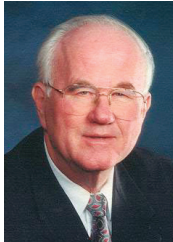


Galvanized fasteners and corrosion in wood

Part 1: The Galvanized Coating

By Thomas J. Kinstler

Zinc coatings to protect steel from corrosion have been used worldwide for well over a century, accumulating an astounding and reassuring record of performance from the Industrial Revolution to present. The corrosion rate of zinc in the natural environment has generally decreased over the last 40 years as a result of higher environmental consciousness, regulation, and investment.



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The corrosion mechanisms and dynamics of zinc are generally well known and predictable. Indeed, the known corrosion reactions of zinc are now used as one factor in the characterization of the corrosivity of atmospheres. Zinc coatings, applied to steel primarily through the galvanizing process, protect steel by a dual barrier and electrochemical mechanism, and have been utilized on projects ranging in size from large bridge and building structures, to fastener components.

Quarles and Tully¹ have pointed out that wood is perhaps the most comfortable and familiar construction material and has long been associated with structures used for human habitation. However, the long-term performance of wood in service is heavily influenced by exposure to biological factors, such as fungal decay and insects, and non-biological factors such as weathering and

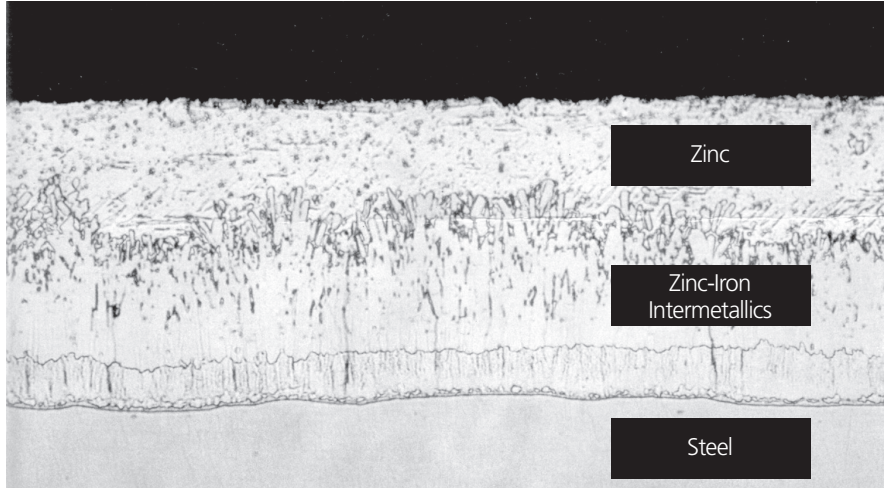


Figure 1: Microstructure of Typical Hot Dip Galvanized Coating

fastener corrosion. The threat from biological decay is often mitigated by the use of preservative treatments, which provide a measure of safety, economy, and environmental stewardship.

A heightened concern about the safety of traditional preservative treatments has led to the introduction of non-arsenic treatments, which are higher in copper than those previously used. These new products, such as ACQ and copper azole, have led to concern about the corrosivity of preserved wood to traditional fasteners. This concern has been heightened by anecdotes and accelerated simulation experiments, the relevance of which should be seriously examined.

The conventional galvanizing process is a “dip and drain” procedure in which properly prepared steel articles are immersed in molten zinc, wherein a reaction creates a zinc-iron intermetallic layer, metallurgically bonded to the steel, which upon withdrawal from the zinc, is encapsulated in solid zinc. The corrosion characteristics of the various components of the unique, layered structure is reasonably constant, and

therefore the corrosion dynamics of the complete galvanized coating can be confidently predicted as similar to zinc alone. The formation of the outer zinc layer is governed by the flow and freezing characteristics of liquid zinc, and the geometry of the article galvanized. Parts galvanized by the conventional method that are relatively small and/or more intricate in shape (such as threaded fasteners) or more critical in surface smoothness (such as collated nails) may experience some non-uniformity of the final coating.

The Galvanized Coating

The result of the galvanizing reaction is a series of zinc-iron intermetallic layers that are metallurgically bonded to the underlying steel, encapsulated in an outer layer of zinc. The unique structure of the coating is shown below:

In the conventional hot dip galvanized coating, the thickness of the complete coating microstructure would range from about 50µm (0.002 inches or 2 mils) to over 100µm (>4 mils) depending on various processing and material

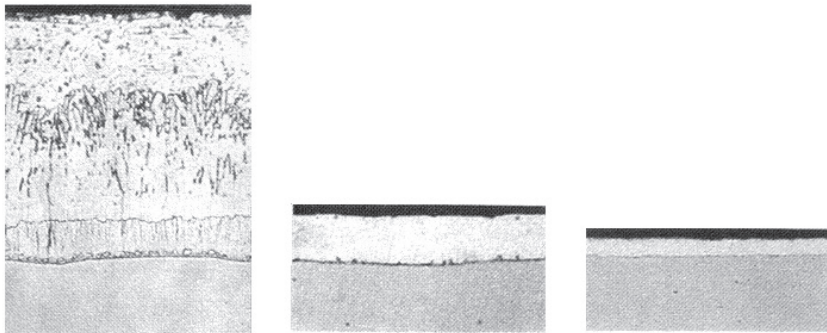


Figure 2: Hot Dip Galvanizing, Continuous Galvanizing, and Electroplating Microstructures

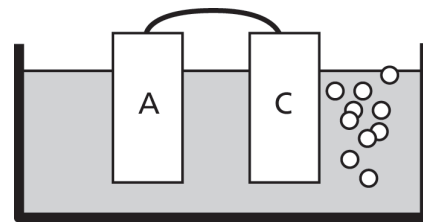


Figure 3: Schematic of General Corrosion Cell

parameters.

There are a number of zinc coatings, some often perhaps erroneously called “galvanizing,” which do not have the unique microstructure shown in Figure 1. As a result they often lack the thickness, mechanical, and adhesion properties inherent in the metallurgical structure above — for example, mechanical plating (a.k.a. mechanical “galvanizing”), electroplating (a.k.a. “electrogalvanizing”). In addition, sheet and wire materials are often galvanized by a continuous process that inhibits the formation of the intermetallic layers, but thereby allows for the further processing of the sheet or wire into articles such as roofing. The typical microstructure of some of these coatings are shown in Figure 2 in correct, relative size for hot dip galvanizing, continuous galvanizing and electroplating.

As a general rule, the corrosion life of zinc coatings is proportional to the coating thickness (more correctly the coating mass). This general rule can be seen in real world practice by the relatively short performance life of galvanized sheet and even shorter life for electroplated hardware, and is a result of the relative thickness shown in Figure 2.

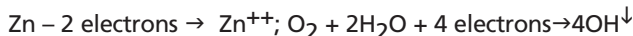
This linear relationship between coating life and zinc thickness is a safe approximation, but in some applications, significantly underestimates the service life of thicker galvanized coatings. The mechanism and kinetics of zinc corrosion fully explains how the thicker coatings have disproportionately longer lives in many applications.

Zinc Corrosion

Most atmospheric and in-service corrosion phenomena are electrochemically driven. The electrochemical cell is based on the confluence of three conditions listed below, and shown schematically in Figure 3:

1. A difference in electrochemical potential between the two surfaces A and C, or more often between two areas along the same surface.
2. A conductive electrolyte, B, connecting the two surfaces allowing for containment and transport of species participating in the reactions, and
3. A supply of material capable of “chemical reduction.”

Corrosion is the “oxidation” of a material. Chemically, oxidation is the loss of electrons, which allows a surface (surface “A” in Figure 3) to dissolve as an ion. This destroys structure, strength and integrity (at least microscopically), and therefore often the utility of that surface. This loss of electrons at “A” must be balanced by the acceptance of those electrons in a “reduction” of some species, which in the case of most corrosion reactions is the reduction of oxygen dissolved in water. The two “electronically opposite but equal” reactions are shown below:



The reduction reaction takes place at the “cathode” of the cell, or surface “C” in Figure 3. Thus the key elements governing zinc corrosion begin to be apparent. The combined reaction for zinc on the adjacent electrode surfaces becomes:

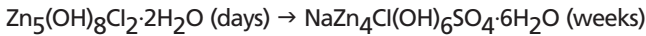
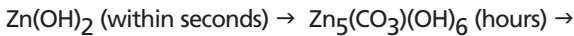


The insolubility of the zinc reaction products (such as zinc hydroxide) lead to a precipitation or “plating out” of the reaction products on the reduction surface, which begin to inhibit the reduction reaction as more and more reaction sites become inactive by the “smothering” blanket of insoluble reaction products. Thus, the reduction reaction slows down. Since the oxidation (or destruction) reaction must be balanced by equal reduction, the oxidation (which we call corrosion) similarly slows down — often to an almost immeasurable pace. The very reactivity of zinc creates a building barrier to further reaction or further zinc corrosion.

The protective nature of zinc corrosion products is generally enhanced by wet and dry cycles. While zinc hydroxide is shown above, it is only one of the reaction products in aqueous corrosion. Dissolved carbon dioxide (the concentration of H_2CO_3 is about 1×10^{-5} M, which is in equilibrium with atmospheric CO_2 level of about 340 ppmv), which has a much greater solu-

bility in water than does oxygen, leads to the formation of a number of zinc, hydroxyl, and carbonate-containing compounds, with varying degrees of insolubility. Upon each drying cycle, the most insoluble precipitate first, and on the next wetting cycle are the last to dissolve. Thus there is a gradual process of sequential dissolution, concentration, redistribution, and precipitation that builds relatively large structures of protective layers on the metal surface.² In an almost “Darwinian” sequence, the zinc corrosion layer (which depends on the environment) becomes more protective over time, given cyclic wetting and drying.

The reaction sequence for this shift in product morphology towards more protection in a marine environment, for example, is generally:³



It is important to recognize from the discussion above, the central fact of zinc corrosion:

The corrosion products of zinc are an integral, necessary, and valuable part of the protective mechanism. The zinc used to create this unique protective layer is not “consumed” as in wasted or degraded, but in general is “converted” into a protective system where the reaction products perform the protective function, and the underlying zinc is the reservoir from which any depletion of the protective layer is repaired and replenished, usually at a slow and equilibrium rate with the surrounding micro-environment.

In addition, Figure 3 depicts a free bulk solution of electrolyte, and uninhibited availability of oxygen, governed only by solubility in the electrolyte. In practice, the availability of oxygen (the reduction “fuel” for the oxidation or “corrosion” reaction), and the amount and mobility of electrolyte is often constrained. In “matrix” materials, such as soil, concrete, and wood, the interstitial spaces present a sometimes convoluted and often tortuous path for the transport of electrolyte, reactants (such as oxygen) and reaction products. Beyond the insolubility mechanism above (which tends to blanket the microscopic reaction sites on the electrode surfaces), the inability to bring more “fuel” to the reaction zone (as well as the difficulty in transporting reaction products away from the reaction zone) leads to a bottleneck technically called “polarization.” This is attributable to the decrease in reaction sites due to deposition or local accumulation of reaction products (Activation Polarization) and the decrease in available fuel (Concentration Polarization) because of diffusion and solubility constraints.⁴ The concentration polarization case is analogous to blowing air on a glowing ember; it enhances the fire. Similarly, encapsulating the ember in a jar retards the transport of carbon dioxide away, and ultimately smothers the fire.

This diminishing of corrosion reaction by a developing pro-

TECTIVE layer of increasing insolubility, as well as the inhibition of retarded diffusion and mobility, have been mathematically modeled and field-verified as the Power Law, where corrosion damage as a function of time is given by:

$$\Delta W = k(T)^n$$

Where:

ΔW = weight of metal consumed

k = a factor related to the corrosivity of the surrounding environment (often taken as the initial corrosion rate before protective film buildup)

T = units of time (for example: years)

n = a factor related to the “protectivity” of the extinguishing reaction product film — the degree of corrosion reaction extinguishment.

The power law, with n usually between 0.5 and 1.0, turns out to be valid for many metals and alloys including galvanized steel and zinc. In very aggressive environments, n -values close to 1.0 are normally observed. This condition reflects a situation in which the corrosion products provide meager protective properties and the corrosion rate is largely determined by the supply of corrodants furnished to the surface. In benign environments that generate corrosion films with increasing protective properties, n is commonly observed to decrease to values of 0.6 or lower.⁵

The importance and validity of this law seems not to have attracted much attention⁶, but the importance and relevance to fastener corrosion in wood cannot be overemphasized. Generally, under corrosion conditions (whether as test or actual long-term exposure) where the reduced species (for example: oxygen) are freely abundant, n tends to be closer to 1.0. However, corrosion cells can only operate when there is sufficient electrolyte at the metal surface.⁷ In cases where there are restrictions on electrolyte availability, ionic diffusion, and other inhibiting conditions, n tends to be lower and the extinguishments of the corrosion reaction with time become more pronounced.

The term k is a constant which relates to the corrosivity of environment. The value of the term k isn't important in the context of this discussion because we are only interested in the relative damage effect of having “ n ” be a number smaller than one. Thus the corrosion (damage) effect is negatively parabolic. That means that as time goes on, the corrosion becomes less and less on a rate basis, and therefore the consumption of zinc slows down. This is very beneficial, and is often overlooked.

If we wanted to know the absolute amount of zinc consumed, “ k ” would matter numerically, but using “ k ” = 1, the corrosion rate numbers are relative. “ k ” may be thought of as the “corrosivity” of the environment, and “ n ” the “protectivity” of the reaction products. If “ n ” < 1, the reaction decelerates, if “ n ” = 1, the reaction rate is linear, and if “ n ” > 1, the reaction

accelerates, which of course is bad news. The corrosion rate decrease noted by the research from France, cited below as reference 8, illustrates and proves the concept.

This author has researched similar conditions such as corrosion within concrete matrix and within soils, and values of n well lower than 1.0 are supported. For example, in studying long-term field and laboratory corrosion of galvanized steel in soils (a corrosion condition somewhat analogous to wood), the authors found that “Whatever the zinc coating thickness, an important gradual decrease in the rate of corrosion was observed with ‘ n ’ approximately 0.33. For uncoated (not galvanized) steel, ‘ n ’ varies between 0.6 and 1.0.⁸

A plot of the shape of the parabola resulting from the corrosion power law is very significant in predicting zinc corrosion in wood. Figure 4 shows the zinc remaining for various values of n , and beginning at the specification for hot dip galvanizing according to ASTM A 153 Class D (which would include nails), and for ASTM A 641 Class 1, according to the requirements of ASTM F 1667-97 (which would include some electroplated nails). The value of $n = 1.0$ would represent the kinetics where no protective layer is created.

From Figure 4, a number of important concepts can be seen:

- The reduced zinc consumption with time has a dramatic effect on coating, and therefore underlying steel life and integrity. For example, in the case of A 153 Class D coating (nominally 43 μm) where $n = 0.7$, the coating has about 67 percent of its thickness remaining when the $n = 1.0$ case (dotted line) unreacted zinc has reached zero. Were the $n = 0.7$ curve plotted to zero, the time would approximate 216 times units, or 5 times that when $n = 1.0$, for the same coating thickness starting point. Thus, coating test conditions, which prevent the build up of the natural protective layers, will drastically understate the coating life under natural

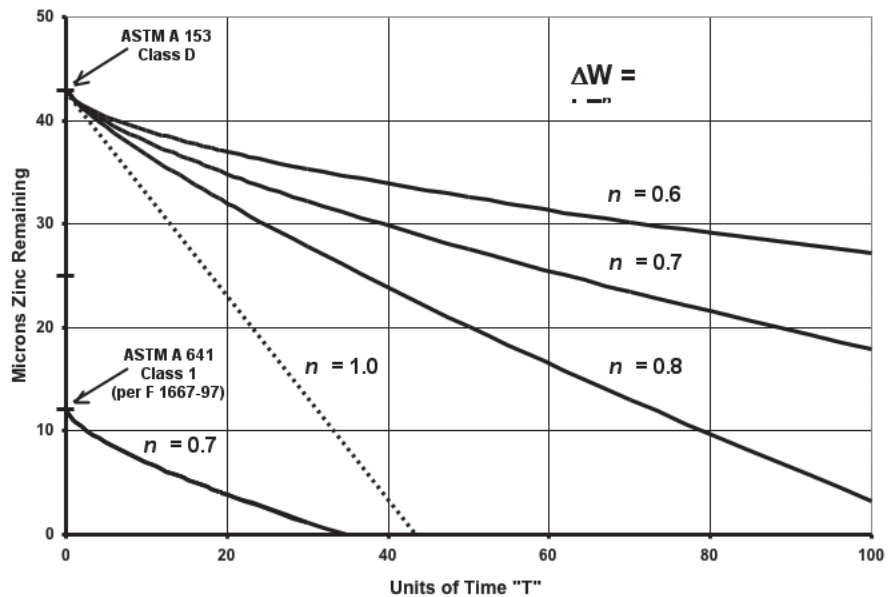


Figure 4: Zinc Remaining as a Function of Time for Various n -Values and Coating Specifications

conditions.

- The nominal coating thickness for the hot dip galvanized versus the electroplated coating is a ratio of about 3.3. At the same n -value, (for example: 0.7), the life of the 43 μm coating (hot dip galvanizing to A 153 Class D) is about 5.5 times that of the 13 μm coating (electroplated to A 641 Class 1) even when governed by the same corrosion kinetics.

Corrosion Testing

Coated fasteners are often subjected to accelerated testing, such as simulated environment cabinet and stagnant solution immersion testing, as a way to rank the corrosion performance and value of the various coatings in natural exposure.

Efforts to correlate accelerated test results and service performance have been characteristically unsuccessful and accelerated tests cannot be used to predict the type of failure likely to occur from natural exposure. Perhaps the greatest disservice provided by the accelerated test approach is encouragement of the fallacy in the minds of the inexperienced that the rougher the treatment

the better the test.⁹ The shapes of the curves in Figure 4 help illuminate the difficulties of accelerated corrosion testing — duplicating the natural exposure conditions, shortening the test period, applying objective and linear criteria, while at the same time not changing the mechanism of corrosion; for example, changing from naturally parabolic (decreasing with time) to artificially linear kinetics.

The corrosion of zinc in water is controlled largely by the impurities present in the water. Rarely are naturally occurring waters pure. Even rainwater, which is partially distilled by nature, contains nitrogen, oxygen, carbon dioxide and other gases as well as entrained dust and smoke particles. Water that runs over the ground carries with it eroded soil, decaying vegetation, living microorganisms, dissolved salts, and colloidal and suspended matter. Groundwater also contains salts of calcium, magnesium, iron, and manganese. Seawater contains many of these salts, plus sodium chloride. All of these substances in natural waters affect the structure and composition of the resulting films and corrosion products on the

surface, which in turn control corrosion of zinc.¹⁰

Water hardness and dissolved salts are particularly significant in retarding the corrosion of zinc over time for film deposition and build up. For example, tests have shown that in the Panama Canal, the corrosion rate of zinc in seawater is initially greater than in fresh water, but after about two years of immersion exposure, the rate in seawater had decreased so that it is approximately the same as that in fresh water.¹¹

Salt Spray Testing (and Salt Fog Testing) has been used since its original development in 1914, often for a number of purposes for which it is not well suited. Indeed, the oft-cited test states in the text that “prediction of performance in natural environments has seldom been correlated with salt spray results when used as stand alone data.”¹² Salt spray testing (SST) often generates material performance rankings which are different from or opposite to those observed in the real environments.¹³ Thus, it can be very misleading to use the results of SST to evaluate the real-life performance of different materials. This is demonstrated clearly in Figure 5 for bare metals and painted metals, where a reversal of performance ranking occurs comparing SST and actual exposure. Similarly, in Figure 5 the ratio of performance between different materials is misleadingly different between accelerated and cabinet testing.

One important reason for the unrealistic results of SST is the use of concentrated salt in the spray solution compared to the salt content in the moisture formed in atmospheric environments, which is much lower. Another reason is the lack of cyclic drying, which is a part of natural atmospheric environments. Salt content and drying effect are both very important to the protectiveness of the corrosion products, which determine the long-term corrosion rate of exposed metals. In particular, the effect of periodic drying increases the adherence and compactness of the corrosion products in zinc but not those of steel,

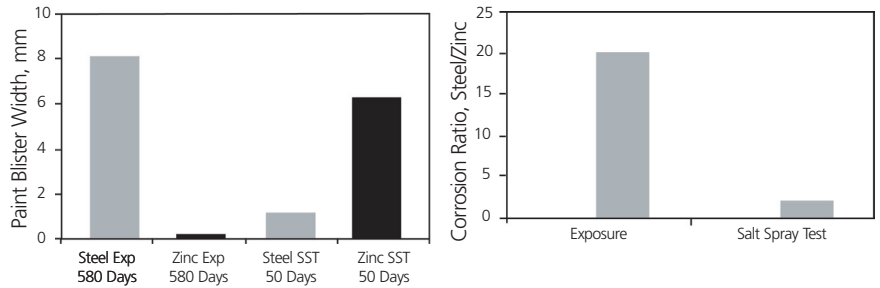


Figure 5: Corrosion of Black Painted Steel and Zinc-Coated Steel as Measured by Paint Blistering¹⁴ Corrosion Ratio, Steel to Zinc as a Function of Evaluation Method¹⁵

¹⁴ Zhang, X.G., Hwang, J., and Wu, W.K., "Corrosion Testing of Steel and Zinc", *Proceedings of Galvatech'98*, Tokyo, Japan, 1998. as quoted by Zhang

¹⁵ Kurokawa, S., Yamato, K., and Ichida, T., "A Study on Cosmetic and Perforation Corrosion Test Procedures for Automotive Steel Sheets", *NACE Corrosion'91 Conference*, Cincinnati, OH, March 11-15, 1991, Paper # 396. as quoted by Zhang

Solution	Zinc Weight Loss g/m ²		
	2 Days	7 Days	14 Days
30 g/L NaCl	19	96	198
30 g/L NaCl = 12 g/L Mg(OH) ₂ ·6H ₂ O	1	2	4
Artificial North Sea Water ^a	1.5	4	5

^a28.4 g/L NaCl; 8.2 g/L MgSO₄·7H₂O; 4.3 g/L Mg(OH)₂·6H₂O; 2.0 g/L CaCl₂·6H₂O

Table 1: Corrosion of Zinc in Solutions of Various Components of Sea Water – Cyclic Immersion

and therefore, greatly increases the corrosion resistance of zinc relative to steel.¹⁶

Indeed, SST cannot even be considered as a surrogate for corrosion performance in seawater. The data¹⁷ in Table 1 show the strong corrosion-inhibiting effect of dissolved magnesium for example, as well as other constituents, on the corrosion rate of zinc in sodium chloride solution. In the case of normally 3 percent NaCl in water, the absence of other ions makes sodium chloride solution corrosion test results relative to expected performance in sea water clearly erroneous, even at the same NaCl concentration.

In short, it is almost universally accepted by corrosion technologists that poor performance in salt spray does not always equate to poor performance in other environments.¹⁸ Similarly, bench top immersion tests in test solutions usually do not authentically duplicate

natural corrosion exposures. Taken by itself, salt spray testing can be useful as a production control test. For example, if periodic samples in continuous production process subjected to salt spray testing routinely indicate “X” hours in the test (without conscientious and purposeful change in the process, feed materials, or process variables), a decrease in the historical performance in a controlled salt spray test would signal a change in the process outcomes. This would require investigation, notwithstanding that such process deviation does not necessarily signal a change in the field performance or expected service of the process output. SST is best used as a process continuity and integrity measure. In the case of zinc coatings, it can be used (subject to test controls) to confirm that a certain coating thickness is being achieved.

In this regard, a general rule is that one micron (1 μm) of hot dip zinc coat-

ing should attain about 10 hours of SST to 5 percent red rust.¹⁹ The application of the rule of thumb depends on whether or not the salt spray test results in generally linear zinc reaction kinetics ($n = 1$), which is uniquely different to the general parabolic performance ($n < 1$) found in most cyclic and diffusion constrained exposures.

Other corrosion tests include immersion tests in solutions or extract solutions. In the case of wood preservatives, such bulk or extract solutions are particularly misleading since they do not represent the chemical activity of the subject chemical in situ, or in actual service. For example, it is well established that wood preservation chemicals undergo a "fixation" over a short period after penetration, which significantly changes the nature and solubility of some components, changing their availability to leaching²⁰ and for corrosion activity. By decreasing solubility, bonding to cell wall components, etc., the corrosivity of the chemicals is altered, and their mobility and activity (chemically) cannot be simply measured by bulk, solution, or testing isolated from their actual environment.

Weight loss is a common measurement method used in assessing corrosion damage. However, it is important to restate the fundamental principle constructed above:

The corrosion products of zinc are integral, necessary, and valuable parts of the protective mechanism. The zinc used to create this unique protective layer is not "consumed" as in wasted or degraded, but in general is "converted" into a protective system where the reaction products perform the protective function, and the underlying zinc is the reservoir from which any depletion of the protective layer is repaired and replenished; usually at a slow and equilibrium rate with the surrounding micro-environment.

Therefore, the removal of the zinc protective layer, including that part which has migrated into the surrounding matrix, overstates the corrosion rate

of zinc by treating it as wastage. In fact, it is an essential part of the protective system. The conversion of zinc into protective constituents is a positive phenomenon. An analogy would be treating uncured concrete, which undergoes significant conversion through hydration reactions, as the surrogate for the ultimate physical and mechanical value of the structure.

This is part one of a two-part article on Galvanized Fasteners and Corrosion in Wood. Part two will focus on corrosiveness of chemicals used to treat wood.

After earning degrees in chemistry and marketing, and gaining experience in lab research and sales development, Thomas J. Kinstler joined the galvanizing industry. During the past 30-plus years Kinstler has researched, written, and published a wide number of technical and marketing topics. Kinstler recently retired from Industrial Galvanizers America to focus more intensely on consulting projects and partnerships involving galvanizing technical and marketing matters through the consulting group "GalvaScience, LLC." He may be reached via email (GalvaScience@alltel.net) or phone (205/296-7236).

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