



Copper Oxidation States Found in Wood Preservatives and their Relationship to Corrosion Factors



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ABSTRACT

Wood preservatives containing metals are widely used for wood protection in residential construction. Preservative systems typically contain copper in various forms paired with organic co-biocides. Past research has indicated that the predominant form of copper found in preservative treated wood is Cu^{2+} , but recent x-ray absorption experiments of wood in contact with aged corroded fasteners indicate Cu^{1+} is the predominant form within the cell wall. There are distinct differences between Cu^{1+} and Cu^{2+} with respect to their solubility and biological activity against microbes.

The goals of these experiments are to characterize Cu valence states in various commercially available wood preservative treatment formulations in order to fill a long standing knowledge gap and establish an improved conceptual model for both wood preservative metal speciation and the initiation of wood decay.

BACKGROUND

The preservatives commonly found in treated wood, such as alkaline copper quaternary (ACQ) and copper azole (CuAz), largely consist of Cu^{2+} in their original treatment solutions. However, after being exposed for a prolonged period of time to an acidic environment, the Cu^{2+} in the preservative is reduced to Cu^{1+} . Because the Cu^{1+} is more soluble than the Cu^{2+} , the former ends up leaching into the environment.

The preserved wood is usually used in outdoor settings, where they are exposed and are in close proximity to other plants and fungi. Fungal growth results in a release of organic acids that increase wood acidity, and even more so during fungal decay. The acidity may also be from the soil itself which has absorbed toxic chemicals and gases dissolved in rain (also known as acid rain). A redox reaction can also occur between the Cu^{2+} and nearby metals. The reduction of Cu^{2+} into Cu^{1+} has a variety of implications for the surrounding environment, including consumption by animals, absorption by other plants, and contamination of our water supply.

SUPPLEMENTAL EXPERIMENTS

To begin our chemical analysis, we placed various wood samples, from the same treated lumber source, into different solutions.

The first solution consisted of an factory-treated wood sample in 1M HCl. The second solution consisted of an factory-treated wood sample in 1M H_2SO_4 . The final solution consisted of an factory-treated wood sample in a 10% cellulase solution. The solutions can be seen in Figure 1.

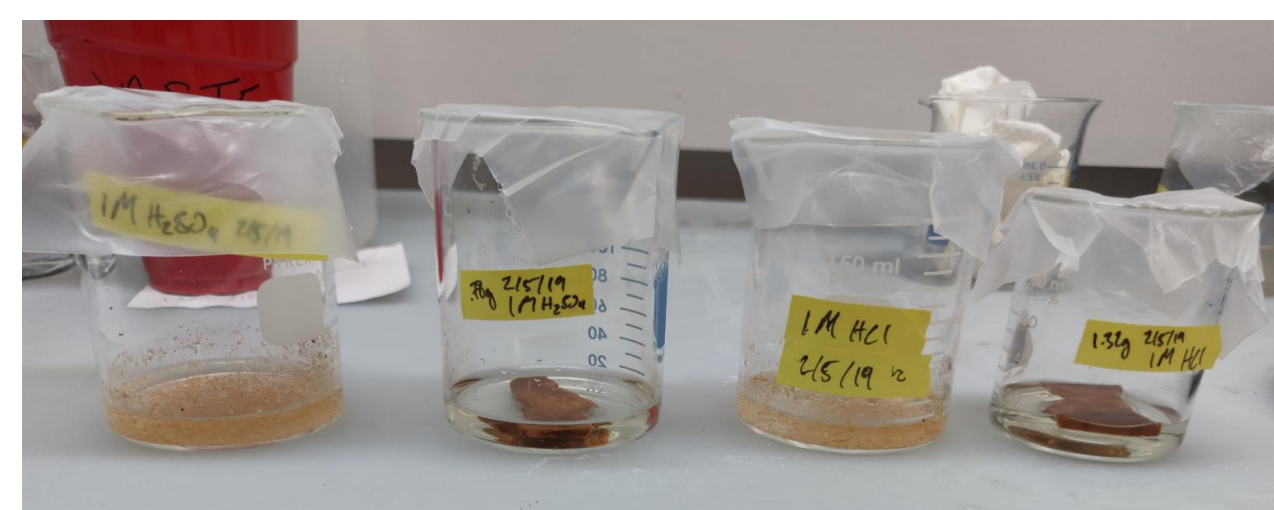


Figure 1: Solutions of factory-treated wood in HCl and H_2SO_4

For the HCl and H_2SO_4 solutions, we experimented with wood dust and pieces of wood. Each of these solutions sat for several days before filtration to allow for most, if not all, the copper to be extracted.

We then conducted an analysis on each of the previously mentioned solutions. The first one was a flame test for both of the acidic solutions to determine the presence of the Cu^{2+} ions in the solution from their distinctive green-blue color. We also added different compounds such as Na_2S and KI to the solutions to isolate different Cu compounds, the former being CuS and the latter being CuI_2 . A spectrophotometric analysis was also done on the solution resulting from wood placed in the cellulase solution, in which several drops of NH_3 were added to convert the colorless complexed Cu ions to the dark blue copper-ammonia complex $[\text{Cu}(\text{NH}_3)_6]^{2+}$.

However, there was very little, if any, free copper present in the solution as no significant traces of color were detected. The supplemental experiments allowed us to determine the presence of copper in the preserved samples. We were not able to obtain an exact quantitative value and breakdown for how much Cu^{2+} and Cu^{1+} were present.



Figure 2: Solution of factory-treated wood and HCl after the addition of KI, forming Lugol's Iodine

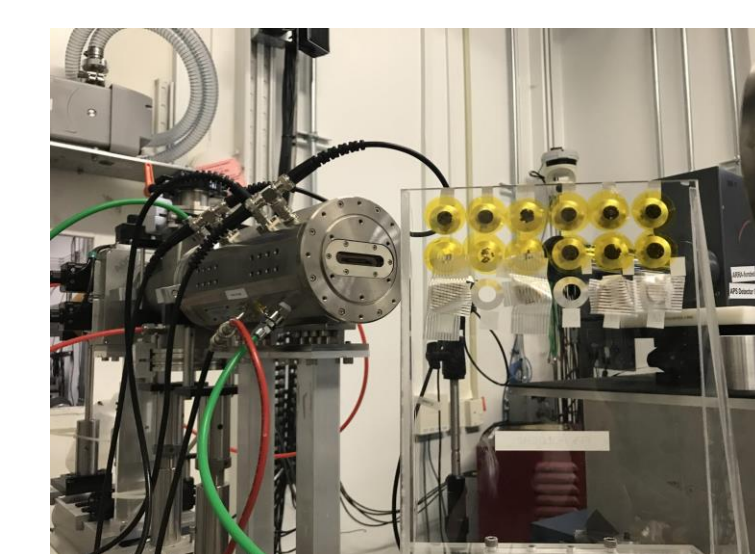
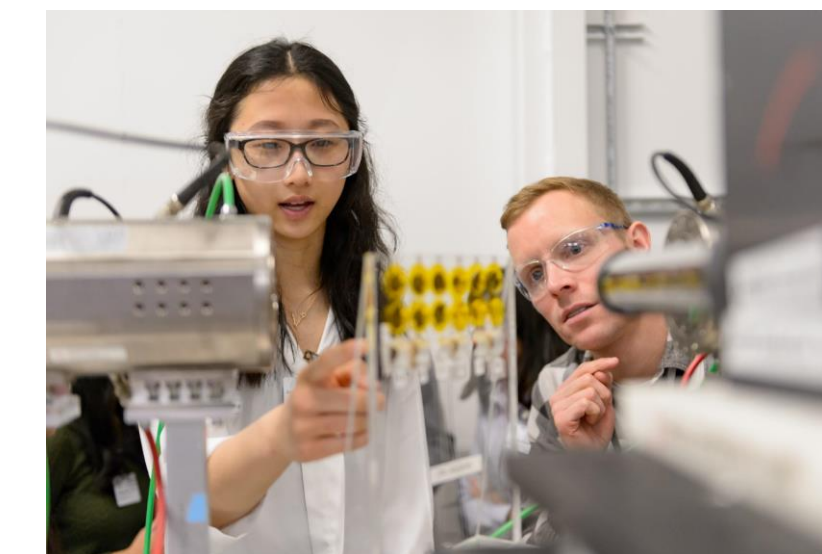
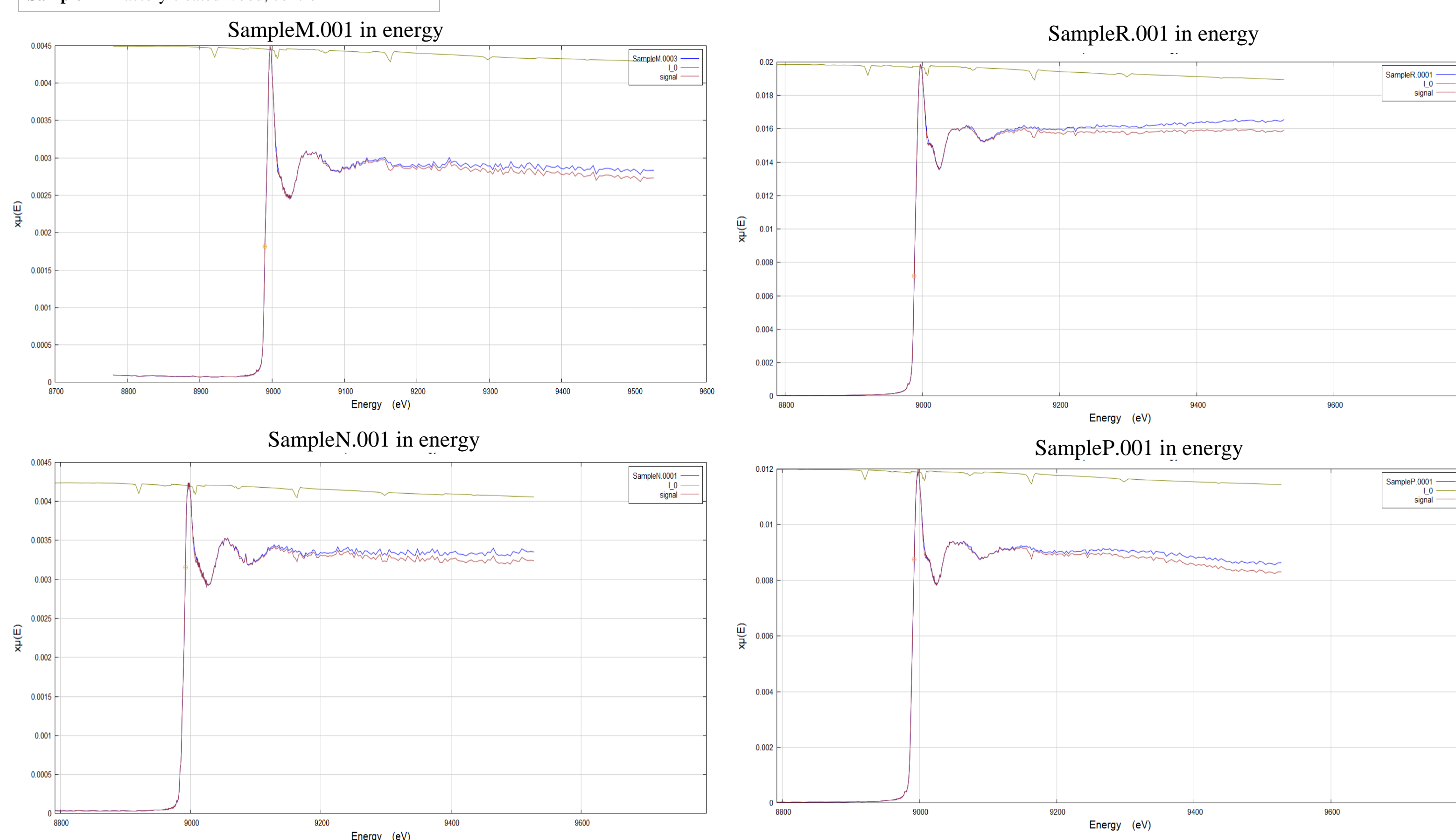


Figure 3: Solution of factory-treated wood and HCl after the addition of Na_2S , forming CuS precipitate

RESULTS OF ARGONNE ADVANCED PHOTON SOURCE DATA

At Argonne APS, we tested our wood samples to obtain more detailed information on the Cu composition in our sample, specifically the presence of Cu in different valence states. We scanned four different samples using x-ray crystallography, analyzing the normalized x-ray fluorescence intensity as a measure of x-ray photon energy shot through the sample.

In the graphs below, the most notable features are the peaks. The largest peak indicates the relative amount of total copper present in the sample. The first pre-edge spike indicates Cu^{2+} , and the second pre-edge spike indicates Cu^{1+} .



FUTURE STEPS

After obtaining a baseline understanding from our supplemental experiments and advanced photon source data regarding the presence of copper in preserved wood, we have formulated new questions that will guide future research on the copper leaching process.

We intend to differentiate between the concentration of Cu^{1+} and Cu^{2+} ions, which we can do through X-ray photoelectron spectroscopy. In addition, we hope that our strategies for analyzing different copper oxidation states can be used for other elements in nature, especially those with oxidation states that impact the environment. We would also like to determine how different chemical environments may affect the function of preservatives and rate at which preservatives leech out of wood.

CONCLUSIONS

The results from the x-ray crystallography show the untreated treated wood samples contain large concentrations of Cu^{2+} . Exposure to H_2SO_4 did not result in any copper being reduced, however, HCl did. This leads us to conclude that the strength of the acid to which the wood is exposed affects the reduction and removal of Cu^{1+} from a wood sample. However, the strength of the acid should theoretically only affect the rate of the reaction and not the success of reducing copper, which we may be able to look further into.

We cannot expect all of the copper in factory-treated wood to leak into the environment, contrary to our initial assumptions, as the wood soaked in cellulase was more effective in releasing copper from the lignin and cellulose bonds in the wood. However, we were still able to confirm that factory-treated wood exposed to an acidic environment will still result in Cu^{1+} being reduced from Cu^{2+} , leaving the wood and entering the environment. This potential leakage into the environment supports the concern regarding current treatment methods.

ACKNOWLEDGEMENTS

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