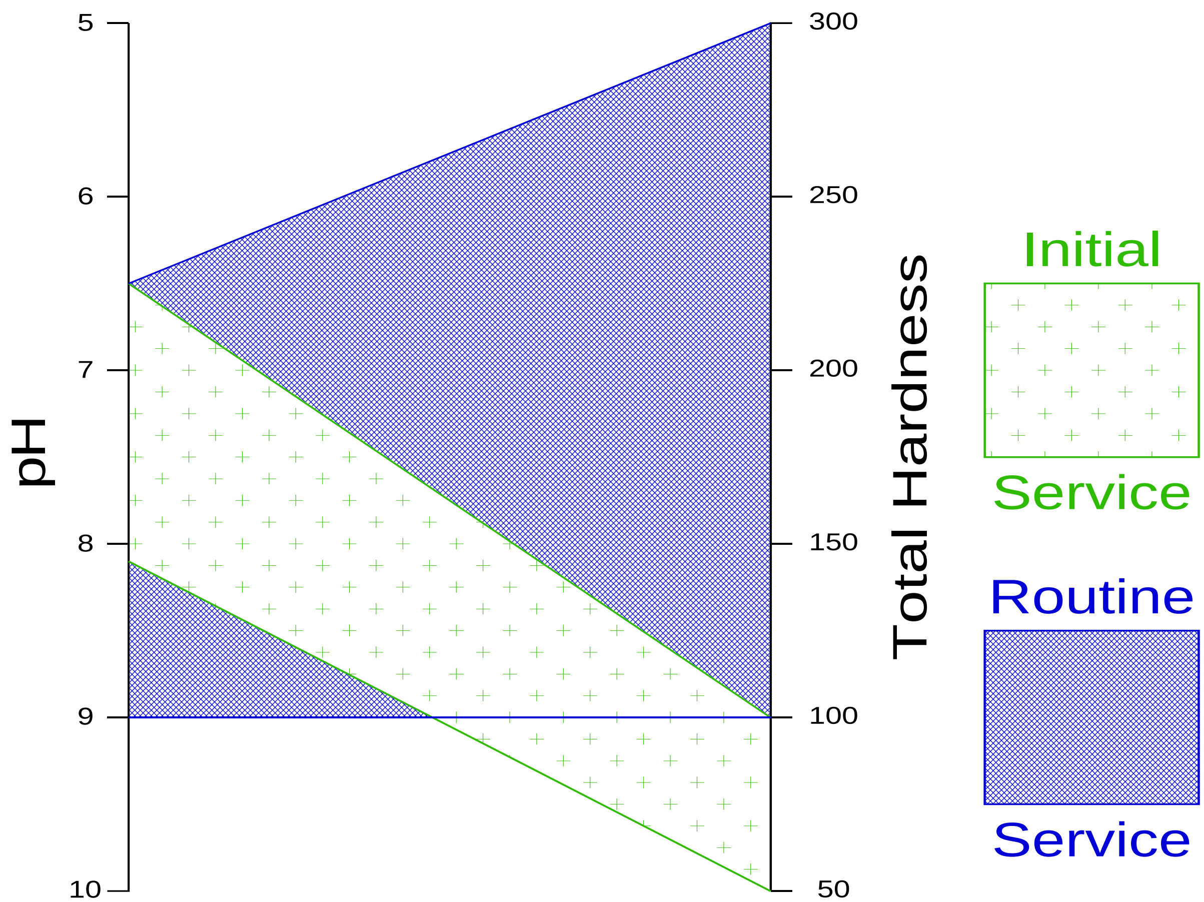
√ All OEM publications reviewed indicate that proper water chemistry and chemical treatment during initial tower start-up is essential to the initial formation of a passive zinc oxide. In particular, alkalinity/pH control and the presence of calcium hardness are emphasized.

√ All OEM publications reviewed emphasize the need to have a water treatment professional, knowledgeable of the topic of white rust prevention, involved in the start-up and operating process.

TABLE 1 COOLING TOWER MANUFACTURERS - RECOMMENDED WATER CHEMISTRIES			
Parameter	**BAC**[2]	**Evapco**[7]	**Marley**[12]
OEM Reference:	BAC Operating Manual	Evapco Eng. Bulletin 036A	Manual 92-114B
Passivation Duration:	4 to 8 weeks	4 to 12 weeks	Minimum of 8 weeks.
pH during Passivation:	>7.0 to <8.2	>7.0 – <8.0	>6.5 – <8.0
pH for Routine Service:	6.5 to 9.0 suggested	>6.0 to <9.0	No specific guide found
Hardness (as $CaCO_3$):	>30 ppm	>50 ppm	100 – 300 ppm
Alkalinity (as $CaCO_3$):	<500 ppm	<300 ppm	100 – 300 ppm
Chlorides (as Cl):	<250 ppm	<250 ppm	No specific guide found
Sulfates (as SO_4):	<250 ppm	<250 ppm	No specific guide found
Conductivity:	<2,400 µS	<2,400 µS	No specific guide found
Chlorine (as Free CL_2):	<1.0 ppm as a routine	<0.5 ppm as a routine	No specific guide found
General Comments:	• BAC offers removal & treatment recommendations for white rust.	• Critical to have a passivation plan and assigned responsibilities prior start-up.	• Chromate rinse used for HMG steel sheet.

NOTE: Cooling OEMs suggest that the system be initially treated with the maximum allowable level of a non-oxidizing biocide and/or sodium hypochlorite (oxidizing biocide) to a level of 4 to 5 mg/l free chlorine at a pH of 7.0 to 7.6. This recommendation is in place as a sound practice for bacteria control in cooling towers (see AWT Position paper on Legionella Guidelines for further discussion of this important issue). Exposure of galvanized steel to elevated chlorine level will increase corrosion potential of new, unpassivated galvanized steel and may damage passivated galvanized steel.

Figure 1 - Galvanized Towers Operating Ranges



Water Treatment Companies' Perspective

Since the water treatment professional is often in the position of being a unit operations consultant, it is important they be aware and communicate the established industry knowledge for maintaining galvanized steel tower surfaces. Also, the water treatment professional can help by communicating (to the specifying company and/or the owner/operator) the likely consequences when these water chemistry and operating requirements are not maintained.

Too often the decisions dealing with design, installation and start-up of a new cooling tower and related equipment are made without any or insufficient review and input from a qualified water treatment professional. Consequently, the requirements for a trouble-free, long operating life of the galvanized steel tower are compromised. In today's competitive environment it is increasingly critical that the owner/operator protect and optimize their investment. Involving a knowledgeable water treatment professional early on in the review process will help minimize problems and will help optimize the owner/operator's investment.

This section will discuss the critical considerations a water treatment consultant should consider and communicate during the *tower-preconditioning phase*, during the *routine operating phase* and during any *idle operation/lay-up phase*.

There are some basic established requirements that ideally should be assessed before deciding on the purchase/use of a galvanized steel tower. These include: 1) raw water chemistry parameters such as alkalinity, calcium hardness, chlorides and sulfates, 2) will the makeup be softened, 3) can the galvanized component be isolated from the system and 4) can the galvanized surface be properly passivated prior to heat load being applied. *Generally speaking, if the existing system conditions make it difficult to effectively accommodate the needs for maintaining galvanized steel, then one should reconsider the purchase and installation of a galvanized steel tower. Refer to Section Five in this document, which will address alternative material of construction selection.*

Tower Preconditioning Phase Check List:

√ Clean and passivate any newly installed cooling system or component prior to or upon initial exposure to circulating water. Galvanized steel surfaces have the same requirement to be cleaned and passivated as other metals, such as steel, but offer some special limitations. During the initial startup phase is when white rust is most likely to occur and consequently impact on the life expectancy of the galvanized steel tower or cooling related component. The startup phase may last several days to accommodate the "system", but passivation of the "galvanized component(s)" may require several weeks to several months to achieve desired results.

√ Control pH/alkalinity during the initial exposure of the galvanized surface to recirculating water: between pH 7.0 to 8.0 being ideal. Cleaners should be buffered to maintain pH between 6.5 and 8.0. The water treater should be capable of selecting an appropriate cleaner, but typically a phosphate-based and/or silicate-based cleaner is used. Specifically, inorganic phosphates are typically used for passivation. An acidic phosphate (such as phosphoric acid) can aid the conditioning process and help buffer the pH. Note each mg/L of phosphoric acid, as PO_4, will neutralize roughly 0.5 to 0.7 mg/L of bicarbonate alkalinity. Phosphate addition can range from 10's of mg/L to 100's of mg/L concentration. However, one should consider calcium phosphate deposition potential before applying the high phosphate residuals.

√ Use an effective copper corrosion inhibitor that will minimize the copper level in the recirculating water and complex any soluble copper to minimize potential for re-deposition. High copper levels in the circulating water can re-deposit on metal surfaces, particularly galvanized metal.

√ Isolate the fresh galvanized surface from any harsh solutions/cleaners. There may be pre-existing parts of the system that require strong acidic or alkaline conditions. Ideally, the system design allows for the galvanized equipment to be isolated and by-passed.

√ A minimum calcium of 30 to 100+ mg/L (as $CaCO_3$) is desired to achieve proper passivation when using phosphate-based or phosphate/molybdate-based treatments. Temporary addition of calcium may be required (i.e., bypassing a makeup water softener or by addition of a calcium source).

√ Halogen products should not be routinely fed to exceed 1.0 mg/L free halogen (as Cl_2). However, it is understood that proper sanitization may require up to 10 mg/L free halogen as Cl_2 for a period of 24 hours. Passivation after sanitization may be required.

√ Avoid starting-up a new unpassivated galvanized steel component with full heat load. Heat load on the system during precleaning and passivation should be minimized or ideally avoided to prevent concentration of salts and minimize corrosion potential.

√ Monitor the galvanized surface prior to and during preconditioning. Monitoring should include as a minimum, visual inspection and documentation. Monitoring may also include trending zinc in the makeup and recirculating water to assess zinc oxide pick-up. Corrosion coupons or a corrosion rate probe have been used with some success. Monitoring will be covered in Section Five of this document.

Routine Operating Phase Check List:

Once the tower and system is precleaned and passivated, the water chemistry and operating conditions can be modified to accommodate process needs. However, there will still be limitations that should be considered for galvanized steel components.

√ The tower pH may exceed 8.0; however, it is recommended the pH be increased slowly (not all at once) to the intended target. A pH of 9.0 is a desired maximum; although some tower treatments can allow a pH greater than 9.0 (consult with the water treatment representative servicing the facility). If excessive pH is identified as a concern, the owner/operator should plan to operate at lower cycles or control pH/alkalinity with acid feed or by dealkalizing the source makeup water.

Note operating at lower cycles is costly and may be precluded due to blowdown limitations. Requirements for proper handling, feed, and control of acid are critical and must be considered to ensure operator and system safety.

√ Control tower chemistry, considering treatment capability, to minimize corrosion potential of steel, copper (if present) and galvanized steel. Care must be taken with the water treatment not to harm the galvanized steel.

√ Overfeed of phosphonates, polymers and other chelating chemistries should be avoided. If the galvanized oxide is harmed, reconditioning of the galvanized steel surface (as identified in the preconditioning phase) may be required. Remove white rust by reducing the pH below 8.0, preferably to neutral pH, and implementing an effective treatment clean-up program (physical and chemical) targeted for galvanized steel.

√ Add maintenance chemicals ensuring they are well mixed and diluted prior to contact with the galvanized surface. As a rule, avoid adding chemical treatment directly to the tray/sump if constructed of galvanized steel. In the case where system upsets may require harsh chemicals to be used, the galvanized component should be isolated from the water circulation or an appropriate galvanized steel inhibitor used.

√ On-going visual monitoring of the tower's galvanized steel surface should be a service visit routine. Other forms of monitoring may be useful and will be covered later in this document.

Idle Operating/Lay-up Phase Check List:

An "operating" system in many ways is much easier to treat and protect than an "idle" cooling system and/or tower. However, for various reasons cooling systems and/or cooling tower(s) will need to be shutdown.

√ Lay-up solutions should be buffered to maintain pH between 7.0 and 9.0. Excessive pH/alkalinity can destroy the protective zinc oxide and result in white rust corrosion. Note, it is most common that the "cooling tower" component will be drained during lay-up.

√ Cleaning and passivation may be required to accommodate special issues such as system sanitization. *For example, sanitization may require high levels of halogen (i.e., > 10 mg/L halogen, as Cl_2) after an extended shutdown.*

Repassivation may be required after the sanitization.

√ If at all possible, water circulation through the system should not be shutdown. Ideally, by-pass the tower completely or least by-pass the tower fill.

Section Three: *White Rust Treatment Basics*

Evolving Technologies

Most water treatment professionals have access to conventional inhibitor technologies capable of maintaining low steel and copper corrosion rates. These conventional technologies are often adequate where galvanized steel is used if the galvanized steel surface has been properly seasoned.

Some newer technologies are being used and have been promoted as having enhanced capability to protect galvanized surface[3,15]. It should be the goal of the general water treatment community to gain a better understanding of these technologies and to continue to develop promising technologies for galvanized steel. This section will review the basis for some of these technologies.

<u>Common Treatment Approaches</u>

The management of white rust in process water can provoke a wide range of treatment approaches. While no one approach is considered standard, three primary treatment themes emerge when field practices are examined: Passivation, Water Chemistry Control and the use of Reactive Inhibitors. *Passivation and Water Chemistry Control* have already been addressed in Section 2. The two approaches remain the most commonly used concepts in mitigating or at least controlling white rust. Reactive inhibitors represent the use of treatment concepts that reportedly mitigate or control white rust and broaden the operating chemistry window tolerable to avoid white rust.

Reactive Inhibitors

Reactive inhibitors refer to those chemical components that are specifically added in order to limit the reactions involved in the formation of white rust. As opposed to protective film formation or water chemistry control, reactive inhibitors are designed to either slow anodic or cathodic reactions or complex with zinc ions as they are liberated from the metal surface to prevent subsequent reaction with free carbonate and hydroxide ions.

Following there are two primary chemical approaches that will be reviewed reportedly capable of controlling white rust with reactive inhibitors.

The first approach is analogous to that of controlling mild steel corrosion where blends of common inhibitors such as molybdate, phosphate, phosphonates, polyphosphates, zinc and/or other compounds believed to work are added to the system using proprietary formulae. There are various reports, industry papers, patents, etc that show data claiming efficacy for such treatments.
While it is not the position of AWT to endorse any specific treatment, the approach of limiting anodic and/or cathodic reactions involved in the destruction of the galvanized surface is a valid approach. However, there does not appear to be a consensus or even a leading series of guidelines within the water treatment community to support a particular combination of inhibitors or formula.

The second approach is the use of strong ligands to react with solubilized zinc to form a complex that has limited or no reactivity with hydroxide or carbonate ions. One class of chemicals with reported success is dithiocarbamates.

Dithiocarbamates are sulfur compounds prepared from the reaction of amines with carbon disulfide. The resultant dithiocarbamate compound can form highly water insoluble complexes with most transition metals. Because of this property, dithiocarbamates are well suited to complex with zinc ions at the water/surface interface and limit the ability of the metal ion to subsequently complex with either hydroxyl or carbonate ions that are necessary to form white rust. The specific composition of dithiocarbamates can vary widely depending upon the starting amine and, as such, a range of dithiocarbamates have reported efficacy in the literature. The addition of other compounds such as phosphonates and molybdate are reported to show significant improvements over the use of dithiocarbamates alone.

Section Four - Removal & Repair of White Rust

<u>Removal of White Rust</u>

Whether or not to remove the White Rust?

As noted, white rust corrosion is characterized as a localized/pitting type corrosion and identified by characteristic white, waxy tubercule-type deposits.

However, not all white deposits found on galvanized steel surface are due to white rust and not all deposits, including zinc-rich deposits, will result in localized/pitting corrosion.

Consequently, it is incumbent of the owner/operator, with guidance from the water treatment professional, to determine if the deposits are better left alone or if removal is required.

Evaluation can include any or all of the following:

- Deposit analysis – determine the inorganic content. It may be the deposits are calcium-based and not zinc oxide.
- Physical inspection of the surface under the deposits – investigate to determine if there is pitting corrosion resulting beneath the deposit. Consider leaving the deposit alone if pitting is not observed.
- Age of the equipment and of the deposits – the deposits may be doing more good than harm. A tower that is far along in life expectancy with white rust that has been present for years is probably better off left alone.

Mechanical Cleaning Methods:
Virtually all information recommends the removal of the white rust by brushing with a stiff (non-metallic) bristle brush and then coating the damaged areas. If the white rust build-up is light or spotty, it should be easily brushed off to allow for the formation of the protective zinc oxide. This process can be enhanced by the addition of inorganic phosphate or by the reduction of the pH/alkalinity during the repassivation step.

Chemical Cleaning Methods:
In mild cases the area should be brushed (using a stiff non-metallic bristle brush) with a mild cleaning solution. Severe cases may require multiple applications of a more concentrated cleaning solution along with brushing. Phosphoric acid is an excellent choice, although other acids such as acetic, glycolic or citric acid have been used with success.

Care should be taken when using these other acids since they can chelate the base zinc coating. Overzealous application of such chelating agents may strip the zinc coating from the steel surface. Follow the cleaning process with a thorough water rinse.

<u>Repairing Damaged Galvanized Surfaces</u>

Re-galvanizing with Zinc-Rich Paints:

- **ZRC Worldwide**
  ZRC Cold Galvanizing Compound
- **Sherwin Williams**
  Zinc Clad XI
- **Benjamin Moore & Co**.
  Epoxy Zinc Rich Primer CM18/19

Non-galvanic finishes

- **Belzona, Inc.**
  Belzona 1111 Supermetal
  Belzona 5811 Immersion Grade
- **Benjamin Moore & Co.**
  Coal Tar Epoxy M47/48
  Low Cure Epoxy Mastic Coating M45L/46
- **PPG Industries**
  COAL CAT® Amine-Cured Coal Tar Epoxy
  COAL CAT® Resinous Cured Coal Tar Epoxy

Please Note: The above list of manufacturers is not meant to represent a complete list of coating suppliers nor is meant to be an endorsement of these products.

Application Guidelines:
To achieve reasonable performance from the post-installation finishes, it is critical to properly prepare the surface. This will require removing debris and deposits, cleaning the base surface (typically with a phosphate-based cleaner) and repairing any areas where failure has occurred.

The surface should be dry before applying the finish. There are products that may be applied to a wet surface; however, results are usually temporary. Best results will typically be achieved by having a professional, experienced in this trade of metal surface finishes, perform the task.

Application instructions will vary somewhat among manufacturers - the basic steps are:

1. Remove sealing compound from corners.
2. Sandblast surface to near-white profile. Grinding the surface and wire brushing the rusted areas may be acceptable, but not as effective as sandblasting.

3. Completely remove debris, clean and dry surface - use fans to promote faster drying.
4. Apply coating according to manufacturer's instruction; typically two coats are required to attain a minimum desired dry film thickness.
5. Allow fully coated surface to dry/cure for specified time period (it can be as short as 1 to 3 days and as long as 14 days with zinc-rich paints). In some cases, application and curing times may be accelerated – check with coating manufacturer.

Notes:

1) Zinc rich compounds require extended cure times (up to 14 days) in order to provide the best possible performance.

2) The most important factors for the success of paint systems are adhesion and continuity – and in the case of zinc-rich paints, electrical conductivity.

Continuity of the paint systems is extremely important for carbon steel, since pinholes and other imperfections quickly become rust pits. Zinc-rich paints must be electrically conductive in order to provide cathodic protection.

3) Surfaces to be reconditioned, which will be subject to immersion should be prepared in accordance with Near White Metal Blast SSPC-SP10.

Refer to ASTM Section A 780 for details on these and other approved repair methods for galvanized steel surfaces.

<u>Leak repair</u>

Quick fix (for sump/pan area): insert a stainless steel bolt through the hole with a rubber gasket on each side of the affected area. The use of tar or an epoxy can help seal this type of repair. For larger areas use a piece of plastic sheet, fasten with rivets and use tar or epoxy to achieve a seal.

Long term repair (for sump/pan area): some cooling tower OEMs will provide a retrofit fiberglass basin. The cost of the sump insert is not a significant expense, but the cost of installation can be expensive since the tower may require partial dismantling.

Section Five - Monitoring for White Rust

Historically physical inspection, mass balance and galvanized steel coupons have been used to ascertain if white rust corrosion of galvanized steel was an ongoing problem in cooling towers. This section will provide some thoughts and guidance to the value and methodology nuances of each.

The simplest method of monitoring is visual observation of the galvanized surface. Physical inspection of cooling towers for white rust has proven to be fairly reliable in that white rust forms an easily identified soft white, waxy deposit on galvanized surfaces which when removed shows a definite area of attack on the metal surface. However, visual inspection is not preventative or proactive and it may not allow for the detection of zinc coating loss, unless gross loss occurs.

Standard mass balance analysis of cooling waters to determine if a white rust problem is occurring is generally not usable as the corroded zinc will deposit as corrosion product (i.e., white rust) and thus is not measured in the cooling water. The exception to this is where sufficiently aggressive treatments are used such that zinc is dissolved into cooling water. This may occur during the initial start-up phase, routine operational phase or during post-operational cleaning events. In these cases, measuring zinc in the makeup and recirculating water (and factoring tower cycles) to determine zinc pick-up can help monitor zinc oxide stability. For example, based on zinc measurement (i.e. $zinc_{blowdown}/zinc_{makeup}$), one can determine if zinc pick-up is occurring at the expense of the galvanized steel surface. It is expected that zinc oxide pick-up may be high to start, but it should level off with time and eventually approach theoretical tower cycles. Note, this monitoring method will not be effective if zinc is fed as part of the treatment program.

Corrosion coupons and to a lesser extent corrosion probes outfitted with zinc coated tips have long been used to monitor for white rust corrosion. Two material options to consider when using corrosion coupons are hot dip galvanized steel or pure zinc corrosion coupons.

Table 2 – Example Coupon Data			
Makeup Water Quality, mg/L	Min. & Max Range, mpy loss		Average, mpy loss
	Min.	Max.	
TH <5, TA 91	5.49	32.55	11.62
Galvanized Coupon	***1.35***	***8.03***	
TH 75, TA15	2.00	5.83	3.09
Galvanized Coupon	***0.49***	***1.44***	
TH 44, TA 52	1.53	3.98	2.65
Galvanized Coupon	***0.38***	***0.98***	
TH 241, TA 235	1.9	5.7	3.23
Galvanized Coupon	***0.47***	***1.41***	
Data is strictly provided as example.			

The field data shown is provided as an example to highlight the difference in data obtained from pure zinc coupons versus the HDG coupons. It suggests that because there is less zinc to be removed from the HDG coupon as compared to a pure zinc corrosion coupon that under the same conditions the reported metal loss will be lower (perhaps understating the actual corrosion result).

There also needs to be some rational given as to when this monitoring approach is best suited. For example, the use of corrosion coupons is ideal when monitoring galvanized surface during system start-up and pre & post operational cleaning events. Furthermore, this monitoring method will work well when using "reactive" white rust inhibitors as part of a maintenance treatment regiment. However, there are some practical issues that need to be considered when using zinc-based coupons to monitor a maintenance treatment that does not employ a "reactive" white rust inhibitor regiment. For example, if the coupon is not pre-passivated, then the water chemistry of the circulating cooling water will have a predominant affect on the coupon regardless of what affect the same water source may have on the actual zinc surfaced equipment. This is because an already "passivated" galvanized metal surface is more tolerant of a broader chemistry window. An unpassivated zinc-based corrosion coupon exposed to water chemistry under heat load, operating conditions will demonstrate white rust, but will not necessarily reflect accurately what is happening to the equipment that has been passivated.

As with all corrosion coupon data, this coupon data needs to be evaluated in the context of other data sources and over time as a trend for each individual operating cooling system.

In the absence of any formally presented data, it is still unclear how to fully interpret the result of zinc-based corrosion coupon data. There is an AWT reference[17] that offers a good overview of best practices for corrosion coupon monitoring. This same project committee is currently looking to establish a specific performance rating system relating to galvanized coupon corrosion rates. Once complete, that specific data will be provided.

Section Six - Alternative Materials

This section will endeavor to provide some guidance on whether the (cooling) system conditions represent a high risk for shortened life expectancy (see figure 2) and will offer suggestions on alternative materials (see Table 4). Included is a summary of the basic features and benefits of alternative materials and some review of their limitations. The most popular alternative MOC choice to galvanized steel cooling towers and evaporative condensers is a hybrid of stainless steel/galvanized steel or all stainless steel (excluding fill, distribution nozzles and louvers). Fiberglass and plastic are gaining somewhat in popularity, but are still a high cost option, especially when structural integrity is fortified.

Selection of Galvanized Steel Material

The decision tree shown on the following page will offer guidance as to whether galvanized steel should be selected. This decision tree is simply a guide and should not be used to draw absolute conclusions as to whether galvanized steel MOC is the right choice or the wrong choice for a particular application.

Table 4 that follows offers a basic overview of the alternative materials one may want to consider if the risk assessment guide suggests that galvanized steel is not appropriate for existing or expected application conditions. Each of the alternative materials may have advantage(s) over galvanized steel; however, the reader is encouraged to pay close attention to the limitations noted for these alternative materials as well.

When in doubt, it is best to consult with one or more tower OEMs and water treatment consultants.

FIGURE 2
Decision Tree - Okay To Use Galvanized?

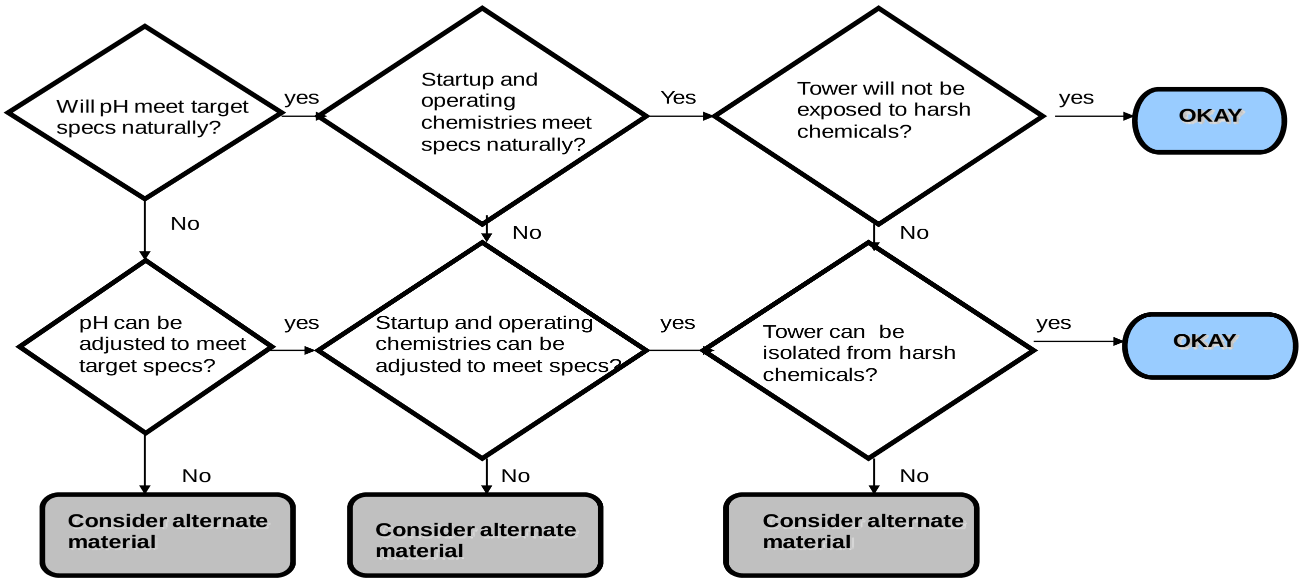


Table Summary:
As one might expect, tower materials with longer life expectancy will tend to have a higher relative cost. Galvanized and epoxy coated galvanized steel towers have the lowest life expectancy, but offer a relatively low-cost option.

If conditions are abusive, the life expectancy of any of the materials shown above may be shortened. However, it is fair to say that the more expensive materials are more forgiving. It holds true that galvanized steel has a narrower window of tolerance.

Epoxy coated galvanized steel is offered by one OEM. The OEM claims that the epoxy coating in combination with the base galvanized steel effectively protects the base steel substrate. If the epoxy coating is disrupted the exposed galvanized steel will become quite anodic (corrosion will be localized to this small exposed area) and white rust-type corrosion is likely to occur.

Consequently, the epoxy coated galvanized steel is considered to be only a minor upgrade at best from galvanized steel.

The seller and buyer should inquire with the manufacturer as to whether this epoxy coating can effectively expand the window of tolerance for operating and chemistry conditions considered to be non-conforming for galvanized steel.

Stainless steel is among the fastest growing alternative materials used, replacing galvanized steel. A stainless steel hybrid with galvanized steel is a common trend as well. The hybrid tower considers the structural components of significant vulnerability for galvanized steel and replaces these components with stainless steel. Stainless steel can be vulnerable to chloride pitting and to stress corrosion cracking (although chloride tolerance is typically greater than that required for galvanized steel). Stainless steel type, temperature, chloride concentration and surface cleanliness are all important factors when using this material.

Fiberglass continues to gain ground as an alternative material, but cost remains an issue and structural integrity can be a limiting factor to size of cooling application. Relatively new manufacturing technique for high-strength structural components will address the structural integrity issue, but cost continues to be an issue.

Wood and concrete materials remain commonplace in medium-sized to large cooling towers applications. However, these materials are not commonly used as an alternative to galvanized steel. Wood has been a viable alternative in the past for smaller cooling applications, but wood material is not readily available today and wood has a fire concern.

TABLE 4			
Material Type & Uses	**Life Expectancy (expected Vs. theoretical)**	**Cost Factor (galvanized = 1.0X)**	**Limitations/Comments (ease of use)**
Ceramic - Tower structure - Tower fill	20+ Vs. 30+ years	2.5 to 3.0X+	• Weight can be an issue • Fill more prone to fouling
Fiberglass/Plastic - Tower structure - Dist. deck & basin - Tower fill & louvers	15-20 Vs. 25+ years	2.5X for small tower >2.5X to increase structural integrity	• Prone to UV degradation • Structural integrity can be a limitation to size • Fastener material can be a weak link • Generally easy to fabricate
Wood - Tower structure - Tower fill & louvers - Distribution deck	20+ Vs. 30+ years	3.0X+	• Availability of wood product • Prone to MB degradation • Can be fire hazard concern
Stainless Steel - Tower structure - Distribution deck	15-20 Vs. 25+ years	1.8X to 2.0X	• Avoid high chlorides • Keep surface clean • Generally easy to fabricate
Concrete - Tower structure - Tower basin	20-25 Vs. 30+ years	3.0X+	• Weight, roof-top installations • Rebar corrosion • Generally easy to use
Epoxy Coated Galvanized Steel - Tower structure - Dist. deck & basin - Louvers	10-15 Vs. 20+ years	1.1X to 1.2X	• Maintain coating to protect gal-vanized surface • Avoid high chlorides and sul-fates • Typical coating life is 2 to 10 years per AWT survey
Galvanized Steel - Tower structure - Dist. deck & basin - Louvers - Evap. condenser	10 Vs. 15-20 years	1.0X	• Prone to white rust • Proper startup conditions are critical • Avoid chemistry upsets. • Generally easy to fabricate

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