EFFECTS OF AMMONIACAL COPPER CITRATE PRESERVATIVE TREATMENT AND REDRYING ON BENDING PROPERTIES OF TWO GRADES OF SOUTHERN PINE 2 BY 4 LUMBER

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ABSTRACT

Ammoniacal copper citrate (CC) is a new preservative recently accepted in many American Wood Preservers' Association standards. This study evaluated the effects of CC preservative treatment on several mechanical properties of two grades of southern pine dimension lumber. For the Dense Select Structural grade lumber, the effects of CC treatment were generally found to be similar to previous reports for chromated copper arsenate and/or other ammoniacal copper preservative treatments — CC treatment to a target retention of 6.4 kg/m^3 (0.4 pcf) caused an average reduction in modulus of rupture (MOR) of only about 5 percent, no reduction in modulus of elasticity (MOE), and a reduction in work to maximum load (WML) of 7 to 18 percent. Reductions in MOR and WML were greater in samples kiln-dried after treatment. Treatment to the marine retention of 40 kg/m^3 (2.5 pcf) caused larger reductions in WML. However, for the No. 2 grade lumber, the effects of CC treatment on MOR were greater (average reduction of 12%) than those noted for Dense Select Structural grade lumber. These effects were also slightly greater than those previously reported for chromated copper arsenate treatment. No comparative data on No. 2 grade material were available for other preservative systems based on ammoniacal copper. As the popularity of arsenic-free ammoniacal copper-based systems increases, this phenomenon of greater strength loss with No. 2 grade treated lumber deserves additional study.

Waterborne ammoniacal copper wood preservatives require ammonia as a co-solvent to solubilize the copper. However, there are only limited data for determining the effects of these ammoniacal treatments on the mechanical properties of defect-free, clear wood and even less data on their effects on various grades of dimension lumber. This problem is accentuated by the immediate need for strength data for determining allowable stress design values and processing limits for redrying for the increasingly popular ammoniacal copper preservative systems. The objective of this report was to evaluate the effect of ammoniacal copper citrate (CC) treatment on the bending properties of Dense Select Structural and No. 2 grade nominal 2 by 4 southern pine (*Pinus* spp.) dimension lumber.[1]

BACKGROUND

In the development of new wood preservative systems, emphasis is often placed on system compatibility and preservative efficacy. However, another important concern is the effect of the preservative on mechanical or strength properties. CC is a new wood preservative recently standardized by the American Wood Preservers' Association (AWPA) (2). Research has demonstrated that this wood preservative system possesses many desirable qualities (3), but its effects on the mechanical properties of the treated lumber have not been evaluated.

Studies using small, clear, straight-grained specimens (commonly called clearwood) have indicated that ammoniacal copper systems cause a reduction in mechanical properties that is equivalent to or slightly less than that caused by the more widely used chromated copper arsenate (CCA) formulations. In tests with clearwood, CC-treated wood was reported to induce slight decreases in modulus of rupture (MOR), an average decrease of 14.7 percent in work to maximum load (WML), and no significant decrease in modulus of elasticity (MOE) (3). These findings generally agree with earlier work on other ammoniacal copper systems, such as ammoniacal copper arsenate (ACA), for which no significant decrease in MOR or MOE but significant decreases in WML at high retentions were reported (7). Although the effects of CC treatment on mechanical properties

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[1] Nominal 2 by 4 refers to nominal 2- by 4-inch (standard 38- by 89-mm) lumber, hereafter called 2 by 4.

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TABLE 1. — Experimental design.

Preservative retention		Type	Number of specimens	
(kg/m^3)	(pcf)	of redry	Select structural	No. 2 (on grade)
Untreated	Untreated	None	60	60
6.4	0.4	Air	60	60
6.4	0.4	Kiln	60	60
40	2.5	Air	60	Not tested

seem comparable to those of other waterborne preservatives in studies using clearwood specimens, additional tests using dimension lumber and AWPA-"standardized" processing techniques were needed.

Another ammoniacal copper system, ammoniacal copper quaternary ammonium chloride (ACQ–Type B), was shown to have a greater effect on the strength properties of knot-free dimension lumber than on the strength properties of similarly treated clearwood (6). Although the strength losses noted were not of great magnitude, kiln-drying after treatment did appear to intensify the negative effects of ACQ treatment. This redrying effect was comparable to previous results for CCA-treated lumber (4,5,11,12). Because limiting the post-treatment redrying temperatures had been proven to be critical in controlling CCA treatment effects, the influence of redrying needed to be evaluated for ammoniacal copper systems. Further, because the influence of lumber quality level (i.e., grade) had also been found to be critical for CCA treatment effects, the influence of lumber grade on CC treatment effects also needed to be evaluated.

MATERIALS AND METHODS

EXPERIMENTAL DESIGN

This study employed a partial factorial experimental design **(Table 1).** The experimental material was two grades (No. 2 and Dense Select Structural) of 2 by 4 southern pine lumber. Targeted CC retentions were 6,4 kg/m^3(0.4 pcf) for two grades and two redrying methods (air and kiln) and 40 kg/m^3(2.5 pcf) for air-redried Dense Select Structural material.

ACQUISITION AND SORTING

Each grade of 2 by 4 lumber was obtained in 2.43-m (8-ft.) lengths from a mill in southwestern Arkansas. A total of 250 pieces of Dense Select Structural and 208 pieces of No. 2 grade were obtained. Both grades of lumber had been kiln-dried at the mill using a 110°C (230°F) dry-bulb temperature and 85°C (185°F) wet-bulb temperature. Total kiln residence time was 29 hours. After shipment to Madison, Wis., the lumber was equilibrated in a conditioning room to 12 percent average equilibrium moisture content (EMC).

Before assignment to treatment groups, each specimen was mechanically evaluated nondestructively by measuring transverse vibrational MOE, hereafter called E-sort, to distinguish it from the bending MOE obtained in destructive testing. The specimens with the 5 highest and 5 lowest E-sort values were discarded from the Dense Select Structural groups (leaving 240 specimens or 4 groups of 60). Specimens with the 14 highest and 14 lowest E-sort values were discarded from the No. 2 grade material (leaving 180 specimens or 3 groups of 60). The remaining pieces for each grade of lumber were then ranked from lowest to highest E-sort value. Specimens were assigned to treatment groups in randomly sorted sequential blocks, which assured that treatment groups for each grade had proportionately equal numbers of high, medium, and low E-sort specimens. This matching allowed much greater statistical inference from results than would a purely random allotment procedure because E-sort and strength were highly correlated,

TREATMENT

Because of the size limitations of the treating cylinder at the USDA Forest Products Laboratory (FPL) (3 m (10 ft.) long, diameter of 0.9 m (3 ft.)), only 30 specimens that were 2.43 m (8 ft.) long could be treated per charge. However, to reduce within-group variability caused by treatment charge, it was desirable to treat each group of 60 specimens in a single charge, which required double-stacking the specimens by length. Consequently, each 2.43-m specimen was cut to 1.5 m (59 in.) long. For the Dense Select Structural grade, the end of the piece furthest from the grade-stamped end was removed; for the No. 2 grade material, the end furthest from the grade-dictating defect was removed.

The 1.5-m-long specimens were then treated to the target retention using a full-cell treatment process at ambient temperature. The initial vacuum was –85 kPa (25 in-Hg) for 30 minutes, followed by maximum pressure of 1.03 MPa (150 psi) for 1 hour. No final vacuum was employed. Treatment was done in 5 batches of 60-specimen groups, Two 208-L (55-gal.) barrels of 12.5 percent CC-treatment concentrate that met AWPA Standard P5 (2) were supplied by the cooperator. Mean concentrations of components in the CC-treatment concentrate were 7.65 percent copper oxide (CUO), 4.72 percent citric acid ($C_6H_8O_7$), 11.12 percent ammonia (NH_3), and 7.95 percent carbon dioxide (CO_2)[2]. The treating solution for the first batch was prepared at the FPL based on preliminary absorption data from preliminary charges of the previously discarded low and high E-sort material of both grades. The treating solution was reused for subsequent batches. For each batch, CC-treatment concentrate was added as needed based on post-treatment chemical analysis of previously used CC-treatment solution concentration and gross absorption of previous CC-treated charges. After treatment, the specimens were removed from the cylinder and wet-stacked under plastic for 1 week to allow complete diffusion of preservative and permit potential reactions of the preservative with the wood components.

REDRYING

After treatment and 1 week of wet storage under plastic, all material was redried. The 6.4-kg/m^3 treated material slated to be air-redried was stickered and redried outside for 6 weeks in early summer to approximately 19 to 20 percent moisture content (MC), then moved to a conditioning room held at 23°C (74°F) and 65 percent relative humidity and equilibrated to constant weight. This material equilibrated quickly when moved inside; there was no odor of ammonia. However, after 12 weeks of outside air-drying, the 40-kg/m^3 treated material still emitted a discernible ammonia odor

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[2] Reported as carbon dioxide, but supplied by adding ammonium bicarbonate (NH_4HCO_3).

within several days after being placed in a closed-loop environmental conditioning chamber. After 4 weeks, the ammonia off-gassing diminished, and the odor became indiscernible.

Material intended to be kiln-redried was stickered and dried using a schedule supplied by Osmose, Inc. **(Table 2).** The specimens were kiln-dried to an average MC of 19 to 20 percent, then equilibrated to constant weight in the 12 percent MC conditioning room (23°C/65% relative humidity).

MECHANICAL TESTING

Static bending tests on treated and untreated specimens were conducted in accordance with ASTM D 4761-93 (1), except that span length was 1.42 m (56 in.) because the 1.5-m specimen was shorter than the length designated in this ASTM standard. The loading rate was 13 mm (0.5 in.)/minute. Load and deflection data were collected by a computerized data-acquisition system. The MOE, Dmax (center-span deflection at failure), Pmax (maximum gross load at failure), MOR, and WML were calculated from these data.

For the first 68 specimens tested (all 60 from the untreated No. 2 grade (Group 7) and the first 8 specimens of the Dense Select Structural untreated controls (Group 1)), a bent sensor stem in a linear variable differential transformer (LVDT) deflection-measuring device caused an intermittent malfunction. This seriously impaired our confidence in the acquired center-span deflection data. Because we could not resolve signal error from real deflection measurements in the deflection data for the 68 specimens, we did not calculate MOE, Dmax, and WML for those specimens.

After mechanical testing, two 25-mm (l-in.) wafers were cut from an undamaged section near the failure location. One wafer was used for determining specific gravity and MC at time of test and the second wafer for CC-treatment analysis.

RETENTION ANALYSIS

For each group, specimens were sorted from lowest to highest density and a 25-mm wafer from the bending test specimens representing the 10th, 25th, 48th, 50th, 52nd, 75th, and 90th density percentiles of that group were selected for CC-treatment assay. These wafers were bored using a 12-mm (1/2 -in.) drill bit, and all the shavings were collected from an outer 15-mm (0.6 -in.) CC-treated assay zone. The drilled shavings were collected and combined from both the tension and compression sides of the bending test specimens.

DATA ANALYSIS

To determine the significance of the differences in bending property results from the various treatments and/or redrying scenarios, the mechanical test data were analyzed using analysis of covariance. Verrill and Green (10) recently repot-ted that newer analytical methods are available for randomly assigned experimental data with limited replicates. However, they also reported that for experimental data assigned to groups based on a predictor variable (recall that we measured and used transverse MOE (E-sort) for each specimen to sort the specimens into groups), analysis of covariance and the new Tight T-test methodology yield similar findings.

RESULTS AND DISCUSSION

Results from CC treatment based on gross uptake and atomic absorption spectrometry (AAS) are summarized in **Table 3.** Mean, standard deviation, and non parametric percentile estimates for E-sort, MOE, MOR, WML, and Dmax are presented in **Tables 4** to 8, respectively. Specific gravity and MC measurements at time of mechanical testing are given in **Table 5.**

We also kept track of rank within the 7 groups of 60 specimens. This blocking variable was then used as a covariant in statistical analysis of covariance when testing differences between groups of comparable grade. The results of a series of statistical analyses of group means are given in **Table 9.** This tabulation describes the correlation between factors (r^2), residual error (root mean square error), and results of Tukey 's comparative test of means.

RETENTION

For each group, assay retention based on AAS analysis **(Table 3)** was lower than comparable retention based on gross uptake of CC-treatment solution. This difference may have resulted from end-grain penetration, which would not

TABLE 3. — Comparative preservative retentions by gross uptake of solution and atomic absorption spectrometry.[a]

Group	Grade[b]	Type of redry	Retention (kg/m^3) Target	Gross absorption	AAS[c]
2	DSS	Air	40	49.3	35.2
3	DSS	Air	6.4	7.2	5.9
4	DSS	Kiln	6.4	6.1	5.1
5	No. 2	Kiln	6.4	5.8	5.0
6	No. 2	Air	6.4	7.4	5.6

[a] All 60 specimens were sampled in gross uptake, but only 10 were sampled in AAS.

[b] DSS = Dense Select Structural.

[c] AAS assay zone was outer 0 to 15 mm (0 to 0.6 in.) zone.

TABLE 2. — Post-treatment kiln-drying schedule.[a]

Time	Dry-bulb temperature		Wet-bulb depression		Wet-bulb temperature		Relative humidity	EMC
(hr.)	(°C)	(°F)	(°C)	(°F)	(°C)	(°F)	- - - - - - - - - (%) - - - - - - - - -	
0 to 24	49	120	6	10	43	110	72	12.1
24 to 28	54	130	8	15	46	115	62	9.7
48 to 72	60	140	11	20	49	120	54	8.0
72 to 96	66	150	17	30	49	120	41	5.8

[a] Specimens were kiln-dried to an average moisture content of 19 to 20 percent, with six sample boards ranging from 16 to 23 percent. Lumber was then conditioned to 12 percent equilibrium moisture content conditions (23°C (74°F)/65% RH). The effect of kiln-drying was evaluated only for specimens treated to 6.4 kg/m^3 (0.4 pcf); the higher retention boards were air-dried only.

been detected in assay samples that were sampled from the midlength of the board. Fortunately, although the CC-treated 2 by 4 lumber may have been slightly undertreated, this probably had little impact on the objectives of this experiment because past work had shown that retention differences in the 4.0-to 9.6-kg/m^3 (0.25 - to 0.6-pcf-) range had no significant differential effect on the strength properties of treated wood (11,12). Comparison of assay and uptake retention across a range of densities revealed little direct relationship between density and retention for either CC retention level.

EFFECTS OF CC TREATMENT ON BENDING PROPERTIES

To evaluate the comparative effects of CC treatment on mechanical properties to matched untreated controls, we calculated a simple equal-rank statistic, called the X-ratio. For any mechanical property (X), the X-ratio at the 25th percentile is the ratio of the 25th percentile X-value for any particular CC-treated group to the comparable 25th percentile X-value for its grade-matched untreated control group. For example, if the particular 25th percentile MOR value for a CC-treated group was 40 MPa (5,850 psi) and the 25th percentile MOR value for the untreated control group was 50 MPa (7,250 psi), then the MOR ratio at the 25th percentile would be 0.80. We calculated X-ratios for each mechanical property (E-sort, MOE, MOR, WML, and Dmax) across the property distribution (10th, 25th, 50th, 75th, and 90th percentiles) for each treated group. We then used X-ratios to compare the strength effects for any group to that for its untreated control.

E-sort. — Our decision to use a predictor variable to sort lumber into experimental groups (rather than random allocation) was very effective in that the between-group variation in transverse vi-

TABLE 4. — E-sort/pre-experimental evaluation of transverse vibrational MOE.[a]

Group	CC	Type of redry	Grade	MOE Mean	MOE SD[b]	5th	10th	25th	50th	75th	90th	95th
						MOE at various percentiles						
	(kg/m^3)			(GPa)								
1	None	None	DSS	13.1	2.28	9.10	10.5	11.4	13.0	15.0	16.6	17.0
3	6.4	Air	DSS	13.1	2.28	9.44	10.1	11.5	13.1	14.6	16.1	17.4
4	6.4	Kiln	DSS	13.2	2.34	9.10	10.3	11.7	12.9	14.4	16.5	17.6
2	40	Air	DSS	13.2	2.41	9.31	10.3	11.4	12.9	14.8	17.0	17.5
7	None	None	No. 2	9.24	1.86	6.14	6.83	7.86	9.38	10.5	11.7	12.1
6	6.4	Air	No. 2	9.31	1.86	6.34	6.96	8.00	9.03	10.8	12.0	12.4
5	6.4	Kiln	No. 2	9.24	1.93	6.14	6.83	7.93	8.96	10.7	12.2	12.6

[a] 1 kg/m^3 = 0.063 pcf; 1 GPa = 1.45 × 10^5 psi.

TABLE 5. — MOE, specific gravity, and moisture content by group at time of test.

Group	CC	Type of redry	Grade	MOE Mean	MOE SD[a]	10th	25th	50th	75th	90th	SG	MC
						MOE at various percentiles						
	(kg/m^3)			(GPa)								(%)
1	None	None	DSS	13.2	2.21	10.1	11.2	12.8	14.8	17.4	0.54	11.7
3	6.4	Air	DSS	13.0	2.21	10.3	11.4	13.0	14.6	16.1	0.53	13.7
4	6.4	Kiln	DSS	13.2	2.41	9.72	11.4	13.2	15.0	16.0	0.54	13.7
2	40	Air	DSS	14.3	2.41	11.3	12.8	14.4	16.6	17.4	0.55	13.7
7	None	None	No. 2	--	--	--	--	--	--	--	0.44	9.9
6	6.4	Air	No. 2	8.34	2.14	5.38	6.76	8.48	9.93	10.7	0.45	12.6
5	6.4	Kiln	No. 2	7.51	2.28	4.76	6.07	7.65	8.55	11.2	0.44	12.9

[a] SD = standard deviation.

TABLE 6. — Evaluation of modulus of rupture (bending strength).

Group	CC	Type of redry	Grade	MOR Mean	MOR SD[a]	10th	25th	50th	75th	90th
						MOR at various percentiles				
	(kg/m^3)			(MPa)						
1	None	None	DSS	80.0	14.4	65.1	72.5	81.0	89.7	98.8
3	6.4	Air	DSS	76.0	12.1	57.2	68.0	77.4	84.5	93.5
4	6.4	Kiln	DSS	74.5	14.3	52.6	65.2	76.1	84.8	91.9
2	40	Air	DSS	77.4	18.8	55.4	65.0	81.6	91.2	99.2
7	None	None	No. 2	38.6	13.3	24.5	29.2	37.2	49.2	56.1
6	6.4	Air	No. 2	33.3	12.3	18.4	23.1	32.1	44.1	50.9
5	6.4	Kiln	No. 2	34.8	13.9	16.2	25.1	33.0	44.1	53.9

[a] SD= standard deviation.

TABLE 7. — Evaluation of work to maximum load.

Group	CC	Type of redry	Grade	WML Mean	WML SD[a]	WML at various percentiles 10th	25th	50th	75th	90th
	(kg/m^3)			(kJ/m^3)						
1	None	None	DSS	80.7	37.9	31.7	51.0	82.7	104	123
3	6.4	Air	DSS	75.1	35.2	31.7	52.4	68.3	88.2	118
4	6.4	Kiln	DSS	66.2	32.4	25.5	40.7	57.9	95.1	116
2	40	Air	DSS	53.8	24.8	24.8	35.2	53.1	69.6	81.4
7	None	None	No. 2	- -	- -	- -	- -	- -	- -	- -
6	6.4	Air	No. 2	16.6	11.7	6.20	6.89	11.7	21.4	33.8
5	6.4	Kiln	No. 2	23.4	20.0	6.20	11.0	19.3	28.3	42.7

[a] SD = standard deviation.

TABLE 8. — Evaluation of maximum center-span deflection in bending.

Group	CC	Type of redry	Grade	Dmax Mean	Dmax SD[a]	Dmax at various percentiles 10th	25th	50th	75th	90th
	(kg/m^3)			(mm)						
1	None	None	DSS	1.42	0.48	0.79	1.09	1.45	1.65	1.96
3	6.4	Air	DSS	1.37	0.38	0.84	1.09	1.32	1.63	1.85
4	6.4	Kiln	DSS	1.27	0.41	0.76	0.97	1.17	1.55	1.93
2	40	Air	DSS	1.04	0.28	0.69	0.86	1.04	1.17	1.35
7	None	None	No. 2	- -	- -	- -	- -	- -	- -	- -
6	6.4	Air	No. 2	0.74	0.25	0.41	0.48	0.71	0.91	1.12
5	6.4	Kiln	No. 2	0.94	0.43	0.46	0.64	0.89	1.22	1.35

[a] SD = standard deviation.

TABLE 9. — Statistical analysis.[a]

Property	Covariable used	Dense Select Structural r^2	RMSE	LSΔ[b]	No. 2 r^2	RMSE	LSΔ[b]
Pmax	None	0.02	741.7	1 2 3 4	- -	- -	- -
	E-sort	0.37	596.5	1 2 3 4	0.26	568.4	7 5 6
	SGT	0.34	610	1 3 2 4	0.19	595.6	7 5 6
	SGS	0.30	629	2 1 3 4	0.17	603.6	7 5 6
MOR	None	0.02	2,190	1 2 3 4	0.03	1,910	7 5 6
	E-sort	0.30	1,859	1 2 3 4	0.25	1,678	7 5 6
	SGT	0.32	1,824	1 3 2 4	0.19	1,748	7 5 6
	SGS	0.29	1,862	2 1 3 4	0.17	1,771	7 5 6
MOE	None	0.05	0.349	2 1 4 3	0.03	0.317	6 5
	E-sort	0.71	0.191	2 1 4 3	0.40	0.251	6 5
	SGT	0.23	0.308	2 1 3 4	0.17	0.297	6 5
	SGS	0.26	0.301	2 4 3 1	0.12	0.305	6 5
WML	None	0.09	4.76	1 3 4 2	0.04	2.36	5 6
	E-sort	0.10	4.74	1 3 4 2	0.13	2.27	5 6
	SGT	0.19	4.49	1 3 4 2	0.17	2.20	5 6
	SGS	0.17	4.55	1 3 4 2	0.18	2.19	5 6
Dmax	None	0.13	0.016	1 3 4 2	0.08	0.014	5 6
	E-sort	0.15	0.015	1 3 4 2	0.08	0.014	5 6
	SGT	0.17	0.015	1 3 4 2	0.11	0.014	5 6
	SGS	0.15	0.015	1 3 4 2	0.12	0.014	5 6

[a] Pmax = maximum gross load at failure; r^2 = coefficient of regression; RMSE = root mean square error; LSΔ = least significant difference. Groups sharing the same line are not significantly different at the 5 percent level of significance using Tukey's test.

[b] Numbers correspond to treatment group, as defined in **Tables 3** to **8**.

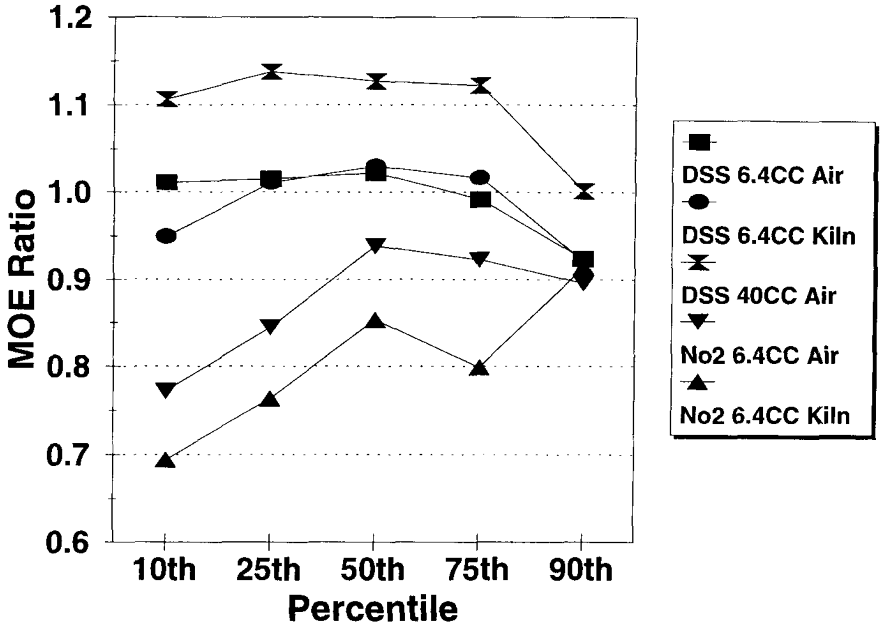

Figure 1. — Ratio of modulus of elasticity (MOE) of each treated Dense Select Structural group to MOE of comparably E-matched untreated control and to MOE of original pretreatment E-sorted No. 2 grade material.

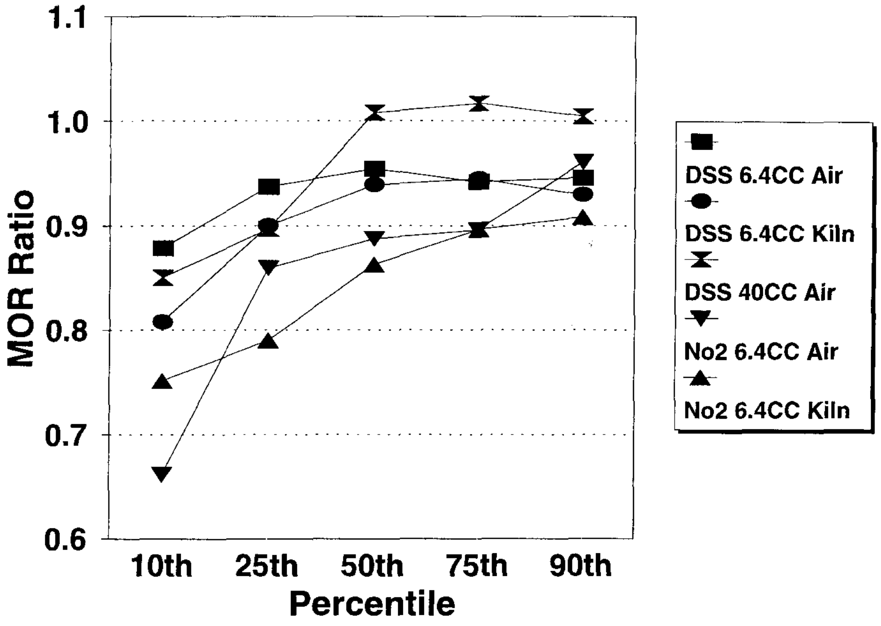

Figure 2. — Ratio of modulus of rupture (MOR) of each treated group to MOR of comparably E-matched untreated control.

brational MOE (E-sort) was less than 5 percent, which is less than might be expected for randomly assigned material. Further, when comparing the variation in E-sort across the distribution of any group to that across any other group, that variation appeared rather random because often, a particular E-sort value for one group might be higher than others at some percentile level and then lower than many or most others at the next percentile level **(Table 4).** Thus, the E-sort method eventually yields significantly more power to subsequent statistical analysis.

Modulus of elasticity. — The MOE of Dense Select Structural 2 by 4 lumber was unaffected by the targeted 6.4-kg/m^3 CC-treatment retention at either level of redrying **(Table 9).** However, at the much heavier 40-kg/m^3 treatment retention, the MOE of CC-treated lumber did significantly increase **(Fig. 1).** Because WML was also simultaneously diminished **(Table 7),** this would suggest embrittlement from CC treatment at marine retention levels. This same embrittling effect was previously noted for other waterborne preservative treatments at heavy marine-use retention levels (8).

Recall that deformation data were lost for the No. 2 grade untreated control group; thus, it was impossible to calculate true MOE ratios (or WML or Dmax ratios) for the No. 2 grade lumber. To obtain some insight into the MOE relationships for the No. 2 grade CC-treated groups (Group 6 (air-dried) and Group 5 (kiln-dried), **Table 3),** we compared each group using its original E-sort values **(Fig. 1).** Although direct qualitative comparisons were somewhat compromised because of the lost MOE data for the No. 2 grade controls, using the pre-treatment E-sort provided a direct comparative basis for noting the trends. There was a statistically significant difference in mean MOE of the No. 2 grade CC-treated specimens, between material air-dried and material kiln-dried after treatment **(Table 9).** Overall, when comparing the two grades of lumber, it appears that CC-treated No. 2 grade material may have experienced a greater reduction in MOE through the lower regions of the MOE distribution (especially when kiln-dried after treatment) when compared to Dense Select Structural material **(Fig. 1).** This difference between grades in the effect of CC treatment on MOE appears to be less for the central and upper regions of the MOE distribution compared to the lower region.

Modulus of rupture. — The bending strength of Dense Select Structural lumber was slightly reduced by CC treatment and various redrying scenarios **(Fig. 2).** In some cases, these reductions in average MOR were significant **(Table 9).** The results for the CC-treated Dense Select Structural lumber followed previously noted trends for high quality CCA-treated lumber in that greater reductions in MOR occurred throughout the lower percentile regions of the bending strength distribution than in the central-to-upper regions (4). The reduction in average MOR was around 5 percent for lumber treated at the targeted 6.4-kg/m^3 CC retention and dried by either method (Groups 3 and 4, **Table 6).** While greater than 75 percent of this CC-treated material experienced less than a 10 percent strength loss, MOR was reduced 12 percent for Group 3 (air-dried) and about 18 percent for Group 4 (kiln-dried) at the 10th percentile MOR level **(Fig. 2).** Also, note that the targeted 40-kg/m^3 group (Group 2) experienced little loss in bending strength **(Table 6),** an increase in MOE **(Table 5),** and a 30 to 35 percent reduction in WML **(Table 7).** Furthermore, this material appeared to generally fail in a slightly brasher manner than did the targeted 6.4-kg/m^3 CC-treated lumber. This exemplifies the embrittling effect noted earlier for MOE at this heavy marine-use retention level of CC. Similar embrittlement has been previously noted with other waterborne preservative treatments (8).

The No. 2 grade material uniformly experienced a greater reduction in bending strength compared to comparably treated and redried Dense Select Structural lumber, especially in the lower regions of the bending strength distribution **(Fig. 2).** This trend was decidedly different than that noted in previous work with CCA-treated No. 2 grade material (11, 12), but not too dissimilar in magnitude to strength losses reported for high quality defect-free ACQ-treated lumber (6). The basic relationship between grade-to-treatment effects might be inherently different for ammoniacal copper-based preservatives than for acid-based treatments (i.e., CCA-A and CCA-C). The difference in bending strength could be related to the increased swelling/shrinkage induced by water-ammonia treatments. More work is needed to elaborate on these issues.

Work to maximum load and Dmax. — For the Dense Select Structural lumber, the targeted 6.4-kg/m^3 CC-treated groups generally experienced less than 25 and 20 percent loss in WML and Dmax, respectively **(Tables 7** and **8).** These results are comparable to results with CCA treatments. Loss in WML was greater for the targeted 40-kg/m^3 CC-treated material than the targeted 6.4-kg/m^3 material, but generally comparable to effects previously noted for CCA-treated clearwood at heavy marine retentions.

As previously noted, interpretation of CC treatment effects on WML and Dmax was greatly impaired for the No. 2 grade lumber because of the loss of deformation data from the No. 2 grade untreated control group. ***However, the comparative*** trends between the air-redried group and the kiln-redried group appear stable across both the WML and Dmax distributions **(Tables 7** and **8).**

Comparison of copper citrate and other waterborne preservatives. — It is informative to compare these data on CC treatment effects to comparable data de-

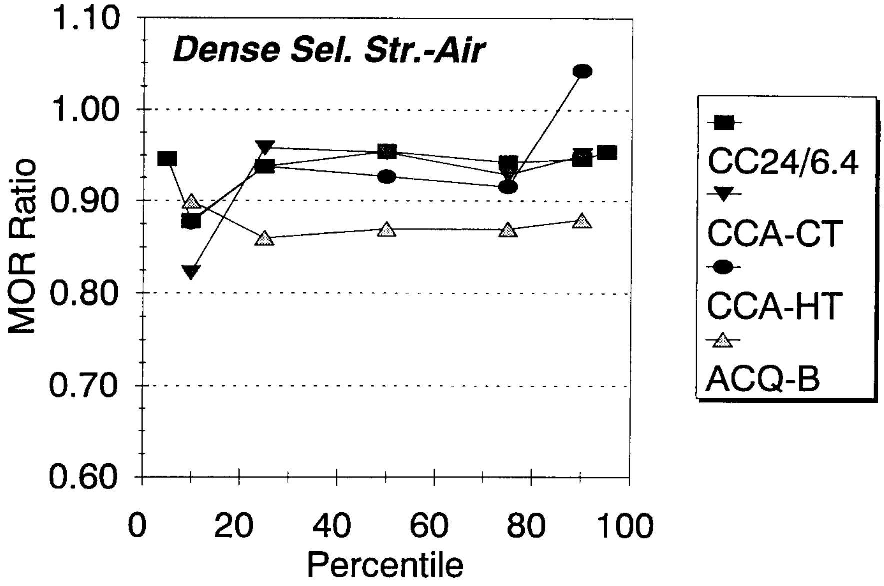

Figure 3. — MOR ratio across distribution for CC-treated air-dried Dense Select Structural specimens (CC24) compared to MOR of specimens treated with CCA-C and redried at conventional (91°C (196°F)) (CCA-CT) and high (116°C (240°F)) (CCA-HT) temperatures (5) and specimens treated with ACQ-B (6).

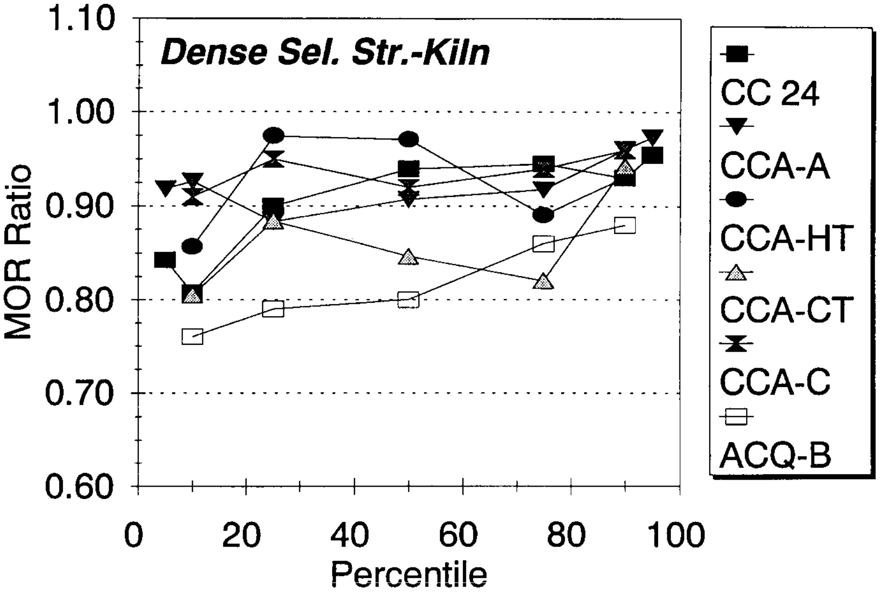

Figure 4. — MOR ratio across distribution for CC-treated kiln-dried Dense Select Structural specimens compared to MOR of specimens treated with CCA-A (4), CCA/redried at conventional temperature (CCA-CT) or high temperature (CCA-HT) (5), and CCA-C and ACQ-B (6).

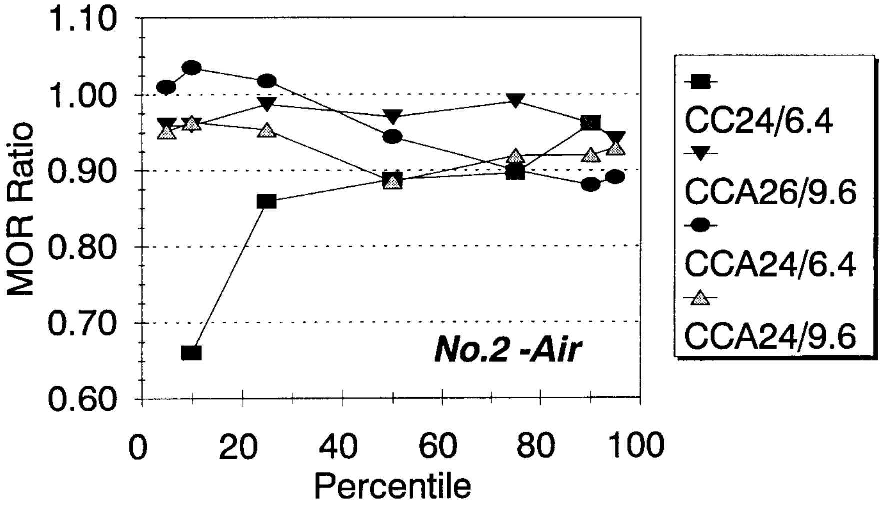

Figure 5. — MOR ratio across distribution for CC-treated air-dried No. 2 grade specimens (CC24) compared to specimens treated with CCA26/9.6 (12) and CCA24/6.4 and CCA24/9.6 (11).

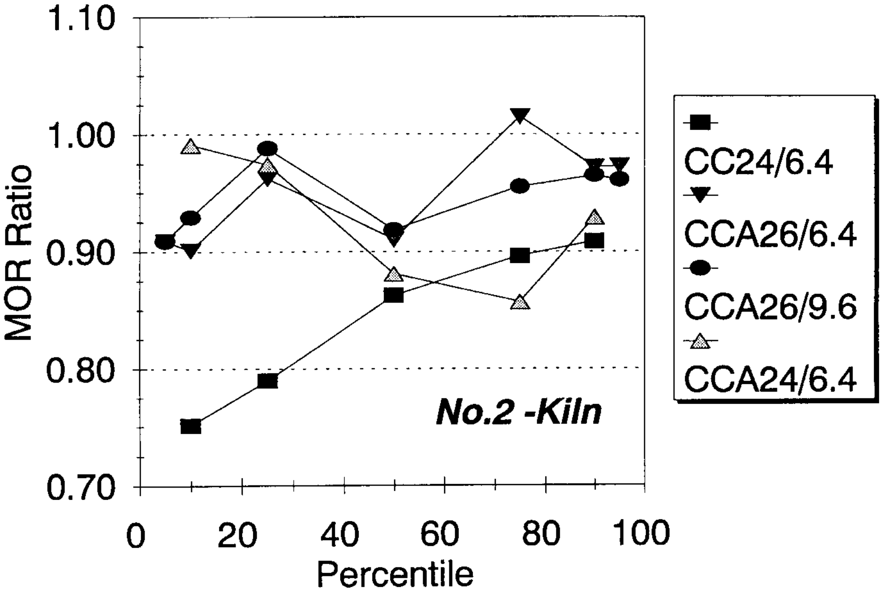

Figure 6. — MOR ratio across distribution for CC-treated kiln-dried No. 2 grade specimens (CC24) compared to specimens treated with CCA26/6.4 and CCA26/9.6 (12) and CCA24/6.4 (9).

rived in previously reported studies of CCA- and ACQ-treatment effects (4-6,9,11, 12). Such comparisons are shown for each grade-redrying combination in **Figures 3** to **6.** It must be remembered that because of the large differences in sample sizes between this study on CC treatment effects and some previous studies (sometimes approaching 4 to 1), we must be careful to not overanalyze the "treatment effect" below the 25th percentile.

In **Figures 3** and **4,** the MOR data from our tests on Dense Select Structural CC-treated lumber (60 replicates per group) are compared to data from 3 different studies on treated Dense Select Structural 2 by 4 southern pine lumber:

1. Lumber treated with ACQ-B or CCA-C, 50 replicates per group (6).
2. Lumber treated with CCA-C and kiln-dried after treatment at 88°C (190°F), 100 replicates (4).
3. Lumber treated with CCA-C and kiln-dried before treatment using conventional (91°C (196°F)) or high temperature (116°C (240°F)) kiln schedules, 92 and 101 replicates, respectively (5).

For the material air- or kiln-dried after treatment, the effects of CCA treatment are very similar to those of CC treatment **(Figs. 3** and **4).** Also note that the CC treatment effects are generally less than those reported for defect-free specimens treated with ACQ-Type B, which is probably more related to a difference in lumber quality than to an actual difference in preservative effect.

In **Figures 5** and **6,** the MOR data from our tests on No. 2 grade CC-treated lumber are compared to data from three different studies on treated No. 2 grade southern pine lumber of different sizes:

1. Nominal 2- by 6-in. (actual 38- by 89-mm) lumber treated to 6.4 kg/m^3 or 9.6 kg/m^3 with CCA and air- or kiln-dried after treatment, 192 specimens (12).
2. 2 by 4 lumber treated to 6.4 kg/m^3 or 9.6 kg/m^3 with CCA and air-dried after treatment, 164 specimens (11).
3. 2 by 4 lumber treated to 6.4 kg/m^3 with CCA and kiln-dried after treatment, 50 specimens (9).

For the No. 2 grade material, the effects of CC treatment are noticeably greater than the effects of comparable CCA treatment at the 25th percentile of the bending strength distribution (< 50th percentile) and generally equivalent at or above the 50th percentile **(Figs. 5** and **6).** As stated earlier, since there are no other comparable data on the effects of ammoniacal-copper treatment for No. 2 grade material, definitive recommendations are probably premature. As the popularity of systems based on ammoniacal copper increases, this phenomenon of greater strength loss with No.2 grade treated lumber deserves additional study with CC and other ammoniacal-copper preservatives.

Finally, additional work is needed to fully define the effects on water-ammonia treatment and to define the effects on lumber properties of amine-copper preservatives that have not as yet been investigated.

CONCLUSIONS

The effects of CC preservative treatment on several mechanical properties were generally found to be similar to previous results for CCA and/or ACQ preservative treatments. The strength effects for higher quality lumber, such as the Dense Select Structural material used in this study, were very similar to results from previous studies on CCA treatment effects. However, the strength effects for lower quality No. 2 grade material were greater than those from previous studies on CCA treatment effects. No comparative data for No. 2 grade material were available for other ammoniacal copper-based systems. As the popularity grows for arsenic-free ammoniacal copper-based systems in the United States, this unexplained phenomenon of increased strength loss when No. 2 grade lumber is treated with ammoniacal copper preservatives will require additional study.

LITERATURE CITED

1. American Society for Testing and Materials. 1995. Standard test method for mechanical properties of lumber and wood-based structural material. D 4761-93. ASTM Book of Standards, Vol. 4.10. ASTM, West Conshohocken, Pa.
2. American Wood Preservers' Association. 1995. Standard for waterborne preservatives. P5-95, Section 16. AWPA Book of Standards. AWPA, Woodstock, Md.
3. Anderson, T.C., R.D. Inwards, R.M. Leach, W.S. McNamara, M.M. Richards, A.D. Williams, and R.J. Ziobro. 1993. Proposal for the standardization of ammoniacal copper citrate. Submitted to AWPA Committee P4 and the General Preservatives Committee. Osmose Wood Preserving, Inc., Buffalo, N.Y.
4. Barnes, H.M. and P.H. Mitchell. 1984. Effects of post- treatment drying schedule on the strength of CCA-treated southern pine dimension lumber. Forest Prod. J. 34(6):29-33.
5. ________, J.E. Winandy, and P.H. Mitchell. 1990. Effect of initial and post-treatment drying on the bending properties of CCA-treated southern pine. J. of Inst. of Wood Sci. 11(6):222- 230.
6. _________, D.E. Lyon, A.R. Zahora, and F. Muisu. 1993. Strength properties of ACQ-treated southern pine lumber. *In*: Proc. American Wood Preservers' Assoc. 88:51-60.
7. Bendtsen, B.A., L.R. Gjovik, and S. Verrill. 1983. The mechanical properties of salt-treated longleaf pine. Res. Pap. FPL-434. USDA Forest Serv., Forest Prod. Lab., Madison, Wis.
8. Eaton, M.L., J.A. Drelicharz, and F. Roe, Jr. 1978. Mechanical properties of preservative treated marine piles — Results of limited full-scale testing. U.S. Naval CEL Tech. Note N-1535, Port Hueneme, Calif.
9. Soltis, L.A. and J.E. Winandy. 1989. Long-term strength of CCA-treated lumber. Forest Prod. J. 39(5):64-68.
10. Verrill, S. and D.W. Green. 1997. Predictor sort sampling, Tight T's, and the analysis of covariance: theory, tables, and examples. Res. Pap. FPL-558. USDA Forest Serv., Forest Prod. Lab., Madison, Wis.
11. Winandy, J.E. 1989. CCA preservative treatment and redrying effects on the bending properties of 2 by 4 southern pine. Forest Prod. J. 39(9):14-21.
12. __________ and R.S. Boone. 1988. The effects of CCA preservative treatment and redrying on the bending properties of 2 by 6 southern pine lumber. Wood and Fiber Sci. 20(3):350-364.