Fixation of CCA-C Treated Red Pine at Moderate Temperatures

By

P.A. Cooper and T. Ung
Faculty of Forestry, University of Toronto
and
Erwin Leonov
TDL Woodtreating Ltd.

INTRODUCTION

CCA fixation is highly temperature dependent. It is well known that CCA can be rapidly fixed at high temperatures (90-110 C) and that at low temperatures, several weeks or longer are required to stabilize the preservative (Peek et. al. 1988, Willeitner et. al. 1988, Rak 1975). TDL Woodtreating Ltd. has installed moderate temperature fixation chambers at their Masson, Quebec plant, designed to accelerate CCA fixation by maintaining fresh treated pine poles at 50-60 C and high relative humidities. Since, there is little published information on the rate of fixation of wood at moderate temperatures, studies were undertaken at the Faculty of Forestry, University of Toronto to simulate these conditioning conditions anf follow the rate of fixation in CCA-PEG treated red pine poles, as a function of time and depth in the pole. Also an attempt was made to determine the relationship between extent and depth of fixation and surface leaching characteristics of wood.

This study was designed to follow the Chromium-VI reduction and Cu, Cr and As surface leaching properties of CCA/PEG treated red pine pole sections conditioned immediately after treatment at 50-60 C and high relative humidity conditions.

MATERIALS AND METHODS

Nine, four-foot long red pine pole sections were selected for study. These sections represented three matched sets of poles that had been air dried or kiln dried by a low temperature schedule (to 65 C) and a higher temperature schedule (to 77 C) respectively.

Immediately following pressure treatment with a 2.5 % CCA-C, 4 % PEG solution (initial vacuum, 20 min.; 150 psi pressure, 60 min.; final vacuum, 20 min.)., two 10 mm diameter borings were taken to the full depth of treatment. Pole sections were placed in a dry kiln at the desired fixation temperature and two additional borings were taken after 1, 3, 6, 12 and 24 hours. Immediately after the borings were taken, one

was cut into 6 mm (1/4") lengths and the segments placed on a large piece of filter paper. Several drops of 0.5 % chromotropic acid solution were placed on each segment and the presence of unreduced chromium-VI noted by the development of a purple stain under the segment (Foster 1988).

The other boring was cut into segments representing the following distances from the pole surface: 0-6 mm, 7-12 mm, 13-18 mm, 19-24 mm, 25-36 mm, 37-48 mm, 49-60 mm, and 61-72 mm. These segments were immediately squeezed in a hydraulic press at 5000 psi to express most of the treating solution from the wood. The expressed solution was analysed for Cr-VI content using a procedure adapted from standard method for formaldehyde emission analysis by the chromotropic acid method (Formaldehyde Council 1982).

The expressed solution was diluted 5 to 1 with 0.5 % chromotropic acid solution and the diluted sample placed in a 50 C water bath for 30 minutes to fully develop the purple chromogen. The sample was analysed for Cr-VI in a visible light spectrophotometer at 580 nm. Because the colour development was time and temperature dependent, Cr-VI standards made up from fresh CCA/PEG solutions were run with each batch of samples for calibration. At the same time that borings were taken, poles sections were subjected to surface leaching as follows:

A 15 cm (6") length of pole was marked and isolated from the rest of the pole by tightly wrapping rubber straps around the pole at 15 com spacing. Half a litre of distilled water at room temperature was sprinkled over the isolated section and the water collected for analysis. At subsequent time periods, a different 15 cm portion was isolated and leached. The area leached was about 0.11 m^2 for each test.

Leachate samples were analysed for Cu, Cr and As using a Unicam SP90A Series 2 atomic absorption spectrophotometer, according to the manufacturers recommendations.

Three end matched pole sections, representing the different drying methods were evaluated at 49 C and 95 % RH. Three other end matched samples were tested at 54 C and a final matched set at 60 C. This approach allowed comparison of effects of drying methods on rate of fixation. However, samples were not matched for comparison at the three fixation temperatures. Two additional pole sections were evaluated at room temperature 21 C for comparison.

RESULTS AND DISCUSSION

The Cr-VI level in the CCA solution absorbed in the cell lumens dropped significantly during the pressure treating cycle (Figs. 1 to 3). The Cr-VI level in samples expressed immediately after treatment were 50-70 % of the concentrations in the fresh solution. This indicates a high reactivity of the cell lumen contents with the CCA solution. This initial

reaction probably accounts for the layer of fixed CCA reaction products observed on the cell lumen surfaces by other investigators (e.g., Chou et al. 1973). The initial drop in Cr-VI concentration appeared to be greater in kiln dried poles than air dried poles.

In the fresh treated pole, the Cr-VI content of the expressed solution dropped with depth in the pole as well (Fig. 4). This probably reflects the well known chromium disproportioning or chromium screening effects noted by many investigators (e.g. Cech and Pfaff 1974) which results in a higher ratio of chromium to copper and arsenic in the outer layers of treated wood. However, with exposure to the higher tempertures, the amount of unreacted Cr-VI was lower at the surface compared to deeper in the pole, in response to the relatively slow heat transfer deeper into the poles.

The rate of drop in Cr-VI content in the expressed solution was very slow in the pole segments maintained at room temperature. More than 10 days were required for complete fixation (Fig. 5). At higher temperatures, Cr VI reduction was greatly accelerated. However, about 12 hours were required for essentially complete fixation in the outer 6 mm. CCA solution at greater depths in the poles required somewhat longer to reach the same degree of fixation.

The filter paper test confirmed the Cr-VI analysis results. At 50-60 C, a purple colour was detectable at the 6 hours fixation period but was not detectable at 12 hours. The three temperatures evaluated gave similar rates of fixation. Apparently, variation among poles had at least as great an effect as the temperature differences.

Surface leaching characteristics generally correlated well with Cr-VI content in the expressate (Figs. 6 to 8). However, the amount of leachable constituents on the surface dropped much more quickly, than the Cr-VI level in the outer 6 mm (Fig. 12). Even at room temperature conditions, Cu, Cr and As concentration in the leachate had dropped significantly in 24 hours. For the higher temperature fixation, the levels were barely detectable after 5 hours.

SUMMARY AND CONCLUSIONS

1. CCA fixation, as measured by Cr-VI reduction and Cu, Cr and As surface leaching, could be greatly accelerated by exposing treated wood to 50-60 C and high humidity conditions.
2. Complete fixation, defined as "no detectable Cr-VI" required about 20 days at 21 C. The same degree of fixation could be obtained in about 12 hours at 50-60 C.

3. Leachable Cu, Cr and As on the pole surface dropped very quickly at higher temperatures with concentrations of leachate

dropping by 90-95 % in less than 5 hours. The As is apparently fixed more rapidly than Cu or Cr.

4. Considerable fixation occurred during the treating cycle at all depths in the treated poles. Cr-VI concentrations in the free solution in the lumens dropped by 30-50 % during the 2 hour period from the time when the preservative was introduced into the retort until the first evaluation was made. This initial Cr-VI reduction increased with increasing depth in the pole.

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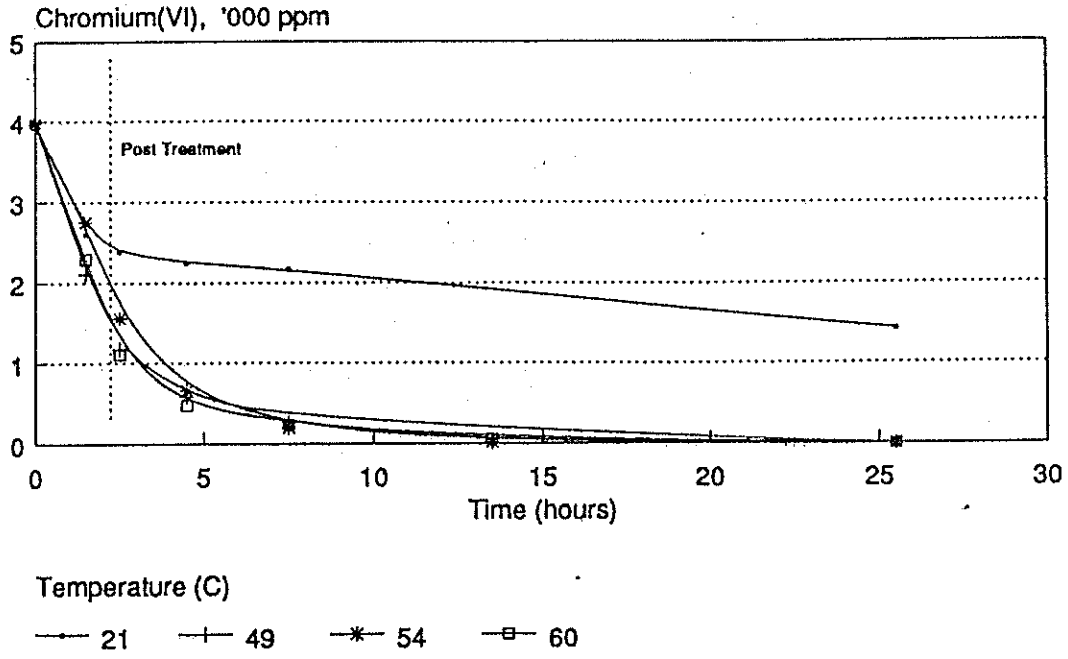
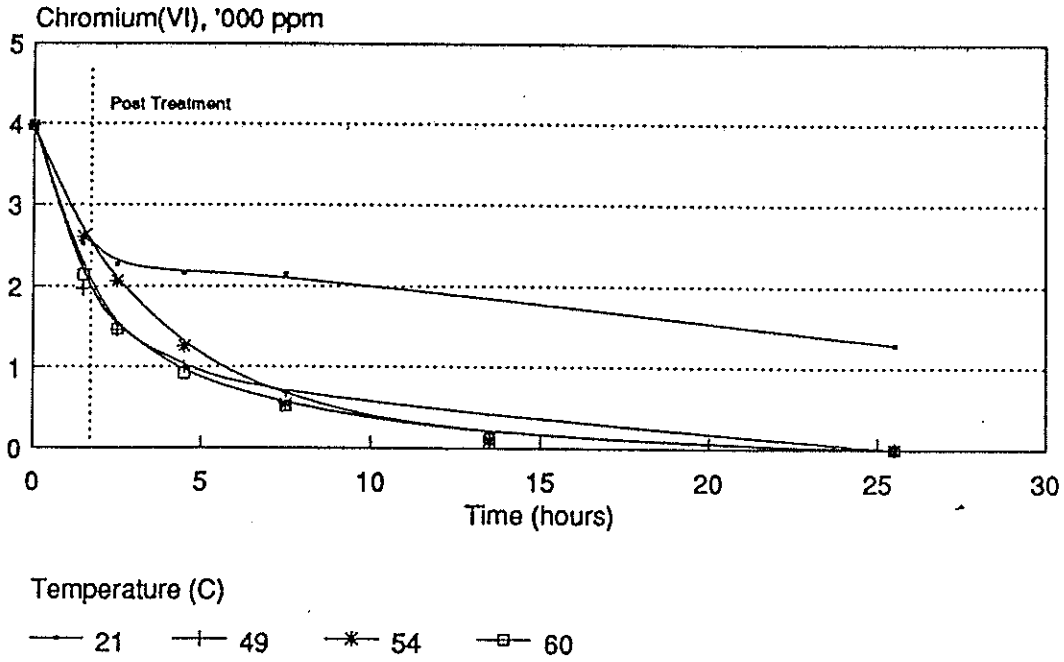
Fig 1. Summary of Cr(VI) concentration change in lumen solution (0-6 mm depth)



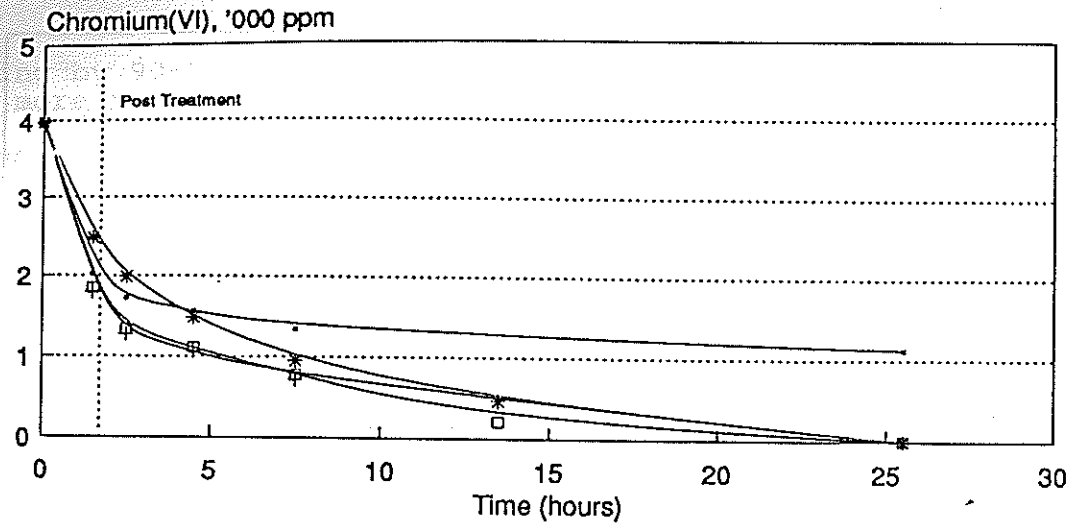
(Each data point is mean of 3 samples)

Fig 2. Summary of Cr(VI) concentration change in lumen solution(20-25 mm depth)



(Each data point is mean of 3 samples)

Fig 3. Summary of Cr(VI) concentration change in lumen solution(51-62 mm depth)

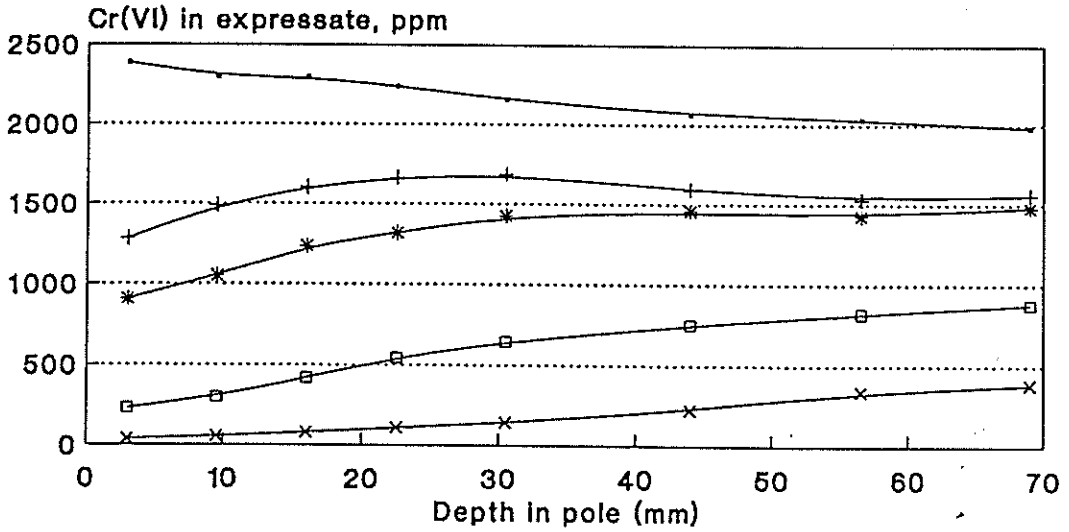


Temperature (C)

21 49 54 60

(Each data point is mean of 3 samples)

Fig 4. Cr-VI distribution in CCA treated red pine at various time after treatment

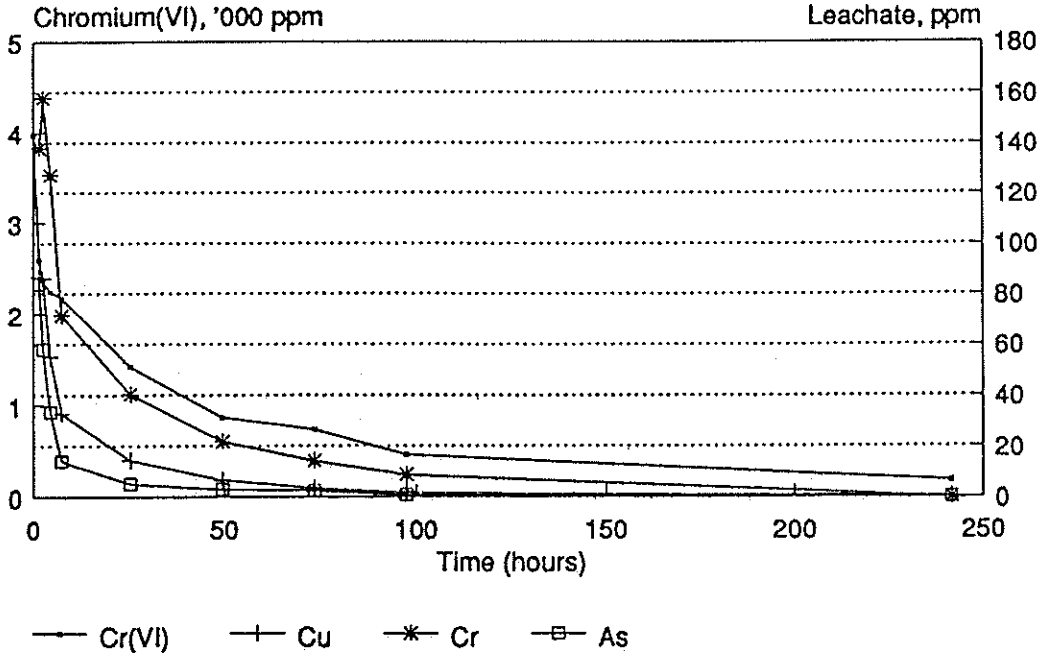


Treatment period:

0 hr. 1 hr. 3 hrs. 6 hrs. 12 hrs.

Temperature(C) 49-60, mean of nine poles

Fig 5. Cr(VI) reduction and leaching of Cu, Cr & As at room temperature(21 C)



Cr(VI) reduction at (0-6 mm depth)

Fig 6. Concentration of Copper in leachate (Average of three poles).

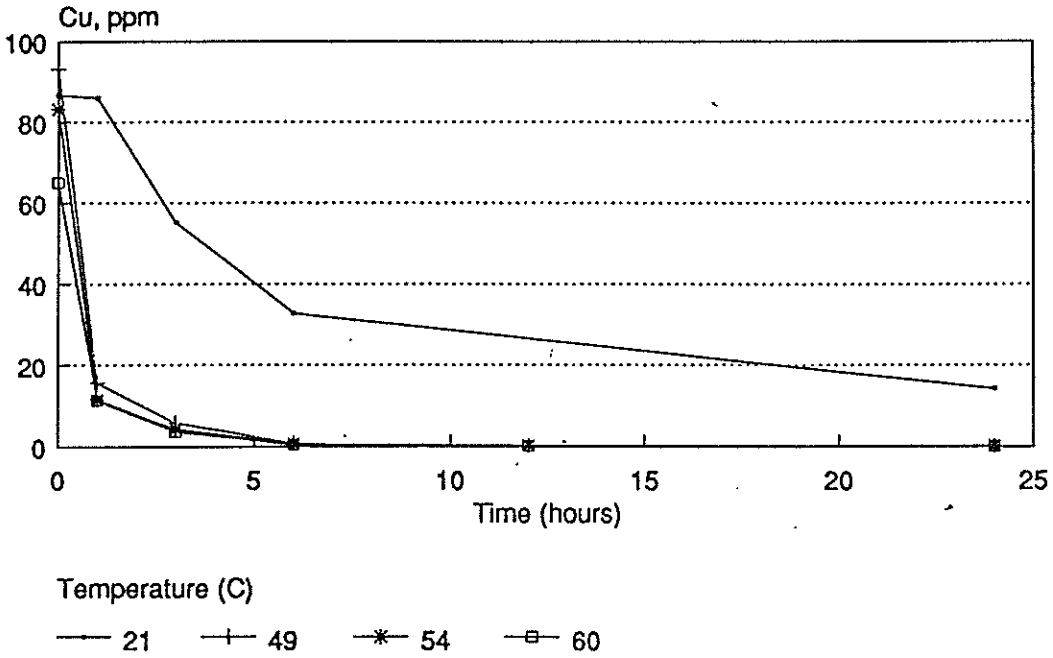


Fig 7. Concentration of Chromium in leachate(Average of three poles).

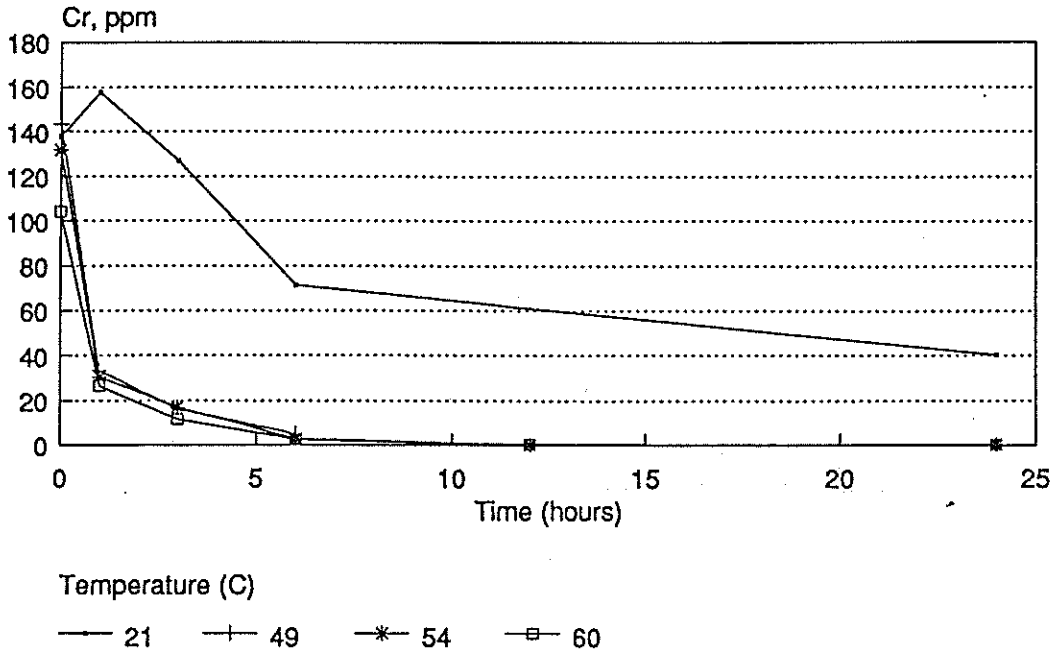


Fig 8. Concentration of Arsenic in leachate(Average of three poles).