Trials on the Efficacy of Micronized Copper in Australia

L. J. Cookson
J. W. Creffield
K. J. McCarthy
D. K. Scown

Abstract

Alkaline copper quat (ACQ) is an established wood preservative that is formulated with solubilized copper in amine solvent. This article describes three separate trials in Australia that investigated whether substituting soluble copper with micronized copper affects performance. ACQ and micronized copper quat (MCQ) performed similarly in *Pinus radiata* against four brown-rot fungi in a soil-block bioassay, while MCQ performed slightly better against two white-rot fungi in *Eucalyptus delegatensis*. A 2.3-year in-ground stake trial in the wet tropics at Innisfail also found that ACQ and MCQ performed comparably in *P. radiata* and *Corymbia maculata*. This was a severe test site with attack caused by soft-rot fungi, white-rot fungi, and termites. An H3 (outside, aboveground) field test against termites in Darwin showed that ACQ- or MCQ-treated *P. radiata* and *C. maculata* performed similarly against *Coptotermes acinaciformis* and *Mastotermes darwiniensis*. These trials demonstrated that MCQ performs comparably to ACQ under the test conditions used.

Amine-solubilized copper-based wood preservatives such as alkaline copper quat (ACQ) and copper azole are commonly used as alternatives to chromated copper arsenate (CCA). The retentions approved for these preservatives in Australian Standard 1604.1 (Standards Australia 2005) are based upon trials that generally show equivalent performance to CCA at the specified retentions (Creffield et al. 1996, Drysdale et al. 1996, Zahora 2002, Lenz et al. 2003). Owing to the higher proportion of mobile copper in their formulation, these amine-solubilized copper-based preservatives can cause increased corrosion of metal (Kear et al. 2008, Zelinka et al. 2008) and suffer increased copper leaching (Temiz et al. 2006, Dubey et al. 2007) when compared with CCA. Micronized copper has been developed in an effort to minimize these characteristics by introducing copper to wood in a relatively insoluble particulate form rather than as solubilized copper (Freeman and McIntyre 2008, Cooper and Ung 2009, Kartal et al. 2009). These inventions have seen the wood preservation industry in North America becoming one of the largest users of microtechnology/nanotechnology for copper (Evans et al. 2008), with the main formulations being micronized copper quat (MCQ) and more recently micronized copper azole (MCA).

A potential concern with micronized copper is that there may be reduced copper penetration into wood and reduced bioavailability for the control of decay fungi and termites (Jin et al. 2008, Preston et al. 2008). Penetration into the cell wall is especially important for the control of soft-rot fungi (Levy and Greaves 1978). Scanning electron microscopy in combination with X-ray microanalysis has been used to examine copper in the cell wall of MCQ-treated wood. Matsunaga et al. (2007) found that copper was present in the cell wall (middle lamella and secondary wall) of MCQ-treated pine. Larger sized deposits of particulate copper (10 to 700 nm) were present in the lumens and pit chambers of MCQ-treated wood, a feature not seen in ACQ-treated wood (Matsunaga et al. 2007). Stirling et al. (2008) found particulate copper in the lumens of both ACQ- and MCQ-treated wood, although larger particles were more obvious in MCQ-treated wood. Furthermore, Stirling et al. (2008) detected copper in the cell wall of both ACQ- and MCQ-treated wood.

In Australia, new wood preservatives should be evaluated according to the protocols of the Australasian Wood Preservation Committee (AWPC 2007). New actives for preservatives require laboratory evaluation and often

The authors are, respectively, Team Leader, Research Scientist, Experimental Scientist, and Experimental Scientist, CSIRO Materials Sci. and Engineering, Private Bag 10, Clayton South, Victoria 3169, Australia (Laurie.Cookson@csiro.au, Jim.Creffield@csiro.au, Kevin.McCarthy@csiro.au, Damian.Scown@csiro.au). This paper was received for publication in September 2009. Article no. 10682.
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Table 1.—Percent mean mass losses of P. radiata *specimens exposed to brown-rotting decay fungi for 12 weeks.*[a]

Treatment and nominal retention (% m/m OD)	Analyzed retention, TAE % m/m OD (oxide basis, kg/m^3)	Mean (SEM) mass loss (%)			
		C. olivacea	*F. lilacinogilva*	*G. abietinum*	*S. lacrymans*
Water	0.0	37.5 (6.4)	62.1 (2.7)	54.6 (2.5)	47.5 (6.0)
CCA (0.14)	0.23 (1.86)	10.1 (0.7)	26.1 (5.8)	0.1 (0.2)	29.6 (1.8)
CCA (0.28)	0.24 (1.94)	3.4 (1.1)	4.1 (3.5)	0.2 (0.1)	7.5 (1.6)
CCA (0.466)	0.37 (3.00)	2.2 (0.7)	2.2 (0.7)	0.0 (0.1)	1.0 (0.4)
CCA (0.745)	0.60 (4.86)	1.5 (0.3)	0.1 (0.2)	0.1 (0.2)	1.1 (0.8)
ACQ (0.226)	0.27 (1.55)	35.9 (3.1)	34.0 (3.2)	0.6 (0.3)	25.7 (3.6)
ACQ (0.45)	0.41 (2.36)	23.5 (5.2)	1.6 (0.7)	0.0 (0.1)	9.1 (2.3)
ACQ (0.75)	0.79 (4.54)	1.9 (1.3)	0.0 (0.2)	0.1 (0.1)	2.0 (0.1)
ACQ (1.21)	1.07 (6.15)	0.2 (0.1)	0.0 (0.1)	0.0 (0.1)	0.0 (0.1)
MCQ (0.226)	0.20 (1.15)	25.5 (9.5)	39.6 (1.5)	2.5 (0.8)	21.8 (6.9)
MCQ (0.45)	0.43 (2.47)	13.7 (6.0)	1.5 (0.5)	0.3 (0.1)	6.1 (3.3)
MCQ (0.75)	0.69 (3.97)	0.0 (0.2)	0.0 (0.1)	0.0 (0.1)	1.6 (0.9)
MCQ (1.21)	1.20 (6.90)	0.0 (0.1)	0.0 (0.1)	0.0 (0.1)	0.0 (0.6)

[a] Values are means of six replicates. OD = ovendry basis; SEM = standard error of the mean.

lengthy field trials. However, the protocols state that formulation change to existing actives can be evaluated using short-term bioassays, and for H4 and H5 preservatives, an accelerated field simulator (AFS) trial. Whether the change of copper from soluble to micronized form can be considered simply a ''formulation'' change has been controversial. Nevertheless, several trials have been undertaken in Australia (Cookson et al. 2008), and this article provides the latest results from that work. The trials undertaken were a fungal soil-block bioassay, an H3 termite field trial, and an H4 in-ground stake trial at Innisfail.

Materials and Methods

Preparation of test specimens

The ACQ and MCQ formulations examined had a copper oxide:quat ratio of 2:1. The current ACQ formulation used in Australia, NatureWood 100, was used as the reference preservative in the termite field trial, and contains didecyldimethyl ammonium chloride (DDAC) as the quaternary ammonium compound. For the fungal bioassay and stake trial, the reference preservative was the same, except that DDAC was replaced with Carboquat (a mixture of didecyldimethyl ammonium carbonate and didecyldimethyl ammonium bicarbonate). MCQ contained micronized copper carbonate particles and Carboquat as the cobiocide. CCA oxide was a further reference preservative.

Pinus radiata D. Don sapwood (air dry density 500 kg/m^3) was used as the softwood substrate, and test specimens were 20 by 20 by 10 mm (fungal bioassay), 25 by 25 by 100 mm (H3 termite trial), and 20 by 20 by 500 mm (Innisfail stake trial). The hardwood sapwood specimens were *Eucalyptus delegatensis* R. T. Baker 20 by 20 by 10 mm (fungal bioassay, air dry density 622 kg/m^3), *Corymbia maculata* (Hook.) K. D. Hill & L. A. S. Johnson 25 by 20 by 100 mm (H3 termite trial, air dry density 878 kg/m^3) and 20 by 20 by 500 mm (Innisfail stake trial, air dry density 909 kg/m^3).

All specimens were conditioned to constant moisture content (10% to 12% MC) and treated to the nominal retentions listed in Tables 1 through 4. The fungal bioassay and H3 termite trial specimens were treated at CSIRO, while the Innisfail stakes were treated by Scion in New Zealand. Spare test specimens from the fungal bioassay and Innisfail stake trials were chemically analyzed for preservative retentions by the Queensland Department of Primary Industries and Fisheries (Qld. DPI&F), and the actual retentions achieved are shown in Tables 1, 2, and 4. The nominal CCA retentions in the Innisfail stake trial were quarter H4, half H4, and H4 specifications, as suggested for field testing by the AWPC (2007).

The test specimens for exposure at Innisfail were not artificially weathered, while those for the fungal bioassay and H3 termite trial were artificially weathered prior to exposure. While keeping treatment groups separate, these test specimens were vacuum impregnated with water and placed in a shaking water bath for 5 days at 35°C. The water was changed daily. After leaching, test specimens were placed on drying racks for 2 to 4 days to surface dry. They were then dried in vacuum ovens at 40°C and −95 kPa for 5 days. After removal from the vacuum ovens, the test specimens were cooled in a desiccator and weighed to obtain initial masses.

Table 2.—Percent mean mass losses of E. delegatensis *specimens exposed to white-rotting decay fungi for 12 weeks.*[a]

Treatment and nominal retention (% m/m OD)	Analyzed retention, TAE % m/m OD (oxide basis, kg/m^3)	Mean (SEM) mass loss (%)	
		P. tephropora	*L. crassa*
Water	0.00	16.3 (3.6)	40.0 (1.6)
CCA (0.14)	0.11 (1.11)	0.6 (0.7)	3.2 (1.0)
CCA (0.28)	0.25 (2.52)	0.7 (0.3)	0.0 (0.4)
CCA (0.466)	0.38 (3.83)	0.1 (0.1)	0.0 (0.1)
CCA (0.745)	0.62 (6.25)	0.2 (0.1)	0.0 (0.2)
ACQ (0.226)	0.25 (1.79)	4.6 (1.0)	13.8 (1.7)
ACQ (0.45)	0.48 (3.43)	3.1 (1.5)	5.9 (2.9)
ACQ (0.75)	0.66 (4.72)	2.2 (1.2)	0.9 (0.5)
ACQ (1.21)	1.16 (8.29)	0.7 (0.4)	0.0 (0.2)
MCQ (0.226)	0.19 (1.36)	2.1 (0.4)	2.9 (1.3)
MCQ (0.45)	0.32 (2.29)	0.5 (0.3)	0.2 (0.3)
MCQ (0.75)	0.52 (3.72)	0.4 (0.2)	0.2 (0.1)
MCQ (1.21)	0.95 (6.79)	0.1 (0.1)	0.1 (0.2)

[a] Values are means of six replicates. OD = ovendry basis; SEM = standard error of the mean.

Table 3.—Percent mean mass losses of treated test specimens after exposure to termites in an aboveground H3 field trial.[a]

Treatment	Nominal retention, TAE m/m OD (oxide basis, kg/m^3)		Mean (SEM) mass loss (%)			
			C. acinaciformis		*M. darwiniensis*	
	P. radiata	*C. maculata*	*P. radiata*	*C. maculata*	*P. radiata*	*C. maculata*
Water	0.00	0.00	91.4 (1.7)	61.0 (14.0)	93.2 (1.3)	98.2 (0.1)
CCA	0.19 (1.54)	0.19 (2.70)	0.6 (0.4)	0.8 (0.2)	1.9 (0.8)	2.4 (0.3)
CCA	0.38 (3.08)	0.38 (5.40)	0.5 (0.2)	1.1 (0.2)	3.0 (1.6)	2.5 (0.2)
ACQ	0.18 (1.03)	0.18 (1.82)	0.5 (0.2)	1.8 (0.5)	6.1 (2.0)	9.3 (2.0)
ACQ	0.35 (2.01)	0.35 (3.53)	0.7 (0.2)	1.9 (0.3)	2.9 (1.0)	3.2 (0.3)
MCQ	0.18 (1.03)	0.18 (1.82)	0.3 (0.1)	1.0 (0.3)	5.4 (2.5)	7.3 (2.6)
MCQ	0.35 (2.01)	0.35 (3.53)	0.3 (0.1)	0.8 (0.2)	1.6 (0.4)	3.1 (0.6)

[a] Values are means of six replicates. OD = ovendry basis; SEM = standard error of the mean.

Fungal bioassay

The fungal bioassay (AWPC 2007) was conducted with *P. radiata* against the brown-rot fungi *Coniophora olivacea* (Pers.) P. Karst, *Fomitopsis lilacinogilva* (Berk.) J. E. Wright & J. R. Deschamps, *Gloeophyllum abietinum* (Bulliard) P. Karst., and *Serpula lacrymans* (Wulfen) J. Schröt., and with *E. delegatensis* against the white-rot fungi *Perenniporia tephropora* (Mont.) Ry. and *Lopharia crassa* (Lév.) Boidin. Six replicates per treatment were selected for each of the decay fungi. Prior to exposure, test specimens were sterilized by gamma radiation at 25 kGy.

Fungi were grown in 250-mL glass jars, partially filled with 150 g of ''Toolangi forest loam soil'' moistened to 100 percent water holding capacity (about 65% MC). Poplar sapwood veneer feeder strips, used for both the hardwood and softwood tests, were soaked overnight in 1 percent malt extract solution and placed on top of the soil in each jar. Metal lids closed the jars, which were then sterilized by autoclaving. Feeder strips were inoculated with actively growing mycelium of the test fungi and incubated at 25°C. When the feeder strips were fully colonized by the fungi, with the exception of *L. crassa*, two sterile test specimens were placed on top. For *L. crassa* the two sterile test specimens were placed below the fully colonized feeder strips and therefore were embedded within soil (Hedley and Foster 1971). Sterile control specimens were included in the trial to determine whether there was any mass loss or gain not attributable to fungal decay. All jars were incubated at 25°C (except for *S. lacrymans,* which was incubated at 20°C) for 12 weeks. Test specimens were then removed from the jars and wiped of adhering mycelium. The test specimens were dried in vacuum ovens at 40°C and −95 kPa for 5 days, weighed, and adjusted according to any changes in the sterile controls; then percentage mass losses were determined.

Termite field trial

Prior to field exposure, test specimens were labeled with stainless steel tags. The test sites were near Darwin in the Northern Territory and known to be inhabited by Australia's most economically destructive species, *Coptotermes acinaciformis* (Froggatt), and the giant northern termite *Mastotermes darwiniensis* Froggatt. Mean annual temperature for the sites is 34°C, and mean annual rainfall is 1,440 mm. *C. acinaciformis* is widely distributed throughout mainland Australia and is responsible for more economic loss than all other Australian species of termites combined. North of the Tropic of Capricorn, *C. acinaciformis* builds aboveground mounds. *M. darwiniensis* is a tropical species; the southern limit of its distribution approximates to the Tropic of Capricorn, both in coastal and inland localities. In this zone it is by far the most destructive termite. Unlike *C. acinaciformis, M. darwiniensis* does not build mounds.

The test method adopted for this field trial was based upon the H3 drum technique described in the AWPC (2007)

Table 4.—Mean ratings for 500 by 20 by 20-mm in-ground stakes exposed at Innisfail for 1.4 and 2.3 years.

Treatment and nominal retention	*P. radiata*				*C. maculata*			
	Mean (SEM) rating[a]				Mean (SEM) rating[a]			
	% m/m (kg/m^3)[b]	1.4 y	2.3 y	No. of failed stakes	% m/m (kg/m^3)[b]	1.4 y	2.3 y	No. of failed stakes
Untreated	0	0.0 (0.0)	0.0 (0.0) A	10	0	0.0 (0.0)	0.0 (0.0) A	10
CCA, quarter H4	0.14 (1.13)	4.7 (1.1)	2.4 (1.0) B	6	0.09 (1.32)	1.6 (0.9)	0.0 (0.0) A	10
CCA, half H4	0.29 (2.35)	6.7 (0.3)	5.6 (0.4) C	0	0.19 (2.80)	5.8 (1.0)	4.0 (1.1) BC	4
CCA, H4	0.65 (5.26)	7.9 (0.1)	7.8 (0.1) CD	0	0.37 (5.45)	3.1 (1.1)	1.4 (0.7) AB	7
ACQ, 3.0 kg/m^3	0.60 (3.45)	7.9 (0.1)	7.4 (0.2) CD	0	0.27 (2.82)	6.5 (0.2)	5.0 (0.7) CD	1
ACQ, 4.0 kg/m^3	0.77 (4.43)	7.9 (0.1)	7.7 (0.2) CD	0	0.33 (3.45)	6.7 (0.2)	5.7 (0.4) CD	0
ACQ, 5.0 kg/m^3	0.95 (5.46)	7.8 (0.1)	7.6 (0.2) CD	0	0.47 (4.91)	6.9 (0.2)	6.0 (0.3) CD	0
ACQ, 6.5 kg/m^3	1.30 (7.47)	8.0 (0.0)	7.8 (0.1) CD	0	0.63 (6.58)	7.5 (0.2)	6.8 (0.3) CD	0
MCQ, 3.0 kg/m^3	0.65 (3.74)	7.9 (0.1)	7.8 (0.2) CD	0	0.19 (2.00)	7.2 (0.3)	6.0 (0.4) CD	0
MCQ, 4.0 kg/m^3	0.89 (5.11)	7.2 (0.4)	7.0 (0.4) CD	0	0.27 (2.82)	7.0 (0.3)	6.2 (0.3) CD	0
MCQ, 5.0 kg/m^3	1.08 (6.21)	8.0 (0.0)	8.0 (0.0) D	0	0.36 (3.76)	7.7 (0.2)	7.2 (0.3) D	0
MCQ, 6.5 kg/m^3	1.12 (6.44)	8.0 (0.0)	8.0 (0.0) D	0	0.38 (3.97)	7.5 (0.2)	7.3 (0.3) D	0

[a] SEM = standard error of the mean. Means with same letters are not significantly different ($P > 0.05$).
[b] Chemical analyses provided by Qld. DPI&F. % m/m = TAE ovendry basis; kg/m^3 = oxide basis.

Table 5.—Rating scale used to assess in-ground stakes at Innisfail for damage by termites and decay fungi.

Rating	Cross-section lost (%)	Depth of damage (mm)		Description of damage
		From each surface	From 1 surface or 2 surfaces added together	
8	No loss, sound	0	0	No damage
7	Up to 15	0–1.5	0–3.0	Light damage
6	15–30	1.5–3.0	3.0–6.0	Light–moderate damage
5	30–45	3.0–4.5	6.0–9.0	Moderate damage
4	45–60	4.5–6.0	9.0–12.0	Moderate–heavy damage
3	60–75	6.0–7.5	12.0–15.0	Heavy damage
2	75–90	7.5–9.0	15.0–18.0	Severe damage
1	90–99	9.0–9.9	18.0–19.8	Severe–destroyed
0	100	10	20	Failed

protocols and is an aboveground trial where test specimens were exposed within 20-liter stainless steel containers. One replicate test specimen of each treatment was placed inside a container, and each test specimen separated by *Eucalyptus regnans* bait-wood. For *C. acinaciformis,* each container was connected to an infested eucalypt tree using plastic piping, and the test duration was 12 months. For *M. darwiniensis,* a container base was placed over a freshly cut stump that had active termite galleries, and the test duration was 40 weeks. For protection against excessive heat and grass fires, all containers were insulated with aluminum foil (Sisalation). Six replicate test specimens were challenged against each species of termite.

At the conclusion of field exposure, test specimens were removed from the containers and cleaned. Test specimens, as well as vacuum oven controls, were then vacuum ovendried at the same conditions used to obtain initial masses (i.e., 5 d at 40°C and −95 kPa), and weighed to obtain percentage mass loss. If necessary, mass losses of test specimens exposed to termites were adjusted to accommodate any changes recorded in vacuum oven control specimens.

In-ground stake trial

The Innisfail in-ground test site is a clearing within a rainforest in Australia's wet tropics. It has a mean annual rainfall of 3,600 mm, and mean maximum annual temperature of 28.1°C. The 500-mm-long stakes were buried in prepared holes to a depth of 300 mm, in rows 300 mm apart. There were 10 rows, with each row containing one replicate of each treatment, which were placed in random order within each row. Stakes were installed on November 24, 2006 and inspected after 1.4 and 2.3 years of exposure by removal from the soil and probing with a knife. They were inspected for fungal decay and termite damage and given a rating from 0 to 8 according to the rating scale described in Table 5. A full factorial analysis of variance (ANOVA) was applied to the data from the 2.3-year inspection with the aid of Statistica software. Significant differences between the means were determined using the Scheffe post hoc test.

Results

Fungal bioassay

The mean mass losses caused by brown-rot fungi to water-treated *P. radiata* ranged from 37.5 to 62.1 percent (Table 1). A treatment is considered to have controlled decay fungi when the mean mass loss was less than 3 percent. The two highest retentions of MCQ, ACQ, and CCA were able to control *C. olivacea*. A comparison of the second lowest set of retentions, 0.45 percent m/m nominal (2.59 kg/m^3 oxide basis), shows that MCQ had a mean mass loss of 13.7 percent compared with 23.5 percent for ACQ. Similarly, *P. radiata* treated to the lowest MCQ retention with 25.5 percent mass loss fell between the lowest and second lowest retentions of ACQ, with mass losses of 35.9 and 23.5 percent, respectively.

Water-treated specimens were severely attacked by *F. lilacinogilva* with 62.1 percent mean mass loss. The three highest retentions of MCQ and ACQ were able to control this fungus, while only the two highest retentions of CCA were effective. *P. radiata* treated with CCA to the next lowest retention (0.24% m/m, analyzed, or 1.94 kg/m^3 oxides) had a mean mass loss slightly above the allowable 3 percent mean mass loss, at 4.1 percent. All treatments at the lowest retention were substantially attacked by *F. lilacinogilva*. *P. radiata* treated with CCA to 0.23 percent m/m (1.86 kg/m^3 oxides), with ACQ to 0.27 percent m/m (1.55 kg/m^3 oxide basis), and with MCQ to 0.20 percent m/m (1.15 kg/m^3 oxide basis) had mean mass losses of 26.1, 34.0, and 39.6 percent, respectively.

While *G. abietinum* was able to cause severe decay to water-treated *P. radiata,* with 54.6 percent mean mass loss, all preservative-treated timber remained sound during the bioassay.

S. lacrymans showed a pattern of susceptibility to preservatives similar to that of *C. olivacea*. The two highest retentions of MCQ, ACQ, and CCA were able to control *S. lacrymans*. A comparison of the second lowest set of retentions (0.45% m/m nominal, 2.59 kg/m^3 oxide basis) shows that MCQ-treated timber had a mean mass loss of 6.1 percent compared with 9.1 percent for ACQ and 7.5 percent for CCA. Similarly, *P. radiata* treated to the lowest MCQ retention was as effective as the lowest retention of ACQ, since mean mass losses were 21.8 and 25.7 percent, respectively.

The white-rot fungus *P. tephropora* caused relatively low mean mass loss to water-treated *E. delegatensis,* at 16.3 percent (Table 2). *P. tephropora* was able to decay the two lowest retentions (0.25% and 0.48% m/m) of ACQ-treated *E. delegatensis* slightly, with mean mass losses of 4.6 and 3.1 percent, respectively. All MCQ- and CCA-treated specimens were not decayed by this fungus.

L. crassa was the more active white-rot fungus in this trial, on test specimens placed under the feeder strips, and

caused 40.0 percent mean mass loss to water-treated *E. delegatensis*. All retentions of MCQ were able to control *L. crassa*. The lowest retention of ACQ (0.25% m/m or 1.79 kg/m^3 oxide basis) was moderately decayed with 13.8 percent mean mass loss, while the 0.48 percent m/m (3.43 kg/m^3 oxide basis) retention was slightly decayed with 5.9 percent mean mass loss. The lowest retention (0.11% m/m or 1.11 kg/m^3 oxides) of CCA was also slightly decayed with a mean mass loss of 3.2 percent.

Termite field trial

At the conclusion of the aboveground H3 field trial, all test specimens within the six exposure containers had evidence of substantial contact by *C. acinaciformis*. All untreated *E. regnans* bait-wood and spacers, used as a susceptible and attractive food source for maintaining the presence of termites, had been destroyed. Water-treated *P. radiata* control specimens were completely destroyed by *C. acinaciformis* (mean mass loss of 91.4%; Table 3). Similarly, water-treated *C. maculata* control specimens were substantially attacked, recording a mean mass loss of 61.0 percent (Table 3). Mass losses of individual water-treated *C. maculata* sapwood specimens ranged from 26.8 to 97.2 percent. The occurrence of variable attack by different colonies of *C. acinaciformis* to the sapwood of high-density hardwoods such as *C. maculata* is not uncommon.

The mean mass losses caused by *C. acinaciformis* to preservative-treated specimens were negligible. The mean mass losses of preservative-treated *P. radiata* specimens ranged from 0.3 to 0.7 percent, whereas the mean mass losses of preservative-treated *C. maculata* specimens ranged from 0.8 to 1.9 percent (Table 3). No dosage effects were evident. Therefore, all retentions of each preservative tested have satisfied the AWPC (2007) performance criterion against subterranean termite attack by *C. acinaciformis* in an H3 field situation, i.e., mean mass losses of test specimens were either equal to or below 5 percent.

Water-treated control specimens of each substrate (*P. radiata* and *C. maculata*) were completely destroyed by *M. darwiniensis,* with mean mass losses of 93.2 and 98.2 percent, respectively (Table 3). The mean mass losses of preservative-treated specimens were generally low. Mean mass losses of preservative-treated *P. radiata* specimens ranged from 1.6 to 6.1 percent, whereas the mean mass losses of preservative-treated *C. maculata* specimens ranged from 2.4 to 9.3 percent (Table 3). In *P. radiata* sapwood, slight dosage effects were evident, i.e., increases in the retention of preservative formulation resulted in a corresponding decrease in mean mass losses of test specimens. However, with the exception of CCA, dosage effects were more noticeable for each preservative formulation when impregnated into *C. maculata* sapwood.

In *P. radiata* sapwood, both retentions of CCA, as well as the highest retentions of MCQ and ACQ, satisfied the AWPC performance criterion against subterranean termite attack by *M. darwiniensis* in an H3 field situation. Similarly in *C. maculata* sapwood, both retentions of CCA and the highest retentions of MCQ and ACQ prevented significant damage by *M. darwiniensis*.

In-ground stake trial

The mean ratings for stakes installed for 1.4 and 2.3 years at Innisfail are given in Table 4. The worst rating obtained in stakes from either decay or termites (decay for most treated stakes) was used to calculate the means.

All untreated *P. radiata* and *C. maculata* test stakes had failed by 1.4 years, and indeed after 6 months the aboveground portions of several stakes were noticed lying on the ground at Innisfail. The decay fungi responsible for most damage to test stakes were white-rot and soft-rot fungi. Soft rot was especially prevalent in the hardwood test stakes. Termite damage to treated and untreated stakes was caused by *Amitermes herbertensis* (Mjöberg) and *Heterotermes paradoxus paradoxus* (Froggatt). *Schedorhinotermes intermedius seclusus* (Hill) and *Microcerotermes serratus* (Froggatt) were also found sporadically during the 2.3-year inspection.

In Australia, the minimum H4 requirements for CCA are 0.63 percent m/m total active ingredients (TAE) in softwoods and 0.70 percent m/m in hardwoods. For this trial, the CCA retentions achieved in *P. radiata* were close to the H4, half H4, and quarter H4 retentions targeted. In contrast, the CCA retentions achieved in *C. maculata* were approximately half those sought. For ACQ the minimum H4 requirements are 0.89 percent m/m TAE for softwoods and 0.98 percent m/m for hardwoods. Termites and decay fungi caused severe damage after 2.3 years in *P. radiata* treated with CCA to 0.14 percent m/m TAE (1.13 kg/m^3 oxides, close to quarter H4 requirements) with a mean rating of 2.4, and light to moderate damage when treated with CCA to 0.29 percent m/m (2.35 kg/m^3 oxides, close to half H4 requirements). *C. maculata* treated with CCA to 0.37 percent m/m TAE (5.45 kg/m^3 oxides, close to half H4 requirements) were also severely attacked with a mean rating of 1.4. In comparison, the lowest mean rating recorded for either of the copper quat–treated *P. radiata* stakes was 7.0 (light damage) when treated with MCQ to 0.89 percent m/m TAE (5.11 kg/m^3 oxides, H4 retention). The lowest mean rating recorded for either of the copper quat–treated *C. maculata* stakes was 5.0 (moderate damage) when treated with ACQ to 0.27 percent TAE (2.82 kg/m^3 oxide basis, close to quarter H4 retention). At equivalent nominal retentions, MCQ generally had similar or slightly higher mean ratings to ACQ in both timber substrates (Table 4).

Discussion

This series of studies has shown that MCQ-treated timber performs as well as ACQ-treated timber against a wide range of biodeterioration agents. Treated wood has been exposed to brown- and white-rot fungi in the fungal bioassay, as well as a high hazard of white- and soft-rot fungi during an in-ground stake trial at Innisfail. Previous research gave conflicting results on whether MCQ has increased susceptibility to copper tolerant fungi such as *Postia placenta* (Fr.) M. J. Larsen & Lombard (Freeman and McIntyre 2008). The main Australian isolates of *S. lacrymans* are considered to be copper tolerant (Thornton 1991, De Groot and Woodward 1999), as demonstrated, for example, by our test isolate (DFP 16508) causing greater mass loss to both copper naphthenate–treated and CCA-treated *P. radiata* than the copper tolerant fungus *Amyloporia xantha* (Fr.) Bondartsev & Singer ex Bondartsev (Johnson et al. 1995; unpublished data, 1992, 1994). In the current study, MCQ-treated *P. radiata* was no more susceptible to *S. lacrymans* than ACQ-treated *P. radiata*. It should be noted, however, that copper tolerance can vary

greatly between isolates of the same species (De Groot and Woodward 1999) and *S. lacrymans* was among the most copper-sensitive species in a study by Green and Clausen (2003).

Published termite bioassay results to date show that all tested retentions of ACQ- and MCQ-treated wood exposed to *Reticulitermes flavipes* (Kollar) and *Coptotermes formosanus* Shiraki had less than 5 percent mass loss, indicating similar performance at the retentions tested (Freeman and McIntyre 2008). Similarly, *C. acinaciformis* was controlled by all tested retentions of ACQ and MCQ in the current H3 field trial. Since no toxic thresholds were found against the above termite species, it is unclear whether one formulation would have proved more active than the other at lower retentions. However, the voracious termite *M. darwiniensis* was able to cause minor damage to the lowest retentions of MCQ and ACQ tested, and performance was similar. This result suggests that the form of copper is unimportant to termites, which attack wood on a macroscopic scale. Treated stakes were also exposed at Innisfail to *A. herbertensis* and *H. p. paradoxus,* which are lesser known species that sometimes cause damage to poles and posts (Hill 1942).

Kartal et al. (2009) noted that the commercial use of micronized copper preservatives is mostly limited to easily treated pine species because of difficulties in penetrating others. The Innisfail stake trial shows that the sapwood of both *P. radiata* and *C. maculata* could be treated and is performing at least as well as ACQ-treated stakes, even though *C. maculata* is a substrate that is particularly susceptible to soft-rot fungi (Greaves 1974, 1979). With questions being raised about the predictive value of 19 by 19-mm stake trials (Lebow et al. 2009), continued inspection and further testing is always warranted. Several other in-ground and soil-bed stake trials have shown that MCQ performs at least as well as ACQ (Larkin et al. 2008, Freeman and McIntyre 2008, Zhang and Ziobro 2009). These results contrast with the field trials of Preston et al. (2008), where in unmatched samples cut from larger treated timbers, MCQ-treated pine performed worse than ACQ-treated pine.

Several of the stake trials suggest that MCQ-treated timber performs slightly better than similar ACQ-treated timber. MCQ is deposited in relatively insoluble form within wood rather than being ''fixed'' by chemical reaction with wood components, and therefore has reduced leaching (Freeman and McIntyre 2008). Reduced loss of actives by leaching may explain the slight improvement in performance. Jin et al. (2008) also found reduced discharge of copper from treated wood when squeezed, raising the question of whether the copper in micronized formulations is sufficiently bioavailable to control a wide range of microorganisms. That MCQ-treated stakes are performing slightly better than ACQ-treated stakes suggests a balance is struck between reduced copper mobility and bioavailability. The micronized copper particles may act as slow-release preservatives, where despite reduced mobility there is sufficient solubilization and movement into the cell wall to control fungi (Stirling et al. 2008, Stirling and Drummond 2009).

Conclusion

These trials have demonstrated that MCQ performs at least as well as ACQ against Australian termites and decay fungi. In the fungal bioassay both preservatives gave similar performance against brown-rot fungi, including the copper tolerant species *S. lacrymans*. MCQ gave slightly improved performance against two white-rot fungi in *E. delegatensis*. Both preservatives prevented attack by *C. acinaciformis* at all retentions examined, while the trial against *M. darwiniensis* where some damage occurred showed that both preservatives had similar toxicity to this termite species. The 2.3-year in-ground stake trial in the wet tropics at Innisfail also found that ACQ and MCQ performed comparably in *P. radiata* and *C. maculata*. White rot, soft rot, and termites were prevalent at the Innisfail site. This research would support the introduction of micronized copper for wood preservation into Australia.

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