

KINETIC MODEL OF CCA FIXATION ON WOOD. PART III. MODEL VALIDATION

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ABSTRACT

In previous studies, models were developed for the initial and main fixation reactions of chromated copper arsenate (CCA-C) on red pine wood as a function of time and isothermal wood temperature conditions following treatment with 1% CCA-C. In this study, these models are used to predict the amount of fixation over sequential short non-isothermal intervals as a way of predicting time to total fixation under variable temperature conditions. The rate of fixation of CCA-C treated red pine pole sections could generally be accurately predicted, using these models, from thermocouple temperature readings in the pole surface, even under a highly variable temperature fixation regime. However, variations in fixation rate were observed even within a single pole, associated with density differences at the butts and tops of the poles. This confirms that fixation time estimates are very sensitive to the model parameters and suggests that the model may not accurately predict fixation rates over a wide range of material sources.

Keywords: Chromated copper arsenate (CCA-C), fixation, *Pinus resinosa* Ait., model, initial reaction, main reaction, kinetics, validation.

INTRODUCTION

Chromated copper arsenate (CCA) preservative reacts with wood components following a series of complex temperature-dependent reactions (Wilson 1971; Dahlgren and Hartford 1972a, b, c; Pizzi 1982; Anderson 1989). CCA components remain somewhat soluble in wood until the fixation reactions are complete. Since the fixation of chromium is slower than that of arsenic and copper (Cooper et al. 1993), the presence of hexavalent chromium (Cr^{VI}) is used as an indicator of CCA fixation on wood. Chromium reduction in wood fol-

lows two reaction zones (Pizzi 1982; Dahlgren 1975), usually designated "initial" and "main" reactions. In red pine (*Pinus resinosa* Ait.), initial reactions are rapid and follow high-order kinetics (Kazi and Cooper 2000). The slow main reactions follow first-order kinetics and take several hours or even weeks to finish, depending on reaction temperatures (Kazi et al. 2000; Alexander and Cooper 1993). A third "conversion" reaction period may extend several weeks after chromium reduction is complete (Dahlgren 1974).

Many treating plants have installed high-temperature fixation chambers to accelerate and control the fixation rate. Chromium fixation is monitored by qualitative or quantitative

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analysis of unreduced chromium (Foster 1988; McNamara 1989; Cooper and Ung 1989, 1993). Mathematical models were developed to predict the percentage of fixation during the initial (Kazi and Cooper 2000) and main reaction (Kazi et al. 2000) as a function of isothermal temperature conditions and fixation time. Adaptation of these models to non-isothermal conditions should provide a methodology for remote monitoring of the fixation of a charge of treated wood based on continuous wood temperature measurement following treatment. This approach has the following advantages over traditional methods of monitoring fixation:

- Feedback is immediate and continuous and the fixation status is known at any time, whatever the temperature and humidity conditions the wood is exposed to, eliminating the time delay for sampling and analysis of hexavalent chromium;
- Temperature probes can be installed while stacking material for treatment or fixation, making it possible to monitor fixation of inaccessible wood such as boards deep in a bundle or stack;
- In high-temperature fixation chambers, there is no need for the operator to enter the chamber to conduct tests, reducing operator exposure to the kiln conditions and heat loss from the chamber;
- The fixation status is computed continuously, allowing for control of the system such as automatic shut-off when fixation is complete or nearly complete or conversion to drying conditions in the chamber.

The objective of this study was to evaluate the ability of fixation models to predict fixation rate in red pine pole samples under non-isothermal temperature conditions.

DESCRIPTION OF THE MODEL

The temperature-dependent kinetic models relate unreduced chromium to the time and temperature history of the wood following pressure treatment. Mathematically, the kinetic behavior of fixation reactions can be effec-

tively described as the rate of change in Cr^{VI} concentration with time t as:

$$-\frac{d\text{Cr}}{dt} = k[\text{Cr}]^n \quad (1)$$

where Cr is the Cr^{VI} concentration, k is the reaction rate constant, and n is the order of the reaction. The integrated form of Eq. (1) for $n = 1$ is:

$$\text{Cr}_t = \text{Cr}_i e^{-kt} \quad (2)$$

and for $n \geq 2$ is:

$$\left(\frac{1}{\text{Cr}_t}\right)^{n-1} = \left(\frac{1}{\text{Cr}_i}\right)^{n-1} + (n-1)kt \quad (3)$$

where Cr_i is the initial hexavalent chromium concentration and Cr_t is the concentration in the wood at time t . At the start of the fixation process, Cr_i is the Cr^{VI} concentration in the treating solution ($= \text{Cr}_0$); for evaluations at subsequent times, where small time increments are evaluated to account for changing temperature conditions, it is the concentration at the beginning of the time increments.

The temperature-dependence of the rate constant, k , can be expressed by the Arrhenius equation as:

$$k = k_0 e^{-E/RT} \quad (4)$$

where E is the activation energy, R the universal gas constant, T the temperature in Kelvin, and k_0 the pre-exponential factor.

The percentage of CCA fixation (F_t) at any time is defined by:

$$F_t (\%) = \frac{\text{Cr}_0 - \text{Cr}_t}{\text{Cr}_0} \times 100 \quad (5)$$

where Cr_0 is the hexavalent chromium concentration in the original treating solution.

APPLICATION OF THE MODEL

In parts 1 and 2 of this study (Kazi and Cooper 2000; Kazi et al. 2000), the three relevant equations (Eqs. 3,4,5 for the initial reaction and Eqs. 2,4,5 for the main reaction) were combined into single models to predict

TABLE 1. Parameters describing the initial and main fixation reaction zones for red pine treated with 1.0% CCA-C (Kazi and Cooper 2000; Kazi et al. 2000).

Reaction zone	Apparent reaction order	k_0	E (kJ/mol)	E/R	% Fixation in each zone
Initial zone	10	8.7×10^{-19} ($\text{h}^{-1} \cdot \text{mol}^{-9} \cdot \text{l}^9$)	37.8	4545	47
Second or main zone	1	2.7×10^{13} (h^{-1})	87.6	10536	53

% fixation in the two reaction zones as a function of elapsed time and temperature of the wood. For non-isothermal fixation conditions, it is easier to solve the equations sequentially, for example using a spread sheet. The steps to be taken to apply the model to wood undergoing accelerated fixation are as follows:

1. Determine the necessary parameters, including length of the initial fixation period, apparent reaction order, and Arrhenius constants for the two reaction zones for the treating conditions by experiment. For 1% CCA-C treatment of red pine sapwood, the relevant factors are shown in Table 1 (Kazi and Cooper 2000; Kazi et al. 2000).
2. Establish the initial Cr^{VI} concentration, C_0 , in the treating solution (by analysis or from the known solution formulation); this was determined to be 2450 ppm for the 1% CCA-C solution used.
3. Monitor the wood temperature at the depth of interest at predetermined measuring intervals ($\Delta t = t_j - t_i$) with a thermocouple or other temperature probe and record the wood temperature at the start and end of the time interval (T_i and T_j in K).
4. Calculate the estimated Cr^{VI} concentrations at different times t during the *initial* reaction period using the model Eq. (6), which combines Eqs. (3) and (4) and applies the appropriate values from Table 1. This equation estimates the Cr^{VI} concentration in the wood at the end of the time interval Δt (hours) using the average rate constant value over the corresponding

temperature change on the interval (Ayres 1964):

$$\left(\frac{1}{\text{Cr}_t}\right)^9 = \left(\frac{1}{\text{Cr}_i}\right)^9 + 9 \times 8.7 \times 10^{-19} \Delta t \left(\frac{e^{-4545/T_j} + e^{-4545/T_i}}{2}\right) \quad (6)$$

5. Calculate the estimated Cr^{VI} concentrations at different times t during the *main* reaction period using the model Eq. (7), which combines Eqs. (2) and (4) and applies the appropriate values from Table 1:

$$\text{Cr}_t = \text{Cr}_i \exp \left[-2.7 \times 10^{13} \Delta t \left(\frac{e^{-10536/T_i} + e^{-10536/T_j}}{2} \right) \right] \quad (7)$$

Note that Cr_i in Eqs. (6) and (7) is the Cr^{VI} concentration in the wood at the beginning of the time increment Δt , i.e., the concentration estimated for the end of the previous time increment.

6. Apply the Cr_t value to Eq. (5) to estimate the cumulative % fixation at that time.

MATERIALS AND METHODS—MODEL VALIDATION

To evaluate the appropriateness of the fixation models, 0.5m-long red pine pole sections were evaluated. Four samples were cut from pole tops and four from pole butts from eight different poles. The pole sections were treated one at a time with 1.0% CCA-C solution at room temperature in a pressure treating chamber (20 min initial vacuum at 21 KPa absolute pressure, followed by 60 min at 700 KPa pressure). A thermocouple was inserted into the pole approximately 5 mm from the surface, and the temperature was recorded using a digital thermocouple (HOBO of Onset Computer Corporation, H08-007-02). The pole sections were subjected to either isothermal or non-isothermal fluctuating temperature schedules in a controlled temperature chamber, where the fixation temperature was varied from -10 to

70°C. During fixation, 10-mm-deep core samples were taken periodically with a 19-mm-diameter plug-cutter. The samples were squeezed in a press at 60 MPa to express treating solution from the wood void space. The expressate was analyzed for unfixed Cr^{VI} in the solution using the diphenylcarbazide method (Coggins and Hiscocks 1978) using a Shimadzu, UV-16 spectrophotometer set at a wavelength of 540nm and the % fixation determined using Eq. (5).

Every 6 min during the fixation schedule, the wood temperature was automatically recorded, and these data were used to estimate the amount of fixation at the end of the interval predicted from the model Eqs. (5), (6), and (7). The initial reaction model (Eq. 6) was applied until the predicted fixation was 47% of total (about 2.5 h after treatment) and subsequently the main reaction model (Eq. 7) was applied. Percent fixation with time through the schedule was plotted at these 6-min intervals to provide the predicted fixation curve. Actual fixation measurements were then compared with the predicted values.

Preliminary results showed considerable differences in results for some pole tops and pole butts, apparently as a result of different wood densities. This was validated using small sapwood cubes (25 × 25 × 25 mm) sawn from the pole sections that showed the greatest discrepancies (top and butt samples). The basic relative densities of the butt and the top sections were 0.47–0.48 and 0.38–0.40, respectively. The samples were conditioned in a saturated environment to about 20% moisture and treated with a 1% CCA-C solution in a pressure treating chamber (20 min initial vacuum at 21 KPa absolute pressure, followed by 10 min at 700 KPa pressure). The blocks were then kept in a plastic bag in a conditioning chamber at 30°C. Two replicate blocks from the top and butt samples were periodically taken out and squeezed in a press at 60 MPa to express treating solution from the wood void space. The expressate was analyzed for Cr^{VI} concentration as above to compare fixation rates as affected by wood density.

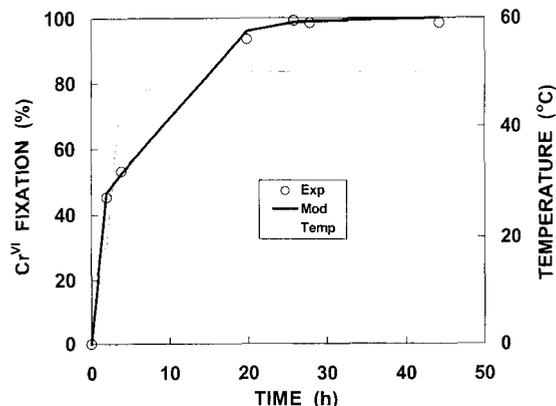


FIG. 1. Predicted and actual fixation status for red pine pole top section exposed to approximately isothermal high-temperature conditions.

RESULTS AND DISCUSSION

Figures 1–8 show the wood temperature variation to which the pole samples were subjected for different fixation schedules and the resulting predicted fixation rate curve and measured fixation status at various times during fixation. In all cases, the predicted fixation rate, based on the model, showed rapid fixation to the end of the initial reaction period (47% of total chromium reduction). Fixation in the main reaction zone proceeded slowly, with steep and flat zones corresponding to high and low wood temperature conditions, respectively.

The essentially isothermal moderately high-temperature fixation schedules (Figs. 1 and 2) resulted in rapid fixation once the chamber reached maximum temperature, and the model predicted fixation rate accurately for both pole top and butt samples (r^2 for predicted vs. measured > 0.985). Similarly, the model predicted the fixation rate very well for more complex temperature cycling from ambient to 50–60°C (Fig. 3— $r^2 = 0.98$). When the cycling ranged from freezing temperatures to high temperatures (Fig. 4), the predicted cessation of fixation during low temperatures was confirmed, and the model predicted the over-all chromium fixation rate very well ($r^2 = 0.984$). The model underestimated the fixation time for the pole

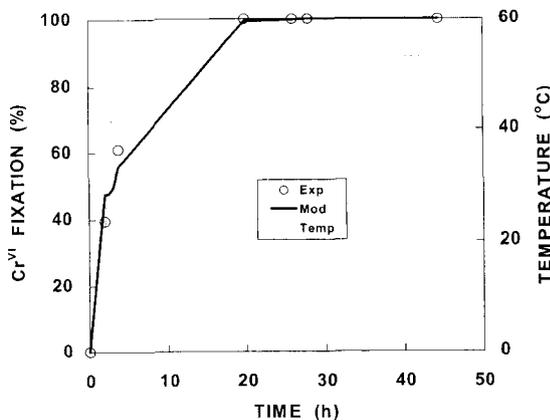


FIG. 2. Predicted and actual fixation status for red pine pole butt section exposed to approximately isothermal high-temperature conditions.

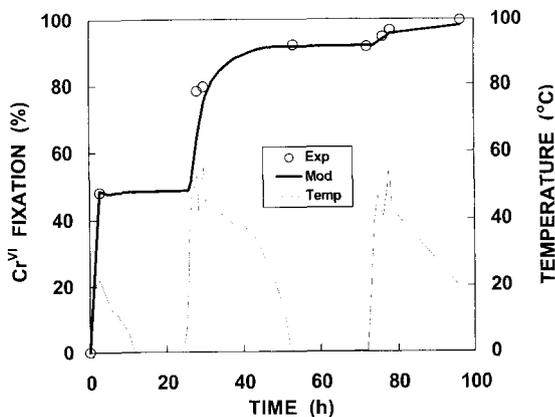


FIG. 4. Predicted and actual fixation status for red pine pole butt section exposed to cyclic temperature conditions after treatment.

top samples and overestimated fixation time for the butt samples with the more complex temperature cycling (Figs. 5 and 6), although in both cases, the general shape of the predicted fixation curve was validated by the fixation measurements. The highly variable temperature schedules (Figs. 7 and 8) resulted in an erratic predicted fixation curve that was closely matched by the measured fixation values when the pole top section was evaluated ($r^2 = 0.975$). However, fixation was faster than predicted for the denser butt section. We attribute this to the higher solution retention in the

low-density tops and the lower ratio of wood substance to CCA treating solution. Osborne (1991) showed that increased CCA retention slowed the CCA fixation rate.

The effect of density on fixation rate for the wood evaluated was confirmed by the small block test results (Fig. 9). Low-density samples from the pole top required more than 70 h to achieve complete chromium fixation at 30°C, while samples from the denser pole butts were fixed in about 40 h.

The model accurately predicted fixation rate for the pole top samples for most of the fixa-

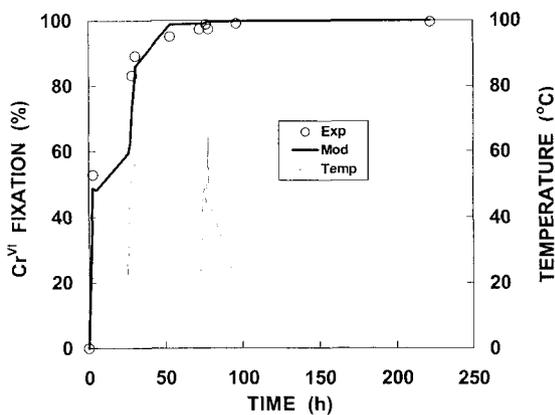


FIG. 3. Predicted and actual fixation status for red pine pole top section exposed to cyclic temperature conditions after treatment.

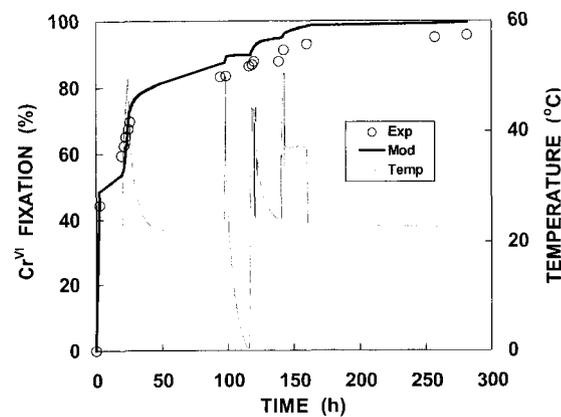


FIG. 5. Predicted and actual fixation status for red pine pole top section exposed to variable temperature conditions after treatment.

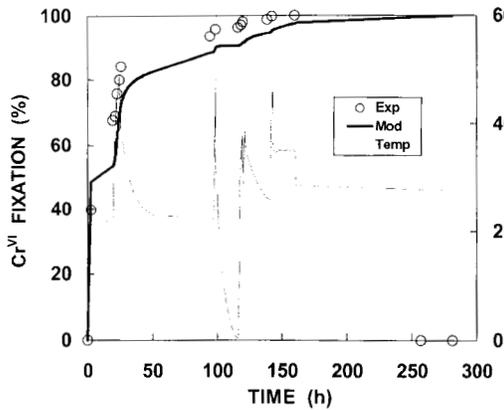


FIG. 6. Predicted and actual fixation status for red pine pole butt section exposed to variable temperature conditions after treatment.

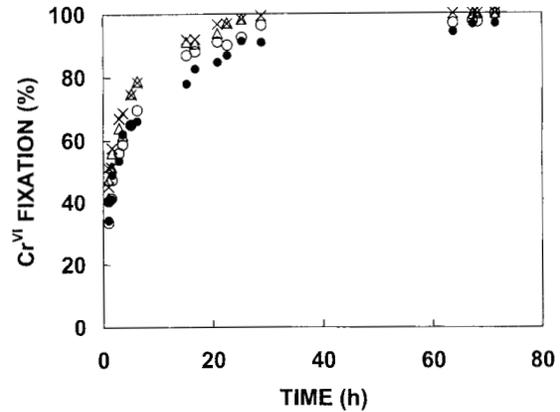


FIG. 9. Effect of wood tissues, collected from top and bottom sections of red pine poles, on fixation rates of 1.0% CCA-C at 30 °C. (○, ●) Top section, (△, X) bottom section.

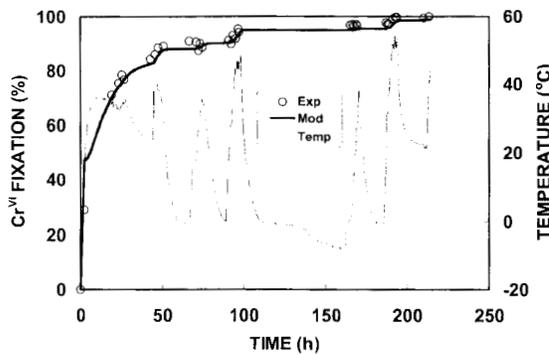


FIG. 7. Predicted and actual fixation status for red pine pole top section exposed to variable temperature conditions after treatment.

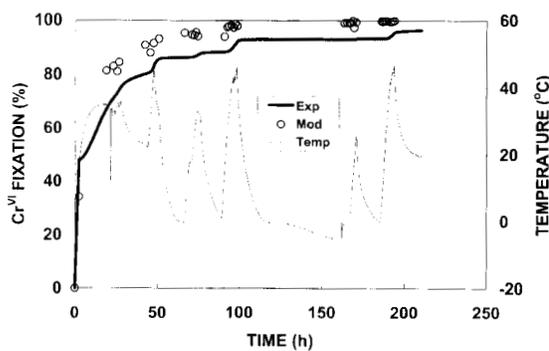


FIG. 8. Predicted and actual fixation status for red pine pole top section exposed to variable temperature conditions after treatment.

tion schedules, since the model parameters were developed from similar wood. The denser bottom sections fixed much faster. This indicates that variations in wood density between pieces in a treatment charge will result in variations in fixation rates. Since wood density in softwoods is higher at the base of trees than at higher elevations (Panshin and deZeeuw 1980), a practical implication of this is that quality control personnel should be monitoring fixation rates at the top of poles rather than the bottom to make sure that the entire pole is fixed completely.

These results show that the fixation model parameters are very sensitive to variations in the wood, and that good conformance to the model will be obtained only if the tests used to determine model parameters represent the wood that is being treated and fixed. The accuracy of the model depends on the validity of the model constants as well as the estimated length of the initial reaction period. These factors will be affected by wood species, wood moisture content when treated, CCA solution concentration, and wood density. Thus for application of this approach to monitoring CCA fixation in wood products, samples monitored should represent those known to take the longest to fix.

CONCLUSIONS

A fixation model based on the temperature-dependence of the reaction rates during the "Initial" and "Main" reaction zones accurately predicted fixation rates when the wood density and treating conditions were similar to those used to develop the model. The fixation rate of higher density wood samples subjected to more complex fixation schedules deviated from the predicted rates. Fixation models must be based on data from material that is similar to that being treated.

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REFERENCES

- ALEXANDER, D.L., AND P.A. COOPER. 1993. Effects of temperature and humidity on CCA-C fixation in pine sapwood. *Wood Protection* 2(2):1-7.
- ANDERSON, D.G. 1989. The accelerated fixation of chromated copper preservative treated wood. *Proc. Can. Wood Preserv. Assoc.* 10:75-111.
- AYRES, F. JR. 1964. *Theory and problems of differential and integral calculus*. 2nd ed. Schaum Publishing Co., New York, NY. P. 254.
- COGGINS, C. AND P. HISCOCKS. 1978. Chromium on the surface of CCA treated wood. *Int. Res. Group on Wood Preserv. Doc. No. IRG/WP/386*.
- COOPER, P. A., AND Y. T. UNG. 1989. Moderate temperature fixation of CCA-C treated poles. *Int. Res. Group on Wood Preserv. Doc. No. IRG/WP/3522*.
- , AND ———. 1993. A simple leaching test for quantitative determination of CCA fixation. *Forest Prod. J.* 43(5):19-20.
- , D. L. ALEXANDER, AND Y. T. UNG. 1993. What is chemical fixation. Pages 7-13 in J. Lang, ed. *Chromium-containing waterborne wood preservatives: Fixation and environmental issues*. Forest Products Society, Madison WI.
- DAHLREN, S. E. 1974. Kinetics and mechanism of fixation of Cu-Cr-As wood preservatives. Part IV. Conversion reactions during storage. *Holzforschung* 28(2):58-61.
- . 1975. Kinetics and mechanism of fixation of Cu-Cr-As wood preservatives. Part VI. The length of the primary precipitation fixation period. *Holzoforschung* 29(4):130-133.
- , AND W. H. HARTFORD. 1972a. Kinetics and mechanism of fixation of Cu-Cr-As wood preservatives. Part I. pH behaviour and general aspects of fixation. *Holzforchung* 26(2):62-69.
- , AND ———. 1972b. Kinetics and mechanism of fixation of Cu-Cr-As wood preservatives. Part II. Fixation of Boliden K₃₃. *Holzforchung* 26(3):105-113.
- , AND ———. 1972c. Kinetics and mechanism of fixation of Cu-Cr-As wood preservatives. Part III. Fixation of Tanalith C and comparison of different preservatives. *Holzforchung* 26(4):142-149.
- FOSTER, D. O. 1988. Proposed A.W.P.A. method for determination of the presence of hexavalent chromium in treated wood. *Proc. Can. Wood Preserv. Assoc.* 9:29.
- KAZI, K. M. E., AND P. A. COOPER. 2000. Kinetic model of CCA fixation on wood. Part I. The initial reaction zone. *Wood Fiber Sci.* 32(3):354-361.
- , ———, AND J. CHEN. 2000. Kinetic model of CCA fixation on wood. Part II. The main reaction zone. *Wood Fiber Sci.* 32(4):442-449.
- MCNAMARA, W. S. 1989. CCA fixation experiments—Part 1. *Int. Res. Group on Wood Preserv. Doc. No. IRG/WP/3504*.
- OSBORNE, P. D. 1991. Effect of high CCA retentions on the percent fixation and fixation rate. *Proc. Am. Wood Preserv. Assoc.* Vol. 87. Report of Subcommittee T-2.
- PANSHIN, A. J., AND C. DEZEEUW. 1980. *Textbook of wood technology*. Vol. 1, 4th ed. McGraw-Hill, New York, NY.
- PIZZI, A. 1982. The chemistry and kinetic behaviour of Cu-Cr-As/B wood preservatives. Part IV. Fixation of CCA to wood. *J. Polym. Sci. Chem. Ed.* 20:739-764.
- WILSON, A. 1971. The effects of temperature, solution strength and timber species on the rate of fixation of a Copper-Chrome-Arsenate wood preservative. *J. Inst. Wood Sci.* 5:36-40.