FIXATION AND LEACHING OF CCA-C TREATED EASTERN HARDWOOD SPECIES[1].

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Summary

Fixation and leaching of CCA type C treated hardwoods and southern pine was investigated using an expressate method to monitor hexavalent chromium reduction and a modified AWPA E11-87 water leaching test to determine CCA components leaching potential after complete chromium reduction. Cubes measuring 19 mm of soft/red maple (Acer rubrum L.), yellow poplar (Liriodendron tulipifera L.), basswood (Tilia americana L.) for hardwood and southern yellow pine (Pinus taeda L.) for softwood were treated to an average retention of 12 kg/m3 with a 2% CCA type C solution. Chromium reduction was monitored for ambient temperature fixation and at high temperature (autoclaved samples). At room temperature, chromium reduction was completed within 72 hours for soft maple, 350-440 hours for yellow poplar, 600-750 hours for basswood and 250-400 hours for southern yellow pine. The rate of chromium reduction (fixation) at room temperature was slower in extracted samples for all species, showing that the extractives contributed to rapid chromium reduction. The percentage of CCA type C components leached was low for species or post treatment conditions that required the longest times for hexavalent chromium reduction. The arsenic loss from soft maple was higher than from the other species at room temperature (17%). Chromium was the most stable with very low (0.2 to 3.8%) losses compared to arsenic (2.7% to 17.6%) and to copper (2.2 to 24.5%).

1. Introduction

Several abundant hardwood species are available in Northeast USA and Canada. They have been used mainly for furniture and other indoor uses where the decay hazard is negligible although a limited volume is treated with creosote and used for crossties. Hardwoods have good physical and structural properties for such commercial uses as decking, guiderail posts and bridge construction.

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With the potential shortage of fiber due to high demand with the increase of world population and the pressure for reduction of logging operations on western Pacific forests, the potential of these local abundant hardwood species for high decay hazard exterior applications is still to be developed.

Creosote and pentachlorophenol can be used for industrial applications such as guide rail posts, ties for rail road and utility posts but are generally not acceptable for residential commodities such as decking or siding applications. There is therefore interest in the treatment of these hardwoods with water based preservtives.

Significant volumes of maple and yellow poplar are already pressure treated with water based preservatives in the northeastern and Appalachian states of the United States and in eastern Canada. Little is known about how the water based preservative chromated copper arsenate (CCA) penetrates and reacts with these species (Englund and Gardner, 1993; Carpenter and Gardner, 1993; Gardner and Slahor, 1994; Smith et al., 1996). In a previous study, we observed that soft maple lumber treated with CCA and reacted ("fixed") at either low or high temperature, had unusually high losses of arsenic when exposed to simulated rain or soaking leaching tests (Cooper et al., 1996). This limits the potential of this species for treated wood products, since poor fixation of the arsenic results in a greater potential for environmental contamination both at the treatment plant site and at the end use location such as timber bridges over streams. It may also reduce the effectiveness of the preservative treatment which will result in a shorter service life (Thomson et al., 1981; Smith and Williams, 1973; Da Costa et al., 1963).

A comparative study of CCA treatment in different hardwood species may provide clues to the fixation mechanism, bioefficacy and how it relates to the chemistry of the wood. Differences in bioefficacy of CCA treated hardwoods was observed and documented by Behr (personal communication). Northern red oak, maples, white ash, birch, elm, hickory, beech and pine stakes measuring 19 by 19 by 200 mm were CCA or pentachlorophenol pressure treated at 0, 1.5, 3 and 6 kg/m3 retention and installed in Florida, Mississippi and Michigan. CCA retention level of 6 kg/m3 protected hardwoods against decay and at a log scale ratio of 70 after 15 years exposure (Morris, 1995) whereas untreated hardwood species were completely destroyed after 2 years on average.

The objective of this study is a comparative study of CCA treatment, fixation, and leaching of soft maple, basswood, yellow poplar and southern pine. The effect of species, fixation temperature, and extractives on the chromium (VI) reduction to chromium (III), and the amount or percentage of CCA component leached after the complete chromium reduction were monitored.

2. Methodology

2.1 Wood Preparation

Soft maple (Acer rubrum L.), Yellow poplar (Liriodendron tulipifera L.), basswood (Tilia americana L.) and southern yellow pine (Pinus taeda L.) species were selected for this study. Air dried defect free sapwood boards of each species were surfaced and cut into 25 mm cubes and conditioned at 68o F and 70% RH for a period of one month before treatment. The equilibrium moisture content of the conditioned samples was approximately 10 %.

Samples from each species were divided into two groups. One group was extracted according to a modified TAPPI method (T208 om 88) as described below before treatment and the other group treated as is. Extractive free samples were soxhlet extracted with a 50:50 mixture of toluene and ethanol for 8 hours, then with ethanol for another 8 hours and finally with water for 2 hours.

2.2 Treatments

A 50% total oxide CCA type C solution from Hickson Corporation was diluted to approximately 2% and used for treatment. The treating solution contained CCA components in the following proportions: 17.3% CuO, 45.0% CrO3 , and 37.7% As2O5. The treatment schedule included an initial vacuum of 24" Hg for 30 minutes, a 95 psi pressure for 1.25 hours and a 30" Hg final vacuum for 30 minutes. After treatment, samples were stored in air tight plastic bags until further testing.

In order to investigate the effect of post steaming on fixation and leaching, half the treated samples were steamed for an hour in an autoclave at 120o C and the other half wrapped in aluminum foil and kept at room temperature around 21o C. After autoclaving, steamed samples were evaluated for chromium fixation status as discussed below and the remaining samples were wrapped in aluminum foil and stored until further test. Cubes (autoclaved and not autoclaved) were removed every twenty four hours and squeezed in a hydraulic press with a vise clamp to obtain expressate solution from wood for chemical analysis. The expressate solution was analyzed for hexavalent chromium by the diphenylcarbazide method (Cooper and Ung, 1992; 1993) with a Perkin Elmer Lambda 4B UV/VIS Spectrophotometer. The rate of chromium fixation or CCA type C fixation was calculated as the percentage of chromium reduced in the expressate solution relative to that initially in the treating solution. After almost complete reduction of chromium (about 99%), four replicate samples of each treatment and each species were subjected to a modified American Wood Preservers' Association E11-87 standard leaching test and the amount of copper chromium and arsenic determined by AAS. The percentage loss of each component in the leachate was determined from the cumulative amount of each element in the leachate after two weeks leaching and the total amount absorbed by wood during the treating as determined by the AAS chemical analysis of acid digested wood.

3. Results and Discussion

3.1 Retention of preservative

The CCA type C retention of the treated cubes averaged 13 .0 kg/m3 for all species. The standard error for retention of CCA by hardwoods species (yellow poplar, basswood, and soft maple) was higher than that of Southern yellow pine indicating a more variable treatment. The retention of cube samples treated after soxhlet extraction was not significantly different from unextracted samples at a 95% level of confidence.

3.2 Fixation

The rates of chromium reduction are represented in Figures 1, 2, and 3. They varied considerably among species. At room temperature, hexavalent chromium reduction in soft maple was completed within 72 hours (Table 2). Yellow poplar and basswood needed 350-440 hours and 600-750 hours, respectively. The chromium reduction in southern yellow pine at room temperature was completed within 250-400 hours.

The chromium reduction or fixation rates of all species were increased by autoclaving treated samples at 220o F for one hour, in agreement with available data on CCA fixation at high temperature (e.g., Peek and Willeitner, 1988). Hexavalent chromium was almost negligible in post autoclaved samples immediately after removal from the autoclave.

Extracted samples of all species fixed more slowly than unextracted samples (Table 2 and Figure 3). For fast fixing species such as maple, this suggests that extractives contribute to the rapid reduction of chromium. However, slow fixing basswood and yellow poplar also contain extractives. The amounts, location (e.g., in lumens or in the cell walls) and types of extractives will affect the rate of fixation. Several studies reported that extractives such as polyflavanoid tannins, catechol and pyrogallol present in some wood species form complexes with metal ions (Pizzi, 1986). Even a slight presence of tannin produced a drastic increase in CCA removal from the treating solution (Pizzi, 1986).

3.3 Leaching

The amount of copper chromium and arsenic leached from treated and fixed cubes, as determined by a 14 day water leaching test, varied with the wood species and the fixation conditions. Table 3 lists the percentage of elements leached from each species. Chromium was the most stable of the three elements with leaching losses from 0.2 to 3.8% of the total absorbed in wood during the treatment. The poorest chromium permanence was in unextracted yellow poplar (3.8% leached), followed by unextracted soft maple (2.5% leached) both at room temperature. In extracted soft maple, only 0.3% of the chromium was leached, suggesting that toluene/ethanol/water extractable compounds contribute to faster reduction of chromium, but produce reaction products that are more accessible to leaching than those produced in extractive free wood. The amount of chromium leached from extracted samples was less than that from unextracted samples for the other species as well. The amount of chromium leached was reduced from 1.2% to 0.5% for extracted southern yellow pine, 3.8 % to 0.8 % for yellow poplar, and 0.4% to 0.3% for basswood by removing the extractives.

Copper losses ranged from 2.2 % to 24.5%. At room temperature for unextracted cubes, southern yellow pine had the greatest copper loss of 24.5%, followed by yellow poplar with 16.3%, soft maple with 9.9% and finally basswood with 8.4%.

Autoclaving resulted in higher amounts of copper being leached from soft maple and yellow poplar. The high copper losses from autoclaved soft maple and yellow poplar might be due to the accelerated chromium reduction under autoclave conditions that did not favor formation of stable copper chromium arsenate complexes. Peek and Willeitner(1988) proposed that steam fixation might increase copper leaching by the mobilization of extractives bound to copper on the wood surface. For extracted samples, copper losses were greatly reduced for all species, supporting the above hypothesis (Table 3).

Arsenic losses ranged from 2.7 to 17.6% with unextracted soft maple CCA treated at room temperature having the greatest loss, followed by southern yellow pine with 10.9%, and yellow poplar and basswood with 8%. Autoclaving appeared to slightly reduce arsenic loss. In general, extracted samples had lower arsenic losses compared to either unextracted or autoclaved samples.

Unextracted soft maple had the fastest chromium reduction rate and exhibited the highest arsenic losses, while yellow poplar and basswood with slowest chromium fixation rates had the lowest arsenic losses. There appears to be a negative correlation between the rate of chromium reduction and the leach resistance of arsenic for hardwood species. The most likely cause of this is the wood extractives; species with extractives that rapidly reduce the hexavalent chromium apparently deposit the reaction products in a form and/or location that are more readily accessible to leaching. The low arsenic and chromium leached from extracted samples, supports this belief that extractive content is an important factor for fixation and the permanence of the CCA components in wood.

4. Conclusions

1. The reduction of Cr(VI) to Cr(III) is affected by wood species. Soft maple fixed chromium more quickly than yellow poplar and basswood. Chromium(VI) reduction at room temperature is complete within 72 hours in unextracted soft maple, whereas 400 hours are needed for yellow poplar and 600-750 hours for basswood. Extractive free samples reduced chromium more slowly, suggesting that extractives play an important role during the chromium reduction. This fixation time can be reduced to about 1 hour by autoclaving or live steaming the samples after treatment.

2. The leaching of CCA components is species dependent. Chromium is the most stable component in CCA treated wood. In general for all species and conditions, copper is the most leachable component. The arsenic losses for soft maple are surprisingly high compared to other species. Extractive free samples exhibit the lowest amount of

component leached, suggesting that there is a clear relationship between the rate of fixation and the permanence of CCA components. The faster a component is fixed, the more it will be leached .

5. Literature

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Table 1: CCA Retention Summary

Wood Species	Condition	Density (kg/m3)	CCA Retention (kg/m3)
Soft Maple	Unextracted	490	13.4
	Extracted	450	13.6
Yellow Poplar	Unextracted	524	12.3
	Extracted	498	13.2
Basswood	Unextracted	350	12.5
	Extracted	335	13.5
Southern Yellow Pine	Unextracted	524	12.6
	Extracted	483	12.9

TABLE 2. Times required to complete chromium reduction for CCA type C treated hardwoods and southern pine.

Wood Species	Extraction Condition	Fixation Condition	Time to Complete Chromium Reduction (h)
Soft Maple	Unextracted	Room Temp.	48 - 72
	Extracted	Room Temp.	192 - 300
	Unextracted	Autoclaved	< 1
Yellow Poplar	Unextracted	Room Temp	350 - 440
	Extracted	Room Temp.	400 - 500
	Unextracted	Autoclaved	< 1
Basswood	Unextracted	Room Temp	600 - 750
	Extracted	Room Temp.	650 - 800
	Unextracted	Autoclaved	< 1
Southern Yellow Pine	Unextracted	Room Temp	250 - 400
	Extracted	Room Temp.	350 - 450
	Unextracted	Autoclaved	< 1

TABLE 3. Leaching of CCA components (AWPA E11-87) from hardwoods and southern pine.

Wood Species	Pre-extracted?	Fixation Condition	% of total leached Cu	Cr	As
Soft Maple	No	Room Temp.	9.9	2.5	17.6
	Yes	Room Temp.	2.2	0.3	8.9
	No	Autoclaved	24.5	1.6	14.8
Yellow Poplar	No	Room Temp.	16.3	3.8	8.0
	Yes	Room Temp.	9.3	1.8	2.7
	No	Autoclaved	23.2	1.7	7.9
Basswood	No	Room Temp.	8.4	0.4	9.2
	Yes	Room Temp.	4.8	0.2	8.1
	No	Autoclaved	7.9	0.2	8.2
Southern Yellow Pine	No	Room Temp.	24.5	1.2	10.9
	Yes	Room Temp.	8.3	0.5	7.2
	No	Autoclaved	24.2	1.1	7.8

Figure 1: Concentration of chromium(6+) in expressate of unextracted samples at RT

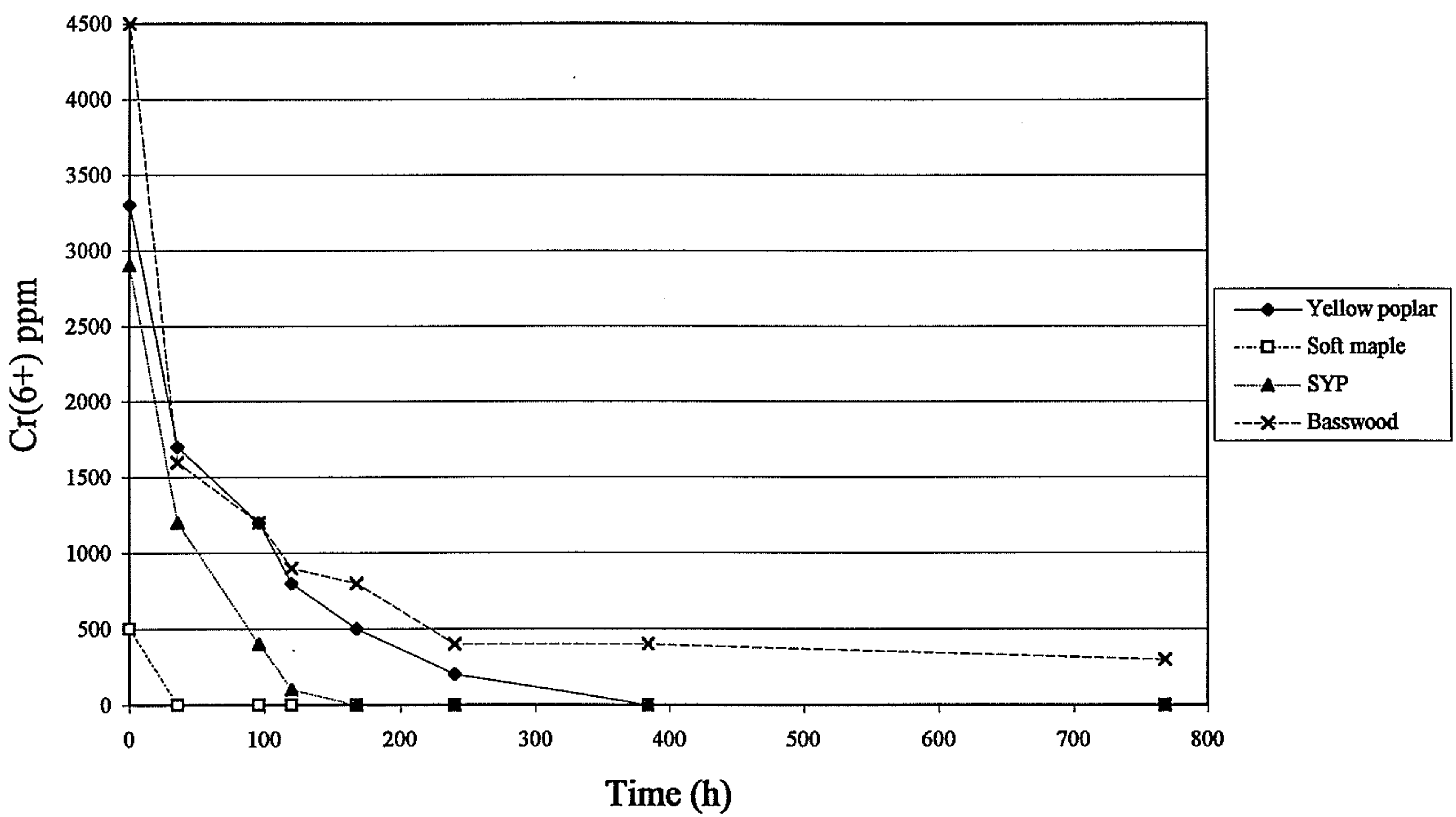

Figure 2: Concentration of chromium(6+) in expressate from autoclaved samples

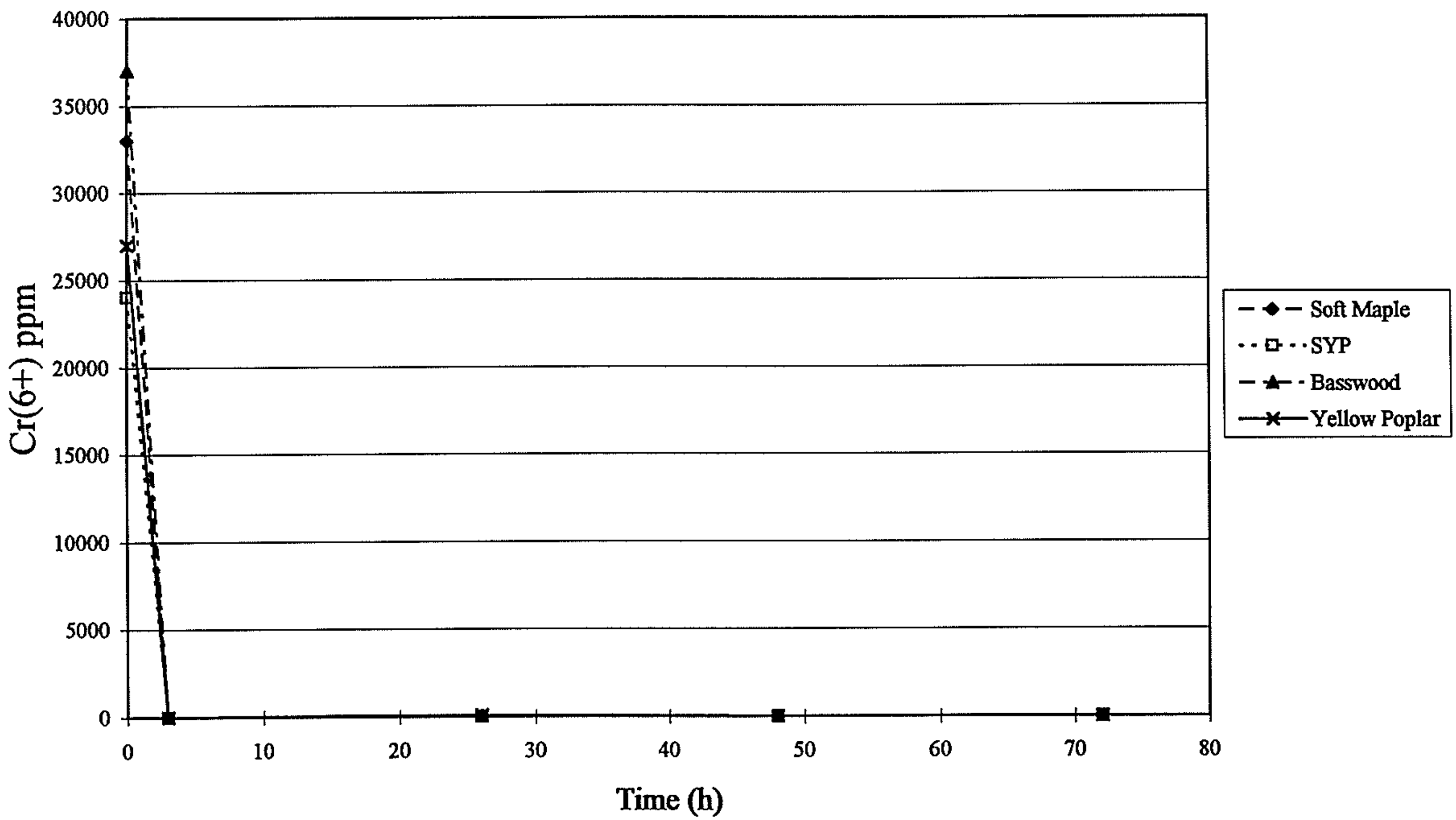

Figure 3: Concentration of chromium(6+) in expressate from extractive free samples