AMERICAN WOOD-PRESERVERS'ASSOCIATION

Appendix 2 to Subcommittee T-4 Report

Fixation Effects On the Release of Copper, Chromium and Arsenic From CCA-C Treated Marine Piles[1]

Report Prepared for American Wood-Preservers' Association Subcommittee P-3, Piles.
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Stan Lebow, Research Forest Products Technologist
S. Nami Kartal, Visiting Scientist
USDA, Forest Service, Forest Products Laboratory
Madison, Wisconsin

Abstract: This study sought to determine the effect offixation time and temperature on the release ofcopper, chromium and arsenic from treated marine piles immersed in seawater under "worstcase" conditions. Sections of piles were CCA-C treated to a target retention of 2.5 lbs/ft³) (40 kg/m3) and then allowed to Condition at 36°F (2°C) for either 3, 7 or 20 days. As a control, one set of "wel1 fixed" pile sections was conditioned at 80°F (27°C) for 20 days prior to leaching. Following the designated fixation period, the sections were leached in seawater maintained at 36 °F (2 °C). Fixation condition was found to greatly affect the leaching of CCA-C components, and especially chromium. After 120 days, average cumulative leaching from the pile sections fixed for3 days at 36°F (2°C) was 19, 169, and 23 times greater than that from piles fixed for 20 days at 80°F (27°C) for copper, chromium, and arsenic respectively. Fixation at 36°F (2°C) for longer periods substantially lessened arsenic leaching, but releases of copper and chromium remained high after fixation for 20 days. The results of this study verify that a high degree of leach-resistance that can be obtained in adequately conditioned CCA-C treated piling, but also demonstrated that much higher release rates may occur with current practices. The authors encourage the adoption offixation standards for marine and fresh-water piles in order to prevent unnecessary releases of CCA-C components into aquatic environments.

Introduction

The copper, chromium and arsenic in chromated copper arsenate (CCA-C) treated wood are resistant to leaching when the wood is placed in service. The leach-resistance of CCA-C is a result of the chemical "fixation" reactions that occur to render the toxic ingredients insoluble in water. The fixation of CCA-C is a complex process, but the essence of CCA fixation is the reduction of chromium from the hexavalent to the trivalent state, and the subsequent precipitation or adsorption of chromium, copper and arsenic complexes in the wood substrate. Some of the these reactions, such as the adsorption of copper and chromium onto wood components, occur within minutes or hours, while others are completed during the ensuing days or weeks. The length of time needed for fixation is greatly dependent on temperature, and the reactions may proceed slowly when the treated wood is stored out-doors in cool weather. Concerns about inadequate fixation have led Canada and European countries to develop standards or guidelines for "fixing" treating wood. The American Wood Preserver's Association (AWPA) has recently formed several task forces to consider the development

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of fixation, or "leaching minimization" standards for CCA-C and other wood preservatives. However, there has been some reluctance to adopt fixation standards because of concerns that such standards are unnecessary. There is little research to demonstrate that leaching from CCA-C products placed in service is significantly affected by degree of fixation.

The type of application and exposure of treated wood can alter how fixation affects the rate and consequences of leaching. For example, a poorly fixed fence post placed during warm weather, with no precipitation occurring within the first few days, would quickly complete fixation with minimal impact. The same fence post placed during cool, rainy weather might unnecessarily release CCA-C components, but these components would probably be adsorbed to the soil immediately adjacent to the post. Poorly fixed boardwalk decking installed during rainy weather may unnecessarily release copper into the wetland below, potentially harming sensitive aquatic species. The same decking installed during warm, dry weather would achieve fixation without negative consequences.

Because it is difficult to assess the effects of all these variables, this study was designed to address a possible worst case scenario: poorly fixed marine piles submerged in cold water. Such a condition might occur ifpiles are treated in the winter in the northeastern US, and then placed in service in cold northern waters. The high CCA retention used in marine piles might be expected to extend the time needed for fixation, while increasing the rate of leaching. Immersion in cool water would provide for continuous leaching while preventing fixation from occurring in-service. In this study, sections of piles were CCA-C treated to a target retention of 2.5 lbs/ft^3 (40 kg/mJ) and then allowed to "fix" at 36°F (2°C) for either 3,7 or 20 days. Following the designated fixation period, the sections were leached in seawater maintained at 36°F (2°C). For comparison, one set of "wel1 fixed" pile sections was conditioned at 80°F (27°C) for 20 days prior to leaching.

Methods

Piles: Four southern pine piles, 6 feet (1.8 m) in length and 8 - 10 inches (20 - 25 cm) in diameter were conditioned to uniform moisture content in a room maintained at 74°F (23° C) and 65% relative humidity. Each pile was cut into twelve, 6 inch (15 cm) long specimens. The specimens were end-coated with two coats of a neoprene rubber sealant, and measured to calculate volume and surface area.

Preservative Treatment: Specimens were pressure treated with a 6.6%, oxide-based CCA-C solution. A full cell treatment was used, with an initial vacuum maintained at 25 inches of Hg (- 85 kPa) for 30 minutes and the pressure maintained at 150 psi (1034 kPa) for 1.5 hours. The solution was than drained from the treating vessel, and a final vacuum of 25 inches of Hg (- 85 kPa) was pulled for 30 minutes. The treating solution was cooled to 9°C (48°F) prior to treatment; the temperature of the used solution immediately following treatment was 15°C (59°F). Following treatment, the specimens were re-weighed and placed in conditioning rooms as described below.

Post-Treatment Conditioning: A total of4 types of post-treatment conditioning were used; 3 time periods under cold conditions and one time period under warm conditions. End-matched specimens from each of the four piles were either placed in a "warm"room maintained at 80°F (27°C) and 80% relative humidity for 20 days, or a "cold" room maintained at 36°F (2°C) and 82% relative humidity for 3, 7 or 20 days.

Leaching Solution: A commercial artificial seawater mix was used to prepare seawater with a salinity of 23 parts per thousand. Before use, this solution was allowed to equilibrate in a room maintained at 36°F (2°C).

Leaching: Following the appropriate conditioning period, the specimens were submerged, individually, in polyethylene containers containing 5 liters of seawater solution. The containers were loosely capped and placed in a room maintained at 36°F (2°C). The leaching solution in the containers was collected and replaced

with fresh solution after periods of 1,3,7,14,30,60 and 120 days.

Assay for Preservative Retention in the Wood: Samples were removed to depths of 0 - 0.5 and 0.5 - 2 inches (0 - 13 and 13 - 50 mm) in specimens reserved for this purpose. Four samples, spaced equally around the circumference, were removed from each specimen and then combined for analysis.

Determination of CCA-C in Leachate and Wood: Copper, arsenic and chromium concentrations in the treated wood and leaching solutions were determined with a Perkin Elmer 5100PC Atomic Absorption Spectrometer (ASS) equipped with a Zeeman Furnace Module. Leaching solutions were analyzed by either graphite furnace or flame atomization, as appropriate. Wood samples were digested in a mixture of hydrogen peroxide and nitric acid using a CEM MD6-2000 Microwave Digester (AWPA Standard A7 - 93). Copper, chromium and arsenic concentrations in the resulting solution were determined by flame atomization.

Results and Discussion

CCA Retention

The average uptake retention of the specimens, as determined by weight gain, was 2.7 lb/ft.^{3} (43 kg/m^3). The average assay retention was 2.5 lb/ft^3 (40 kg/m^3) in the 0 - 0.5 inch (0 - 13 mm) assay zone, and 2.0 lb/ft^3 (32 kg/m^3) in the 0.5 - 2 inch (13 - 50 mm) assay zone.

Effect of Fixation Condition on Leaching

Copper: Fixation condition greatly affected the rate of copper release from the pile sections (Table 1, Figure 1). During the first 60 days of leaching, average release from samples conditioned at 36°F (2°C), regardless of fixation time, was at least 10 times greater than that from samples conditioned at 80°F (27°C). This difference lessened considerably after 120 days of leaching, although specimens fixed in cold conditions still released copper at a rate 3 to 4 times higher than those conditioned at 80°F (27°C). The cumulative effect of fixation condition on leaching, for the entire 120 day period, is shown in Figure 2. The average total amount of copper released from specimens conditioned for 3, 7 and 20 days at 36°F (2°C) was approximately 19, 16 and 8 times greater than that leached from specimens fixed for 20 days at 80°F (27°C), respectively.

Chromium: As expected, fixation condition had the greatest effect on the rate of chromium release. During the initial stages of leaching, average chromium release was 100 to 200 times greater from the specimens conditioned at cold temperatures than from those conditioned at 80°F (27°C) (Figure 1). Although this difference gradually decreased, average release from specimens conditioned at 36°F (2°C) was still at least 20 times greater than that for those conditioned at 80°F (27°C) after 120 days of leaching. In addition, yellow coloration of the leaching water, indicating the presence of hexavalent chromium, remainea readily evident after 120 days. The cumulative effect offixation condition on leaching, for the entire 120 day period, is shown in Figure 2. The average total amount of chromium released from specimens conditioned for 3, 7 and 20 days at 36°F (2°C) was approximately 169, 165 and 67 times greater than that leached from specimens fixed for 20 days at 80°F (27°C), respectively.

Arsenic: Fixation condition had less effect on the release of arsenic than it did on the release of copper or chromium (Figure 1). Although the average release of arsenic was initially 40 to 50 times greater from piles conditioned for 3 or 7 days at 36°F (2°C) than from piles conditioned at 80 F (27 C) for 20 days, this difference became quite small after 30 to 60 days of leaching. In addition, it is interesting that average arsenic release from piles conditioned at 36°F (2°C) for 20 days was much less than for those conditioned for 3 or 7 days. This cold temperature fixation after 20 days is also reflected in the cumulative leaching of arsenic as shown in Figure 2. The average total amount of arsenic released from specimens conditioned for 20 days at

80°F (27°C) was approximately 20 times less than that leached from specimens fixed for 3 and7 days at 36°F (2°C) but only 2 times less than those fixed for 20 days at 36°F (2°C). It appears that substantial arsenic fixation can occur even at cold temperatures. This may indicate that the reaction ofchromium with arsenic is less temperature sensitive than other chromium reduction reactions.

Conclusions and Recommendations

This study clearly shows that fixation time and temperature has the potential to greatly affect the release of CCA components, and particularly chromium and copper, from treated marine piles placed in service, After 120 days, average cumulative release of chromium from poorly conditioned piles was as much as 169 times greater than from well conditioned specimens. On the positive side, the data from this study again demonstrate the high degree of leach resistance that can be obtained when CCA-C treated wood is adequately conditioned.

Admittedly, the conditions used in this study are worst case, and are not typical of those encountered in practice. However, ocean temperatures only slightly warmer than those employed in this study are common in northern waters during winter months, and ambient storage-yard temperatures below 40°F (4°C) can and do occur. It is the concern of these authors that current AWPA standards do far too little to prevent the placement of poorly fixed marine piles into service. Very recently, the association included optional fixation guidelines for poles, but it is likely that the need for fixation standards is much more critical for marine piles. Marine piles are treated to a higher retention, and by definition are placed into an environment that provides continual leaching and contains aquatic organisms. In the opinion of these authors, we should work to prevent the placement of poorly fixed piles by including verifiable fixation standards for CCA-C treated marine and fresh water piles in AWPA Standard C3. Without such standards in place it will become increasingly difficult to defend these products against claims of leaching and environmental harm.

Table 1. Average release rates for pile sections. Values represent four replicates.

Fixation Condition	Days Leached	Copper		chromium		Arsenic	
		Average	Std. Dev.	Average	Std. Dev.	Average	Std. Dev.
3 Days, 36 F (2 C)	1	222.88	*54.95*	1095.81	*136.21*	139.76	*20.83*
3 Days, 36 F (2 C)	3	63.90	*14.85*	323.25	*47.61*	56.59	*5.54*
3 Days, 36 F (2 C)	7	30.55	*4.14*	173.17	*25.23*	27.98	*1.14*
3 Days, 36 F (2 C)	14	13.64	*2.95*	49.06	*10.20*	3.68	*0.13*
3 Days, 36 F (2 C)	30	5.75	*1.77*	17.90	*5.12*	2.43	*0.26*
3 Days, 36 F (2 C)	60	2.22	*0.71*	8.52	*3.88*	0.17	*0.00*
3 Days, 36 F (2 C)	120	0.63	*0.16*	0.89	*0.97*	0.30	*0.05*
7 Days, 36 F (2 C)	1	158.17	*51.97*	1085.73	*204.42*	105.74	*6.64*
7 Days, 36 F (2 C)	3	54.88	*9.82*	289.65	*28.47*	49.78	*1.59*
7 Days, 36 F (2 C)	7	24.57	*3.35*	146.95	*39.67*	24.34	*1.35*
7 Days, 36 F (2 C)	14	10.63	*3.24*	44.06	*10.92*	3.19	*0.12*
7 Days, 36 F (2 C)	30	5.40	*1.66*	24.88	*8.31*	0.32	*0.00*
7 Days, 36 F (2 C)	60	1.86	*0.80*	6.80	*3.56*	0.74	*0.10*
7 Days, 36 F (2 C)	120	0.58	*0.23*	0.75	*0.83*	0.20	*0.04*
20 Days, 36 F (2 C)	1	162.95	*140.10*	572.34	*251.70*	11.64	*1.86*
20 Days, 36 F (2 C)	3	38.69	*20.57*	182.55	*54.63*	3.11	*0.67*
20 Days, 36 F (2 C)	7	14.80	*5.77*	86.98	*16.71*	1.35	*0.02*
20 Days, 36 F (2 C)	14	8.05	*3.70*	28.25	*4.83*	1.60	*0.19*
20 Days, 36 F (2 C)	30	3.57	*1.64*	18.46	*4.85*	0.33	*0.00*
20 Days, 36 F (2 C)	60	1.19	*0.45*	5.54	*2.40*	0.20	*0.00*
20 Days, 36 F (2 C)	120	0.56	*0.17*	0.91	*0.74*	0.13	*0.03*
20 Days, 80 F (27 C)	1	6.62	*5.24*	4.58	*4.89*	2.45	*0.41*
20 Days, 80 F (27 C)	3	4.06	*1.87*	1.66	*1.43*	0.86	*0.08*
20 Days, 80 F (27 C)	7	0.98	*0.44*	1.10	*0.98*	0.52	*0.12*
20 Days, 80 F (27 C)	14	0.50	*0.11*	0.43	*0.40*	0.43	*0.10*
20 Days, 80 F (27 C)	30	0.21	*0.05*	0.28	*0.30*	0.21	*0.05*
20 Days, 80 F (27 C)	60	0.13	*0.04*	0.09	*0.16*	0.16	*0.03*
20 Days, 80 F (27 C)	120	0.17	*0.05*	0.04	*0.05*	0.10	*0.04*

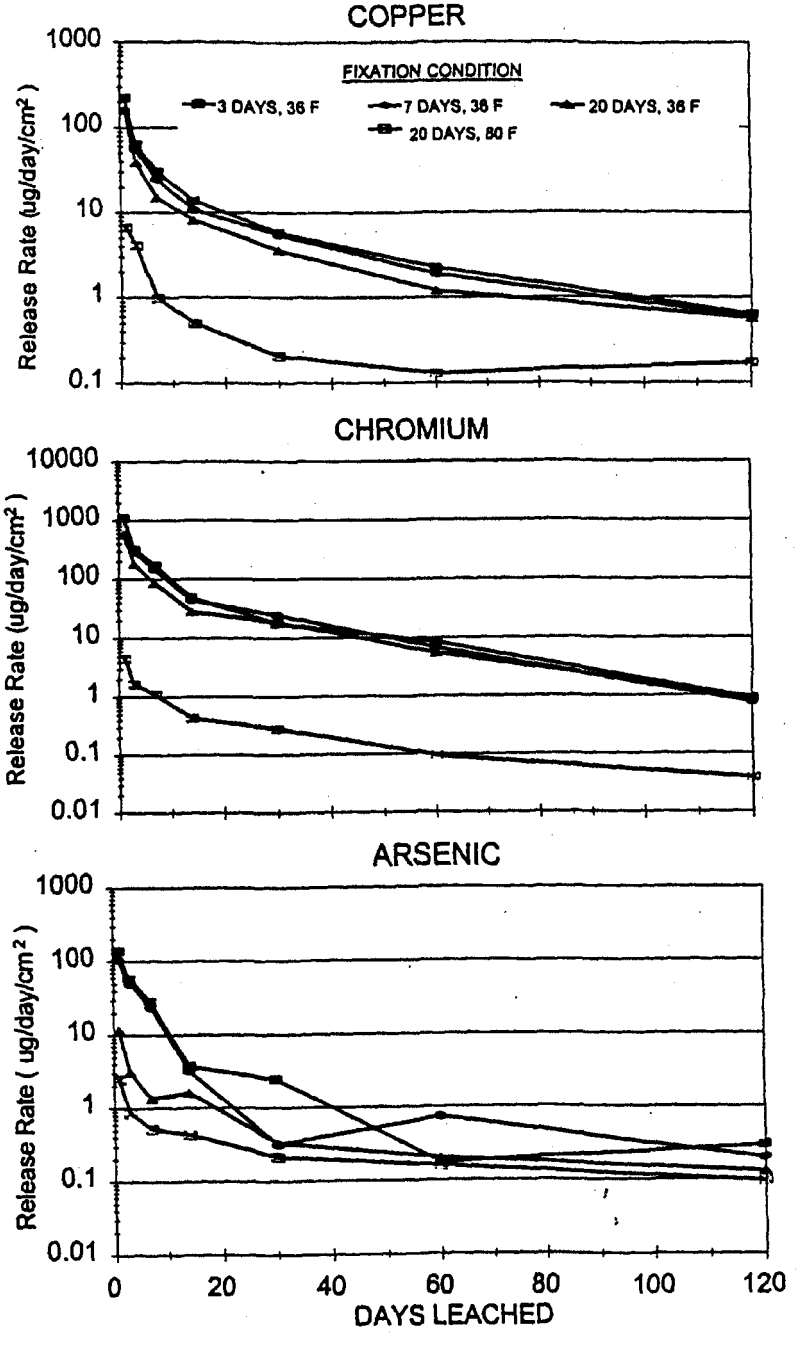

Figure 1. Effect of fixation time and temperature on release of copper, chromium, and arsenic.

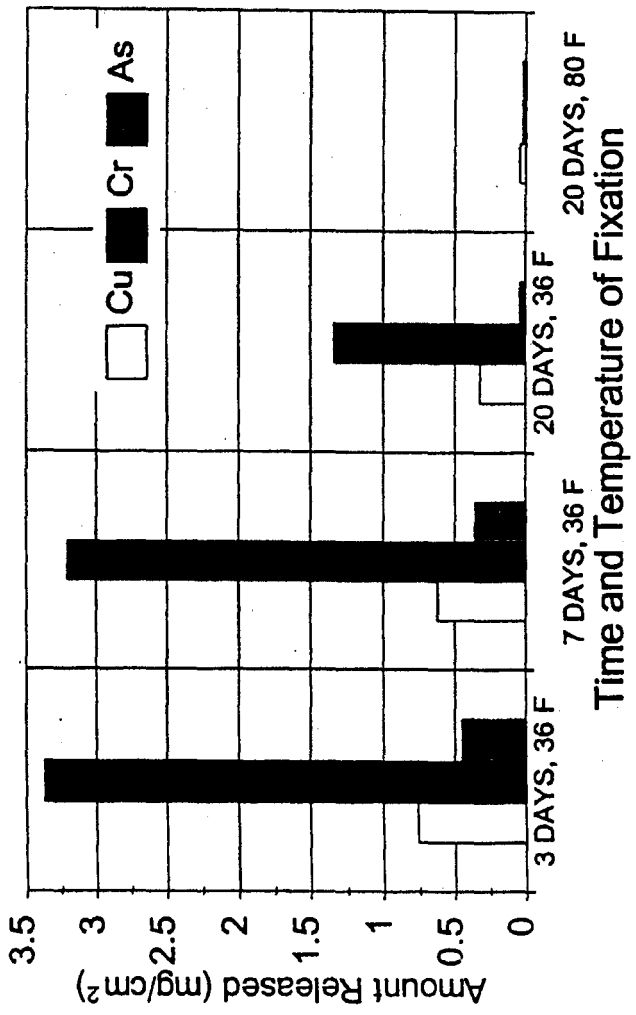

Figure 2. Effect of fixation time and temperature on cumulative release of copper, chromium, and arsenic after 120 days of leaching.

PROCEEDINGS

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P.O. BOX 5690 **GRANBURY, TEXAS 76049**