EFFECT OF COMPRESSION WOOD ON LEACHING AND FIXATION OF CCA-C TREATED RED PINE

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ABSTRACT

In this study, we investigated the effect of compression wood on the release rate of chromium, copper, and arsenic elements from red pine (*Pinus resinosa* Ait.) and the rate of fixation of hexavalent chromium in the wood. Wood blocks from red pine, some containing compression wood and some with normal wood, were treated with a 1.0% CCA-C solution and then allowed to fix at 23°C ± 2 (74°F ± 4) for 0, 6, 24, 48, 96, 192, and 336 h. After each fixation period, sets of blocks removed from the conditioning room were subjected to 336 h of leaching. The percentage of hexavalent chromium reduced to the trivalent state was determined for solution pressed from matched sets of blocks. The blocks containing compression wood released significantly less chromium and copper elements. For chromium, the biggest effect was seen after the 192- and 336-h fixation periods. In the normal wood blocks fixed for 336 h, the average chromium release rate after 6 h of leaching was almost five times greater than that of the compression wood blocks. Copper and arsenic release was also affected by compression wood, but for these two elements, the effect diminished during the later stages of fixation. A higher percentage of hexavalent chromium was reduced to trivalent chromium in compression wood compared with that in normal wood after most fixation periods, and this difference was significant after 0, 48, 96, and 192 h.

Keywords: Compression wood, red pine, CCA, fixation, leaching.

INTRODUCTION

Compression wood is a reaction wood formed in gymnosperms as a response to various growth stresses. It develops on the underside of leaning trunks and branches. Compression wood in logs is usually indicated by eccentric annual rings that appear to contain an abnormally large proportion of latewood in the region of fastest growth (Panshin and De Zeeuw 1980).

Compression wood develops most frequently and rapidly in vigorous, fast-growing trees and is very common and probably more widespread than is generally thought. Compression wood is a common defect in southern pine species growing in the United States; it has been reported that 10% of the wood in southern pine consists of severe compression wood and that 25% contains mild compression wood. Plantation-grown *P. resinosa* trees in New York that were leaning 5 degrees contained 5% to 40% compression wood, while those inclined 10 to 40 degrees contained 40% to 70%. In the spruce forests of Canada, 15% of the wood might be compression wood (Timell 1986). Under adverse environmental con-

ditions, forest and plantation stands can contain as much as 40% compression wood in their trunks. Even in the most-improved and best-managed conifer forest, no tree stem can be expected to be entirely without compression wood (Timell 1986).

Compression wood is generally characterized by rounded thick-walled tracheids, large fibril angles, spiral checks in the cell walls and highly lignified secondary cell walls (Timell 1986). Compression wood has different chemical properties compared with normal wood. Normal softwood is composed of cellulose (40%–45%), hemicellulose (25%–30%), lignin (25%–35%), and small amounts of ash and extractives. In general, compression wood contains 30% to 40% more lignin and 20% to 25% less cellulose than normal wood. Compression wood differs from normal wood not only in the proportion of the major constituents but also in their distribution in the cell walls. In addition to different lignin and carbohydrate contents, compression wood is more soluble in both water and dilute alkali than normal wood. Although most studies have stated that stem compression wood contains more extractives than normal wood, sometimes the opposite trend was noted (Timell 1986).

CCA-C is currently the predominant preservative for many applications and is widely used in the United States (Lebow 1996). CCA-C contains 18.5% CuO, 67.5% CrO_3, and 34% As_2O_5 as specified by AWPA standards (AWPA 1999c) and is stabilized in the wood by means of chemical reactions called fixation. Fixation is considered to be the state of the chemical components of the preservative and other wood or substrate when all chemical reactions and interactions are completed (Cooper et al. 1993). Properties of wood such as pH, lignin structure and content, and extractive content can influence fixation. The fixation reactions are highly dependent on treating factors such as preservative formulation, preservative retention, and processing techniques as well as post-treatment conditioning factors such as temperature, humidity, and air flow

(Lebow 1996). The effects of wood species on the fixation and efficacy of treated wood and the fixation reactions of CCA with lignin, cellulose, and their model compounds have been extensively investigated (Cooper and Roy 1994; Pizzi 1990a, b, 1980, 1981, 1982; Greaves 1972, 1973, 1974; Wilson 1971; Dahlgren 1975; Henshaw 1979; Yamamoto and Matsuoka 1989; Yamamoto and Rokoba 1991; Pizzi et al. 1984; Carpenter and Gardner 1993; Englund and Gardner 1993). According to these studies, differences in the distribution of preservative components in soft- and hardwoods and in the fixation mechanism of the preservative can play a significant role in fixation and leaching rates of treated wood. Lignin or extractives in wood have been considered to be possible causes of the differences in CCA-C efficacy. Ostmeyer and others (1988) showed that preservative components react with lignin via aromatic and possibly alkene substitution. The nature of this substitution is expected to be through the formation of chromate esters. Dahlgren (1975) showed that wood properties affecting the leaching of CCA from treated wood were the natural pH, the chemical composition, and the anatomy of the wood to be treated. Pizzi and others (1984) concluded that low solubility chromium arsenates precipitated or lightly fixed in both lignin and wood carbohydrates appear to be a majority of the CCA reaction products in wood, followed by Cu fixed on both holocellulose and lignin and copper chromates and by chromium irreversibly complexed on lignin. A certain portion of the CCA preservative reacts with lignin to form stable complexes—esters. A further portion of the CCA appears to be weakly bound, or just precipitated, on the wood carbohydrates, possibly cellulose (Pizzi 1990a). The final reaction products of CCA fixation have been theorized to include precipitates of basic copper arsenate, chromium hydroxide, chromium arsenate, and chromium chromate. The copper cation adsorbs to, or forms complexes with, lignin or cellulose, while copper chromates and chromium arsenates form complexes with lignin or extrac-

tives. Phenolic hydroxyls of lignin and extrac-
tives react with copper and chromium, al-
though it is probable that hexavalent chromi-
um also reacts with other cell-wall
components. In addition to the effects of lignin
and carbohydrate content, extractives play an
important role in CCA fixation, as well. Fla-
vonoids, which are made up of subgroups such
as flavones, flavanes, flavanones, isoflavones,
readily form complexes with metal ions (Fen-
gel and Wegener 1984). Metal-flavonoid com-
plexes apparently form more readily than
those with other wood compounds. Flavonoid-
CCA mixtures precipitate almost instantly at
room temperature, while it may take a few
hours for a lignin-CCA mixture to precipitate
completely (Pizzi et al. 1986).

The literature indicates that differences in
the chemical composition of wood, and espe-
cially the type and content of lignin, may af-
fect the rate of CCA fixation and its subse-
quent leachability. Because compression wood
differs significantly from normal softwood in
both lignin and carbohydrate content, it is
probable that the rate of fixation in compres-
sion wood will be different from that of nor-
mal softwood and that the fixation products
may also differ. Consequently, the rate of
leaching of CCA components from compres-
sion wood may differ significantly from that
of normal wood. Understanding these rates
will be important in developing models to pre-
dict leaching rates from various wood species,
especially when compression wood percent-
ages vary widely among tree sources.

MATERIALS AND METHODS

Wood blocks

A leaning red pine tree, 30.5 cm (12 in.) in
diameter, was cut from central Wisconsin,
United States. Two 80-cm-(31.5-in.-) long sec-
tions were cut from the tree and delivered to
the USDA Forest Service, Forest Products
Laboratory in Madison, WI, where they were
placed in a room maintained at 2°C (36°F).
Four boards, 3.2 cm (1.25 in.) thick by 10 to
20 cm (4 to 8 in.) wide, were cut from the

sapwood portion of the compression wood and
normal wood zones of each log section. The
boards were then dried to below 20% moisture
content (MC) and planed to 19 mm (0.75 in.)
thick. The boards were then cut to obtain 19-
mm (0.75-in.) blocks. The blocks were free of
knots and visible concentration of resins and
showed no visible evidence of infection by
mold, stain, or wood-destroying fungi. The
blocks were conditioned to 12% MC in a con-
ditioning room maintained at 23°C ± 2 (74°F
± 4) and 65% ± 5% relative humidity (RH),
and all blocks were numbered and weighed to
the nearest 0.01 g.

Chemical analyses of compression and
normal wood

Twelve randomly selected blocks from each
of the four boards were retained for chemical
analysis. These blocks were ground to pass
through a 20-mesh screen (0.841-mm open-
ings), and the ground wood was analyzed for
Klason lignin content, acid-soluble lignin con-
tent, wood sugar content, cold water solubility,
hot water solubility, 1% sodium hydroxide
solubility, ethanol solubility, ethanol-benzene
solubility, and pH. Wood sugars were deter-
mined by subjecting the samples to acid hy-
drolysis and then analyzing the hydrolysates
using high pH anion exchange chromatogra-
phy with pulsed ampermetric detection (Davis
1998). Cold and hot water solubilities, 1% so-
dium hydroxide solubility, and ethanol and
ethanol-benzene solubilities of compression
and normal wood were determined according
to TAPPI Test Methods T207 om-93, T212
om-93, and T204 om-88 (TAPPI 1996), re-
spectively. The loss in weight of extracted
wood was determined and calculated as per-
centage solubility. For pH determination of
compression and normal wood, one part by
weight of ground sawdust (to pass 40-mesh
screen (0.420-mm openings)) was placed in
three parts of distilled water. The sample and
water were mixed until the sawdust was wet,
and the pH was then measured by a glass elec-

trode with a digital pH meter after 10 min and after 24 h.

Scanning electron microscope examinations of compression and normal wood

The specimens were soaked in water and surfaced on a sliding microtome. The specimens were then dried and mounted on aluminum stubs with silver paste and coated with gold. The compression and normal wood specimens were then imaged using a scanning electron microscope at 15 kV.

Preservative treatment

All of the blocks were vacuum-treated in a single charge using an oxide-based 1.0% CCA-C solution. The blocks were placed in a treatment cylinder, and the pressure was reduced to 14 kPa (4 inHg) for 20 min. Then the treating solution was introduced and the vacuum was released. After 30 min, the blocks were removed from the solution, wiped lightly to remove surface preservative solution, and immediately weighed to the nearest 0.01 g. Then the amount of preservative absorbed by the blocks was calculated. The treated blocks were stored in plastic bags at 23°C ± 2 (74°F ± 4) and 65% ± 5 RH for fixation periods of 0, 6, 24, 48, 96, 192, or 336 h.

Analysis of preservative retention

After post-treatment conditioning, 15 blocks were randomly selected from each board to determine chromium, copper, and arsenic retention. Each block was ground to pass a 30-mesh screen (0.595-mm openings) and analyzed for preservative content by X-ray fluorescence spectroscopy (AWPA 1999a).

Leaching procedure

The leaching procedures were similar to AWPA Standard Method E11-97 (AWPA 1999b). After each fixation period (0, 6, 24, 48, 96, 192, and 336 h), four replicate samples of four blocks were removed from the conditioning room and reweighed. One replicate set of four blocks was obtained from each of the four original compression wood and normal wood boards. Each set of four blocks was submerged in 200 mL of deionized water in a 250-mL bottle and subjected to a vacuum to impregnate the blocks with the leaching solution. The sample bottles were subjected to mild agitation for a total of 336 h (14 days) with leachates collected after 6, 24, 48, 96, 144, 240, and 336 h. The leachates were analyzed for the amounts of chromium, copper, and arsenic with an atomic absorption spectrometer (AAS), using flame atomization for higher concentrations and graphite furnace atomization for lower concentrations of the elements.

Hexavalent chromium reduction

After each fixation period, two blocks from each of the four original compression and normal wood boards were removed from the conditioning room. The blocks were then squeezed in a hydraulic press at 69 MPa (10,000 lb/in.^{2}) pressure to express solution from the wood. Solution from the blocks was analyzed for hexavalent chromium according to ASTM D 1687, Test Method A, Photometric Diphenylcarbohydrazide (ASTM 1991) using a UV/VIS spectrophotometer with absorbance read at 540 nm. The percentage of hexavalent chromium reduced was determined by comparing the Cr^{6+} concentration in the expressed solution to that originally in the treating solution.

Data analyses

The cumulative amounts of copper, chromium, and arsenic leached after each fixation period were analyzed using a nonparametric analysis of variance (ANOVA) with wood type (compression vs. normal) as the independent variable. A nonparametric ANOVA was also used to compare the percentage of chromium reduced from the hexavalent to trivalent state in normal wood and compression wood.

TABLE 1. *Composition and solubilities of compression and normal wood.*

| Log-board #	Percentage of total sample									Solubility (%)					pH	
	Klason lignin	Acid-soluble lignin	Arabinose	Galactose	Rhamnose	Glucose	Xylose	Mannose	Total carbohydrates	Cold water	Hot water	Ethanol	Ethanol-benzene	1% NaOH	10 min	24 h
Compression wood																
1-1	37.60	64.13	1.10	8.10	0.10	33.20	5.20	6.70	54.60	1.13	2.50	0.38	4.59	16.47	6.29	6.73
1-2	36.20	58.88	1.20	7.30	0.10	35.10	5.40	7.70	56.90	1.26	2.44	0.35	4.47	16.11	5.94	6.71
2-1	34.90	59.40	1.40	5.80	0.10	36.40	5.60	7.90	57.20	1.11	2.30	0.61	5.56	12.80	5.71	6.55
2-2	36.30	59.10	1.30	7.20	0.10	34.40	5.70	7.30	56.20	1.25	2.30	0.60	5.48	14.58	5.59	6.44
Average	36.30	60.38	1.30	7.10	0.10	34.80	5.50	7.40	56.20	1.19	2.39	0.49	5.03	14.99	5.88	6.61
Normal wood																
1-1	28.40	61.60	1.60	1.40	0.10	43.20	5.70	12.00	63.90	1.23	2.25	0.31	3.59	13.38	5.46	6.17
1-2	28.70	61.30	1.70	1.50	0.10	43.00	6.00	11.30	63.60	1.07	1.95	0.30	4.98	13.35	5.47	5.94
2-1	28.50	62.45	1.60	1.50	0.10	43.00	6.00	11.30	63.60	1.11	1.90	0.50	4.94	13.11	5.42	5.73
Average	28.50	61.78	1.60	1.50	0.10	43.10	5.90	11.50	63.70	1.14	2.03	0.37	4.50	13.28	5.45	5.95
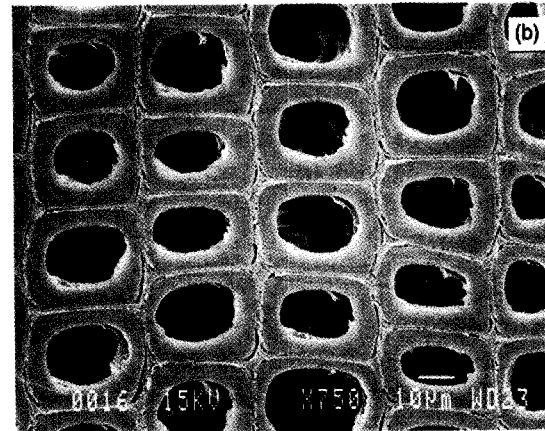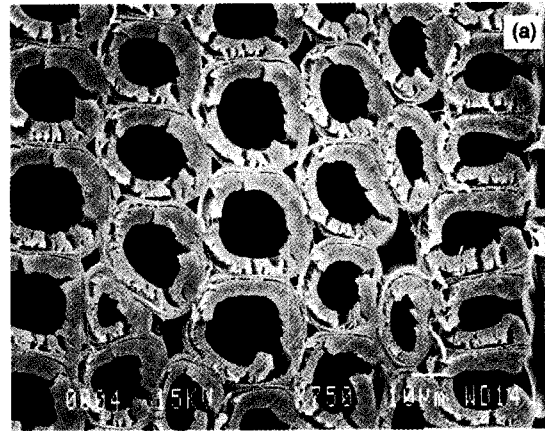
FIG. 1. Scanning electron microscope micrographs showing the structure of (a) compression and (b) normal wood samples.

RESULTS

Chemical analyses of compression and normal wood

Klason lignin content was found to be 36.3% and 28.5% in compression wood and normal wood blocks, respectively (Table 1). Compared with normal wood, compression wood contained about 27% more lignin. Rhamnose, xylose, and arabinose contents were about the same in both wood types; however, galactose content in compression wood was much higher than in normal wood (Table 1). In contrast, compression wood contained

TABLE 2. *Retention of chromated copper arsenate (CCA) in compression and normal wood (oxide basis).*

Log-board #	Retention (kg/m³)											
	Specific gravity		By weight gain CCA		CrCO₃		CuO		As₂O₅		CCA	
	Average	SD	Average	SD	Average	SD	Average	SD	Average	SD	Average	SD
Compression wood												
1-1	0.41	0.02	6.42	0.40	3.31	0.22	1.35	0.05	2.46	0.12	7.12	0.35
1-2	0.40	0.00	6.91	0.60	3.46	0.15	1.41	0.03	2.65	0.14	7.52	0.26
2-1	0.38	0.02	7.08	0.31	3.52	0.17	1.42	0.06	2.65	0.13	7.59	0.33
2-2	0.40	0.02	6.87	0.38	3.66	0.20	1.43	0.06	2.55	0.11	7.64	0.35
Average	0.40	0.02	6.82	0.28	3.49	0.15	1.40	0.04	2.58	0.09	7.47	0.24
Normal wood												
1-1	0.41	0.02	7.10	0.38	3.62	0.17	1.47	0.05	2.73	0.10	7.82	0.29
1-2	0.37	0.01	7.31	0.11	3.68	0.17	1.47	0.05	2.74	0.11	7.89	0.30
2-1	0.36	0.02	7.23	0.39	3.63	0.16	1.43	0.04	2.69	0.07	7.75	0.23
Average	0.38	0.02	7.23	0.11	3.64	0.03	1.46	0.02	2.72	0.03	7.82	0.07

about 35% less mannose compared with normal wood.

The average solubility of compression wood appeared slightly higher than that of normal wood for all of the solvents evaluated (Table 1). This suggests higher solubility of both the carbohydrate and lignin fractions of the compression wood. The higher ethanol and ethanol-benzene solubilities may also be an indicator that the compression wood contains a higher proportion of phenolic compounds such as flavonoids, phlobaphenes, tannins, and stilbenes (Fengel and Wegener 1984). However, the variation between boards within the compression wood and normal wood zones indicates that some of the differences in solubility are a function of vertical location within the tree.

The pH of compression wood was slightly, but consistently, higher than that of normal wood (Table 1). Wood pH is affected by acidic groups, extractives, and mineral salts and also indicates content of carboxyl groups and hydrogen ions (Fengel and Wegener 1984).

SEM examinations of compression and normal wood

In the cross sections of the compression wood samples, the tracheids had a rounded or oval outline, while those in normal wood were more rectangular (Fig. 1). In addition to the circular shape of compression wood tracheids, compression wood had intercellular spaces where three or four tracheids met (Fig. 1a). The rounded outline of the tracheids and numerous intercellular spaces are useful diagnostic features of compression wood (Panshin and De Zeeuw 1980). Another feature in the tracheids of compression wood is the presence of spiral cavities, as shown by the roughness of the cross-sectional surface in Fig. 1a. It has been suggested that these cavities form in the S2 layer because of the large amounts of lignin (Panshin and De Zeeuw 1980). Wall thickness of tracheids is another indicator of compression wood formation, but no profound differences in wall thickness of compression and normal wood tracheids were observed in this study.

Retention of CCA-C

Average retention of CCA-C, as determined by both uptake and chemical analysis, was in the range of 6.8 to 7.8 kg/m³ (0.43 to 0.49 lb/ft³) (Table 2). Retentions were slightly higher when determined by chemical analysis than by uptake and also appeared to be slightly higher in normal wood than in compression wood.

Leaching of copper, chromium, and arsenic

The average amounts of copper, chromium, and arsenic released from the compression and

TABLE 3. *Leaching of chromium, copper, and arsenic from compression and normal wood after various fixation periods.*

Leaching time (h)	Amount released (ppm, elemental basis)[a]								
	0 h[b]			6 h			24 h		
	Cr	Cu	As	Cr	Cu	As	Cr	Cu	As
Compression wood									
6	93.75	22.96	71.74	70.75	14.68	41.25	47.70	3.78	19.63
	3.17	*1.17*	*2.83*	*4.47*	*2.28*	*2.17*	*6.28*	*0.69*	*0.79*
24	41.09	8.21	29.61	44.90	6.66	25.54	34.03	2.74	9.67
	5.26	*1.64*	*2.49*	*5.52*	*1.16*	*2.11*	*5.66*	*1.00*	*1.16*
48	11.47	1.47	6.62	12.29	1.66	8.70	9.48	1.00	6.09
	1.40	*0.17*	*1.18*	*1.40*	*0.21*	*0.94*	*0.94*	*0.25*	*0.39*
96	2.07	0.80	5.83	1.77	0.95	5.36	0.57	0.82	5.91
	0.64	*0.09*	*2.05*	*0.59*	*0.15*	*0.67*	*0.16*	*0.13*	*0.23*
144	0.14	0.22	3.29	0.13	0.30	4.12	0.14	0.35	5.40
	0.06	*0.03*	*0.33*	*0.05*	*0.04*	*0.24*	*0.06*	*0.07*	*0.49*
240	0.15	0.35	4.49	0.19	0.48	5.66	0.17	0.40	6.99
	0.05	*0.05*	*0.33*	*0.04*	*0.07*	*0.45*	*0.05*	*0.04*	*0.32*
336	0.12	0.14	2.04	0.08	0.17	3.14	0.10	0.19	3.74
	0.05	*0.05*	*0.05*	*0.02*	*0.02*	*0.09*	*0.03*	*0.05*	*0.35*
Total	**148.8**	**34.1**	**123.6**	**130.1**	**24.9**	**93.8**	**92.2**	**9.3**	**57.4**
	8.18	***2.92***	***8.43***	***8.43***	***3.14***	***3.06***	***12.80***	***1.91***	***3.26***
Normal wood									
6	104.3	24.80	88.86	82.75	19.86	47.05	59.78	6.34	20.35
	5.19	*0.33*	*3.81*	*3.25*	*1.24*	*2.72*	*2.61*	*0.87*	*1.43*
24	50.12	13.24	32.67	56.40	10.97	27.91	45.40	5.18	11.32
	5.08	*2.54*	*3.23*	*4.81*	*1.60*	*2.18*	*3.12*	*0.69*	*1.70*
48	16.30	2.82	7.47	16.09	2.73	12.04	11.55	1.71	6.58
	1.47	*0.38*	*0.40*	*0.72*	*0.31*	*2.23*	*0.25*	*0.21*	*0.79*
96	3.17	1.09	5.65	2.67	1.17	6.13	1.11	1.07	6.54
	0.51	*0.07*	*0.23*	*0.66*	*0.16*	*0.70*	*0.31*	*0.19*	*0.42*
144	0.14	0.22	3.50	0.16	0.27	4.50	0.15	0.47	5.86
	0.03	*0.05*	*0.07*	*0.02*	*0.06*	*0.26*	*0.02*	*0.12*	*0.40*
240	0.17	0.30	4.66	0.16	0.58	5.31	0.17	0.53	7.24
	0.01	*0.03*	*0.16*	*0.03*	*0.22*	*0.34*	*0.03*	*0.06*	*0.13*
336	0.12	0.12	1.97	0.10	0.19	3.37	0.12	0.22	3.94
	0.03	*0.03*	*0.08*	*0.01*	*0.02*	*0.15*	*0.02*	*0.05*	*0.22*
Total	**174.3**	**42.6**	**144.8**	**158.3**	**35.8**	**106.3**	**118.3**	**15.5**	**61.8**
	6.39	***3.06***	***3.98***	***7.23***	***3.28***	***7.84***	***5.27***	***1.94***	***4.81***
P value[c]	**0.0062**	**0.0151**	**0.0132**	**0.0032**	**0.0165**	**0.0097**	**0.0218**	**0.014**	**0.2661**

[a] Numbers in italics represent one standard deviation from the mean.
[b] Fixation time.
[c] *P* value indicates the statistical probability of observing a difference greater than or equal to that observed between the total amount leached from the normal wood samples and that leached from the compression wood samples.

normal wood blocks are shown Table 3, while the percentage of each element leached is shown in Fig. 2. The presence of compression wood significantly ($\alpha = 0.05$) lessened the leaching of chromium for all fixation periods (Table 3). This effect was proportionately greatest after 192 and 336 h of fixation, when the amount of chromium released from both types of wood was relatively small. After 0, 6, 24, 48, and 96 h of fixation, the average total amount of chromium leached from the normal wood blocks was 17% to 32% greater than that of compression wood blocks. However, in the blocks fixed for 336 h, the total chromium release from the normal wood blocks was almost three times greater than that

TABLE 3. *Extended.*

| Amount released (ppm, elemental basis)[a] | | | | | | | | | | | |
| 48 h | | | 96 h | | | 192 h | | | 336 h | | |
Cr	Cu	As	Cr	Cu	As	Cr	Cu	As	Cr	Cu	As
Compression wood											
25.35	1.46	8.72	15.30	0.63	1.50	6.94	0.30	1.01	0.42	0.29	0.40
3.09	*0.20*	*2.46*	*2.60*	*0.18*	*0.22*	*2.51*	*0.05*	*0.76*	*0.09*	*0.04*	*0.16*
21.44	1.47	8.15	15.57	0.91	2.58	6.38	0.43	1.59	0.51	0.41	0.65
2.10	*0.23*	*0.99*	*2.45*	*0.27*	*0.40*	*2.97*	*0.08*	*0.21*	*0.04*	*0.03*	*0.26*
7.56	0.70	3.78	5.97	0.37	2.50	1.16	0.24	1.09	0.40	0.35	1.18
0.26	*0.05*	*0.17*	*1.14*	*0.08*	*0.43*	*0.61*	*0.04*	*0.13*	*0.06*	*0.05*	*0.35*
0.52	0.46	5.49	0.73	0.36	3.22	0.31	0.27	1.16	0.34	0.33	1.59
0.11	*0.03*	*0.20*	*0.34*	*0.09*	*0.54*	*0.02*	*0.05*	*0.17*	*0.05*	*0.06*	*0.40*
0.15	0.29	5.25	0.16	0.38	3.60	0.20	0.17	1.17	0.24	0.23	2.13
0.05	*0.03*	*0.24*	*0.02*	*0.05*	*0.70*	*0.06*	*0.02*	*0.05*	*0.03*	*0.03*	*0.31*
0.17	0.41	5.06	0.18	0.27	2.89	0.21	0.32	3.06	0.24	0.35	3.19
0.03	*0.08*	*0.30*	*0.04*	*0.03*	*0.43*	*0.02*	*0.06*	*0.40*	*0.04*	*0.04*	*0.19*
0.11	0.24	3.80	0.18	0.22	4.50	0.18	0.30	3.84	0.19	0.35	3.24
0.03	*0.03*	*0.43*	*0.05*	*0.03*	*0.25*	*0.02*	*0.05*	*0.27*	*0.04*	*0.04*	*0.19*
55.3	**5.0**	**40.2**	**3.81**	**3.1**	**20.8**	**15.4**	**2.0**	**12.9**	**2.3**	**2.3**	**12.4**
5.28	***0.41***	***4.58***	***6.27***	***0.56***	***2.68***	***6.08***	***0.15***	***1.14***	***0.17***	***0.11***	***2.44***
Normal wood											
29.79	2.49	7.85	19.75	0.95	1.51	12.02	0.44	0.54	2.00	0.38	0.32
0.82	*0.36*	*0.61*	*0.87*	*0.08*	*0.30*	*0.59*	*0.06*	*0.07*	*1.21*	*0.06*	*0.05*
26.77	2.73	9.01	19.82	1.33	2.35	12.81	0.62	1.27	2.14	0.59	0.44
0.79	*0.34*	*0.31*	*1.29*	*0.22*	*0.39*	*1.09*	*0.13*	*0.09*	*1.15*	*0.06*	*0.05*
9.88	1.20	4.32	8.85	0.54	2.52	3.51	0.32	0.88	1.01	0.39	0.90
0.81	*0.13*	*0.22*	*0.79*	*0.14*	*0.36*	*0.67*	*0.05*	*0.06*	*0.45*	*0.06*	*0.11*
0.73	0.59	5.84	1.29	0.51	3.17	0.91	0.26	0.97	0.48	0.40	1.20
0.09	*0.09*	*0.33*	*0.31*	*0.04*	*0.37*	*0.28*	*0.01*	*0.11*	*0.08*	*0.02*	*0.16*
0.17	0.44	5.77	0.15	0.40	3.33	0.15	0.14	1.26	0.30	0.26	1.66
0.03	*0.07*	*0.36*	*0.01*	*0.01*	*0.30*	*0.01*	*0.01*	*0.19*	*0.06*	*0.03*	*0.24*
0.19	0.50	5.77	0.16	0.31	2.52	0.23	0.32	2.58	0.27	0.33	2.60
0.01	*0.10*	*0.25*	*0.02*	*0.05*	*0.30*	*0.01*	*0.04*	*0.20*	*0.07*	*0.07*	*0.25*
0.13	0.28	4.43	0.14	0.20	4.57	0.18	0.25	3.54	0.21	0.43	2.48
0.01	*0.05*	*0.23*	*0.01*	*0.04*	*0.27*	*0.02*	*0.04*	*0.47*	*0.04*	*0.08*	*0.23*
67.7	**8.2**	**43.0**	**50.1**	**4.2**	**20.0**	**29.8**	**2.3**	**11.0**	**6.4**	**2.8**	**9.6**
1.89	***1.00***	***1.61***	***2.51***	***0.49***	***2.22***	***2.15***	***0.26***	***0.91***	***2.72***	***0.26***	***0.79***
0.0137	**0.0085**	**0.3989**	**0.0229**	**0.0566**	**0.6128**	**0.014**	**0.1233**	**0.0762**	**0.0256**	**0.0239**	**0.142**

of the compression wood blocks. Differences in the amount of chromium released were also a function of the number of hours that the samples had been leached. The compression wood effect was most apparent during the early stages of leaching, when the rate of release was greatest. For example, after 192 h of fixation, average chromium release from the normal wood blocks was two to three times greater than that of compression wood blocks during the first 96 h of leaching, but this difference largely disappeared during the latter stages of leaching. A similar trend was apparent in samples that had been fixed for 336 h.

Compression wood blocks also released less copper than normal wood blocks. However, compared with chromium, this relative difference was most apparent during the early and intermediate stages of fixation (Table 3). The average total amount of copper released from
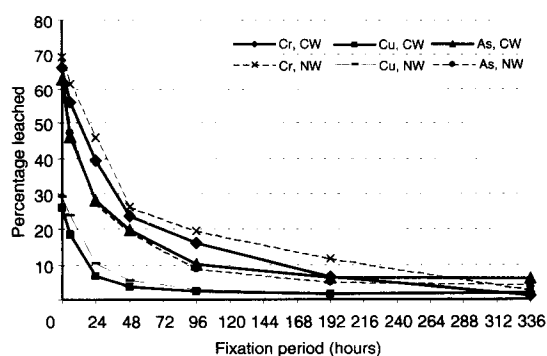
FIG. 2. Percentage of chromium, copper, and arsenic leached from normal (NW) and compression wood (CW) after various fixation periods.

TABLE 4. *Percentage of hexavalent chromium reduced after each fixation period.*

Fixation time (h)	Cr^{6+} reduction (%)				
	Compression wood		Normal wood		
	Mean	SD	Mean	SD	P value[a]
0	42.03	3.30	37.24	2.45	0.008
6	51.29	7.25	46.09	4.70	0.1348
24	64.63	2.38	64.08	4.99	0.7932
48	75.63	4.61	67.00	4.76	0.0051
96	83.21	2.66	76.08	2.99	0.0005
192	94.86	1.32	91.84	2.65	0.0127
336	99.93	0.03	98.61	2.36	0.1472

[a] P value indicates the statistical probability of observing a difference greater than or equal to that observed between the percentage reduced in the normal wood samples and the percentage reduced in the compression wood samples.

the normal wood blocks was 67% and 63% greater than that from the compression wood blocks after 24 and 48 h, respectively, but only 15% greater after 192 h of fixation. Statistically, the release of copper from compression wood was found to be greater than that from normal wood after 0, 6, 24, 48, and 336 h of fixation ($\alpha = 0.05$). However, the significance of the difference at 336 h must be noted with some skepticism, given the small absolute difference between the two values (2.3 ppm for compression wood compared with 2.8 ppm for normal wood). Thus, although copper is fixed more rapidly to compression wood than to normal wood, there is little difference in the rate of release from well-fixed compression wood and normal wood.

The effect of compression wood on the release of arsenic was more complex than that noted for copper or chromium (Table 3). As with copper, arsenic release was significantly ($\alpha = 0.05$) lower from the compression wood than from normal wood blocks during the early stages of fixation. However, this trend disappeared and then eventually reversed during the latter stages of fixation (Fig. 2). Although the difference was not statistically significant, arsenic release from compression wood was 29% greater than that of normal wood after 336 h of fixation.

Hexavalent chromium reduction

Reduction of Cr^{6+} was more complete in compression wood at most fixation times; this

difference was statistically significant after 0, 48, 96, and 192 h of fixation (Table 4). The effect of compression wood on fixation rate was most apparent in the blocks conditioned for 0, 48, and 96 h. In the compression wood blocks fixed for 48 h, percentage Cr^{6+} reduction was about 13% greater than that of normal wood blocks. At 0 h of fixation, Cr^{6+} reduction was 42% in compression wood while only 37% in normal wood. On the other hand, in blocks fixed for 336 h, Cr^{6+} reduction rate reached 99.9% and 98.6% for compression and normal wood blocks, respectively.

DISCUSSION

The results of this study indicate that differences in wood structure and chemical composition, even within sapwood of the same tree, can significantly affect fixation and leaching of CCA-C. It is likely that lignin content, which proved to be different between compression and normal wood in this study, plays a major role in CCA fixation. Previous comparative studies generally agreed that CCA components are more leachable from hardwoods than softwoods (Becker and Buchmann 1966; Cooper 1990; Nicholson and Levi 1971; Yamamoto and Rokoba 1991). This phenomenon has been attributed to the lower content and type of lignin in hardwoods (Butcher and Nilsson 1982; Cooper 1990; Gray 1993). Softwood species also differ in susceptibility to the leaching of CCA. Slow fixation and high

leaching rates have been noted for Japanese cedar (Yamamoto and Rokoba 1991), and Cooper (1990) reported that CCA leaching rates from small red pine specimens were approximately double those from lodgepole pine, Douglas-fir, and redcedar. Lignin content may be important in explaining some of these species differences, and the greater lignin content of the compression wood appears to be a likely source of additional reaction sites.

Extractive content also plays an important role in CCA fixation. Table 1 shows that ethanol solubility of compression wood was slightly higher than normal wood, and ethanol particularly dissolves flavonoids from wood. Metal-flavonoid complexes precipitate much faster than lignin-CCA complexes (Pizzi et al. 1986). Of CCA components, chromium forms the most stable complexes with flavonoids, while arsenic reacts at a much slower rate than chromium and copper (Pizzi et al. 1986). It has been reported that the higher extractive content in Douglas-fir heartwood accelerated CCA fixation relative to the sapwood (Forsyth and Morrell 1990) and that extractives contribute to rapid fixation in eucalyptus (Dahlgren 1975). Also, Kennedy and Palmer (1994) reported that arsenic leaching from CCA-C treated pine heartwood was approximately twice that from sapwood, and they suggested that the presence of extractives in the heartwood interfered with the fixation process. This phenomenon might explain why arsenic leaching in compression wood after the 96-, 192-, and 336-h fixation periods appeared higher than the normal wood in this study.

CONCLUSIONS

The results of this study show that presence of compression wood can affect both the rate of CCA fixation and the amount of CCA elements leached from the treated wood. Differences in the chemical composition of compression wood caused more rapid reduction of chromium from the hexavalent to trivalent valence state compared with normal wood. This, in turn, led to a decrease in the amount of

leachable chromium at each stage of fixation. Leaching of copper was also less in compression wood. These results indicate a greater abundance of reactive sites for copper and chromium within the wood structure of compression wood. Leaching of arsenic was also initially lower from compression wood, but this trend appeared to reverse as fixation proceeded. These findings support the premise that reactive sites within lignin play an important role in CCA fixation and may also help explain some of the species-related differences in CCA fixation and leaching that have been noted in previous studies. These findings may also allow us to better predict the relative rate of fixation for a particular species or source of wood.

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