COMPARISON OF COPPER LEACHING FROM ALKALINE COPPER QUAT TYPE-D TREATED CHINESE FIR AND MONGOLIAN SCOTS PINE AFTER DIFFERENT POSTTREATMENTS

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(Received March 2010)

Abstract. Chinese fir (*Cunninghamia lanceolata* Hook.) and Mongolian Scots pine (*Pinus sylvestris Linn.* var. *mongolica* Litv.) sapwood were treated with alkaline copper quat type D (ACQ-D) solutions at two concentration levels (0.5 and 1.1%) followed by three posttreatments: oven-drying, conditioning in a humidity chamber, or exposed to boiling water. The effects of treatment on copper leaching from ACQ-D-treated wood were investigated by performing tests according to AWPA E11-06. Analysis of chemical composition and pH values were determined to evaluate the effects of wood species on copper leaching. The results showed that copper leaching from ACQ-D-treated Mongolian Scots pine without posttreatment was lower than that of treated Chinese fir. However, after posttreatment, more copper leaching was observed from ACQ-D-treated Mongolian Scots pine than Chinese fir. For example, after conditioning posttreatment, the percentage of copper leached from 1.1% ACQ-D-treated Chinese fir decreased 58.6 to 1.8%, while for Mongolian Scots pine, it decreased 49.5 to 19.4%. The difference was considered to be related to different chemical compositions and pH levels.

Keywords: Alkaline copper quat (ACQ), wood species, copper leaching, posttreatment.

INTRODUCTION

Chinese fir (*Cunninghamia lanceolata* Hook.) is one of the most widely planted species in Chinese plantation forests and it has been one of the major species used in historical wood construction (Ren et al 2006). Mongolian Scots pine (*Pinus sylvestris Linn.* var. *mongolica* Litv.) is currently the main wood species used for wood preservation in the Chinese market. The sapwood of both species is vulnerable to fungus attack. Water-borne wood preservatives are widely used

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in the preservation industry; among them, alkaline copper quat (ACQ) is commonly used in residential and garden construction, outdoor furniture, and playground equipment. The active ingredients in the ACQ formulation bind to a limited number of ion exchange sites in wood. The absence of chromium, which can oxidize various lignocellulosic groups to form strong fixation sites for copper, results in relatively higher levels of copper leaching compared with chromium-based preservatives (Stook et al 2005). Recent work has proved that posttreatments such as hot air (Ung and Cooper 2005; Cao and Yu 2007), steaming (Kang et al 2008), microwave heating (Cao and Kamdem 2004), and hot water posttreatments (Barnes 1988; Yu et al 2009a) can effectively promote fixation and reduce copper loss from wood treated with copper-containing preservatives. In our previous study, we evaluated copper immobilization in Chinese fir. However, the chemical compositions in various wood species are quite different and can affect copper leaching (Stevanovic-Janesic et al 2000). In this study, Chinese fir and Mongolian Scots pine were used to evaluate the effects of wood species and posttreatment processing on copper leaching.

MATERIALS AND METHODS

Samples and Treatment

Defect-free sapwood cubes (19 mm) of Chinese fir (*Cunninghamia lanceolata* Hook.) (basic relative density: 360 kg/m^3, oven-dry basis) and Mongolian Scots pine (*Pinus sylvestris Linn.* var. *mongolica* Litv.) (basic relative density: 430 kg/m^3, oven-dry basis) were impregnated with 0.5 or 1.1% ACQ-D solutions (CuO and DDAC-based), respectively, using a full-cell process. The process was as follows: –80 kPa vacuum (relative to atmospheric pressure) for 30 min; pressure at 2 MPa for 2 h; and final vacuum at –80 kPa for 30 min. Immediately after removal from the retort, samples were posttreated to accelerate copper fixation. Three posttreatment conditions were used: oven-drying (110°C, RH uncontrolled, with air circulation, 24 h), conditioning (chamber at 70°C and 80% RH, with air circulation, 24 h), or boiling (100°C, 15 h). After posttreatments, the samples were leached according to E11-06 (AWPA 2008). Six replicates were used for each condition and the leachate was replaced at prescribed intervals: 6, 24, and 48 h and thereafter every 48 h for 14 da. After the leaching test, the blocks were air-dried, ground to pass through a 30-mesh sieve, oven-dried at 103 ± 2°C for 24 h, and the copper retention analyzed by X-ray fluorescence spectroscopy (XRF). Additionally, two groups of 0.5 and 1.1% ACQ-D-treated samples without posttreatment were used as controls to immediately perform leaching tests, and the other two groups of 0.5 and 1.1% ACQ-D-treated samples without posttreatments and leaching were used to determine the original copper retention. Percentage of copper leaching was calculated according to the original copper retention in wood and the amount of copper remaining in the samples after leaching.

Analysis of Chemical Composition

Wood extractives in Chinese fir and Mongolian Scots pine were qualified by soxhlet extraction of sapwood powder (40-60 mesh) of these species without ACQ-D treatment by using benzene–ethanol solutions (2:1 volume ratio) for 6 h according to standard 2677.6-94 (GB/T 1994a). The contents of acid-soluble and -insoluble lignin in the extracted sapwood powder were determined by 72 and 3% of analytical reagent-grade sulphuric acid according to standards 10337-08 (GB/T 2008) and 2677.8-94 (GB/T 1994b), respectively. The content of holocellulose was determined by delignification of wood with acidified sodium chlorite using the methods described in standard 2677.10-95 (GB/T 1994c). The unextracted sapwood powder was immersed in the mixture of nitric acid and ethanol solution in a boiling water bath to prepare the cellulose (Shi and He 2006). Three replicates were used in each experiment of wood composition analysis.

Determination of pH

The pH of Chinese fir and Mongolian Scots pine was determined according to standard 6043-09 (GB/T 2009) with five replicates, ie 30 mL distilled water without carbon dioxide was added to 3 g sapwood powder (40-60 mesh) without ACQ-D treatment, stirred for 5 min, let stand for 15 min, stirred another 5 min, and let stand for 20 min. The pH of wood powder was then determined with a pH meter (microprocessor pHB-5).

Statistical Analysis

The significance of differences in retentions, percentage of copper leaching, and wood chemical compositions between and among groups were analyzed statistically. One-way analysis of variance (ANOVA), linear regression, and parameter estimation analysis were conducted by using SPSS Data Editor Version 13.0. The results of variance for significance were evaluated at a 95% confidence level.

Table 1. Retentions (kg/m^3) of Chinese fir and Mongolian Scots pine treated with 0.5 and 1.1% alkaline copper quat type D (ACQ-D) solutions (standard deviations in parentheses).

Wood species	0.5% ACQ-D	1.1% ACQ-D
Chinese fir	5.74 (0.08)	12.29 (0.33)
Mongolian Scots pine	5.18 (0.04)	12.76 (0.14)

RESULTS AND DISCUSSION

According to the results of XRF analysis, the ACQ-D retention in treated Mongolian Scots pine was significantly lower ($p < 0.05$) than that in Chinese fir at a 0.5% concentration, while at 1.1%, the ACQ-D retentions of both species were not significantly different ($p > 0.05$) because of the relatively high standard deviations (Tables 1 and 2).

The percentages of copper leached from ACQ-D treated Chinese fir and Mongolian Scots pine with or without posttreatment are listed in Table 3, and the corresponding ANOVA analysis for the significance of copper leaching between these two species after different treatments are presented in Table 4. It is clear that for unconditioned samples, more copper leached from treated Chinese fir than Mongolian Scots pine. The result may be attributed to the significantly higher extractive contents in Mongolian Scots pine ($p = 0.001 < 0.05$) (Tables 5 and 6). Extractives have been proved to be an important factor on the fixation process of wood preservatives in treated wood, which are primarily located in the wood pore structure and the effect will be mainly in the cell lumens (Stevanovic-Janesic

Table 2. Analysis of variance for the significance of retentions in Chinese fir and Mongolian Scots pine treated with 0.5 and 1.1% alkaline copper quat type D (ACQ-D) solutions.

Treatment		Sum of squares	df	Mean square	F	P	Significance
0.5% ACQ-D	Between groups	0.477	1	0.477	123.761	0.000	*
	Within groups	0.015	4	0.004			
	Total	0.492	5				
1.1% ACQ-D	Between groups	0.320	1	0.320	4.960	0.090	
	Within groups	0.258	4	0.064			
	Total	0.578	5				

* Significant at a confidence level of 95% ($\alpha = 0.05$).

Table 3. Percentage of copper leached from alkaline copper quat type D (ACQ-D)-treated Chinese fir and Mongolian Scots pine after various posttreatments (standard deviations in parentheses).

	Cu leaching (as % of original retention)[a]							
	0.5% ACQ-D				1.1% ACQ-D			
Wood species	Control[b]	Drying	Conditioning	Boiling	Control[b]	Drying	Conditioning	Boiling
Chinese fir	37.1	26.8	13.7	10.7	58.6	11.6	1.8	10.4
	(1.90)	(4.93)	(2.38)	(3.80)	(1.14)	(3.80)	(2.14)	(3.17)
Mongolian Scots pine	26.2	24.9	20.5	19.0	49.5	30.8	19.4	24.9
	(6.05)	(6.10)	(3.35)	(4.53)	(1.57)	(2.24)	(1.89)	(7.13)

[a] Mean values of six replicates for each treatment condition with standard deviations in parentheses.
[b] Samples leached immediately after ACQ-D treatments.

Table 4. Results of the analysis of variance for the significance of copper leaching from alkaline copper quat type D (ACQ-D)-treated Chinese fir and Mongolian Scots pine after different treatments.

Treatment		Total sum of squares	df	F	P	Significance
0.5% ACQ-D	Control	687.244	11	31.856	0.000	*
	Drying	95.242	11	1.291	0.282	
	Conditioning	444.983	11	4.481	0.060	
	Boiling	334.573	11	9.168	0.013	*
1.1% ACQ-D	Control	268.446	11	132.650	0.000	*
	Drying	1139.738	11	270.537	0.000	*
	Conditioning	1744.890	11	169.444	0.000	*
	Boiling	1135.925	11	25.157	0.001	*

* Significant at a confidence level of 95% ($\alpha = 0.05$).

Table 5. Chemical composition of Chinese fir and Mongolian Scots pine (standard deviations in parentheses).

			Lignin (%)		
Wood species	Cellulose (%)	Holocellulose (%)	Acid-soluble	Acid-insoluble	Extractives (%)
Chinese fir	46.9 (0.0131)	78.3 (0.0032)	0.3 (0.1098)	33.8 (0.0003)	2.3 (0.0006)
Mongolian Scots pine	43.7 (0.0067)	77.5 (0.0251)	0.2 (0.0529)	26.8 (0.0008)	5.2 (0.0049)

Table 6. Results of the analysis of variance for the significance of wood compositions in Chinese fir and Mongolian Scots pine.

Wood composition	Total sum of squares	df	F	P	Significance
Extractives	13.154	5	102.122	0.001	*
Acid-soluble lignin	0.014	5	2.389	0.197	
Acid-insoluble lignin	68.764	5	19097.042	0.0001	*
Cellulose	10.331	5	5.548	0.078	
Holocellulose	3.606	5	0.145	0.723	

* Significant at a confidence level of 95% ($\alpha = 0.05$).

et al 2000). Although the effects of wood extractives on the fixation process are quite different with the varying amounts and types in wood species, it is apparent that the extractives in the Mongolian Scots pine could promote the fixation process of copper, as shown in previous research on complexing copper in ACQ-treated wood (Ruddick 2003). The research of the effects of different extractives types on copper leaching is still in progress, and we expect more detailed information in the future.

However, copper leaching results were reversed after posttreatments with copper leaching from ACQ-D-treated Chinese fir mostly lower than that from treated Mongolian Scots pine. All three posttreatments had positive effects on accelerating copper fixation, and this effect was much more obvious for Chinese fir. Conditioning posttreatment reduced the percentage of copper leaching from ACQ-D-treated Chinese fir from 58.6 to 1.8%, which is nearly complete fixation. The lower copper loss was consistent with our previous results in that 4.1% of copper leached out from ACQ-D-treated Chinese fir after the same posttreatment using shorter treatment duration (10 h) (Yu et al 2009b). These results demonstrated that after well-fixed conditions, the leaching resistance of copper in treated wood was dependent on the chemical composition and pH of wood species, which are closely related to the reaction sites in treated wood. From Tables 5 and 6, Chinese fir has higher lignin and cellulose contents than Mongolian Scots pine, but the difference in holocellulose content is negligible ($p = 0.723 > 0.05$). This means that Chinese fir has more reaction sites for copper, because although lignin and hemicelluloses are primarily responsible for copper adsorption on wood (Bland 1963; Lebow and Morrell 1995; Thomson and Pasek 1997), copper is much more easily fixed to lignin than to holocellulose (Zhang and Kamdem 1999). Another explanation for better leaching resistance of ACQ-D-treated Chinese fir after well-fixed conditions is attributed to its higher pH (5.1 compared with 4.3 for Mongolian Scots pine). Rennie et al (1987) showed that a relatively high wood pH should favor copper adsorption because this will result in a higher treating solution pH in the initial stages of treatment. Although wood has a pH-dependent number of sites for reaction with copper (Cooper 1991), the cation exchange capacity increases with increased treating solution pH (Lee and Cooper 2010). Moreover, according to the results of Jin et al (2010), the solubility of copper could increase significantly with a decrease in the treated solution pH. As a result, we conclude that the higher copper losses from ACQ-D-treated and well-fixed Mongolian Scots pine also resulted from the more soluble copper in treated wood at lower pH.

After posttreatments, a lower percentage of copper leaching was found from the Chinese fir samples with higher retentions, which is different from the control samples. One of the reasons is considered to be the pH of treating solutions, in which the higher pH in the higher concentration of ACQ-D solutions has promoted a cation exchange between copper and wood constituents and formed stable Cu-wood complexes. Lee et al (1993) also proposed that more leaching could be observed at higher retentions for samples that have not fixed completely, while for well-fixed samples, the reverse could be observed, ie more leaching at lower retention levels. Therefore, it is essential to perform suitable posttreatments to ensure the better fixation quality of ACQ-D-treated wood, especially for treated wood with higher retentions.

CONCLUSIONS

Wood species has a substantial influence on copper leaching from ACQ-D-treated wood, especially on the accelerating effect of posttreatments. Chinese fir showed good copper fixation after ACQ-D treatment and three different posttreatments, while Mongolian Scots pine showed much less accelerating effect by the posttreatments. The reasons were considered to be mainly related to the different chemical composition and pH of these species. The experimental results confirmed that wood species with higher lignin content and pH could display excellent copper leaching resistance after ACQ-D-treated and suitable posttreatments. Research is in progress to evaluate the effect of pH of ACQ-D-treated wood with different posttreatments on copper leaching and will be reported in the future.

ACKNOWLEDGMENT

We thank the Fok Ying Tong Education Foundation (No.101028) for its financial support.

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