EFFECTS OF HOT WATER POSTTREATMENT ON ACCELERATING COPPER FIXATION IN ACQ-D-TREATED CHINESE FIR

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Abstract. The effects of hot water posttreatments on accelerating copper fixation in alkaline copper quat-type D (ACQ-D) -treated Chinese fir [*C. lanceolata* (Lamb.) Hook] were evaluated. The rate and extent of copper fixation in treated wood posttreated at 60, 80, and 100°C were monitored by analyzing the copper content in the expressed solution over time. The fixation qualities of copper in treated wood after different hot water posttreatments were evaluated by the AWPA E11-06 leaching test. The valence conversion of copper in treated wood was investigated by UV/visible spectroscopy. The expressing results showed that copper stabilized much faster during hot water posttreatments, especially at 80 and 100°C; more than 90% of copper could be fixed in treated wood in less than 2 h. The valence conversion of copper was highly dependent on the temperature and duration of the treatment. After a 100°C hot water bath of 6 h, more than 40% of cupric copper was reduced to cuprous forms. Based on the results of leaching tests of ACQ-D-treated wood, the best copper leaching resistance was obtained at 100°C; the percentage of copper leaching was reduced to about 12% when posttreated for 9 h. The compressive strength of treated wood was not impaired significantly in that condition.

Keywords: Chinese fir [*C. lanceolata* (Lamb.) Hook], alkaline copper quat-type D (ACQ-D), hot water, posttreatment, copper leaching, valence conversion, compression strength.

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INTRODUCTION

As a result of the growing pressure from environmental concerns, waterborne wood preservative systems containing arsenate or chromium such as chromated copper arsenate (CCA) were prohibited or limited for residential applications in many countries or regions. Accordingly, new environmentally friendly wood preservatives such as alkaline copper quat (ACQ) and micronized or dispersed systems of copper-based wood preservatives are used much more widely in the market. These copper-based preservative systems do not contain arsenic or chromium, which is a benefit for safety issues; however, this is also a drawback considering the copper leaching resistance in treated wood because many studies have shown that Cr(VI) could oxidize various lignocellulosic groups to form strong fixation sites for copper and possibly form other low-solubility copper compounds in the matrix (Pizzi 1982; Milowych et al 1992).

After preservative impregnation, fixation reactions between the chemicals and wood components take place and during this process, the active ingredients are fixed in the treated wood. The fixation mechanisms of alkaline copper preservatives (amine or ammonia-based) in the treated wood have been reported in many studies. Such studies have shown that copper amine could react with the acidic groups in wood by ion exchange, especially with the carboxylic acid of hemicelluloses and phenolic of lignin (Butcher and Nilsson 1982; Jin et al 1990; Cooper 1991, 1998). Some copper can react with cellulose to form new complexes through formation of hydrogen bonds between cellulosic hydroxyl groups and amine nitrogen (Hinojosa et al 1974; Zhang and Kamdem 2000) and in ammoniacal systems through the replacement of one ammonium group in the cupriammonium ions with the hydroxyl ion of cellulose (Baugh et al 1968). The fixation process is strongly dependent on the fixation conditions such as temperature, duration, RH, and wood MC (Boone et al 1995; Kaldas and Cooper 1996; Ung and Cooper 2005). Copper fixes much more slowly at ambient temperature conditions, requiring days to weeks to be completed (Ung and Cooper 1996, 2005). Efforts have been undertaken to accelerate the fixation of active ingredients through posttreatments. Electromagnetic radiation such as microwave and radio-frequency, dielectric heating, kiln drying, and steaming accelerate the fixation process of CCA chemicals in the treated wood with improved leaching resistance and reduced processing time (Peek and Willeitner 1988; Cooper and Alexander 1991; Boone et al 1995; Smith et al 1996; Cao and Kamdem 2004).

Different methods have some drawbacks related to the higher cost, need for special equipment, or complicated factors within the entire process. A number of commercial hot water bath fixation technologies have emerged such as the MSU Process (Kelso 1981) and other patented technology (Bergervoet et al 1997, 1998). The MSU Process uses hot water (70 – 115°C water for 1 – 8 h depending on the wood dimensions) as the heating medium in an empty cell process (no initial vacuum), which prevents solution kickback by holding the pressure in the wood with hot water until the fixation process is complete. As a result, the fixation of active ingredients is accelerated. The advantages of hot water posttreatment are obvious; for example, it is easy to perform and does not need to consider the cooling effects of drying on the fixation process (Christensen 1990; Chen et al 1994). Weaver (1981) treated CCA-treated southern pine pole sections using the MSU Process at 138 MPa initial air pressure and fixed the preservative using hot water at 49, 66, 93, and 116°C for 3 h. He showed that over 96% of the CCA components were precipitated at 66°C. Bergervoet et al (1997, 1998) described an improved process in the patents for the fixation of preservatives in wood, which initiates the fixation process in a fixation vessel with an aqueous liquid heating medium preheated to a temperature of 54 – 93°C for a period of 0.5 – 2 h, and after the removal of heating medium and the final vacuum, the treated and fixed wood is rinsed in the fixation vessel with heated clean water with a temperature of about 93°C. Limitations of in-retort hot water fixation include longer processing times, the

Table 1. *Treatment and posttreatment conditions for samples used in different experiments.*

Experiment	ACQ-D treatment			Posttreatment		Replicates
	Concentration of treating solution (%)	Retention in treated wood (kg/m^3)	SD	Temp. (°C)	Duration (h)	
Copper fixation	1.35	12.8	0.17	60, 80, 100	0, 2, 4, 6, 8,10	6
Copper conversion	1.35	12.8	0.17	60, 80, 100	0, 1, 3, 6, 9	3
Copper leaching	1.35	12.8	0.17	60, 80, 100	0, 1, 3, 6, 9	6
	0.90	8.5	0.13	100	0, 1, 3, 6, 9	6
	0.60	5.6	0.15	100	0, 1, 3, 6, 9	6

potential for creating large volumes of contaminated water, and the potential for strength reduction (Winandy and Boone 1988).

Posttreatments may bring about some reductions in performance. For example, some conditions used in posttreatment may promote the valence conversion of cupric copper to less soluble cuprous copper. It was reported that copper in the cuprous form is more stable than in the cupric form and biologically less available and therefore less effective against fungi compared with the initial cupric form in ACQ-D (Zhang et al 1997; Zhang and Kamdem 2000; Kamdem et al 2001).

Therefore, this investigation investigates the overall effects of hot water posttreatment on ACQ-D-treated wood, including the fixation rate of copper, the quality of the fixation based on copper leaching performance, the valence conversion of copper, and the compression strength of the conditioned wood. Based on the experiment results, optimal conditions for hot water posttreatment of ACQ-treated wood can be obtained.

MATERIALS AND METHODS

Samples and Treatment

Defect-free cubes measuring 19 × 19 × 19 mm were cut from pole sections of Chinese fir (*Cunninghamia lanceolata* Hook.) sapwood from Sichuan Province, China, and were stored in a conditioning room maintained at 23 ± 0.5°C with 65 ± 2% RH until they reached EMC of 9 ± 1%. The ACQ-D concentrate used in this study was about 15% concentration (66.7% CuO and 33.3% didecyldimethylammonium chloride) produced by a local wood preservation plant. It was diluted with deionized water to the concentrations of 1.35, 0.90, and 0.60%. The samples used in different experiments underwent the treatments and posttreatments shown in Table 1.

Vacuum treatment procedures were as follows: vacuum at 0.1 MPa for 30 min or 1 h depending on the number of treated blocks, introduce the preservative solution, release the vacuum, remove the beaker to air exposure, cover the beaker with plastic film to minimize evaporation, and leave the blocks submerged in solution for 1 h.

Fixation Rates of Copper

After ACQ-D impregnation, the blocks were weighed and divided into groups with six replicates in each group to carry out different hot water posttreatments. For each group after hot water posttreatment, the extent of fixation of copper was monitored by the expressing technique (McNamara 1989). After posttreatments in different temperature water baths for various durations as listed in Table 1, 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 PhoenixII XRF). The extent of copper fixation was computed as the percentage decrease in copper oxide content compared with the initial concentration in the treating solution.

Copper Conversion

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 analysis of digested wood samples (AWPA A11-93; AWPA 2006) of six control samples per treatment. After posttreatments as shown in Table 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. About 0.1 g of wood powder was extracted with 30 mL of 2, 2′-biquinoline reagent by ultrasonic means for 10 min using an ultrasonator (Model KQ-250VDB; Kunshan Instrument Co. Ltd.). After centrifugation, the supernatant was analyzed by a UV/VIS spectrophotometer (Unix 7200). 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 (Felsenfeld 1960; Cui 1999).

Laboratory Leaching

To evaluate the copper leaching performance of samples after different ACQ-D treatments and hot water posttreatments, samples were divided into different groups to perform hot water posttreatments with six replicates in each group. The concentration of treating solution, temperature, and duration of hot water bath posttreatments are listed in Table 1. For each ACQ-D treatment, a group of six samples was leached immediately without posttreatment.

The leaching tests were performed according to AWPA E11-06 (AWPA 2006). Treated wood blocks were immersed in deionized water for 14 da. Deionized water was changed after 6, 24, and 48 h and thereafter at 48-h intervals. When the leaching test was finished, the blocks were air-dried, ground to pass through a 30-mesh sieve, and dried in an oven at 103 ± 2°C for 24 h. The copper content was analyzed by X-ray fluorescence spectroscopy. Percentage of copper leached out was calculated according to the following equations:

$$L_0 = \frac{R_0 - R_1}{R_0} \times 100 \quad (1)$$

$$L_1 = \frac{R_1 - R_2}{R_1} \times 100 \quad (2)$$

$$L = \frac{R_0 - R_2}{R_0} \times 100 \quad (3)$$

where L_0 is the percentage of copper leached out from ACQ-D-treated wood after different hot water posttreatments, L_1 is the percentage of copper leached out after the leaching test, and L is the total loss of copper during hot water posttreatment and leaching test. R_0 is the original copper retention in the samples after ACQ-D impregnation, R_1 is the copper retention after different hot water posttreatments but before leaching, and R_2 is the copper remaining in the treated wood after 14-da leaching.

Strength Test

The reduction in wood strength as an indicator of decay and an evaluation of treatment condition on the mechanical properties have been well documented (Morrell and Zabel 1985; Ruddick 1986; Poncsák et al 2006). To determine the impact of hot water on the compressive strength of ACQ-D-treated wood, samples with better copper leaching resistance were selected to perform the compression strength parallel to grain test with three replicates in each group, and another three Chinese fir samples without any treatment were used as a reference.

RESULTS AND DISCUSSION

Effect of Hot Water Posttreatments on Copper Fixation

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 hot water posttreatments is shown

in Fig 1. It is evident that samples posttreated in a higher temperature water bath fixed much faster than those in a lower temperature water bath. Samples posttreated at 60°C require 6 h or more to achieve almost complete copper fixation, but the fixation time can be significantly shortened in an 80 or 100°C water bath. At 80 or 100°C, over 90% of copper can be fixed in less than 2 h. It seems that copper reacted with wood components rapidly with hot water posttreatments. However, even with longer hot water treatments, copper cannot fix completely in the treated wood at these temperatures. This is partly attributed to the copper available in the wood void space and there appears to be equilibrium between the amount of copper reacted in the wood cell walls and the amount remaining dissolved in excess ethanolamine in the wood void structure (Ung and Cooper 2005). Also, as discussed subsequently, some free copper was leached out during the hot water posttreatment.

Effect of Hot Water Posttreatments on the Valence Conversion of Copper

Percentages of copper reduced from cupric form to cuprous form after different hot water posttreatments are compared in Fig 2. Cupric copper was prone to reduction to cuprous forms during hot water posttreatments, and the temperature of the hot water posttreatment had a great effect on accelerating the valence conversion of copper. After a hot water bath at 60°C for 9 h, only 14% of cupric copper was reduced to cuprous form; however, after a hot water bath at 100°C for 9 h, up to 40% cupric copper was reduced to cuprous form. The percentage of the valence conversion of copper generally increased with increased duration of the posttreatment conditioning. From these results, it can be concluded that hot water posttreatment with higher temperature and water could promote the reduction of cupric copper to cuprous forms. It is considered that Cu amine induces oxidation of wood to create additional cation exchange sites, and during this process, some Cu is reduced from cupric to cuprous form, as stated by Tascioglu et al (2008). This is also supported by the known ability of Cu amines to oxidize various organic compounds under aerobic conditions (Li and Trush 1993; Marko et al 1996; Kumbhar and Kishore 2003). For ACQ-treating solutions exposed to elevated temperatures in the absence of wood, no Cu(I) is detected in the solutions (Tascioglu et al 2008), which is likely the result of the availability of reducing sugars, a key factor in copper conversion from cupric

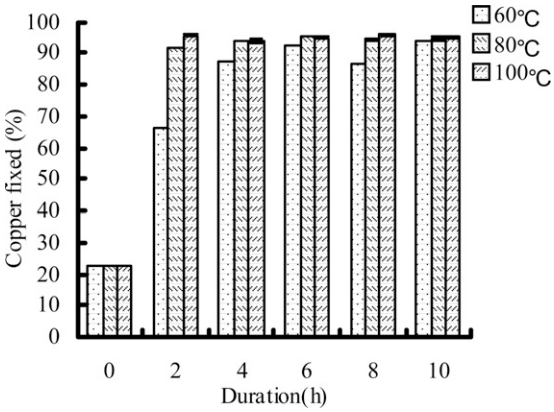

Figure 1. Percentage of copper fixed in ACQ-D-treated Chinese fir with a copper retention of 6.8 kg/m^3 (ACQ retention 12.8 kg/m^3) after different hot water posttreatments.

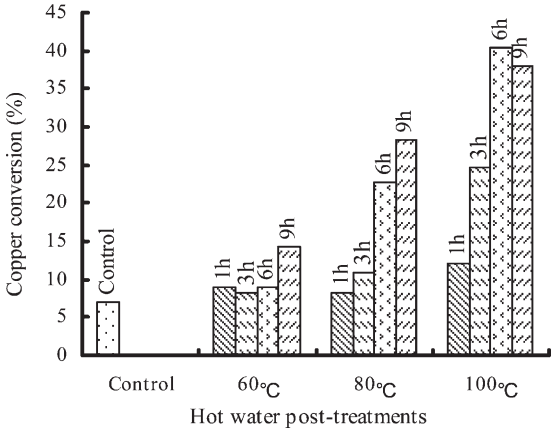

Figure 2. Copper conversions from Cu(II) to Cu(I) in ACQ-D-treated Chinese fir with a copper retention of 6.8 kg/m^3 (ACQ retention 12.8 kg/m^3) after different hot water posttreatments.

to cuprous form (Kamden et al 1998). Although the cuprous copper–wood complexes are more stable than the cupric copper–wood ones, the bioefficacy may be impaired with higher levels of valence conversion. The effect of valence conversion on the bioefficacy in ACQ-D-treated wood will be further investigated by field tests and also laboratory decay tests, and the results will be reported in the future.

As observed in Fig 3, the percentages of copper leaching (L_1 and L_2) are related with the percentage of copper conversion from cupric to cuprous form. Generally, in these two phases of copper leaching, higher copper conversion corresponds to a lower copper leaching rate. The better copper leaching resistance in treated wood is attributed to the low water solubility of cuprous copper formed during hot water posttreatments.

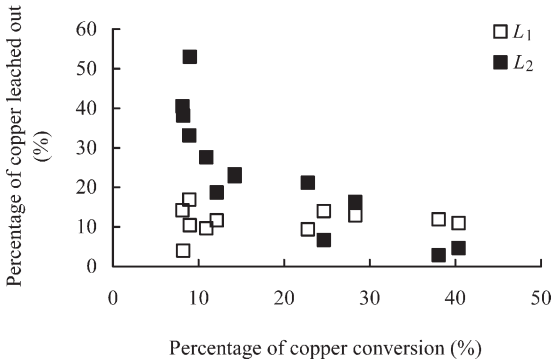

Figure 3. Relationship between copper leaching and copper conversion from cupric to cuprous form.

Effect of Hot Water Posttreatments on Copper Leaching Performance

Percentages of copper leached out from ACQ-D-treated wood (L) include two parts, one during hot water posttreatments (L_1) and the other during the AWPA leaching tests (L_2). Their average values as well as the corresponding standard deviations are shown in Table 2. The percentage of copper leached is highly temperature- and duration-dependent. The total copper leached decreases with increasing temperature and prolonged duration of hot water posttreatment. After 9 h in a 100°C hot water bath, the total copper leaching was reduced from 61% (control without posttreatment) to only 12.5%.

The amount of copper leached during the hot water posttreatment (L_1) ranges from 4 – 23% depending on the temperature and duration. At 60 and 80°C, more copper was lost with prolonged duration of leaching, whereas at 100°C, there is no clear trend between copper loss and duration, which may be related to the rapid copper fixation in high temperature hot water. Although the L_1 in 80°C hot water is the lowest, the copper loss during AWPA leaching tests (L_2) is still high for samples posttreated in

Table 2. *Comparison of the percentages of copper leached out during hot water posttreatments and AWPA leaching tests with corresponding standard deviations.*

R_0 (kg/m^3)	Temp. (°C)	Duration (h)	R_1 (kg/m^3)	SD	L_1 (%)	R_2 (kg/m^3)	SD	L_2 (%)	L (%)
6.8	—	—	—	—	—	—	—	—	61.0
	60	1	6.1	0.4	10.4	2.9	0.04	53.0	57.0
		3	5.8	0.1	14.2	3.4	0.07	40.5	47.8
		6	5.6	0.2	16.9	3.8	0.04	33.1	43.2
		9	5.3	0.1	22.8	4.0	0.06	23.3	39.4
	80	1	6.5	0.1	4.0	4.1	0.04	38.1	39.2
		3	6.2	0.4	9.6	4.4	0.05	27.6	33.1
		6	6.2	0.2	9.4	4.9	0.09	21.1	26.9
		9	5.9	0.4	12.9	5.0	0.04	16.3	25.5
	100	1	6.0	0.1	11.6	4.9	0.04	18.7	26.5
		3	5.9	0.2	14.0	5.4	0.06	6.7	18.0
		6	6.1	0.1	10.9	5.8	0.07	4.6	13.1
		9	6.0	0.2	11.9	5.8	0.04	2.8	12.5

80°C hot water, which gives a relatively high total copper leaching. The samples posttreated in 100°C hot water performed best during AWPA leaching tests, especially for those posttreated more than 3 h. After 9 h posttreatment in a 100°C hot water bath, only 2.8% of copper (as a percentage of copper in samples after hot water posttreatments) leached out during leaching tests.

Effect of Copper Retention on Copper Leaching Performance

The wood samples were treated with 1.35, 0.9, and 0.6% ACQ-D solutions, which corresponded to ACQ-D retentions of 12.8, 8.5, and 5.6 kg/m^3 and copper retentions of 6.8, 4.5, and 2.8 kg/m^3, respectively. The percentages of copper leached from treated samples (L) after different durations of hot water posttreatment at 100°C and leaching exposure are shown in Fig 4. The effect of copper retention on copper leaching seems inconsistent for different durations of hot water posttreatment. Within 3 h posttreatment, more copper was observed to be leached at higher copper retentions, whereas after 3 h, a reverse trend was observed. It suggests that the duration of hot water posttreatment should be chosen according to the copper retention. For wood treated at lower copper retentions, shorter duration of hot water posttreatment is possible. This result is consistent with the previous investigations on CCA and ACQ leaching performance. It was reported that the fixation of the active ingredients in CCA-treated wood would take more time at higher retentions (Cooper 1996; Ruddick 1996; Ung and Cooper 2005). For the samples that have not fixed completely, more leaching could be observed at higher retentions, whereas for well-fixed samples, a reverse result could be observed, that is, more leaching was observed at lower retention levels (Lee et al 1993).

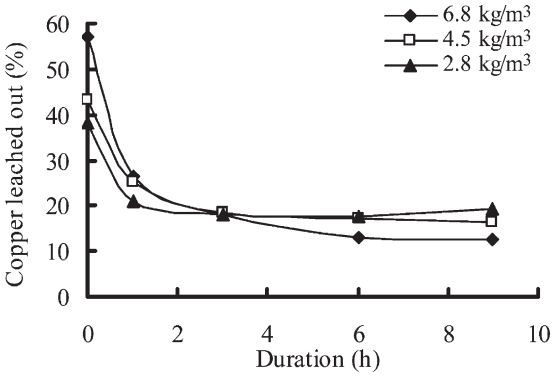

Figure 4. Percentage of copper leached out from ACQ-D-treated Chinese fir samples posttreated in a 100°C hot water bath at different copper retention levels.

Effect of Hot Water Posttreatments on Compression Strength of Treated Wood

On the basis of the copper leaching results, samples for compression strength test were posttreated in 100°C hot water bath for 0, 1, 3, 6, and 9 h, and after air-drying, the compression strength parallel to grain was recorded and compared with untreated Chinese fir samples (Table 3). The parallel to grain compression strength values of all samples were very close. Hot water posttreated samples had slightly lower average strength values, but the differences were not statistically significant. A larger

Table 3. *Compression strength parallel to grain of ACQ-D-treated Chinese fir samples posttreated in a 100°C hot water bath.*

Treatment	Duration in 100°C hot water bath (h)	Compression strength parallel to grain (MPa)	SD
Untreated control	—	46.1	3.5
ACQ-D-treated and posttreated	0	45.8	3.8
in hot water bath	1	42.9	3.1
	3	45.0	5.2
	6	43.3	2.8
	9	42.7	3.6

sample size should be evaluated to determine whether significant strength losses occur.

CONCLUSIONS

Hot water posttreatment at suitable conditions was shown to be an effective method to improve the leaching resistance of copper in ACQ-D-treated wood. At higher temperatures of hot water posttreatment such as 80 or 100°C, copper fixed very quickly in treated wood. The rate of copper fixation had a very clear relation with the copper leaching performance of treated wood. A higher rate of copper fixation corresponds to better copper leaching resistance. Although after 10-h hot water posttreatments, it appeared that all temperatures produced similar percentages of copper fixation. The different copper leaching resistance suggests that copper is fixed in treated wood by different mechanisms at different temperatures. At low temperatures, copper is inclined to be fixed in treated wood with weak interactions such as physical absorption and formed less low solubility cuprous copper resulting in the higher copper leaching in the treated wood. The copper retention has an obvious influence on the copper leaching performance of wood posttreated in 100°C water. Shorter duration of hot water posttreatment is adequate for wood treated at lower copper retentions levels.

The drawback of hot water posttreatment is the significant leaching of copper during the treatment and increasing percentage of reduction of copper to Cu(I) during hot water posttreatment with increasing temperature and duration of the hot water posttreatment. The influence of the valence conversion of copper on the bioefficacy of ACQ-D-treated wood will be investigated by field tests and laboratory decay tests in a future study.

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