FIXATION OF CCA-C COMPONENTS IN ASPEN, RED PINE AND RED MAPLE

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Summary

The fixation of CCA-C preservative was investigated in red pine (*Pinus resinosa* Ait.), trembling aspen (*Populus tremuloides* Michx.) and red maple (*Acer rubrum* L.) at target retentions of 6.4 and 30.0 kg/m^3. Treated wood sawdust was extracted at close time intervals during the fixation and analyzed for the contents of unfixed hexavalent chromium, total Cr, Cu and As. Fixation curves are similar for red pine and aspen. Chromium fixation is extremely fast in red maple and significant amount of unfixed arsenic was present at the time of complete fixation of chromium. Strength of the CCA solution has diverse effect on the course of fixation. Further research is needed to better understand the particular influence of each of the investigated variables on the course of fixation.

Introduction

Treatment of wood with chromated copper arsenate (CCA) has been one of the most common and efficient means of preserving the wood against the attack of wood decaying organisms. Typical composition of CCA-C formulation that is at present almost exclusively used is an oxide based mixture of CuO, CrO_3, and As_2O_5 in ratios 18.5% : 47.5% : 34.0%.

CCA belongs to the group of waterborne inorganic preservatives that are "fixed" by the chemical reactions that occur between CCA components and wood substance, resulting in the formation of essentially leach resistant forms. The term "fixation", repeatedly used in the literature dealing with CCA, is an object of ambiguity. In general, "fixation" is related to the process of conversion of water-soluble CCA components into stabilized, definitely bound and permanently retained chemical compounds in wood. "Fixation" is furthermore associated with any of the chemical reactions or interactions that occur in the wood-CCA system that ultimately lead to the withdrawal of CCA elements from the treating solution. Fixation is commonly monitored by the degree of chromium reduction and considered complete when no detectable Cr(VI) is present in the system.

The chemical reactions involved in the fixation process are numerous and diverse. Reaction modes suggested in the literature include a combination of adsorption, desorption, ion-exchange, oxidation-reduction, precipitation, proton transfer and organometallic complex formation (Dahlgren and Hartford 1972, 1972a, 1972b; Pizzi 1982, 1990; Cooper 1991).

The critical reaction, governing the whole course of CCA fixation is reduction of water soluble Cr(VI) to essentially insoluble Cr(III) forms. Although the fixation mechanism is not completely understood, a number of intermediate and end fixation products is suggested. Different chromic chromates and chromium arsenates are suggested to be formed in early fixation stages, but as the fixation proceeds accompanied by the rise

in pH, those will transform to more stable, precipitated inorganic products such as $Cr(OH)_3$ and $CrAsO_4$. The withdrawal of anionic species from the solution results in the overall increase in pH, toward the value that favors the adsorption of Cu from treating solution and it's fixation on cation-exchange sites in wood components. Under acidic conditions, which dominate during the early stages of fixation, the adsorption of Cu from the treating solution is very small.

As fixation reactions occur consecutively and simultaneously in a very complex and dynamic chemical system, each variable that has an affect on one of the fixation reactions is likely to act upon the following ones. Therefore, the conclusions about the course of fixation reactions, nature of end fixation products, and their relative distribution, need to be made with regard to the specific conditions of the treatment.

The temperature, pH, and the concentration of the treating solution are designated as most important factors affecting the fixation kinetics (Pizzi 1983). The rates of chemical reactions employed in fixation increase with temperature. The affect of pH of the treating solution is hard to distinguish from the concentration effect since, for the same formulation, pH decreases with increasing concentrations. In general, authors agree that the most distinct expression of pH effect is the acceleration of Cr reduction at lower pH and retardation of Cu fixation. Relative humidity does have pronounced affect on the fixation kinetics inasmuch as the presence of water is necessary for ionic chemical reactions to occur.

The role of major wood constituents such as lignin, cellulose and hemicelluloses has been determined in terms of their activity and chemical affinity towards individual CCA ingredients, but the clear understanding of their fixation chemistry is still lacking. The assessment of the interference and contribution of wood extractives during the fixation is even more difficult. A number of observed anomalies are ascribed to the presence of extractives. For example, those species with the highest rate of Cr fixation (beech, red oak, red maple) (Stevanovic-Janezic *et al.* 2000) have the poorest quality of fixation, especially of As. Slowly fixing species (yellow poplar, aspen and basswood) were most leach resistant.

The results presented here are part of a broader research program which is being conducted with an aim to investigate the chemical reactions involved in fixation and nature of fixation end-products as affected by relevant treatment/fixation variables.

Methodology

Experiments were performed on sawdust prepared from the sapwood of three wood species: red pine (*Pinus resinosa* Ait.), trembling aspen (*Populus tremuloides* Michx.) and red maple (*Acer rubrum* L.). Wood free from heartwood, knots, and visible reaction wood was separated and milled in a Willey mill and the fraction 25-40 mesh was used for the fixation experiments.

Samples were treated with CCA type C preservative solution (approximately 19.0% CuO, 47.0% CrO_3, 34.0% As_2O_5) at a target retention levels resembling real conditions: 6.4 kg/m^3 - used under normal conditions, and 30 kg/m^3 applied for marine use. CCA treating solutions of predetermined strengths were prepared in order to achieve the above target retentions of CCA in sawdust. Another consideration was not to exceed the moisture content of wood-CCA system above maximum natural moisture content of wood. Precise

concentrations of Cr, Cu and As in treating solutions were analyzed by ICP-AES according to AWPA Standard A21-93 (1996), and the content of hexavalent Cr by spectrophotometry using diphenylcarbazide as color developing reagent (Coggins and Hiscocks 1978).

Each fixation experiment was performed in a way that wood sawdust was mixed with the preservative solution, homogenized, placed in polyethylene bags, closed and conditioned at temperature of $30^{o}C$ and high relative humidity until the fixation was completed. The assumption was made that unfixed CCA elements are soluble in water. Two replicates of approximately 2g of sample were taken from the bulk treated wood at close time intervals and extracted. Extraction was conducted using oscillatory shaker, twice with 100 ml aliquots of deionized water, filtered through a Buchner funnel by vacuum filtration and after the dry suction, washed with additional 50 ml of water to assure complete removal of unfixed material. The non fixed ingredients collected in filtrate were analyzed for the content of hexavalent chromium and total chromium, copper and arsenic.

Results and Discussion

The fixation curves (Graphs 1-6) are generated based on the data points representing the average values for two replicate extractions of sample during different stages of the fixation.

Results presented in Graphs 2-5 show that fixation of chromium in aspen and red pine was the slowest among three CCA components, thus justifying its application for the overall fixation monitoring.

Fixation rates for three investigated wood species for the retention of 6.4 kg/m^3 are presented in Graph 1. The results indicate extremely fast chromium fixation in red maple compared to aspen and red pine as observed in earlier research (Cooper *et al.* 1997). Since all the fixation and treatment parameters were similar, and the contribution of the anatomical properties minimized, differences in the observed rates of fixation are attributed to the variability in the chemical composition among these three wood species. It is well known that oxidation of smaller organic molecules, such as most of the extraneous wood constituents, is faster compared to large organic polymerized compounds. Other researches have proved that wood extractives are predominantly responsible for different rates of chromium fixation (Stevanovic *et al*., 1997; Pizzi *et al*., 1986). The extent of the interference depends on their reducing capability and amounts of extractives present. High content of low molecular weight reducing sugars in maple is mostly responsible for the rapid chromium reduction.

The effect of the strength of treating solution is revealed in differences in the fixation curves of Cr for two target retentions (Graph 2-5). Time needed for complete fixation of chromium (at 99.9% of available Cr(VI)) was longer for the treatments with solutions of higher CCA concentrations for all three wood species. This is expected due to the higher contents of chromium. However, the pH has a pronounced effect on the rate of chromium fixation, as chromium reduction is increased at lower pH. Faster chromium reduction for more concentrated CCA solutions is apparent after comparison of curves for both, red pine and aspen.

Another anomaly observed from the fixation curves of red maple (Graph 6) in comparison to two other species, is slower fixation of arsenic compared to chromium.

Incomplete fixation of arsenic at the point of complete chromium fixation leads to the conclusion that formation of chromium arsenates, which are the predominant fixation end-product in species such as red pine or aspen is somehow retarded in red maple. High leaching of arsenic from the treated maple observed in earlier studies (Stevanovic Janezic *et al.* 2000) could be explained by the failure of complete fixation of arsenic from the treating solution. A discrepancy observed between Cr (VI) determined by the diphenyl carbazide method and total chromium leached during fixation, determined with ICP-AES analysis is considerable for red maple. This suggests the formation of chromium fixation products, which are characteristic for this species. The formation of water soluble Cr(III) complexes with oxidized extractives can be hypothesized. Another possibility is the formation of short-living Cr(V) species (Ruddick *et al.* 1994), which are known to be water soluble. This possibility would give rise to environmental concerns as it is believed that Cr(V) poses high environmental hazard being toxic itself or when releasing Cr(VI) after disproportionation to Cr(III) and Cr(VI)

Fixation of aspen and red pine to the Rtn=30kg/m^3 are both characterized by very fast disappearance of arsenic from the treating solution. Fast arsenic fixation is probably related to the pH of the treating solution, which decreases with increasing solution strength. Acidic conditions favor chromium reduction, and Cr(III) is most likely precipitated in the form of Cr(III) arsenates above the pH of 2.4. Higher arsenic leaching from wood treated with CCA solutions of lower concentrations was observed earlier. Further research is needed to understand how the stability of formed arsenic species is affected by the solution strength.

Copper fixation proceeded faster in samples treated with higher concentrations of treating solution. Copper was adsorbed in less then 1 hour in maple treated to retention of 6.4 kg/m3, while in red pine and aspen treated to comparable retention of 6.4 kg/m3, equivalent times were around 25 and 52 hours. The mechanism of copper fixation in wood is mostly accomplished through cation exchange reactions with its weak acidic functional groups, and therefore fundamentally affected by the pH of the fixation system (Cooper 1991). Dissociation of weak-acidic ion-exchange sites is low at the beginning of fixation when the pH of the system is around 2, but it increases sharply, as fixation proceeds and pH of treated wood approaches its final value which is around 4-5. The trend of pH increase is closly related to the course of chromium reduction, which may explain significantly shorter fixation in maple compared to other two species. Observed longer Cu fixation from treating solutions of higher concentration is linked to their higher acidity accordingly.

Conclusions

- The effects of investigated fixation variables, namely; the strength of treating solution and chemical properties of wood are confirmed as most responsible for the course of fixation.
- The rate of arsenic fixation is affected by the strength of the treating solution for red pine and aspen, while in red maple other factors interfere with fixation reactions of arsenic.

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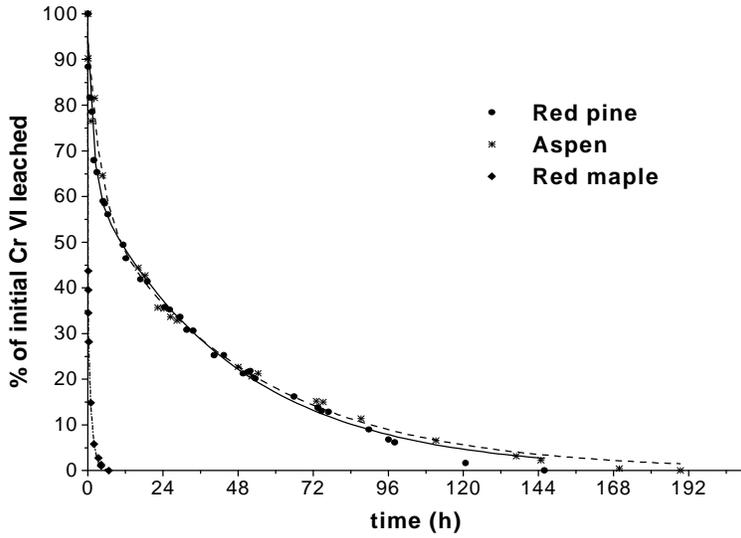
Graph 1.
Fixation of Cr(VI) in three wood species
T=30°C; Rtn=6.4kg/m³
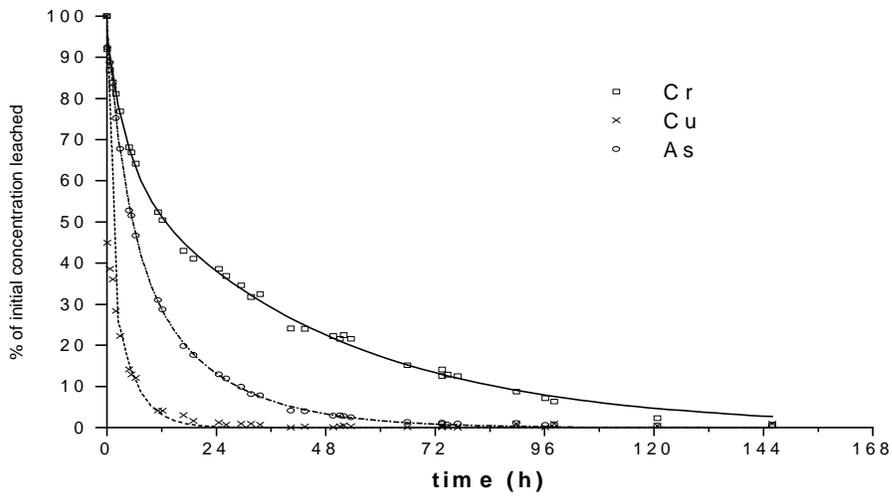
Graph 2.
CCA Fixation in Red Pine
T=30°C; Rtn=6.4kg/m³
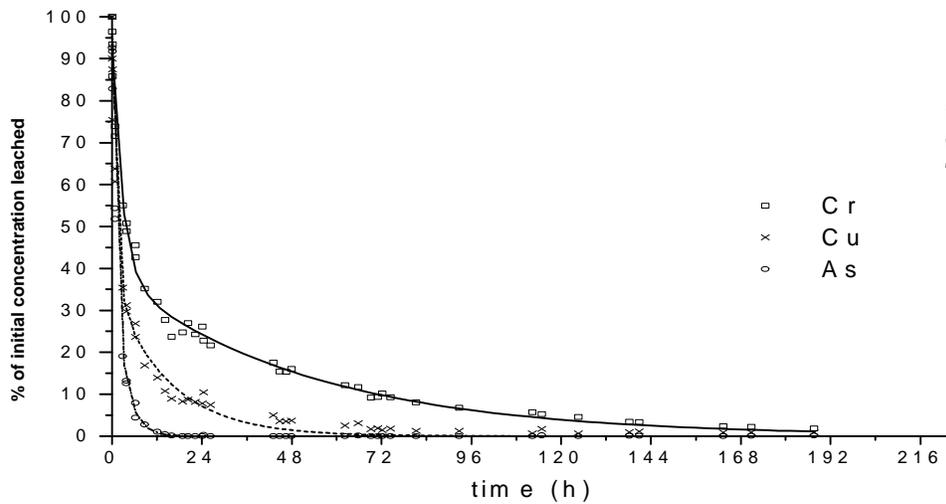
Graph 3.
CCA Fixation in Red Pine
T=30°C; Rtn=30kg/m³
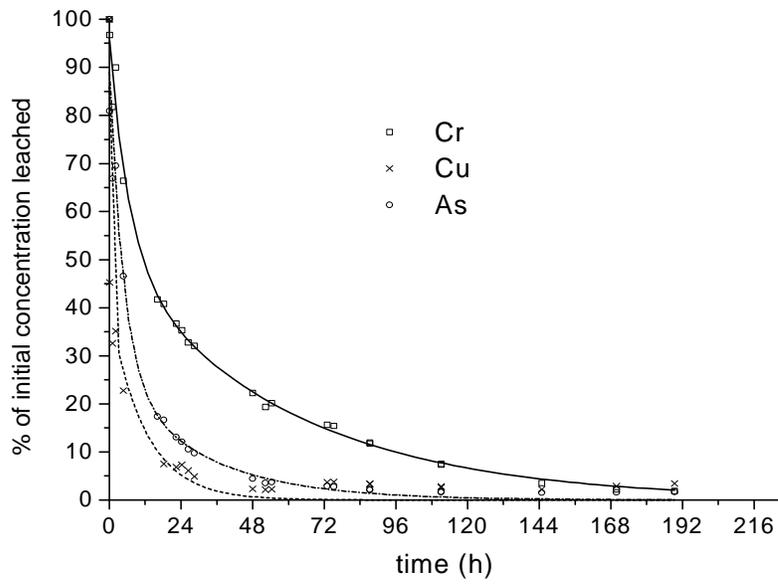
Graph 4.
CCA Fixation in Aspen
T=30°C; Rtn=6.4 kg/m³
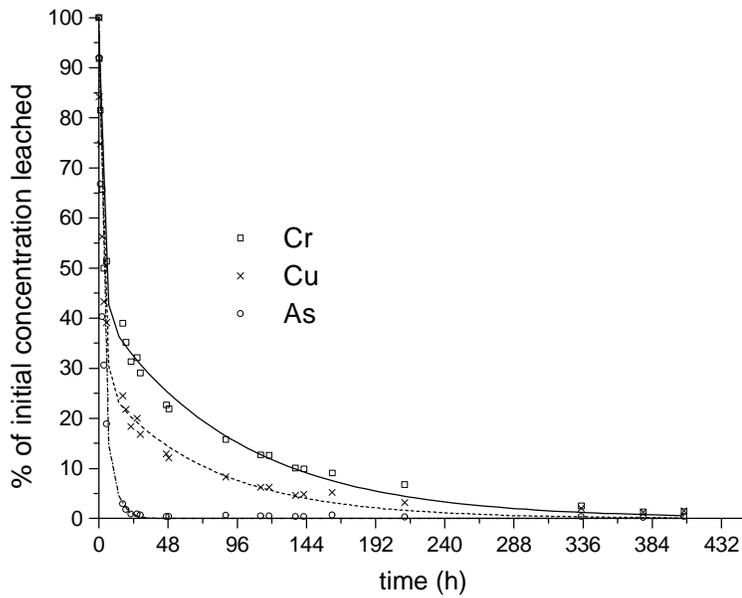
Graph 5.
CCA Fixation in Aspen
T=30°C; Rtn=30 kg/m³
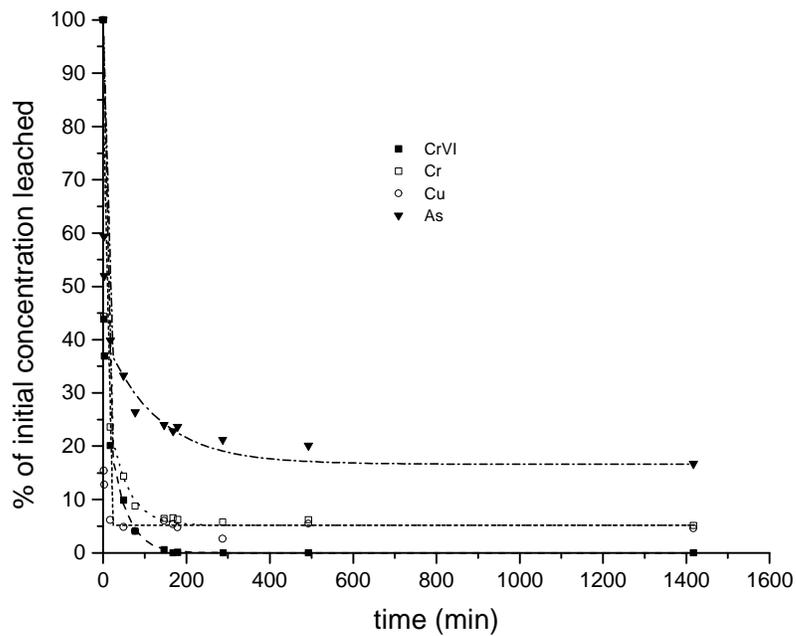
Graph 6.
CCA Fixation in Red Maple
T=30°C
Rtn=6.4 kg/m³