Short communication

Leachability, metal corrosion, and termite resistance of wood treated with copper-based preservative

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A B S T R A C T

Health-awareness and concern for the environment have resulted in voluntary removal of chromated copper arsenate (CCA) from wood preservatives in residential applications worldwide. Copper-based preservatives have been formulated as replacements, but these may not provide a permanent solution to all of the related problems, including copper contamination of aquatic environments and corrosion of fasteners. In this study, the copper retention (before and after the leaching process) of five softwood specimens vacuum-treated with alkaline copper quaternary (ACQ) and copper azole (CA) at three target retention levels was investigated by X-ray fluorescence studies. The metal corrosion and termite (Coptotermes formosanus) resistance of treated specimens were studied under laboratory conditions. Except for treated Japanese larch wood, the copper retention levels of the other wood specimens were able to meet the target copper retention values (use classes 2–4) in Chinese National Standard 3000. The copper leaching rates of iron nails due to corrosion tests (CNS 6717) were influenced significantly by the 1.2% ACQ and 1.2% CA treatments; whereas the metal corrosion rates of zinc-galvanized steel nails were less than 2 and could meet the tested standard. Even though the ACQ and CA treatments caused higher copper leaching rates from the treated specimens, they also increased termite mortalities and reduced the mass loss significantly after termite-resistance tests (JIS K 1571).

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1. Introduction

Biodegradation of wood by termites is recognized as one of the most serious problems for wood utilization in countries such as Taiwan, Japan, and parts of the U.S. (Cheng et al., 2007). Many toxic wood preservatives were used in the past in attempts to minimize termite damage. Recognition of risks for human health and potential damage of the environment have prompted changes in the types of preservatives used commercially in recent years. The use of preservatives that include arsenic, chromium, and other heavy metals has decreased in most European countries and in North America (Green and Clausen, 2005; Humar et al., 2006b).

Some alternative methods, including chemical modification and the use of arsenic/chromium-free preservatives, have been developed to enhance the durability of wood without the use of conventional toxic biocides. Chemical modification is accomplished by treating the wood with selected chemicals that modify the cell wall wood polymers without leaving toxic residues within the wood (Papadopoulos et al., 2002). The use of chemical modification to stabilize wood against the activities of decay organisms has been the subject of numerous studies (Rowell, 1983; Hon, 1996; Papadopoulos et al., 2008). Arsenic/chromium-free alternatives based on copper compounds have also been introduced recently as alternative chemicals, because copper exhibits good biocidal activity (Nicholas and Schultz, 1997). Some of these new preservative systems include alkaline copper quaternary (ACQ), copper azole (CA), ammoniacal copper citrate (CC), copper dimethyl-dithio-carbamate (CDDC), and Cu-HDO (bis-(N-cyclohexyldiazene-m-dioxy)-copper) (Cao and Kamdem, 2004; Lebow et al., 2005).

There have been some reports about the properties of penetration, retention, leaching, and resistance to fungi and termites, as well as long-term field testing of some softwoods and hardwoods treated with these new preservatives (Creffield et al., 1996; Slahor et al., 1997; Hassler et al., 1999; Drysdale et al., 2000; Fox et al., 2000; Morris et al., 2002; Terziev, 2002; Rhatigan et al., 2004; Temiz et al., 2004, 2005; Lebow et al., 2005; Arango et al., 2006; Humar et al., 2006a; Yildiz, 2007).

However, copper-based preservatives may not provide a permanent solution to all related problems; some of these issues include concern over copper in aquatic environments and corrosion...
of fasteners (Jin et al., 1992; Anon., 1994; Lebow, 1996; Stook et al., 2005; Arango et al., 2006; Temiz et al., 2006). In this study, copper retention (before and after the leaching process) of five softwood specimens vacuum-treated with ACQ and CA at three target retention levels was investigated by X-ray fluorescence studies. The metal corrosion and termite (Coptotermes formosanus) resistance of treated specimens were studied under laboratory conditions. These results can provide information for estimating the applicability of copper-based preservatives in architectural design.

2. Materials and methods

2.1. Wood specimens and preservative treatments

Specimens, measuring 20 mm (radial) × 20 mm (tangential) × 10 mm (longitudinal), were cut from sapwood portions of Taiwania (Taiwania cryptomerioides, average density: 325 kg m⁻³), Japanese cedar (Cryptomeria japonica, average density: 483 kg m⁻³), China fir (Cunninghmania lanceolata, average density: 372 kg m⁻³), Japanese larch (Larix leptolepis, average density: 566 kg m⁻³), and Western hemlock (Tsuga heterophylla, average density: 484 kg m⁻³). Before treatment, all wood specimens were kept at 20 °C and 65% relative humidity (RH) for 2 weeks. All specimens were numbered and weighed to the nearest 0.01 g. The specimens were free of knots and visible concentration of resin, and showed no visible evidence of infection by mold, stain, or wood-degrading fungi.

The specimens were vacuum-treated with two different copper-based preservatives at various concentrations: 0.3%, 0.6%, and 1.2% alkaline copper quaternary (ACQ-A; Koshii Preserving Co., Japan; including 7.2% alkylbenzylimethimethyl ammonium chloride (C8-C18) and 9.2% copper oxide) and copper azole (Wolman CA-B; Arch Wood Protection; including 10.0% copper (w/w) and 0.40% azole (Tebuconazole) (w/w)). The specimens were placed in a desiccator and subjected to a 700 mm Hg vacuum for 20 min. The treatment solution was introduced and the vacuum was released. After 30 min, the specimens were removed from the solution, wiped lightly to remove preservative solution from the surface, and immediately weighed to the nearest 0.01 g. These specimens were stored in plastic bags at 20 °C for 2 weeks before analyses for copper retention.

2.2. Leaching of treated wood specimens

The leaching test was conducted according to Chinese National Standard 6717 (2000) to reproduce the effect of weathering. The procedure involves immersing the wood specimens in distilled water, stirring with a magnetic follower (400–450 rpm) at 27 °C for 8 h, followed by drying at 60 °C for 16 h. This cycle was repeated 10 times. After each leaching cycle, the water was replaced with fresh distilled water at a ratio of 10 volumes of water to 1 volume of wood. After the leaching process, the specimens were stored in plastic bags at 20 °C for 2 weeks before analyses for copper retention.

2.3. Analyses of treated wood for copper retention

After the fixation period and leaching process, copper retention (in kg m⁻³) was assessed according to Chinese National Standard 14730 (2003) with an energy dispersive X-ray fluorescence spectrometer (ED-XRF, Oxford Lab-X 3500 analyzer, UK). The leaching rate of copper (formula (1)) in the wood specimens was calculated on the basis of the initial amount of copper in the specimens.

Leaching rate of copper(%) = \( \frac{R_1 - R_2}{R_1} \times 100 \)  

where \( R_1 \) and \( R_2 \) represent the average copper retention (before and after the leaching process) of wood specimens investigated by X-ray fluorescence studies, respectively.

2.4. Metal corrosion tests

Iron nails and hot dip, zinc-galvanized steel nails, both 38 mm long and with a diameter of 2.35 mm, and Japanese cedar wood specimens measuring 20 mm (radial) × 20 mm (tangential) × 45 mm (longitudinal) were selected for metal corrosion tests of wood treated with copper-based preservatives, according to the method described in Chinese National Standard 6717 (2000). Two nails (both iron or both galvanized steel) were pushed into the cross section of the vacuum-treated wood specimens. The specimens were conditioned at 40 °C and 97% RH for 10 days. The mass loss of the nails due to these corrosion tests was calculated as the difference between the initial weight and the final weight of the nails after withdrawal from the wood and removal of the rust with 10% ammonium citrate. The metal corrosion rate was evaluated using the following formula:

Metal corrosion rate(%) = \( \frac{M_2 - M_1}{M_1} \times 100 \)  

where \( M_1 \) and \( M_2 \) represent the average mass loss rates of the nails after withdrawal from the wood without and with preservative treatment, respectively. Metal corrosion rate is considered to be the important quantity index of the wood preservative and must be less than 2.

2.5. Termite-resistance tests

Untreated control and treated specimens (without and after the leaching process) were exposed to the subterranean termite C. formosanus Shiraki according to the method detailed in Japanese Industrial Standard K 1571 (2004). An acrylic cylinder (80 mm in diameter, 60 mm in height) with the lower end sealed with a 5-mm-thick hard plaster was used as a container. The test specimen was placed at the center of the plaster bottom of the test container. A total of 150 worker termites collected from a laboratory colony of National Taiwan University were introduced into each test container together with 15 termite soldiers. Five wood specimens per treatment were exposed to the termites. The assembled containers were set on damp cotton pads to supply water to the specimens, and kept at 28 °C and >85% RH in darkness for 3 weeks. The mass loss of the specimens due to termite attack was calculated as the difference between the initial weight and final oven-dried (60 °C, 3 days) weights of the specimens after the debris from the termite attack was cleaned off. Termite mortality was also recorded.

3. Results and discussion

3.1. Copper retention of treated wood specimens after the leaching process

In this study, the designated conditions for exposure of treated wood were use classes 2–4 according to Chinese National Standard 3000 (2001): (1) leaching from treated wood used indoors at 70% RH (use class 2); and (2) treated wood used outdoors was exposed indirectly (use class 3) or directly (use class 4) to weathering and not in contact with the ground or water. The principal agent for causing leaching from wood in use class 4 is rainfall. Rainfall on the treated wood could produce leaching, which runs off into surface water and/or soil. Wood exposed in an above-ground situation is subjected to the intermittent wetting of rainfall and the drying of the wood surface between rainfall events. These wetting and drying
cycles were simulated under laboratory conditions. We assumed that leaching obtained by exposure to rainfall is identical with leaching obtained by immersion in water. According to CNS 3000, ACQ and CA treatments were not appropriate when the treated wood was constantly in contact with the ground, fresh water, or seawater (use class 5).

Table 1 shows the copper retention of five softwood specimens at three target retention levels after vacuum-treatment with ACQ and CA. Except for treated Japanese larch wood, the copper retentions of the other wood specimens were able to meet the target copper retention values (use classes 2–4) in CNS 3000. The treated Japanese larch wood was able to meet the target copper retention values (use classes 2 and 3) in CNS 3000 because of resins in the tracheids of Japanese larch. Generally, the copper retentions of treated specimens increase with an increase of preservative concentration. A high coefficient of relationship ($r = 0.7074$) between copper retention and preservative concentration was found. Taking specimen density into consideration, there was a negative linear relationship ($r = 0.7074$) between copper retention of treated specimens and density of the wood.

Table 1 also indicated copper retention of treated wood specimens after the leaching process. Except for treated Japanese larch wood, the copper retention of the other wood specimens after the leaching process met the target copper retention values for use classes 2–4 in CNS 3000 (Table 1). After the leaching process, the treated Japanese larch wood could meet the target copper retention value only for use classes 2 and 3 in CNS 3000. For all ACQ- and CA-treated wood specimens, the copper leaching rates were 6.92–19.54% and 9.38–22.46%, respectively. Generally, the copper leaching rates of treated specimens increased with increased concentration of treated preservative, possibly because of better copper fixation when the wood was treated with lower concentrations of preservatives.

These results support the findings reported by Anon. (1990, 1994) and Jin et al. (1992). Anon. (1994) showed that copper leaching rates were 17.4% from ACQ-B-treated wood and 15.4% from ACQ-D-treated wood (both retentions: 6.4 kg m$^{-3}$) as measured by a soil-bed test, whereas the copper leaching rate (10–14%) decreased due to an above-ground depletion test (Jin et al., 1992; Anon., 1994). Moreover, the leaching rate increased from that of ACQ-B-treated wood, with a higher retention of 9.6 kg m$^{-3}$ (Jin et al., 1992), and decreased with a lower retention of 0.4 kg m$^{-3}$ (Anon., 1990). Furthermore, Temiz et al. (2006) found the greatest loss of copper from wood treated with ACQ-1900 and ACQ-2200 in the first periods of the leaching process. The percentage of copper leached from the wood treated with the alternative copper-based preservatives was greater than that from the CCA-treated wood. By using various leaching procedures, including the toxicity characteristic leaching procedure, the synthetic precipitation leaching procedure, the synthetic seawater leaching procedure, and the deionized water leaching procedure, Stook et al. (2005) found that 15–40% of copper leached from ACQ-D-treated wood and 18–39% of copper leached from CBA-A-treated wood, respectively. The average copper leaching rates from treated wood, in decreasing order, were toxicity characteristic leaching procedure > synthetic seawater leaching procedure > synthetic precipitation leaching procedure > deionized water leaching procedure. The copper leaching rate after the deionized water leaching procedure was close to our results after the distilled water leaching procedure.

3.2. Metal corrosion

Fig. 1 shows the metal corrosion rate of wood treated with ACQ and CA. The results indicate that the metal corrosion rate of the iron nails due to corrosion was influenced significantly by the treatment with 1.2% ACQ and 1.2% CA (metal corrosion rate > 2). This is because serious metal corrosion may be caused by ammonia and chloride in the preservatives tested (Lin and Chen, 2004; Ayrilmis, 2007). Ayrilmis (2007) also pointed out that waterborne inorganic salts may be hygroscopic and corrosion metal fillers in treated wood may be increased. The metal corrosion rates of the iron nails

![Fig. 1. Metal corrosion rate of wood treated with alkaline copper quaternary (ACQ) and copper azole (CA).](image-url)
were 1.65–3.11% for ACQ-treated specimens, and 1.55–2.83% for CA-treated specimens.

The metal corrosion rates of the zinc-galvanized nails after the corrosion tests were less than 2 (Fig. 1). The rates showed no significant difference among specimens treated with 0.3% ACQ, 0.6% ACQ, 0.3% CA, and 0.6% CA (1.17–1.22%). However, a significant difference was found between 1.2%-ACQ- (or 1.2%-CA-)treated specimens (1.59–1.62%) and the other specimens.

The metal corrosion rates of the zinc-galvanized steel nails were lower than those of the iron nails for the same preservative at the same concentration. This suggests that the use of zinc-galvanized steel nails is preferred for connecting ACQ- and CA-treated woods.

3.3. Termite resistance of untreated specimens

The termite-resistance tests showed that untreated Japanese larch suffered the greatest mean mass loss (mean 13.94%; Table 2) and had the lowest termite mortality (9.5%; Table 3) (a positive relationship \[ r = 0.6442 \] between specific gravity and mass loss, but a negative correlation between termite mortality and mass loss \[ r = 0.6923 \], and between specific gravity and termite mortality \[ r = 0.5970 \]). The hypothesis that woods with a higher specific gravity show a greater natural resistance to degradation by termites appears contradictory to the results of our study. However, the density is not the sole factor affecting the durability of wood. A study carried out by Peralta et al. (2004), which focused on wood consumption rates of different forest species by termites under field conditions, did not find a strong correlation between wood density and termite resistance. Chang et al. (1999) also indicated that extractives have a significant effect on the durability of wood, and certain extractives from wood tissues can provide protection against harmful insects. In a study of Arango et al. (2006), six hardwoods and six softwoods were evaluated for their ability to resist termite damage by Reticulitermes flavipes. Mass loss versus specific gravity showed an inverse correlation in tropical hardwood species, but a slightly positive correlation in native softwood species. Similar results were also found by Esenther (1997) in a study of the natural resistance of 21 native and exotic woods. However, observation of the mean mass loss and mean termite mortality showed no statistically significant difference between the sets of specimens in this study. It appeared that there was a greater percentage of termite deaths associated with woods of a lower specific gravity. However, these results are limited to the wood species chosen for the experiment.

3.4. Termite resistance of treated specimens

Even at low retention values, ACQ- and CA-treated specimens showed lower mass loss and greater termite mortality in comparison to those shown by the untreated specimens. All treated

### Table 2

<table>
<thead>
<tr>
<th>Treatment solution</th>
<th>Leaching treatment</th>
<th>Mass loss (%), mean (SD)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>China fir</td>
</tr>
<tr>
<td>Untreated control</td>
<td></td>
<td>12.02 (1.44)</td>
</tr>
<tr>
<td>0.3% ACQ</td>
<td>Leached</td>
<td>0.60 (0.23)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.16 (0.60)</td>
</tr>
<tr>
<td>0.6% ACQ</td>
<td>Leached</td>
<td>0.55 (0.15)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.98 (0.38)</td>
</tr>
<tr>
<td>1.2% ACQ</td>
<td>Leached</td>
<td>0.29 (0.02)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.32 (0.05)</td>
</tr>
<tr>
<td>0.3% CA</td>
<td>Leached</td>
<td>0.84 (0.24)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.74 (0.56)</td>
</tr>
<tr>
<td>0.6% CA</td>
<td>Leached</td>
<td>0.85 (0.14)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.20 (0.38)</td>
</tr>
<tr>
<td>1.2% CA</td>
<td>Leached</td>
<td>0.45 (0.09)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.54 (0.09)</td>
</tr>
</tbody>
</table>

Values in parenthesis are standard deviations.

### Table 3

<table>
<thead>
<tr>
<th>Treatment Solution</th>
<th>Leaching treatment</th>
<th>Termite mortality (%), mean (SD)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>China fir</td>
</tr>
<tr>
<td>Untreated control</td>
<td></td>
<td>26.5 (9.8)</td>
</tr>
<tr>
<td>0.3% ACQ</td>
<td>Unleached</td>
<td>72.0 (9.0)</td>
</tr>
<tr>
<td></td>
<td>Leached</td>
<td>52.5 (7.9)</td>
</tr>
<tr>
<td>0.6% ACQ</td>
<td>Unleached</td>
<td>89.8 (10.0)</td>
</tr>
<tr>
<td></td>
<td>Leached</td>
<td>79.8 (15.6)</td>
</tr>
<tr>
<td>1.2% ACQ</td>
<td>Unleashed</td>
<td>87.3 (11.3)</td>
</tr>
<tr>
<td></td>
<td>Leached</td>
<td>87.7 (10.1)</td>
</tr>
<tr>
<td>0.3% CA</td>
<td>Unleashed</td>
<td>72.0 (10.5)</td>
</tr>
<tr>
<td></td>
<td>Leached</td>
<td>53.8 (14.0)</td>
</tr>
<tr>
<td>0.6% CA</td>
<td>Unleashed</td>
<td>88.3 (7.6)</td>
</tr>
<tr>
<td></td>
<td>Leached</td>
<td>82.8 (16.4)</td>
</tr>
<tr>
<td>1.2% CA</td>
<td>Unleashed</td>
<td>97.3 (1.2)</td>
</tr>
<tr>
<td></td>
<td>Leached</td>
<td>97.0 (1.8)</td>
</tr>
</tbody>
</table>

Values in parenthesis are standard deviations.
specimens had significantly less mass loss and greater termite mortality than untreated specimens. The treatments with ACQ and CA appeared to improve the resistance of wood to termite attack. Even though the leaching process caused higher leaching rates of copper from the treated specimens, ACQ and CA treatments also increased termite mortality significantly and reduced the mass loss.

We examined the relationship between termite mortality, mass loss, and specific gravity using linear statistical analysis. According to this test, the mass loss and the termite mortality of treated specimens were inversely associated \( r = 0.5972 \). The rate of termite mortality and specific gravity were also inversely related \( r = 0.3292 \), while mass loss had a marginally positive association with specific gravity \( r = 0.2629 \).

4. Conclusions

Evaluation of leachability, metal corrosion, and termite resistance of wood treated with copper-based preservatives is becoming increasingly important in the wood preservation industry, because there has been a great deal of focus on preservative contamination of aquatic environments and corrosion of fasteners in residential applications. In this study, copper retention (before and after the leaching process) of five softwood specimens vacuum-treated with ACQ and CA at three target retention levels was investigated by X-ray fluorescence studies. The metal corrosion and termite resistance of treated specimens were studied under laboratory conditions. The results indicate that the copper retentions of treated specimens increase with an increase of preservative concentration. A high coefficient of relationship \( r = 0.9763 \) between copper retention and preservative concentration was found. Taking specimen density into consideration, there was a negative linear relationship \( r = 0.7074 \) between copper retention of treated specimens and density of the wood. For all ACQ- and CA-treated wood specimens, the copper leaching rates were 6.92–19.54% and 9.38–22.46%, respectively. Generally, the copper leaching rates of treated specimens increased with increased concentration of treated preservative.

The metal corrosion rates of the zinc-galvanized steel nails were lower than those of the iron nails for the same preservative at the same concentration. The rates of the iron nails due to corrosion were 1.65–3.11% for ACQ-treated specimens, and 1.55–2.83% for CA-treated specimens. The rates were influenced significantly by the treatments with 1.2% ACQ and 1.2% CA (metal corrosion rate > 2%). The metal corrosion rates of the zinc-galvanized nails after the corrosion tests were less than 2. The rates showed no significant difference among specimens treated with 0.3% ACQ, 0.6% ACQ, 0.3% CA, and 0.6% CA (1.17–1.22%). However, a significant difference was found between 1.2% ACQ- (or 1.2% CA-)treated specimens (1.59–1.62%) and the other specimens.

After the leaching process, treatment with ACQ and CA also increased termite mortality significantly and reduced the mass loss. However, the effects of wood treatments on human health and the environment need to be assessed by all aspects of wood preservatives. Further studies of preservative fixation and metal corrosion of copper in wood treated with copper-based preservatives should be conducted in the future with concern for human health, the environment and architectural aspects.

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