Research paper

Leachability of Commercial Ammoniacal Copper Quat and Micronized Copper Quat Used in Taiwan

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【Summary】

In order to meet the needs of the Taiwanese wood preservation industry to obtain domestic research information to verify the possible leaching property improvement of micronized copper quat (MCQ) declared by Osmose Inc., a leaching test which followed CNS 6717 "Qualitative standards and testing methods of wood preservatives" was carried out. The test was conducted using southern yellow pine (SYP, *Pinus* spp.) wood blocks with currently used commercial chromated copper arsenate (CCA), ammoniacal copper quat (ACQ), MCQ, and copper azole (CA) with various preservative retention levels.

Results indicated that among CCA-, ACQ-, and MCQ-treated SYP blocks, the average leaching percentage of MCQ-treated blocks with various retention levels was the lowest (4.94%), followed by CCA-treated blocks (5.42%, which did not statistically differ from the MCQ-treated ones), and then ACQ-treated blocks (10.19%). Components of CCA, ACQ, and MCQ did not leach in proportion to the active ingredient composition of these preservatives. The percentage of Cu compounds leached from CCA-treated SYP blocks was the highest among the 3 active ingredients in CCA, followed by Cr compounds then As compounds. The quats made up over 90% of the leachate leached from ACQ- and MCQ-treated SYP wood blocks. Dispersed micronized copper compounds in MCQ leached less (0.40%) from the treated SYP blocks than did the soluble copper compound in ACQ-treated blocks (0.69%), however, the lower leachability of the didecyl dimethyl ammonium chloride (DDAC) in MCQ (14.15%) than the N-alkyl benzyl dimethyl ammonium chloride (BKC) in ACQ (22.31%) significantly accounted for the lower leachability of MCQ compare to ACQ.

Different preservative and component leaching patterns were noted and were categorized into 3 different types by the ratios of the first leachate amount to the total leachate amount collected throughout the leaching sequence (10 times). These patterns may serve as basic data to understand the probable leachability of preservatives from treated wood in service.

When the leachability of CA was estimated by the percentage of Cu leached from treated SYP wood blocks, CA seemed to possess the lowest leaching percentage compared to the other preservatives tested.

Key words: micronized copper quat, ammoniacal copper quat, chromated copper arsenate, wood preservative, leachability.

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研究報告

台灣地區商用木材防腐劑－銅‧烷基銨與微米化銅‧烷基銨之流失性

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摘　要

微米化銅‧烷基銨(MCQ)為2007年自國外引進台灣之木材防腐藥劑，由其製造廠商及國外相關試驗結果顯示，其流失性較同系列之銅‧烷基銨(ACQ)者為低。為因應台灣市場與防腐處理材生產及進口廠商對台灣本土相關試驗結果的需求，依照中國國家標準(CNS 6717)製備5個藥劑吸收量的鉻化砷酸銅(CCA)、ACQ、MCQ及銅‧唑(CA)等四種木材防腐劑處理之南方松(SYP)木材試塊，進行藥劑流失試驗。

結果顯示，經CCA、ACQ及MCQ三種藥劑處理各吸收量之SYP試塊，其平均藥劑流失率以MCQ處理者為最低(4.94%)，CCA處理者次之(5.42%，統計上與MCQ處理者無差異)，ACQ處理者為最高(10.19%)。三種藥劑的處理試塊，皆未依其個別的藥劑有效成分組而呈比例流失。CCA處理試塊中以銅的流失率最高、鉻次之、砷最低。MCQ處理試塊中銅成分流失率(0.40%)較ACQ者(0.69%)為低，此二藥劑處理試塊中四級銨(quat)的流失率顯著的較銅高出許多，MCQ中的DDAC為14.15%，ACQ中的BKC為22.31%。DDAC相對於BKC的流失性顯著較低，應是MCQ流失性較ACQ者為低的主因。

由流失試驗中依序收集的10次流失液樣本分析，可將防腐藥劑及其組成分的經時流失情形歸納為三種類型，以作為使用環境中防腐處理材藥劑流失模式的基礎資料。

若以CA處理試塊之銅成分流失率推估其整體藥劑流失率，相較於CCA、ACQ及MCQ的流失率，CA似乎為四種藥劑中流失性最低者。

關鍵詞：微米化銅‧烷基銨、銅‧烷基銨、鉻化砷酸銅、木材防腐劑、流失性。

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INTRODUCTION

A recent restriction of chromated copper arsenate (CCA) usage in many countries has increased the use of copper-quaternary systems, especially ammoniacal copper quaternary (ACQ) for the protection of nondurable timber. However, some disadvantages with the use of nitrogen-containing solvents and chlorine in quat compounds create negative effects, i.e., mold growth and metal fastener corrosion. To improve ACQ systems, a modified formulation of a non-alkaline solvent and micronized copper compound particles is promoted by Osmose Inc. (Baffalo, NY, USA) as MicroPro$^{\text{TM}}$ (Osmose 2007, abbreviated locally in Taiwan as MCQ).

Comparing ACQ with MCQ, the major differences are: 1. instead of being dissolved in the preservative solutions as Cu compounds are in ACQ, micronized Cu compound particles (of < 1000 nm) are dispersed in preservative solutions with the aid of polymer dispersing agents; 2. chlorine is substituted in didecyl dimethyl ammonium chloride (DDAC) by carbonate; and 3. the preservative solutions are free of ammonia and/or amines (Freeman and McIntyre 2008). In soluble copper-based wood preservative systems such as chromated copper arsenate (CCA), ACQ, and copper azoles (CA), a great part of the Cu^{+2} ions are believed to be chemically "fixed" in the treated wood, whereas micronized copper particles with polymeric dispersant molecules attached to the particle surface in MCQ are physically deposited into the treated wood structure. The micronized particles are believed to "fix" to treated wood through strong adhesion between the polymeric dispersants and wood fibers with similar mechanisms as occur in wood-coating applications. The majority of Cu^{+2} ions fixed in micronized systems are believed to be a simple deposition as opposed to a reaction (Archer and Preston 2007). A study using energy dispersive x-ray analysis (EDXA) on the microdistribution of treated southern yellow pine (SYP) wood indicated that micronized copper was abundantly present in pit chambers and tertiary wall layers adjacent to the lumens of tracheids and ray parenchyma cells as separate particles (Matsunaga et al. 2007). While part of the dispersed type of copper which resembles the water-soluble type of copper was mainly in the middle lamella and secondary wall layer, it is possible that minor amounts of free Cu^{+2} ions associated with the micronized particle formulations bind to various wood components by similar mechanisms as the other soluble copper preservatives. However, most of the fixation in micronized systems is believed to be simple deposition as opposed to a reaction (Matsunaga et al. 2007, Stirling et al. 2008).

Micronized copper quat (MCQ) was imported into Taiwan in 2007 as a substitution/competitor for ACQ. Arguments as to the advantages of MCQ over ACQ and vice versa have been put forth by individual supporters. Tests were conducted to verify the purported properties. In this article, results from preservative leaching tests of commercial CCA, ACQ, and MCQ currently used in Taiwan are reported, and the leachabilities of the preservatives are compared. The Cu leaching property of commercially used copper azole (CA) preservative is also mentioned.

MATERIALS AND METHODS

Wood blocks

SYP wood blocks with dimensions of 20 × 20 × 20 mm were prepared for preservative treatment and leaching tests.

Preservatives

CCA (CNS 14495 CCA no. 3, and AWPA P5-08 CCA-C, Arch Inc., Norwalk, CT, USA), ACQ (CNS 14495 ACQ no.1, Koshii Inc., Osaka, Japan), MicroPro™. (MCQ, Osmose Inc., Baffalo, NY, USA), and CA (AWPA P5-04 CA-B, Arch Inc.) were prepared as solutions of various active ingredient concentrations for wood block treatment to treat SYP-treated wood blocks with preservative retention levels of 12.0, 9.6, 6.4, 4.0, and 2.4 kg m^{-3}. The compositions of the preservatives are shown in Table 1.

Wood block treatment and leaching test

Wood block treatment and the leaching test were performed according to CNS 6717 (Bureau of Standards, Metrology, and Inspection, 2000a). Ten blocks (as a set)

Table 1. Compositions of preservatives

Preservative	Active ingredient composition (%)						
	CrO_3	CuO	As_2O_5	Cu	BKC	DDAC	Tebuconazole
CCA	47.5	18.5	34.0	–	–	–	–
ACQ	–	56.1	–	–	43.9	–	–
MCQ	–	66.7	–	–	–	33.3	–
CA	–	–	–	96.1	–	–	3.9

BKC, N-alkyl benzyl dimethyl ammonium chloride; DDAC, didecyl dimethyl ammonium chloride; CCA, chromated copper arsenate; ACQ, ammoniacal copper quaternary; MCQ, micronized copper quaternary; CA, copper azole.

were treated with each preservative and concentration combination. After treatment, each set of wood blocks was divided into 2 subsets; leaching tests and determinations of preservative retentions before leaching were performed on the 2 subsets. Leachate solutions from the leaching test were collected according to the leaching sequence for leachate analysis.

Retention and leachate analysis

Unleached treated wood blocks were grounded up to a powder which could pass a 20-mesh sieve, and their preservative component retentions were analyzed with the following procedures.

1. Metallic components (Cr, Cu, and As)

Wet ashing procedure described in CNS 14730 (Bureau of Standards, Metrology, and Inspection, 2000b) was applied to turn the wood powder into a solution, followed by analyzing individual metallic elements with inductively coupled plasma spectrometry (ICP, Perkin Elmer ICP-OES Optima 2100 DV, Waltham, MA, USA). The metal contents of the leachate solutions were directly analyzed by ICP.

2. Quats

Extraction and titration (autotitrator, Metrohm 794, Herisau, Switzerland) following AWPA A37-08 (American Wood Protection Association, 2008a) were applied to determine the quat contents in ACQ- and MCQ-treated wood blocks. Quat contents in leachate solutions were determined by direct titration.

Data management

Wood blocks for the leaching test were of similar volumes but different weights. In order to compare test results collected from wood block sets of different treatments and to match the analysis output format of ICP (mainly in ppm), preservatives and component concentrations of the wood blocks were presented in grams of preservative active ingredient per gram of oven dried wood blocks (in units of ppm) for further processing. Leachate concentrations in the solutions were also recorded in ppm, and transformed to a ratio (in units of %) of preservative retention levels acquired from the unleached treated wood blocks.

RESULTS AND DISCUSSION

This article mainly compares the leaching properties of ACQ with those of MCQ, but we were unable to analyze the tebuconazole contained in CA-treated wood and leachate solution. The discussion focuses on ACQ, MCQ, and CCA (as a reference). The leaching properties of CA are only briefly mentioned according to the Cu data collected.

Total preservatives leached

Preservatives and their components leached from treated SYP blocks with varieous preservative retention levels of CCA, ACQ, and MCQ are summarized in Table 2. The average leaching percentages of CCA-, ACQ-, and MCQ-treated SYP blocks of various retentions showed that MCQ had the lowest preservative leaching percentage (4.94%), and ACQ had the highest (10.19%), while CCA (5.42%) was only numerically slightly higher than MCQ and statistically showed no difference, in spite of the block of 2.4 kg m^{-3} preservative retention level obviously being higher than that of MCQ ones at the same retention level.

The highest preservative leaching percentage of ACQ-treated SYP blocks may be explained by lignin depolymerization caused by ethanolamine in the copper-ethanolamine-based wood preservative system, resulting in leachable complexes of copper-ethanolamine-lignin monomers (Humar et al. 2007). Results of an AWPA standard E11 leaching test performed by Stirling et al. (2008) coincided with the results of this test, i.e., MCQ-treated SYP blocks leached less than ACQ-treated

Table 2. Preservatives and their components leached from southern yellow pine blocks of various preservative retention levels

Preservative	Preservative retention (kg m^{-3})	Preservative and component leached in relation to the original retention (%)				Reduction in retention (kg m^{-3})
		CrO_3	CuO	As_2O_5	Total	
CCA	12.0	4.07	4.87	0.44	2.98	0.371
	9.6	3.85	6.18	0.76	3.23	0.278
	6.4	5.48	8.75	1.29	4.66	0.252
	4.0	5.71	10.13	3.92	5.92	0.261
	2.4	10.09	13.87	8.66	10.31	0.233
	Avg.	**5.84**	**8.76**	**3.01**	**5.42**	**0.285**
			CuO	BKC	Total	(kg m^{-3})
ACQ	12.0		0.91	15.93	7.50	0.891
	9.6		0.61	25.12	11.37	0.650
	6.4		0.69	19.33	8.87	0.500
	4.0		0.62	22.60	10.27	0.421
	2.4		0.62	28.59	12.90	0.301
	Avg.		**0.69**	**22.31**	**10.19**	**0.553**
			CuO	DDAC	Total	(kg m^{-3})
MCQ	12.0		0.17	10.39	3.54	0.320
	9.6		0.18	12.76	4.33	0.329
	6.4		0.49	17.47	6.09	0.227
	4.0		0.45	16.57	5.77	0.189
	2.4		0.70	13.56	4.94	0.105
	Avg.		**0.40**	**14.15**	**4.94**	**0.234**

CCA, chromated copper arsenate; ACQ, ammoniacal copper quaternary; MCQ, micronized copper quaternary.

SYP blocks which may also be explained by lignin depolymerization caused by the ethanolamine in the ACQ solvent system.

The preservative leachability seemed to decrease as the preservative retention levels of the treated blocks increased for these 3 preservatives (Fig. 1). Wood blocks with higher preservative retention levels leached less than lower-retention ones in proportion to the original preservative retention before leaching. However, as shown by the preservative retention leached in Table 2, the absolute amounts (kg m^{-3}) of preservatives leached from the higher-retention blocks were as expected, i.e., higher than the lower-retention blocks.

The only exception to the above discussion was the leaching percentage of ACQ-treated SYP blocks at 9.6 kg m^{-3} retention which showed an exceptionally high leaching percentage rendered by the abruptly increased N-alkyl benzyl dimethyl ammonium chloride (BKC) leaching percentage that remains unexplainable, except perhaps an experimental error.

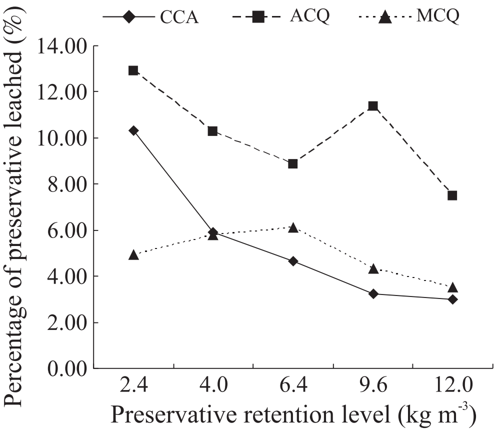

Fig. 1. Percentage of preservative leached from chromated copper arsenate (CCA), ammoniacal copper quaternary- (ACQ), and micronized copper quaternary (MCQ)-treated southern yellow pine blocks with various retention levels.

Components of the preservatives leached

It is obvious that the components of the preservatives tested did not leach equally (Table 2). The average leaching percentage of the 5 retentions revealed that CCA-treated SYP blocks leached the least As_2O_5 (3.01%) of the 3 components of CCA, while CuO leached the most (8.76%) and CrO_3 was in between (5.84%). This feature also held for blocks of all 5 retention levels individually (Fig. 2). Possible explanations of the higher leaching percentage of Cu compounds involve the fixation mechanisms of CCA components in treated wood structures. In Pizzi's works (1982a, b) on CCA fixation mechanisms, it was revealed that the reduction of Cr^{+6} to Cr^{+3} is crucial for the formation of insoluble chromium arsenate and chromium hydroxide in CCA-treated wood, while the products formed between copper and wood carboxylate are relatively more soluble.

The difference between the 2 components (CuO and Quat) in ACQ and MCQ was notable. The average percentage of leaching from quats were 22.32 and 14.15% for ACQ and MCQ, respectively, and 0.69 and 0.40% for CuO. It appears that the quats in ACQ and MCQ accounted for the major loss of these

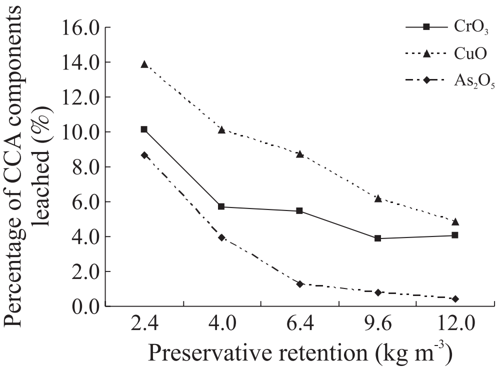

Fig. 2. Percentage of individual components leached from chromated copper arsenate (CCA)-treated southern yellow pine blocks.

2 preservatives by leaching. Generally, more of both components leached from ACQ than from MCQ (Fig. 3), which resulted in a higher preservative leaching percentage of ACQ than of MCQ. The higher percentage of the quat component (BKC, 43.9%) in ACQ than in MCQ (DDAC, 33.3%), also gave ACQ higher leachability than MCQ.

However, it is interesting to note that the leaching percentage of Cu compounds in MCQ increased as the preservative retention level of MCQ-treated SYP blocks decreased and leached more Cu compounds at a retention level of 2.4 kg m^{-3} than ACQ-treated blocks of a similar retention level, which coincides with the result of an AWPA E19 leaching test summarized by Freeman and McIntyre (2008) that MCQ-treated wood lost more copper in percentage as the retention level of preservative decreased.

Comparatively, quats (BKC and DDAC) leached exceedingly more than did CuO in ACQ and MCQ. Although not as high as the differences shown in this study, research conducted by Mississippi State University found a similar result of obviously higher leachability of quats over Cu compounds in ACQ- and MCQ-treated wood stakes (Preston et al. 2008). This may have been caused by the non-chemical bonding or lack of chelate formation in ACQ-treated wood and no adhesion particle formation in MCQ-treated wood between quats and wood components which do occur between Cu^{+2} ions and wood components.

It was also noted that a higher percentage of CuO in CCA leached (8.76%) than CuO in the other 2 preservatives (0.69 and 0.40% respectively for ACQ and MCQ), which may have been a result of the occupation of Cu^{+2} ion binding sites on the wood components by the other 2 metallic elements in CCA-treated wood (Bull 2001, Fu 2006), which did not occur in ACQ- and MCQ-treated wood. However, the actual causes remain to be revealed.

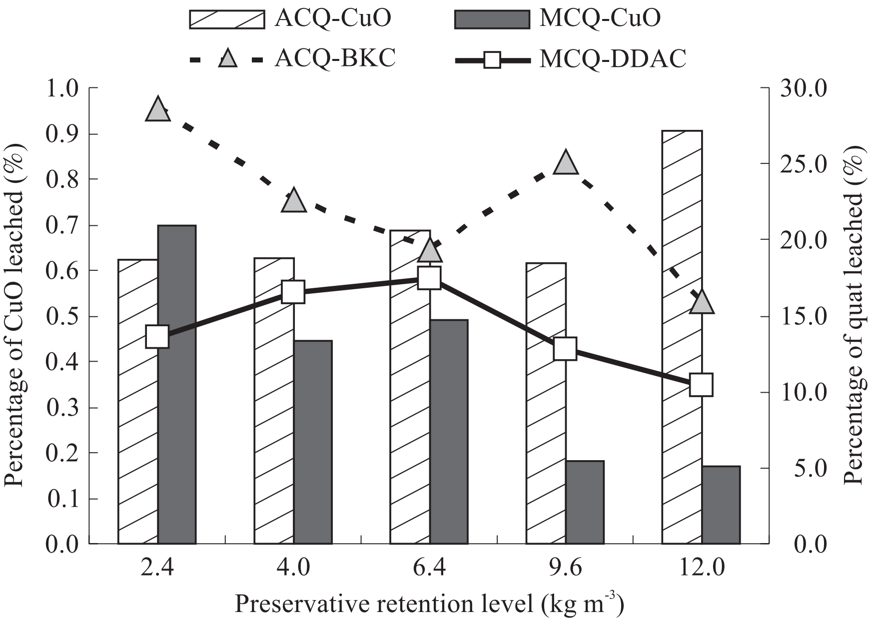

Fig. 3. Percentages of CuO and quats leached from ammoniacal copper quaternary (ACQ) and micronized copper quaternary (MCQ)-treated southern yellow pine blocks.

Leachability of preservatives and components in leaching sequence

As was expected from leachates obtained from the first few times, the first leaching sequence had obviously higher percentages than the following times in the sequence (Table 3). However, some details and the leaching tendency of individual components are worthy of comment.

Varied leaching patterns of leachate percentage in sequence were observed. The major differences among these patterns were indicated by differences between the amount of the first leachate and those of the following times. These leaching patterns were also noted from the percentage of the amount of the first leachate to the total amount leached as shown in Table 4, and decreasing patterns were sharp (> 40%), moderate (20~40%), and slight (< 20%).

Table 3. Percentages (%) of components and preservative leached from chromated copper arsenate- (CCA), alkaline copper quaternary- (ACQ), and micronized copper quaternary (MCQ)-treated southern yellow pine blocks in leaching sequence with different preservative retention level

Preservative retention: 12.0 kg m^{-3}

Type	CCA				ACQ			MCQ		
Seq.	CrO_3	CuO	As_2O_5	Total	CuO	BKC	Total	CuO	DDAC	Total
1	2.223	0.753	0.279	1.290	0.719	7.484	3.689	0.048	3.939	1.332
2	0.439	0.534	0.094	0.339	0.142	2.308	1.093	0.025	1.188	0.409
3	0.250	0.492	0.036	0.222	0.004	1.513	0.666	0.018	1.016	0.347
4	0.203	0.489	0.033	0.198	0.004	1.151	0.508	0.011	0.782	0.265
5	0.177	0.459	0.002	0.170	0.004	0.833	0.368	0.012	0.274	0.098
6	0.162	0.422	0	0.155	0.004	0.636	0.281	0.013	0.700	0.240
7	0.160	0.460	0	0.161	0.004	0.556	0.246	0.011	0.621	0.212
8	0.157	0.451	0	0.158	0.004	0.535	0.237	0.011	0.645	0.220
9	0.148	0.399	0	0.144	0.011	0.450	0.204	0.014	0.578	0.200
10	0.148	0.409	0	0.146	0.014	0.463	0.211	0.008	0.645	0.218
Sum.	**4.067**	**4.868**	**0.444**	**2.983**	**0.910**	**15.929**	**7.503**	**0.171**	**10.388**	**3.543**

Preservative retention: 9.6 kg m^{-3}

Type	CCA				ACQ			MCQ		
Seq.	CrO_3	CuO	As_2O_5	Total	CuO	BKC	Total	CuO	DDAC	Total
1	1.405	0.800	0.555	1.004	0.362	11.376	5.197	0.062	3.757	1.281
2	0.347	0.682	0.163	0.346	0.083	3.845	1.735	0.027	1.852	0.629
3	0.285	0.639	0.026	0.262	0.044	2.441	1.096	0.018	1.251	0.425
4	0.269	0.617	0.013	0.246	0.030	1.807	0.810	0.011	0.860	0.291
5	0.267	0.629	0	0.243	0.023	1.233	0.554	0.013	1.021	0.346
6	0.261	0.596	0	0.234	0.015	0.940	0.421	0.014	0.943	0.321
7	0.261	0.590	0	0.233	0.017	0.922	0.414	0.006	0.752	0.252
8	0.252	0.545	0	0.221	0.015	0.867	0.389	0.011	0.821	0.278
9	0.249	0.524	0	0.215	0.012	0.867	0.387	0.01	0.733	0.249
10	0.252	0.56	0	0.223	0.013	0.824	0.369	0.01	0.772	0.261
Sum.	**3.848**	**6.182**	**0.757**	**3.229**	**0.614**	**25.122**	**11.373**	**0.182**	**12.762**	**4.333**

(con't)

Preservative retention: 6.4 kg m^{-3}

Type	CCA				ACQ			MCQ		
Seq.	CrO_3	CuO	As_2O_5	Total	CuO	BKC	Total	CuO	DDAC	Total
1	1.472	1.034	0.946	1.212	0.391	8.501	3.951	0.168	5.063	1.783
2	0.518	0.911	0.238	0.496	0.088	3.157	1.435	0.077	2.093	0.742
3	0.459	0.885	0.058	0.401	0.050	2.041	0.924	0.043	1.535	0.535
4	0.451	0.901	0.052	0.399	0.036	1.127	0.515	0.035	1.596	0.550
5	0.435	0.833	0	0.361	0.027	1.032	0.468	0.031	1.527	0.525
6	0.425	0.809	0	0.352	0.022	0.846	0.384	0.033	1.283	0.446
7	0.436	0.885	0	0.371	0.022	0.750	0.342	0.025	1.176	0.405
8	0.431	0.852	0	0.362	0.019	0.676	0.307	0.027	1.146	0.396
9	0.421	0.799	0	0.348	0.015	0.592	0.268	0.026	1.138	0.393
10	0.427	0.844	0	0.359	0.018	0.609	0.277	0.023	0.909	0.315
Sum.	**5.475**	**8.753**	**1.294**	**4.660**	**0.688**	**19.331**	**8.872**	**0.488**	**17.466**	**6.091**

Preservative retention: 4.0 kg m^{-3}

Type	CCA				ACQ			MCQ		
Seq.	CrO_3	CuO	As_2O_5	Total	CuO	BKC	Total	CuO	DDAC	Total
1	1.225	1.455	2.383	1.661	0.35	9.259	4.261	0.127	4.528	1.579
2	0.606	1.107	0.725	0.739	0.083	3.593	1.624	0.059	2.242	0.779
3	0.546	1.078	0.456	0.614	0.048	1.841	0.835	0.045	1.745	0.606
4	0.493	0.941	0.238	0.489	0.016	1.491	0.664	0.025	1.300	0.446
5	0.498	1.003	0.122	0.464	0.029	1.491	0.671	0.038	1.396	0.486
6	0.477	0.930	0	0.399	0.023	1.223	0.550	0.030	1.091	0.380
7	0.476	0.924	0	0.397	0.023	1.118	0.504	0.026	1.099	0.380
8	0.477	0.953	0	0.403	0.020	0.954	0.430	0.036	1.056	0.373
9	0.449	0.855	0	0.371	0.016	0.835	0.376	0.025	1.099	0.379
10	0.461	0.881	0	0.382	0.018	0.798	0.360	0.036	1.012	0.358
Sum.	**5.708**	**10.127**	**3.924**	**5.919**	**0.626**	**22.603**	**10.274**	**0.447**	**16.568**	**5.767**

Preservative retention: 2.4 kg m^{-3}

Type	CCA				ACQ			MCQ		
Seq.	CrO_3	CuO	As_2O_5	Total	CuO	BKC	Total	CuO	DDAC	Total
1	1.967	1.681	6.329	3.397	0.298	12.013	5.441	0.191	1.222	0.531
2	1.031	1.403	1.452	1.243	0.065	3.553	1.596	0.091	2.059	0.740
3	0.958	1.371	0.699	0.946	0.065	2.175	0.991	0.057	1.428	0.509
4	0.918	1.354	0.182	0.748	0.035	2.030	0.911	0.039	1.364	0.476
5	0.896	1.358	0	0.677	0.031	2.320	1.036	0.048	1.312	0.465
6	0.870	1.342	0	0.662	0.027	1.595	0.715	0.066	1.377	0.499
7	0.882	1.336	0	0.666	0.027	1.789	0.801	0.065	1.222	0.447
8	0.870	1.350	0	0.663	0.024	0.918	0.416	0.048	1.287	0.457
9	0.842	1.341	0	0.648	0.023	0.906	0.411	0.042	1.287	0.453
10	0.860	1.334	0	0.655	0.029	1.293	0.584	0.052	1.004	0.366
Sum.	**10.094**	**13.870**	**8.662**	**10.306**	**0.624**	**28.592**	**12.902**	**0.699**	**13.562**	**4.944**

1. CCA

Leaching patterns of CCA and its individual components of CCA-treated SYP blocks are shown in Fig. 4. On average, CCA and CrO_3 had moderately decreasing patterns with As_2O_5 showing a sharp decrease and CuO a slight decrease. From the figure, it is clear that a lot of As_2O_5 leached the first few times and ceased leaching after the 5th time of the leaching sequence. CuO leached steadily during the test, and the percentage of CrO_3 leached gradually dropped over the

Table 4. Ratio (%) of the first leachate amount to the total leachate amount obtained from the leaching sequence (10 times) of treated southern yellow pine blocks with various preservative retention levels

Retention	CCA				ACQ			MCQ		
(kg m^{-3})	CrO_3	CuO	As_2O_5	Total	CuO	BKC	Total	CuO	DDAC	Total
12.0	54.66^{a}	15.47^{c}	62.99^{a}	43.24^{a}	79.01^{a}	46.98^{a}	49.16^{a}	28.07^{b}	37.92^{b}	37.60^{b}
9.6	36.51^{b}	12.94^{c}	73.23^{a}	31.10^{b}	58.96^{a}	45.28^{a}	45.70^{a}	34.07^{b}	29.44^{b}	29.57^{b}
6.4	26.89^{b}	11.81^{c}	73.11^{a}	26.01^{b}	56.83^{a}	43.98^{a}	44.54^{a}	34.43^{b}	28.99^{b}	29.28^{b}
4.0	21.46^{b}	14.37^{c}	60.75^{a}	28.07^{b}	55.91^{a}	40.96^{a}	41.47^{a}	28.41^{b}	27.33^{b}	27.39^{b}
2.4	19.49^{c}	12.12^{c}	73.07^{a}	32.96^{b}	47.76^{a}	42.02^{a}	42.17^{a}	27.32^{b}	9.01^{c}	10.75^{c}
Avg.	31.80^{b}	13.34^{c}	68.61^{a}	32.28^{b}	59.69^{a}	43.84^{a}	44.61^{a}	30.46^{b}	26.54^{b}	26.92^{b}

The superscripts a, b, and c refer to the leaching patterns; a, great difference; b, moderate difference; c, lower difference leaching pattern. CCA, chromated copper arsenate; ACQ, ammoniacal copper quaternary; MCQ, micronized copper quaternary.

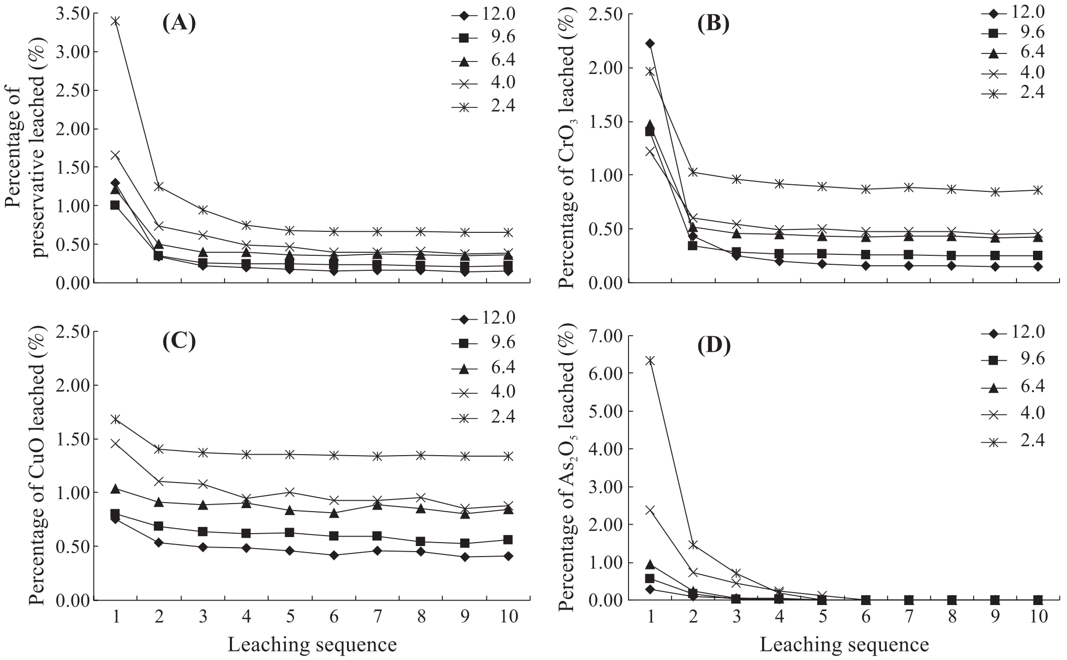

Fig. 4. Leaching patterns of chromated copper arsenate (CCA) and its individual components obtained from CCA-treated southern yellow pine blocks. (A) CCA, (B) CrO_3, (C) CuO, (D) As_2O_5.

first 5 times then became steady in subsequent times. Comparing the leaching patterns of CCA components obtained from CCA-treated blocks with various preservative retention levels, it appears that CuO continued to slightly decrease and As_2O_5 maintained a sharply decreasing leaching pattern regardless of the retention level of the block, while CrO_3 shifted from a sharply to a slightly decreasing leaching pattern as the retention level of the blocks decreased from 12.0 to 2.4 kg m^{-3}.

2. ACQ and MCQ

Leaching patterns of the preservatives and their individual components of ACQ- and MCQ-treated SYP blocks are shown in Fig. 5. The figure shows that both Cu compounds and BKC in ACQ-treated blocks had a sharply

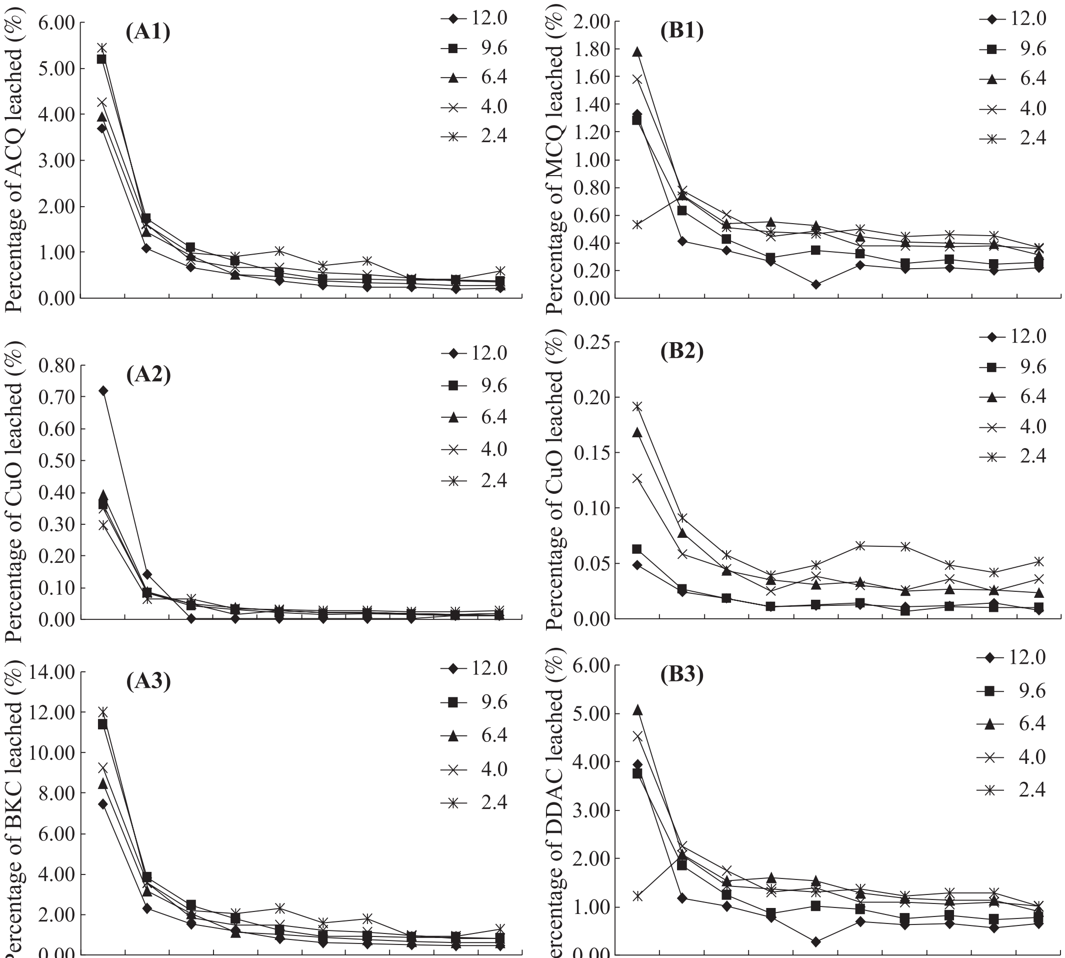

Fig. 5. Leaching patterns of preservatives and their individual components obtained from ammoniacal copper quaternary (ACQ) and micronized copper quaternary (MCQ)-treated southern yellow pine blocks. (A1) ACQ, (A2) CuO in ACQ, (A3) N-alkyl benzyl dimethyl ammonium chloride (BKC) in ACQ, (B1) MCQ, (B2) CuO in MCQ, (B3) didecyl dimethyl ammonium chloride (DDAC) in MCQ.

Table 5. Percentage of amounts of total and first copper leached from copper azole (CA)-treated southern yellow pine blocks in the leaching sequence

Cu leached (%)	Preservative retention level (kg m^{-3})					Avg.
	12.0	9.6	6.4	4.0	2.4	
Total	0.810	1.103	0.561	0.755	0.637	0.773
1st time[1)]	0.506 (62.47)	0.763 (69.17)	0.315 (56.15)	0.447 (59.21)	0.356 (55.89)	0.477 (61.74)

[1)] Percentage of the first time Cu leachate amount to the total Cu leached.

decreasing leaching pattern despite the preservative retention of the blocks, which gave ACQ, as a total of its 2 components, a similar leaching pattern. MCQ and its components in blocks with various preservative retention levels mostly had moderately decreasing leaching patterns, except for those with 2.4 kg m^{-3} retention levels from which a slightly decreasing leaching pattern was observed for MCQ and the DDAC, one of its components.

Leachability of CA

Since tebuconazole makes up only 3.1% of the CA treating solution, the percentage of total copper leached from CA-treated SYP blocks was between 0.561 and 1.103% (Table 5). Even if all of the tebuconazole had leached out, CA-treated SYP blocks would still possess the lowest preservative leaching percentage (a maximum of approximately 4.203%) compared to blocks treated with the other 3 test chemicals.

CA-treated SYP blocks with various preservative retention levels leached more than 55% of the total copper the first time of the leaching sequence (Table 5), which caused the leaching pattern of copper in CA to greatly vary (Fig. 6) and differ from the leaching patterns of the other Cu components of the other 3 preservatives.

The total percentage of Cu compounds leached from SYP blocks treated with ACQ, MCQ, and CA (Cu/organic compound-type preservatives) were 0.69, 0.40, and 0.77%, respectively. This indicates that with a different fixation mechanism from ethanolamine and/or ammonium solvent-type preservatives, micronized Cu compounds in MCQ seemed to fix better than did the other 2 preservatives in the SYP blocks.

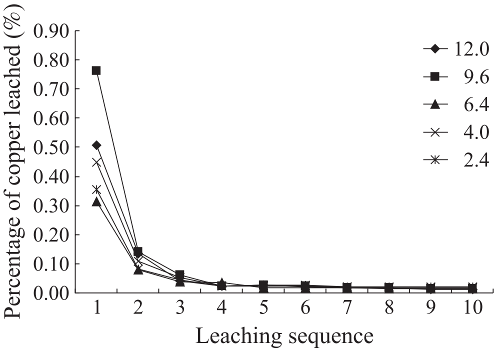

Fig. 6. Leaching patterns of copper obtained from copper azole (CA)-treated southern yellow pine blocks.

CONCLUSIONS

Among CCA, ACQ, and MCQ, MCQ leached the least (4.94%) from the treated SYP wood blocks tested, followed by CCA (5.42%, with no statistical difference with MCQ) then ACQ (10.19%). The components of CCA, ACQ, and MCQ did not leach in proportion to the active ingredient compositions of these preservatives. The percentage of Cu compounds leached from CCA-treated SYP blocks was the highest among the 3 active ingredients in CCA, followed by Cr compounds and As compounds.

The quats made up over 90% of the leachate derived from ACQ- and MCQ-treated SYP blocks. The lower leachability of DDAC in MCQ than BKC in ACQ significantly accounted for the better fixation property of MCQ over ACQ.

Different preservative and component leaching patterns were noted and were categorized into 3 different types by the ratios of the 1st leachate amount to the total leachate amount collected throughout the leaching sequence. These patterns can serve as basic data for understanding the probable leachability of preservatives from treated wood in service.

When the leachability of CA was estimated by the copper leached from treated SYP blocks, CA seemed to possess the lowest leaching percentage compared to the other 3 preservatives tested.

LITERATURE CITED

American Wood Protection Association. 2008a. Standard for determination of quaternary ammonium compounds in wood by and wood treating solutions by potentiometric titration using sodium tetraphenylborate (A37-08). In: 2008 AWPA Book of Standards. Birmingham (AL): American Wood Protection Association. 5 p.

American Wood Protection Association. 2008b. Standard for waterborne preservatives (P5-08). In: 2008 AWPA Book of Standards. Birmingham (AL): American Wood Protection Association. 6 p.

Archer KJ, Preston AF. 2007. An overview of copper-based wood preservative systems. In: Barnes HM, editor. Wood protection 2006. Proceedings of the symposium at 2006 wood preservation conference of the Forest Products Society; 2006 Mar 21-23; New Orleans (LO): Forest Products Soc. p 287-8.

Bull DC. 2001. The chemistry of chromated copper arsenate II. Preservative-wood interactions. Wood Sci Tech 34(6):459-66.

Bureau of Standards, Metrology, and Inspection. 2000a. Qualitative standards and testing methods of wood preservatives. Chinese National Standard, CNS 6717. Taipei, Taiwan. 22 p. [in Chinese].

Bureau of Standards, Metrology, and Inspection. 2000b. Wood preservatives. CNS 14495. Taipei, Taiwan. 56 p. [in Chinese].

Bureau of Standards, Metrology, and Inspection. 2000c. Method of test for absorption of wood preservatives. Chinese National Standard, CNS 14730. Taipei, Taiwan. 12 p. [in Chinese].

Freeman MH, McIntyre CR. 2008. A comprehensive review of copper-based wood preservatives with a focus on new micronized or dispersed copper systems. For Prod J 58(11):6-27.

Fu Q. 2006. Studies on the pyrolysis of chromated copper arsenate-treated wood: analytical methodology and optimization [dissertation]. Raleigh (NC): North Carolina State University. 123 p. Available from: http://www.lib.ncsu.edu/theses/available/etd- 12152006-062858/unrestricted/etd.pdf.

Humar M, Bucar B, Zupancic M, Zlindra D, Pohleven F. 2007. Influence of ethanolamine on lignin depolymerization and copper leaching treated Norway spruce and beech wood. IRG/WP/07-30423. Stockholm: International Research Group on Wood Preservation, IRG Secretariat. 11 p.

Matsunaga H, Kiguchi M, Evans P. 2007. Micro-distribution of metals in wood treated with a nano-copper wood preservative. IRG/WP/07-40360. Stockholm: International Research Group on Wood Preservation, IRG Secretariat. 10 p.

Osmose Inc. 2007. Micronised copper revolutionises the way the industry treats timber. Micro Pro article for China. Griffin (GA):

Osmose Inc. 8 p.

Pizzi A. 1982a. The chemistry and kinetic behavior of Cu-Cr-As/B wood preservatives. IV. Fixation of CCA to wood. J Polym Sci Polym Chem Ed 20:739-64.

Pizzi A. 1982b. The chemistry and kinetic behavior of Cu-Cr-As/B wood preservatives III. Fixation of the Cu/Cr system on wood. J Polym Sci Polym Chem Ed 20:725-38.

Preston A, Jin L, Nicholas D, Zahora A, Walcheski P, Archer K, Schultz T. 2008. Field stake tests with copper-based preservatives. IRG/WP/08-30459. Stockholm: International Research Group on Wood Preservation, IRG Secretariat. 15 p.

Stirling R, Drummond J, Zhang J, Ziobro R. 2008. Microdistribution of micronized copper in southern pine. IRG/WP/08-30479. Stockholm: International Research Group on Wood Preservation, IRG Secretariat. 16 p.