Fixation and leaching characteristics of Douglas-fir treated with CCA-C

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Abstract

Fixation and leaching characteristics of chromated copper arsenate (CCA)-treated Douglas-fir sapwood and heartwood were evaluated using the expressate method and the American Wood Protection Association (AWPA) E11–97 leaching procedure. CCA fixation, monitored by hexavalent chromium reduction, was much faster in heartwood than in sapwood; copper and arsenic fixation in heartwood appeared to be incomplete, regardless of the duration of the fixation time. Poor fixation of copper and arsenic in heartwood was confirmed using leaching tests. Based on the results, we conclude that CCA is not an appropriate preservative for Douglas-fir heartwood because of its poor fixation quality. Therefore, the use of CCA-treated Douglas-fir products in environmentally sensitive areas should be restricted or banned.

Douglas-fir (*Pseudotsuga menziesii* [Mirb.] Franco var. *menziesii*) imported from North America and New Zealand is one of the major wood species for exterior applications that require protection with preservatives in Korea. This refractory species is treated exclusively with ammoniacal copper zinc arsenate (ACZA) or ammoniacal formulations of copper-based preservatives, such as alkaline copper quat (ACQ-B) in the North American wood-treating industry. In the Korean preservation industry, however, chromated copper arsenate (CCA) is still used to treat Douglas-fir. All CCA-treated products should be properly fixed before shipment because incomplete fixation may allow preservative components to leach out from the treated wood into the surrounding environment. The leaching of CCA components has raised public concern about the risk for environmental pollution and hazards to human health.

Although it has long been recognized that complete fixation of CCA components in treated wood is important before shipment, the fixation and leaching characteristics in Douglas-fir remains poorly understood (Forsyth and Morrell 1990, Guo et al. 2002). This study was, therefore, conducted to investigate the fixation and leaching characteristics of CCA-treated Douglas-fir sapwood and heartwood.

Materials and methods

Douglas-fir trees approximately 45 to 50 years in age and 35 cm in diameter at breast height were harvested from plantation forest at the northern South Island of New Zealand. Average heartwood content was around 50 percent and average growth ring width of heartwood and sapwood was 8.5 and 4 mm, respectively. Each tree was bucked into 3.6-m-long logs. Logs were randomly selected from shipments into Korea and then sawn into 40-mm-thick boards, and then conditioned to approximately 15 percent moisture content (MC). Sapwood and heartwood samples measuring 25 by 25 mm in cross section by 80 mm in length were cut from air-dried boards. Ten sapwood and heartwood samples were used to provide a range of estimates of the extent of fixation over time. Samples were treated using a full-cell process consisting of a 30-minute initial vacuum of 760 mm Hg, and then the cylinder was filled with 2 percent (w/v) CCA-C solution, followed by a pressure of 14 kg/cm^2 until refusal. No final vacuum was employed. Samples were not end-coated to guarantee full absorption

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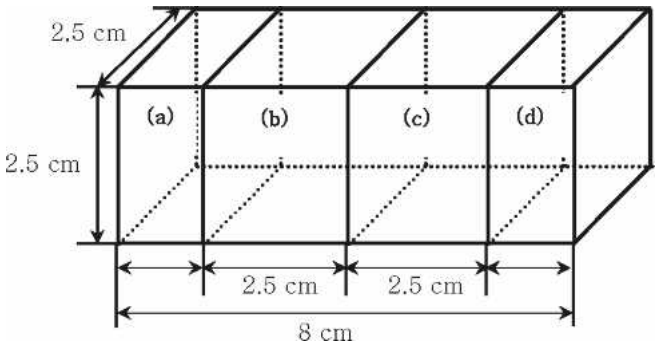

Figure 1. — Schematic diagram for preparing test blocks: a block for fixation test (b), a block for leaching test (c), and blocks for the initial retention measurement (a, d).

of the CCA solution through transverse surfaces. CCA retention of both sapwood and heartwood, which were estimated from the solution uptake and solution concentration, was 8.35 ± 0.19 kg/m^3 and 8.45 ± 0.25 kg/m^3, respectively.

After treatment, the treated samples were wrapped in plastic bags and allowed to undergo fixation without drying at 21 °C for different periods of time. At selected times following treatment, two samples were randomly removed from each type of wood in a controlled chamber and cut into four blocks (a, b, c, and d) as shown in **Figure 1**. Two 25-mm cubes were used for the fixation and leaching tests, respectively, and remnants were used for analyzing initial CCA retention of treated samples.

The rates of fixation in treated Douglas-fir samples were evaluated using the expressate method (McNamara 1989). Blocks were squeezed in a hydraulic press to express free treating solution from the wood void spaces, and the expressed solution was analyzed for its hexavalent chromium content using the diphenylcarbazide colorimetric method (ASTM 1996) and for its total chromium, copper, and arsenic content using inductively coupled plasma-atomic emission spectroscopy (ICP–AES) (AWPA 2001a). The rate of fixation at any given time was evaluated by comparing the hexavalent chromium concentration of the expressed solution with that of the initial treating solution.

The leaching tests were performed according to the American Wood Protection Association (AWPA) standard E11–97 (AWPA 2001b) with some modifications. Two 25-mm cubes were impregnated and leached with approximately 170 mL of deionized water calculated using the water-to-wood ratio specified by AWPA E11–97 standard method. After a 14-day leaching period, the combined leachate samples from the nine sampling times were analyzed by ICP–AES method to determine their CCA components. The total leaching was expressed as the percent loss of each CCA component relative to the amount initially retained in the treated samples.

Results and discussion

CCA fixation

CCA fixation, defined by rate of reduction of hexavalent chromium to trivalent chromium, was substantially faster in heartwood (**Fig. 2**) than in sapwood (**Fig. 3**); this is similar to the findings of Forsyth and Morrell (1990) and Guo et al. (2002). In **Figure 2** it can be seen that the heartwood chromium was reduced in approximately 1 day, but sapwood required approximately 7 days. This rapid heartwood chromium

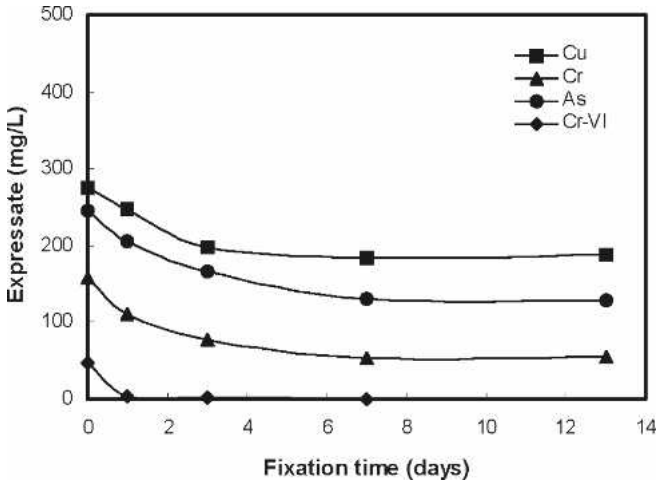

Figure 2. — Fixation of CCA components in Douglas-fir heartwood at 21 °C.

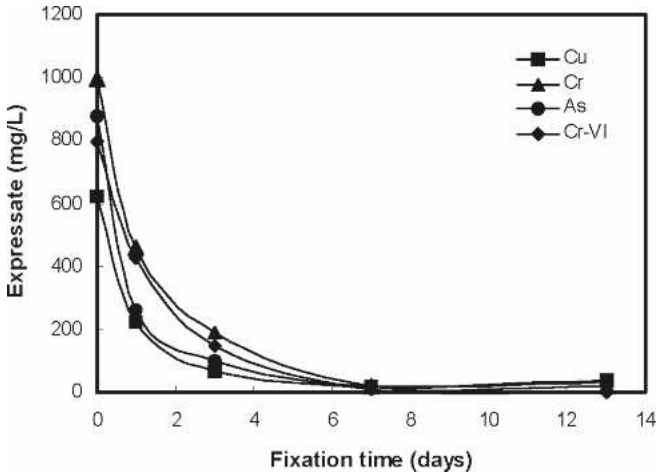

Figure 3. — Fixation of CCA components in Douglas-fir sapwood at 21 °C.

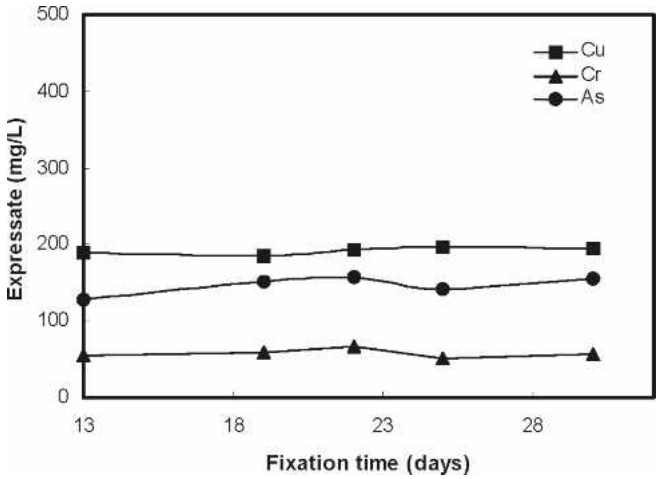

Figure 4. — Fixation of CCA components with extended fixation time in Douglas-fir heartwood at 21 °C.

Table 1. — The degree of CCA components leaching from treated Douglas-fir heartwood and sapwood.

Fixation time	Wood tissue type	Average concentration in leachate			Total leached		
		Cr	Cu	As	Cr	Cu	As
(days)		----------(ppm)----------			----------(%)----------		
1	Heartwood	0.19	0.74	4.26	2.0	12.3	20.1
	Sapwood	0.42	0.13	3.10	3.9	2.5	13.6
3	Heartwood	0.18	0.66	3.32	3.3	13.6	18.7
	Sapwood	0.08	0.04	2.22	2.7	4.0	9.9
7	Heartwood	0.23	0.61	3.30	2.9	11.4	22.7
	Sapwood	0.14	0.09	2.00	3.6	1.4	7.3
13	Heartwood	0.19	0.69	3.12	3.8	12.1	25.1
	Sapwood	0.14	0.33	1.50	2.0	4.2	7.2
19	Heartwood	0.15	0.76	3.34	1.3	7.1	19.6
	Sapwood	0.04	0.14	1.32	2.6	3.7	5.5
22	Heartwood	0.19	0.85	3.66	3.9	10.6	19.6
25	Heartwood	0.19	0.69	3.45	4.3	8.3	24.3
30	Heartwood	0.09	0.46	3.12	2.7	8.3	29.6
35	Heartwood	0.05	0.26	2.78	2.8	9.2	22.1
40	Heartwood	0.08	0.17	2.74	1.0	12.6	24.4

fixation is attributed to the reaction of hexavalent chromium with wood extractives. The effects of reactive extractives on accelerating the chromium reduction process were evident from the formation of dark brown precipitates observed in heartwood expressates, as Stevanovic-Janezic et al. (2000) pointed out in CCA-treated red maple fixation study. The fast CCA fixation in heartwood has also been reported in tamarack studies (Srinivasan et al. 1999). We are currently conducting further studies to investigate the possible cause for the fast rate of reduction for hexavalent chromium in Douglas-fir heartwood through extractive chemistry studies.

During the analysis of expressed solutions for total chromium, copper, and arsenic, we found that a relatively high amount of copper and arsenic remained in the unfixed state, but virtually all of the hexavalent chromium had been reduced to trivalent chromium in the solution expressed from heartwood (**Fig. 2**). Copper and arsenic levels in the expressed solution from heartwood did not decrease appreciably after approximately 7 days (**Fig. 2**). By contrast, the copper and arsenic components in sapwood were fixed almost completely before the chromium was reduced (**Fig. 3**). Our findings in the heartwood samples are in contradiction with presently held concepts of CCA fixation, which indicate that both copper and arsenic are stabilized in treated wood long before all of the hexavalent chromium is reduced. Thus, diphenylcarbazide methods, which are the most common techniques used to assess the degree of CCA fixation based on the reduction of hexavalent to trivalent chromium, may be not appropriate for monitoring CCA fixation, at least in the case of Douglas-fir heartwood.

We investigated further to determine whether copper and arsenic would be fixed adequately if fixation time was extended up to 30 days even though all the hexavalent chromium had been already reduced. Methods of CCA treatment, fixation conditions after treatment, block preparation from treated samples, and squeezing method were identical to those described earlier. The expressed solution was analyzed as described previously to determine the fixation status of copper and arsenic. Regardless of the extension of fixation time, copper and arsenic fixation did not improve, presumably because of a deficiency of hexavalent chromium (**Fig. 4**).

CCA leaching

Leaching tests confirm the poor copper and arsenic fixation in the heartwood samples. The copper and especially the arsenic losses were much higher in heartwood than in sapwood at the end of each fixation time period as summarized in **Table 1**, but the copper and arsenic losses from fully fixed sapwood samples (estimated fixation time: 7 days) were within the normal range that have been observed for other softwoods (e.g., Cooper 1991). There was no difference in chromium loss between sapwood and heartwood. The unusually large amount of copper and arsenic leached from the heartwood could be explained by the deposition of CCA fixation reaction products in the cell lumens due to higher extractive levels where they would be more readily accessible to leaching (Cooper et al. 1997, Srinivasan et al. 1999, Stevanovic-Janezic et al. 2001). The large amount of copper and arsenic leached from the heartwood samples in which the chromium has been fully fixed might be a cause for public concern for CCA-treated Douglas-fir products used in environmentally sensitive areas.

Conclusion

Douglas-fir heartwood samples fixed faster than sapwood, confirming the effects of extractives on chromium reduction. After the complete reduction of hexavalent chromium to trivalent chromium, however, a relatively high amount of copper and arsenic remained in an unfixed state in heartwood expressed solution. These poor copper and arsenic fixation characteristics were confirmed by leaching tests. The poor leaching performance of CCA-treated Douglas-fir heartwood suggests that CCA is not a proper preservative for this species.

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