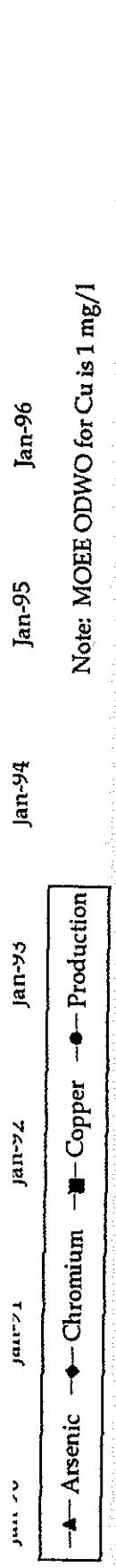

FIXATION CHEMISTRY OF CCA AND HOW IT RELATES TO PRODUCTION OF SAFE AND EFFECTIVE TREATED WOOD

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Summary

Our basic understanding of the chemistry of fixation of chromated copper arsenate (CCA) wood preservatives is reviewed and discussed in relation to practical production of a high quality treated product. The reaction with CCA-C components after treatment can be divided into two and possibly three reaction periods: an almost instantaneous "initial reaction" characterized by a rapid rise in pH, a 30 - 60% decrease in available hexavalent chromium, and a significant drop in available copper and arsenic; a main reaction period during which the arsenic and copper components are stabilized rather early in this step and the available hexavalent chromium is reduced to the trivalent form; and possibly a third stage where conversion reactions occur in the wood which result in formation of more stable reaction products. Fixation conditions, such as temperature, humidity, solution concentration and retreatment may affect both the physical and chemical aspects of fixation and the quality of treated product. The potential consequences of fixation under other than optimum conditions, such as higher leaching losses and surface deposition must be considered in the design of controlled fixation systems.

1.0 Introduction

In the more than sixty years since chromated copper arsenate (CCA) wood preservatives were first developed, tremendous research and development effort has been expended on "fine-tuning" the formulations, determining the properties of treated wood and exploring mechanisms of fixation of the chemicals with wood. At this time, there is still much unknown about the specific reactions that result in the high resistance to leaching and other losses from wood and CCA's long term effectiveness against most wood degrading organisms. However, in recent years some of the reactions have been clarified and more importantly, their relevance to the industry are becoming more clear.

Much of the recent work on CCA fixation mechanisms focuses on accelerated fixation at elevated temperatures. Most CCA treating plant operators in Canada now recognise the benefits of faster and controlled fixation of CCA treated products by these systems. The rate of fixation increases exponentially with fixation temperature allowing manufacturers to rapidly move treated material off the drip pad and out of protected storage. Environmental and health consequences of dripping and leaching of CCA components from incompletely fixed material and handling of this material by unprotected workers can

be virtually eliminated. By speeding up this phase of the process, manufacturers of treated wood are better able to implement "just-in-time" production of their product. Furthermore, wood treated to CSA specifications must be certified fixed by the chromotropic acid method and it is becoming more common for regional environmental agencies to require assurance of chromium fixation before treated wood is allowed to leave the treating plant. Controlled accelerated fixation is the only sure way of producing fixed material in a reasonable time, especially in the winter.

However, of the estimated 20+ treating plants in Canada that use some type of accelerated fixation, virtually no two are the same and the efficiency and ultimate quality of product varies considerably. It is important to identify the factors that not only affect the rate of fixation, but also the quality of fixation. In this paper, we will discuss some of the recent findings on CCA fixation and the factors affecting the production of high quality CCA treated wood - a product that is safe to handle, has optimized resistance to leaching after treatment and maintains its resistance to biological deterioration.

2.0 Chemistry of CCA Fixation

The complexity of the CCA fixation process derives to a great extent from the fact that three complex CCA components are interacting with many complex wood cell wall components and the chemical environment (especially pH) is changing continuously during fixation. As a result, the many scientists that have investigated this problem (see references by Wilson, Smith and Williams, Dahlgren and Hartford, Pizzi and co-workers, Ostmeyer and co-workers, Yamamoto and Ruddick and co-workers for example) have hypothesized a number of intermediate and final reactions, few of which have been unequivocally proven or are universally agreed to.

Researchers (e.g., Dahlgren and Hartford 1972) have defined three reaction periods during CCA fixation:

Initial reaction period Significant reactions occur by the time that treated wood is removed from the treating vessel. This is even observed in laboratory tests where the total time to treat and unload the samples may be only a matter of minutes. These reactions are assumed to be almost instantaneous. The most noticeable initial reaction is the increase in pH from about 2.0 in the 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 is drawn from the treating solution which is usually attributed to pH dependent ion exchange of copper on wood (e.g., Dahlgren and Hartford 1972). 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, not consumed, this does not help explain the observed increase in pH. The Cr(VI) concentration in the CCA solution in the wood drops immediately after treatment by 30 - 60% which is generally taken to support the view that some hexavalent chromium is temporarily

adsorbed to the wood (Schema 1) and other is reduced by sugars and other low molecular weight extractives (Dahlgren and Hartford 1972b), although we have found (Cooper, Kaldas and Ung 1995) that the effect is as great in solvent extracted wood as in unextracted wood.

Schema 1: Consumption of H^+ by adsorption of hexavalent chromium on wood during the initial reaction

$$2CrO_3 + H_2O \;\text{®}\; Cr_2O_7^{2-} + 2H^+ (+H_2O) \;\text{®}\; 2HCrO_4^- + 2H^+ \;\text{®}\; 2H_2CrO_4$$

$$\text{Wood} + H_2CrO_4 \;\text{®}\; \text{Wood}.H_2CrO_4$$

Also, a smaller fraction of arsenic is rapidly immobilized, presumably due to formation of chrome arsenates and perhaps copper arsenates. With higher concentration solutions, and with wood retreated with CCA, the relative copper adsorption is reduced, consistent with there being a fixed number of sites for copper adsorption, but the arsenic immobilization is increased (Wilson 1971, Cooper, Kaldas and Ung 1995). Thus, even in this initial reaction phase, treatment variables can affect the route and possibly the quality of fixation. There may be different overall fixation mechanisms and end reaction products for example for material treated to high retentions such as marine material and for wood that is retreated due to failing retention.

Main reaction period

Following the "initial reactions" there is an extended period of steadily increasing pH during which the majority of the CCA components react. The decrease in solubility of copper, chromium and arsenic with time is highly temperature dependent. The kinetics describing the insolubilization or fixation of CCA components has been described as both first order (e.g., Alexander and Cooper 1993, Chen 1994) and second order (e.g., Dahlgren and Hartford 1972b, Pizzi 1982c). In either case, fixation is characterized by a "diminishing returns" type curve where long times are needed to achieve small changes in the degree of fixation as it approaches completion.

During this period, the pH of the wood solution continues to rise from about 3.2 to 5.5. One scenario for this large pH change can be represented by oxidation of a primary alcohol group (Schema 2) with consumption of protons and reduction of Cr(VI) to the trivalent state.

Schema 2: Oxidation of a primary alcohol with Cr(VI)

$$3RCH_2OH\ 3RCH_2OH + 16H^{+} + 2Cr_2O_7^{2-} \ \textcircled{R}\ 3RCOOH + 11\ H_2O + 4Cr^{3+}$$

$$3RH + 3CO_2$$

The amount of Cr(VI) decreases steadily accompanied by oxidation of various wood components. Studies based on reaction of CCA with model compounds and on sawdust and more recent studies on solid wood by X-ray photoelectron spectroscopy (XPS), diffuse reflectance Fourier transform infrared spectroscopy (DRIFT), electron spin resonance spectroscopy (ESR) and other techniques provide conflicting evidence of the types of reactions occurring.

XPS and DRIFT studies (Ostmeyer *et al* 1988, 1989) provided evidence of chromium oxidation of lignin and the formation of chromium esters with lignin components. These reactions have been supported by Pizzi's work. Other studies (e.g., Yamamoto *et al* 1991, Kaldas and Cooper 1991) show that there is a relative decrease in carbons reacted with one oxygen that is best explained by oxidation of -OH groups on hemicellulose and cellulose (Schema 2). However, there is not an increase in highly oxidized (carbonyl and carboxylic acid groups) components expected from such an oxidation. This is explained by decarboxylation reactions with the release of CO_2 (Williams and Feist 1984, Yamamoto *et al* 1991). Again, the fact 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 suggests that the fixation products and the quality of fixation may differ significantly depending on the fixation conditions.

Pizzi (1982c, 1990) concluded that most of the chromium was strongly fixed to lignin and that arsenic and copper were mainly associated with this lignin bound chromium as copper chromates and chromium arsenates. He concluded that copper arsenates were not formed. He concluded that a lesser amount of chromium was weakly bound to the polysaccharides along with some arsenate as chromium arsenate on the cellulose.

It is becoming more clear that the relative importance of these competing oxidation reactions depend on treating conditions such as concentration and formulation of the treating solution, time of contact of the solution with wood, pH of the solution and wood temperature and moisture content during fixation. The practical significance of this has not been made clear yet, although presumably, it may affect the quality of fixation. The implications are discussed in general terms by Pizzi (1982c, 1993) and Anderson (1989).

In the process of reduction of chromium 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). This is further evidence that the progress of fixation depends on the fixation conditions.

Conversion reactions
Dahlgren and Hartford (1972a) observed that the pH of sawdust mixed with CCA solution fluctuated over a several month period after treatment, indicating competitive proton consuming such as hydrolysis of chromate complexes to $Cr(OH)_3$ and proton liberating reactions such as conversion of tertiary copper arsenates and copper chrome arsenates to basic copper arsenates and tertiary chromium arsenates take place over an extended period.

The most probable final reaction products of CCA fixation are (Dahlgren and Hartford 1972, 1973, Pizzi 1982c, 1990a,b):
Wood-Cu complexes
Lignin-Cr complexes
$CrAsO_4$
$CuCrO_4$
$Cu(OH)CuAsO_4$
$Cr(OH)_3$

3.0 How do we define and measure CCA fixation?

A number of physical and chemical changes occur in wood as a result of the reactions with CCA chemicals. This results in a number of options for monitoring the progress of the reactions and of determining when the reactions are more-or-less complete:

j **Electrical conductivity** As the CCA components become insoluble, their ability to conduct electrical charges decreases and the point of minimum solubility can be measured from the electrical resistance of the wood (Evans and Nossen 1991).

j **Change in pH** The acidic CCA solution in wood is neutralized as the reactions progress. Expressed solution increases from the initial solution pH of about 2 to about 5 when fixation is complete. Unfortunately, the pH fluctuates in the latter stages of fixation and the end point can vary considerably both within and between wood species so this approach is not very reliable.

j **Change in available copper, chromium and arsenic** This may be measured as concentration of components in expressed solution or as leachable element when exposed to a defined leaching exposure.

j **Change in available hexavalent chromium - Cr(VI)** This may be measured in expressed solution or by a leaching test.

Measurement or detection of hexavalent chromium has become the accepted way of monitoring fixation for several reasons:

j Cr(VI) is very reactive and develops strong colour reactions with several reactants; thus it is easy to detect or measure as discussed above.

j Cr(VI) is the last component of CCA solutions to be immobilized during the fixation process (Figure 1); therefore it is a conservative method that ensures that once the chromium is fixed, the copper and arsenic components are fixed.

j Cr(VI) is perhaps the most hazardous of all CCA solution components since it has both acute and chronic toxicity properties and, unlike arsenic, is very mobile in the soil and can be significantly absorbed through human skin.

Both the AWPA and the CSA cite the chromotropic acid test method as standard method to determine when a satisfactory level of fixation has been achieved. The procedure is a sensitive qualitative detection of the presence of unreduced or hexavalent chromium from the original treating solution. The detection limit is about 15 to 50 ppm Cr(VI) in the wood which corresponds to about 99.5 % chromium reduction or fixation depending on the initial solution concentration. Typically a small core is taken from representative samples of the treated wood and placed on white porous paper such as filter paper and 1 - 2 drops of chromotropic acid solution (e.g., Foster 1988) placed on the core. If a purple colour develops under the core in a few minutes, there is detectable hexavalent chromium present in the wood and it is considered to be incompletely fixed. Thus, it is a qualitative "GO/NO GO" procedure that gives no real indication of how close the wood is to an acceptable fixation level.

Several quantitative procedures have been developed and adapted for use in treating plant quality control labs (e.g., Cooper *et al* 1994). One approach that has been adopted by several treating plants involves taking small increment borings (e.g. 4 - 0.5" long cores in 50 ml) from representative pieces in the charge, shaking them in distilled water or dilute sulfuric acid, adding a colouring hexavalent chromium reactant (diphenyl carbazide) and measuring the absorbance at the specified wavelength in a visible light spectrometer. The concentration in the leachate can be related to the percent fixation as determined by the expressing method so the % fixation can be estimated quantitatively in this way. One advantage of this approach is that it allows one to choose different fixation criteria than the approximately 99.5% of the chromotropic acid method. Also, it provides an estimate of how far fixation has progressed in incompletely fixed material so the operator can judge how much longer is required to complete fixation.

The main disadvantages of measuring Cr(VI) availability as a measure of fixation are that it does not relate directly to the availabilities of copper and arsenic and it does not characterize the quality of fixation. It is possible to have complete chromium reduction but unacceptable leaching characteristics as discussed below.

How does measured fixation relate to surface leaching of CCA products?

Use of a fixation test as a quality control procedure at treating plants presumes that the test results relate in some way to the availability of unreacted components to leaching or dislodging. It is important to validate this assumption, as questions can be raised about the suitability of using Cr(VI) content as the fixation criterion. Since the copper and arsenate components of CCA are fixed before the chromium (e.g., Figure 1), it is of interest to relate the surface leachability of all CCA components to the chromium fixation status. Also, fixation measuring procedures use corings to a specified depth in wood while leaching of wood exposed to rainfall is very much a surface phenomenon because of the relatively slow

rate of diffusion of the CCA components from deeper in the wood to the surface. This could result in poor correlation between fixation status and surface leaching properties.

We have compared the surface leaching properties of jack pine boards (Cooper *et al* 1995) and southern pine boards (Cooper and Ung 1995) with their chromium fixation status, as determined by the expressing method. Representative samples were exposed to the desired fixation conditions (either 21°C or 60 °C) and assessed for chromium fixation status at different stages of fixation. They were then placed in a recirculating water spray unit and exposed to approximately 150 mm (6") of vertical simulated rainfall applied as a misting spray. The water was analysed for Cr(VI), and total Cr, Cu and As content so the leaching characteristics could be related to the fixation level.

In both cases, (Figures 2 and 3), the copper and arsenic concentrations in the leachate dropped to low consistent values at only moderate levels of chromium fixation (80 - 95% depending on the species and fixation temperature). However, measurable hexavalent chromium could be detected in the leachate until very high levels (> 99%) of chromium fixation were achieved. High temperature fixation resulted in lower surface leaching at a given level of chromium fixation, presumably because leaching occurs at the very surface which fixes faster than the interior at high temperatures. This suggests that the chromotropic acid procedure is overly sensitive if the main concern is copper and arsenic availability but if Cr(VI) is of concern, it is an appropriate test.

4.0 Implications of Temperature/Humidity/Moisture content conditions

Many have discussed the effects and interactions of ambient and wood temperature, relative humidity and wood moisture content (e.g., Avramidis and Ruddick 1989, Lee *et al* 1993, Chen *et al* 1994, Boone *et al* 1995). Based on these studies and our own recent work, we believe that these effects can be summarized as follows:

j The rate of fixation increases exponentially with **wood** temperature. The relationship we have observed for red pine at moderate temperatures is summarized in Figures 4 and 5 (Chen 1994).

SIGNIFICANCE: Time to complete fixation can be controlled and selected from a wide range of acceptable fixation times frame 1 hour to several days by design of a fixation unit that can achieve higher than ambient temperatures.

j Wood temperature depends not only on the ambient or "dry bulb" temperature in the fixation chamber but also on the relative humidity which defines the wet bulb temperature. Under drying conditions, water evaporates from the wood surface cooling the surface so the wood temperature is below the dry bulb temperature and as long as there is significant water to evaporate, approximately equal to the wet bulb temperature (Figure 6). The fixation rate is reduced accordingly.

SIGNIFICANCE: The use of high temperature fixation chambers without high humidity wastes energy, since the fixation time depends on the wet bulb temperature.

j The surface drying effect may result in wicking of solution containing unreacted CCA components to the wood surface where it takes longer to fix and may result in more easily leached surface reacted CCA. It may also contribute to surface deposition of CCA fixation reaction products and unreduced chromium.

As water from the solution evaporates from the wood surface, the liquid meniscus recedes into the small pit membrane pores resulting in a strong capillary pull on the solution below. If the wood is highly saturated and relatively permeable, a large volume of solution may be brought to the surface. Any dissolved CCA components will be deposited on the surface where they may or may not react with the wood surface and each other to form CCA fixation reaction products. Surface deposits on CCA treated wood at the point of sale or use is a major concern of the industry since they can result in unacceptable surface dislodgeability and exposure of users to CCA components.

This effect, in combination with evaporative drying of pools of CCA solution on the wood surface is most likely responsible for the brown wood surface discolouration, sometimes called "fish tailing" which is often associated with accelerated fixation. This is a serious problem that must be avoided since the stained area contains a high concentration of unreduced chromium which will be readily leached or dislodged when exposed to the environment or to handling. The stain appears to be related to evaporation of CCA solution at points on the wood where the temperature is high and the relative humidity low, such as near the inlet of gas furnaces or unsaturated steam used to heat the fixation chamber. The hot air or steam causes rapid evaporation of the solution before the components can react with the wood surface. It may result from the drying of puddles of solution laying on horizontal surfaces but more often appears to be related to the wicking of unfixed material to the wood surface and rapid evaporation of the water in the solution near the heat source.

This condition, if observed, must be eliminated. One solution to the problem is to increase the relative humidity in the chamber to prevent drying and to ensure that the dry bulb/wet bulb depression is low during the initial heat up period. Also, heat sources should have deflectors to disperse incoming heat streams uniformly through the chamber.
SIGNIFICANCE: If wood dries during fixation, the components are more easily leached, perhaps because of concentration of reaction products near the surface. There may also be more surface deposits that make the wood more dangerous to handle.

j If the wood surface moisture content drops significantly below the fibre saturation point, not only is the rate of fixation greatly reduced (Figure 7), but also the quality of fixation is impaired. Even though the wood may test fixed (complete Cr(VI) reduction) arsenic and copper leaching properties will be much worse than for wood fixed at high humidity (Figure 8).

One possible explanation for this effect is that the relative distribution of CCA components between the cell walls and the lumen surfaces depends on the fixation conditions. CCA

components presumably diffuse into the cell walls in relation to their ionic characteristics (size of hydrated ion and charge). Cations such as copper are attracted into the cell wall while anions such as chromates and arsenates tend to be excluded (Cooper and Roy 1994). The capacity of the cell wall water for these chemicals is limited and for significant cell wall penetration, the chemicals must react and become insoluble so more unreacted components can diffuse in. If wood drops below the fibre saturation point moisture content before fixation is complete, diffusion of chemicals into the cell walls is impeded and more reacted product will be deposited in the cell lumens. It has not been proven, but it seems likely that this effect contributes to the well documented poor leaching characteristics of wood that has been dried during the fixation process (Conradie and Pizzi 1987, Lee *et al* 1991, Boone and Winandy 1995).

SIGNIFICANCE: It must be understood that Dry [1] Fixed.
Surface drying is not a substitute for proper fixation and in fact is deleterious to the health and environmental safety of the "fixed" product. The wood moisture content must be maintained at above 25 - 30% moisture content to avoid poor leach resistance of the treated product.

5.0 Case Studies of Facility Design and Its Effect on Fixation

The following case studies demonstrate some of the above principles.

1. Ambient temperature fixation of bulk piled Southern pine lumber

Bulk piled southern pine lumber was monitored for temperature for about 3 days and the fixation status estimated by the boring leaching method described above (Figure 9). The wood temperature was higher inside the pack than on the surface as a result of surface drying and at the end of the test, the interior wood (sample A) was fixed to a higher degree than the wood on the surface (sample B) or in the stickered pile (sample C).

2. High temperature fixation of bulk piled Southern pine lumber

In this example, bulk piled and stickered Southern pine was placed in a fixation chamber with high dry bulb temperature, moderately high humidity and good air circulation. The wood temperature of the stickered lumber reached the wet bulb temperature rather quickly and was 99 % fixed in 8 hours (Figure 10). The interior of the bulk pile heated up slowly and the wood reached only 78 % fixation in the same time period.

3. High temperature fixation of stickered 4" X 4" SPF with poor humidity control and air circulation (Figure 11)

This direct fired fixation chamber results in a large dry bulb/wet bulb depression indicative of very low relative humidity. The energy expended to achieve the high dry bulb temperature is essentially wasted since the wood temperature only approaches the wet bulb temperature. The rate of heating of the wood is low because of the poor air circulation. Wood produced by this chamber is surface dry, but incompletely fixed because of the low

temperatures achieved in the wood. There will be the additional problems of surface deposits and poor leaching resistance of the product.

4. **High temperature fixation of 2" X 4" SPF with good humidity control but poor air circulation (Figure 12).**

The sample near the outside of the bundle achieved the high wet bulb temperature and a high level of fixation in 7 hours. Samples deeper in the piles do not heat adequately because of the poor air circulation and reach only moderate levels of fixation in this time period.

5. **Moderate temperature fixation of 2" X 6" SPF with good humidity control and air circulation (Figure 13)**

6. **High temperature fixation of 2" X 8" SPF with good humidity control and air circulation (Figure 14)**

In both cases, the wood temperature is close to the kiln temperature because of the high humidity and good air circulation. Complete fixation is achieved in both cases, but requires a much shorter time in the high temperature chamber

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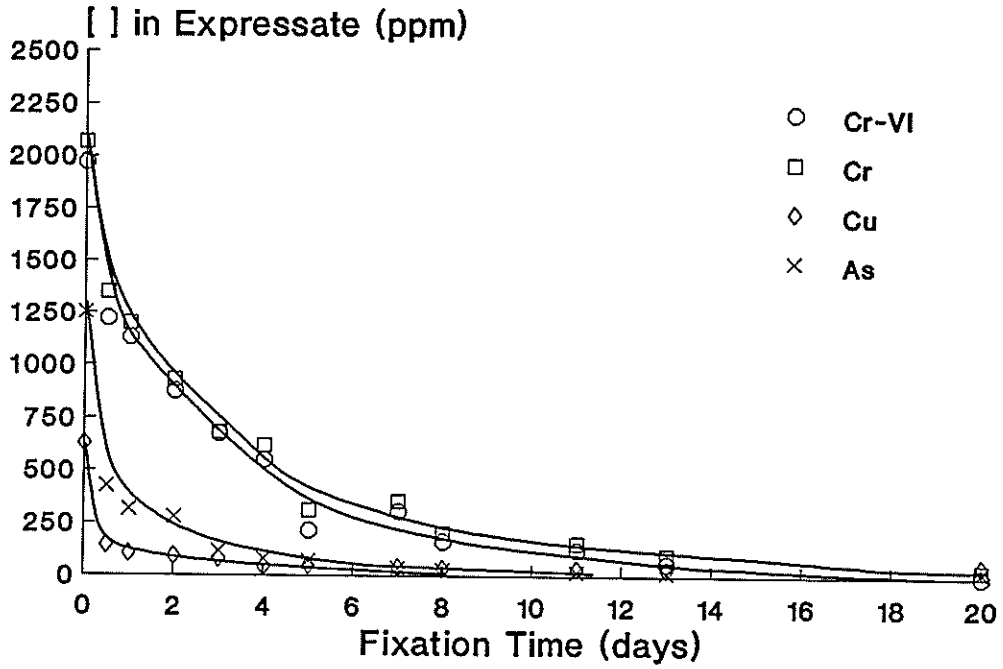


Figure 1: Fixation of CCA components in southern pine lumber treated with 1.6 % CCA-C at 21°C-Expressate method.

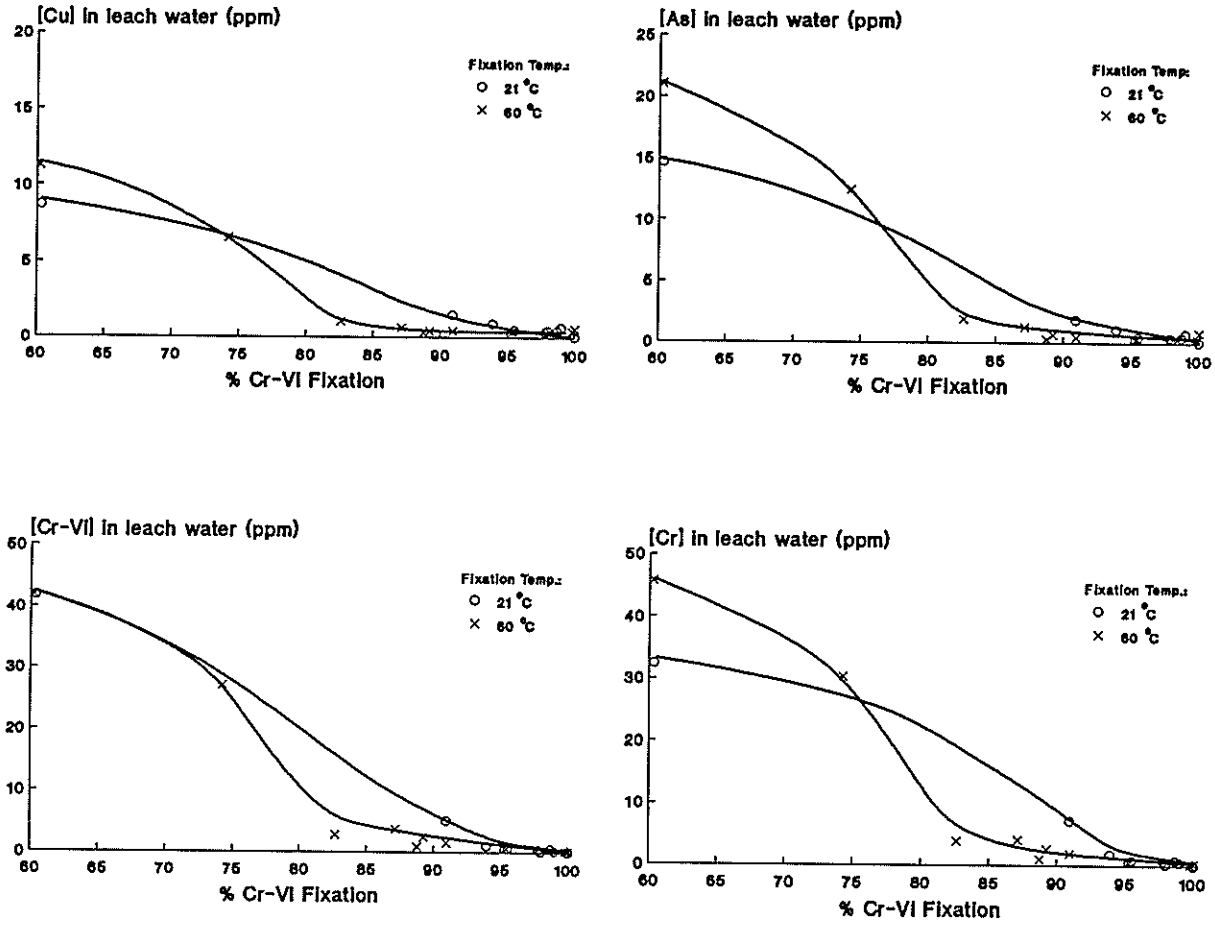


Figure 2: Surface leaching of CCA components at different chromium fixation levels.
(jack pine lumber @ 1.6 % CCA-C)

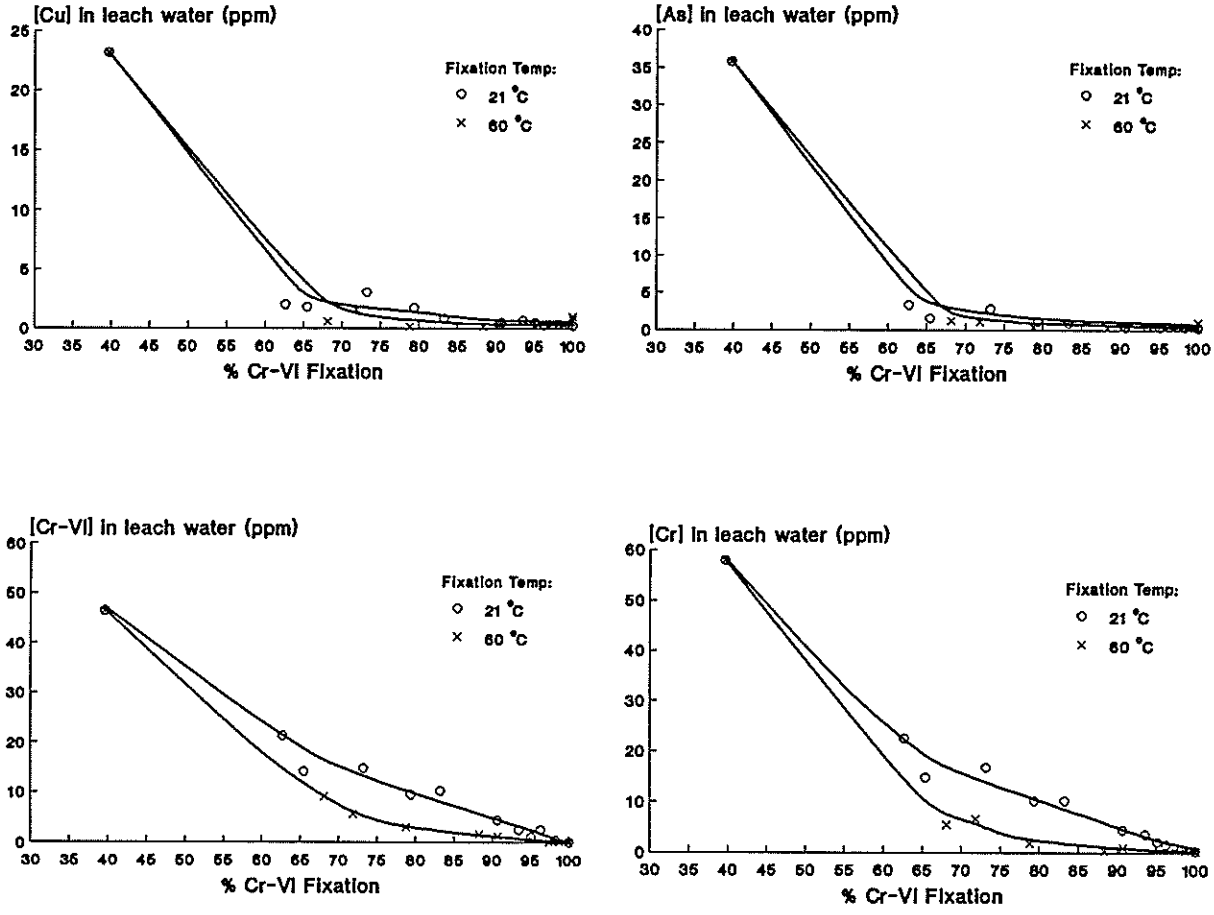


Figure 3: Surface leaching of CCA components at different chromium fixation levels.
(Southern pine lumber @ 1.6 % CCA-C)

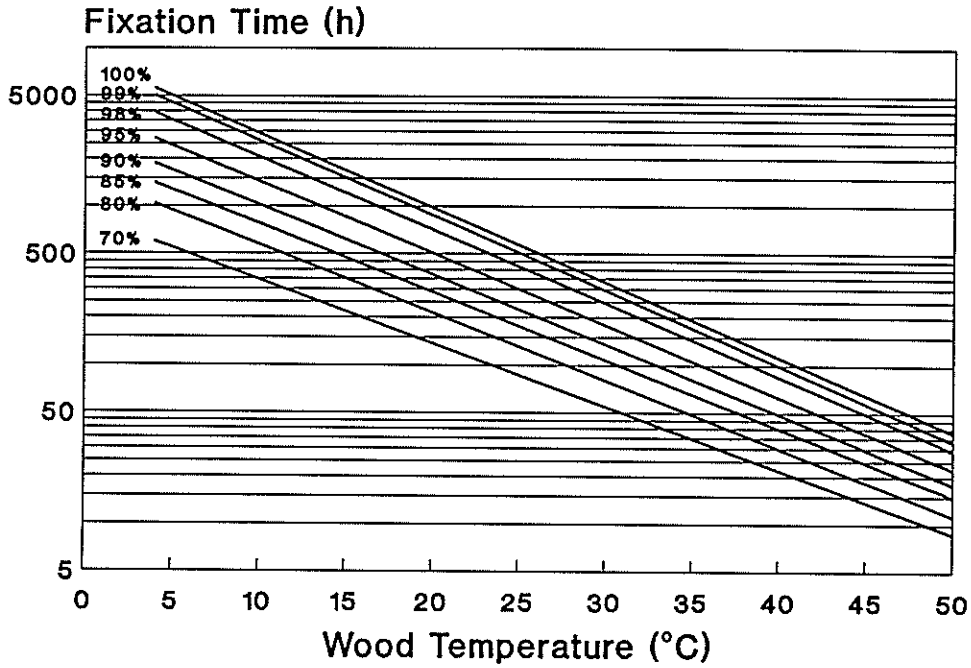


Figure 4: Relationship between wood temperature & fixation time for red pine treated with 1% CCA-C (4 - 50°C).

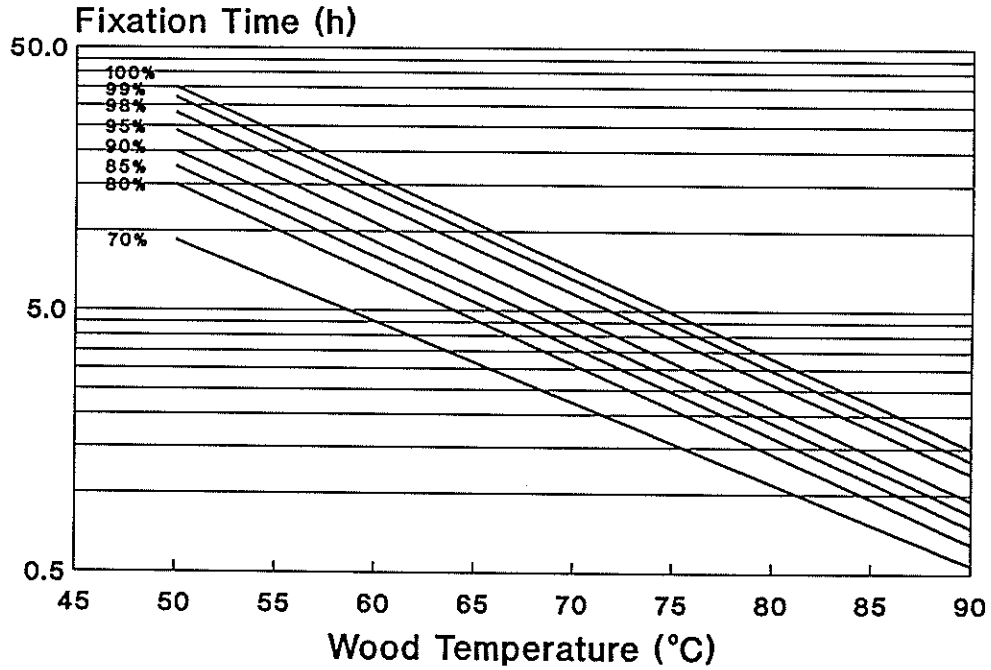


Figure 5: Relationship between wood temperature and fixation time for red pine treated with 1% CCA-C (50 - 90°C).

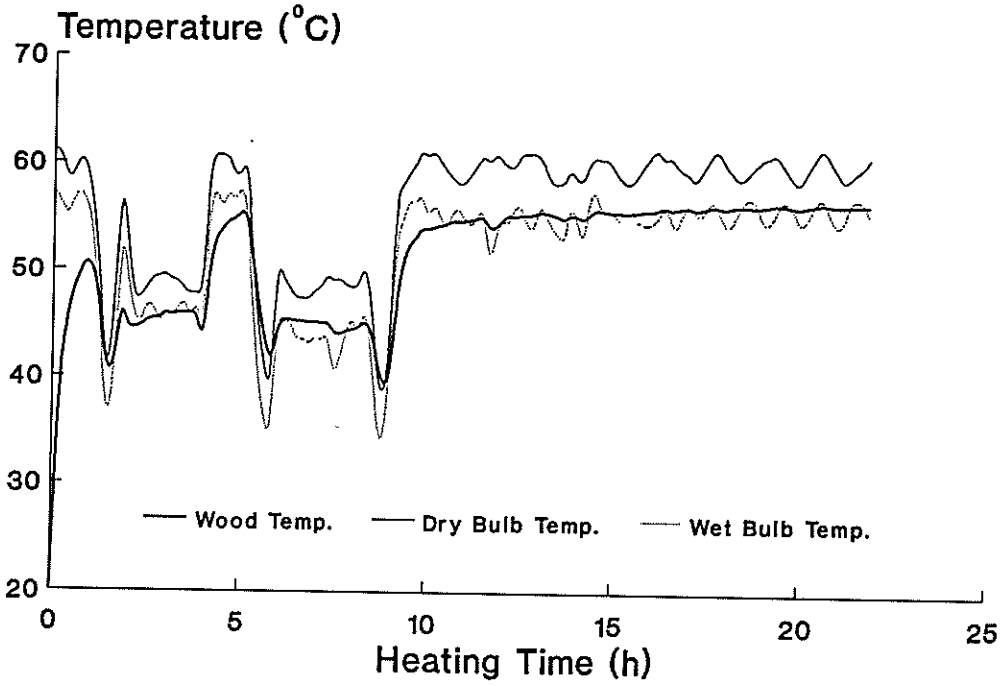
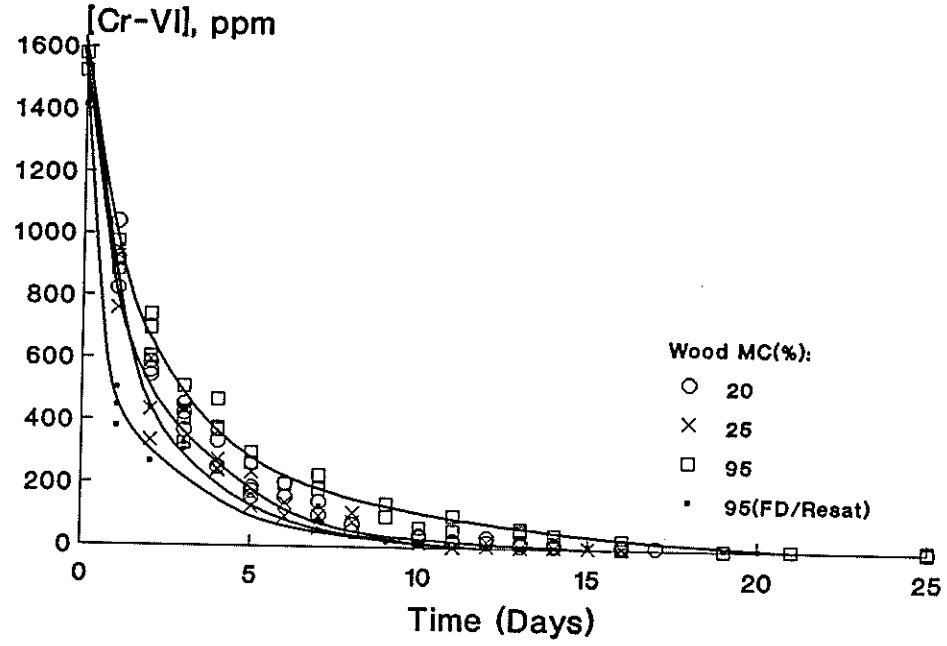


Figure 6: Wood temperature under fluctuating temperature and humidity conditions (red pine poles @ 12.5 mm depth).



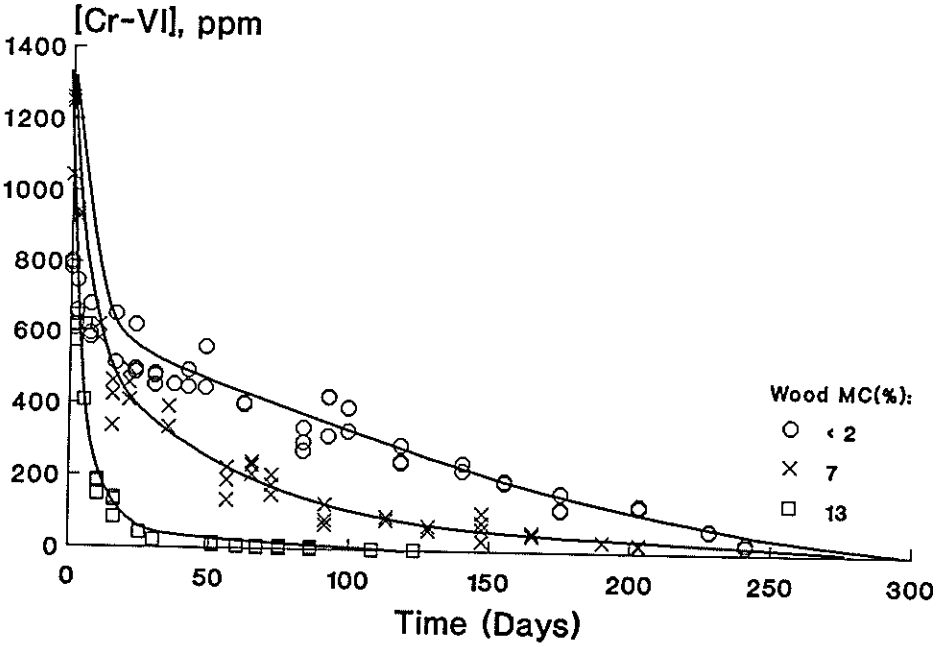


Figure 7: Effect of wood moisture content on rate of chromium fixation at 21 °C (Kaldas & Cooper 1995).

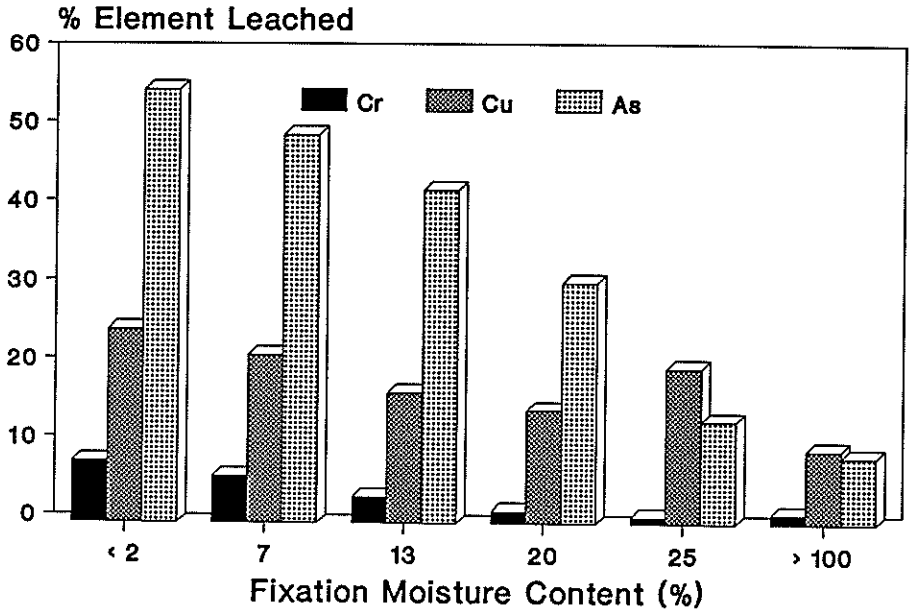


Figure 8: Effect of wood moisture content during fixation on AWPA-E11 leaching of CCA components (Kaldas & Cooper 95).

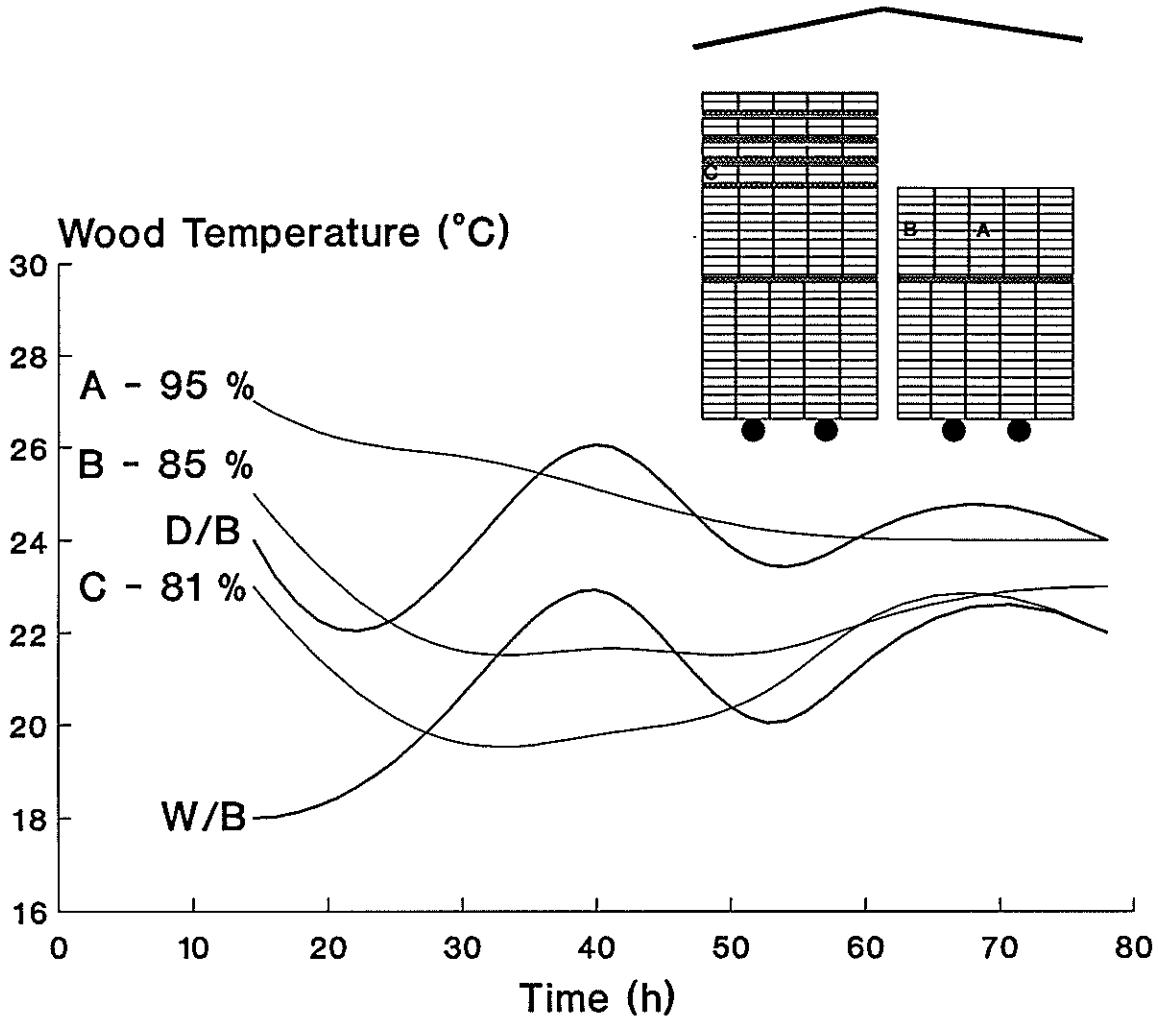


Figure 9: Temperature development and fixation achieved in 78 hours in bulk piled or stickered southern pine under ambient summer conditions.

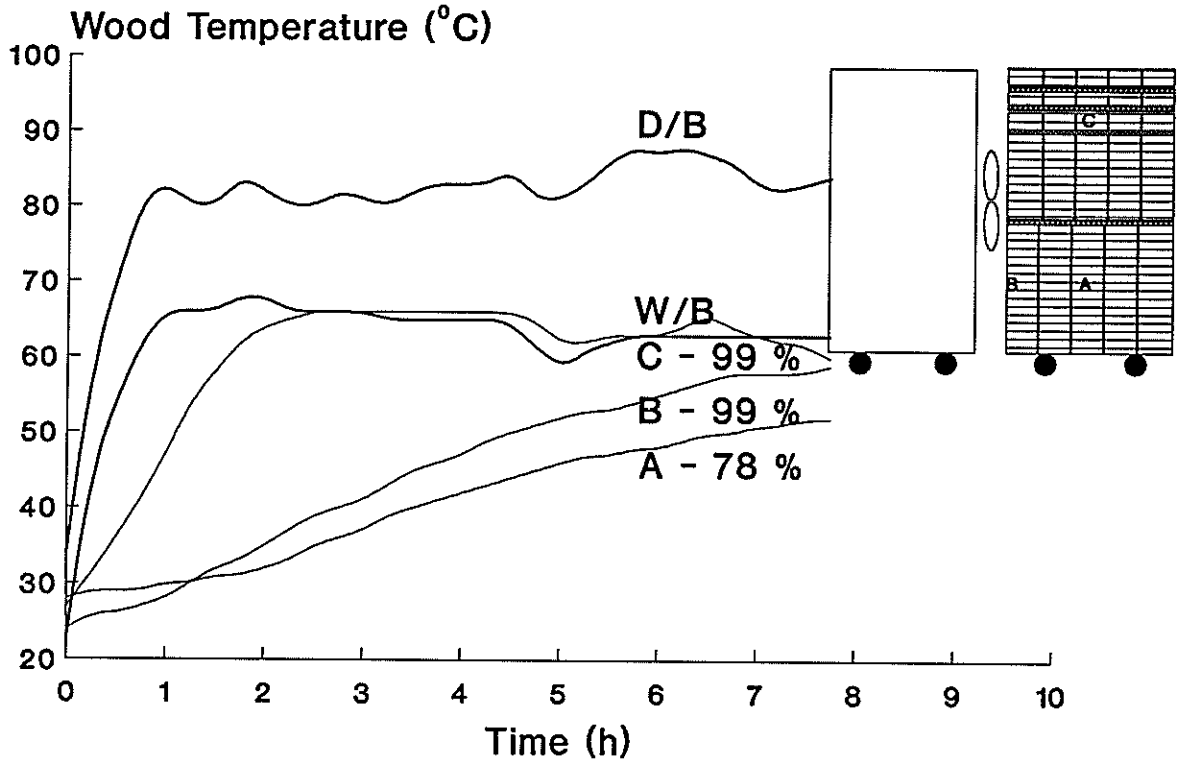


Figure 10: Temperature development and fixation achieved in 8 hours in bulk piled or stickered southern pine (5/4"x6") in a fixation chamber.

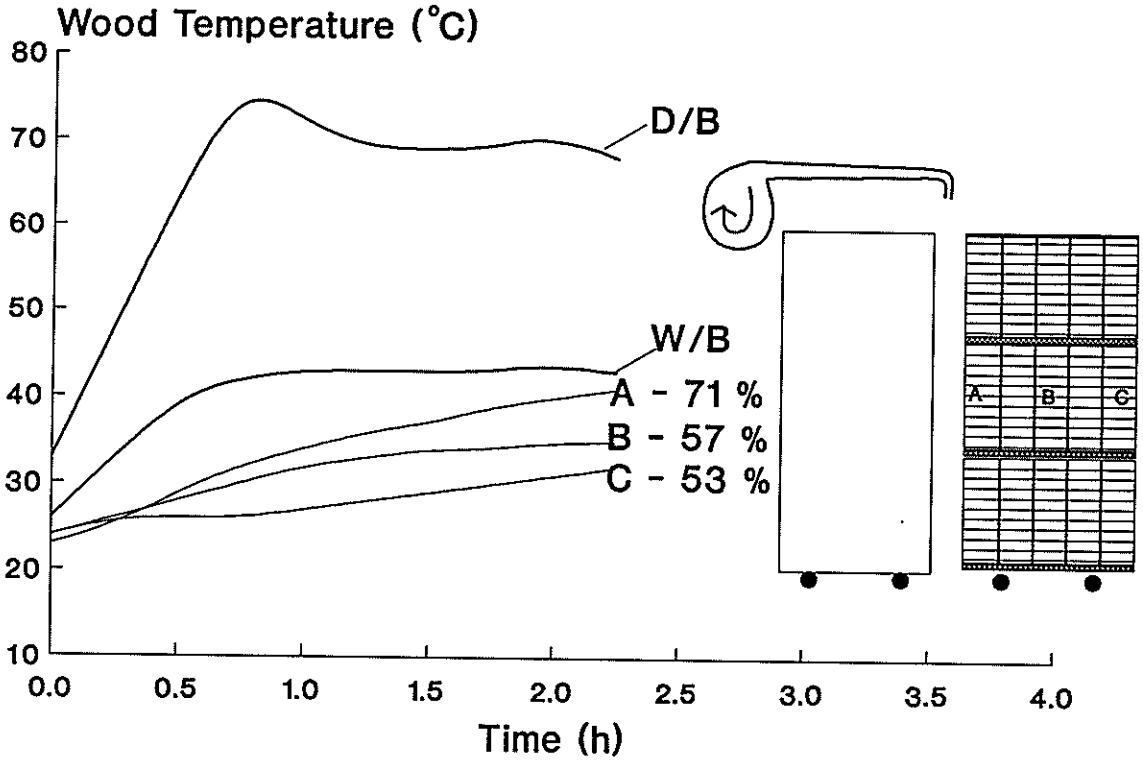


Figure 11: Temperature development and fixation achieved in stickered 4"x4" SPF in high temperature with low humidity and poor air circulation.

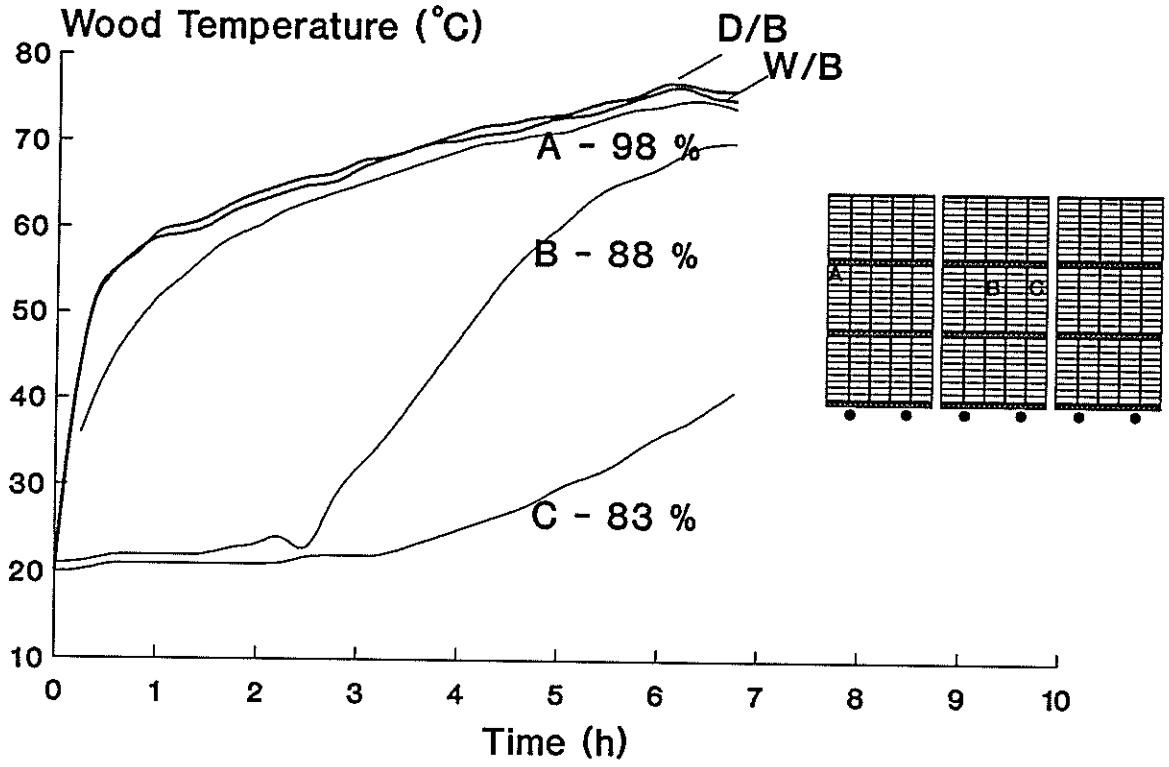


Figure 12: Temperature development and fixation achieved in 2"x4" SPF before fans added to the chamber.

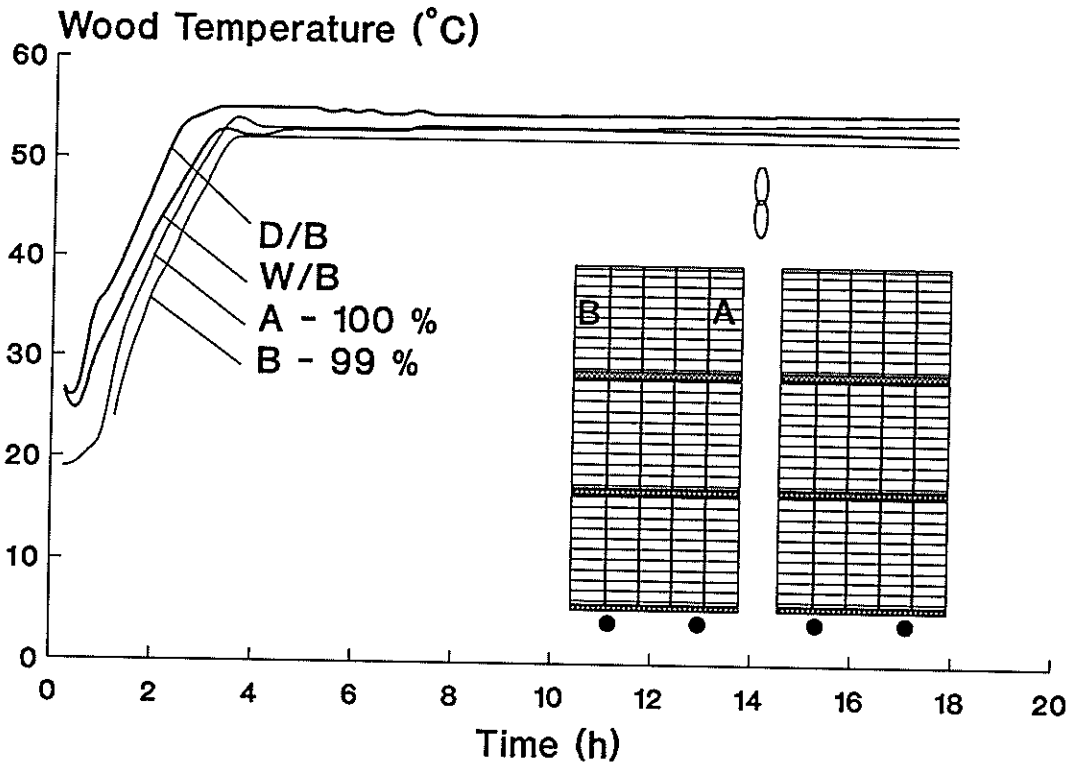


Figure 13: Temperature development and fixation achieved in 2" x 6" SPF in moderate temperature fixation chamber.

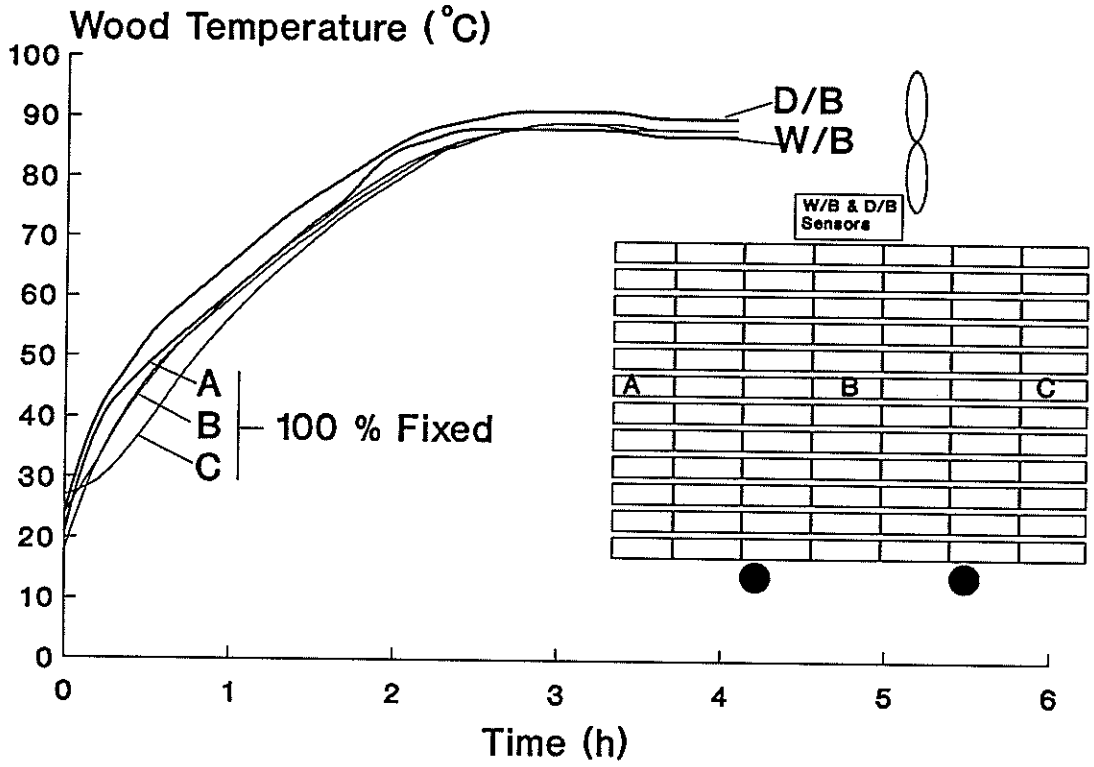


Figure 14: Temperature development and fixation achieved in 4 hours in stickered 2"x8" SPF in a high temperature and humidity chamber with good air flow.