

Effectiveness of CCA fixation to avoid hexavalent chromium leaching

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Abstract

It is generally assumed that hexavalent chromium in wood treated with chromated copper arsenate (CCA) preservative is substantially reduced to trivalent chromium during fixation and that the potential to leach the more toxic Cr^{VI} is minimal. However, there are occasional claims that some hexavalent chromium remains in wood after fixation and that small amounts of Cr^{VI} are available for leaching. A number of CCA-treated wood samples of different wood species and ages, as well as wood-cement and wood-plastic composites containing CCA-treated wood were collected and exposed to laboratory leaching. The leach water and expressate from water-saturated wood samples were analyzed for Cr^{VI} , total Cr, Cu, and As. For CCA-treated wood and wood-plastic composites, Cr^{VI} in the leachate was near or below the detection limit for analysis by ion chromatograph (< 1 ppb) compared to total chromium levels of 200 to 2700 ppb. The amount of hexavalent chromium relative to total chromium leached was generally less than 0.1 percent. Leachate from wood-cement composites showed significant levels of Cr^{VI} (up to 50% of the total chromium leached). However, both hexavalent and total chromium levels in the leachate were low (200 to 400 ppb). These results show that once the CCA is properly fixed in wood, there is little health or environmental risk associated with toxic hexavalent chromium being released from treated wood by water leaching.

Hexavalent chromium (Cr^{VI}) is an important component of chromated copper arsenate (CCA) wood preservative treating solutions, as its reduction by wood components leads to the precipitation and stabilization of copper and arsenic components of the preservative in wood. This is responsible for the low leachability of the preservative and its long-term efficacy in protecting treated wood against decay and insect attack. The components of CCA react with one another and with wood by reactions termed "fixation," which are driven by the reduction of hexavalent chromium to low toxicity trivalent chromium (Cr^{III}) by the wood components. These reactions result in an increase in wood pH and formation of low solubility Cr^{III} complexes

with arsenic and possibly copper (Dahlgren and Hartford 1972).

The completeness of this reaction is an important issue, since hexavalent chromium is water soluble and much more toxic than trivalent chromium. If unreduced chromium remains in wood in service, it will leach out and be available for transfer to clothes and exposed skin of people that contact the wood in service. Hexavalent chromium is a strong oxidizing agent and known human carcinogen. It may cause lung cancer when inhaled as dust, although there

is no conclusive evidence that ingested Cr^{VI} is carcinogenic (GRAC 2001). Thus, there is concern for health implications of Cr^{VI} in the use of CCA during the treating process and through the life cycle of CCA-treated wood.

Hexavalent chromium is managed during the treating process through controls on airborne emissions of the treating solution and safety precautions taken by workers when handling freshly treated wood. Emissions of Cr^{VI} into the environment are minimized by ensuring that the treated wood is at a high state of

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Table 1. — CCA components in leached water after different soaking times.

Sample	CCA retention (kg/ m ³)	No. of replicates	Time leached (hr.)	Cr ^{VI} (ppb)	Cr (ppm)	Cr ^{VI} /Cr (%)	Cu ----- (ppm) -----	As
Wood cement	5.5	1	24	33	0.18	18	0.03	0.0
	5.5	1	96	177	0.35	50	0.10	0.04
Wood plastic	12.0	2	24	< 0.5	0.12	< 0.4	0.11-0.26	0.18-0.33
	12.0	2	96	< 0.5	0.28-0.56	< 0.2	0.53-2.44	0-2.6
Jack pine (1 by 6 in.)	4.5	1	24	< 0.5	0.76	< 0.07	3.2	1.7
weathered 6 months	4.5	1	96	0.6	1.33	0.04	5.1	3.2
Jack pine (2 by 6 in.)	4.8	2	24	< 0.5	0.31-0.76	< 0.06	1.3-2.0	0.9-1.3
weathered 1 year	4.8	2	96	< 0.5-1.3	1.0-1.2	< 0.10	3.2-5.6	3.4-3.9
Southern pine (2 by 6 in.) new	9.5	2	24	< 0.5	0.7-0.9	< 0.07	1.3-2.7	2.3-4.0
	9.5	2	96	< 0.5	1.6-1.9	< 0.05	2.4-4.4	6.6-9.1
Southern pine (2 by 6 in.)	9.5	2	24	< 0.5	0.5	< 0.10	0.8-2.0	1.5-2.2
weathered 1 year	9.5	2	96	< 0.5	0.8	< 0.06	0.9-2.3	2.4-3.4
Douglas-fir (2 by 6 in.) new	5.7	2	24	< 0.5	0.6-1.2	< 0.10	2.0-2.5	1.8-3.8
	5.7	2	96	0.5-1.1	0.9-1.7	0.06	2.7-2.9	2.5-6.1
Jack pine (2 by 2 in.) new	4.3	1	24	< 0.5	1.08	< 0.05	4.5	3.3
	4.3	1	96	< 0.5	1.6	< 0.05	6.0	4.8
Red pine pole, weathered 1 year	10.9	1	24	< 0.5	0.9	< 0.05	2.5	2.7
		1	96	< 0.5	2.7	< 0.05	5.6	7.6

chromium fixation (Cr^{III}) before wood is removed off drip pads or other protected storage.

While it is known that the hexavalent chromium component of CCA is reduced during the fixation process (Dahlgren and Hartford 1972), some scientists have raised the question of whether some of the chromium can persist in treated wood for some time after treatment. Pizzi (1990) and Ostmeier et al. (1988, 1989) suggest that some chromate reacts with lignin to form organic chromates. It is suggested that these may be eventually reduced to Cr^{III}. Other studies show that pentavalent chromium (Cr^V) can persist for several months after treatment when the wood is dried (Rudnick et al. 1994, Andersone et al. 2000) although it is not clear under what conditions this is promoted. Cr^V can disproportionate back to Cr^{VI} and Cr^{III} resulting in possible leaching of Cr^{VI}.

However, other studies on treated wood, using magnetic susceptibility analysis (Wright and Banks 1989, Jorge et al. 1999) and x-ray photoelectron spectroscopy (Kaldas et al. 1998) indicate that there is little or no Cr^{VI} retained in the treated wood.

Cooper (1993) collected and analyzed rain drippage from CCA-treated telephone poles in service for different times. The leachate was analyzed for total Cu, Cr, and As and for Cr^{VI} by the diphenyl-carbazide method (Coggins and Hiscock 1979). Generally, Cr^{VI} lev-

els were below the detection limit of 0.01 ppm, representing less than 1 percent of the total chromium concentration. Occasionally, a slight color reaction was noted when high volumes of leachate were used in the test. The estimated Cr^{VI} concentration in these cases was less than 0.05 ppm, or less than 5 percent of total chromium content. Taylor (2001) did not detect Cr^{VI} in leachate from treated decking samples exposed to natural rainfall over a 1-year period.

Other ions such as iron can result in a positive color reaction with diphenyl-carbazide (EPA 1994) and natural wood extractives sometimes absorb at the same wavelength, resulting in false positive readings. Thus, it is important to use a more precise ion chromatography technique (EPA 1994) to avoid interference and provide higher analytical sensitivity when low concentrations are being investigated.

Materials and methods

A number of samples of different species of CCA Type C treated wood were collected: 1) laboratory-treated samples exposed to 1 year of natural weathering in Toronto, Canada (Taylor 2001); 2) fresh treated wood produced both commercially and in the laboratory; and 3) aged commercially treated wood (Tables 1 and 2). Cross-sectional samples of each wood specimen were ground in a Wiley mill and the CCA retention determined by x-ray fluorescence spec-

trometry (Oxford Instruments Ltd.). One or two replicate samples (25 mm by 25 mm by thickness) were cut for leaching tests.

Laboratory-manufactured wood-cement (1:3 by mass) and wood-polyethylene (1:1 by mass) composites made using CCA-treated wood particles were also evaluated. Wood-cement boards were made using CCA-treated wood from the sapwood of a red pine pole removed from service. Treated wood was ground in a Wiley mill to pass a 1-mm mesh screen. The CCA retention was determined by x-ray fluorescence spectrometry (Oxford Instruments Ltd.) to be 11.5 kg/m³. The wood was mixed with Portland cement and water (wood: cement:water = 1:3:2), placed on caul plates, and pressed at 1.5 MPa pressure at room temperature for 24 hours to a density of 1200 kg/m³. After a 28-day hydration period, 25- by 25- by 15-mm-thick samples were evaluated for leaching. Ground treated wood from the same source at 8 percent moisture content was mixed in equal mass ratios in a high-speed K-mixer with high density polyethylene and the hot mixture was pressed between platens at 2.0 MPa pressure to form a composite 12 mm thick. This composite was also cut into 25- by 25-mm samples for leaching tests.

All solid wood and composite samples (Table 1) were submerged and weighed down in tap water (water

Table 2. — CCA components in expressed water after 72 hours.

Sample	CCA Retention (kg/m ³)	Cr ^{VI} (ppb)	Cr (ppm)	Cr ^{VI} /Cr (%)	Cu ---- (ppm) ----	As ---- (ppm) ----
Red pine pole, weathered 1 year	10.9	< 0.5	7.2	< 0.01	22.9	9.2
Southern pine (2 by 6 in.) new	9.5	< 0.5	4.7	< 0.01	13.3	20.7
Untreated	--	< 0.5	< 0.01	--	< 0.01	< 0.03

volume = 2 × wood volume) at 21°C for various times. Ten-mL samples of leachate were collected, filtered, and analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES) for total chromium, copper, and arsenic using a Perkin Elmer Optima 3000 instrument. Leachate samples were also analyzed by ion chromatography (Dionex DX-600, AD25 absorbance detector at 520 nm, 4 mm Ionpac CS5A column) using post column reaction with diphenyl-carbazide for Cr^{VI} content (EPA 1994). The ratios of Cr^{VI} to total Cr were determined.

Some treated samples (Table 2) were cut from the same sources as used for the leaching tests and impregnated with water and held for 72 hours. The water was expressed from the wood cells by squeezing the samples at 60 MPa in a hydraulic press and the expressate was analyzed as described previously.

Results and discussion

For the leachate samples (Table 1), the wood-cement composites showed very low leaching of copper and arsenic, but relatively high levels of chromium leaching, of which up to 50 percent was in the hexavalent form (33 to 177 ppb Cr^{VI} depending on the leaching period). These results confirm earlier indications using the diphenyl-carbazide method that chromium could be partially oxidized in the high pH cement matrix (Qi 2000). These values are comparable to USEPA Maximum Contaminant Levels (MCL) of 100 ppb for total chromium in drinking water. However, because of the higher toxicity of Cr^{VI} compared to Cr^{III}, some jurisdictions such as California EPA are considering a Public Health Goal of 2.5 ppb for Cr^{VI} (GRAC 2001). This could limit the applicability of wood-cement composites as a means of recycling spent CCA-treated wood.

The wood-plastic composite generally had lower leaching of CCA components than solid treated wood. No measurable Cr^{VI} was detected.

For all treated solid wood samples, Cr^{VI} in the leachate was near or below the detection limit of the ion chromatograph (< 1 ppb) and the amount of Cr^{VI} relative to total chromium leached was generally less than 0.1 percent. The leachate concentrations of Cr^{VI} were consistently below the most stringent public Health Goal under consideration by California EPA (2.5 ppb).

For the expressed samples, higher concentrations of chromium, copper, and arsenate were measured (Table 2) compared to the leachate samples. However, Cr^{VI} levels were below the 0.5 ppb detection limit, indicating that the ratio of Cr^{VI} /total Cr was less than 0.01 percent, again confirming the absence of significant amounts of available Cr^{VI} in fixed CCA-treated wood.

Conclusions

These results show that once the CCA is properly fixed in wood, there is no health or environmental risk associated with toxic hexavalent chromium being released from treated wood. However, CCA-treated wood recycled into wood-cement composites has some chromium oxidized to the more soluble hexavalent state. Methods should be sought to stabilize chromium in wood-cement composites if this material is to be used for recycling spent CCA-treated wood.

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