Effect of Weathering on Chromated Copper Arsenate (CCA) Treated Wood: Leaching of Metal Salts and Change in Water Repellency

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Abstract: Wood pressure-treated with chromated copper arsenate (CCA) wood preservative is commonly used for outdoor construction. Oxides of arsenic, copper, and chromium are bound in the wood by a complex series of chemical reactions, but a small percentage of these compounds are gradually released by leaching and weathering. Recent studies suggest that the release of these compounds can be minimized by applying finish to the surface of the treated wood, but little is known about how or to what degree finish properties affect release. This study evaluated the effects of water repellents in clear penetrating finishes on the amount of arsenic, copper, and chromium released from CCA-treated wood through leaching and ultraviolet (UV) radiation. End-matched specimens were cut from CCA-treated deck boards and either left unfinished or dipped in a finish prepared with 1%, 3%, or 5% concentration of water repellent. All specimens were exposed to leaching from simulated rainfall and a subset of specimens was also exposed to UV radiation. Water from the simulated rain was collected and analyzed for arsenic, copper, and chromium. The water repellent greatly decreased the amounts of these elements in the runoff, but the water repellent concentration did not make a difference for the short duration of this study. It is possible that water repellent content would have a greater effect over a longer exposure period. Exposure to UV radiation caused a large increase in leaching from both finished and unfinished specimens. This effect may be a result of increased surface area via checking, as well as loss of fibers from the wood surface caused by UV-induced surface erosion. The results indicate that UV radiation plays an important role in the release of preservative components from CCA-treated wood and that the effect of UV exposure must be considered when developing methods to assess the ability of finishes to minimize preservative release. In a matching study to investigate the effects of UV radiation on water repellency, small wafers of CCA-treated wood were treated with the same water repellent. Water repellency increased slightly for specimens exposed to both simulated rain and exposure to UV radiation compared with specimens exposed only to simulated rain.

Keywords: Water repellent, chromated copper arsenate, CCA, wood, leaching, weathering, ultraviolet radiation, arsenic, chromium, copper, deck, treated wood

Introduction

For several decades, consumers have been able to purchase pressure-treated wood at local lumber yards. This type of treated wood, commonly known as green treated, is pressure impregnated with a preservative called chromated copper arsenate (CCA). Chromium, copper, and arsenic oxides are deposited in the wood cell wall through a complex series of chemical fixation reactions that involve the reduction of chromium VI to chromium III and the formation of chromium and copper arsenate compounds. Although the mechanism of this process is not fully understood, the reaction products become highly insoluble in the wood under normal pH conditions. However, a small percentage of CCA components is gradually released from the wood through leaching and weathering.

Background

The amount of leaching of arsenic, chromium, and copper can be influenced by a number of factors, including the dimensions and wood species of the treated product, preservative concentration in the wood, and the exposure environment (Lebow 1996). Preservative concentration can have conflicting effects on

leaching, depending on the preservative components. Several researchers have noted that the percentage of leachable arsenic decreases with increased concentration of CCA components in the treating solution and wood (Archer and Preston 1994, Arsenault 1975, Coetze 1980, Hagar 1969, Irvine and others 1972, Lee and others 1993, Wood and others 1980). The effect appears to be attributable to the increased proportion of available chromium in the treating solution and treated wood. At high solution concentrations, increased amounts of chromium are available to react with arsenic because a lower proportion of the total chromium is adsorbed into wood components (Arsenault 1975). It has also been suggested that higher CCA concentration levels provide more water repellency to the wood, thus limiting leaching (Coetze 1980). The effect of CCA concentration on leaching of copper and chromium is less clear. Increased concentration has been reported to both increase (Irvine and others 1972) and decrease (Lee and others 1993, Wood and others 1980) the percentage of these elements leached.

The size and dimension of wood products determine the surface area/volume ratio and the wood-grain angle that is exposed. Because the leaching rate is a function of the rate of movement of water into and out of the wood, leaching is more rapid when water is able to move along the wood grain rather than across it. Therefore, products with a high proportion of exposed end-grain are more susceptible to leaching. The American Wood Preservers' Association (AWPA) standard method of determining the leachability of wood preservatives (El 1-97, AWPA 2001) specifies the use of 19-mm cubes. Rates of leaching using this method are many times greater than that of most products in service because of the small specimen dimension and the large proportion of exposed end-grain. CCA leaching has also been shown to be greatest from exposed end-grain in seawater exposures (Shelver and others 1991) and to be higher from flat-grain than edge-grain Douglas Fir exposed in cooling towers (Gjovik and others 1972). A similar effect has been noted with some wood species; more permeable species tend to leach at a higher rate because of more rapid movement of water through the wood structure (Cockroft and Laidlow 1978, Wilson 1971).

Water pH may also affect leaching of CCA, although it is unclear how important this effect is under most naturally occurring conditions. In one study, sulfuric acid/nitric acid solutions were used to investigate the effect of pH on CCA leaching from western hemlock blocks (Kim and Kim 1993). The study showed that 16% to 25% of copper was leached from the wood at pH 3, compared with about 1% at pH 4. The percentage of arsenic leached from the wood was less affected by pH—generally around 2% to 3% at pH 4 and above. In a similar study, the amount of CCA leached from pine blocks was generally less than 5% for any element, even at pH levels as low as 3.5 (Cooper 1991). A study of the effect of acid rain on leaching of CCA from pine stakes yielded somewhat similar results (Murphy and Dickinson 1990). Although 4% of copper was lost at pH 3, there was no detectable loss of copper at pH 5.6 (normal acidity of rain caused by absorption of CO_2 from atmosphere), and no detectable loss of chromium or arsenic at either pH. However, the pH of rainfall is not necessarily the same as that which contacts CCA components within the wood because the wood also contains compounds that can buffer the acid. Cooper (1990) pointed out that in acid rain situations where the volume of water is relatively low, wood has the capacity to neutralize the acid. He noted field observations in which water dripping from treated wood was consistently 0.8 to 1.2 pH units less acidic than that of the rainfall. Although the low pH of acid rain may be a concern for aboveground exposures in some areas, these studies generally suggest that the conditions encountered in service are not acidic enough (typically well above pH 4) to cause much increase in the leach rate of CCA-treated wood.

For treated wood exposed above ground, the pattern or rate of rainfall may also affect leaching. A recent study evaluated this effect by comparing the rate of leaching from CCA-treated decking specimens at simulated rainfall rates of 2.5, 8.0, and 25.4 mm/h (Lebow and others, in press). The greatest effect was for arsenic, where 2 to 3 times more arsenic was released at a rainfall rate of 2.5 mm/h than at 25 mm/h. The total amount of water was the same. The amounts of copper and chromium leached were less sensitive to rate of rainfall, although the effect was still noticeable. Previous studies have also shown that rate of rainfall affects leaching. In one study, runoff from CCA-treated pine roof boards revealed that concentrations of copper, arsenic, and chromium were greater when exposed to drizzling rain than to heavy showers (Evans 1987). Others have observed that for an equivalent amount of rainfall, more leaching is caused by slow, steady rain than by intermittent showers (Cockroft and Laidlaw 1978, Lebow and others 2000). The amount of time the wood is in contact with water seems to have a greater effect than the amount of water.

The contribution of weathering to release of CCA components from treated wood into the environment is largely unknown. However, a vast amount of information is available on wood weathering and its mechanism and the degradation of the surface (Williams 2001a,b,c and citations therein). Browne (1960) reported that the average erosion rate resulting from weathering for most commercial American softwoods is about 6 mm per century. Feist (1990) and Feist and Hon (1984) described in detail the mechanisms of the degradation of wood in aboveground outdoor exposure. The degradation of the wood surface begins with the UV-radiation-induced degradation of lignin, followed by loss of fibers from the wood surface (erosion of the surface). Information on weathering rates has been obtained from exposure of wood to high-intensity artificial UV radiation and from outdoor exposure. Feist and Mraz (1978) reported good correlation between the erosion rate of wood and wood density. They also found that the outdoor erosion rates correlated well with erosion rates measured using artificial W radiation (carbon arc). The exposure cycle was 20 h of UV radiation and 4 h of water spray daily. Erosion from the surface of western red cedar (*Thuja plicata*) was about the same for 2,400 h of artificial weathering and 5 years of outdoor exposure near Madison, Wisconsin. Williams and others (2001a,b,c) reported the effect of weathering on many commonly used American wood species from 16 years of outdoor exposure.

It is also well established that treatment of wood surfaces with chromium VI salts gives the chemically modified surface resistance to degradation by UV radiation (Black and Mraz 1974). A comparison of untreated wood, chromium VI modified wood, and CCA-treated wood clearly showed that the chromium in the wood greatly decreased the erosion rate of finished and unfinished wood (Feist and Williams 1991). The CCA-treated wood still eroded, but at a rate about 4 times slower than that for untreated wood (Figure 1).

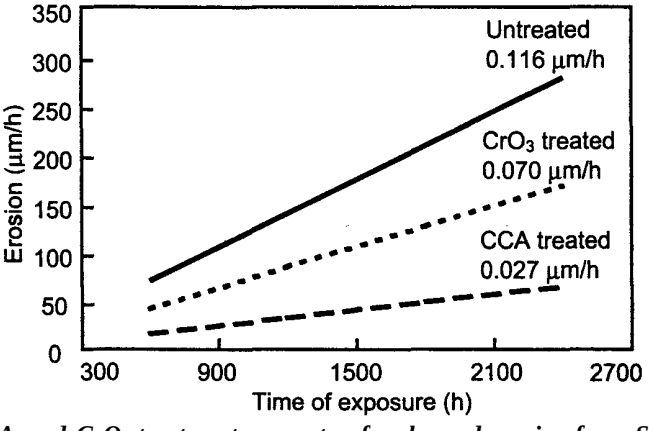

Figure 1. Effect of CCA and CrO_3 treatments on rate of earlywood erosion from Southern Pine. Adapted from Feist and William (1 991).

Although past studies show that a small percentage of CCA components is released from treated wood by leaching and weathering, the environmental significance of this release is unclear. In studies of the environmental impact of a CCA-treated wetland boardwalk (Forest Products Laboratory 2000) and CCA-treated wooden bridges (Brooks 2000), no measurable impact on aquatic insect populations was found, even when a large volume of treated wood was used in slow-moving water. However, concerns about human arsenic exposure from decks and playground equipment led to a recent agreement between the Environmental Protection Agency (EPA) and CCA producers to phase out the use of CCA-treated wood for most residential applications. It is difficult to determine if this decision was based on documented risks or a general desire to decrease use of arsenical wood preservatives. According to their Web site, the EPA has not concluded that CCA-treated wood poses any unreasonable risk to the public or the environment. Nevertheless, arsenic is a known human carcinogen, and, thus, the Agency believes that decrease of exposure to arsenic is desirable (EPA 2003). The EPA Web site also states that citizens may want to take extra precautions by applying a coating to exposed deck surfaces on a regular basis. The EPA action has greatly increased interest in using finishes to minimize arsenic exposure, but little information is available

on the types of finishes that should be applied. The properties of various types of finish vary greatly, and factors such as water repellent content, pigment concentration, binder system, and additives may affect the ability of a finish to prevent release of CCA components.

One report indicated that a clear water-repellent finish greatly decreased CCA release from fencing (Cooper et al. 1997). After 2 years, arsenic concentration in rainwater samples collected from the finished portion of the fence was approximately five times less than that from the unfinished portion. However, horizontal surfaces such as decking present a more severe challenge to a wood finish than do vertical surfaces because they are more directly exposed to UV radiation. A clear water-repellent finish generally lasts only 1 year on decks.

In most previous long-term outdoor exposures of wood to determine weathering rate, the wood was exposed vertically. In previous work at the Forest Products Laboratory comparing vertical and horizontal exposures, the erosion rate was found to be two to three times more rapid for boards exposed horizontally (Williams and others 2001c). Horizontal exposure increases the overall direct sun exposure and the amount of indirect UV radiation. In addition, many decks are located on the sunny side of structures and therefore receive reflected radiation from the structure. Decks and other structures that are fully exposed to the weather undergo diurnal cycles of dew at night followed by rapid drying as they warm by the sun. This tends to cause surface checking and cupping of the boards. The cupped boards tend to hold water longer after rain, which allows more time for leaching from the wood. Of all wood structures, decks are the most vulnerable to UV degradation and leaching by rain.

A survey of the concentrations of arsenic, copper, and chromium in soil under residential decks indicated that levels appear to be lower under a painted deck (Stilwell and Gorny 1997). However, the design of that study did not have a controlled comparison. A more rigorous laboratory study showed that latex paint, oil-based paint, and semi-transparent penetrating stain are all effective in decreasing leaching from horizontal surfaces (Lebow and others 2002). End-matched CCA-treated deck boards were exposed to simulated rainfall and the leachate analyzed for arsenic, copper, and chromium. All three types of finish decreased the leaching of arsenic, copper, and chromium by over 99% in comparison to leaching from unfinished specimens. None of the water collected from specimens coated with latex or oil-based paint contained detectable levels of CCA elements. The greatest concentration of arsenic detected in any single sample was 14 ug/L for the semitransparent penetrating stain. This is only slightly above the allowable level (10 ug/L) for arsenic in drinking water set by the EPA (Federal Register 2001). However, the study by Lebow and others (2002) did not include the effects of UV radiation induced degradation of the surface on the ability of the finish to decrease leaching. Further evaluation is needed to determine the effect of weathering on the ability of finishes to prevent leaching and to determine the longevity of their efficacy. At least two mechanisms are at work to release arsenic, copper, and chromium from the wood: leaching and weathering. These processes work in combination to degrade the wood surface, thus releasing the preservative components. In addition, in the absence of a water repellent finish, the weathering process decreases the natural water repellency of wood (Kalnins and Knaebe 1992).

Because the release of arsenic, copper, and chromium can involve leaching as well as weathering of the surface, the mitigation of this release must involve both increasing the water repellency of the wood and protecting the surface from weathering. It is not practical to evaluate all finish formulations available to consumers because the formulations are constantly changing and their composition is usually proprietary. Therefore, it seems more appropriate to develop an understanding of the role of finish components in minimizing leaching and providing protection against weathering. The type and amount of binder, pigment, and water repellent in the finish will undoubtedly affect the rate of release of CCA components from treated wood. Some coatings, such as paints, form a film or barrier that prevents water from entering wood (Feist and others 1986). In the case of clear penetrating finishes for decks, the water repellent component is expected to play a major role. For pigmented finishes, the pigment will greatly decrease the weathering rate. The effects of water repellent and pigment on leaching of arsenic have not been previously quantified. The first step in quantifying the effect of finish components on the release of arsenic, copper, and chromium from CCA-treated wood focused on the effect of water repellent concentration in the finish.

Objectives

Using an apparatus to simulate rain and collect rainwater runoff for analysis and a xenon arc weathering device, the first objective of this research was to evaluate the effect of water repellent at three concentrations to prevent leaching and weathering of CCA-treated decking specimens. A second objective was to develop technologies needed to establish a standardized procedure for evaluating finishes for their ability to mitigate the release of CCA components. A third objective was to evaluate the change in water repellency of water-repellent-treated CCA-treated specimens caused by exposure to xenon-arc UV radiation.

Experimental

Specimen Preparation

Specimens were obtained from five Southern Pine boards, 38 mm thick and 140 mm wide (nominal 2 by 6 inches), that had been commercially treated with chromated copper arsenate Type C (CCA-C) to a target retention of 6.4 kg/m^3. The boards were randomly selected except for the criterion of being free of heartwood. The boards were conditioned to constant weight in a room maintained at 65% relative humidity and 23°C. Six defect-free 254-mm-long specimens were then cut from each board. Ten replicate specimens for water repellency tests using the swell-o-meter method were also cut from the same boards. The specimens were 25 by 25 by 6 mm (radial, tangential, longitudinal).

Each specimen was assayed for arsenic, copper, and chromium content in a manner similar to that used to determine retention in commercial charges (AWPA 2001). Samples of wood 9.5 mm in diameter and 15 mm in depth were removed from the narrow faces (vertical grain) of each specimen, digested, and analyzed in accordance with AWPA Standard A21-00 (AWPA 2001). The AWPA standard density value for Southern Pine (512 kg/m^3) was used to calculate preservative concentration on a weight/volume basis (AWPA Standard A12-01, AWPA 2001).

Water repellent finishes were formulated with paraffin wax concentrations of 1%, 3%, or 5% using mineral spirits as the solvent and a 20% concentration of a commercial urethane varnish as the binder (solids content of varnish was 50%). To minimize variability resulting from uncontrolled board properties (i.e., growth rate, permeability), matched specimens for each treatment group were cut from each of the original five boards. The 3% water repellent formulation was applied to two of the six specimens cut from each board; the 1% and 5% formulations were each applied to only one specimen from each board. These specimens were dipped in finish for 30 s. Two specimens cut from each board were not finished. This pattern of application provided five replicates (each) of specimens finished with the 1% and 5% water repellent formulations and 10 replicates (each) of the unfinished specimens and the specimens finished with the 3% water repellent formulation. Each original board was equally represented in each treatment group.

Swell-@Meter Test

Using a specially designed swell-0-meter apparatus capable of testing small wafers of wood (Figure 2), the water repellency of specimens treated with 1%, 3%, and 5% water repellent formulations was evaluated after each 5-day simulated rainfall. In addition, a second set of specimens treated with 3% water repellent was subjected to 240 h of xenon-arc W radiation after each rain event. The swelling of CCA/water-repellent-treated specimens was compared to that of end-matched CCA-treated specimens.

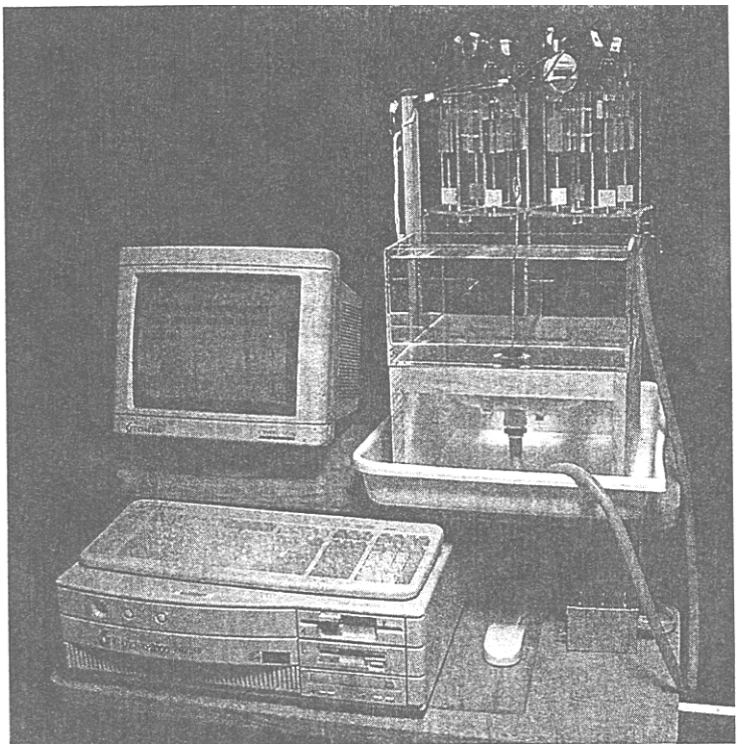

Figure 2. Swell-o-meter test apparatus.

Leaching, Weathering, and Analytical Methods

The leaching methodology was intended to simulate leaching from horizontal decking exposed to either rainfall alone or rainfall and UV radiation. A device was constructed to spray deionized water onto the flat specimens from above, with the rate of rainfall controlled by adjusting the ratio of air:water pressure supplied to the nozzles. Ten air-atomizing wide-angle round spray nozzles were supported on a 1.2- by 2.4-m wire grid at a height of 1 m above the specimens. Each nozzle was supplied with air and water through flexible hoses. Air pressure to the nozzles was regulated at 345 kPa and water pressure was regulated at 241 kPa. This pressure combination produced a spray of fine droplets at a rate of 3.0 mm/h.

Preliminary experiments were used to place the nozzles in positions that minimized differences in rainfall delivered to the specimen containers below. Removable plexiglass walls were assembled to enclose the apparatus and minimize evaporation and air movement. The specimen containers were supported on a 1.2- by 2.4-m platform below the nozzles. Thirty polyethylene trays, 280 mm long by 150 mm wide by 1 14 mm deep, were used to collect rainwater runoff from the specimens. Hoses attached to the bottom of the trays drained the runoff into 19-L collection containers placed below the platform. Each specimen was placed horizontally in the tray with a wide face oriented upward. Specimens were supported 20 mm above the bottom of the tray so that they did not contact standing water. The assignment of specimens to the trays was random prior to the first phase of the simulated rain, and the specimens were returned to the same position for each subsequent rainfall episode.

The specimens were sprayed for 9 h/day, 5 days/week, resulting in approximately 140 mm of rainfall after 5 days (45 h simulated rain). At the end of this 5-day period, the water in the collection container was weighed, acidified with nitric acid, and sub-sampled for analysis. The leachate samples were analyzed for arsenic, chromium, and copper by inductively coupled plasma emission (ICP) spectrometry. The detection limits of the method were approximately 5 µg/L for arsenic and 2 µg/L for chromium and copper. The collection container was then emptied before reattaching it to the specimen tray; the water was not re-used or re-circulated. Five replicates of the unfinished specimens and five replicates of the specimens finished with the 3% water repellent formulation were then removed from the rainfall simulator and transferred to a xenon-arc weathering chamber. They were attached in the chamber so that the face that was exposed to

rainfall would also be exposed to UV radiation. Specimens were exposed to UV radiation for 10 days (240 h) without water spray. The relative humidity was maintained above 30% during the weathering phase to prevent excessive drying. The irradiance was about 65 W/m^2 for the 300- to 400-nm range. The remaining specimens, not exposed to UV light, remained at ambient conditions in the rainfall simulator during this time. After UV exposure, specimens were returned to the rainfall simulator and all the specimens were exposed to rainfall for an additional 5 days. This process was repeated until all the specimens had been exposed to 6 rainfall episodes and selected specimens had been exposed to 5 episodes of UV radiation exposure. This exposure pattern simulated approximately 838 mm of rainfall (270 h simulated rain) and 1,200 h of UV radiation exposure over a period of 5.5 months.

Statistical Analysis

Leachate data—components leached were analyzed as repeated measures experimental designs with the Mixed procedure in the statistical software SAS7 (version 8.2, SAS Institute 1999). The Mixed model structure for both arsenic and copper included a heterogeneous variance structure for each treatment with a separate variance estimate and autoregressive parameter estimate. The Mixed model structure for chromium assumed compound symmetry over time, with separate variance estimates for weathered and non-weathered treatments to accommodate heterogeneity across the two types of treatments.

Estimates of total leaching and individual degree of freedom contrasts to test for differences in these totals were constructed and evaluated in SAS7. Since all treatment totals were contrasted within each component leached, multiple comparison adjustments for each component were made with the Bonferroni method to hold the family-wise error rate at 0.05. For each of the 15 comparisons, the comparison-wise error rate was 0.05/15 = 0.0033. The probability values (*p*-values) and multiplicity adjustment are considered approximate for complicated repeated measurement structures (Westfall and others 1999).

Swell-o-meter data—Water repellent effectiveness (WRE) was also analyzed as a repeated measures experimental design with the Mixed procedure in the SAS statistical software (SAS Institute 1999). The Mixed model structure for WRE included a heterogeneous variance structure for each water repellent treatment group with a separate variance estimate and autoregressive parameter estimate. Subsample measurements were averaged before analysis.

Least squares estimates of WRE and contrasts to test for differences in WRE after similar exposure periods were constructed and evaluated in SAS. The water repellent treatment by exposure interaction was partitioned by time period and treatments compared within exposure period using the slice option in SAS. These comparisons were further broken down with multiple comparison adjustments for contrasting treatments within each period. The simulation method by Westfall and others (1999) was used to hold the family-wise error rate for each exposure period at 0.05. For each exposure period, three primary comparisons were considered: comparison of 3% to 1% wax water repellent treatments, 3% to 5% treatments, and 3% treatment with and without UV exposure. The *p*-values and multiplicity adjustment are considered approximate for complicated repeated measurement structures (Westfall and others 1999).

Results and Discussion

CCA Retention and Penetration

The average concentration of arsenic, chromium, and copper oxides in the decking specimens was relatively uniform between treatment groups (Table 1). Because of this uniformity, it is unlikely that observed differences in leaching between treatment groups are attributable to differences in retention. The CCA retentions were also very close to the 6.4-kg/m^3 target retention for this commodity (AWPA 2001). Visual inspection of the cross sections showed that penetration of preservative was complete in most specimens, although a few had a small amount (about 5% of cross section area) of untreated wood at the center of the board.

Table 1. Average retention of CCA components in specimens assigned to each treatment group

Finish and Exposure	Average retention (kg/m^3)[a]			
	As_2O_5	CrO_3	CuO	Total CCA (oxide basis)
1% Wax, No UV	2.28 (0.67)	2.65 (0.50)	1.47 (0.26)	6.40 (1.42)
3% Wax, No UV	2.32 (0.77)	2.74 (0.70)	1.50 (0.30)	6.57 (1.76)
3% Wax, With UV	2.27 (0.71)	2.67 (0.64)	1.45 (0.30)	6.39 (1.65)
5% Wax, No UV	2.29 (0.52)	2.68 (0.47)	1.47 (0.22)	6.43 (1.19)
No Finish, No UV	2.23 (0.63)	2.66 (0.62)	1.42 (0.26)	6.31 (1.48)
No Finish, With UV	2.32 (0.57)	2.70 (0.45)	1.48 (0.21)	6.51 (1.21)

[a] values in parenthesis represent one standard deviation from the mean.

Effect of Water Repellent Finish

Application of the water repellent finish to the specimens greatly decreased leaching compared to that of unfinished specimens. The greatest effect was observed for arsenic, which appeared to be the most leachable element from unfinished wood. As reported previously (Lebow 1996), chromium was the least leachable CCA element. The decrease in leaching of arsenic is similar to that reported by Cooper and others (1997), but less than that reported by Lebow and others (2002) in an evaluation of paints and a semitransparent stain. It is likely that the binder in paints and stains forms a protective film that is more effective in decreasing leaching than is a water repellent alone. The percentage of wax in the finish did not have a significant effect on leaching for the duration of this study. The total amounts leached for each formulation are shown in Table 2; for each component, average total amounts leached over the course of the experiment are marked with the same alphabetic letter if they are not statistically different. For the unweathered specimens, wax content did not significantly affect the total amount of copper, chromium, or arsenic leached. This may indicate that the 1% water repellent was sufficient to prevent water movement in the wood, or it may indicate that the varnish binder component of the finish had a large role in leaching inhibition. It is possible that water repellent content may have a greater effect after a longer exposure, as the water repellency begins to decline. A concern with water repellent finishes is that they will gradually lose their ability to retard leaching and that the rate of leaching might increase to levels similar to that from unfinished wood. During the course of this study, no increase in leaching was observed over time, although the quantity of each element released from the unfinished specimens declined more rapidly than that from the finished specimens. Cooper and others (1997) reported that a commercial water repellent finish continued to limit leaching from fence units 2 years after application.

The results from the swell-o-meter test showed that the water repellency of the specimens treated with water repellents having 3% and 5% paraffin wax remained at about 75% WRE over the period of exposure (Figure 3). The WRE of specimens treated with the 1% formulation dropped to about 50%. One of the interesting outcomes of the swell-o-meter test was the increase in WRE for the specimens placed in the weathering chamber compared with similar specimens that were exposed only to the simulated rain. After five rain/UV radiation cycles, the average WRE for specimens treated with the 3% formulation and exposed to rain only was 73.6±3.1 versus 81.4±3.4 for specimens exposed to both simulated rain and UV radiation. An ANOVA showed this difference to be significant (Table 3). We believe this was caused by heat in the weathering chamber, which melted the paraffin wax and drew it to the end-grain surface.

At each exposure period, an equivalent set of comparisons were broken down comparing the 3% to the 1% treatment, 3% to 5%, and 3% with and without UV exposure. Table 3 lists the least squares mean estimates of WRE for each water repellent treatment group after the specified period of exposure. Means marked with an asterisk are significantly different from the corresponding 3% water repellent treatment group exposed for the same length of time at an adjusted p-value of <0.05. The swell-o-meter test also showed that UV radiation did not affect the water repellency of the specimens in a negative way during the period of exposure. The drop in the line at week 3 for the specimens exposed to UV radiation was caused by insufficient swelling of the controls. We suspect that these specimens inadvertently got wet prior to the test. The same specimens were evaluated throughout the test.

Table 2. Average amount leached after each rainfall episode Values in parentheses are coefficients of variation (standard deviation divided by mean).

Finish and exposure	Rainfall episode	Average amount leached (mg) Arsenic	Chromium	Copper
1% wax	1	1.85 (0.31)	1.44 (0.49)	1.86 (0.32)
No UV Exposure	2	0.88 (0.22)	0.27 (0.20)	0.72 (0.09)
	3	1.13 (1.18)	0.18 (1.13)	0.64 (1.01)
	4	0.50 (0.32)	0.06 (0.08)	0.32 (0.14)
	5	0.36 (0.25)	0.02 (1.37)	0.20 (0.13)
	6	0.29 (0.26)	0.00 (0.00)	0.20 (0.08)
	Total	5.00 (0.48) **A**	1.97 (0.83) **A**	3.94 (0.27) **A**
3% Wax	1	1.90 (0.47)	1.70 (0.61)	1.76 (0.21)
No UV Exposure	2	0.83 (0.22)	0.27 (0.31)	0.76 (0.31)
	3	0.52 (0.20)	0.09 (0.31)	0.43 (0.22)
	4	0.45 (0.39)	0.10 (0.58)	0.32 (0.28)
	5	0.35 (0.37)	0.03 (1.39)	0.23 (0.21)
	6	0.26 (0.46)	0.02 (2.24)	0.21 (0.21)
	Total	4.32 (0.28) **A**	2.20(0.74) **A**	3.70(0.14) **A**
3% wax	1	1.65 (0.33)	1.52 (0.56)	1.71 (0.11)
With W Exposure	2	6.48 (0.18)	2.79 (0.09)	4.02 (0.08)
	3	4.50 (0.17)	1.63 (0.08)	2.99 (0.07)
	4	4.23 (0.13)	1.56 (0.08)	3.14 (0.12)
	5	3.23 (0.19)	1.32 (0.16)	2.45 (0.12)
	6	3.07 (0.18)	1.31 (0.14)	2.08 (0.14)
	Total	23.17 (0.14) **B**	10.13 (0.26) **C**	16.39 (0.07) **C**
5% wax	1	1.57 (0.30)	1.53 (0.64)	1.65 (0.21)
No W Exposure	2	0.67 (0.17)	0.21 (0.40)	0.61 (0.07)
	3	0.48 (0.27)	0.07 (0.16)	0.33 (0.21)
	4	0.42 (0.31)	0.05 (0.65)	0.29 (0.27)
	5	0.34 (0.51)	0.01 (2.24)	0.22 (0.19)
	6	0.30 (0.54)	0.04 (1.43)	0.25 (0.32)
	Total	3.79 (0.29) **A**	1.91 (0.83) **A**	3.36 (0.09) **A**
No Finish	1	5.03 (0.20)	2.80 (0.19)	3.49 (0.15)
No W Exposure	2	3.81 (0.22)	1.23 (0.13)	2.48 (0.16)
	3	3.57 (0.29)	0.91 (0.10)	1.90 (0.24)
	4	2.88 (0.32)	0.50 (0.27)	0.93 (0.37)
	5	1.94 (0.37)	0.26 (0.33)	0.46 (0.34)
	6	1.44 (0.33)	0.14 (0.43)	0.31 (0.34)
	Total	18.67 (0.22) **B**	5.84 (0.25) **B**	9.57 (0.17) **B**
No Finish	1	4.48 (0.22)	3.26 (0.30)	3.34 (0.25)
With W Exposure	2	9.86 (0.18)	3.86 (0.10)	6.24 (0.14)
	3	10.10 (0.12)	3.24 (0.10)	6.61 (0.12)
	4	10.48 (0.23)	2.76 (0.22)	5.77 (0.16)
	5	9.96 (0.26)	2.31 (0.34)	4.83 (0.25)
	6	8.71 (0.21)	2.04 (0.14)	4.00 (0.12)
	Total	53.58 (0.15) **C**	17.47 (0.15) **D**	30.79 (0.11) **D**

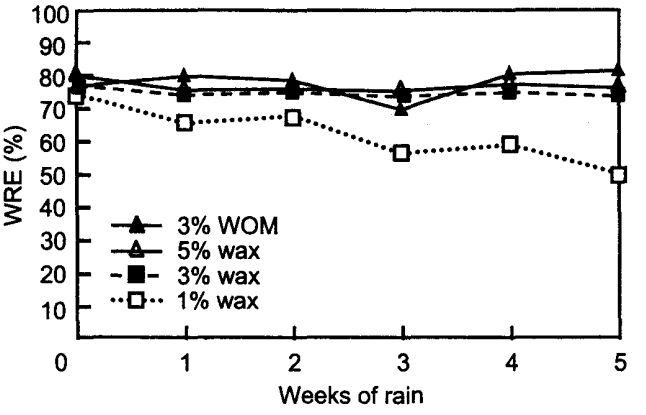

Figure 3. Water repellent effectiveness (WRE) of water repellents with 1%, 3%, or 5% wax after 5 weeks of simulated rain.

Table 3. Average WRE after UV radiation exposure.

Treatment group	WRE (%) least squares mean after various exposure times [a]					
	0 h	240 h	480 h	720 h	960 h	1,200 h
1%	74.3	65.4	67.8	56.3*	58.8*	50.2*
3%	76.9	73.9	74.8	73.5	74.7	73.6
5%	79.9*	75.3	75.9	75.2	77.2*	76.1*
3% + UV exposure	76.7	79.6	78.4	69.6	80.3*	81.4*

[a]Values marked with asterisk (*) are significantly different.

In this study, leaching of all three CCA components decreased during the repeated rainfall episodes for all specimens (Table 2). For the water-repellent-treated specimens, the rate of arsenic, chromium, and copper release neared an asymptote; for the unfinished specimens, however, the rate of release continued to decrease until the termination of the experiment. This decline was most rapid for copper and chromium. This pattern of release is typical for preservative-treated wood and is even more evident when wood is leached via submersion (Lebow 1996, Kartal and Lebow 2002). The initial leaching reflects the loss of poorly fixed or readily available preservative components (Lebow 1996); it may be that these more readily leachable forms of the preservative are prevented from leaching by the wood finish.

Greater leaching occurs from the end grain of treated wood than from other surfaces because water is able to move more readily along than across the grain. Because the specimens used in this study are much shorter than typical deck boards and therefore have a greater proportion of exposed end-grain, we might expect less leaching from a typical deck board in outdoor exposure. The contribution of end grain to leaching can be estimated by comparing the results of this study to those of a previous study (Lebow and others, in press) that used nearly identical methods except that the specimens were end-sealed to prevent leaching In that study, unfinished specimens leached an average total of 10.3 mg arsenic, 5.7 mg chromium, and 6.5 mg copper. Those amounts can be compared to the average total release of 18.7 mg arsenic, 5.8 mg chromium, and 9.6 mg copper for specimens that were not finished or exposed to weathering in the study reported here (Table 2). This comparison indicates that arsenic release is nearly doubled by the contribution of end-grain leaching, with lesser effects on leaching of chromium and copper. As a result, the ability of the finish to prevent leaching from the end grain of the short pieces of wood was more critical than it would be for full-length decking. The amount of arsenic, chromium, and copper leached decreased with each rain event (Figure 4).

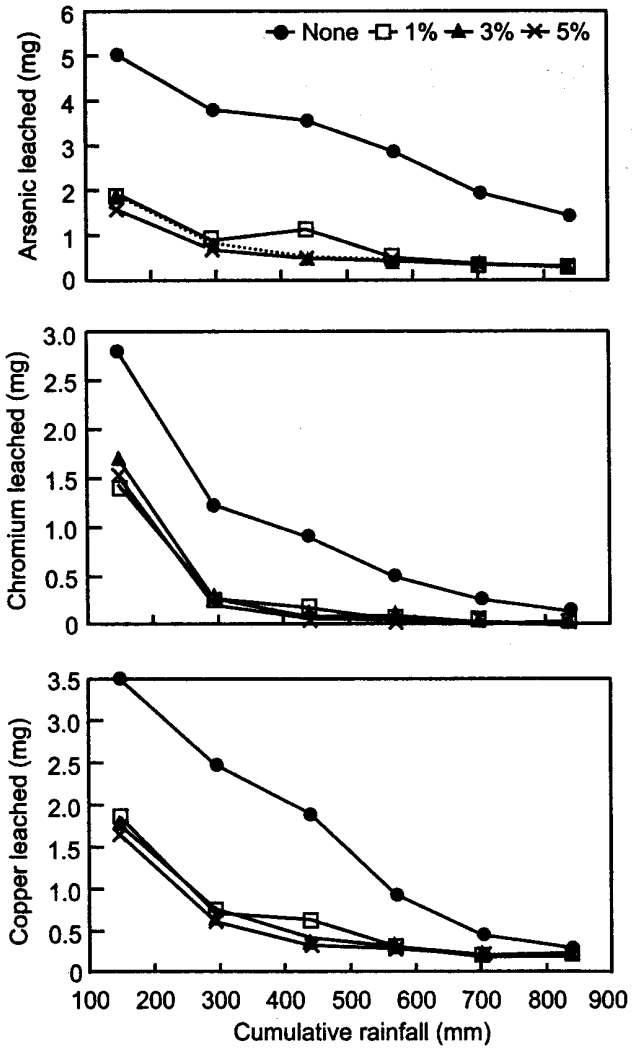

Figure 4. Effect of water repellent (wax) content on ability of finish to prevent leaching of arsenic, chromium, and copper.

Effect of UV Radiation Exposure

Exposure of specimens to W radiation in the weathering chamber resulted in substantial increases in the amounts of arsenic, chromium, and copper leached (Table 2, Figure 5). This effect was observed for both finished and unfinished specimens. For the unfinished specimens, the W exposure increased leaching of all three CCA elements by a factor of 3 (Table 2). The proportional increase was even greater for specimens that had been coated with the finish containing 3% wax, although leaching from the finished specimens remained significantly below that from the unfinished UV-exposed specimens (Table 2). The large increase in leaching after W exposure may be a result of the combined effects of surface erosion and checking. (Surface erosion is the loss of wood fiber from the surface; checking is the formation of small cracks in the surface parallel to the wood grain.) A considerable increase in surface checking, surface roughening, and loosening of the fiber was observed on the boards exposed to W radiation.

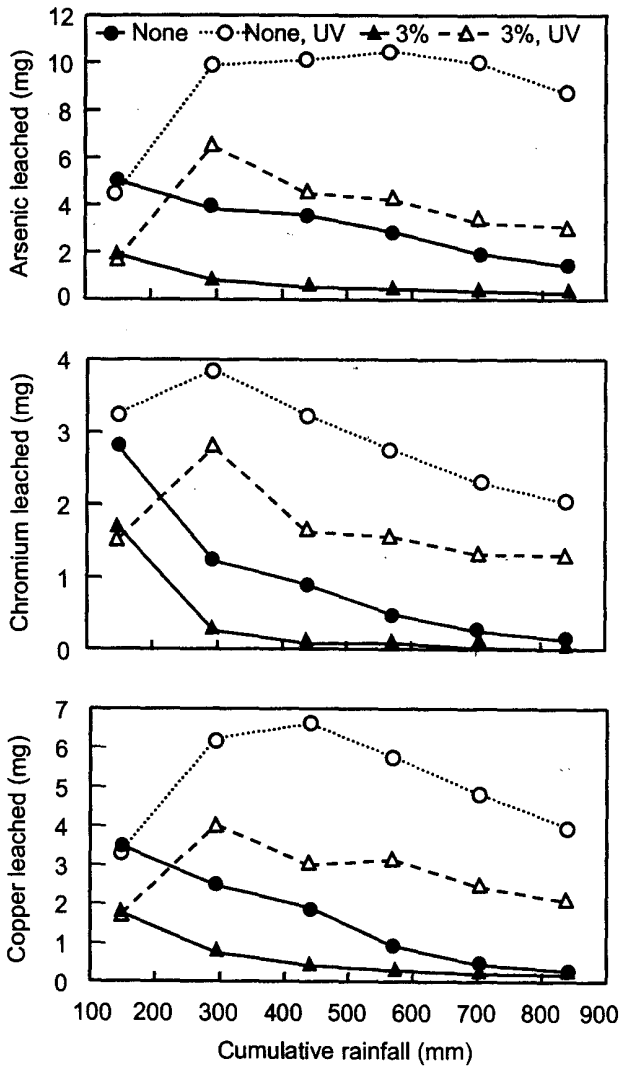

Figure 5. Effect of UV exposure on leaching of arsenic, chromium, and copper.

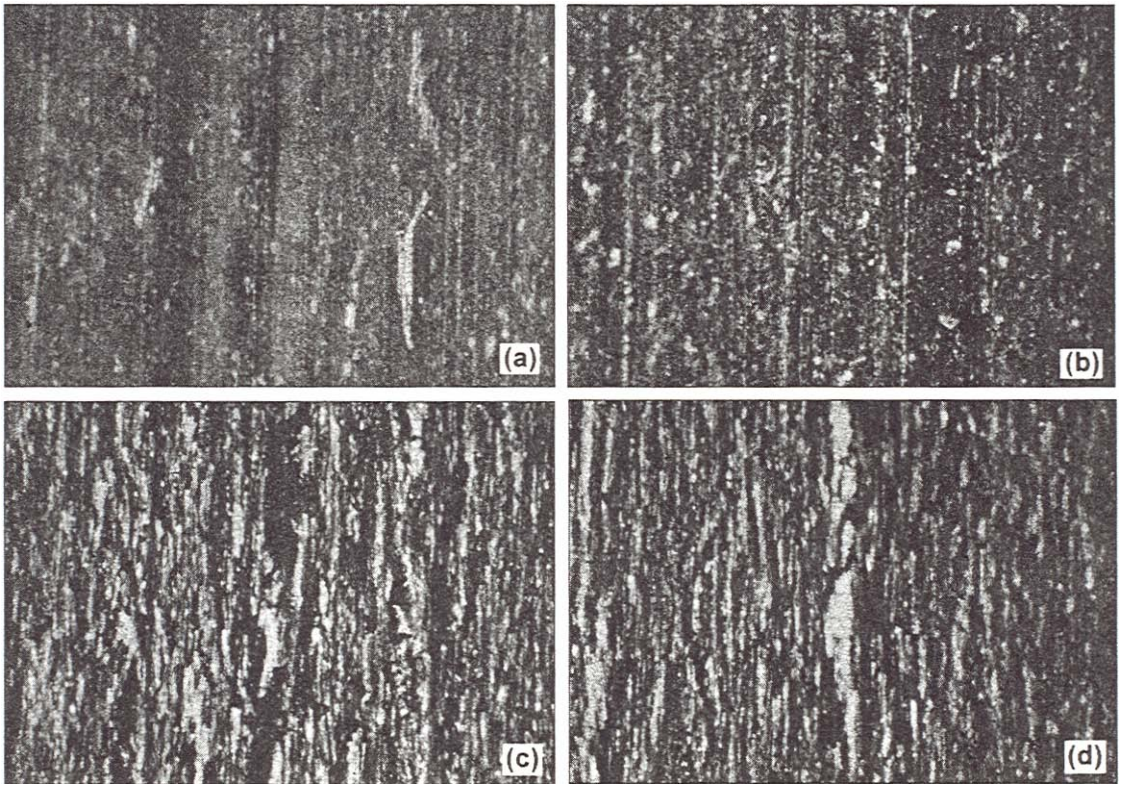

Figure 6. Surface of clear cellophane tape following pull-offtest of wood surfaces after exposure: (a) no UV radiation (0% wax), (b) no UV radiation (3% wax), (c) UV radiation (0% wax), (d) UV radiation (3 % wax).

When the specimen surfaces were subjected to a pull-off test using clear cellophane tape, fibers were only observed on the tape from the weathered surface (Figure 6). X-ray dispersive analysis of the fibers on the tape removed from the weathered surfaces showed considerable arsenic, copper, and chromium in comparison to the tape removed from the unweathered surfaces (Figure 7). This effect was particularly notable for the unfinished specimens.

When wood is exposed to UV light, it is the lignin that preferentially degrades, which leads to a loss of wood fiber. Although chromium in the CCA formulation slows this process, the surface will still degrade, thus releasing wood fibers containing CCA. In a previous study in which xenon arc radiation was used with 4 h of water spray each day, Feist and Williams (1991) showed the erosion rate of CCA-treated wood to be about 0.027 µm/h. This was approximately one-fourth the rate for untreated southern pine (Figure 1).

For 1,200 h of accelerated UV radiation exposure, erosion would be expected to be about 30 µm. Although we did not measure loss of fiber, the tape test clearly showed that the surface had been degraded and that the fibers were loosened. If wood fibers had been lost during the simulated rain exposure, arsenic, copper, and chromium could have been extracted by acid treatment of the leachate. (Acid treatment of the leachate was used to ensure that the arsenic, chromium, and copper ions stayed in solution.)

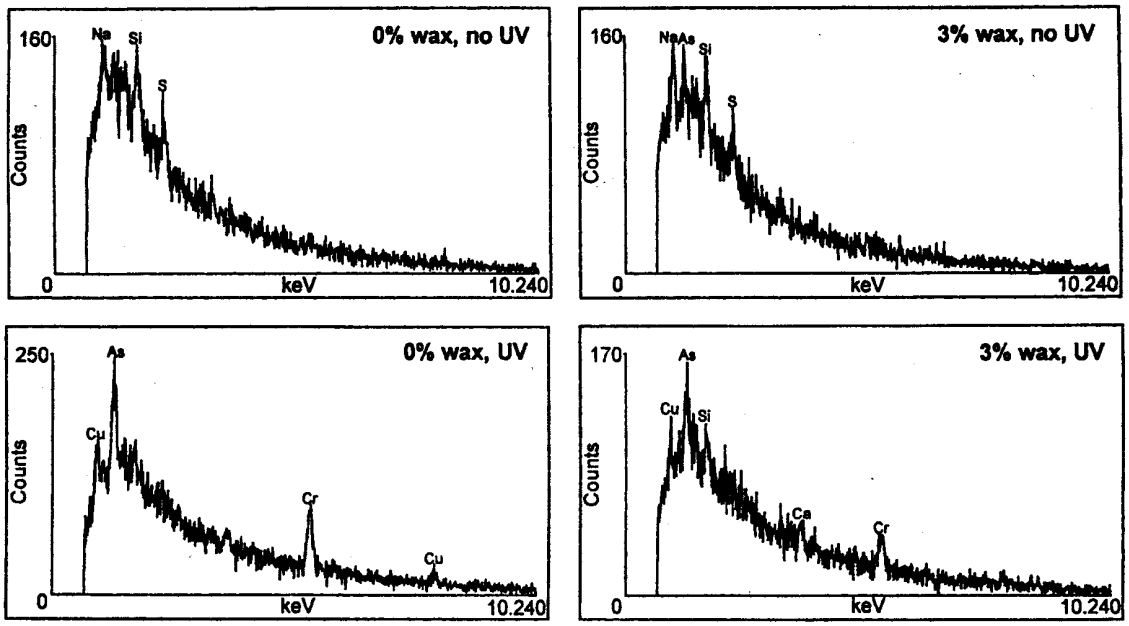

Figure 7. X-ray dispersive analysis of wood fibers attached to clear cellophane tape.

Williams and others (2001c) reported that an average of 87 &year is lost from the tangential surface of Southern Pine earlywood exposed horizontally. Using the factor of 4 difference between CCA-treated and untreated Southern Pine, expected loss from CCA-treated decking would be expected to be about 22 µm/year for CCA-treated wood (on the basis of 87 µm/year for untreated Southern Pine). The arsenic oxide content of CCA-treated wood is about 2.3 kg/m^3 (Table 1), which equates to about 1.5 kg/m^3 As^{+5}. By multiplying this concentration by the volume of wood that erodes from a square meter of CCA-treated wood during a year (2.2×10^{-5} m^3), the amount of arsenic that could be released by the weathering mechanism is about 33 mg AS+5/m2 year (calculated on the basis of As_2O_5). It is interesting that this amount is of the same order of magnitude as we obtained for the unfinished CCA-treated wood that was exposed to leaching and W radiation (53.58 mg, Table 2).

Surface checking from the combined effect of UV degradation and wetting and drying cycles also may have provided a mechanism for the release of CCA components. The water repellent protection is limited to the surface and to a rather shallow depth into the wood. The surface checks give a route for entry of water into the wood and thus may also increase the leaching of CCA. Regardless of the mechanism, the role of W exposure in leaching appears to be an important factor for both water-repellent-treated finished and unfinished CCA-treated wood. Further investigation of this UV effect is underway.

Conclusions

As suggested in previous studies, penetrating deck finishes have the potential to greatly decrease the amount of arsenic, copper, and chromium leached from CCA-treated decking. Although the decrease in leaching in this study was not as great as that noted with pigmented finishes, the amounts of arsenic released were 3 to 5 times less than that from unfinished wood. The amounts of arsenic, copper, and chromium released were the same for all three concentrations of water repellent for the duration of this study. This suggests that to differentiate the effect of water repellent concentration on leaching, longer exposure periods are necessary. The water repellent effectiveness (WRE) of swell-0-meter specimens treated with the 3% and 5% wax formulations remained about the same over the period of leaching; however, WRE of specimens treated with the 1% wax formulation decreased from about 75% to 50%. Specimens treated with the 3% formulation and exposed to both leaching and W radiation increased slightly. A notable outcome of this study is the observation that significantly more arsenic, copper, and

chromium were released from specimens exposed to W radiation. Although the proportion of preservative released from leaching, W radiation, or the combination of these effects was not clear, the effect of W degradation of the surface must be considered when developing finishes for mitigating the release of preservatives from wood. Finishes with pigments will undoubtedly slow W degradation. Research is underway on further evaluating the effect of pigments and binders in combination with W exposure and leaching.

Acknowledgments

We thank John Gangstad for conducting the W exposure of the specimens and initial data plots, Tom Kuster for preparing the micrographs and x-ray analysis, and Dan Foster for ICP analysis.

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Discussion

Dr. Morrell: Thank you, Sam. We'll hold questions until the end for that presentation please. Our next speaker in the FPL Series will be Stan Lebow, and he will be talking about FPL stake evaluations of arsenic free copper preservatives. Stan Lebow, please come on up.

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Ninety-Ninth Annual Meeting

of the

AMERICAN WOOD-PRESERVERS' ASSOCIATION

Boston Marriott Copley Place
Boston, Massachusetts
April 27-30,2003

VOLUME 99

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