The Chemistry of Micronized Metal Treated Wood

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Summary

Following the successful confirmation of the rapid mobilization of copper from micronized copper preservative treated wood, further research has focused on quantifying the amount of copper that is mobilized and then bound to the wood. Electron paramagnetic resonance (EPR) spectroscopy was used in combination with x-ray fluorescence spectroscopy (XRF) to quantify both the total copper and the portion solubilised in the wood. A calibration graph was prepared from copper sulphate treated wood. The standardized relationship was then used to convert the EPR signal intensity to the percent copper present in the MCQ treated southern pine sawdust. Interestingly it was found that after initially increasing with increasing solution concentration, the signal intensity then decreased with further increases in copper concentration. This observation was interpreted as being due to increasing competition from the quat co-biocide for the reactive protons in wood. Further studies were made of the mobilized copper present in red pine "4 x 4" samples treated with MCQ or MCA. Differences in the total copper in earlywood and latewood were observed, which were much less apparent than that of the mobilized and bound copper. The influence of the presence of aminecopper in wood containing micronized copper treatments was examined. As predicted, the amount of mobilized copper was greatly reduced.

Background

In conventional wood treatment biocides are dissolved in a solvent to form a solution which is then impregnated into the timber to be protected. For inorganic metal based preservatives the most common strategies have been to either use metal salt formulations that are water soluble and which react with wood to form insoluble metal-wood complexes, or to use a suitable solvent which can solubilise insoluble metal compounds and these solvated metal complexes react with wood to form insoluble metal-wood complexes. An example of the first type of reaction is chromate copper arsenate (CCA) which in early formulations used copper sulphate, sodium dichromate and sodium arsenate as the preservative components. Subsequently it was found that the use of the insoluble copper carbonate or hydroxide could be solubilised in arsenic acid and chromic acid to produce a treating solution which reacted to wood to form the “fixed” preservative. An example of the second type of preservative was the early use of copper carbonate and arsenic pentoxide (or trioxide) which when solubilised in ammonium hydroxide (with air in the case of the trioxide) produced a deep blue solution of ammoniacal copper arsenate (ACA). The ACA solution reacted with wood to form copper-ammonia-wood complexes as well as some precipitated copper compounds. Unfortunately the evaporative loss of excess ammonia which stimulated the reaction with the breakdown of the tetramminocupprate ion caused the surface of the treated wood to be often discoloured by precipitated copper compounds. This rendered the treated wood unsuitable for residential end-uses.

As the industry developed the adaptation of the alkaline copper preservatives from the use of ammonium hydroxide to monoethanolamine allowed the alkaline copper preservatives to become widely accepted in North America and Europe. Now the fundamental driver for fixation was the acid nature of the wood. Thus the copper-monoethanolamine complexes formed in solution reacted with the wood acid groups. The pH of the solution was lowered leading to reactive copper species which bound to reactive sites in wood. One can summarize this reaction using the following reaction schematic.

$\mathrm{Cu(Mea)_2}$ + wood $\longrightarrow$ $\mathrm{(CuMea.MeaH)^+}$ + wood $\longrightarrow$ insoluble Cu.Mea.wood complexes
Mea.wood complexes
precipitated copper compounds
unreacted soluble copper.Mea.MeaH

This is further complicated when reactive co-biocides like didecyldimethylammonium carbonate (or chloride) are included in the formulation since they have been shown to react with wood by ion exchange and will also form complexes with wood (Doyle and Ruddick, 1994; Lee and Cooper, 2010a).

Nevertheless in summary the reaction of an alkaline copper preservative such as alkaline copper quat (ACQ) or alkaline copper azole (CA) with wood will result in fixed copperamine – wood products, precipitated copper compounds, and soluble unreacted copper-amine complexes being present in the treated wood. This reaction driven by the wood pH causes the soluble copper compounds to become insolubilized.

The reaction chemistry of the solution containing the micronized metal dispersion also uses the wood pH to cause the chemical reaction. But these reactions are diametrically opposite to those of the copper-amine (such as alkaline copper quat or ACQ) or CCA preservative reactions. In the former the soluble metal complexes are rendered insoluble by the wood while in the latter the insoluble metal compounds are rendered soluble by the acid nature of the wood. In the micronized metal reactions, the reactants are already insoluble. So any unreacted chemical remains insoluble. Only metal solubilized by the acidic protons in wood will be mobilized. This obviously will limit the amount of metal solubilised by this process. In addition, the reaction of the protons from wood will cause reactive sites also to be generated in wood so released metals can also be rapidly fixed. In this way the loss of soluble metal compounds from treated wood can be greatly reduced. Just as before we can identify a reaction schematic for this solubilisation of basic copper carbonate.

$CuCO_3.Cu(OH)_2$ + wood $\longrightarrow$ insoluble Cu-wood complexes
unreacted insoluble copper carbonate (precipitate)
soluble copper ions not reacted with wood

So we can compare the two chemistries and see a strong parallel between the products formed in the wood in each case. For the ACQ the unreacted and mobile metal components are the same (or similar), whereas in the micronized metal system the unreacted component is insoluble.

This research is focused on studying the chemistry of the reactions of micronized metals with wood. The early research focused on confirming the solubilisation of the basic copper carbonate, and the relative rate at which it took place in sapwood of pine. The technique of choice is electron paramagnetic resonance (EPR) since it allows us to focus on the solubilised and fixed copper while the basic copper carbonate is EPR silent. This allows us to examine the mobilized copper with respect to the total copper determined by conventional-ray analysis (XRF).

In the first phase it was possible to establish that the copper reaction with wood was rapid (Xue, Kennepohl and Ruddick, 2010). Solubilized copper could be detected within 2 hours of wood treatment. The lower limit of the time is dictated by how rapidly the sawdust could be treated and then cooled to liquid nitrogen temperature for measurement. The signal intensity continued to increase for about 3 to 4 days before becoming constant – indicating completion of the reaction. Immediately, the question arose – how much of the copper is mobilized and complexed to wood?

The objective of this phase of the research is to quantify the amount of copper mobilized and fixed to wood in micronized copper quat (MCQ), micronized copper azole (MCA) and micronized copper (MC) treated southern pine sawdust.

Methodology

The detailed methodology has been described previously (Wei, Kennepohl and Ruddick, 2010). So only a summation is provided here. Initially the EPR sample tube was filled with wet sawdust to maximize the EPR signal. However, it was found that for best reproducibility it was important that all of the sawdust is exposed to the magnetic field so that the total EPR signal is detected. In addition to be able to relate the different samples, the EPR signal must be normalized with the amount of treated sawdust present. To do this effectively, required the used of dried sawdust. In order to quantify the EPR signal, a reference treated wood sample having an EPR spectrum similar to that found in the preservative treated sawdust needs to be prepared. From the previous research we were able to show that copper sulphate treated wood provided EPR parameters very similar to those of the micronized copper treated wood. Several samples having copper retentions from very low to above the upper range of copper expected in the treated wood were prepared. The total copper in the copper sulphate treated sawdust was measured by x-ray fluorescence spectroscopy (XRF).

In the sampling of earlywood and latewood in red pine, sawdust was collected from sections cut from MCQ and MCA treated sawdust, using a fine drill bit to recover the sawdust. The sections of the latewood were also hand sectioned. Figure 1.

Figure 1. Drilling sample of treated red pine section (left) cut from a treated “4 x 4” (right).

Results and Discussion

The EPR signal intensity was plotted against total copper in the copper sulphate treated sawdust to generate the calibration curve (Figure 2).

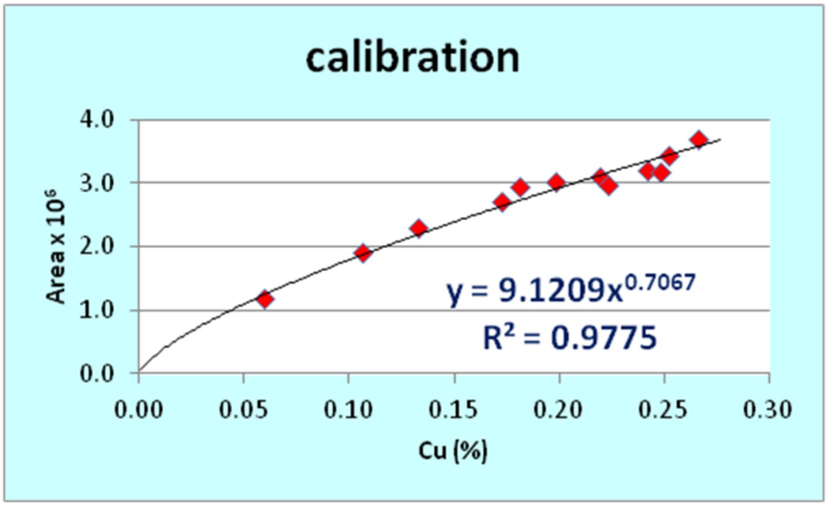

Figure 2. Calibration graph of copper sulphate treated southern pine sapwood sawdust

The spectra were then recorded for MCQ treated southern pine sawdust, Figure 3. Several interesting observations can be seen from the results in Figure 3. The first is that as the MCQ solution concentration increased from 0.02% Cu to 0.05% Cu the EPR spectral intensity increased. However, further increase in the copper concentration caused a lowering of the EPR signal, with the lowest value being recorded for the highest MCQ concentration. This observation is interpreted as being due to competition between the quat ion exchange mechanism and the availability of the protons to mobilize and fix the mobile copper in MCQ treated wood.

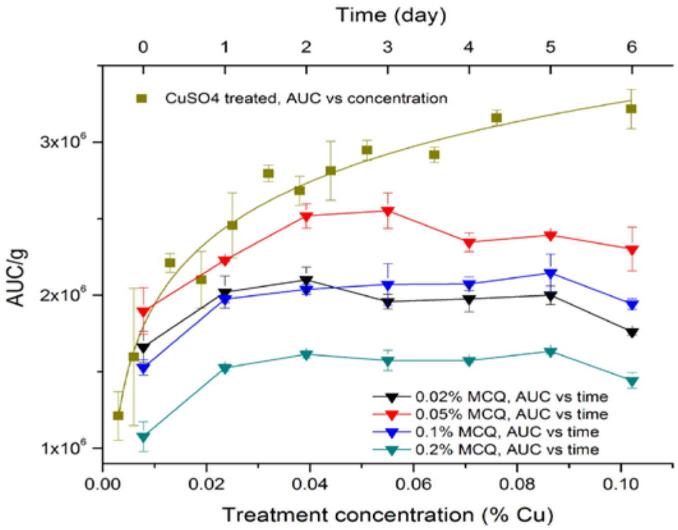

Figure 3. EPR spectra of MCQ treated and dried southern pine sawdust at 0 to 6 days following treatment

Also of interest is the fact that in Figure 3, the copper sulphate standard graph also reaches a maximum. The value appears to be about 3 x 10^6 AUC. From the calibration graph in Figure 2, this would correspond to about 0.25% Cu. This figure is consistent with the predicted cation exchange capacity for red pine determined by Lee and Cooper (2010a and 2010b) for solution pH values about 5 to7. It can also be noted from Figure 3 that the maximum copper retention determined by EPR corresponds to about 0.17% Cu. This is equivalent to about 1 kg/m^3 of Cu in southern pine.

A second study attempted to quantify the amount of mobilized and fixed copper present in earlywood and latewood of different wood species. Red pine commercially treated with MCQ was sectioned and earlywood and latewood sawdust samples were collected and analysed by x-ray and EPR. The results are shown in Figure 4. The mobilized and fixed copper content was fairly constant in both latewood and earlywood at about 0.2 % Cu while the total copper as determined by XRF was greater in earlywood than latewood. It ranged from 1.8% Cu to 1.6% Cu in earlywood and from 1.1 % Cu to 1.0 % Cu in latewood. Further, as expected the values gradually from the outer sampling to the inner sampling. A similar study on MCA treated red pine showed similar trends, Figure 5. The total copper uptake was somewhat lower but again the copper retentions were greater in earlywood than in latewood and showed a gradually reducing trend from the surface of the “4 x 4” towards the interior.

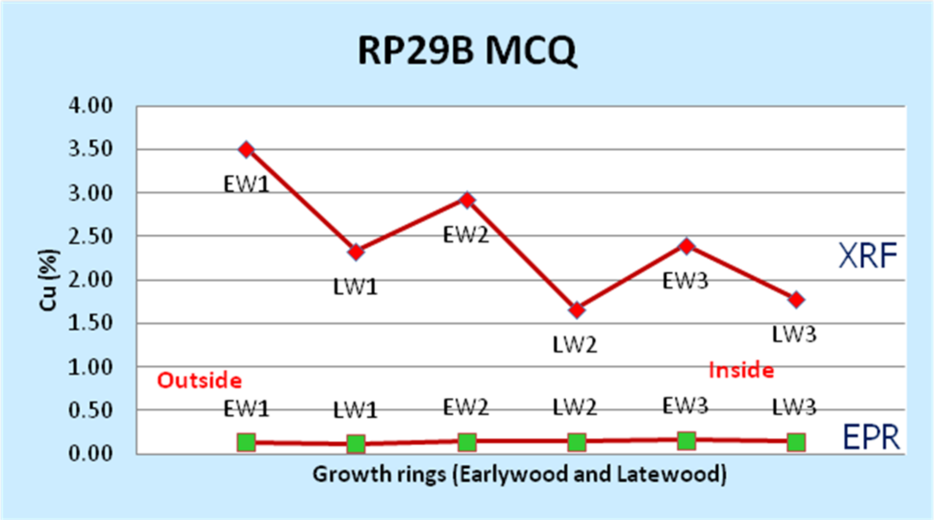

Figure 4. Earlywood (EW) and latewood (LW) retentions of mobilized copper determined by EPR and total copper determined by XRF measured in 3 consecutive rings of an MCQ treated red pine “4 x 4”.

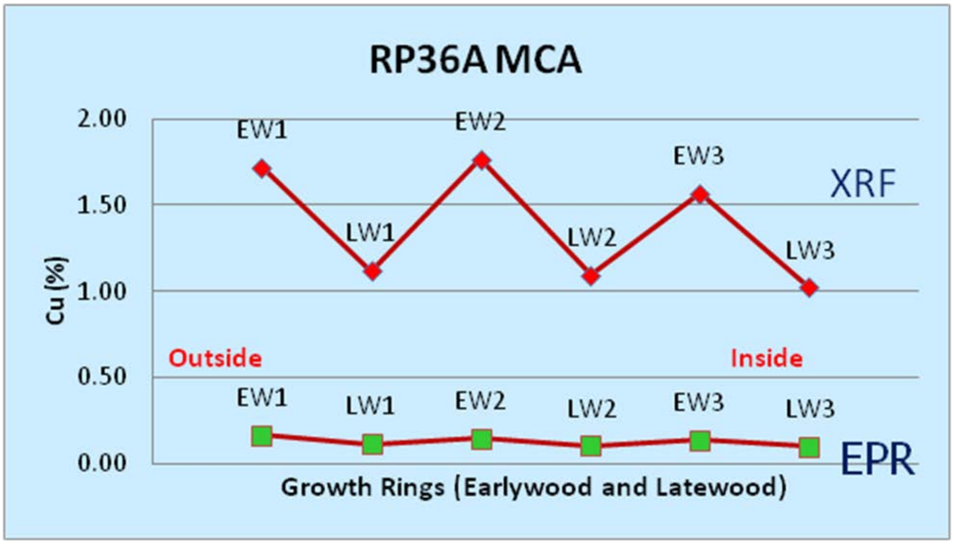

Figure 5. Earlywood (EW) and latewood (LW) retentions of mobilized copper determined by EPR and total copper determined by XRF, measured in 3 consecutive rings of an MCA treated red pine “4 x 4”.

In a third study, the measurement of mobilized copper in combinations of micronized copper carbonate in MCQ when combined with monoethanolamine copper in wood was examined. This required separate calibration graphs to be developed for both copper-oxygen bonded species as well as copper – nitrogen bonded species. Based on our understanding of the chemistry of micronized copper preservatives, the increase in the pH of the wood will inhibit the mobilization of copper from the MCQ. This was observed, as can be seen in Figure 6.

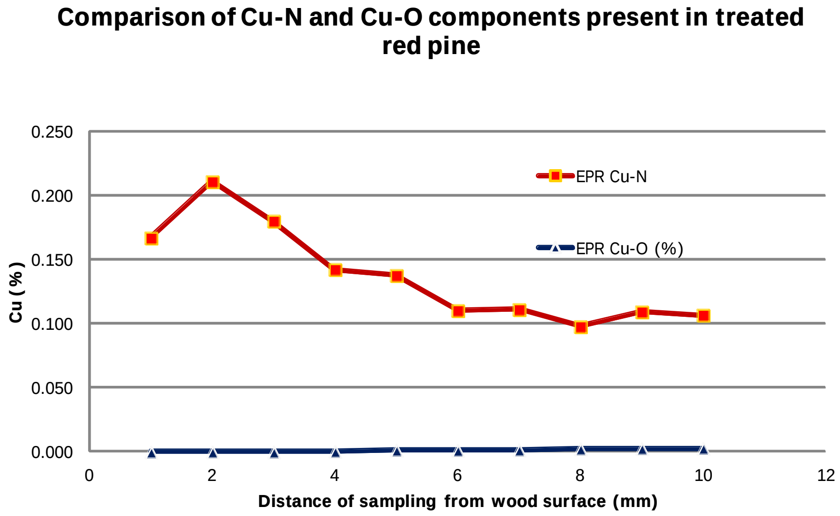

Figure 6.Influence of monoethanolamine copper on the mobilization of copper from MCQ in red pine sapwood.

Conclusions

It was concluded from this study that in MCQ treated southern pine sawdust, the maximum mobilized and fixed copper was about 0.17% Cu or1.0 kg/m^3 of Cu. From the reference standard samples a maximum copper fixation from copper sulphate solution was about 0.25% which corresponds to the cation exchange capacity reported previously by Lee and Cooper, (2010) for red pine at a pH range of 5 to 7. Measurement of both total copper and solubilised and fixed copper in red pine `4 x 4``s` treated with MCQ or MCA showed that more total copper was present in earlywood compared to latewood. However, differences in the mobilized copper in the earlywood and latewood were small. As expected, combinations of alkaline copper with micronized copper lead to a sever reduction in the mobilization of copper from the micronized basic copper carbonate.

References

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