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Corrosion of metal fasteners embedded in acetylated and untreated wood at different moisture contents

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ABSTRACT

Acetylated wood is now commercially available and designed to be used in certain outdoor applications as an alternative to preservative-treated wood. Fastener corrosion can be a concern in preservative treated wood when the wood remains wet for long periods. However, little data on the corrosiveness of acetylated wood exists beyond the product literature. Here we examine the corrosiveness of commercially obtained acetylated wood and compare it against unmodified (untreated) southern pine (*Pinus spp.)*. Corrosion rates of plain carbon steel, hot dip galvanized steel, and stainless steel were calculated gravimetrically after a one year exposed in the wood. Four different moisture conditions were examined: 90% relative humidity (RH), 95% RH, 100% RH, and a fully water saturated condition. When compared to literature data on the corrosion of fasteners in preservative treated wood at 100% RH, the acetylated wood had much lower steel corrosion rates than all preservatives examined; the measured corrosion rates for galvanized steel were lower than all preservatives except chromated copper arsenate. These measured corrosion rates across a range of moisture conditions can be used to inform the selection of appropriate corrosion resistant fasteners when building with acetylated wood.

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Wood modification; fastener corrosion; acetylated wood; moisture dependent wood properties

Introduction

Metal fasteners are used to hold wood members together. When the wood moisture content is high, embedded metal fasteners can corrode. Corrosion of fasteners in wood has been studied for over 90 years (Heim *et al*. 1923), and the mechanisms of corrosion in wood are well understood. In general, wood is not corrosive; measured corrosion rates evaluated in untreated wood are generally less than 5 µm yr^{-1} for steel and galvanized steel embedded in untreated wood as measured in laboratory and field tests (Zelinka *et al*. 2010, Zelinka *et al*. 2016a). However, preservative treatments that protect the wood from biotic attack are known to greatly accelerate fastener corrosion and in some cases cause lead to failure of the fasteners (Burkholder, 2004).

Most commercially available waterborne wood preservatives utilize copper as one of the preservative components (Lebow 2010). In the treated wood, the majority of the copper is in a Cu^{+} or Cu^{2+} oxidation state (Xue *et al*. 2012, Xue *et al*. 2013, Xue *et al*. 2015, Xue *et al*. 2016, Zelinka *et al*. 2016c) as opposed to reduced, metallic copper. For these wood preservatives, the corrosion mechanism involves an electron transfer between the copper ions which are reduced as the metal is oxidized (Baker 1988, Zelinka 2014, Zelinka *et al*. 2016b). Corrosion rates for copper containing wood preservatives can be as high as 300 µm yr^{-1}, 60 times higher than those measured in untreated wood (Freeman and McIntyre 2008, Zelinka 2014).

Corrosion of embedded metals is a strong function of the wood moisture content. At low moisture contents, fasteners do not corrode in wood, regardless of treatment (Baker 1980, Zelinka 2013, Zelinka *et al*. 2014). As the wood moisture content is increased above 15%–18%, corrosion begins to occur (Dennis *et al*. 1995, Short and Dennis 1997). The corrosion rate increases until it plateaus at a maximum which occurs between 25% and 40% depending on the treatment (Zelinka *et al*. 2014). Zelinka *et al*. have empirically characterized the corrosion rate (R in units of µm yr^{-1}) as a function of moisture content (M) by

$$R = \frac{A}{1 + \exp\left[B(C - M)\right]} \quad (1)$$

where A, B, and C are fitting parameters that represent the maximum corrosion rate, steepness of the transition from zero to the maximum amount of corrosion, and the location of the transition, respectively. This function can then be implemented into hygrothermal models to predict the amount of corrosion fasteners will exhibit in different environments (Zelinka *et al*. 2011, Zelinka *et al*. 2016a).

Wood modification is an alternative method for wood protection whereby the chemical structure of wood is altered to make it less susceptible to decay without the use of regulated pesticides (Hill 2006). The most studied form of modified wood is acetylation (Tarkow 1945, Rowell *et al*. 1994, Brelid *et al*. 2000, Hill *et al*. 2005, Hill *et al*. 2009, Rowell *et al*. 2009, Popescu *et al*. 2014, Meyer *et al*. 2015, Hosseinpourpia and Mai 2016). In the acetylation process, wood is reacted with acetic anhydride, and one of the hydroxyl groups in the cell wall is replaced by an ester group per hydroxyl reacted;

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acetic acid is produced as a byproduct. The acetylation process results in bulking of the cell wall and a decrease in the hygroscopicity of the wood (Hill 2006, Temiz *et al*. 2006, Popescu *et al*. 2014).

Because the acetylation process results in the production of additional acetic acid, there is a potential for this acid to make the wood more corrosive. On the other hand, acetylated wood does not contain copper ions, which drive the corrosion in traditional preservative treated wood. While acetylated wood is now commercially available, there is a lack of information on its corrosiveness compared to preservative and untreated wood. The product recommendations for acetylated wood suggest that stainless steel fasteners should be used, although no information is given regarding measured corrosion rates in acetylated wood (Anon. 2015).

The goal of this work is to determine the corrosion rates of fasteners embedded in acetylated wood. A secondary objective is to determine the effect of wood MC on the corrosion rates of fasteners in acetylated and untreated wood so that they can be added to the combined hygrothermal corrosion model. This work is focused on the corrosion of fasteners used in outdoor applications and cannot be used to determine whether organic vapors produced by these woods may cause corrosion in indoor applications (Clarke and Longhurst 1961, Bartel-Kornacka 1967, Knotkova-Cermakova and Vlckova 1971, Berndt 1987, Chiavari *et al*. 2008).

Materials and methods

Commercial acetylated wood was purchased through a distributor. The wood was radiata pine (*Pinus radiata D. Don*). The wood was sold as planks with a transversal section of 50 mm (R) × 200 mm (T). From these planks, four members with 810 mm (L) × 50 mm (R) × 100 mm (T) were obtained. The acetylated wood was compared against four untreated southern pine (*Pinus spp. L.*) members with the same dimensions. While the pH of the wood was not measured, previous research has classified these two species as acidic, with a pH of between 4 and 4.5 (Bootle 1983, Zelinka and Stone 2011b). Holes were then drilled in one of the radial surfaces of each member at 25 mm (1 inch) intervals for the placement of fasteners; the first and the last fastener were spaced 25 mm from the ends.

Each wood member held 30 fasteners, which included ten replicates of three different fastener types: carbon steel, hot dip galvanized steel, and 304 stainless steel; fasteners were placed next to fasteners of the same type. The fasteners were all nominally "8d" in size and had a nominal diameter of 3.4 mm and length of 64 mm. The actual surface area of each fastener was measured using the method of Rammer and Zelinka (Rammer and Zelinka 2010). The carbon steel and galvanized steel fasteners came from the same batch that was tested in previous corrosion studies (Zelinka *et al*. 2010, Zelinka and Stone 2011a, Zelinka *et al*. 2014). The carbon steel and galvanized steel nails were made on the same production run and the steel nails were pulled immediately prior to galvanization. The thickness of the galvanized coating was measured with a magnetic thickness gauge and ranged between 10 and 25 μm. Prior to driving the nails into the wood, they were cleaned in an ultrasonic bath with a soap solution for 5 min, rinsed with deionized water in an ultrasonic bath for 5 min, rinsed with acetone, and then weighed to the nearest 0.1 mg.

Four different moisture conditions were examined: 90% relative humidity (RH), 95% RH, nearly 100% RH, and a water saturated condition. These conditions were chosen so that the moisture content dependence could be fit with a function previously developed by the authors for relating the corrosion rate to the wood moisture content (Zelinka *et al*. 2011, Zelinka *et al*. 2014). All tests were conducted at 27°C (80°F). The 90% and 95% environments were achieved by placing the wood inside chambers (Associated Environmental Systems, Acton, MA, USA) that had computer controlled humidification systems. The nearly 100% RH condition was achieved by placing samples approximatively 2 cm above a reservoir of deionized water in a closed plastic container. The water saturated samples were first end-coated with neoprene paint to prevent moisture uptake along the grain so that moisture content was relatively uniform throughout the length of the member. The samples were then vacuum impregnated with water by pulling a vacuum to a gauge pressure of 95 kPa for 30 min after which the fasteners were driven. Throughout the exposure period, these samples were partially submerged in water. For the three lowest moisture conditions, the wood was allowed to equilibrate for several weeks prior to driving in the fasteners to start the test. For the saturated condition, the nails were driven in shortly after they were removed from the vacuum impregnation.

The test continued for one year, the minimum exposure time was 8832 h (water saturated condition) and the maximum was 9048 h (90% relative humidity). After the test was finished, the fasteners were removed by sawing in between the fasteners, cutting closely on each side of the fastener, the wood surrounding each fastener was used to determine the wood moisture content. The fasteners could then be easily removed without damage by breaking remaining wood around the fastener. To measure the gravimetric corrosion rate, the corrosion products were removed by placing the fasteners in an ultrasonic bath with a 50:50 (volume) mixture of water and a proprietary chelating agent[1] for 60 min. The corrosion rate (R) was then calculated as

$$R = K\frac{m_f - m_i}{A\rho(t_f - t_i)} \quad (2)$$

where m_f and m_i are the final and initial masses (g), respectively, A is the surface area of the fastener (cm^2), ρ is the density (g cm^{-3}), $t_f - t_i$ is the length of the experiment (h) and K is a constant needed for unit analysis (87.6×10^6 μm cm^{-1} h y^{-1}). It should be noted that K is not a fitting factor but rather harmonizes the various units used in the equation. Ten nails were driven for all conditions. However, some nails were damaged when trying to remove the fasteners, mostly in the acetylated board held at 90% relative humidity. For this condition, there was only one stainless steel fastener that was not damaged, four carbon steel nails, and five galvanized steel nails. The rest of the conditions had between seven and ten successful replicates.

Results and discussion

The wood moisture contents, determined gravimetrically from the wood surrounding the fasteners, are presented in Figure 1. For the acetylated wood, no correction was made for the added weight of the modification agent as the exact weight percent gain of the treatment was unknown (Thybring 2013). It is well known that acetylation reduces the equilibrium moisture content in the hygroscopic moisture regime (conditioned with water vapor) (Popescu *et al*. 2014, Himmel and Mai 2015, Thybring *et al*. 2018, Garay and Henriquez 2012). The commercially acetylated wood strongly affected the equilibrium moisture content, reducing the moisture contents to less than 6% MC for each of the 3 conditions tested. For the vacuum saturated samples, both the unmodified and acetylated wood had moisture contents greater than 100%. For the unmodified wood, the moisture content measured for all conditions was above 20% MC, which is above the previously observed moisture threshold for corrosion in treated wood (Baker 1988, Dennis *et al*. 1995, Short and Dennis 1997, Zelinka *et al*. 2014).

Figure 2 presents the measured corrosion rates in acetylated and untreated wood for steel, hot-dip galvanized steel, and stainless steel fasteners for each of the four moisture conditions examined. It is clear from the figure that the stainless steel nails exhibited negligible corrosion for all of the conditions examined. In previous studies on treated wood (Dennis *et al*. 1995, Short and Dennis 1997, Zelinka *et al*. 2014), small increases in the corrosion rate with moisture content were observed until a rapid jump occurred in the corrosion rate (parameter C in Eq. 1). This behavior is also observed in the current data for untreated wood for steel and galvanized steel. However, in the acetylated wood, the corrosion rate of galvanized steel fasteners is constant (between 10 and 15 µm yr^{-1}) for all conditions. The corrosion rate of the steel fasteners in acetylated wood in the saturated condition is higher than those conditioned hygroscopically, and a widespread corrosion rate is observed in the hygroscopic measurements even though the wood MCs were all around 6%. A major goal of this study was to examine whether acetylated wood presented any additional corrosion risk for fasteners. From the data in Figure 2, it appears that in general, the corrosion rates of acetylated wood are similar to those measured in untreated wood. For stainless steel fasteners, corrosion is not a concern in either environment. For the steel and galvanized steel fasteners, it appears that the corrosion rate is slightly higher than that of untreated wood under hygroscopic conditions but less than untreated wood in the fully water saturated state. Even though the corrosion rates are slightly higher in the hygroscopic region, they remain below 15 µm yr^{-1}. Zelinka and Rammer have estimated that at a corrosion rate of 15 µm yr^{-1} it would take more than 30 years for a commonly used 8 d nail (diameter 3.4 mm) to reach 50% of its original lateral capacity (Zelinka and Rammer 2012). Therefore, it seems likely that corrosion may not be the limiting design concern in these scenarios, as other rehabilitation of the structure should be expected within a 30 year period.

In addition to comparing the corrosion rates of acetylated wood against untreated wood, it makes sense to also compare the corrosion to that of preservative treated wood, as both acetylated wood and preservative treated wood are designed to be used in outdoor applications. Figure 3 presents data from a previous study where the corrosion rates of steel and galvanized fasteners were exposed to wood treated with alkaline copper quaternary type D (ACQ-D), a common copper based wood preservative, using the same relative humidity conditioning methods examined in this study (Zelinka *et al*. 2014). From Figure 3, it is clear that for all moisture conditions and fasteners, the corrosion rate of acetylated wood was less than that the ACQ-treated wood. The largest differences between the ACQ-treated wood and the acetylated wood were observed at the 100% RH condition.

While the 2014 work of Zelinka *et al*. was the only previous study to examine corrosion under the same moisture conditions as the present study, several other papers have

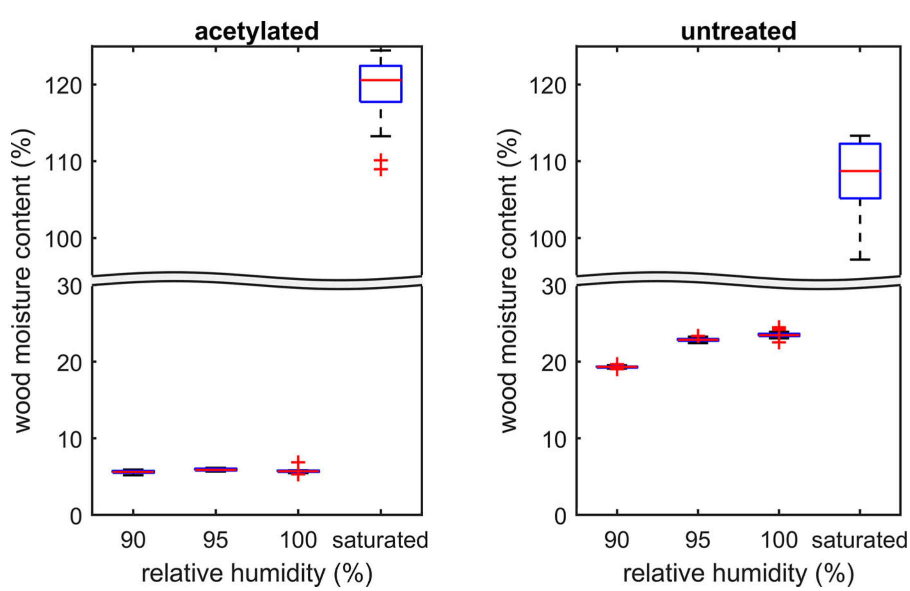

Figure 1. Average wood moisture contents of the acetylated (left) and untreated (right) wood specimens.

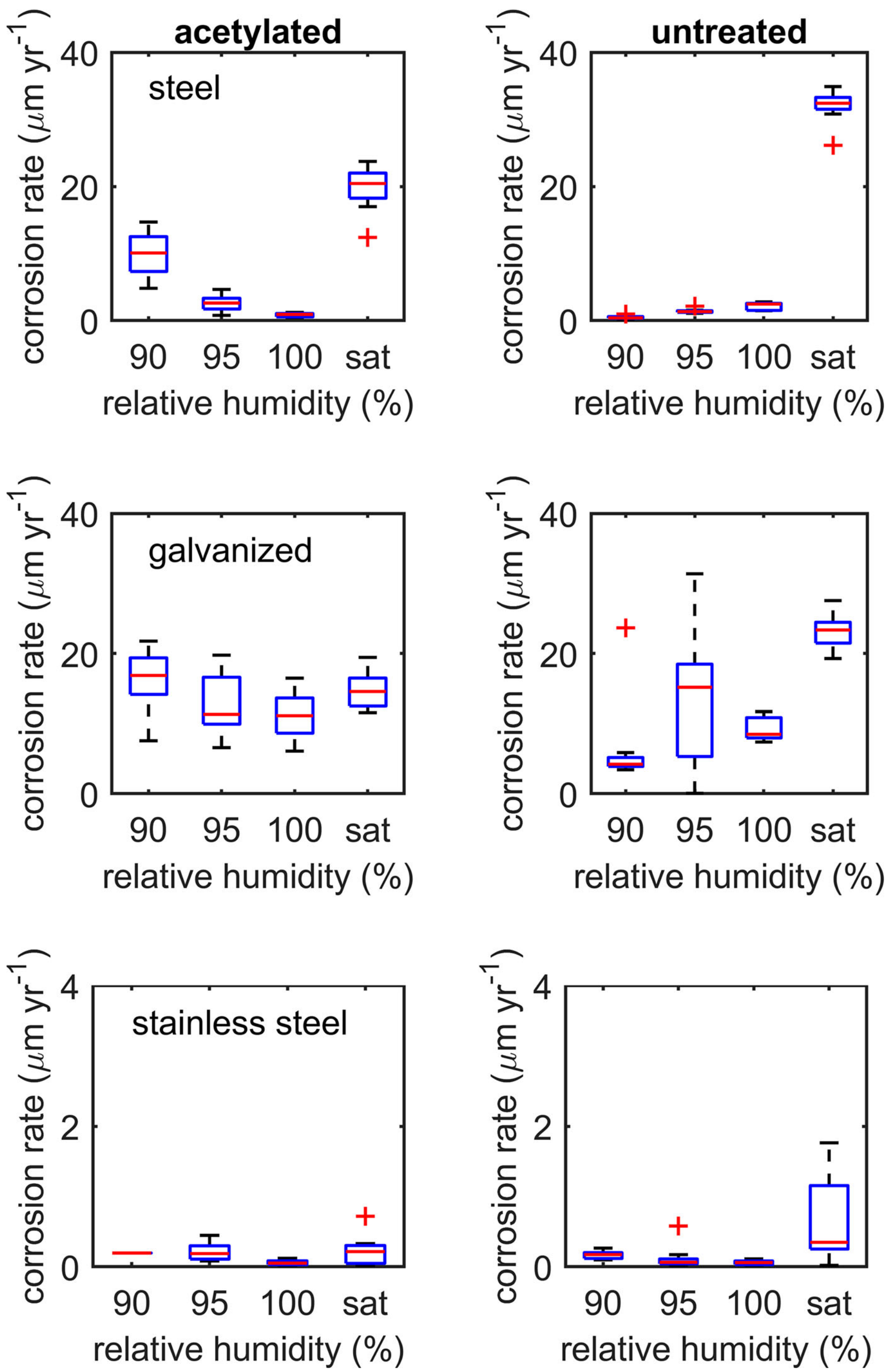

Figure 2. Corrosion rates measured in acetylated (left) and untreated wood (right) for steel (top) hot dip galvanized steel (middle) and stainless steel (bottom) fasteners. The solid line represents the median. Note the difference in scale for the bottom panel. The "+" represents an outlier of the box-and-whiskers plot.

measured corrosion rates at 100% relative humidity (Baker 1992, Zelinka 2007, Zelinka and Rammer 2009, Zelinka *et al.* 2010). Figure 4 presents the corrosion rates for many different wood preservatives along with those found for acetylated wood and untreated wood (this work). The data come from a previous compilation performed by Zelinka (Zelinka 2014). The circles represent the average value from a single study and the lines represent the range of reported average values where data from multiple studies are available. From Figure 4 it is clear that the measured corrosion rates for acetylated wood are low when compared to preservative-treated wood. The corrosion rate of the steel fasteners in acetylated wood was lower than that of all preservative treated wood and within the range of untreated wood. The corrosion rates of galvanized fasteners in acetylated wood were lower than all of the wood preservatives except chromated copper arsenate (CCA); corrosion rates measured in acetylated wood were within the range of reported corrosion rates of CCA. From these data, it appears that acetylated wood does not present a larger corrosion risk than preservative treated wood, and in fact, is less corrosive than many wood preservatives.

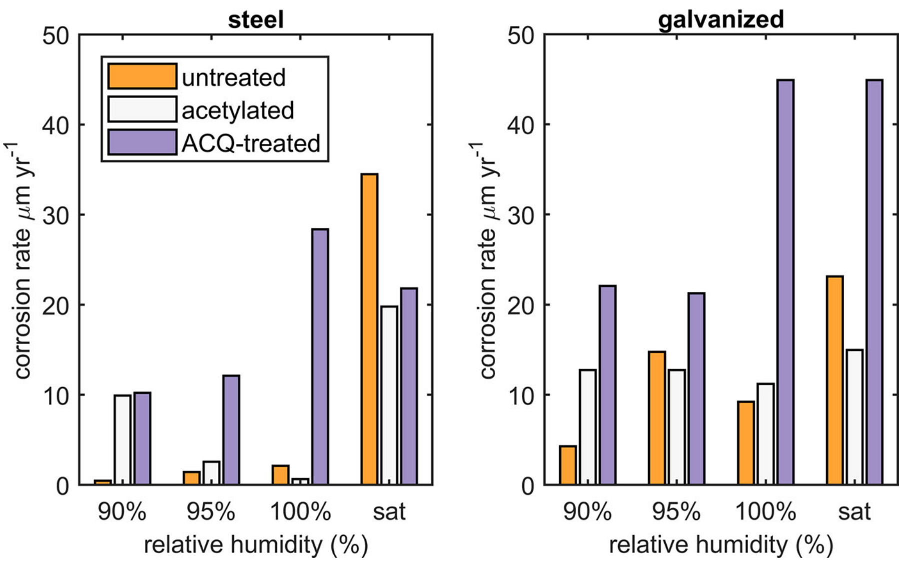

Figure 3. Corrosion rates from this study and from Zelinka *et al.* (2014) which examined alkaline copper quaternary (ACQ) treated wood.

The steel fasteners in untreated wood at the saturated condition exhibited unusually high corrosion for untreated wood (Figure 2). Previously reported corrosion rates for steel in untreated pine exposed to 100% relative humidity were less than 1 μm yr^{-1} (Zelinka *et al.* 2010). The corrosion rates measured in this study for untreated wood in the saturated condition were higher than those previously measured in ACQ-treated wood in both the 100% RH and saturated conditions (Zelinka *et al.* 2010, Zelinka *et al.* 2014). However, in the previous study it was found that under saturated conditions, copper from the wood preservative plated on the steel fasteners which greatly reduced the corrosion rate. Using an inverse calculation from previous field measurements, it was estimated that the corrosion rate of carbon steel fasteners in saturated conditions should be approximately 20 μm yr^{-1} (Zelinka *et al.* 2016a). It is unclear what is causing the high corrosion rates in this study, and the results may not be indicative of actual performance in untreated wood. On the other hand, the results from this study may be used as a conservative, upper bound on the amount of corrosion that can be expected in untreated pine.

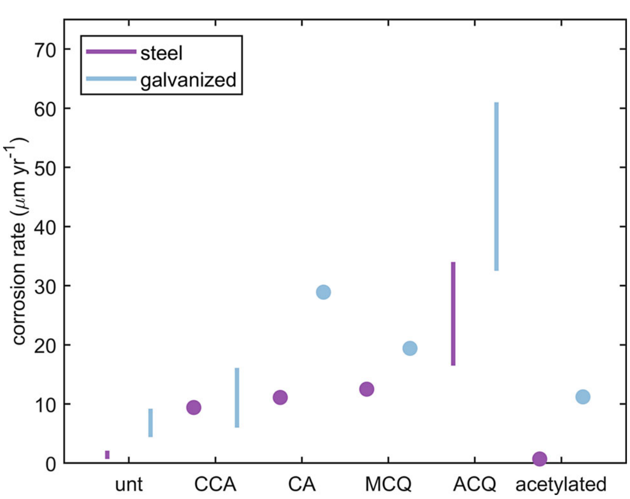

Figure 4. Corrosion rate of steel and galvanized steel fasteners measured at 100% RH for various preservative treatments. CCA, chromated copper arsenate; CA, copper azole; MCQ, micronized copper quaternary; ACQ, alkaline copper quaternary. The circles represent the average value from a single study and the lines represent the range of reported average values where data from multiple studies are available.

An interesting aspect of the data in the previous figures is the dependence on the corrosion rate on the wood moisture content. Previous research in unmodified preservative treated wood reported a threshold moisture content, between 15% and 18% MC, at which fastener corrosion does not occur (Baker 1988, Dennis *et al.* 1995, Short and Dennis 1997, Zelinka *et al.* 2014). After this corrosion threshold, there is a steep increase in the rate of corrosion until it plateaus at some maximum value. Interestingly, for the acetylated wood, all of the unsaturated conditions tested were well below this threshold moisture content. In fact, under these conditions, the wood moisture contents were within 1% of each other and there was no increase of the corrosion rate with moisture. In comparison, for the unmodified wood, the moisture trend appears to mimic the previously observed sigmoidal shaped behavior, especially for steel and galvanized fasteners. This behavior can be better seen in Figure 5, where the corrosion rates for steel and galvanized steel fasteners in untreated wood are plotted as a function of moisture content with the model fit of Eq. 1 overlaid. The model fit parameters are given in Figure 5. Such a fit was not possible for the acetylated data as there was not a sufficient spread in the moisture content data and it appears that the corrosion rates measured in acetylated wood do may follow the same trend with wood moisture content as they do in untreated wood.

It is worthy to note that the corrosion rates of galvanized steel fasteners in acetylated wood do not appear to depend on MC (Figure 1); the corrosion rates measured between 5% and 6% MC are not statistically different from those measured under saturated conditions. For the steel fasteners, the

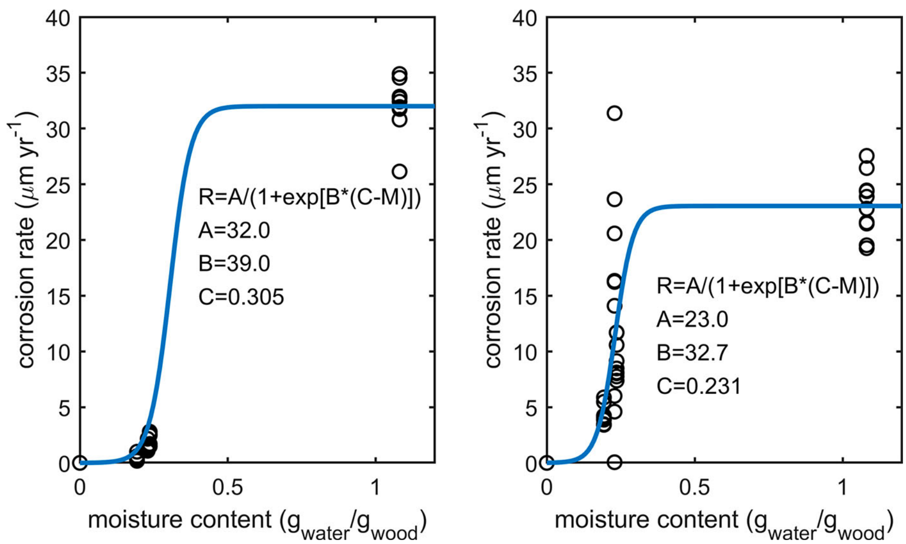

Figure 5. Corrosion rates of steel (left) and galvanized steel fasteners (right) in untreated wood as a function of moisture content with the fit of Eq. 1 overlaid.

corrosion rates were higher in the saturated condition than the hygroscopic conditions but for these conditions differences could be observed between the three conditions with the highest corrosion rates occurring under the 90% relative humidity condition. For the stainless steel fasteners no significant corrosion was observed for any of the conditions. These trends suggest that for acetylated wood, the corrosion mechanism may be completely different than for unmodified wood. For instance, corrosion was observed in acetylated wood even below the moisture content threshold at which corrosion occurs in unmodified wood for both steel and galvanized steel fasteners. Furthermore, the corrosion rate was independent of moisture content, whereas corrosion strongly depends on moisture for unmodified wood. One possibility for this difference may have to do with the diffusivity of corrosive agents within the wood. In in unmodified wood, the increase in moisture softens hemicelluloses which allows diffusion, whereas diffusion has shown to be inhibited in acetylated wood (Jakes *et al*. 2013, Hunt *et al*. 2018). These differences in corrosion mechanism suggest further study is needed. Developing a better understanding of the corrosion mechanism in modified wood has important practical implications as corrosion prevention strategies for preservative-treated wood may not be successful for acetylated wood. Additionally, it is also important to examine the potential for acid vapors from modified wood to cause corrosion on metal surfaces.

Conclusions

This paper presented a comprehensive look at the corrosion of fasteners in acetylated wood at four different moisture content conditions for carbon steel, galvanized steel, and stainless steel fasteners. The results were compared to data collected in untreated pine, as well as literature data on preservative treated wood.

From the data, it can be concluded that acetylated wood does not present a larger corrosion risk than preservative treated wood. In fact, in most situations, the measured corrosion rates were within a few μm yr^{-1} of untreated pine, and therefore suggests corrosion should not be a design concern for fasteners in outdoor applications.

Stainless steel fasteners exhibit essentially no measurable corrosion after a one year exposure embedded in both acetylated and untreated wood.

The acetylated wood had a very low moisture content, even when conditioned over liquid water (100% RH environment). Because of this, the wood moisture content was essentially independent of RH in the 90%–100% range and it was not possible to determine whether acetylated wood had a moisture content threshold for corrosion, nor was it possible to fit a corrosion model to the data.

For the untreated wood, the spread in moisture contents allowed a corrosion model to be fit to the data. This is the first time that the corrosion of untreated wood was examined as a function of moisture content. These model parameters can be input into combined hygrothermal corrosion models to predict the amount of corrosion that may be expected in outdoor environments in treated wood.

Note

1. EvapoRust, Orison Marketing, Abilene TX.

Disclosure Statement

No potential conflict of interest was reported by the authors.

Notes on Contributors

Samuel L. Zelinka is the Project Leader of the Building and Fire Sciences work unit of the US Forest Service Forest Products Laboratory.

Leandro Passarini was a post doc at the Forest Products Laboratory when the paper was written. Currently employed by Université du Québec en Abitibi-Témiscamingue.

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