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CORROSION OF METALS IN CONTACT WITH TREATED WOOD: DEVELOPING TEST METHODS

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ABSTRACT

With the voluntary withdrawal of wood treated with chromated copper arsenate (CCA) for use in residential construction in January 2004, the corrosiveness of treated wood has become a concern. Preliminary research has shown the replacements for CCA, which include copper azole (CuAz) and alkaline copper quaternary (ACQ) are more corrosive than CCA. Since rapid tests cannot easily be run in solid wood, an electrochemical method has been developed that measures the corrosiveness of water-extracts of wood. Corrosion rates of steel and galvanized steel fasteners measured in the extract of ACQ treated wood correlate well with gravimetric data in solid wood.

Keywords: wood, fastener, polarization resistance, galvanized steel, alkaline copper quaternary (ACQ)

INTRODUCTION

The corrosion of metals in contact with wood has been studied for over 80 years' and in most situations wood is not corrosive. Recently however, there have been concerns about the durability of fasteners in *pressure treated wood,* wood that is injected with chemicals to resist decay. The major wood preservative of the past fifty years, chromated copper arsenate (CCA), was recently voluntarily withdrawn for use in residential construction in January 2004. Replacements to CCA, such as Copper Azole (CuAz) and Alkaline Copper Quaternary (ACQ), have been shown in accelerated[2] and long term exposure tests[3] to be more corrosive than CCA.

Structurally, wood is a matrix of cell walls with open space called *lumens.* Chemically, wood is mostly comprised of cellulose, hemicellulose, and lignin, the remainder is divided between small organic molecules called *extractives* and inorganic substances *(ash content).* It is believed[4-6] that corrosion in wood is an aqueous process that occurs in the free water present in cell walls and in lumens at higher moisture contents.

An aqueous corrosion mechanism is reasonable since the corrosiveness of wood depends strongly on wood moisture content. There is a threshold moisture content[7-11], between 15%-18% below which no corrosion takes place, a region where corrosion rate increases with increasing moisture content, and a plateau above which the corrosion rate is constant with moisture content[7,8]. These three regions correspond with the stages of water adsorption in wood, which at low moisture contents gets bound to hydroxyl sites within the wood cell wall, and as these sites get filled, free (unbound) water exists within the cell walls, and eventually the lumens. Interestingly, the threshold moisture content for corrosion is the same threshold moisture content for ionic conduction[12], which is also believed to depend upon free or loosely bound water in the cell walls[13].

The effect of the treatment chemicals on the corrosion mechanism is less clear. Baker[4] proposed a mechanism of galvanic corrosion between the cupric ions (Cu^{++}) in the wood preservative and the metal fasteners. His theory is based upon 17 year gravimetric exposure data for metals embedded in CCA treated wood[14]. Metals that were noble with respect to copper on the galvanic series in seawater[15] did not corrode and metals active to copper exhibited significant corrosion. However, the noble metals that Baker tested, monel (alloy N04400), bronze, copper, and two types of stainless steel, in addition to being noble or equal to copper on the galvanic series, are also more kinetically stable than aluminum and zinc, so it is hard to separate galvanic effects and kinetic effects. In a related study, Simm and Button[16] examined the surfaces of fasteners embedded in CCA treated wood with energy dispersive X-ray spectroscopy (EDX). They did not find copper on the surface of the fasteners, which would be expected if the corrosion was galvanic and the cathodic reaction was the reduction of the cupric ion.

Even though the mechanism of corrosion of metals in contact with treated wood is not entirely understood, there have been several attempts to develop electrochemical corrosion tests in wood. Two researchers[7,17] have run polarization resistance tests in solid wood. Although they used different geometries, both embedded the working and counter electrodes in treated wood. The reference electrode was connected to a salt bridge that was also embedded in the wood. They found that that the corrosion rate depended strongly upon moisture content, which is consistent with gravimetric corrosion tests[5,14]. However, while the corrosion rate is sensitive to moisture content, the resistivity of wood (Figure 1) also changes with moisture content and can vary by over six orders of magnitude[18]. Neither paper stated whether they corrected for the “solution resistance’’ of solid wood. If they did not correct for this solution resistance, they would have large errors since the resistivity of wood is high and changes with moisture content. Therefore it is not clear whether the reported change in corrosion rate, as measured by polarization resistance, was due to a change in corrosion rate, or a change in solution resistance, or some convolution of the two.

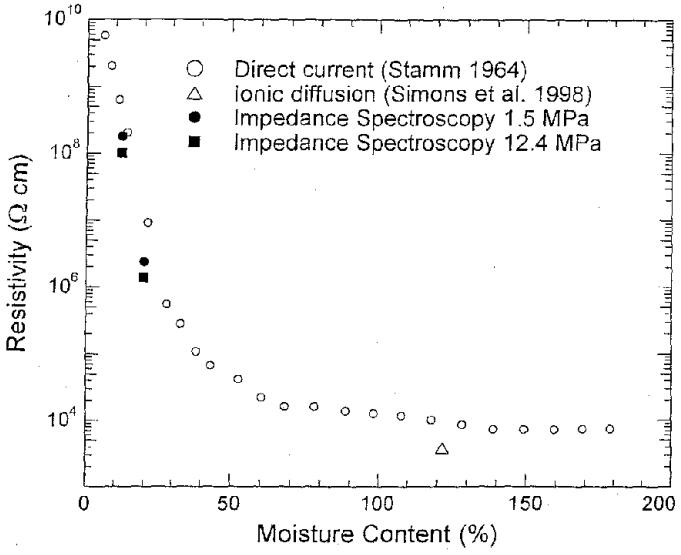

Figure 1: Resistivity of various species of Pine *(Pinus)* over a wide range of moisture contents, measured by several techniques: direct current resistance measurements (()[18], calculated from the diffusion coefficients of ions within the wood (¶)[19], and calculated from the resistance in baseline EIS measurements (&,⁻)[13] at two different electrode contact pressures.

A similar approach was taken by Jack and Smedley[20] who used electrochemical impedance spectroscopy (EIS) with embedded electrodes. In theory, EIS is better suited for taking measurements in solid wood since the "solution resistance" of solid wood can be separated out in equivalent circuit modeling. However, Jack and Smedley fit their impedance data with the complicated model in Figure 2 and the paper contains little explanation of the model. It is not clear if physical meaning can be attributed to any of the components in the model because of the number of components. Furthermore, the baseline impedance spectra of wood measured with graphite electrodes is non-trivial, and changes with moisture content[13]. At low moisture contents, it exhibits a single time constant, and at higher moisture contents (~20%), exhibits a low frequency tail (Figure 3- frequency is contained implicitly), which has been attributed to ionic diffusion. While EIS in solid wood may be a viable corrosion test, a more practical equivalent circuit model needs to be developed which accounts both accounts for the baseline electrical properties of wood and has components with physical meaning.

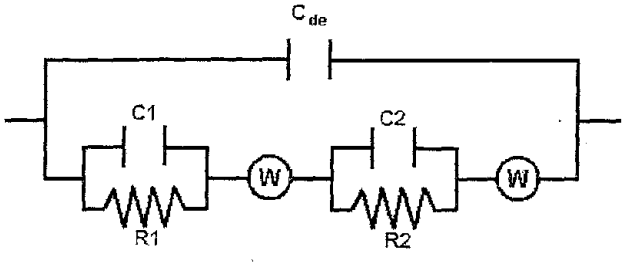

Figure 2: Equivalent circuit model of Jack and SmedleVo for corrosion in CCA treated wood.

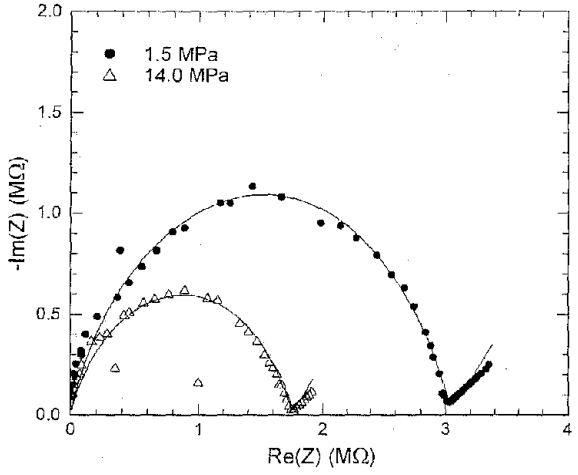

Figure 3: Baseline EIS spectra of untreated wood at 20% moisture content with graphite electrodes with different applied pressures[13].

In short, while an electrochemical corrosion test would be useful for prototyping new fasteners or wood preservatives, the complicated electrical properties of solid wood make the interpretation of electrochemical tests difficult. An initial attempt to circumvent this problem by measuring polarization resistance of metals in solutions of the wood preservative (an aqueous chemical) did not correlate to the corrosion of metals in treated solid wood[21]. In retrospect, the lack of correlation is not surprising as it is known that the preservative interacts with the wood. This paper reports on an improved method where electrochemical tests were conducted on metals immersed in a water-extract of treated wood. The new method is based upon the assumption that corrosion in wood is an aqueous mechanism and the components in the water extract are similar to the free water within the wood cell walls and lumens.

EXPERIMENTAL

Full details of the procedure, and a discussion thereof have been accepted for publication elsewhere[22]. The details most pertinent to the results are included here for clarity.

The extract was made by mixing sawdust and distilled water and later filtering off the sawdust. The sawdust came from Southern pine *(Pinus Spp.)* treated with ACQ to a retention of 4kg m^{-3}. The ratio of sawdust to water was 1:10 (weight), and the extraction time was one week at room temperature. The concentration of copper in the extract was measured using an inductively coupled plasma mass spectrometer (ICP) was 19.85 mg L^{-1}. The pH of the extract was 6.6.

Four types of commercial fasteners were tested. The fasteners were machined to a length of 41 mm to fit in the 5-neck corrosion test flask recommended in ASTM G5[23]. Likewise, the machined edge of the fastener was drilled and tapped such that it could be incorporated into the standard[23] polytetrafluoroethylene gasket system. The four types of fasteners tested were a bright carbon steel 8d nail, an 8d hot-dip zinc galvanized carbon steel nail, a 4d aluminium alloy (UNS AA5056) nail, and a 64 mm long electroplated zinc galvanized screw. The surface areas of the fasteners were calculated using the projection from a silhouette photograph and an algorithm developed by Rammer and Zelinka[24]. Immediately prior to immersion, the fasteners were cleaned with soapy water and ultrasonic agitation, rinsed with distilled water, acetone, and rinsed a second time with distilled water.

The corrosion rate was evaluated by measuring the polarization resistance after recording the open circuit potential (OCP) for an hour. The solutions were tested without a gas purge or stirring. The scan rate was swept potentiodynamically from -30mV (vs. OCP) to +30mV (vs. OCP) at a scan rate of 0.166mV/s. The solution resistance was compensated automatically using the algorithm built into the potentiostat. The Tafel slopes were calculated by using Mansfeld's method[25,26].

RESULTS AND DISCUSSION

Steel and Galvanized Steel in ACQ Extract

The results of the polarization resistance tests are shown in Figure 4. Also shown in the figure are gravimetric data from a 1 year exposure test where fasteners were embedded in ACQ treated wood in an 27°C (80°F), 100% relative humidity environment[3]. The 27°C (80°F), 100% relative humidity environment has been used as a baseline by many researchers[14,16,27] to study the corrosion of metals in treated wood. Baker[14] has shown that the corrosion rate of metals in treated wood in this environment is constant with time between 1 and 17 years. Uniform corrosion was observed for all of the exposure specimens.

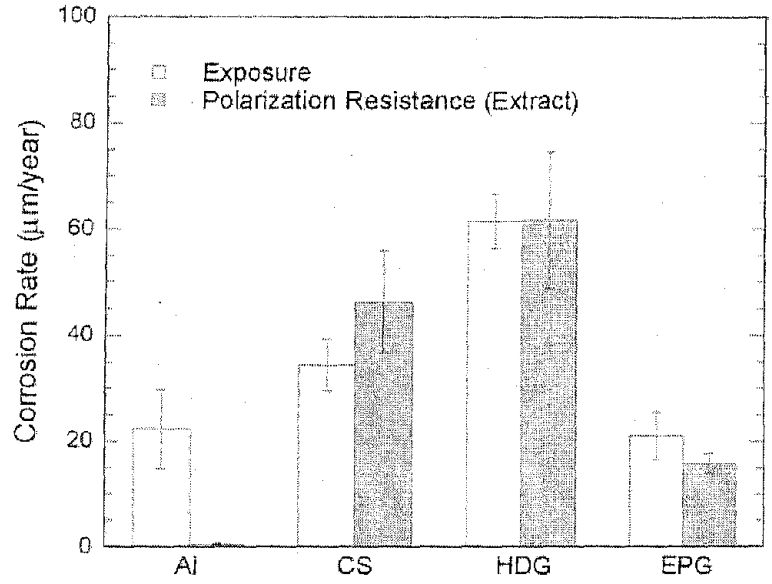

Figure 4: Corrosion rates for aluminum (Al), carbon steel (CS), electroplated galvanized (EPG) and hot dip galvanized (HDG) fasteners measured by two different test methods: exposure in ACQ treated wood at 27°C, 100% relative humidity (white) and polarization resistance measured in the extract of ACQ treated wood (gray).

From the figure, it is clear that there is good correlation between exposure and electrochemical extract tests for the carbon steel, hot dip galvanized and electroplated galvanized fasteners. It therefore seems plausible that these fasteners corrode in the extract through a similar mechanism to solid wood, and this extract test method may be a viable accelerated test method.

Results of aluminum fasteners in ACQ extract

Unlike the steel and galvanized steel fasteners, there was not a good correlation between corrosion rates measured in solid wood and the extract for aluminum fasteners. One possibility is the mechanism of corrosion is different in the extract. Some evidence of a different mechanism can be seen in the open circuit potential of the aluminum fastener. The open circuit potential of the aluminum fastener was constant at -0.42 V vs SCE prior to polarization. However, the asymptotic limit of the aluminum polarization curve was -0.3 V vs SCE (Figure 5). It is interesting that (1) the asymptotic limit was higher than the open circuit potential measured prior to polarization and (2) that both potentials are higher than steel (-0.67 V vs SCE), hot dip galvanized steel (-0.88 V vs SCE), and electroplated galvanized steel (-0.77 V vs SCE).

In the galvanic series for seawater[15] , aluminum has a more negative potential than carbon steel. While the extract is not seawater, the potentials of carbon steel and the galvanized steel are close to their published potentials in seawater and it is unlikely that the potential of the aluminum fastener in the extract would deviate more than the carbon and galvanized steel. We believe the difference in open circuit potentials may be due to a passive layer on the aluminum fasteners. In a separate experiment, the aluminum fasteners were polished prior to polarization and they had a lower open circuit potential (-0.8V vs SCE), which agrees more closely with the galvanic series.

However, a passive layer cannot explain the difference between the asymptotic limit of the polarization curve and the open circuit potential. We believe that during cathodic polarization, the cupric ions in solution were reduced, which plated the surface of the aluminum fastener with copper, and raised the potential since copper is more noble than aluminum. What is not

clear is why the plating occurred on the aluminum fastener, but not the carbon steel or galvanized steel, whose asymptotic limit agreed with the open circuit potential.

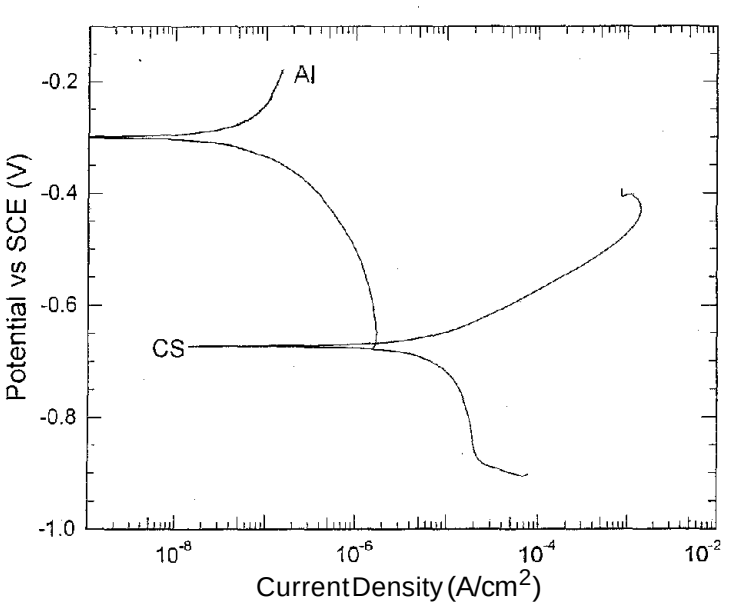

Figure 5: Polarization curves for aluminum (Al), carbon steel (CS). The asymptotic limit of the polarization curve for aluminum was higher than its open circuit potential (-0.42 V vs SCE).

Results of steel in an untreated extract

To better understand the mechanism of corrosion in the treated extract, we ran tests in an extract made from untreated Southern pine as a control, which had a pH of 4.5. Additional tests were run to study the effect of dissolved oxygen. Three conditions were tested: deaerated, which were purged with nitrogen gas; aerated, which were purged with compressed air; and undisturbed solutions, where no gas was bubbled and the solution was not stirred. The results of these tests are shown in Figure 6. Unlike the treated extract, the untreated results do not correlate well with exposure tests; the corrosion rate of steel in untreated pine is about 20 µm/year[27]. What is even more surprising is that the untreated extract was more corrosive than the treated extracts because we know that treated wood is much more corrosive than untreated wood. We believe that both these deviations are related, and arise from chemical reactions in the wood.

The first question that must be answered is why the untreated extract is more corrosive than the solid wood. Several wood researchers[11,28,29,] have shown that when wood or sawdust is exposed to water, it breaks down to produce acetic acid. Acetic acid is not an extractive, but rather is produced by a chemical reaction between the wood and the water. In our extraction process, the wood has a much greater surface area, and is mixed with an excess of water, accelerating the production of acetic acid, making the extract more acidic, and more corrosive. Secondly, during in-service conditions a portion of the acetic acid leaves the wood[5,9,11,30] because it is volatile. However, in the extract it cannot volatize since it is always in a closed container.

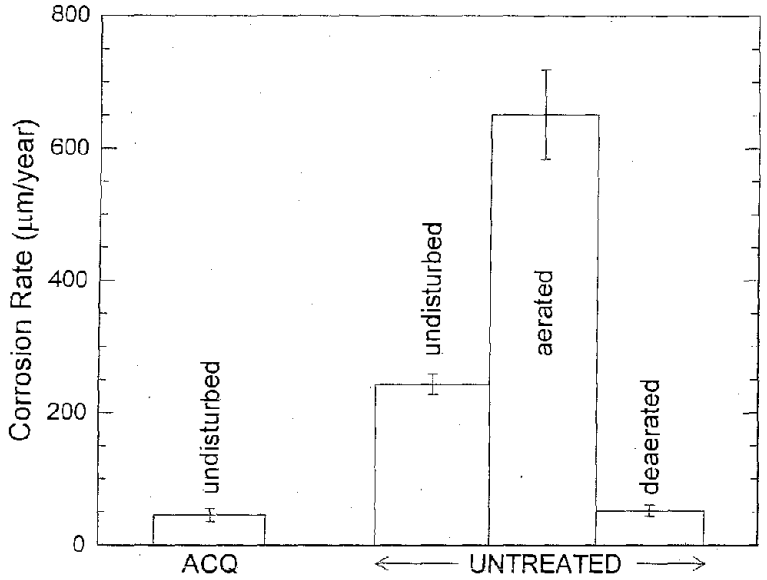

Figure 6: Corrosion rates measured by polarization resistance in extracts of untreated and ACQ treated Southern Pine *(Pinus spp.).*

If the untreated extract is more corrosive than the tgreated extract because it is more acidic, it poses the following question, why wasn"t this observed in the ACQ extracts? ACQ treating solutions are alkaline, with a pH of 9.5[21]. While pH of solid wood is not defined, it is possible to measure of the pH of extracts. We observed the pH of the ACQ treated wood extract was nearly neutral, 6.6. Therefore, we believe the ACQ neutralized the acid that was produced during the extraction process, and made the extract less corrosive.

SUMMARY AND CONCLUSIONS

Currently, polarization resistance tests in ACQ treated wood extracts have shown good correlation with gravimetric data in solid wood for steel and galvanized steel fasteners. However, this correlation did not exist for aluminum fasteners, or fasteners in untreated extracts. The explanation for the untreated wood is based upon observations by other researchers that damp sawdust produces acid. if we can understand why the extract test has a correlation in some cases, but not others, it will help us to understand the mechanism of corrosion in treated wood as well as understand the limitations of the extract test as an accelerated test.

The next logical step in understanding the relation between corrosion in the extract and corrosion in solid wood is to compare the correlation between extract and solid wood tests for wood treated with different chemical treatments. For example, CCA solutions are acidic. If our hypothesis that the ACQ, neutralized the acetic acid produced in the extraction process is correct, then the CCA extract should be more corrosive than both the ACQ extract and untreated wood extract. The CCA extract should also be more corrosive than the CCA treated wood. Conversely, CuAz, another alkaline preservative, should have a good correlation between the extract and solid wood, similar to ACQ.

In addition to testing different chemical treatments, additional information can be gained by testing different genera of wood. Elm *(Ulmus)* is known to be one the least acidic and least corrosive genera of wood whereas Oak *(Quercus)* is known to be acidic, and corrosive. The effect of acetic acid in the extract can be examined by making extracts from different genera and looking for correlations between its corrosiveness (polarization resistance) as well as their total acidity measured by titration.

The development of an electrochemical test to measure corrosion in treated wood has been hampered by the complicated electrical properties of wood. Electrochemical tests in water extracts of wood have had mixed results. We believe the acid produced in the extraction process caused the untreated data to not correlate well. Because the extract method uses real fasteners and has been shown to have good correlation to exposure tests for ACQ treated wood, it may be an effective method to prototype new fasteners for use in ACQ treated wood.

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