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Copper leached from Micronized Copper Quaternary (MCQ) Treated Wood: Influence of the Amount of Copper in the Formulations

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Abstract

The objectives of this study was to evaluate the influence of the amount of copper uptake in the amount of copper leached from Micronized copper quat treated wood at target retention of 3.60 kg/m3. Red pine (*pinusresinosa*) and southern pine were used as softwood reference species. Leaching protocol described in AWPA standard E11 was used. The amount of copper leached from treated wood was proportional to the amount of copper uptake during the treatment in good agreement with data published in the literature for ACQ and MCQ.

The percentage of Cu leached increases with the increase of quatin the formulation suggesting competed reactions between copper and quat for the available interactions sites in wood. This competition between copper and quat made the ratio of CuO to quat in the preservative formulation an important factor to be investigated on the long term efficacy of MCQ treated wood. No considerable difference was observed for red or southern pine.

Key word: ratio of CuO to DDAC, leaching, competition, wood preservative

Introduction

Alkaline copper quat (ACQ) and micronized copper quat (MCQ) are emerging commercial copper based wood preservatives used to replace arsenic and chromium containing formulations to protect wood used for residential and commercial applications where decay and insects are known to be a considerable menace. This emerging formulation contains two major ingredients known to be effective against decay and insects destroying wood for centuries: copper and quaternary ammonium salt. One of the major obstacles of copper based formulations used to treated wood has been the bioavailability of copper versus the migration in the surrounding environment that may create issues on the prediction of their long term efficacy. To alleviate the problem, micronized basic copper carbonate with low water solubility and reduced migration has been proposed in the formulations of copper based preservatives formulations (Zhang and Leach, 2005). However, limited information is available on the migration of the ingredients from treated wood to the surrounding environment, mostly the influence of the amount of quat on the migration/fixation of copper from micronized copper quat treated wood.

It has been proposed andassumed that positively charged copper ions or copper complexes chemically or/and physically interact with the negatively charged phenolate/carboxylate groups of lignin/hemicellulose/cellulose/extractives present in wood to limit the migration of copper in copper preservatives treated wood (Rennie et al. 1987; Cooper 1991; Thomason and Pasek 1997; Kamdem et al. 2001; Ruddicket al. 2001; Cooper and Lee, 2010). The interaction of other positively charges moieties in the formulations such as quaternary ammonium, monoethanolamine (MEA)werereported for the ACQ soluble copper based preservative system by several authors (Tascioglu et al. 2005; Lee and Cooper 2011;Pankras and Cooper 2012).They suggest the existence of competition between copper and other positively charged moieties for the negatively interaction sites in wood.Data for solid copper particulate with low water solubility but dispersed in water formulations containing quat and dispersant are not available in the open literature.

Understanding the interaction of copper and quaternary ammonium salt and wood substrate is useful to predict the long term efficacy of this type of wood preservatives. The objective of this study was to evaluate the amount of copper leached from red pine and southern pine wood treated with formulations of MCQcontaining various proportion of copper oxide toquat using AWPA protocol (AWPA 2009).

Material And Methods

Micronized copper and quaternary salts were obtained graciously from Osmose INC and used as received without further analysis in our formulations. A series of formulations were made using the CuO to quat following ratios: 3:1, 2:1, 1:1, 1:2, and 1:3. A 1% formulation was made afterwards by adding water.

Defect free kiln dried sapwood of red pine and southern pine were selected and used to 19mm cubes with no visible defect. They were placed in a chamber conditioned at 20 °C and 70% to a constant weight before further testing. Conditioned blocks were selected based on similar density and used for treatments following AWPA E11 (2009).

Copper content in the treating solutions, leachates and treated wood were analyzed by atomic absorption spectroscopy (AAS) following standard protocol listed in AWPA A 11-93 (2007).

Results And Discussion

Tables 1 and 2 listed the copper oxide content in MCQ treating solutions used and the total copper in mg leached from 6 cubes after the leaching periods (2 weeks) for SP and RP, respectively. The copper contents in treating solutions for RP and SP vary from 0.85 to 0.26%, and almost similar for each target concentrations levels.

The total amount of copper leached from treated SYP and RP samples increased with the increase of ratio of CuO toquat in the MCQ formulation. This indicated that more copper leached from high copper retention in good agreement with previous studies on alkali water soluble copper based wood preservatives (Lebow et al 2006). The total amount of copper leached from MCQ treated wood vary with initial copper uptake for wood treated with formulation in the range of CuO to quat ratio used in this study.

Table 3 contains the total copper and the percentage of copper leached from MCQ treated wood at various CuO to quat ratios. This clearly shows that less copper is leached from MCQ treated wood in comparison of alkali water soluble systems published in the literature. A maximum of less than 10% level was observed for the worst case scenario for both species treated with MCQ.At CuO to quat ratio of 2:1, about 4% copper was leached from MCQ treated wood. The Ratio of 2:1 is the ratio commercially used for treatment.

The percentage of copper leached increased with the decrease of ratio of CuO to quat in the preservative formulation. Even though less copper amount contained in the lower ratio of CuO to quat preservative formulation, high percentage of copper leached from the treated both SYP and RP. This strongly suggested that quat competed with the limited available sites in wood with copper. In formulation with low ratio of CuO to quat preservative formulation, more quat is present in the formulation and can compete with copper resulting in less copper interacting with the available sites in wood to form a less mobile/leachable copper.

The pH values of the leachate measured vary from 5.6 to 6.0. Even though the 1% MCQ treating solution used to treat wood was alkaline and ranged from 8.9 to 9.7, the leachate was not influenced that much. The pH values of leaching at less than 6 confirm that leaching was conducted in an acidic environment.The different ratio of CuO to quat used did not influence the pH of leachate too much; therefore pH did not play a major role on the leaching of copper. Low value of copper migration from MCQ treated wood observed here in comparison of water soluble copper based wood preservatives formulations was attributed to the low water solubility of copper used in the formulations of MCQ in good agreement with the previous researches (Cooper and Ung 2009; Wang and Kamdem 2011).

Conclusion

Higher value of copper were leached from RP and SP wood treated with 1% MCQ preservative formulation containing higher levels of CuO and low levels of Quat. However, the value of the percentage of copper leached calculated as the amount of copper leached divided by total copper retention was lower for formulation containing high levels of copper/low quat.

This result strongly suggested that quat competes with copper for the same limited available sites in wood during the treatment. At concentration of MCQ 1%, copper had low leaching resistance when MCQ contained copper less than quat.

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Table 1 CuO concentration in MCQ treating solution

	MCQ for SP	MCQ for RP
Target CuO concentration (%)	AAS analyzed CuO concentration (%)	AAS analyzed CuO concentration (%)
0.75%	0.85%	0.80%
0.66%	0.70%	0.71%
0.50%	0.51%	0.53%
0.33%	0.35%	0.34%
0.25%	0.26%	0.26%

Table 2 Total Cu amount leached out from six 19 mm treated cubes (mg)

Ratio CuO:Quat	SP	RP
3:1	3.27	3.69
2:1	3.15	3.96
1:1	3.09	3.69
1:2	2.74	3.17
1:3	2.34	2.65

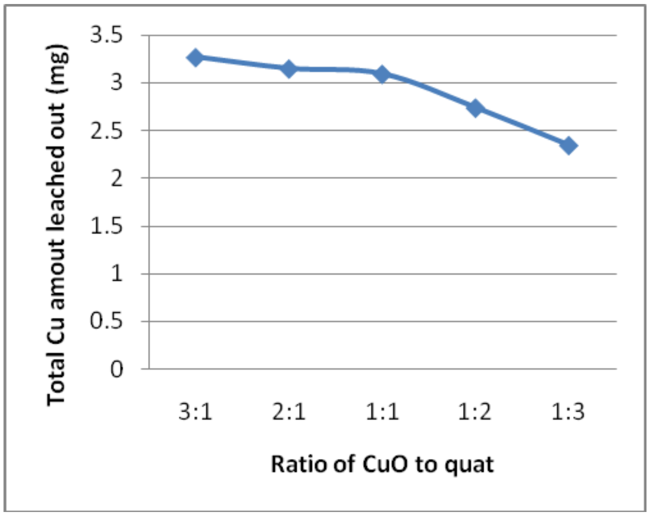

Figure 1 Total Cu amount leached out from treated SP VS ratio of CuO to quat

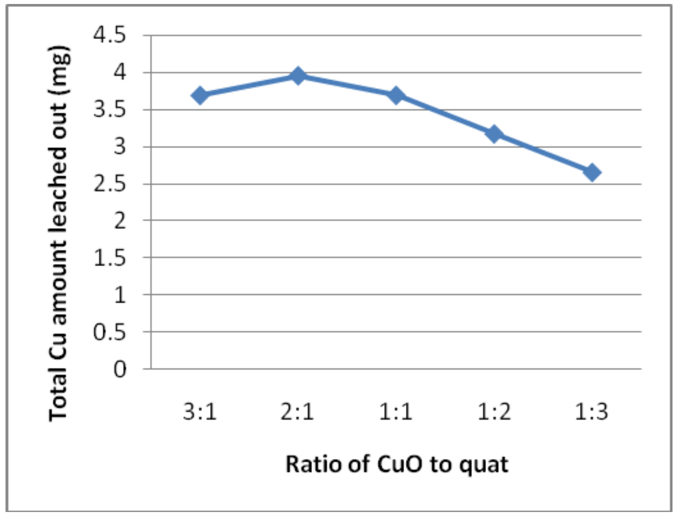

Figure 2 Total Cu amount leached out from treated RP VS ratio of CuO to quat

Table 3Percentage of Cu leached out VS ratio of CuO to quat

SP			
Ratio of CuO to quat	Total Cu amount leached out(mg)	Initial Cu amount (mg)	Percentage of Cu leached out (%)
3:1	3.27	84.96	3.85%
2:1	3.15	81.70	3.85%
1:1	3.09	61.15	5.06%
1:2	2.74	35.87	7.63%
1:3	2.34	26.28	8.91%
RP			
Ratio of CuO to quat	Total Cu amount leached out (mg)	Initial Cu amount (mg)	Percentage of Cu leached out (%)
3:1	3.69	88.82	4.16%
2:1	3.96	78.87	5.02%
1:1	3.69	60.44	6.11%
1:2	3.17	37.29	8.51%
1:3	2.65	29.05	9.13%

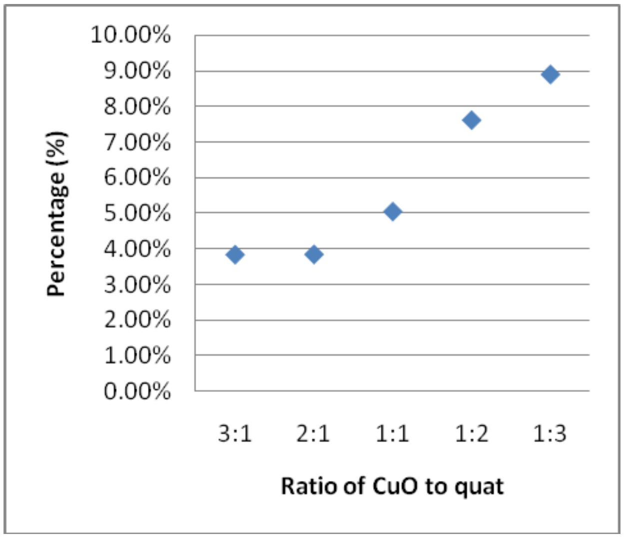

Figure 3 Percentage of Cu leached out from treated SP

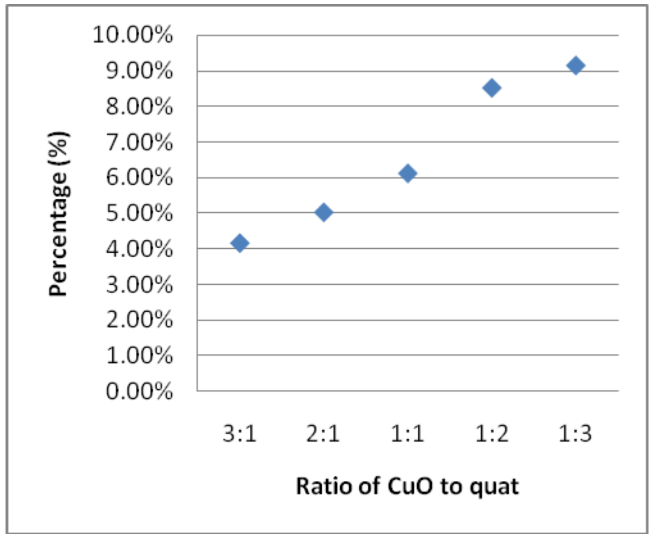

Figure 4 Percentage of Cu leached out from treated RP

Table 4 pH of treating solution

Ratio of CuO to quat	pH of solution for treating SP	pHof solution for treating RP
3:1	9.51	9.53
2:1	9.56	8.87
1:1	9.43	9.71
1:2	9.34	9.45
1:3	9.40	9.49

Table 5 pH of leachate during two weeks leaching process

SP	
Ratio of CuO to	Duration (hour)

quat											
	0 hour	6 hrs	24 hrs	48 hrs	72 hrs	96 hrs	144 hrs	192 hrs	240 hrs	288 hrs	336 hrs
3:1	5.62	5.96	5.98	5.84	5.84	5.93	5.9	5.83	5.97	5.73	5.79
2:1	5.72	5.8	6.00	5.91	6.04	5.91	5.81	5.92	5.93	5.74	5.87
1:1	5.75	5.81	5.97	5.90	5.87	5.96	5.92	5.85	5.86	5.79	5.75
1:2	5.71	5.73	5.9	5.87	5.81	5.84	5.79	5.86	5.77	5.73	5.69
1:3	5.64	5.67	5.87	5.85	5.73	5.8	5.76	5.86	5.74	5.74	5.7
RP											
Ratio of CuO to quat	Duration (hour)										
	0 hour	6 hrs	24 hrs	48 hrs	72 hrs	96 hrs	144 hrs	192 hrs	240 hrs	288 hrs	336 hrs
3:1	5.67	5.73	5.87	5.85	5.82	5.79	5.9	5.79	5.77	5.67	5.77
2:1	5.63	5.68	5.88	5.86	5.85	5.78	5.83	5.72	5.75	5.65	5.72
1:1	5.58	5.63	5.77	5.82	5.84	5.73	5.69	5.63	5.77	5.60	5.67
1:2	5.60	5.76	5.9	5.72	5.78	5.68	5.74	5.65	5.74	5.63	5.6
1:3	5.59	5.63	5.76	5.76	5.8	5.64	5.61	5.57	5.78	5.58	5.64

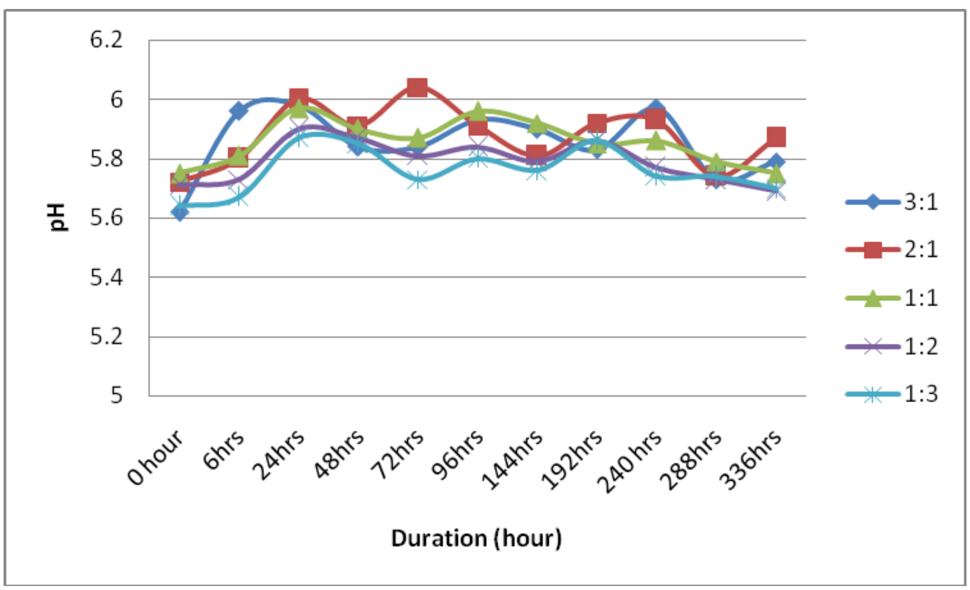

Figure 5 pH of leachate from SP

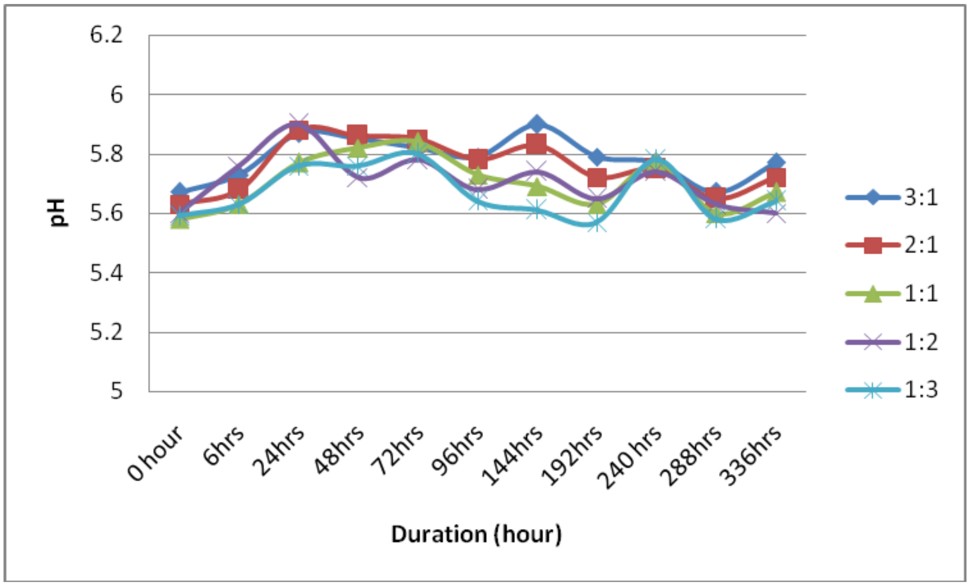

Figure 6 pH of leachate from RP