

# EFFECT OF PRESERVATIVE TYPE AND NATURAL WEATHERING ON PRESERVATIVE GRADIENTS IN SOUTHERN PINE LUMBER

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**Abstract.** The effects of preservative type and natural weathering on preservative component distribution in southern pine boards were evaluated. Lumber was treated by a modified full-cell process with chromated copper arsenate (CCA-C), alkaline copper quat (ACQ-D), and micronized copper quat (MCQ), and samples were exposed to natural weathering. After treatment, the copper and arsenic components of CCA were uniformly distributed across the board thickness, whereas the chromium component was higher near the surface. The copper amine component of ACQ was preferentially adsorbed near the board surface, whereas MCQ had lower copper concentration near the surface compared with inside the board. The quat component (didecyltrimethylammonium carbonate [DDACb]) of both preservatives was preferentially adsorbed near the surface resulting in a steep concentration gradient. After 330 da of exposure to natural weathering, the average amounts leached were 2.9% for ACQ-Cu, 0.36% for MCQ-Cu, 0.24% for CCA-Cr, 0.59% for CCA-Cu, and 2.05% for CCA-As. For ACQ and MCQ, the ratio of CuO to quat increased significantly with weather exposure indicating a higher DDACb rate of leaching compared with copper. For both preservatives, it was estimated that DDACb leaching was about 20% for ACQ and 16% for MCQ.

**Keywords:** Preservative, preservative gradient, leaching, CCA, ACQ, micronized copper, DDACb, mass balance.

## INTRODUCTION

When preservative chemicals penetrate wood products during pressure treatment, there may be a preservative gradient as a result of physical screening and/or rapid chemical reaction of the preservative with wood. The nature of this gradient has implications for leaching of preservatives and efficacy of the treatment. Leaching occurs mainly from the exposed surface and a higher surface concentration may increase the overall leaching rate; a deficiency of active ingredients deeper in treated sapwood may make the interior of products susceptible to decay by organisms invading wood through checks.

As different wood preservative systems are introduced, it is of interest to compare preservative component gradients after treatment and the effects of leaching exposure on the preservative distribution. Pine sapwood is easily treated by preservatives and is usually fully penetrated, but there is limited information on gradients of water-based preservatives after treatment. Osborne and Fox (1995) showed a decreasing chromated copper arsenate (CCA) concentration in Southern pine (*Pinus* spp.) poles with depth. Red pine (*P. resinosa* Ait.) poles had a relatively uniform CCA concentration gradient with depth, whereas lodgepole pine (*P. contorta* var. *latifolia* Engelm.) had a steep concentration gradient (Cooper et al 1994). A disproportioning of individual preservative components occurs with CCA as a result of rapid adsorption of chromium near

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the wood surface (Cech and Pfaff 1974). Steeper preservative gradients are expected in preservative systems that bind components to wood through rapid fixation processes such as ion exchange reactions, for example, of copper amines and quaternary ammonium compounds (Jin and Preston 1991; Zhang and Kamdem 2000).

Leaching of preservative components under natural weathering exposure is a complex process involving wetting of the wood by rain, penetration of moisture deeper into wood, dissolution of soluble preservatives, and diffusion out of wood. Naturally, these processes are affected by many variables, including the preservative type and its distribution in wood. Recent comparisons of leaching properties among CCA, alkaline copper quat (ACQ), and micronized copper systems (MCQ) (Cooper and Ung 2008; Freeman and McIntyre 2008) show that copper losses in laboratory and field leaching exposures are much higher for ACQ compared with CCA or MCQ. In this article, the preservative component distributions are compared for southern pine decking material treated with three preservatives—CCA, ACQ, and MCQ—either without leaching exposure or exposed horizontally to natural weathering for 330 da.

#### MATERIALS AND METHODS

Flat-sawn southern pine boards, 38 mm × 140 mm × 1.5 m, were treated in a pilot plant treating retort using a modified full-cell treating schedule (vacuum at -44 kPa for 5 min to fill the retort; pressure at 895 kPa for 20 min; and final vacuum at -95 kPa for 30 min; all pressures relative to gauge). Wood was treated to target retentions of 4.0 kg/m<sup>3</sup> with waterborne preservatives, CCA-C, ACQ-D, and MCQ consisting of submicron copper carbonate particles (at least 90% of the particles <1-μm dia) and quaternary ammonium compound, didecyldimethylammonium carbonate (DDACb), in a 2:1 ratio of copper as CuO to DDACb. The ACQ formulation had the same ratio of CuO to DDACb dissolved in monoethanolamine (MEA). Three different replicate boards were treated with each preser-

vative system. After laboratory fixation of the preservatives for 5 da, 300-mm-long samples were cut from each board and end-sealed with a silicone adhesive. One sample from each board was mounted horizontally over containers in Toronto in July 2007, removed in November 2007, reinstalled in April 2008, and left until October 2008 for a total exposure time of 330 da. Over this period, the cumulative rainfall was 1067 mm as measured by a rain gauge. Leach water was collected after each significant rainfall and the cumulative losses of inorganic preservative components were estimated from the volumes of leach water, concentrations of components in the leach water, and the original retentions of the samples. An unexposed sample from each board was retained in the laboratory.

Two cross-section samples (5- and 10-mm thick) were cut from the midpoint of weathered and end-matched unexposed samples. The 5-mm section from each board was ground to pass a 30-mesh (0.68-mm opening) screen and samples were analyzed for copper (all preservatives), chromium (CCA), and arsenic (CCA) as oxides by X-ray fluorescence spectroscopy (Oxford Instruments LAB X 3000). For ACQ and MCQ, two 0.5-g samples were extracted with denatured ethanol by ultrasonic extraction according to AWPA A16-93 (AWPA 2006). Extracts were analyzed for DDACb retention by ion chromatography (Dionex DX 600) suppressed conductivity using a CS12A analytical column (4 mm) and run isocratically at 1.0 mL/min flow rate. The eluents used for DDACb analysis were 20% 20 mM methanesulfonic acid and 80% acetonitrile. The 10-mm-thick wafers were accurately sliced into 8 depth zones using a band saw (blade kerf of 0.7 mm) with the blade centered at depths of 3, 8, 12, 19, 26, 30, and 35 mm. These zones were ground and analyzed for Cu, Cr, As, and DDACb as previously described.

#### RESULTS AND DISCUSSION

##### Cumulative Leaching

Based on analysis of leachate samples collected during exposure, the average leaching losses of

inorganic components (standard deviations in brackets) were: ACQ-Cu, 2.9% (1.54); MCQ-Cu, 0.36% (0.11); CCA-Cr, 0.24% (0.05); CCA-Cu, 0.59% (0.19); and CCA-As, 2.05% (0.33).

### CCA-Treated Samples

The average retention of CCA in the unexposed samples was 3.85 kg/m<sup>3</sup>. There was a considerable change in the mass balance of CCA components in wood after treatment compared with the original solution balance; the relative amounts of chromium and copper were higher in the wood than in the solution, whereas the relative amount of arsenic was lower (Table 1). The effects observed here may result from the modified full-cell treatment, which causes a significant amount of solution to be expelled during the pressure release and final vacuum treatment. Hedley et al (1990) reported significant changes in the mass balance of CCA components after empty-cell treatments with increased chromium and copper and decreased arsenic proportions. Slower-reacting components will be expelled in greater amounts from

the wood with these treatments. This suggests that chromium and copper reacted more quickly and were expelled to a lesser extent than arsenic. Hexavalent chromium is rapidly adsorbed on wood during treatment, reducing the concentration in free solution (Dahlgren and Hartford 1972), and a small amount of copper is rapidly ion-exchanged to wood even at the low pH conditions during treatment. Arsenic is not expected to precipitate until chromium is reduced to the trivalent state.

Chromium preferentially reacted near the surface resulting in a significantly (by t-test comparison) higher surface concentration (Fig 1a) as observed by others (eg Cech and Pfaff 1974). The arsenic (Fig 1a) and copper (Fig 1b) components of CCA were quite uniformly distributed across the thicknesses of the samples with slight elevations (statistically significant for arsenic based on t-test comparison) in the surface layers. Although copper in these systems is considered to be fixed primarily through rapid ion-exchange mechanisms, these reaction sites are few and easily saturated during solution penetration because the solution is very

Table 1. Comparison of copper (as CuO), DDACb, Cr (as CrO<sub>3</sub>), and As (as As<sub>2</sub>O<sub>5</sub>) distribution in unexposed and naturally weathered 38- × 140-mm ACQ, MCQ, and CCA samples (means [SD]).

Preservative component	Weather-exposed	Retention (kg/m <sup>3</sup> )	Percent of formula <sup>a</sup>
ACQ-Cu	No	2.97 (0.29)	65.0 (0.40)
	Yes	2.47 (0.17)	69.4 (2.23)
ACQ-DDACb	No	1.60 (0.11)	35.0 (0.40)
	Yes	1.09 (0.04)	30.6 (2.34)
ACQ Total	No	4.57 (0.38)	
	Yes	3.56 (0.14)	
MCQ-Cu	No	3.29 (0.45)	67.2 (1.83)
	Yes	3.24 (0.48)	71.1 (1.90)
MCQ-DDACb	No	1.60 (0.11)	32.7 (0.40)
	Yes	1.32 (0.04)	28.9 (2.34)
MCQ Total	No	4.89 (0.66)	
	Yes	4.56 (0.61)	
CCA-CrO <sub>3</sub>	No	1.97 (0.06)	52.2 (2.19)
	Yes	1.93 (0.07)	49.9 (1.36)
CCA-CuO	No	0.80 (0.06)	21.2 (0.96)
	Yes	0.88 (0.04)	22.7 (0.40)
CCA-As <sub>2</sub> O <sub>5</sub>	No	1.00 (0.05)	26.5 (0.94)
	Yes	1.06 (0.05)	27.4 (0.52)
CCA-total	No	3.77 (0.12)	
	Yes	3.87 (0.14)	

<sup>a</sup> Balances in treating solutions were CuO:DDACb = 66.7:33.3 for ACQ and MCQ (nominal) and CrO<sub>3</sub> = 48.0, CuO = 18.2 and As<sub>2</sub>O<sub>5</sub> = 33.8 for CCA (by analysis).

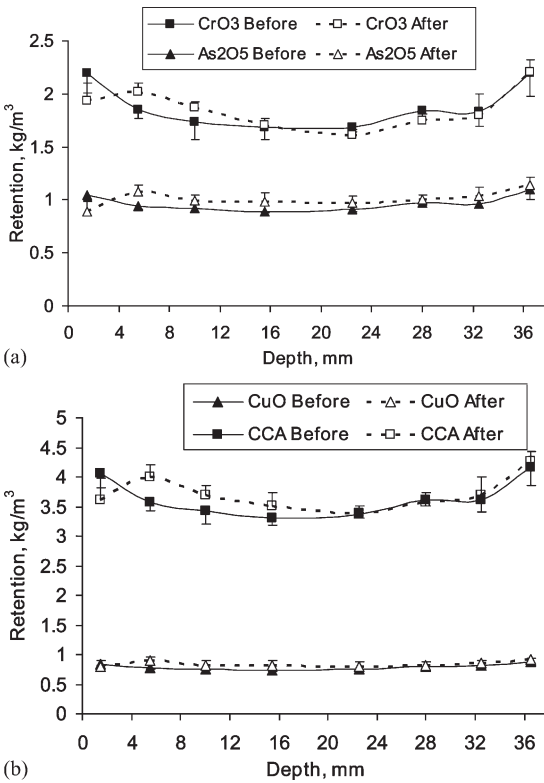


Figure 1. Average chromium and arsenic (a) and copper and total CCA (b) retention gradients in CCA-C-treated southern pine in unexposed samples (before) and those exposed to natural leaching (after); note error bars are presented as  $-1$  SD for unexposed samples and  $+1$  SD for leached samples for visibility.

acidic and weak acid groups in wood are not significantly dissociated. As a result, no significant gradient develops. Similarly, the precipitation of arsenates is driven by the slow chromium reduction that occurs over a longer time than required to fully penetrate the wood. As a result, CCA solution penetrates the wood uniformly without significant chemical screening of the components, except for some rapid adsorption of chromium near the surface.

The shape of the distribution profile was affected by natural weathering only near the top surface, where there appeared to be some depletion of chromium and arsenic. The chromium effect was surprising because the amount measured in the leachates was lowest of the three components.

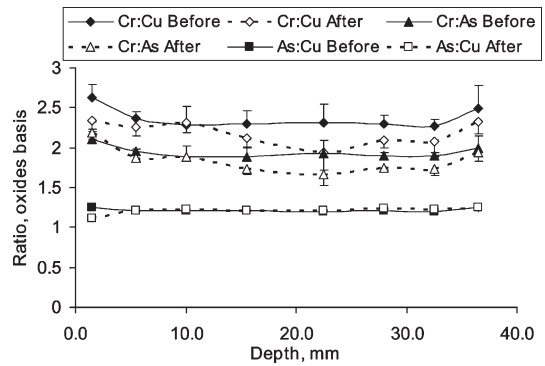


Figure 2. Average ratio of Cr to Cu and As (all expressed on oxides basis) at different depths for CCA-treated southern pine in unexposed samples (before) and those exposed to natural leaching (after); note error bars are presented as  $-1$  SD for unexposed samples and  $+1$  SD for leached samples for visibility.

The ratios of components (oxides basis) through the depth of the boards (Fig 2) shows the main differences in the mass balance of unexposed and weathered boards to be deeper in the boards, suggesting initial differences in chromium proportions among the boards rather than effects of leaching. The arsenic-to-copper ratios are very similar in both cases, except for a decrease in the top surface layer, indicative of higher arsenic leaching compared with copper. The higher component levels below the top surface after weathering (Fig 1) suggest that there might have been some migration of components from the top surface to deeper in the wood; however, considering the natural variability along the boards, this would have to be confirmed by careful evaluation of perfectly end-matched samples.

### ACQ-Treated Samples

The unexposed ACQ samples retention averaged  $4.56 \text{ kg/m}^3$  (Table 1) with a CuO:DDACb ratio of 1.86:1 compared with the target retention of  $4.0 \text{ kg/m}^3$  and nominal 2:1 ratio in the formulation. The copper concentration was about 25% higher near the surface (Fig 3), indicating preferential adsorption of the copper-MEA complex at the surface as the preservative penetrated the wood. These differences were statistically significant (t-test comparison).

After leaching, the gradient was similar, although the average concentration profile was substantially below that of the unleached material. This difference represented about 17% lower average retention (Table 1), which is much higher than expected from the analysis of all of the collected leachates from the exposed samples (2.9% loss). Thus, it is likely that the samples, although end-matched, had different initial retentions. However, it appeared that there was more depletion from the top surface than from other depths.

The DDACb retention profile showed an even steeper gradient from the surfaces to the center (Fig 3) indicative of the strong ion exchange adsorption of quats to wood (Jin and Preston 1991). As the solution penetrates wood, DDACb is stripped from the solution resulting in a steep gradient and increasing ratio of CuO to DDACb with depth in the wood (Fig 5). DDACb appears to be leached to a greater extent than copper with substantial decreases in concentration, especially near the top surface, but also to a lesser extent near the bottom surface. The ratio of CuO to DDACb increased at the center of the boards (Fig 3) after exposure, although these estimates were highly variable. It is possible that the lower uptake in these samples resulted in more complete removal of DDACb from the solution near the surface,

resulting in low retentions deep in the wood and high copper-to-DDACb ratios.

### MCQ-Treated Samples

The MCQ retention of unexposed boards averaged  $4.86 \text{ kg/m}^3$  (Table 1) with a CuO:DDACb ratio of 2.07:1 compared with the target retention of  $4.0 \text{ kg/m}^3$  and nominal 2:1 ratio in the formulation. There was no preferential absorption near the surface, because the copper is injected as low-solubility particulate matter rather than cationic complexes, as present in ACQ. In fact, the micronized copper formulation showed about 20% lower (significant by t-test) surface retentions than interior retentions (Fig 4). This could result from displacement of particles absorbed near the surface with solution kickback during the final vacuum step of the modified full-cell treatment. The fact that there was no decrease in concentration with depth indicates that the particles are small enough to avoid being screened out as they pass through ray tissue and bordered pits as the preservative penetrates the wood. The concentration profiles are similar before and after leaching with some variation as expected when comparing different (although end-matched) samples. The difference in average retention between unexposed and leached samples of MCQ-treated wood was

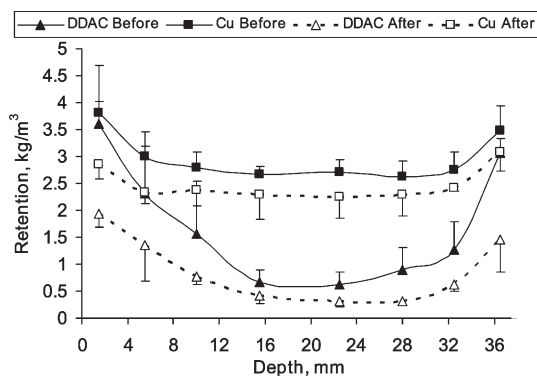


Figure 3. Average copper and DDACb retention gradients in ACQ-treated southern pine in unexposed samples (before) and those exposed to natural leaching (after); note error bars are presented as +1 SD for unleached samples and -1 SD for leached samples for visibility.

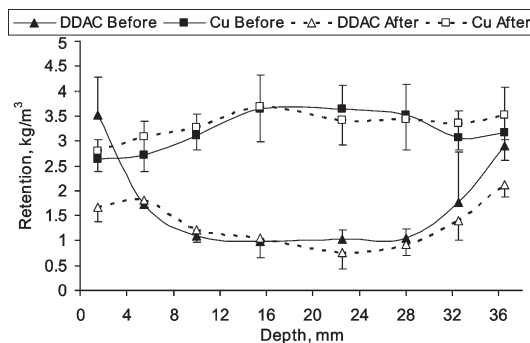


Figure 4. Average copper and DDACb retention gradients in MCQ-treated southern pine in unexposed samples (before) and those exposed to natural leaching (after); note error bars are presented as +1 SD for unleached samples and -1 SD for leached samples for visibility.

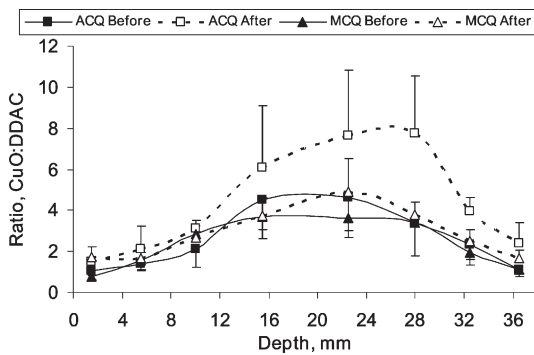


Figure 5. Average ratio of CuO:DDACb at different depths for ACQ- and MCQ-treated southern pine in unexposed samples (before) and those exposed to natural leaching (after); note error bars are presented as  $-1$  SD for unleached samples and  $+1$  SD for leached samples for visibility.

relatively low (1.5%) compared with an estimated average loss based on leachate analysis of 0.36%.

DDACb showed a similar retention profile with depth in MCQ-treated wood as in ACQ-treated wood with a high concentration and low CuO:DDACb ratio (Fig 5) near the surface and the reverse in the interior of the sample. After leaching, the DDACb profile was similar except for obvious high depletion near the top surface and less depletion from the bottom surface and little or no apparent leaching from the centers of boards.

The differences in DDACb retentions of unexposed and leached samples were much higher than for copper (Table 1) averaging about 32% for ACQ and 16% for MCQ. Considering the discrepancy in copper retentions between unexposed and leached ACQ samples, which suggests that the leached sample initially had a lower retention than the unexposed sample, it is likely that the DDACb percentage loss is lower than 32% for ACQ. However, higher DDACb leaching compared with copper leaching for both preservatives is confirmed by the significant increase in CuO:DDACb ratios in leached samples for both preservative systems; the ratio increased from 1.86 to 2.27 (+22%) for ACQ and from 2.07 to 2.45 (+18%) for MCQ (Table 1).

If it is assumed that the true copper leaching losses are as determined by cumulative analyses of the leachates (2.9% for ACQ and 0.36% for MCQ), the DDACb loss can be estimated from the change in component ratios as follows:

For ACQ, the ratio in unexposed wood is

$$\frac{[CuO]_i}{[DDACb]_i} = 1.86 \quad (1)$$

and after leaching exposure, the ratio is

$$\frac{0.971}{x} \frac{[CuO]_i}{[DDACb]_i} = 2.27 \quad (2)$$

whereas for MCQ, the ratio in unexposed wood is

$$\frac{[CuO]_i}{[DDACb]_i} = 2.07 \quad (3)$$

and after leaching exposure, the ratio is

$$\frac{0.9964}{x} \frac{[CuO]_i}{[DDACb]_i} = 2.45 \quad (4)$$

where  $x$  is the fraction of DDACb remaining after exposure and  $[ ]_i$  represents the unexposed concentration. Solving (1) and (2), for ACQ,  $x = 0.795$ , it is estimated that an average of 20.5% of the DDACb leached from the ACQ samples. Solving Eqs 3 and 4,  $x = 0.842$ , corresponding to an estimated DDACb loss of 15.8% for MCQ. It is evident from Fig 4 that most of this leaching loss is of the higher retention quat near the wood upper surface, and as a result, the surface retention approaches the low values in the interior. This suggests that the uneven distribution and high surface loading of DDACb on the surface contribute to its relatively high leaching in service.

## CONCLUSIONS

Southern pine 38- × 140-mm boards pressure-treated with CCA by a modified full-cell process had a relatively uniform distribution of copper and arsenic through the board thickness, whereas the chromium component was higher close to the surface. The copper-amine component in the ACQ-D solution was preferentially



adsorbed near the treated wood surface resulting in, on average, about 25% lower concentration in the interior compared with the surface. For the micronized copper system, the copper gradient was reversed with, on average, about 20% lower concentration near the surface compared with the interior of the board. The DDACb component of both ACQ and MCQ was strongly adsorbed near the wood surface resulting in steep concentration gradients and low DDACb content and high CuO:DDACb ratio inside the boards.

After 330 da of horizontal exposure to natural weathering in Toronto, leaching losses, estimated by analysis of leachates, averaged 2.9% for ACQ-Cu, 0.36% for MCQ-Cu, 0.24% for CCA-Cr, 0.59% for CCA-Cu, and 2.05% for CCA-As. For both systems, copper and DDACb were preferentially leached from the top surface, but there also appeared to be some leaching from the bottom surface. DDACb in the ACQ and MCQ treatments leached to a greater extent than the copper, approximately 20% for ACQ and 16% for MCQ, mainly from the high concentration surfaces.

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