

KINETIC MODEL OF CCA FIXATION IN WOOD. PART II. THE MAIN REACTION ZONE

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(Received September 1999)

ABSTRACT

Fixation of chromated copper arsenate type C (CCA-C) solution on wood, measured by hexavalent chromium reduction, follows different rates in different reaction zones. We identify two main zones: an initial reaction and a second main reaction. The main reaction zone in red pine (*Pinus resinosa* Ait.) starts once approximately 47% of the total Cr^{VI} in the impregnated CCA-C solution is fixed on wood matrix. The second main fixation reaction follows first-order reaction kinetics, and an Arrhenius type of correlation can be used in modeling the fixation kinetics. We obtained similar values of Arrhenius parameters for CCA-C concentrations of 1% and 3%. The activation energies for fixation reactions in the second zone were 87.6 and 88.1 kJ/mol for 1% and 3% CCA-C concentrations, respectively. The pre-exponential factors of the reaction rate constant were 2.7×10^{13} and 2.2×10^{13} h⁻¹ for 1 and 3% solutions, respectively. By combining the reaction rate equations and the temperature-dependence (Arrhenius) relationship, a mathematical model for the main reaction of 1% CCA-C fixation in red pine was produced.

This model estimates the percentage of CCA-C solution fixation on red pine for a given time (in hours)/temperature (K) history of the wood following treatment.

Keywords: Preservative, CCA-C, wood, red pine (*Pinus resinosa* Ait.), fixation, main reaction, model, activation energy.

INTRODUCTION

When chromated copper arsenate (CCA) preservatives come into contact with wood, a large increase in pH occurs. This rise of pH is at first rapid, then slow, and finally oscillates until pH reaches its final values. Based on observations of pH behavior, Dahlgren and Hartford (1972a) assumed that a series of consecutive and parallel reactions occur during CCA fixation processes, although the basic reaction

is described as the reduction of chromium from the hexavalent to trivalent state. The course of fixation consists of two or three zones (Dahlgren 1975; Pizzi 1982). In the first zone, the initial fixation reactions occur so fast that they are often regarded as instantaneous. Kazi and Cooper (2000) observed that the first reaction zone ends when Cr^{VI} concentration reaches approximately 50% of its initial value, and the second or main reaction takes over for the remainder of the fixation process.

There is an extended period of increasing

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pH from approximately 3.2 to 5.5 following the initial reactions, during which the majority of the CCA components react. Reactions in this zone are thought to involve HCrO_4^- ion with lignin to form polymeric insoluble complexes; while additional Cr^{VI} (hexavalent chromium) is adsorbed by cellulose (Pizzi 1981). Cr^{VI} is also consumed during the oxidation of primary alcohol groups with consumption of protons and reduction of Cr^{VI} to the trivalent state (Dahlgren and Hartford 1972a).

Studies based on the reaction of CCA with model compounds and on sawdust and more recent studies on solid wood by X-ray photon spectroscopy (XPS), diffuse reflectance Fourier transform infrared spectroscopy (DRIFT), electron spin resonance spectroscopy (ESR), and other techniques provide conflicting evidence for the types of reactions occurring. XPS and DRIFT studies (Ostmeyer et al. 1988, 1989) suggest chromium oxidation of lignin and formation of chromium esters with lignin components. These reactions support Pizzi's (1981, 1982) work. Other studies (Kaldas et al. 1998; Yamamoto and Rokova 1991) show that there is a relative decrease in carbon reacted with one oxygen that is best explained by oxidation of $-\text{OH}$ groups on hemicellulose and cellulose. However, there are not increases in highly oxidized carbonyl and carboxylic acid groups that would be expected from such oxidations. This is explained by decarboxylation reactions that release CO_2 (Williams and Feist 1984; Yamamoto and Rokova 1991; Porandowski et al. 1998). It is apparent that oxidation of the wood can occur on different components, located at different sites within the cell wall, and forming different types of reaction products. In the chromium reduction process, it is apparent by ESR that intermediate chromium oxidation states, in particular Cr^{V} , exist for significant times, which depend on the fixation conditions (Yamamoto et al. 1993; Hughes et al. 1992).

The rate of CCA fixation on wood in the main reaction zone has been reported to follow either first-order (Alexander and Cooper 1991) or second-order (Dahlgren and Hartford

1972b; Pizzi 1982) reactions with respect to hexavalent chromium concentration. Since chromium is the last CCA component to be stabilized in wood (Cooper et al. 1993), CCA fixation is usually monitored by following the reduction of hexavalent chromium in wood following treatment through qualitative or quantitative tests for Cr^{VI} (Foster 1988; Cooper and Ung 1993).

This study focuses on the reaction kinetics of red pine to develop a kinetic fixation model for the main reaction zone. This model, in conjunction with the initial reaction model, should predict overall fixation levels by simply monitoring wood temperature following treatment, and computing the level of fixation based on time/temperature history. Since CCA fixation is temperature-dependent, we selected a wide range of treatment temperatures (4, 22, 35, 50, 70, and 90°C) to develop a generalized kinetic model.

KINETIC MODEL DEVELOPMENT

In the process of CCA fixation, Cr^{VI} is reduced to Cr^{III} by reducing agents in the wood matrix, accompanied by pH changes. The kinetic behavior of a given fixation reaction zone can be described in a generalized form:

$$r = -\frac{d\text{Cr}}{dt} = k[\text{Cr}]^n[\text{WOOD}]^m[\text{H}^+]^p \quad (1)$$

where,

r = reaction rate

k = reaction rate constant

t = reaction time for the main reaction zone

Cr , WOOD , H^+ :

= concentrations of reactants Cr^{VI} , reducing agents in the wood matrix, and hydrogen ion respectively, and

n , m , p

= reaction order of the corresponding components Cr^{VI} , reactive sites of reducing agent in wood matrix and hydrogen ion.

In fixation reactions, the reducing agent remains mainly insoluble and is present in large excess in the wood matrix, so its concentration can be considered constant (Dahlgren and Hartford 1972a). Also, chromium reduction and adsorption account for most of the pH change (Dahlgren and Hartford 1972a) and the H^+ effect can be combined with the Cr^{VI} effect. Thus the rate expression can be modified to pseudo nth order of the form:

$$r = -\frac{d[Cr]}{dt} = k[Cr]^n \quad (2)$$

where k is a pseudo rate constant that depends on concentrations of Cr^{VI} , reactive wood sites, and H^+ and other CCA components (Pizzi 1981, 1982). The pseudo reaction order, n , could have any value. When $n = 1$, the rate equation describes a first-order reaction.

The transition from one reaction zone to another and the reaction orders (n) for the different reaction zones can be determined by applying the van't Hoff differential form of Eq. (2) (Steinfeld et al. 1989):

$$\ln\left(-\frac{\Delta[Cr]}{\Delta t}\right) = \ln(k) + n \ln[\overline{Cr}] \quad (3)$$

where $[\overline{Cr}]$ is the average chromium concentration over the interval $\Delta[Cr]$. The kinetic data are plotted as $\ln[-\Delta Cr]/(\Delta t)$ versus $\ln[\overline{Cr}]$. Slopes of each curve in the plot show the reaction orders of the corresponding zones.

The integral form of the first-order reaction Eq. (2) can be written as:

$$[Cr_t] = [Cr_i]e^{-kt} \quad (4)$$

or

$$\ln[Cr_t] = \ln[Cr_i] - kt \quad (4a)$$

where $[Cr_i]$ is the chromium concentration in the absorbed solution in wood at the beginning of the second or main reaction and $[Cr_t]$ is the concentration at time t . When $n = 2$, the reaction is second-order with the integral form:

$$1/[Cr_t] = 1/[Cr_i] + kt \quad (5)$$

The temperature-dependence of the rate

constant can be defined by the Arrhenius equation:

$$k = k_0 e^{-(E/RT)} \quad (6)$$

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

If it is assumed that $R_1\%$ of total fixation occurs during the initial reaction, then $(100 - R_1)\%$ occurs during the main reaction. The percentage of total chromium fixation, F , on the wood matrix in the main reaction zone at a given time is:

$$F(\%) = \frac{[Cr_i] - [Cr_t]}{[Cr_i]} \times (100 - R_1) \quad (7)$$

For a first-order fixation reaction, we can substitute the integral rate Eq. (4) into the fixation Eq. (7), to obtain:

$$F(\%) = (1 - e^{-kt}) \times (100 - R_1) \quad (8)$$

For a first-order reaction, the effect of initial concentration drops out and the equation indicates that fixation in the main zone is independent of the initial CCA solution concentration. Combining this with the temperature-dependence Eq. (6) yields a fixation model that predicts percentage chromium fixation in the main reaction zone as a function of time and temperature:

$$F = (100 - R_1) \times (1 - e^{-t \times k_0 \times e^{-(E/RT)}}) \quad (9)$$

MATERIALS AND METHODS

Sapwood cubes ($25 \times 25 \times 25 \text{ mm}^3$) were sawn from a fresh air-dried red pine (*Pinus resinosa* Ait.) pole section. The samples were conditioned in a saturated environment to moisture contents ranging from 25–35%. CCA-C solutions of 1% and 3% concentrations (oxides basis) were prepared from a 50% CCA-C solution. Six different target fixation temperatures were evaluated: 4, 22, 35, 50, 70, and 90°C. For each fixation trial, 15 blocks each were vacuum impregnated with the 1% or 3% CCA-C solutions. Vacuum was applied at 20 kPa absolute pressure for 30 min; then

the solution at the test temperature was drawn in and the vacuum released. This produced CCA retentions of approximately 6.4 and 20 kg/m³ for the 1% and 3% solutions, respectively. After treatment, the samples were immediately weighed and equipped with thermocouples to measure the actual wood temperatures, then allowed to fix in a temperature-humidity-controlled fixation chamber. Throughout the fixation process, about 95% relative humidity was maintained to minimize the evaporative cooling effect and to more rapidly equilibrate wood temperatures near the wet-bulb temperatures. The samples were then randomly removed from the chamber at different intervals and squeezed in a hydraulic press at 60 MPa pressure. The expressed solution was analyzed for Cr^{VI} concentration by the diphenylcarbazide method (Coggins and Hiscocks 1978) using a spectrophotometer (Shumadzu, UV-16) at a wavelength of 540 nm. The Cr^{VI} concentration data at various treatment intervals and temperatures were used in the kinetic modeling studies.

RESULTS AND DISCUSSION

A van't Hoff plot of fixation kinetic data at a treatment temperature of 22°C (room temperature) and 1% CCA-C solution concentration showed two distinct linear curves with slopes of 9.4 and 0.99 (Fig. 1). The 9.4 slope component represents the initial reaction zone, while the 0.99 value represents the main reaction zone and indicates that the process is a first-order reaction. In an earlier study (Kazi and Cooper 2000), we obtained an average slope of approximately 10 for the initial reaction zone (i.e., a pseudo tenth-order reaction). The intersection point of the two reaction zones indicates the change-over point from the initial reaction to the main reaction zone. The concentration of Cr^{VI} at the intersection point is the interzone concentration [Cr_i] or the initial concentration of the main reaction zone. The interzone concentration of Cr^{VI} was about 53% of the total Cr^{VI} concentration initially used. This concentration was

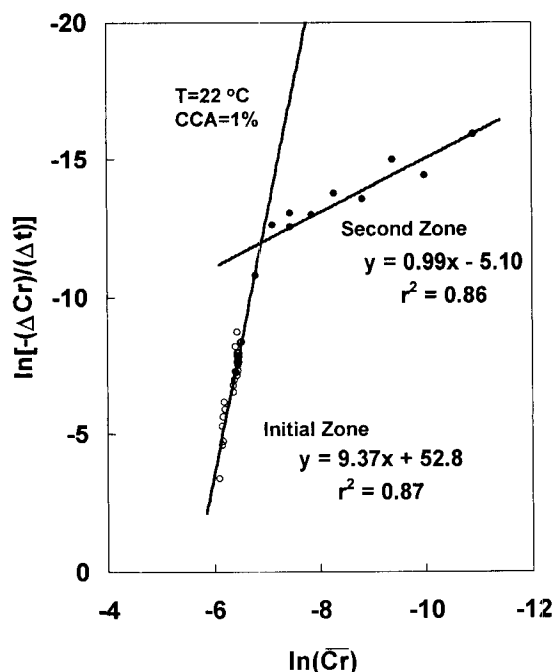


FIG. 1. van't Hoff plot showing the two reaction zones for 1% CCA-C fixation in red pine at 22°C.

used as the starting point in all of the main reaction plots.

The measured wood temperatures during the fixation studies were 4, 22, 35, 49, 70, and 88°C for 1% CCA-C and 4, 22, 35, 49, 71, and 90°C for 3% CCA-C. The measured Cr^{VI} concentration in wood with fixation time at various treatment temperatures fit first-order reaction kinetics (Eq. (4)). Examples of plots of logarithmic concentrations, $\ln[Cr^{VI}]$ vs. fixation time (t) for the two concentrations at 49°C are shown in Fig. 2. The reaction rate constants (k), derived from these plots for all temperatures, and the regression coefficients (r^2), defining the goodness of the fit of the linear equations, are summarized in Table 1. The linear behavior of the kinetic plots in Fig. 2 confirms that fixation reactions in the main zone followed first-order reaction kinetics for both of the treating solution concentrations.

Plots for the second-order reaction, by comparison, were not linear (Fig. 3) and showed an upward trend indicating that the fixation ki-

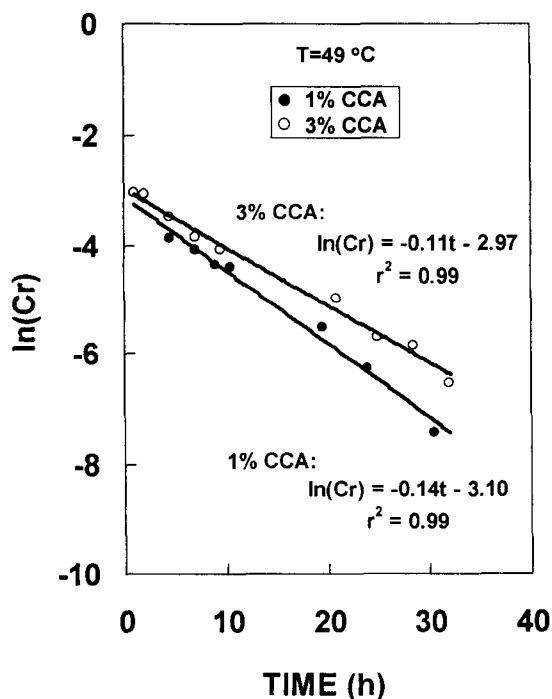


FIG. 2. Experimentally obtained kinetic data fitted in a first-order reaction model for 1% and 3% CCA in red pine fixed at 49°C.

netics in the main zone followed a lower order than a second-order kinetics (Hill 1977).

The exponential drop in Cr^{VI} concentration with time is analogous to a radioactive decay curve (also a first-order reaction), and a value similar to the "half life" of a radioactive isotope can be determined for the unreduced Cr^{VI} in the main reaction zone. This "half life" for fixation is the time needed to reduce available Cr^{VI} at any time to 50% of its present value. The estimated "half life" values for the experimental temperature conditions are summarized in Table 1. For example, at 4°C and 1% CCA solution, assuming that the main reaction started at 50% chromium fixation, the time to reach 75% total fixation was approximately 690 h; an additional 690 h was required to reach 87.5% fixation, etc. In all cases, the "half life" was longer for 3% CCA treatment, confirming that higher concentration treatments fix more slowly (e.g., Osborne 1991).

TABLE 1. First-order reaction rate constants, fixation "half times," and goodness-of-fit of linear relationship of $\ln \text{Cr}$ vs. t .

T (°C)	[CCA] Conc. (%)	Rate constant (h^{-1})	Fixation "half life" (hours)	r^2
4	1.0	0.0010	690	0.981
4	3.0	0.0007	990	0.982
22	1.0	0.0062	112	0.971
22	3.0	0.0042	165	0.968
35	1.0	0.0424	16.3	0.919
35	3.0	0.0244	28.4	0.910
49	1.0	0.1347	5.1	0.987
49	3.0	0.1064	6.5	0.988
70	1.0	1.3225	0.52 (31 minutes)	0.973
71	3.0	0.7808	0.89 (53 minutes)	0.984
88	1.0	6.2657	0.11 (6.6 minutes)	0.962
90	3.0	4.7146	0.15 (8.8 minutes)	0.986

The Arrhenius plots of $\ln(k)$ vs. $1/T$ for the different temperatures and two concentrations are shown in Fig. 4. The activation energy term (E/R) and pre-exponential factor term ($\ln k_0$) were obtained from the slopes and the intercepts of the Arrhenius plot (Fig. 4). Ac-

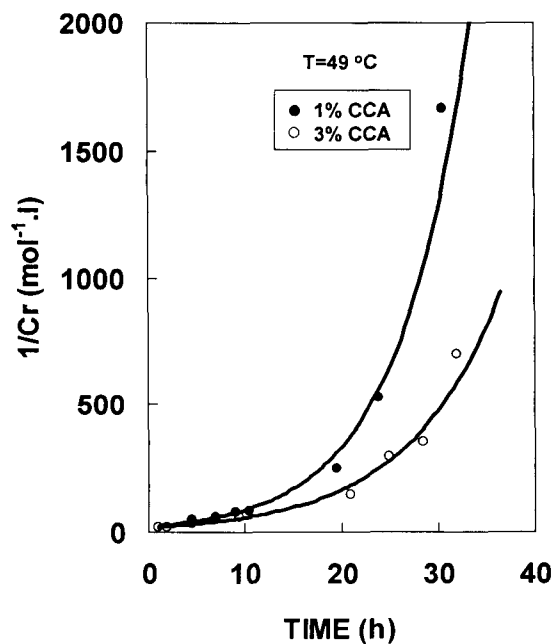


FIG. 3. Experimentally obtained kinetic data fitted in a second-order reaction model for 1% and 3% CCA in red pine fixed at 49°C.

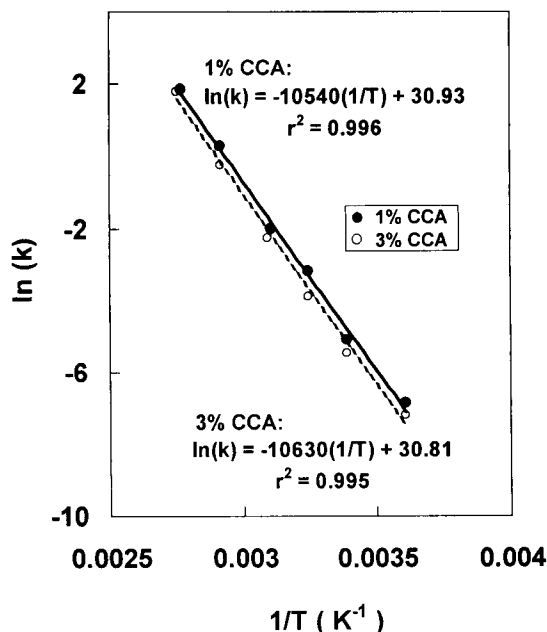


FIG. 4. Plots of Arrhenius curves for temperature-dependence of first-order rate constants for fixation of 1% or 3% CCA in red pine.

tivation energies and pre-exponential factors were calculated from these values for the two different concentrations. CCA-C solution strength had a minor effect on the reaction mechanisms within the main fixation zone over the concentration range studied. Activation energies for the second fixation reaction zone were 87.6 and 88.1 kJ/mol for 1% and 3% CCA-C solution concentrations, respectively. Pre-exponential factors (k_0) were 2.7×10^{13} and $2.2 \times 10^{13} \text{ h}^{-1}$ for 1% and 3% CCA-C solution concentrations, respectively. The activation energies for this zone correspond to an approximate doubling of reaction rate with each 6.0°C (10.8°F) increase in temperature.

The activation energies determined were somewhat higher than those estimated by others. Dahlgren and Hartford (1972c) observed values of approximately 75.8 kJ/mol in softwoods, Alexander and Cooper (1991) reported values of 65–75 kJ/mol in red pine, and Pizzi (1982) observed values of about 77.5 kJ/mol for reaction of glucose with CCA. These values were considerably higher than for the ini-

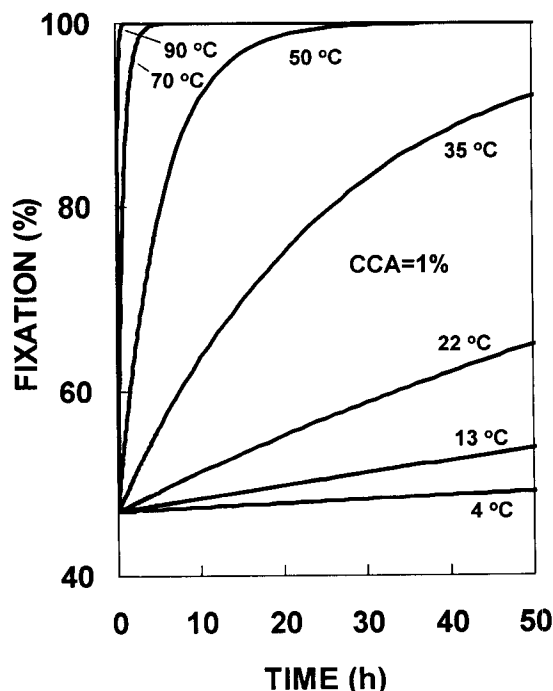


FIG. 5. Model simulation of 1% CCA-C solution fixation in red pine at different treatment temperatures over a 50-h period beginning at the start of the main reaction zone.

tial reaction zone (approx. 38 kJ/mol—Kazi and Cooper 2000) indicating that the main reaction zone was much more sensitive to temperature than the initial reaction zone.

Application of these constants for 1% CCA-C treatment of red pine to Eq. (9) and assuming the initial reaction accounts for 47% chromium fixation yielded the following fixation model:

$$F(\%) = 47\% + 53\{1 - \exp[-2.7 \times 10^{13} \times t \times e^{-(10,540/T)}]\} \quad (10)$$

where t is in hours and T in K.

Application of this model at fixation temperatures of 4, 13, 22, 35, 50, 70, and 90°C for the 1% CCA-C solution, produced estimated fixation rates over a 50-h period (Fig. 5) where fixation time commenced at the start of the main reaction zone.

The above fixation model, when used in conjunction with the tenth order model developed for the initial reaction, provides accurate estimates of CCA fixation in wood by monitoring wood temperature during fixation.

CONCLUSIONS

Fixation of CCA-C solution on red pine is a time- and temperature-dependent process, which follows first-order kinetics in the second or main reaction zone. For 1% CCA-C solution, the second zone starts after approximately 47% of the total Cr^{VI} is fixed onto the wood matrix. Based on this first-order reaction and the Arrhenius temperature-dependence of the reaction rate constants, a kinetic model was developed that expresses percent fixation in terms of elapsed time (hours) and temperature (K). The activation energies for fixation of wood treated with 1% and 3% CCA-C treatment solutions were determined to be 87.6 and 88.1 kJ/mol, respectively. The models were similar for the 1% and 3% solutions although the fixation times were slightly greater for the 3% solution.

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