# Chemistry of Micronized Copper Treated Wood

John N. R. Ruddick,
Mychem Wood Protection Consultants Ltd., West Vancouver, B.C.

## Abstract

Recently two studies of copper treated wood using X-ray absorption near edge structure (XANES) have revealed the presence of Cu(I) in the treated wood. Since previous studies on freshly treated wood had not shown Cu(I) the potential causes of the formation of the Cu(I) were assessed. In one of the studies freshly treated wood was found to contain no Cu(I), but up to about 14% was recorded in material recovered during a wipe test following one and two month exposures above ground. It was suggested that this is related to the weathering of wood. The second study examined wood adjacent to metal fasteners as part of a corrosion study. Very high levels of Cu(I) which ranged from 68% to 83% were observed. It was suggested that the corrosion chemistry which is known to lead to reduction of Cu(II) to Cu(I) or copper metal was the prime cause of the Cu(I) formation. It is recommended that further XANES studies be undertaken on copper treated wood after extended periods of storage or use taking care to avoid influences of weathering and corrosion chemistry.

## Introduction

Recently researchers reported high Cu(I) content in wood treated with copper based wood preservatives, including micronized copper Zelinka et. al. (2016). This is important since the usual techniques used to investigate the chemistry of the micronized copper would not be able to detect the presence of the cuprous form. Currently much of the chemical information on micronized copper reactions in wood during treatment has been based on X-ray fluorescence spectroscopy (XRF) for quantifying total copper and electron paramagnetic resonance (EPR) for speciating and quantifying the reacted Cu(II) formed (Xue, Kennepohl and Ruddick, 2012; 2013a and 2013b; 2014, 2015 and 2016). The EPR detection is based on the paramagnetic behaviour of the Cu(II) compounds. It is already known that certain copper(II) compounds are not detectable by EPR, for example basic copper carbonate, and copper oxalate. This is because they are antiferromagnetic – the spins on adjacent copper atoms couple. However, Cu(I) compounds are diamagnetic and so are not observed in EPR. The early research on quantification had observed excellent agreement between the XRF and EPR data. The question therefore, was whether the formation of the Cu(I) was due to particular exposure conditions of the samples or an inherent property of copper treated wood. This paper seeks to identify the possible answers to this question.

## Methodology

The EPR data reported by Xue, Kennepohl and Ruddick, was acquired at 77K. Three replicates were made for each sample. Sample height in all the EPR tubes were controlled to a maximum height of 4.5 cm so they did not exceed that of the vertical height of the microwave cavity (i.e., the sample is kept within the sampling volume of the instrument). A Bruker Elexsys E500 series continuous wave EPR spectrometer was used to carry out data acquisition. The spectrometer was operated at a frequency of 9.40 GHZ (X-band), 100 KHz field modulation and 1G modulation amplitude. DPPH (g = 2.0036) was the standard for spectra frequency calibration (Krzystek *et al.*, 1997).

OriginPro 8 was used to integrate, perform baseline correction and calculate the area under the curve (AUC) for the spectra. AUC values were normalized over EPR sample weight of the dried sawdust (AUC/mass).

The XRF data is usually acquired by bombarding a sample with a low energy source of X-rays. During this process the specific energy required to excite a copper atom is provided so that an inner shell electron is excited to an outer shell. In the second part of the process an outer electron falls back to fill the inner shell and an x-ray is emitted characteristic of the energy of the emitting atom. In this way the identity and amount of the emitting atom is determined. The elemental quantification is independent of the spin and redox state.

Two other techniques that have been reported. These are extended X-ray absorption fine structure (EXAFS) spectroscopy and X-ray absorption near edge structure (XANES). Both require a synchrotron radiation source. In EXAFS, calibration using a metallic foil assigning 8979 eV to the pre-edge peak of copper and 10355 to the pre-edge peak of lead. XANES involves the filling of a core hole by capture of an electron from another shell plus fluorescence, filling in of the core hole by the emission of an Auger electron. Detailed descriptions of these techniques are available from various sources.

## Discussion

Gaur, Shrivastava, and Joshi (2009) used XANES to quantify Cu(I) and Cu(II) oxide in mixtures, Figure 1. The goodness of fit confirmed the ability of the XANES to quantify a 3:1 mixture of the two oxides.

Dupont et. al. (2002), have used XANES to study the retention of copper and lead by a lignocellulosic material (wheat bran) which was used to treat wastewaters as a biosorbent. The XANES allowed the speciation of the metal and by comparing the spectra of the Cu-lignocellulose derivative to selected model Cu compounds, information on the geometry of the copper lignocellulosic derivative was obtained (Figure 2).
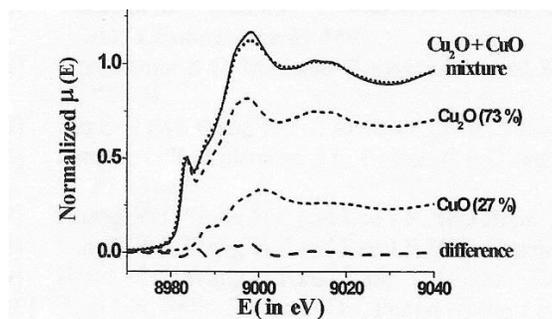


**Figure 1.** XANES spectra of mixtures of $Cu_2O$ and CuO, compared to samples of pure $Cu_2O$ and CuO. (from Gaur, Shrivastava and Joshi, 2009)

Interestingly, in the spectra of Cu(II) compounds in both studies, no reduction of Cu(II) to Cu(I) was detected, so it is possible to eliminate the X-ray exposure as a source of Cu(I) formation.

Such reduction has been reported for X-ray photoelectron spectroscopy (XPS) when copper compounds were studied (Jiang and Ruddick, 1999)
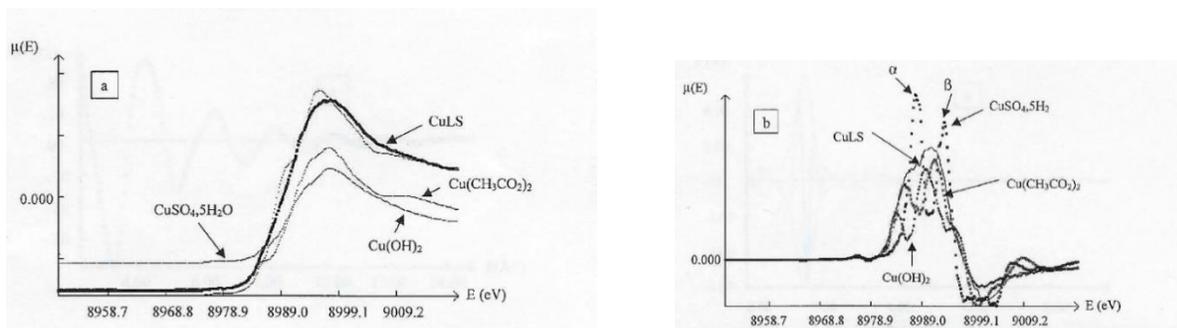


**Figure 2** Normalized XANES spectra (pre- and near edge region) of CuLS, $Cu(OH)_2$, $Cu(CH_3CO_2)_2$, $Cu(SO_4)_4,5H_2O$ a) and their first derivative b). (from Dupont et al., 2002)

The authors concluded that the similar spectra suggested similar geometries for the bonding leading to the further conclusion that the copper was bonded to the lignocellulosic molecule by the carboxylic groups.

Considering now the recent papers where Cu(I) species were detected using XANES. The first was reported by Platten III et al. in 2016. In this study commercially treated "2 x 6" boards were purchased from a retail outlet. They had each been treated with one of three wood preservatives, described by the authors as two micronized copper treatments (MCA-1 and MCA-2) and an ionic aqueous copper azole treatment (ACA). It is assumed that this treatment was copper azole solubilized in monoethanolamine, and usually identified as CA-B. Three boards treated with each formulation were left outdoors for approximately one year in Cincinnati, Ohio. Each board was divided into four sections. Three sections were used for total copper analysis while the fourth was used for particulate analysis. Each section was sampled by wiping using a polyester cloth at 0 to 399 days. Two additional boards were stored indoors and were also wiped repeatedly without any weathering. Interestingly, before weathering no Cu(I) was detected by XANES (Table 1).

**Table 1**  Linear combination fitting results for Cu Kα XANES first derivative spectra for materials wiped off of the treated wood samples exposed to the environment after 1 and 2 months of exposure

| Sample | Month | Cu-Organic | $Cu_2O$ | $Cu_2CO_3(OH)_2$ | $CuCl_2$ (aq) |
|---|---|---|---|---|---|
| | | Average/Standard Deviation % | | | |
| MCA-1 as-purchased | 0 | 88/1 | | 12/1 | |
| MCA-1 Wipe 1 | 1 | 49/4 | 10/1 | 41/4 | |
| MCA-1 Wipe 2 | 2 | 20/5 | 5/2 | 76/8 | |
| MCA-2 as-purchased | 0 | 42/3 | | 58/2 | |
| MCA-2 Wipe 1 | 1 | 52/5 | 14/2 | 34/5 | |
| MCA-2 Wipe 2 | 2 | 16/5 | 14/3 | 70/5 | |
| ACA as-purchased | 0 | 90/5 | | 10/2 | |
| ACA Wipe 1 | 1 | 73/3 | 10/1 | | 18/2 |
| ACA Wipe 2 | 2 | 67/5 | 5/2 | | 28/4 |

*The summation of Cu-Acetate and Cu-Oxalate

(From Platten et. al. 2016)

After one month of exposure, Cu(I) was detected in all three treated samples at about 10% which did not appear to increase in the second month. After two months of exposure the wipe did not contain sufficient Cu to be characterized. The authors cited research by Pham, Rose and Waite (2002) which studied the kinetics of the reduction of Cu(II) by natural organic matter. Interestingly Platten et al., noted that the XANES also revealed the main components present to be copper(II) carbonate, aqueous Cu(II), $Cu_2O$, and copper complexed with acetate type bonding, (Figure 3).
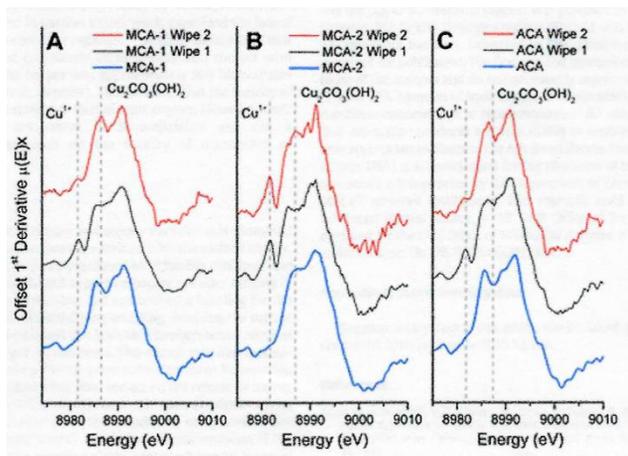


**Figure 3**. Cu Kα XANES spectra for the as purchased pressure treated wood, and material dislodged from the wood surface and retained on a 0.45-µm filter after 1 month (wipe 1) and two months (wipe 2). MCA-1 (A), MCA-2 (B), ACA (C). Dashed lines indicate the energy positions associated with $Cu^{1+}$ and malachite. (From Platten III et al., 2016)

Clearly some reduction of Cu(II) to Cu(I) does occur during weathering. However, it is known that weathering is a surface phenomenon, so that the reduction of Cu(II) is likely to be occurring predominately at the surface. Never-the-less the study also confirms that freshly treated wood does not contain Cu(I), so that previous studies on the chemistry are valid in excluding discussion of Cu(I) formation.

The second paper which also reported Cu(I) in treated wood was by Zelinka et al. (2016). It also used XANES to study the copper speciation in copper preservative treated wood. However, in this case the amounts of Cu(I) reported ranged from 68% in CA-B treated wood, to 83% for chromated copper arsenate (CCA) treated wood. The micronized copper was 71% Cu(I). Clearly these values are considerably different from those reported elsewhere. However, the most plausible reason for these very high figures becomes clear from the material used.

The samples were recovered from wood used for previous corrosion tests. Indeed, the aim of the XANES study had been to examine the corrosion products. During the corrosion test the samples had been exposed at 100% humidity for one year after which the wood was split to remove the fasteners. The samples were stored under dry conditions for several (possibly 5 or more) years. The sections (2 µm) were then recovered from the area containing wood cells in contact with the fastener. The results are shown in Figure 4 where the Cu(I) in the region of 8981 eV can be clearly seen.
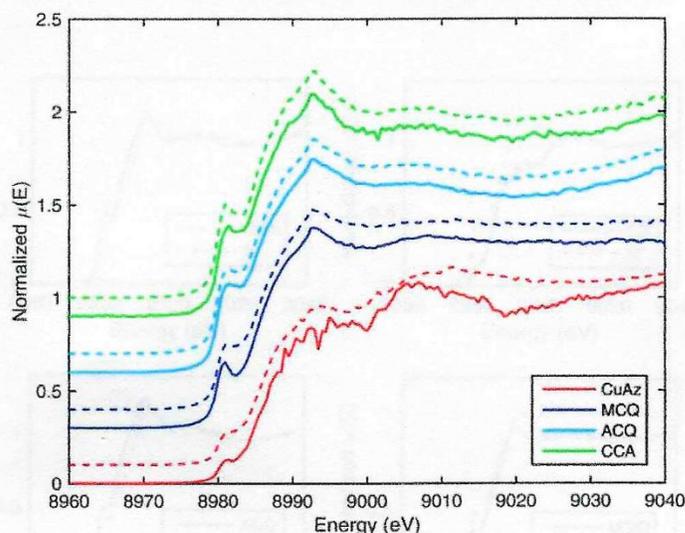
**Figure 4.** Copper XANES patterns taken from locations within the secondary cell wall (solid line) and the middle lamella (dashed line) in wood sections cut from different wood preservatives. (from Zelinka et al. 2016)

The authors suggested that the reason for the high concentration of Cu(I) was that these samples had been subjected to a high humidity for one year followed by several years of dry storage. At present no study of conventionally exposed wood has shown such high Cu(I) concentrations. An alternative explanation is more likely to be found in the use of the wood to evaluate corrosion of metal fasteners, where the oxidation of iron fasteners is well established.

It is also well known that the corrosion of fasteners is enhanced by the presence of Cu(II). Indeed, the deposition of metallic copper on the surface of metal fasteners has also been reported by Simm and Button in 1985. These authors used electrochemical measurements on metals placed in CCA-treated wood cell. They ranked the corrosion potential from the greatest - zinc metal and CCA-treated wood, to the lowest – stainless steel and untreated wood. From the corrosion potential vs pH plots they noted that cuprous ions are stable in contact with stainless steel. This suggests that the reduction of Cu(II) to Cu(I) is a first step in the corrosion process. This likely to be greatest in the treated wood close to the fastener, the location of the samples selected by Zelinca et al. In other studies, Baker (1980) recommended that "in moist ammoniacal copper arsenate and CCA treated wood, fasteners should be selected from those metals that are cathodic to copper in the galvanic series". An excellent discussion on Corrosion of Metals in Wood Products has been produced by Zelnka (2014). Here Zelinka points out that the corrosion mechanism clearly involves reduction of the cupric ions.

However, in solution cuprous ions are relatively unstable compared to cupric ions, although the stabilities do depend on the nature of anions present and water solubility of any products formed.

$$2Cu^+ = Cu + Cu^{2+} \quad E^0 = 0.367 \text{ v}; \text{ K} = [Cu^{2+}]/[Cu^+]^2 = \sim 10^6$$

Thus in aqueous environments the free $Cu^+$ ion can exist only at exceedingly low concentrations. Obviously the formation of relatively insoluble compounds can increase the potential for increased concentration. In the samples studied by Zelink et al. (2016) the extremely high concentrations of Cu(I) suggest that either a very insoluble Cu(I) species was formed, or that the samples were extremely dry. Support for this is observation by Tascioglu et al. (2008) who evaluated the conversion of Cu (II) to Cu(I) in alkaline copper quat (ACQ) treated wood.

Essentially 100% conversion was achieved by steaming but rewetting or leaching converted most of the microbial copper to the divalent form. It may be concluded that in dry wood, $Cu_2O$ which is insoluble in water will be relatively stable, but in moist wood the natural acids present will cause it to oxidize to Cu(II) products.

Thus it may be concluded that in the two papers citing significant formation of Cu(I) in micronized copper treated wood, both involved an external influence which would lead to reduction of some Cu(II) to Cu(I). In the case of the weathering aspect the reduction was low and limited to the wood surface. For the corrosion study the actual corrosion process at the metal-treated wood interface induces a chemical reaction which quantitatively will reduce the Cu(II) in the wood adjacent to the wood metal interface to Cu(I). The subsequent dry condition would limit any re-oxidation of the Cu(I).

It is recommended that XANES studies of copper treated wood that has been in use for extended periods be undertaken, with specific attention to wood not exposed to weathering or fastener corrosion. The role of coatings in preventing the reduction to Cu(I) could be investigated. The impact of the Cu(I) on protection of the wood against decay is not clear, since Horsfall, Marsh and Martin (1937) have suggested that efficacy against fungi is greater for Cu(I) than Cu(II) and has been used as a seed protectant.

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