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Solubilisation and chemical fixation of copper(II) in micronized copper treated wood

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Wood preservatives using micronized particulate copper as the main active ingredient recently introduced in the USA have generated controversies due to their limited intrinsic solubility compared to the conventional soluble copper treatments. Because the availability of soluble copper ions is essential for these preservatives to provide an effective treatment, concerns are centered on whether they are able to produce soluble copper when introduced into wood, and the copper fixation mechanism of the treatment is little understood. Micronized copper treated wood were studied using a combination of Electron Paramagnetic Resonance (EPR) spectroscopy and X-ray Fluorescence (XRF) spectroscopy. The identification and characterization of soluble and chemically fixed copper species were discussed. A calibration standard was developed to quantify the solubilized and fixed copper species in the micronized copper treated wood, which also contains unreacted particulate copper. On the basis of the experimental results, the fixation mechanism is thought to be triggered by the reaction between the carboxylic acid protons in hemicellulose of wood with the particulate copper, and the quantities of the solubilized and fixed copper species are determined by the availability of these acidic protons.

1. Introduction

As one of the most important products of nature, wood has long been used as a fuel, a chemical raw material and a construction material. Data released by the Food and Agriculture Organization Statistics Division (FAOSTAT) of the United Nation shows that global wood extraction in 2013 exceeded 3.6×10^9 m^3, of which about half was used for fuel and half processed for use by industry. The decrease of total forest area from 2000-10 is estimated at 5.2 million hectares per year, which equals a loss of 0.13% of the remaining forest area each year.[1] The net loss in this period is ~35% lower than that in the 1990s as a result of both decreased deforestation (logging) and increased reforestation (planting). Wood used in construction and for utility distribution is prone to degradation by various biological organisms including insects, bacteria and fungi. This is particularly relevant when wood is placed in direct contact with soil, or fresh water or sea water, when enhanced biodegradation will occur unless it is protected. Wood preservation makes great environmental sense by protecting timber against deterioration, thus maximizing the longevity of a renewable resource.

1.1. Major wood structural chemical components

Cellulose, hemicellulose and lignin are the three major structural building blocks of wood cell walls. The integrity of these components are vital to the mechanical strength of lumber, and therefore represent the targets for wood preservation; the structural integrity of wood is ensured by these components. Cellulose constitutes approximately 40-55% of the total cell wall mass and is the most abundant constituent of wood; hemicellulose constitutes another (25-40% of the dry wood mass) and lignin (18-33%) account for the rest.[2]

Cellulose is a linear homopolysaccharide derived from β-D-glucopyranose units linked by $\beta(1\rightarrow4)$ glycosidic bonds. Naturally occurring cellulose microfibers are rich in hydroxyl groups and yields a crystalline structure. Hemicelluloses are amorphous polymers consisting of extensively branched heteropolysaccharides; 5-10% of hemicelluloses are xylans, which contain carboxylic acid sidechains in the form of uronic acids. Unlike cellulose and hemicellulose, lignin is an amorphous macromolecule with no defined primary structure. It consists of cross-linked aromatic alcohols known as monolignols, which contains an abundant numbers of methoxy, phenol, and benzyl alcohol groups.

1.2. Copper based wood preservatives

Chemical wood preservatives are either oilborne or waterborne. Because of the strong petrochemical odor emitted by the oilborne preservatives, waterborne preservatives are exclusively used in residential consumer products in North America due to their excellent effectiveness, low cost, lack of odor and relatively low toxicity to larger organisms. A key ingredient of most waterborne preservative formulae is copper in the form of cupric salts, which are combined with organic biocides to protect against copper tolerant organisms. Even though development of new preservatives in recent years has focused increasingly on organic biocides, copper(II) remains the most extensively used biocidal component due to its excellent performance against a wide range of wood-destroying microbial.[3,4]

Other than production costs and product performance, increasing public awareness of health and environmental safety over the past several decades has become an important factor influencing the development of new preservatives. The negative public perception regarding chromium and arsenic led to the voluntary withdrawal of chromated copper arsenate (CCA) in the North American residential treated wood market in 2003; prior to this, CCA had been the most widely used preservative in wood preservation for almost 30 years. Several alkaline copper based preservatives have been successfully commercialized as replacements. These conventional soluble copper based wood preservatives, such as alkaline copper quaternary (ACQ), copper azole (CA), copper citrate, and bis-(N-cyclohexyldiazeniumdioxy)copper (Cu-HDO), contain copper(II) solubilized in aqueous amine solutions. For a comprehensive review of current soluble copper-based wood preservatives, see Freeman and McIntyre.[5] ACQ and CA are the most commonly used copper preservatives in both Europe and North America for protecting residential products such as decking and fencing. Both formulations contain solubilized copper(II) salts in an aqueous monoethanolamine (MeaH) solution as the primary biocide. The major difference being that ACQ formulations use quaternary ammonium compounds ("quats") as the co-biocide, whereas the amine-solubilized cupric salts in CA are augmented by an azole co-biocide (Figure 1). In MeaH solubilized formulations, the treatment solution contains $Cu(Mea)_2$ as the primary copper species.

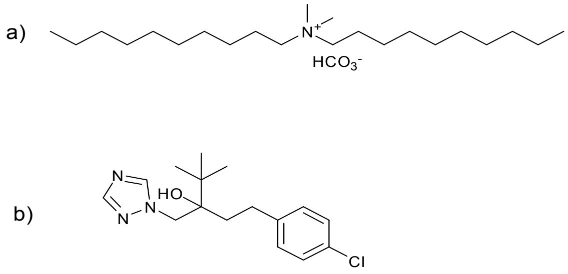
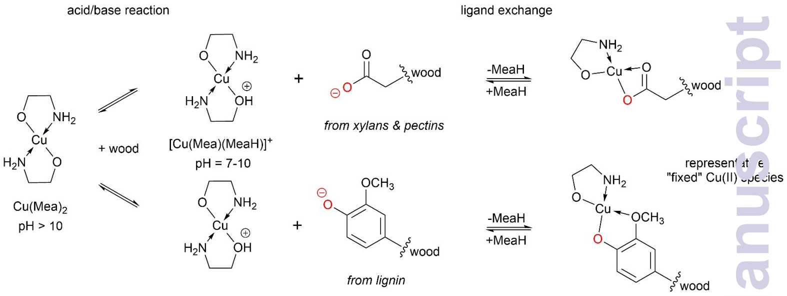


Figure 1 Co-biocides: a) didecyldimethylammonium bicarbonate/carbonate (DDA bicarbonate/ carbonate) used in ACQ-B and ACQ-D; b) tebuconazole used in CA-B

It has been long recognized that copper-based preservatives assert their fungicidal action through free cupric ions in a biological system.[6,7] Therefore, the availability of *soluble* copper(II) ions is essential for the wood preservatives to provide an effective treatment. Copper-amine complexes formed in the impregnating solution (*i.e.* $Cu(Mea)_2$ for Cu(II) methanolamine formulations) can be physically trapped in the polymeric matrices of wood cell walls by weak Van der Waals forces, and they are easily removed during leaching.[8,9] However, the alkaline copper complexes can also react with acidic wood components, such as carboxylic acid, aromatic esters and phenolic hydroxyl groups, causing the copper(II) to be bound (fixed) to the wood (Figure 2). These forms of chemically fixed copper(II) complexes are less prone to leaching as it requires ligand substitution to mobilize the Cu(II) ion; maximizing such fixed Cu(II) species reduces preservative depletion and environmental impact. The highly pH dependent mechanism is triggered by the interaction of the basic preservative solution with the most acidic protons of the carboxylic acids in a rapid acid base reaction.[10] Protonation of the Mea^- ligand leads to rapid ligand exchange with available carboxylates and phenolates in the wood structure. Overall, the chemistry leads to a lowering of the pH to around 7 to 9 and formal cation exchange between the metal complexes and the acidic protons in wood (Scheme 1). [11]



Scheme 1 Chemical fixation of Cu(II) complexes in alkaline methanolamine treatments.

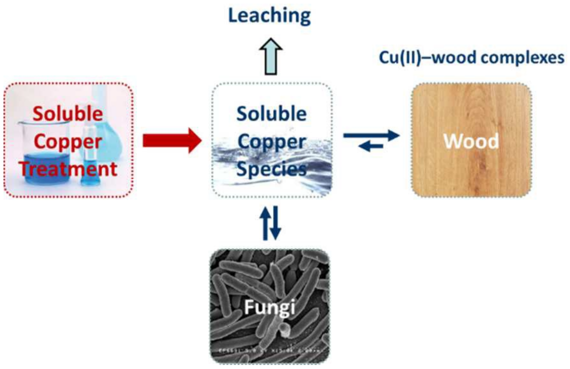


Figure 2 Activity model of soluble copper preservatives

Studies conducted by Lee and Cooper show that the overall *cation exchange capacity* (CEC) of wood is 0.6% w/w Cu per gram of wood at pH 7, and the value doubles to 1.3% at pH 11.[10] However the total amount of copper(II) loaded in wood treated by alkaline copper formulations may exceed the CEC, which implies that a large fraction of copper(II) ions in alkaline copper formulations are *not* chemically bound to wood components (*i.e.*, they are soluble copper species such as $Cu(Mea)_2$; Figure 2) and thus highly susceptible to leaching in high moisture conditions. Whether this poses a higher biological hazard has been a matter of debate.[11] Elevated levels of unfixed metal ions in alkaline copper treated wood have been found in ACQ treated wood compared to CCA[12–14]; which also coincides with enhanced potential for corrosion in alkaline copper treated wood. [15]

Recently, a new strategy for copper-based wood preservation has emerged in the North American market in the form of 'micronized' particulate basic copper carbonate [$CuCO_3{\cdot}Cu(OH)_2$] (BCC) as the active ingredient.[16,17] The micronized BCC particles are produced by mechanical grinding with the aid of dispersing/wetting agents resulting in 90% or more of the particles being less than 1000 nm size. In contrast to the soluble copper(II) species used in alkaline copper preservatives, BCC has extremely low Cu(II) solubility ($K_{sp}=10^{-33.78}$ for malachite) at neutral pH.[18] Insoluble BCC particles are dispersed in aqueous solution in combination with quat or azole co-biocides. These new preservatives, which are known as micronized copper quat (MCQ) and micronized copper azole (MCA), provide an alternative to the widespread alkaline copper preservatives. Reported advantages of the micronized formulations include lower leachability and decreased corrosion of metal fasteners. [5,19]

Even though the availability of *soluble* Cu(II) ions is essential for providing an effective treatment, such a requirement has not been a central concern for conventional water-based preservative formulations because the copper complexes employed are all inherently water soluble. However, the limited intrinsic solubility of micronized copper suggests that such concerns are vital in such formulations. Cupric ions have been detected in laboratory leaching of MCQ treated wood.[20] Field exposure tests have also shown small but significant amounts of copper leached from MCQ treated wood.[21]

The poor intrinsic solubility of the newly developed formulations has sparked great interest regarding whether they are able to produce soluble copper(II) species and thus provide efficient biocidal protection. There is also a great need for more detailed information on the chemistry of their reaction with wood together with information on the underlying mechanisms for their apparent preservative performance.

1.3. Spectroscopic probes of wood preservatives

A number of analytical techniques have been employed to probe the effects of copper treatment on wood samples. For example, energy dispersive X-ray (EDX) spectroscopy, scanning electron microscopy (SEM) and X-ray fluorescence (XRF) have been frequently applied in the surface characterization of copper distribution and quantification of total copper loadings.[22–27] However, these techniques can neither distinguish different possible copper species deposited in treated wood, nor can they provide details of the local chemical environment of these copper species. By contrast, electron paramagnetic resonance (EPR) spectroscopy offers molecular level insights into the chemical nature of Cu(II) complexes, affording the opportunity to characterize, quantify and differentiate the concentration and speciation of various copper complexes in complex systems such micronized copper preservative treated wood.

EPR has previously been applied to *in situ* monitoring of copper-based wood preservative reactions present in wood.[9,28–32] Previous studies, including the seminal contributions of Peisach and Blumberg have shown that the unpaired electron chemical shift in mononuclear S=1/2 Cu(II) species and the hyperfine coupling to the I=3/2 copper nucleus along the axial direction (g_z *and* A_z, respectively) are most sensitive to electronic and geometric perturbations in the coordination sphere of the Cu(II) ion.[9,30,33,34] Peisach and Blumberg[33] investigated a series of natural and artificial Cu proteins for the relation of their chemical structures to the EPR parameters. From these data, systematic changes in both g_z and A_z correlated with the relative number of oxygen vs. nitrogen-based ligands. The relationship of g_z and A_z in different Cu compounds bound to oxygen and/or nitrogen is summarized in Figure 3. [33,35]

Based on this, EPR has been used to probe the nature of copper(II) complexes relevant to wood preservation. Most notably, the complex formed from reaction alkaline copper formulations with vanillin, a lignin model compound, affords an EPR spectrum that is consistent with a single nitrogen–based ligand, in excellent agreement with the solid-state molecular structure of the complex.[36] EPR studies on the fate of alkaline $Cu(Mea)_2$ treated wood samples indicate formation of copper species of the type CuN_2O_2.[28,29,31] In *amine-free* treatment solutions (e.g. using simple salts such as $CuSO_4$ and $Cu(NO_3)_2$), the EPR data of the Cu(II) complexes have larger g_z values and lower A_z, consistent with formation of complexes with four oxygen ligands (CuO_4). [9,28–30]

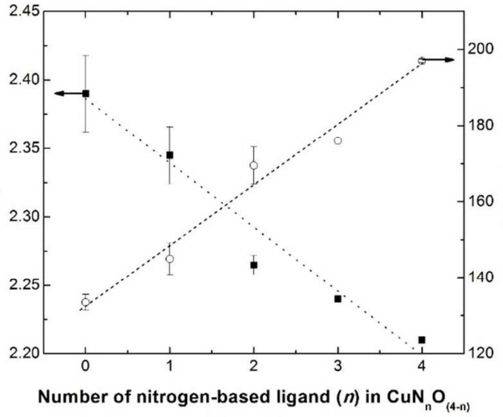


Figure 3 The relationship between the EPR spectral parameters g_z (■) and A_z (○) for a series of Cu(II) compounds (based on data reported in Peisach and Blumberg 1974; Ruddick 1992; Ruddick et al. 2001)

2. Speciation of copper in micronized copper treated wood

2.1. Characterization of copper(II) species

EPR spectra of southern pine sawdust revealed only very weak signals reflecting low intrinsic concentrations of

Mn(II) (Figure 4). Aqueous suspensions of micronized copper (MC) are also devoid of any EPR features as the Cu(II) ions in BCC are antiferromagnetically coupled in the solid state[37] and hence EPR silent. However, a strong EPR signature ($g_z = 2.365$ and $A_z = 130\ G$) is observed in southern pine after two hours of immersion in an aqueous suspension of MC; the resulting spectrum is similar to that obtained from treatment with $CuSO_4$ (Figure 4). The monomeric Cu(II) species formed upon treatment are chemically fixed to the wood, with only minimal leaching.[38] Clearly, despite the low inherent solubility of BCC, wood treatments result in formation of stable Cu(II)-wood complexes. These results imply that treatment of wood with BCC generates at least some soluble (aquo) copper(II) species, which rapidly react with wood components resulting in Cu(II)-wood complexes. Cupric ions have also been detected during laboratory leaching of MCQ treated wood.[20,21] Figure 5 shows the activity model that has been derived from this work.

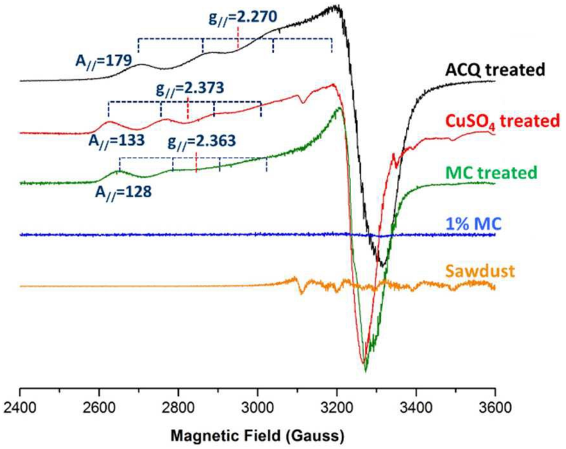
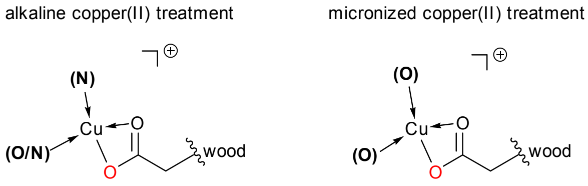


Figure 4 EPR spectra of de-ionized water treated southern pine sawdust, micronized copper suspension containing 1% Cu, and commercial red pine sapwood treated with MC, $CuSO_4$ and ACQ

Commercial MCQ and MCA treated wood yields very similar results to that obtained from laboratory treated samples (see Figure 4). By contrast, commercial alkaline treatments (*e.g.* ACQ) yield very different EPR spectra, which are in good agreement with laboratory treated samples with ammoniacal copper carbonate treated wood.[29,31,35] Taken together, these results imply that copper(II) species formed in both laboratory and commercial treatments using micronized copper differ substantially from that obtained from soluble alkaline copper formulations. The differences between the mononuclear Cu(II) complexes formed under these different conditions are summarized in Scheme 2. Most importantly, we find that even highly insoluble MC formulations allow for formation of Cu(II)-wood complexes, indicating that solubilisation and fixation of Cu(II) into wood does occur from BCC treatment.



Scheme 2 Representative model structures of fixed Cu(II) as derived from EPR studies. The resulting fixed Cu(II) species differ for alkaline copper(II) treated wood (left, EPR $g_{||}$=2.27, $A_{||}$~180G) and micronized copper(II) treated wood (right, EPR $g_{||}$=2.36, $A_{||}$~130G). The differences in EPR parameters reflect a change in the exogenous ligands (N vs. O-based) in the fixed Cu(II) complexes.

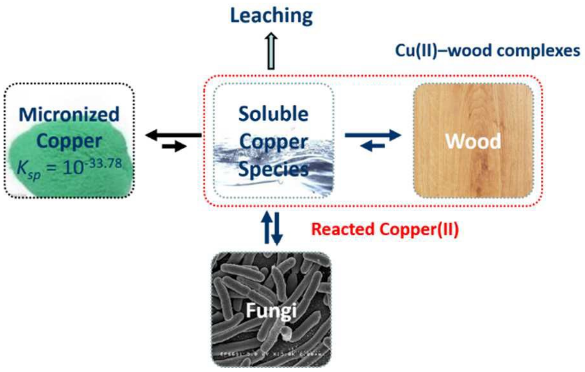


Figure 5 Activity model of micronized copper preservatives

2.2. Quantification of reacted Cu(II) species

The overall activity models for both alkaline and micronized copper formulations imply very different copper speciation in treated wood. In the former case (Figure 2), any copper(II) in excess of that which can be bound directly to wood components must be retained as soluble copper species, which are susceptible to rapid leaching into the environment. By contrast, the latter treatment option (Figure 5) allows for a pool of *insoluble* copper(II) – in the form of BCC – embedded in the wood, which would be significantly less prone to leaching. To address questions that arise from these differing activity models, it becomes imperative to adequately quantify the amount of different copper species in treated wood samples.

Traditional methods for elemental quantification (EDX and/or XRF) provide accurate measures of total copper content but do not allow for efficient speciation between different forms of copper. EPR, however, allows for the quantification of unpaired spins and thus allows for good quantification of *EPR active* copper species. In principle, XRF can provide the total amount of copper in the system and EPR can determine the amount of “reacted copper(II)” (see Figure 5), which consists of the sum of Cu(II)-wood complexes and soluble Cu(II) complexes. Importantly, The amount of reduced copper species (Cu(0) and/or Cu(I)) in treated wood samples has been determined to be <5% by Cu K-edge X-ray absorption spectroscopy. We have exploited a combined XRF/EPR methodology (with appropriate calibration between the two techniques) to allow us to determine the fate of copper in MC treated wood.[39]

***in vitro* treatment kinetics.** MC-treated samples were monitored for 7 days after treatment to determine whether copper speciation changed after initial treatment. Although the chemical nature of the reacted copper species does not change over the first 7 days after treatment, the amount of reacted copper increases over the first 1-3 days before reaching saturation (Figure 6). At low treatment concentrations, most of the copper is converted to reacted copper but at higher treatment concentrations, the amount of unreacted BCC in the wood is substantial.

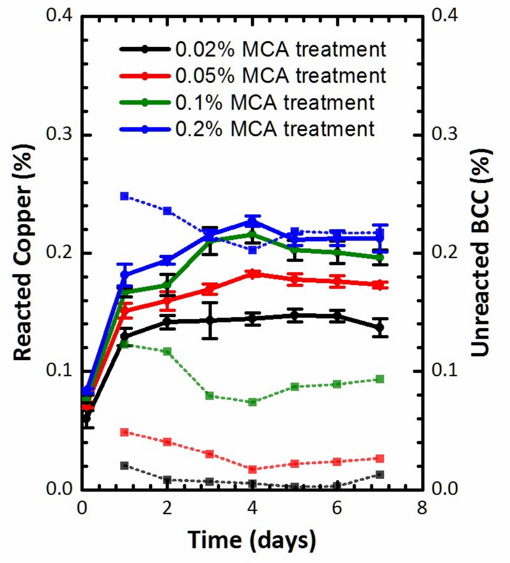


Figure 6 Time evolution of copper(II) speciation in sawdust samples using different MCA treatment concentrations. Solid lines show profile for reacted wood concentrations (measured by EPR) whereas dashed lines show remaining unreacted BCC. Note that even at very high treatment concentrations, the total reacted copper never exceeds 0.25% even though there is significant unreacted copper remaining.

Table 1 Total Cu contents and reacted Cu concentrations of southern pine sawdust treated by MC, MCA and MCQ with increasing Cu concentration (% w/w on Cu basis) after 7 days. [a]Standard error estimated at ±0.02%; [b]Standard error within ±0.01%

Treatment conc. (% Cu)	[a]Total Cu (%)			[b]Reacted Cu (%)		
	MC	MCA	MCQ	MC	MCA	MCQ
0.02	0.19	0.15	0.14	0.19	0.14	0.14
0.05	0.24	0.20	0.36	0.20	0.18	0.18
0.10	0.35	0.29	0.56	0.23	0.22	0.14
0.20	0.52	0.43	0.46	0.25	0.23	0.10

Lee and Cooper studied the CEC of red pine with alkaline copper quat solutions and observed the CEC increased with increasing pH.[10] The profile reflects the pH titration of carboxylates found in hemicellulose and pectin (pH 3-5), and phenolates in lignin (pH 7-11). The same study also showed that chemisorption of Cu^{2+} mirrored that of the CEC pH profile up to pH 5, corresponding to the binding of Cu^{2+} to carboxylates in hemicellulose. It is thus possible to estimate a theoretical maximum amount of reacted Cu(II), which can bind to wood as only carboxylic acids are sufficiently acidic to solubilize copper in BCC under the experimental conditions. From these data, we estimate ~0.05 mmol Cu(II) g^{-1} of sapwood will be produced at pH 4, which corresponds to approximately 0.32% Cu. The observed maximum reacted copper(II) in treated samples is ~25% lower than this theoretical limit. We currently hypothesize that complete cation exchange of the carboxylate groups is kinetically limited and that allowing for longer reaction times (e.g. at high humidity levels to allow for ion transport) may further increase the reacted copper levels closer to the CEC limit.

The CEC limit also becomes important in treatments where other cations may also compete with copper(II) for hemicellulosic carboxylates. This has been observed when quaternary ammonium cobiocides are used in conjunction with MC, i.e. in MCQ treatments. In this cases, we observe that increasing MCQ treatment levels leads to decreased levels of reacted copper species. The competitive effect of the cationic cobiocide is clearly shown when independently varying the relative amount of Cu(II) and quat cobiocide (Figure 7). At low quat concentrations, there is increased formation of reacted copper – likely due to the surfactant properties of the cobiocide, which would enhance the permeability of the wood towards MC particulates. However, at high quat concentrations, the amount of reacted copper decreases substantially as it is outcompeted for available carboxylate sites by the high concentration of quaternary ammonium cations. [40]

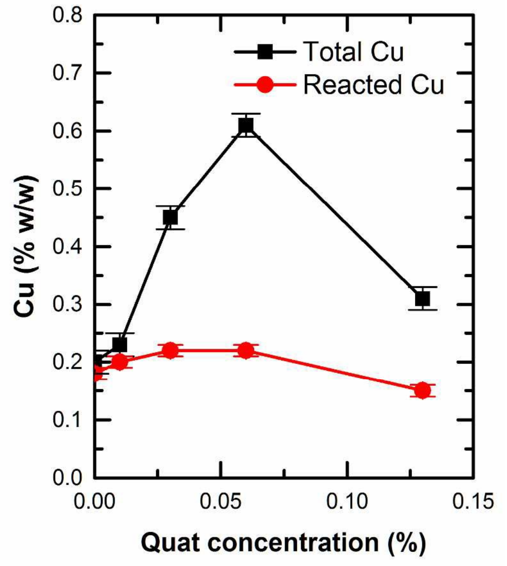


Figure 7 Total Cu and reacted Cu concentrations of southern pine sawdust treated by 0.05% (w/w on Cu basis) MC with varying quat concentrations.

Implications for commercial samples. The general model of copper(II) fixation into wood – and the important role played by free carboxylic acids in the wood structure – identifies several factors that may have significant implications for commercial treatment using micronized copper formulations. For example, depth profiling of commercial MCQ-treated red pine (Figure 8) demonstrates that although the total amount of copper deposited in the wood and the amount of quaternary cobiocide both decrease over the first 10mm from the treatment surface, the availability of reacted Cu(II) increases slightly over the same depth range. These data reflect the fact that as long as there is sufficient micronized copper in the vicinity, the reacted copper content will be limited and controlled by the availability of carboxylic acid groups in the wood and by the duration of treatment. The observed (slight) increase is also consistent with decreased competition with quaternary cobiocide further away from the treatment surface.[39]

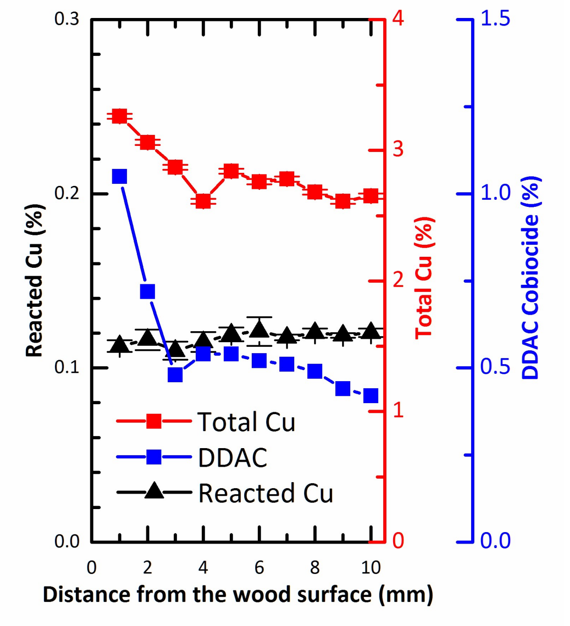


Figure 8 Depth profiling of commercially MCQ-treated red pine. Reacted Cu, total Cu and quat content at sampling locations 0-10 mm from the wood surface.[39]

These results reinforce the idea that the relative amount of total and reacted copper content in treated wood may vary quite substantially as their behaviour is determined by different factors. We would expect this to potentially have a great influence when investigating more localized effects and probing treatment results in chemically different wood types.

In softwood, cells formed early in the growth periods (known as earlywood) have larger cavities and thinner walls, as opposed to the thick-walled and densely packed cells formed later (known as latewood) as rain fall or temperature decrease.[41] In commercial micronized copper treated red pine and western hemlock, the total Cu loadings were found to be distinctly different between the earlywood and the latewood, whereas the concentrations of reacted Cu(II) were very similar in earlywood and latewood(Figure 9).[42] These results again reflect that the primary solubilization and fixation of reacted Cu(II) is controlled by the reaction with the acidic components in the wood structure, whereas the total copper uptake and retention is defined by solution uptake during treatment.

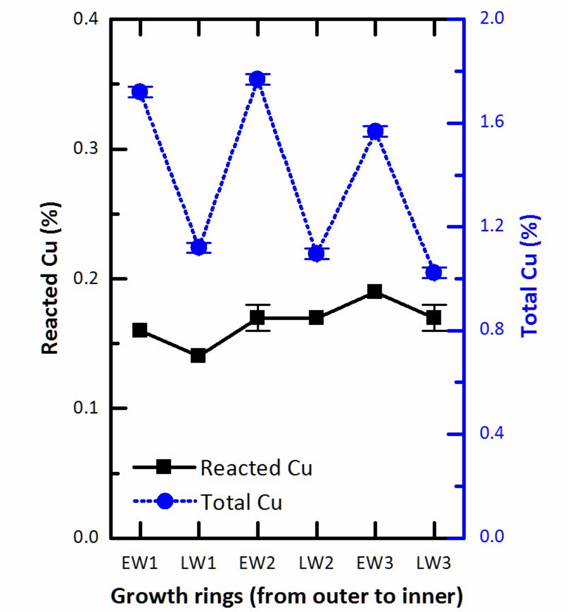


Figure 9 Earlywood (EW) and latewood (LW) retentions of reacted Cu(II) and total Cu, measured in three consecutive rings of MCA treated red pine.

Another feature of wood that has been explored are the differing treatment results in sapwood and heartwood.[43] The live sapwood contains far fewer organic deposits (known as extractives) such as fatty acids and resin acids. The greater prevalence of acidic extractives in heartwood allows for additional BCC solubilisation and thus higher reacted Cu(II) concentrations.

Lastly, one would anticipate that other external factors could modulate the fate of copper(II) species in treated wood samples. The potential effects of chelators in the service environment,[44,45] the presence of additional acidic compoments such as humic acids and fulvic acids in soil,[46–50] and certain low molecular weight metal chelating agents released by some fungi during colonization,[51–53] could all influence copper distribution and speciation in treated wood. Ongoing efforts seek to quantify and evaluate the roles of each of these factors in micronized copper treated wood.

3. Conclusions

Investigations of micronized copper treatments and the resulting speciation of copper(II) in treated wood demonstrates that coordination chemistry is of fundamental importance in understanding and improving the formulation of copper-based wood preservatives. Importantly, the insolubility of basic copper carbonate does not inhibit rapid formation of Cu(II)-wood complexes that are of great importance in biocidal activity. At lower treatment pH, it is found that the degree of complexation to the wood is limited by the availability of appropriate metal binding sites (specifically carboxylates in hemicelluloses). Leaching of copper(II) into the environment is dramatically decreased as there are only very low concentrations of free Cu(II) ions in the wood matrix after treatment. A general protocol for the quantification of copper(II) species in micronized copper treated wood allows further exploration of specific differences in copper distribution and speciation as a function of wood type and structure; for example differences observed between early wood and late wood are easily explained based on the general equilibrium speciation model that has been developed.

4. Acknowledgements

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