

Synchrotron Based X-ray Fluorescence Microscopy Confirms Copper in the Corrosion Products of Metals in Contact With Treated Wood

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ABSTRACT

Copper based waterborne wood preservatives are frequently used to extend the service life of wood products when subjected to frequent moisture exposure. While these copper based treatments protect the wood from fungal decay and insect attack, they increase the corrosion of metals embedded or in contact with the treated wood. Previous research has shown the most plausible corrosion mechanism involves the migration of copper ions from the wood treatment through the wood to the metal surface, where they are then reduced. Despite this, under almost all conditions, copper has not been detected in the corrosion products as the proposed mechanism would imply.

Recently, synchrotron based X-ray fluorescence microscopy (XFM) was used to examine the wood that had been in direct contact with metal fasteners in a corrosion test. These measurements showed a copper depleted region in the wood directly adjacent to the metal fastener. Based on the size of the region and the copper concentration, the amount of copper in the corrosion products was calculated to be on the order of 500 parts per million. This low concentration explains why previous attempts to find copper in the corrosion products using scanning electron microscopy, energy dispersive X-ray spectroscopy, and powder X-ray diffraction were unsuccessful.

Here, we present XFM maps of corrosion products removed from corroded fasteners that had been in contact with preservative treated wood. The XFM maps of the corrosion products clearly show the presence of copper. These measurements definitively confirm the mechanism of corrosion in treated wood and give further insights into where and how the cathodic reaction takes place.

Key words: preservative treated wood, steel, cupric ions, corrosion mechanisms

INTRODUCTION

In typical wood construction, metal fasteners are used to join wood to wood or other construction materials. These metal connectors are subject to corrosion from moisture and organic acids within the wood.¹⁻⁵ In certain cases, wood preservatives or fire retardants are added to the wood and these chemicals affect the corrosiveness of the wood.⁶

Waterborne wood preservatives are commonly used to protect wood from fungi and other insects. These wood preservatives typically contain copper.⁷ It is believed that a portion of the copper within the wood remains as cupric ions and that these cupric ions are partly responsible for the wood protection.⁸ Therefore, the treated wood environment lends itself to corrosion because it contains cupric ions which are thermodynamically unstable in the presence of steel and galvanized steel fasteners.⁹ In 2004, there was a change in the regulation of wood preservatives in the United States. Following this regulation change, many new copper-based formulations of wood preservatives were introduced to the marketplace, and the use of chromated copper arsenate (CCA), the most common preservative prior to 2004, was greatly reduced.¹⁰ One commonality between these new copper-based preservatives is that they all have more copper than CCA. After the 2004 regulation change, corrosion became a bigger concern within the wood construction industry.¹¹

Previous work on the corrosion of metals in wood has shown that the corrosion mechanism involves the migration of copper ions through the wood to the metal surface where it is reduced as part of the cathodic reaction illustrated in Figure 1.¹²⁻¹⁴ This proposed mechanism has been supported by thermodynamic and kinetic arguments. Thermodynamically, the open circuit potential of steel and galvanized steel in wood are in a region where copper metal is the stable phase.¹⁵ Kinetically, the corrosion rate of embedded metals increases as the amount of wood preservative (copper ions) increases.¹⁶ Furthermore, differences in corrosion rates between different wood preservatives could be explained solely by the differences in the amount of copper and the pH of the different treatments. Despite the evidence for the mechanism illustrated in Figure 1, in nearly all of the experiments, copper metal could not be detected on the corrosion products using scanning electron microscopy (SEM) or powder x-ray diffraction (XRD).¹⁷

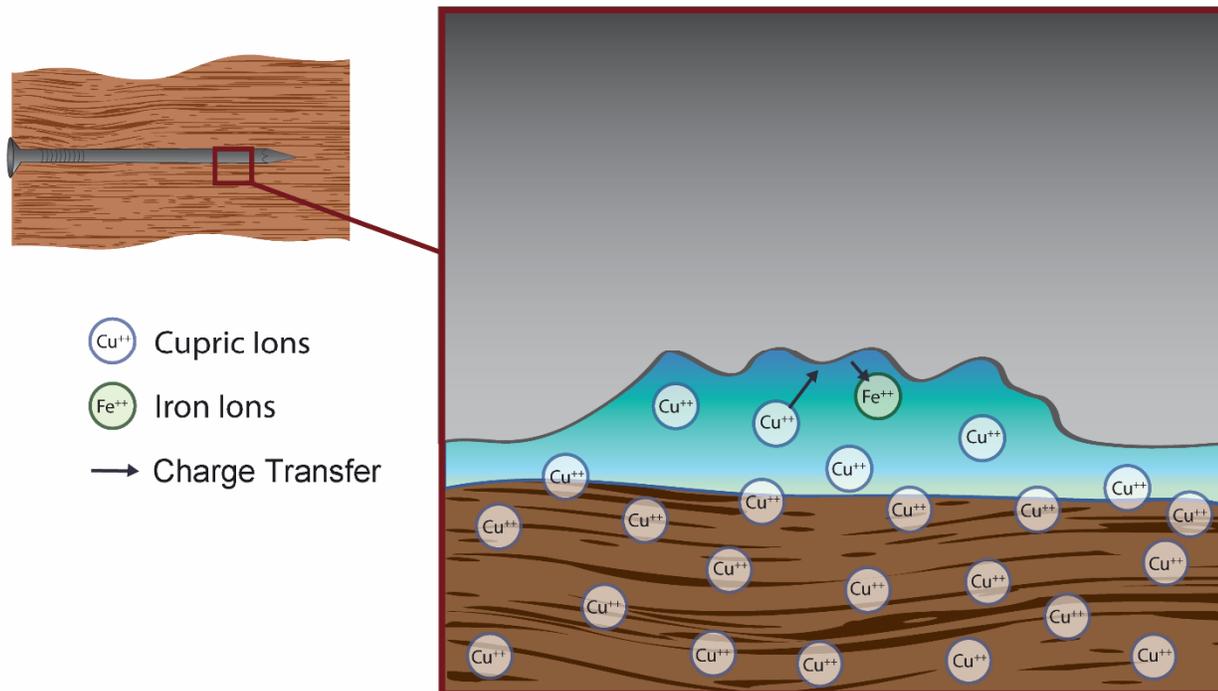


Figure 1: Illustration showing the mechanism of corrosion of metals in treated wood where cupric ions from the wood preservative migrate to the metal surface where they are reduced as the iron is oxidized.

Recent work used synchrotron based x-ray fluorescence microscopy (XFM) and x-ray absorption near edge spectroscopy (XANES) to further examine and test the mechanism of corrosion in treated wood.¹⁸ In these experiments, the wood immediately next to embedded metals was analyzed. Using XFM, the amount of copper in the wood cell walls was quantified down to trace levels. Using XANES, the oxidation state of the copper was determined. Figure 2 presents example data from the experiment. There was a clear “corrosion affected” zone which was depleted in copper and extended approximately 50 μm from the fastener surface. This corrosion affected zone also corresponded roughly with the distance that the iron corrosion products diffused into the wood cell wall. The XANES patterns revealed a peak consistent with a copper (I) oxidation state. The oxidation state was the same across both the corrosion affected zone and the control wood.

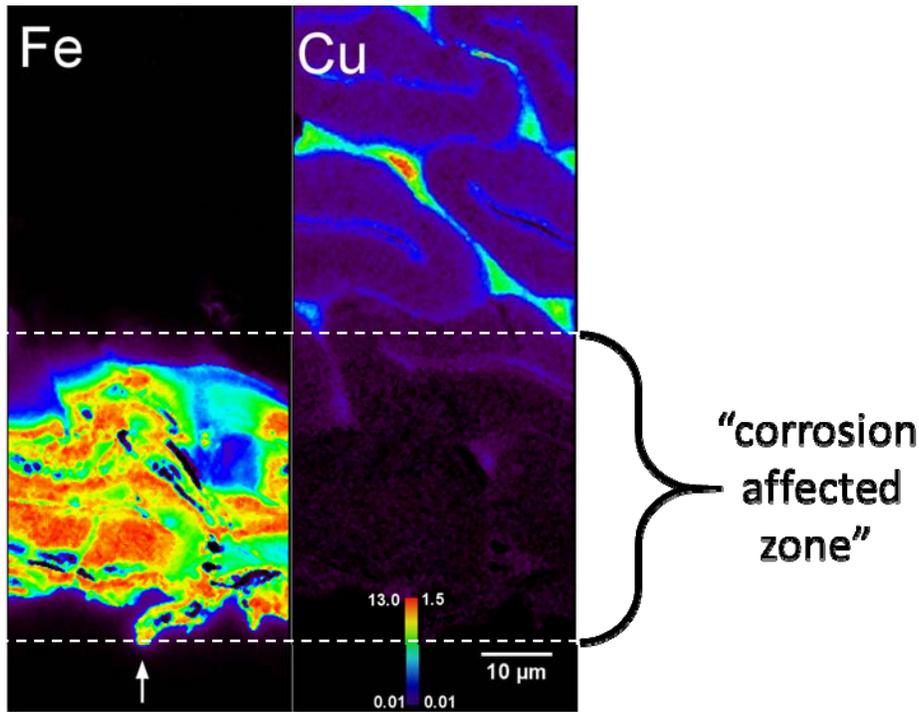


Figure 2: XFM map of wood showing the iron and copper concentrations immediately adjacent to a steel fastener (fastener location indicated by arrow).

The data in Figure 2 gives insight into why the previous attempts to observe copper in the corrosion products were unsuccessful. The size of the copper depleted zone was used to calculate the amount of copper that was consumed in the reaction and therefore presumably would be in the corrosion products. Based on the differences in the copper concentration between the depleted zone and non-depleted zone, and the size of the zone, it was estimated that the amount of copper consumed was approximately 32 micrograms for the entire fastener. Given that the fastener weight loss caused by corrosion was between 60-80 mg, this amount of copper represents at most 500 parts per million of weight. This concentration is well below the detection limit of the techniques previously used to identify copper in the corrosion products of treated wood. In this paper, we utilize the high brilliance of the synchrotron light source of the Advanced Photon Source[†] at (APS) at Argonne National Laboratory[†] (ANL) to examine the corrosion products of metals exposed to treated wood with XFM.

EXPERIMENTAL PROCEDURE

Corrosion products were examined from a previous test where metals were placed in contact with preservative treated wood. Plain carbon steel nails that were 64 mm long and a diameter of 3 mm were driven into southern pine (*Pinus spp.*) and exposed for 1 year at 80°F, 100% relative humidity. Several different wood preservatives were examined, chromated copper arsenate type C (CCA), alkaline copper quaternary type D (ACQ), micronized copper quaternary (MCQ), and copper azole type C (CA-C). The wood was treated at the retention specified for above-ground retention in the American Wood Protection (AWPA) standard U1.¹⁹ Full details of the preservative formulations can be found in the AWPA standard P5 and ICC-ES Evaluation Report ESR-1980.^{20, 21} At the end of the exposure period, the loosely adherent corrosion products were collected by scraping the surface of the fastener with a razor blade. These corrosion products were stored in a sealed glass vial in dry (office) conditions for several years prior to analysis.

[†] Trade name.

XFM was performed at APS beamline 2-ID-E. To prepare the corrosion products for XFM, the corrosion products were spread onto the adhesive side of Kapton[†] tape that was attached to the beamline aluminum mounting stick. The XFM measurements were taken with a focused beam measuring approximately 0.3 μm in diameter at an energy of 10.15 keV. For each corrosion product a 0.6 mm by 0.2 mm map was built up using 1 μm steps and 5 ms dwell times. An Al filter was also used to attenuate the beam to prevent detector overload. The XFM maps were created using the MAPS software package.²² Full spectra were fit to Gaussian peaks, background iteratively calculated and subtracted, and the results were compared to a standard reference materials (RF8-200-S2453, AXO GmbH, Dresden).

RESULTS

Figure 3 shows XFM maps for corrosion products collected from steel fasteners. The figure can best be understood by examining the iron maps. Corrosion product particles appear as high intensity regions. The reported concentrations are the 2D projection of a 3D X-ray measurement; the exact concentration density is unknown as the corrosion product particles varied in size, and in some cases the X-rays may not have penetrated through the full particle. The copper map shows the presence of copper clustered in particle regions. Figure 4 shows the XFM spectra from a small ROI within a copper containing region (labeled with a black star in Figure 3). The peak locations confirm that the copper on the XFM map is indeed from a copper K_{α} peak, and not the shoulder of a peak of a different element.

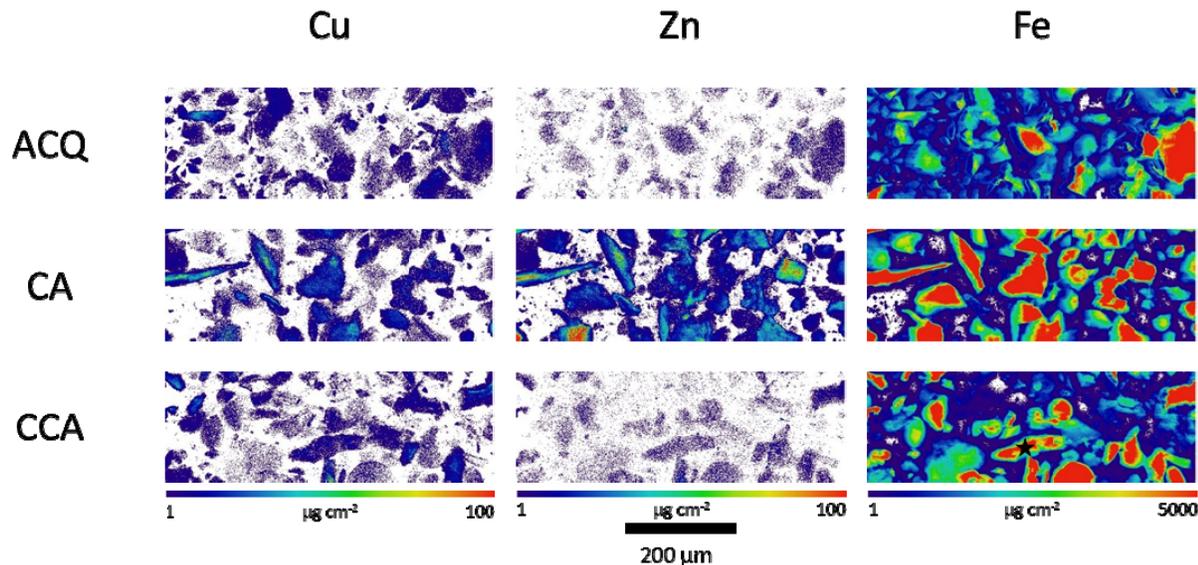


Figure 3: XFM maps of the corrosion products collected from steel fasteners embedded in ACQ treated wood (top), CA treated wood (middle), or CCA treated wood (bottom).

[†] Trade name.

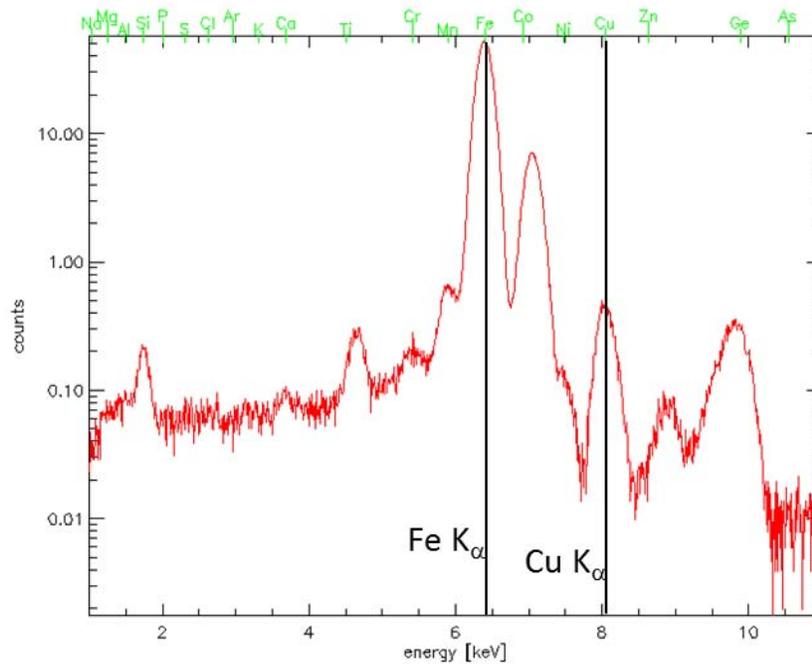


Figure 4: XFM spectra from taken from a small region of interest within the map collected from CCA treated wood showing the copper K α peak.

From the data in Figure 3 and Figure 4, it is clear that there is copper in what was collected with the corrosion products. However, it is unclear how the copper is distributed throughout the corrosion products. Figure 5 presents co-localization maps of iron, zinc, and copper. In these maps, copper is clearly co-located with iron. In some particles, it appears to occur in small veins. In others it appears more equally distributed across the corrosion products. This co-localization suggests that the copper was formed with the oxide and hydroxide corrosion products instead of being formed with copper-rich wood particles.

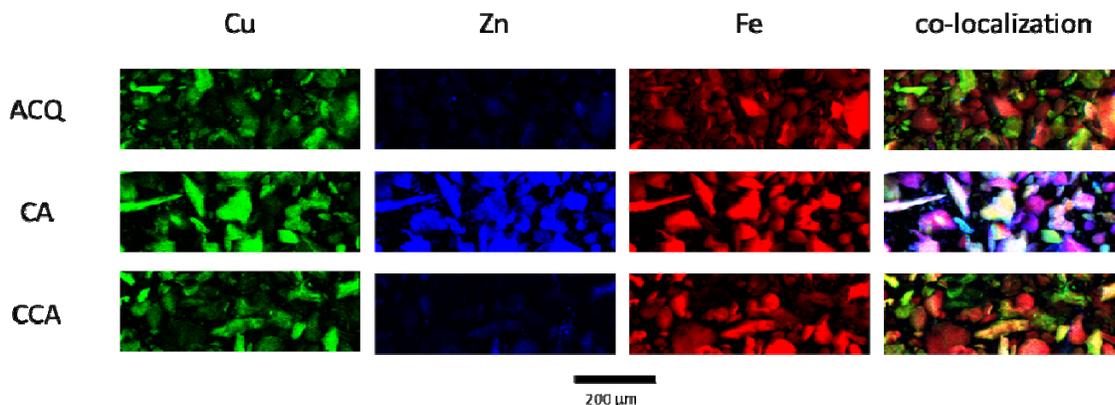


Figure 5: XFM maps collected on steel corrosion products that show the co-localization of copper, iron, and zinc in the corrosion products.

DISCUSSION

The corrosion products of steel exposed to preservative treated wood contain copper. The copper is co-located within regions of iron rich corrosion product particles. These results are consistent with the previously proposed mechanism of corrosion in treated wood where copper from the wood preservatives diffuses to the metal surface where it is reduced. The presence of copper in the corrosion products answers one of the last questions in the corrosion mechanism, namely, what happens to the reduced copper.

Previous attempts to locate copper in the corrosion products using scanning electron microscopy and powder X-ray diffraction were unsuccessful. One reason for this may be that the copper concentrations were low compared to the other elements in the corrosion product. Based upon Figure 2, the copper concentration was estimated at no more than 500 parts per million. The median copper concentration found in the corrosion products for the fastener embedded in CA-treated wood was $0.9 \mu\text{g cm}^{-2}$ (Figure 3). The corresponding median concentration of iron was found to be $1000 \mu\text{g cm}^{-2}$. These data suggest a concentration of 900 parts per million, within a factor of 2 from what was estimated from the XFM maps of the wood by itself. These concentrations are on the edge of what may be resolvable with SEM and XRD, and the current findings highlight the low achievable levels of quantification inherent in synchrotron based XFM.

CONCLUSIONS

Using synchrotron based XFM (this work) and XANES,¹⁸ we were able to confirm the corrosion mechanism in treated wood involves the reduction of cupric ions from the wood preservative at the metal surface. Furthermore, we were able to quantify the amount of copper removed from the wood cell walls and semi-quantitatively determine the amount of copper in the corrosion products. Together, these measurements have confirmed previous hypotheses of the mechanism of corrosion of metals in treated wood and this understanding can be used in the development of new anti-corrosion strategies for metals in treated wood.

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