



# Corrosion of metals in wood: Comparing the results of a rapid test method with long-term exposure tests across six wood treatments

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## ABSTRACT

This paper 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 the reduction of cupric ions is the cathodic reaction in both the solid wood and the 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 the 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 the understanding of the mechanism of corrosion of fasteners in treated and untreated wood.

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## 1. Introduction

The current mechanism for corrosion of metals in contact with preservative treated wood was proposed by Baker in the 1980s [1,2]. 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 the transport of the cupric ions through the 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 since the corrosion rate depends strongly on wood moisture content and there is a threshold moisture content below which corrosion does not occur in wood [2–4]. We have illustrated the mechanism schematically in Fig. 1 specifically highlighting the ion transport through the wood.

Based upon Baker's proposed corrosion mechanism, and the assumption that the migration of ions was not the rate determining step, a new accelerated test method was developed at the US Forest Service, Forest Products Laboratory [5]. The method consisted of grinding the 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 [5,6]. The results suggested the cathodic reaction is the reduction of cupric ions as

Baker [2] 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 [7]. Furthermore, the untreated extract was more corrosive than the ACQ extract; a surprising result considering cupric ions increase the corrosiveness in solid wood. While 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 [8] and matched specimens from the exposure test were also examined with an electrochemical method in water extracts of the treated wood [9]. This work examines the similarities and differences between the exposure test and the electrochemical extract test and from these cases infers the corrosion mechanisms. To test the inferred corrosion mechanisms, additional experiments to separate the effects of pH and copper from other differences in preservative chemistry were performed. In addition to having practical implications for

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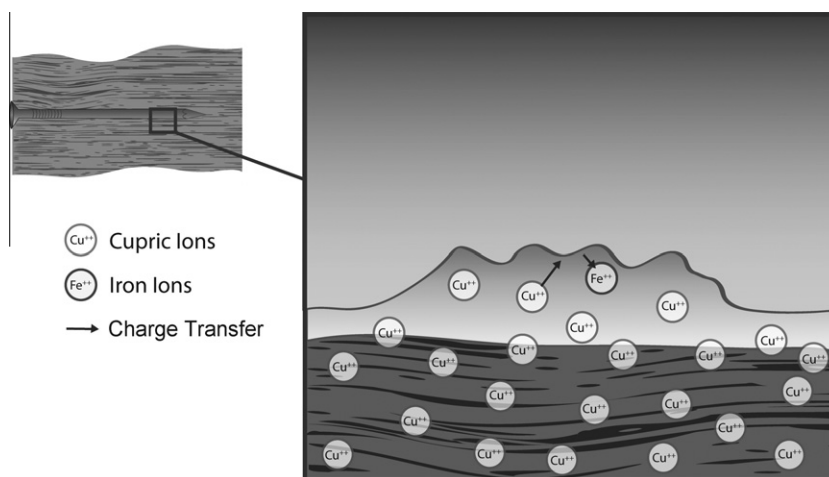


Fig. 1. Schematic illustration of the mechanism in corrosion in treated wood as proposed by Baker [1,2].

accelerated corrosion testing, this study adds to the understanding of the mechanism of corrosion of metals in wood.

## 2. 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  $\mu\text{m}$  as measured by an eddy-current thickness gage. The compositions of the 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 [16].

Southern pine (*Pinus* spp.) lumber was treated with one of five wood treatments or left untreated as a control for a total of six dif-

ferent groups; the compositions and retentions are given in Table 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 the 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 [10] – however, the total amount of copper and the ratio of the other biocides is the same as ACQ. Although the MCQ treating solutions contain insoluble copper, it is believed that the copper becomes soluble in the treated wood, and cupric ions are available [11,12]. The fifth treatment, didecyldimethylammonium carbonate (DDAC), is the cobicide 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.

The 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.

The exposure tests were conducted for 1 year in a 27 °C, 100% relative humidity environment that was achieved by placing

Table 1

Type, composition, and retention of the wood preservatives tested as well as the physical properties of the extracts made from these wood treatments.

|                               | Nominal composition (wt.%)                                        | Retention <sup>a</sup> (kg m <sup>-3</sup> ) |              | Extract physical properties |                                        |                          |                          |                          |
|-------------------------------|-------------------------------------------------------------------|----------------------------------------------|--------------|-----------------------------|----------------------------------------|--------------------------|--------------------------|--------------------------|
|                               |                                                                   | Nominal                                      | Actual       | pH                          | Conductivity ( $\mu\text{S cm}^{-1}$ ) | Cu (mg L <sup>-1</sup> ) | Cr (mg L <sup>-1</sup> ) | As (mg L <sup>-1</sup> ) |
| ACQ (type D)                  | 66.7% CuO                                                         | 4.0                                          | 1.6          | 6.6                         | 596                                    | 51.0                     | <sup>c</sup>             | <sup>c</sup>             |
| Alkaline copper quaternary    | 33.3% DDAC <sup>b</sup>                                           |                                              |              |                             |                                        |                          |                          |                          |
| CuAz (type C)                 | 96.8% CuO                                                         | 1.0                                          | 0.7          | 6.5                         | 446                                    | 23.9                     | 0.06                     | 0.22                     |
| Copper Azole                  | 1.6% Tebuconazole <sup>d</sup><br>1.6% Propiconazole <sup>e</sup> |                                              |              |                             |                                        |                          |                          |                          |
| MCQ                           | 66.7% CuO                                                         | 4.0                                          | 5.0          | 5.1                         | 220                                    | 32.5                     | <sup>f</sup>             | 0.09                     |
| Micronized copper quaternary  | 33.3% DDAC                                                        |                                              |              |                             |                                        |                          |                          |                          |
| CCA (type C)                  | 47.5% CrO <sub>3</sub>                                            | 4.0                                          | 2.9          | 4.9                         | 195                                    | 33.4                     | 6.20                     | 9.30                     |
| Chromated copper arsenate     | 18.5% CuO<br>34.0% As <sub>2</sub> O <sub>5</sub>                 |                                              |              |                             |                                        |                          |                          |                          |
| DDAC <sup>b</sup> (carbonate) | 100.0% DDAC                                                       | 1.3                                          | <sup>c</sup> | 4.6                         | 173                                    | 0.2                      | <sup>f</sup>             | 0.33                     |
| Untreated (control)           |                                                                   |                                              |              | 4.5                         | 190                                    | 0.3                      | <sup>c</sup>             | <sup>c</sup>             |

<sup>a</sup> Nominal compositions from AWP standard P5 [28], with the exception of MCQ, which comes from ICC-ES evaluation report ESR-1980.

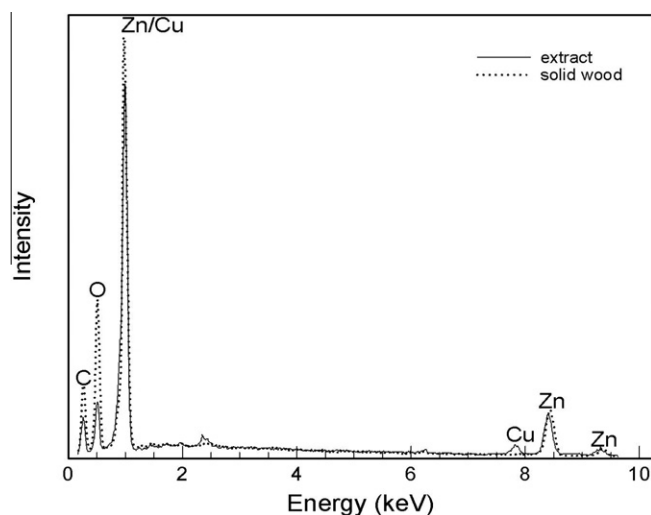
<sup>b</sup> DDAC: didecyldimethylammonium carbonate- IUPAC formula (C<sub>10</sub>H<sub>21</sub>)<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub>N(CO<sub>3</sub>)H and (C<sub>10</sub>H<sub>21</sub>)<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub>N(CO<sub>3</sub>)(C<sub>10</sub>H<sub>21</sub>)<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub> (mixture).

<sup>c</sup> Not assayed.

<sup>d</sup> IUPAC formula: (RS)-1-(4-Chlorophenyl)-4,4-dimethyl-3-(1,2,4-triazol-1-ylmethyl)pentan-3-ol.

<sup>e</sup> IUPAC formula: 1-[[2-(2,4-dichlorophenyl)-4-propyl-1,3-dioxolan-2-yl]methyl]-1,2,4-triazole.

<sup>f</sup> Assayed, but not detected.



**Fig. 2.** EDS measurements of the surface of a galvanized fastener exposed to MCQ-treated wood in both the solid wood and the extract test. Note the presence of copper in the fastener exposed to the extract test.

wood/metal assemblies over water in sealed desiccators. The average wood moisture content in this environment, determined gravimetrically on untreated specimens, was  $24.6 \pm 0.6\%$  (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 TX, USA) for 60 min while ultrasonic agitation was applied. It was found that this cleaning method produced a mass change on uncorroded fasteners of  $2.9 \pm 1.4$  (standard deviation) mg for the galvanized fasteners and  $-0.9 \pm 0.9$  mg for the steel fasteners. On additional specimens, the corrosion products were analyzed with powder X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy dispersive X-ray spectroscopy (EDS).

The extract test method involved making an extract from the wood, and then electrochemically measuring the corrosion rate of a fastener immersed in the 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 the 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 the corrosiveness of the extract is not affected by the heat produced during grinding [5]. After it was produced, the extract was stored near  $0^\circ\text{C}$  and tests were run within two weeks to minimize biologically induced changes in the extract. The physical properties of the extracts are summarized in Table 1.

The electrochemical testing used a similar procedure to ASTM G59 [13], and the fasteners were machined to fit in the standard 5-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  $-30$  mV vs. OCP to  $+30$  mV vs. OCP with a scan rate of  $0.166 \text{ mV s}^{-1}$ . The automatic IR correction of the potentiostat was applied during the test. Tafel slopes and the resulting corrosion rate were ascertained from the non-linearities of the polarization resistance curve using Mansfeld's method [14,15]. Nine replicates were tested for both steel and galvanized steel for all six treatments.

### 3. Results and discussion

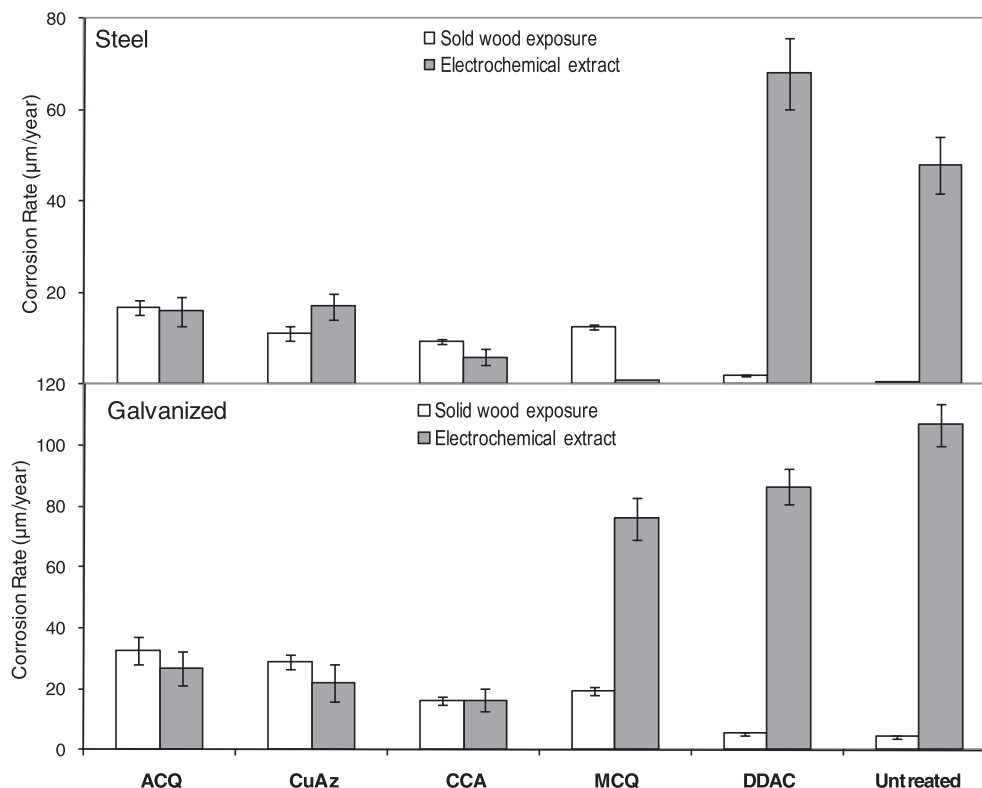
Corrosion product analyses from XRD, SEM, and EDS for the solid wood tests have been published elsewhere [8]; only the pertinent details needed for the present discussion are included here. For all six treatments, the steel corrosion products consisted of goethite ( $\alpha\text{-FeOOH}$ ) and magnetite ( $\text{Fe}_3\text{O}_4$ ); for galvanized steel namuwite  $\{\text{Zn}_2(\text{SO}_4)(\text{OH})_6 \cdot 4\text{H}_2\text{O}\}$ , and hydrozincite  $\{\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6\}$  were clearly identifiable, although smithsonite ( $\text{ZnCO}_3$ ), simonkolleite  $\{\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot (\text{H}_2\text{O})\}$ , and zincite ( $\text{ZnO}$ ) may also have been present. Importantly, the EDS revealed different elemental compositions between the surfaces of fasteners corroded in the extract and in the solid wood (Fig. 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 Fig. 3. There are three types of behavior present in Fig. 3. The traditional, soluble copper, wood preservatives (CCA, ACQ, and CuAz) have similar corrosion rates in both the extract and solid wood. For both the untreated and DDAC treated wood, which do not contain copper in any form, the extracts are much more corrosive than the solid wood. Finally, the MCQ-treated wood does not behave like either the traditional wood preservatives or the copper-free treatments. The differences in behavior can be ascribed to different reaction mechanisms occurring in these treatments. To further discuss these mechanisms, the treatments will be grouped depending on whether or not they contain copper and what form it is in.

#### 3.1. Preservatives containing cupric ions

For the traditional wood preservatives (ACQ, CCA, and CuAz), good correlation was found between the exposure test and the extract test. These results agree with the preliminary work in ACQ treated wood [5]. In that work, EDS of polarized fasteners in the extract revealed the presence of reduced copper on the fastener surface. It was concluded that the cathodic reaction in the extract was the reduction of cupric ions. Furthermore, since the extract and exposure tests had similar corrosion rates across several different metals [5], it was concluded that the mechanism in solid ACQ treated wood also involved the reduction of cupric ions and the rate determining step was the same in both cases. The 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 who examined steel, zinc, and aluminum fasteners exposed to CCA treated wood [17]. While the 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 the cupric ions are reduced because the 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 the 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 et al. [18] found correlation between the amount of copper and the corrosiveness of the wood preservative. While the correlation between exposure and extract tests suggests that the reduction of cupric ions is the cathodic reaction in both the extract and solid wood, it is not clear what happens to the reduced copper in the solid wood. It is possible that



**Fig. 3.** Corrosion rates measured in the electrochemical extract test [17] and a 1 year exposure test [8] for steel (top) and galvanized steel (bottom). Note the difference in scale on the ordinate axis.

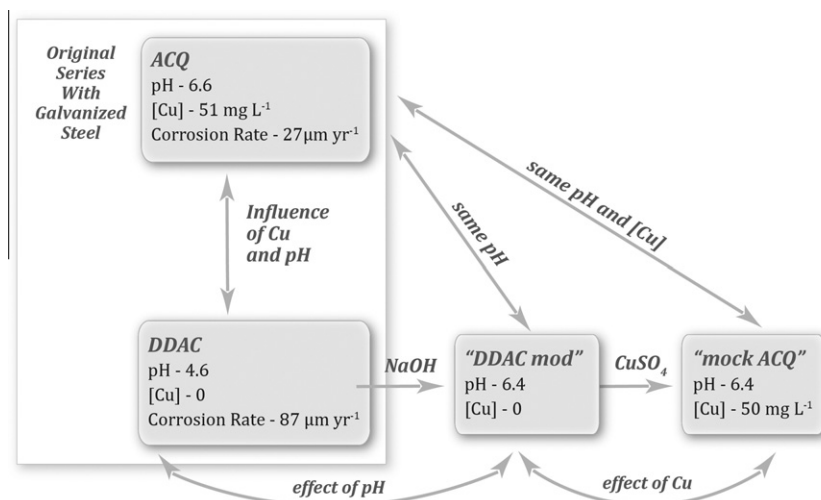
the reduced copper dissolves again in a different reaction or that the copper is reduced near the metal surface but remains on the wood instead of the metal, although EDS measurements taken in the region adjacent to the fastener showed no difference in copper concentration.

### 3.2. DDAC and untreated wood

For the DDAC and untreated wood, which do not contain copper in any form, the expected cathodic reactions are the reduction of acids and dissolved oxygen [1,19–21]. In a previous investigation [7], 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 deacetylation [22]. 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



**Fig. 4.** Graphical explanation of the model DDAC extracts used to examine the effect of pH and cupric ions on the corrosion of polished zinc sheet.

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 [23,24].

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  $30 \mu\text{m year}^{-1}$  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  $87 \mu\text{m year}^{-1}$  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. 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 sulfate was added so that the resultant copper concentration in the solution was  $50 \text{ mg L}^{-1}$ . Cupric sulfate 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 [25,26]. 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<sup>1</sup> 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 Fig. 5; for the DDAC extract (pH 4.6), the corrosion rate (in  $\mu\text{m year}^{-1}$ ) in zinc was  $185 \pm 32$  (standard error) for the “DDAC mod” extract (pH 6.4) it was  $21 \pm 4$  and for the “mock ACQ” extract (DDAC pH 6.4 with  $50 \text{ mg L}^{-1} \text{ CuSO}_4$ ) it was  $63 \pm 4$ . 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 cupric ions increase the corrosion rate. The corrosion rates cannot be directly compared to those in Fig. 2 because a different metal was tested to reduce variation between replicates. However, what can be compared is the ratio of the corrosion rates in DDAC/ACQ (or mock ACQ). For the galvanized fasteners, the ratio of the DDAC/ACQ corrosion rate was 3.2 and for the zinc sheet, the ratio of the DDAC/mock ACQ was 2.9. The similarities in ratios suggests that the 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.

### 3.3. MCQ-treated wood

For the solid wood, MCQ corrosion rates were similar to those measured in wood treated with soluble copper systems (CCA, ACQ, CuAz). However, the corrosion rates measured in MCQ extracts exhibited unique behavior; the galvanized fasteners had a

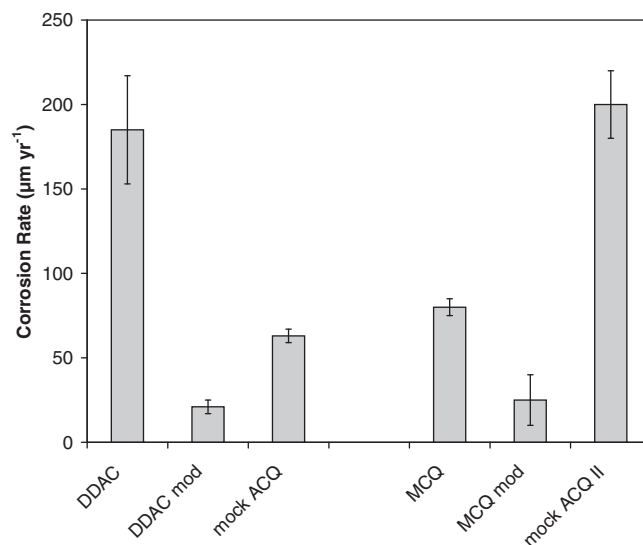


Fig. 5. Results of ancillary experiments of polished zinc sheet in model extracts used to examine differences between the wood preservatives which contain DDAC (DDAC, ACQ, and MCQ-treated wood).

higher corrosion rate in the extract than the solid wood whereas the corrosion rate of the steel fasteners in the extract was so low it could barely be detected. These data present two main questions: (1) why did the 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 [27] (Fig. 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 1). Additionally, the Pourbaix

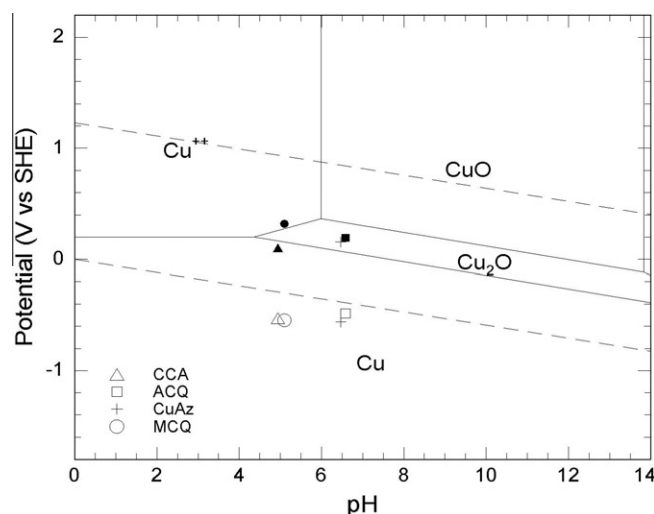


Fig. 6. Potential-pH diagram of copper with an assumed ion solution activity of  $10^{-4}$ . The average open-circuit potential data of steel (filled symbols) and galvanized steel (open symbols) are plotted. Error bars are not presented as they are smaller than the symbols.

<sup>1</sup> 99% Pure, Alfa Aesar (Ward Hill, MA).



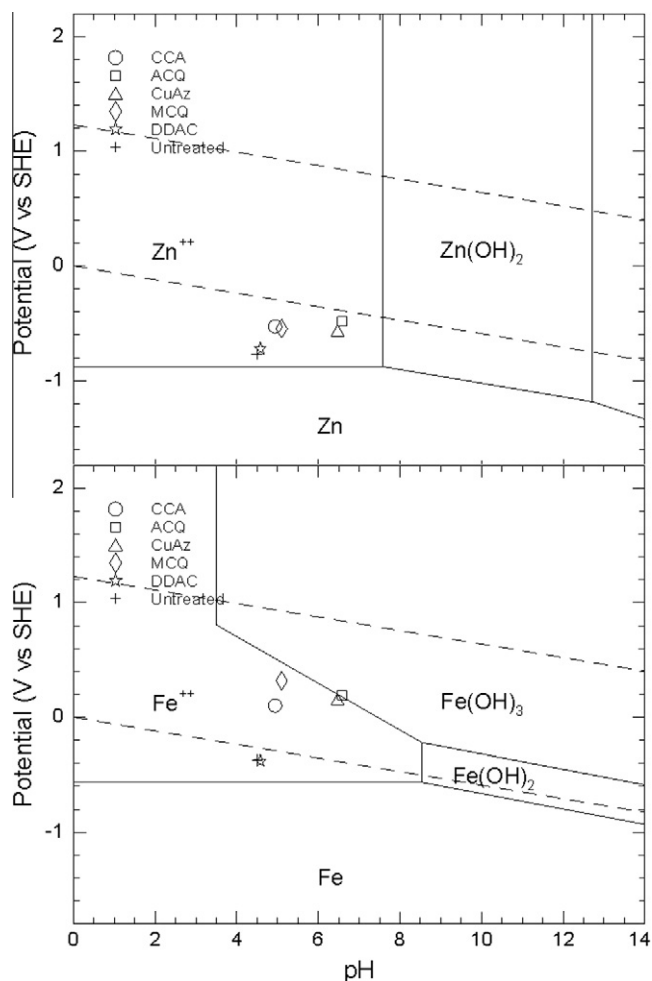


Fig. 7. Potential-pH diagram of zinc and steel where the ion activity is assumed to be  $10^{-4}$ . The average pH and open-circuit potential for each treatment are overlaid.

diagrams of steel and zinc are included in Fig. 7 with the 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. 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, since they are in a region where cupric ions are stable; this agrees with the corrosion rate data (Fig. 2). Furthermore, the surface of fasteners polarized in the extract was 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 the MCQ extract even though the treating solution is comprised of particles of nearly insoluble copper. The open-circuit potential of the galvanized fasteners places them in a region where copper metal is the stable phase, and the cupric ions are reduced on the metal surface as the fastener oxidizes. Conversely, the steel fasteners are more noble, at a potential where cupric ions are stable, and therefore do not corrode.

The behavior of the steel fastener in the MCQ extract appears to be controlled by the thermodynamics of the cupric ions in solution. One interesting aspect of this study was the open-circuit potential (OCP) of the steel fasteners is unusually high when compared to the galvanized fasteners. For example, in previous work in ACQ extracts [5], the average OCP for steel fasteners was  $-0.33$  V vs. the standard hydrogen electrode (SHE) whereas it was  $0.19$  V in the current study. For reference, the OCP of the galvanized fasteners was  $-0.62$  V in the previous and  $-0.48$  V in the current work. Although the OCPs were high for the steels in extracts with copper, this was not the case for extracts without copper; the OCP in the DDAC and untreated extracts were  $-0.38$  and  $-0.37$  V, respectively. Interestingly, in an auxiliary experiment in this study where polished steel was tested in an ACQ extract, a high ( $>0.25$  V vs. SHE) open-circuit potential was measured and the steel did not corrode. Whatever the reason for the high open-circuit potentials in MCQ-treated wood, it clearly limits the usefulness of the electrochemical extract test in these cases.

In contrast to the steel fastener, the galvanized fastener in the MCQ extract has a much higher corrosion rate than in the solid wood, and the EDS confirmed cupric ions were present. Because the data suggest the MCQ extract contains cupric ions, and cupric

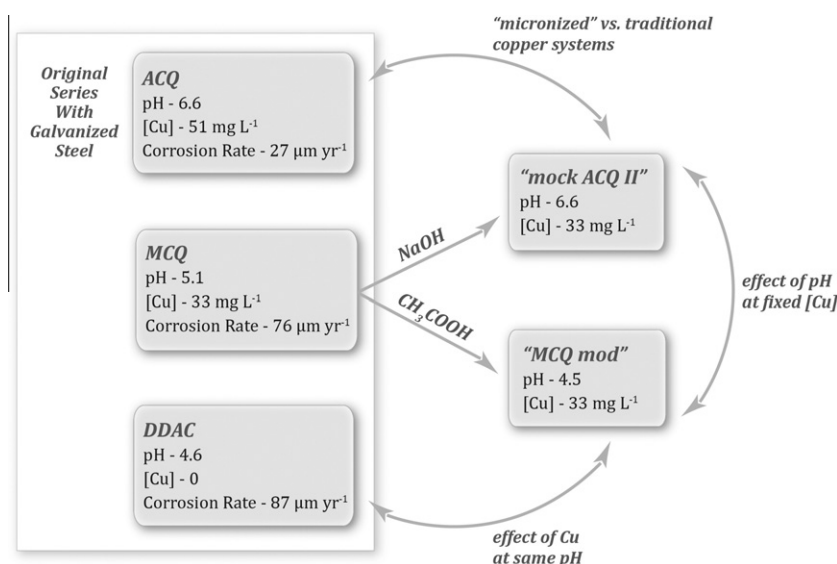


Fig. 8. Graphical explanation of the model MCQ extracts used to examine the effect of pH and cupric ions on the corrosion of polished zinc sheet.

ions are not stable for the open-circuit potentials measured for galvanized steel, we would expect this system to behave like the 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. 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  $80 \pm 5$  (standard error)  $\mu\text{m year}^{-1}$ . The pH 6.6 (mock ACQ II) extract had a corrosion rate of  $25 \pm 15$  and the pH 4.5 had a corrosion rate of  $200 \pm 20$  (Fig. 5).

Not surprisingly, the changes in pH caused large changes in the corrosion rate. The 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 the cupric ions were not contributing to the corrosiveness, the 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.

#### 4. 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 the 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 ( $\sim 0.25$  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.

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