Distribution and Oxidation State of Copper in the Cell Walls of Treated Wood Examined by Synchrotron Based XANES and XFM

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ABSTRACT

Recently, synchrotron based X-ray fluorescence microscopy (XFM) and X-ray absorption near edge spectroscopy (XANES) were used to examine the mechanism of metal fastener corrosion in copper-treated wood. XFM is able to map the copper concentration in the wood with a spatial resolution of 0.5 µm and is able to quantify the copper concentration to within 0.05 µg cm^{-3}. XANES was used as a complementary technique to differentiate between oxidation states of copper in the wood. While the primary goal of these measurements was to better understand the corrosion mechanisms, the measurements also give insights into the amount, distribution, and ionic states of copper in various wood preservatives. In this paper we show how synchrotron based XFM and XANES can be used to map out the concentration of copper within the cell walls along with the oxidation state, as a potential tool for better understanding treatment and fixation with copper based preservatives. Data are presented for alkaline copper quaternary (ACQ-D), chromated copper arsenate (CCA-C), copper azole (CA-C), and a micronized copper quaternary formulation (MCQ). The data suggest a large fraction of the copper is in a copper (I) oxidation state.

Keywords: copper, oxidation states, micronized copper, wood preservatives

INTRODUCTION

Waterborne wood preservatives are used to protect wood from biotic attack when the wood will be placed into high moisture environments and are the preferred preservative system when the wood is painted or used in residential construction [1]. Nearly all waterborne wood preservatives use copper as part of the preservative system [2]. The copper in the preservative systems start as either solubilized copper or sub-micron particles of copper compounds. These solutions are then introduced to the wood through vacuum and pressure cycles to force them into the wood structure where the treatment chemicals react with the wood polymers through a process called "fixation." After reacting with the wood polymers, the fixed wood preservatives exhibit relatively low amounts of leaching [3].

Understanding the amount, distribution, and binding interactions of copper in treated wood is important for understanding how the treated wood will perform and is also important for understanding differences between preservatives. A better understanding could potentially lead to new ways of delivering copper in the treated wood. Traditionally, the fixation reaction and the binding of copper have been studied with electron paramagnetic resonance (EPR). In this technique, the unpaired spins of the copper metal complexes are excited with a magnetic field, and the resulting data gives information on the type and geometry of the organometallic bonds in the copper (II) complexes [4]. EPR has been used to examine the fixation of chromated copper arsenate (CCA), the solubilization of micronized copper formulations, and the complexing of copper in treated wood [4-9]. These papers have only examined the copper (II) bonds; Xue et al. suggest that over 95% of the copper in treated wood exists in the copper (II) oxidation state [8]. Also, EPR is limited in its spatial resolution and therefore cannot examine differences in the copper oxidation state within different regions of the cell wall. Measurements are taken on sample tubes that are 4-5 mm in diameter and filled to a height of 100 mm [9].

The distribution of copper within the cell walls has been examined with scanning electron microscopy (SEM) or field-emission scanning electron microscopy (FESEM) in combination with energy dispersive X-ray spectroscopy (EDS) [10-14]. Much of this work has focused on examining differences in the copper distribution between micronized and traditional copper systems. For instance, Matsunaga et al. [11, 12] and Stirling et al. [14] used these techniques to identify copper

particles and copper distribution in wood treated with micronized formulations. More quantitative work was performed by Cao and Kamdem [13] who examined differences in X-ray intensity (counts) across cell wall layers to determine a semi-quantitative copper distribution within cell wall layers of wood treated with copper-ethanolamine.

In short, EPR and SEM/EDS give information on the oxidation state of copper within the wood on a bulk level and also some clues about how the copper is distributed in the wood. Here we show how synchrotron based techniques can give a clearer understanding of the spatial distribution and oxidation states of copper within the wood. Specifically, we use X-ray fluorescence microscopy (XFM) to map the copper concentration with a concentration resolution of 0.05 µg cm^{-3} and X-ray absorption near edge spectroscopy (XANES) to determine the oxidation state within the secondary layer of the wood cell wall and within the cell corner compound middle lamella.

MATERIALS AND METHODS

The wood material came from samples that were used in previous corrosion tests that examined the effect of different wood preservatives on the corrosion of carbon steel fasteners. The wood was treated in 2007 with either chromated copper arsenate (CCA-C), alkaline copper quaternary (ACQ-D), copper azole (CA-C), or a micronized copper quaternary formulation (MCQ). The retentions for all treatments were targeted for an above ground application (UC3B) [16]. The actual retention was later verified using inductively coupled plasma atomic emission spectroscopy (ICP-AES). The actual retentions for ACQ, CCA, and CA were lower than the targeted retention, MCQ was higher. Table 1 summarizes the preservatives used, their compositions, and their targeted and actual retentions along with the corresponding concentration of copper in the wood based off ICP-AES.

Table 1. Preservatives tested along with the actual retentions as measured by ICP-AES. The final column is the bulk concentration of copper in the treated wood.

	Composition	Nominal Retention (kg of preservative per m^3 of wood)	Actual Retention (kg of preservative per m^3 of wood)[a]	Bulk copper concentration (g of copper per m^3 of wood)
CCA Chromated Copper Arsenate (type C)	47.5 wt% CrO_3 18.5 wt% CuO 34.0 wt% As_2O_5	4	1.6	236
ACQ Alkaline Copper Quaternary (type D)	66.7 wt% CuO 33.3 wt% DDAC[b]	4	2.9	1529
CA Copper Azole (type C)	96.1 wt% Cu 1.95 wt% Tebuconazole 1.95 wt% Propiconazole	1	0.7	541
MCQ Micronized Copper Quaternary	66.7 wt% CuO 33.3 wt% DDAC	4	5.0	2636

[a]Actual retention in bulk wood as determined by (ICP-AES) in previous work [15]
[b]DDAC, didecyldimethylammonium carbonate

Prior to synchrotron analysis, the wood specimens were placed in a chamber at 27°C (80°F) and 100% relative humidity for a year during the corrosion test. Following the corrosion test, the wood was split along the grain so the fasteners could be removed and then was stored in dry (office) conditions for several years.

To examine the wood with fluorescence microscopy, the samples were cut into 2 µm sections. The 2 µm-thick sections were prepared using a diamond knife fit into a Leica EM UC7 Ultramicrotome (Wetzlar, Germany). Transverse sections in Figure 2 were cut under ambient temperature and dry. The sections were secured between two Norcada 200 nm–thick silicon nitride windows (Edmonton, AB, Canada) for the experiments. The sections were cut so that one part of the section came from the cells that had been in contact with the corroded fastener. The sections were cut at different depths for the different preservative treatments. The CA, CCA, MCQ, and ACQ samples were cut 12, 44, 6, and 47 mm below the surface, respectively; all measurements are within ± 3 mm. One section from each wood preservative was examined.

The fluorescence microscopy experiments were performed at beamline 2-ID-D at the Advanced Photon Source at the Argonne National Laboratory. The XFM data were collected with a beam energy of 9 keV with 0.2 micron step sizes and a 5 ms dwell time. To calculate and visualize the 2D representation of the elemental concentrations, the MAPS software package

was used [17]. MAPS fit the full spectra to modified Gaussian peaks, iteratively calculated and subtracted the background, and the spectra were then compared to standard reference materials NBS 1832 and 1833 [17]. The intensities of the quantified element maps had units of mass per area. Volumetric concentrations were calculated by dividing the intensities by the known 2 µm section thickness.

Copper XANES data were collected by scanning in energy space over the copper K-edge (8980 eV) from 8960 eV to 9040 eV with a step size of 0.5 eV. The beam spot size was approximately 0.2 µm, which allowed measurements to be taken in both the secondary cell wall and the cell corner compound middle lamella. The dwell time at each energy depended on the amount of copper in the wood cell wall and ranged from 2s-10s per energy step. Data were analyzed by first exporting the copper fluorescence signal and the total absorption from MAPS. The ratio of the copper signal to the absorption was then analyzed in ATHENA (version 0.9.22) [18]. Using the software, the data were edge step normalized so that they could be directly compared to other XANES data. Because the scans from adjacent cells were nearly identical, they were "merged" in ATHENA by averaging the normalized absorption at each energy. Merging scans reduces the noise within the XANES scans and allows for easier comparison across different samples. Standards were also tested so the experimental data could be compared against known compounds.

RESULTS AND DISCUSSION

Figure 1 shows XFM maps of the copper concentration in the wood cell walls. The color intensity is proportional to the amount of copper and was scaled so that all the wood preservatives are presented on the same color map. The XFM maps for all preservatives were taken on the part of the wood section that was far away from the corroded fastener. Coarse overview scans (Figure 2) showed that the copper concentration was relatively uniform across the sections, except in the immediate area (<20 µm) next to the fastener [19].

The cells appear twisted because of the crushing that occurred when the fastener was driven in (Figure 1). In all preservatives, the concentration of copper was higher in the middle lamella than in the secondary cell wall. The copper concentration also appears slightly higher in the cell wall directly adjacent to the cell lumen for CCA, CA, and MCQ. The amount of copper in the cell walls across the wood preservatives is roughly correlated with the amount of copper in the bulk wood (Table 1). The copper loading was lightest in the CCA treatment which had the least amount of copper in the XFM maps. Likewise, the MCQ treatment had the highest loading of copper and has the highest concentration of copper in the XFM maps of the cell walls.

The distribution of copper is relatively uniform within the secondary cell wall and the middle lamella, although the copper amounts are clearly different between these two regions. During the corrosion test, the wood was held at high humidity for over a year. Copper is mobile within the cell wall when the wood is in equilibrium with a relative humidity greater than 65% [20]. Therefore, we would expect the copper to diffuse throughout the year long test to minimize any differences in the chemical potential and therefore have a generally uniform distribution, as we have observed within a given cell wall layer. However, the fact that there are differences in concentration between the secondary cell wall and middle lamella may suggest that these cell wall layers have different affinities for copper.

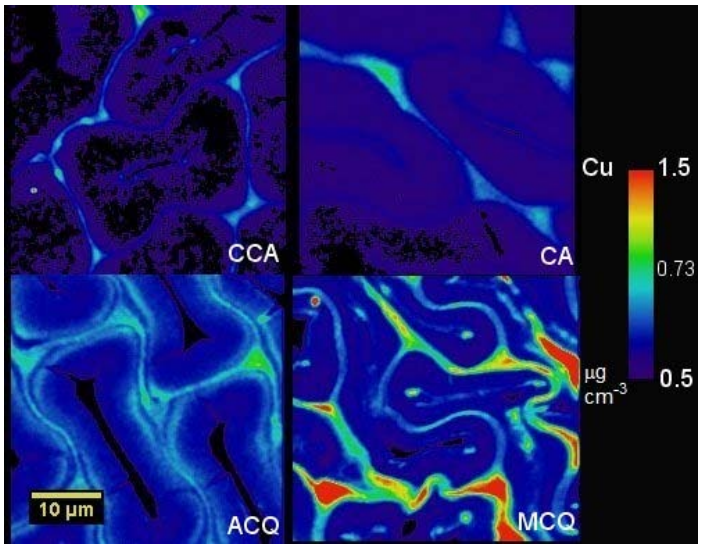

Figure 1. XFM maps of the copper concentration and distribution within the cell walls of wood treated with different wood preservatives. The images are scaled so that the color intensity map is the same across all four preservatives.

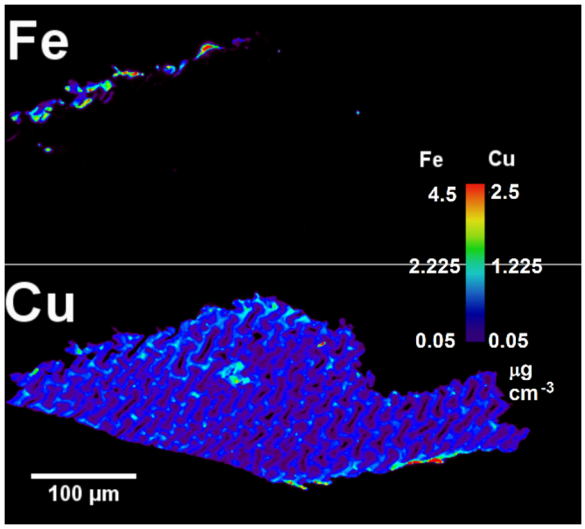

Figure 2. Coarse overview scan of the entire ACQ section showing the concentration maps of both iron (top) and copper (bottom). The top left edge of the sample was in contact with the corroded fastener and has a higher concentration of iron and less copper.

Figure 3 presents XANES patterns for the different wood preservatives. The data represent merged (averaged) scans from within the secondary cell wall region (solid line) or taken in the cell corner compound middle lamella (dotted line). For a given wood preservative, the curves are very similar suggesting that the oxidation state of copper in treated wood does not depend upon the cell wall layer. Because of the similarities, data from the secondary cell wall and middle lamella were merged in further analysis.

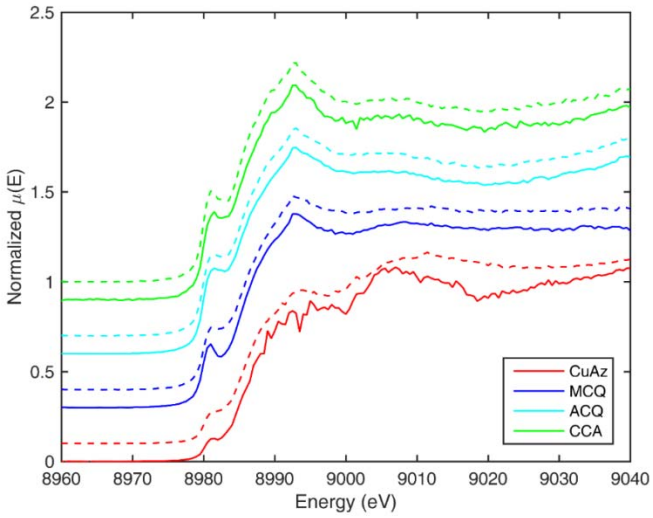

Figure 3. Copper XANES patterns taken from locations within the secondary cell wall (solid line) and the middle lamella (dashed line) in wood sections cut from different wood preservatives.

The oxidation state of the copper in the treated wood was determined by comparing the data to curves taken on known compounds (standards) using the linear combination fitting routines in ATHENA, where the data were fit to a linear combination of standard spectra. The data could be best represented by a linear combination fit of the copper (I) oxide standard and the copper (II) carbonate standard. Adding more standards to the linear combination fitting did not improve the goodness of fit. The XANES pattern for these standards is presented in Figure 4 along with the resulting linear combination fit for CCA.

Figure 5 shows the linear combination fits for all wood preservatives. The percentage of copper (II) carbonate and copper (I) oxide from the fit is given in Table 2. The linear combination fit appears to capture most of the features of the CCA, MCQ, and ACQ data. However, the fit cannot capture the ratios of the peak heights within the CA data, suggesting that the fit is not optimal, and also that CA may contain a different copper species. More work is needed to find appropriate standards for the linear combination fitting of the CA data.

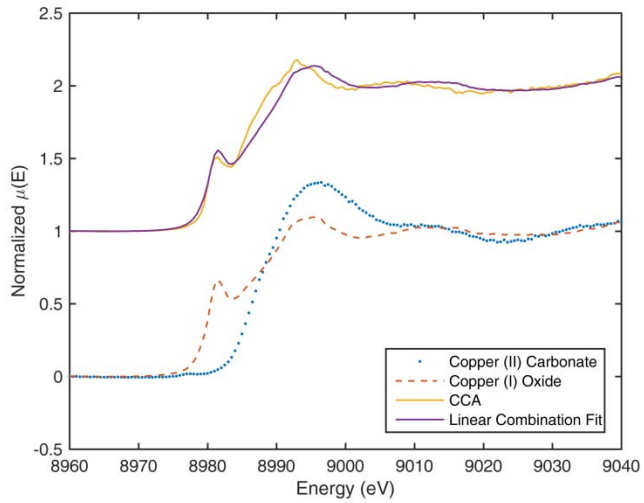

Figure 4. Comparison of the linear combination fit (purple) to the CCA XANES pattern (gold). The standard from which it was fit are included below. The best fit linear combination contained 83% copper (I) oxide and 17% copper (II) carbonate.

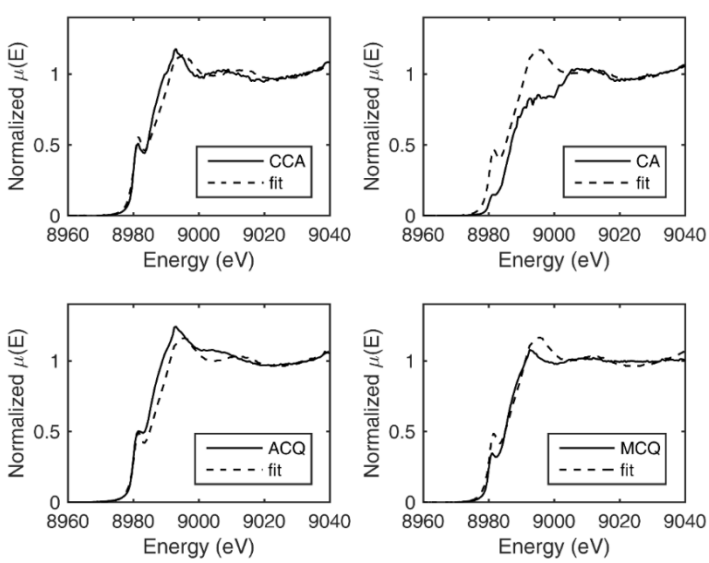

Figure 5. Comparison of the XANES patterns to their best linear combination fit of copper (I) oxide and copper (II) carbonate.

Overall, the XANES patterns were found to be very similar for the middle lamella and the S2 layer of the cell walls for all preservatives. This suggests that even though these layers are different in the amount of copper that they can hold, the oxidation state of the copper is the same in these distinct cell wall layers. The XANES spectra are very similar between the

ACQ, MCQ and CCA data which suggests that the oxidation states of copper in the wood cell wall are similar for these different preservative systems. On the contrary, the CA data exhibited a different spectra and the fit was not as good to the standards it was tested against.

Table 2: The percentages of copper (I) oxide and copper (II) carbonate in the best fit of the XANES data to the two standards.

	% copper (I)	% copper (II)
CCA	83	17
ACQ	73	27
MCQ	71	29
CA	68	32

The XANES patterns were compared against a copper (II) carbonate and copper (I) oxide standard and fit with a linear combination fit. The results of the fit suggested that for all wood preservatives, the majority of the copper was in a copper (I) oxidation state (Table 2). The spatial resolution of the technique allowed a confirmation that the oxidation state was the same between cell wall layers for a given wood preservative. The high amount of reduced copper found with XANES is in contrast to previous work that suggested that over 95% of the copper in treated wood was in a copper (II) oxidation state [8]. One difference is that the previous work examined freshly treated wood whereas this work examined wood that had been in damp conditions for a year, followed by several years of storage under dry conditions. One possible explanation for these differences is that the oxidation state of copper in treated wood changes over long time periods. More work is needed to better reconcile these differences.

CONCLUSIONS

This paper illustrated how synchrotron based XANES and XFM can be used to examine the distribution and oxidation state of copper in preservative-treated wood. The data presented herein examined wood that had been in a 1-year corrosion test and showed the distribution and oxidation state of copper in the wood cell walls of wood that was held at 80°F and 100% RH for one year. The quantitative XFM maps showed that there was more copper in the middle lamella than in the secondary cell wall layer. However, the copper concentrations were uniform throughout the S2 layer for the ACQ, MCQ, and CA treatments. The XANES spectra revealed that for all treatments, there were higher amounts of copper (I) than copper (II) compounds.

ACKNOWLEDGEMENTS

Joseph E. Jakes and Samuel L. Zelinka acknowledge funding from the Presidential Early Career Award for Scientists and Engineers (PECASE). The use of Advanced Photon Source facilities was supported by the US Department of Energy, Basic Energy Sciences, Office of Science, under contract number W-31-109-Eng-38.

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