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Corrosion of Metals in Wood Products

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1. Introduction

The corrosion of metals in contact with wood has been studied for over 80 years, and in most situations wood is not corrosive [1]. Recently, however, the durability of fasteners in preservative-treated wood has become a concern. Changes in legislation and certification in the United States, the European Union, and Australasia have restricted the use of chromated copper arsenate (CCA), which was previously the most extensively used waterborne wood preservative [2, 3]. Following these changes, several different wood preservatives have come to the market, some of which are much more corrosive than CCA [4-7]. Although a lot of recent research has been conducted in this area, no attempt has been made to summarize all the recent advances, and confusion exists about the corrosiveness of alternatives to CCA and proper materials selection for use in treated wood. In this chapter, we summarize information on why metals corrode in wood, how fast this corrosion occurs, and techniques to minimize corrosion in wood products.

2. Wood as an electrolyte

Understanding the microstructure and chemistry of wood is helpful in understanding how and why metals corrode in wood. Wood is an anisotropic, cellular material; long, hollow, narrow cells are orientated along the root-to-crown direction of the living tree. The types of cells and the structure of the wood material depend on if the tree was a hardwood (angiosperm, deciduous leaves) or softwood (gymnosperm, evergreen). Many of the structural differences between hardwoods and softwoods are highlighted in Figure 1 [8].

Despite the diversity in wood microstructure across genera and species, the cell wall of all wood species is composed of the same three structural polymers: cellulose, hemicelluloses,

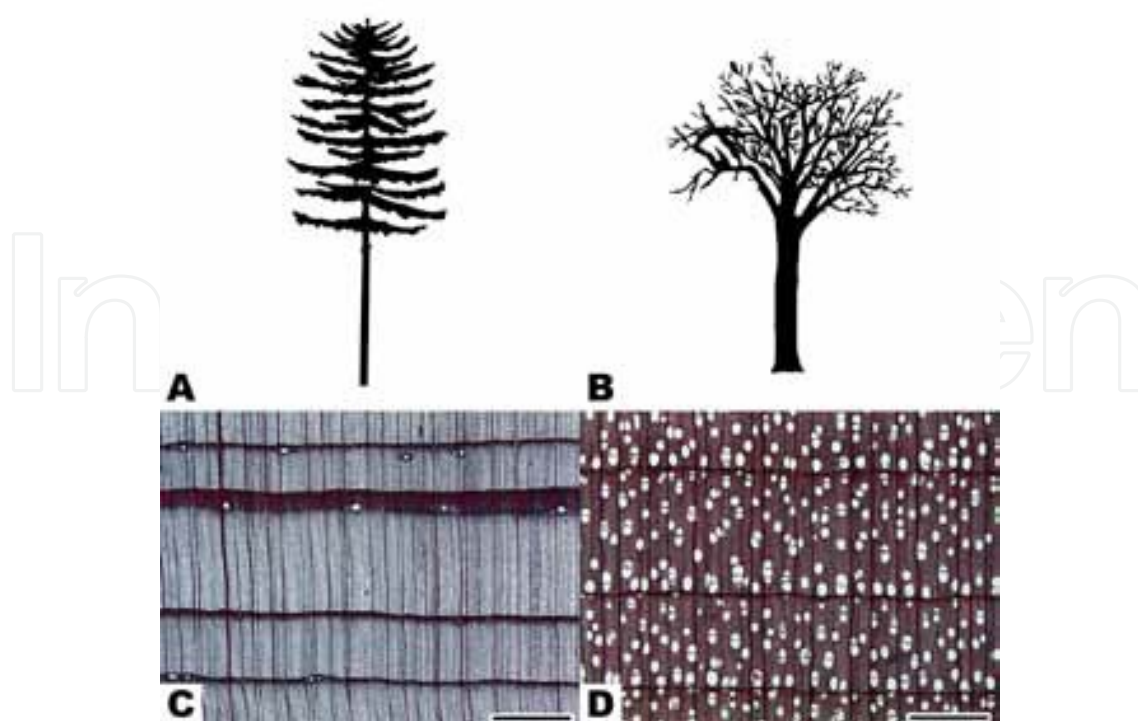


Figure 1. Generic shape of a softwood (A) and hardwood (B) and the corresponding microstructure (in cross section) of a softwood (C) and hardwood (D). Scale bar represents 780 μm . From [1].

and lignin, in roughly the same proportions [9]. In addition to the structural polymers, wood also contains a wide range of extractives, or chemicals that can be removed from the wood with various solvents. The types and amounts of extractives vary widely between wood species, and some of these extractives can affect the corrosion of embedded fasteners (see Section “Role of wood chemistry on corrosion”).

Given the porous microstructure and relatively benign chemistry, wood may not seem like a challenging environment for corrosion. However, wood has complex interactions with water that greatly affect its physical, mechanical, and chemical properties, including corrosion. Wood is a hydrophilic material and can hold over 200% of its dry weight as water [10]. Moisture can exist in wood as free water (liquid water or water vapor in cell lumina and cavities) or as bound water (held by intermolecular forces within cell walls). The moisture content at which only the cell walls are completely saturated (all bound water) but no water exists in cell lumina is called the fiber saturation point. The fiber saturation point occurs at approximately 30% moisture content (MC, weight of water/weight of dry material) for many wood species [11].

In the absence of liquid water (and the resulting capillary water uptake), wood freely exchanges moisture with its environment until it reaches an equilibrium (that depends upon the relative humidity). The relationship between equilibrium moisture content and relative humidity at a given temperature is called a sorption isotherm. The sorption isotherm depends on the wood species and previous history of the wood, however the data in Figure 2 are frequently used for practical purposes to estimate moisture content for a given relative humidity and temperature in the absence of better data [10].

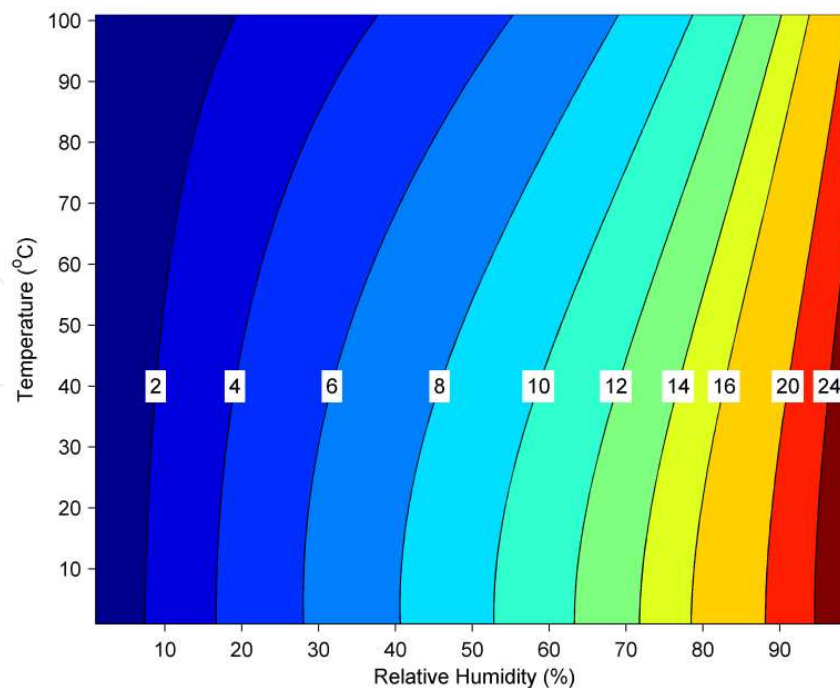


Figure 2. Moisture content (contours) as a function of relative humidity and temperature; data represent an average of adsorption/desorption and should be used for approximations only [3].

Even below fiber saturation, bound water is able to solvate and conduct ions. Zelinka et al. showed that ionic conduction in wood is a percolation phenomenon and that at approximately 16% MC, there is a continuous pathway for ion conduction in wood [12]. For reference, 16% MC corresponds with a relative humidity range of approximately 75%-85% [13]. The percolation threshold is related to a threshold moisture content for corrosion of metals in contact with wood (see Section “Role of wood moisture content on corrosion”).

3. Wood preservatives

Wood preservatives are chemicals that are injected into the wood to help the wood resist attack by decay fungi, mold, and/or termites. Waterborne wood preservatives are commonly used when the wood may be in contact with humans or will be painted. Although many different formulations of waterborne preservative treatments have been developed, only a few of these have been used commercially. Most commercial treatments contain cupric ions, which give treated wood its characteristic greenish-brown coloration (Figure 3).

In 2004, regulation changes in the United States restricted the use of chromated copper arsenate (CCA), which had previously dominated the preservative market for many years. Similar regulation changes happened in the European Union and Australasia. Since the regulation change, alternatives to CCA have been introduced to the market. A brief summary of the commercially important alternative wood preservatives is provided below; more information is available in references [2, 3]. Although the exact formulations of the newer wood preserva-



Figure 3. (From left to right) Wood treated with MCQ, DDAC, and ACQ. Cupric ions from the wood preservative cause the dark coloration of the wood. Excess copper has deposited on the MCQ (green splotches) and the ACQ (along the end grain) samples. SCALE: The boards are approximately 38 x 140 mm.

tives are different from each other, they are similar in that they all have a higher percentage of copper than that of CCA. This is important because the corrosion mechanism involves the reduction of cupric ions from the preservative and the corrosion rate depends upon cupric ion concentration [14].

Alkaline copper quaternary (ACQ) is composed of copper oxide (67%) and a quaternary ammonium compound (DDAC- didecyldimethylammonium chloride or carbonate 33%). When it was first commercially available, the quaternary ammonium compound was made with a chloride formulation but was later almost exclusively replaced with a carbonate formulation. Several formulations of ACQ have been commercialized, and it can be treated with an amine or ammonia carrier.

Copper azole (CA) types B and C are composed of ammine copper (96%) and an azole (4%). In CA type B, the azole is entirely composed of tebuconazole. In type C, the azole is 50/50 mixture of tebuconazole and propiconazole. Although copper azole contains a higher percentage of copper than does ACQ, the retention required for aboveground use (Category U3 [15]) is lower and, therefore, the total amount of copper in the treated wood is less.

In addition to these preservatives (CCA, ACQ, CA) standardized by the American Wood Protection Association, several commercially important preservatives have been introduced

to the market by ICC-ES evaluation reports. These preservatives include “micronized” formulations of ACQ and CA, which have various trade names. In these formulations, soluble copper is not injected into the wood, rather solid copper, copper oxide, or copper carbonate is ground into submicron particles, or “micronized,” and suspended in solution prior to injection. Several different formulations of these preservatives are covered by different ICC-ES evaluation reports. These formulations differ in listed uses and required retentions and have slight differences in formulations, but in general require less copper than the nonmicronized counterparts.

A summary of wood preservatives highlighting copper concentration is given in Table 1. Preservative composition is given in column 2; aboveground retention needed to meet Use Category 3b for aboveground use according to AWP A U1 is given in column 3 [15]. Column 4, calculated from columns 2 and 3, lists the amount of copper metal per volume of wood. Several studies have shown that as copper concentration in the wood is increased, corrosion of metal fasteners increases [4, 16].

Preservative	Composition	Aboveground retention (kg of preservative per m ³ of wood)	Copper concentration (g of copper per m ³ of wood)
CCA	47.5% chromium trioxide 34.0% arsenic pentoxide 18.5% copper as copper oxide	4	591
ACQ	67% copper as copper oxide 33%DDAC	4	2141
CA-B	96.1% amine copper as Cu 3.9% Tebuconazole	1.7	1634
CA-C	96.1% amine copper as Cu 1.95% Tebuconazole 1.95% Propiconazole	1.0	961
ESR-1721 (MCA-B)	96.1% amine copper as Cu 3.9% Tebuconazole	1.0	961
ESR-1721 (MCA-C)	96.1% amine copper as Cu 1.95% Tebuconazole 1.95% Propiconazole	0.8	769
ESR-1980	67% copper as copper oxide 33%DDAC	2.4	1285
ESR-2240	25/26 copper particles 1/26 Tebuconazole	1.0	961

Table 1. Summary of some waterborne wood preservatives and aboveground retentions highlighting the difference in copper concentration between preservatives. Data are combined from ([17, 18]).

4. Mechanism of corrosion in wood treated with copper-containing wood preservatives

Many of the concerns over corrosion of metals in treated wood involve wood treated with copper-based wood preservatives (e.g., those in Table 1). For wood treated with these preservatives, the corrosion mechanism involves the reduction of cupric ions available in the wood, which are reduced as the construction material, normally a steel or zinc galvanized connector, is oxidized. Figure 4 illustrates this mechanism of corrosion highlighting the transport of cupric ions to the metal surface, where there is a charge transfer reaction resulting in oxidation of the fastener and reduction of the cupric ions in the wood preservative.

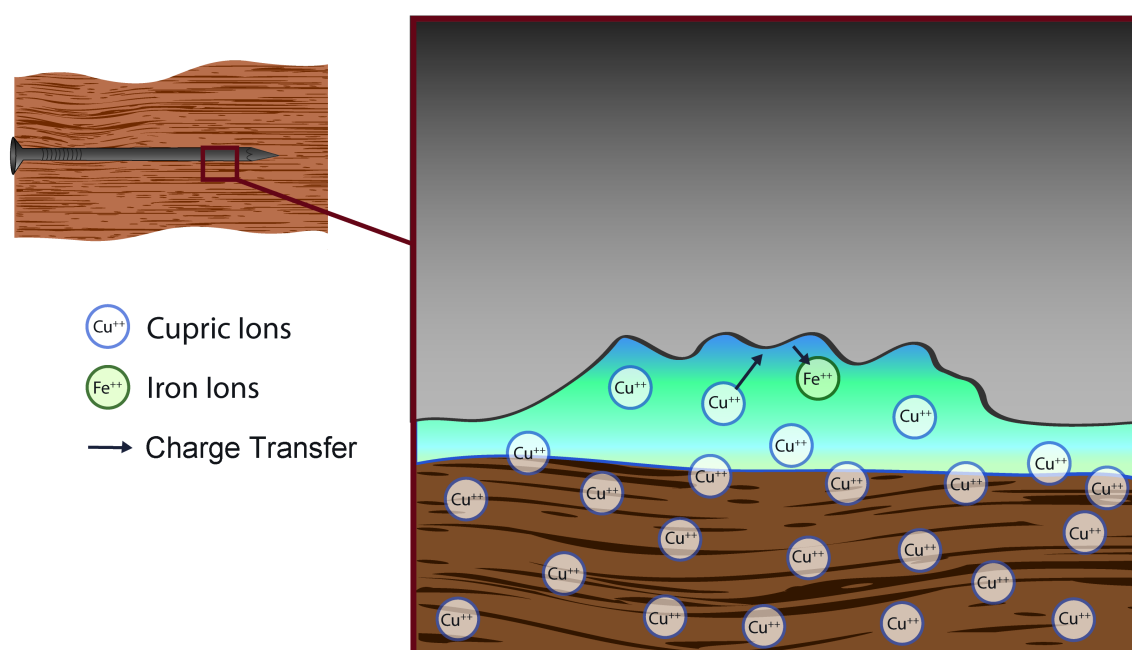


Figure 4. Schematic illustration of the mechanism of corrosion in treated wood (not to scale).

The role of cupric ions in the corrosion mechanism was first hypothesized by Baker [19] and later confirmed by work of Zelinka et al. [5, 14] and Kear et al. [4, 20] through energy dispersive x-ray analysis, Pourbaix diagrams, and examinations of the role of cupric ion concentration and acidity. Zelinka et al. performed electrochemical corrosion tests in water extracts of treated wood, which were later found to result in similar corrosion rates to those measured in solid wood [6, 14, 21]. Because the medium was aqueous and electrochemical techniques were used, ion concentrations, pH, and potentials could be measured and a Pourbaix diagram could be constructed. Figure 5 shows the Pourbaix diagram of copper with measured potentials in extracts of wood treated with different wood preservatives. The diagram shows that zinc-galvanized steel lies in a region where copper metal is the stable phase, and therefore cupric ions in the preservatives are thermodynamically unstable. Further work using energy dispersive x-ray spectroscopy (EDS) showed that fasteners placed in the extract had copper metal deposited on them.

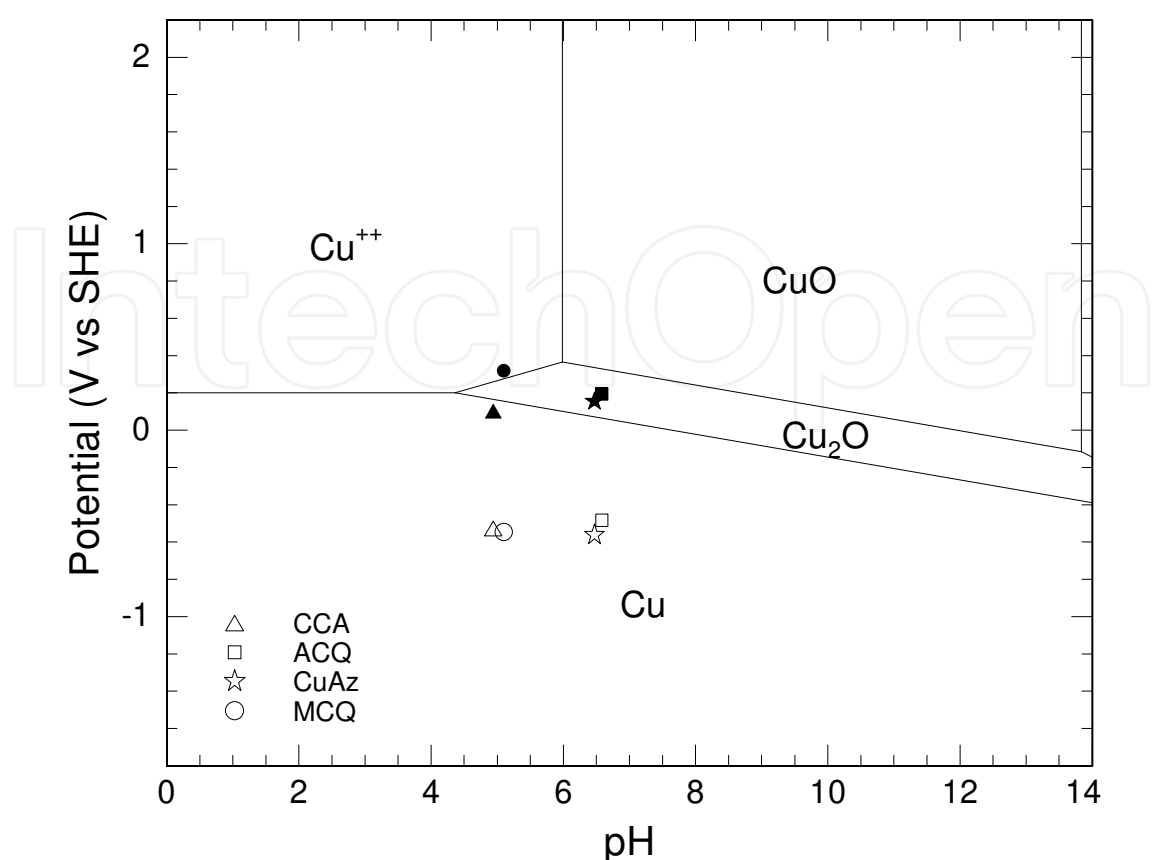


Figure 5. Pourbaix diagram with an assumed cupric ion concentration of 10^{-4} with the open circuit potentials of steel (filled symbols) and galvanized steel (open symbols) in water extracts of different wood preservatives.

Several researchers have shown that corrosion rate of metals in treated wood increases with increasing cupric ion concentration [4, 14, 16]. The clearest evidence of this was found in an unpublished report by the Forest Products Laboratory, the results of which were synthesized and republished by Zelinka and Rammer [16]. In these experiments, living trees were allowed to imbibe a copper-containing wood preservative before felling, and corrosion rate was measured in logs cut from these trees; corrosion rate quadrupled as copper concentration increased from 1 to 11 kg m^{-3} . Zelinka and Stone [14] examined differences in corrosion rates observed in different wood preservatives and showed that most differences could be explained by differences in cupric ion concentration and pH (MCQ, CCA were acidic, ACQ was alkaline). For example, at a given copper concentration, the preservative with the lower pH was more corrosive. Similarly, at a given pH, the preservative with the higher copper concentration was more corrosive.

Despite the fact that the corrosion mechanism clearly involves reduction of cupric ions in the preservative, several experiments that examined corrosion products of fasteners embedded in treated wood found no evidence of copper metal on the fasteners [5, 6]. This raises the question of what is happening to the reduced cupric ions: do they get bound to the wood near the metal surface, or do they get reoxidized or redissolved in a different reaction step? Further research is needed to explain this enigma.

5. Role of wood moisture content on corrosion

The most important environmental variable controlling corrosion of metals embedded in wood is moisture content of the wood. Below a threshold moisture content of 15%–18% MC, embedded metals do not corrode [12, 22–24]; above the threshold, corrosion rate increases with moisture content and plateaus at a maximum corrosion rate near or above fiber saturation point. Despite the importance of wood moisture content on corrosion rate, very little research has been conducted to examine the role of moisture on corrosion.

Two different long-term exposure tests examined the role of wood moisture content on corrosion by placing wood with embedded fasteners in chambers with a fixed relative humidity. Baechler [25, 26] used three chambers at 30%, 65%, and 90% RH. Kear et al. [4] examined 75% and 90% RH and “moisture saturated air.” In these studies, corrosion rate was effectively zero at 30% and 65% RH and barely measureable at 75% RH. Corrosion rate then had noticeable increases between both the 75% and 90% RH and the 90% RH and moisture saturated air conditions.

The number of moisture contents at which a gravimetric corrosion rate can be determined is limited experimentally by time, expense, and difficulty maintaining the wood moisture content constant for long periods of time. To develop a more detailed curve, Dennis et al. used electrochemical tests to measure corrosion rate as a function of moisture content in solid wood treated with CCA [22]. In these tests, thin sheets of wood were pressed around a zinc working electrode and stainless steel counter electrode and corrosion rate was measured with the polarization resistance technique. A subset of the data are plotted in Figure 6. The data exhibit hysteresis with moisture content, which suggests that the wood specimens were not in equilibrium when measurements were taken. These data have been used to create a combined hygrothermal/corrosion model to predict the amount of corrosion one can expect in different environments [27]. The model calculates wood moisture content from hourly climatic data and calculates the hourly amount of corrosion from the wood moisture content.

6. Differences between atmospheric corrosion and corrosion of metals in wood products

Corrosion of metals embedded in wood has several differences from atmospheric corrosion, with implications for both materials selection and service life of metals in wood. The two most important differences are that (1) galvanized steel corrodes more rapidly than carbon steel when in contact with wood and (2) long-term corrosion kinetics are different in wood than in atmospheric conditions. Both of these differences can be attributed to the fact that corrosion products of metals in contact with wood are different than those that form in atmospheric conditions and therefore the passivation is different.

In atmospheric corrosion, zinc oxidizes to form hydrozincite $\{Zn_5(CO_3)_2(OH)_6\}$ and smithsonite ($ZnCO_3$), which passivate the zinc surface; that is, these oxidized species protect the metal from

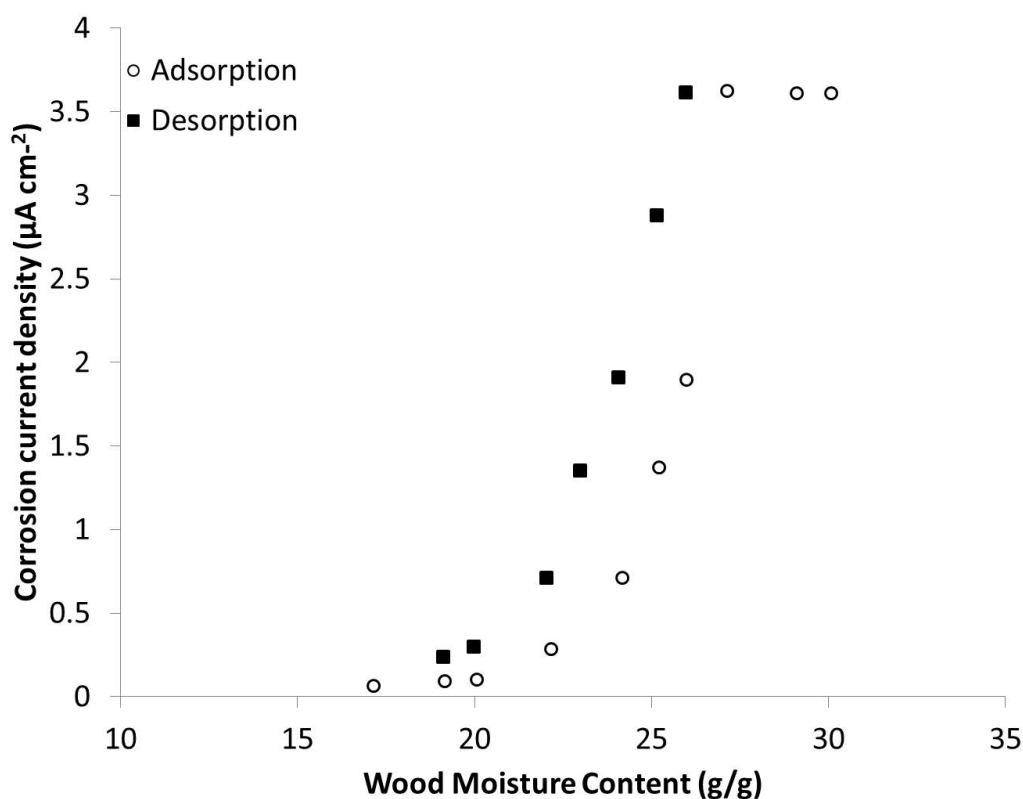


Figure 6. Selected data of Dennis et al. replotted to show the dependence of corrosion rate on wood moisture content. Data from [5].

further corrosion. Conversely, steel forms goethite ($\alpha\text{-FeOOH}$), also called “red rust” in atmospheric conditions. Kinetically, hydrozincite and smithsonite are better at protecting the underlying metal than goethite, which is why zinc corrodes more slowly than steel in atmospheric conditions [28]. In certain environments, such as immersion in saltwater [29] or in environments with volatile acetic and formic acids [30], different corrosion products form and zinc corrodes more rapidly than steel. In addition to measuring corrosion rates, Zelinka et al. [5] examined corrosion products on fasteners removed from steel and galvanized steel fasteners in wood using X-ray diffraction and did not observe smithsonite on the zinc fasteners. Instead, they observed namuwite $\{\text{Zn}_2(\text{SO}_4)(\text{OH})_6 \cdot 4\text{H}_2\text{O}\}$, simonkolleite $\{\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot (\text{H}_2\text{O})\}$, and in some cases hydrozincite. The lack of a protecting passive layer explains why galvanized fasteners corrode more rapidly than steel fasteners in solid wood.

Passivation in atmospheric corrosion also causes a decrease in corrosion rate with time. Legault and Preban described corrosion kinetics under atmospheric conditions by

$$\Delta W = Kt^n \quad (1)$$

where ΔW is the change in weight, K is a constant (the 1-year corrosion rate), t is time in years, and n is an exponent that controls the kinetics and is less than or equal to unity [31]. Corrosion

of metals in wood exhibits a constant rate with time (i.e., $n = 1$). This behavior was first observed by Baker [32], who found that the weight loss increased linearly with time in a 17-year exposure test. Zelinka et al. observed further evidence of activation control in measurements performed in water extracts of treated wood. They observed that corrosion rates measured in the extract were similar to those measured in solid wood, where the diffusion is slower [33].

7. Role of wood chemistry on corrosion

Even a single species of wood can have more than 700 different extractives, chemicals that can be solubilized in water or another solvent, and could, in theory, affect the corrosion of embedded metals [34]. Despite the large number of extractives that could potentially affect corrosion, very few of these compounds have been associated with corrosion of embedded metals. Zelinka and Stone [35] reviewed the literature on the role of extractives on corrosion and found that previous researchers had identified only three different compounds that affect corrosion of metals embedded in wood or exposed to the black liquors of wood pulp: small organic acids (acetic and formic acid) [30, 36-39], tannins (or more broadly, polyphenols) [34, 40-49], and phenols with two or three adjacent hydroxyl groups (e.g., catechol and pyrogallol) [45-50]. For solid wood, only organic acids and tannins have been mentioned in the literature; catechol (1,2-dihydroxybenzene) and pyrogallol (1,2,3-trihydroxybenzene) are formed as lignin is destroyed in the pulping process [51, 52].

Zelinka and Stone further investigated the role of tannins and pH by making water extracts of different wood species known to vary in both tannin content and pH: pine (low pH, low tannin), oak (low pH, high tannin), elm (high pH, low tannin), and black locust (high pH, high tannin). A blue-black precipitate formed on the surface of steel in the extracts, suggesting the formation of a passive layer of iron-tannate (Figure 8). In further experiments they adjusted the extracts by changing the amount of tannins or the pH. In these experiments they observed that at a given pH, increasing the tannins decreased the corrosion rate; and at a given level of tannins, lowering the pH increased the corrosion rate. Based upon their measurements and simple kinetic models, Zelinka and Stone developed an isocorrosion map for the water extracts of different wood species (Figure 7). While absolute corrosion rates are higher than would be expected in solid wood, the same general trends are expected to apply.

8. Test methods to examine corrosion of metals in wood

One year after the 2004 regulation change in wood preservatives, Zelinka and Rammer [53] summarized 22 different methods that had been previously used to evaluate corrosion of metals in contact with wood. The review was divided into “exposure tests,” where temperature and relative humidity were kept near realistic conditions, “accelerated tests,” where temperature and/or a fog were used to accelerate corrosion, and “electrochemical tests,” where the metal was polarized to evaluate corrosion rate. In general, many of the tests were for “com-

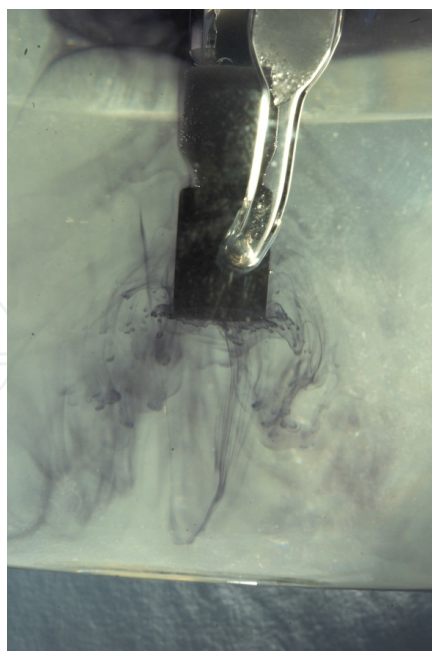


Figure 7. Iron-tannate precipitate forming on a steel plug in a solution with the same tannin concentration and pH as white oak. SCALE: The steel plug is approximately 9.5 mm in diameter.

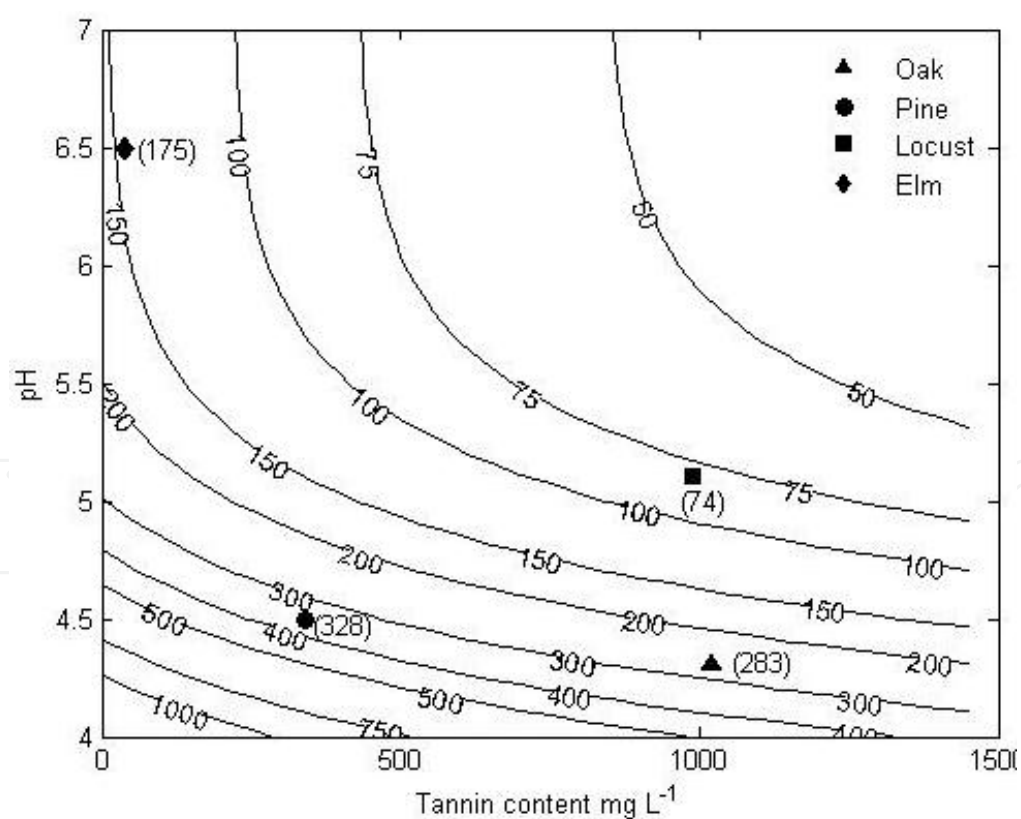


Figure 8. Showing the interplay between tannins (abscissa) and pH (ordinate). Contours represent combinations of tannins and pH that result in the same corrosion rate

parative purposes only,” where conclusions could be drawn only between a treatment and a control group. In many cases, corrosion was reported as a percentage weight loss instead of a true corrosion rate because the surface area of threaded fasteners could not be calculated. It has been shown that this way of reporting corrosion rates distorted the performance of aluminum fasteners, which have a lower density than steel and galvanized steel fasteners [7].

Since the Zelinka and Rammer review of test methods, several new test methods have been developed. A new standard has been written to measure the corrosion rates of fasteners driven into treated wood [54], and the American Wood Protection Association (AWPA) E-12 standard has been greatly revised [55]. Furthermore, Rammer and Zelinka developed a method to calculate the surface area of threaded fasteners from digital images [56-58], which allows for true corrosion rates to be measured. The remainder of this section summarizes new developments in test methodologies.

AWPA standard E12, “Standard method of determining corrosion of metal in contact with treated wood,” was the first standardized test method used to measure corrosion of metals in contact with wood [55]. The test method places metal coupons between two blocks of treated wood and exposes the “sandwich” to a high-temperature (50°C) high-humidity (90% RH) environment for 120 days. The blocks of wood are held together with nylon bolts. The E12 standard was revised and greatly improved in 2008. The new standard specifies an effective torque for the nylon bolts and gives much more detailed instructions for cleaning the corrosion products. Although the E12 test can be used to make a relative ranking between preservatives, information on the effect of temperature on the corrosion of embedded metals is lacking and it is impossible to relate corrosion rates measured in the E12 test to realistic temperatures for building enclosures or outdoor wood structures.

ASTM International standard G198, “Standard test method for determining the relative corrosion performance of driven fasteners in contact with treated wood,” was published in 2011 [54]. The goal was to develop a test method to evaluate fasteners, which may have different metallurgical characteristics or coatings than the sheet metal used in the AWPA E12 test. Beyond the geometry of the metal sample, the biggest difference between the ASTM and AWPA standards is the exposure conditions. The AWPA test is conducted at a temperature of 50°C; the ASTM test is conducted at a lower and potentially more realistic temperature of 32°C. Relative humidity conditions are also different between the two standards. In the ASTM test, the wood and fasteners are exposed either to a “steady state” test of 95% RH or to a “cyclic fog” test where the fasteners are exposed to 48 hours of fog followed by a 72-hour dry cycle. Both tests are conducted for 120 days. The reasoning for including a cyclic fog test is that in accelerated testing conditions, galvanized fasteners perform better when exposed to alternating wet and dry cycles, which is similar to the environment they see in service [28, 29]. However, Zelinka recently showed that wood acts as a moisture buffer and does not dry out during the dry cycles; rather, it gains moisture throughout the entire test [59]. From this analysis it appears that the cyclic fog test may be more challenging than the steady-state moisture test.

Results of several exposure tests in newer wood preservatives have been reported as actual corrosion rates rather than percentage weight loss. Kear et al. exposed nails and metal coupons to treated wood exposed to three different relative humidity environments [4] (75% RH, 90%

RH, “moisture saturated air”). The surface area of the nails was calculated from the diameter and tip geometry. Zelinka et al. measured the corrosion rates of screws and nails at 100% relative humidity [5, 7]. Furthermore, using photographs from Baker’s laboratory notebook, Zelinka and Rammer were able to convert Baker’s seminal data from a 17 year exposure test in CCA- and ACA-treated wood from percentage weight loss to actual corrosion rates [7].

Additional work has further advanced electrochemical methods as a rapid technique to measure corrosion of metals in treated wood. Both Zelinka et al. [60] and Kear et al. [61, 62] have measured corrosion of metal fasteners in dilute solutions of wood preservatives. Zelinka et al. used the polarization resistance technique and concluded that these measurements could not be used to predict corrosion of metals embedded in treated wood. Kear et al. used impedance spectroscopy, large perturbation potentiodynamic polarization, and polarization resistance measurements to characterize the corrosion performance of mild steel, stainless steel, and galvanized steel in dilute solutions of wood preservatives. Kear et al. observed good correlation between trends found in these electrochemical measurements and gravimetric measurements in dilute solutions of wood preservatives as specified in the AWWA E17 test for measuring the corrosiveness of wood treatment solutions [20, 63], but not for metals embedded in treated wood.

Although these measurements in dilute solutions of wood preservatives were unable to predict the corrosion of embedded metals, a different method developed by Zelinka et al. [6] has good correlation to laboratory exposure tests of metals in treated wood. In this method, extracts of treated wood were made by grinding the treated wood, adding water (1:10 weight ratio), and extracting the water-soluble components of the treated wood for one week, after which the milled wood was filtered off. The rationale for the method was that corrosion of embedded metals is aqueous and that the water extract would have a similar chemistry to the micro-chemistry within the wood structure. Corrosion rates determined from polarization resistance measurements in the extract had excellent correlation to corrosion rates of fasteners embedded in wood conditioned at 100% RH for 1 year [7].

9. Review of corrosion rates measured in wood treated with different preservatives

Since the 2004 change in wood preservative regulation, several investigations of the corrosiveness of metals in contact with treated wood have been reported. The studies cover a wide range of preservatives, preservative retentions, wood moisture contents, and metals tested. Not surprisingly, a wide variation in corrosion rates has been reported (e.g., from 2–113 $\mu\text{m yr}^{-1}$ for galvanized steel in ACQ-treated wood). Table 2 summarizes the corrosion data. Because of the wide variations of test conditions used, it is best to compare results only within a single study or across different studies with very similar conditions. The remainder of this section summarizes how the data in Table 2 were obtained.

Many design recommendations for materials selection in wood are based off the recommendations of Baker [32], who conducted a 17-year investigation of corrosion of metal fasteners embedded into chromated copper arsenate (CCA) and ammoniacal copper arsenate (ACA)

treated wood exposed either underground or in a room maintained near 100% RH. From these data, Baker concluded that at a minimum, hot-dip galvanized fasteners should be used in treated wood and cautioned against the use of aluminum fasteners. Importantly, Baker presented the corrosion data as percentage weight loss instead of corrosion rate because he could not calculate the surface area of threaded fasteners. Zelinka and Rammer reanalyzed Baker's data using data in Baker's laboratory notebook and an algorithm they had developed to measure surface area of threaded fasteners [7, 56, 57]. They found that when the corrosion rate was adjusted to a true corrosion rate, the corrosion rate of aluminum was in fact less than that of hot-dip galvanized steel.

Zelinka has published results of several different corrosion tests that were conducted at 27°C (80°F) and 100% RH [5, 7, 14, 64]. In one study [7], Zelinka and Rammer examined the corrosion of five different metal fasteners (carbon steel, hot-dip galvanized steel, electroplated galvanized steel, aluminum, and stainless steel) embedded in wood treated with ACQ-D to a retention of 4 kg m⁻³. They found that the corrosion rate of hot-dip galvanized steel was the highest (62 μm yr⁻¹). The corrosion rate of stainless steel was statistically indistinguishable from zero. In another study [5], steel and hot-dip galvanized steel fasteners were exposed to six different wood treatments: chromated copper arsenate (CCA-C), alkaline copper quaternary (ACQ-D), copper azole (CA-B), micronized copper quaternary (MCQ), and didecyldimethylammonium carbonate (DDAC, or the "quat" in ACQ and MCQ). ACQ was found to be the most corrosive to both steel and galvanized steel.

Kear et al. examined the corrosion of three different metals (316 stainless steel, hot-dip galvanized steel, and plain carbon steel) in three different preservatives (CCA, ACQ, and CA) treated to three different retention levels with four different test methodologies [4]. Retention levels were specified in a New Zealand standard that specifies a mass basis (i.e., kg/kg) instead of a density basis and therefore cannot be directly compared to traditional U.S. retentions (in lbs ft⁻³ or kg m⁻³). Differences in the corrosiveness of the preservatives were most apparent in a constant exposure to 90% RH.

Simpson Strong Tie corporation published a technical bulletin on the results of in-house AWWA-E12 [55] corrosion tests [65]. In this test method a metal plate is sandwiched between two blocks of wood and exposed to a high-temperature (50°C), high-humidity (90% RH) environment. They found that the corrosiveness of ACQ-D (carbonate) was roughly equivalent to that of CA, and both of these were more than twice as corrosive as CCA-C. They also found that ACZA was more than three times more corrosive than CCA and that borates were less corrosive than CCA. A footnote in the table mentioned that for micronized formulations like MCQ the "relative corrosiveness is somewhat lower than ACQ-D."

Copper naphthenate is sometimes used as a preservative in timber bridges. Although no peer-reviewed data on the corrosiveness of copper naphthenate have been reported, Anthony Forest Products company published a technical bulletin with the results of AWWA E12 tests that compares both waterborne and oilborne formulations of copper naphthenate against ACQ-D and CCA-C for mild steel, hot-dip galvanized steel, aluminum, and red brass [66]. Although no data are reported on variability between replicates, the data clearly suggest that either formulation of copper naphthenate is much less corrosive than ACQ and possibly less corrosive than CCA (Table 2). This bulletin was published by a company that supplies products treated

with copper napthenate; nevertheless, the data suggest that copper napthenate is much less corrosive than ACQ and less than or equal in corrosiveness to CCA.

	Plain steel	Hot-dip galvanized steel	Stainless steel	Aluminum
17 years, 27 C (80 F), 100% RH [7, 32]		9 CCA I 6 CCA II	<1 CCA I <1 CCA II	3 CCA I 4 CCA II
1 year, 27 C (80 F), 100% RH [7]	34 ACQ	61 ACQ	1 ACQ	22 ACQ
1 year, 27 C (80 F), 100% RH [5]	9.4 CCA	16.1 CCA		
	16.8 ACQ	32.5 ACQ		
	12.5 mCQ	19.4 mCQ		
	11.1 CA-B	28.9 CA-B		
	1.9 DDAC	5.5 DDAC		
	0.7 Untreated	4.4 Untreated		
1 year, 27 C (80 F), "moisture saturated air" [4]	62 CCA	26 CCA	≤1 CCA	
	176 ACQ-B	113 ACQ-B	≤1 ACQ-B	
	84 CA-B	87 CA-B	≤1 CA-B	
1 year, 27 C (80 F), 90% RH [4]	4 CCA	5 CCA	≤1 CCA	
	45 ACQ-B	26 ACQ-B	≤1 ACQ-B	
	14 CA-B	16 CA-B	≤1 CA-B	
1 year, 27 C (80 F), 75% RH [4]	1 CCA	1 CCA	<1 CCA	
	3 ACQ-B	2 ACQ-B	<1 ACQ-B	
	2 CA-B	2 CA-B	<1 CA-B	
AWPA E12 [66]	4 CuN-W	11 CuN-W		(-1) CuN-W
	1 CuN-O	2 CuN-O		2 CuN-O
	124 ACQ-D	23 ACQ-D		185 ACQ-D
	27 CCA-C	10 CCA-C		7 CCA-C
AWPA E12 [67]	140 mCA	23 mCA		18 mCA
	107 CA	51 CA		(-3) CA
AWPA E12 [67]	66 mCA	69 mCA		3 mCA
	180 CA	76 CA		0 CA
	41 mCQ	41 mCQ		0 mCQ
	196 ACQ-D	81 ACQ-D		3 ACQ-D
	41 CCA-C	53 CCA-C		3 CCA-C
AWPA E12 [67]	89 mCQ	25 mCQ		10 mCQ
	307 ACQ-D	28 ACQ-D		10 ACQ-D
	76 CCA-C	20 CCA-C		5 CCA-C

Table 2. Summary of published corrosion rates (in $\mu\text{m yr}^{-1}$) in treated wood. The table represents a wide variety of test methodologies—comparisons should be made only within a single row.

Freeman and McIntyre [67] summarized results of several unpublished corrosion tests of pressure-treated wood in contact with different metals that compared traditional (ACQ and

CA) against their micronized formulations (MCQ and mCA). Most of the data shown were from AWWA E-12 tests. The results were inconclusive. In one test, the micronized formulation of CA was less corrosive than the standard formulation for galvanized steel but more corrosive for plain carbon steel, and the micronized formulation was much more corrosive to aluminum. The remainder of the E-12 data have similar trends; in some cases the micronized formulations show lower corrosiveness, in other cases, the traditional formulations appear less corrosive. The only results that consistently show that the micronized formulations are less corrosive than the traditional formulations are from a test conducted using a protocol from the International Staple and Nail Tool Association (ISANTA). In this test, the micronized formulations appear slightly (approximately 30%–40%) less corrosive, with the notable exception of aluminum, in which case the micronized formulations are more corrosive.

Table 2 summarizes corrosion rates measured in a variety of test methods over a range of wood preservatives and metals. Each row in the table represents a paper or report, and the test method is briefly summarized in the first column. Corrosion rates for each metal are contained in columns followed by the type of wood preservative. The data can be used for observing general trends or relative comparison of a preservative or a metal type; however, it is dangerous to compare across rows because different test methods were used.

10. Effects of corrosion on the structural capacity of connections

The main effect of corrosion of fasteners embedded in wood is to reduce the strength of the connection. Recently, Zelinka and Rammer used the yield theory equations and measured corrosion rates to calculate how fastener corrosion reduces the structural capacity of connections [68]. Fastener connection performance can be calculated by the yield theory developed by Johansen, which treats both the wood and metal as elastic/perfectly plastic materials [69]. The yield theory equations are now the standard method for calculating design capacity for any dowel type connector (nail, screw, lag screw, bolt, etc.) in the United States through the National Design Specification for Wood Construction (NDS). Lateral design load, *Z* (in N), is determined by

$$Z = \min \left\{ \begin{array}{ll} \frac{DT_s F_{es}}{2.2} & \text{(Mode I}_s\text{)} \\ \frac{k_2 D l_p F_{em}}{2.2(1 + 2R_e)} & \text{(Mode III}_m\text{)} \\ \frac{k_3 D T_s F_{em}}{2.2(2 + R_e)} & \text{(Mode III}_s\text{)} \\ \frac{D^2}{2.2} \sqrt{\frac{2F_{em} F_{yb}}{3(1 + R_e)}} & \text{(Mode IV)} \end{array} \right. \tag{2}$$

where

$$k_2 = -1 + \sqrt{2(1 + R_e) + \frac{2F_{yb}(1 + 2R_e)D^2}{3F_{em}l_p^2}}$$

$$k_3 = -1 + \sqrt{\frac{2(1 + R_e)}{R_e} + \frac{2F_{yb}(2 + R_e)D^2}{3F_{em}t_s^2}} \quad (3)$$

and
 $R_e = F_{em}/F_{es}$

and D is dowel diameter (mm), F_e is dowel bearing stress of the main (m) or side (s) member (MPa), F_{yb} is bending yield stress of the nail (MPa), l_p is length of penetration into main member, and t_s is thickness of the side member.

Zelinka and Rammer took measured corrosion rates and converted them to reduction in fastener diameter. Because corrosion does not affect joint geometry, wood dowel bearing stress, or bending yield stress of the uncorroded fastener, design load becomes a function of fastener diameter only. Zelinka and Rammer observed that for most decking fasteners, a Mode IV failure would be observed. This is especially problematic since Mode IV failure is the most sensitive to corrosion rate; design load scales as the diameter squared in this case. Figure 9 illustrates reduction in relative capacity of a nailed joint with time for different corrosion rates. For the range of measured corrosion rates in wood (~ 1 – $100 \mu\text{m yr}^{-1}$), relative capacity drops quickly with increasing corrosion rate.

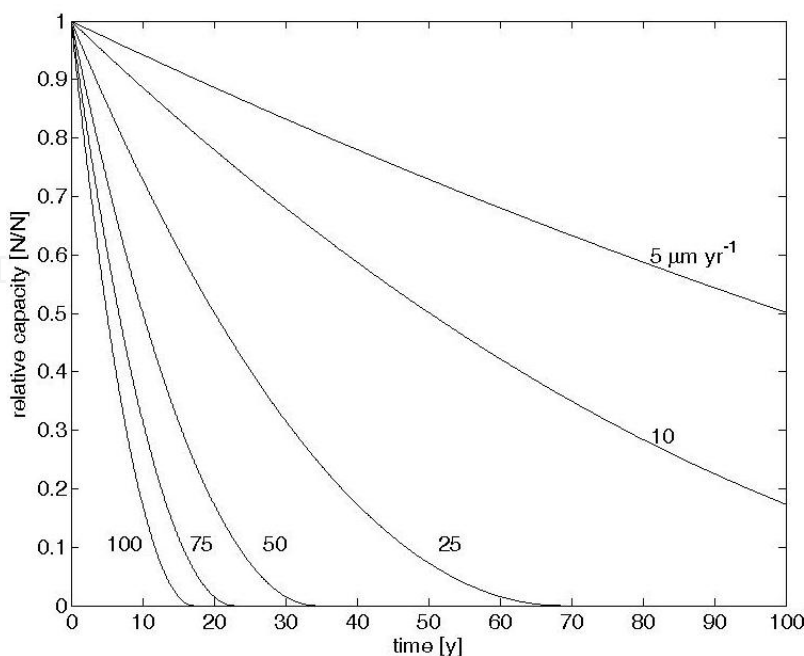


Figure 9. Loss of capacity as a function of time for different corrosion rates (labeled lines in $\mu\text{m yr}^{-1}$). The figure was constructed for a 3.4-mm nail exhibiting a Mode IV failure.

11. Design considerations for minimizing corrosion in wood

Metal fasteners are an essential part of wood construction, and their use in preservative-treated wood cannot be avoided. Therefore, it is important to design and utilize metals in wood so that they exhibit the least amount of corrosion. Here we discuss three design considerations that will help prolong the service life of metals in wood: proper moisture management, proper use of nonmetallic coatings and barriers, and avoiding mixed metals in construction.

11.1. Moisture management

Proper moisture management is the most important factor in reducing corrosion of metals in treated wood. If wood is kept dry, both the wood and the fasteners can last for centuries [70]. In most cases, preservative-treated wood is specified because the wood will be exposed in an outdoor environment where it will be exposed to moisture. However, sound design principles can maximize drainage of rainwater and minimize the amount of moisture that is absorbed by the wood.

Clausen and Glass recently published a design guide for minimizing wood decay in residential construction by keeping the wood dry [70]. Pertinent strategies that also apply to exterior structures involve (1) keeping rainwater from seeping in through the end grain and (2) designing roofs and overhangs so they do not drain onto lower structures.

11.1.1. End grain

Moisture transport in the longitudinal direction (along the grain) is more than 10 times faster than in the radial or tangential directions. Therefore, if the end grain of the wood member is allowed to come into contact with liquid water, the entire member will absorb significant amounts of moisture. It is important to design the structure so that end grain is not exposed to water. This frequently happens at joints between two members if the connection is improperly designed or installed and the joint traps water. Vertical members (i.e., posts) are especially prone to water uptake along the end grain. For these members, impermeable coatings or end caps should be used to prevent water uptake through the end grain.

11.1.2. Roof

For outdoor wooden structures with a roof, such as covered bridges, proper roof design and detailing can shield much of the structure from water and keep the wood moisture content low. The larger the overhangs of the roof, the less likely it is that drainage from the roof will strike the walls below (Figure 10).

11.2. Coated metals

Paints and other nonmetallic coatings are frequently used to protect metals from corrosion by isolating the metal from the corrosive environment. The annual cost of coatings used to prevent corrosion is estimated at \$100 billion USD, which is 36% of the total cost of corrosion in the



Figure 10. Illustration of the importance of roof overhangs for protecting wood from biodeterioration and corrosion. The right side of the beam is protected by the large roof overhang, whereas the left side is exposed to rain. SCALE: The beam supporting the trellis is 0.66 m deep.

Unites States and 1.1% of the entire U.S. gross domestic product (GDP) [71]. Although many different formulations of organic coatings are available, the goal of nearly all coatings is to isolate the metal from the environment.

Coatings fail when the corrosive environment can reach the metal substrate. This can happen if the coating is mechanically damaged during installation (Figure 11). Zelinka et al. observed that screws with a nonmetallic coating had much worse corrosion performance after they had been driven into the wood or driven through a joist hanger into the wood [72] and attributed this decrease in performance to damage in the coating caused by inserting the fastener into wood. Extreme care should be taken if using coated metals in construction with wood so that the coating does not get damaged before or during installation.

11.3. Mixed metals

Special design consideration is needed if two different metals are used in contact with each other. Galvanic corrosion happens when three conditions are satisfied: (1) two dissimilar metals (2) are placed in electrical contact (3) in the presence of an electrolyte. Galvanic corrosion is a design concern in wood when a joist hanger or sign is attached to wood with a fastener. If the fastener is a different metal than the sheet metal, conditions for galvanic corrosion exist, wood acts as the electrolyte and the metals are in electrical contact between the head of the fastener and the sheet metal.



Figure 11. Corrosion underneath a coating failure. This lamp post was in service for less than 5 years before corrosion was visible at defects in the coating. SCALE: The lamp post is approximately 115 mm.

An example of galvanic corrosion with wood was observed by the Wisconsin Department of Transportation (WisDOT) [73]. In this case, aluminum signs were attached to sign posts made of treated wood using galvanized lag screws. The aluminum signs exhibited excessive corrosion around the lag screw, causing the sign to fall off in some cases. In this case, aluminum was acting as the anode; the galvanized lag screw, the cathode; and wood, the electrolyte. Because it would be difficult to change the sign material, and aluminum lag screws do not exist, it is impossible, from a design perspective to change one of the metals to avoid corrosion. A better design solution would be to electrically isolate the aluminum sign from the galvanized lag screw.

12. Conclusions

This chapter summarized recent research on the corrosion of metals in wood focusing on how metals corrode in wood, how fast this corrosion occurs, and techniques to minimize corrosion in wood products. Despite the complexity of the corrosion mechanism in wood, the most

important considerations for materials selection and design can be summarized in two short phrases:

“Corrosion in wood is not atmospheric corrosion” Corrosion in wood is different from atmospheric corrosion. There are different thermodynamics, different kinetics, and different corrosion products form. It is not safe to assume that just because a solution works for atmospheric corrosion that it is a good idea to apply it to fastener corrosion in wood.

“Keep the wood moisture content below 18%” The corrosion of metals in wood is aqueous. The threshold moisture content at which moisture content occurs is between 15-18%, and the corrosion rate experiences a steep transition around 20% MC. The structural degradation of the joint depends strongly upon the corrosion rate, so even a few percent moisture content difference can make a large difference in the service life of the fasteners.

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