

EFFECTS OF CCA-C PRESERVATIVE RETENTION AND WOOD SPECIES ON FIXATION AND LEACHING OF CR, CU, AND AS

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ABSTRACT

Fixation of chromated copper arsenate (CCA-C) preservative was investigated using ground sapwood of trembling aspen, red pine, and red maple at treatment retentions of 4.0, 6.4, 9.6, and 30 kg/m³ at 30°C. The fixation of (CCA) wood preservative differed considerably among the wood species and was affected by treatment retention, resulting in differences in subsequent leaching of the “fixed” components. For the wood species considered, the fixation times increased with increasing retention for the Cr and Cu components but decreased with increasing retention for As. Red pine and aspen had similar fixation patterns and similar leaching trends and levels of leaching losses. Red maple had significantly faster CCA fixation than red pine and aspen but had elevated Cr and As leaching. These fixation anomalies decreased with an increase in treatment retention, and after removal of hot-water-soluble extractives. It is postulated that extractives impair the quality of fixation owing to their high reducing capacity toward Cr(VI) and capability to complex Cu(II) and Cr(III). Irregular CCA fixation in red maple results in incomplete fixation of As due to reduced availability of Cr in a form that can complex As.

Keywords: CCA, fixation and leaching, CCA retention, red maple, red pine, aspen.

INTRODUCTION

When wood is treated with chromated copper arsenate (CCA) preservative, its chromium, copper, and arsenic components react with wood constituents through a series of redox and complexation reactions to form chemically fixed products with low water solubility. CCA fixation and water leaching have been extensively studied and comprehensively reviewed (e.g., Lebow 1996; Cooper 2003). Nevertheless some phenomena and trends, in particular those pertaining to the effects of wood species and preservative retention on fixation and leaching, re-

main inadequately understood. They include differences in CCA fixation and leaching among wood species, inconsistent reports on the sequence of Cu and As fixation, and the lack of a reasonable explanation for high As leaching associated with certain hardwoods and with very low treatment retentions in both softwoods and hardwoods.

Cu and As fixation are considerably less well understood in comparison to Cr fixation, which has been commonly considered an indication of the overall fixation progress and therefore more systematically studied. Cr fixation is the slowest reaction, and its length increases with treatment retention for a given wood species and fixation conditions (Wilson 1971). In contrast, As has

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been reported to fix before (e.g., McNamara 1989) at the same time (e.g., Cooper and Ung 1992) and following Cu fixation (e.g., Wilson 1971). These inconsistencies may be accounted for by differences in concentrations of the treating solutions, since higher concentrations were observed to accelerate As and delay Cu fixation from salt-based Tanalith C preservative (Wilson 1971).

While softwoods generally require similar fixation times, substantial variability is observed in hardwoods, ranging from those that rapidly fix Cr (e.g., beech, red oak and red maple), to species such as yellow poplar, aspen and basswood, which require longer fixation times than typical softwoods (Wilson 1971; Cooper and Ung 1992; Carpenter and Gardner 1993; Stevanovic-Janezic et al. 2000). More variable and often higher leaching is associated with hardwoods in general, and those that fix Cr fast (i.e. red maple) have elevated Cr and especially As leaching (Kamdern et al. 1996; Cooper et al. 1997; Stevanovic-Janezic et al. 2000, 2001). These studies offer substantial evidence that rapid fixation and elevated leaching are associated with the interference of the water-soluble fraction of wood extractives, and suggest simple sugars such as dextrose and reducing mono-, di- and oligo-saccharides as most probable reactants. Nevertheless, while their reactivity is consistent with rapid Cr(VI) reduction, it does not explain the elevated As leaching. Since wood extractives are present in small and limited amounts in comparison to the structural wood constituents—holocellulose and lignin, which are the main CCA reactants, it can be expected that the relative effect of extractives will be higher with low retention treatments.

Previous studies have focused on either species effects or concentration effects and often investigated older CCA formulations with different chemical compositions from the CCA type C used exclusively now. Also, due to variability in sample parameters (i.e. size, preservative retention) and leaching regimes employed in leaching studies (Cooper 2003), the relationship between treatment retention and water solubility of fixed CCA is not clear. Better understanding

of complex interaction effects of CCA concentration and wood species on fixation rates and quality (leaching) is needed.

This work aims to improve the current understanding of some of the observed anomalies by investigating overall CCA-C fixation pattern and water solubility of fixation products, as affected by different wood species with variable chemical compositions and by the treatment level. Red pine (*Pinus resinosa* Ait.) was chosen as a typical North American softwood that is commonly and effectively treated with CCA. Trembling aspen (*Populus tremuloides* Michx.) is a diffuse porous hardwood species, which has very similar CCA fixation pattern as conifer red pine, in spite of different gross chemical composition. Red maple (*Acer rubrum* L.) is a diffuse porous hardwood with similar chemical composition to trembling aspen, but is known to respond differently to CCA treatment (Kamdern et al. 1996; Cooper et al. 1997; Stevanovic-Janezic et al. 2000). Preservative retentions were chosen to represent standard treatments for commercial applications (AWPA 1996) in the range from 4 to 30 kg/m³. Wood sawdust was used in experiments instead of solid wood blocks to minimize the effect of diffusion of chemicals during the treatment and during their extraction, and to provide a more homogenous distribution of chemicals in wood.

MATERIALS AND METHODS

Logs of trembling aspen (*Populus tremuloides* Michx.) and red maple (*Acer rubrum* L.), approximately 30 and 25 years old, were cut in Northern Ontario in the spring of 2001. A red pine (*Pinus resinosa* Ait.) pole top approximately 35 years of age was obtained from a Canadian pole producer. The logs were cut into 25-mm-thick slabs and air-dried for two months. Sapwood free from knots and visible reaction wood was separated, cut into chips, and milled in a Wiley mill. The 25–40 mesh fraction of sawdust was collected and used for the CCA treatment.

To evaluate the influence of water-soluble extractives on the course of fixation of red maple,

a sample of red maple was pre-extracted with hot water and the content of hot-water solubles determined according to ASTM D 1110-84 (2001). Following extraction, the sample was washed with 1 L of hot water, filtered, and air-dried.

The chemical composition of investigated wood species was determined by standard wood analyses (Table 2), using 30-mesh wood sawdust. All analyses were performed on two replicate samples.

Treatment solutions were prepared from CCA-C wood preservative commercial formulation K-33TM (C-60), manufactured by Timber Specialties Ltd., containing 29.50% chromic acid, 20.00% arsenic pentoxide, and 10.50% copper oxide. All dilutions were made with distilled water. Concentrations of treating solutions were 0.5–4.1% for aspen, 0.5–3.7% for red pine, and 0.4–2.9% for red maple. Precise concentrations were calculated to achieve treatment retentions equivalent to 4.0, 6.4, 9.6, and 30 kg/m³ in solid wood, when wood sawdust was mixed with the treating solution at 1:2 mass ratio based on the oven-dry weight of wood. This solution to wood ratio approximates the moisture to wood ratio of solid wood full-cell pressure-treated with preservative. Conversions of treatment retentions to standard units (kg/m³) were based on basic relative densities (ASTM D 2395-93) of matched sapwood samples. The relative density values were: 0.388 (red pine), 0.551 (red maple), and 0.390 (aspen). Pre-extracted red maple, was treated only to 6.4 and 30 kg/m³.

Treated sawdust was homogenized by mixing, sealed in polyethylene bags, and conditioned at 30°C and high relative humidity to prevent drying during fixation. The fixation level was monitored by extracting two replicate treated sawdust samples of approximately 2 g, according to a defined time schedule. Depending on the concentrations of unfixed components, samples were extracted at least twice with 100 ml aliquots of deionized water, on an oscillating shaker for 20 minutes. This time interval assured maximum dissolution of unfixed CCA elements. Filtrate was collected by vacuum filtration through a 0.45- μ m PTFE filter and analyzed for

the contents of Cr(VI) and total soluble Cr, Cu, and As. Fixation was monitored until completion, or when the Cr(VI) content in the extract fell below the analytical detection limit of 0.1ppm, corresponding to more than 99.9% total Cr reduction.

Cr(VI) in treating solutions and water extracts was determined by UV-Vis spectroscopy at 540 nm using 1,5-diphenylcarbazide (DPC) as a color developing agent (Coggins and Hiscocks 1978) within 4 to 5 hours following the extraction. Contents of total Cr, Cu, and As were determined by inductively coupled plasma Auger electron spectroscopy (ICP-AES) on a Perkin Elmer Optima 3000 ICP AES instrument in accordance with AWWA Standard A21-93 (AWWA 1996).

Two replicate samples were found to be adequate, because of the high reproducibility of results. The relative standard deviations for most concentration measurements with ICP-AES and UV-Vis spectrophotometry were in the range of 1 to 4%, and not higher than 7%, and the major source of the variability in concentrations of unfixed components was caused by analytical and instrumental errors, and not by the sample variability. Fixation curves were generated from at least two independent fixation experiments, and data plotted as average concentration values of two simultaneous extractions.

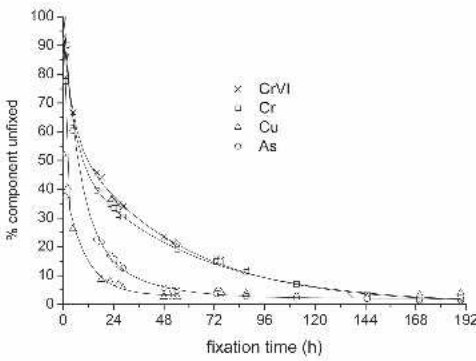
Treatments of unextracted red maple with one-component solutions of CrCl₃ (0.13%) and CuSO₄ (0.09%) were performed to evaluate the potential of the wood substrate for binding Cu(II) and Cr(III). These treatments corresponded to Cr and Cu loadings in CCA-treated sawdust for retention of 6.4 kg/m³.

Water leaching of sawdust was investigated following the complete fixation, based on Cr(VI) reduction, for all preservative retentions in red pine, aspen, and red maple. Duplicate samples of approximately 2 g of treated sawdust were leached with 100 ml of deionized water for 20 min on an oscillating shaker to characterize their leaching properties. Leachates were filtered and analyzed for the CCA components as above.

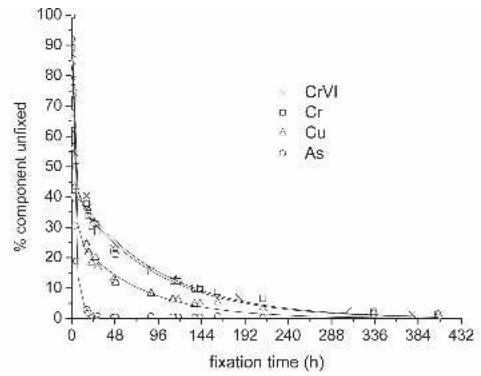
RESULTS AND DISCUSSION

Fixation curves, which represent quantitative changes of unreacted CCA components as a function of time, are shown for representative species/retention combinations in Figs. 1 and 2. CCA fixation curves for red pine and aspen (Fig. 1) show essentially complete fixation of all three elements, with Cr fixation being slowest. Durations of fixation reactions were slightly longer in aspen than in red pine, not only for Cr(VI), as observed by Stevanovic-Janezic et al. (2000), but for Cu and As as well. In contrast, CCA fixation curves in low retention red maple (Fig.

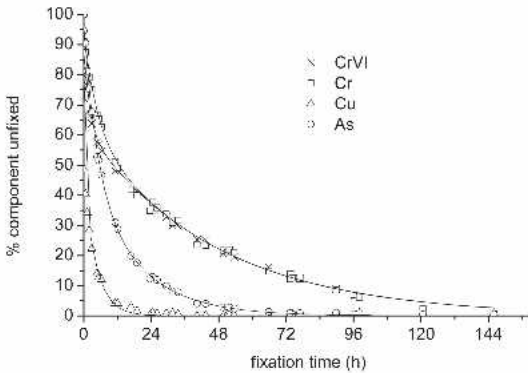
2a) had rapid, but complete Cr(VI) reduction and rapid Cu fixation to a high degree, and similarly fast, but incomplete fixation of As, as observed previously for red maple solid blocks treated with 2% CCA solution (Cooper et al. 1997; Kamdem et al. 1996; Stevanovic-Janezic et al. 2000, 2001). The proportion of residual unfixed As (Fig. 3c) decreased with retention with unfixed levels of approximately 32%, 21%, 10%, and 1% corresponding to 0.42, 0.44, 0.32, and 0.10 kg/m³ of soluble or unfixed As₂O₅ for retentions of 4.0, 6.4, 9.6, and 30 kg/m³ respectively. Significant water-soluble Cr, unreactive



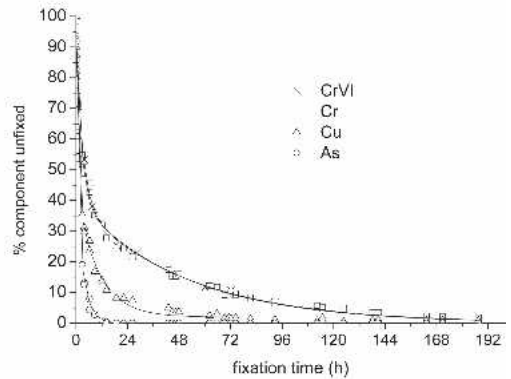
a) Aspen Ret. = 6.4 kg/m³



b) Aspen Ret. = 30.0 kg/m³

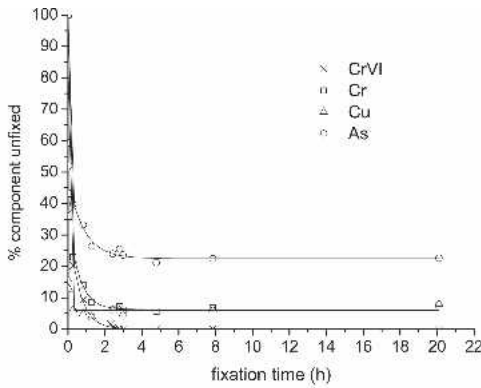


c) Red pine Ret. = 6.4 kg/m³

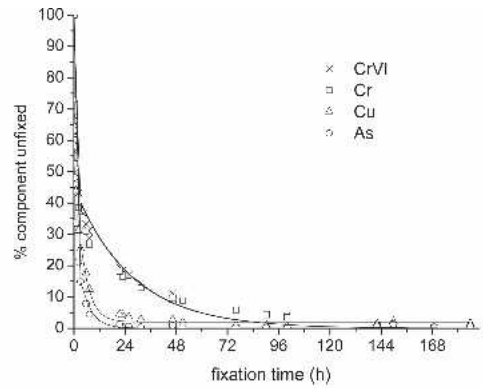


d) Red pine Ret. = 30.0 kg/m³

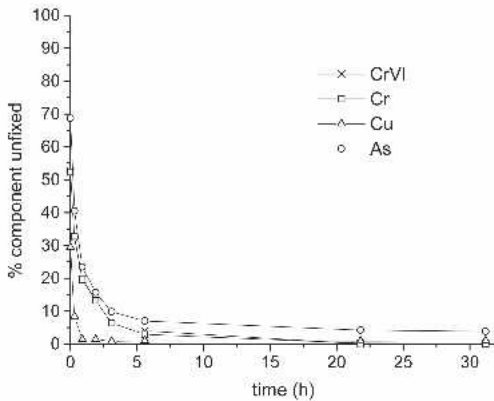
FIG. 1. Comparison of CCA fixation at 30 °C in red pine and aspen at two retentions (6.4 and 30 kg/m³).



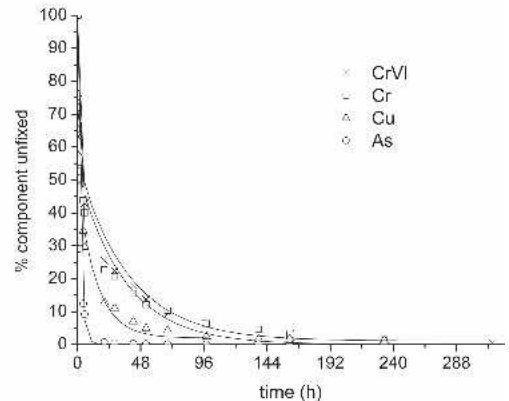
a) Red maple (6.4 kg/m³)



b) Red maple (30 kg/m³)



c) Red maple pre-extracted (6.4 kg/m³)



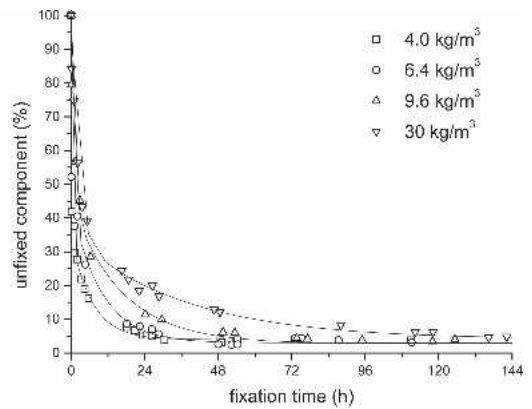
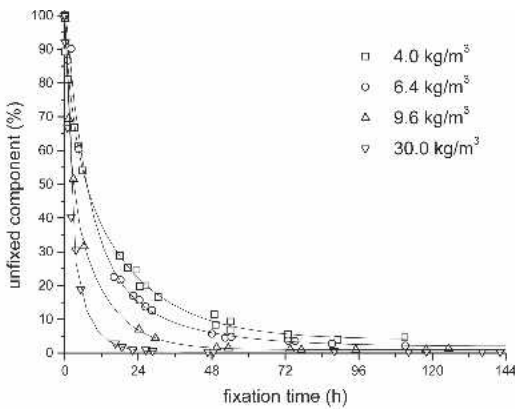
d) Red maple pre-extracted (30 kg/m³)

FIG. 2. Comparison of CCA fixation at 30 °C in unextracted and pre-extracted red maple at two retentions (6.4 and 30 kg/m³).

to diphenylcarbazide and assumed to be Cr(III), was observed after all of the Cr(VI) had been reduced in red maple treated to the lower retentions (Fig. 2a), in contrast to red pine or aspen. The levels of soluble Cr(III) decreased proportionally with increasing retention and were not noticeable at 30.0 kg/m³.

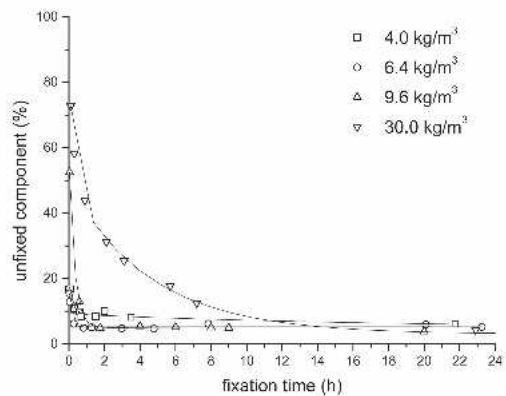
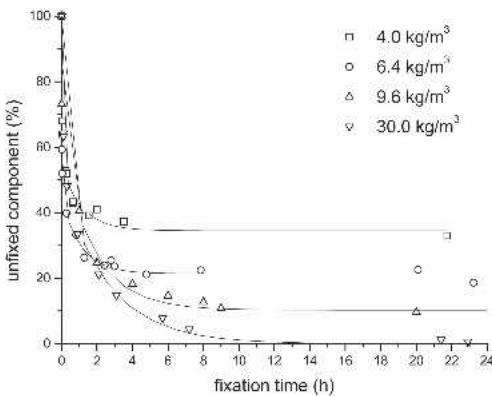
We observed less than 10% of Cr or As fixed during the initial 2–3 minute fixation period in red pine and aspen at all CCA retentions (data not shown), in contrast to findings of Ste-

vanovic-Janezic et al. (2000), who reported approximately 55% and 60% of Cr and As initially fixed in the same species using an expressing technique. The discrepancy in reported values for the initial Cr(VI) fixation may be related to the experimental approach used for its determination. Extensive Cr(VI) fixation of 30–60% immediately after the treatment, has been also reported in other studies utilizing the expressing method (Kazi and Cooper 2000). This method is based on applying a mechanical force to wood



a) Aspen As fixation

b) Aspen Cu fixation



c) Red maple As fixation

d) Red Maple Cu fixation

Fig. 3. Effect of CCA retention on Cu and As fixation in aspen and unextracted red maple.

blocks to express the preservative solution from the cell lumens, under the assumption that its concentration of unfixed CCA is representative of the whole sample. However, adsorption of H_2CrO_4 by chemical/physical interactions on wood constituents during early stages of fixation would result in lower Cr(VI) concentration in the lumens in comparison to Cr(VI) concentration in the cell wall, and would lead to overestimation of fixed Cr(VI). The temporary adsorption of H_2CrO_4 on cellulose was suggested

by Dahlgren and Hartford (1972a) and Pizzi (1982) as a major cause of extensive proton-consuming reactions and increase in pH in treated sawdust observed during initial reactions. Their studies also suggest that the level of H_2CrO_4 adsorption decreases with an increase in pH and with the dilution of Cr(VI) concentrations. Prolonged water extraction of treated sawdust used in this study would desorb and dissolve adsorbed H_2CrO_4 as a result of increased pH and the high dilution factor, completely re-

moving unreduced Cr(VI). A similar mechanism might be responsible for the discrepancy in initial As fixation between different techniques.

Initial copper fixation corresponding to the Cu fraction insoluble in water following the first 3 min after the treatment was rapid in all wood species, resulting in as much as 66% of Cu fixation in red pine treated to 4.0 kg/m³ (Table 1). These initially fixed amounts correspond to 0.8–0.9 mg Cu per gram of oven-dry wood (mg Cu/godw) in aspen, and 1–1.3 mg Cu/godw in red pine. The absolute amounts of initially fixed Cu, which have been hypothesized to depend predominantly on the cation exchange capacity of wood, and thus on the concentration, and pH of the treating solution (Dahlgren and Hartford 1972a; Cooper 1998), were found to increase with the solution strength (Table 1), as observed by others (e.g. Dahlgren and Hartford 1972b). Corresponding percentages of fixed Cu, however, decrease with solution strength.

Cr, Cu, and As fixation times in all three wood species depended strongly on the treating solution concentration and were similar in aspen and red pine. Arsenic fixation time decreased (Figs. 3a, 3c), and Cr and Cu fixation times increased (Figs. 1, 2, 3b, 3d), in response to an increase in CCA solution strength (retention level). Consequently, in red pine and aspen, Cu fixation was faster than As fixation for lower retentions (4.0, and 6.4 kg/m³) as illustrated for 6.4 kg/m³ in Figs. 1a and 1c, slower for the highest investigated retention (30 kg/m³) (Figs. 1b, 1d), and of similar length for the retention of 9.6 kg/m³.

Removal of the hot-water-soluble extractives (4.24% by weight) from red maple prior to CCA treatment resulted in slower fixation reactions,

marked by lower initial fixation of all three elements, and longer overall fixation times (Fig. 2). The levels of unfixed As decreased; for example, at 6.4 kg/m³, unfixed As was reduced from 25% in unextracted samples to 3.5% in pre-extracted samples (Fig. 2a, 2c). These results are in agreement with the findings of Stevanovic-Janezic et al. (2001) and Kamdem et al. (1996), who reported a significant decrease in As leaching from red maple after extraction with water/5% ethanol. In addition, the soluble Cr(III) content of approximately 7% in unextracted red maple decreased to about 0.2% in pre-extracted samples (Fig. 2a, 2c). This suggests that elevated Cr(III) water solubility originates from chemical complexation with water-soluble extractives, such as low molecular weight carbohydrates, which have been shown to yield soluble complexes with Cr(III) upon their oxidation (Pizzi 1981; Jorge et al. 1999).

Leaching of CCA components from completely fixed sawdust is shown in Fig. 4. Relative leaching of Cr, Cu, and As decreased with an increase in the preservative retention in all investigated species, except for Cu in red pine. Absolute leaching, expressed as micrograms of CCA component leached per gram of oven-dry wood (µg/godw), however, varied considerably among wood species and retentions. Absolute Cr leaching was relatively constant in aspen and red pine irrespective of the retention, and higher in aspen than in red pine. Absolute Cr leaching in red maple was substantially higher than in other two species for 4.0 and 6.4 kg/m³, but decreased with increased retention to levels comparable to aspen. Absolute As leaching decreased with retention in all three species, and was similar for red pine and aspen. High absolute As leaching in

TABLE 1. Initial fixation of copper as % of available Cu and as µg of fixed Cu per gram of oven dry wood substance—godw (means ± 1 s.d., 3–5 determinations per sample).

Retention (kg/m ³)	Aspen		Red pine		Red maple			
					unextracted		pre-extracted	
	(µg/godw)	(%)	(µg/godw)	(%)	(µg/godw)	(%)	(µg/godw)	(%)
4	798 ± 75	53	1000 ± 92	66	861 ± 14	83	—	—
6.4	731 ± 99	31	1067 ± 65	47	1342 ± 49	84	734 ± 81	46
9.6	814 ± 15	23	1242 ± 73	34	1184 ± 63	48	—	—
30	893 ± 59	8	1349 ± 114	16	1974 ± 213	25	715 ± 77	9

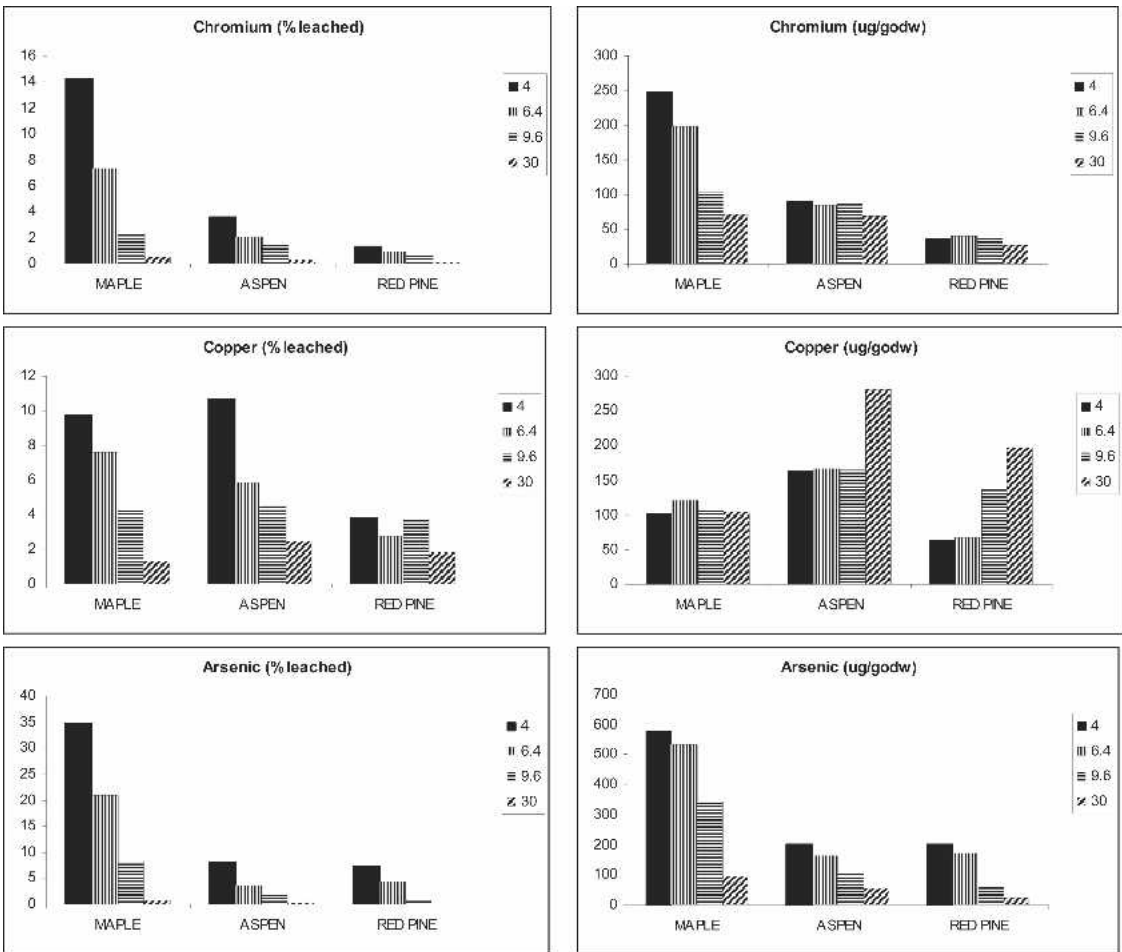


FIG. 4. Water leaching of CCA components from red pine, aspen, and red maple treated to four retentions after completed fixation at 30 °C.

red maple is consistent with incomplete As fixation (Figs. 2a, 3c). In contrast, absolute Cu leaching in red maple was relatively constant (about 100 $\mu\text{g/godw}$) for investigated retentions, and lower than in aspen. Copper leaching in red pine was lower than in either hardwood for retentions of 4.0 and 6.4 kg/m^3 , while at retentions of 9.6 and 30 kg/m^3 it was higher than in red maple, but lower in comparison to aspen.

This study demonstrates similar CCA fixation patterns, comparable solubilities of fixation products, and analogous effects of treatment retention in aspen and red pine, and different fixation and leaching patterns in red maple. In general, differences in contents (Table 2), composi-

tion, and reactivity of main chemical constituents between softwoods (red pine) and hardwoods (aspen) contribute little variability to the overall CCA fixation pattern. In contrast, differences in composition of extractives, as indicated by the effect of removal of hot-water solubles from red maple, in otherwise chemically similar hardwoods red maple and aspen (Table 2), may lead to radically different CCA fixation pattern. It may be hypothesized that dominant fixation reactions involve structural wood components in “regularly fixing” wood species (i.e. red pine and aspen), in absence of significant amounts of highly reactive wood extractives which react preferentially with CCA, and render it unavail-

TABLE 2. Chemical composition of wood used in this study.

Wood component (%)	Aspen	Red maple	Red pine	Analytical method
Holocellulose	80.3–80.6	79.0–79.4	74.5–75.6	Wise et al. 1946
Alpha cellulose	44.0–44.8	41.8–43.0	52.6–53.0	Zobel and McElwee 1966
Hemicellulose	35.5–36.6	36.0–37.6	21.5–23.0	Calculated*
Lignin–Klason	18.6–19.3	22.5–23.5	27.2–29.4	Effland 1977
Total extractives	6.4–6.5	5.8–6.3	3.6–3.7	TAPPI T204 os-76
Hot water	1.2–1.6	1.0–1.2	0.9	TAPPI T204 os-76
Ethanol	0.1–0.2	0.2–0.3	0.1	TAPPI T204 os-76
Ethanol/Toluene	4.8–5.1	4.6–4.9	2.6–2.7	TAPPI T204 os-76

* – Difference between holocellulose and α -cellulose contents

able for the reactions with structural wood constituents, as seen in red maple.

The effect of red maple extractives on As fixation and leaching and the relative decrease of these effects with an increase in CCA loading can be better understood upon consideration of probable As fixation mechanism in red maple. In regularly fixing species, As is almost exclusively fixed through precipitation with Cr(III) (Dahlgren and Hartford 1972a; Bull 2001). In contrast, it appears that in red maple, Cr(III) reacts preferentially with extractives forming reaction products that either do not include As, or do to a considerably lower extent in comparison to normal Cr-As fixation products. If the consumption of Cr(III) by wood extractives exceeds the amounts necessary for complete As fixation, it results in a surplus of unfixed and leachable As. Higher CCA loadings provide sufficient Cr contents for reactions with available extractives as well as for normal As fixation. Incomplete As fixation is more evident when reactive extractives are abundant relative to CCA contents, and more pronounced at low retentions. This is consistent with the observed high As leaching from formulations with low Cr/As ratios (Smith and Williams 1973).

The reactivity of water-soluble extractives in red maple is manifested through two distinct types of reactions: (1) rapid Cr(VI) reduction and (2) complexing of Cu(II) and Cr(III). Soluble reducing-carbohydrates suggested previously as probable interfering compounds in red maple by Cooper et al. (1997) and Stevanovic-Janezic et al. (2000), are readily oxidized by Cr(VI) compounds under acidic conditions and can contribute to reaction (1). However,

their oxidation, depending on the pH and their molar ratio to Cr(VI), can range from the mild oxidation and formation of COOH groups to severe oxidation terminated by CO₂ evolution. Carboxylic acid derivatives form only water-soluble complexes with Cr(III) (Pizzi 1981; Jorge et al. 1999), while the mass balance indicates substantial fixation of Cr(III) in insoluble form other than in association with As. Severe oxidation of sugars would lead to the formation of free Cr(III), which would ultimately precipitate As, contrary to what has been observed. The reactivity of soluble carbohydrates is therefore not consistent with reactions (2).

Substantial *in situ* capacity of red maple for binding Cu(II) and Cr(III) was confirmed by treatment with one component solutions of CuSO₄ and CrCl₃ (Table 3). Around 30% of total Cr(III) was fixed from CrCl₃ solution without any redox modifications of wood and in the absence of As, supporting the argument that newly formed Cr(III) can be fixed without As by chemical compounds present in wood *in situ*. Similarly, over 65% of Cu fixed from CuSO₄ solution compares well with amounts fixed initially from CCA. Substantial reduction in initial

TABLE 3. Initial (2–3 min) fixation of Cr and Cu from CCA (Ret. = 6.4 kg/m³) and one-component solutions of CrCl₃ and CuSO₄ in red maple.

Component	Treatment	pH	Fixed amount		
			(mM/godw)	(μ g/godw)	(%)
Cr(III)	CCA	2.3	30	1560	55
	CrCl ₃	2.1	17	870	31
Cu(II)	CCA	2.3	21	1342	84
	CuSO ₄	4.5	20	1282	67

Cu fixation in pre-extracted red maple (Table 1) also suggests that Cu reacts with soluble extractives. Pizzi et al. (1986) showed that tannins can complex Cu and Cr causing the underfixation of As, and similar effect has been attributed to oak tannins by Stevanovic-Janezic et al. (2000). While tannins are not present in maples (Rowe and Conner 1979), water-soluble phenolic extractives, which were investigated in connection with stain formation in red maple (Levitin 1972), may be hypothesized as likely reactants based on their known chemistry. Tattar and Rich (1973) found total phenol contents in water extracts of red and sugar maple of around 1% in clear wood, containing at least six different phenols similar to gallic acid or catechin. Similarly, Taylor and Cooper (2002) found phenol levels of about 1% in red maple compared to about 0.02% in red pine sapwood while both species had significant levels of soluble polysaccharides. Catechin was also identified in beech (Zule and Može 2003), which fixes CCA similarly to red maple, but it was not reported in any *Populus* species. Another low molecular phenolic procyanidin dimer was also found in red maple wood (Narayanan and Seshadri 1969). These phenolic compounds are readily oxidatively polymerized (Rowe and Conner 1979) and can form insoluble complexes with metals such as Cr(III) and Cu(II), as indicated by the elevated ash content of stained wood (Levitin 1972). It is possible that these compounds can act as additional Cr reduction agents and can complex and fix Cr(III) and render it unavailable for As fixation.

The limiting retention below which the consumption of Cr by extractives exceeds amounts necessary for proper As fixation is between 9.6 and 30 kg/m³ in red maple. Even in regularly-fixing red pine and aspen, the As fixation curve closely followed the Cr fixation curve at 4.0 kg/m³, (figures not shown) suggesting that this retention is close to the lower retention limit at which Cr can adequately complex As in these species. At retentions lower than 4.0 kg/m³, the effect of Cr-consuming extractives will be more pronounced and possibly result in incomplete As fixation and its leaching. Jin and

Preston (1993) reported exceptionally high As leaching at low retentions in CCA-treated southern pine. Arsenic losses increased during the two-week leaching period from 18% at 4.0 kg/m³ to 36% at 2.0 kg/m³, and 87% at 1.0 kg/m³. Dawson-Andoh et al. (2000) reported high As losses from yellow-poplar, red oak, and southern pine treated to 2.6 kg/m³. Such under-fixation of As in regularly fixing species is expected only in very low retention treatments due to low contents of interfering extractives. The variability in extractive contents and composition among individual trees of the same species in response to genetic or growth factors and between different parts of the xylem, will be reflected accordingly on the extent of the "via-extractives fixation" reactions for a particular wood. For example, the seasonal variability in extractive content was manifested in variability in CCA fixation in red maple (Cooper et al. 1997; Ung et al. 1998). Kennedy and Palmer (1994) observed twice as high As leaching from extractive-rich heartwood as from sapwood of slash pine.

Higher than normal preservative loadings are recommended for wood species as red maple, to ensure complete Cr and As fixation and to minimize As and Cr leaching. High preservative loadings can also provide sufficient amounts of CCA for fiber tissue treatment, since at low retentions, preservative distribution may be confined to more accessible and extractive-rich lumens of vessels and parenchyma cells. Under the light microscope, we observed dense colored deposits in parenchyma cells of CCA-treated red maple that were not present in untreated samples.

The limitations of this approach are related to the effects of particle size and diminished effect of wood anatomy on the availability of wood components for reactions with preservative, and should be considered for the interpretation of results with respect to solid treated wood products. However, the results and observations are consistent with those studies where solid wood samples were evaluated.

CONCLUSIONS

- CCA fixation and leaching are comparable in aspen and red pine and similar to other “regularly fixing species.”
- In both species, Cr and Cu fixation times increase, and As fixation time decreases with increasing chemical retention.
- CCA fixation in red maple is characterized by rapid fixation in comparison to red pine and aspen, incomplete As fixation, and elevated contents of leachable Cr(III) and As. These effects decrease in proportion to increasing treatment retention.
- Soluble reducing-sugars and phenolic compounds are proposed as the major red maple extractives which impede CCA reactions with structural wood components by acting as preferential Cr reducing agents (sugars), and by forming complexes with Cu(II) and Cr(III) (phenolics).
- This complex formation results in Cr(III) becoming largely unavailable for fixation of As in low retention treatments. Because of the limited amounts of extractives, the effect is greater at lower than at higher retentions.
- Higher treatment retentions, in species such as red maple, should be considered to provide sufficient amounts of Cr to offset reactions of extractives and minimize leaching of As.

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