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Effect of Copper Retention on Copper Leaching in Wood Treated with Copper-based Preservatives*1

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ABSTRACT

This research investigates the effect of copper retention on copper leaching in wood treated with copper-based preservatives. Radiata pine (*Pinus radiata* D. Don) sapwood samples were ground in a Wiley mill equipped with a 20-mesh screen. The ground wood was vacuum-treated with various concentrations of alkaline copper quat (ACQ), bis-(N-cyclohexyl-diazeniumdioxy)-copper (CB-HDO), and copper azole (CUAZ). The treated samples were conditioned at 70°C and 100% RH for 72 hours. The samples were leached by using the distilled water for four weeks, and the copper contents in each sample were measured by X-ray spectroscopy. As expected, the copper leaching was increased with increasing of copper retention. The copper leaching from the ACQ and CB-HDO treated samples were gradually decreased with increasing copper retention: however, the copper losses from the CUAZ treated samples appeared to be proportionally increased with the increase in copper retention in all retention levels tested. The results indicate that at the conditions of the same copper retention ACQ and CB-HDO treated wood have a better leaching resistance compared to CUAZ treated wood.

Keywords : ACQ, CB-HDO, CUAZ, copper retention, copper leaching

1. INTRODUCTION

Copper-based wood preservatives have been worldwidely used in wood preservation industry since the use of chromated copper arsenate (CCA) was prohibited or restricted for industrial purpose in many countries. The Ministry of Environment, Korea banned the manufacture and use of CCA in 2007, which resulted in the wide use of alkaline copper quat (ACQ), bis-(N-cyclohexyl-diazeniumdioxy)-copper (CB-HDO), and copper azole (CUAZ) as alternatives to CCA. The preservatives have gained good recognition as excellent preservatives because they appeared to offer a good protection against wood decay fungi as well as lower environmental impacts compared with CCA due to the absence of arsenic and chromium.

ACQ, CB-HDO, and CUAZ resist leaching during service because of fixation reactions that

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take place within the treated wood. The factors affecting on the fixation include preservative formulation, preservative retention, pH, and post-treatment conditioning parameters such as temperature, and humidity. Many researches have been performed to investigate the fixation reaction of copper-based preservatives (Copper, 1988, 1991; Kamdem and Zhang, 2000; Manriquez *et al*., 1996; Morris *et al*., 2002; Ruddick, 1996; Zhang and Kamdem, 1999).

Although there remains a need for a better understanding of the fixation and leaching of copper, the assumption that there are a limited number of sites available for copper reaction in wood appears to be generally accepted. The assumption explains the increase of copper leaching in treated wood with high retention levels by the relatively high amount of unreacted copper. Copper adsorption increase with increasing the number of available reaction sites were supported by the results of several experiments (Cooper, 1991; Jin and Preston, 1991; Tascioglu *et al*., 2005). But it is still unclear whether or not all of excessive levels of unreacted copper with wood functional groups could be leached at high retention levels.

The objective of this research was to investigate the effect of retention on leaching resistance of copper in wood treated with copper-based preservatives. The maximum leaching amount of copper dependent on copper retention were evaluated.

2. MATERIALS and METHODS

2.1. Sample Preparation

Defect-free radiata pine sapwood was used in this research. The sapwood was air-dried to 8% MC and milled to 20 meshes prior to preservative treatment. Although wood blocks are generally used in a leaching test, we may gain some useful information about fixation and leaching by using ground wood because almost all of unfixed copper components will be leached from the treated ground wood during the leaching test. The use of ground wood results in much higher amount of leaching compared to actual service conditions. However, it may offer useful guideline about maximum environmental impacts that could be caused by the unfixed copper in preservative treated wood.

2.2. Treating Solution

The samples were treated with various concentrations of alkaline copper quat (ACQ), bis-(N-cyclohexyl-diazeniumdioxy)-copper (CB-HDO), and copper azole (CUAZ) solutions. The percents of total active ingredients in the obtained ACQ-2, CUAZ-2, and CB-HDO were 16%, 12%, and 25%, respectively. The preservatives were diluted to 10, 20, 40, 80, and 160 times by adding distilled water prior to the preservative treatment.

2.3. Treatment of Wood with Preservative

The prepared samples (20 g) were put into glass jars and each of the prepared preservative solutions (100 g) was added into them. After well mixed and then vacuum-treated at 84.6 kPa for 30 minutes, the glass jars were capped to prevent distilled water from being evaporated. The samples were conditioned at 70°C for three days for the complete fixation. Then they were uncapped and dried at 60% RH and 30°C for two weeks. The fixation reactions in the treated samples were considered to be completely finished. After conditioning was over, half amounts of the treated samples in each treated group were removed for the analysis of initial copper retentions and the rest were stored for a labo-

Table 1. Copper retention in the leached and unleached samples treated with ACQ, CB-HDO, and CUAZ

Dilution	ACQ		CB-HDO		CUAZ	
	Unleached	Leached	Unleached	Leached	Unleached	Leached
(times)	(kg/m^3)					
10	22.08	17.83	64.81	50.36	38.54	16.74
20	12.16	9.54	32.00	26.77	17.01	10.03
40	5.86	4.88	16.97	13.43	9.24	6.19
80	2.94	2.49	9.32	7.60	4.65	3.33
160	1.36	1.26	4.09	3.51	2.31	1.77

ratory leaching test.

2.4. Leaching

A laboratory leaching test was carried out on the treated samples to determine the amount of copper leached as a percentage of the initial copper retention. The 10 g of each treated sample were placed in a beaker of 500 mℓ of distilled water. They were vacuum-treated at 84.6 kPa for one hour to submerge the treated ground wood. The leaching tests were carried out for four weeks at 25°C. The leachates were removed at 24 hours intervals and replaced with an equal volume of fresh distilled water. The leachates were not collected for the analysis of copper.

2.5. Analysis of Copper

After leaching test, the samples were oven-dried to measure the copper content. The copper contents in treated samples were analyzed using an x-ray spectroscopy. The values of wood density used to determine the retention in kg/m^3 of copper oxide in each test samples was 0.5 g/cm^3. The densities determined on the oven dried weight and the volume at 8% MC were in the range from 0.49 g/cm^3 to 0.53 g/cm^3.

3. RESULTS and DISCUSSION

The copper retentions of ACQ, CB-HDO, and CUAZ treated wood are shown in Table 1. As expected, the CB-HDO treated samples showed the highest copper retention, followed by CUAZ and ACQ. The different elemental copper concentrations in ACQ, CB-HDO, and CUAZ solutions caused the differences of copper retention in the treated samples. When the preservatives were diluted to 10 times, the theoretically predicted copper retentions of the treated samples with ACQ, CB-HDO, and CUAZ were 24 kg/m^3, 44 kg/m^3, and 30 kg/m^3, respectively, and the measured values were 22 kg/m^3, 65 kg/m^3, and 39 kg/m^3. The copper retentions of CB-HDO and CUAZ treated samples were higher than the predicted retentions.

Fig. 1 shows the trends of copper losses with the change of copper retention. ACQ and CB-HDO treated samples appeared to have a similar trend of leaching. Although the copper leaching of ACQ and CB-HDO increased with the increase of copper retention, the leaching rates were gradually decreased. About 10 to 15 percent of copper were leached for the samples with about 5 kg/m^3 copper retention, and maximum leaching amount of copper was not exceeded 25 percent based on the initial copper retention in all copper retention levels. CUAZ treated samples showed the different leaching results compared to ACQ and CB-HDO treated samples. The amount of copper leached seemed to proportionally increased with the increase of copper retention. No gradually decreased rates found in ACQ, and CB-HDO treated samples

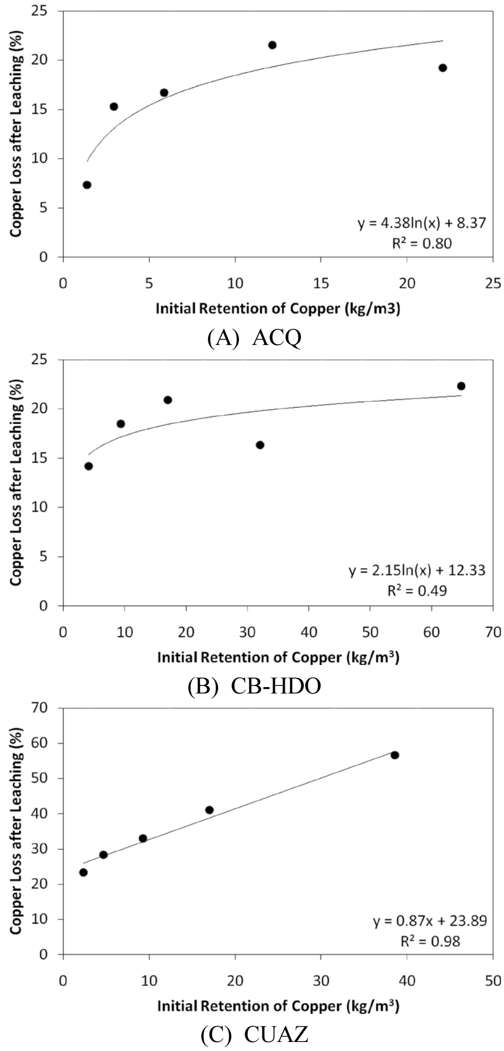

Fig. 1. The change of Cu losses (%) according to the change of copper retentions measured as a percentage of the original copper present in the treated samples.

were observed in CUAZ treated sample.

The copper-based wood preservatives require fixation periods to ensure that their components become water insoluble and have leaching resistance under severe decay conditions. The fixation can be achieved by proper conditioning treatments. However, the fixation cannot completely prevent the active ingredients from leaching into environments. The active ingredients will be leached into environments very slowly. At about 3 kg/m^3 copper retention, the copper losses in the CUAZ treated samples were about 25 percent, and those of ACQ and CB-HDO treated samples did not exceed 15 percent. meaning that unfixed amounts of copper exist although wood has enough bonding sites in wood (Fig. 1).

According to the previous researches about the fixation and leaching of ACQ, the copper adsorption in wood is limited by the number of sites available for copper adsorption in wood, and the unabsorbed coppers with wood functional groups could be leached (Cooper, 1991; Jin and Preston, 1991; Tascioglu *et al*., 2005). The maximum capacity for various species was reported to be in the range from 0.06 to 0.24 mmol of copper per gram of dry wood (Kamdem and Zhang, 2000; Lucas and Ruddick, 2002; Tascioglu *et al*., 2005). Tascioglu *et al*. (2005) reported that only the 35% copper were fixed when the copper retention of treated samples with ACQ was 18.5 kg/m^3, and didecyldimethyl ammonium chloride (DDAC) could compete with copper for the same adsorption sites in wood. However, our research showed all the unfixed coppers with the functional groups in wood were not leached. At near the 20 kg/m^3 of copper retention, the copper losses of ACQ, CB-HDO treated samples were around 20% and that of CUAZ was around 40% (Fig. 1). Although the reason is unclear, the results may indicate that the physical or chemical bonds between the preservative components and the components reacting with wood functional groups give an additional leaching resistance to treated wood.

4. CONCLUSIONS

The result obtained from this experiment suggests that all of excessive levels of unreacted copper with wood functional groups were not leached at high copper retention levels, and at the conditions of the same copper retention ACQ and CB-HDO treated samples have a better leaching resistance compared to CUAZ treated wood. Further research should be required to compare the environmental impacts of those preservatives because their copper retentions required for the hazard class 3 or 4 conditions are different.

REFERNCES

1. Cooper, P. A. 1988. Diffusion and interaction of components of water-borne preservatives in the wood cell wall. Int. Res. Group on Wood Pres. Document No: IRG/WP/3474.
2. Cooper, P. A. 1991. Cation exchange adsorption of copper on wood. Wood Protection 1(1): 9-14.
3. Jin, L. and A. F. Preston. 1991. The interaction of wood preservatives with lignocellulosic substrates. 1. Quaternary ammonium compounds. Holzforschung 45: 455～459.
4. Kamdem, P. D. and J. Zhang. 2000. Contribution of wood components on the absorption of copper amine. Int. Res. Group on Wood Pres. Document No: IRG/WP/00-30216.
5. Kang, S.-M., I.-Y. Hwang, and S.-k. Kim. 2008. Effect of steam on fixation of Cu-amine preservative treated wood. Int. Res. Group on Wood Pres. Document No: IRG/WP 08-50251.
6. Lucas, N. and J. N. R. Ruddick. 2002. Determination of the amine to copper ratio remaining in wood after water leaching. Int. Res. Group on Wood Pres. Document No: IRG/WP/02-30285.
7. Manriquez, V., M. C. Vallette, N. Lara, N. G. Tejeda, O. Wittke, G. Diaz, S. Munoz, and L. Kriskovic. 1996. Crystal structure and vibrational spectra of polyamine-copper (II) complexes. J. Chem. Crystal. 26(1): 15～22.
8. Morris, P. I., S. M. McFarling, and A. Zahora. 2002. Treatability of refractory species with amine and amine/ammoniacal formulations of ACQ. Forest Prod. J. 52(10): 37～42.
9. Ruddick, J. N. R. 1996. The fixation chemistry of ammoniacal copper wood preservatives. Proc. Amer. Wood Pres. Assoc. 92: 32～49.
10. Tascioglu, C., P. Cooper, and T. Ung. 2005. Adsorption of ACQ and CuMEA wood preservatives in red pine. Int. Res. Group on Wood Pres. Document No: IRG/WP/05-30374.
11. Zhang, J. and P. D. Kamdem. 1999. Interaction of copper-amine complexes with wood: Influence of copper source, amine ligands and amine to copper ratio on copper retention and leaching. Int. Res. Group. On Wood Pres. Document No. IRG/WP/99-30203.