EFFECTS OF TEMPERATURE AND HUMIDITY ON CCA-C FIXATION IN PINE SAPWOOD

By Dave L. Alexander, and Paul A. Cooper
Faculty of Forestry, University of Toronto

ABSTRACT

The rates of CCA fixation in blocks of jack pine, red pine, and southern yellow pine sapwood are compared at temperatures of 50°C, 70°C, and 90°C and relative humidities of 50%, 70% and 90%. Fixation is monitored by the rates of depletion of free chromium VI, and total copper, chromium, and arsenic in the cell lumens of the blocks. The fixation rates of jack pine and red pine are almost identical, while southern pine fixes more rapidly. The rates of fixation of all species are significantly inhibited if the wood is allowed to dry extensively during the fixation process.

INTRODUCTION

The post-treatment handling of freshly-treated wood is a great source for potential hazard to the environment and worker health at most Chromated-Copper-Arsenate (CCA) treatment facilities in Canada. To this effect Environment Canada (EPS 2/WP/3, 1988), has made recommendations to minimize the loss of preservative chemicals from CCA-treated wood. One such recommendation allows for the fixation of CCA in wood, and states that CCA treatment facilities should *provide for sufficient storage area to hold all freshly-treated wood for a minimum of 48 hours under cover or 96 hours in a specially designated uncovered area, with assured recovery of dripped material and precipitation*. However, significant chromium losses can still occur from CCA-treated wood after a 96 hour fixation period at 21°C, (McNamara, 1988; Cooper *et al.* 1989; and Sheard, 1991). This potential source for chemical release in the environment could result in serious long-term toxic effects if the treated wood is allowed to be rained upon while in the storage yard.

Accelerating the fixation of CCA by means of heating will remove most of the risks associated with the post-treatment handling of CCA-treated wood. Peek and Willeitner (1988), achieved almost complete fixation of chromium VI in pine by steaming the treated wood at 110°C for about 60 minutes, while Cooper *et al.* (1989), achieved complete fixation in red pine sapwood in about 12 hours at 50-60°C and 90-100% relative humidity conditions. However, not all heating conditions are suited to accelerate fixation. Avramidis and Ruddick (1989), showed that wet-bulb temperature was more important than dry-bulb temperature in determining the time required to fix CCA in a mixture of hem-fir treated wood, while Conradie and Pizzi

(1987), suggested that rapid drying using high temperatures might impair fixation and even reduce the efficacy of the preservative.

The chemistry and mechanism of fixation of Cu-Cr-As wood preservatives have been extensively investigated by many authors, and have recently been summarized by Anderson (1989). In most studies, the rate of fixation has either been monitored via the leaching of sawdust samples or by direct pH measurements. These techniques, however, present an impossible task when dealing with solid wood samples.

Recently, a simple expressing technique has been demonstrated for the monitoring of CCA fixation in solid wood, (McNamara, 1988; Cooper *et al.* 1989). This method involved squeezing excess CCA solution out of the treated wood cells, and analyzing the resulting expressate for the remaining CCA component elements. This expressing technique is only applicable to situations where a little or no drying of the wood occurs, because as the moisture content approaches the fibre-saturation-point of wood the removal of excess solution becomes increasingly difficult. However, by resaturating the wood samples with water before expressing is done, an excess supply of solution can be ensured even under severe drying conditions.

This study was, therefore, designed to use a refined expressing technique to evaluate the effects of temperature and relative humidity on CCA-C fixation in pine sapwood.

MATERIALS AND METHODS

A 3^3 factorial design was used to assess the effects of temperature, relative humidity (RH), and species on the rate of CCA fixation. Three pine species: southern yellow pine (*Pinus sp.*); jack pine (*Pinus banksiana*); and red pine (*Pinus resinosa*), were selected for study based on their commercial importance to the wood preservation industry. Each species was represented by a sample of 10 individual pole-sections which were tested at 3 temperatures (50, 70, and 90°C), and 3 relative humidity conditions (50, 70, and 90%). A total of 27 experimental runs were conducted where each run was monitored over 5 selected time intervals.

Sapwood blocks measuring 25×25×25mm were carefully cut and labelled from each of the 10 pole-sections for each species. Five blocks were then selected from each pole-section and vacuum treated at room temperature (approximately 23°C), with a 1.058% CCA Type-C solution (w/w basis) to achieve a target retention of 6.44 Kg/m^3. Immediately after treatment, the blocks were weighed to determine gross retention, before being placed in a humidity chamber at one of the above temperature/humidity conditions (e.g. 50°C and 50% RH), where they were monitored until the complete reduction of chromium VI was achieved.

At selected time intervals, 10 blocks were taken from the chamber and weighed to determine moisture loss, before being resaturated under a 1 minute vacuum with 1000 mL of distilled water. After resaturation the blocks were again weighed to determine moisture pick-up, before being squeezed in a hydraulic press to remove excess treating solution from the wood. Approximately 6mL of expressate were collected from each sample and stored in glass vials for later analysis. On an average, all treatment combinations were tested over a period ranging from 0 to 28 hours in the humidity chamber to determine the extent of CCA fixation under the different exposure conditions.

Expressate samples were analyzed for copper, chromium, and arsenic content by using an x-ray fluorescence analyzer (ASOMA unit), and the reduction of chromium VI to chromium III was monitored using the Diphenylcarbazide Method (ASTM D1687-86).

RESULTS AND DISCUSSION

A summary of actual fixation conditions are presented in Table 1, along with estimated times to achieve 99% fixation of chromium VI under the given conditions. These estimated times were based on a first order kinetic model that was fitted to data obtained at each experimental condition. An example of such a fit is presented in Fig 1, while Fig 2 shows an example of the relationship between the elements of CCA during the fixation process. The almost instantaneous adsorption of copper generally accounts for its rapid fixation rates, followed by arsenic and then chromium. The reactions of arsenic are also generally chromium dependent for CCA solutions, (Dahlgren and Hartford (1972c); (Pizzi 1982c); and Wilson (1971)). Concentrations of chromium VI were lower than that of total chromium and both species of chromium were fixed at similar rates. Similar observations with chromium VI were also noted by other authors such as McNamara (1988) and, Sheard (1991). The rates of chromium VI fixation were, therefore, used for comparing the different experimental conditions.

There were no differences between the fixation rates of jack pine and red pine (Fig's 3 - 6), however, southern pine showed considerably faster fixation rates at all the conditions tested. The different temperature and relative humidity conditions all exhibited different rates of fixation, with the higher combination of these conditions having the fastest fixation times. The rates of fixation are significantly inhibited if the wood is allowed to dry excessively during the fixation process. This trend is again consistent with what have been reported by other authors such as Avramidis and

Ruddick (1989). The relationship between wet-bulb temperature and the rate of fixation is, therefore, very important. However, this phenomenon cannot be explained at this point in time. It is suspected that a high wet-bulb temperature is necessary to facilitate proper heat transfer in the wood, while also maintaining moisture which is essential for the interactions of chromium with the other preservative components and wood.

The rates of copper fixation, also showed similar relationships to those of chromium VI fixation, however, no differences were observed between species when the rates of arsenic fixation were taken into account.

CONCLUSIONS

The rate of CCA-C fixation in wood is highly temperature dependent with wet-bulb temperature apparently playing an important role in the process. Jack pine and red pine gave identical rates of fixation under the conditions tested, however, southern yellow pine exhibited faster fixation rates at the same conditions. The rates of fixation of total chromium and chromium VI are almost identical, and the chromium component is the slowest fixing component in a CCA preservative. Tests involving the monitoring of chromium are, therefore, good indicators of the rate and extent of CCA fixation in wood.

ACKNOWLEDGMENTS

The authors wishes to thank Timber Specialties Ltd., Campbellville, Ont.; LPB Poles Inc., Masson, Que.; and the Ministry of Colleges and Universities (URIF Program) for their financial, and technical support in conducting this study.

REFERENCES

ASTM, D1687-86. 1987 Annual Book Of ASTM Standards. Standard Test Method for Chromium in Water. Vol. 11.01. Philadelphia. PA.

Anderson, D.G. 1989. The accelerated fixation of chromated copper preservative treated wood. Proc. Can. Wood Preserv. Assoc. 10: 75-110.

Avramidis, S., and J.N.R. Ruddick. 1989. Effect of temperature and moisture on CCA fixation. Proc. Can. Wood Preserv. Assoc. 10: 125-126.

Cooper, P.A., T. Ung, and E. Leonov. 1989. Fixation of CCA-C treated red pine at moderate temperatures. Proc. Can. Wood Preserv. Assoc. 10: 111-118.

Conradie, W.E. and A. Pizzi. 1987. Progressive heat inactivation of CCA biological performance. Proc. Amer.

Wood Pres. Assoc. 83: 32-49.
Dahlgren, S.E. and W.H. Hartford. 1972c. Kinetics and mechanism of fixation of Cu-Cr-As wood preservatives. Part III. Fixation of Tanalith C and comparison of different preservatives. Holzforschung 26; 142-149.
Report EPS 2/WP/3. 1988. Chromated Copper Arsenate (CCA) Wood Preservation Facilities: Recommendations for Design and Operation. Environment Canada. Ottawa. Ontario. 90p.
McNamara, W.S. 1988. CCA fixation experiments. Osmose Wood Preserving Inc. Research Report 22-1876.
Peek, R.D., and H. Willeitner. 1988. Fundamentals on steam fixation of chromated wood preservatives. Int. Res. Group on Wood Preserv. Doc. IRG/WP/3483.
Pizzi, A. 1982c. The chemistry and kinetic behaviour of Cu-Cr-As/B wood preservatives. Part III. Fixation of a Cr/As system on wood. J. Polym. Sci. Chem. Ed. 20; 725-738.
Sheard, L. 1991. A study of the rate of fixation of various chromium-containing preservatives. Int. Res. Group on Wood Preserv. Doc. IRG/WP/3653.
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(6); 36-40.

TABLE 1: **Summary of fixation relationships**

Specie	Temp (°C)		Rel Hum	Retention	Avg Drying Rate	Time to 99% Fixation
	Db	Wb	(%)	(Kg/m^3)	(%/min)	(min)
J	50	39	50	6.29 ± 1.05	0.06 ± 0.01	1395.7 ± 483.0
A	50	44	70	6.33 ± 1.14	0.06 ± 0.02	851.1 ± 226.4
C	50	48	90	6.22 ± 1.13	0.01 ± 0.01	752.5 ± 159.7
K	70	56	50	6.54 ± 1.05	0.12 ± 0.03	391.6 ± 108.7
	70	62	70	5.70 ± 0.98	0.10 ± 0.04	216.4 ± 14.5
P	70	68	90	6.17 ± 0.97	0.02 ± 0.01	158.9 ± 16.7
I	90	73	50	6.41 ± 1.10	0.19 ± 0.05	85.9 ± 4.2
N	90	81	70	6.41 ± 1.05	0.53 ± 0.16	81.1 ± 2.4
E	90	87	90	6.57 ± 1.35	0.18 ± 0.08	69.0 ± 4.5
R	50	39	50	5.86 ± 0.64	0.08 ± 0.02	1708.8 ± 288.2
E	50	44	70	6.07 ± 0.66	0.07 ± 0.02	1005.3 ± 314.1
D	50	48	90	6.04 ± 0.66	0.03 ± 0.01	752.4 ± 32.5
	70	56	50	6.20 ± 0.61	0.17 ± 0.05	368.0 ± 24.8
P	70	62	70	6.17 ± 0.73	0.09 ± 0.02	230.4 ± 7.7
I	70	68	90	6.15 ± 0.64	0.05 ± 0.02	200.3 ± 6.0
N	90	73	50	5.96 ± 0.61	0.19 ± 0.05	91.2 ± 0.7
E	90	81	70	5.84 ± 0.63	0.66 ± 0.10	80.0 ± 2.3
	90	87	90	5.73 ± 0.76	0.12 ± 0.09	52.9 ± 14.5
S	50	39	50	6.33 ± 0.45	0.06 ± 0.01	1314.7 ± 163.5
O	50	44	70	6.79 ± 0.37	0.06 ± 0.01	793.4 ± 124.8
U	50	48	90	6.50 ± 0.42	0.02 ± 0.01	541.9 ± 28.8
T	70	56	50	6.62 ± 0.42	0.13 ± 0.04	341.4 ± 4.0
H	70	62	70	6.50 ± 0.44	0.10 ± 0.02	155.9 ± 9.7
P	70	68	90	6.76 ± 0.42	0.03 ± 0.01	111.2 ± 2.5
I	90	73	50	6.38 ± 0.44	0.19 ± 0.03	84.8 ± 26.9
N	90	81	70	6.41 ± 0.44	0.18 ± 0.03	52.7 ± 1.1
E	90	87	90	6.23 ± 0.45	0.50 ± 0.16	39.1 ± 1.5

Fig 1: First order transformation of chromium VI data for southern pine at 70oC & 70%RH

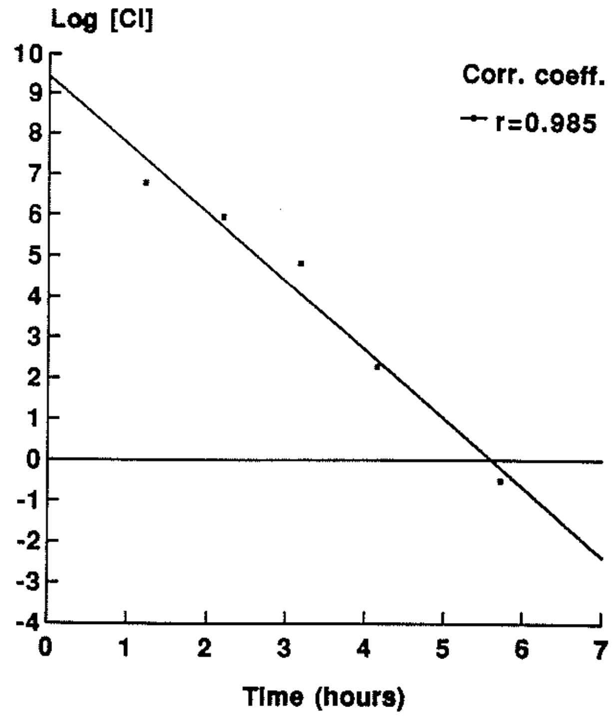


Fig 2: Fixation of CCA in southern pine at 70oC & 70%RH

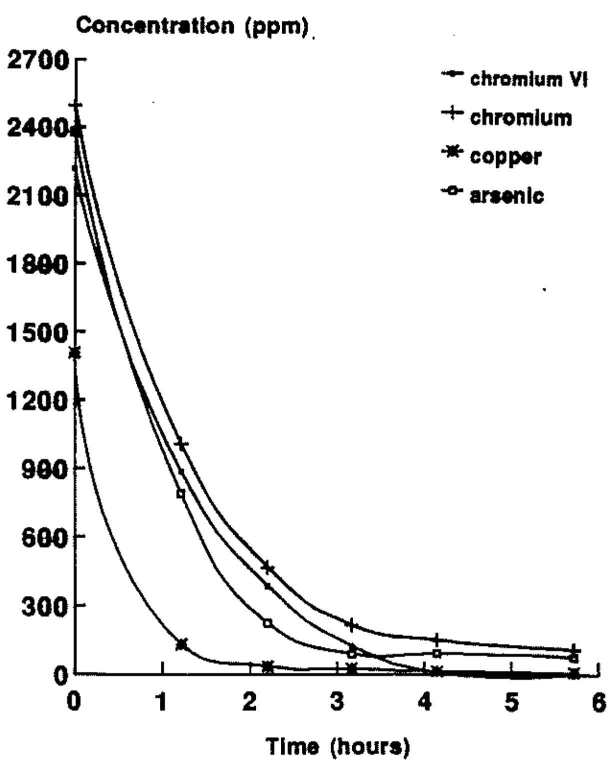
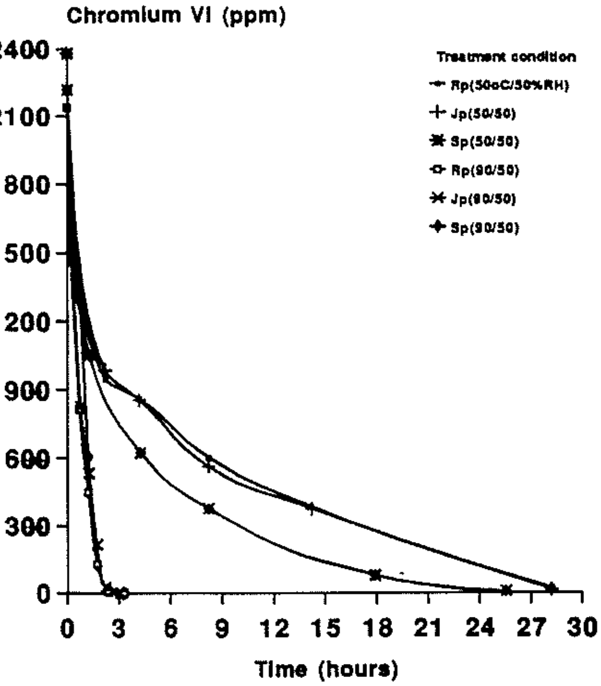
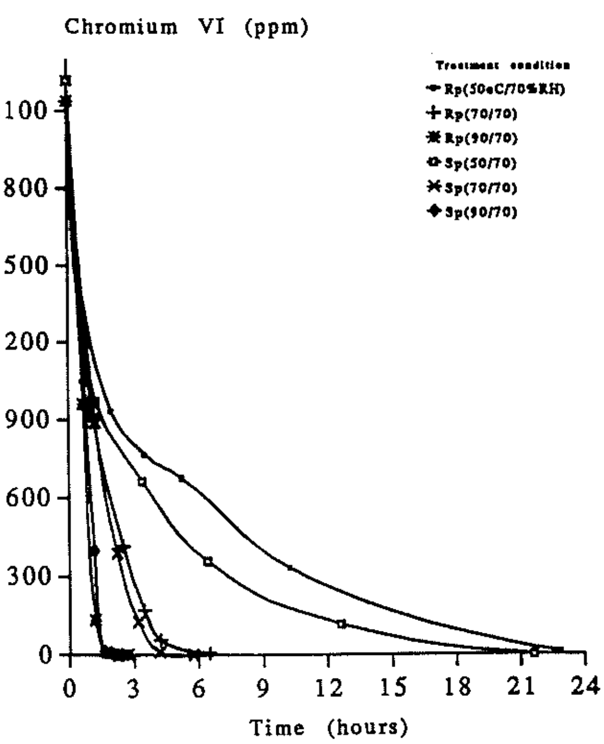


Fig 3: Fixation of chromium VI among pine species at different conditions



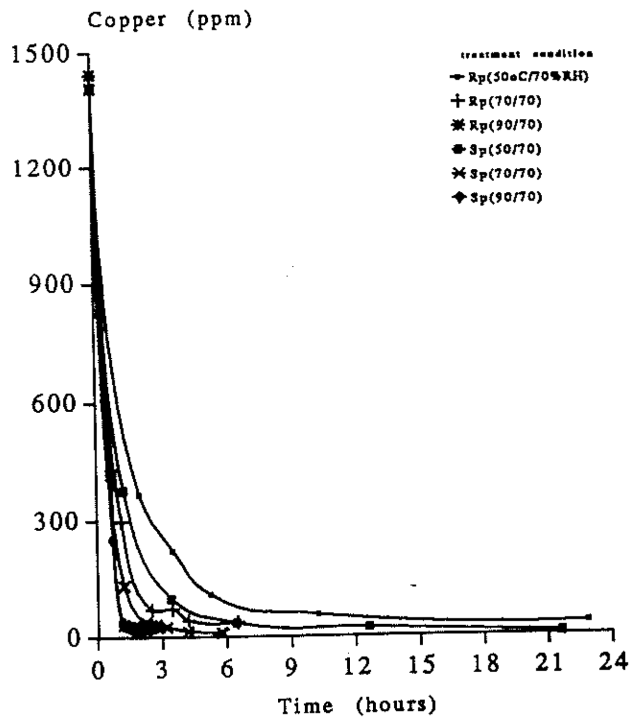
Rp=red pine
Jp=jack pine
Sp=southern pine

Fig 4: Fixation of chromium VI at various temperatures among pine species



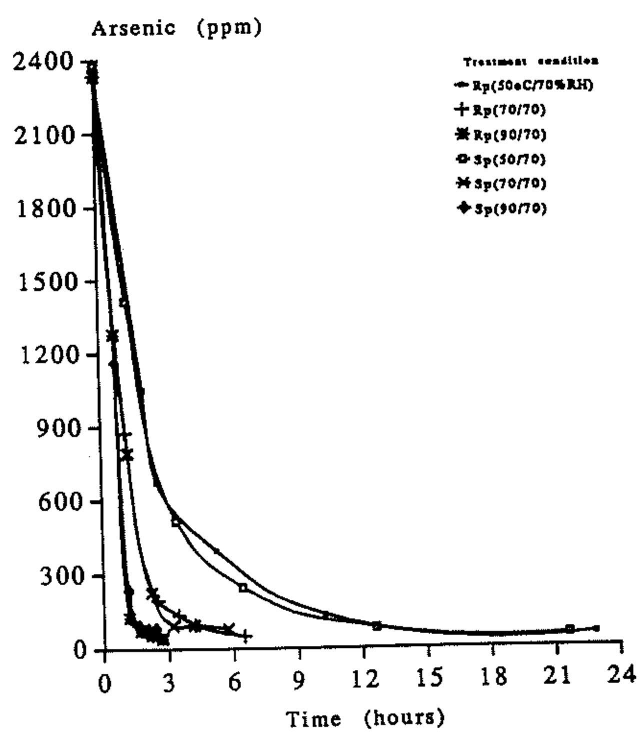
Rp=red pine
Sp=southern pine

Fig 5: Fixation of copper at various temperatures among pine species



Rp=red pine
Sp=southern pine

Fig 6: Fixation of arsenic at various temperatures among pine species



Rp=red pine
Sp=southern pine