THE EFFECT OF POST-STEAMING ON COPPER NAPHTHENATE-TREATED SOUTHERN PINE

D. Pascal Kamdem

Assistant Professor

Jun Zhang

Graduate Student

Department of Forestry
Michigan State University
East Lansing, MI 48824

and

Mike H. Freeman

Industrial Biocides Division
ISK Biosciences Corporation
416 East Brooks Road, P.O. Box 9158
Memphis, TN 38109

ABSTRACT

The reduction of copper from cupric (Cu^{2+}) to cuprous (Cu^{1+}) form in post-steamed copper naphthenate-treated southern pine was monitored. The amount of cuprous oxide formed after the post-steam treatment was determined by X-ray diffraction (XRD). About 50% of copper was reduced from cupric to cuprous in post-steamed samples treated to a retention of 0.31 to 0.51% total copper. Less than 15% of the copper was reduced to cuprous in the post-steamed samples containing 0.71% total copper. Environmental scanning electron microscopy (ESEM) was used to collect images of the crystalline cuprous oxide deposits on the wood cell walls.

Keywords: XPS, XRD, ESEM-EDXA, copper naphthenate, cuprous oxide, steam, wood preservatives, southern yellow pine.

INTRODUCTION

With increasing social pressure against use of creosote, pentachlorophenol, and arsenical wood preservatives, researchers are looking for an effective wood preservative with low human toxicity and environmental impact. Copper naphthenate (Cu-N) might satisfy these requirements, but it is now only marginally competitive economically (Freeman 1994). It is active against a wide range of decay fungi and termites for both softwoods and hardwoods (Kamdem et al. 1995; Freeman 1994; De Groot et al. 1988; Hartford 1973). Copper loss from Cu-N-treated wood is relatively low (Freeman 1994) compared to other waterborne preservatives. The surface of copper naphthenate-treated wood becomes hydrophobic; thus, the absorption of water, which promotes the solubility or migration of copper, is reduced.

Much research has been conducted on fungal and termitic attack of Cu-N-treated wood (Freeman 1994; Bratt et al. 1992), the properties of Cu-N-treated wood or wood composites, and treatment methods (Kalnins et al. 1990; Barnes and Hein 1988). The performance of Cu-N-treated wood is variable. Some Cu-N-treated poles have been destroyed by decay after only two years in service, while others are still in service after 20 years. Early decay failure could result from the naphthenic

acid characteristics, the oil or solvent/carrier used, low retention achieved during the treatment, the form of copper in treated wood, and/or the presence of unrecognized early decay in wood before treatment (Kamdem 1997).

Freshly treated Cu-N products have a green color and a strong odor that negatively impact their use (De Groot et al. 1988). To reduce the green color and the strong odor, and to obtain a clean dried surface, Cu-N-treated products are post-steamed at 240°F (115°C) as suggested in the footnote in the AWPA standards (AWPA 1996). The duration of steaming varies from one half to 15 hours, depending upon the strength of the treating solution, the moisture content, and the dimensions of the treated wood (Harp and Grove 1993). However, the effects of such post-steaming on the chemical properties or biological performance of copper naphthenate-treated products is not addressed in the available literature.

It is widely reported in organometallic chemistry that copper in its cupric form is reduced to cuprous both in an alkaline and acidic medium in the presence of sugar. These reactions are energy-sensitive following Arrhenius's law (Ayres 1958). Either reaction may take place in wood after post-steaming, or even after exterior exposure, since reducing sugars are present in wood.

The objective of this study is to determine the form of copper present in Cu-N-treated wood before and after post-steaming. This information may help to understand the effect of post-steaming on the chemical properties and physical modification, as well as the biological performance, of Cu-N-treated wood.

EXPERIMENTAL

Treatment

Defect-free 5 by 10 by 180 cm long (2 by 4 in. by 6 ft) kiln-dried sapwood boards of southern yellow pine (SP) obtained from a sawmill located in Alabama were used in this study. Cubes measuring 19 mm (0.75 inch) were prepared from these boards and stored in a conditioning room maintained at 65% rela-

tive humidity (RH) and 68°F (20°C) until they reached an equilibrium moisture content (EMC) of 15 ± 3%. A stock solution of Cu-N containing 2% elemental copper, received from ISK Biosciences Corporation, was diluted with toluene. Samples were pressure-treated with Cu-N solution containing 0.5, 1, and 2% elemental copper to achieve different copper retentions. The treatment schedule included an initial vacuum at 84.6 kPa (25 inches of mercury) for 5 min, followed by pressure at 690 kPa (100 psi) for 40 min, and then a final vacuum for 30 min. Treated samples were post-steamed at 240°F (115°C) for 40 min and stored at room temperature.

Chemical analysis

ESEM-EDXA.—Environmental scanning electron microscopy coupled with energy-dispersive X-ray analysis was performed with an ESEM ElectroScan model 2020 with an accelerating voltage of 20 kV at 77°F (25°C) and a vacuum level of 2.0 to 3.5 torr (2 to 3.5 mm Hg). The EDXA detector was equipped with an Oxford Atmospheric thin window capable of detecting elements with atomic number greater than 6 and less than 99. The acquisition time for each spectrum was set at approximately 500 seconds with 1,600 to 2,500 counts per second.

AAS.—Total copper content of the samples was determined by using a Perkin Elmer atomic absorption spectrometer (AAS) model 3110, as described in the AWPA standard A11-93 (AWPA 1997).

X-ray diffractometry

X-ray diffractograms were obtained with a Rigaku XRD diffractometer using Cu Kα radiation of λ equal to 1.5418 Å, and a voltage of 45 kV at 100 mA. The diffraction patterns were measured using 2θ angle values from 5° to 65°. Crystal size was measured using Bragg Equation (2d sinθ = λ) and the 2θ angle values from the diffractograms (Klug and Alexander 1954). XRD was used to identify and semi-

quantify the crystals present in post-steamed samples.

To develop a quantitative protocol, southern pine wood meal was mixed with various amounts of solid cuprous oxide. The total copper content of the wood meal was determined by AAS analysis. The XRD diffractograms of wood meal mixed with cuprous oxide were deconvoluted, and peak areas were calculated using Peak-Fit software V.3 from Jandel Scientific.

The XRD pattern of crystalline cellulose was not modified after the Cu-N and/or the post-steaming treatment. Therefore, the cellulose peaks were used as references. The most intense peak for Cu_2O at $2\theta = 36.20°$ was used for quantification. Since cellulose has two peaks, three peak area ratios were calculated: Cu_2O/Cellulose peak 1, Cu_2O/Cellulose peak2, and Cu_2O/Cellulose (peak1 + peak2). The three calibration curves were obtained by plotting peak area ratio versus the actual amount of Cu_2O determined by AAS. The curve corresponding to Cu_2O/Cellulose (peak1 + peak2) versus the copper content, with $R^2 = 0.95$ was selected and used as a calibration curve for the determination of Cu_2O content.

RESULTS AND DISCUSSION

ESEM-EDXA

No solid particles were observed in ESEM images of Cu-N-treated southern pine (Fig. 1A), while solids were present in the samples Cu-N-treated and post-steamed (Fig. 1B). The EDXA in Fig. 2 with no background substraction confirms that the solids formed in post-steamed Cu-N-treated southern pine contained copper, carbon, and oxygen. The carbon X-ray count in Fig. 2A and B was out of the range with maximum count per second (CPS) at $10,000 \pm 1,500$, while the maximum was about 2,000 for oxygen and 1,500 for copper. The use of an appropriate CPS to include the carbon peak reduces the peak of copper and oxygen to negligible. A cps of $3,000 \pm 500$ was used to illustrate the contrast between the copper and oxygen.

The post-steaming resulted in formation of solid deposits on the cell-wall surfaces of the treated wood. The EDXA in Fig. 2 confirms that the solids formed in post-steamed Cu-N-treated southern pine contained copper, carbon, and oxygen. The EDXA scan in Fig. 2B was obtained by focusing the electron beam on the solids present on the surface of the cell wall. This indicates that the solids in post-steamed samples are relatively rich in copper and oxygen with high ratios of Cu/O. The ratio of copper to oxygen was determined semi-quantitatively using the height and the area of copper and oxygen peaks of the EDXA scan. EDXA spectra of samples that were not post-steamed were obtained by scanning the cell-wall surface, since no solid particles were present. The relative intensity of the copper and oxygen from the post-steamed treated samples and those which were not post-steamed was different. It indicated that the solids in the post-steamed samples may have a different chemical composition than the non-particulate accumulations on the cell walls of the samples that were not post-steamed. The copper to oxygen ratio of the post-steamed samples was higher than that of samples that were not post-steamed. Total copper content of the various samples, as determined by AAS, is shown in Table 1.

XRD analysis

X-ray diffractograms of samples are shown in Fig. 3. The two characteristic peaks of cellulose with 2θ at $15.60°$ and $22.20°$ were present in all wood samples, indicating that copper naphthenate pressure treatment did not significantly change the cellulose crystal lattice structure. New peaks, or significant modifications, were not detected in copper naphthenate-treated wood as illustrated in Fig. 3A.

Cu-N-treated and post-steamed samples (Fig. 3B) contained two new peaks at $2\theta = 36.40°$ and $42.20°$, suggesting the presence of solid crystals, which were absent from samples that were not post-steamed. They were formed during the steaming of copper naph-
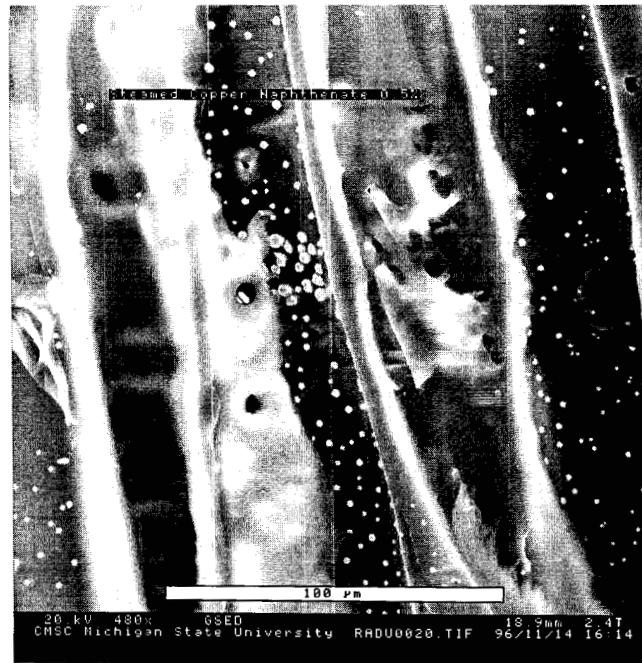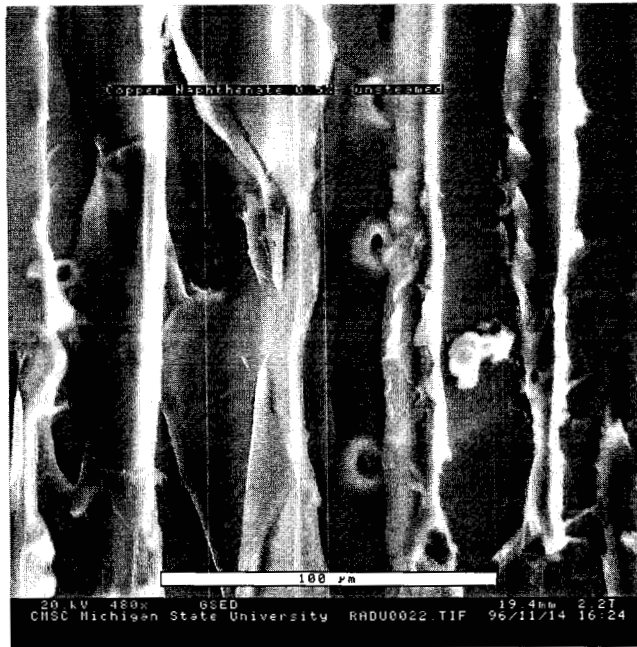
Fig. 1.   ESEM images of southern pine. (A) Cu-N-treated without post-steaming. (B) Cu-N-treated and post-steamed.
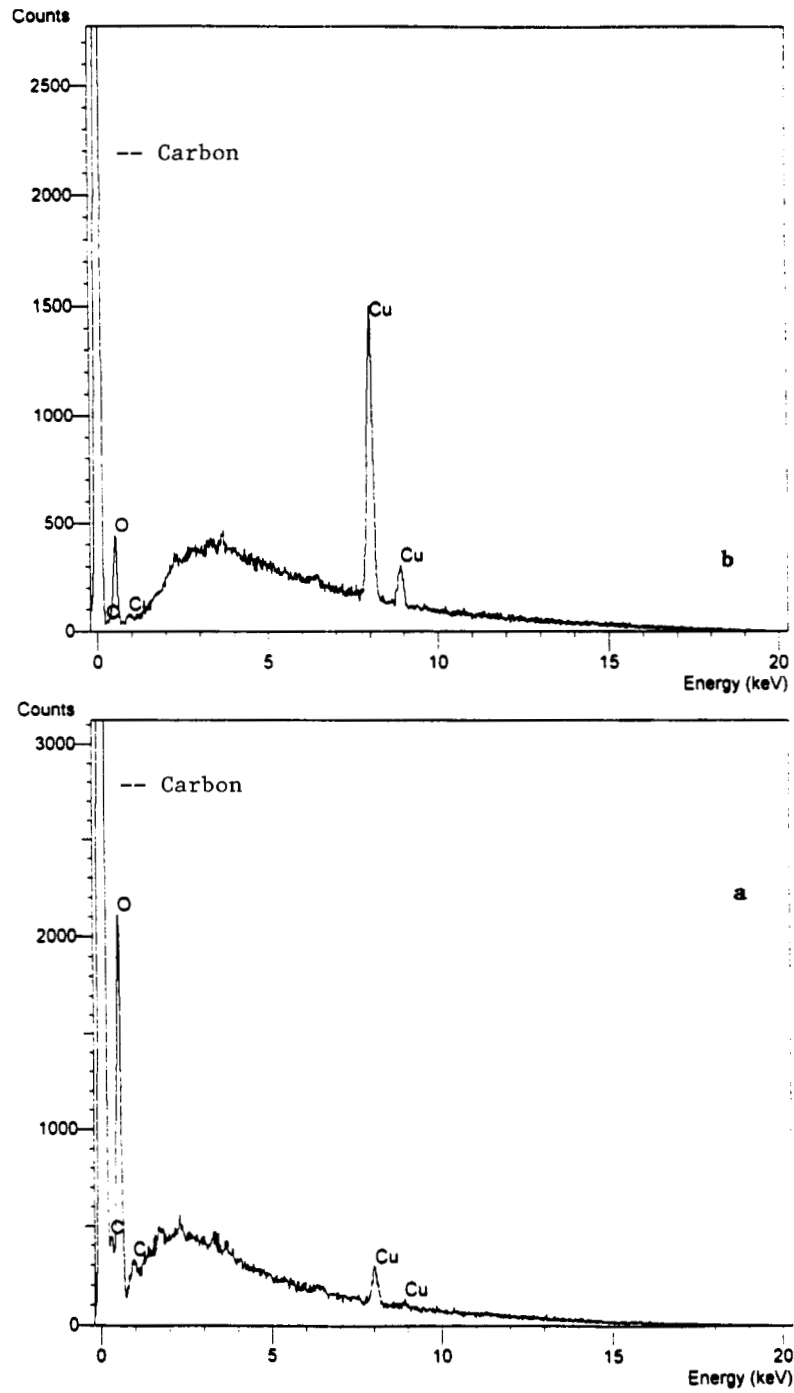
FIG. 2.   EDXA of southern pine. (A) Cu-N-treated without post-steaming. (B) Cu-N-treated and post-steamed.

TABLE 1.   *Copper content determined by AAS, XRD, and conversion rate in percentage (%).*

Treatment solution strength, Cu(%)	Sample description		Conversion rate %
	Total Cu (AAS) Cu(%)	Cu^{1+} (XRD) Cu(%)	
0.0	0.0	0.0	0
0.5	0.31	0.17	55
1.0	0.50	0.24	48
2.0	0.71	0.11	15

thenate-treated southern pine. No similar crystals were detected after oven-drying copper naphthenate-treated samples. The absence of crystals after oven-drying of Cu-N-treated samples indicates that the formation of crystals in Cu-N-treated southern pine required both water and high temperatures. Based upon this information, the crystals detected in post-steamed samples could be either cupric oxide (CuO), cuprous oxide (Cu$_2$O), copper hydroxide (Cu(OH)$_2$), copper sulfate, copper oxalate, or any other copper oxygen combination in crystalline form.

To identify the crystals in post-steamed Cu-N-treated wood, standard XRD patterns of pure Cu$_2$O, CuO, Cu(SO$_4$)$_2$, and Cu(OH)$_2$ were acquired and used as references. The diffraction angles at $2\theta = 36.50°$ and $42.10°$ in post-steamed samples were similar to the values obtained with pure Cu$_2$O. Untreated wood meal was mixed with approximately 0.4% Cu$_2$O (Fig. 3C). Post-steamed Cu-N-treated samples were spiked with 0.2% cuprous oxide, and specific peaks at 36.5° and 42.10° increased as illustrated in Fig. 3D. The XRD patterns of wood meal mixed with Cu$_2$O (Fig. 3C), post-steamed Cu-N-treated wood (Fig. 3B), and Cu$_2$O (Fig. 3E) are comparable at 36.5° and 42.10°. The diffractogram of pure CuO in Fig. 3F and of pure Cu$_2$O (Fig. 3E) indicates that crystals in the post-steamed Cu-N samples (Fig. 3B) are different from cupric oxide but rather similar to cuprous oxide with peaks at 36.5° and 42.10°.

Table 1 shows the results of total copper analysis by AAS and the calculation of conversion to cuprous oxide from XRD data.
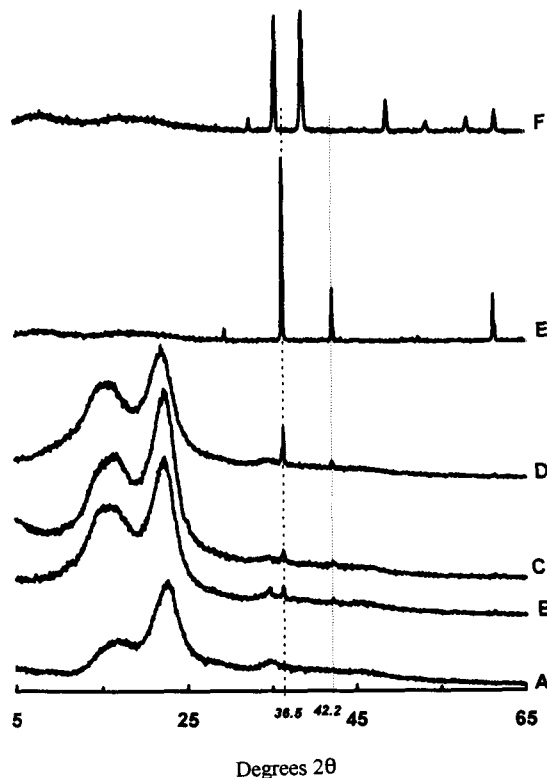

Fig. 3.   XRD of southern pine. (A) Cu-N-treated without post-steaming. (B) Cu-N-treated and post-steamed. (C) Physical mixture of wood meal and Cu$_2$O. (D) Cu-N-treated, post-steamed, and spiked with 0.2% Cu$_2$O. (E) Pure Cu$_2$O. (F) Pure CuO.

Copper absorbed in wood increased from 0.31 to 0.71% as the copper in the treating solutions increased from 0.5 to 2%. Nearly half of the total copper came from cuprous oxide in the 0.5% treating solution, with conversion efficiency decreasing with increasing solution concentration. Figure 4 shows the X-ray diffraction patterns of post-steamed samples with different copper naphthenate retentions.

The XRD peak intensity of Cu$_2$O in the post-steamed samples increased with the increase of copper naphthenate retention from 0.31 to 0.51%, as illustrated in Fig. 4B and C. The intensity of peaks specific to cuprous oxide in post-steamed Cu-N-treated samples with 0.71% copper did not increase proportionally with the copper content as compared to the 0.51% copper content samples (Fig. 4C, D).
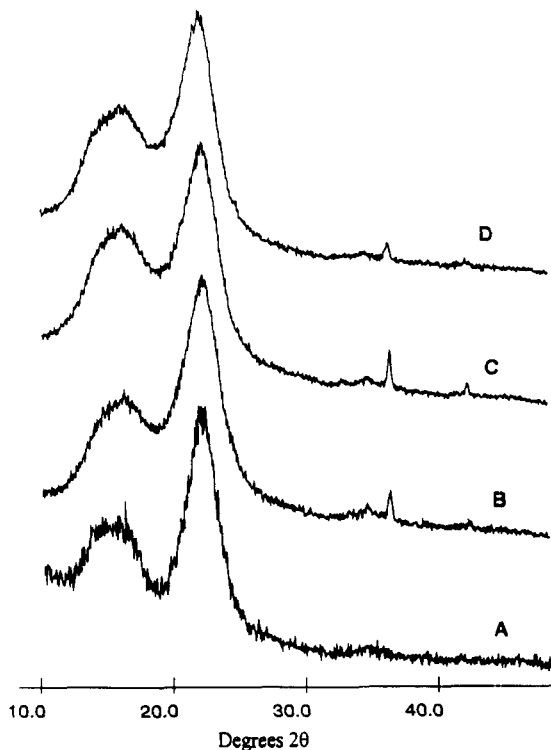
FIG. 4. XRD of southern pine. (A) Cu-N-treated without post-steaming. (B) Treated with Cu-N solution containing 0.5% Cu and post-steamed. (C) Treated with Cu-N solution containing 1% Cu and post-steamed. (D) Treated with Cu-N solution containing 2% Cu and post-steamed.

The conversion rate of cupric to cuprous, was calculated by dividing the percentage of cuprous copper determined by XRD to the total copper analyzed by AAS, since no cuprous oxide was detected in copper naphthenate-treated samples without post-steaming. The conversion rates are listed in Table 1. About 50 ± 5% copper was reduced or converted to Cu_2O for the 0.31 to 0.51% total copper containing samples, and 15% in the post-steamed samples containing 0.71% copper. This suggests that all the Cu^{2+} was not reduced to Cu^{1+} (Cu_2O), with the conversion rate increasing with post-steaming and decreasing with an increase in copper content.

As stated earlier, the formation of Cu_2O in Cu-N-treated southern pine requires water and energy. The low conversion rate in the sam-

ples with 0.71% copper content may be due to more hydrophobic Cu-N in that sample. The most concentrated treating solution contained a greater proportion of copper naphthenate complex with a high viscosity, resulting in a more hydrophobic medium than in the dilute treatments. This may have reduced the penetration and uptake of water (steam) into the sample during post-steaming and thereby limited the formation of Cu_2O. The formation of Cu_2O is promoted by the carboxylic acids generated during the steaming of wood. These wood acids can protonate the naphthenate ligand of Cu-N into naphthenate acid and the formation of copper carboxylate/acetate/formate/glucuronate/hydroxide. Under some specific conditions, the new form of copper may be transformed partially or totally into Cu_2O. The amount of organic acid liberated during the steaming, which is a function of species, steam temperature, and duration, will limit the conversion rate of Cu_2O. The higher the concentration of Cu-N, the lower the Cu_2O conversion rate. A greater proportion of stable Cu-N, less energy, and less water may generate a more stable cupric than cuprous copper as proposed in the following equation:

$$R\text{-}CHO + 2Cu^{++} + 2H_2O \overset{\Delta}{\rightleftharpoons}$$

$$\overset{\Delta}{\rightleftharpoons} R\text{-}COOH + Cu_2O + 4H^+ \qquad (1)$$
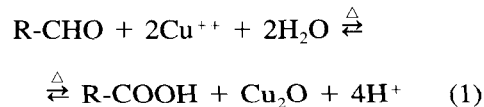
The formation of Cu_2O may be promoted by the removal of naphthenate ligands with the regeneration of naphthenic acid. Copper in Cu_2O is a stable compound that is insoluble in water and in several organic solvents. It is also less biologically available and may be less toxic than copper (II) from unaltered copper naphthenate. To evaluate the extent of the modification of Cu-N in post-steamed samples, it is important to quantify the amount of Cu_2O/CuO present in treated wood after post-steaming. AAS or ICP (inductively coupled plasma) emission spectrometric techniques cannot be used to quantify the amount of Cu_2O in wood because they yield information on the total copper content. XRD was suc-

cessfully used to obtain valuable information on the identity and the quantity of crystals formed after a treatment.

Further research is underway to determine the mechanism of copper reduction after post-steaming treatment as well as the bioefficacy of cuprous oxide.

CONCLUSIONS

The rate of the copper reduction in copper naphthenate-treated wood was affected by the initial copper content as well as the post-steam treatment. Approximately 48–55% of the cupric copper in southern pine treated with 0.30–0.50% copper containing copper naphthenate and post-steamed can be reduced to cuprous oxide.

ESEM-EDXA showed solid deposits rich in copper and oxygen on cell-wall surfaces in the post-steamed samples. XRD patterns of the crystalline deposits were similar to those of cuprous oxide (Cu_2O). The presence of solid crystal deposits of cuprous oxide leads us to conclude that the post-steaming of copper naphthenate-treated southern pine may alter the efficacy of copper naphthenate for preserving wood, if the less soluble Cu_2O is shown to be less fungitoxic than CuO.

ACKNOWLEDGMENTS

REFERENCES

AMERICAN WOOD PRESERVERS' ASSOCIATION (AWPA). 1996. Standard method of determining the leachability of wood preservatives. AWPA standard E11-87. AWPA, Woodstock, MD.

AYRES, G. H. 1958. Quantitative chemical analysis. Harper & Brothers, New York, NY.

BARNES, M., AND R. W. HEIN. 1988. Treatment of steam-conditioned pine poles with copper naphthenate in hydrocarbon solvent. Rec. Ann. Conv. BWPA, 3-33.

BRATT, R. P., D. J. SQUIRRELL, S. MILLINGTON, G. MANTON, AND W. HOSKINS. 1992. Comparison of the performance of several wood preservatives in a tropical environment. Int. Biodeterior. Biodegrad. 29(1):61–73.

DE GROOT, R. C., C. L. LINK, AND J. B. HUFFMAN. 1988. Field trials of copper naphthenate treated wood. Proc. Am. Wood Preserv. Assoc. 84:186–200.

FREEMAN, M. H. 1994. Copper naphthenate: An effective wood pole and cross arm preservative. Pages 68–77 *in* Proc. First Southern Pole Conference. Forest Products Society, Madison, WI.

HARP, K. L., AND S. L. GROVE. 1993. Evaluation of wood and soil samples from copper naphthenate-treated utility poles in service. Proc. Am. Wood Preserv. Assoc. 89: 167–191.

HARTFORD, W. H. 1973. Chemical and physical properties of wood preservatives. *In* D. D. Nicholas, ed. Wood deterioration and its prevention by preservative treatment. Syracuse Univ. Press, Syracuse, NY.

KALNINS, M. A., R. S. BOONE, AND D. I. GUTZMER. 1990. Practical preservation procedures for beehive bodies. Am. Bee J. 130(5):337–340.

KAMDEM, D. P., K. GRUBER, AND M. FREEMAN. 1995. Laboratory evaluation of copper naphthenate as wood preservative for northern red oak. Forest Prod. J. 45(9):72–76.

————. 1997. Unpublished report.

KLUG, H. P., AND L. E. ALEXANDER. 1954. X-ray diffraction procedures for polycrystalline and amorphous materials, 1st ed. John Wiley and Sons Inc., New York, NY.