

ADVANCES IN CORROSION TESTING OF METALS IN CONTACT WITH TREATED WOOD

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ABSTRACT

A January 2004 change in the regulation of wood preservatives used in the U.S. has increased the use of newer wood preservatives, such as alkaline copper quaternary (ACQ) and copper azole (CuAz). These preservatives contain high amounts of cupric ions, which may be reduced to copper metal at the expense of less noble steel and galvanized fasteners in the wood. Preliminary testing using extreme accelerating conditions suggested newer preservatives are more corrosive than the previously used chromated copper arsenate (CCA), although it is unclear how corrosion rates measured in these extreme conditions relate to milder in-service conditions. This paper presents preliminary results of a 1 year solid wood exposure test. The results are compared to electrochemical data collected in wood extracts obtained in a previous study. Additionally, the results of a small exploration on the effect of tannins on the corrosion of metals in wood extracts are presented.

Keywords: wood, wood extractives, tannins, fastener, polarization resistance, steel, galvanized steel, alkaline copper quaternary (ACQ), chromated copper arsenate (CCA), pH

INTRODUCTION

Historically, the most common wood preservative for residential construction was chromated copper arsenate (CCA). Corrosion of metals in CCA treated wood has been well studied¹⁻⁴ and these studies have led to corrosion-design recommendations for fasteners in CCA treated wood⁵ of hot-dip galvanized, stainless steel, silicon bronze or copper fasteners. Due to regulation changes in the United States (January 1, 2004), Europe, and Australasia, CCA can no longer be used for residential construction. Currently, newer wood preservatives, such as alkaline copper quaternary (ACQ), copper azole (CuAz), and micronized copper systems are commercially available; preliminary studies have shown that these preservatives are more corrosive than CCA⁶⁻⁹.

Despite its practical importance, the mechanism of corrosion of metals in contact with treated wood is not well understood. Corrosion in CCA treated wood has generally been attributed to reduction of cupric ions in the wood preservative¹⁰. Baker¹ found that metals noble to copper in the galvanic series did not corrode in CCA treated wood whereas metals active to copper did corrode. One aspect of wood-metal corrosion that is well understood is the strong dependence of corrosion on wood moisture content. The role of wood moisture content is similar to the role of relative humidity in atmospheric corrosion. The corrosion rate of metals in contact with wood drop sharply when the wood moisture content is below fiber saturation (where there is no free water in the lumina) and eventually at a "threshold" moisture content of 15%-18%, no corrosion occurs^{11,4}. It is believed that corrosion between the threshold moisture content and fiber saturation is related to a type of water with properties between bound and free water (so called "freezable bound water")¹². While freezable bound water has been confirmed in cellulose¹³, its presence in solid wood is not yet proven.

Recently the authors developed a new test method for measuring the corrosion of metals in contact with wood^{8,14,15}. The method involves measuring the polarization resistance of a metal fastener in a water extract of treated wood, and was developed under the assumptions that (1) the corrosion mechanism in wood is aqueous, and (2) the extract contains the water soluble components in wood and therefore should have a similar composition to moisture within the wood.

In preliminary work good correlation was found between corrosion rates measured in the extract and a 1 year exposure of steel and galvanized steel in ACQ treated wood¹⁴. Using EDS, copper was found on fasteners that had been polarized in the extract, suggesting the reduction of cupric ions was the cathodic reaction in the extract. The correlation between the extract and the solid wood suggests the cathodic reaction in the solid wood is also the reduction of cupric ions as Baker¹⁶ hypothesized. Recent work⁸ measured the corrosion rates in extracts of wood treated with several wood preservatives to test the effects of the preservative chemistry on the corrosion rate. However, the effectiveness of the extract test method could not be evaluated because there were no solid-wood exposure data at the time to compare them against. This work presents exposure data and compares it to these previously collected extract corrosion rates to solid wood corrosion rates.

Although the corrosion mechanism in the extract involves the reduction of cupric ions, it is also largely influenced by the presence of wood extractives. Corrosion in solutions of wood preservatives show completely different behavior than corrosion in solid wood^{7,17,18} even at the same copper concentration. Although a single piece of wood can contain over 700 different extractives²¹, only three types extractives have been thought to affect the corrosion of metals in contact with wood or the black liquors of wood pulp: organic acids³⁰, tannins (or more broadly polyphenols), and phenols with a second hydroxyl groups in the ortho position, (i.e. catechol and pyrogallol). For solid wood, only organic acids and tannins have been mentioned

in the literature; catechol (1,2 dihydroxobenze) and pyrogallol (1,2,3 trihydroxobenze) are formed as the lignin is destroyed in the pulping process^{24,25}.

It is widely known that pH affects metallic corrosion. The earliest literature on corrosion in wood stated that more acidic wood species were more corrosive³¹. Later, Smith²⁷ tabulated the pH and corrosiveness of different wood species and found that the most corrosive wood species had a pH less than 5.

Tannins can chelate with iron to form a dark blue/black precipitate^{23,32-34}. In many cases, this chelation reaction is used to protect metals either by using tannins as an inhibitor, or incorporating them into a priming system³⁵⁻³⁹. Literature on corrosion in the pulp and paper industry has generally also accepted wood tannins as corrosion inhibitors^{19-23,32}. However, the literature on the role of tannins in solid wood corrosion has stated that tannins increase the corrosion rate in solid wood^{28,29,40-43}. These papers examined the corrosion of saw blades, where the corrosive environment contains high temperature and friction, and it is not clear how these results pertain to fasteners in wood.

In short, there is agreement that pH and tannins affect corrosion in wood, although the literature presents two conflicting viewpoints on the role of tannins. This work examines wood species that were chosen because of their differences in both tannins and pH to explore how these variables affect corrosion in wood.

EXPERIMENTAL

Southern pine (*Pinus spp.*) sapwood with an oven-dry specific gravity of 0.6 was tested either in an untreated state, or with one of four preservatives: CCA, ACQ, CuAz, or dimethyldidecyl ammonium carbonate (DDAC). The preservative loadings were in accordance with American Wood Protection Association use category UC3 for use in above ground applications⁴⁴, except for DDAC which was treated to have the same amount of DDAC as the ACQ treated wood contained. Three of these treatments (CCA, ACQ, CuAz) contained cupric ions, and the other two treatments (DDAC and untreated) did not. DDAC, the co-biocide in ACQ, was chosen as a control to separate out the effects of copper from the effects of DDAC in the ACQ treated wood.

Steel and hot-dip galvanized steel fasteners were tested a long term exposure test at 27°C, 100% relative humidity, or with electrochemical methods in a wood extract. The conditions for the exposure test were maintained by placing the specimens over water in sealed desiccators; the resulting wood moisture content was 24.6% ± 0.6% (standard deviation). After exposure fasteners were either cleaned and weighed for a corrosion rate measurement, or the corrosion products were examined. The extract consists of a 1:10 weight ratio of sawdust to water, and the extraction time is 1 week. Chemical properties of the extracts have been reported elsewhere⁸. The polarization resistance was measured after the fastener had been immersed in the extract for an hour. The potential was varied from -30mV to +30mV with respect to the open circuit potential at a scan rate of 0.166 mV/s. The Tafel slopes and corrosion rate were calculated from the polarization resistance data using Mansfeld's method^{47,48}.

Four wood species known to have differences in pH and tannin were investigated with the extract method: white oak (*Quercus spp.*) was chosen as it is very acidic and high in tannins, elm (*Ulmus sp.*) was chosen because it is low in extractives and is one of the least acidic woods, black locust (*Robinia pseudoacacia*, hereafter referred to as locust) was chosen because it is a naturally durable species, and the extractives that protect the wood may affect corrosion, and southern pine (*Pinus spp.*) was chosen to connect with the work on treated wood.

For the untreated woods, the pH was measured with a double junction glass bulb electrode in conjunction with a pH meter. The amount of tannin was also quantified colorimetrically with the method of Amin⁴⁹ with two modifications. The tetrazolium blue did not dissolve in water at a concentration of 0.01M so the tetrazolium blue solution was made to a concentration of 0.005M and twice the volume used instead. Also, when solutions were heated in 10 mL volumetric flasks the solutions boiled over and the samples could not be tested quantitatively. Instead, solutions were heated in a 50 mL Erlenmeyer flask and after heating, transferred to a 10 mL volumetric flask where the total volume was brought to 10 mL with ethanol. The corrosion rate of a 1018 steel plug (UNS G10180) was measured using the polarization resistance method with the same parameters used for the treated wood specimens.

RESULTS

For the treatments that contain cupric ions, there was good correlation between corrosion rates measured in the solid wood and in the extract for both steel and galvanized steel (Figure 1). However, the extracts without cupric ions were much more corrosive than both the solid wood and the cupric ion containing extracts (Figure 2).

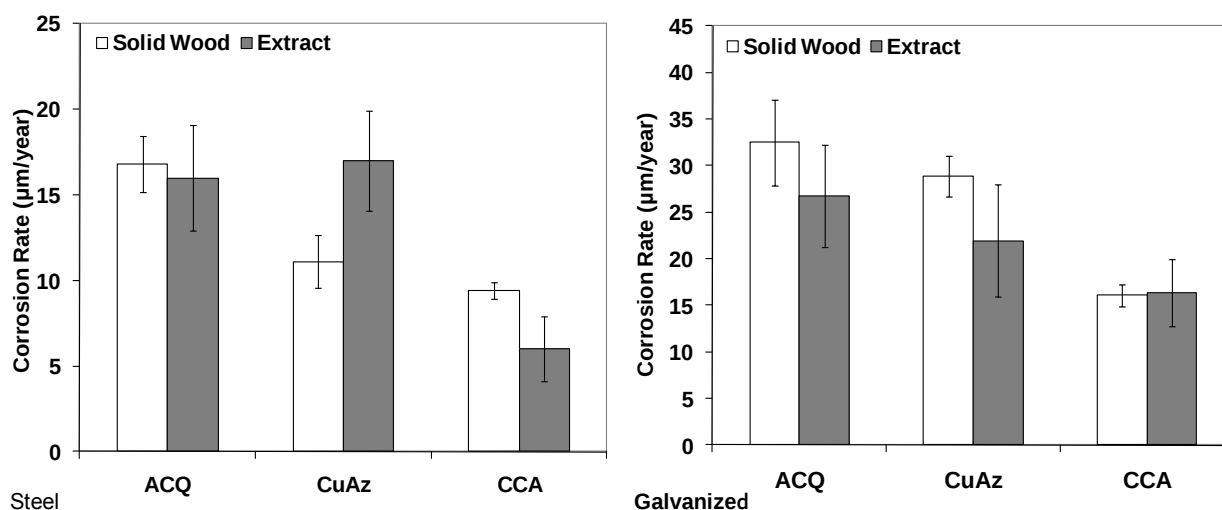


Figure 1: Comparison of corrosion rates of steel (left) and hot-dip galvanized steel (right) fasteners measured in either a one year exposure test (Solid Wood) or electrochemically in wood extracts (Extract) for preservatives with cupric ions.

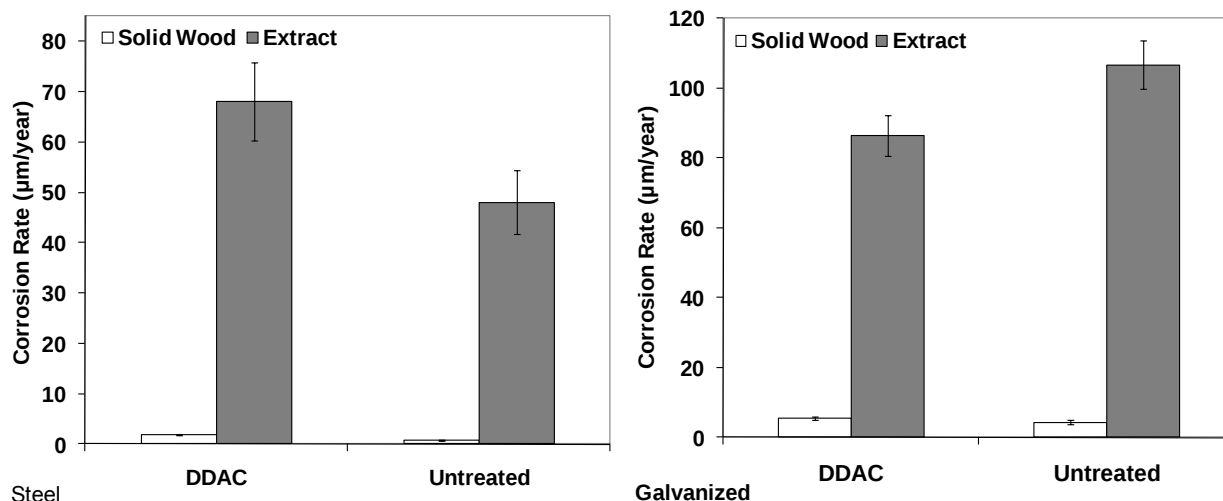


Figure 2: Comparison of steel (left) and hot-dip galvanized steel (right) fasteners measured in a one year measured in either a one year exposure test (Solid Wood) or electrochemically in wood extracts (Extract) for preservatives without cupric ions.

The surfaces and cross sections of the fasteners were analyzed with SEM and energy dispersive X-ray spectroscopy (EDS). Copper was not detected with EDS on either the steel or galvanized fasteners exposed to any of the preservative treatments.

The pH, tannin content, and corrosion rate of the extracts of the different wood species tested are given in Table 1. The pH of the pine and oak extract were similar, and the tannin content of locust and oak were also similar. This allows a limited discussion of the effect of tannin and pH holding the other variable constant.

Table 1: Physical and corrosive properties of the untreated wood extracts tested.

		pH	Tannins ^(a) (mg L ⁻¹)	Corrosion rate of steel (μm yr ⁻¹)	
Extract	Oak	4.3	1020	279	±10 ^(b)
	Pine	4.5	340	334	±26
	Locust	5.1	990	74	±24
	Elm	6.5	40	159	±33

^(a)Expressed as tannic acid

^(b)Standard error

DISCUSSION

It was found that the corrosion rates of galvanized fasteners were higher than the corrosion rates for carbon steel fasteners for all of the preservatives tested. This may seem surprising as it is generally accepted that zinc corrodes more slowly than steel in atmospheric conditions. However, research has shown that wood vapors cause zinc to corrode more rapidly than steel⁵⁰ and it has been shown that zinc corrodes more rapidly than steel when immersed in water⁵¹. Differences between the relative corrosion rates of zinc and steel have been attributed to the type and morphology of the corrosion products formed in a given environment⁵². Future research on fasteners embedded in treated wood should include X-ray diffraction as a means to classify the corrosion products formed.

Assuming the corrosion mechanism involves the reduction of cupric ions, there are two possible rate determining steps; the migration of cupric ions to the metal surface, or the

corrosion reaction at the surface of the fastener. Three results suggest that the rate determining step is not the migration of ions. The first is that the measured corrosion rate in solid wood is independent of time⁹. The second involves the diffusion distance. We measured corrosion rates on the order of 5-30 μ m per year, which corresponds to a depletion of copper in a zone $\sim$ 0.5cm around the fastener. Based upon ionic diffusivities measured in our previous work⁴⁶, we estimate the diffusion distance is approximately 1.5 cm per year, bigger than what is needed to sustain a corrosion rate of 30 μ m per year. Finally, we observe good correlation between corrosion rates measured in the solid wood and corrosion rates measured in the extract when cupric ions are present.

Good correlation was found between the solid-wood test and the extract test for the wood preservatives containing cupric ions (ACQ, CCA, and CuAz). These results agree with the preliminary work in ACQ treated wood¹⁴. EDS of fasteners polarized in the extracts reveal the presence of copper, which suggests that the reduction of cupric ions is the cathodic reaction. Because of the similarity in corrosion rates between the solid wood and the extract, it is plausible that the reduction of cupric ions is also the cathodic reaction in solid wood. However, no copper was detected on fasteners exposed to the solid wood. While this is surprising, it agrees with the work of Simm and Button who did not detect copper on steel, zinc, and aluminum fasteners exposed to CCA treated wood². While it appears that the cathodic reaction in solid wood may be the reduction of cupric ions, it is not clear what happens to the reduced copper. One possibility is that it is reduced near the metal surface but remains on the wood instead of the metal, although at this point in time, the wood near the metal has not been analyzed.

For the treatments that do not contain copper (untreated/DDAC), the extracts were much more corrosive than the solid wood. In these extracts, likely cathodic reactions are the reduction of acids and dissolved oxygen[10,31,3,38]. It is not surprising that these extracts are more corrosive than the solid wood since the transport of oxygen is likely much higher in the extract and there is more acid; it has been shown that acetic acid is produced (not extracted) as the wood spontaneously undergoes deacetylation in the presence of water²⁶. What is surprising however is that these extracts are more corrosive than the extracts with cupric ions since the cupric ions increase corrosion in solid wood.

The two extracts that did not contain cupric ions were approximately three times more corrosive than the extracts with cupric ions. From an experimental perspective, the DDAC and untreated extracts were different in two regards; these extracts had the lowest pH and also did not contain cupric ions. There are three possibilities: (1) in extracts containing cupric ions, reduction of cupric ions is the preferred cathodic reaction and this reaction occurs at the same rate regardless of the pH, or (2) the difference in corrosion rates is entirely an effect of pH, and if one of the extracts with cupric ions had a lower pH, it would exhibit behavior like the untreated and DDAC extracts. The third possibility is the copper deposited on the metal surface reduced the amount of surface area for corrosion. While it is impossible to differentiate between these expected behaviors from the current data, we hope to identify a technique that will clarify this mechanism. It may be possible to analyze the amount and valence of the copper in the wood near the metal surface and compare it to bulk wood.

The effect of pH and tannins can best be observed by comparing pine and locust to oak. Pine and oak have the nearly the same pH but oak has more tannins than pine and a lower corrosion rate. This suggests that tannins act as an inhibitor and at a given pH, an increase in the tannin content lowers the corrosion rate. Likewise, the locust and oak have nearly the same tannin content, but the pH of oak is lower, and it has a higher corrosion rate. It is difficult to discuss the corrosiveness of elm without invoking kinetic models with the influence of tannins and pH on the corrosion rate. Elm has the highest pH and the lowest amount of

tannins and since the corrosion kinetics may depend non-linearly on both tannins and pH it is unclear whether the measured corrosion in elm is consistent with the other measurements. It may eventually be possible, by collecting more data and applying the appropriate models, to develop an isocorrosion map for tannins and pH in wood.

CONCLUSIONS

- Preservatives with cupric ions exhibited the same corrosion rate in the extract and the solid wood. It is believed that the cathodic reaction in both cases is the reduction of cupric ions and migration of cupric ions through the wood is not the rate determining step. Future work should focus on determining what happens to the reduced copper in solid wood. The untreated and DDAC treated extracts were more corrosive than the solid wood and these extracts were also more corrosive than the extracts with cupric ions. It is not yet clear why these extracts are more corrosive than the extracts with cupric ions.
- The limited data on the influence of tannins and pH on the corrosion of wood extracts suggest that at a given pH, tannins inhibit corrosion in wood extracts. This is not consistent with the literature on saw blade corrosion; differences are most likely due to the high temperatures and friction that occur in saw blades. At a given level of tannins, a lower pH increases corrosion. Future work should combine the data with kinetic models to create an isocorrosion diagram of the role of these compounds in wood.

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