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Section 3

Wood Protecting Chemicals

**Effect of Compression Wood
on Leaching of Chromium, Copper, and Arsenic
From CCA-C Treated Red Pine (*Pinus resinosa* Ait.)¹**

S. Nami Kartal
Visiting Scientist
USDA Forest Service, Forest Products Laboratory
Madison, WI, USA

Stan Lebow
Research Forest Products Technologist
USDA Forest Service, Forest Products Laboratory
Madison, WI, USA

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Sweden

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Abstract

In this study, the effect of compression wood formation on the release rate of chromium, copper, and arsenic elements from red pine (*Pinus resinosa* Ait) was investigated. Wood blocks from red pine containing compression and normal wood portions were treated with a 1.0% CCA-C solution and were then allowed to fix at $23 \pm 2^\circ\text{C}$ ($74 \pm 4^\circ\text{F}$) for 0, 6, 24, 48, 96, 192, and 336 hours. After each fixation period, the blocks removed from the conditioning room were subjected to 336 hours of leaching. Less chromium and copper elements were released from the compression wood blocks. For chromium, the biggest effect occurred after the 192- and 336-hour fixation periods. In the normal wood blocks fixed for 336 hours, the average chromium release rate after 6 hours of leaching was almost five times greater than that of blocks containing compression wood. Copper and arsenic release was also affected by compression wood, but for these two elements, the effect diminished during the later stages of fixation.

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

Introduction

Compression wood is a reaction wood formed in gymnosperms in response to various growth stresses. This wood has different properties than 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. In addition, compression wood has significantly different carbohydrate and lignin composition than that of normal wood. Compression wood differs from normal wood not only in the proportion of the major constituents but in their distribution in the cell walls as well (Timell, 1986).

Compression wood develops most frequently and rapidly in vigorous, fast growing trees and is very common and probably more widespread than is generally thought. There is hardly a forest or plantation tree that does not have at least some compression wood in its stem (Timell, 1986). 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 pines consists of severe compression wood, and that 25% contains mild compression wood (Timell, 1986). Plantation-grown *P. resinosa* trees in New York that were leaning 5 degrees contained 5% to 40% compression wood, while those leaning 10 to 40 degrees contained 40% to 70% (Timell, 1986). In the spruce forests of Canada, 15% of the wood might be compression wood (Timell, 1986). Under adverse environmental conditions, forest and plantation stands can contain as much as 40% compression wood. Even in the most improved and best-managed conifer forest, no tree stem can be expected to be entirely free of compression wood (Timell, 1986).

CCA-C, the most widely used waterborne preservative in the United States, 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 (Pizzi, 1990a,b, 1980, 1981, 1982; Pizzi et al., 1984; Cooper and Roy, 1994; Greaves, 1972, 1973, 1974; Wilson, 1971; Dahlgren, 1975; Henshaw, 1979; Yamamoto and Matsuoka, 1989; Yamamoto and Rokoba, 1991; Carpenter and Gardner, 1993; Englund and Gardner, 1993). According to those 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 one of the causes of the differences in CCA-C efficacy. Ostmeyer et al. (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 et al. (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 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 extractives. Phenolic hydroxyls of lignin and extractives react with copper and chromium, although it is probable that hexavalent chromium also reacts with other cell wall components (Lebow, 1996).

The literature indicates that differences in the chemical composition of wood, and especially the type and content of lignin, may affect the rate of CCA fixation and its subsequent leachability. Because compression wood differs significantly from normal softwood in both lignin and carbohydrate content, it is probable that the rate of fixation in compression wood will be different than that of normal softwood and that the fixation products may also differ. Consequently, the rate of leaching of CCA components from compression wood may differ significantly from that of normal wood. Understanding these rates will be important in development of models to predict leaching rates from various wood species, especially where compression wood percentages vary widely among tree sources.

Materials and Methods

Wood Blocks: A leaning red pine tree *P. resinosa*, 30.5 cm (12 in.) in diameter, was cut from central Wisconsin, USA. Two 80-cm (31.5-in.) sections were cut from the tree and sent to the USDA Forest Service, Forest Products Laboratory (FPL), where they were placed in a room maintained at 2°C (36°F). Four boards, 3.2 cm (1.25 in.) thick by 10 cm (4 in.) to 20 cm (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 conditioning room maintained at $23 \pm 2^\circ\text{C}$ ($74 \pm 4^\circ\text{F}$) and at $65 \pm 5\%$ 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 openings), and the ground wood was analyzed for klason lignin and wood sugar content. Wood sugars were determined by subjecting the samples to acid hydrolysis, and then analyzing the hydrolysates using high pH anion exchange chromatography with pulsed amperometric detection (Davis, 1998).

Preservative Treatment: All of the blocks were treated in a single charge using an oxide-based 1.0% CCA-C solution. The blocks were placed in a treatment cylinder, subjected to -14 kPa (4 in.) vacuum for 20 min, 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. The amount of preservative absorbed by the blocks was calculated.

Post-Treatment Conditions: The treated blocks were stored in plastic bags at $23 \pm 2^\circ\text{C}$ ($74 \pm 4^\circ\text{F}$) for fixation periods of 0, 6, 24, 48, 96, 192, or 336 hours.

X-Ray Analyses of the Blocks: 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 using an ASOMA X-ray fluorescence analyzer (ASOMA Instruments, Austin, Texas).

Leaching Procedure: The leaching procedures were similar to AWWA Standard Method E11-97 (AWWA, 1997). After each fixation period (0, 6, 24, 48, 96, 192, and 336 hours), 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 placed into a 250-mL bottle, submerged in 200 mL of deionized water, 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 hours (14 days) with leachates collected after 6, 24, 48, 96, 144, 240, and 336-hour intervals. 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.

Data Analysis: Statistical analysis of the data generated in this study is in progress. Preliminary analysis has been completed on total (cumulative) amounts of copper, chromium, and arsenic released, using a nonparametric analysis of variance (ANOVA) with wood type (compression vs. normal) and fixation period as independent variables.

Results and Discussion

Lignin and sugar analyses for compression and normal wood are presented in Table 1. Klason lignin content was found to be 36.3% and 28.5% in compression wood and normal wood blocks, respectively. 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. In contrast, compression wood contained about 35% less mannose than did normal wood.

Average retention of CCA-C, as determined by both uptake and chemical analysis, was slightly higher in normal wood than in compression wood (Table 2). However, preliminary statistical analysis found no significant difference in uptake retention between the two groups.

Average release rates from the compression and normal wood blocks are shown in Table 3. The presence of compression wood appeared to reduce leaching for all fixation periods, but this effect was proportionately greatest after 192 and 336 hours of fixation. This effect was most apparent during the early stages of leaching, when the rate of release was greatest. In the normal wood blocks fixed for 192 hours, average chromium release was three times greater than that of compression wood blocks after 96 hours of leaching, while the release rate was almost the same value after 144 hours of leaching in both types of wood. In 336-hour fixed normal wood samples, average chromium release after 6 hours of leaching was almost five times greater than that of compression wood samples. However, the difference in release rate between compression and normal wood blocks decreased gradually after the 96-hour leaching.

The effect of fixation time on the cumulative release of chromium from compression and normal wood blocks after 336 hours of leaching is shown in Figure 1. After 0, 6, 24, 48, 96, and 192 hours 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 hours, the cumulative chromium release from the normal wood blocks was almost three times greater than that of the compression wood blocks. Preliminary statistical analysis indicates that cumulative chromium release from normal wood blocks was greater than from compression wood blocks for all fixation periods.

Compression wood blocks also released less copper, although this effect was most pronounced in the early stages of fixation (Fig. 1). The average total amount of copper released from the normal wood blocks was 67% and 63% greater than that of the compression wood blocks after 24 and 48 hours, respectively, but only 20% greater after 336 hours of fixation. Thus, although copper is fixed more rapidly to compression wood than normal wood, there is less difference in the rate of release from well-fixed compression wood and normal wood. However, as for chromium, preliminary statistical analysis indicates that cumulative copper release from normal wood blocks was greater than from compression wood blocks for all fixation periods.

Compression wood had less effect on the rate of release of arsenic from the blocks. As with copper, the rate of release was slower from the compression wood blocks but only during the early stages of fixation. Total arsenic release in the normal wood fixed for 0, 6, 24, and 48 hours was greater than that of compression wood, but less than that of compression wood fixed for 96, 192, and 336 hours (Fig. 1). Statistical analysis of arsenic release rate differences between normal and compression wood is complicated by this interaction with fixation period, and more detailed analysis is in progress.

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 is one difference between compression wood and normal wood, plays a major role in CCA fixation. Previous comparative studies generally agree 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 smaller amount and different 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 fast 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 an important variable in explaining some of these species differences.

Conclusions

Release of copper and chromium from compression wood blocks used in this study was less than that from the normal wood blocks. In general, compression wood contains high contents of lignin and galactose, and the compression wood blocks used in this study contained 27% more lignin than the normal wood blocks. It is possible that the CCA components, especially chromium and copper, reacted and formed complexes with the higher lignin content in the compression wood blocks, thus reducing the rate of leaching. This finding may help to explain some of the species related differences in CCA fixation and leaching that have been noted in previous studies, and it may also allow us to predict the relative rate of fixation for a particular species or source of wood. Better understanding of the factors that affect the fixation and leaching of CCA may help mitigate environmental concerns with CCA treated wood. However, further studies are needed to better understand reaction mechanisms and products of CCA fixation in compression wood. As a first step, we are conducting a study to examine the reduction of Cr^{6+} to Cr^{3+} in compression wood.

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Table 1. Lignin content and carbohydrate composition of the compression and normal wood boards.

Log-board No.	Percentage of total sample							
	Klason lignin	Arabinose	Galactose	Rhamnose	Glucose	Xylose	Mannose	Total carbohydrate
Compression wood								
1-1	37.6	1.1	8.1	0.1	33.2	5.2	6.7	54.6
1-2	36.2	1.2	7.3	0.1	35.1	5.4	7.7	56.9
2-1	34.9	1.4	5.8	0.1	36.4	5.6	7.9	57.2
2-2	36.3	1.3	7.2	0.1	34.4	5.7	7.3	56.2
Average	36.3	1.3	7.1	0.1	34.8	5.5	7.4	56.2
Normal wood								
1-1	28.4	1.6	1.4	0.1	43.2	5.7	12.0	63.9
1-2	28.7	1.7	1.5	0.1	43.0	6.0	11.3	63.6
2-1	28.5	1.6	1.5	0.1	43.0	6.0	11.3	63.6
Average	28.5	1.6	1.5	0.1	43.1	5.9	11.5	63.7

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

Log-board No.	Specific gravity	Retention (kg/m ³)				
		By weight gain	By x-ray analyses			
		CCA	CrO ₃	CuO	As ₂ O ₅	CCA
Compression wood						
1-1	0.41	6.42	3.31	1.35	2.46	7.12
1-2	0.40	6.91	3.46	1.41	2.65	7.52
2-1	0.38	7.08	3.52	1.42	2.65	7.59
2-2	0.40	6.87	3.66	1.43	2.55	7.64
Average	0.40	6.82	3.49	1.40	2.97	7.47
Normal wood						
1-1	0.41	7.10	3.62	1.47	2.73	7.82
1-2	0.37	7.31	3.68	1.47	2.74	7.89
2-1	0.36	7.23	3.63	1.43	2.69	7.75
Average	0.38	7.23	3.64	1.46	2.72	7.82

Table 3. Release rates from the compression and normal wood blocks treated with CCA. Each value is the average of four replicates.

Fixation time (h)	Leaching time (h)	Release rate (ppm/h, elemental basis)					
		Compression wood			Normal wood		
		Cr	Cu	As	Cr	Cu	As
0	6	15.62	3.84	11.98	17.40	4.13	14.81
	24	2.28	0.46	1.65	2.79	0.74	1.82
	48	0.48	0.06	0.28	0.68	0.12	0.31
	96	0.04	0.02	0.12	0.07	0.02	0.12
	144	<0.01	<0.01	0.07	<0.01	<0.01	0.07
	240	<0.01	<0.01	0.05	<0.01	<0.01	0.05
	336	<0.01	<0.01	0.02	<0.01	<0.01	0.02
6	6	11.79	2.45	6.88	13.80	3.31	7.84
	24	2.49	0.37	1.42	3.13	0.61	1.55
	48	0.51	0.07	0.36	0.67	0.11	0.50
	96	0.04	0.02	0.11	0.06	0.02	0.13
	144	<0.01	0.01	0.09	<0.01	0.01	0.09
	240	<0.01	0.01	0.06	<0.01	0.01	0.06
	336	<0.01	<0.01	0.03	<0.01	<0.01	0.04
24	6	7.95	0.63	3.27	9.96	1.06	3.39
	24	1.90	0.15	0.54	2.52	0.29	0.63
	48	0.40	0.04	0.25	0.48	0.07	0.27
	96	0.01	0.02	0.12	0.02	0.02	0.14
	144	0.03	0.07	0.11	0.03	0.01	0.12
	240	<0.01	<0.01	0.07	<0.01	0.01	0.08
	336	<0.01	<0.01	0.04	<0.01	<0.01	0.04
48	6	4.22	0.24	1.45	4.97	0.42	1.31
	24	1.19	0.08	0.45	1.49	0.15	0.50
	48	0.32	0.03	0.16	0.41	0.05	0.18
	96	0.01	0.01	0.11	0.02	0.01	0.12
	144	<0.01	0.01	0.11	<0.01	0.01	0.12
	240	<0.01	<0.01	0.05	<0.01	0.01	0.06
	336	<0.01	<0.01	0.04	<0.01	<0.01	0.05
96	6	2.55	0.10	0.25	3.29	0.16	0.25
	24	0.87	0.05	0.14	1.10	0.07	0.13
	48	0.25	0.02	0.10	0.37	0.02	0.11
	96	0.02	0.01	0.07	0.03	0.01	0.07
	144	<0.01	0.01	0.08	<0.01	0.01	0.07
	240	<0.01	<0.01	0.03	<0.01	<0.01	0.03
	336	<0.01	<0.01	0.05	<0.01	<0.01	0.05
192	6	1.16	0.05	0.17	2.00	0.07	0.09
	24	0.35	0.02	0.09	0.71	0.03	0.07
	48	0.05	0.01	0.05	0.15	0.01	0.04
	96	0.01	0.01	0.02	0.02	0.01	0.02
	144	<0.01	<0.01	0.02	<0.01	<0.01	0.03
	240	<0.01	<0.01	0.03	<0.01	<0.01	0.03
	336	<0.01	<0.01	0.04	<0.01	<0.01	0.04
336	6	0.07	0.05	0.07	0.33	0.06	0.05
	24	0.03	0.02	0.04	0.12	0.03	0.02
	48	0.02	0.02	0.05	0.04	0.02	0.04
	96	0.01	0.01	0.03	0.01	0.01	0.03
	144	0.01	0.01	<0.01	0.01	0.01	0.03
	240	<0.01	<0.01	0.03	<0.01	<0.01	0.03
	336	<0.01	<0.01	0.03	<0.01	0.01	0.03

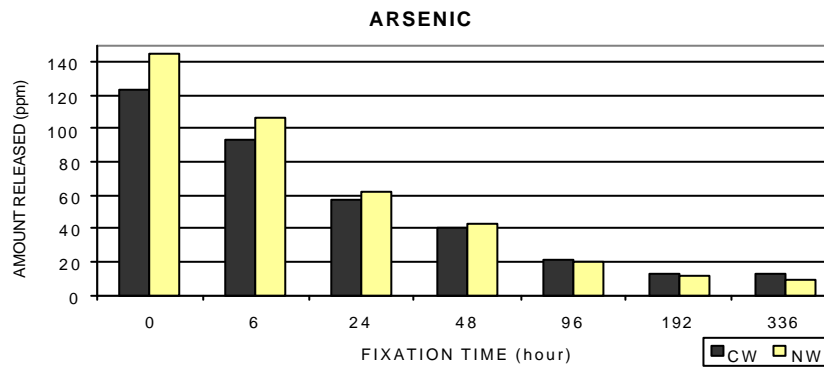
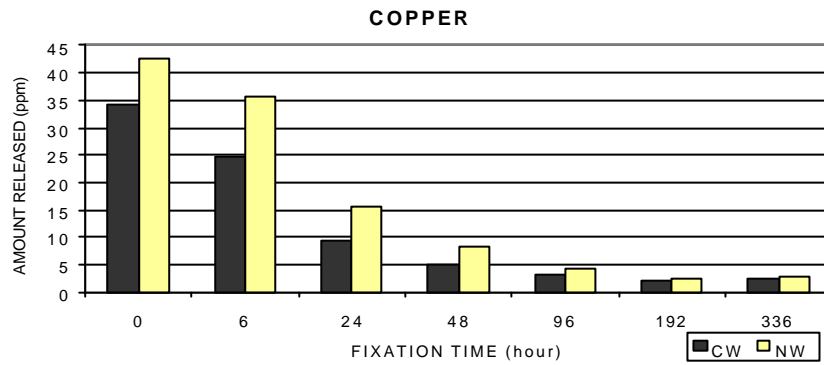
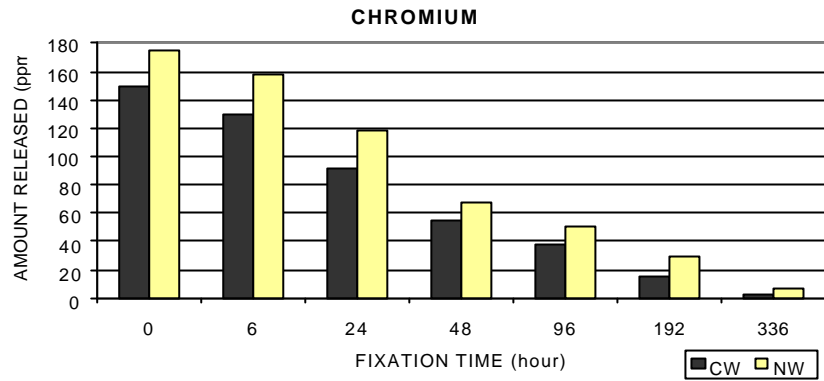


Figure 1: Effect of fixation time on cumulative release of chromium, copper, and arsenic from compression and normal wood blocks after 336 hours of leaching (CW, compression wood; NW, normal wood).