KINETIC MODEL OF CCA FIXATION ON WOOD. PART I. THE INITIAL REACTION ZONE

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ABSTRACT

The fixation process for chromated copper arsenate (CCA-C) preservative treated wood has at least two distinctly different zones. One of these is a fast "Initial Reaction," characterized by a rapid increase in pH and a decrease in available hexavalent chromium (Cr^{VI}). In the present study we develop a mathematical model that describes the initial reaction kinetics for red pine (*Pinus resinosa* Ait.) treated with 1% CCA-C. The results show that the initial fixation reactions follow *pseudo* 10th order kinetics. The activation energy and pre-exponential factors were found to be 37.8 $kJ.mol^{-1}$ and 8.7 × 10^{-19} h^{-1} mol^{-9} l^9, respectively. At all treatment temperatures tested, the initial reaction resulted in approximately 47% chromium reduction. At 4°C the time required to complete the initial reaction is approximately 4.5 h; at room temperature the initial reaction is complete in about 1.7 h. At 50°C the initial reaction is complete in about 25 min. The complete model incorporates the rate equation, Arrhenius temperature dependence, and the fixation definition into a single equation that expresses % chromium fixation as a function of initial chromium concentration in the treating solution and time and temperature history of the wood following treatment.

This model can also be used as an integral part of an overall fixation model that can be used to predict the percent fixation at a given treatment condition based on knowledge of the temperature history of the wood during fixation.

Keywords: Activation energy, CCA-C, fixation, initial reaction, kinetics.

INTRODUCTION

Chromated copper arsenate (CCA) is one of the most reliable general-purpose preservatives commercially used, usually providing excellent protection against all types of fungal and wood-borer deterioration (Richardson 1978). The long service life and clean outward appearance of treated products have made CCA the highest volume wood preservative used in North America. As a waterborne chemical, however, the toxic ingredients of CCA in wood remain susceptible to leaching until the 'fixation' process is finished. Therefore, improperly fixed treated products could result in environmental contamination at treatment sites, storage yards, and in service. Traditionally, treated products are stored in a yard at the treating plant to achieve fixation before being shipped out. Under normal temperate climatic conditions, the fixation process may require several days or weeks depending on the wood species and CCA retention. In winter, the fixation period may extend over several months, while elevated temperature fixation conditions can shorten this process to several hours (Wilson 1971; Peek and Willeitner 1988; Anderson 1989; Cooper and Ung 1992).

During fixation, the three components of CCA (copper, chromium, and arsenic) react with each other and with wood components at
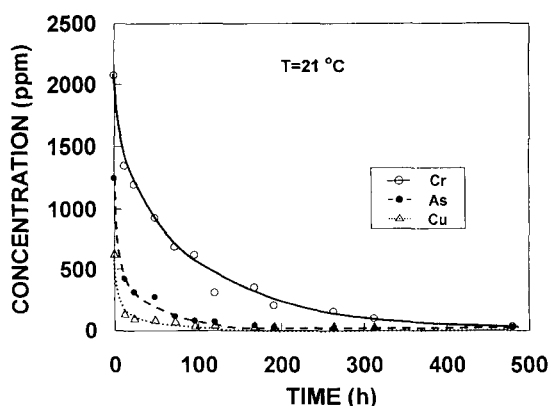
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FIG. 1.   Fixation profiles of the individual components of CCA-C treating solution during the fixation process (Cooper et al. 1993).
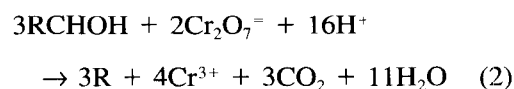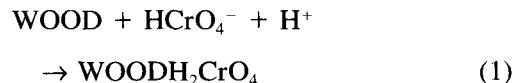
different rates. Copper and arsenic fix on the wood matrix most quickly, followed by chromium, which takes significantly longer. Typical fixation curves for Cu, Cr, and As on wood, determined by the expressing procedure, are shown in Fig. 1 (Cooper et al. 1993). Since the fixation of chromium is slowest among the three components, chromium is used as a marker of CCA fixation on wood. Chromium fixation is usually evaluated qualitatively by determining the presence of unreduced hexavalent chromium (Cr^{VI}) with chromotropic acid (Foster 1988). However, it can be measured more quantitatively by measuring the leaching of CCA components during the fixation process (Dahlgren and Hartford 1972b; Cooper and Ung 1993), or by analyzing liquid expressed out of the treated wood and comparing its CCA content with that of the initial treating solution (Cooper and Ung 1989; McNamara 1989).

During fixation, a series of consecutive and parallel reactions occur. There are thought to be two or three chromium fixation reaction zones (Pizzi 1982; Dahlgren 1975):

(1) The initial reaction

This reaction is so rapid that it is often considered to be finished while the wood is still in the treating vessel. This reaction stage is characterized by a sudden increase in pH of

the system from about 2.0 in treating solution to greater than 3 in solution expressed from the wood immediately after treatment. This change represents a 50–80% drop in hydrogen ion concentration. At the same time, copper reacts with the wood, which is usually attributed to pH dependent ion exchange of copper on wood (Dahlgren and Hartford 1972a). This involves the displacement of protons from weak acid groups in wood, which are more highly dissociated and therefore have a higher cation exchange capacity as the pH rises (Rennie et al. 1987; Cooper 1991). Since protons are released and not consumed, this does not help explain the observed increase in pH. The Cr^{VI} concentration in CCA solution in wood drops immediately after treatment by 30–60%. This is generally attributed to temporary adsorption of some hexavalent chromium onto the wood constituents (Pizzi 1981) (Eq. (1)), while other chromium is reduced by sugars and other lower molecular weight extractives (Eq. (2)), (Dahlgren and Hartford 1972a). Both of these reactions consume hydrogen ions. Also, a smaller fraction of arsenic is rapidly immobilized, presumably due to formation of chrome arsenates and perhaps copper arsenates.

$$WOOD + HCrO_4^- + H^+$$

$$\rightarrow WOODH_2CrO_4 \qquad (1)$$

$$3RCHOH + 2Cr_2O_7^= + 16H^+$$

$$\rightarrow 3R + 4Cr^{3+} + 3CO_2 + 11H_2O \qquad (2)$$

(2) The second or main reaction phase

This zone has been described as both first order with respect to chromium reduction (Alexander and Cooper 1993; Chen 1994) and second order (Dahlgren and Hartford 1972a–c). The pH continues to increase and the adsorbed and unreacted hexavalent chromium is reduced, but at a slower rate than for the initial reaction (Dahlgren 1975).

(3) The third reaction phase

Some authors (Dahlgren 1974; Pizzi 1982) reported the existence of a third reaction zone

where the precipitated or adsorbed CCA compounds react further to produce the final form of immobilized CCA precipitated components. This occurs when all of the CrO_3 is consumed, and it involves the reduction of the adsorbed Cr^{VI} species to Cr^{III}. This phase also involves very slow reactions, and the corresponding pH increase in the system is also slow and may fluctuate due to conversion reactions of precipitated products (Dahlgren 1974).

KINETIC MODEL DEVELOPMENT

Currently, to ensure the completion of CCA fixation, treating plant quality control personnel must enter the fixation chamber/kiln or remove the charge from the chamber to test samples. The proposed kinetic model relates unreduced chromium to the time and temperature history of the wood following pressure treatment. From this model, the percentage of fixation at any treatment conditions can be obtained simply by monitoring the treating wood temperature history. In the present study, we are focusing on the development of a kinetic model for the initial reaction zone.

Mathematically, the kinetic behavior of this initial fixation reaction zone can be described in a generalized form as:

$$r = -\frac{d[Cr]}{dt} = k[Cr]^n[Wood]^m[H^+]^p \quad (3)$$

where,

r:	reaction rate
k:	reaction rate constant
t:	time
n, m, p:	reaction order of the corresponding components, Cr^{VI}, reactive sites in wood and hydrogen ions
[Cr], [Wood],	concentration of reactants,
[H$^+$]:	Cr^{VI}, reactive sites in wood, and hydrogen ions

In the initial reaction zone, the dominant reactions are assumed to be between Cr^{VI} and reactive sites on the wood matrix. While hydrogen ion concentration is also an important factor in the reaction, fixation is mainly monitored by following the reduction of hexavalent chromium and the proposed model will not consider [H$^+$] (pH). We also assume that the reactive sites in the wood matrix are present in very large excess, and the number of these sites that can be consumed by these reactions is negligible compared to the total number present. Thus the rate expression can be modified to the pseudo nth order of the form:

$$r = -\frac{dCr}{dt} = k[Cr]^n \quad (4)$$

where, k is a pseudo rate constant that will depend on the concentrations of Cr^{VI} and reactive wood sites (Hill 1977). The pseudo reaction order, "n", could have any value: 0, 1, 2, 3, ... n.

Traditionally, kinetic data are plotted assuming they follow a particular reaction order (1st order, 2nd order, etc.). For CCA fixation, the reactions do not follow a particular type of reaction order throughout. To estimate the reaction order (n) for the different reaction zones, van't Hoff's technique (Steinfeld et al. 1989) can be applied (differential method), where Eq. (4) is expressed as:

$$\ln\left[-\frac{\Delta Cr}{\Delta t}\right] = \ln(k) + (n)\ln[\overline{Cr}] \quad (5)$$

Kinetic data are plotted in the form of $\ln\{-\Delta[Cr]/\Delta t]\}$ versus $\ln[\overline{Cr}]$, where $[\overline{Cr}]$ is the average Cr^{VI} concentration over the interval ΔCr. The slope of the resulting linear relationship indicates the reaction order (n). If the reaction follows different orders within the zone under investigation, the van't-Hoff plot shows the zones with different slopes. From the plot, we can also identify where the one zone finishes and the other starts.

Since we are dealing with a highly heterogeneous reaction system with scattered experimental data, we will be interested to test those data further with the integral form of kinetic model using the reaction order obtained from van't-Hoff's differential technique. Integrating

Eq. (4) from time, t = 0 and Cr = Cr_0 to t = t and Cr = Cr_t we obtain:

$$\left(\frac{1}{Cr_t}\right)^{n-1} = \left(\frac{1}{Cr_0}\right)^{n-1} + (n - 1)kt \qquad (6)$$

For nth order reaction kinetics (where, n = 0, 2, 3, 4, 5 ... n), a plot of the concentration term, $(1/Cr)^{n-1}$ versus reaction time, t, will show a straight line with a slope of (n − 1)k. From the slope, the reaction rate constant, "k", can be obtained. The temperature dependence of the reaction constant can be determined by the Arrhenius equation expressed as:

$$k = k_0 e^{-(E/RT)} \qquad (7)$$

or (logarithmic form),

$$\ln(k) = \ln(k_0) - \left(\frac{E}{R}\right)\frac{1}{T} \qquad (7a)$$

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

The percentage of CCA fixation onto wood matrix at a given treatment temperature and time can be calculated from the following expression.

$$F(\%) = \frac{Cr_0 - Cr_t}{Cr_0} \times 100 \qquad (8)$$

where,

F: percentage of chromium fixation

Cr_0: initial concentration in the treating solution

Cr_t: concentration of Cr^{VI} at a given time

Combining Eqs (6), (7), and (8) results in the fixation model:

$$F(\%) = 100$$

$$- \frac{100}{Cr_0}\left[\left(\frac{1}{Cr_0}\right)^{n-1}\right.$$

$$\left. + (n - 1)k_0\exp\left(\frac{-E}{RT}\right)t\right]^{-[1/(n-1)]}$$

$$\qquad (9)$$

The model predicts % chromium fixation during the initial reaction zone for a given solution hexavalent chromium concentration (Cr_0) as a function of fixation temperature (T in K) and elapsed time (in hours), once the reaction order (n) and Arrhenius constants (k_0, E) are known.

MATERIALS AND METHODS

Studies on the initial reaction zone were conducted with 19-mm cubes of red pine (*Pinus resinosa* Ait.) sapwood. The wood blocks were equilibrated at 21°C and 80% relative humidity to an equilibrium moisture content of about 18% (dry mass basis) and sealed in polyethylene bags until treated.

A 1% CCA-C treating solution was prepared from concentrated (50%) solution by diluting it with distilled water. The concentration of Cr^{VI} in the treating solution was analyzed by the diphenylcarbazide method using a Shumadzu, UV-16 spectrophotometer set at a wavelength of 540 nm (Coggins and Hiscocks 1978).

Kinetic studies of the initial reaction zone were carried out at four different treatment temperatures: 4, 13, 22, and 32°C. For each temperature, 30 wood blocks and the CCA solution (1%) were conditioned overnight to the treatment temperature prior to vacuum impregnation. Samples were submersed in the CCA treating solution and then put in a vacuum impregnator controlled to the desired temperature in a water bath. Vacuum (approximately 15 kPa absolute pressure) was applied for 30 min and the vacuum broken to allow CCA penetration of the samples. Impregnated samples were placed in polyethylene bags in a conditioning chamber to maintain the specified temperature. The CCA-impregnated wood blocks were withdrawn from the conditioning chamber at different time intervals. Samples were squeezed in a press at 60 MPa to express treating solution from the wood void space. The expressate solution was analyzed for Cr^{VI} as above.
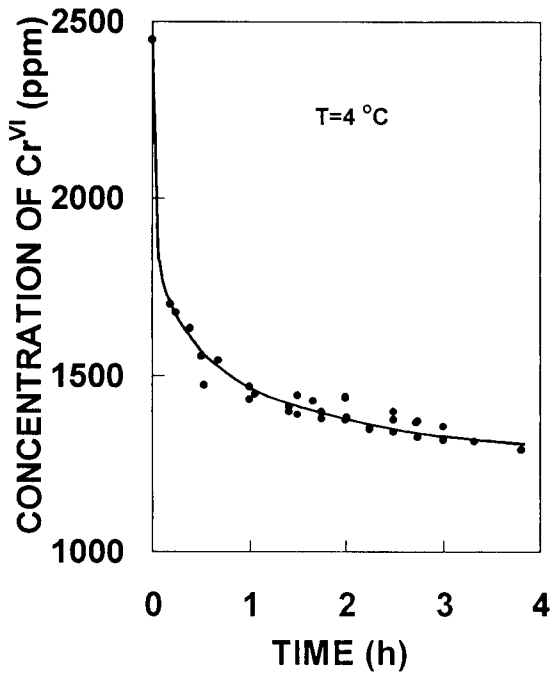
The reaction constants and Arrhenius con-

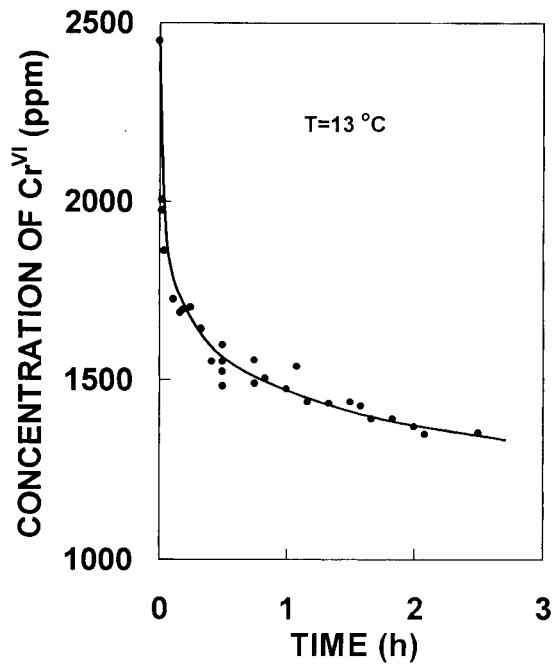FIG. 2. Change of Cr^{VI} concentration in the expressate in the initial reaction zone at 4°C.

FIG. 3. Change of Cr^{VI} concentration in the expressate in the initial reaction zone at 13°C.

stants were estimated for the treatment of red pine from the fixation monitoring results by using Eqs. (5) to (7) and the fixation model developed from these parameters.

RESULTS AND DISCUSSION

The initial concentration of hexavalent chromium in the 1% CCA-C treating solution (Cr$_0$) was determined to be 2,450 ppm. The changes in Cr^{VI} content in the expressate with time, at the three test temperatures, are shown in Figs. 2–5. At each treatment temperature, Cr^{VI} concentration diminishes exponentially, then levels off.

An example of the van't Hoff plot for the entire fixation range is shown in Fig. 6 for 1% CCA at 22°C. There is a definite break in the slope of the relationship; this was observed at all temperatures and occurred at approximately 47% total chromium reduction (47% chromium fixation). The duration of this initial effect is a function of temperature. At 4°C, this typical fixation pattern exists for about 4.5 h.

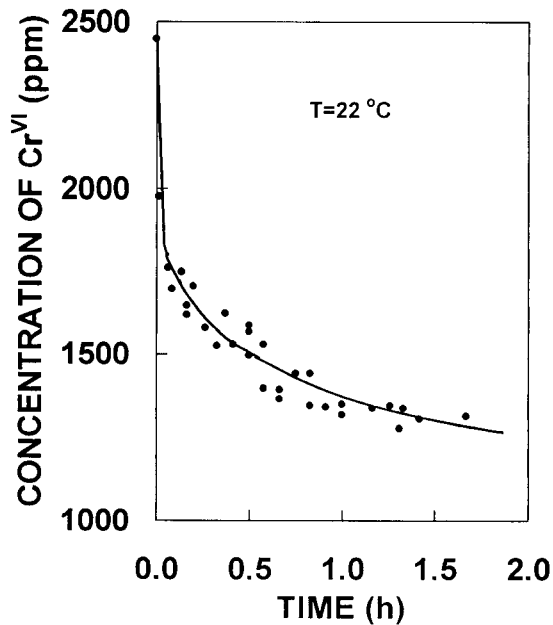FIG. 4. Change of Cr^{VI} concentration in the expressate in the initial reaction zone at 22°C.

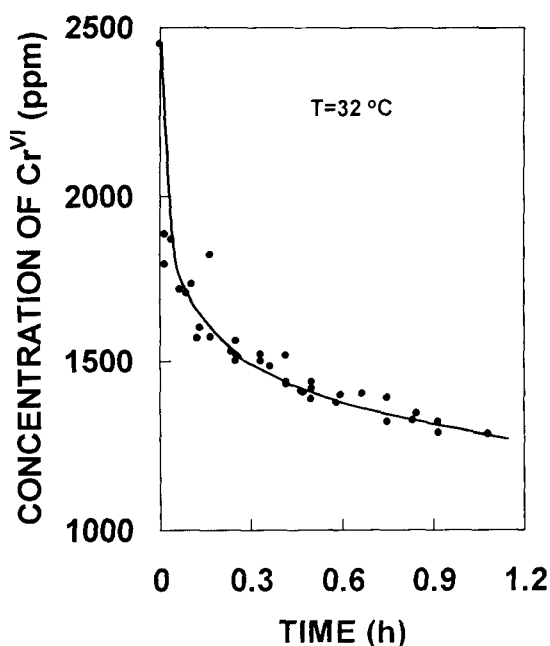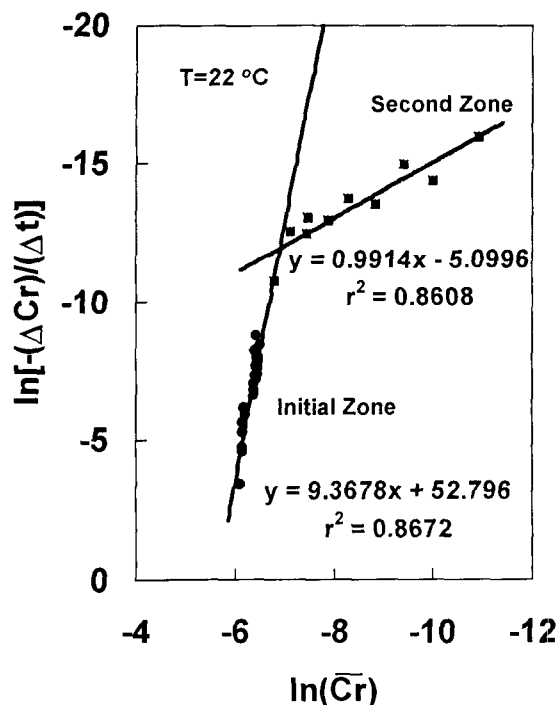FIG. 5. Change of Cr^{VI} concentration in the expressate in the initial reaction zone at 32°C.

FIG. 6. Van't-Hoff plot of kinetic data for the initial and main reaction zones at 22°C.

When the temperature is increased to 13, 22, and 32°C, the duration is reduced to 2.5, 1.7, and 1 h, respectively. The slopes of the van't-Hoff plots of $\ln\{-\Delta[Cr]/\Delta t\}$ against $\ln[Cr]$ for the early stages of fixation at the four test temperatures are summarized in Table 1 with the r^2 values as indicators of the goodness-of-fit of the linear model. All the plots showed a linear behavior, with a slope of approximately 10. From Eq. (5), this slope represents the order of the reaction, "n". That means that the initial reaction follows a *pseudo* 10th order reaction.

These data were further verified by plotting them in an integrated form of 10th order reaction model (Eq. 6, n − 1 = 9). The reaction rate constants k, derived from the slopes of these plots along with the r^2 values for the goodness of the linear fit, are summarized in Table 1.

Higher order reactions are reported to occur in reactions between different chemical species to give two or more different products such as the formation of ortho-, meta-, para-

derivatives of an aromatic compound (Hill 1977). CCA fixation involves the reaction of Cr^{VI} with the wood matrix, where wood has three different main constituents, cellulose, lignin, and hemicellulose, plus various aromatic and other extractives. Initially Cr^{VI} reacts with several different kinds of functional groups present in the wood matrix, and we can expect a higher reaction order in the initial zone. Also, the rate constants associated with the effect of pH on chromium reduction are incorporated in the *pseudo* rate constant. Our

TABLE 1. *Van't Hoff parameters and reaction rate parameters for initial reaction zone.*

Temperature (°C)	van't Hoff parameters		Rate constant parameters	
	Slope (n)	r^2	Rate constant k $(mol^{-9} \cdot h^{-1})$	r^2
4	9.90	0.90	7.32×10^{12}	0.88
13	10.55	0.86	8.20×10^{12}	0.94
22	9.37	0.87	1.80×10^{13}	0.86
32	9.62	0.77	2.91×10^{13}	0.94
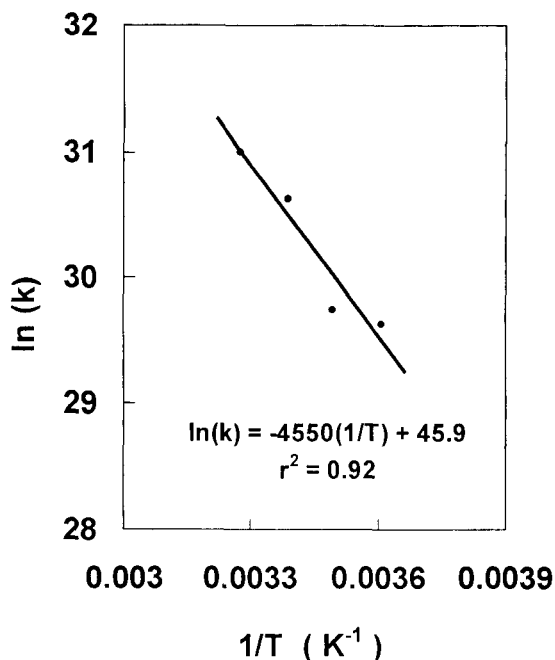
FIG. 7. Arrhenius plot of temperature dependence of the initial reaction (Equation 7a).

In the plot: $\ln(k) = -4550(1/T) + 45.9$, $r^2 = 0.92$, with y-axis $\ln(k)$ from 28 to 32 and x-axis $1/T\ (K^{-1})$ from 0.003 to 0.0039.

FIG. 8. Model estimates (for initial zone) prediction of the time needed to reach 47% of fixation at different temperatures 0 to 50°C.

kinetic data were also used to fit 1st and 2nd order reaction models, which are more common in reaction kinetics (curves not shown). All of the curves at every treatment temperature, 4, 13, 22, and 32°C, deviated from a straight line and bent downwards indicating that the actual reaction order is much higher than 1st or 2nd order (Hill 1977).

The rate constants in Table 1 were applied to the Arrhenius Eq. (7a) by plotting $\ln(k)$ vs $1/T$ (K) (Fig. 7). From the slope, we obtained the activation energy term, $E/R = 4,550$, and thus the value of the activation energy, $E = 37.8$ kJ/mol. From the intercept we obtained the pre-exponential factor $k_0 = 8.7 \times 10^{19}$ $h^{-1}.mol^{-9}.l^9$. The activation energy value is relatively small compared to other estimates for the main reaction zone (Dahlgren and Hartford 1972c: approx. 75.8 kJ/mol; Alexander and Cooper 1993: 65–75 kJ/mol), indicating that this reaction is less sensitive to temperature than the main reaction.
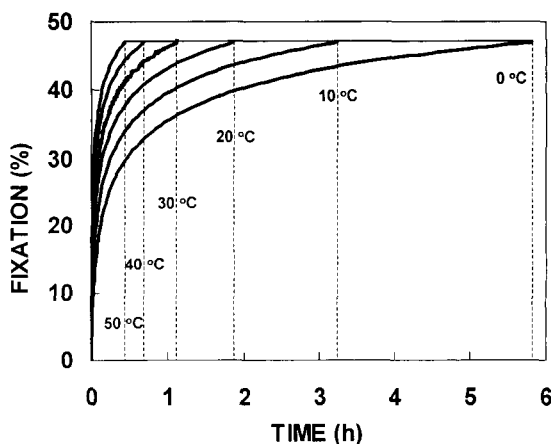
Applying all of the estimated parameters to

the generalized fixation model (Eq. (9)) yields the following for the initial reaction zone:

$$F(\%) = 100 - \frac{100}{Cr_o}\left[\left(\frac{1}{Cr_o}\right)^9 + 78.3 \times 10^{19} \times \exp\left(\frac{-4,550}{T}\right)t\right]^{-(1/9)}$$

(9a)

This generalized equation predicts the extent of chromium fixation during the initial reaction phase as a function of time (hours) and temperature (K) history for a given initial Cr^{VI} concentration in the treating solution (Cr_o). Using this equation, the predicted fixation rates as a function of isothermal temperature conditions between 0°C and 50°C are shown in Fig. 8.

In future work, the initial reaction model will be coupled with a model for the slower main reaction zone to develop an overall kinetic model that can predict the percentage of fixation at any given fixation conditions.

CONCLUSIONS

The initial rapid reaction of CCA fixation on wood matrix can be modeled by 10th order reaction kinetics. The initial reaction zone

controls approximately 47% of the total fixation. Once that percentage of fixation is completed, reactions of the second or main zone take over. The developed model can be used as a tool to predict the rate of the initial fixation reaction in a treating plant. The temperature dependence of the initial reaction estimates an activation energy of 37.8 kJ/mol.

In future studies now in progress, we will develop a model to describe the second or main reaction zone and test the ability of the models for the two reaction zones to predict the rate of CCA fixation in red pine pole sections.

ACKNOWLEDGMENTS

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