THE STUDY OF CCA (CHROMATED COPPER ARSENATE) AND PEG (POLYETHYLENE GLYCOL) TREATED SOUTHERN AND RED PINE WOOD USING FIELD EMISSION SCANNING ELECTRON MICROSCOPY

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Summary

The bulking of polyethylene glycol (PEG) treated softwood was observed for the first time by the use of field emission scanning microscopy (FE-SEM). When PEG was used as an additive in conjunction with chromated copper arsenate (CCA) for treating red pine and southern pine utility poles, not only did PEG increase the softness and the dimensional stability of the wood, but PEG also seemed to enhance the microdistribution of the metal ions of the CCA preservative as demonstrated by the environmental scanning electron microscope (ESEM) equipped with an energy dispersive X-ray elemental analysis system.

1. Introduction

Polyethylene Glycol is known to interact with wood to provide unusual dimensional stability to its structure (Forest Product Laboratory, 1972). Recently, PEG is also known for providing softness to CCA-treated utility poles to improve their climbability (Cooper et al., 1995). However, its physical and chemical interactions with wood are still not well understood. Wood structures containing PEG in the presence of CCA wood preservative have never been characterized.

In this paper, FE-SEM was employed to investigate and compare the structures of untreated red pine and southern pine wood to those of CCA- and CCA/PEG-treated. The micro-distribution of CCA in PEG-treated wood was also investigated.

2. Methodology

Field Emission Scanning Electron Microscope (FE-SEM)

The field emission scanning electron microscope (FE-SEM) photomicrographs in the present study were taken using a cold cathode JEOL JSM-6300F FE-SEM, which is capable of high resolution imaging at low accelerating voltage (e.g., 2kV) for image enhancement.

Wood cross-section cuts for FE-SEM observation, and X-ray analysis, were prepared by using a vibrating-blade sectioning device (OTS-3000-03 EMS Oscillating Tissue Slicer from Electron Microscopy Sciences) to slice 60μ-thick sections from ~1/8" bore plugs.

Several of the thin sections were mounted on SEM sample stubs covered with carbon conductive double-sided adhesive tape. For imaging with the FE-SEM, a thin coating (~40-60Å) of chromium was sputtered onto the samples using a high-resolution sputter coater (CrC-100 Planar Magnetron Sputtering System from Plasma Sciences, Inc.). The thin conductive coating eliminated surface charging that might develop from the electron beam during FE-SEM observation.

Environmental Scanning Electron Microscope (ESEM) / Energy Dispersive X-Ray Spectrometer (EDS)

The X-ray analyses were collected using a Noran Voyager EDS X-ray analysis system mounted on an ElectroScan Environmental Scanning Electron Microscope (ESEM). Since it was not necessary with the ESEM to sputter coat the sample to dissipate charge build-up from the electron beam, this set-up eliminated the need to compensate for background interference in the X-ray signals due to a coating material. Results of the elemental analysis could then be used for comparison without further background signal correction. However, from time to time, within the same samples, slight variations in results did occur. This could be attributed to artifacts such as the size of the samples and their geometry, which could affect the sensitivity of the X-ray analysis. To minimize such an effect, the data reported in Tables 1 and 2 were averages of analyses of multi-spots on multi-samples. Typically, a minimum of two different specimens with five random areas per specimen were analyzed.

EDS Analysis - Data Generation and Comparison

The calibration of the EDS system on the ESEM for elemental analysis was done using CCA solution. The chromated copper arsenate type C formulation used was commercial grade material known by the trade name K 33-C®, as a 50% concentrated aqueous solution. The contained solids were comprised of 47.5% CrO_3, 18.5% CuO and 34% As_2O_5 as metal oxides. Based on the formulation, the weight per cent of chromium, copper and arsenic was calculated to be 40.32%, 24.60% and 35.08% respectively. The ratio of Cr : Cu : As was calculated to be 1 : 0.61 : 0.87 for the metal ions content.

Droplets of the CCA solution discussed above were placed on microscope slides and the water was evaporated. The residual solids were analyzed by ESEM/EDS. The average weight per cents of Cr, Cu and As obtained through multiple analyses on different samples over a period of time were 40.04%, 23.72% and 36.24% respectively. The ratio of Cr : Cu : As was then calculated to be 1 : 0.60 : 0.91 which was considered to be very close to the theoretical ratio of the CCA solution discussed above. This calibration exercise was repeated during the course of the study to ensure the instrument was well aligned for metal ions analyses and data were accurate and reproducible.

CARBOWAX® PEG PLUS™

CARBOWAX® PEG PLUS™ wood treating additive, a proprietary formulation containing a high molecular weight polymer of ethylene oxide manufactured by Union Carbide Corporation, Inc., was used for this study.

Untreated Wood Samples

Sections of untreated red pine and southern pine utility poles were obtained directly from utility pole treaters. 3/4 inch x 3/4 inch x 3-3/4 inch rectangular blocks were cut from the sapwood region of the log sections and further sub-divided into five 3/4 inch cubes, as shown in Figure 1.

CCA- and CCA/PEG-Treated Wood Samples

To ensure wood sample consistency for comparison purposes, only end-matching cubes (meaning cubes from the same rectangular block) were used. In general, one cube from the same block would be treated with 2.5% CCA, another with 2.5% CCA/PEG PLUS™ 4% solution, etc. If more samples were required, a new block would be secured in a similar manner to ensure samples were from the vicinity of one another to minimize any background variation.

The chemical treating procedure used was similar to commercial utility pole treatment. It consisted of subjecting 2-4 wood cubes to 30 minutes of vacuum (28 in. Hg), followed by introducing about 500 ml of the pre-mixed treating solution (e.g., 2.5% CCA, etc.) into a ½ liter stainless steel vessel (a modified Paar reactor). Then the vessel with its contents was pressurized with nitrogen to 150 psig and maintained at that pressure for 2 hours. The solution was then removed and the wood samples subjected to another 30-minute vacuum cycle to remove any residual liquid.

The treated samples were weighed before and after treatment to determine chemical uptakes. In almost all cases, the weights gained by the samples were over 100% of the initial wood weight, indicating that the wood was saturated with the treatment solution. The treated samples were stored in a 90°C oven for at least 48 hours to allow CCA fixation to take place and the samples to dry.

3. Results and Discussion

Untreated Red Pine (*Pinus Resinosa Ait.*)/Southern Pine (*Pinus Spp.*)

Observing the transverse sections of the untreated wood by FE-SEM reveals several important cellular structures. The late wood cell walls of southern pine are much thicker than the late wood of red pine, Figures 2 and 3. This explains the more distinct and darker year rings of the former. The lumen surface of the red pine tracheids is spotted with warts, Figure 4. They are believed to be the localized thickening of microfibular bundles, and chemically composed of a combination of lignin and amorphous carbohydrates (Kuo and Manwiller, 1986). Their function is not clear, but could be related to water absorption and storage. Figure 4 also depicts the structure of the pit membrane of a tracheid bordered pit. The apparent smooth surface is actually quite porous. Minute particles up to 0.2μm can easily pass through the membrane (Panshin and Zeeuw, 1980).

Earlier work (Côté, 1958 and 1963) had demonstrated that the circular pit membranes are attached to the aperture of the bordered pits by a network of microfibrils as shown in Figures 5-A and B. They are responsible for the aspiration of the pit membranes onto the pit apertures to seal off passages between tracheids.

CCA Treated Pine Wood

Evidence of CCA in treated wood can be easily found in areas the treatment solution has passed through, such as the pit membrane. Figure 6 shows a high concentration of CCA solid with sizes as large as 0.5μm at and around the pit membrane and the surrounding lumen surface of red pine wood. This phenomenon has also been observed by others (Vick and Kuster, 1992). Some researchers (Greaves, 1972) attributed this to the filtration effect of tracheid bordered pits where crystals from the treatment solution were filtered out. Yet another plausible explanation is that the aqueous CCA solution present in the area had evaporated, leaving solid CCA behind.

While the presence of CCA in the cell wall region cannot be easily seen by the FE-SEM, it can be detected by X-ray elemental analysis. The EDS dot map, Figure 7, generated using the ESEM shows the locations of the individual metal ions in the wood fibers. The apparent even distribution of the chromium, copper and arsenic ions suggests that the wood is very evenly treated.

CCA/PEG PLUS™ Treated Pine Wood

The photomicrograph of southern pine treated with CCA/PEG PLUS™ at the bordered pit area, Figure 8, reveals a substantial amount of solid PEG mixed in with the CCA particles. By the changes in cellular details, such as the loss in the distinction of the striation of the microfibular bundles, and the loss of surface roughness around the bordered pits and lumen areas, the deposition is considered to be relatively massive. Similar results were also found for the CCA/PEG PLUS™-treated red pine, Figure 8-B.

The Bulking Effect of PEG on Wood

By comparing the photomicrographs obtained for the untreated, CCA-only treated and the CCA/PEG PLUS™-treated pine wood, PEG-induced bulking of wood can be observed for the first time using FE-SEM. The untreated early wood sample, Figure 9-A, appears to be thin walled and full of voids as a result of drying/loss of moisture content. After treating with the preservative CCA, Figure 9-B, some bulking occurred as indicated by the disappearance of most of the void spaces; but maximum bulking of wood seems to be effected by the combined CCA/PEG treatment, Figure 9-C. Although a visual comparison of the result is only qualitative, this series of photomicrographs provides direct evidence to support the belief that PEG PLUS™ molecules can penetrate into the void region of the microfibrils and cause the wood fibers to expand.

Such bulking effect on wood by PEG could be significant in real life. Figure 10 captures the severe ring delamination effect on a CCA-treated red pine telephonic transmission pole

after only three years in service (Bariska et al., 1988). This same phenomenon is observed for a CCA-treated southern pine pole section after 2 years of field exposure, Figure 11. On the other hand, the CCA/PEG PLUS™-treated pole section shown in Figure 11 remains dimensionally stable throughout the same time period.

Microanalysis of CCA in Treated Wood

Several different cellular structures in wood were analyzed for CCA distribution using the ESEM/EDS as described above. These included pit membranes, the cross-sections of early and late wood, and the middle lamella for both the CCA- and the CCA/PEG PLUS™-treated wood.

A typical elemental dot map of CCA on the cross-section of the early wood has been shown in Figure 7. The distribution of the metal ions in the cell wall structure appears to be very uniform. The intensity of the metal ions on the map, however, does not necessarily indicate their concentrations. Table 1 gives the average weight per cent distribution of Cr, Cu and As for the various cellular structures in the sapwood region of treated red pine.

Figure 12 depicts the microdistribution of metal ions in various structures of CCA-only treated wood. The weight per cent of Cr, Cu, and As for the late wood and the compound middle lamella has a metal ions distribution pattern quite similar to that of the CCA solution. However, those of the early wood and the pit membrane deviate to some extent. This suggests that the disproportionation of the CCA preservative has occurred in these areas, although it does not necessarily imply that the preservation of the wood has been compromised. Based on the overall average of Cr, Cu, As distribution (41.55%, 26.08% and 32.37% respectively) shown in Table 1, the present results compared well with those (38.46%, 23.46% and 38.08% respectively) reported for softwood species (Greaves, 1974) and with those (44.1%, 24.6%, and 31.3% respectively) for CCA treated red pine (Petty and Preston, 1968).

In comparison, the distribution for the metal ions within different structures of the CCA/PEG PLUS™-treated wood is even more similar to that of the CCA treatment solution, Table 1 and Figure 13. Little or no disproportionation of CCA seems to have occurred.

The almost-identical metal ions microdistribution data based on the overall average of all the tabulated cellular structures for the two different treatments imply that PEG has not affected the overall retention of the preservative in the red pine wood. On the contrary, PEG seems to have caused less disproportionation of the CCA in the treatment process.

With the exception of the late wood, the same effect that PEG causes less disproportionation of the CCA solution throughout the early wood region in treated southern pine wood can be seen in Table 2 and Figures 14 and 15.

It is not certain why the disproportionation of CCA is much more severe for the late wood of southern pine. The thicker cell wall, hence, a higher wood density and possibly a higher

concentration of lignin with which chromium (VI) ions tend to rapidly react could all contribute to the severe disproportionation. Other possible reasons may include how the samples were prepared and how quickly the CCA fixation process had occurred.

Of all the cellular structures analyzed in this study, the early wood and the compound middle lamella appear to be consistently well treated in the CCA/PEG PLUS™ cases. Some early researchers (Drysdale, et. al.1980), attributed phenomena such as this to the possibility that the preservatives probably entered into the middle lamella through the pit areas if there were a great number of large size pits present. However, PEG, being a bulking agent, could simply swell the cell wall effectively enough to allow a better penetration of the CCA preservative. Regardless of the mechanisms involved, based on the present CCA retention data generated for the CCA/PEG PLUS™-treated wood, the addition of PEG PLUS™ to the CCA solution for wood treating could have a beneficial effect on the efficacy of the CCA preservative.

4. Conclusions

The field emission scanning electron microscope allows the direct observation of the bulking effect of wood by polyethylene glycol for the first time. The expansion of the wood fibers by PEG restores most of the structural integrity of dry and CCA-treated wood.

Aside from providing dimensional stability to CCA treated wood, based on x-ray elemental analyses, PEG appears to be capable of providing a metal ions distribution ratio similar to that of the treatment solution. As a result, CCA/PEG PLUS™-treated wood should be well preserved and protected.

In future work, it will be valuable to correlate the fixation conditions of CCA in treated wood to the microdistribution of the metal ions in the sapwood region, not only to optimize the process, but also to maximize the efficacy of CCA.

Acknowledgment

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5. Literature

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Figure 1

Schematic Diagram of Wood Sample Preparation

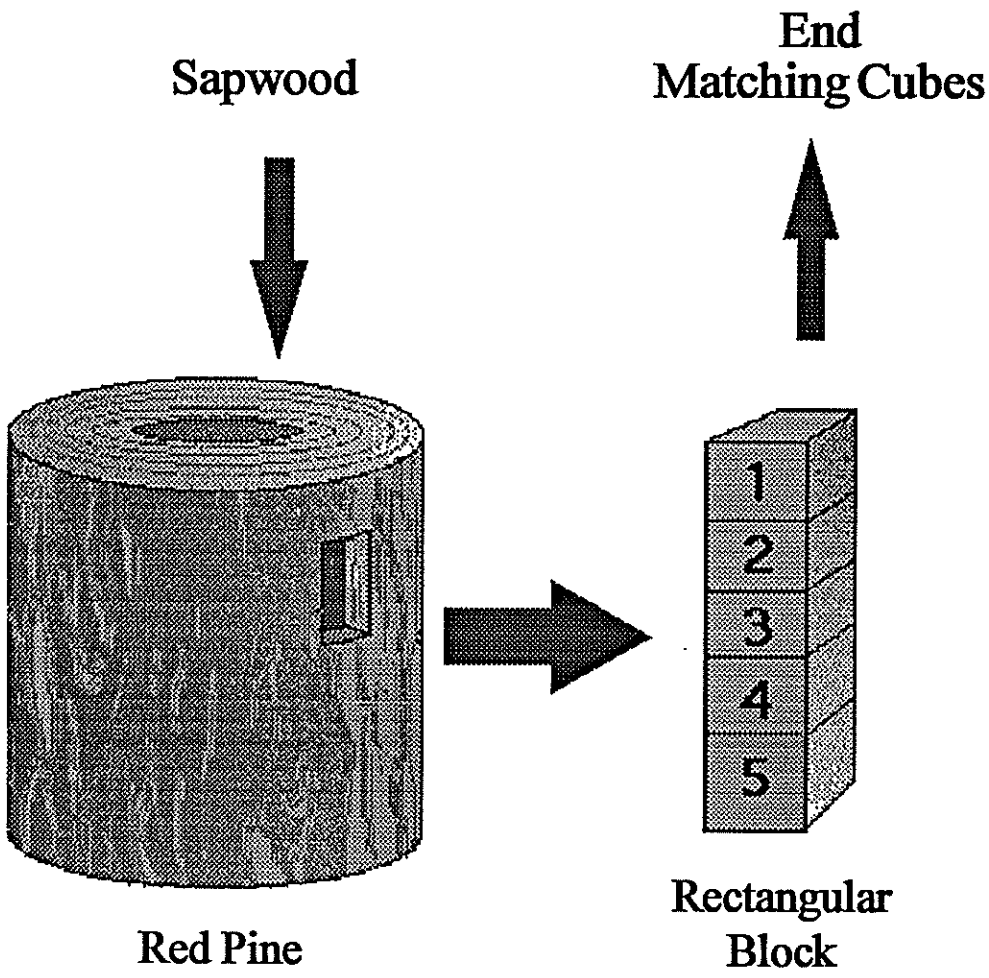
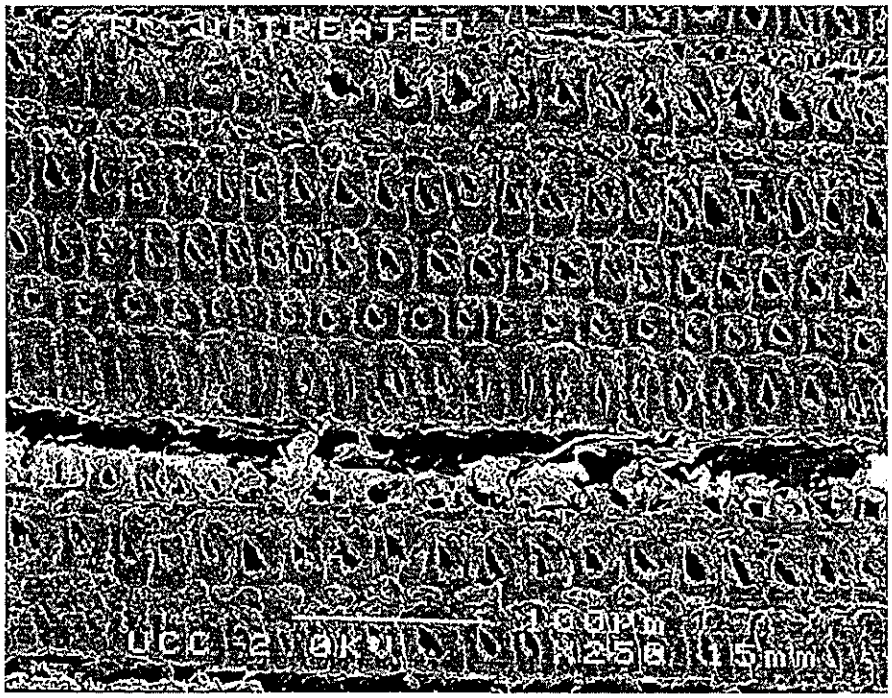


Figure 2
Southern Pine, Untreated, 250X



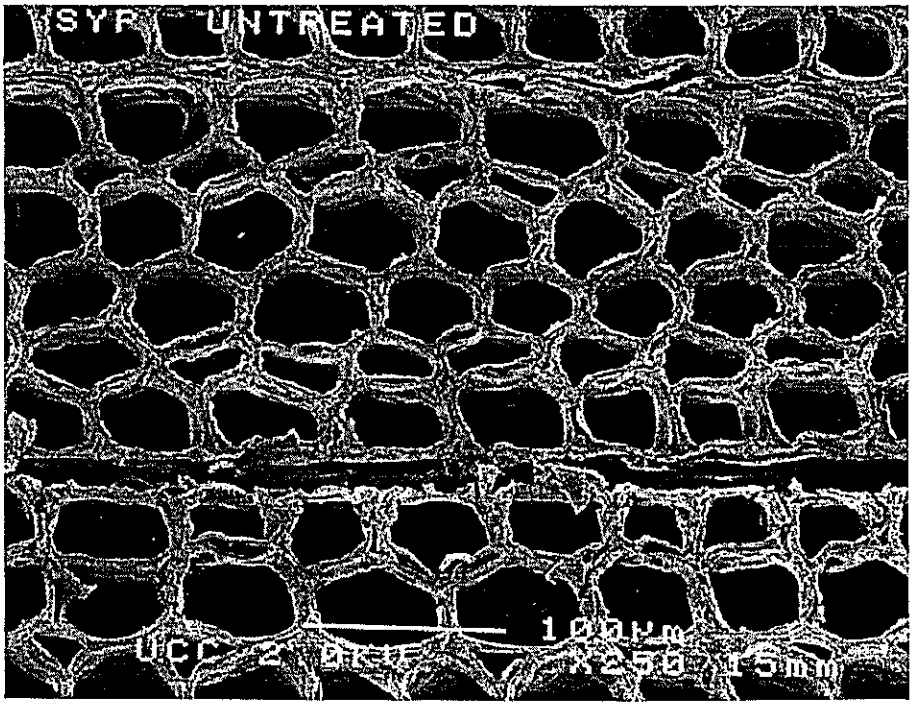
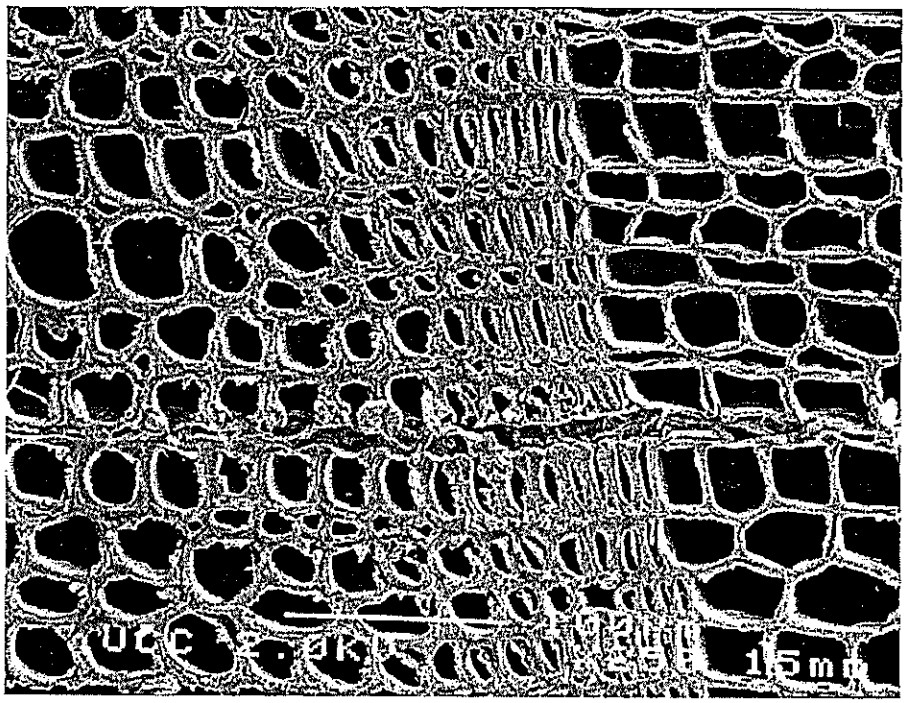


Figure 3
Red Pine, Untreated, 250X



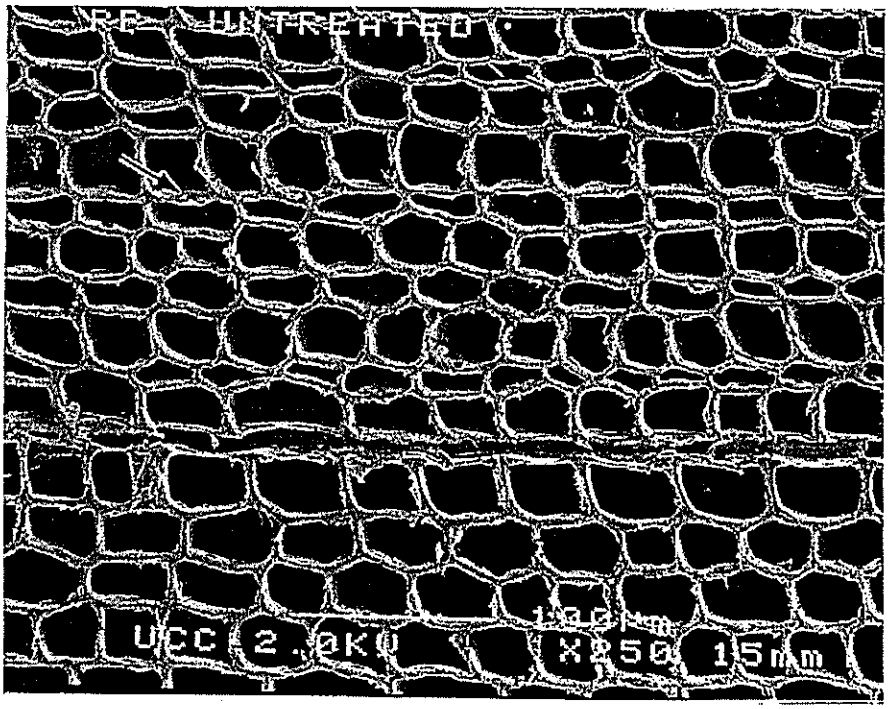


Figure 4
Tracheid Bordered Pit and Lumen Surface of Red Pine

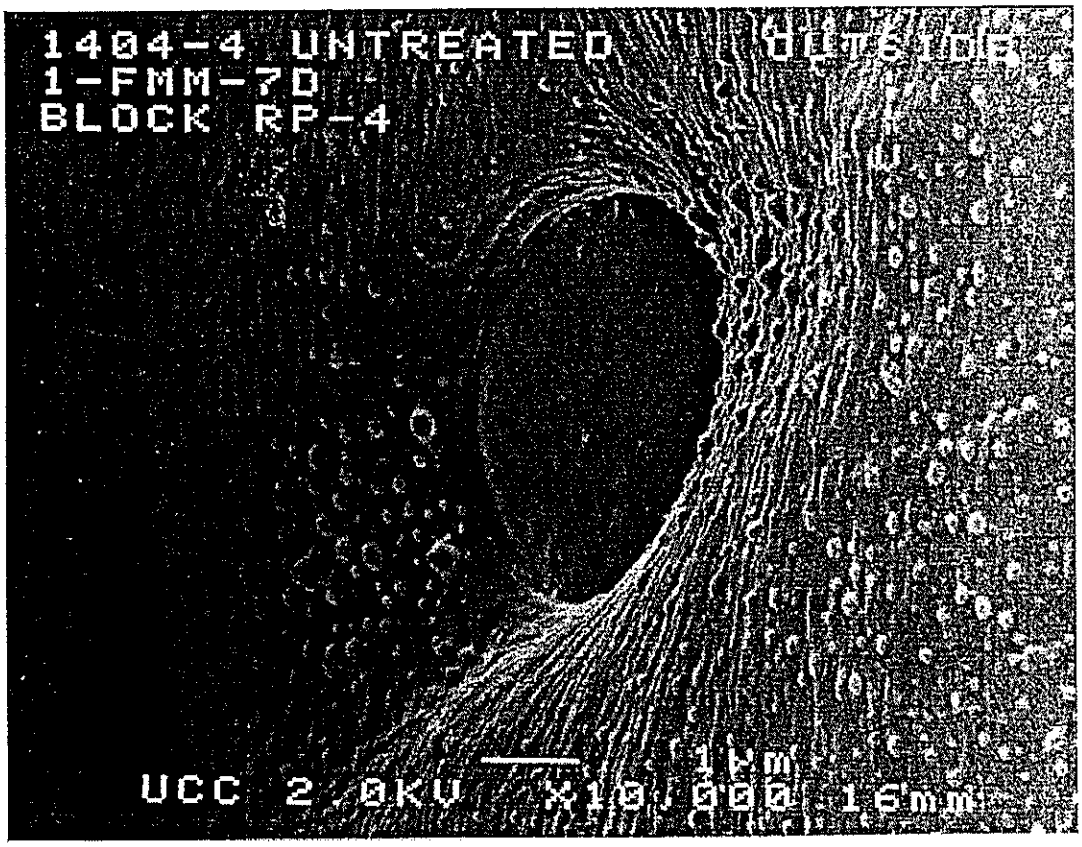
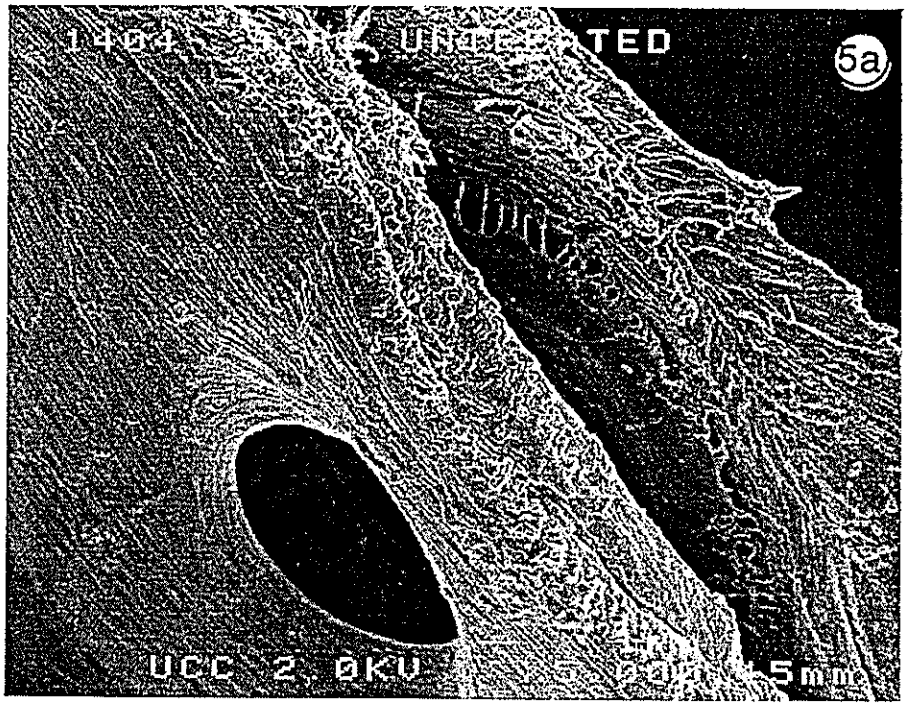


Figure 5A and 5B
Attachment of the Pit Membrane in the Bordered Pits by Microfibrils



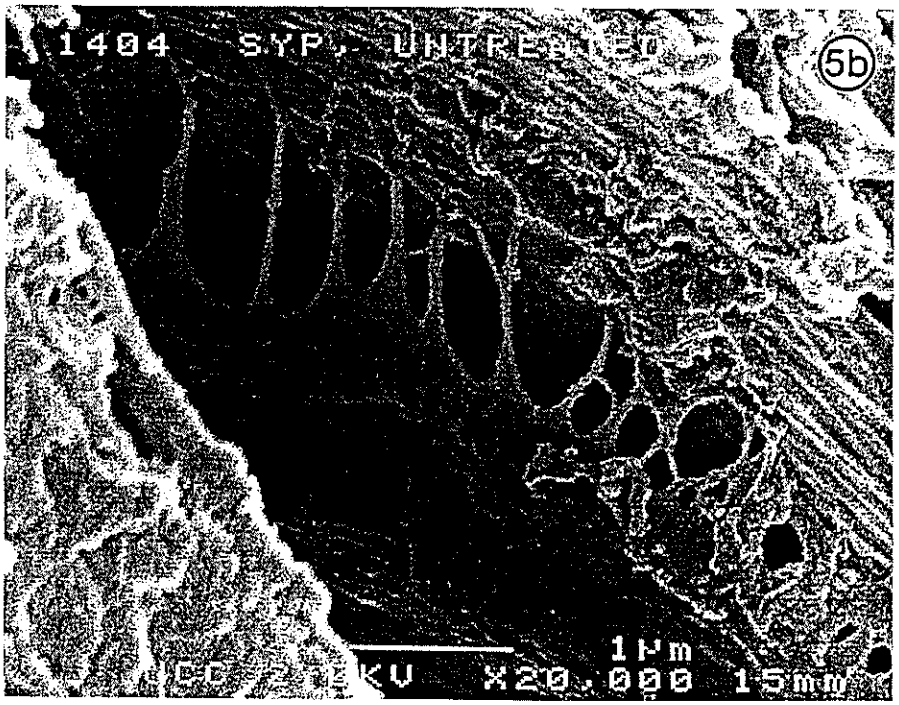


Figure 6
Red Pine, CCA-Only Treated

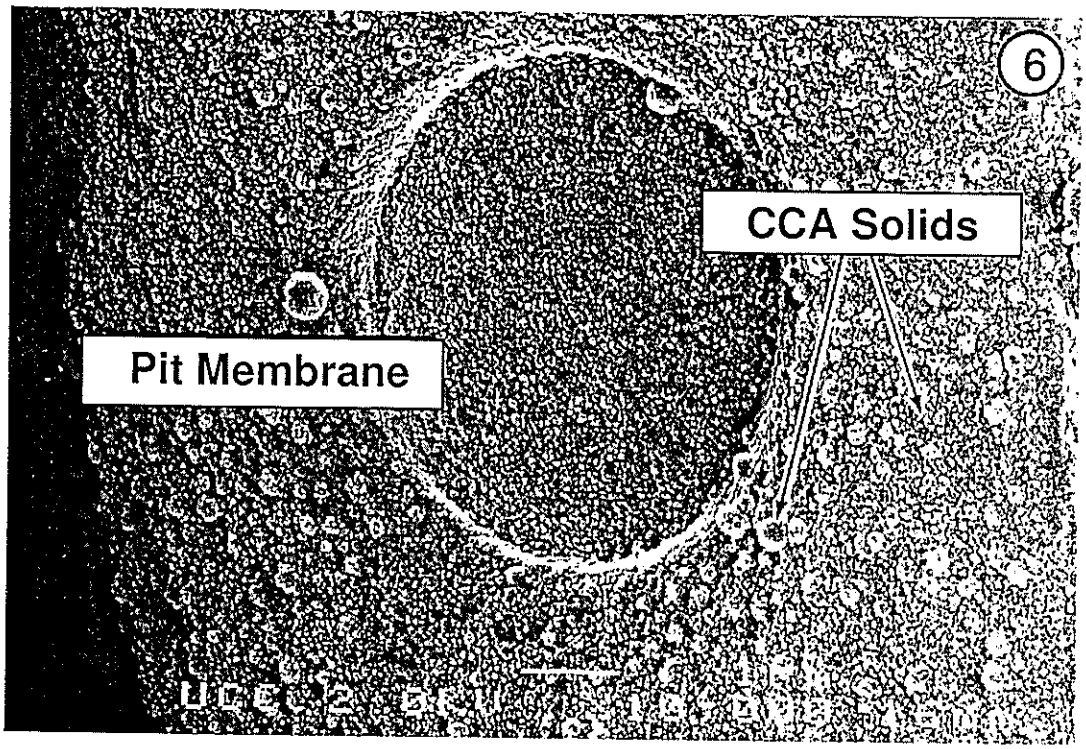


Figure 7

Microdistribution of CCA Metal Ions in Red Pine as Detected by ESEM/EDS

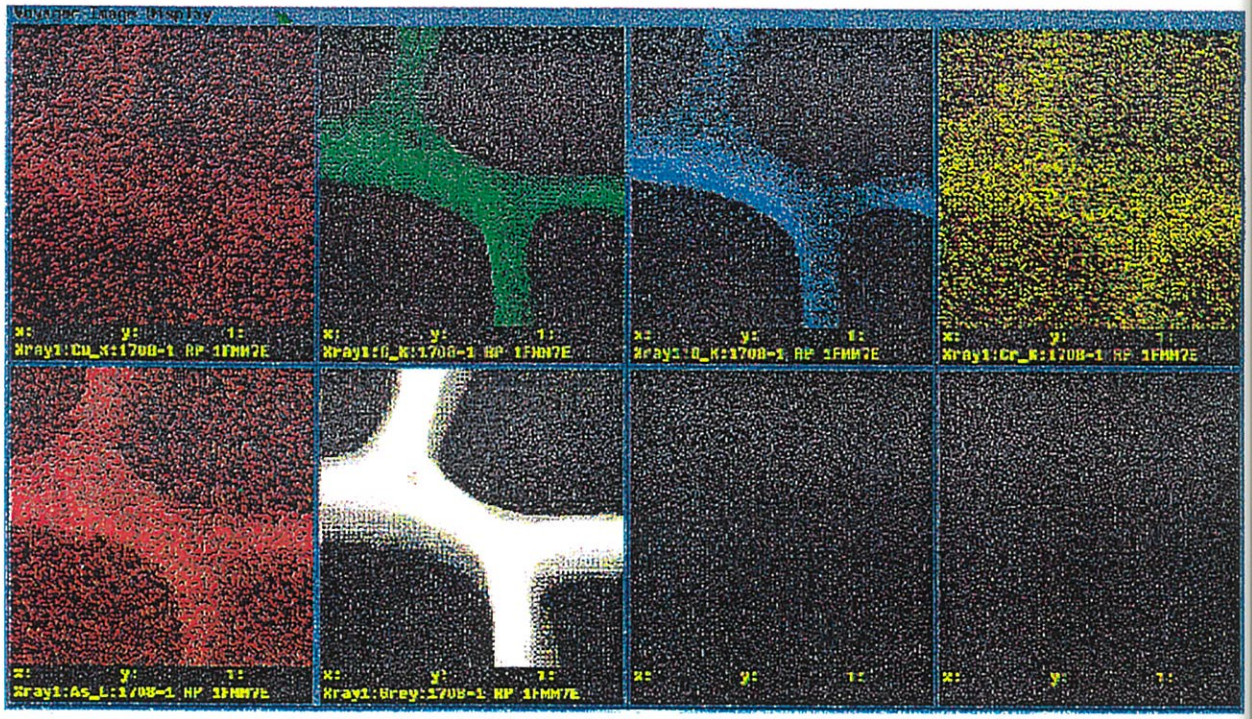
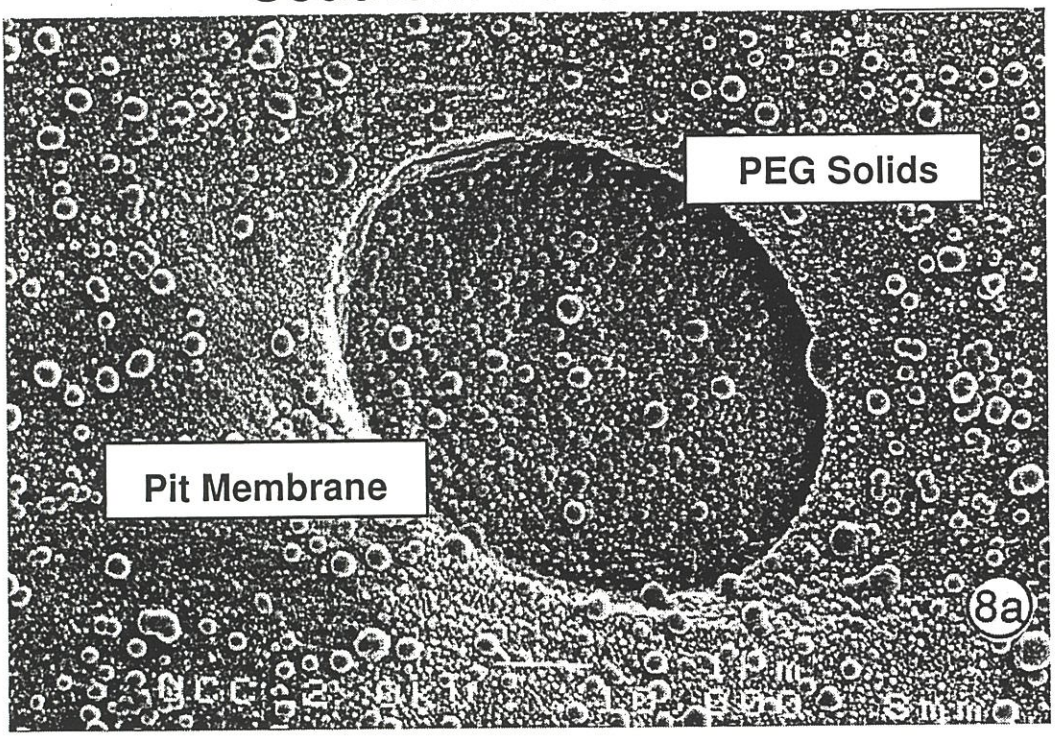


Figure 8A and 8B
Southern Pine and Red Pine, CCA/PEG Treated

Southern Yellow Pine



Red Pine

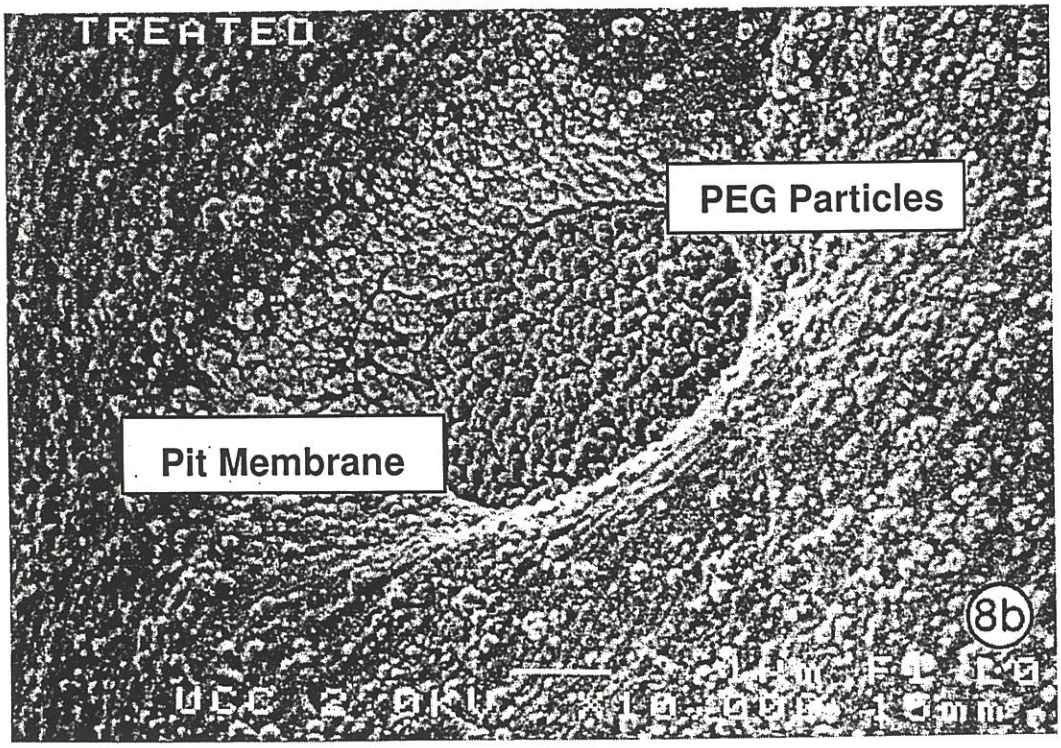
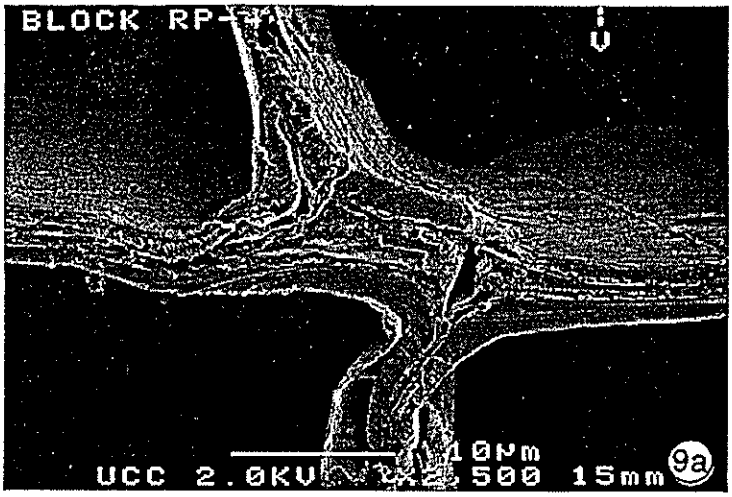
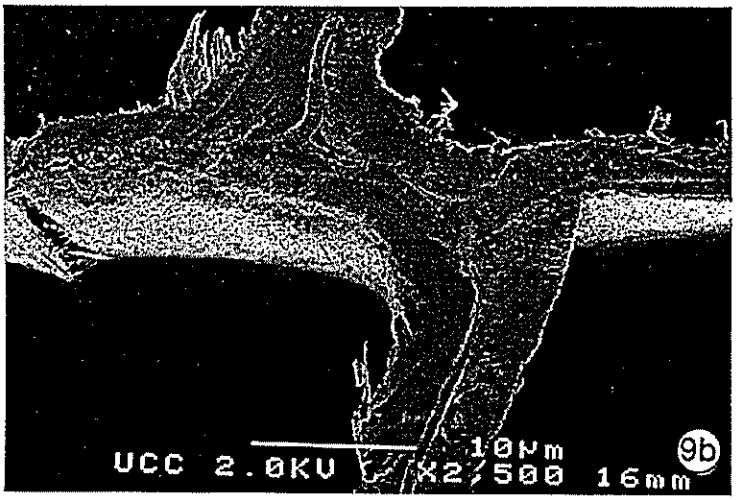


Figure 9A, 9B and 9C
Cross-Sections of
Untreated and Treated Red Pine, 2500x

Red Pine, Untreated



Red Pine, CCA Only



Red PineCCA/PEG

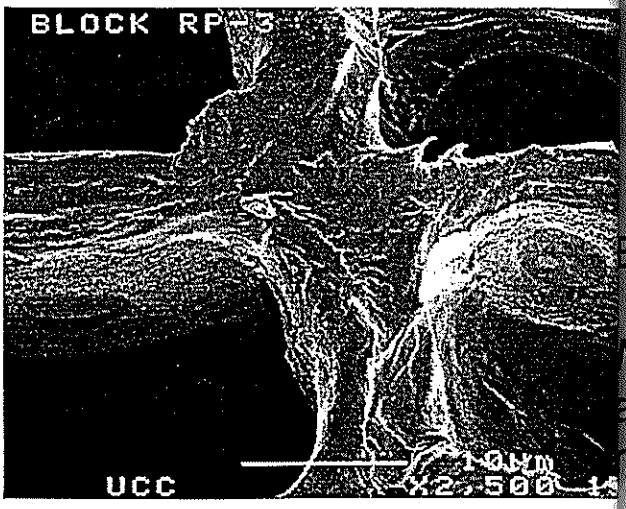
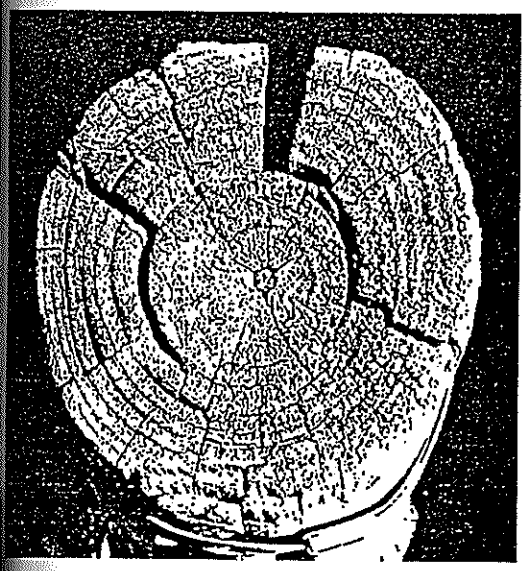


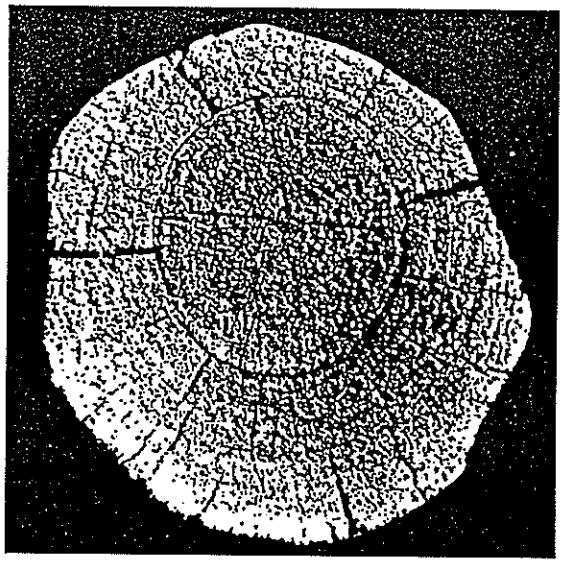
Figure 10

Transmission Poles
Ring Delamination Effect

Pinus radiata, diameter 150mm, retention 16 kg/m^3

Bariska et al., 1988. "Structural Weakening of CCA-Treated Timber", Holzforschung 42 (5), 339-45





Exposed for 3 years in service.

Note: multiple delamination along several of the growth rings.

Exposed for 4 years in the field, from Pienaars River termite testing ground, Transvaal, South Africa.

Note: complete annular delamination along one of the inner growth rings and partial rings and partial annular delamination along other growth rings.

Figure 11
Dimensional Stability of CCA
vs
CCA/PEG PLUS™ Treated Poles

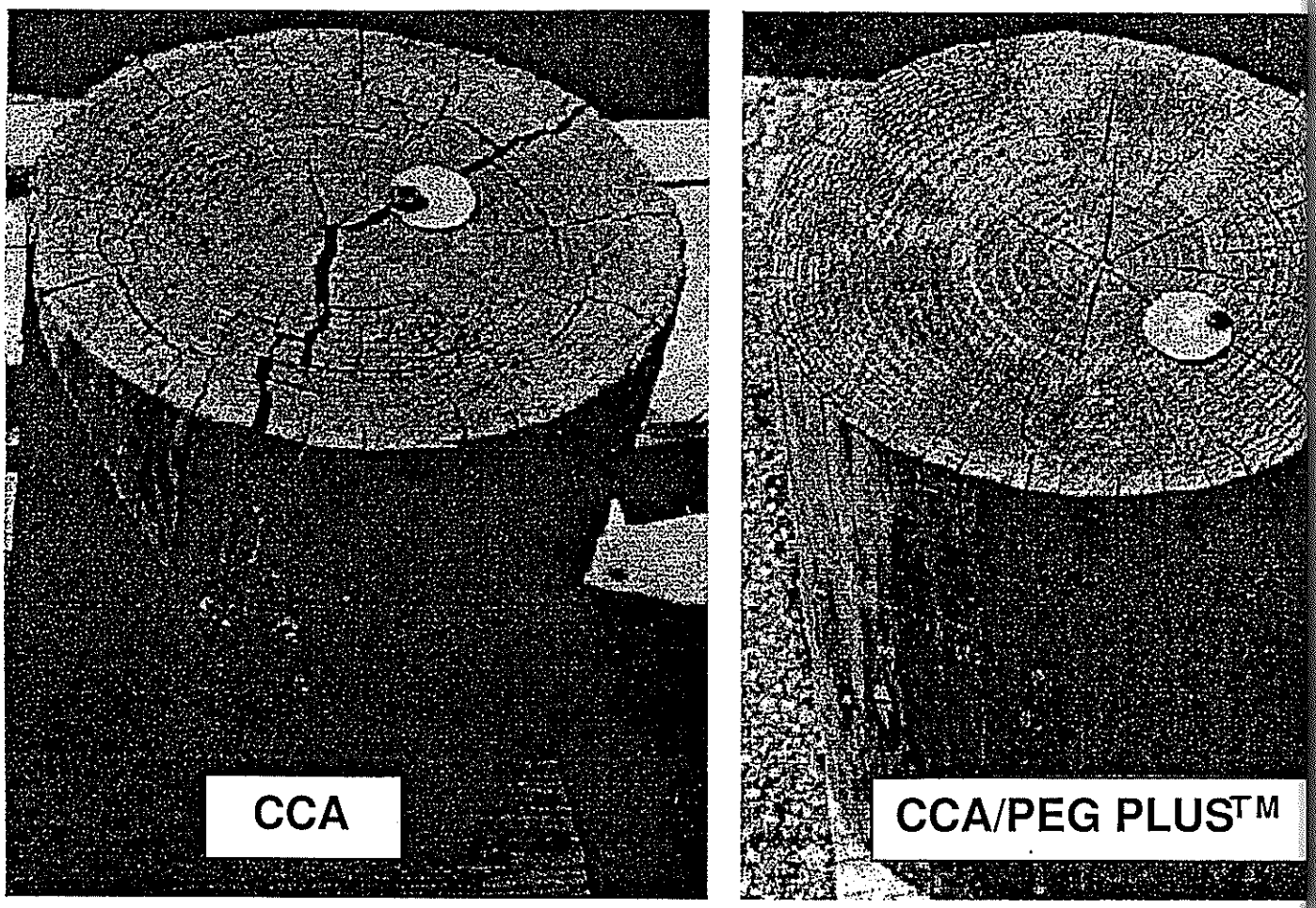


Table 1
EDS Analysis of CCA in Red Pine

Wood Structure	Weight %		
Treatment Type: CCA only	Cr	Cu	As
Late Wood, cross section	42.38	25.02	32.61
Early Wood, cross section	48.17	27.74	24.09
Compound Middle Lamella	38.70	20.09	41.21
Pit Membrane	36.96	31.47	31.57
Overall Average	41.55	26.08	32.37
Treatment: CCA/PEG PLUS	Cr	Cu	As
Late Wood, cross section	45.96	26.41	27.63
Early Wood, cross section	37.07	26.76	36.17
Compound Middle Lamella	37.10	27.37	35.53
Pit Membrane	46.55	22.09	31.36
Overall Average	41.67	25.66	32.67

Table 2
EDS Analysis of CCA in Southern Pine

Wood Structure	Weight %		
Treatment Type: CCA only	Cr	Cu	As
Late Wood, cross section	52.04	31.63	16.33
Early Wood, cross section	45.67	29.81	24.52
Compound Middle Lamella	35.42	25.93	38.65
Pit Membrane	38.39	21.57	40.04
Overall Average	42.88	27.24	29.89
Treatment: CCA/PEG PLUS	Cr	Cu	As
Late Wood, cross section	52.43	30.49	17.08
Early Wood, cross section	43.68	25.27	31.05
Compound Middle Lamella	42.74	23.93	33.33
Pit Membrane	43.27	24.31	32.41
Overall Average	45.53	26.00	28.47
* CCA Solution Composition	40.04	23.72	36.24

Figure 12
Microdistribution of CCA Treated RP

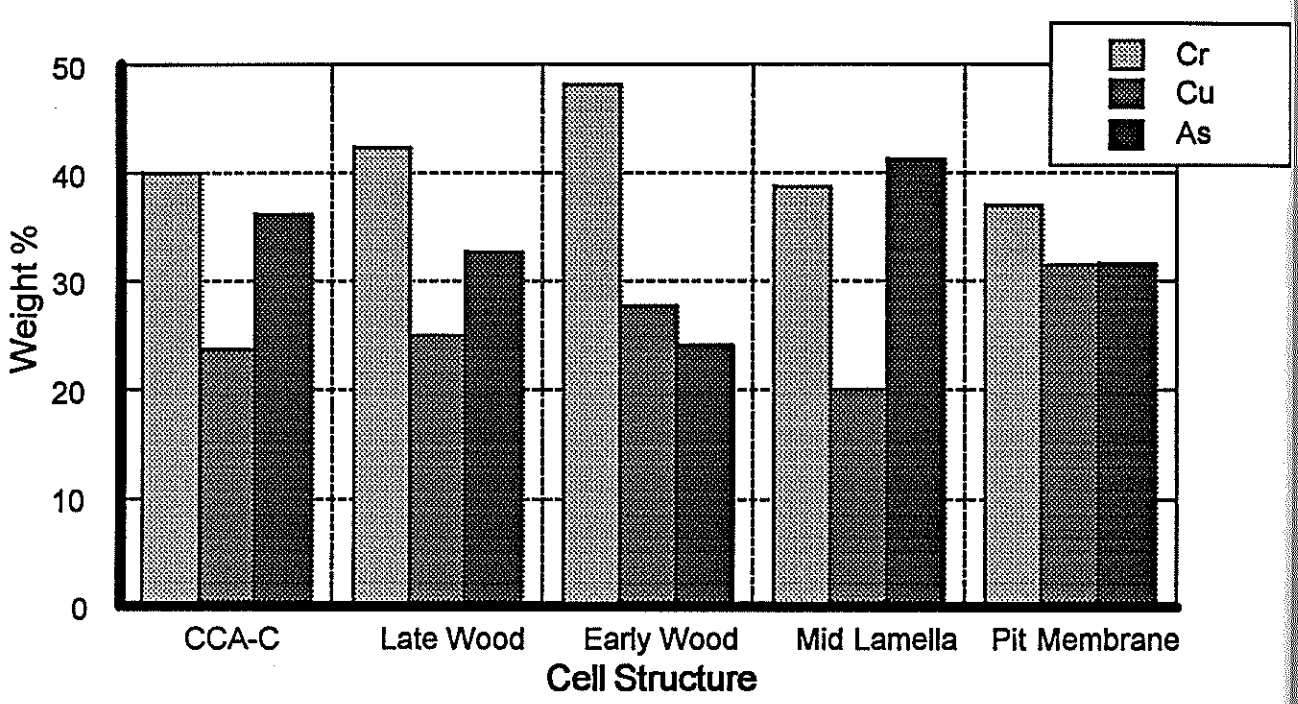


Figure 13
Microdistribution of CCA/PEG Treated RP

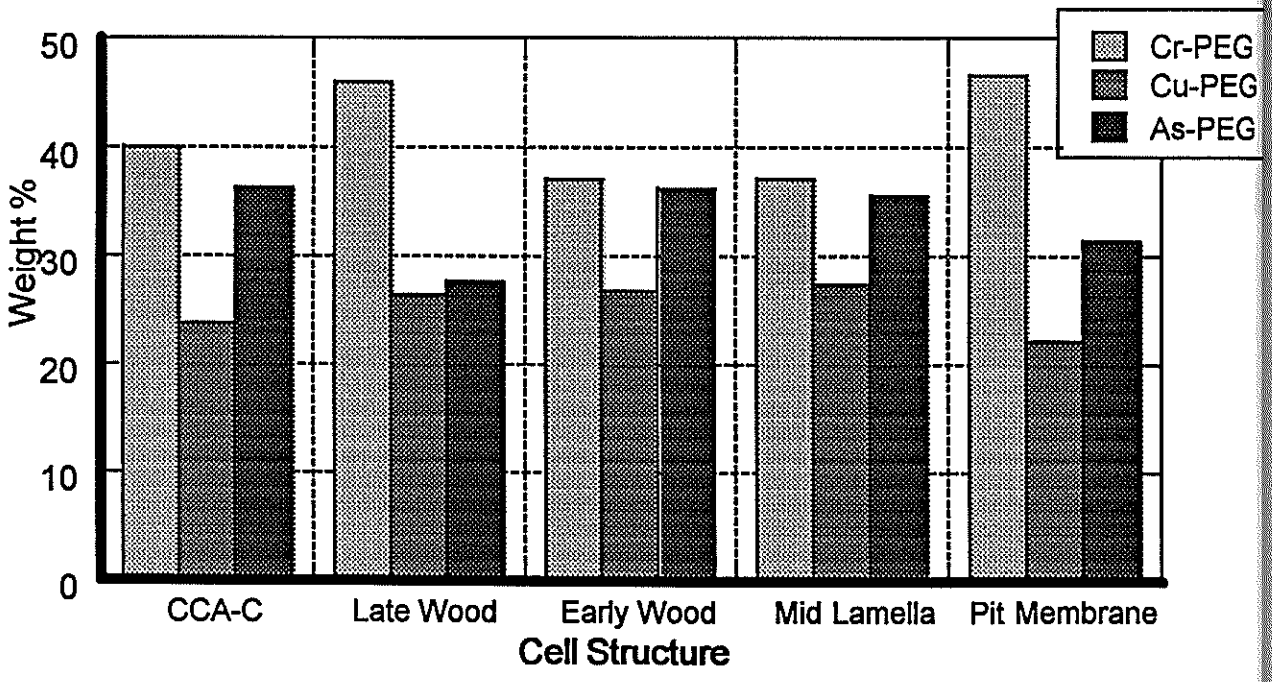


Figure 14
Microdistribution of CCA treated SYP

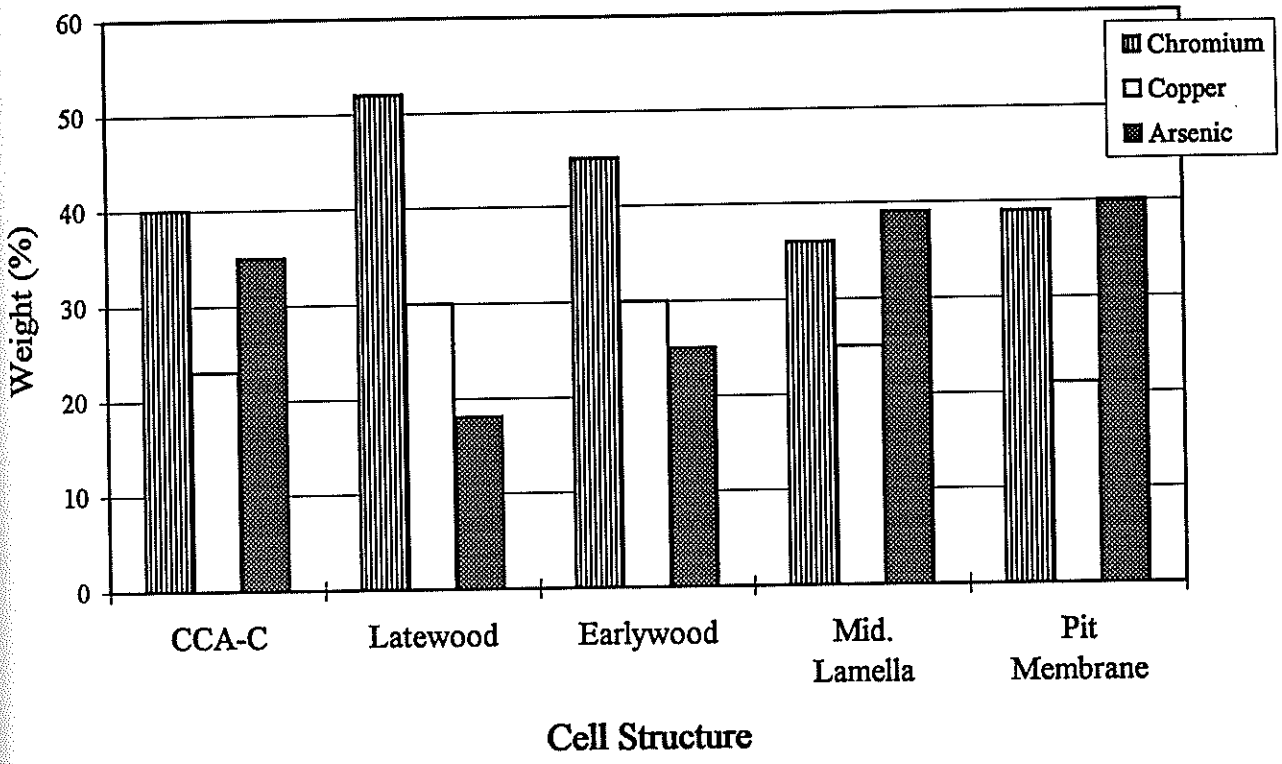


Figure 15
Microdistribution of CCA/PEG treated SYP