MODELLING OF THE RELATIONSHIP BETWEEN WOOD TEMPERATURE AND CCA FIXATION TIME*

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1. INTRODUCTION

CCA fixation is highly temperature dependent. Many investigators (e.g. Cooper and Ung 1992, Anderson 1989) have demonstrated that fixation can be accelerated at higher ambient temperature. Our studies also found that fixation time was greatly reduced by increasing temperature, from more than six months at 4^0C to about one hour at 90^0C and high relative humidity conditions. These results suggest that there is a definite relationship between ambient temperature and CCA fixation time.

However, wood temperature is distinctly lower than the ambient temperature during the heating or cooling period in fixation chamber (Figure 1). The difference between wood temperature and ambient temperature can be attributed to many factors, such as unsaturated relative humidity in the chamber which may cause a cooling effect when water evaporates from the wood surface and wood species which have different thermal conductivities.

It is clear that wood temperature is the true factor to affect CCA fixation rate and any study of temperature effect on CCA fixation time is preferred to be based on wood temperature instead of the ambient temperature. However, the calculation of wood temperature from ambient temperature is a multi-factor involved process and hence is complex. Therefore, we believe that monitoring wood temperature directly during fixation should provide more reliable information in regard to the estimation of temperature effect on CCA fixation time.

This study was designed to develop a CCA fixation model which defines the relationship between wood temperature and fixation time quantitatively. Ultimately, it may lead to the development of an industrial fixation control system.

2. MATERIALS AND METHODS

Small red pine blocks (25x25x25 mm) with moisture content 25-35% were cut from red pine sapwood to evaluate wood temperature effect on fixation time. Six wood temperatures, ranging from 4^0C to 90^0C, were selected for the study. Wood temperatures were measured by thermocouples inserted at the midpoint of blocks and recorded by computer.

In total, 540 blocks were used representing: 2 concentrations x 6 temperatures x 3 replicates x 15 blocks per test. For each experimental run, 15 samples were vacuum treated at room temperature

*This paper was selected for the student award 1994 for 30 minutes with 1% or 3% CCA-C solution respectively to achieve target retention of 6.4 or 20.0 Kg/M^3. Following treatments, the blocks were immediately weighed and then fixation allowed to take place in a fixation chamber. Throughout fixation time, about 95% relative humidity was maintained to minimize the cooling effect.

Fixation rates at six different wood temperatures were monitored by Cr^{+6} contents in expressed solutions. Samples were randomly taken out from chamber at different fixation time, e.g. 0 hour, 24 hours, and then squeezed in a hydraulic press. The concentration of unreacted Cr^{+6} in solution expressed from the wood void space, which is an indicator of CCA fixation level, was analyzed by the diphenylcarbazide procedure (McNamara, 1989).

3. MODELLING

With the nature of chemical reactions, CCA fixation is affected by many factors, such as temperature, concentration, pH, wood species and wood moisture content, etc. (Anderson 1989). Our experiment results (Figure 2) indicate that the effect of wood temperature is of primary importance. When wood temperature increased from 4^0C to 90^0C, the fixation time was reduced from 4391 hours to about 1 hour. The strength of the treating solution or the initial concentration in wood (at "0" fixation time) also had a positive effect on fixation time with 3% CCA fixation treated blocks taking longer to fix than that of 1% CCA treated blocks.

The experiment information suggested that the extent of Cr^{+6} reduction is depends on wood temperature and fixation time, and the relationship between them could then be expressed as:

$$Cr^{+6} \text{ concentration} = f\text{ (wood temperature, fixation time)}$$

Therefore, we hypothesized that a fixation model could be developed by applying the theory of chemical kinetics which deals with how the chemical reaction rates depend on factors such as concentration and temperature (Laidler 1987).

1) Determination of Chemical Reaction Order of Cr^{+6} Reduction

The rate of chemical reaction is a positive quantity that tells us how the concentration of a reactant or product changes with time. The reduction of Cr^{+6} could be related to the rate equation with the form of

$$\text{rate} = d[Cr^{+6}]/dt = K[Cr^{+6}]^n \qquad (1)$$

where

K = rate constant

n = reaction order of Cr^{+6} reduction

From Table 1, the functions (X, LnX, and 1/X), when plotted against t, give a straight line for zero, first, and second order reactions, respectively. These relations offer a simple method of deciding upon the order of a reaction (Masterton and Slowinski 1973). From our experimental data, the

Linear relationship was established by plotting $Ln(Cr^{+6}/M)$ vs t, suggesting a first order reaction type of Cr^{+6} reduction during fixation (Figure 3).

Table 1. Determination of chemical reaction order: A _ products
(X, X_0 = conc.A at t and t=0, respectively)

Order	Rate Expression	Conc.-Time Relation	Linear Plot
0	rate = K	$X_0 - X = Kt$	X vs t
1	rate = Kt	$Ln(X_0/X) = Kt$	LnX vs t
2	rate = $K X^2$	$(1/X)-(1/X_0) = Kt$	1/X vs t

Equation (1) can now be written as rate = K $[Cr^{+6}]$ with a corresponding differential rate equation

$$\text{rate} = - d[Cr^{+6}]/dt = K\,[Cr^{+6}] \qquad (2)$$

Equation (2) can be solved by separating the variables and integrating between the limits of Cr^{+6}_t (Cr^{+6} concentration at time "t") and Cr^{+6}_0 (Cr^{+6} concentration at time "0"). After integration, Eqs. (3) and (4) are the equivalent forms of the integrated first-order rate equation

$$Ln([Cr^{+6}_t]/[Cr^{+6}_0]) = - Kt \qquad (3)$$

$$\text{or } Cr^{+6}_t = Cr^{+6}_0\, e^{-Kt} \qquad (4)$$

In equation (4), Cr^{+6}_t, the unreacted Cr^{+6} at any fixation time t, is related to its original concentration Cr^{+6}_0, fixation time t and the rate constant K.

2) Estimating Wood Temperature Dependence of the Rate Constant K

The rate of Cr^{+6} reduction is a sensitive function of wood temperature. Experimentally, the rate constant K can usually be connected with temperature by Arrhenius' equation

$$K = A\, e^{-E/(RT)} \qquad (5)$$

$$\text{or its linear form: } LnK = LnA - E/RT \qquad (6)$$

where R is the gas constant and T is the wood temperature in absolute scale. Equation (6) contains two parameters: A is called the pre-exponential factor with the same units of rate constant and E is the experimental activation energy (J/Mole). K can be calculated from Equation (3) at six different wood temperatures and then plotted LnK against 1/T to estimate E and A. If E and A are indeed temperature independent, the plot should give a straight line with the slope equal to -E/R and the intercept equal to A (Connors 1990). The plotting of LnK vs. 1/T did yield linear relations with our 1% and 3% CCA data (Figure 4). The parameters estimated are listed in Table 2. If we insert values of parameter E, A and the gas constant into Equation (5), we get an estimated Arrhenius' equation

$$K = 4.0 * 10^{10} * e^{-69811/(8.314*T)} \qquad (7)$$

which relates the rate constant K to wood temperature T. Therefore, we can calculate K value or evaluate temperature effects from (7).

Table 2. Estimated parameters in Arrhenius' equation

Parameters	1% CCA	3% CCA	Gas constant R
A	$1.7*10^{10}$	$4.0*10^{10}$	
E	80643 J/M	69811 J/M	8.314 J/(K Mole)

3) Model Building

In the first order integrated rate equation (4), we have defined the relationship between unreacted Cr^{+6} concentration in wood and initial Cr^{+6} concentration, fixation time, and the rate constant K. We can also evaluate wood temperature effect on rate constant K from equation (7) based on Arrhenius' equation. The combination of Equations (4) and (7) yielded the fixation model:

$$Cr^{+6}_t = Cr^{+6}_0\, e^{-4.0 * 10\wedge 10 * e\wedge(-69811/(8.314*T)) * t} \qquad (8)$$

from the model, unreacted Cr^{+6} in wood during fixation can be calculated or predicted at any given fixation time on the basis of wood temperature history.

4. VALIDATIONS AND RESULTS

To examine the applicability of the fixation model, red pine and southern yellow pine pole sections, about 110 cm long with diameters of 30 to 40 cm, were conditioned to initial moisture content 10~25%. Wood sections were treated with 2% CCA-C solution and fixed at different ambient/wood temperatures, relative humidities and heating schedules.

During fixation, wood temperatures were monitored by thermocouples and fixation time recorded by computer. Cr^{+6} contents in wood were predicted from the fixation model. During the model validations, the actual Cr^{+6} contents in wood sections were also measured by the diphenylcarbazide procedure as the control. Then the calculated or predicted Cr^{+6} concentrations were compared with the measured values to evaluate the predictability of the fixation model.

Figure 5 shows the validation results of red pine poles at 55% and 95% relative humidities. At both fixation conditions, the predicted (solid line) and the measured (dashed line) Cr^{+6} concentrations were quite similar. Further tests were designed by combining high humidity fixation with low humidity to achieve some degree of drying. Again, the predicted and the measured values were well matched as shown in Figure 6. These suggest that the fixation model can be used in combined/mixed humidity conditions which is now applied by some treating plants in order to partially dry the wood during fixation. Tests were also conducted at an extreme conditions in which kiln temperature was deliberately changed dramatically by opening the kiln door or shutting off the kiln for 1 hour, and then closing the door or reheating for 1 hour. These processes were repeated several times for the initial 10-hour fixation period (Figure 7). Similarly, the predicted fixation time is very close to the measured fixation time (Figure 8).

The model was also tested with southern yellow pine pole sections. Figure 9 shows that the predicted and measured values are almost superimposed, indicating that the fixation model can also be applied to this species as well.

5. DISCUSSION

The hypothesis that wood temperature should give a better estimation of CCA fixation than the ambient temperature has been positively approved. By using wood temperature to predict CCA fixation we can avoid involving too many factors in our model. Though these factors do contribute somehow to heat transfer of wood and consequently affect the rates of CCA fixation, their influences have been included in the wood temperature effect.

This model has given a simple equation to define the relationship between wood temperature and fixation time. It could also provide treating industry with a straightforward way for process control. Based on our fixation model, a computer-aided fixation monitoring system has been established for experimental purposes. A further goal is to develop an industrial control system to follow the fixation process automatically and remotely (Figure 10). The application of the model will result in minimization of environmental contamination at treating sites and will save energy by allowing fixation to take place at optimum time and wood temperature.

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Figure 1. Comparison of Wood Temperature with the Kiln Temperatures at 95% Relative Humidity (60/58°C)

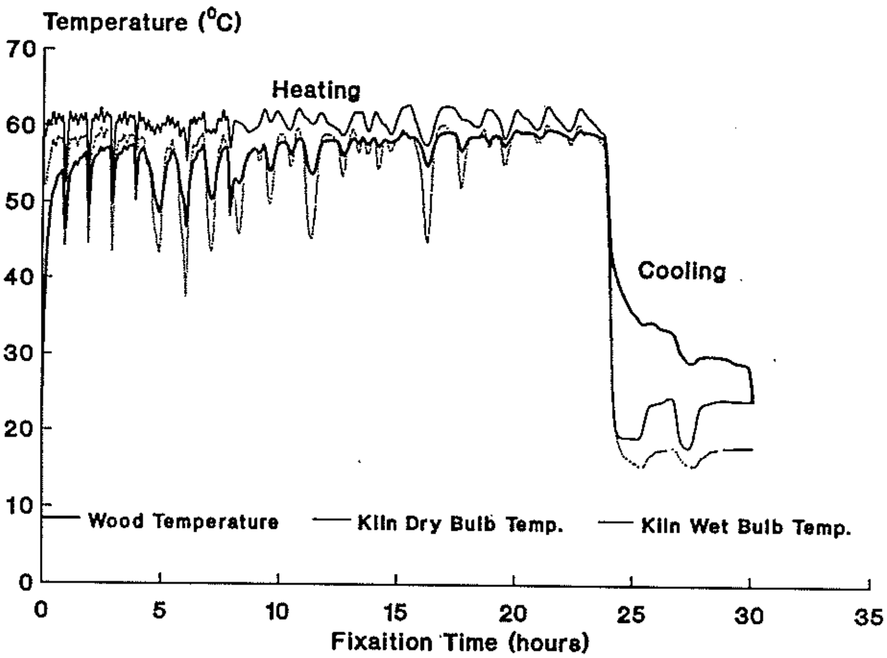

Figure 2. The Reduction of Cr^{+6} in 3% CCA-C Treated Red Pine Blocks at Six Different Wood Temperatures

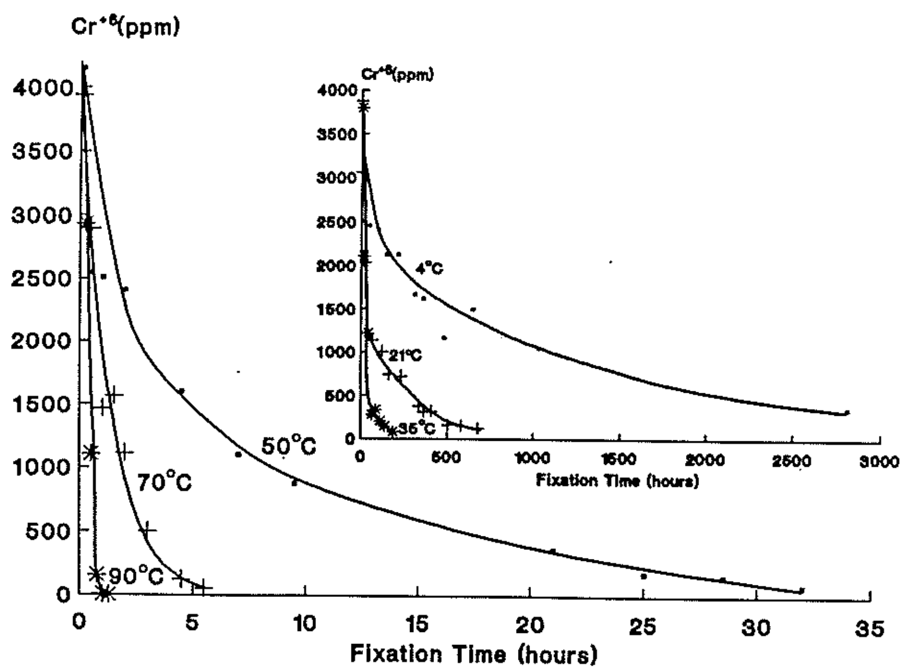

Figure 3. Examples of the Relationship between LnCr^{+6} and the Fixation Time: First Order Linear Relation

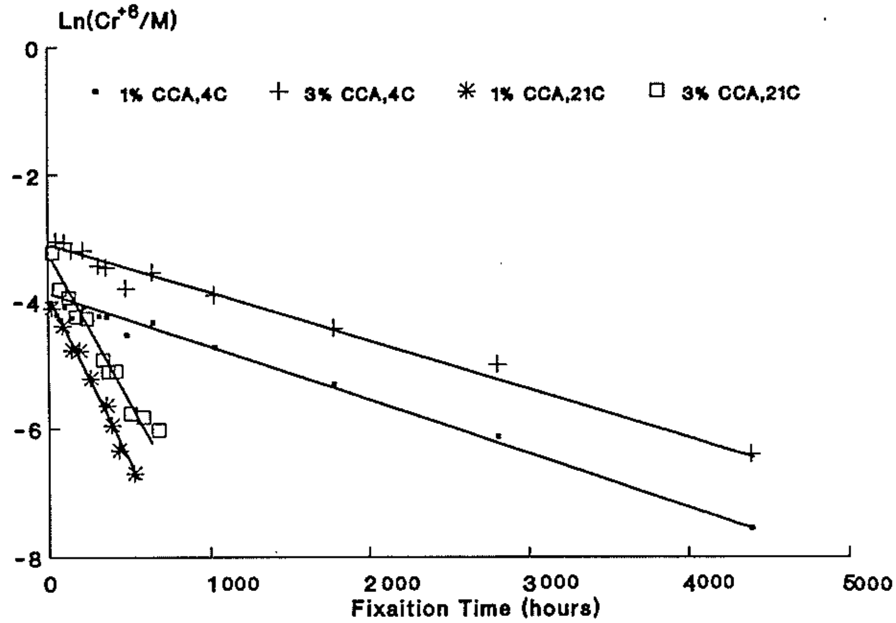

Figure 4. The Relationship between Rate Constant (K) and Wood Temperature (T): Activation Energy Estimation

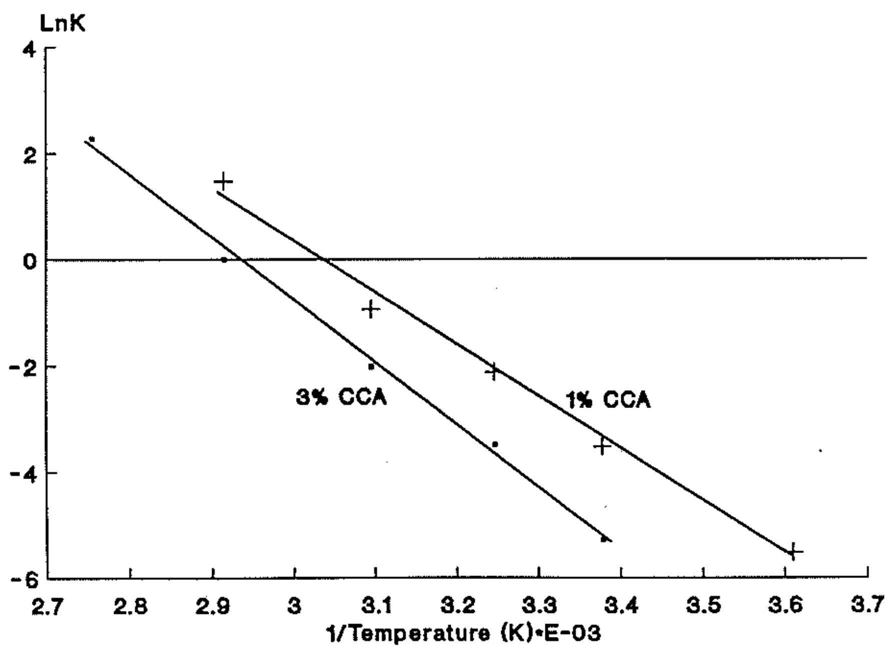

Figure 5. Comparison of Predicted and Measured Cr^{+6} Reduction at 95% and 55% Relative Humidities

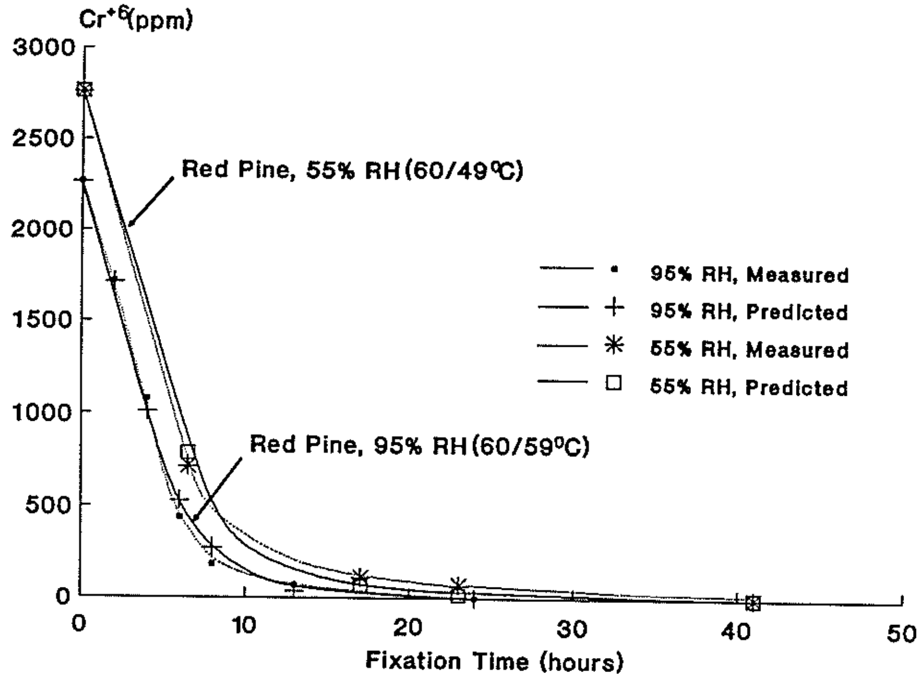

Figure 6. Comparison of Predicted and Measured Cr^{+6} Reduction at High Humidity Followed by Low Humidity

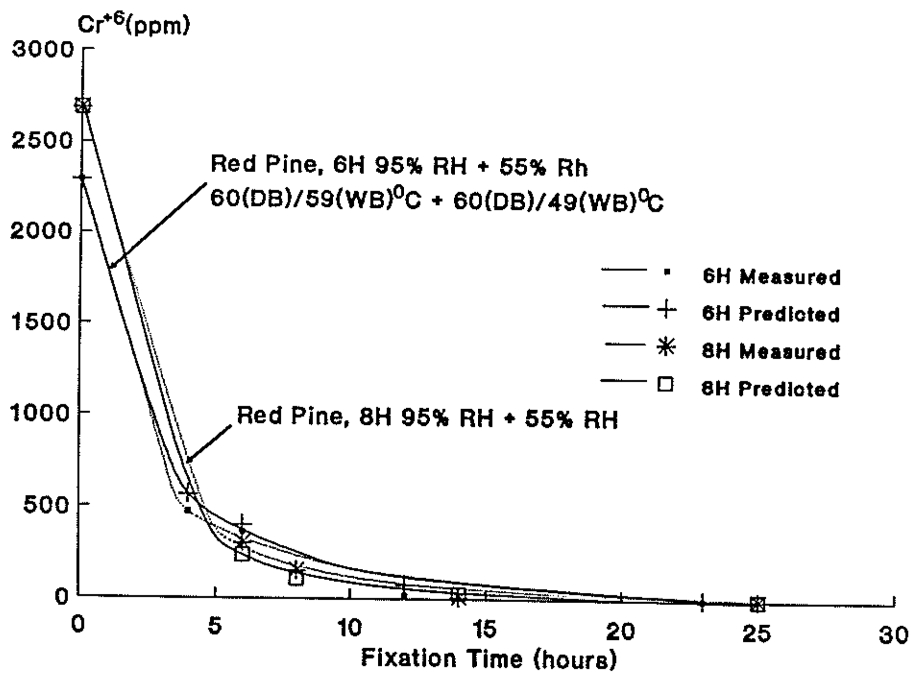

Figure 7. Fluctuating Wood and Kiln Temperatures Caused by a Changed Heating Schedule

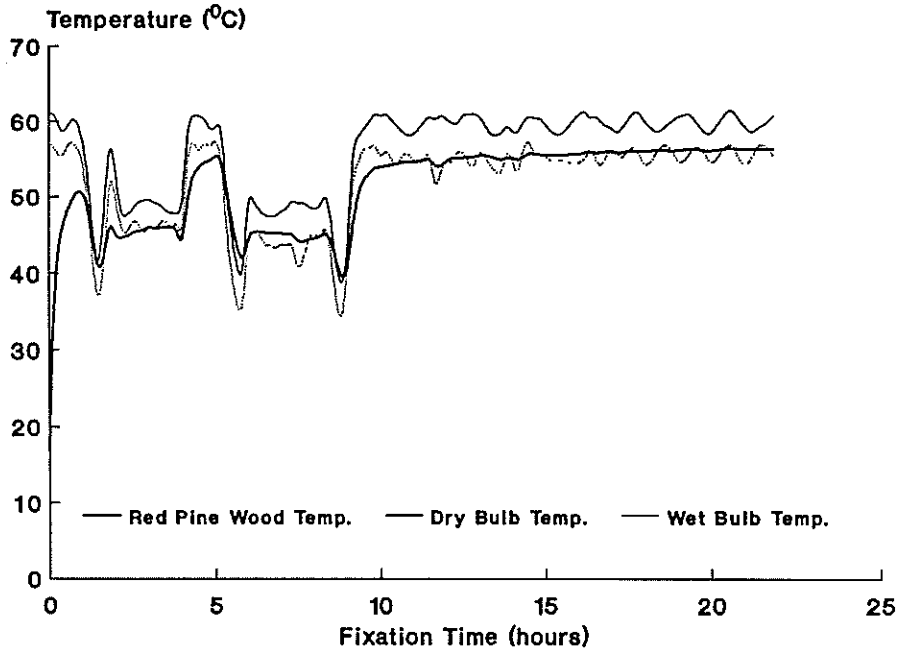

Figure 8. Comparison of Predicted and Measured Cr^{+6} Reduction at Fluctuating Wood Temperature

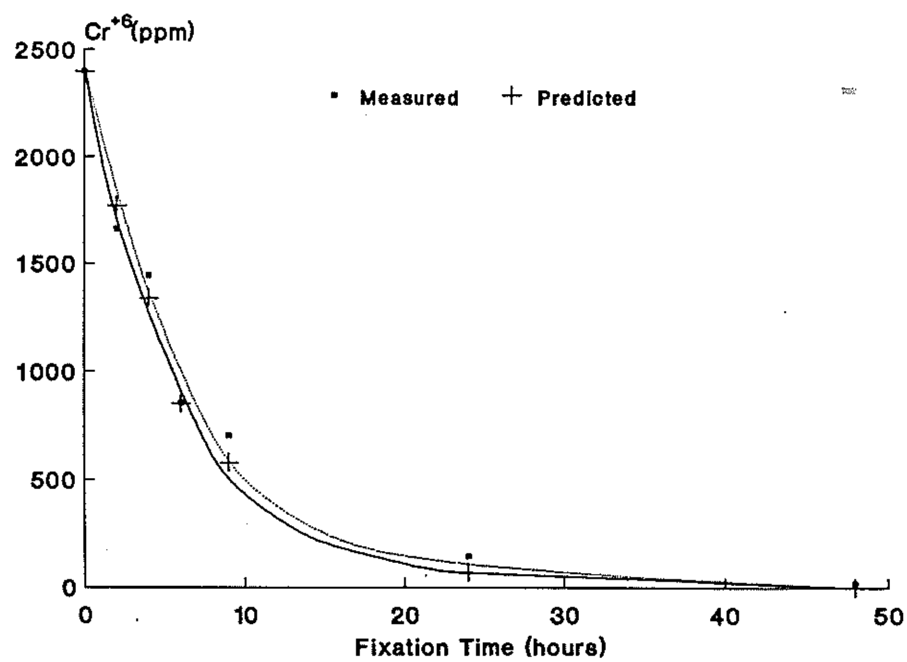

Figure 9. Comparison of Predicted and Measured Cr^{+6} Reduction in Southern Yellow Pine Pole Section

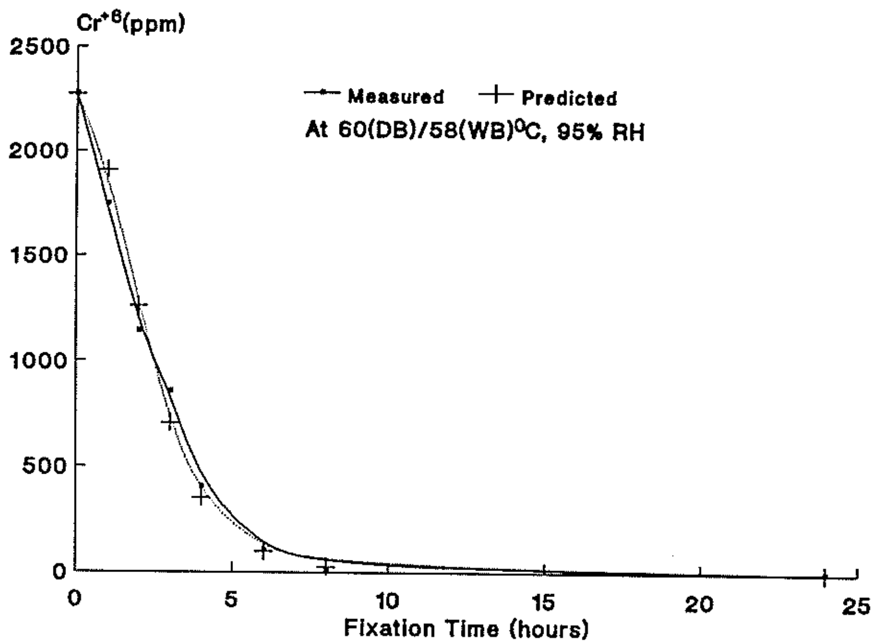

Figure 10. Schematic Diagram of a CCA Fixation Monitoring System for Fixation Control