DIFFUSION OF COPPER IN WOOD CELL WALLS FOLLOWING VACUUM TREATMENT

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ABSTRACT

The rate and extent of copper redistribution in the wood structure of red pine (*Pinus resinosa* Ait.) and trembling aspen (*Populus tremuloides* Michx.) sapwood samples vacuum-treated with alkaline copper solutions were monitored using an expressing technique. Diffusion coefficients (D) for copper movement into the cell-wall substrate were determined from the rate of change of copper concentration in the cell lumens, using a finite bath model for unsteady state Fickian diffusion. D values were in the range of 0.1–165 $\times$ 10^{-10} cm^2/s, depending on the wood species and treating conditions. These D values are about 1/10 to 1/10,000 those for bound water diffusion. Equalization times were much longer for aspen than for red pine, partly as a result of the greater average diffusion distances in aspen; however, estimated D values were more than 100 times lower for aspen even with correction for the different diffusion path lengths. There was no significant species effect on the concentration of copper in the cell walls at equilibrium. Depending on the solution pH, the cell walls retained from 2 to 4 mg Cu per g dry wood with higher retentions for high pH treatments. The rate of diffusion increased with temperature, while wood moisture content had no consistent effect. Ammoniacal and monoethanolamine copper solutions at similar initial pH had similar rates of copper diffusion and equilibrium adsorption. Arsenate anions formulated with copper in ammoniacal copper arsenate solutions were initially excluded from the cell-wall substrate but eventually penetrated into the cell wall, but to a lesser degree than copper.

Keywords: Diffusion, wood cell wall, copper, cation exchange, finite bath, *Pinus resinosa, Populus tremuloides,* amine, ammoniacal copper arsenate (ACA), moisture content, pH.

INTRODUCTION

Copper's effectiveness against decay fungi makes it an important constituent of several commercial wood preservatives and new or proposed systems. There have been many studies assessing the equilibrium distribution of copper and other preservative components in the wood cell-wall matrix and its effect on performance against decay organisms. Investigation of chromated copper arsenate (CCA) components in treated hardwood tissues by micro-analytical analysis (e.g., Dickinson 1974) indicates that copper is not well distributed through the wood tissue. Early soft rot degradation of chromated copper arsenate (CCA)-treated hardwoods may be related to poor distribution of copper in the fiber tissue of these species.

Other studies on the micro-distribution of preservative components in softwood and hardwood tissues after treatment indicate that copper is relatively well distributed in the wood cell walls surrounding treated cells (Yata et al. 1979; Ryan and Drysdale 1988). Ryan and Drysdale (1988) suggest that other factors such as differences in the inherent susceptibility to soft rot of the different species are responsible for the poor soft rot resistance of some hardwoods. Compared to softwoods, some hardwood species may require more copper in the S_2 cell-wall layers to protect against soft rot, and it is important to understand the factors affecting both the rate of movement and the equilibrium concentration of wood-protecting chemicals in the wood cell walls.

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There has been less work on the rate of diffusion of copper and other wood preservative components into the wood cell walls. Yata et al. (1978, 1979, 1983) used microscopic staining techniques to follow the diffusion of CCA components in wood substance. Wood samples were pretreated with staining agents that reacted as copper and other preservative components diffused in the cell walls. This pretreatment with reacting chemicals could influence the interaction of the diffusing species with the cell-wall components.

Understanding of factors influencing the rate of movement of wood preservative components in the cell-wall matrix may help explain differences in performance and mechanisms of fixation.

Following treatment with water-based wood preservatives, the ionic components are expected to diffuse through the bound water system unless or until they become immobilized by various fixation mechanisms. Wood is weakly acidic, and charged solutes interact with the cell-wall/bound water system during diffusion. Cations such as Cu^{++} are adsorbed onto the wood substrate by ion exchange or other pH-dependent mechanisms, resulting in a higher concentration in the cell wall than that resulting from solution in the bound water (Rennie et al. 1987; Cooper 1991a; Thomason and Pasek 1997). This results in changing boundary conditions at the interface between the cell lumen solution and the S_3 layer of the cell wall since the copper concentration drops in the cell lumen solution as it is adsorbed in the cell wall (Cooper 1988; Kumar et al. 1996). The equilibrium copper concentration in the cell-wall matrix should be much higher from basic treating solutions than from acidic solutions as a result of higher adsorption of cations on wood under high pH conditions where the weak acid groups in wood are more highly dissociated. The presence of dissociated acid groups on the wood substance may cause anionic components of preservative solutions to be excluded from the swollen cell wall due to Donnan exclusion effects (e.g., Briggs et al. 1961; Cooper and Roy 1994). This could result in lower diffusion rates and lower equilibrium concentrations of these solutes in the cell walls. The nature of the accompanying "co-ions" and the presence of solubilizing agents such as ammonium hydroxide may also influence the distribution and concentration of copper in the cell-wall matrix.

In this study an expressing technique is used to compare the effects of wood characteristics, ambient conditions, and solution properties on both the rate of diffusion and the equilibrium distribution of copper and other ionic species in the wood cell-wall matrix following vacuum impregnation of the wood. At different times following treatment, solution is squeezed out of wood and analyzed. Changes in concentration of this expressed solution are taken to represent the relative uptakes of water and solutes into the cell walls after treatment.

THEORY

Following vacuum or pressure treatment with a copper-based preservative, some of the copper in the cell lumen solution diffuses into and reacts with the cell wall. By following the change in copper concentration in the wood void space, the progress of its diffusion can be indirectly followed. The movement of solutes in the wood cell-wall matrix can be quantified by a simple membrane diffusion model where it is assumed that a plane membrane of average thickness 2L separates adjacent saturated cell lumens. For wood with the void space completely saturated with solution, 2L should approximately correspond to the double cell-wall thickness. To compensate for the drop in cell lumen concentration with time, a "finite bath" diffusion model should be used.

Consider a wood sample of dry mass (m_0), initial fractional moisture content (u_i), and fractional fiber saturation point (f) treated with a copper-based treating solution of concentration (C_i-mg Cu/g solution) with a solution pickup of P g. We can define C_0 (in mg/g) as the effective initial copper concentration in the treated cell lumens. It represents the concen-

tration of copper that would be in the cell void space if the treating solution and the water contained in the wood were in equilibrium, but no copper had yet diffused into the cell walls. The value of C_0 depends on the initial wood moisture content. If $u_i > f$, the excess free water in the cell void space dilutes the treating solution and $C_0 < C_i$; if $u_i < f$, water from the treating solution diffuses into the wood cell walls and $C_0 > C_i$. For wood treated at its fiber saturation point moisture content, $C_0 = C_i$.

This theoretical initial concentration can be estimated from the copper and water mass balances in the cell lumens and cell walls (Cooper 1991b) as:

$$C_0 = C_i P/[P - (f - u_i)m_0] \quad (1)$$

If the copper concentration in the cell void space at equilibrium is C_E (mg/g), then the ratio of copper retained in the solution to that in the wood substance at equilibrium is given by:

$$\alpha = C_E/[C_0 - C_E] \quad (2)$$

α is the "effective ratio" of solution to wood substance and is an important parameter in the finite bath analysis.

The solution of the Fickian nonsteady-state diffusion equation under these varying solute concentrations for a well-stirred solution in contact with a plane membrane of thickness 2L is shown in Eq. (3). The amount of chemical that has entered the membrane at time t (m_t) as a fraction of the amount that has entered the membrane at equilibrium (m_E) is given by:

$$m_t/m_E = 1 - \sum_{n=1}^{\infty} \frac{2\alpha(1 + \alpha)}{1 + \alpha + \alpha^2 q_n^2} \cdot \exp[-Dq_n^2 t/L^2] \quad (3)$$

(Carmen and Haul 1954; Crank and Park 1968). Since C_0 is the effective concentration of solute in the free solution in the lumens at $t = 0$ and C_E is the concentration in the lumens at equilibrium, then:

$$1 - m_t/m_E = [C_t - C_E]/[C_0 - C_E] \quad (4)$$

where C_t is the concentration in the cell lumens at time t.

The q_n values are the non-zero positive roots of $\tan q_n = -\alpha q_n$ and α is as defined above. Crank (1970, p. 55, Table 4.6) has plotted graphs of m_t/m_E vs. $(Dt/L^2)^{1/2}$ for various values of $100\%/[1 + \alpha]$, the percentage of total solute finally taken up by the membrane.

To apply Eq. (3), values of $(Dt/L^2)^{1/2}$ corresponding to experimental m_t/m_E and α values are taken from this graph and if L is known, the diffusion coefficient D can be estimated. In this study, values of $m_t/m_E = 0.5$ were used and the corresponding times to half equalization ($t_{1/2}$) determined.

A procedure is required to estimate L, the half thickness of the membrane. In the treatment of wood, there is not a single constant membrane thickness. The maximum distance that a given ion must diffuse to achieve full saturation of an individual sample depends on the cell shapes, cell-wall thicknesses, and on whether all adjacent cells are saturated with preservative solution. in this study, average effective diffusion path lengths (L_e) were estimated for each species on the basis of their rates of water swelling following vacuum treatment with water (Cooper and Churma 1990). In a separate study using wood from the same source. Cooper (1996) found that the L_e values in aspen were not significantly affected by relative density or by degree of saturation of the void space and that the average L_e value was about 26.5 μm. Thus, this value is used in this study. For red pine, it was shown that the estimated L_e values varied approximately inversely with the percentage of total void space (F_{VL}) filled during treatment but was also independent of the relative densities of the samples. The best fit equation was:

$$L_e = 1035F_{VL}^{-0.98} \quad (5)$$

This equation is used in this study to estimate the effective diffusion path length in red pine.

The copper concentration in the wood cell-wall matrix at equilibrium was estimated as

follows. If x (mg) copper enters the cell walls, then:

$$C_E = [PC_i - x]/[P - x/1{,}000 - (f - u_i)m_0] \quad (6)$$

and:

$$x = [PC_i - PC_E + C_E(f - u_i)m_0] \div [1 - C_E/1{,}000] \quad (7)$$

or approximately:

$$x = PC_i - PC_E + C_E(f - u_i)m_0. \quad (8)$$

and the retention in the wood (mg copper per dry g of wood) is x/m_0.

The percentage of total void space saturated by the treatment (F_{VL}) was estimated for each sample (Siau 1971). Assuming a dry wood substance density of 1.53, fractional fiber saturation point f = 0.35, density of sorbed water = 1.0 and, if the volume of treating solution absorbed is V_s and the basic relative density of the wood is G_b, then the porosity at fiber saturation point is given by:

$$V_{ai} = 1 - G_b[1/1.53 + 0.35] = 1 - 1.004G_b \quad (9)$$

and the porosity after treatment is:

$$V_{af} = 1 - G_b[0.654 + V_s/m_0] \quad (10)$$

Then:

$$F_{VL} = 100[V_{ai} - V_{af}]/V_{ai} \quad (11)$$

MATERIALS AND METHODS

Twenty-five millimeter cubes of red pine (*Pinus resinosa* Ait.) and trembling aspen (*Populus tremuloides* Michx.) sapwood were cut from machined sticks, sawn from untreated air-dry red pine pole sections and from three fresh-cut 30–35-year-old aspen trees from near Sault Ste. Marie, Ontario. For each study, 18 end-matched specimens were prepared. The samples were equilibrated to either "low" moisture contents (4 to 10% oven-dry basis) or "high" moisture contents (approximately 30%) and weighed (m_i). Three samples were randomly selected, saturated with water, and the green volumes (V_g in cm^3) determined by water buoyancy measurements. These specimens were oven-dried at 103°C, weighed (m_0 in g), and the average initial moisture content (u_i) and basic relative densities ($G_{FSP} = m_0/V_g$) of the samples determined. The 15 remaining end-matched specimens were equilibrated to the test moisture content in a humidity chamber, then weighed individually (m_i), and sealed in a desiccator. A vacuum of 24 in. Hg (20 KPa absolute pressure) was applied for 20 min and the selected copper based solution drawn in until the specimens were submerged. The vacuum was released ($t = 0$) and the specimens rapidly removed from the desiccator, wiped with a damp paper towel, weighed (m_f), sealed in three layers of polyethylene bags, and stored at the test temperature. Most samples were evaluated at room temperature (20°C), but some low temperature tests were done for comparison (4°C). For these samples, the treating solution, vacuum desiccator, and wood samples were conditioned at 4°C in a cooled circulating water bath; the treatment and post-treatment conditioning of samples were conducted in this environment.

At periodic intervals following treatment, the specimens were removed from their plastic wraps, and a sample of free lumen solution was expressed by squeezing the sample in a hydraulic press at 69 MPa (10,000 psi) pressure. Three or more replicate runs were performed for each test condition.

After expressing, the wood samples were oven-dried and weighed (m_0). The pH of the expressed solution was measured and the solution analyzed for Cu (and As for ACA) by X-ray fluorescence spectroscopy (ASOMA Instruments Inc.). Standard copper (and As) solutions were prepared representing the concentration range of interest to provide a calibration curve for the X-ray fluorescence analysis.

The percentage of total void space saturated by the treatment (F_{VL}) was estimated for each sample (Eq. 11).

From the plots of expressate concentration vs. time, the equilibrium concentrations (C_E)

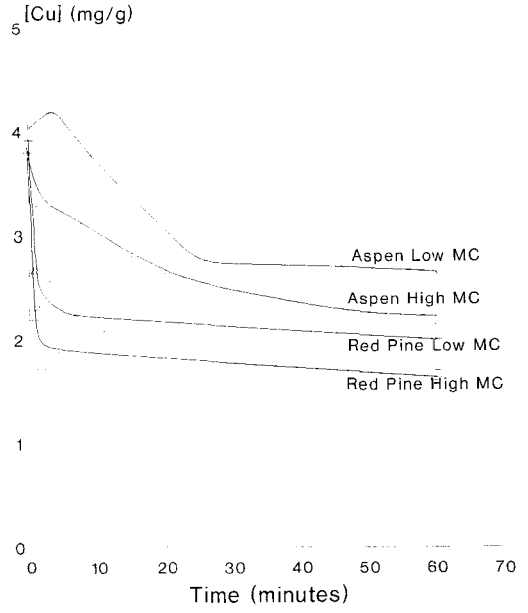

FIG. 1. Change in concentration of copper in solution expressed from wood void space as affected by species and wood moisture content.

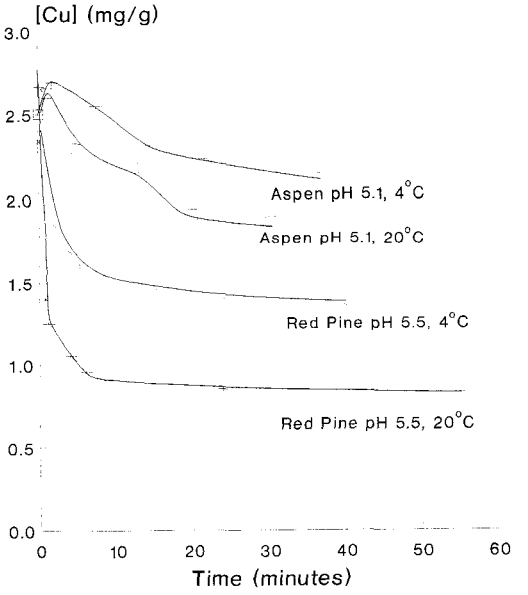

FIG. 2. Change in concentration of copper in solution expressed from wood void space as affected by species and ambient temperature.

and half diffusion times ($t_{½}$) were estimated graphically and α, x/m_0 and D values estimated. Based on the solution uptake and the above parameters, the P, C_0, F_{VL} and L_e values were estimated. Since a different wood sample was evaluated at each time interval, these values varied from sample to sample, and the average value for a run was used to characterize a given trial. The x/m_0 and D values were estimated from these average results for each run.

The temperature dependence (two temperatures only) was determined using the Arrhenius relationship for temperature-activated processes:

$$D = Ae^{-Q/RT} \text{ or } \ln D = \ln A - Q/RT \quad (12)$$

where A is a constant, Q the activation energy in KJ per mole, R is the gas constant (8.314 J/°K·mol), and T the temperature (°K). Then the slope of the plot of ln D vs. 1/T provides an estimate of the activation energy.

The solutions and test conditions evaluated are summarized in the tables.

RESULTS AND DISCUSSION

General

The effects of the different variables evaluated on copper diffusion and equilibrium in the cell wall can be seen from the plots of copper concentration in the cell lumens at various times after treatment (Figs. 1–4). The rate of drop of the concentration reflects the diffusion rate, while the total change in concentration defines the extent of adsorption of copper on the cell wall at equilibrium. The parameters calculated from the solution absorption and these curves provide quantitative comparisons of affinity of the preservative components for the wood cell-wall substance (α and x/m_0) and the rates of equalization ($t_{½}$ and D) for the different treatments (Tables 1–3). Low α and high x/m_0 values denote high equilibrium concentrations of copper in the cell-wall substance; high $t_{½}$ and low D values indicate slow diffusion of solutes into the cell wall.

The D values were relatively low, ranging from 0.1 to 165 $\times$ 10^{-10} cm^2/sec depending on the species and conditions. This compares to

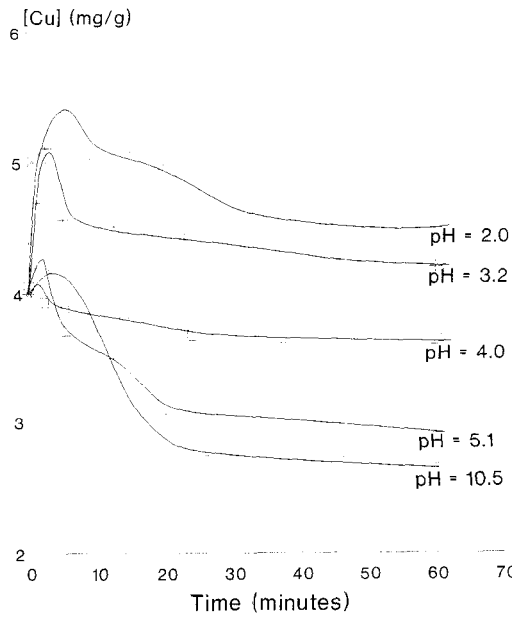

FIG. 3. Change in concentration of copper in solution expressed from wood void space as affected by solution pH—aspen at low moisture content.

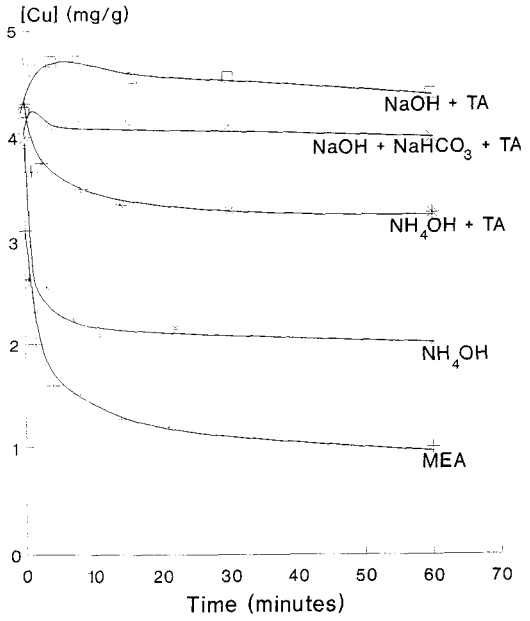

FIG. 4. Change in concentration of copper in solution expressed from wood void space from various high pH systems—red pine at initial pH = 10.5.

about 1,000–2,000 × 10^{-10} cm^2/sec for transverse bound water diffusion in the cell wall (Stamm 1960). Thus, in dry wood, water resaturates and swells the cell walls much faster than copper equalizes in the water saturated cell walls.

Effect of species (red pine vs. aspen)

The copper concentration of the expressed solution increased initially in aspen samples treated at low moisture contents as water from the solution penetrated the cell-wall matrix faster than the copper ions (Fig. 1). After a few minutes, as the cell walls approached saturation with the water, the rate of copper adsorption exceeded that of water and the copper concentration in the expressed solution decreased. The rate of concentration change was rapid at first, but several days were required to reach equilibrium. The data are plotted only for the initial 60 min of the process, but the equilibrium copper concentrations (C_E) in the cell lumens can be seen in Tables 1 and 2. The fractional void space penetrated in aspen was relatively low (about 50%). Presumably, vacuum-treated aspen is initially penetrated through the vessels (Stone and Green 1958; Perng et al. 1985) and the copper and solution water diffuse outwards into the surrounding fiber tissue.

In red pine, the rates of water and copper equalization in the cell walls were much faster than in aspen. By the first measurement at less than 1 min after treatment, the copper levels had already dropped significantly below the initial solution concentration. This can be partially explained by the better initial distribution of solution in the red pine cells and the resulting shorter diffusion path lengths and by the greater relative area of cell lumen surfaces exposed to the solution. Generally, about 80% or more of the total void space in red pine was saturated by the vacuum treatment.

The estimated diffusion path length of red pine, based on the solution absorption and Eq. (6), was about 15 μm compared to the 26.5 μm assumed for aspen. These values are much greater than the double cell-wall thickness in

TABLE 1. *Effect of species and initial wood moisture content on equalization of copper in the wood cell wall matrix—high pH systems (average of three values—standard deviations in bold).*

Solution	Initial Conc mg/g	Initial pH	Final pH	Species	C_0 mg/g	C_E mg/g	u_i (%)	F_{VL} (%)	L_e (μm)	$t_{½}$ (sec)	α	x/m_0 mg/g	D $cm^2sec \times 10^{-10}$
$CuSO_4$ in NH_4OH	4.00	10.5	7.65	Aspen	5.42	0.66	7.0	49	26.5	2,240	0.14	3.78	0.22
					0.16	**0.17**	**0.90**	**7.3**		**765**	**0.04**	**0.29**	**0.12**
$CuSO_4$ in NH_4OH	4.00	10.5	8.22	R. Pine	5.01	0.96	9.0	67	16.8	20	0.14	4.16	22.0
					0.16	**0.46**	**0.5**	**13**	**4.2**	**4.9**	**0.04**	**0.91**	**19.2**
$CuSO_4$ in NH_4OH	4.00	10.5	7.53	Aspen	3.99	0.51	36	54	26.5	2,030	0.19	3.46	0.39
					0.05	**0.16**	**8.0**	**3.5**		**55**	**0.01**	**3.07**	**0.07**
$CuSO_4$ in NH_4OH	4.00	10.4	8.71	R. Pine	3.90	0.21	30.5	62	18.0	105	0.057	3.36	0.57
					0.18	**0.05**	**0.7**	**3.5**	**1.3**	**21**	**0.01**	**0.16**	**0.11**
$CuSO_4$ in MEA	4.00	9.5	6.73	Aspen	6.44	0.29	6.3	31	26.5	1,490	0.049	3.39	0.07
			0.45		**0.52**	**0.05**	**2.0**	**5.6**		**590**	**0.01**	**0.38**	**0.03**
$CuSO_4$ in MEA	4.00	9.4	7.78	R. Pine	5.59	0.25	7.4	42	26.2	24	0.047	3.68	3.97
			0.64		**0.16**	**0.02**	**0.20**	**5.0**	**3.1**	**0.7**	**0.004**	**0.71**	**0.30**
$CuSO_4$ in MEA	4.07	9.5	7.45	Aspen	4.17	0.29	30	46	26.5	1,800	0.071	2.64	0.12
			0.11		**0.11**	**0.04**	**1.0**	**10**		**415**	**0.01**	**0.60**	**0.05**
$CuSO_4$ in MEA	3.75	9.5	8.21	R. Pine	3.98	0.28	30	54	20.7	24	0.087	3.36	6.2
			0.02		**0.11**	**0.04**	**2.0**	**0.9**	**0.30**	**3.5**	**0.021**	**0.14**	**1.2**

different cell types in both species. The longer diffusion path lengths result from factors such as the incomplete saturation of all cells and cell corner effects (Cooper 1996). As a general rule, the diffusion time increases with the square of the membrane thickness for non-steady-state diffusion processes (Crank 1970). Thus, if the copper diffusion rates in the wood cell walls were similar for the two species, we would expect the $t_{½}$ values for aspen to be less than 4 times greater than those for red pine. For red pine, the $t_{½}$ values were shorter than

TABLE 2. *Effect of solution concentration and temperature on equalization of copper in the wood cell wall matrix (average of three values—standard deviations in bold.)*

Solution	Initial Conc mg/g	Initial pH	Final pH	Species	C_0 mg/g	C_E mg/g	u_i (%)	F_{VL} (%)	L_e (μm)	$t_{½}$ (sec)	α	x/m_0 mg/g	D $cm^2/sec \times 10^{-10}$
Cu Acetate 20°C	4.00	5.1	4.34	Aspen	5.40	1.27	7.4	52	26.5	855	0.31	3.58	2.02
			0.04		**0.24**	**0.05**	**4.0**	**8.2**		**225**	**0.03**	**0.04**	**0.46**
Cu Acetate 4° C	4.00	5.1	4.31	Aspen	5.63	1.24	7.4	47	26.5	2,550	0.285	3.34	0.70
			0.05		**0.17**	**0.04**	**1.0**	**6.1**		**1,050**	**0.005**	**0.44**	**0.35**
Cu Acetate 20°C	2.60	5.5	4.34	Aspen	3.38	0.79	7.6	52	26.5	820	0.31	2.24	2.11
			0.04		**0.14**	0.03	**1.0**	**8.2**		**122**	**0.03**	**0.22**	**0.24**
Cu Acetate 4°C	2.60	5.5	4.33	Aspen	3.40	1.24	7.4	47	26.5	3,200	0.285	2.54	0.56
			0.05		**0.17**	**0.04**	**1.0**	**7.0**		**1,000**	**0.005**	**0.44**	**0.20**
Cu Acetate 20°C*	2.60	5.5	4.54	R. Pine	3.29	0.87	7.3	68	16.6	20	0.36	2.43	38
Cu Acetate 4°C*	2.60	5.5	4.53	R. Pine	2.90	1.28	6.5	80	14.1	60	0.79	2.04	20.7
$CuSO_4$ in NH_4OH	4.00	10.5	7.65	Aspen	5.42	0.66	7.0	49	26.5	2,240	0.14	3.78	0.22
			0.05		**0.16**	**0.17**	**0.90**	**7.3**		**765**	**0.04**	**0.29**	**0.12**
$CuSO_4$ in NH_4OH	1.04	10.5	7.86	Aspen	1.30	0.06	13.9	55	26.5	260	0.043	1.03	0.47
			0.06		**0.02**	**0.01**	**0.70**	**0.75**		**140**	**0.014**	**0.02**	**0.40**
ACA 20°C*	4.00	10.7	n.m.	R. pine	4.46	2.47	5.6	74	15.2	22	1.24	3.3	92
ACA 20°C*	2.80	9.5	n.m.	R. pine	3.58	1.09	7.1	63	17.8	18	0.44	2.50	65
ACA 20°C*	1.58	10.3	n.m.	R. pine	2.01	0.32	4.2	75	15.0	18	0.19	1.91	14.4

* 1 replication only.
n.m. Not measured.

TABLE 3. *Effect of solution formulation on equalization of copper in the wood cell wall matrix—pH, amine vs ammonia (average of three values—standard deviations in bold).*

Solution	Initial Conc mg/g	Inital pH	Final pH	Species	C_0 mg/g	C_E mg/g	u_j (%)	F_{VL} (%)	L_e (μm)	$t_{½}$ (sec)	α	x/m_0 mg/g	D $cm^2/sec \times 10^{-10}$
$CuSO_4 + H_2SO_4$	4.00	2.0	3.36	Aspen	5.41	2.73	6.9	50	26.5	1,840	1.00	2.09	3.07
			0.31		**0.06**	**0.05**	**0.30**	**1.8**		**350**	**0.05**	**0.09**	**0.66**
$CuSO_4$	4.00	3.22	3.52	Aspen	5.25	2.58	10.2	58	26.5	820	0.79	2.13	4.2
			0.03		**0.35**	**0.38**	**3.0**	**18**		**40**	**0.09**	**0.23**	**0.60**
$CuSO_4$	4.00	4.0	3.36	Aspen	5.41	2.73	6.9	50	26.5	1,840	1.00	2.09	2.60
			0.31		**0.06**	**0.05**	**0.30**	**1.8**		**350**	**0.05**	**0.09**	**0.567**
Cu Acetate	4.00	5.1	4.34	Aspen	5.40	1.27	7.4	52	26.5	855	0.31	3.58	2.02
			0.04		**0.24**	**0.05**	**4.0**	**8.2**		**225**	**0.03**	**0.04**	**0.46**
$CuSO_4$ in NH_4OH	4.00	10.55	7.65	Aspen	5.42	0.66	7.0	49	26.5	2,240	0.14	3.78	0.22
					0.16	**0.17**	**0.90**	**7.3**		**765**	**0.04**	**0.29**	**0.12**
$CuSO_4 + H_2SO_4$	4.00	2.0	2.61	R. Pine	4.86	3.83	8.3	89	9.0	17.5	4.68	0.86	70
			0.05		**0.05**	**0.10**	**0.10**	**13**	**1.5**	**3.5**	**0.39**	**0.23**	**11**
$CuSO_{4*}$	4.00	4.0	3.2	R. Pine	4.91	3.62	8.0	90	8.6	20	2.81	1.52	48
$CuSO_4$ in NH_4OH	4.00	10.5	8.22	R. Pine	5.01	0.96	9.0	67	16.8	20	0.14	4.16	22.0
					0.16	**0.46**	**0.5**	**13**	**4.2**	**4.9**	**0.04**	**0.91**	**19.2**
$CuSO_4$ in NH_4OH	4.00	10.5	7.65	Aspen	5.42	0.66	7.0	49	26.5	2,240	0.14	3.78	0.22
					0.16	**0.17**	**0.90**	**7.3**		**765**	**0.04**	**0.29**	**0.12**
$CuSO_4$ in MEA	4.00	9.5	6.73	Aspen	6.44	0.29	6.3	31	26.5	1,490	0.049	3.39	0.07
			0.45		**0.52**	**0.05**	**2.0**	**5.6**		**590**	**0.01**	**0.38**	**0.03**
$CuSO_4$ in NH_4OH + TA	4.31	10.57	7.61	Aspen	6.27	2.51	5.6	40	26.5	2,340	0.67	2.40	1.73
			0.07		**0.18**	**0.14**	**0.10**	**3.5**		**470**	**0.09**	**0.15**	**0.53**
$CuSO_4$ in NaOH + TA	4.15	10.5	5.60	Aspen	5.88	4.58	5.5	36	26.5	240,000	3.96	0.83	0.60
			0.15		**0.09**	**0.16**	**0.10**	**1.4**		**20,000**	**0.40**	**0.04**	**0.40**
$CuSO_4$ in NaOH + TA + $NaHCO_3$	4.00	10.55	8.13	Aspen	6.21	3.97	3.5	37	26.5	585	1.02	3.12	3.9
			0.34		**0.06**	**0.03**	**0.30**	**2.4**		**75**	**0.08**	**0.05**	**0.10**
$CuSO_4$ in NH_4OH	4.00	10.5	8.22	R. Pine	5.01	0.96	9.0	67	16.8	20	0.14	4.16	22.0
					0.16	**0.46**	**0.5**	**13**	**4.2**	**4.9**	**0.04**	**0.91**	**19.2**
$CuSO_4$ in MEA	4.00	9.4	7.78	R. Pine	5.59	0.25	7.4	42	26.2	24	0.047	3.68	3.97
			0.64		**0.16**	**0.02**	**0.20**	**5.0**	**3.1**	**0.7**	**0.004**	**0.71**	**0.30**
$CuSO_4$ in NH_4OH + TA	4.31	10.5	9.23	R. Pine	5.27	2.59	8.6	70	16.0	20.7	0.97	3.13	93
			0.15		**0.03**	**0.04**	**0.60**	**0.4**	**0.09**	**2.5**	**0.04**	**0.10**	**9.4**
$CuSO_4$ in NaOH + TA	4.23	10.5	5.95	R. Pine	5.37	4.04	8.6	63	18.1	30	3.27	1.35	165
			0.20		**0.27**	**0.38**	**0.80**	**9.6**	**3.1**	**4.1**	**1.05**	**0.35**	**42**
$CuSO_4$ in NaOH + TA + $NaHCO_3$	4.31	10.5	9.62	R. Pine	5.47	2.76	6.2	66	17.2	21	1.02	3.12	2.5
			0.04		**0.13**	**0.04**	**0.20**	**5.4**	**1.4**	**4.5**	**0.08**	**0.05**	**0.10**

the time to the first reading (<60 sec) and were estimated by graphic interpolation. Based on these estimates, the half diffusion times are 50 to 100 times greater for aspen than for red pine (Table 1). Only a small part of this difference can be explained by the differences in the diffusion path length, suggesting that the diffusion of copper in aspen wood substance is inherently slower than in red pine cell walls.

As a result, the estimated copper diffusion coefficients were much higher for red pine than for aspen, even though these calculations take into account the short effective diffusion path length (membrane thickness) of the softwood estimated from rates of water swelling. Thus, the rate of copper equalization in the cell-wall substrate is not proportional to the rate of moisture equalization and is lower in the diffuse porous hardwood than predicted on the basis of the relative swelling rates of the two species.

This may result from the greater heterogeneity effect in the aspen, although moisture diffusion should be equally affected. Another possibility is that if treatment is primarily through the vessels in vacuum-treated aspen and the copper must diffuse through several of the surrounding fiber cells, Cu diffusion may be retarded because the ions must cross a number of intercellular joins (compound middle lamellae). Yata et al. (1979) presented microscopic evidence that diffusing fronts of copper in the cell-wall matrix are delayed at the compound middle lamellae. This is consistent with higher Cu adsorption in this lignin- and pectin-rich area. Also, copper penetration into the cell walls of red pine may be facilitated by penetration into the compound middle lamella through bordered pits in the radial walls.

The estimated D values were low compared to the values for free diffusion of copper in solution (about 0.75×10^{-5} cm^2/sec). For a homogenous material with large "mesh size" compared to solute size, the ratio of observed D to the free solute diffusion coefficient (D_s) is predicted to be (Meares 1968):

$$D/D_s = ([1 - v_p]/[1 + v_p]) \quad (13)$$

where v_p is the volume fraction of polymer in the swollen membrane. For wood with a dry wood substance density of 1.53 and estimated FSP = 35%, $v_p = 0.66$ and $D/D_s = 0.04$. However, the estimated ratio from the results obtained here is in the range $0.25–250 \times 10^{-5}$, indicating greatly inhibited diffusion of copper in the cell-wall matrix of wood. This may result from a number of factors, such as, tortuosity effects, reduced cross-section for diffusion, electrical drag effects, and resistance of the cell-wall polymers to displacement Meares 1968).

Low α and high x/m_0 values indicate high affinities of the wood substrate for copper. Under identical treatment conditions, the two species appear to have similar affinities to copper. Based on an assumed fiber saturation moisture content of 35% for both species, the estimated equilibrium copper concentration in the cell walls (x/m_0) at pH 10.5 is about 4 mg copper per gram dry wood for both species. These values are consistent with those reported by Thomason and Pasek (1997) for their lower range of concentrations of copper with boric acid in MEA (4.32 to 4.50 mg/g Cu adsorption for concentrations of 2.5–10 mg Cu/g solution).

The equalization of Cu in the cell-wall matrix of both species was rapid in relation to normal fixation times for CCA preservatives (requiring several days at room temperature). However, red pine reached equilibrium much faster than aspen. In higher density diffuse porous hardwoods such as maple (*Acer* sp.) and ring porous species such as oak (*Quercus* sp.) where the effective diffusion path lengths are considerably longer (Cooper and Churma 1990), complete distribution of copper in the wood tissue may not be possible before fixation is complete.

Effect of initial moisture content

For aspen specimens treated at close to the fiber saturation point moisture content, there was no measurable increase in copper concen-

tration of the expressate (Fig. 1). At this moisture content, little water leaves the solution in the cell lumens to saturate the cell walls. The copper concentration dropped steadily with both species. One might expect faster equalization of preservative components in the cell walls with the treatment of dry wood since the turbulence created by the sorption of water into the cell wall should reduce diffusion boundary layer effects at the lumen surface. Also, the initial increase in concentration of solute in the cell lumens creates a higher solute concentration gradient that should increase the diffusion rate in initially dry wood. For samples treated with ammoniacal copper solutions (Table 1), D values were higher for the initially dry samples, and the equilibrium adsorption of copper (x/m_0) was also higher. However, for copper-MEA treatments, the D values were lower for the samples treated dry, although the x/m_0 values were higher.

Effect of solution concentration

The solution concentration effect can be compared using the copper acetate and ACA (Table 2) results. It is apparent that there was a limit to the amount of copper that could be accommodated in the cell-wall matrix, depending on the solution pH. This is shown by the higher C_E and α values for the higher solutions strengths and the fact that the x/m_0 values were not greatly affected by the different initial concentrations. This is consistent with ion exchange type reactions between the copper cations and the weak acidic groups in the cell wall. The diffusion coefficients were higher for the higher concentrations, but this is more a reflection of the effect of the calculated α on D. In terms of practical significance, the equalization times (as represented by the $t_{½}$ values) were similar at all concentrations.

Effect of temperature

As expected, $t_{½}$ values were lower and D values higher in samples treated and maintained at higher temperatures (Table 2 and Fig. 2). Only two temperature conditions were evaluated, and estimates of activation energies using the Arrhenius equation using only two values are not very precise; however, it is useful to compare such estimates with activation energies for CCA fixation. The estimated activation energies for copper diffusion were 47,000 J/M for aspen and 19,350 J/M for red pine compared to values of about 75,000 J/M for CCA-C fixation in red pine (Chen 1994). This indicates that the temperature dependence for CCA fixation is much greater than for copper diffusion and that it is possible that at high temperatures, fixation may occur before redistribution of the copper is complete, as was suggested by Preston and McKaig (1983). Thus accelerated fixation of hardwood species should not be considered until these implications have been explored more fully.

Effect of solution formulation

Effect of pH.—At both low and high initial wood moisture contents, the high pH samples had a greater adsorption of copper during the diffusion reaction period than low pH formulations (Fig. 3). This may be attributed primarily to pH-dependent ion exchange adsorption of copper ions to the wood substrate (Rennie et al. 1987; Cooper 1991a; Thomason and Pasek 1997). With an initial solution copper concentration of 4 mg/g, the add-on to the wood at pH 10.5 is in the order of 4 mg Cu/g dry wood, compared to 1–2 mg/g at pH = 2 (Table 3). At all solution pHs, wood buffers the treating solution, increasing the pH of the acidic solutions and reducing that of the basic solution (Tables 1–3). This tends to reduce the effect of initial pH on cation adsorption.

Even though the $t_{½}$ values were lower for the basic solutions, the estimated diffusion coefficients, based on the finite bath model, were actually lower than for the more acidic solutions. This results from the fact that a large component of the concentration drop in high pH systems is related to rapid adsorption on the cell-wall substance.

Effect of ammonia and amine.—There have been many studies on the mode of fixation of

ammoniacal copper based wood preservatives on wood (e.g., Jin and Archer 1991; Jin and Preston 1991; Pohleven et al. 1994; Ruddick 1992, 1995; Lebow and Morrell 1993, 1995). While the commonly presumed fixation modes of precipitation of low solubility copper arsenate products on evaporation of the ammonia (Hulme 1979; Hartford 1973) and ion exchange to weak acid groups on wood (Cooper 1991a) are no doubt important, there is considerable evidence that ammonia and amines are involved in the fixation beyond their effects on the pH of the system. Copper amine complexes are detected after the volatile ammonia is gone (Pohleven et al. 1994; Ruddick 1992). To investigate the effect of ammonia on the copper diffusion and reaction in the cell-wall matrix, copper monoethanolamine (MEA) systems and copper formulated with sodium hydroxide were compared with the ammoniacal systems (Fig. 4 and Table 3).

Copper was adsorbed into the cell walls from copper-MEA solutions and copper ammonia solutions at similar rates and equilibrium adsorption values. The solution absorption was lower for the copper-MEA solutions, which resulted in lower C_E and α values. This resulted in lower estimated D values, even though the half times were similar.

High pH copper/NaOH solutions could not be made because of the formation of low solubility $Cu(OH)_2$. Thus, basic copper tartrate solutions were prepared by dissolving copper acetate with a stoichiometric equivalent of tartaric acid (TA) in water and adjusting the pH to 10.5 with NaOH. This was compared with identical copper tartrate solutions adjusted to high pH with ammonium hydroxide or with sodium bicarbonate ($NaHCO_3$) and NaOH. Solutions formulated with ammonium hydroide with TA adsorbed copper into the cell-wall matrix at a slower rate than from copper ammonium solutions without TA; also the equilibrium amount adsorbed tended to be lower than with ammonium hydroxide alone. Solutions formulated with NaOH with tartaric acid did not have significant adsorption of copper into the cell-wall matrix. However, it was observed that the pH of this system dropped very rapidly (Fig. 5). The addition of $NaHCO_3$ as a buffer to this system reduced the rate of drop of the pH and resulted in significant adsorption of copper into the cell walls, although not to the extent seen with the ammonia and amine treatments (Table 3). This effect may be attributed to pH-controlled ion exchange to weak acid groups in the wood substance. However, the rate of adsorption was much slower than with the ammoniacal systems (Fig. 4).

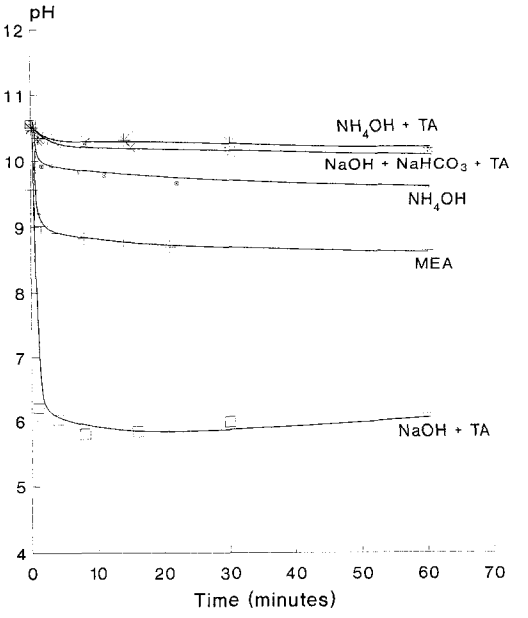

FIG. 5. Change in pH of expressed solution of different high pH copper solutions—red pine.

One interpretation of these observations is as follows: pH-dependent copper adsorption did not occur with NaOH systems because of the immediate pH drop on contact with wood. The presence of sodium bicarbonate allowed the copper to adsorb on the cell-wall components. However, the extent of reaction is lower because of the absence of ammonia or amine. The diffusion of copper into the cell wall with the ammonia and bicarbonate solutions with tartaric acid was much slower than with ammoniacal solutions with or without TA. It is possible that the larger copper tartrate com-

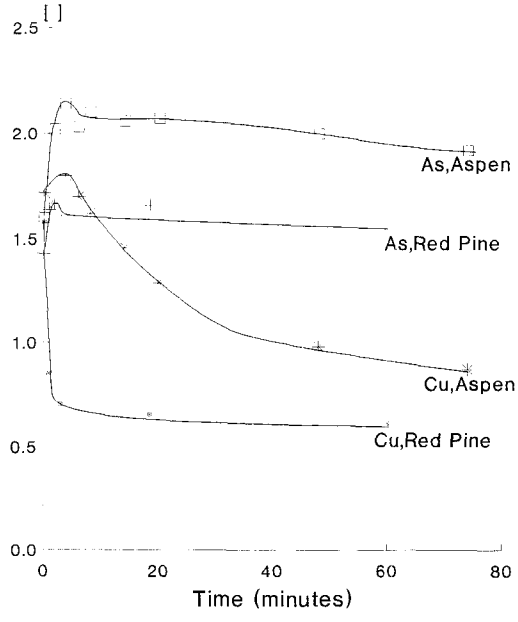

FIG. 6. Change in concentration of copper and arsenic in solution expressed from wood void space following treatment with ammoniacal copper arsenate.

plex develops in the absence of ammonia, but cuprammonium ions are preferentially formed when ammonia is present. The slow penetration of copper into the cell wall in the above system may also result from competition between the tartaric acid in the cell lumens and the exposed anions in the cell wall for the dissolved copper in the solution.

Ammoniacal copper arsenate (ACA).—In addition to the effect of pH on copper diffusion and equalization in the cell wall, there appear to be effects from the accompanying anions as well. In ammoniacal copper arsenate formulations, copper was rapidly depleted from the cell lumens as it was adsorbed in the cell walls (Fig. 6); but the equilibrium copper concentration in the wood cell walls was lower than for systems without arsenic. Also, the arsenate concentrations increased in the cell lumens and remained high compared to the copper concentrations. The cell wall contains a high concentration of "fixed" anions at the high pHs of these formulations (Cooper 1991b), and exclusion of mobile anions such as the arsenate ions is predicted by the Donnan membrane effect (e.g., Cooper and Roy 1994). Eventually, the arsenate concentration in the cell lumens dropped; this may have resulted from precipitation of metal arsenate complexes as ammonia evaporates from the wood (Lebow and Morrell 1995) over the long test period, or from a slow diffusion of the arsenate into the cell walls and reaction with the adsorbed copper. However, in the time frame of this study, the equilibrium concentration of arsenate in the cell lumens was much higher than the copper concentration. This raises the question of whether there is adequate copper in the cell lumens for stoichiometric formation of copper arsenate complex (Lebow and Morrell 1995). This may help explain the relatively poor arsenic leaching resistance in conventional ACA solutions compared to ammoniacal copper zinc arsenate (ACZA) formulations with much higher metal to arsenate ratios. Kumar et al. (1996) showed that expressate from ACZA treated Douglas-fir had more copper than arsenic during the entire reaction/precipitation period.

SUMMARY AND CONCLUSIONS

Diffusion coefficients for copper movement into the cell-wall substrate, as determined from the rate of change of copper concentration in the cell lumens, using a finite bath model for unsteady-state Fickian diffusion are in the range of 0.1 to 4 $\times$ 10^{-10} cm^2/sec for aspen and 1 to more than 100 $\times$ 10^{-10} cm^2/sec for red pine. These correspond to about 1/10,000 to 1/250 of the bound water diffusion coefficient for aspen and about 1/1,000 to 1/10 of the bound water diffusion value for red pine. Thus, even with correction for different effective path lengths, diffusion of copper in aspen is greatly retarded compared to pine. Wood moisture content did not have a consistent effect on rate of copper diffusion or equilibrium copper concentration in the cell walls.

High pH formulations resulted in a greater distribution of copper in the cell walls of the treated wood than low pH systems. This is at-

tributed to pH-dependent cation exchange to weak acid groups in wood and to formation of amine copper complexes in the wood cell wall. Times to half equalization were shorter for high pH systems, but calculated diffusion coefficients (based on a finite bath model) were smaller for the high pH systems.

High pH copper ammonia and copper amine solutions resulted in greater copper adsorption on the wood than high pH systems based on sodium hydroxide, tartaric acid, and sodium bicarbonate.

Multisalt formulations such as ACA resulted in reduced rates and equilibrium amounts of copper in the cell wall substrate at equivalent pHs compared to copper salts alone. The arsenic component of ACA lags behind the copper and is excluded from the cell-wall matrix compared to copper.

Although the rate of diffusion is accelerated at higher temperatures, the temperature dependence is not as strong as that for CCA fixation. This suggests that in hardwood, fixation may be completed before the CCA components have a chance to completely saturate the wood cell wall matrix.

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