TECHNICAL NOTE

Effect of Polyvinyl Alcohol on Copper Leaching from Treated Wood

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Abstract

The new copper-based preservative systems leach a relatively high level of copper and, thus, generate some environmental concerns. Polyvinyl alcohol (PVOH) is known to complex with copper(II) and is water soluble. The effect of co-addition of fully hydrolyzed PVOH on the leaching of copper from wood treated with three different copper salts was examined. Southern pine sapwood wafers were treated with copper sulfate, copper acetate, and ammoniacal copper carbonate, all with 1 percent elemental copper in the waterborne solution, with and without 2 percent PVOH. The wafers were then dried and water leached for 2 weeks. PVOH co-addition greatly reduced the copper leached from wood treated with alkaline ammoniacal copper carbonate but not from wood treated with a slightly acidic solution of copper acetate or highly acidic copper sulfate.

The first-generation waterborne arsenical wood preservatives were recently replaced by second-generation copper-based systems (Schultz et al. 2007) for residential applications in North America due to environmental and health concerns. While these second-generation systems do not contain arsenic or chromium, they have relatively high copper(II) levels. The high copper content in the new systems paired with a lack of chromium(VI) that oxidizes various lignocellulosic groups to form strong fixation sites for the copper results in relatively high levels of copper leaching with resulting environmental concerns (Lebow et al. 2002, Stook et al. 2005, Townsend and Solo-Gabriele 2006). Copper depletion will also negatively impact the efficacy of treated wood against wood-destroying organisms over its expected long service life.

Various additives have been examined to reduce copper leaching. One additive known to bind with copper(II) is polyvinyl alcohol (PVOH; Mori et al. 1995, Yokoi et al. 1995, Wan Ngah et al. 2004). Since it is water soluble, PVOH can be formulated in waterborne systems.

The objective of this study was to determine the effect of PVOH co-addition on the amount of copper leached from wood immersed in water. The wood was treated with three different copper(II) salts to obtain treating solutions with a range of pHs so that the effect of acidity could also be determined.

Experimental Methods

Solutions containing 1 percent (wt/vol) copper as the metal were prepared with copper sulfate, copper acetate, and ammoniacal copper carbonate in deionized water. The pH values of the copper sulfate, copper acetate, and ammoniacal copper carbonate solutions were 3, 5.5, and 12, respectively, and did not change when 2 percent PVOH was added. The PVOH employed was Airvol Polyvinyl Alcohol 09 to 125 from Air Products, a super-hydrolyzed PVOH with 99.3 to 100 percent hydrolysis of the original acetate groups. Two southern pine boards (*Pinus* spp.) were cut to make 5 by 19 by 19-mm (longitudinal by radial by tangential) wafers. Six wafers from each of the two boards, for a total of 12 wafers, were used for each treatment. The wafers were treated by a vacuum/atmospheric pressure immersion process and then dried. The dry wafers were ground to 20 mesh and then analyzed by inductively coupled plasma spectroscopy (American Wood Protection Association [AWPA] Standard A21; AWPA 2009).

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Table 1.—Effect of co-addition of PVOH on the amount of copper leached during a 2-week water immersion.[a]

Treatment	Unleached copper retained (kg/m^3)	Leached copper retained (kg/m^3)	% copper loss
Copper sulfate	13.9	4.3	67
Copper sulfate + PVOH	16.3	3.8	77
Copper acetate	15.9	9.3	42
Copper acetate + PVOH	17.6	10.3	41
Ammoniacal copper carbonate	17.9	14.4	20
Ammoniacal copper carbonate + PVOH	25.2	24.7	2

[a] The copper sulfate solution was highly acidic, copper acetate mildly acidic, and ammoniacal copper carbonate highly alkaline, with all solutions containing 1 percent copper as metal. The results are the average of 12 treated wafers, with wafers cut from two boards with six wafers from each board.

Samples were leached using the AWPA Standard E11 (AWPA 2009). Dried wafers were placed in a beaker, covered with a weight, and immersed in deionized water. The beaker was then subjected to a 10-minute vacuum followed by atmospheric pressure. Samples were left immersed in the water, with the water changed daily during the 2 weeks of leaching. Samples were then air-dried for 48 hours before inductively coupled plasma analysis.

Results and Discussion

The average copper retentions of the unleached and leached wafers treated with the three copper solutions, with and without co-added 2 percent PVOH, are given in Table 1. For the samples without co-added PVOH, the amount of copper leached increased as the treating solution became more acidic. This effect was anticipated based upon basic chemical metal–organic binding principals and prior studies that examined the effect of copper leached from treated wood in soils or aquatic environments with different pHs (e.g., Lebow et al. 2006, Edwin et al. 2006).

In samples with co-added PVOH, the polymer did not reduce the extent of copper leached by water for wood treated with copper sulfate (highly acidic treating solution) or copper acetate (mildly acidic solution). Indeed, slightly more copper was leached from wood treated with copper sulfate and co-added PVOH, but this may be simply due to the high variation typically observed in leaching studies. However, for the alkaline ammoniacal copper carbonate treatment, wafers without PVOH leached an average of 20.1 percent copper but only 2.0 percent when PVOH was co-added. Thus, we conclude that co-addition of PVOH will reduce the amount of copper leached in water for wood treated with ammoniacal copper carbonate. (Unfortunately, the former graduate student who performed this experiment has long left MSU and only the summary/average data are available. Consequently, a statistical analysis could not be performed to test the significance of the results).

The increase in copper retention for unleached wood for all copper salts (Table 1) can be explained by formation of a coordination complex between copper(II) and one or more hydroxy groups of the PVOH polymer, which helps immobilize the copper ion. Examples of copper(II) coordination complexes of this nature are known (Bebendorf et al. 1996, Gack and Klüfers 1996, Kogane et al. 1996, Boever et al. 1999, Lehtonen et al. 2002). As with many chelating ligands, the stability or strength of the metal polymer interaction is dependent on the pH of the solution. At high pH, one or more of the hydroxy groups is deprotonated, leading to a stronger bond to the metal. Consequently, a strong complex between copper(II) and deprotonated PVOH hydroxy groups forms only under alkaline conditions (Shirai et al. 1973, 1978; Yushko et al. 1975; Kurose et al. 1980; Suzuki et al. 1983) so that the preservative system alkaline copper quat gives a relatively insoluble copper–PVOH complex and improved copper retention for the leached samples. Conversely, in acidic solutions the interaction is much weaker and the copper ion can be solubilized and subsequently leached.

Conclusions

The co-addition of PVOH to a waterborne treating solution of ammoniacal copper carbonate greatly reduced the extent of water leaching of copper from treated wood. The PVOH increases the binding sites in the matrix for the copper ion. The strength of the interaction between these sites and the metal are enhanced under the alkaline conditions of an ammoniacal copper carbonate–treating solution.

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