Corrosion of Fasteners in Wood Treated with Newer Wood Preservatives

Samuel L. Zelinka
Abstract

This document compiles recent research findings related to corrosion of metals in preservative treated wood into a single report on corrosion of metals in wood. The research was conducted as part of the Research, Technology and Education portion of the National Historic Covered Bridge Preservation (NHCBP) Program administered by the Federal Highway Administration. The compilation addresses: corrosion rates of metals embedded in treated wood, the mechanism of corrosion in treated wood, the effect of extractives on corrosion, methods for predicting the service life of metals in treated wood, and suitable non-metallic replacement fasteners. The document was created to serve as a desk reference for engineers to aid in materials selection when building with treated wood.

Keywords: preservative treated wood, corrosion, timber bridge, fastener, fiber reinforced polymers

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This study is part of the Research, Technology and Education portion of the National Historic Covered Bridge Preservation (NHCBP) Program administered by the Federal Highway Administration. The NHCBP program includes preservation, rehabilitation and restoration of covered bridges that are listed or are eligible for listing on the National Register of Historic Places; research for better means of restoring, and protecting these bridges; development of educational aids; and technology transfer to disseminate information on covered bridges in order to preserve the Nation’s cultural heritage.

This study is conducted under a joint agreement between the Federal Highway Administration–Turner Fairbank Highway Research Center, and the Forest Service – Forest Products Laboratory.

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Corrosion of Fasteners in Wood Treated with Newer Wood Preservatives

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Executive Summary

Most metals are thermodynamically unstable in the environment and corrode to form the more stable ceramics (metal-oxides or metal-hydroxides) from which they were at one time extracted. Because of the thermodynamic favorability of corrosion, it is a war that Nature will eventually win, but humankind may prolong the fight, in some cases indefinitely, through careful materials selection and design.

Metal fasteners are an essential part of modern timber construction; these fasteners, like all metals, are subject to corrosion, which may lessen the structural capacity of the joint. If the wood remains dry, the fasteners will not corrode. Timber bridges are exposed to the natural environment and the wood will invariably get wet during the life of the structure. It is therefore necessary in rehabilitating timber bridges to understand the corrosion of metals in wood so that the bridge can be properly inspected for corrosion and durable materials can be selected for replacement.

Even when wet, the wood of most species is a relatively benign environment for corrosion. However, wood preservatives are frequently added to wood used in exterior environments to protect it from wood decay fungi and termites. Although wood preservatives increase the service life of wood, in some cases these preservatives increase the corrosiveness of the wood toward metal fasteners.

The corrosiveness of preservative-treated wood has been studied since the 1920s when the first treatments were being developed for railroad ties. The amount and intensity of the corrosion research has changed throughout time as wood preservatives of varying corrosivity have been developed and introduced. Prior to 2004, the most common waterborne wood preservative in the United States was Chromated Copper Arsenate (CCA). The corrosion of metals in CCA-treated wood was studied by several researchers who found that it was more corrosive than untreated wood and suggested that at a minimum, hot-dip galvanized fasteners should be used in treated wood. The hot-dip galvanized fasteners were widely used in CCA-treated wood for many years with few corrosion problems.

In 2004, CCA-treated wood was voluntarily withdrawn for use in residential construction in the United States and similar changes in regulation have decreased the use of CCA-treated wood in Europe and Australasia. At that time, several alternatives to CCA became commercial available, the most popular being alkaline copper quaternary (ACQ) and copper azole (CuAz). Like CCA, these preservatives used copper as a biocide, but in a higher concentration than CCA. Shortly after this transition, anecdotal evidence of corrosion failures was found with these new preservative treatments. Likewise, the results of accelerated high-temperature, high-humidity testing suggested that these new preservative treatments may be more corrosive than CCA. However, it was unclear how these accelerated tests and reported failures related to an expected corrosion lifetime for fasteners in treated wood.

Although it was accepted that galvanized fasteners were sufficiently durable for service in CCA-treated wood, it was unclear how the results of the accelerated testing could be applied to designing durable structures in other wood preservatives. There were two reasons for this. First, even though the corrosion of metals in CCA-treated wood had been examined, the actual corrosion rates were not reported, but instead percentage weight loss was used because the surface area of the fasteners, which was necessary for calculating a corrosion rate, was, at the time, impossible to calculate for threaded fasteners. Second, there was also no way to connect the results from a metal corrosion test to the residual strength of the nailed connection in wood.

The USDA Forest Service, Forest Products Laboratory (FPL), with funding from the Federal Highway Administration, conducted an investigation of the corrosion of fasteners in new wood preservatives. The goals were to understand and quantify the corrosion of ferrous and non-ferrous metal fasteners in new preservative treatments and to examine the feasibility and performance of non-metallic fasteners that eliminate the potential for corrosion altogether. Key to this investigation was an apparatus recently developed at FPL that made it possible to measure the surface area of threaded fasteners.

This final report represents a single-volume compilation of the major research findings. The research addresses these pertinent questions on designing durable connections with new preservative treatments:

- How rapidly do embedded metals corrode in wood?
- What is the mechanism of corrosion in treated wood?
- Do extractives affect corrosion?
- How can we rapidly determine the service life of metals in wood?
• How can we use corrosion data to predict service life of metals in wood?
• Do suitable non-metallic fasteners for use in wood exist and how durable are they?

These questions were explored over a period of several years and the findings were published as they were found. Papers are compiled here to have all of the pertinent data in a single report. Although each chapter is self-contained, it addresses at least one and sometimes more than one of these questions. This Executive Summary briefly connects the previously published papers to the scientific questions that they answer and highlight key results. Citations to the originally published papers are provided in this Executive Summary.

How Rapidly Do Embedded Metals Corrode in Wood?

Arguably, the most important questions are how fast do embedded metals corrode in wood, and how do wood preservatives affect these corrosion rates. The corrosion rates of steel and galvanized steel were measured in a one year exposure test. Five different wood preservatives and untreated wood were tested. The results of the exposure test are given in Chapter 1.


What Is the Mechanism for Corrosion in Treated Wood?

This question is more broad than the first question, but equally important to eventual development of non-corrosive preservatives and corrosion resistant fasteners. Different aspects of this question were explored in different papers. For example, corrosion products that formed in different preservatives are detailed in Chapter 1; the type and amount of corrosion products are a key part of how fast underlying metals corrode. The role that cupric ions in preservatives play on further corrosion is detailed in Chapter 2.


Do the Extractives Affect Corrosion?

Research has shown that different wood species contain different extractives that may affect the corrosion of embedded metals. For instance, many of the individual extractives in wood are being used as “green” corrosion inhibitors in the corrosion industry. The role of two classes of extractives, tannins and small organic acids, are examined in Chapter 3. Zelinka, S.L.; Rammer, D.R. 2013. Environmental degradation of fiber-reinforced polymer (FRP) fasteners in wood. ASCE Journal of Materials in Civil Engineering. 25(5):627-631.


How Can We Rapidly Determine the Service Life of Metals in Wood?

A rapid test was developed at FPL to measure corrosion of metals in contact with wood, wherein metals are electrochemically polarized in water extracts of treated wood. Chapter 2 describes the rapid test and compares results from this test against the exposure test presented in Chapter 1.

How Can We Use Corrosion Data to Predict Service Life?

One of the key aspects of applied science of any sort is relating laboratory measurements to the “real world.” This requires knowledge of the failure mechanism, models that describe the breakdown in service, and a failure criteria. Chapters 1 and 2 detail the failure mechanism. In Chapter 4, the corrosion mechanism is combined with a hygrothermal model to determine how rapidly fasteners will corrode in different U.S. climates. Finally, Chapters 5 and 6 show how corrosion affects the structural capacity of nailed joints.


Do Suitable Non-Metallic Fasteners for Use in Wood Exist and How Durable Are They?

Metals corrode because they are thermodynamically unstable in nearly every environment. Ceramics and polymers are generally thermodynamically stable, but may have other challenges that make them unsuitable to replace metals. In the course of this research, a ceramic-fiber reinforced polymer nail for use in wood became commercially available. This fastener was evaluated for use in treated wood and the results are presented in Chapter 7.
Chapter 1

Exposure Testing of Fasteners in Preservative Treated Wood: Gravimetric Corrosion Rates and Corrosion Product Analyses

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Abstract

Research was conducted to determine the corrosion rates of metals in preservative-treated wood and also understand the mechanism of metal corrosion in treated wood. Steel and hot-dip galvanized steel fasteners were embedded in wood treated with one of six preservative treatments and exposed to 27 °C at 100% relative humidity (RH) for 1 year. The corrosion rate was determined gravimetrically and the corrosion products were analyzed with scanning electron microscopy, energy dispersive x-ray spectroscopy, and x-ray diffraction. Although the accepted mechanism of corrosion in treated wood involves the reduction of cupric ions from the wood preservative, no reduced copper was found on the corrosion surfaces. The galvanized corrosion products contained sulfates, whereas the steel corrosion products consisted of iron oxides and hydroxides. The possible implications and limitations of this research on fasteners used in building applications are discussed.

Keywords: Steel, zinc, preservative-treated wood, timber, XRD X-ray diffraction, scanning electron microscopy (SEM)

Introduction

The corrosiveness of wood treated with chromated copper arsenate (CCA), the major wood preservative of the past 30 years, was studied in accelerated (Simm and Button 1985b; Dennis and others 1995) and long-term tests (Baker 1992; Simm and Button 1985a) in the 1980s and 1990s. These test results led to design recommendations for minimizing metal corrosion of metals in contact with CCA-treated wood (Anon 2003). However, CCA was voluntarily withdrawn for use in residential applications in the United States on December 31, 2003; similar changes in regulation have taken place in Europe and Australasia. Whereas alternatives to CCA are commercially available, there has only been limited work studying corrosion of metals in contact with these alternatives.

Recent work has investigated corrosion of metals in contact with alternatives to CCA using accelerated test methods. The Simpson Strong Tie Corporation (Pleasanton, California) published a technical bulletin (Anon 2008) based upon over 6,000 replicates using a high-temperature high-humidity test method (AWPA 2007a) and reported relative corrosion rankings of hot-dip galvanized steel exposed to several wood preservatives. They found that alkaline copper quaternary (ACQ) and copper azole (CuAz) were roughly twice as corrosive as CCA. However, the high-temperature high-humidity test method has been shown to have poor correlation with in-service performance (Jin and Preston 2000). Both Zelinka and others (2007) and Kear and others (2008a,b) examined corrosion in solutions of the preservative chemical as opposed to treated wood and found that the corrosion behavior of metals in treating solution was very different from behavior in treated wood. The lack of success with these accelerated methods highlights the importance of long-term tests; recently, several papers have presented non-accelerated wood-metal corrosion data for newer wood preservatives.

Thorough work by Kear and others (2009) examined the behavior of mild steel, hot-dip galvanized steel, and stainless steel (UNS S31600) exposed to CCA (type C), CuAz (type B), and ACQ (types B and C) treated at several retention levels. A unique aspect of this work was that both metal plates specified in the AWPA standard (AWPA 2007a) as well as metal fasteners were tested. The wood–metal assemblies were exposed to either accelerated (49 °C, 90% RH for ~400 h) or nonaccelerated conditions (21°C, various RH}
for ~1 year). The data were presented as corrosion rate (mm y⁻¹). Similar to accelerated tests, Kear and others (2009) found that CuAz and ACQ were more corrosive than CCA and attributed this to differences in fixation between the preservative systems.

Zelinka and Rammer (2009) re-examined a 14-year exposure study of CCA-treated wood published by Baker (1992), which is the basis for the International Building Code’s recommendations for fasteners used in treated wood (Anon 2003). Using archived photographs, Baker’s laboratory notebook, and a new surface area algorithm (Rammer and Zelinka 2008), Zelinka and Rammer were able to convert Baker’s percent weight loss data into a corrosion rate (μm y⁻¹). Additional tests were conducted for 1 year in ACQ-treated wood at the same temperature and RH conditions that Baker tested (27 °C, 100% RH). The authors found that ACQ-treated wood was more corrosive than CCA-treated wood and that the relative corrosiveness of wood treatments depended on the metal tested.

In addition to these long-term laboratory tests, Li (2009) has published results of outdoor field exposure tests of steel, galvanized steel, and stainless steel fasteners embedded in ACQ-, CuAz-, and CCA-treated wood.

The work by these authors has quantified the difference in corrosion rates between CCA, the historical baseline, and new wood preservatives such as ACQ and CuAz. These measured corrosion rates have practical implications for designing treated wood structures. The current work expands upon these earlier works with the goal of better understanding the mechanism of corrosion in treated wood. In addition to gravimetric tests, the current work examines corrosion products with several techniques to find correlations between preservative chemistry and corrosion products in both treated and untreated wood.

### Experimental

Southern Pine (*Pinus* spp.) boards, 38 mm by 140 mm by 2.5 m from the same plantation were split into five groups for treatment with either chromated copper arsenate (CCA-C), alkaline copper quaternary with a carbonate formulation (ACQ-D), micronized (<1000 nm) copper quaternary (MCQ), didecyl dimethyl ammonium carbon (DDAC), or left untreated as a control. The newer carbonate formulations of ACQ-D use didecyl dimethyl ammonium carbonate instead of didecyl dimethyl ammonium chloride; formulations were changed so that they would be less corrosive than the chloride formulations. Lumber treated with copper azole (CuAz) was also tested in this study, but the lumber came from a different plantation and had starting dimensions of 38 mm by 89 mm by 1.2 m. The retention of the preservatives was verified using inductively coupled plasma atomic emission spectroscopy (ICP-AES). The ACQ and MCQ formulations tested in this study are similar in that they both contain the same nominal amount of copper and DDAC; however, they differ in how the copper was applied to the wood structure. ACQ is comprised of soluble copper in a waterborne solution, whereas MCQ is comprised of sub-micron sized particles of insoluble copper compounds. More information on the differences between preservatives and a comprehensive review of the biological and wood-treatment aspects of these wood preservatives has recently been published by Freeman and McIntyre (2008). Details on the composition and specified and actual treatment retentions for the preservatives used in this study are given in Table 1-1.

Two types of box nails used for siding (8d) were tested in this study, a plain carbon steel nail, and a hot-dip galvanized nail. Both nails came from the same batch; the plain carbon steel nails were culled from the production line just prior to

### Table 1-1. Composition and retention of preservatives tested

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Nominal compositionᵃ (percentage weight)</th>
<th>Retention (kg m⁻³)</th>
<th>Nominal</th>
<th>Actual</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCA (type C)</td>
<td>47.5 CrO₃; 18.5 CuO; 34.0 As₂O₅</td>
<td>4 1.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chromated copper arsenate</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ACQ (type D)</td>
<td>66.7 CuO; 33.3 DDACᵇ</td>
<td>4 2.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alkaline copper quaternary</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CuAz (type C)</td>
<td>96.8 uO; 1.6 Tebuconazole; 1.6 Propiconazole</td>
<td>1 0.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Copper azole</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MCQ</td>
<td>66.7 CuO; 33.3 DDAC</td>
<td>4 5.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Micronized copper quaternary</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DDAC (carbonate)</td>
<td>100.0 DDAC</td>
<td>1.3 n.a.ᶜ</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alkyl ammonium compound</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

ᵃNominal compositions from AWPA Standard P5 (AWPA 2007b), with the exception of MCQ, which comes from ICC-ES evaluation report ESR-1980.
ᵇDDAC is didecyl dimethyl ammonium carbonate.
ᶜThis preservative could not be analyzed with ICP-AES.
Corrosion of Fasteners in Wood Treated with Newer Wood Preservatives

analyzed gravimetrically and after approximately 7 months removed after 1 year of exposure (366 days) for specimens was 24.6% ± 0.6% (standard deviation). The blocks were made, determined gravimetrically from untreated specimens, as dictated by the Gibbs phase diagram. The resulting environment inside the desiccator was kept in a room held at 27 °C, 100% RH; the resulting environment inside the desiccator was kept in a room held at 27 °C, 90% RH; the resulting environment inside the desiccator was kept in a room held at 27 °C, 90% RH; the resulting environment inside the desiccator was kept in a room held at 27 °C, 90% RH; the resulting environment inside the desiccator was kept in a room held at 27 °C, 90% RH. The blocks were then placed above a reservoir of high-purity distilled water into a block of wood. The wood-fastener assemblies were degreased, and weighed. The fasteners were cleaned in a bath of distilled water that was ultrasonically agitated for 5 min. Finally, the fasteners were degreased with acetone and allowed to dry. Once dry, the fasteners were weighed to the nearest 0.1 mg and hand-driven through the pilot hole into a block of wood. The wood-fastener assemblies were then placed above a reservoir of high-purity distilled water inside a sealed desiccator that was kept in a room held at 27 °C, 90% RH; the resulting environment inside the desiccator was 27 °C, 100% RH as dictated by the Gibbs phase rule. The average wood moisture content in this environment, determined gravimetrically from untreated specimens, was 24.6% ± 0.6% (standard deviation). The blocks were removed after 1 year of exposure (366 days) for specimens analyzed gravimetrically and after approximately 7 months for the qualitative specimens.

Fasteners were removed from the wood in a way that minimized damage to the corrosion products. Notches were sawn in the wood block, and the block was then placed into a vise. As pressure was applied, the wood split apart and the fastener could be removed by hand.

For gravimetric specimens, the corrosion products were removed with a combination of ultrasonic agitation and chemical solvents. Fasteners were placed in a 50:50 (volume ratio) mixture of water and Evapo-Rust™ (Orison Marketing, Abilene, Texas). Ultrasonic agitation was then applied for 60 min. The fasteners were then wiped with a lint-free paper towel and allowed to dry before being weighed to the nearest 0.1 mg. The same process and solvents were used on both the galvanized and steel fasteners; this process was able to successfully remove both red and white rusts. The amount of base metal removed by the cleaning processes, $m_c$, was measured by cleaning uncorroded specimens; $m_c$ was $-2.9 ± 1.4$ (standard deviation) mg for the galvanized fasteners and $-0.9 ± 0.9$ mg for the steel fasteners.

To analyze the corrosion products, corroded fasteners were examined in a Zeiss (Oberkochen, Germany) EVO 40 scanning electron microscope (SEM) with a Thermo Noran Vantage (Waltham, Massachusetts) energy dispersive X-ray spectroscopy (EDS) analyzer. The surfaces of the corroded fasteners were examined with SEM and EDS after being removed from the treated wood with no further cleaning. For cross-sectional analysis, corroded fasteners were mounted in conductive phenolic resin, rough polished to 1200 grit, and final polished with a 1.0 micron alumina slurry.

X-ray powder diffraction was used to qualitatively identify phases in the corrosion products. Powder samples were prepared by removing the corrosion products with a razor blade. An Inel (Artenay, France) CPS 120 wide angle diffractometer with a Cu K-α source was used to collect the powder X-ray diffraction patterns.

### Results

The corrosion rate ($R$ in μm y⁻¹) was calculated by the following:

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

(1.1)

where

- $m$ is mass (g),
- $t$ is time (h),
- $A$ is surface area (cm²) calculated from the digital image,
- $\rho$ is density as tabulated in ASTM G1 (ASTM 2005), and
- $K$ is constant for unit analysis (87 600 000 μm cm⁻¹ h y⁻¹).

<table>
<thead>
<tr>
<th>Table 1-2. Elemental composition of the fasteners tested</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon steel</td>
</tr>
<tr>
<td>Weight percentage $±2\sigma$</td>
</tr>
<tr>
<td>Bi</td>
</tr>
<tr>
<td>Co</td>
</tr>
<tr>
<td>Cr</td>
</tr>
<tr>
<td>Cu</td>
</tr>
<tr>
<td>Fe</td>
</tr>
<tr>
<td>Mo</td>
</tr>
<tr>
<td>Mn</td>
</tr>
<tr>
<td>Ni</td>
</tr>
<tr>
<td>Pb</td>
</tr>
<tr>
<td>Si</td>
</tr>
<tr>
<td>Ti</td>
</tr>
<tr>
<td>Zn</td>
</tr>
<tr>
<td>Zr</td>
</tr>
</tbody>
</table>

The nails had a nominal length of 64 mm and a nominal head diameter of 7 mm; the galvanized nails had a nominal shank diameter of 3 mm, with the carbon steel nails being slightly smaller. Each fastener was digitally imaged, the surface area for each fastener was determined from the digital image using an algorithm developed previously. Alloy compositions were analyzed with a Niton XL3 x-ray fluorescence (XRF) analyzer (Thermo Scientific, Billerica, Massachusetts) (Table 1-2). Galvanized coating thicknesses were measured on several fasteners with eddy-current thickness gages; thicknesses ranged between 10 and 25 μm.

Prior to exposure, the lumber was sectioned into blocks 50 mm by 38 mm by 90 mm. A pilot hole (1.5 mm in diameter) was drilled into the center of the 50 mm by 38 mm face of the block. These blocks were then allowed to equilibrate over several weeks in a room that was kept at 27 °C, 90% RH.

Immediately prior to exposure, the fasteners were cleaned, degreased, and weighed. The fasteners were cleaned in a bath with soap and water that was ultrasonically agitated for 5 min. Afterward, the fasteners were rinsed and placed in a bath of distilled water that was ultrasonically agitated for 5 min. Finally, the fasteners were degreased with acetone and allowed to dry. Once dry, the fasteners were weighed to the nearest 0.1 mg and hand-driven through the pilot hole into a block of wood. The wood-fastener assemblies were then placed above a reservoir of high-purity distilled water inside a sealed desiccator that was kept in a room held at 27 °C, 90% RH; the resulting environment inside the desiccator was 27 °C, 100% RH as dictated by the Gibbs phase rule. The average wood moisture content in this environment, determined gravimetrically from untreated specimens, was 24.6% ± 0.6% (standard deviation). The blocks were removed after 1 year of exposure (366 days) for specimens analyzed gravimetrically and after approximately 7 months for the qualitative specimens.

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The subscripts i and f refer to initial, and final, respectively, and \( m \) was defined earlier. The 1-year corrosion rate for hot-dip galvanized and steel fasteners is shown in Figure 1-1.

The surfaces of the corrosion products on the nail head, which was exposed directly to the 27 °C, 100% RH environment as well as the nail shank, which was embedded in the wood, were analyzed with SEM and EDS. The morphology and elemental composition of the corrosion products were similar for the head and shank and were also similar across preservative treatments for both the steel and galvanized nails. Characteristic SEM images of the corrosion products are given for steel and galvanized steel in Figure 1-2. Cross-sectional images for steel and galvanized steel are shown in Figure 1-3 and Figure 1-4, respectively. The micrographs in most cases represent the areas with the largest corrosion product. Pitting was observed in the cross-sectional image of the steel fastener exposed to untreated wood.

The most important result from the EDS testing was that copper was not detected on any of the corroded fasteners. Carbon, iron, and oxygen were detected on all of the corroded steel fasteners. Likewise, carbon, oxygen, and zinc were detected on all of the corroded galvanized fasteners. For galvanized fastener that had clearly visible red rust (ACQ and CuAz), iron was also detected in the EDS. Finally, arsenic was detected on both the steel and galvanized steel fastener exposed to CCA-treated wood. The arsenic likely came from the arsenate in the preservative; Zelinka and others (2007) have shown that the arsenates may play a role as a corrosion inhibitor in the CCA preservative systems.

For the steel nails, the predominant corrosion products across all treatments were goethite (\( \alpha \)-FeOOH) and magnetite (Fe\(_3\)O\(_4\)). The galvanized corrosion products depended on the treatment to which the fasteners were exposed (Fig. 1-5). For fasteners in CuAz-treated wood, namuwite \( \{\text{Zn}_2(\text{SO}_4)(\text{OH})_6\cdot4\text{H}_2\text{O}\} \) and hydrozincite \( \{\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6\} \) were clearly identifiable in the x-ray diffraction (XRD) pattern, although it is possible that smithsonite (ZnCO\(_3\)) and simonkolleite \( \{\text{Zn}_5(\text{OH})_8\text{Cl}_2\cdot(\text{H}_2\text{O})\} \) were also present. For the fasteners exposed to other treatments, namuwite and hydrozincite were the clearly identifiable phases, with possibly smithsonite and zincite (ZnO).

**Discussion**

It is instructive to compare ACQ and MCQ to DDAC, as these preservatives all contain the same organic biocide, and differences in these treatments are due to the presence and type of copper used in the formulations. For both steel and galvanized steel, the DDAC-treated wood was only slightly more corrosive than the untreated wood. This suggests that the corrosiveness of these wood preservatives comes from...
the copper rather than the organic biocides and is congruent with previous theories (Baker 1988) that the cathodic corrosion reaction is the reduction of cupric ions. The MCQ and ACQ both have nominally the same amount of copper. In ACQ, the treatment solution consisted of copper solubilised in ammonia or ethanolamine, whereas the MCQ solution contains a suspension of insoluble submicron-sized copper compounds (Lebow 2010). The fact that the MCQ-treated wood is more corrosive than DDAC-treated wood suggests that after treatment, some of the copper becomes soluble and participates in the corrosion reaction. ACQ-treated wood was the most corrosive. Kear and others (2009) showed that the corrosion rate can depend on the amount of copper in the wood. Even though in these tests the MCQ-treated wood had more total copper than the ACQ-treated wood, it is possible that the ACQ-treated wood was more corrosive than the MCQ-treated wood because there was more copper available to participate in the corrosion reaction. This comparison of the relative corrosiveness of MCQ and ACQ is limited to the specific conditions of this study and does not
necessarily reflect the relative corrosivity under a range of in-service exposure conditions.

The most important results from the SEM and EDS data is the absence of deposited copper in the corrosion products because the currently accepted mechanism of corrosion in treated wood (Baker 1980) involves the reduction of cupric ions in the preservative. The absence of copper on the corroded fasteners could have two explanations: either cupric ions are not reduced as part of the corrosion reaction or cupric ions are reduced in the reaction but are not deposited on the surface. We believe it is the latter because several key experiments (Kear and others 2009; Zelinka and others 2008) have shown the importance of cupric ions on wood–metal corrosion. For instance, Kear and others (2009) found a weak correlation between the corrosiveness of the wood preservative and the amount of copper in the preservative. When polarization measurements were made in liquid extracts of treated wood containing cupric ions, reduced copper was detected with EDS on the corroded fasteners (Zelinka and others 2008). Furthermore, the extract tests have good correlation to solid wood exposure when the preservatives contain cupric ions (Zelinka and others 2009) but do not correlate for preservatives that do not contain cupric ions. The present work suggests that the mechanism of corrosion in both extract and solid wood is the reduction of cupric ions; however, this raises the question that if the cupric ions are being reduced, why are they not being deposited on the corroded surface? It is possible that the cupric ions are reduced near the metal surface, but instead of depositing on the fastener, the reduced copper remains in the wood.

In all cases, the galvanized fasteners had a higher corrosion rate than the steel fasteners. This has practical applications because of the widespread use of galvanized fasteners.

Although zinc coatings cathodically protect the underlying steel at coating defects, the main protection mechanism of the zinc coatings is barrier protection because in many environments, zinc corrodes more slowly than steel (Zhang 2003). In atmospheric corrosion, zinc usually forms hydrozincite and smithsonite, which passivate the surface and cause the zinc to have a lower corrosion rate than steel. However, when exposed to certain conditions, such as air at 100% RH (Zhang and others 1998) and in closed containers with wood vapors containing volatile acetic and formic acids (Knotkova-Cermakova and Vlckova 1971), zinc corrodes more rapidly than steel. Several researchers have observed that zinc fasteners have corroded more rapidly than carbon steel fasteners in treated wood, although the zinc corrosion products were not identified (Simm and Button 1985a; Duncan 1988). We found that in addition to hydrozincite, namuwite also formed for fasteners embedded in treated wood. The presence of non-passivating compounds in zinc corrosion products exposed to treated wood may explain why galvanized fasteners corroded more rapidly than steel fasteners.

Other work using different exposure conditions has found that galvanized fasteners corroded more slowly than steel fasteners in treated wood, although corrosion products were not identified in that study (Kear and others 2009). It is possible that different corrosion products formed under the two different conditions, which may explain the relative differences between steel and galvanized steel in these two studies. Comparing between these two studies, it seems that the type and morphology of zinc corrosion products play a large role in the corrosion of metals in wood products. Furthermore, corrosion products are sensitive to the test method. Future work should compare corrosion products from field exposure studies to those formed under different laboratory test protocols to optimize laboratory test methods. Until a better understanding of the relationship between laboratory and field measurements can be developed, caution should be used when extrapolating laboratory corrosion rates.
Conclusions

Corrosion rates were measured for steel and galvanized steel in Southern Pine treated with several wood preservatives. Corrosion rates over all treatments were small in absolute terms (~1–35 μm y⁻¹). For each treatment, the steel fasteners had lower corrosion rates than the galvanized fasteners. Zinc corrosion products contained namuwite and hydrozincite. The type and morphology of corrosion products may explain why zinc corrosion rates were greater than steel corrosion rates. Future work should focus on identifying the phases in corrosion products for both field and laboratory measurements.

Copper was not detected in any of the corrosion products. However, we believe that the corrosion mechanism in treated wood involves the reduction of cupric ions, but the reduced copper does not deposit on the corroding fastener.

Acknowledgments

The authors thank Forest Products Laboratory staff Thomas A. Kuster and Daniel O. Foster for their assistance with the SEM and ICP-AES, respectively.

References


Corrosion of Metals in Wood: Comparing the Results of a Rapid Test Method to Long-Term Exposure Tests Across Six Wood Treatments

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Abstract

This chapter compares two methods of measuring the corrosion of steel and galvanized steel in wood: a long-term exposure test in solid wood and a rapid test method where fasteners are electrochemically polarized in extracts of wood treated with six different treatments. For traditional wood preservatives, the electrochemical extract method correlates with solid wood exposure, which suggests that reduction of cupric ions is the cathodic reaction in both solid wood and extract. For treatments without copper, the extract method predicted a higher corrosion rate than the solid wood exposure. For these treatments, the cathodic reaction appears to be reduction of acid and dissolved oxygen. The practical implication of this work is that in some cases, the rapid test method could be used to screen new fasteners and wood preservatives. Scientifically, this work increases understanding of the mechanism of corrosion of fasteners in treated and untreated wood.

Keywords: Steel, zinc, preservative-treated wood, timber, polarization resistance, weight loss

Introduction

The current mechanism for corrosion of metals in contact with preservative-treated wood was proposed by Baker in the 1980s (1980, 1988). The wood preservatives that Baker studied contained cupric ions, which are thermodynamically unstable in the presence of steel and galvanized steel fasteners. Baker’s mechanism involves transport of cupric ions through wood to the metal surface where they are reduced at the expense of the fastener, which is oxidized. Furthermore, the mechanism is believed to be aqueous because the corrosion rate depends strongly on wood moisture content and there is a threshold moisture content below which corrosion does not occur in wood (Baker 1988; Dennis and others 1995; Short and Dennis 1997). We have illustrated the mechanism schematically in Figure 2-1 specifically highlighting the ion transport through the wood.

Based on Baker’s proposed corrosion mechanism and the assumption that migration of ions was not the rate-determining step, a new accelerated test method was developed at FPL (Zelinka and others 2008b). The method consisted of grinding wood into sawdust, steeping the sawdust in distilled water, and then running an electrochemical corrosion test in the resulting extract. The electrochemical extract test method was found to correlate well with long-term exposure tests of alkaline copper quaternary- (ACQ-) treated wood (Zelinka and others 2008b; Zelinka and Rammer 2009). The results suggested that the cathodic reaction is reduction of cupric ions as Baker (1988) hypothesized, and the reaction is not diffusion controlled in solid wood at the moisture of the solid wood exposure test.

In untreated wood, however, the extract test produced a much higher corrosion rate than the exposure tests (Zelinka and others 2008a). Furthermore, the untreated extract was more corrosive than the ACQ extract—a surprising result considering that cupric ions increase the corrosiveness in solid wood. Whereas these results may partially be explained by the difference in pH between untreated (pH 4.5) and ACQ-treated extracts (pH 6.6), it was not possible to conclusively identify the reason for the differences in corrosion rate between these two extracts because both the pH and concentration (presence) of copper were different.

In summary, solid wood and electrochemical extract tests have correlated well for ACQ-treated wood but do not correlate for untreated wood. This paper is part of a broad examination of corrosion in wood with the ultimate aim of understanding the mechanism in treated wood. For this large investigation, six different wood treatments were chosen to interrogate different aspects of corrosion. Previous studies in this examination have included long-term exposure tests in solid wood (Zelinka and others 2010), and matched
specimens from the exposure test were also examined with an electrochemical method in water extracts of the treated wood (Zelinka and others 2009). This work examines similarities and differences between the exposure test and the electrochemical extract test and from these cases infers corrosion mechanisms. To test the inferred corrosion mechanisms, we performed additional experiments to separate the effects of pH and copper from other differences in preservative chemistry. In addition to having practical implications for accelerated corrosion testing, this study adds to the understanding of the mechanism of metal corrosion in wood.

**Methods and Materials**

Plain carbon steel and hot-dip galvanized steel nails (8d) from the same lot were examined in both the long-term exposure and the electrochemical extract test. The galvanized fasteners had nominal dimensions of 64 mm (length) by 3 mm (shank diameter) with a head diameter of 7 mm. Carbon steel fasteners had the same nominal dimensions except for the shank diameter, which was slightly smaller. Galvanized coating thicknesses ranged between 10 and 25 μm as measured by an eddy-current thickness gage. Compositions of carbon steel nails and hot-dip galvanized coatings were analyzed by x-ray fluorescence. The carbon steel nail contained 0.73 wt% Mn, 0.27 wt% Cu, 0.16 wt% Si, 0.15 wt% Ni, 0.10 wt% Cr, 0.04 wt% Zn, and 0.01 wt% Mo, with the remainder as Fe. The surface of the galvanized coating contained 3.8 wt% Fe, 1.7 wt% Bi, 0.14 wt% Pb, 0.12 wt% Co, 0.06 wt% Cr, 0.01 wt% Ti, and 0.01 wt% Zr. Prior to testing, the surface areas of each fastener was calculated from a high resolution digital photograph using an algorithm developed by the authors (Rammer and Zelinka 2010).

Southern Pine (Pinus spp.) lumber was treated with one of five wood treatments or left untreated as a control for a total of six different groups; the compositions and retentions are given in Table 2-1. Three of these preservatives, chromated copper arsenate (CCA), alkaline copper quaternary (ACQ), and copper azole (CuAz), are traditional, soluble-copper waterborne wood preservative systems where copper is dissolved in solution and impregnated into wood in a pressure vessel. In contrast, micronized copper quaternary (MCQ) consists of a suspension of “micronized” (<1000 nm) particles of nearly insoluble copper carbonate (Zhang and Leach 2006); however, the total amount of copper and the ratio of other biocides is the same as ACQ. Though the MCQ treating solutions contain insoluble copper, research indicates that the copper becomes soluble in treated wood, and cupric ions are available (Zhang and Ziobro 2009; Stirling and Drummond 2009). The fifth treatment, didecyldimethylamonium carbonate (DDAC), is the cobiocide in ACQ and MCQ, and the nominal retention was set so that the DDAC-treated wood would have the same concentration of DDAC as the ACQ and MCQ treatments. Finally, untreated Southern Pine was tested as a control.

Treatments were applied to boards 38 mm by 140 mm by 2.5 m, with the exception of the CuAz-treated wood, which had dimensions of 38 mm by 89 mm by 1.2 m. Specimens were treated and then separated for use in either the long-term exposure test or the electrochemical extract test. Exposure tests were conducted for 1 year in a 27 °C, 100% RH environment that was achieved by placing wood–metal assemblies over water in sealed desiccators. The average wood moisture content in this environment, determined gravimetrically on untreated specimens, was 24.6% ± 0.6%.
Corrosion of Fasteners in Wood Treated with Newer Wood Preservatives

(standard deviation). Nine replicates were tested for both steel and galvanized steel for all six treatments. The corrosion rate was measured gravimetrically after removing the corrosion products, which was accomplished by placing the fasteners in a 50:50 mixture of water and Evapo-Rust™ (Orison Marketing, Abilene, Texas) for 60 min while ultrasonic agitation was applied. We observed that this cleaning method produced a mass change on uncorroded fasteners of 2.9 ± 1.4 (standard deviation) mg for the galvanized fasteners and −0.9 ± 0.9 mg for the steel fasteners. On additional specimens, corrosion products were analyzed with powder XRD, scanning electron microscopy (SEM), and energy dispersive X-ray spectroscopy (EDS).

The extract test method involved making an extract from wood and then electrochemically measuring the corrosion rate of a fastener immersed in extract. For each treatment, a single batch of extract was made to reduce intra-treatment variability. The extract was made by grinding the wood into sawdust, placing sawdust in distilled water (1:10 ratio weight basis) for one week, at which time the sawdust removed with a Büchner funnel. Previous testing has shown that corrosiveness of the extract is not affected by the heat produced during grinding (Zelinka and others 2007). After it was produced, the extract was stored near 0 °C and tests were run within two weeks to minimize biologically induced changes in the extract. Physical properties of extracts are summarized in Table 2-1.

Electrochemical testing used a similar procedure to ASTM G59 [c], and the fasteners were machined to fit in the standard five-neck flask. Immediately prior to testing, the fasteners were cleaned with ultrasonic agitation in a soap solution for 5 min, then rinsed with distilled water before a final 5-min ultrasonic bath in distilled water. The open circuit potential (OCP) was measured for an hour; at the end of the hour, the OCP was recorded and the potential was swept from −30mV vs. OCP to +30mV vs. OCP with a scan rate of 0.166 mV s⁻¹. The automatic IR correction of the potentiostat was applied during the test. Tafel slopes and the resulting corrosion rate were ascertained from the nonlinearity of the polarization resistance curve using Mansfeld’s method (1973a,b). Nine replicates were tested for both steel and galvanized steel for all six treatments.

Results and Discussion

Corrosion product analyses from XRD, SEM, and EDS for the solid wood tests have been published elsewhere (Zelinka and others 2010), and only the pertinent details needed for the present discussion are included here. For all six treatments, the steel corrosion products consisted of goethite (α-FeOOH) and magnetite (Fe₃O₄); for galvanized steel namuwite {Zn₆(SO₄)(OH)₈•4H₂O}, and hydrozincite {Zn₆(CO₃)₆(OH)₈} were clearly identifiable, although smithsonite (ZnCO₃), simonkollete {Zn₅(OH)₆C₁₂( H₂O)}, and zincite (ZnO) may also have been present. Importantly, the EDS revealed different elemental compositions between the surfaces of fasteners corroded in the extract and in solid wood (Fig. 2-2). In every case except the CCA treatment, the solid wood exposure tests, EDS only detected carbon, oxygen, and the base metal; those exposed to CCA also contained arsenic. In contrast, for most of the electrochemical tests in CCA-, CuAz-, ACQ- and MCQ-treated wood, copper was detected in the corrosion products.

Corrosion rates from the extract and solid wood tests are compared in Figure 2-2. There are three types of behavior present in Figure 2-2. There are three types of behavior present. Traditional, soluble copper, wood preservatives (CCA, ACQ, and CuAz) have similar corrosion rates in both the extract and solid wood. For both untreated and DDAC-treated wood, which do not contain copper in any form, extracts are much more corrosive than solid wood. Finally, MCQ-treated wood does not behave like either traditional wood preservatives or copper-free treatments. Differences in behavior can be ascribed to different reaction mechanisms occurring in these treatments. To further discuss these mechanisms, treatments will be grouped depending on whether or not they contain copper and what form it is in.

Preservatives Containing Cupric Ions

For traditional wood preservatives (ACQ, CCA, and CuAz), we found good correlation between the exposure test and the extract test. These results agree with preliminary work in ACQ-treated wood (Zelinka and others 2008b). In that work, EDS of polarized fasteners in the extract revealed the presence of reduced copper on the fastener surface. Zelinka and others (2008b) concluded that the cathodic reaction in the extract was the reduction of cupric ions. Furthermore, because the extract and exposure tests had similar corrosion rates across several different metals, they concluded that the
mechanism in solid ACQ-treated wood also involved reduction of cupric ions and the rate-determining step was the same in both cases. Current results agree with these original conclusions and suggest that they are applicable to other treatments with cupric ions as well as ACQ.

It should be noted, however, that while EDS detected copper on fasteners exposed to the extract, none of the fasteners exposed to solid wood exhibited detectable copper in the corrosion products. This result is in agreement with the work of Simm and Button (1985), who examined steel, zinc, and aluminum fasteners exposed to CCA-treated wood. Whereas absence of copper in the solid wood specimens could mean that cupric ions are not reduced as part of the corrosion reaction, we believe that cupric ions are reduced because preservatives with cupric ions are much more corrosive than untreated wood in the 1-year exposure tests, and they exhibit similar corrosion rates in the extract where EDS confirmed reduction of cupric ions. Indeed, Simm and Button did not rule out the reduction of cupric ions as a possible cathodic reaction and, in more recent work, Kear and others (2009) found correlation between the amount of copper and corrosiveness of the wood preservative. While the correlation between exposure and extract tests suggests that reduction of cupric ions is the cathodic reaction in both the extract and solid wood, it is not clear what happens to reduced copper in solid wood. It is possible that reduced copper dissolves again in a different reaction or that the copper is reduced near the metal surface but remains on the wood instead of the metal, although EDS measurements taken in the region adjacent to the fastener showed no difference in copper concentration.

DDAC and Untreated Wood

For the DDAC-treated and untreated wood, which do not contain copper in any form, the expected cathodic reactions are the reduction of acids and dissolved oxygen (Farmer 1962; Bailey and Schofield 1984; Kubler 1992; Baker 1980). In a previous investigation (Zelinka and others 2008a), the role of oxygen was studied in an untreated extract. Deaerating the solutions lowered the corrosion rate by approximately half, which confirmed that reduction of dissolved oxygen was one of the cathodic reactions. When sawdust is exposed to water, additional acetic acid is produced (not extracted) as the wood spontaneously undergoes

Figure 2-3. Corrosion rates measured in the electrochemical extract test (Zelinka and others 2010) and a 1-y exposure test (Zelinka and others 2008) for steel (top) and galvanized steel (bottom). Note the difference in scale on the ordinate axis.
deacetylation (Farmer 1962). Because of the increased availability of acids and dissolved oxygen in the extract, it might not be surprising that the extract is more corrosive than the solid wood. Using the same arguments, we would expect extracts from the treated wood to also be much more corrosive than the extracts from untreated wood, although this was not observed. Some further insight to the differences between extracts with and without cupric ions can be gained by examining their chemical properties.

The major differences among all six extracts are the pH and the presence/amount of cupric ions. The pH of the solutions ranged from 4.5 for untreated wood to 6.6 for ACQ-treated wood. This pH range spans two regimes in the corrosion kinetics of steel and zinc; below pH 5, the kinetics are dominated by the hydrogen ion concentration (pH) as well as the counter-ion of the acid, whereas in neutral solutions, the corrosion of steel and zinc is nearly independent of pH (Silverman 2003; Andrzejaczek 1984).

It is useful to compare the DDAC and the ACQ treatments as they both contain the same quaternary ammonia compound but have differences in pH and presence of copper. The ACQ extract had a pH of 6.6 and the corrosion rate was approximately 30 μm y⁻¹ for the galvanized steel in both the solid wood and the extract. The DDAC treatment had a pH of 4.6 and galvanized steel corrosion rates of 6 and 87 μm y⁻¹ in solid wood and the extract, respectively. From the above data, the high corrosion rate in the DDAC extract could be due to the low pH, or due to the lack of cupric ions if the cupric ions reduced to form a protective corrosion product on the metal surface during the time the OCP was measured.

To examine the effects of pH and cupric ions separately, two “model” extracts were made starting with the DDAC extract (summarized in Fig. 2-4). In the first model extract, “DDAC mod,” the pH of the DDAC extract was raised with sodium hydroxide to pH 6.4. This extract can be thought of as a model of the ACQ extract without cupric ions. The second model extract “mock ACQ” was like the first extract except that cupric sulphate was added so that the resultant copper concentration in the solution was 50 mg L⁻¹. Cupric sulphate was used instead of copper ethanolamine, the source of cupric ions in ACQ-treated wood, because of problems with copper ethanolamine solubility at this pH (Zelinka and others 2007; Lee and Cooper 2010). The mock ACQ extract has the same pH and copper concentration as the ACQ extract and allows for the role of copper to be examined independently by comparing it to the pH adjusted extract without copper. Zinc sheet (99% pure, Alfa Aesar, Ward Hill, Massachusetts) polished to 600 grit was used instead of hot-dip galvanized fasteners to eliminate variability caused by surface roughness. This allowed a clearer examination of the effect of pH and cupric ions.

The electrochemically determined corrosion rates of the polished zinc in the model extracts are summarized in Figure 2-5; for the DDAC extract (pH 4.6), the corrosion rate (in μm y⁻¹) in zinc was 185 ± 32 (standard error) for
the “DDAC mod” extract (pH 6.4) it was 21 ± 4 and for the “mock ACQ” extract (DDAC pH 6.4 with 50 mg L⁻¹ CuSO₄) it was 63 ± 4. These data suggest pH is responsible for high corrosion rates in DDAC extract because raising the pH to that of the ACQ greatly reduced the corrosion rate. The data also suggest that cupric ions increase the corrosion rate. The corrosion rates cannot be directly compared to those in Figure 2-3 because a different metal was tested to reduce variation between replicates. However, what can be compared is the ratio of corrosion rates in DDAC/ACQ (or mock ACQ). For galvanized fasteners, the ratio of DDAC/ACQ corrosion rate was 3.2 and for the zinc sheet, the ratio of the DDAC/mock ACQ was 2.9. Similarities in ratios suggest that differences in corrosion between DDAC and ACQ extracts can be explained exclusively by the differences in pH and cupric ions. The modified extracts suggest that the DDAC extract is much more corrosive than ACQ because its pH is much lower, even though ACQ has cupric ions, which indeed increased the corrosion rate.

**MCQ-Treated Wood**

For solid wood, MCQ corrosion rates were similar to those measured in wood treated with soluble copper systems (CCA, ACQ, CuAz). However, corrosion rates measured in MCQ extracts exhibited unique behavior; galvanized fasteners had a higher corrosion rate in the extract than solid wood, whereas the corrosion rate of steel fasteners in the extract was so low it could barely be detected. These data present two main questions: (1) why did steel and galvanized steel behave so differently in the extracts, and (2) why was there correlation between exposure and extract tests for CCA-, ACQ-, and CuAz-treated wood but not for MCQ-treated wood?

The large difference between the corrosion rate of steel and galvanized steel in the extract suggests that corrosion of steel may be thermodynamically unfavorable. To examine the thermodynamic differences between steel and galvanized steel in these solutions, we overlay the open circuit potentials of steel and galvanized steel in different solutions on the potential-pH diagram (Pourbaix diagram) of copper (Pourbaix 1973, Fig. 2-6) where the stability region of water is denoted by the dashed lines. The diagram was drawn using a copper ion solution activity of 10⁻⁴; measured concentrations are within an order of magnitude (Table 2-1). Additionally, the Pourbaix diagrams of steel and zinc are included in Fig. 2-7 with data from each treatment overlaid.

From the potential-pH diagram we see that the steel and galvanized steel in MCQ solutions are in two distinct regions of copper stability. The steel is in a region where cupric ions are stable, whereas the galvanized steel is in a region where copper metal is stable. Furthermore neither metal is immune from corrosion in this regime (Fig. 2-7). Assuming that the corrosion mechanism involves the reduction of cupric ions to copper metal, the potential-pH diagram predicts that steel fasteners will not corrode, as they are in a region where cupric ions are stable; this agrees with the corrosion rate data (Fig. 2-3). Furthermore, the surface of fasteners polarized in the extract were examined with EDS. The EDS detected copper on the galvanized fasteners but not on the steel fasteners.

When the results of the EDS are combined with the polarization resistance measurements and the potential-pH diagram, a coherent picture of corrosion in the MCQ extract
emerges. These results suggest that cupric ions are available in MCQ extract even though the treating solution is comprised of particles of nearly insoluble copper. The open circuit potential of galvanized fasteners places them in a region where copper metal is the stable phase, and cupric ions are reduced on the metal surface as the fastener oxidizes. Conversely, steel fasteners are more noble at a potential where cupric ions are stable, and therefore do not corrode.

Behavior of the steel fastener in the MCQ extract appears to be controlled by thermodynamics of the cupric ions in solution. One interesting aspect of this study was that the open-circuit potential (OCP) of the steel fasteners was unusually high when compared to the galvanized fasteners. Conversely, steel fasteners are more noble at a potential where cupric ions are stable, and therefore do not corrode.

In contrast to the steel fastener, the galvanized fastener in the MCQ extract has a much higher corrosion rate than in solid wood, and the EDS-confirmed cupric ions were present. Because the data suggest the MCQ extract contains cupric ions, and cupric ions are not stable for the open circuit potentials measured for galvanized steel, we would expect this system to behave like traditional wood preservatives (CCA, ACQ, CuAz), which had the same corrosion rate in the extract and the solid wood. This was not the case, although MCQ had the lowest pH of any of the systems with soluble copper. Interestingly, the corrosion rate in the MCQ extract was not statistically different from that measured in the DDAC extract, which did not contain cupric ions but had a slightly lower pH. To examine the role of pH and cupric ions in MCQ, ancillary tests were carried out on polished zinc where the pH of the MCQ extracts was adjusted. Two pH-modified MCQ extracts were made, and the corrosion rate of zinc sheet was measured with polarization resistance (Fig. 2-8). In the first modification, the pH was raised with sodium hydroxide to the same pH as the ACQ extract (pH 6.6) “mock ACQ II”. In the second modification, the pH was lowered with acetic acid to nearly the same pH as the DDAC extract (pH 4.5). The pH of the unadjusted MCQ extract was 5.1, and the corrosion rate of the zinc sheet in this extract was 80 ± 5 (standard error) μm y⁻¹. The pH 6.6 (mock ACQ II) extract had a corrosion rate of 25 ± 15 and the pH 4.5 had a corrosion rate of 200 ± 20 (Fig. 2-5).

### Table 2-1. Type, composition, and retention of the wood preservatives tested and the physical properties of extracts made from these wood treatments

<table>
<thead>
<tr>
<th>Nominal composition (weight percentage)</th>
<th>Retention(^a) (kg m(^{-3}))</th>
<th>Extract physical properties</th>
<th>pH</th>
<th>Conductivity (μS cm(^{-1}))</th>
<th>Cu (mg L(^{-1}))</th>
<th>Cr (mg L(^{-1}))</th>
<th>As (mg L(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>ACQ (type D)</strong></td>
<td></td>
<td></td>
<td></td>
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<td></td>
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</tr>
<tr>
<td>Alkaline copper quaternary</td>
<td>66.7 CuO</td>
<td>4.0</td>
<td>6.6</td>
<td>596</td>
<td>51.0</td>
<td></td>
<td></td>
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<tr>
<td>DDAC(^b)</td>
<td>33.3 DDAC</td>
<td>1.6</td>
<td>6.5</td>
<td>446</td>
<td>23.9</td>
<td>0.06</td>
<td>0.22</td>
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<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Copper azole</td>
<td>96.8 CuO</td>
<td>1.0</td>
<td>6.5</td>
<td>220</td>
<td>32.5</td>
<td></td>
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<tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>f</td>
</tr>
<tr>
<td>Micronized copper quaternary</td>
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<td>4.0</td>
<td>5.0</td>
<td>220</td>
<td>32.5</td>
<td></td>
<td>f</td>
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<td>0.2</td>
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<td>f</td>
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</tr>
<tr>
<td>Chromated copper arsenate</td>
<td>47.5 CrO(_3)</td>
<td>4.0</td>
<td>4.9</td>
<td>195</td>
<td>33.4</td>
<td>6.20</td>
<td>9.30</td>
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<td></td>
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</tr>
<tr>
<td>Chromated copper arsenate</td>
<td>18.5 CuO</td>
<td>4.0</td>
<td>4.9</td>
<td>195</td>
<td>33.4</td>
<td>6.20</td>
<td>9.30</td>
</tr>
<tr>
<td>DDAC(^b)</td>
<td>34.0 As(_2)O(_3)</td>
<td>3.0</td>
<td>4.9</td>
<td>195</td>
<td>33.4</td>
<td>6.20</td>
<td>9.30</td>
</tr>
<tr>
<td><strong>DDAC</strong></td>
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<td>1.3</td>
<td>4.6</td>
<td>173</td>
<td>0.2</td>
<td></td>
<td>f</td>
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<tr>
<td><strong>Untreated (control)</strong></td>
<td></td>
<td></td>
<td></td>
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<td>f</td>
</tr>
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</table>

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\(^a\)Nominal compositions from AWPA standard P5 (AWPA 2007), with the exception of MCQ, which comes from ICC-ES evaluation report ESR-1980.

\(^b\)DDAC: didecyldimethylammonium carbonate- IUPAC formula (C\(_{10}\)H\(_{21}\))(CH\(_3\))(CH\(_3\))N(CO\(_3\))H and (C\(_{10}\)H\(_{21}\))(CH\(_3\))(CH\(_3\))N(CO\(_3\))(C\(_{10}\)H\(_{21}\))(CH\(_3\))(CH\(_3\)) (mixture).

\(^c\)Not assayed.

\(^d\)IUPAC formula: (RS)-1-(4-Chlorophenyl)-4,4-dimethyl-3-(1,2,4-triazol-1-y)pentan-3-ol.

\(^e\)IUPAC formula: 1-[[2-(2,4-dichlorophenyl)-4-propyl-1,3-dioxolan-2-yl]methyl]-1,2,4-triazole.

\(^f\)Assayed, but not detected.
Not surprisingly, changes in pH caused large changes in the corrosion rate. Data from the “mock ACQ II” suggest the corrosion rate of the MCQ extract was higher than the ACQ extracts because it was more acidic. Conversely, lowering the pH to 4.5 more than doubled the corrosion rate. If cupric ions were not contributing to corrosiveness, results of the pH modifications suggest that the MCQ extract should be much lower than the DDAC extract. In summary, the high corrosion rate measured in the MCQ extract for galvanized steel appears to be caused by both the presence of cupric ions and the pH of the solution.

**Conclusions**

Steel and galvanized steel exposed to CCA, ACQ, and CuAz treatments have similar corrosion rates in the solid wood and in extracts made from the solid wood. We believe that the reduction of copper is the cathodic reaction in these solutions and this reaction proceeds at the same rate in both the extract and the solid wood. Conversely, for untreated and DDAC-treated wood, the extract is much more corrosive than treated wood. The cathodic reaction is the reduction of acids and dissolved oxygen and these proceed much more rapidly in the extract.

Steel fasteners did not corrode in the MCQ extract. The open circuit potential for steel in these extracts was in a region where cupric ions were stable and therefore there was not a thermodynamic driving force for cupric ion reduction. These results were duplicated inadvertently in an ACQ extract with a different type of steel. In short, if the open circuit potential of the metal to be tested is above cupric ion stability line (~0.25 V vs SHE), the electrochemical extract test method will not work. The galvanized fasteners in the MCQ extract had a much higher corrosion rate than fasteners exposed to ACQ and CuAz extracts, which was attributed to the lower pH of the MCQ extract. However, the cupric ions in the extract still affected corrosion.

**Acknowledgments**

The authors thank the assistance of USDA Forest Products Laboratory employees Thomas A. Kuster, Daniel. O. Foster, and James T. Gilbertson for their assistance with the experimental work, and Tivoli Gough for drawing Figures 2-1, 2-4, and 2-8.

**References**


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treated with copper azole and alkaline copper quaternary compounds. Corrosion Science. 51: 252–262.


Figure 2-8. Graphical explanation of the model MCQ extracts used to examine the effect of pH and cupric ions on the corrosion of polished zinc sheet.


Chapter 3

The Effect of Tannins and pH on the Corrosion of Steel in Wood Extracts

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Abstract

Tannins and pH are often cited as factors that affect the corrosiveness of wood yet there are few data to confirm these statements. The purpose of this paper is to systematically investigate the effect of tannins and pH on corrosion of metals in wood. Four wood species known to vary in both their pH and extractives were chosen and extracted with water. The pH, tannin content, and corrosion rate of carbon steel were determined for each extract. To test if pH and tannin were the only factors influencing corrosion, “synthetic” extracts were made by adding tannins to distilled water and adjusting the pH. At a given pH, increasing the tannin content inhibited corrosion and at a given level of tannin content, lowering the pH increased corrosion. An isocorrosion map as a function of pH and tannins was developed by using simple kinetic models to extrapolate the data. The data may be useful in estimating the relative corrosiveness of new, non-metallic wood preservatives based upon the chemistry of naturally durable wood species.

Keywords: wood, wood extractive, tannins, pH, corrosion, isocorrosion diagram

Introduction

Recently several papers have been published on corrosion of metals in wood treated with copper-based wood preservatives. Although the corrosion mechanism involves reduction of cupric ions (Baker 1988), it also depends on the wood extractives. Kear and others (2008a,b) studied corrosion behavior of metals in solutions of wood preservatives and concluded that these solutions cannot be used to predict corrosion in solid wood. Zelinka and others (2008) found that water extracts of treated wood were much more corrosive than dilute solutions of the wood preservative with roughly the same copper concentration. These studies suggest that wood extractives affect corrosion of metals in treated wood; however, the literature on this topic is sparse, and the role of several extractives remains controversial.

Although a single piece of wood can contain over 700 different extractives (Hazlewood and others 2006) only three types of extractives have been thought to affect the corrosion of metals in contact with wood or the black liquors of wood pulp: small organic acids (acetic and formic acid), tannins (or more broadly polyphenols), and phenols with two or three adjacent hydroxyl groups (e.g., catechol and pyrogallol). 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 (Clark and Green 1968; Niemelä 1989).

Small Organic Acids

Although the pH of wood, a solid material, is not well defined, water extracts of nearly all wood species are acidic (Packman 1960; Bootle 1983; Balban and Uçar 2003). The reason for this acidity is that in the presence of water, acetyl and formyl groups in the hemicelluloses are hydrolyzed to form acetic and formic acid (Packman 1960). Research has shown that this process is chemical, rather than biological (Packman 1960; Arni and others 1965b; Smith 1982), and that over 90% of the acid produced is acetic (Balban and Uçar 2003).

The earliest papers on corrosion of metals in wood attribute corrosiveness of wood to its acidity. Farmer (1962) lists the pH of several wood species and suggests a correlation between the most corrosive wood species and the most acidic wood species. Farmer emphasizes corrosiveness of western red cedar (Thuja plicata) and lists the pH in the range 2.9 to 4.7. Bartel-Kornacka (1967) studied the corrosiveness of 23 tropical wood species by placing iron in contact with water-saturated sawdust and found no difference in corrosiveness for species with a pH greater than 5; some species with a lower pH were more corrosive. Knothкова-Cermakova and Vlčkova (1971) cite the presence of acetic and formic acids as the only corrosive factors in wood. Smith (1982) ranks 16 species of wood according to their corrosivity, lists their pH, and concludes that, “a strongly acid [sic] wood, pH less than 4.0, is potentially dangerous, and a less acid [sic] wood, pH more than 5.0, is likely to be relatively safe.” This concurs with the accepted knowledge that the corrosion rate of carbon steel, while generally constant in the range of pH
5–9, increases rapidly with decreasing pH below pH 5 (Silverman 2003).

To summarize, many researchers have found correlations between the acidity of wood and its corrosiveness, and pH is largely controlled by formation of acetic and formic acid. However pH cannot be the only variable that affects corrosion. For example, Bartel-Kornacka (1967) found differences in corrosion between species with the same pH; Cynometra ananta and Nauclea diderrichii both had a measured pH of 4.5, but the corrosion rate in Cynometra was twice as high as in Nauclea. Furthermore, when Terminalia ivorenensis was extracted with a mixture of ethanol and water, it was much less corrosive. Similarly, Arni and others (1965a) removed all the volatile acids and phenolics from the wood and found the extracted wood was not corrosive toward mild steel.

**Tannins**

Tannins and other polyphenolic extractives are often mentioned in the literature as compounds that affect corrosion in wood. Polyphenols complex with metals; adjacent hydroxyl groups interact with metal ions (Maclean and Gardner 1953; Gust and Suwalski 1994; Kannan and Kelly 1996) forming metal tannates that are insoluble and form a dark blue/purple precipitate (McDonald and others 1996). However, researchers disagree about whether this chelation increases or decreases corrosion. Papers that examine the corrosion of metals in solid wood state that tannins increase corrosion (Krilov and Gref 1986; Winkelmann and others 2009a; Winkelmann and others 2009b; Pugsley and others 2001; Pugsley and others 2002), whereas studies on corrosion in the pulp and paper industry state that tannins are corrosion inhibitors (Maclean and Gardner 1953; Kannan and Kelly 1996; Hazlewood and others 2006; Singh and others 2001; Singh and Anaya 2001; Singh and Anaya 2007), although only one of these papers explicitly examined their effect (Hazlewood and others 2006). In the broader corrosion literature, wood tannins are frequently used to protect metals as either a primer or as an inhibitor (Mallow and Gardner 1953; Gust and Suwalski 1994; Pelikán 1966; Mammala and others 2000; Gust and Bobrowicz 1993; Nasrazadan 1997; Oguzie 2008; Rahim and others 2008).

Most of the research on the effect of tannins on corrosion in solid wood have examined the wear resistance of sawblades. Krilov and Gref (1986) listed the pH and polyphenol content for 15 different hardwoods, although all but two of the species were from the genus Eucalyptus. No corrosion data were reported, but a mechanism for corrosion involving the chelation of ferric ions was proposed. Winkelmann and others (2009a,b) claim that tannins accelerate the corrosion process by both lowering the pH and forming complexes with iron that do not adhere to the surface. Pugsley and others (2001, 2002) examined the role of tannins in the corrosion of sawblades by measuring the strength of ceramic reinforced tool-steels exposed to a 5 mM (8.5 g L$^{-1}$) solution of tannic acid. The strength of all steels decreased with exposure time, and some alloys exhibited stress-corrosion cracking.

In contrast to the above studies, in the broader corrosion literature tannins are often cited as corrosion mitigators. For example, Matamala and others (2000) tested tannins extracted from radiata pine (Pinus radiata) and black acacia (Acacia melanoxylon) as part of an anti-corrosive paint system and found that tannins increased the time to failure by over 250% when compared to an equivalent paint system without the tannins. Similarly, researchers have found that tannins extracted from radishes, honey, and various other plant species inhibit corrosion in acid and sodium chloride solutions (Oguzie 2008; Radojcic and others 2008; Rahim and others 2008).

The different behavior of tannins in these papers is most likely due to the studied application. In sawblade corrosion, it is possible that the iron-tannates are removed from the surface due to friction or heat and chelation results in a more active surface than normal corrosion processes, whereas in other situations, iron-tannates protect the surface. Regardless, the effect of tannins on the corrosion of metals in wood remains unclear.

**Catechol and Pyrogallol**

Although catechol and pyrogallol are not expected to be found in large quantities in solid wood, they warrant discussion in this work because they have been well studied in pulp and paper corrosion and are chemically similar to tannins. All of these compounds form complexes with iron at adjacent hydroxyl groups. Gust and Suwalski (1994) used Mössbauer spectroscopy to study the interaction of iron with catechol, pyrogallol, gallic acid, and oak tannins. They found that iron formed a complex with the same Mössbauer parameters for all compounds; that is, the interaction of iron and the phenolic molecule only depended on whether the molecule contained hydroxyl groups in adjacent positions. Furthermore, they found no difference in the type of complex formed between catechol and pyrogallol. These similarities suggest that catechol and pyrogallol should affect corrosion in the same way as tannins; however, the literature does not support this.

Seminal work by MacLean and Gardner (1953) found that catechol increased corrosion of equipment used to pulp western red cedar. Kannan and Kelly (1996) found that the critical current density for steel passivation in alkaline media was unaffected by 1,3-dihydroxybenzene and 1,4-dihydroxybenzene but was greatly increased in the presence of catechol and pyrogallol. Similarly, Singh and others (Singh and others 2001; Singh and Anaya 2001; Singh and Anaya 2007) examined the role of catechol on corrosion and found that it interacted synergistically with other components of the black liquor to increase corrosion.
Corrosion of Fasteners in Wood Treated with Newer Wood Preservatives

Objectives of This Research

The literature points to the importance of pH, tannins, and catechols as important factors in the corrosion of metals in wood and wood pulp. In this work, we systematically investigated the effects of tannin content and pH in extracts of four wood species exhibiting a range of both pH and tannins to see if there is a trend. These might not be the only factors affecting corrosion. If they were, “synthetic” extracts with the same pH and amount of tannin content as the wood extracts should give the same results. To test the influence of other factors, corrosion rates of synthetic extracts were made and compared to the wood extracts.

Materials and Methods

Four wood species known to vary across a range of acidities and quantity of extractives were investigated in this study by examining their water extracts. White oak (Quercus spp.) was chosen, as it is very acidic (Packman 1960), one of the most corrosive solid woods (Smith 1982), and is also high in tannins (De Rosso and others 2009). Elm (Ulmus spp.) was chosen because it is low in extractives and is one of the least acidic woods; literature values of the pH range from 6.0 to 7.2 (Farmer 1962; Smith 1982). Black locust (Robinia pseudoacacia, hereafter referred to as locust) was chosen because it is a naturally durable species (Scheffer and Hopp 1949; Pollet and others 2008). It has been shown that the extractives that protect the wood are water soluble (Scheffer and Hopp 1949) and contain ortho-phenolic groups (Pollet and others 2008) so it is therefore reasonable to expect that these extractives may also affect the corrosiveness of locust. Southern Pine (Pinus spp.) was chosen to connect with existing work on treated wood (Zelinka and others 2008). Additionally, other researchers have noted the corrosivity of Southern Pine black liquor (Singh and others 2001; Singh and Anaya 2001; Singh and Anaya 2007). Elm and locust were harvested near Madison, Wisconsin, and stored in a temperature- but not humidity-controlled room for several years before testing. The Southern Pine and white oak were purchased commercially and had been kiln-dried prior to testing. No effort was made to separate heartwood from sapwood; rather, one homogenized extract was made for each wood species tested.

Corrosion of steel in water extracts was determined by the method of Zelinka and others (2008). The extract was made by combining sawdust and distilled water in a 1:10 ratio by weight for one week at room temperature. After the extraction period, the sawdust was removed with vacuum filtration and the extract was stored at 1 °C until just before testing to minimize any possible biological activity. No effort was made to control particle size of the sawdust because in previous work we found that the corrosion rate did not depend on the size of particles used to form the extract (Zelinka and others 2008).

Corrosion of a 1018 steel plug (UNS G10180) was measured electrochemically. The potential was varied from −30 mV to +30 mV with respect to the open circuit potential at a scan rate of 0.166 mV/s. Prior to polarization, the open circuit potential was measured for an hour. The corrosion rate was determined by simultaneously measuring polarization resistance and Tafel slopes, which were ascertained from the non-linearity in the polarization resistance curve using Mansfeld’s method (Mansfeld 1973a,b). For each extract, the pH was measured with a double junction glass bulb, and the amount of tannin was quantified colorimetrically with the method of Amin (1997) with minor modifications. In this method, tetracoluline blue is reduced in the presence of tannins and the absorbance at 527 nm is measured. The color is compared against a calibration curve made with tannic acid, and the tannin content is expressed as an equivalent concentration of tannic acid. Two modifications were made to the method. First, tetracoluline blue solution was made to a concentration of 0.005 M and twice the volume used because it did not readily dissolve in water at 0.01 M. Second, when solutions were heated in 10-mL volumetric flasks, boiling over occurred, 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 “Synthetic” extracts were made by first adding tannic acid to distilled water and then adjusting the pH by addition of sodium hydroxide.

Results and Discussion

The pH, tannin concentration, and corrosion rate (with standard error) are given in Table 3-1. Fortuitously, the pH of pine and oak were similar, and tannin concentrations were nearly equal in oak and locust. This allows a limited examination of the effect of pH and tannin individually while holding the other variable constant. Corrosion rates in synthetic extracts were much lower than in wood extracts, and they exhibited a different response to changes in pH and tannins.

The steel plug exposed to oak and locust extracts formed a blue/black patina after the polarization resistance test. This behavior was replicated in the synthetic extracts, and small amounts of the patina could be found on the plug after it had been exposed to synthetic pine and elm extracts. Furthermore, in all the synthetic extracts, a blue/black cloud of precipitate was visible around the electrode (Fig. 3-1). This cloud was most visible in the synthetic oak and locust extract. The precipitate cloud may also have been present in the wood extracts but the extracts were translucent prior to testing so the precipitate cloud would not have been visible. It is assumed that the patina and precipitate were iron-tannate, since these solutions contained tannins, and iron-tannates are also blue/black in color (Pelikán 1966; Gust and Bobrowicz 1993; Matamala and others 2000).
Because of the similar pH between pine and oak extracts and the similar tannin content in oak and locust extracts, ancillary tests were conducted on modified extracts of pine and locust. The pine extract was modified by adding tannic acid until the total concentration was 1,000 mg L\(^{-1}\) and the locust extract was acidified with acetic acid until the pH was 4.3; these modified extracts both had nominally the same pH and tannin acid concentration as the unmodified extract of oak. The properties of these extracts are given in Table 3-1 and the corrosion rates are shown graphically in Figure 3-2.

**Discussion**

Although only four species were tested, some general trends can be observed in the data. Similarity in pH between pine and oak allow us to examine the role of tannins holding pH constant. It appears that increasing tannins at a given pH decreases the corrosion rate; that is, tannins are acting as an inhibitor. Interestingly, modified pine extract, having the same concentration of tannins as oak extract, had the same corrosion rate. This suggests that the difference in corrosiveness between unmodified pine and oak is due to differences in tannin content, which is remarkable considering the complexity of wood chemistry.

Likewise, the effect of pH at a given tannin concentration can be examined by comparing locust and oak extracts. Oak had a lower pH and a higher corrosion rate. When acetic acid was added to the locust extract until it had the same pH as the oak extract, the corrosion rate increased, but the modified locust was not as corrosive as oak, even though they had the same pH and tannin concentration. This suggests that locust may contain one or more compounds that act as corrosion inhibitors not present in either oak or pine.

Corrosion rates in the synthetic extract are all much lower than in the solid wood extracts, and there is a different trend across the species. This can be seen most clearly by plotting the extract corrosion rate against the synthetic extract corrosion rate (Fig. 3-3). From the data appear two possibilities. The first is that oak is an outlier and all of the synthetic extracts have a corrosion rate of roughly 30 µm y\(^{-1}\). The other possibility is that pine is an outlier and there is a linear trend between the extract and the synthetic extract. In either case, one or more chemicals in the wood extract appear to affect corrosion in addition to tannins and the pH.

For a clearer understanding of the effects of tannin and pH on corrosion rate, it is necessary to invoke kinetic models. A general form for the dependence of corrosion rate \(r\) on the concentration of hydrogen ions \((\text{H}^+)\) in acidic conditions (below pH 5) is given by

\[
r = k_1(\text{H}^+)^n \tag{3.1}
\]

where \(k\) and \(n\) are constants; the corrosion rate of steel is largely independent of pH between pH 5 and 9 (Silverman 2003). We have modeled this transition from a power-law dependence \((\text{H}^+)\) to no dependence on \((\text{H}^+)\) at pH 5 with a decaying exponential by adding unity to Eq. (3.2) that is

\[
r = k_1(\text{H}^+)^{n(5-\text{pH})} + 1 \tag{3.2}
\]
Radojcic and others (2008) showed that the Langmuir isotherm can be used to describe the inhibitor efficiency of tannins as a function of concentration. Rearranging terms in the Langmuir equation, the corrosion rate can be written as a function of the concentration of tannins ($c$) by

$$r = \frac{r_0}{1 + k_2c}$$  \hspace{1cm} (3.3)

where $r_0$ is the corrosion rate when there are no tannins, and $k_2$ is a second constant. Assuming that the effects of tannins and pH are orthogonal, it is possible to combine these models as

$$r = r'_0 (1 + k'_c)^{-1} \left( e^{m (5 - \text{pH})} + 1 \right)$$  \hspace{1cm} (3.4)

where $r'_0$, $k'$, and $m$ are fitting parameters and $m > 0$. Fitting this model to our data allows us to examine more clearly the effects of tannin concentration and pH.

Figure 3-4 is an isocorrosion diagram created by fitting our model to the wood-extract data in Table 3-1. This model was based on the following assumptions: (1) effects of tannin and pH are orthogonal; (2) literature models for the effects of tannins and pH are valid for wood extracts; (3) transition from pH-dependent to pH-independent corrosion occurs at pH 5 and can be modeled with a decaying exponential; and (4) the small data set is sufficient to fit the model.

More data would be needed for any reliable prediction given the model assumptions, the possibility of synergistic effects, the lack of agreement between real and “synthetic” extracts, and the need to show correlation between corrosion in extracts and in solid wood under outdoor exposure.

Despite its limitations, Figure 3-4 may be used for visualizing the effects of tannins and pH. One possible application is in development of new, completely non-metallic wood preservative systems. These preservatives are based on the chemistry of naturally durable species come to the market (Thevenon and others 2009; Binbuga and others 2008; Donoso-Fierro and others 2009) and contain antioxidants, including tannins, that might complex with iron. This isocorrosion map could be used to predict the relative effects of adding tannins or adjusting the pH of these preservatives.

**Summary and Conclusions**

Corrosion of steel in wood extracts was studied. Specifically, the corrosion rate was studied as a function of pH and tannin content. In the extracts, at a given level of tannins, a lower pH increases corrosion. In contrast, at a given pH, a decrease in tannin content increases corrosion. It appears that in wood extracts, tannins act as a corrosion inhibitor. This is in contradiction to findings in the literature on sawblade corrosion. The difference is most likely due to the friction and heat produced during sawing.

By combining kinetic models in the literature, an isocorrosion map was created for wood extracts as a function of pH and tannin content. In the extracts, a lower pH increases corrosion. In contrast, at a given pH, a decrease in tannin content increases corrosion. It appears that in wood extracts, tannins act as a corrosion inhibitor. This is in contradiction to findings in the literature on sawblade corrosion. The difference is most likely due to the friction and heat produced during sawing.

By combining kinetic models in the literature, an isocorrosion map was created for wood extracts as a function of pH and tannin content. This map is based on limited data and it does not explain why synthetic extracts behave differently; nevertheless, in the future with additional data such maps may be able to assess the relative effects of these chemicals when developing a new, non-metallic preservative system.

Synthetic extracts exhibited lower corrosion rates and different relative rankings between wood species. It appears there is one or more chemicals not accounted for in this study that affect corrosion. These chemicals (or chemical) may act synergistically with tannins and pH or also may be unevenly distributed among the wood species tested.
Table 3-1. Acidity, tannin content, and corrosion rate of the solutions tested

<table>
<thead>
<tr>
<th></th>
<th>pH</th>
<th>Tannins (mg L⁻¹)</th>
<th>Corrosion rate of steel (µm y⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Mean</td>
<td>Standard error</td>
</tr>
<tr>
<td>Extract</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oak</td>
<td>4.3</td>
<td>1,020</td>
<td>279</td>
</tr>
<tr>
<td>Pine</td>
<td>4.5</td>
<td>340</td>
<td>334</td>
</tr>
<tr>
<td>Locust</td>
<td>5.1</td>
<td>990</td>
<td>74</td>
</tr>
<tr>
<td>Elm</td>
<td>6.5</td>
<td>40</td>
<td>159</td>
</tr>
<tr>
<td>Synthetic extract</td>
<td>4.3</td>
<td>1,000</td>
<td>49</td>
</tr>
<tr>
<td>Oak</td>
<td>4.3</td>
<td>1,000</td>
<td>49</td>
</tr>
<tr>
<td>Pine</td>
<td>4.5</td>
<td>350</td>
<td>31</td>
</tr>
<tr>
<td>Locust</td>
<td>5.1</td>
<td>1,000</td>
<td>27</td>
</tr>
<tr>
<td>Elm</td>
<td>6.5</td>
<td>40</td>
<td>33</td>
</tr>
<tr>
<td>Modified extract</td>
<td>4.2</td>
<td>1,000</td>
<td>285</td>
</tr>
<tr>
<td>Pine</td>
<td>4.2</td>
<td>1,000</td>
<td>285</td>
</tr>
<tr>
<td>Locust</td>
<td>4.3</td>
<td>990</td>
<td>198</td>
</tr>
</tbody>
</table>

*a*Expressed as tannic acid equivalent.

*b*The modified pine extract was made by adding tannic acid to the pine extract until the total concentration of tannic acid of 1,000 mg L⁻¹ was reached. The modified locust extract was made by adding acetic acid until the pH was 4.3.

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Combining Hygrothermal and Corrosion Models To Predict Corrosion of Metal Fasteners Embedded in Wood

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Abstract

A combined heat, moisture, and corrosion model is presented and used to simulate the corrosion of metal fasteners embedded in solid wood exposed to the exterior environment. First, the moisture content and temperature at the wood–fastener interface is determined at each time step. Then, the amount of corrosion is determined spatially using an empirical corrosion rate model and the inputs of the first step. The result is a corrosion profile along the length of the fastener generated by summing the corrosion depths determined at each time step. We apply the combined model to predict the annual corrosion depth along a metal fastener in wood decks situated in nine different U.S. cities. Corrosion profiles are found to exhibit the same general shape independently of climatic load, with the largest amount of corrosion occurring at 1 to 5 mm from the wood surface with corrosion depths ranging from 5 μm in Phoenix, Arizona, to 45 μm, in Hilo, Hawaii. Corrosion is confined to the first 7 to 20 mm of the fastener below the wood surface. By varying the climatic loads, we found that although there is a definite relation between total annual rain and total annual corrosion, under the same rain loads, corrosion is higher for a climate with more evenly distributed rain events. The proposed combined model is capable to capture corrosion behavior under varying loading. A sensitivity analysis gives guidelines for future corrosion modeling work for fasteners in wood.

Keywords: corrosion, hygrothermal modeling, decks, wood preservatives

Introduction

Wood structures that are exposed to the exterior environment, such as terrace decks, balconies, and playground equipment, are susceptible to moisture damage such as wood rot and metal corrosion. Frequently, softwoods (pine, spruce) are treated with wood preservatives to be durable and suitable for these exterior applications. The durability of treated wood depends not only on protecting the wood from biological attack but also on minimizing the corrosion of embedded fasteners. The corrosion rate of embedded fasteners depends on the moisture and temperature conditions at the metallic surface, which fluctuate considerably in outdoor wood constructions considered here. In this paper, we present a modeling approach that combines heat and mass transport in the wood exposed to environmental loading with corrosion of the metallic fasteners in contact with the wood.

The specific context of this paper stems from a wood preservation regulation change that occurred in the United States in January 2004. Alkaline copper quaternary (ACQ) and copper azole (CuAz) replaced chromated copper arsenate (CCA) in residential applications (Lebow 2004). These alternative wood preservatives were suspected to be more corrosive to embedded metal fasteners than CCA (Burkholder 2004; Anon 2008). Since the regulation change, the corrosiveness of CuAz and ACQ has been evaluated in several laboratory tests. Most of this work used the American Wood Protection Association AWPA E-12 standard, which places metal coupons between blocks of wood at 49 °C and 90% RH for at least 240 h (Freeman and McIntyre 2008; Kear and others 2009). Other procedures using more realistic temperatures were developed. Kear and others (2009) exposed fasteners embedded in treated wood at 21 °C to three different relative humidities ranging from 75% to 98% RH for 1 year.

Zelinka and Rammer (2009) embedded fasteners in blocks of treated wood exposing them to 27 °C and 100% RH for one year. Furthermore, electrochemical tests in a water extract of treated wood were found to have the same corrosion rates as those measured at the 27 °C 100% RH conditions (Zelinka and others 2008). These tests all show that ACQ
and CuAz are more corrosive than CCA. However, mainly because of the variations of testing conditions, the measured corrosion rates from these tests have a wide range of values, for example, from 2 to 113 μm y⁻¹ for hot-dip galvanized steel in ACQ-treated wood (1-26 μm y⁻¹ for CCA). As the corrosion rate of metals in contact with wood is shown to depend on the moisture content and temperature conditions at the interface, in-service conditions along the interface are needed for durability prediction. In-service moisture content (MC, the ratio of the mass of water to the mass of oven dry wood) of wood decks experience large fluctuations (from 8% to 80% MC) and nonuniform distribution depending on the environmental conditions (Lebow and Lebow 2007; Glass and TenWolde 2007). Therefore, a steady-state approximation of the MC conditions or of the corrosion rate would not be able to capture these changes and could not lead to prediction of corrosion lifetime.

For predicting the corrosion lifetime of fasteners in treated wood, we propose to predict the corrosion rate using the conditions at the wood–fastener interface determined under environmental conditions by combining a heat and moisture transport model with a corrosion model. An existing, validated heat and moisture transport model (Janssen and others transport model with a corrosion model. An existing, validated heat and moisture transport model (Janssen and others 2007a) is used to calculate the conditions at the wood–fastener interface with a complete set of climatic data applied as boundary conditions including air temperature and relative humidity, rain precipitation, and wind conditions. The model is also able to account for solar radiation, although in this paper, its effect was not considered. The corrosion of the embedded fastener is computed from the calculated temperature and moisture content at the wood–fastener interface at each time step. In the next section, we describe this modeling approach, including the geometry of the application problem and the determination of the required material properties. We use this modeling approach in comparing the corrosion depth profiles of fasteners for constructions under nine different climatic conditions and present the results of this study. We then discuss two key aspects of this study: the selection of the appropriate year of climatic data and sensitivity of the results to variations of the three parameters of the corrosion model.

**Combined Heat Moisture and Corrosion Model—Geometry of the Physical Problem**

Most of the previous work on corrosion in treated wood has focused on residential decks; similarly, we simulate the corrosion of the fastener that connects the decking to the joists (i.e., a deck screw). The American Forest and Paper Association recently published a Prescriptive Residential Wood Deck Construction Guide based on the 2009 International Residential Code (IRC), which gives the minimum construction requirements for single level residential wood decks. The guide specifies an “8d” nail (64 mm long, ~3 mm in diameter), 38-mm thick deck boards spaced 3.2 mm apart, and 38-mm thick joists.

In this work, two simplifications are made to the configuration. The geometry and meshing of the calculation domain are shown in Figure 4-1. The first simplification is that the fastener is modeled within a single wood member, which can be thought of as a joist with the deck board removed. The second simplification is that the problem can be treated two-dimensionally, which is equivalent to assuming that the fastener is in the middle of an infinitely long joist. Symmetry considerations are used so that only half of the width needs to be modeled. The two-dimensional mesh is 20 by 90 mm and consists of 1,965 wood elements, of exponentially decreasing size going towards the exterior boundaries and nail interface, 336 steel elements, and 2,400 nodes. Heat transport was simulated in the nail to account for possible thermal bridging effects; however, the nail was assumed to be impermeable to moisture and had no moisture capacity.

**Corrosion Model**

Research indicates the corrosion mechanism for metals embedded in wood is aqueous (Baker 1988; Short and Dennis 1997; Dennis and others 1995; Duncan 1988) and many researchers have observed a threshold moisture content (between 15% and 20%) below which corrosion in wood does not occur (Baker 1988; Short and Dennis 1997). This parallels the mechanism in atmospheric corrosion, where a liquid film is required for corrosion. The simplest such model for calculating the risk of atmospheric corrosion is found in the ISO 9223 standard and assumes that a liquid film capable of causing corrosion forms when the relative humidity is greater than 80% and the temperature is greater than the freezing temperature of water (0 °C) (ISO 1992). Our empirical corrosion model maintains this temperature threshold for corrosion, but includes the dependence of the corrosion rate on moisture content above the corrosion temperature threshold.

Short and Dennis (1997) used electrochemical techniques to measure the corrosion rate of zinc as a function of moisture content. They placed a small strip of CCA-treated wood between a stainless steel counter electrode and a zinc-working electrode. Two more pieces of wood were placed on the outside of the working and counter electrodes to create a “sandwich.” The wood moisture content was adjusted by placing the assembly in various conditioning chambers and the corrosion rate was measured at 11 different moisture contents using polarization resistance. The relationship between polarization and the corrosion rate was explored first by Mansfeld (1973) and this relationship has been recently exploited to study a diverse range of phenomena such as the corrosion of rebar in concrete (Poupard and others 2003b; Poupard and others 2003a; Ait-Mokhtar and others 2006). The polarization resistance data indicated a sigmoidal dependence of the corrosion rate on moisture content between 15 and 27% MC. In addition, below 15% MC,
there was no corrosion and above 27% MC, the corrosion rate was constant at its maximum value. We have fit their experimental corrosion rate data \( R, \mu \text{m y}^{-1} \) as a function of moisture content, \( M \text{ (kg kg}^{-1} \text{ expressed as a percentage)} \), with the following:

\[
R = \frac{A}{1 + e^{B(C-M)}}
\]  

(4.1)

where \( A \) represents the maximum corrosion rate \((\mu \text{m y}^{-1})\), \( B \) represents the steepness of the transition from 0 to \( A \), and \( C \) represents the moisture content at which \( R = A/2 \), i.e., a metric of the moisture content threshold of corrosion. The parameters \( B (0.83) \) and \( C (24) \) are taken from our fit of the published data of Short and Dennis (1997). The parameter \( A \), which is physically the asymptotic corrosion limit, is taken as 52.3 \( \mu \text{m y}^{-1} \) from recent electrochemical measurements of hot-dip galvanized steel in an extract of ACQ-treated Southern Pine (Zelinka and others 2008). A graph of the corrosion rate as a function of moisture content is shown in Figure 4-2, with the data of Short and Dennis overlaid (Short and Dennis 1997) (scaled to the maximum corrosion found by Zelinka and Rammer (2008)).

There are no data on the temperature dependence of corrosion in treated wood. However, because the corrosion mechanism in wood is believed to be aqueous, it is unlikely that corrosion occurs below freezing. Therefore our model enforces a “no-corrosion” condition when the wood near the metal surface is less than 0 °C, similar to the ISO 9223 model (ISO 1992).

**Heat and Mass Transport Model**

The coupled heat and moisture transport is calculated using an existing, validated heat and moisture transport model implemented with a finite element code (Janssen and others 2004, 2007a,b) which uses capillary pressure, \( p_c \) as

![Figure 4-1. Calculation mesh (domain) used in the simulations with physical dimensions. The elements with steel material properties are black to clearly identify the nail. Top, side, and bottom refer to the boundary conditions, e.g., exposed to environmental conditions. The heavy line represents the symmetry plane.](image)

![Figure 4-2. Corrosion model in this study derived from Short and Dennis (1997) and Zelinka and others (2008).](image)
the driving potential for moisture transport. The governing equations are the following:

\[
\frac{\partial w}{\partial t} + \nabla \cdot (g_{m,l} + g_{m,v}) = 0
\]  

(4.2)

\[
(c_0 \rho_0 + c_1 w) \frac{\partial T}{\partial t} + \left( c_1 T \frac{\partial w}{\partial c_p} \right) \frac{\partial c_p}{\partial t} = -\nabla \cdot (g_{h,c} + g_{h,a})
\]  

(4.3)

\[
g_{m,l} = -K_l \nabla p_c
\]  

(4.4)

\[
g_{m,v} = \frac{\delta_v \rho_v}{\rho_l R_v T} \nabla p_c - \frac{\delta_v \rho_v}{\rho_l R_v T} (\rho_l L_v + \rho_c (T_T - 1)) \nabla T
\]  

(4.5)

\[
g_{h,c} = -\lambda \nabla T
\]  

(4.6)

\[
g_{h,a} = (c_1 T) g_{m,l} + (c_1 T + L_v) g_{m,v}
\]  

(4.7)

where

- \( w \) is volumetric moisture content [kg m\(^{-3}\)]
- \( t \) time [s]
- \( \tau \) the transpose
- \( g_m \) moisture flux [kg m\(^{-2}\) s\(^{-1}\)], and the subscripts \( l \) and \( v \) stand for liquid and vapor, respectively
- \( c \) specific heat [J kg\(^{-1}\) K\(^{-1}\)], and the subscript \( 0 \) stands for dry solid
- \( \rho \) density [kg m\(^{-3}\)]
- \( T \) absolute temperature [K]
- \( g_h \) heat flux [W m\(^{-2}\)], and the subscripts \( c \) and \( a \) stand for conductive and advective, respectively
- \( K_l \) liquid water permeability [s]
- \( \delta_v \) vapor permeability [s]
- \( \rho_v \) vapor pressure [Pa]
- \( R_v \) the specific gas constant for water vapor [J kg\(^{-1}\) K\(^{-1}\)]
- \( L_v \) heat of vaporization [J kg\(^{-1}\)]
- \( \gamma \) the normalized thermal derivative [K\(^{-1}\)]
- \( \lambda \) thermal conductivity [W m\(^{-1}\) K\(^{-1}\)]

The model can handle the full range of moisture content of wood from dry to capillary saturation as it includes liquid transport. The non-linearity as well as the temperature and moisture content dependence of the material properties are implemented. Time stepping is adaptive while the temperature and moisture content of the wood at each node are written to an output file at one hour intervals.

**Boundary Conditions**

To simulate the moisture conditions of a deck, atmospheric boundary conditions including air temperature and relative humidity, precipitation, and wind dependent convective heat and mass transfer coefficients are applied on the top surface. Precipitation is applied as an hourly average liquid thickness of rain, snow is treated as its liquid water equivalent. On the “side” and “bottom” surfaces (Fig. 4-1), only the air temperature and relative humidity are taken from the climatic data while the convective heat and mass transfer coefficients are taken as constant (20 W m\(^{-2}\) K\(^{-1}\) and \(2.4 \times 10^{-8}\) s m\(^{-1}\), respectively).

**Material Properties**

The accuracy to which the hygrothermal model can predict the wood moisture content, and thus the corrosion rate, is dependent on appropriately determined material properties, namely, full moisture retention curve over both the hygroscopic (sorption isotherm) and overhygroscopic regimes, moisture diffusivity (from vapor permeability and liquid water conductivity), thermal conductivity, and heat capacity. In this work, the moisture retention curve and diffusivity are functions of capillary pressure, the thermal conductivity is a function of moisture content, and the heat capacity is a constant. No temperature dependency is included at this stage of the work.

Few measurements have been published on the hygrothermal properties of treated Southern Pine. Sorption isotherms of preservative-treated and untreated Southern Pine have recently been published (Zelinka and Glass 2010) and there were only small differences between the isotherms of ACQ, CCA, and untreated Southern Pine. However, the vapor permeability of treated wood, its liquid water conductivity, and its moisture retention curve in the overhygroscopic regime have not been characterized.

In the present work, the material properties are taken from work on untreated Scots pine (Pinus sylvestris) (Zillig and others 2006). While it is likely that there are differences in the hygrothermal properties of Scots pine and Southern Pine, the data were chosen because of the quality and completeness of the data and because the data are from the same genus. The liquid, vapor, and total permeabilities were taken from measurements in the tangential direction, and utilized the diffusivity approach presented by Carmeliet and others (2007). Heat capacities and thermal conductivity values for loblolly pine (Pinus taeda) were taken from the Wood Handbook (Glass and Zelinka 2010). The sensitivity of the model to these properties has been examined previously (Zelinka and others 2010).
Combining Models

Modeling the corrosion of fasteners in treated wood involves two steps: first, calculating the wood moisture content and temperature at the wood-metal interface; and second, calculating the metal corrosion rate, which is dependent on this moisture content. We calculate the corrosion rate at each output time step (every hour) at each node along the wood–metal interface from Equation (4.1) and the wood-moisture content. We assume the corrosion rate to be constant over the entire following hour. If the temperature of the wood at the interface is less than zero for a given hour, the corrosion rate at that node is set to zero. The total amount of corrosion during the simulation is found by summing the amounts determined hourly.

Since combining the models does not introduce additional physical models, validation of the combined model reduces to a validation of the hygrothermal model and the corrosion model separately. The hygrothermal model has been validated previously (Janssen and others 2007a) and the corrosion model is empirical.

In the next section we apply the combined models approach for a parametric study.

Examination of the Corrosion Potential in Different U.S. Climates

Corrosion in outdoor structures is expected to depend upon climate. Intuitively, it should depend upon the amount of precipitation, the way in which precipitation is distributed over time, drying potential, temperature, and possibly other climatic variables. Drying potential likely depends on temperature, humidity, solar radiation, and wind speed. To examine the possibility for corrosion in different climates, we apply the combined models approach to nine cities in the United States. The cities are chosen based on the climate zones proposed by Briggs and others (2003), which have been adopted by the American Society of Heating, Refrigerating and Air-Conditioning Engineers (ASHRAE) and the International Energy Conservation Code (IECC). The methodology splits the continental United States into seven zones (1–7) based upon temperature; each of these temperature zones is then assigned a moisture classification, “a” for humid, “b” for dry, or “c” for coastal. Eight cities from the continental United States are examined, from six of the seven climate zones, including all moisture subclassifications (Table 4-1 and Fig. 4-3). Additionally, Hilo, Hawaii, is chosen to simulate corrosion in what was expected to be an extreme environment (more than 5 m of annual rainfall).

Climatic Data

The climatic data for the simulations are obtained from the Solar and Meteorological Surface Observation Network (SAMSON) dataset that includes hourly weather observations for 237 weather stations throughout the United States during the period 1961–1990 (NCDC 1993), including the nine locations selected above. It would have been possible to use the whole set of 30 years to perform the simulations. A more common approach is the selection of the dataset of a specific year, based on one or several criteria of particular relevance for the problem studies. Examples of such selection in building physics deal mainly with the hygrothermal behavior of wall assemblies. For example, ASHRAE 160 recommends 10th percentile hottest and coldest years as moisture design reference years (ASHRAE 2009). We ran the combined hygrothermal/corrosion model in preliminary simulations with several reference years proposed for wall assemblies (ASHRAE 2009; Salonvaara and others 2010). We found that these reference years do not result in large amounts of corrosion compared to other years. This may be expected as wall assemblies and terrace decks experience very different boundary conditions and hygrothermal gradients.

During preliminary simulations, we observed that the climatic parameter that has the most impact on the total corrosion depth is rain. Thus, the reference years are selected based upon precipitation, using two rain parameters as simplified simulations (Zelinka and others 2010) show that the amount of corrosion is sensitive to both the total amount

<table>
<thead>
<tr>
<th>Zone</th>
<th>City</th>
<th>State</th>
<th>Year</th>
<th>Maximum predicted corrosion depth (µm)</th>
<th>Yearly</th>
<th>Total number of hours T &gt; 0°C Rain</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Hilo</td>
<td>HI</td>
<td>1990</td>
<td>45</td>
<td>23.0</td>
<td>5.36</td>
</tr>
<tr>
<td>1</td>
<td>Miami</td>
<td>FL</td>
<td>1968</td>
<td>12</td>
<td>23.4</td>
<td>2.12</td>
</tr>
<tr>
<td>2a</td>
<td>New Orleans</td>
<td>LA</td>
<td>1961</td>
<td>20</td>
<td>19.6</td>
<td>2.12</td>
</tr>
<tr>
<td>2b</td>
<td>Phoenix</td>
<td>AZ</td>
<td>1978</td>
<td>5</td>
<td>23.3</td>
<td>0.39</td>
</tr>
<tr>
<td>3a</td>
<td>Atlanta</td>
<td>GA</td>
<td>1975</td>
<td>17</td>
<td>15.9</td>
<td>1.68</td>
</tr>
<tr>
<td>4a</td>
<td>Baltimore</td>
<td>MD</td>
<td>1989</td>
<td>16</td>
<td>12.6</td>
<td>1.32</td>
</tr>
<tr>
<td>4c</td>
<td>Seattle</td>
<td>WA</td>
<td>1971</td>
<td>26</td>
<td>10.1</td>
<td>1.10</td>
</tr>
<tr>
<td>5a</td>
<td>Chicago</td>
<td>IL</td>
<td>1983</td>
<td>11</td>
<td>9.7</td>
<td>1.25</td>
</tr>
<tr>
<td>5a</td>
<td>Minneapolis</td>
<td>MN</td>
<td>1983</td>
<td>12</td>
<td>7.8</td>
<td>0.99</td>
</tr>
</tbody>
</table>
of annual rainfall as well as the number of hours with a rain event. For each city, the years 1961–1990 are ranked based upon the total amount of annual precipitation. From this list, the top 5 years are selected and the hourly data are analyzed for the number of hours with non-zero precipitation. From the five analyzed years, the year with the most hours of rain is selected as the reference year. The reference years selected by this method from the SAMSON data set are given in Table 4-1. To simulate a worst case scenario for corrosion, for example, a deck that is constantly in the shade, solar radiation is excluded from the climatic data. The years selected, along with some rainfall and temperature mean or total values, are included in Table 4-1.

**Results of the Simulations**

Simulations are run for one calendar year for each city, starting in January. The starting temperature of the wood and metal is set to be equal to the air temperature at the first time step and the starting moisture content is 13%. The results of the 1-year simulation for each city are shown in Figure 4-4, where the amount of corrosion is given as a function of the depth below the wood surface.

The curves in Figure 4-4 have several features in common: the total corrosion penetration increases with depth for the first few millimeters, reaches a maximum, and then decreases with depth until it reaches zero. The similarities between these curves can be explained by the physics of the phenomenon. During a rain event, the wood moisture content at the surface is above the corrosion threshold; the depth of this high moisture region is dependent on the amount of rainfall and duration of the rain event. At depths far below the surface, the moisture content is not affected by the rain and remains below the corrosion threshold. In between these two locations, moisture is transported into the wood by diffusion and a gradient of moisture content is expected. Also, following a rain event, the wood begins to dry out from the surface, and surface drops quite quickly below the corrosion threshold. After the rainfall stops, the first few millimeters of the wood are at the capillary saturation threshold moisture content, which is why the maximum is not at the surface that gets wet by rain, but a short distance below it.

An example of the relationship between moisture content and rain events is given in Figure 4-5, which plots the hourly precipitation and moisture content for one month (April) using the Baltimore climate data. The data are taken at 1.8 mm below the fastener surface, where the maximum yearly average moisture content occurred for this city. At this depth, the moisture content reaches a maximum quickly after a rain event (in a few hours), and then dries out over tens of hours. Another illustration of the effect of precipitation on the moisture content, and therefore corrosion, is given in Figure 4-6, which plots the entire corrosion profile after the rain event corresponding to approximately 350 hours in Figure 4-5 (time = 0 in Fig. 4-6 corresponds to time = 353 in Fig. 4-5). After 60 h, the peak in the moisture content graph has disappeared.

To make comparisons between the cities easier, the maxima of the curves in Figure 4-5 have been tabulated in Table 4-1. As expected, Hilo, with over 5 m of rainfall, has the most corrosion and Phoenix, with less than 0.4 m, is the environment leading to the least corrosion. After Hilo, Seattle has the next highest corrosion rate. This city, while relatively
low in annual rainfall, has 50% more hours with a rain event than the next highest city (Baltimore).

Surprisingly, Miami and New Orleans, which have the same total rainfall (2.12 m) and nearly the same number of hours (588 vs 593 h) of precipitation, have very different amounts of corrosion (67% difference). Since this behavior cannot be explained in terms of the annual totals in Figure 4-7, the rain events are plotted as a time series in Figure 4-7. From this figure, it qualitatively appears that the rain events in New Orleans are spread more evenly throughout the year.
whereas the Miami rain events appear more concentrated between hours 3000 to 8000. This difference in distribution of rain throughout the year could explain the differences in corrosion between these two cities. Likewise, Chicago and Minneapolis have a similar number of hours of rain, but Chicago has more rain (1.25 m as opposed to 0.99 m) and more hours with the air temperature above freezing, yet the simulation results indicate slightly less corrosion for Chicago than for Minneapolis.

The corrosion profiles had a similar shape in all climates with a maximum 2 to 5 mm below the wood surface. The fact that no corrosion is observed at 10 to 20 mm below the surface is a result of the relatively low starting moisture content. After the lumber is preservative treated, it is completely saturated with water and preservative chemicals. Although best construction practices suggest that the wood should be kiln dried after treatment and before construction, in reality decks are frequently built from lumber that is still wet from treating. To simulate the effect of a “built-wet” construction, a simulation was run for Baltimore with the wood starting in a capillary saturated state. This analysis assumes that the freshly treated lumber is chemically the same as dried and retreated lumber. The corrosion profile is shown as a function of time in Figure 4-8, along with the 1-year data with a 13% starting moisture content shown as a baseline. The corrosion profile after 3 months is nearly uniform at ~3 µm and represents the corrosion that occurred from the initially high moisture content. After the first 3 months, the amount of corrosion remains at 3 µm, as the wood has dried to below the corrosion threshold and non-precipitation related corrosion is no longer occurring. This analysis suggests that while building with freshly treated lumber increases corrosion, it only affects the first few months after construction and should have a small effect compared to atmospherically induced corrosion.

Discussion

The combined model was used to determine the corrosion profile of metal fasteners embedded in wood for several different climates. Here, we discuss issues relating to the selection of a reference year for corrosion and the sensitivity of the corrosion model parameters.

Selection of the Reference Year

The results show that the corrosion of fasteners depends on the environmental loading. Although only the amount and number of hours of rain are examined in selecting the reference years, there is not a strict correlation between either of these variables and the simulated corrosion. This suggests that other climatic variables are also affecting the corrosion of metals in wood in outdoor exposure. While there has been much work on selecting reference years for analysis of building envelope assemblies (Salonvaara and others 2010; ASHRAE 2009; Cornick and others 2003; Sanders 1996; David and others 2010; Kershaw and others 2011; Zhu and others 1995; Blocken and Carmeliet 2010), and using climate year data to assess rain loads (Blocken and Carmeliet 2007; Abuku and others 2009; Blocken and Carmeliet 2010), the moisture loads on exterior structures have not been assessed so systematically. Structures such as decks are clearly different from walls as they receive the entire amount of horizontal rainfall, and do not have interior/exterior temperature and moisture gradients.

The method for selecting the years is based on the results of a few preliminary simulations, which are used to select the important climatic variables, and then deduce what parameters should be used to select the climate years. However, the results of simulations in different climates with nearly the same controlled climate parameters produce different corrosion rates, which suggests that not all of the physics is
captured in the original parameters used to select reference years. A more systematic approach seems warranted for the selection of reference years for outdoor structures.

**Examination of the Sensitivity of the Corrosion Model**

The corrosion profile is the result of two models: a hygrothermal model that determines the wood moisture content and temperature distribution over the calculation domain, and a corrosion model that translates this moisture content into a corrosion rate at the nail surface. While hygrothermal models have been developed and improved for many years, this work presents a first model relating wood moisture content to a corrosion rate. There are only a few examples in the literature where corrosion was examined as a function of moisture content or relative humidity. Because of the limited quality of the data used to construct the corrosion model, the sensitivity of the corrosion profile to the corrosion model parameters is here examined.

The sensitivity of the corrosion rate as a function of moisture content is examined by running simulations for Baltimore where only the corrosion function (Eq. (4.1)) is varied. The parameter $A$ is not studied, as it changes the whole corrosion profile proportionally; that is, if $A$ were doubled, the result would be doubling the entire corrosion profile. The parameter $B$, physically the width of the distribution, is varied from 0.1 to 2 in increments of 0.1 (compared with the original value of 0.83) (Fig. 4-9a). The threshold value, represented by $C$ is varied from 14 to 34 in increments of 1 (compared with the original value of 24) (Fig. 4-10a).

Of the two parameters, the corrosion profile is less sensitive to $B$. Increasing $B$ from 0.83 to 2 results in nearly no change.
in the profile. Intuitively, this can be expected because $B$ represents the steepness of the transition. Because the original function already had a steep transition, and the function approaches the Heaviside function as $B$ gets arbitrarily large, the corrosion profile is nearly at its limiting case to begin with. Decreasing $B$ causes an increase in the total corrosion and a smoothing of the transition from the corrosion maximum to the lowest amount of corrosion. At the lowest values shown, corrosion occurs along the entire length of the fastener. However, a close examination of Figure 4-9a reveals that in these cases, the corrosion rate is non-zero at very low moisture contents, which may be unphysical. For example, Baechler measured no corrosion for metals embedded in wood at 27 °C and 65% RH (~12% MC) for 20 years (Baechler 1949). In short, it appears that within physical limits, the corrosion profile is not highly sensitive to $B$.

The parameter $C$, a measure of the transition moisture content, affects both the shape and magnitude of the corrosion profile. As $C$ is increased to higher moisture contents, the curve retains its shape; however, the corrosion maximum is decreased and the depth at which there is no corrosion moves towards smaller values. Even with a threshold value of 34% MC, which is greater than the fiber saturation point of southern pines where free water exists in the lumina (Stamm 1929), the corrosion profile retains its shape. As $C$ is decreased to lower moisture contents, the profile increases in magnitude and begins to broaden. The maximum in the corrosion profile increases rapidly as the threshold decreases, nearly doubling as the threshold is lowered from 24 to 14.

In summary, the corrosion profile is much more sensitive to the moisture content threshold of corrosion, i.e., parameter $C$, than to the steepness of the corrosion model, parameter $B$. As $B$ increases, the corrosion rate as a function of moisture content approaches a Heaviside function, which would only require two parameters. The goal of this sensitivity analysis was to aid future experiments determining the corrosion rate function. From this analysis, it appears that most of the work should involve carefully determining the corrosion threshold by focusing the measurements around this value rather than taking measurements over a broad range of moisture contents to precisely observe the distribution.

Conclusions

This paper presents a combined hygrothermal/corrosion model for simulating the corrosion of metals embedded in wood. The model is developed to aid in the design of wood/metal assemblies used in exterior construction. Several U.S. cities are examined with the model using reference years based upon precipitation. Although in general cities with a high annual rainfall or number of hours of rain exhibit high corrosion, there are several exceptions.

The simulations show that in most cases, corrosion is confined to the first 10 mm below the wood surface. The highest corrosion occurs 1–3 mm below the surface of the wood. For built-wet construction, the simulated wood joist dries to below the corrosion threshold within the first 3 months. The sensitivity of the function that relates moisture content to corrosion is examined. We found that the corrosion profile is more sensitive to the corrosion threshold than the width of the transition from no corrosion to the maximum corrosion rate.

There are several logical extensions to the currently presented work. First, the combined model could be compared with a field corrosion test that includes monitoring of environmental conditions and wood moisture content. Second, the hygrothermal properties of ACQ-treated Southern Pine could be better characterized, including temperature dependencies. Third, the corrosion model could be improved with further experiments to locate the corrosion threshold. Finally, it may be worthwhile to develop a more systematic method for selecting reference years for exterior structures.

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Inc.


Chapter 5

Synthesis of Published and Unpublished Corrosion Data from Long-Term Tests of Fasteners Embedded in Wood: Calculation of Corrosion Rates and the Effect of Corrosion on Lateral Joint Strength

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Abstract

In the past 5 years, several accelerated test methods have been developed to measure the corrosion of metals in contact with wood. It is desirable to contrast these accelerated results against those of long-term exposure tests. While there have been several published long-term exposure tests performed on metals in treated wood, the data from these studies could not be used as a comparative baseline because the formulations and retentions of the preservatives were not reported or the amount corrosion was presented as percent mass loss instead of a true corrosion rate because the surface areas of the fasteners were unknown. This work reexamines four reports (two unpublished) that measured the corrosion of metals in treated wood. Where possible, the composition of the preservatives is reported from the original laboratory notebooks. In all cases, the percent mass loss data are presented in terms of a true corrosion rate by calculating the surface areas of the fasteners. The second part of this paper uses the long-term corrosion rates to calculate the reduction in capacity of the joint using the yield theory equations from the National Design Specification for Wood Construction. Specific examples illustrate the loss of capacity with time using measured corrosion rates for wood treated with chromated copper arsenate and alkaline copper quaternary.

Keywords: preservative-treated wood, corrosion, yield theory, chromate copper arsenate (CCA), alkaline copper quaternary (ACQ)

Introduction

In the past five years, there have been numerous studies on corrosion of metals in treated wood (Kear and others 2009; Zelinka and others 2008b; Kear and others 2008a,b; Zelinka and others 2007, 2009; Zelinka and Rammer 2009). These studies were focused on determining the corrosiveness of new wood preservatives that have become widely used since chromated copper arsenate (CCA) was voluntarily withdrawn for residential use in the United States on January 31, 2003. These studies have shown that wood treated with new preservatives such as alkaline copper quaternary (ACQ) and copper azole (CuAz) are more corrosive than CCA-treated wood by a factor of between 2 and 19 depending on the metal and the environment (Kear and others 2009; Anon 2008). CCA-treated wood has been successfully used for many years with few corrosion problems (Burkholder 2004); however, the original research on CCA-treated wood never measured corrosion rates, nor was the effect of corrosion on joint strength analyzed. In other words, while CCA-treated wood may present an “acceptable” level of corrosion, this level is not well characterized. Furthermore, even if it were well characterized, knowing the difference in corrosion rates between ACQ and CCA lacks meaning unless it can be put into the context of mechanical performance.

To answer these questions, we conducted a review of two papers that measured long-term corrosion rates (14–20 years). The goal was to convert the data, which were originally published as a percent weight loss into corrosion rate so that it could be compared with current work on newer wood preservatives. On conducting this investigation, two additional unpublished reports on fastener corrosion were found in the archives at FPL. While these reports pre-date the use of CCA as a preservative, they contain valuable information about the mechanism of corrosion in treated wood: one report examines the effect of copper on the corrosion rate, and the other examines combining copper with arsenates and chromates individually (the building blocks of CCA). All four of these reports, with pertinent experimental details, are summarized here along with the
data, which we transformed from the originally reported percent weight loss to a corrosion rate. The conversion was accomplished by finding archived photographs, and using a novel method to calculate the surface area of the fastener from a photograph (Rammer and Zelinka 2008, 2010). To give a common basis to compare different treatments, the concentration of copper is presented as kilograms of copper per cubic meter of dry wood is included along with the more traditional “retention” of the preservative.

The second part of this paper explores how corrosion, through a reduction in fastener diameter, affects the lateral strength of nailed connections. The reduction in capacity is calculated from yield theory equations given in the National Design Specifications for Wood Construction (NDS). Specific examples are shown comparing the reduction in capacity as a function of time for corrosion rates measured for ACQ and CCA-treated wood.

### Part I: Synthesis of Published and Unpublished Data

#### Corrosion of Nails in CCA- and ACA-Treated Wood in Two Environments (Baker 1992)

**Significance and Overview**

In his study, “Corrosion of Nails in CCA- and ACA-Treated Wood in Two Environments,” Baker (1992) conducted the most recent long-term corrosion study on metal fasteners in preservative treatments. This work has special significance as it strongly influenced the International Building Code’s statements on corrosion of metals in treated wood (Anon 2003). Despite its widespread use, implications for design codes and building practices, data from this report were only presented in the form of percent weight loss. The original laboratory notebook, which contained photographs of the fasteners, was used to calculate a corrosion rate in µm yr⁻¹. In going through the laboratory notebook, we discovered unpublished experimental details such as the exact compositions of the preservatives used. Additionally, uncorroded galvanized fasteners from the original study were found that have now been analyzed to obtain the coating thickness and elemental composition. We first present a brief summary of the test details, followed by the new information on the preservative treatment and galvanized fasteners, before finishing with the transformation of percent weight loss data to corrosion rates.

**Experimental Details**

Southern Pine (*Pinus* spp.) was treated to a retention of 9.7 kg/m³ (0.6 lb/ft³) with one of three different preservatives: “CCA-I,” “CCA-II,” or ammoniacal copper arsenate (ACA) (Table 5-1). The resulting copper concentrations for CCA-I and II were 1.39 and 1.50 kg m⁻³, respectively. Nails were driven through two pieces of preservative-treated wood to simulate how nails are used in service. There was a 0.8-mm (1/32-in.) spacer between the two pieces of wood so that all test replicates had the same availability of water and oxygen. Specimens were either buried underground at a test site near Madison, Wisconsin, or exposed to a constant 27 °C (80 °F), 95% RH environment; replicates were removed at 1, 3, and 17 years for the underground exposure, and at 1, 3, and 14 years for the humidity chamber exposure. Eleven different fasteners were tested, which included six different materials (copper, silicon bronze, two stainless steels- UNS S30400 and S30160, a nickel alloy-UNS 04400, and an aluminum alloy- UNS A95056) and five different types of coated steel (hot-dip galvanized, mechanically galvanized, electroplated galvanized, cadmium coated steel, and a tin-cadmium alloy coated steel).

**Treating Statistics**

Official correspondence (Letter from Andrew Baker to Ray Lindberg of Reynolds Metal Company, Richmond, Virginia, dated December 13, 1973) found in Baker’s study file contained detailed information on the preservative treatments used in the study and are given in Table 5-1. It is instructive to compare these formulations to the standardized CCA formulations also summarized in Table 5-2 (AWPA 2007). The standardized formulations vary in the ratio of copper, chromium, and arsenic with the current formulation referred to as CCA-C. It is clear from the table that the composition of Baker’s CCA-II is the same as the formerly standardized CCA-B. It also appears that Baker’s CCA-I is similar to the formerly standardized CCA-A. However, it should be noted that the preservatives that Baker used were made from the “salt” formulation of chromic acid and arsenic acid, which is

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**Table 5-1. AWPA standardized formulations (Anon 2007) of CCA (A-C) as well as the formulations used by Baker (1992)**

<table>
<thead>
<tr>
<th></th>
<th>Copper (weight percentage as CuO)</th>
<th>Chromium (weight percentage as CrO₃)</th>
<th>Arsenate (weight percentage as As₂O₅)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCA-A</td>
<td>18.1</td>
<td>65.5</td>
<td>16.4</td>
</tr>
<tr>
<td>CCA-B</td>
<td>19.6</td>
<td>35.3</td>
<td>45.1</td>
</tr>
<tr>
<td>CCA-C</td>
<td>18.5</td>
<td>47.5</td>
<td>34.0</td>
</tr>
<tr>
<td>CCA-II*</td>
<td>17</td>
<td>61</td>
<td>22</td>
</tr>
<tr>
<td>CCA-II*</td>
<td>20</td>
<td>35</td>
<td>45</td>
</tr>
</tbody>
</table>

Corrosion of Fasteners in Wood Treated with Newer Wood Preservatives

Recent work on corrosion in treated wood has used CCA-C as a baseline preservative. Therefore, it is instructive to have a short discussion on the differences in these preservatives and how these differences may affect corrosion. It has been shown that the corrosion mechanism in wood involves the reduction of cupric ions and that the higher the copper concentration in the treated wood, the higher the corrosion rate (Kear and others 2009; Zelinka and others 2008b). On the other hand, hexavalent chromium is widely known as a corrosion inhibitor and it has been speculated that the arsenates in CCA may also act as inhibitors (Zelinka and others 2007). From this information, we would expect CCA-B, with the highest copper concentration and the lowest chromate concentration to be the most corrosive, and CCA-A with the lowest amount of copper and the greatest amount of chromates to be the least corrosive. In fact, however, the opposite was observed; based on percent weight loss, CCA-II was less corrosive than CCA-I. Regardless, CCA-I and CCA-II should give lower and upper bounds on the corrosiveness of the CCA-C used in modern experiments because the composition of CCA-C lies between these two extremes.

Galvanized Fastener Details

A hot-dip galvanized nail with the same stock number as those used in the experimental work was found in the study file. To determine the galvanized coating thickness the fastener was cross sectioned, polished, and viewed in SEM. The coating thickness was measured at several locations and the average coating thickness was 24 µm (Fig. 5-1). Additionally, EDS was used to detect the composition of the galvanized coating (Fig. 5-2). Chromium was found on the fastener, which suggests that a chromate conversion coating was applied to the fastener post-galvanizing.

**Table 5-2. Corrosion rates measured by Baechler (1949) after 20 years of exposure for carbon steel. The ‘—’ indicates that the corrosion rate was much smaller than the uncertainty in the measurement. Measurements at a specified RH were taken at 27 °C.**

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Relative humidity (%)</th>
<th>Test fence</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>— — 6 &lt;1</td>
<td></td>
</tr>
<tr>
<td>11.3 kg m⁻³</td>
<td>— — 17 1</td>
<td></td>
</tr>
<tr>
<td>Zn Cl (s)a</td>
<td>— — 21 1</td>
<td></td>
</tr>
<tr>
<td>22.6 kg m⁻³</td>
<td>— — 21 2</td>
<td></td>
</tr>
<tr>
<td>Zn Cl (ns)b</td>
<td>— — 21 1</td>
<td></td>
</tr>
<tr>
<td>ZnCl + Na₂Cr₂O₇ (ns)</td>
<td>— — 21 2</td>
<td></td>
</tr>
</tbody>
</table>

*aSeasoned (allowed to dry) after treatment.

*bNot seasoned.

Corrosion Rates

The study file contained several different pictures that were suitable for calculating the surface areas of the fasteners (for example, Fig. 5-3). However, because the photographs were not taken with a scale marker in the picture, an approximation was needed to convert the surface area (in pixels) to physical units. The image was calibrated by setting the width of the UNS30160 stainless steel fastener in Table 5-2 to its standardized width. Combined with the starting and final masses recorded in the laboratory notebook, we were then able to calculate a corrosion rate for Baker’s data. The results for galvanized steel and aluminum exposed in a humidity room are shown graphically in Figure 5-4; we found that the corrosion rates for stainless steel and the nickel alloy were negligible given the uncertainties in the measurements. Baker found a linear relationship between percent
weight loss and time between 1 and 17 years. Given this constant corrosion rate, 1-year corrosion rate data should be sufficient for extrapolation of long-term corrosion performance (Baechler 1949).

H2 Corrosion of Metal Fastenings in Zinc Chloride-Treated-Wood After Twenty Years (Baechler 1934)

Significance and Overview

In his study, Baechler conducted the longest known study on the effect of chemical treatments on the corrosion of metal fasteners. This work is significant in two regards: (1) it contains the only long-term (>1 year) corrosion data on untreated wood and (2) it measures the corrosion rate at several moisture contents. More recent research has shown that the corrosion rate depends strongly on wood moisture content, although the only quantitative observations of this dependence used polarization resistance in solid wood. However, these measurements fail to take into account that the resistivity of solid wood changes by several orders of magnitude in this moisture content regime (Short and

![Figure 5-3. Photograph of the fasteners tested by Baker after 1-year exposure to soil. Several similar photographs were found and used to calculate the surface areas of fasteners tested to get a true corrosion rate.](image)

![Figure 5-4. Corrosion rates (in µm y⁻¹) measured by Baker in a 27 °C, 95% RH environment. Error bars represent the uncertainties in the mean.](image)
Dennis 1997; Zelinka and others 2008a). As with the work of Baker, we discovered additional unpublished photographs in the study file. These photographs are included, as well as the corrosion rates based off of the weight loss measurements and surface areas calculated from the photographs. We present a brief description of the experimental testing before presenting the corrosion rate data. Because the two unpublished studies used the same fasteners and same methods for removing the corrosion products as this study, these details are highlighted in more thoroughly in this summary.

Experimental Details

Baechler measured the weight loss of three different fasteners in contact with treated and untreated ponderosa pine (Pinus ponderosa) exposed to four different environmental conditions. The treatments consisted of four different levels of zinc-chloride preservative and an untreated control. Two treatments, one with a net retention of 22.6 kg m\(^{-3}\) of dry zinc-chloride and the other with a net retention of 11.8 kg m\(^{-3}\) were applied and then allowed to return to their original moisture content prior to the corrosion tests. The time it took for the specimens to return to their pretreatment moisture content was approximately 6 months. Two other treatments were applied shortly before the corrosion test and were not allowed to dry. The first of these treatments had a net retention of 24.2 kg m\(^{-3}\) zinc chloride and the second treatment was a mixture of two parts zinc chloride to one part sodium dichromate by weight, with a net retention of 24.2 kg m\(^{-3}\) of total salt. Untreated pine was also tested.

Three different fasteners were tested: a No. 4 common wire nail, a No. 6 brass screw, and a 38-mm long galvanized steel nail. The mass loss of the galvanized fasteners was not recorded, although visual observations were recorded. The corrosion products were removed by immersing the fasteners in a solution of 10% ammonium citrate in water. This procedure was found to reduce the mass of uncorroded nails in an ancillary experiment by 0.25% (a 0.04-g change on 10 fasteners with an original weight of 16.16 g). We have accounted for extra mass loss due to cleaning in the corrosion rate calculations.

The outdoor exposure took place on a fence at Madison, Wisconsin. It is unclear whether the test pieces were exposed parallel or perpendicular to the ground but it was stated the specimens had a southern exposure. Photographs of the laboratory during this time frame show test fences on the second floor roofs, and we believe that the Baechler's corrosion specimens may have been exposed on these racks. In addition to running outdoor exposure experiments, sets of similar specimens were exposed to a constant temperature of 27 °C, (80 °F) and a constant relative humidity of 30%, 60%, or 90% for 20 years. The estimated equilibrium moisture contents associated with those conditions are 6%, 12%, and 20% (Glass and Zelinka 2010).

Corrosion Rates

A photograph of the fasteners after the exposure test (Fig. 5-5) was found in Baechler's study file and used to calculate the surface area of the fasteners. Because no scale bar was included in the photograph, we assumed that the width of the carbon steel fastener was equal to its standardized width when calculating the surface area. The resulting corrosion rates for carbon steel nails are given in Figure 5-4; the corrosion rates for the brass screws were smaller than the uncertainties in the calculations for all conditions. The uncertainties in the measurement are large because the balance used by Baechler could only measure to the nearest 0.01 g. Corrosion rates for times fewer than 10 years are not presented for the same reason. Although measurements were taken at several moisture contents, the trend in corrosion rate with moisture content cannot be inferred from the data because the corrosion rates are so low. The difference between the seasoned and unseasoned results most likely occurred because of a high initial corrosion rate during the first 6 months as the boards dried from a completely saturated condition. From the 20-year study, a baseline corrosion rate for untreated wood in a 20% moisture content environment is 6 µm/y, whereas the 6%, 12%, and exposed test fence indicated little or no corrosion.

Significance and Overview

In his unpublished report, Tests on Stakes Treated With Copper Arsenate and Copper Chromate By the Double Diffusion Process, (filed March 13,1944), Baechler evaluated wood treated with copper arsenate and copper chromate. In addition to the corrosion tests, which will be presented in detail, the treated wood was also examined for decay and termite attack. One significant aspect of this work is that it is possible, in a limited sense, to evaluate the effects of chromates and arsenates separately. In dilute CCA studies, we observed that both the chromates and arsenates were acting as corrosion inhibitors, although no published studies have examined the role of the individual components on fastener corrosion (Zelinka and others 2007).

Experimental Details

In addition to untreated controls, Southern Pine (Pinus spp.) was treated with one of two different preservative combinations; each combination was tested at two retentions (Table 5-3). The first combination contained copper sulfate and sodium arsenate, with a copper sulfate retention of 5 kg m\(^{-3}\) (light) or 11 kg m\(^{-3}\) (heavy) and a sodium arsenate concentration of 3 kg m\(^{-3}\) (light) 12 kg m\(^{-3}\) (heavy). The other combination contained copper sulfate with a retention of 5 kg m\(^{-3}\) (light) or 14 kg m\(^{-3}\) (heavy) and sodium chromate with a retention of 8 kg m\(^{-3}\) (light) or 25 kg m\(^{-3}\) (heavy).

Specimens were then placed outdoors in Saucier, Mississippi, and Madison, Wisconsin, although no data are reported
from the specimens located at Madison, Wisconsin. Specimens were exposed for 2 years.

Three types of fasteners, nominally the same as those in the 20-year study, were tested: a No. 4 common wire nail, No. 6 brass screw and a 38 mm long galvanized steel nail (Baechler 1949). The same cleaning methods that were described earlier were used in this study. Weight loss was only determined for the carbon steel nails. All fasteners were graded qualitatively on a four point scale from “perfect condition” to “very rusty.” For the fasteners where weight loss was measured, individual measurements were not taken because the balance had a precision of only 0.01 g, and the average mass of an uncorroded steel fastener was ~1.5 g. Instead, to decrease the uncertainties in the mass loss measurements, the entire group of 5 fasteners was weighed before and after exposure to get an average percent weight loss. Using the surface areas calculated from the 20-year study, we have converted these to a corrosion rate.

**Results**

The corrosion rate data are given in Table 5-3. Although none of these formulations are currently used as wood preservatives, they represent subcomponents of CCA. For this reason, it is interesting to look at differences between the preservatives with only chromates and those with only arsenates to better understand the corrosiveness of CCA-treated wood. For the treatments with the light copper retention, the corrosion rate of the treatment with chromate was roughly the same as that of the untreated wood, whereas the corrosion rate was 4 times larger with the arsenates. Similar trends were also seen in the data with a higher amount of copper. From this data it appears that the chromates are primarily responsible for mitigating the corrosiveness of CCA. Previously, it had been speculated that arsenates may also play a role in inhibition but these data suggest that at best it is secondary to the effect of chromates.

**Significance and Overview**

In their study, *The Corrosion of Wire Nails in Wood Treated With Copper Sulphate*, Bateman and Baechler (1938) evaluated an experimental method for wood preservation
Corrosion of Fasteners in Wood Treated with Newer Wood Preservatives

where the preservatives are injected into a living tree. Corrosion tests were performed on shortleaf pine (*Pinus echinata*) specimens that had been injected with copper sulfate prior to felling. Because of the unusual treating method, each group of fasteners was exposed to a different amount of copper. The actual copper concentration in the wood near each group of fasteners was measured in a separate experiment. No untreated controls were included.

Experimental Details

Trees were injected with copper sulphate and then felled. Sections along the length of tree were then cut. The nails were driven directly into these sections around the circumference. No. 4 common wire nails, nominally the same as those used in previous studies, were used in this study and the corrosion products were removed with the same methods described previously (Baechler 1949). The wood–metal assemblies were exposed to one of two constant temperature, constant humidity conditions: 27 °C, 30% RH or 27 °C, 75% RH and removed at intervals between 3 and 24 months. It is not clear from the study documents whether the wood was conditioned prior to the test. However, data appear to indicate that the wood must have been green when the fasteners were driven; the corrosion rate decreases with exposure time, and even fasteners exposed to the 30% RH condition have a high corrosion rate (10–47 µm yr⁻¹), contrasted with the negligible corrosion rates found for the same conditions in Table 5-2. The report includes the actual copper retentions in each section of wood, but the method used to measure the retention is not given.

Experimental Results

Selected data from the 75% RH condition are shown in Figure 5-6. Two major trends can be seen in the data. The same trends appear in the remainder of the data, which were removed from the figure for clarity. The first trend is that the corrosion rate increases with increasing copper concentration. For example, between the extreme points on the curve, the copper concentration changes by a factor of ~12 and the corrosion rate changes by a factor of ~5. This ratio remains constant over all exposure times. The second trend is that the corrosion rate decreases with time. Two possibilities can explain this decrease. The first is that the nails were driven into green wood and the specimen was drying during the exposure period. An alternate explanation is that protective corrosion products were formed during this period that reduced the corrosion rate. However, because corrosion rates are so high for this environment, we believe the former explanation is the correct one.

**Part II: Effect of Corrosion on the Lateral Joint Strength**

The single-fastener connection performance is dependent on the joint geometry (thickness of main and side members), fastener diameter, dowel bending-yield strength, dowel-bearing strength, and direction of load to the grain. Yield expressions relating these parameters were developed by Johansen using a static analysis that assumes the wood and the metal dowel fastener are both perfectly plastic (Johansen 1949). After nearly a decade of development, the yield model became the standard for dowel connection design in the 1991 NDS and is applicable to all types of dowel fasteners—nails, lag screws, and bolts (Aune and Patton-Mallory 1986; McLain 1992; McLain and Thangjitham 1983; Soltis and Wilkinson 1987; Soltis and others 1986; Wilkinson 1993). The yield model theory selects the worst case of yield modes based on different possibilities of wood bearing and nail bending. Mode I is a wood-bearing failure in either the main or side member; mode II is a rotation of the fastener in the joint without bending; modes III and IV are a combination of wood-bearing failure and one or more plastic hinge yield formations in the fastener. For a two member nailed joint, the lateral design load $Z$ (N) of a joint is determined by the minimum of the following yield expressions:

$$Z = \min\left\{ \frac{Dk_sF_{es}}{2.2} \quad \text{(Mode I_s)} \right\}
\left\{ \frac{k_2Dl_pF_{em}}{2.2(1+2R_e)} \quad \text{(Mode III_m)} \right\}
\left\{ \frac{k_3Dk_sF_{em}}{2.2(2+R_e)} \quad \text{(Mode III_s)} \right\}
\left\{ \frac{D^2}{2.2} \sqrt{\frac{2F_{em}F_{yb}}{3(1+R_e)}} \quad \text{(Mode IV)} \right\}$$

where
where $D$ is the dowel diameter (mm), $F_e$ is the dowel bearing stress of the main (m) or side (s) member (MPa), $F_{yb}$ is the bending yield stress of the nail (MPa), $l_p$ is the length of penetration into main member, and $t_s$ is the thickness of the side member. For determining the effect of corrosion on the lateral fastener strength two assumptions are made. The first is that corrosion occurs uniformly along the length of the fastener and the corrosion rate can be treated as a constant reduction in diameter with time. The second assumption deals with the effect of moisture content on the wood dowel bearing strength. We assume that the wood moisture content at failure is greater than 19% MC; in this regime, the dowel bearing strength does not depend on moisture content (Rammer 2001). This is reasonable as it is likely that the moisture content is greater than 19% if corrosion is occurring.

Figure 5-7 illustrates the effect of corrosion on the lateral strength of single shear nailed joint for a hot-dip galvanized 8d nail (3.05 mm) for different wood preservatives using historical CCA data from Baker (Fig. 5-4) and recent data collected by Zelinka and Rammer (2009) on ACQ-treated wood (retention of 4 kg m$^{-3}$). The below analysis assumes a constant corrosion rate with time, even after the galvanized coating has been consumed. Future work could include a change in corrosion rate once the reduction in diameter exceeds the coating thickness. The reduction in capacity depends upon the side member thickness, which, along with the diameter, determines the failure mode.

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

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

and

$$R_e = \frac{F_{cm}}{F_{es}}$$

Figure 5-7. Percentage reduction of capacity as a function of time for an 8d (3.05 mm) fastener embedded in wood with an assumed corrosion rate of 10 (A) or 60 (B) $\mu$m y$^{-1}$, which correspond to corrosion rates measured in hot-dip galvanized steel at 27 °C, 100% RH for CCA- and ACQ-treated wood, respectively (Baker 1992, Zelinka and Rammer 2009). Each contour represents a 10% loss in capacity; note the difference in the time axes.

For the narrow side member, the reduction is directly related to the reduction of nail diameter due to corrosion. As the side member thickness increases, the reduced diameter will affect both the bearing and nail bending performance. For large enough side member thicknesses, the joints will fail in Mode IV, which is independent of the wood thicknesses. Because most of the work on corrosion in wood has examined decking nails, and the most common decking material in the United States of America is “5/4 radial deck board” (25 mm thick), it can be expected that decking nails will exhibit a Mode IV failure, in which case a simpler diagram can be made (Fig. 5-8). In this failure mode, the capacity of the connection is proportional to the square of the fastener diameter.
In all cases, corrosion rates from laboratory experiments were used to calculate the reduction in capacity with time. Wood exposed in outdoor conditions will most likely experience fluctuations in moisture content, and may have higher or lower corrosion rates than those used in these calculations. Recent changes to ACQ formulations and treatment retentions may have also lessened the corrosiveness to treated wood.

**Summary and Conclusions**

This paper reevaluated two classic reports on the corrosion of metals in wood and presented the data as a corrosion rate. Two smaller, unpublished reports were also summarized that give insight into role of the components which comprise CCA. One of these reports highlighted the effect of copper concentration on the corrosion rate of carbon steel. The other report showed that the chromate in CCA acts as a corrosion inhibitor, whereas the arsenate has a smaller if any effect.

From these uniform, constant corrosion rates, a reduction in diameter with time was calculated, and this in turn was used in the yield theory equations to calculate the reduction in lateral joint strength. For decking materials, the fasteners are expected to exhibit a Mode IV failure where the reduction in joint capacity is related to the square of the diameter. This dependence results in the capacity being quite sensitive to the corrosion rate.

**References**


Chapter 6

Modeling the Effect of Nail Corrosion on the Lateral Strength of Joints

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Abstract
This article describes a theoretical method of linking fastener corrosion in wood connections to potential reduction in lateral shear strength. It builds upon published quantitative data of corrosion rates of metals in contact with treated wood for several different wood preservatives. These corrosion rates are then combined with yield theory equations to calculate a loss in lateral capacity as a function of time. The calculations are straightforward and can be performed in a spreadsheet or simple computer program. They can accommodate time-dependent and moisture-dependent corrosion rates. The latter of these capabilities can easily be recognized as important inasmuch as corrosion rates of fasteners are recognized as being dependent on moisture content of the wood in which they are embedded. The calculation method is dependent on corrosion rates, and the method is therefore limited by the lack of agreement in corrosion rates presented in the literature. Within these limitations, the article examines how different corrosion rates and changes in corrosion rates affect the mechanical properties and service life of nailed wood joints.

Keywords: Corrosion, metal, wood, yield theory, preservative-treated wood

Introduction
Since the voluntary withdrawal of chromated copper arsenate (CCA) as a wood preservative for residential construction in January 2004, the corrosion of metals in contact with preservative-treated wood has been a research emphasis. In addition to numerous articles on the mechanism of corrosion in treated wood (e.g., Kear and others 2009; Zelinka and others 2010; Zelinka and Stone 2010, 2011), a standard has also been developed to measure the corrosion rates of metals embedded in treated wood (ASTM 2011). The emphasis of corrosion research has been on quantifying the metal corrosion rate in units of depth of metal wastage per unit of time. The previous work represents a significant improvement in the understanding of how metals in wood corrode. However, because metals in wood are used to fasten two wooden members together, the loss in joint strength with time is just as important as the amount of metal that has corroded. Nguyen and others (2011) have highlighted the importance of incorporating corrosion into a reliability based timber engineering design code and proposed a preliminary model to do so based upon time of wetness for untreated and CCA-treated wood.

This article extends previous work on the degradation of wood–metal connections by examining how metal corrosion leads to a loss of structural capacity of a laterally loaded nailed joint. The reduction in lateral capacity is calculated from yield theory equations given in the National Design Specifications (NDS) for Wood Construction (American Wood Council 2012). Specific examples are shown comparing the reduction in lateral capacity as a function of time for corrosion rates measured for untreated, alkaline copper quaternary (ACQ)-treated and CCA-treated wood.

Method for Calculating the Loss of Lateral Capacity

Yield Theory Equations
Single-fastener connection performance is dependent on joint geometry, fastener diameter, dowel bending-yield strength, dowel-bearing strength, and direction of load to the grain. Yield expressions relating these parameters were developed by Johansen (1949) using a static analysis that assumes the wood and the metal dowel fastener are both perfectly plastic. After nearly a decade of development, the yield model became the standard for dowel connection design in the 1991 NDS and is applicable to all types of dowel fasteners—nails, lag screws, and bolts (Aune and Patton-Mallory 1986; McLain 1992; McLain and Thangjitham 1983; Soltis and others 1986; Soltis and Wilkinson 1987; Wilkinson 1993). The yield theory model selects the worst case of yield modes based on different possibilities of wood bearing and nail bending. Mode I is a wood-bearing failure in either the main or side member, Mode II is a rotation of the fastener in the joint without bending, and Modes III and IV are a combination of wood-bearing failure and one or more plastic hinge yield formations in the fastener. In addition to yield modes, we have included the transverse shear
of the fastener as a possible failure mode. For a two-member nailed joint, the lateral design load \(Z(N)\) of a joint is determined by the minimum of the following yield expressions because a Mode II failure is not expected for smaller diameter fasteners such as nails:

\[
Z = \min \left\{ \frac{DT_p F_{es}}{2.2} \left( \frac{k_2 D l_p F_{em}}{2.2(1 + 2R_c)} \left( \frac{k_3 D l'_p F_{em}}{2.2(2 + R_c)} \right) \right) \right. \\
\left. \left. \frac{D^2}{3(1 + R_c)} \left( \frac{2F_{em} F_{yb}}{2F_{em}} \right) \right) \right. \\
\left. \frac{3nd^2}{16} \left( F_v \right) \right. \right. \\
\left( \text{Mode I}_s \right) \\
\left( \text{Mode III}_m \right) \\
\left( \text{Mode III}_b \right) \\
\left( \text{Mode IV} \right) \\
\left( \text{Fastener shear} \right)
\]

where

\[
k_2 = -1 + \sqrt{\frac{2F_{yb}(1 + 2R_c)D^2}{3F_{em}^2}} \\
k_3 = -1 + \sqrt{\frac{R_c}{3F_{em} T_s^2}} \\
R_c = \frac{F_{cm}}{F_{es}} \quad \text{and} \quad F_v = \frac{F_{yb}}{\sqrt{3}}
\]

and where \(D\) is the dowel diameter (mm), \(F_{es}\) is the dowel bearing stress of the main (\(m\)) or side (\(s\)) member (MPa), \(F_{yb}\) is the bending yield stress of the nail (MPa), \(l_p\) is the length of penetration into the main member, and \(T_s\) is the thickness of the side member. For a shear failure, the yield shear stress is determined from \(F_{yb}\) because pure shear occurs on \(45^\circ\) planes and \(F_{yb}\) is representative of the material tensile yield stress for a fully plastic section.

In the following examples illustrating the effect of corrosion on the lateral fastener strength, several assumptions were made. The first assumption is that the corrosion only reduces the section modulus of the nail, not \(F_{yb}\) or the elastic modulus of the fastener. Practically, this assumption is implemented also assuming uniform corrosion over the entire nail and using the corrosion rate as a constant reduction in diameter with time. The other assumptions deal with the dowel-bearing strength. It is assumed that the corrosion byproducts do not affect \(F_e\) and that at failure, the wood moisture content is greater than 19%; in this regime, the NDS treats dowel-bearing strength as independent of moisture content (Rammer 2001). This is reasonable because it is likely that the moisture content is greater than 19% if corrosion is occurring (Baker 1988; Short and Dennis 1997).

For a given joint geometry, wood species, and fastener-bending yield stress, the equations depend only on the fastener diameter, which is a function of the corrosion rate. Corrosion rates for metals in wood will be reviewed in the following section. These corrosion rates will then be used throughout the article to examine the relative lateral capacity of nailed joints in many different scenarios.

### Corrosion Rates of Metals in Contact with Treated Wood

Since the voluntary withdrawal of CCA for use in residential construction, many experiments have measured the corrosion of metals in ACQ- and CCA-treated wood (Freeman and McIntyre 2008; Kear and others 2009; Zelinka and Rammer 2009; Zelinka and others 2008). However, there is little agreement between these measurements; the measured corrosion rates from these tests have a wide range of values, for example, from 2 to 113 µm y\(^{-1}\) and from 1 to 26 µm y\(^{-1}\) for hot-dip galvanized steel in ACQ- and CCA-treated wood, respectively. These wide differences in measured corrosion rates most likely result from experimental differences in temperature, relative humidity, and wood moisture content. The emphasis of this article is on the framework for analyzing how the relative lateral capacity depends upon corrosion rate; therefore, only a few representative corrosion rates will be used in the ensuing analysis. The representative condition chosen for further analysis is 27 °C, 100% RH, which Baechler (1949) chose to simulate outdoor exposures. The condition is chosen because data exist under these conditions for hot-dip galvanized steel in untreated and CCA- treated and ACQ-treated wood and it is one of the most tested environments for wood–metal corrosion (Baechler 1949; Baker 1992; Kear and others 2009; Zelinka and Rammer 2009; Zelinka and others 2010).

The corrosion rate for CCA-treated wood comes from a study conducted by Baker (1992), which reported the percent weight loss for “CCA-I” and “CCA-II”, which were essentially equivalent to modern CCA-A and CCA-B. Zelinka and Rammer (2009) later converted the percent weight loss to a true corrosion rate. Baker’s study involved 11 different types of metal fasteners embedded in CCA-treated and ammoniacal copper arsenate (ACA)-treated wood at 27 °C and 97% to 100% RH for periods of 1, 3, and 14 years. Baker found a linear relationship between percent weight loss and time, which implies a constant corrosion rate assuming a constant surface area. The corrosion rate for CCA-I, which was found constant between 1 and 14 years, is used in the remainder of this article (Table 6-1).

The untreated and ACQ-treated wood corrosion rates come from 1-year exposure tests at 27 °C and 100% RH (Zelinka and Rammer 2009; Zelinka and others 2010). These corrosion rates are assumed to be constant with time, as was observed by Baker in CCA-I-treated wood. This assumption
and its implications are further examined in the Section “Examination of a time-dependent corrosion rate.”

The corrosion rates, treatments, and original source for the data are summarized in Table 6-1 and will be referred to throughout the paper.

### Effect of Corrosion on the Lateral Joint Strength

To illustrate how the yield theory equations can be used to calculate the corrosion in lateral joint strength, we examine the corrosion of an 8d common nail (length, 63 mm; \(D = 3.4 \text{ mm}\)) in treated Southern Pine (\(\text{Pinus spp}.; F_{yb} = 620 \text{ MPa}, F_{cm} = F_{en} = 38 \text{ MPa}\)). We first illustrate how these equations can be used to predict the loss in lateral strength with time for all yield theory modes. We then focus on Mode IV yielding and show the percentage of the original capacity as a function of time. If an arbitrary failure criterion (e.g., 50% of original capacity) were defined, the time to failure could be determined with these data. To illustrate the flexibility and robustness of this methodology, three additional cases are examined. In the first case, a coated fastener is examined. The final two cases examine what happens when the corrosion rate varies with time and moisture content.

### Examination of All Failure Modes

Figure 6-1 presents the reduction in capacity of the lateral strength of single shear nailed joint for corrosion rates of 10 \(\mu\text{m y}^{-1}\) (Fig. 6-1a) and 60 \(\mu\text{m y}^{-1}\) (Fig. 6-1b). These corrosion rates are roughly equivalent to those measured for hot-dip galvanized steel at 27 °C, 100% RH. Each line on the graph represents a 10% reduction in capacity, and the second order discontinuities are a result of a change in failure mode. For a narrow side member that exhibits Mode I behavior, the reduction is directly related to the reduction of nail diameter because of corrosion. As the side member thickness increases, the reduced diameter will affect both the bearing and nail bending performance. For large enough side member thicknesses, the joints will fail in Mode IV, which is independent of the wood thicknesses. Transverse...
fastener shear is never the controlling failure mechanism. Importantly, joints governed by Mode IV have the fastest reduction in capacity with time. Because most of the work on corrosion in wood has examined decking nails, and the most common decking material in the United States is “5/4 radial deck board” (25 mm thick), we can expect that decking nails will most likely exhibit a Mode IV yielding in service. Because of its importance, and because it represents the quickest time to complete strength loss, only Mode IV failures will be considered in the next four cases.

**Examination of Mode IV Yield Mode**

For Mode IV failures, which are expected in decking applications, the reduction in lateral capacity depends only upon the corrosion rate and the initial diameter of the fastener. Figure 6-2 illustrates the reduction in lateral capacity for an 8d nail in a Mode IV failure with several different corrosion rates. The 5 µm y⁻¹ corrosion rate corresponds to galvanized steel in untreated wood, and the 10 and 60 µm y⁻¹ corrosion rates have been described previously (Table 6-1). For Mode IV failures, the yield strength is inversely related to the square of the diameter, which results in the lateral capacity decreasing rapidly with increasing corrosion rate. By arranging the terms, it is possible to express the time to a given percentage of the original capacity, \( t_{50} \), can be given by the following:

\[
 t_{50} = \frac{d_o \left(2 - \sqrt{2}\right)}{4r} \quad (6.3)
\]

This expression is shown graphically for an 8d fastener in the inset of Figure 6-2.

**Examination of a Galvanized Fastener**

For galvanized and other metal-coated fasteners, corrosion rate in the initial stages, when the coating is continuous and completely intact, is equivalent to the corrosion rate of the coating metal by itself. Once the coating has completely corroded away, corrosion proceeds at the rate of the base metal. The measured corrosion rates (Table 6-1) are high enough that a typical hot-dip galvanized fastener (with a coating on the order of 100 µm) would last only a few years before the base metal was completely exposed. Therefore, it is instructive to examine how the above calculations change for coated fasteners, where the corrosion rate experiences a change when the coating has disappeared, that is,

\[
r = \begin{cases} 
r_{\text{coat}} & 0 < t < t_{\text{crit}} \\
T_{\text{coat}} & t > t_{\text{crit}} 
\end{cases} \quad (6.4)
\]

where \( t_{\text{crit}} \) is the time at which the galvanized coating has completely corroded away, given by

\[
t_{\text{crit}} = \frac{T_{\text{coat}}}{r_{\text{coat}}} \quad (6.5)
\]

where \( T_{\text{coat}} \) is the thickness of the coating. Although Equation (6.4) is generally valid, literature values on the ratio of corrosion rates of galvanized steel to plain steel corrosion rates in treated wood vary greatly. Kear and others (2009) and Zelinka and others (2010) both measured the corrosion of metals embedded in wood for 1 year in an environmental chamber at 100% RH. Surprisingly, Kear and others observed that the corrosion rate of galvanized steel was less than that of plain steel, whereas Zelinka observed that the corrosion rate of galvanized steel was greater than that of plain steel.

Given this uncertainty in relative corrosion rates, it is possible that the corrosion rate of a galvanized fastener could increase or decrease once the coating has completely corroded. In either case, the relative lateral capacity as a function of time will depend upon the corrosion rates of both the coating and base metal. The total loss in capacity can be determined by Equations (6.4) and (6.1). Figure 6-3 illustrates the importance of accounting for the corrosion rate of the coating for an 8d nail exhibiting a Mode IV failure, where the galvanized coating is 100 µm thick and has a corrosion rate of 10 µm y⁻¹ (CCA-I, Table 6-1). Along with the “baseline case” where the entire thickness of the fastener has the same corrosion rate, two different scenarios are plotted. In the first case, the ratio of the steel corrosion rate to the galvanized corrosion rate is assumed to be 2.5, as found by Kear and others (2009); in the second, it is assumed to be 0.5, as found by Zelinka and others (2010). It is clear from Figure 6-3 that the corrosion rate of the base metal plays an
Corrosion of Fasteners in Wood Treated with Newer Wood Preservatives

Examining the Role of Corrosion Rates with Time

The above analysis assumes the corrosion rate is constant with time, which is consistent with observations by Baker (1992) for galvanized fasteners embedded in treated wood for times ranging between 1 and 14 years. This is consistent with literature observations of the corrosion rate of galvanized steel exposed to atmospheric corrosion; Legault and Pearson (1978) reviewed the corrosion kinetics of galvanized steel and found that in most industrial and marine environments, galvanized steel exhibited a constant corrosion rate because the corrosion products dissolve in low-pH water/rainwater. Because it is well known that wood is acidic, it is not surprising that galvanized steel exhibits a constant corrosion rate in wood. However, for most other metals and for galvanized steel exposed to less acidic conditions, the corrosion rate usually decreases with time (Zhang 2003).

Many empirical sources have observed that the corrosion kinetics for atmospheric corrosion can be described by

\[ \Delta W = Kt^n \]  

where \( \Delta W \) is the change in weight, \( K \) is a constant (the 1-year corrosion rate), \( t \) is the time in years, and \( n \) is an exponent that controls the kinetics and describes the resistance for ion transport to the metal surface through the corrosion product once it has formed. The limiting case, \( n = 1 \), observed by Baker (1992), corresponds with a constant corrosion rate with time and physically represents a case where the corrosion products do not remain on the surface, or they remain but do not decrease the rate of corrosion. In theory, \( n = 0.5 \) should represent the lower bound, where the reaction is limited by the diffusion of ions to the metal surface. However, values of \( n \) as low as 0.36 have been observed in carbon steels exposed to atmospheric conditions (Legault and Preban 1975).

Although the data suggest that metals in wood exhibits a constant corrosion rate with time (i.e., \( n = 1 \)), only one article examined this behavior (Baker 1992). It is possible that the corrosion rate is not constant, but rather changes with time. If the commonly accepted atmospheric corrosion kinetic model holds for wood, the \( n = 1 \) case represents a worst-case scenario. It is possible but physically unlikely that the corrosion of metals in wood increases with time. In this case, Equation (6.6) would no longer be applicable and a different kinetic model would need to be developed.

By combining Equation (6.6) with the yield theory equation (Eq. (6.1)), it is possible to examine how a decreasing corrosion rate would affect the relative lateral capacity of nailed joints. Fig. 6-4 examines the same case as Fig. 6-2 with a time-dependent corrosion rate (i.e., the 60 µm y\(^{-1}\) curve in Fig. 6-4 is equivalent to the \( n = 1 \) case in Fig. 5-4). The values of \( n \) were selected to be representative of those observed for different classes of materials as observed by Legault and Preban (1975), and the corrosion rate as a function of time is shown as an inset. Any change in \( n \) represents not only a decrease in the corrosion rate but also a deceleration with time and therefore has a large effect on the relative capacity with time.
Examination of a Moisture-Dependent Corrosion Rate

The wood moisture content is the most important environmental variable to the corrosion of metals embedded in wood. Below 15% to 18% moisture content, embedded metals do not corrode (Baker 1987; Short and Dennis 1997). Above this threshold, the corrosion rate increases with increasing moisture content before eventually reaching a plateau (Kear and others 2009; Short and Dennis 1997). Because of this sensitivity, most laboratory corrosion rate measurements have been under conditions where the wood moisture content is either constant or well characterized (e.g., Anon 2007). However, in actuality, wood exposed to the environment can experience large fluctuations in moisture content (Cui and Zahora 2000; Gaby and Duff 1978; Miller and Boxall 1987). Because of these large fluctuations in moisture content and the resulting fluctuations in corrosion rate, a steady-state approximation of the corrosion rate can be misleading.

Recently, Zelinka and others (2011) developed a combined hygrothermal/corrosion model to predict the cumulative corrosion at various points along the length of an embedded fastener as a function of time. The process consists of two steps; the first step is to calculate the wood moisture content profile from hourly climatic data using a hygrothermal model. The second step is to use the moisture content calculated from the hygrothermal model to calculate the metal corrosion rate, which is assumed to be constant over the hour. The hourly amounts of corrosion are summed, resulting in a final output of the depth of the corrosion attack (in micrometers) along the entire length of the fastener. The hygrothermal model uses an existing, validated two-dimensional finite element code to solve the coupled heat and mass transport equations using hourly climatic data as an input (Janssen and others 2007). It predicts moisture content and temperature at various depths within the wood. In the subsequent calculation of corrosion rate, two simplifying assumptions are made: corrosion ceases at temperatures below freezing, regardless of moisture content, and at temperatures above freezing, corrosion rate is solely dependent on moisture content.

The moisture dependence of the corrosion rate was incorporated by fitting the empirical polarization resistance data of Short and Dennis (1997) with

$$ R = \frac{A}{1 + e^{B(C-w)}} $$

(6-7)

where $A$ represents the maximum corrosion rate ($\mu$m y⁻¹), $B$ represents the steepness of the transition from 0 to $A$, $C$ represents the moisture content at which $R = A/2$, and changing $C$ changes the corrosion threshold moisture content. The parameters $B$ (0.83) and $C$ (24) are taken from a fit of the published data of Short and Dennis (1997). The parameter $A$, which is physically the asymptotic corrosion limit, is taken as 52.3 $\mu$m y⁻¹ from recent electrochemical measurements of hot-dip galvanized steel in an extract of ACQ-treated Southern Pine (Zelinka and others 2008).

The result of these simulations is the corrosion profile—the depth of corrosion penetration into the nail shank as a function of position along the length of the nail and of time. Results from a 1-year simulation for a specific reference year in Baltimore, Maryland, are included in Figure 6-5. The reference year was 1989. This year was chosen on the basis of being the 10th percentile year in terms of number of hours of precipitation from 1960 to 1990. For further discussion of the choice of references years see Zelinka and others (2011). As Figure 6-5 shows, the maximum amount of corrosion occurs 0.18 cm below the surface, and the corrosion profile changes throughout the year. This is consistent with empirical observations of corroded fasteners (Kubler 1992). The combined hygrothermal/corrosion model illustrates how fluctuations in moisture content affect the corrosion of embedded fasteners, and the model can be extended using Equation (6-1) to predict the loss in capacity as a function of time.

To illustrate the importance of moisture fluctuations on the corrosion and the resulting loss in lateral capacity, Figure 6-6 was created based upon the 1-year simulation for Baltimore (Fig. 6-5). The analysis uses the same assumptions, but the corrosion rate is calculated from Equation (6-5). Although the moisture content (and therefore the corrosion rate) depends upon the depth below the surface (Fig. 6-5), the analysis assumes a worst case scenario and uses the moisture content at 0.18 cm. Two scenarios are presented in the figure. The first assumes a constant corrosion rate based upon the yearly mean moisture content (33%), and the second uses a different corrosion rate for every hourly output of the simulation. The two analyses...
give quite different results. This is most likely a result of the highly non-linear shape of Equation (6-5), which is nearly a Heaviside function. Because the yearly average moisture content was greater than \( C \), the assumed corrosion rate was higher than the average of the hourly corrosion rate data. Although the average annual moisture content overestimated the amount of predicted corrosion, it should give a conservative bound for design in most cases.

**Summary and Conclusions**

Although the corrosion rates of metals embedded in treated wood are small in absolute terms, this work has shown that fastener corrosion can have a large effect on the lateral strength of nailed joints in outdoor structures. Although the major aim of the article was to present a methodology for practicing engineers to make informed design decisions for specific wood-metal combinations, several interesting conclusions can be drawn from the scenarios examined in this article:

- In most decking applications, a Mode IV yielding of the fastener is expected. In this case the lateral capacity is proportional to the square of the fastener diameter, resulting in the most rapid time to failure (Fig. 6-1). If “failure” is defined as an arbitrary percentage of the original capacity, the time to failure is proportional to the reciprocal of the corrosion rate (Fig. 6-2).

- For galvanized fasteners, the measured corrosion rates suggest that the coating will be completely corroded within a few years. If the base metal has a different corrosion rate than the coating, this results in a large change in the reduction of capacity as a function of time (Fig. 6-3).

- Only a few measurements have examined the corrosion rate of zinc in treated wood as a function of time. The results from the most comprehensive study (Baker 1992) are consistent with a constant, time-invariant corrosion rate. If the corrosion rate decreased with time, this would drastically increase the service life of fasteners (Fig. 6-4). If the kinetics are indeed consistent with Equation (6-6), a constant corrosion rate assumption gives a conservative service life estimation.

- Hygrothermal simulations and a moisture-dependent corrosion rate model give practicing engineers tools to make more accurate predictions of the corrosion rate of fasteners in a given structure. Using an average yearly moisture content gives a conservative bound on the residual capacity (Fig. 6-6).

**Acknowledgments**

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**Literature Cited**


Environmental Degradation of Fiber-Reinforced Polymer (FRP) Fasteners in Wood

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Abstract
This paper examines the durability of fiber-reinforced polymer (FRP) nails in treated wood. FRP nails were exposed to four conditions: (1) accelerated weathering consisting of exposure to UV light and condensation, (2) 100% relative humidity (RH), (3) driven into untreated wood and exposed to 100% RH, (4) driven into ACQ-treated wood and exposed to 100% RH. Changes in the physical, mechanical, and chemical properties were examined with weight loss, dynamical mechanical analysis (DMA), and near-infrared spectroscopy (NIR), respectively. Although fasteners exhibited changes after exposure to treated wood, the changes were not statistically different than the changes that occurred in untreated wood or in the humid environment. Under these three conditions, the fasteners gained 2% to 3% of their starting mass and the storage modulus also increased by 20% after exposure. The results suggest that moisture is more important than the wood chemistry or preservative chemistry in determining the durability of FRP fasteners in wood.

Keywords: nail, preservative-treated wood, dynamical mechanical analysis (DMA), near-infrared spectroscopy (NIR)

Introduction
Although not generally considered an aggressive environment, wood can be corrosive to metal fasteners if it is wet or has been treated with a wood preservative or fire retardant. Prior to 2004, the major wood preservative used in the United States was chromated copper arsenate (CCA) (Lebow 2004). The corrosion of metal fasteners in CCA-treated wood was examined extensively by Baker (1992), who found that fasteners made from hot dip galvanized steel, stainless steel, silicon bronze, and copper gave adequate service life in CCA-treated wood (Anon 2003). However, in 2004, CCA was voluntarily withdrawn by industry for use in residential construction, and its market share has been taken up by a number of alternatives, such as alkaline copper quaternary (ACQ), copper azole (CA), and their corresponding “micronized” formulations (MCQ and MCA, respectively) (Lebow 2004).

The corrosiveness of alternatives to CCA has been researched heavily in the past 5 years as preliminary research (Anon 2008), and anecdotal evidence (Burkholder 2004) suggested that these alternatives were more corrosive than CCA. This recent research has confirmed that in most cases, these preservatives are more corrosive than CCA. For example, Kear and others (2009) tested galvanized steel in many different preservative formulations and exposure conditions and found that ACQ-treated wood was between 3 and 19 times more corrosive than CCA and that CA-treated wood was between 3 and 11 times more corrosive (the range represents differences in retention levels and exposure conditions). Similarly, Zelinka and others found that CA and ACQ were 1.8 and 2.0 times more corrosive than CCA-treated wood for hot-dip galvanized fasteners exposed to a 100% relative humidity environment for one year (Zelinka and others 2010). Zelinka and Rammer have examined the effect of corrosion rate on the degradation in lateral strength of joints in decks and shown that increasing the corrosion rate from 10 to 60 µm yr⁻¹ decreases the time to failure (defined as 50% of the original capacity) by 500% (Zelinka and Rammer 2012). Because alternatives to CCA are more corrosive than CCA and because this difference in corrosion affects the usable life of structures, corrosion of fasteners and joist hangers must be considered when designing and building with treated wood.

There are several ways to minimize corrosion in treated wood. Since the mechanism of corrosion in treated wood involves the reduction of cupric ions, metals noble to copper, such as stainless steel, have much lower corrosion rates in treated wood (Zelinka and Rammer 2009). Another option for minimizing corrosion is using a polymer or ceramic coated fastener to chemically isolate the metal from the treated wood. Finally, a completely non-metallic fastener would be immune to traditional forms of corrosion.
Most of the focus on minimizing corrosion in wood has focused on either using stainless steel or coated fasteners, as these products dominate the market. However, there are disadvantages to these products. Stainless steel fasteners are several times more expensive than galvanized fasteners. Polymer-coated fasteners, while less expensive, are only as good as the polymer coating, which can be damaged during or prior to placement in wood. Zelinka and others (2009) have shown that in some coated wood screws, the polymer coating can be entirely stripped upon driving them into the wood. Recently, a non-metallic fastener has been introduced to the marketplace. This fastener, made from an FRP, by definition cannot experience corrosion because it is completely non-metallic and is cheaper than stainless steel. While the fastener is immune from corrosion, it may experience other forms of environmental degradation, such as crazing, embrittlement, or even possibly softening, in treated wood. It is important to understand the durability of these non-metallic fasteners as the fasteners become established in the marketplace.

This paper examines the durability of a commercial FRP nail for potential use in treated wood by exposing the fastener to different environments including treated and untreated wood. As opposed to metals, whose weight loss is proportional to the amount of corrosion (degradation) that occurred, a simple weight loss measurement would not be able to capture the degradation of an FRP nail. For this reason, the chemical, mechanical, and physical properties of FRP nails were quantified before and after the exposures. While the interpretation of these chemical and physical changes is more nuanced than just a simple weight loss, these measurements give clues to the various changes that might occur to the FRP fasteners in wood.

**Methods and Materials**

**Fasteners**

One type of commercially available, non-metallic fastener was examined. The material safety data sheet that revealed the fastener was a composite of a high strength polymer and fiberglass dust. Fasteners were roughly the size of a common 8d nail and had a rectangular cross section that was 3.2 mm by 2.6 mm by 56.9 mm in length and weighed 0.686 g (median of 100 measurements). Ten fasteners (replicates) were tested in each exposure condition.

**Exposure Conditions**

The fasteners were subjected to one of four different environmental exposure conditions in a laboratory setting: “accelerated weathering,” “100% relative humidity,” “untreated wood,” or “ACQ-treated wood.” A detailed explanation of these exposure conditions are given below.

The accelerated weathering exposure test followed the ASTM G154 “Cycle 1” protocol with a modified temperature during the condensing cycle (ASTM 2006). The fasteners were exposed to 0.89 W/m²/nm of irradiance using UVA-340 bulbs for 8 h at 60 °C followed by a 4-h long dark cycle where water condensed on the fasteners at 40 °C. These cycles were repeated until the combined exposure totaled 1,000 h. Fasteners were suspended on sample racks exposed directly to the UV radiation (not embedded in wood).

Fasteners were exposed to 100% RH to examine the moisture resistance of the fasteners. Fasteners were tested by suspending the fasteners over a reservoir of water in a sealed desiccator at 27 °C; the resulting relative humidity within the desiccator was 100% as dictated by the Gibbs phase rule. Fasteners were exposed for 6 months.

The solid wood exposure tests (untreated and ACQ-treated wood) closely followed common procedures for measuring the corrosion of metallic fasteners embedded in treated wood (Zelinka 2007; Zelinka and Rammer 2009; Zelinka and others 2010). The fasteners were hand-driven into predrilled holes in blocks of Southern Pine (Pinus spp.) (38 mm by 50 mm by 90 mm) that had been equilibrated at 27 °C and 90% RH prior to the exposure test. Predrilled holes were either exactly the largest dimension of the nails or in some cases 0.4 mm (1/64 in.) oversized. We found that the fasteners would fracture if driven into undersized holes or directly into the pine. These wood–fastener assemblies were then placed in a desiccator suspended over a reservoir of water with a resulting relative humidity of 100% at 27 °C. To minimize experimental differences, all the lumber was purchased at the same time, and half of the lumber was treated to 4 kg m⁻³ ACQ (carbonate formulation); suggested retention for above ground use (AWPA 2007). Fasteners were exposed for 6 months, after which they were carefully removed by sawing grooves in the wood near the fastener, placing the wood in the vise, and extracting the fastener by hand.

**Property Evaluation**

Before and after the fasteners were exposed, their physical, mechanical, and chemical properties were evaluated to detect changes caused by the exposure. Physically, the fasteners were examined for swelling caused by water uptake by measuring the fasteners to the nearest 0.01 mm at four key points along the length of the fasteners before and after exposure; these points are illustrated in Figure 7-1. Likewise, the fasteners were weighed to the nearest 0.1 mg before and after to see if they gained weight (water uptake) or lost weight (environmental degradation).

Changes in the surface chemistry were measured with near-infrared spectroscopy (NIR) using an ASD AgriSpec spectrophotometer (Analytical Spectral Devices, Boulder, Colorado), capable of measuring wavelengths from 350–2500 nm with a 10-mm spot size. The light source was provided with a tungsten halogen bulb that was fed through
a fiber optic sampling probe to deliver illumination to the physical sample. The reflected light from the sample was carried by a separate fiber optic bundle to the spectrophotometer. The baseline spectrum was obtained by measuring a white reference and this spectra was automatically applied and subtracted to each raw spectra. Because the fastener was smaller than the spot size, a special methodology was developed. The fastener was placed in a special white reference with a groove machined in it so that the fastener would lay flat. The grooved reference also assured that the spot region before and after exposure would be the same. Spectra were collected over the 10-mm spot size, which included both the nail and the white reference. To isolate changes in the surface chemistry of the fastener, spectra were taken before and after exposure using the same white reference, and relative differences between spectra were examined. Specific peaks were located and identified using the freely distributed “Extrema” program written for Matlab (Vargas-Aguilera 2007).

Changes in the mechanical properties were measured using dynamical mechanical analysis (DMA). Fasteners were placed in the tension fixture of a Q800 DMA (TA Instruments, New Castle, Delaware). A frequency sweep was performed from 0.1 to 100 Hz with 10 measurements per decade of frequency at 35 °C. The storage modulus (E’, i.e., the in-phase component of the dynamic modulus) and the loss modulus (E”, the out-of-phase component of the dynamic modulus) were recorded at each frequency step.

**Results and Discussion**

**Physical Changes**

Changes in the dimensions and weights of the fasteners are summarized in Table 7-1. Practically speaking, the dimensions of the fasteners exposed to the 100% RH, ACQ-treated wood, and untreated wood conditions remained the same before and after exposure. For these fasteners, some of fasteners slightly elongated in one dimension, while others decreased in size. The average change in any given dimension was very close to the standard error of the measurements. Whereas in some cases the relative changes appear to be non-negligible (i.e., several percent), it is only because the starting dimensions were so small (3 mm) that slight fluctuations in the absolute dimensions cause a large percentage shift. It should be noted however, that the fasteners exposed.

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**Table 7-1. Absolute and percentage change in mass and dimensions of the fasteners for different exposure conditions. The number in parentheses represents the standard error. **i, ii, iii represent groupings from the Tukey HSD test and ** represents no difference from the original (pre-exposure) mass.**

<table>
<thead>
<tr>
<th></th>
<th>Mass (mg)</th>
<th>Length (mm)</th>
<th>Diameter (mm)</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>100% RH</td>
<td>687 (1.2)</td>
<td>56.85 (0.01)</td>
<td>6.17 (0.004)</td>
<td>3.17 (0.005)</td>
<td>2.56 (0.007)</td>
<td>3.02 (0.013)</td>
<td></td>
</tr>
<tr>
<td>ACQ-treated wood</td>
<td>687 (1.2)</td>
<td>56.85 (0.03)</td>
<td>6.17 (0.005)</td>
<td>3.16 (0.005)</td>
<td>2.56 (0.004)</td>
<td>3.04 (0.007)</td>
<td></td>
</tr>
<tr>
<td>Untreated wood</td>
<td>687 (1.2)</td>
<td>56.87 (0.02)</td>
<td>6.17 (0.004)</td>
<td>3.16 (0.005)</td>
<td>2.57 (0.005)</td>
<td>3.04 (0.010)</td>
<td></td>
</tr>
<tr>
<td>Accelerated weathering</td>
<td>686 (0.3)</td>
<td>56.92 (0.03)</td>
<td>6.16 (0.002)</td>
<td>3.16 (0.004)</td>
<td>2.56 (0.005)</td>
<td>3.03 (0.003)</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>100% RH</th>
<th>ACQ-treated wood</th>
<th>Untreated wood</th>
<th>Accelerated weathering</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absolute changes</td>
<td>16.3 (0.1)i</td>
<td>–0.08 (0.04)</td>
<td>0.02 (0.005)</td>
<td>–0.03 (0.01)</td>
</tr>
<tr>
<td></td>
<td>14.4 (0.7)i</td>
<td>–0.20 (0.17)</td>
<td>0.01 (0.01)</td>
<td>–0.01 (0.02)</td>
</tr>
<tr>
<td></td>
<td>14.8 (0.1)i</td>
<td>–0.27 (0.17)</td>
<td>0.00 (0.01)</td>
<td>–0.02 (0.01)</td>
</tr>
<tr>
<td></td>
<td>–6.2 (0.15)iii</td>
<td>–0.17 (0.02)</td>
<td>–0.02 (0.003)</td>
<td>–0.02 (0.004)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Relative changes (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100% RH</td>
<td>2.4 –0.2 0.31 –0.84 –0.69 1.30</td>
</tr>
<tr>
<td>ACQ-treated wood</td>
<td>2.1 –0.4 0.19 –0.24 0.10 –2.77</td>
</tr>
<tr>
<td>Untreated wood</td>
<td>2.2 –0.5 0.02 –0.64 –0.04 –3.85</td>
</tr>
<tr>
<td>Accelerated weathering</td>
<td>–0.9 –0.3 –0.39 –0.72 –0.84 –0.92</td>
</tr>
</tbody>
</table>

The locations associated with these numbers are shown in Figure 7-1.
to accelerated weathering experienced consistent shrinkage. Although this change was only a few hundredths of a millimeter, it occurred nearly identically for all fasteners and unlike the other exposure conditions, no fasteners elongated. It appears therefore that the fasteners slightly shrink with exposure to accelerated weathering, and that the other exposure conditions cause small positive and negative fluctuations in diameter.

Although for the most part, the fasteners seem dimensionally stable, there was a noticeable and statistically significant change (α = 0.05) in mass for each of the exposure conditions. Differences among groups were analyzed using a Tukey HSD test (α = 0.05). The groupings from the Tukey HSD test are indicated by Roman numerals i, ii, and iii in the mass column of Table 7-1. The fasteners exposed to 100% RH, ACQ-treated and untreated wood gained more than 2% of their starting mass (i in Table 7-1), were statistically different than the control (unexposed) fasteners (ii in Table 7-1) but differences among these three treatments were not statistically different. The increase in mass in these groups most likely arises from water ingress into the fasteners. In contrast, the fasteners exposed to accelerated weathering with UV-light lost nearly 1% of their starting mass (iii in Table 7-1), which suggests some UV attack of the fasteners. It should be noted that as part of the ASTM G154 protocol, these fasteners were cycled through “condensing” periods of where the RH was 100% at 40 °C, so one would expect that these fasteners would have gained mass like those exposed to the 100% RH for 6 months, all other things equal. Therefore, it is possible that the fasteners would have lost more mass if the accelerated weathering test did not have the condensing periods.

### Chemical Changes

The pre-test NIR spectra were similar across all specimens except for some small differences in intensity between spectra that manifested themselves as slight distortions along the y axis. To make the data analysis easier, the y data were scaled by the intensity of the peak at 1518 nm. Once scaled, the data were virtually identical; the coefficient of variation of the peak with the biggest variability was at most 0.04%. The peak at 1518 nm was chosen to normalize the other peaks because it was clearly identifiable and remained at nearly the same frequency and intensity after all exposures. The scaled NIR spectra are shown in Figure 7-2. The NIR spectra for the control fasteners exhibited 8 distinctive peaks, which are highlighted with black dots in Figure 7-2. The frequency and intensity of each peak are summarized in Table 7-2 for each treatment. Most of the changes that occurred during the exposure test were minor; the peaks were either shifted in intensity or frequency by a small amount. The most noticeable feature from the NIR spectra was the peak at 1336 nm where there was distinct behavior difference between exposure conditions. The fasteners in the control group exhibited a peak at 1336 nm, which became more

### Table 7-2. Wavelength (λ) and peak intensity (I) for the peaks in the NIR reflectance spectra. The data are normalized to the peak intensity at 1518 nm.

<table>
<thead>
<tr>
<th>Control</th>
<th>Accelerated weathering</th>
<th>ACQ-treated wood</th>
<th>Untreated wood</th>
<th>100% RH</th>
</tr>
</thead>
<tbody>
<tr>
<td>λ (nm)</td>
<td>I (arb)</td>
<td>λ (nm)</td>
<td>I (arb)</td>
<td>λ (nm)</td>
</tr>
<tr>
<td>1</td>
<td>989</td>
<td>1.22</td>
<td>996</td>
<td>1.15</td>
</tr>
<tr>
<td>2</td>
<td>1,044</td>
<td>1.16</td>
<td>1,044</td>
<td>1.10</td>
</tr>
<tr>
<td>3</td>
<td>1,219</td>
<td>1.22</td>
<td>1,229</td>
<td>1.19</td>
</tr>
<tr>
<td>4</td>
<td>1,336</td>
<td>1.02</td>
<td>1,341</td>
<td>1.04</td>
</tr>
<tr>
<td>5</td>
<td>1,518</td>
<td>1.00</td>
<td>1,517</td>
<td>1.00</td>
</tr>
<tr>
<td>6</td>
<td>1,578</td>
<td>0.86</td>
<td>1,579</td>
<td>0.86</td>
</tr>
<tr>
<td>7</td>
<td>1,633</td>
<td>0.82</td>
<td>1,633</td>
<td>0.82</td>
</tr>
<tr>
<td>8</td>
<td>1,756</td>
<td>0.89</td>
<td>1,762</td>
<td>0.86</td>
</tr>
</tbody>
</table>
prominent after exposure to accelerated weathering. However, this peak was not present in those fasteners exposed to ACQ-treated wood, untreated wood, or 100% RH.

**Mechanical Changes**

The storage and loss moduli are shown in Figure 7-3 for typical curves for each exposure condition. The storage modulus was nearly constant across the frequencies tested, increasing very slightly with frequency; the slope was dependent on exposure condition. Likewise, the loss modulus decreased slightly with frequency and the amount of decrease also depended on exposure conditions. Because there were no peaks in the frequency spectra, the data can be compared at a given frequency to make data easier to examine.

The storage and loss moduli (taken at 1 Hz) are presented in Table 7-3. Control fasteners had a storage modulus of 8.0 GPa. Fasteners exposed to accelerated weathering had a lower, but not statistically different, storage modulus whereas fasteners exposed to treated wood, untreated wood, and 100% RH had a statistically significant higher storage modulus.

**Summary and Conclusions**

The purpose of the investigation was to examine the compatibility of a non-metallic fastener for use in treated wood. After 6 months, exposure to treated wood, small but noticeable changes occurred to physical, chemical, and mechanical properties of the fasteners. These changes were similar to the changes that occurred to fasteners that were placed in untreated wood, and also the fasteners exposed to the 100% RH environment that the wood was conditioned in. It therefore appears that most of the changes caused during the exposure period are caused by moisture. Wet conditions caused the fasteners to have a higher storage modulus and caused the peak at 1336 nm in the NIR spectra from the control group to disappear. From the perspective of using FRP fasteners in treated wood, the data after 6 months suggest that their performance will not be much worse than if the FRP fasteners were used in wet or humid environments.

**References**


