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EVALUATION OF THE CORRELATIONS BETWEEN COPPER STABILIZATION AND VALENCE CONVERSION ON COPPER LEACHING FROM ACQ-D TREATED WOOD

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ABSTRACT

Red pine (*Pinus resinosa* Ait.) wood cubes (19.0•19.0•19.0 mm) were treated with amine copper quat (ACQ-D) solution and fixed in different post-treatment conditions. The correlations between copper leaching, copper conversion and copper stabilization were analyzed. The results showed that higher temperature and relative humidity are positive conditions for copper fixation. The copper leaching resistance of ACQ-D treated red pine post-treated at 50°C for more than 24 h is similar to that post-treated at 120°C only for 2 h. During different post-treatments, a higher copper conversion rate usually corresponds to a lower copper leaching, the same trend also can be found in the relationship between copper fixation and copper leaching, which demonstrates post-treatment conditions bring about higher copper conversion and copper stabilization during copper fixation process are positive measurements for improving copper leaching resistance of ACQ-D treated wood.

KEYWORDS: ACQ-D treated wood, copper leaching, copper stabilization, valence conversion, post-treatment.

INTRODUCTION

Red pine (*Pinus resinosa* Ait.) is one of the most widely species used in wooden structures and other landscape architectures because of its lower price and better permeability. However, the content of starch and monosaccharide in its sapwood is rather higher, which is vulnerable to fungus and termite attack (Tao et al. 2013, Tascioglu et al. 2009). Copper based preservative formulations without chromium and arsenic have been introduced into the treated wood market over the past decade, and these systems have much less environmental impact when compared to heavy-metal containing formulations. ACQ (alkaline Cu quat), CA (Cu azole), Cu citrate, and Cu ethanolamine as Cu-based preservatives have emerged over this period as the most widely available wood preservatives. Besides these "water-soluble copper" formulations, micronized-Cu based systems have been recently introduced into the North American and European market (Kartal et al. 2015). Among of them, alkaline copper quat (ACQ-D) is one of the most widely used wood preservatives in the market nowadays especially for the outdoor constructions and playground equipments (Mazela et al. 2003, Freeman et al. 2003, Evans 2003, Shi et al. 2007).

However, the active ingredients in the ACQ-D formulation bind to a limited number of ion exchange sites in wood and are easily leached out during outdoor exposure (Craciun et al. 2009, Humar et al. 2007a, b, Tascioglu et al. 2005, Lee and Cooper 2010). The absence of chromium, which can oxidize various lignocellulose 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 post-treatments 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 (Yu et al. 2009) post treatments can effectively promote fixation and reduce copper loss from wood treated with copper-containing preservatives. The fixation extent of treated wood will be affected by many factors, such as copper fixation duration, temperature, relative humidity, air ventilation (Tao et al. 2013, Humar et al. 2007a, b; Tascioglu et al. 2005; Cao and Yu 2007). Especially, the effect of the temperature on copper fixation, in which the data provided from Humar et al. (2007a, b) is in contradiction with the other results and the possible reasons were concluded as follows: Different ethanolamine originates in ethanolamine, mass flow of copper aqueous solution to the surface of the specimens (Zhang and Kamdem 2000a, b), and a high moisture content level facilitates and ensures the development of copper fixation process (Cao and Kamdem 2004). During different post-treatments, some of the active ingredient cupric copper would be converted to less soluble cuprous copper form. Copper in the cuprous form is more stable than in cupric form and biologically less available, and therefore less toxic than the initial cupric form in ACQ-D (Zhang et al. 1997, Yu et al. 2009).

From the previous researches, it can be found that the correlations between copper stabilization and valence conversion on copper leaching from ACQ-D treated wood after different post-treatments has not been clarified clearly. Therefore, in this study, we take two promissing post-treatment as the expample to evaluate the effects of copper conversion and copper stabilization on copper leaching from ACQ-D treated wood after some promissing post-treatments. These results will give some useful information about the positive post-treatment conditions during some promising post-treatments, which could improve copper leaching resistance of the treated wood.

MATERIAL AND METHODS

Material and treatment

Wafers (5.0•20.0•50.0 cm long) of red pine (*Pinus resinosa* Ait.) sapwood was cut into small cubes with dimensions of 19.0 ± 0.2 mm and stored in a conditioning room to reach an equilibrium moisture content of 8-10 %. Then the weight of the cubes was taken, and those with similar weight were selected as test samples. The ACQ-D concentrate used in this study was about 15 % concentration (66.7 CuO and 33.3 % didecyldimethylammonium chloride (DDAC)).

It was diluted with deionized water to two different concentrations, which were 1.0 and 0.6 % respectively as determined by using atomic absorption spectroscopy (AAS), and pH value of the solution is about 10.8.

Samples were vacuum-treated in following procedures: Vacuum at 0.1 MPa for 30 min, admit preservative solution, release the vacuum, and remove the beaker, then cover the beaker with plastic film to minimize evaporation and leave the blocks submerged in solution for another hour. The samples used in different experiments underwent the treatments and post-treatments shown in Tab. 1.

Tab. 1: Treatment and post-treatment conditions for samples used in different experiments.

Experiment	Concentration of ACQ (%)	Hot air post-treatment		Steaming post-treatment	
		Temp. (°C)	Duration (h)	Temp. (°C)	Duration (h)
Copper stabilization	0.6, 1.0	50	0,2,7,24,48,120	120	2
Copper conversion			0, 24,48,120		
Copper leaching			0,2,7,24, 120		

Copper stabilization

After ACQ-D impregnation, the blocks were weighed and divided into groups with six replicates in each group to carry out different post-treatments. For each group after different post-treatment (Tab. 1), the extent of copper fixation was monitored by the expressing technique: 10 samples were squeezed in a press at high pressure to express the free treating solution, and the expressate solution was analyzed for copper oxide content by x-ray fluorescence spectroscopy (Spectro Phoenix II XRF). The extent of copper fixation was computed as the percent decrease in copper oxide content compared to the initial concentration in the treating solution.

Leaching test

Samples were performed the laboratory leaching test after post-treatment according to AWPA E11-2009 standard. Six replicates were used for each condition and the leachate was exchanged at prescribed intervals; the first interval was 6 h and then after 24, 48 and thereafter at 48 h intervals. The leaching test lasted for a total of 14 days. After the leaching test, the blocks were air-dried, milled to powder, and then dried at 103±2°C for 24 h. 0.15 g wood powder of each replicate was weighed and digested with the acid mixture of nitric acid and perchloric acid. Then the copper content was analyzed by using atomic absorption spectroscopy (AAS).

Copper valence conversion by UV/VIS

The percentage of copper conversion was expressed as the percentage of copper reduced from cupric copper (Cu(II)) to cuprous copper (Cu(I)) based on the ratio of cuprous copper to the total copper content in the samples. The total copper content in the treated samples was determined by atomic absorption spectroscopy (AAS) analysis of digested wood samples of six control samples per treatment. After post-treatments as shown in Tab. 1, a colorimetric method based on the specific reaction of Cu (I) and 2,2′-biquinoline in acetic acid matrix was used to monitor and to quantify Cu(I) in the treated wood. The blocks were ground to pass through a 40-mesh sieve and then air dried. 30 ml of 2, 2′-biquinoline reagent was used to extract about 0.1 g wood powder by ultrasonic extraction for 10 min using ultrasonator. After centrifugation, the supernatant was analyzed by UV/VIS spectrophotometer. The absorption of the solution was measured at 540 nm, which is the wavelength of the maximum absorbance for Cu(I)- 2,2′-biquinoline complex in glacial acetic acid (Cui 1999).

RESULTS AND DISCUSSION

Evaluation the correlations between copper leaching and copper stabilization

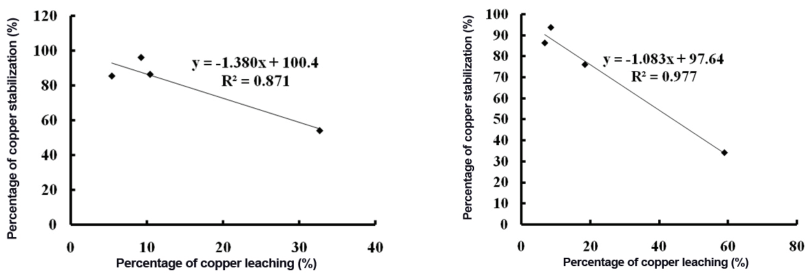
The percentages of copper leached out from ACQ-D treated red pine are showed in Tab. 2. For the samples of control group (leaching directly after impregnation without any post-treatment), about 32.7 and 58.9 % of copper in ACQ-D treated wood would leach out from 0.6 % ACQ-D treated wood and 1.0 % ACQ-D treated wood respectively. From Tab. 2, it is clearly showed that all post-treatment conditions used in this study could reduce copper leaching to a certain extent and the effect is dependent on the conditions of post-treatments. The extent of copper fixed in the treated wood as determined by analyzing the copper content of expressate in the samples taken at different times after different post-treatments is shown in Tab. 2. It can be observed that samples post-treated at 120°C temperature fixed much faster than those post-treated at 50°C hot air post-treatments with longer duration, in which more than 90 % of cupic copper has converted to cuprous form.

Tab. 2: Percentage of copper stabilization, valence conversion and leaching for samples after different post-treatments.

Post-treatment	Experiment	Concentration of ACQ (%)	Temp.(°C)	Duration (h)	Percentage of leaching (%)	SD
Hot air	Copper stabilization	0.6	50	0	54.0	1.8
				2	62.9	3.0
				7	77.4	2.9
				24	86.4	3.3
				48	89.0	1.7
				120	85.4	2.6
Steaming			120	2	96.1	0.8
Hot air		1.0	50	0	34.0	2.9
				2	45. 7	0.7
				7	58.4	1.5
				24	76.0	2.7
				48	81.2	2.2
				120	86.3	3.5
Steaming			120	2	93.7	1.0
Hot air	Copper conversion	0.6	50	0	5.2	0.5
				24	46.5	3.1
				48	48.0	1.3
				120	52.5	0.6
Steaming			120	2	100	5.5
Hot air		1.0	50	0	9.0	2.7
				24	33.9	1.2
				48	35.0	1.5
				120	47.3	1.8
Steaming			120	2	99.9	2.7

Hot air	Copper leaching	0.6	50	0	32.7	1.5
				2	26.7	1.3
				7	18.3	2.0
				24	10.4	1.0
				120	5.4	0.9
Steaming			120	2	9.2	0.3
Hot air		1.0	50	0	58.9	5.4
				2	44.8	3.3
				7	33.2	4.6
				24	18.5	2.5
				120	6.9	1.4
Steaming			120	2	8.6	0.8

As observed from the equations of linear correlations in Fig. 1a and 1b, the percentage of copper leaching is closely related with the percentage of copper stabilization in different post-treatments, especially for the samples treated with 1.0 % ACQ-D solution.



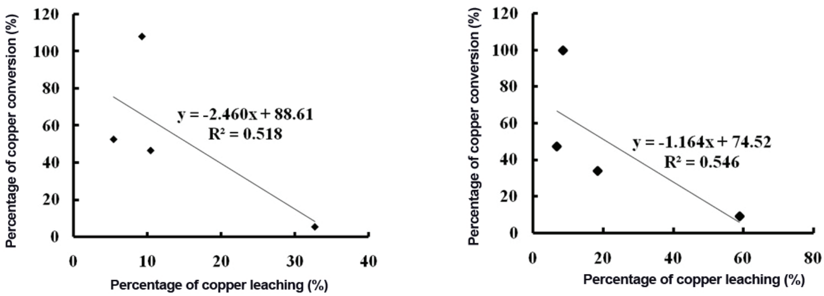
a) 0.5 % ACQ-D b) 1.0 % ACQ-D

Fig. 1: Correlations between copper stabilization and copper leaching.

It seems that 50°C is a mild temperature to promote the fixation process of copper in the treated wood, for 0.6 % ACQ-D treated wood post-treated at that temperature, the copper leaching resistance will be improved much slowly as post-treatment duration prolonged, and it needs to be treated for more than 24 h to reach the similar copper leaching resistance compared to samples post-treated at 120°C only for 2 h. For 1.0 % ACQ-D treated wood, the difference of copper leaching resistance between 50°C hot air post-treatment and 120°C steaming post-treatment is much more obvious, and the samples treated with higher ACQ-D concentration needs much more fixation time to improve copper leaching resistance. This phenomenon may be attributed to the complicated copper fixation process between wood components and ACQ-D constituents, in which the fixation temperature is a very critical factor to promote copper fixed into wood as justified by Ruddick and Yu (Ruddick et al. 2001; Yu et al. 2010a). At 120°C, both of the samples treated with 0.6 and 1.0 % ACQ-D solutions can be reached to almost complete fixation for only 2 h. However, at 50°C, the samples needs several days to reach about 80 % copper fixation, and the fixation process in the samples is rather slow, especially for 1.0 % ACQ-D treated wood. This is also proved that fixation reactions between ACQ-D constituents and wood components are quite active at higher temperatures, and this trend also has been found in other wood species, such as Chinese fir and Mongolian Scotch pine (Yu et al. 2010b).

Evaluation the correlations between copper leaching and copper valence conversion

Percentages of copper reduced from cupric form to cuprous form after different hot water post-treatments are compared in Tab. 2. Cupric copper was prone to reduction to cuprous forms during 120°C steaming post-treatment, and almost 100 % of cupric copper has been converted to cuprous form after only 2 h post-treatment. However, the percentage of copper conversion is only about 50 % for samples post-treated in 50°C hot air post-treatments for several days.



a) 0.5 % ACQ-D b) 1.0 % ACQ-D

Fig. 2: Correlations between copper conversion and copper leaching.

As observed from the equations of linear correlations in Fig. 2a and 2b, the percentage of copper leaching is also related with the percentage of copper stabilization in different post-treatments, although the linear relationship is not so obvious as between the percentage of copper leaching and the percentage of copper stabilization. Generally, higher copper conversion also corresponds to a lower copper leaching rate. The most reason can be concluded to the better stability of cuprous copper product in fixation reactions. From these results, it can be concluded that the complex produced during copper fixation reactions in the wood contain the cuprous form of copper, which is much more stable than the cupric ones, which is a positive factor for improving copper leaching resistance and can be regarded as a rational reason for the better copper leaching resistance in the samples post-treated at 120°C for 2 h. Compared to the almost complete conversion for steaming post-treatment, similar copper leaching resistance also can be obtained in the samples post-treated in hot air post-treatments for longer duration, which means the chemical complex contained cuprous form produced during copper fixation reactions in the wood is not the only stable product as pointed by Kitanovski et al. (2009). The lignin model compounds represent a suitable opportunity for copper stabilization in wood. The basic lignin model compounds are mostly of three types, namely guaiacyl, syringyl and p-hydroxyphenyl (Sakakibara 1991) and we can choose the reasonable condition to obtain better copper leaching resistance of ACQ-D treated wood. Because some research also pointed that the toxicity of cuprous copper is lower than cupric forms, which means higher copper conversion may be impair the termite and decay resistance of ACQ-D treated wood by means of EPR and FITR (Zhang and Kamdem 2000a, Ruddick et al. 2001).

CONCLUSIONS

Positive post-treatments with higher temperature and relative humidity could effectively increase the leaching resistance of copper in ACQ-D treated wood. The correlations among copper leaching, stabilization and valence conversion can be concluded that a higher copper conversion rate and a higher extent of copper fixation usually correspondes to a lower copper leaching. These results demonstrates that it is an effective way to accelerate the fixation process and valence conversion rate of copper in the treated wood by providing idea fixation conditions for ACQ-D treated wood, such as sufficient fixation duration, higher fixation temperature or reasonable post-treatment method. For example, in this study, ACQ-D treated samples could archive better leaching resistance both after 50°C hot air post-treatments for longer duration (120 h) and after higher temperature and relative humidity post-treatment (120°C steaming) for only 2 h.

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