IRG/WP 08-30479

THE INTERNATIONAL RESEARCH GROUP ON WOOD PROTECTION

Section 3 Wood Protecting Chemicals

Micro-Distribution of Micronized Copper in Southern Pine

Rod Stirling[1], James Drummond[2], Jun Zhang[3], Richard J. Ziobro[4]

[1]FPInnovations – Forintek Division
2665 East Mall Vancouver, BC, V6T 1W5, Canada

[2]FPInnovations – Paprican Division
3800 Wesbrook Mall Vancouver, BC, V6S 2L9, Canada

[3]Osmose Inc.
980 Ellicott St. Buffalo, NY, 14209-2398, U.S.A.

[4]Osmose Inc.
1016 Everee Inn Rd., Griffin, GA, 30224-4733, U.S.A.

Paper prepared for the 39th Annual Meeting
Istanbul, Turkey
25-29 May 2008

IRG SECRETARIAT
Box 5609
SE-114 86 Stockholm
Sweden
www.irg-wp.com

Micro-Distribution of Micronized Copper in Southern Pine

Rod Stirling[1], James Drummond[2], Jun Zhang[3], Richard J. Ziobro[4]

[1] FPInnovations – Forintek Division, 2665 East Mall, Vancouver BC, Canada, V6T 1W5. rod@van.forintek.ca

[2] FPInnovations – Paprican Division, 3800 Wesbrook Mall, Vancouver BC, Canada, V6S 2L9. jdrummond@paprican.ca

[3] Osmose Inc., 980 Ellicott St. Buffalo, NY, 14209-2398, U.S.A. jzhang@osmose.com

[4]Osmose Inc., 1016 Everee Inn Rd., Griffin, GA, 30224-4733, U.S.A. rziobro@osmose.com

ABSTRACT

For copper-based preservatives to be used in ground contact, penetration of copper into the cell wall is believed to be important to protect the wood from soft rot fungi. Preservatives containing soluble copper are known to do this. It is not known whether preservatives containing particulate copper will also migrate into the cell wall in sufficient quantities to control soft rot decay. An AWPA standard E11 leaching test found that leachate from southern pine blocks treated with a preservative containing particulate copper (Micronized copper quat) contained copper ions, suggesting that copper-containing particles in the treated wood slowly release mobile copper. Southern pine sapwood samples treated with wood preservatives containing soluble (ACQ-D) and particulate copper (Micronized copper quat), as well as untreated southern pine sapwood, were analyzed by Environmental Scanning Electron Microscopy (ESEM) and Energy Dispersive X-Ray Spectrometry (EDS). Copper was detected in the lumens of wood treated with both preservatives, and not in the untreated control. Moreover, the presence of small amounts of copper in the cell walls of samples treated with Micronized copper quat and ACQ-D was indicated by ESEM and EDS. This was further supported by the results of a fungal cellar test and a field stake test which demonstrated that wood treated with Micronized copper quat is resistant to soft rot attack. Future work will investigate copper mobility from particles lodged in the lumens.

Keywords: Micronized Copper, Alkaline Copper Quat, Environmental Scanning Electron Microscopy, Micro-distribution, Cell wall, Southern pine.

1. INTRODUCTION

Copper has a long history of use as a wood preservative due to its excellent control of decay fungi, including those causing soft rot. The efficacy of copper-based preservatives depends on many things, one of which is micro-distribution within the cell wall. The micro-distribution of wood preservatives has been studied for more than half a century (Belford et al., 1957; Petty and Preston, 1968; Dickinson, 1973; Greaves, 1974; Levy and Greaves, 1978; Drysdale et al., 1980; Peters and Parameswaran, 1980; Reimão and Palacios, 1990). The components of CCA have been shown to distribute into the cell wall to varying degrees depending on wood species (Levy and Greaves, 1978) and are largely associated with lignin distribution (Daniel and Nilsson, 1987). While other factors such as tannin content (Pizzi and Conradie, 1986), the presence of nutrients (Hulme and Butcher, 1977), and the distribution of preservative outside the S_2 layer (Ryan and Drysdale, 1988) may affect the amount of copper needed in the cell wall to control soft rot fungi, a certain threshold is still required in the cell wall to inhibit soft rot activity. Insufficient distribution of the preservative into the cell wall could make treated wood susceptible to soft rot decay (Levy and Greaves, 1978). More recently the presence of copper has been demonstrated in the cell walls of wood treated with copper azole (Matsunaga et al., 2004), copper ethanolamine (Cao et al., 2004) and ammoniacal copper and copper carboxylates (Petrič et al., 2000).

Micronized copper quat is a novel wood preservative containing a quaternary ammonium compound and particulate copper carbonate. The use of copper in a particulate form has raised questions about whether the micro-distribution of copper would be the same as in preservatives containing copper in solution (Archer, 2007; Matsunaga et al., 2007). Both Matsunaga et al. (2007) and Archer (2007) showed that the micro-distribution of particulate copper was different than that of soluble copper because of particulate accumulation in the lumens and pit chambers. Deposits in wood treated with preservatives containing soluble copper may also have abundant deposits in lumens and pit chambers (Matsunaga et al., 2004), but the particles are much smaller. Although Archer (2007) could not detect copper above detection limits in the cell wall of the sample treated with particulate copper, vulnerability to soft rot was not demonstrated. These data were also confounded by embedding the samples in epoxy resin which can produce significant movement or loss of preservative (Ryan, 1986). Archer (2007) and Matsunaga et al. (2007) also used commercially obtained material for their analysis, so the soluble and particulate copper preservatives tested were not from matched wood samples. Natural variations in wood anatomy or chemistry could have influenced these analyses. When spectra were corrected for total copper content, x-ray microanalysis revealed no significant difference between wood treated with ACQ and wood treated with micronized copper (Matsunaga et al., 2008).

Choi et al. (2004) and Morris et al. (2004) showed that copper redistributes within wood treated with chromated copper arsenate to protect untreated wood exposed in checks against germination of basidiospores above ground. Since copper carbonate has extremely low but detectable solubility, it seems possible that this copper may re-distribute into the cell wall in sufficient quantities to protect against soft rot when wood remains wet in ground contact. The question is does this redistribution happen rapidly enough to deter soft rot. Promising performance data for Micronized copper quat at sites where other preservative systems fail rapidly to soft rot, suggest that it does. Further work was therefore planned to investigate copper re-distribution. The use of an Environmental Scanning Electron Microscopy (ESEM) eliminates the need for the type of sample preparation that might itself cause loss or redistribution of copper. It also allows for examination of samples in a wet condition.

The present work investigates the loss of copper from wood treated with Micronized copper quat in a leaching test, and the initial distribution of copper in southern pine sapwood treated with Micronized copper quat using ESEM. Future microscopic work will look at re-distribution of copper from the lumen into the cell wall. The results of a fungal cellar test and field stake test are also provided to demonstrate the resistance of wood treated with Micronized copper quat to attack by soft rot fungi.

2. EXPERIMENTAL METHODS

2.1 Leaching Test

Southern pine sapwood was cut into 19 mm x 19 mm x 19 mm (¾" x ¾" x ¾") blocks. Two concentrations of Micronized copper quat solutions were prepared and the southern pine blocks were treated with the solutions as shown in Table 1 following the procedures described in AWPA Standard E11-97 (AWPA, 2003). The preservative retentions were calculated and are summarized in Table 1. The treated samples were air-dried for two weeks prior to the leaching test. Copper leaching was evaluated following the procedures described in AWPA Standard E11-97. The concentration of copper in the leachates was analyzed by ICP.

Table 1: Treating Solutions and Preservative Retentions

Preservative	Solution Strength %	A.I. Retention kg/m^3 (pcf)
Micronized	0.714	4.0 (0.25)
copper quat	1.143	6.6 (0.41)

2.2 Environmental Scanning Electron Microscopy

Southern pine sapwood stakes (4 x 38 x 254 mm) were cut into paired 4mm x 4mm x 125 mm samples. Randomly selected pairs were either left untreated or were treated with 0.8% Micronized copper quat or 0.8% alkaline copper quat (ACQ-D). To treat the samples an initial vacuum was pulled for 15 minutes at approximately 29.3 mm Hg, followed by 30 minutes at 60 psi. No final vacuum was drawn. Sections were taken from one sample in each group and examined and analyzed using a FEI Quanta FEG 400 Environmental Scanning Electron Microscope (ESEM) and EDAX Genesis energy dispersive X-ray spectrometer with a 10mm^2 SiLi SUTW (super ultra thin window).

Each of the samples was cut with a narrow-kerf Dozuki saw to yield blocks representing the middle and the end of the stake (Figure 1). The surfaces of the resultant blocks were cleaned with compressed air (Dust-off®) to remove any particles dislodged in the sawing process.

Each of the middle and end samples were subsequently hand cut using single-edged, uncoated stainless steel razor blades. Separate radial, tangential and cross-section sub-samples were produced in this manner. The radial samples represent more of a split surface than a sectioned surface since the wood split easily in this plane.

All samples were mounted on aluminum SEM stubs using spectroscopically-pure, double-sided adhesive carbon tabs. The stubs were placed in the ESEM and imaged in low-vacuum mode at 1 Torr pressure. Images were collected using a solid-state back-scattered electron detector. In back-scattered electron mode, elastically-scattered, high-energy electrons are collected and lower-energy secondary electrons are largely undetected. Therefore the image formed is based on atomic number contrast. Accordingly, higher atomic number material such as Cu appears brighter than organic material such as wood. Images and X-ray spectra were collected using an accelerating voltage of 20kV. X-ray spectra were collected using a live time of 100s. A short pre-amplifier time (1.6μs) was used to improve the detection of heavier elements (i.e. Cu).

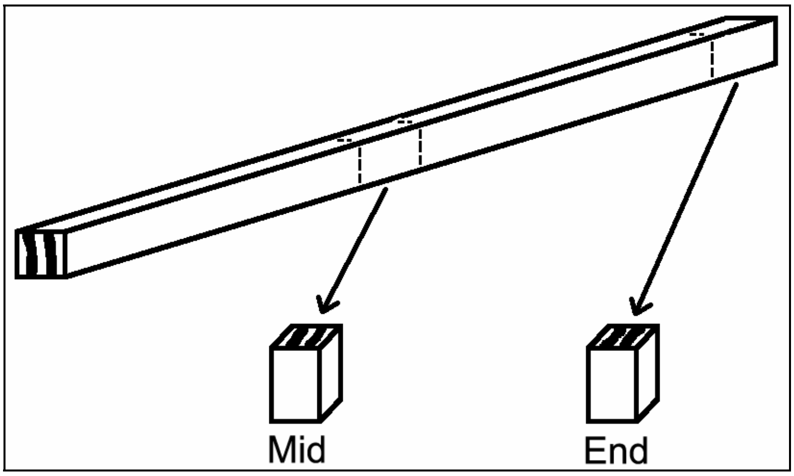

Figure 1: Schematic representation of cutting of the stake to yield samples from the middle and one end.

2.3 Fungal Cellar Test

FRI (New Zealand) treated, installed and inspected samples in a fungal cellar test. Radiata pine samples were treated with ACQ-D and Micronized copper quat to a range of retentions, plus untreated controls measuring 10 x 5 x 160 mm were evaluated by the protocol given in the Australasian Wood Preservation Committee (AWPC), Protocols for Assessment of Wood Preservatives. The stock soil was taken from the Scion experimental forest nursery and contained NPK fertilizers of unknown amounts. The top 200mm of soil was replaced with fresh soil prior to testing. Prior to installing the stakes the soil was wetted up until its moisture content was greater than 100% water holding capacity (around 50% moisture content). Soil temperature was maintained at 25-27°C by heating pipes which are embedded in the concrete block which forms each fungal cellar. Moisture was maintained by gently hosing the soil surface using a fine rose head. The amount added was, again, until it felt right (based on 30 years experience of staff at the facility). Samples were rated after 6, 9, 12, 15 and 18 months of exposure.

2.4 Field Test with Stakes

Michigan Technological University treated, installed and inspected samples in field test. Southern pine stakes were cut and treated with Micronized copper quat as well as an organic preservative to four retentions. These, along with untreated controls, were placed in a field test in Keaau, Hawaii (near Hilo). This site has a mean temperature of 23°C, receives an average of 322 cm of precipitation annually and has a Scheffer Index of approximately 350. The soil is a silty clay loam (Hilo series). After approximately three years stakes were moved to another site in Maunawili, Hawaii (near Honolulu). This site has a mean temperature of 23°C, receives an average of 228 cm of precipitation annually and has a Scheffer Index of approximately 300. The soil is a silty clay (Lolekaa Series). Stakes were inspected after 12, 24, 33 and 45 months and rated according to AWPA E7-03, Standard Method of Evaluating Wood Preservatives by Field Tests with Stakes.

3. RESULTS AND DISCUSSION

3.1 Copper Leaching

The copper concentration in the leachates after each leaching period is summarized in Table 2. At both retentions copper was detectable throughout the experiment. This suggests that the copper particulate in the treated wood is slowly releasing soluble copper. The presence of some soluble copper is important since it has been shown in other systems to migrate into the cell wall and protect the wood from soft rot attack (Hulme and Butcher, 1977) and spore germination by migrating into checks (Choi et al., 2004).

Table 2: Leaching of Copper from Southern Pine Sapwood Treated with Micronized Copper Quat

Preservative System	Retention kg/m^3 (pcf)	Copper Detected in Leachates Over Leaching Time, ppm							
		6 hrs.	Day 1	Day 2	Day 4	Day 7	Day 9	Day 11	Day 14
Micronized	4.0 (0.25)	2.72	1.6	1.0	0.98	1.0	0.19	0.11	0.21
Copper Quat	6.6 (0.41)	2.9	2.2	1.4	1.7	1.4	0.38	0.17	0.58

3.2 Copper Distribution

3.2.1 Copper in Lumens

Copper-containing particles were detected in lumens of both the Micronized copper quat and ACQ-treated samples. In both, the obvious presence of particles in lumens occurred sporadically. Relatively few lumens in the samples contained obvious particles. The Micronized copper quat-treated sample had significantly more obvious particles present compared to the ACQ sample. Examination and analysis of radial sections of the samples showed that there were copper-containing particles in some of the lumens, rays, and resin canals in both the Micronized copper quat and ACQ-treated samples. Again, the presence of particles was more obvious in the Micronized copper quat-treated samples versus the ACQ samples. In the ACQ mid samples, there were almost no observable particles.

Figures 2 and 3 show images of copper-containing particles in the Micronized copper quat-treated sample. Figure 4 shows radial sections of Micronized copper quat-treated, ACQ-treated, and untreated samples. The difference between samples in terms of observable copper-containing particles is obvious. Note that in the Micronized copper quat-treated sample there is a resin canal exposed in the section. There is a significant amount of copper-containing material in the canal. In the ACQ-treated sample, there is Cu-containing material visible in an exposed tracheid lumen in the upper right-hand quadrant. There are also a few pit borders that show the presence of Cu particles. The presence of Cu in all these locations was confirmed by energy dispersive X-ray spectroscopy (EDS). An example is shown in Figure 5.

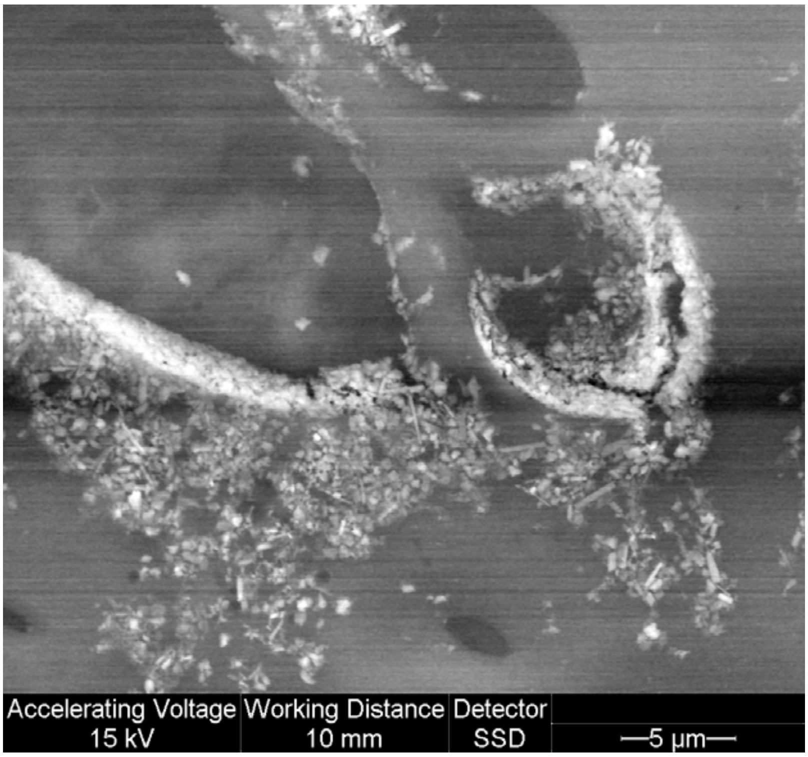

Figure 2. Copper-containing particles in radial section of a Micronized copper quat-treated sample. The particles appear to be coming from a ray parenchyma cell through a cross-field pit.

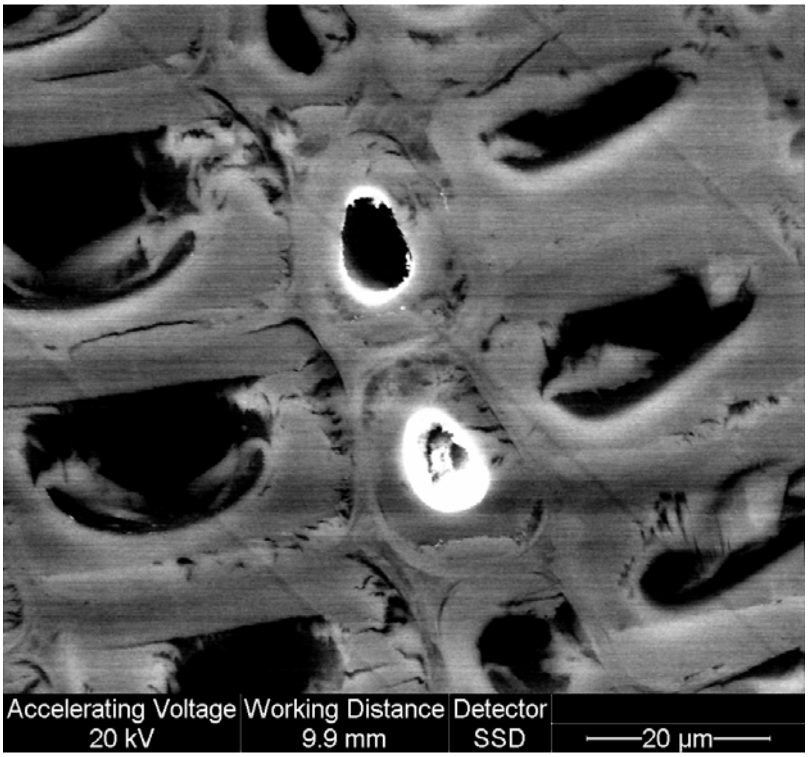

Figure 3. Copper-containing particles in the lumens of two tracheids in a cross-section of a Micronized copper quat-treated sample.

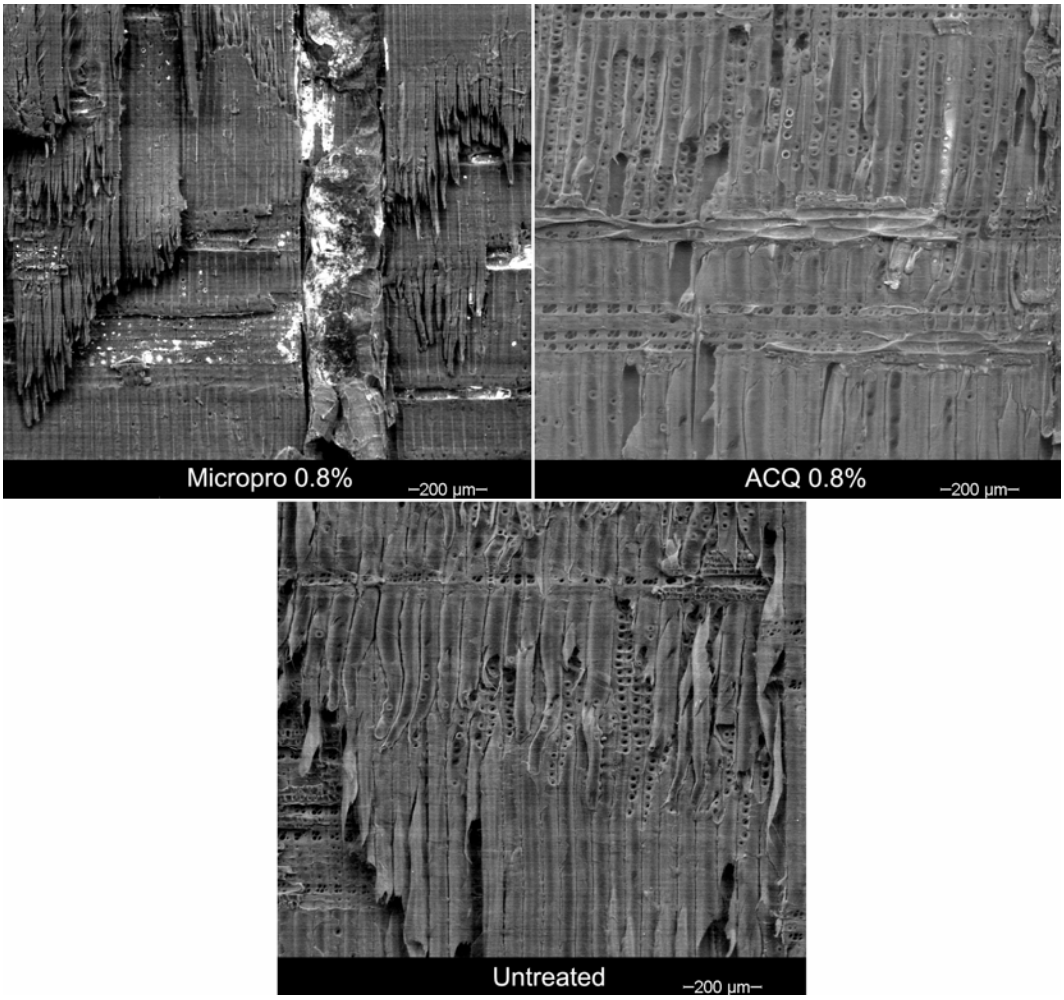

Figure 4. Radial sections of end samples in back-scattered electron mode.

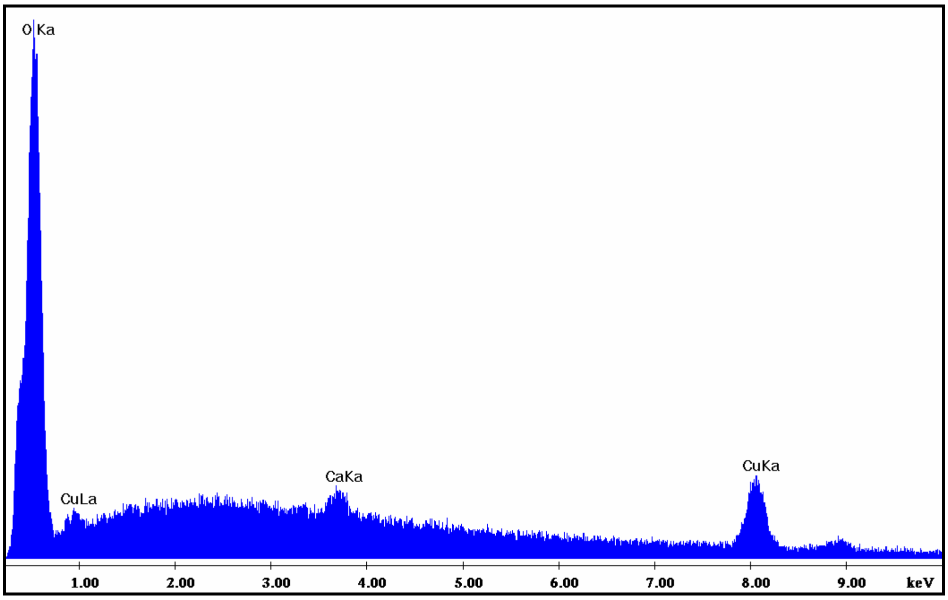

Figure 5. X-ray spectrum of particles in lumen of radial section of a Micronized copper quat-treated sample.

3.2.2 Detection of copper in the cell wall

Confirming the presence of copper in the cell wall is difficult. The first attempts at analyzing the cell wall were performed by centring the beam on the middle lamella between four adjacent thick-walled latewood tracheids. A field of view was selected to include about half of the cell wall thickness of the adjacent tracheids and therefore avoid including any lumens where particles might reside. There were small peaks for Cu found in both Micronized copper quat and ACQ-treated samples in analysis of cross-sections in the centre of latewood tracheids at 500,000X magnification. Figures 6 and 7 show the area analyzed and the resulting X-ray spectrum for the Micronized copper quat-treated sample. Note the damage incurred to the sample by the electron beam. It is important to remember that this small copper peak was determined just after fixation. Given time and the appropriate storage conditions, additional copper may re-distribute from the lumens into the cell wall.

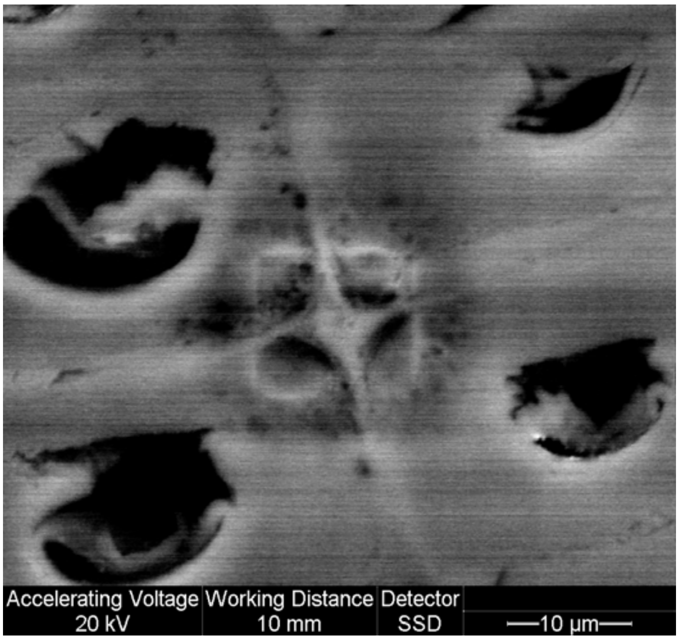

Figure 6. Cross-section of Micronized copper quat-treated middle sample after X-ray analysis of the middle lamella and four adjacent cell walls.

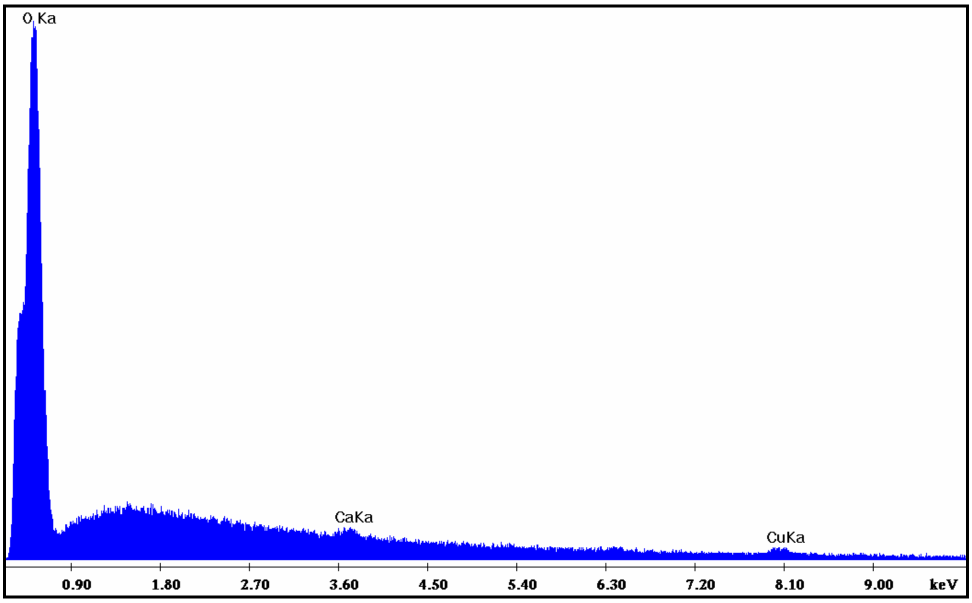

Figure 7. X-ray spectrum of the area shown in Figure 6. There is a very small copper peak.

To attempt to analyze the S_2 only, the beam was centred at low magnification in the middle of the cell wall of a latewood tracheid and then a magnification of 500,000X was selected and the X-ray signal collected. Under these conditions, the horizontal field width scanned was 0.54µm.

A micrograph of the area taken after analysis (Figure 8) shows that there is significant spread of the beam in the sample as indicated by the observable damage. It is well established in electron microscopy that the electrons from the beam spread out in the sample below the surface. There is usually a tear-drop shaped interaction volume, whose size depends on many factors including the density and composition of the sample. The concern in these samples would be that the volume includes some of the lumen, and the potential for surface particles in the lumen to contribute to the signal (Ryan, 1986). We cannot conclusively state at this time that we are sampling only the S_2. However, in the experiments analyzing four adjacent walls and the middle lamella, it appears from the after photos (Figure 6 for example) that the damage zone is contained within the cell walls (i.e. no lumen contribution) and thus it seems to indicate that there is Cu in the walls. It would seem unlikely that the copper would be solely contained in the middle lamella, though it may be more abundant in regions with greater lignin content (Daniel and Nilsson, 1987).

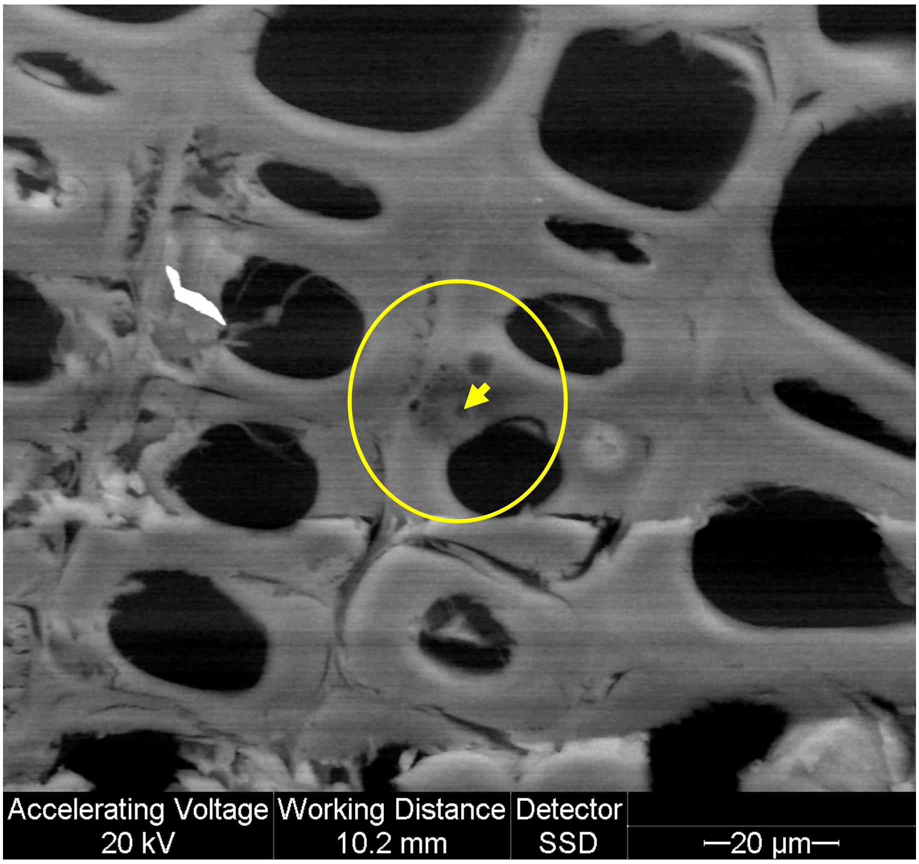

Figure 8. Cross-section of ACQ-treated middle sample. The area scanned by the beam during X-ray analysis is inside the yellow circle. The beam was focused on the spot indicated by the arrow. The dark area around this spot indicates damage to the sample and possibly the extent of the beam interactions inside the sample.

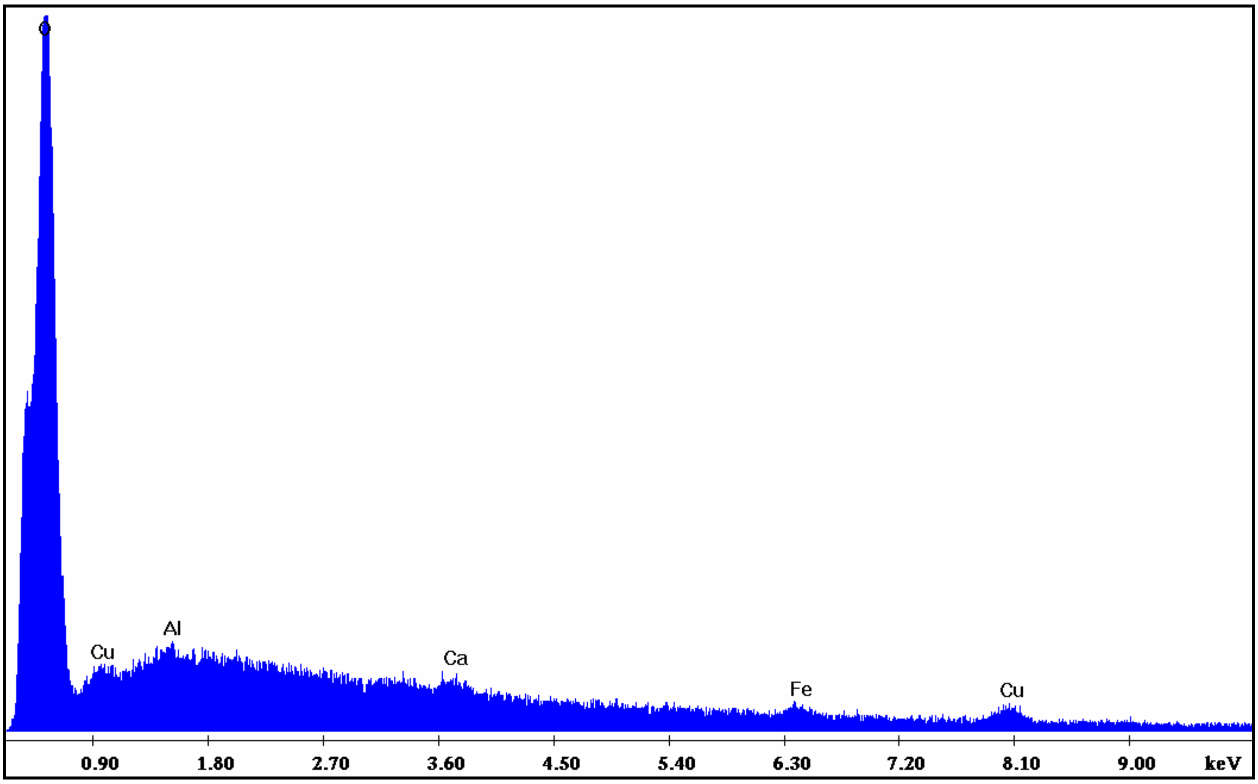

Figure 9. X-ray spectrum of cell wall area shown in Figure 8. There is a small copper peak along with other inorganic peaks.

3.2.3 Untreated sample

Copper was not detected in the untreated sample, indicating that the Cu detected in small amounts in the cell wall is not an inherent component of the sample.

Figure 10 shows overlaid spectra from analyses at 500,000X of single latewood tracheid walls in cross-sections of Micronized copper quat-treated and untreated samples. There are no copper peaks in the untreated sample. The ACQ- and Micronized copper quat-treated samples have similar, small copper peaks.

Materials used in the preparation of the samples, such as the compressed air and razor blades, were analyzed by X-ray under similar conditions and the absence of copper in both was confirmed. Only Cr and Fe peaks were found in the razor blade spectrum. The compressed air was sampled by impinging compressed air for 30s against the surface of a carbon adhesive tab. No inorganic peaks were found in subsequent X-ray analysis; therefore the compressed air is not a source of potential contamination.

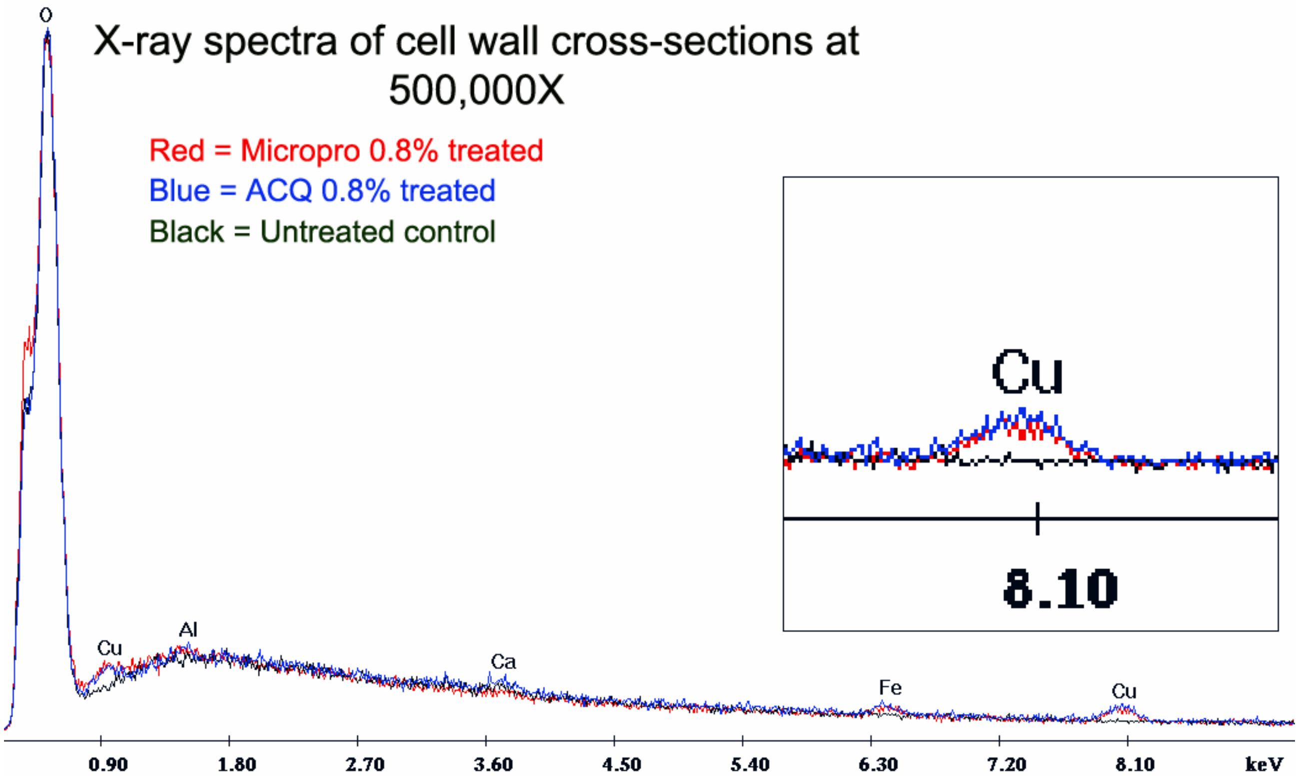

Figure 10. Comparison of X-ray spectra from the cell wall in cross-sections of Micronized copper quat-treated, ACQ-treated and untreated samples.

3.3 Fungal Cellar Test

Table 3 shows the results of a fungal cellar test after 6, 9, 12, 15 and 18 months. Untreated controls had an average life time of 8.7 months which was very typical and indicates that decay conditions were pretty near optimum. After 18 months Micronized copper quat-treated samples outperformed ACQ-treated samples at all retentions tested. These data indicate that wood treated with Micronized copper quat is highly resistant to decay by soil-inhabiting fungi.

Table 3: Summary of Fungus Cellar Stakelets' Condition (Index of Condition)

Preservative/Retention (kg/m^3 a.i.)	6 months	9 months	12 months	15 months	18 months
ACQ-D					
3.0	9.5	9.4	8.8	6.6	5.7
4.0	9.4	9.2	8.2	7.2	6.8
5.0	9.5	9.5	9.4	8.3	7.6
6.5	9.7	9.6	9.5	9.1	8.6
Micronized Copper Quat					
3.0	9.9	9.7	9.4	8.4	7.7
4.0	9.7	9.7	8.8	8.3	7.7
5.0	9.6	9.5	9.5	8.4	7.2
6.5	9.9	9.9	9.9	9.9	9.5
Untreated Controls	5.4 (1)*	0.4 (9)*	Average life 8.7 months		

* Number of complete failures

3.4 Field Test with Stakes

Table 4 shows the results of the field stake test. Untreated controls failed rapidly to decay (33 months) and termites (45 months). Both soft-rot and white-rot decay were evident in untreated controls examined by light microscopy (Figure 11). Stakes treated with organic biocides showed some resistance to decay and insect attack, but after 33 months the highest retention was rated 2.3 for decay and 8.3 for termites. Both soft-rot and white-rot decay were evident in stakes treated with organic biocides when examined by light microscopy (Figure 12). The stakes treated with Micronized copper quat were resistant to degradation by fungi and insects. After 45 months stakes treated to 6.0 kg/m^3 still had perfect ratings. Even stakes treated to only 1.5 kg/m^3 were rated 7.0 for decay and 9.0 for insects after 45 months. These data indicate that wood treated with Micronized copper quat is resistant to soft-rot decay.

Table 4: Summary of Ratings of 19mm Stakes from a Field Test in Hawaii

Preservative System	Retention kg/m^3	12 months		24 months		33 months		45 months	
		Decay	Insect	Decay	Insect	Decay	Insect	Decay	Insect
Organic Biocides	#1	8.8	10	8.7	9.3	5.0	9.0	-	-
	#2	8.5	10	8.3	8.8	1.6	8.1	-	-
	#3	9.1	10	7.2	9.4	2.6	9.4	-	-
	#4	8.5	10	6.9	9.5	2.3	8.3	-	-
Micronized Copper Quat	1.5	9.9	10	9.9	10	8.8	10	7.0	9.0
	3.0	9.8	10	9.95	10	9.7	10	8.6	10.0
	4.5	10	10	10	10	9.8	9.95	9.0	10.0
	6.0	9.9	10	10	10	10	10	10.0	10.0
Untreated Controls	-	5.9	9.8	1.6	6.2	0.0	7.5	0.0	0.0

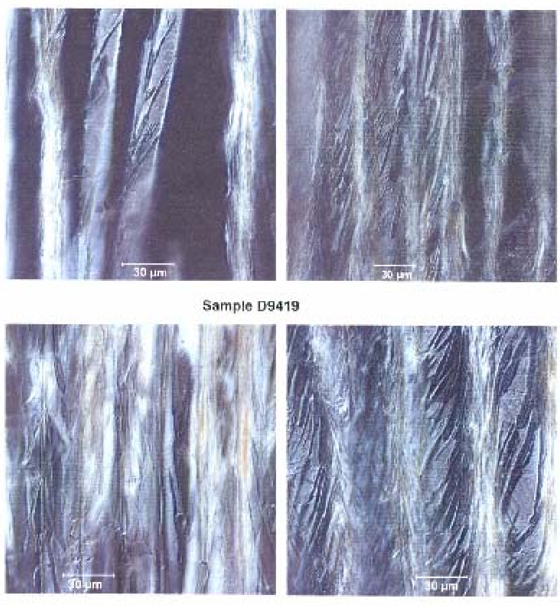

Figure 11. Light Micrographs from an untreated field test control show extensive soft-rot degradation in the forms of soft rot cavities. Dark hyphae are associated with the cavities. In addition, erosion around intertracheid pits indicates white rot.

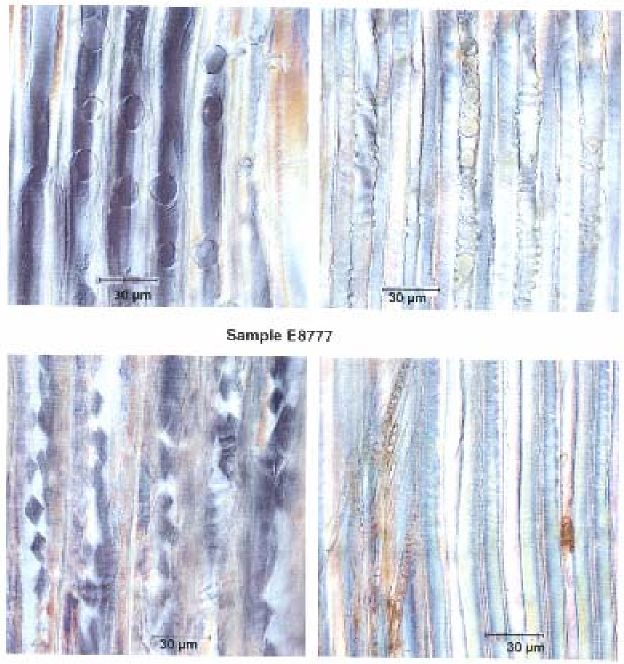

Figure 12. Light micrographs from a field stake treated with organic biocides indicate the presence of both soft-rot and white-rot decay. Soft rot is indicated by cavities and narrow bore holes. Dark hyphae are associated with cavities and bore holes.

4. CONCLUSIONS AND RECOMMENDATIONS

Low levels of copper were detected at every stage of an AWPA E11-97 leaching test of wood treated with Micronized copper quat suggesting micronized copper may be capable of redistributing into cell walls. Copper-containing particles were detected in the lumens of Micronized copper quat- and ACQ-treated samples but were not present in untreated samples. While confirming the presence of copper in the cell wall was difficult, X-ray analysis indicated that there was a small amount of Cu in the cell walls in both Micronized copper quat- and ACQ-treated samples, and not in the untreated samples. Fungal cellar and field stake test data indicate that wood treated with Micronized copper quat is highly resistant to decay by soft-rot fungi. This resistance to soft-rot attack is likely due to soluble copper released from the Micronized copper particles entering the cell wall. While we have shown that low levels of copper can be leached out of wood treated with Micronized copper quat and that this copper is detectable in the cell wall, further work is needed to conclusively determine whether this soluble copper re-distributes from the lumens into the cell wall and whether this level of copper in the cell wall is sufficient to explain the resistance to soft-rot decay.

5. ACKNOWLEDGEMENTS

The Light Microscopic work was conducted by State University of New York College of Environmental Science and Forestry.

6. REFERENCES

American Wood-Preservers' Association (2003): Standard Method of Determining the Leachability of Wood Preservatives: E11-97. AWPA, Selma, AL. pp. 430-432.

American Wood-Preservers' Association (2003): Standard Method of Evaluating Wood Preservatives by Field Tests with Stakes: E7-01. AWPA, Selma, AL. pp. 403-411.

Archer, K J (2007): Cell Wall Penetration of Particulate Copper Wood Preservative Systems in Southern Pine. International Research Group on Wood Protection. Oral presentation at the 38th Annual Meeting; no paper.

Belford, D S, Preston, R D, Cook, CD, Nevard, EH (1957): Timber Preservation by Copper Compounds. *Nature*. 4595: 1081-1083.

Cao, J, Kamdem, D P, Pasek, E (2004): Microdistribution of Copper in Copper-Ethanolamine (Cu-EA) Treated Southern Yellow Pine (*Pinus* spp.) Related to Density Distribution. International Research Group on Wood Preservation. Document No. IRG/WP/04-40270. 18p.

Choi, S., Ruddick, J.N.R., Morris, P.I. 2004. Chemical redistribution in CCA-treated decking. *Forest Products Journal*. 54(3): 33-37.

Daniel, G F, Nilsson, T. (1987): Comparative Studies on the Distribution of Lignin and CCA Elements in Birch Using Electron Microscopy X-Ray Microanalysis. International Research Group on Wood Preservation. Document No. IRG/WP/1328. 19p.

Dickinson, D J (1973): The Micro-Distribution of Copper-Chrome-Arsenate in *Acer Pseudoplatanus* and *Eucalyptus maculate*. International Research Group on Wood Preservation. Document No. IRG/WP/319. 12p.

Drysdale, J A, Dickinson, D J, Levy J F (1980): Micro-distribution of a CCA Preservative in Five Timbers of Varying Susceptibility to Soft Rot. *Material und Organismen*. 15: 287-303.

Greaves, H (1974): The Microdistribution of Copper-Chrome-Arsenic in Preservative Treated Sapwoods using X-ray Microanalysis in Scanning Electron Microscopy. *Holzforschung*. 28(6): 193-200.

Hulme, M A, Butcher, J A (1977): Soft-rot Control in Hardwoods Treated with Chromated Copper Arsenate Preservatives. I. Treatment Problems. *Material und Organismen*. 12(2): 81-95.

Levy, J F, Greaves, H (1978): Penetration and Distribution of Copper-Chrome-Arsenic Preservative in Selected Wood Species. *Holzforschung*. 32(6): 209-213.

Matsunaga, H, Kiguchi, M, Evans, P (2007): Micro-Distribution of Metals in Wood Treated with a Nano-Copper Wood Preservative. International Research Group on Wood Protection. Document No. IRG/WP/07-40360. 10p.

Matsunaga, H, Kiguchi, M, Roth, B, Evans, P D (2008): Visualisation of metals in pine treated with preservative containing copper and iron nanoparticles. *IAWA J*. (In-Press)

Matsunaga, H, Matsumura, J, Oda, K (2004): X-Ray Microanalysis Using Thin Sections of Preservative-Treated Wood: Relationship of wood anatomical features to the distribution of copper. *IAWA Journal*. 25(1): 79-90.

Morris, P.I., Ingram, J.K., Ruddick, J.N.R., Choi, S.M. 2004. Protection of untreated wood by adjacent CCA-treated wood. *Forest Products Journal* 54(3): 29-32.

Peters, G A, Parameswaran, N (1980): Transmission Electron Microscopical Localization of Salt Preservative Components in Wood Cell Walls. *Wood Science and Technology.* 14: 81-88.

Petrič, M, Murphy, R J, Morris, I. (2000): Microdistribution of Some Copper and Zinc Containing Waterborne and Organic Solvent Wood Preservatives in Spruce Wood Cell Walls. *Holzforschung*. 54(1): 23-26.

Petty, J A, Preston, R D (1968): Electron Probe Microanalysis of Metals in Cell Walls of Conifer Wood Treated with Preservatives. *Holzforschung*. 22(6): 174-177.

Reimão, D, Palacios, J M (1990): Microdistribution of water-borne preservatives in blue gum wood treated by full-cell process. International Research Group on Wood Preservation. Document No. IRG/WP/3617. 11p.

Ryan, K G (1986): Preparation Techniques for X-ray Analysis in the Transmission Electron Microscope of Wood Treated with Copper-Chrome-Arsenate. *Material und Organismen*. 21(3): 223-234.

Ryan, K G, Drysdale, J A (1988): X-Ray Analysis of Copper Chromium and Arsenic Within the Cell Walls of Treated Hardwoods – New Evidence Against the Microdistribution Theory. *J. Inst. Wood Sci.* 11(3): 108-113.