Effect of Simulated Rainfall and Weathering on Release of Preservative Elements from CCA Treated Wood

STAN LEBOW,* R. SAM WILLIAMS, AND PATRICIA LEBOW
USDA Forest Service, Forest Products Laboratory, One Gifford Pinchot Drive, Madison, Wisconsin 53726-2398

The release of arsenic from wood pressure-treated with chromated copper arsenate (CCA) can be decreased by application of wood finishes, but little is known about the types of finishes that are best suited for this purpose. This study evaluated the effects of finish water repellent content and ultraviolet (UV) radiation on the release of arsenic, copper, and chromium from CCA-treated wood exposed to simulated rainfall. Deck boards treated with CCA were either left unfinished or dipped in a finish prepared with 1%, 3%, or 5% water repellent. All specimens were exposed to leaching from simulated rainfall, and a subset of specimens was also exposed to UV radiation. The rainfall was collected and analyzed for total elemental arsenic, copper, and chromium. The water repellent significantly decreased the amounts of these elements in the runoff, but for the short duration of this study there was no difference among the three water repellent concentrations. It is possible that water repellent content would have a greater effect over a longer exposure period. Exposure to UV radiation caused a significant increase in leaching from both finished and unfinished specimens. This effect may be a result of increased surface area during weathering as well as loss of fibers caused by UV-induced surface erosion.

Introduction

For several decades consumers have been able to purchase pressure-treated wood at local lumberyards. This type of treated wood, commonly known as green treated, is pressure impregnated with the preservative chromated copper arsenate (CCA). Chromium, copper, and arsenic oxides in CCA-treated wood 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 (1). However, a small percentage of CCA components gradually release from the wood through leaching and weathering. The amount of leaching can be influenced by a number of factors, including the dimensions and wood species of the treated product, the preservative concentration in the wood, and the exposure environment (2–4).

The contribution of weathering to release of CCA components from treated wood is largely unknown, but there is substantial information available on wood weathering and its mechanism and the degradation of the surface (5–7). These studies indicate that surface degradation begins with UV-radiation-induced degradation of lignin followed by loss of fibers (surface erosion). However, it has also been determined that treatment with hexavalent chromium solutions makes the surface resistant to degradation by UV radiation (8, 9). Accelerated weathering of untreated wood, wood treated with hexavalent chromium, and CCA-treated wood demonstrated that CCA was even more effective than hexavalent chromium in protecting the wood surface (10). In that study, untreated southern pine eroded at a rate of 0.116 mm/h, whereas wood treated with hexavalent chromium and CCA-treated wood eroded at 0.070 and 0.027 μm/h, respectively (10). Although erosion of CCA-treated wood is limited in comparison to that of untreated wood, any erosion that does occur is expected to contribute to overall arsenic release and surface availability.

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 (11). The EPA has greatly increased interest in using finishes to minimize arsenic exposure from existing structures, but little information is available on the types of finishes that should be applied for this purpose. The properties of various types of finish vary greatly (12), 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 (13). Even after 2 years, arsenic concentration in rainwater collected from finished samples was approximately five times less than that from unfinished samples. However, the relation of these findings to decking is uncertain because horizontal surfaces such as decking receive more overall direct sun exposure and more indirect UV radiation. In previous work comparing vertical and horizontal exposures, the erosion rate was found to be two to three times more rapid for boards exposed horizontally (7). Horizontal surfaces are also more likely to retain rainwater.

In an observational study of arsenic, copper, and chromium concentrations in soil under residential decks, Stilwell and Gorny (14) noted that levels appeared to be lower under a painted deck. However, the study design did not allow a controlled comparison. A preliminary study in our laboratory (4) indicated that latex paint, oil-based paint, and semi-transparent penetrating stain are all effective in decreasing leaching from horizontal surfaces. All three types of finish decreased the leaching of arsenic, copper, and chromium by over 99% in comparison to leaching from unfinished specimens. However, that study did not include the effect of UV-radiation-induced surface degradation 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 decrease leaching and to determine the longevity of their efficacy.

Because the release of arsenic, copper, and chromium can involve leaching as well as surface weathering, 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 formula-
tions available to consumers because formulations often change 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 paint, form a film or barrier that prevents water from entering wood (15). In the case of clear penetrating deck finishes, the water repellent component is expected to play a major role. For pigmented finishes, the pigment will greatly decrease the weathering rate. However, these assumptions have not been quantified.

This study focused on the effect of finish water repellent content on the release of arsenic, copper, and chromium from CCA-treated wood. Using an apparatus to simulate rainfall and a commercial weathering device, we evaluated the effect of water repellent at three concentrations on leaching and weathering of CCA-treated decking specimens.

**Experimental Section**

**Specimen Preparation.** Specimens were taken from five Southern Pine boards 38 mm thick × 140 mm wide (nominal 2 × 6 in. lumber) that had been commercially treated with chromated copper arsenate Type C (CCA-C) to a target retention of 6.4 kg/m³. The boards were randomly selected; the only selection criterion was absence of heartwood. The nonlining center of a tree, is relatively impermeable and typically contains very little preservative after treatment. 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.

Each specimen was assayed for arsenic, copper, and chromium content in a manner similar to that used to determine retention in commercial charges (16). Samples of wood 9.5 mm in diameter and 15 mm in depth were removed from the narrow (vertical grain) face of each specimen and digested and analyzed in accordance with American Wood-Preservers Association (AWPA) Standard A21-00, Standard Method for the Analysis of Wood and Wood Treating Solutions by Inductively Coupled Plasma Emission Spectrometry (16). This method details the procedure for digesting a wood sample and analyzing the resulting solution for preservative components. The AWPA standard density value for Southern Pine (512 kg/m³) was used to calculate preservative concentration on a weight/volume basis (AWPA Standard A12-01) (16).

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 urethane varnish as the binder (50% varnish solids content). 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 (total of 10 replicates) so that five replicates could be exposed to UV radiation; the 1% and 5% formulations were each applied to only one specimen from each board (5 replicates each). The specimens were dipped in finish for 30 s. The remaining two 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 (total of 10 replicates) so that five replicates could be exposed to UV radiation; the 1% and 5% formulations were each applied to only one specimen from each board (5 replicates each). The specimens were dipped in finish for 30 s. The remaining two replicates were not finished.

**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. Although naturally occurring rainfall may contain components such as sulfur and nitrogen oxides as well as chlorine and sodium ions, we chose to use deionized water in this study. The pH and composition of natural rainwater vary by region and climate conditions, and no single composition is broadly representative. Previous researchers have concluded that in all but the most extreme cases, the pH of naturally occurring rainfall is not sufficiently low to significantly increase leaching of CCA components (17, 18). A device was constructed to spray deionized water onto the flat specimens. Ten air-atomizing, wide-angle, round spray nozzles were supported on a 1.2- × 2.4-m wire grid at a height of 1 m above the specimens. Each nozzle was supplied with air and water through a flexible hose. The rate of rainfall was controlled by adjusting the ratio of air:water pressure supplied to the nozzles. Air pressure was regulated at 345 kPa and water pressure at 241 kPa. This pressure combination produced a spray of fine droplets at a rate of 3.0 mm/h. Preliminary experiments were conducted to position the nozzles so that differences in rainfall on the specimens were minimized. This was accomplished by repeatedly collecting and weighing the rainwater delivered to the empty specimen containers. The apparatus was enclosed by removable plexiglass walls to minimize evaporation and air movement.

High-density polyethylene specimen containers were supported on a 1.2- × 2.4-m platform below the nozzles. Specimens were laid horizontally, with the wide face turned up, in trays 280 mm long × 150 mm wide × 114 mm deep; the specimens were supported 20 mm above the bottom of the trays so that they did not contact standing water. Hoses attached to the bottom of the trays drained water runoff into 19-L low-density polyethylene collection containers below the platform.

Specimens were assigned randomly to the trays prior to the first phase of the simulated rainfall and were returned to the same position for each subsequent rainfall episode. The specimens were sprayed for 9 h/day for 5 days, resulting in approximately 140 mm of rainfall. At the end of the 5-day period, the water in the collection container was weighed, acidified with nitric acid, and subsampled for analysis. The leachate samples were analyzed for total elemental arsenic, chromium, and copper by inductively coupled plasma (ICP) emission spectrometry. The detection limits of the method (defined as the concentration of the element producing a signal-to-noise ratio of 2.0) were approximately 5 μg/L for arsenic and 2 μg/L for chromium and copper. The collection container was emptied before reattaching it to the specimen tray; the water was not reused or recirculated. Care was taken to minimize risk of sample contamination. The specimen and collection containers were prewashed with dilute nitric acid. Sample vials used in ICP analysis were prewashed and were not reused. With the exception of the stainless steel nozzles, metallic components were not used in construction of the rainfall simulator. Tubing and attachments were constructed of poly(vinyl chloride), rubber, nylon, or polypropylene. The support frame was constructed of untreated wood.

At the end of each 5-day period, five replicates of unfinished specimens and five replicates of specimens finished with the 3% water repellent formulation were then removed from the rainfall simulator and transferred to a xenon-arc weathering chamber. Specimens were attached in the chamber so that the face exposed to rainfall would also be exposed to UV radiation. Specimens were exposed to UV radiation for 10 days (240 h) without water spray. Relative humidity was maintained above 30% during the weathering phase to prevent excessive drying. The irradiance was about 65 W/m² for the 300–400 nm range. The remaining specimens were not exposed to UV light and remained at ambient conditions in the rainfall simulator during this time.

The UV-exposed specimens were then 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 six rainfall
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, with statistical mean differences indicated for each element. For 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 is sufficient to prevent water movement in the wood or that the varnish binder component of the finish has a large role in inhibiting leaching. It is possible that water repellent concentration 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 over time the amount 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 unfinished specimens declined more rapidly than that from finished specimens. Cooper et al. (13) reported that a commercial water repellent finish continued to limit leaching from fence units 2 years after application.

In this study, leaching of all three CCA components decreased with repeated rainfall episodes for all specimens (Table 2). The amounts of arsenic, chromium, and copper released for the water repellent treated specimens began to plateau after the fourth rainfall episode, while release from the unfinished wood continued to decline in the final leaching episode. This decline was most rapid for copper and chromium. This pattern of release is typical for preservative treated wood, and it is even more evident when wood is leached via submersion (2, 21). Initial leaching reflects the loss of poorly fixed or readily available preservative components (2), and it may be that these more readily leached forms of the preservative are contained within the wood by the finish.

The amount of leaching from the end grain of treated wood is greater than that from other surfaces because water is able to move more readily along than across the grain. Because the specimens used in this study were much shorter than typical deck boards and therefore had a greater proportion of exposed end-grain, we might expect less leaching from a typical deck board in outdoor exposure. In this study, specimens were not end-sealed to maximize leaching and to better differentiate the effects of the finishes. The contribution of end grain to leaching can be estimated by comparing the results of this study to those of a previous study in which end-sealed samples were exposed to the same simulated rainfall conditions (22). In the previous study, unfinished specimens leached an average total of 10.3 mg of arsenic, 5.7 mg of chromium, and 6.5 mg of copper. In the study reported here, average total release from unfinished, unweathered specimens was 18.7 mg of arsenic, 5.8 mg of chromium, and 9.6 mg of copper (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 used in this study was more critical than it would be for full-length decking.

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**TABLE 1. Average Retention of CCA Components in Treatment Groups**

<table>
<thead>
<tr>
<th>finish and exposure</th>
<th>average retention (kg/m²)*</th>
<th>As₂O₃</th>
<th>Cr₂O₃</th>
<th>CuO</th>
<th>total CCA (oxide basis)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1% wax, no UV</td>
<td>2.28 (0.67) 2.65 (0.50) 1.47 (0.26)</td>
<td>6.40 (1.42)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3% wax, no UV</td>
<td>2.32 (0.77) 2.74 (0.70) 1.50 (0.30)</td>
<td>6.57 (1.76)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3% wax, with UV</td>
<td>2.27 (0.71) 2.67 (0.64) 1.45 (0.30)</td>
<td>6.39 (1.65)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5% wax, no UV</td>
<td>2.29 (0.52) 2.68 (0.47) 1.47 (0.22)</td>
<td>6.43 (1.19)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>no finish, no UV</td>
<td>2.23 (0.63) 2.66 (0.62) 1.42 (0.26)</td>
<td>6.31 (1.48)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>no finish, with UV</td>
<td>2.32 (0.57) 2.70 (0.45) 1.48 (0.21)</td>
<td>6.51 (1.21)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Values in parentheses represent one standard deviation from the mean.

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episodes, and selected specimens had been exposed to five episodes of UV radiation exposure. This exposure pattern simulated approximately 838 mm of rainfall and 1200 h of UV radiation exposure over a period of 5.5 months. These exposures correspond to approximately 1 year of outdoor exposure averaged across the mainland United States.

Specimens were subjected to a pull-off test using clear cellophane tape. Pieces of tape approximately 50 mm long were pressed to the surface and burnished firmly with thumb. Tape was pulled from the surface at a 90° angle. The tape was analyzed by X-ray dispersive analysis (EDXA). Specimens with pulled-off fibers were mounted on carbon stubs using double-stick carbon tape. These specimens were analyzed in a scanning electron microscope. Spectra were acquired at 15 kV for 60 s.

**Statistical Analysis.** The amounts of arsenic, chromium, and copper leached from the wood were analyzed as repeated measures experimental designs using the Mixed procedure within the Statistical Analysis Software (SAS) (19). 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 unweathered 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 SAS. 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 (0.05/15) was 0.0033. The probability (p) values and multiplicity adjustment are considered approximate for complicated repeated measurement structures (20).

**Results and Discussion.**

**CCA Retention and Penetration.** The average concentrations of arsenic, chromium, and copper oxides in the docking specimens were relatively uniform between treatment groups (Table 1). Consequently, it is unlikely that observed differences in leaching between the treatment groups are attributable to differences in retention. The CCA retentions were also very close to the 6.4-kg/m³ target retention for this commodity (16). 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.

**Effect of Water Repellent Finish.** Application of water repellent finish greatly decreased leaching compared with leaching from unfinished specimens (Table 2). The greatest effect was observed for arsenic, which appeared to be the most leachable CCA element from unfinished wood. As reported previously (2), chromium was the least leachable element. The effect of water repellent on leaching of arsenic was similar to that reported by Cooper et al. (13) but less than that reported by Lebow et al. (4) 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.

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

When the specimens were subjected to a pull-off test using clear cellophane tape, fibers were observed only on the tape from the unweathered surfaces (Figure 1). X-ray dispersive analysis of the tape from the weathered surfaces showed considerable arsenic, copper, and chromium in comparison to tape from the unweathered surfaces (Figure 2). This effect was particularly notable for the unfinished specimens.

Lignin is preferentially degraded when wood is exposed to UV light, leading to a loss of wood fiber. Although CCA treatment slows this process, some degradation does occur. UV exposure, as part of weathering, has been reported to erode the wood structure, particularly earlywood cells. The accelerated weathering study by Feist and Williams (10) indicated that CCA decreased the erosion rate by a factor of about 4 (0.116 – 0.027 μm/h). In another recent outdoor study (7), the rate of erosion of fibers from the surface of horizontally exposed Southern Pine was found to be 87 μm/year. Although we did not measure loss of fiber, the tape test indicated 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 would have been extracted by the acid treatment of the leachate. Thus, the greater preservative release detected after UV exposure may have partially resulted from mechanical loss of wood substrate rather than from leaching. The mechanism of release from the treated wood may have practical implications. Copper, chromium, and arsenic leached into the environment might be expected to be most bioavailable if released in the ionic form. Further studies are needed to clarify the bioavailability of leached CCA elements in the environment.
form, but studies on leaching of these components have not revealed whether they are leached in ionic form, as copper or chromium arsenates, or as complexes with inorganic or organic ligands (2). CCA elements released in the form of treated wood fibers would be expected to have lower bioavailability than those that are solubilized in rainwater (23). Even without UV effects, activities such as foot traffic or refinishing may cause fibers to dislodge from treated wood, contributing to environmental concentrations. This mechanism of release may partially explain the relatively high concentrations of chromium, copper, and arsenic reported in a survey of soil beneath residential decks (14). Surface checking from the combined effect of UV degradation and wetting and drying cycles may have also increased the wood surface area and provided a mechanism for the increased leaching of CCA components.

The water repellent protection is limited to the surface and to a rather shallow depth into the wood. Surface checks provide 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 UV exposure in leaching appears to be important for both CCA-treated wood finished with water repellent and unfinished CCA-treated wood. These findings suggest that finishes that prevent UV degradation of the surface of CCA-treated wood may be of great value in minimizing release of preservative elements. Further investigation of this UV effect is underway.

Acknowledgments

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