CCA fixation and its implications on availability of hexavalent chromium (Cr^{VI}) for dislodgeability and leaching

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Prepared for:

The American Chemistry Council
Arsenicals Wood Preservative Task Force

August 20, 2003

Introduction

Hexavalent chromium (Cr^{VI}) is an important component of chromated copper arsenate (CCA) wood preservatives. Its presence in CCA formulations contributes to the low leaching and ultimately to the long-term efficacy of the system as a wood preservative.

It has long been recognized that the primary components of chromated copper arsenate wood preservatives react with one another and with the chemical components of wood through a complex series of reactions that are collectively termed as "fixation". Fixation reactions are driven by the reduction of Cr^{VI} into trivalent chromium (Cr^{III}) by the wood components. The completion of the reaction process is characterized by an increase in wood pH and the formation of low solubility Cr^{III} complexes with arsenic and possibly copper effectively immobilizing all three components in the wood (Dahlgren and Hartford 1972).

The completeness of this reaction is an important issue, since hexavalent chromium is water soluble and much more toxic than trivalent chromium. Hexavalent chromium is a strong oxidizing agent and a known human carcinogen. It may cause lung cancer when inhaled as dust, although there is no conclusive evidence that ingested Cr^{VI} is carcinogenic (Groundwater Resource Association of California 2001). If unreduced chromium remains in wood in service, it may leach out and be transported by water; Cr^{VI} can move in the ground water until it is reduced by organic matter in the soil (Rouse and Pyrih, 1990). Thus it is important to understand the bio-availability of Cr^{VI} in wood during the treating process and during the service life of CCA treated wood.

While the available evidence indicates the conversion of Cr^{VI} to insoluble Cr^{III} is close to 100% when the fixation is complete, it is possible to conceive of two mechanisms by which hexavalent chromium could be released from CCA - treated wood in service. For example if fixation is not complete and unreduced chromium remains in the wood when it is placed in service then it could potentially leach or if the fixed trivalent chromium in wood is exposed to an extremely strong oxidizer such as that found in certain deck cleaning/brightening formulations .

The purpose of this report is to assess the likelihood of those possibilities and to quantify the potential of CCA treated wood to release Cr^{VI}.

The valence of chromium in CCA treated wood

CCA fixation in wood may be monitored by following the reduction of chromium using reagents that are highly sensitive to the presence of Cr^{VI}, such as chromotropic acid or diphenylcarbazide (DPC). The color reaction with chromotropic acid is recommended as an AWPA standard method for determining the presence of hexavalent chromium in treated wood. This procedure gives a positive color reaction until the Cr^{VI} level in the liquid preservative in the wood drops to below about 15 ppm (McNamara 1988). In practice this generally corresponds to more than 99 % reduction of the water soluble Cr^{VI} to insoluble Cr^{III} within a relatively short (temperature dependent) time after treatment. When the more sensitive diphenylcarbazide reagent is used the evidence shows that even higher conversion of Cr^{VI} to Cr^{III} occurs during the fixation process (less than 0.5 ppm Cr^{VI} in the retained solution (Cooper and Ung 1991).

Some scientists have raised the question of whether some unreduced chromium can persist in treated wood for some time after treatment. Pizzi (1982) and Ostmeyer et al (1988, 1989) suggested that some chromate reacts with lignin to form organic chromates (hexavalent). It is suggested (Pizzi 1982) that these may be eventually reduced to trivalent chromium. Other studies show that, under special conditions, hexavalent chromium can also be reduced to pentavalent chromium, which persists for several months after treatment (Ruddick et al 1994, Andersone et al 2000), although exposure to water leaching rapidly eliminated the Cr^{V}. It is not clear what conditions promote Cr^{V} persistence in wood, but it appears to be related to removal of significant amounts of moisture by air or kiln drying the wood before fixation is complete. Drying during fixation is not recommended as the evaporation of moisture from the wood surface cools the wood surface which slows the fixation rate and may prevent complete reduction of the chromium (Kaldas and Cooper 1996). High temperature steam fixation results in rapid disproportioning of the Cr^{V} to reducible Cr^{VI} and low solubility Cr^{III} (Hughes et al 1994).

Other studies on CCA treated wood, using more sophisticated magnetic susceptibility analysis (Wright and Banks 1989, Jorge et al 2001) or X-ray photoelectron spectroscopy (Kaldas et al 1998) confirm that there is no

detectable hexavalent chromium retained in treated wood (limit of detection about 25 ppm for XPS; LOD not reported for magnetic susceptibility). These results indicate that if there is unreduced chromiumVI retained in wood after completion of the fixation reactions, it represents a very low proportion of the total chromium retained in the wood (< 1 %) and it likely is eventually reduced to trivalent chromium in the wood.

Experimental measurements of Cr^{VI} in expressate and leachate from treated wood

There have been a number of studies where expressed liquid squeezed from freshly treated wood and leachate from treated wood exposed to water have been analyzed for the presence of Cr^{VI}.

McNamara (1988) showed that the chromotropic acid test can be used until the Cr^{VI} level in expressed solution drops below 15 ppm (about 99 % fixation). Beyond that point, the test loses it sensitivity. Cooper et al (1996) used the diphenylcarbazide reaction to simultaneously follow Cr^{VI} content in expressed solution from the treated southern pine wood and in leachate from boards subjected to two hours of laboratory shower leaching (with recycled water) at different stages of the fixation process (Table 1). This procedure has a limit of detection of about 0.2 ppm and a limit of quantification of about 0.5 ppm for expressate samples. These limits can be decreased by increasing the size of sample added to the reagent (e.g. 25 ml leachate vs 1 ml for the expressate) for leachate samples resulting in LOD values of about 0.01 ppm (LOQ about 0.05 ppm). For expressate samples, wood extractives sometimes interfere with the reading, resulting in false positives and it is advisable to correct readings using expressed samples from distilled water treated samples.

By the time that samples approached full reduction of the available chromium (complete fixation), levels of Cr^{VI} in the expressate and leachate were near the limit of detection corresponding to about 0.005 % of the chromium initially present as hexavalent chromium in the treating solution. This confirms that once the fixation reaction is measured as complete, there is no detectable Cr^{VI} available for leaching.

Taylor (2001) exposed jack pine, spruce and southern pine boards to natural leaching exposure for one year and collected natural leach water after each rainfall for total chromium, copper and arsenic analysis. During the winter,

he observed a yellow color in the leachate and analyzed the water for Cr^{VI} by the diphenylcarbazide method. No Cr^{VI} was detected at the 0.05 ppm detection limit (total Cr was in the 0.5 – 1.0 ppm range).

Table 1: Relationship between fixation status and amount of Cr^{6+} leached in rain exposure in southern pine 4 - 2"X6"X4' boards – exposed to 12 cycles of 6" vertical simulated rainfall -Cooper *et al* (1996).

Fixation conditions/CCA retention (kg/m^3)	Fixation time	[Cr^{VI}] in expressate (ppm)	% Cr Fixation	[Cr^{VI}] in Leachate (12 recycles) (ppm)	% of original Cr present
Low temperature 21ºC	0.5 days	1219	62.1	21.4	1.0
	1 day	875	73.2	14.2	0.63
	4 days	547	83.2	10.2	0.47
9.3 kg/m^3	5 days	213	92.1	2.55	0.13
	8 days	162	94.8	1.08	0.47
	11 days	122	96.1	2.48	0.12
	13 days	57	97.6	0.48	0.02
	20 days	0.8	99.3	0.01	0.001
High temperature 60ºC	1 hour	1039	71.0	9.10	0.46
	2 hours	918	73.6	5.60	0.25
	3 hours	673	81.0	3.08	0.14
9.1 kg/m^3	4.5 hours	381	89.7	1.60	0.07
	7 hours	85	92.5	0.02	0.002
	8 hours	42.5	98.6	0.02	0.001
	16 hours	<0.2	99.9+	0.03	0.001
	20 hours	<0.1	99.9+	0.04	0.002
Untreated wood		<0.1	N/A	<0.02	N/A

Cooper (1993) collected rain drippage from CCA-treated telephone poles that had been in service for different times. The leachate was analyzed for total Cu, Cr and As and for Cr^{VI} by visible light spectroscopy using the diphenylcarbazide method. Generally, levels of Cr^{VI} were below the detection limit of 0.01 ppm (LOQ 0.05 ppm), representing less than 1 % of

the total chromium concentration. Occasionally, a slight color reaction was noted when high volumes of leachate were used in the test. The estimated Cr^{VI} concentration in these cases was less than 0.05 ppm or less than 5 % of total chromium content.

Recognizing that other metals such as iron can result in a positive color reaction with diphenylcarbazide (EPA 1994), we (Cooper et al 2001) recently analyzed leachate from treated wood using a more precise ion chromatography technique (EPA Method 218.6) that avoids these interferences and provides a higher analytical sensitivity. A number of samples of different species of CCA treated wood were collected, including laboratory treated samples exposed to 1 year natural weathering, freshly treated wood produced from both commercially and in the laboratory and new and aged commercially treated wood (Tables 2 and 3).

Some samples (red pine and southern pine sapwood) were impregnated with water and held for 72 hours, then the water expressed from the wood cells and analyzed by ion coupled plasma spectroscopy (ICP) for total chromium, copper and arsenic and by ion chromatography for Cr^{VI} content (EPA Method 218.6). This procedure separates Cr^{VI} from interfering ions and quantifies it by a post column reaction with diphenylcarbazide and analysis by UV-vis spectroscopy. Other samples were submerged in water of a volume equal to that of the wood specimen for various times and the leachate collected and analyzed as above. The ratios of Cr^{VI} to total Cr were determined.

For the expressed samples, relatively high levels of chromium copper and arsenate were obtained (Table 2), but Cr^{VI} levels were below the 0.5 ppb detection limit (LOQ 1.0 ppb) for the ion chromatograph procedure indicating that the ratio of Cr^{VI} /total Cr was less than 0.01%. For the leachate samples (Table 3), Cr^{VI} in the leachate was near or below the detection limit of the ion chromatograph (<1ppb) and the amount of hexavalent chrome relative to total chromium leached was generally less than 0.1 %.

Table 2: CCA components in expressed water after 72 hours. (Cooper et al 2001)

Sample	CCA Retention (kg/m^3)	[Cr^{VI}] ppb	Total [Cr] ppm	[Cr^{VI}]/[Cr]	[Cu] ppm	[As] ppm
CCA red pine	10.1	< 0.5	7.2	<0.01%	22.9	9.2
CCA SYP	9.5	< 0.5	4.7	<0.01%	13.3	20.7
Untreated	-	< 0.5	<0.01	-	<0.01	<0.03

Table 3: CCA components in leached water after different soaking times (ratio of water to wood = 2:1) *(Cooper et al 2001)*

Sample/CCA Retention (kg/m^3)	# reps.	Time soaked (h)	[Cr^{VI}] ppb[1.]	[Cr] ppm[2.]	[Cr^{VI}]/[Cr] (%)	[Cu] ppm[3.]	[As] ppm[4.]
Jack pine (1"X6") New 4.5 kg/m^3	1	24 96 240	<0.5 0.6 4.1	0.76 1.33 1.87	<0.07 0.04 0.22	3.2 5.1 6.3	1.7 3.2 5.8
Jack pine (2"X6") weathered 1 year 4.8 kg/m^3	2	24 96 240	<0.5 <0.5-1.3 <0.5-1.1	0.3-0.8 1.0-1.2 1.6-1.8	<0.06 <0.10 <0.05	1.3-2.0 3.2-5.6 1.7-8.0	0.9-1.3 3.4-3.9 5.9-6.2
Southern pine (2"X6") new 9.5 kg/m^3	2	24 96 240	<0.5 <0.5 <0.5-0.8	0.7-0.9 1.6-1.9 3.1-3.2	<0.07 <0.05 <0.02	1.3-2.7 2.4-4.4 3.8-6.7	2.3-4.0 6.6-9.1 16.7-18.1
Spruce (2"X6") weathered ½ year 3.3 kg/m^3	2	24 96	<0.5 0.6-0.8	0.2 0.3-0.5	<0.10 <0.06	0.1 0.7-1.1	0.6-1.1 1.7-3.2
Spruce (2"X6") weathered 1 year 3.1 kg/m^3	2	24 96 240	<0.5 <0.5 <0.5-0.8	0.5 0.8 1.6	<0.10 <0.06 <0.04	0.8-2.0 0.9-2.3 0.6-0.7	1.5-2.2 2.4-3.4 7.0-7.8
Douglas-fir (2"X6") new 5.7 kg/m^3	2	24 96 240	<0.5 0.5-1.1 1.6-2.6	0.6-1.2 0.9-1.7 1.6-2.3	<0.10 0.06 0.11	2.0-2.5 2.7-2.9 3.0-6.5	1.8-3.8 2.5-6.1 6.5-12.4
Jack pine (2"X2") new 4.3 kg/m^3	1	24 96 240	<0.5 <0.5 0.9	1.2 1.6 2.4	<0.05 <0.05 0.03	4.5 6.0 6.8	3.3 4.8 8.9
Red pine pole, weathered 1 year 10.9 kg/m^3	1	24 96 240	<0.5 <0.5 1.4	0.9 2.7 6.6	<0.05 <0.05 0.02	2.5 5.6 12.1	2.7 7.6 15.1
Untreated red pine	1		<0.5	<0.05		<0.05	<0.05

[1.] The amounts leached correspond to from less than 1/1,000,000 to 1/250,000 of the original chromium in the wood
[2.] The amounts leached correspond to from about 0.03 % to 0.23 % of the original chromium in the wood
[3.] The amounts leached correspond to from 0.02 % to 1.3 % of the original copper in the wood
[4.] The amounts leached correspond to from 0.13 % to 0.95 % of the original arsenic in the wood

The expressate and leachate samples evaluated here are more concentrated than typical rain water leachate, and even so, the levels of Cr^{VI} measured are generally below the most stringent drinking water standards. For example, a proposed but recently withdrawn drinking water standard by the California Environmental Protection Agency Office of Environmental Health Hazard Assessment was for 2.5 ppb total Cr (GRAC 2001) and the current Canadian guideline for drinking water is 50 ppb Cr^{VI} (Pawlitz et al 1997).

In conclusion, based on the results reproduced above and the other published information, there is no evidence to show that significant amounts of Cr^{VI} are present in treated wood after the fixation reaction is complete or that CrVI is produced as a result of oxidation of trivalent chromium in the wood. This latter observation is expected, since normal in-service exposure conditions where CCA treated wood is used are not strongly oxidizing enough to facilitate the conversion of CrIII to CrVI. Only under special circumstances and under severe exposure conditions, will some trivalent chromium be re-oxidized to the more toxic and mobile hexavalent state. Examples are when there is a high manganese content (Mn^{III}, Mn^{IV}, Mn^{VII}) present in the soil (Bartlett & James, 1979) or when oxidizing deck cleaners are used (Taylor et al 2001). However, the amount liberated in this way is very low and is quickly reduced by organic matter in the soil or diluted to insignificant levels.

Experimental measurements of Cr^{VI} dislodged from treated wood

Coggins and Hiscock (1979) concluded that chromium (mainly hexavalent) on the surface dropped rapidly during fixation and except when frozen, they

stated wood was safe to handle after about 2 days. Wipe tests with wet glass wool showed initial levels of about 5 $\mu g/cm^2$ total chromium (mainly hexavalent) to about 0.5 $\mu g/cm^2$ in 48 hours at 20°C stabilizing eventually to about 0.1$\mu g/cm^2$ (Cr^{3+}). When cotton swabs were used, more Cr was removed (speciation not determined). Wipe tests done at lower temperature (10°C) showed little effect of temperature after 4 days. After 48 hours at room temperature, only about 10% of wiped chromium was hexavalent.

In a field evaluation of fixation of CCA treated southern pine under cold winter conditions, (Janesville Wisconsin, January 8-11, 2001 and Conyers, Georgia, March 2001 - Cooper 2001a), bundles of dead-packed nominal 2-inch southern pine lumber were assessed for chromium fixation status and tested for Cr^{VI} dislodgeability using a kimwipe test. Samples that tested at 96 % chromium fixation or higher had Cr^{VI} dislodgeability values of less than 0.1 $\mu g/cm^2$. Laboratory studies on CCA treated southern pine (Cooper 2001b), confirmed the low potential for dislodgeability. Samples determined to be 99.5 % fixed or higher had dislodged Cr^{VI} levels of 0.01 $\mu g/cm^2$ or lower.

There is a strong correlation between the extent of fixation, the amount of Cr^{VI} leached from wood and the amount available for dislodging, as determined by the kimwipe test (Table 4).

Table 4: Relationship among % fixation, leaching (2 hour shower test –300 mm rain) and dislodgeability of Cr^{VI} – southern pine lumber. (Cooper et al 1996, Cooper 2001a,b)

% Chromium fixation	% Cr^{VI} leached	Dislodgeable Cr^{VI} ($\mu g/cm^2$)
65	1.01	0.38
84	0.47	0.20
95	0.05	0.05
99.5	0.001	<0.01

Summary and Conclusions

Most research shows that virtually all of the chromium injected into wood during the treating process is eventually reduced to low toxicity trivalent chromium. Re-oxidation of this chromium to the hexavalent state would only occur in alkaline environments or in the presence of strong oxidizing agents, and there is no evidence that this is significant in treated wood applications (except where deck cleaners are used). The amount of hexavalent chromium re-oxidized from trivalent chromium or liberated in this way from adsorbed trivalent chromium is very low and is quickly reduced to Cr^{III} by organic matter or diluted to insignificant levels.

As the chromium fixation process proceeds, the amounts of Cr^{VI} available for leaching and dislodging decrease proportionally. Studies on the speciation of chromium in leach water collected from CCA treated wood show that once the chromium fixation reaction with wood is complete, there is virtually no hexavalent chromium available in the wood for leaching. Similarly, dislodgeability (kimwipe) studies on treated wood at close to complete fixation confirm that levels of dislodgeable hexavalent chromium are very low (about 0.01 $\mu g/cm^2$). While there are no reported studies on the speciation of dislodged chromium from CCA treated wood that has been in service for any extended length of time, it is likely that these values will be even lower and most likely undetectable.

These results suggest that during the service life of a typical piece of CCA treated wood, more than 99.9 % of any chromium that is leached or dislodged from the wood will be in the trivalent oxidation state and will remain so in the environment.

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