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Performance of copper-based wood preservatives in soil bed exposures

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1. Introduction

Copper-based biocides are widely used to protect wood from biological attack in a variety of environments. Chromated copper arsenate (CCA) is the dominant copper-based preservative for wood protection (J. T. MICKLEWRIGHT, 1989). First developed in India in the 1930s, CCA contains a very effective combination of materials. Copper provides protection against most organisms, chromium aids in the fixation of copper and arsenic to the wood. and arsenic provides supplemental protection against those organisms that are copper tolerant (W. H. HARTFORD, 1973). CCA provides excellent protection in most environments. but increasing perceptions of toxicity, leaching, and other potential environmental effects have stimulated the development of alternative systems that, while still containing copper. incorporate materials other than chromium or arsenic. A number of these systems use ammonia to solubilize copper. The fact that many of these alternative biocides perform variably with site suggests a vulnerability to copper-tolerant fungi (A. F. PRESTON *et al.,* 1994: G. R. WILLIAMS *et al.,* 1994). The implications of copper tolerance for the performance of these materials has been the subject of much speculation. but relatively little in the way of comparative data under high decay hazard conditions currently exists.

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To develop a better understanding of the effects of substituting alternative materials for chromium and arsenic in copper-based biocides, we performed the trials described in this paper.

2. Materials and methods

2.1 Treatment methods

Stakes (10 mm by 25 mm by 40 mm long) were cut from Douglas-fir (*Pseudotsuga menziesii* [Mirb.] Franco) sapwood or heartwood and red alder (*Alnus rubra* Bong.) lumber. The stakes were conditioned to a stable moisture content at 25 °C and 70% relative humidity. weighed (nearest 0.1 g), and then treated with chromated copper arsenate me C (CCA-C) (Osmose Wood Preserving, Buffalo, NY), ammoniacal copper zinc arsenate (ACZA) (J. H. Baxter & Co., Eugene, OR), ammoniacal copper citrate (CC) (Osmose Wood Presenting, Buffalo, NY), or ammoniacal copper quaternary (ACQ-B) (Chemical Specialties Inc., Charlotte, NC). Treatment consisted of submerging the stakes in pans containing the desired preservative and placing the pans in a treating cylinder. A vacuum (−85 KPa) was drawn over the specimens for 20 minutes, then the pressure was raised to 800 KPa and held for 4 hours. The pressure was released and the specimens were wiped clean of residual solution and weighed (nearest 0.1 g). The difference between pre- and post-treatment weights was used to calculate gross preservative retention. The stakes were treated either with CCA-C to target retentions of 0.8, 2.4, 4.0, and 10.0 kg/m^3 (oxide basis); or with ACZA, CC, or ACQ-B to a single retention of 6.4 kg/m^3. Following treatment. stakes were stored in plastic bags for 48 hours at 23–25 °C to permit any fixation reactions to proceed. then air-dried and shipped to the Swedish University of Agricultural Sciences (SUAS), Uppsala, Sweden. for exposure trials.

2.2 Pure culture exposures

At SUAS one set of treated stakes was exposed for two or four months at 25 °C to a pure culture of the brown rot fungus *Postia placenta* (Isolate #QM1010, U.S. Army, Natick, MA) growing on Scots pine feeder strips on a commercial potting soil in glass jars. This procedure was similar, in principle, to that described in American Wood Preservation Association Standard E10 (1999). Weight loss following exposure was used as the measure of microbial attack. Treatments were replicated on six stakes of each mood type.

2.3 Terrestrial microcosm exposures

Another set of treated stakes was exposed to microbial attack in terrestrial microcosms (TMCs). The TMCs consisted of plastic containers filled with one of three soils with different dominant decay types (T Nilsson and G. Daniel. 1990). The soils used were (1) soil from a test site in Simlångsdalen, Sweden (main hazard; brown rot): (2) humus-rich soil from a coniferous forest in Sweden (main hazards; white rot and soft rot); and (3) garden compost soil (main hazards; soft rot and tunneling bacteria). The pH levels of these soils were 4.5, 6.8, and 3.5, respectively. The

Simlångsdalen soil and the forest soil had a nitrogen content of ca. 0.1%, and the compost soil had a nitrogen content of ca 0.5%. Prior to placing the soils in the plastic containers, soil moisture was adjusted to ca. 95% of its water-holding capacity. The filled TMC containers were covered with a loose sheet of plastic to retain this moisture level; deionized water was also sprinkled evenly over the soil as necessary to maintain the original moisture content.

The TMCs were kept at 25 °C and 85% relative humidity. The samples were evaluated after 6 or 12 months of exposure, again using weight loss as the measure of microbial attack. In addition. sections were cut from selected samples for microscopic examination to characterize the nature of microbial attack as soft rot, brown rot. or tunneling or erosion bacteria.

2.4 Residual chemical analysis

At the end of each fungal exposure period for both the pure-culture and TMC trials, the Douglas-fir sapwood stakes were evaluated for residual chemical content, Stakes treated with CCA-C (2.4 and 4.0 kg/m^3 loadings). ACZA, and CC were ground to pass a 20 mesh screen and the resulting dust was analyzed for copper, chrome, arsenic, or zinc using an ASOMA 8620 x-ray fluorescence analyzer. The results were expressed on a wt/volume basis.

3. Results and discussion

3.1 Pure culture exposures

Weight losses in untreated controls exposed to *P. placenta* for 2 or 4 months varied from 40.9% to 65.2%, indicating that conditions were suitable for active decay by the test fungus (Table 1). Within the control group, weight losses for Douglas-fir heartwood differed little from those for Douglas-fir sapwood. These results suggest that Douglas-fir heartwood has little decay resistance. but *P. placenta* is frequently isolated from decaying Douglas-fir heartwood and must therefore be somewhat tolerant of the extractives present in this wood (R. D. GRAHAM and M. E. CORDEN, 1980).

The difference in weight loss between Douglas-fir sapwood and red alder was small, indicating that the higher lignin content of Douglas-fir sapwood compared to that of alder had little influence on the decay activity of the brown rot fungus. This confirms earlier observations of brown rot decay in wood with varying lignin contents (T. NILSSON and G. DANIEL, 1987).

Weight losses in preservative-treated stakes were generally lower than those found in the untreated controls, although weight losses in stakes treated with CC and exposed for 4 months approached those found with the controls. Weight losses were also higher in Douglas-fir sapwood

Table 1: Average weight losses of treated Douglas-fir heartwood. Douglas-fir sapwood. and red alder stakes exposed to *Postia placenta* in pure-culture exposure.

		Wood weight loss (%)					
	Retention	Douglas-fir sapwood		Douglas-fir heartwood		Red alder	
Treatment	(kg/m³)	2 mo	4 mo	2 mo	4 mo	2 mo	4 mo
CCA-C	0.8	6.4	44.6	7.2	29.4	15.0	43.1
CCA-C	2.4	4.3	25.2	2.3	12.7	2.7	18.3
CCA-C	4.0	4.3	20.2	0.8	4.9	2.1	19.7
CCA-C	10.0	8.0	7.5	1.4	3.3	0.3	4.0
ACZA	6.4	5.4	12.3	0.6	15.6	0.2	1.5
CC	6.4	22.2	43.5	23.5	52.7	24.1	54.9
ACQ-B	6.4	–[1]	2.0	–[1]	3.6	–[1]	0.9
Control	–	50.1	57.2	41.4	65.2	40.9	64.3

[1] Not tested.

stakes treated to a CCA-C retention of 0.8 kg/m^3 and exposed for 4 months. In CCA-C-treated heartwood stakes, weight losses after 4 months of exposure were generally lower than those for sapwood stakes at the same retentions, suggesting that the combination of heartwood and CCA-C provided enhanced protection. This phenomenon has also been observed on ponderosa pine sapwood and heartwood treated to low retentions with CCA (P. I. MORRIS and J. INGRAM, 1991). The concept of synergistic protection may be especially useful in Douglas-fir. a species that contains large percentages of difficult-to-treat heartwood.

Stakes treated with the ammoniacal-based solutions containing copper and a co-biocide experienced little weight loss after 2 months of exposure; after an additional 2 months of exposure, however, ACZA-treated Douglas-fir stakes experienced elevated weight losses. Interestingly, 4-month weight losses were minimal for ACZA-treated alder stakes. Alder has little natural decay resistance and the difference in performance between this species and Douglas-fir is perplexing. It is possible that the ammonia-based systems react differentially with hardwood species that contain lower levels of lignin. These reactions and their potential effect on performance of ammoniacal-based systems merit further study.

3.2 TMC exposures

The three different soils produced variable weight losses as well as differences in decay types. In general, the garden compost soil produced markedly large weight losses on both untreated and treated stakes compared to the other two soils (Table 2): the only exception to this occurred

Table 2: Average weight losses of treated Douglas-fir sapwood, Douglas-fir heartwood, and red alder stakes exposed in three forest soils for 6 or 12 months.

Wood species	Chemical treatment	retention (kg/m³)	Wood weight loss (%)[1] Simlångsdalen		Acid forest soil		Garden compost soil	
			6 mo	12 mo	6 mo	12 mo	6 mo	12 mo
Douglas-fir sapwood	CCA-C	0.8	6.7	25.3 S/B	4.2	14.3 W	28.1	49.6 S/T
	CCA-C	2.4	3.9	10.1 S/B	1.5	7.0W	14.5	38.4 S/T
	CCA-C	4.0	1.1	5.9 S/B	0.8	5.0 W	8.7	24.5 S/T
	CCA-C	10.0	0.9	1.8	1.0	2.3	0.9	8.6 S/T
	ACZA	6.4	3.2	4.6	3.1	5.5	4.6	21.1 S/T
	ACQ-B	6.4	3.4	4.2	3.1	4.3	1.7	11.4 T
	CC	6.4	2.5	7.9 B	2.3	11.3	5.0	26.2 S/T
	Control	–	9.8	33.9 B	15.1	58.5 W	37.2	55.9 S/T
Douglas-fir heartwood	CCA-C	0.8	5.9	15.2 S/B	2.7	10.9 W	16.35	2.9 S/T
	CCA-C	2.4	3.8	6.7 S	0.5	4.8 W	5.0	25.4 S/T
	CCA-C	4.0	1.9	4.2	1.5	2.7 W	2.6	15.1 S/T
	CCA-C	10.0	1.6	2.3	1.2	2.4	0	2.3 T
	ACZA	6.4	3.4	4.6 S	3.1	3.2	7.2	31.1 T
	ACQ-B	6.4	3.7	4.5	3.0	4.4	1.9	12.1 T
	CC	6.4	2.4	4.9 S	2.4	4.5 W	8.8	33.9 T/E
	Control	–	10.9	30.8 B	19.4	45.7 S/W	30.2	61.4 S/T
Red alder	CCA-C	0.8	19.0	41.9 S	12.3	34.2 S	44.4	65.8 S/T/E
	CCA-C	24	10.5	40.3	2.6	22.9 S	45.1	70.8 S/T
	CCA-C	4.0	9.2	29.5 S	1.0	11.0 S	34.1	65.0 S/T
	CCA-C	10.0	3.8	6.1 S	0.6	2.7 S/W	22.1	39.6 S/T
	ACZA	6.4	4.9	8.7 S/E	5.5	8.6 S	9.2	34.5 S/T
	ACQ-B	6.4	4.5	7.7 E	4.3	7.9	4.1	26.3 S/T
	CC	6.4	4.1	8.5 S/B	2.7	10.6 W	21.1	66.5 S/T
	Control	–	12.1	42.0 S/B/E	20.4	28.7 S	43.1	74.7 S/T

[1] Letters following 12 mo. weight loss data indicate dominant microbial activity, if detected: S = soft rot. B = brown rot. W = white rot. T = tunneling bacteria. E = erosion bacteria

with the 12-month Douglas-fir sapwood control. Stakes exposed in the compost soil for 12 months had the greatest incidence of soft rot attack, possibly reflecting the higher nitrogen content of this soil. Attack by tunneling bacteria was also prominent among stakes in the compost soil and in several instances, this bacteria type was the dominant damaging agent for these stakes. Remarkably, tunneling bacteria caused a weight loss of more than 30% in the ACZA-treated Douglas-fir heartwood stakes in compost soil. In contrast, tunneling bacteria were absent from stakes exposed in the other two soils. Tunneling bacteria have also been noted as prominent decay agents in ammoniacal copper arsenate (ACA)-treated stakes (P I. MORRIS and J. INGRAM, 1991), suggesting these ammoniacal solubilized metal systems may be more sensitive to these organisms.

All CCA-C treatments. with the exception of Douglas-fir heartwood treated to 10 kg/m^3, failed to provide protection in the compost soil, demonstrating that this soil is very aggressive. The CCA-C-treated alder stakes suffered more from soft rot attack compared with the CCA-C-treated Douglas-fir samples in all three soils. This confirms that CCA-C does not perform as well in hardwoods with a low lignin content (cf. J. BUTCHER and T. NILSSON, 1982). As with the pure-culture trials, treatment performances of ammoniacal and acid-based systems did not appear to differ markedly in any of the three soils.

With the exception of the 0.8 kg/m^3 CCA-C retention. weight losses of CCA-C-treated Douglas-fir sapwood stakes after 12 months tended to be slightly higher than comparably treated heartwood samples. Overall. CCA-C seemed to do a better job of protecting Douglas-fir heartwood than Douglas-fir sapwood at comparable retentions. Conceivably, CCA-C components reacted with the heartwood extractives to render them less susceptible to leaching. Weight losses of Douglas-fir heartwood stakes treated with ammonia-based systems were slightly higher than those found with comparably treated sapwood stakes. Impregnation with ammonia-based treatments may have caused dissolution of heartwood extractives and so altered their distribution and effectiveness.

Brown rot, the predominant damaging agent in the samples exposed in the Simlångsdalen soil – and the dominant microflora in this soil – was not observed on stakes exposed in the other two soils. Despite the presence of this decay type. however, the weight losses in the Simlångsdalen control samples were quite modest after 6 months of exposure. This effect may be explained by the extremely high soil moisture. Previous research has shown that weight losses of 45% or more may occur when the soil is kept slightly drier (M.-L. EDLUND and T. NILSSON, 1999). The suboptimal brown rot activity in our tests likely led to an increase in soft rot attack and erosion bacteria.

The differential modes of attack among the soils and biocides observed in this study clearly illustrate the benefits of employing multiple-test conditions to evaluate biocide performance. For example, the fact that white rot attack was found only in the acid forest soil exposures and most often in the CCA-C-treated conifer stakes may be related to the better performance of CCA-C-treated conifer wood against soft rot compared to that of the low-lignin alder. The results from different selected soils can identify specific susceptibilities of various woods to different modes of attack. Potentially, such data could be used to modify treatment standards or establish multiple retentions for these applications.

White rot in the CCA-C-treated Douglas-fir was of two different types. One was a typical white rot characterized by cell wall erosion. The other type, which was predominant at the higher CCA-C retentions, was characterized by hyphae growing in highly branched networks within the tracheid cell walls, in a manner reminiscent of tunneling bacteria. This form of attack has been observed earlier (T. NILSSON and G. DANIEL, 1990) but has not yet been attributed to any specific species of white rot fungus. The ability of white rot to degrade CCA-C-treated wood, even at high retentions, indicates a high level of copper tolerance.

3.3 Residual chemical analysis

Analysis of Douglas-fir sapwood stakes following fungal exposures suggested that CCA-C-treated stakes lost relatively little of their original chemical loadings (Table 3). ACZA- and CC-treated stakes both tended to lose substantial quantities of preservative components during soil exposure. Loss of copper from CC is particularly critical since this system lacks a second biocide to supplement protection. Little evidence of either zinc or arsenic was found in ACZA-treated stakes after the various exposures. The loss of these components is perplexing since controlled studies suggest that zinc and arsenic are complexed following ammonia evolution (S. T. LEBOW and J. J. MORRELL, 1995). Possibly, strongly acidic soil affects this complex, resulting in leaching from the wood. This would be particularly important in stakes with such high surface-to-volume ratios but may be less important in full-sized commercially treated materials.

Table 3: Residual preservative content of Douglas-fir sapwood stakes exposed for 2 to 12 months in pure-culture and TMC trial.

		Residual preservative retention (kg / m³)[1]					
		Postia placenta		Simlångs-dalen	Acid forest soil	Garden compost soil	
Chemical	Retention	2 mo	4mo	12mo	12mo	6 mo	12 mo
CCA-C	2.4	2.39(0.29)	2.13(0.54)	5.40(1.38)	3.34(0.20)	3.60(0.38)	4.00(0.21)
CCA-C	4.0	4.46(0.56)	3.93(0.51)	8.65(2.10)	5.63(0.56)	6.91(0.72)	7.89(0.39)
ACZA	6.4	3.07(0.40)	2.23(1.66)	2.22(0.82)	1.16(0.32)	–	1.61(0.28)
CC	6.4	2.76(0.18)	2.58(0.48)	2.03(0.18)	1.28(0.16)	2.42(0.15)	1.64(0.10)

[1] Oxide basis. Values for ammoniacal copper citrate do not include residual citrate, if any. Valuer represent means of 6 analyses. Figures in parentheses represent one standard deviation.

4. Conclusions

The results of this study illustrate preservative performance differences that result from varying wood species and soil conditions. While the decay susceptibility of some of the ammoniacal copper systems appeared higher than that of CCA-C in the pure culture *P. placenta* evaluation, little difference among these systems was found in the TMC exposures, where much of the decay was attributed to soft rot or tunneling bacteria. The ACQ-B system, with its quaternary ammonium chloride eo-biocide, appeared to perform well against attack by soft rot and tunneling bacteria. CCA-C tended to perform well in Douglas-fir heartwood and sapwood but was less effective in red alder. The combination of CCA-C and the extractives in Douglas-fir heartwood may enhance resistance to biodegradation in comparison to CCA-C alone.

5. Summary

The abilities of chromated copper arsenate (CCA), ammoniacal copper zinc arsenate (ACZA), ammoniacal copper quaternary (ACQ), and ammoniacal copper citrate (CC) to protect Douglas-fir sapwood and heartwood and red alder from deterioration were evaluated in single-culture decay tests and soil burial tests. In nearly all treatments. tests stakes incurred some weight losses over the test period. Tunneling bacteria and soft rot fungi were especially prevalent in the garden compost soil, while white rot fungi were more prevalent in the acid forest soil. Protection was often greatest for Douglas-fir heartwood stakes, suggesting some interaction of preservatives with extractives in this wood, with regard to either fixation or efficacy. In general. CC provided the lowest level of protection under most conditions, while the remaining chemicals performed well on a majority of species / soil combinations. The results highlight the importance of testing preservatives on multiple wood species under an array of environmental conditions

Zusammenfassung

Zur Wirksamkeit von kupferhaltigen Holzschutzmitteln inErdeingrabeversuchen

Die Fähigkeit von einem Kupfer-Chrom-Arsen-Schutzmittel (CKA), ammoniakalischem Kupferzinkarsenat (ACZA), quartärem ammmoniakalischem Kupfer und ammoniakalischem Kupfercitrat (CC), Douglasien-Splintholz und -Kernholz sowie Roterle gegen Pilzbefall zu schützen, wurde in Versuchen mit einem einzigen Organismus und in Erd-Eingrabeversuchen untersucht. Bei fast allen Behandlungen wurden Gewichtsverluste an den Prüfhölzern im Laufe der Versuchszeit festgestellt. Bakterien und Moderfäulepilze waren hauptsächlich in der Komposterde ventreten, während Weißfäulepilze in der sauren Walderde vorherrschten. Der Schutz war bei Prüfhölzern aus Douglasien-Kernholz oft am besten, was auf eine Wechselwirkung der Schutzmittel mit Holzextraktstoffen hinweisen könnte, die sich auf die Fixierung oder Wirksamkeit ausgewirkt haben könnte. Im allgemeinen bot CC den geringsten Schutz bei den meisten Prüfbedingungen, während die übrigen Substanzen bei der Mehrzahl der Kombinationen von Organismenanen und Erdetypen einen guten Schutz boten. Die Ergebnisse unterstreichen die Wichtigkeit, Holzschutzmittel mit mehreren Holzarten und unter verschiedenen Umwelteinflüssen zu untersuchen.

5. Résumé

Caractéristiques des produits de protection du bois á base de cuivre exposés dans un lit de terre

Les capacités du cuivre-chrome-arsenic (CCA), ammoniac cuivre zinc arsenic (ACZA), ammoniac cuivre quaternaire (ACQ) et ammoniac cuivre citrique (CC) de protéger l'aubier et le coeur du Douglas fir et de l'aubier contre la détérioration ont été évaluées par simples tests de pourriture et par tests dans un lit de terre. Pour presque tous les traitements, les tuteurs testés ont subi des pertes de poids pendant la période des tests. Bactéries faisant des tunnels et les champignons des pourritures molles étaient specialement prédominants dans une terre de composte, tandis que les champignons des pourritures étaient plus courant dans une forêt à sol acide. La protection était souvent meilleure pour les tuteurs en coeur de Douglas fir, suggérant des interactions entre les produits de protection et les extractifs du bois, en ce qui concerne la fixation ou l'efficacité. En général, CC fournit le plus faible niveau de protection sous fortes conditions, tandis que le reste des produits chimiques fonctionnent bien sur la majorité des combinaisons espéces / terre. Les résultats soulignent l'importance des tests de produits de protection sur plusieurs espèces de bois sous différentes conditions environnementales.

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