INTERACTIONS OF AMMONIACAL COPPER ZINC ARSENATE (ACZA) WITH DOUGLAS-FIR[1]

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ABSTRACT

Tests were conducted to determine the effect of ACZA composition on fixation and the roles of adsorption and precipitation in fixation. The sites of copper and zinc adsorption within the treated wood and the bonding environment of adsorbed copper were also examined. The results generally support the finding that arsenic fixation occurs by precipitation of metal/arsenate complexes. Arsenic leaching was minimized with high solution ratios of metal oxide:arsenic pentoxide, and with formulations containing zinc. Zinc precipitated the majority of arsenic when ammonia was allowed to evaporate from the treating solution. The metal cations were leach-resistant regardless of ACZA formulation because of their low water solubility and their ability to adsorb to the wood. Copper was readily adsorbed by lignin and by model compounds that possessed phenolic hydroxyl groups, which suggests that phenolic hydroxyl groups were the primary reaction sites. Fourier Transform Infrared (FTIR) and Fast Atom Bombardment (FAB) mass spectroscopy analysis also supported this conclusion. Multiple copper species and increased free radical content were detected within lignin that had adsorbed copper. Adsorption of copper and zinc has important ramifications for arsenic fixation.

Keywords: Ammoniacal copper zinc arsenate (ACZA), Douglas-fir, fixation, adsorption, precipitation, leaching.

INTRODUCTION

The use of water-borne wood preservatives to protect poles, pilings, and timbers has increased steadily in recent years because of environmental and economic concerns associated with pentachlorophenol and creosote. Although chromated copper arsenate (CCA) remains the most commonly used water-borne preservative for many applications, ammoniacal copper zinc arsenate (ACZA) is replacing oil-borne preservatives, especially in refractory western species such as Douglas-fir [*Pseudotsuga menziesii* (Mirb.) Franco]. As the use of ACZA increases, the resistance of ACZA to leaching will become more important from both environmental and performance standpoints. Although ACZA has shown excellent performance in service, relatively little research has been done to clarify the mechanisms of copper, zinc, and arsenic stabilization or "fixation" in the wood.

ACZA fixation has generally been assumed to result from precipitation; as the ammonia evaporates from the treated wood, the metals become insoluble and are deposited within the wood structure. Within the treating solution, arsenic probably exists as $H_2AsO_4^-$ or $HAsO_4^{-2}$ (Bodek et al. 1988), while copper and zinc are believed to occur primarily as tetra-ammonia cations, with one to four ammonia groups replacing water to form amine complexes (Hulme 1979). As ammonia evaporates, substitution decreases and the metal ions precipitate. Arsenic is relatively water-soluble and does not precipitate unless it forms insoluble complexes with metal cations. However, there is also evidence that adsorption reactions influence ACZA fixation. Copper undergoes adsorption reactions with wood; zinc and arsenic are also adsorbed, but to a lesser degree (Cooper 1991). Copper adsorption increases with increasing pH, possibly as a result of dissociation and exposure of anions in wood, which can react with copper or zinc amines (Cooper 1991). In addition to limited studies of copper adsorption from amine solutions, there is a wealth of research examining copper adsorption in chromated copper arsenate (CCA) (Eadie and Wallace 1962; Dahlgren 1972; Pizzi 1982; Gray and Dickinson 1988). Under the low pH regimes typical of CCA, uronic acids in hemicelluloses appear to be primary sites for ion exchange (Rennie et al. 1987; Cooper 1991), while wood extractives and lignin become increasingly important exchange sites as pH increases (Pizzi 1982). The sites of copper adsorption from ACZA, however, remain unknown.

Adsorption of copper and zinc may play an important, but poorly understood, role in arsenic fixation (Hulme 1979). Leaching studies indicate that arsenic losses are markedly reduced at metal:arsenic oxide ratios exceeding 2.0, and substitution of zinc for copper further diminishes losses (Rak 1976; Best and Coleman 1981). More recent studies indicate that arsenic precipitation began at approximately 1.1% ammonia, while copper precipitated much more slowly (Lebow and Morrell 1993).

These effects suggest that a portion of the metals, and especially copper, undergo adsorption reactions with the wood and thus are unavailable to precipitate the arsenic.

Environmental concerns associated with wood preservatives are becoming increasingly important. Data on fixation and leach resistance will help regulators and wood treaters to make informed decisions regarding the safety of preservative formulations. In this report, we describe a series of experiments designed to identify potential mechanisms for ACZA fixation in wood.

MATERIALS AND METHODS

Effect of ACZA composition on fixation

The interaction of copper, zinc, and arsenic in ACZA fixation was studied by treating wooden cubes with ACZA components at various ratios, leaching the wood, and comparing the levels of these elements in the leachate to those in the original treating solution. Eighty sapwood and eighty heartwood cubes (1.5 × 1.5 × 1.5 cm) were cut from adjacent sapwood and heartwood zones on each of four Douglas-fir boards. The cubes were conditioned to 10% moisture content (MC) (oven-dry basis). Solutions of ACZA (Table 1) were prepared by adding $Cu(CO_3)_2$, ZnO, or H_3AsO_4 to an ACZA solution containing 50% CuO, 25% ZnO, and 25% As_2O_5 (AWPA 1991). Ammoniacal copper arsenate (ACA) solutions were also prepared with $Cu(CO_3)_2$ and H_3AsO_4 solutions, with NH_4OH and ammonium bicarbonate added according to the American Wood Preservers' Association (AWPA) Standards (1991). Concentrations were determined with an ASOMA 8620 X-ray Fluorescence Analyzer (XRF) and were adjusted to 2.65% (oxide basis).

Eight heartwood and sapwood cubes were treated (0.5 h of 635 mm Hg vacuum, 0.5 h of 862 kP pressure) with each of the 10 solutions, and the treatments were replicated four times. Treated cubes were air-dried for 10 days, and then split into six 0.25-cm-thick wafers. One-third of the wafers from each treatment

group were combined, ground to pass a 30-mesh screen, and analyzed by XRF to determine preservative content. The remaining wafers were agitated in distilled water for 72 h. The leachate was then filtered to remove particulates and analyzed for ACZA components with atomic absorption spectroscopy.

Role of adsorption in fixation

Cellulose, Douglas-fir sapwood, xylan (a polyose model compound), Douglas-fir heartwood, and a high-quality spruce organosolve lignin (Lora et al. 1989) were tested for their ability to adsorb ACZA components. All materials were ground to pass a 60-mesh screen before testing. Five grams of each substrate were combined with 50 g of 1.5% ACZA solution (0.75% CuO, 0.38% ZnO, 0.37% As_2O_5) in 125-ml flasks. The flasks were stoppered, agitated for 0.17, 0.67, 1.5, 20, or 74 h and allowed to settle for 5 min. Twenty grams of preservative solution was decanted, filtered, and analyzed by XRF to determine remaining levels of ACZA components. Concentration differences between original and used solutions were presumed to reflect adsorption to test substrates. Treatments were evaluated in triplicate.

Role of precipitation in fixation

Procedures used were identical to those described above except that the ammonia was allowed to evaporate from the reaction flasks, only lignin, heartwood, and sapwood were tested, and exposure times were 1.5, 20, or 74 h because little evaporation occurred with shorter exposures. Ammonia contents of the original and used solutions were determined with a rapid acid-base titration, where methyl red was added to the ACZA to produce a green color, and then 0.1 N HCL was added until the solution turned red (Jin 1992). The accuracy of this technique was verified with an Alpkem RFA-300 Colormetric Analyzer and Kjeldahl analysis (Fig. 1). Concentration differences between original and used solutions were used to estimate the combined effects of adsorption and precipitation.
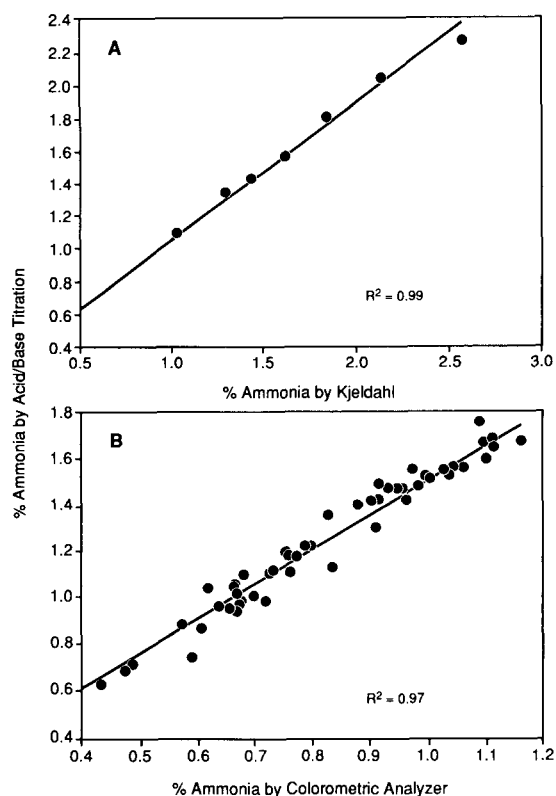

FIG. 1. Correlation between acid/base titration method and (A) Kjeldahl analysis or (B) Alpkem RFA-300 colorometric analysis for determining ammonia content in ACZA.

Adsorption by extractives

Twenty grams of Douglas-fir heartwood flour was refluxed with 300 ml of 2:1 toluene : ethanol in a soxhlet extraction thimble for 6 h. Extracted and unextracted wood flour samples were dried (60 C) for 36 h; then 3.6 g of each sample and 36 g of a 2.2% ACZA solution were weighed (0.01 g) into 125-ml flasks. Three replicates of each substrate were agitated for 1 h and allowed to settle for 30 min. Fifteen grams of ACZA solution was then decanted, filtered through glass fiber filters, and analyzed for ACZA components with XRF spectroscopy. Differences in preservative component concentration between original and used solutions were attributed to adsorption by wood substrates.

Adsorption by lignin model compounds

Two grams of tannic acid, 3,5 dimethoxybenzyl alcohol (DMA), or quercetin and 20–50 grams of 0.91% ACZA solution (0.31% CuO, 0.30% ZnO, 0.31% As$_2$O$_5$) were agitated for 40 min. The proportions of ZnO and As$_2$O$_5$ were increased in this solution to improve XRF quantification of changes in solution ratios after reaction with the lignin model compounds. In addition, 3.65 g of eugenol was agitated in 32.12 g of 1.5% ACZA (0.75% CuO, 0.38% ZnO, 0.38% As$_2$O$_5$) for 3 h. The mixtures were allowed to precipitate for 24 h; then the used ACZA solution was decanted, filtered, and analyzed. Concentration differences between original and used solutions provided estimates of the combined effects of adsorption and precipitation.

FTIR analysis

Initial trials indicated that copper and zinc adsorption did not affect enough bonding sites in ACZA-treated heartwood or lignin to significantly alter the Fourier Transform Infrared (FTIR) spectra. To overcome this problem, FTIR analysis was performed on precipitates produced by ACZA treatment of vanillin, an NH$_4$OH-soluble compound possessing some of the same reactive sites present in lignin.

Two grams of vanillin was agitated for 1 h in 50 ml of 3.8% ACZA, then allowed to settle for 24 h. The resulting precipitate was washed with water (adjusted to pH 9.8 with NH$_4$OH) to remove unreacted preservative. No precipitate formed when control samples containing only vanillin were dissolved in aqueous 5% NH$_4$OH, although the solution turned first yellow then brown. Consequently, the control was obtained by evaporating a vanillin/ammonia solution and analyzing the remaining solids. The precipitates were dried for 48 h (50 C) before spectra were determined on KBr pellets at 4,000–400 cm^{-1} with a Nicolet 5DXB FTIR spectrophotometer.

FAB mass spectroscopy

Tests were performed with vanillin to sim-plify spectral interpretation and insure that a significant proportion of reaction sites were involved in metal adsorption. Fast Atom Bombardment (FAB) solid state mass spectroscopy avoided the unknown effects of dissolving and volatilizing the ACZA/vanillin substrate. Vanillin as solid, vanillin dissolved in dilute NH$_4$OH (5% ammonia), a 3.8% ACZA solution, and precipitates formed when vanillin was mixed with 3.8% ACZA, were suspended in glycerol on the end of a probe, inserted into a Kratos MS-50 Mass Spectrophotometer and bombarded with high-energy xenon atoms to produce ions for mass analysis.

Bonding environment of copper

Earlier sections have examined fixation mechanisms on the basis of the effect of metal adsorption reactions on a treated substrate. Another approach is to use techniques such as electron paramagnetic resonance spectroscopy (EPR) to examine the bonding environment of the metal itself. Because copper atoms in a solid cannot rotate freely about all axes, absorption corresponding to both parallel and perpendicular orientation of the magnetic field to the rotational axis of the atom is observed. The absorption proportionality constant (g-value) for copper in the parallel section of the spectrum typically varies between 2.08–2.42, and that in the perpendicular part of the spectrum between 2.04–2.06, depending on the molecular environment (Plackett et al. 1987).

Spruce lignin, which appeared to readily adsorb copper, was treated with dilute NH$_4$OH, ACZA, or a solution of CuO in dilute NH$_4$OH. For the ACZA treatment, 7.97 g of lignin and 85.3 g of 0.008% ACZA (0.004% CuO, 0.002% ZnO, and 0.002% As$_2$O$_5$) were agitated for 15 min in a 125-ml flask, then allowed to precipitate for 5 min. Similarly, 8.12 or 8.11 g of lignin were agitated with 81.30 g of 0.004% CuO or 81.02 g of 0.25% ammonia (from NH$_4$OH), respectively. The precipitates were washed five times with 50 ml of distilled water (adjusted to pH = 9.8 with NH$_4$OH) to maximize the proportion of adsorbed copper.

The reacted lignin was stored in plastic bags

for 24 h to retard drying and to simulate conditions in treated wood, then air-dried for 5 days, and analyzed with XRF techniques for ACZA components. The ACZA-treated lignin contained approximately 0.04% CuO, 0.03% ZnO, and no detectable arsenic; the CuO-treated lignin contained 0.05% CuO. A Varian EPR Spectrometer was used for EPR analysis.

Data analysis

Where appropriate, data generated by the various experiments were subjected to an Analysis of Variance, and mean separation procedures were performed with Duncan's Multiple Range Test at $\alpha < 0.05$ (Steel and Torrie 1980).

RESULTS AND DISCUSSION

Effect of ACZA composition on fixation

Copper and zinc were leach-resistant regardless of formulation, but arsenic loss was strongly influenced by formulation (Figs. 2 and 3). Our results concur with previous leaching studies of ACZA (Rak 1976; Best and Coleman 1981). The leach resistance of copper and zinc reflects reactions with wood components and the low water solubility of these metals.

The percentage of arsenic leached ranged from over 60% to near zero, depending on the cation : anion ratio, the type of cation, and whether sapwood or heartwood was treated (Figs. 2 and 3). Arsenic leaching was virtually eliminated from sapwood treated with solutions containing zinc when the metal oxide : arsenic pentoxide ratio exceeded 1.5:1. Arsenic losses from heartwood samples, however, were not minimized until the cation : anion ratio exceeded 2:1. These findings generally agree with previous studies of ACZA leaching from spruce (Rak 1976).

Solutions that contained copper as the sole cation were less effective in fixing arsenic, especially with heartwood, where 15% of the arsenic leached at a 2:1 $CuO:As_2O_5$ ratio. Arsenic leaching from sapwood was also minimized at higher copper levels within solutions without zinc, but fixation was consid-
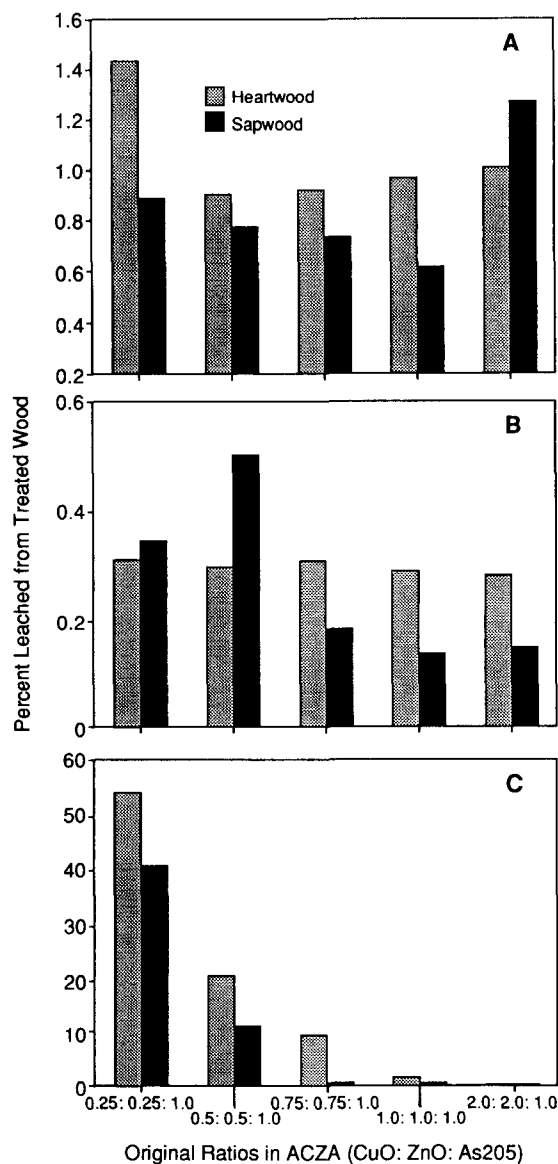
Fig. 2. Percentage of (A) copper, (B) zinc, or (C) arsenic leached from Douglas-fir heartwood and sapwood following treatment with ACZA solutions of varying component ratios.

erably better in the presence of zinc. Other researchers have suggested that the availability of copper to complex with arsenic may be reduced by competitive adsorption reactions with wood (Hulme 1979). Arsenic leaching from heartwood was higher than from sapwood for
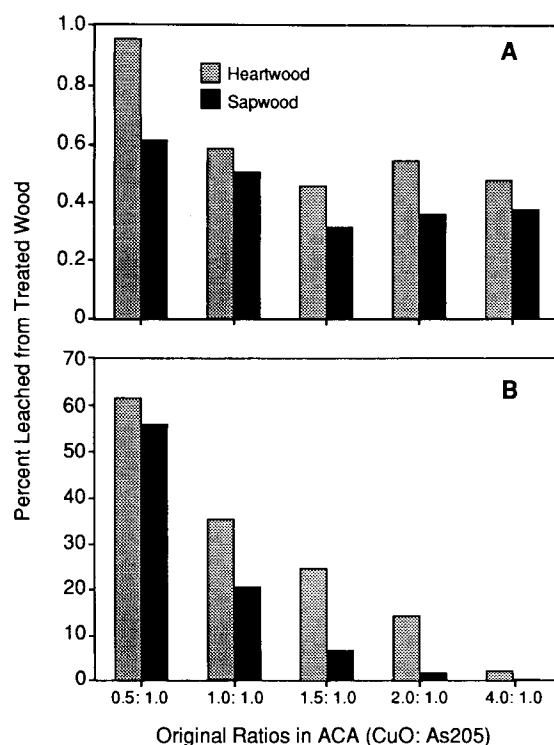
FIG. 3. Percentage of (A) copper or (B) arsenic leached from Douglas-fir heartwood and sapwood treated with ACA solutions of varying component ratios.

TABLE 1. *Effect of ACZA formulation on leaching of arsenic from Douglas-fir heartwood or sapwood.*

Solution ratios	Average % leached[a]	
$CuO : ZnO : As_2O_5$	Heartwood	Sapwood
2.00:2.00:1.00	0.16 a	0.13 a
1.00:1.00:1.00	1.09 ab	0.12 a*
0.75:0.75:1.00	8.36 bc	0.31 a*
0.50:0.50:1.00	20.20 de	10.56 a*
0.25:0.25:1.00	54.13 g	40.58 c*
4.00:0:1.00	2.26 ab	0.12 a*
2.00:0:1.00	14.84 cd	1.51 a*
1.50:0:1.00	24.63 e	6.66 a*
1.00:0:1.00	35.22 f	20.76 b*
0.50:0:1.00	61.51 h	56.21 d

[a] Values in a given column followed by the same letter are not significantly different with Duncan's Multiple Range Test at $\alpha = 0.05$.

[b] Values followed by an asterisk are significantly different from those in heartwood with Duncan's Multiple Range Test at $\alpha = 0.05$.

all formulations tested, although these differences were significant in only eight treatments (Table 1). Increased arsenic leaching from heartwood may also reflect competitive adsorption reactions that reduced copper availability because heartwood adsorbed copper from the treating solutions more readily than did sapwood.

Role of adsorption in fixation

Although ACZA fixation is believed to be primarily a precipitation process (Nicholas 1973), ours and previous reports (Cooper 1991) suggest that copper adsorbs to wood substrates. This test, which did not account for the effects of ammonia evaporation, was designed to determine which wood components participated in adsorption of ACZA components.

Substantial quantities of copper and lesser amounts of zinc were adsorbed onto some substrates (Fig. 4). Lignin, in particular, adsorbed significantly more copper and zinc than other substrates (Table 2). Heartwood also adsorbed more copper than other substrates, but adsorbed less zinc. In contrast, xylan and sapwood adsorbed significantly more zinc than did heartwood, which suggests that copper and zinc do not always compete for similar reaction sites.

The high affinity of copper for lignin suggests that phenolic groups are primary reaction sites, a possibility also suggested by the increased heartwood reactivity relative to sapwood. Heartwood contains phenolic extractives, and the cell walls are coated with lignin-like phenolic incrustations (Krahmer and Côté 1963).

Low cellulose reactivity may reflect intramolecular hydrogen bonding, which decreases hydroxyl-group availability relative to the more branched xylan structure. The uronic acid groups in xylan may have also provided reactive sites, however, since copper is reportedly adsorbed by carboxylic acid groups in plant materials (Bayley and Rose 1960; Knight et al. 1961). Copper adsorption was rapid; the majority of copper was withdrawn from solution after only 0.17 h, and no significant increases occurred over time except with lignin. Rapid copper adsorption from ACZA and CCA
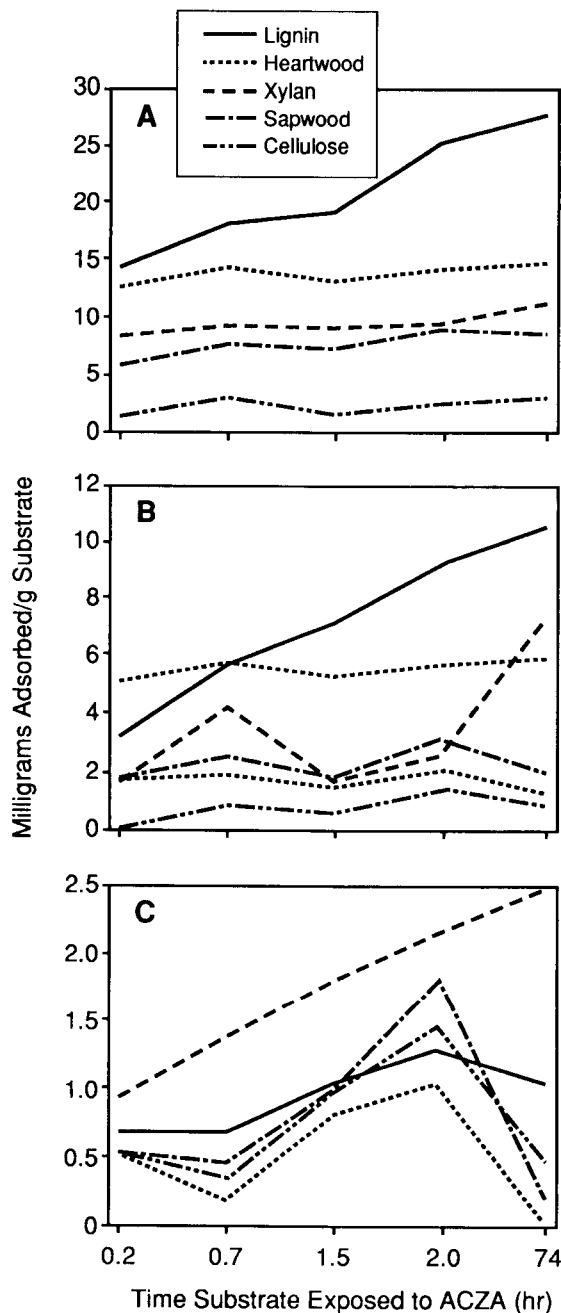
FIG. 4. Adsorption of (A) copper, (B) zinc, or (C) arsenic from a 1.51% ACZA solution by heartwood, sapwood, lignin, cellulose, and xylan.

TABLE 2. *Effect of wood component and exposure time on adsorption of copper, zinc, and arsenic from a 1.51% ACZA solution.*

Substrate	Average adsorption[a] (mg/g substrate)				
	0.17 h	0.67 h	1.5 h	20 h	74 h
Copper					
Cellulose	1.1 a	2.6 a	1.1 a	1.9 a	2.5 a
Sapwood	5.6 b	7.6 b	7.0 b	8.6 b	8.2 b
Xylan	8.4 c	9.2 c	8.9 b	9.2 b	11.0 bc
Heartwood	12.8 d	14.4 d	13.0 c	13.9 c	14.5 c
Lignin	14.5 d	18.2 d	19.1 d	25.1 d	27.7 d
Zinc					
Cellulose	0.0 a	0.7 a	0.5 a	1.3 a	0.7 a
Sapwood	1.9 b	2.5 b	1.7 b	3.1 b	1.8 b
Xylan	1.7 b	4.2 c	1.6 c	2.5 bc	7.5 b
Heartwood	1.7 b	1.9 b	1.4 b	2.0 ab	1.1 a
Lignin	3.3 c	5.8 d	7.3 c	9.4 c	10.7 c
Arsenic					
Cellulose	0.5 b	0.4 a	1.0 a	1.5 ab	0.5 a
Sapwood	0.5 a	0.5 a	1.0 a	1.8 ab	0.2 a
Xylan	1.0 a	1.4 b	1.8 b	2.2 b	2.5 b
Heartwood	0.5 a	0.2 a	0.8 a	1.1 a	0.0 a
Lignin	0.7 a	0.7 a	1.1 a	1.3 a	1.1 ab

[a] For each element, values followed by the same letter are not significantly different with Duncan's Multiple Range Test at $\alpha = 0.05$.

has been attributed to cation exchange reactions (Dahlgren 1972; Pizzi 1982; Cooper 1991). Although zinc also undergoes similar reactions, it has a lower charge density and ionization potential than copper, and so may be adsorbed less readily by the wood (Cooper 1991).

In contrast to copper, little arsenic was adsorbed by the wood substrates, although arsenic adsorption by xylan was significantly higher than by other substrates, except after 74 h (Table 2). Low arsenic adsorption conflicts with previous research where arsenic adsorption by pine and aspen sawdust exceeded zinc adsorption (Cooper 1991). Arsenic adsorption has been attributed to the reaction of arsenic with copper bonded to the wood by ion exchange reactions (Cooper 1991), an effect not noted in the current study.

Role of precipitation in fixation

The adsorption study was extended to examine the effect of ammonia evaporation on adsorption and precipitation of ACZA com-

ponents. The open-flask results of this test are best understood in comparison to those of the closed-flask study described above, in which the ammonia was not allowed to evaporate. In general, copper was less sensitive to solution ammonia content than was zinc; no significant copper loss was detected. In addition, zinc precipitation appeared to be closely associated with arsenic precipitation (Fig. 5). Since relatively little ammonia was lost after 90 min and precipitation was insignificant, the amount of copper, zinc, and arsenic lost from solution was primarily attributed to adsorption. Accordingly, results after 90 min compare closely to those in the closed-flask study. However, after 20 and 74 h, zinc and arsenic losses from the open solutions became more noticeable

(Table 3). Zinc and arsenic losses from open solutions after 74 h of aeration were significantly higher than those from closed solutions for all substrates, which suggests that ammonia loss caused zinc precipitation. Arsenic, which is not dependent on ammonia for solubility, was lost in direct proportion to zinc, which suggests the formation of zinc arsenate complexes such as $Zn_2AS_2O_7$, with a 1:1 zinc:arsenic ratio, or the more common ortho zinc arsenate, $Zn_3(AsO_4)_2$, with a 3:2 zinc:arsenic ratio (Farnsworth and Kline 1973). Consistent differences between zinc and arsenic losses from solution reflect adsorption of zinc, especially by lignin. Copper losses agree closely with the above results (Fig. 4) where the losses were confined to adsorption, which suggests that ammonia evaporation caused little precipitation. This finding implies that zinc is primarily responsible for the "fixation" of arsenic in ACZA, and it supports earlier results in which the replacement of a portion of copper with zinc reduced arsenic leaching (Fig. 2). Increased copper stability relative to zinc in ACZA solutions is in accordance with the metal amine dissociation constants of copper and zinc (Dean 1985).
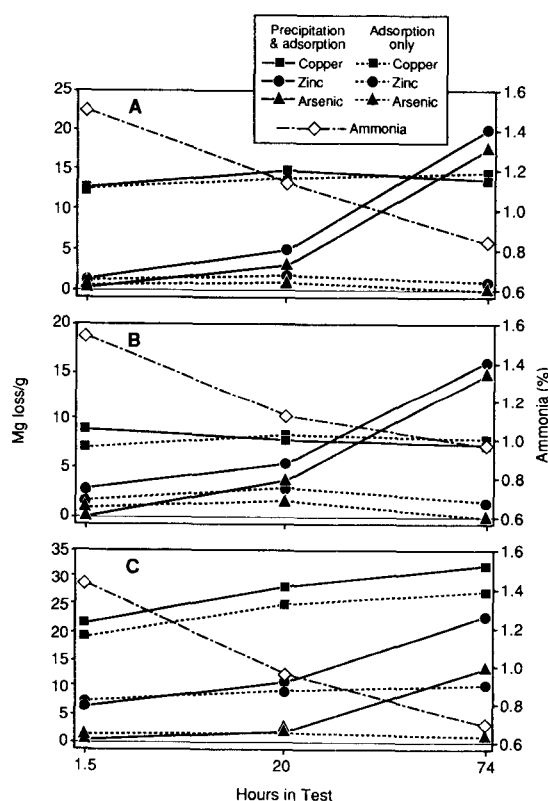

FIG. 5. Adsorption or combined precipitation and adsorption of copper, zinc, and arsenic from an ACZA solution in the presence of (A) heartwood, (B) sapwood, or (C) lignin over a 74-h period at 23–25 C.

TABLE 3. Amounts of zinc and arsenic lost from ACZA solutions exposed to wood components in open or closed systems for 20 or 74 hours.[a][b]

	Loss of ACZA component (mg/g substrate)			
	Zinc			
	20 h		74 h	
Component	Open	Closed	Open	Closed
Heartwood	5.2	2.0	20.2	1.1*
Sapwood	5.5	3.1	16.4	1.8*
Lignin	11.0	9.3	23.5	10.7*
	Arsenic			
	20 h		74 h	
Component	Open	Closed	Open	Closed
Heartwood	3.3	1.1	12.6	0.0*
Sapwood	3.7	1.8	15.0	0.24*
Lignin	1.8	1.3	13.8	1.06*

[a] Values represent the means of 3 samples. Closed system values followed by an asterisk are significantly different from corresponding open system values by Duncan's Multiple Range Test at $\alpha = 0.05$.

[b] No precipitation was detected for copper at any time period, or for arsenic or zinc after 90 min.

TABLE 4. *ACZA component adsorption by solvent extracted and unextracted Douglas-fir heartwood powder.*

Treatment	mg adsorbed from solution/gram wood		
	Cu	Zn	As
Unextracted	18.6	1.8	−0.8
Extracted	15.1	0.5	−0.8

Adsorption by extractives

High copper adsorption by heartwood (Table 2) suggests that phenolic extractives may provide reactive sites for copper. In this test, the ACZA adsorption capabilities of unextracted Douglas-fir heartwood were compared to extractive-free heartwood.

Toluene and ethanol extraction caused slight decreases in copper adsorption; the difference was significant at the 90th percentile (Table 4). Copper has been reported to bond with phenolic hydroxyl groups, coordinating with one to three polyflavanoid tannins (Pizzi et al. 1986). The decreased copper adsorption in extracted heartwood, however, does not appear to account for the entire difference in copper adsorption between heartwood and sapwood (Table 2). It is probable that the buildup of insoluble phenolic incrustations coating the heartwood cell walls also increased copper adsorption. Zinc adsorption by extracted wood was also significantly lower (90th percentile) than by unextracted wood (Table 4). Arsenic adsorption from the solutions appeared to be negative for both types of samples, suggesting that solvent was adsorbed by the wood more readily than arsenic.

Adsorption by lignin model compounds

Earlier tests demonstrated that lignin strong-

ly adsorbed copper (Table 2). Further adsorption tests with lignin model compounds were conducted to help identify the reaction sites involved. These results were strongly influenced by substrate solubility in the preservative solution since soluble-adsorbed preservative components were not detected. Although incomplete precipitation may result in underestimates of adsorption, lignin model compounds, with the exception of DMA, adsorbed over 60% of the copper and some zinc from the ACZA solutions (Table 5). In contrast, little copper adsorption occurred with DMA, suggesting that the phenolic hydroxyls were much more reactive than the methoxyl groups. However, the reactivity of DMA may have been lower because none of the reactive sites was adjacent to the aromatic ring.

FTIR analysis

FTIR was employed to clarify the reactive sites involved in the adsorption of ACZA components. Adsorption bands of functional groups in a lignin model compound, vanillin, were evaluated before and after ACZA treatment.

Spectra of ammonia-treated vanillin were significantly altered by the addition of ACZA components (Fig. 6). Although the spectra were complex and difficult to interpret, vanillin bands that were shifted or reduced by ACZA treatment provided insights into the functional groups involved in metal adsorption.

The broad peak in the 3,500–2,500 cm^{-1} region, attributed to oxygen-hydrogen stretching (Harrington et al. 1964; Sarkanen and Ludwig 1971), was significantly altered, revealing previously hidden or small shoulder peaks. These peaks probably reflect C-H stretching

TABLE 5. *Adsorption of ACZA components in solutions containing selected lignin model compounds and 0.91 or 1.5% ACZA.*

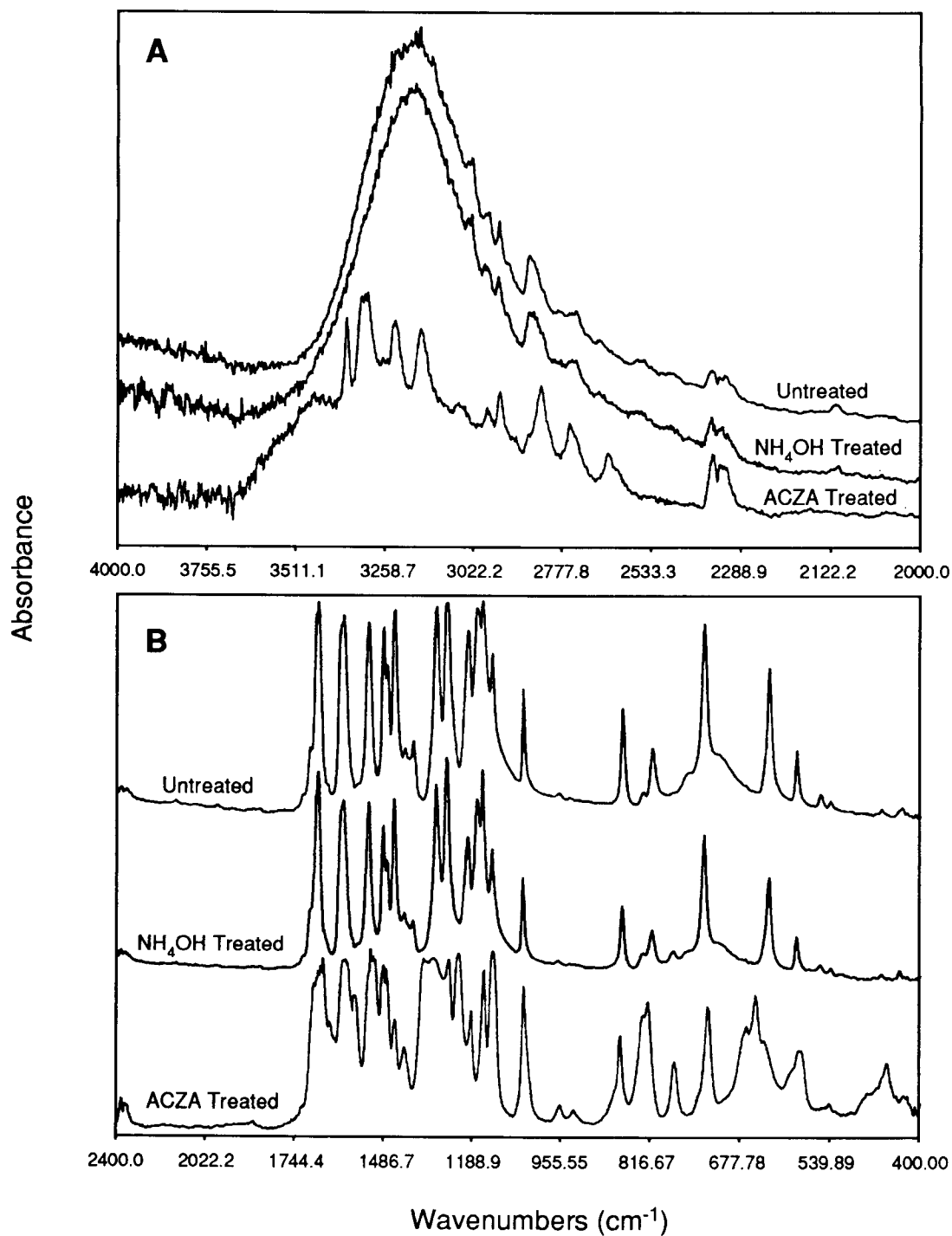| Compound	Chemical levels in original solution (%)			Chemical levels in reacted solution (%)		
	CuO	ZnO	As$_2$O$_5$	CuO	ZnO	As$_2$O$_5$
Tannic acid	0.305	0.303	0.310	0.026	0.020	0.303
Quercetin	0.305	0.303	0.310	0.029	0.097	0.319
3,5 dimethoxybenzyl alcohol	0.305	0.303	0.310	0.302	0.304	0.308
Eugenol	0.759	0.378	0.356	0.325	0.235	0.347

FIG. 6. FTIR spectra of untreated vanillin and vanillin after ammonia or ACZA treatment for (A) 4,000–2,000 cm⁻¹ or (B) 2,500–400 cm⁻¹.

vibrations, although they may be due to water or ammonia bands if metals were adsorbed while still complexed to these components. Disappearance of the 1,370 and 1,173 cm^{-1} peaks assigned to phenolic hydroxyls (Sarkanen et al. 1967a), provides further evidence that hydroxyl groups are major adsorption sites. In addition, the peak at 1,203 cm^{-1}, probably due to O-H bending frequency (Sarkanen et al. 1967a), was substantially reduced.

Conversely, there was less evidence that the methoxyl-methyl group was displaced during metal adsorption. The band associated with aromatic C-O stretching, 1,610–1,590 cm^{-1} (Sarkanen and Ludwig 1971) appeared to shift to a slightly lower frequency; but the 1,470–1,460 cm^{-1} band, associated with C-H deformation in methyl groups (Sarkanen and Ludwig 1971), was affected very little.

Several peaks appear to have been shifted, broadened, or reduced after ACZA treatment, including those at about 1,666 cm^{-1}, a region associated with the carbonyl stretching of aldehyde groups (Sarkanen et al. 1967b), and 1,594 and 1,427 cm^{-1}, assigned to aromatic skeletal vibrations (Sarkanen and Ludwig 1971). The 1,427 cm^{-1} band was highly sensitive to ring substituents (Sarkanen and Ludwig 1971), and decreased intensity implies substituent changes.

Bands associated with the hydroxyl group were most substantially altered, especially in comparison to methoxyl-group adsorption bands. This finding further suggests that phenolic hydroxyl groups have an important role in metal adsorption.

FAB mass spectroscopy

Fast Atom Bombardment (FAB) mass spectroscopy provided further insights into the reaction products formed when copper and zinc adsorbed to vanillin.

Mass spectra of ACZA-treated vanillin revealed that the most common mass/charge ratio, once preservative and glycerol lines were subtracted, was vanillin itself (m/e—152.9) (Fig. 7). The lowest mass/charge ratio detected that may reflect a vanillin-metal complex was

m/e—200.9. This mass could be formed by the displacement of hydroxyl hydrogen and methoxyl-methyl groups and the bonding of both oxygens to a copper atom. Similarly, the line at 215.9 could be attributed to vanillin losing a hydrogen and gaining a copper atom, and the line at 217.9 to the same phenomenon involving zinc.

Copper complexes also appeared to be involved in adsorption reactions. For example, the line at 232.8 could be attributed to vanillin plus CuO, or vanillin minus H + CuOH$^+$, and the line at 234.8 could be attributed to similar zinc-vanillin complexes. Similarly, the stronger line at 250.8 could be attributed to vanillin plus Cu(OH)$_2$, and the line at 322.8 to vanillin plus Cu(NH$_3$)$_2$4(H$_2$O) or minus H + Cu(NH)5(H$_2$O). Copper may also complex with two vanillin molecules by dislodging the hydroxyl hydrogen from each vanillin (m/e = 366.7).

Many of the mass/charge ratios suggest displacement of a hydrogen from vanillin, followed by copper or zinc bonding. FTIR analysis and adsorption tests with lignin model compounds suggest that hydroxyl hydrogens were involved, but many of the same mass/charge ratios would result from bond formation with the aldehyde group oxygen.

Bonding environment of copper

Comparison of spectra of ammonia-, ACZA-, and CuO-treated lignin revealed alterations caused by the presence of Cu^{2+} (Fig. 8). The spectra of lignin treated with ACZA (g parallel/perpendicular—2.405/2.046) or CuO (g parallel/perpendicular = 2.392/2.043) were similar. These g-parallel values were higher than previous reports of pine sapwood impregnated with an ammoniacal copper complex (g parallel < 2.25) (Hughes et al. 1992). The proportion of adsorbed copper was presumably lower in that study, as whole wood was treated and no effort was made to remove unfixed copper. The g-parallel value tends to increase as copper distorts from a tetrahedral configuration (Hughes et al. 1992), as might occur with bonding to bulky substituents such
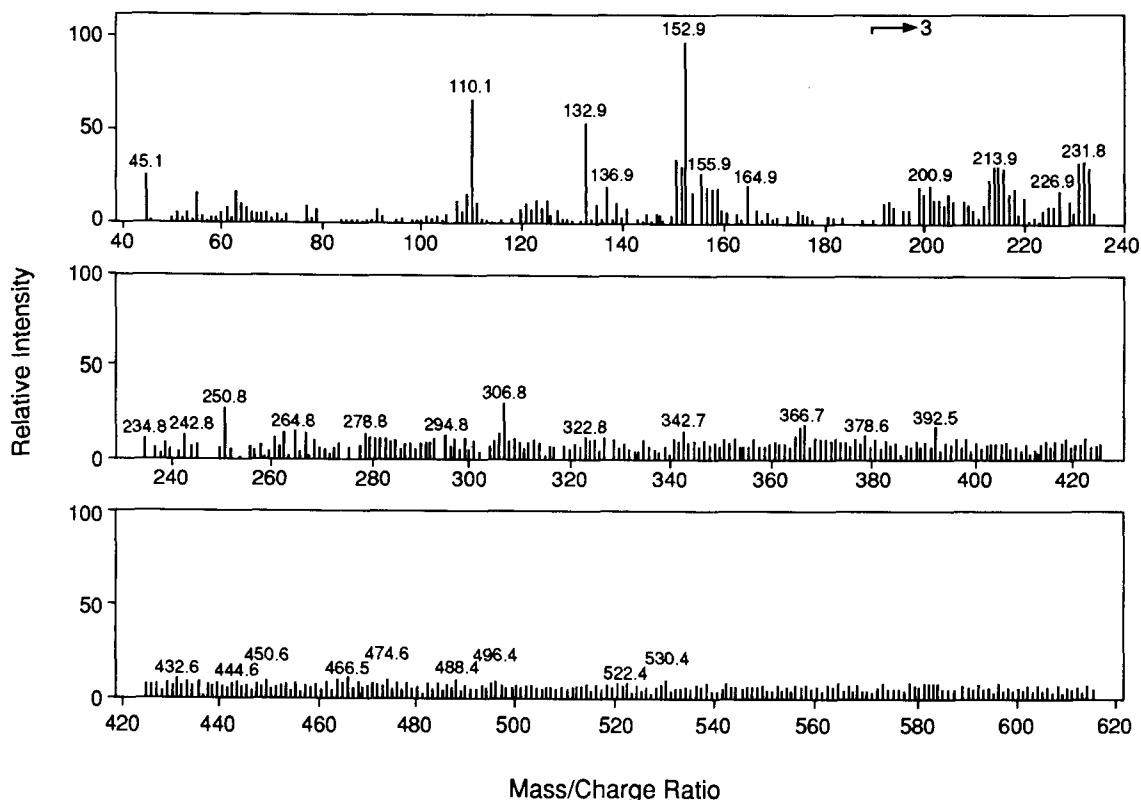
Fig. 7.   FAB mass spectroscopy spectra of vanillin in ACZA.

as lignin. The nonhomogeneous broadening of peaks in the g-parallel region of both spectra indicates that copper species were present in multiple molecular environments, but that at least one of the environments involved some type of bonding. The uneven hyperfine splitting in the g-perpendicular region also indicates the presence of multiple copper species. This type of hyperfine splitting may reflect copper bonding to nitrogen atoms, as in ammonia molecules.

A dominant feature in the spectra was the free radical signal of lignin. Lignin normally has a strong free radical signal, but copper enhanced this signal even further. ACZA- or CuO-treated lignin had free radical signals 1.4 or 1.3 times higher, respectively, than ammonia-treated lignin. Reactions occurring during the copper adsorption may have induced free radical formation, possibly by transforming some

phenolic groups into quinone-type structures. If copper served as an electron acceptor in these reactions, Cu^+ would be present within the lignin.

The generation of free radicals may also contribute to the efficacy of ACZA against decay fungi. Wood decay fungi have produced two-to-three-fold increases in free radical content of pine and sweet gum, which may reflect the enzymatic oxidation of phenolic constituents to produce quinone moieties, which in turn react with other phenolic groups to produce stable radical anions trapped within the lignin structure (Steelink 1966). Treatment with ACZA may interfere with this pathway for fungal degradation of wood.

The intensified free radical peak, combined with the g-perpendicular hyperfine splitting, was consistent with the presence of copper in a square planer configuration, perhaps bonded
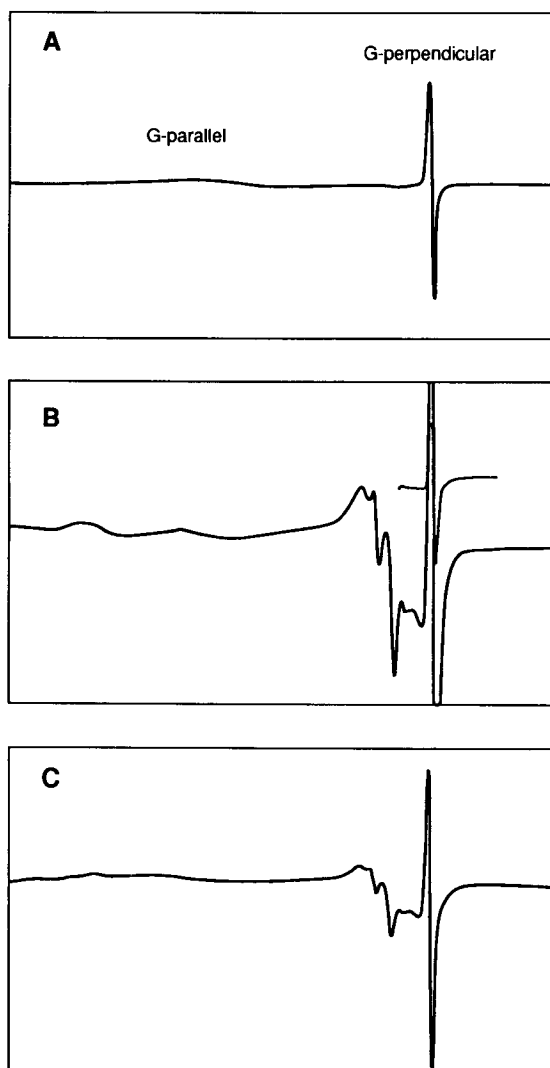
FIG. 8. EPR spectra of spruce organosolve lignin after (A) ammonia treatment, (B) CuO treatment, or (C) ACZA treatment.

to two oxygens from a lignin phenolic group and two ammonia molecules. The spectra also suggested, however, that copper was present in several forms, making other types of lignin-copper bonding possible.

CONCLUSIONS

The stabilization or fixation of ACZA components in wood appears to occur through both adsorption and precipitation reactions. The results generally support previous conjecture that arsenic fixation occurs by precipitation of metal/arsenate complexes as ammonia evaporates from treated wood. Arsenic leaching was minimized when metal oxide : As_2O_5 ratio in the treating solutions exceeded 2.0, and when copper was partially replaced with zinc. Zinc also precipitated the majority of arsenic as ammonia evaporated from the treating solution. Thus, the addition of zinc to ACA has important implications for preservative stability in wood. In contrast, the metal cations were not dependent on arsenic for fixation because of their low water solubility and their ability to adsorb to the wood. Copper, in particular, was readily adsorbed by the lignin and heartwood, which suggests that phenolic groups were primary reaction sites. Model compound tests further indicated that copper reacted preferentially with phenolic hydroxyl groups. Copper adsorption reactions increased lignin free-radical content, suggesting that copper displaced hydroxyl hydrogens or methoxy-methyl groups on catechol-type moieties. Multiple copper species were detected within ACZA-treated lignin, including at least one possible ammonia-associated form.

Metal adsorption to wood can interfere with arsenic fixation by reducing metal cation availability in the preservative solution. Wood treatment variables that favor adsorption over precipitation reactions, such as longer treating schedules and storage practices that limit drying, may increase the proportion of leachable arsenic. Further research is needed to determine if treatment variables significantly affect ACZA fixation, and if these variables can be manipulated to minimize the potential for arsenic leaching while the wood is in service.

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