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Implication of chromium speciation on disposal of discarded CCA-treated wood

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Abstract

The wood preservative chromated copper arsenate (CCA) contains hexavalent chromium [Cr(VI)] and the conversion of Cr(VI) to trivalent chromium [Cr(III)] drives fixation of the treatment chemicals to the wood fibers. Since the toxicity of Cr depends on its valence state, an assessment of the Cr species occurring in CCA-treated wood, as well as leachates and ashes from CCA-treated wood, is helpful when assessing implications for disposal. In this study, both new and weathered wood samples of CCA-treated wood and their ashes were evaluated for total Cr and Cr(VI) within the solid matrices and within leachates. Results show that for both new and weathered CCA-treated wood, Cr(VI) occurred in the range of 0.7–4% of the total Cr. Greater Cr leaching occurred at the pH extremes, with Cr(VI) only measured under alkaline pH values (pH > 9.0). Total chromium concentrations from synthetic precipitation leaching procedure (SPLP) leachates from CCA-treated wood were consistently less than 3 mg/L with Cr(VI) below detection limits. The results suggest that leaching of Cr(VI) from discarded CCA-treated wood should not be a concern in most landfill environments. One exception would be disposal in landfills with alkaline leachate; Cr(VI) was observed to leach from CCA-treated wood in the presence of alkaline leachate from crushed concrete. When CCA-treated wood is combusted, chromium becomes concentrated in the ash. Cr(VI) in ash from the combustion of CCA-treated wood was found between 4 and 7% of the total chromium. In ash from the combustion of wood recovered from construction and demolition (C&D) debris (which contained some CCA-treated wood), Cr(VI) accounted for as much as 43% of the total Cr. Nearly, all of the Cr in SPLP leachates produced from the ash was in the Cr(VI) form. The degree of Cr(VI) leaching from the ash was highly dependent upon the alkalinity of the ash, with higher ash leachate pH resulting in greater concentrations of Cr(VI).

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1. Introduction

Chromated copper arsenate (CCA) has been used as a wood preservative for several decades because of its excellent performance in prolonging the structural integrity of wood products used in outdoor environments. The amount of chemical added to the wood depends upon its intended use with more chemical added in wood to be used in harsher environments. The amount of chemical in units of kilograms of chemical added as CuO, CrO_3 , and As_2O_5 per cubic meter of wood varies from 4 to 40 kg/m^3 [1]. While arsenic and copper act as biocides, chromium acts as a fixing agent to bind the metals to the wood. Fixation results from the conversion of hexavalent chromium [Cr(VI)] present in CCA solution to trivalent chromium [Cr(III)] in the wood matrix [2]. The primary chromium precipitates reported to occur in CCA-treated wood products include CrAsO₄,

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CuCrO₄, and Cr(OH)₃ [3,4]. The bulk of the fixation process occurs in a few days, and the rate of chromium fixation depends on factors, such as temperature, time, and wood species [5,6]. While the metals are considered fixed from a wood preservation efficacy standpoint, a number of researchers have reported that chromium, copper, and arsenic do leach from CCA-treated wood products over time when exposed to water or when disposed in the environment [2,3,5-7].

The potential impacts of CCA preservative leaching on human health and the environment have been investigated [8–14], but in most studies, only the total chromium concentration has been reported. Since Cr(VI) is much more toxic to humans than Cr(III) [15], and because Cr(VI) also tends to be more mobile in the environment, a detailed assessment of risk from Cr must consider the species present. The research reported in this paper examines the potential impact of Cr on the management of discarded CCA-treated wood, with a focus on characterizing the species of Cr occurring in different waste-management scenarios. The total and leachable chromium concentrations were measured for both CCA-treated wood and ash that was produced from the combustion of wood mixtures containing CCA-treated wood. The results are assessed with respect to the existing regulations and risk-based guidelines for management of solid and hazardous wastes.

2. Materials and methods

Both unburned wood and ash were evaluated in this study. The total concentrations of Cr and Cr(VI) in mg/kg were measured in every sample, with Cr(III) assumed to represent the difference. The leachable concentrations of Cr and Cr(VI) in mg/L were also measured. A summary description of the sample preparation and analytical methods fol-

Table 1

Sample details and retention	values for	CCA-treated	wood samples
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lows. Detailed procedures have been reported elsewhere [16,17].

2.1. Sample collection and preparation

New CCA-treated dimensional lumber (i.e., wood that had not been exposed to weathering in the environment) was purchased from a variety of home improvement stores in Gainesville and Miami, FL. The manufacturer-reported CCA retention levels of these samples, also referred to as the "rated retention," are provided in Table 1. Several pieces of new untreated dimensional lumber were purchased to serve as a control. These samples were prepared for leaching analysis by chipping the wood with a chipper-shredder and for total analysis by grinding the chipped wood with a laboratory mill or by collecting the cuttings from a power drill. One weathered wood sample was collected by selecting an aged CCA-treated utility pole from a stockpile located at a Florida electric utility company (estimated at 22 years in age). The pole was chipped as described above with a fraction of the chipped samples ground for total analysis. A second weathered wood sample consisted of sawdust produced from the cutting of wood from a demolished playground (estimated at 15 years in age [17]).

Samples of shredded construction and demolition (C&D) wood waste were collected from two recycling facilities in Florida. These facilities accept mixed loads of C&D debris and separate the major material types, including wood, for recycling. The C&D debris wood contains a mixture of treated and untreated wood [18]. The C&D debris samples were not further processed prior to leaching, but were ground in a laboratory mill prior to total analysis. Several of the chipped wood samples described above were combusted using an industrial furnace to produce an ash. A description of the ash samples is presented in Table 2. These ash samples were prepared as a part of an earlier study and the details

Sample category Sample ID		Rated retentionAverage Cr(kg/m³)concentration (mg/kg)		Average Cr(VI) concentration (mg/kg)	Cr(VI) (%)	Remarks	
	UN	_	1.2	<0.8	_	Untreated SYP ^a	
	А	4	2850 ± 18	90 ± 26	3.2		
	В	6.4	5440 ± 200	36 ± 5	0.7		
	С	6.4	2820 ± 43	43 ± 3	1.5		
	D	6.4	1310 ± 2	22 ± 7	1.7		
N 1	Е	6.4	2720 ± 70	45 ± 4	1.7		
New wood	F	6.4	2860 ± 33	55 ± 3	1.9		
	G	6.4	3150 ± 72	45 ± 8	1.4		
	Н	4.0	1800 ± 131	71.3 ± 15	4.0		
	Ι	9.6	6350 ± 920	113 ± 26	1.8		
	J	40.0	15800 ± 230	248 ± 52	1.6		
	pH-N	6.4	1470 ± 46	29.4 ± 14	2.0	Used for pH impact	
	Pole	9.6	5340 ± 122	42.4 ± 10	0.8		
T T .1 1 1	C&D A	_	278 ± 100	6.9 ± 1.2	2.5		
Weathered wood	C&D B	_	421 ± 20	29.7 ± 4.3	7.1		
	pH-W	_	2550 ± 55	16.8 ± 6.7	0.7	Used for pH impact	

^a SYP: Southern yellow pine.

Table 2	
Sample details for CCA-treated wood ash samples	

Sample category	Sample ID	Average Cr concentration (mg/kg)	Average Cr(VI) concentration (mg/kg)	Cr(VI) (%)	Remarks
Ash from new wood	UN-ash H ash I ash J ash	$\begin{array}{c} 10.2 \pm 1.1 \\ 15400 \pm 2400 \\ 40400 \pm 6000 \\ 108000 \pm 2400 \end{array}$	<0.8 1090 ± 214 1600 ± 18 6340 ± 450	- 7.1 4.0 6.0	Ash from corresponding new wood sample
Ash from weathered wood	Pole-ash C&D A ash C&D B ash	52000 ± 8150 2100 ± 97 1960 ± 380	2300 ± 450 600 ± 27 840 ± 90	4.4 28.6 43.0	Ash from corresponding weathered wood sample

concerning the incineration and collection procedures can be found elsewhere [19].

2.2. Laboratory analysis

Analysis for total Cr and Cr(VI) in the solid samples required two different extraction procedures and measurement techniques. The total Cr-extraction procedure (Method 3050B [20]) involved digesting the samples with a sequence of strong acid and hydrogen peroxide additions. The acid digestates were analyzed for total Cr using an inductively coupled plasma atomic emission spectrometer (ICP-AES, Model: Thermal Jarrel Ash Enviro 36, Method 6010B [20]). The Cr(VI) extraction procedure (Method 3060A [20]) required an alkaline digestion to preserve the chromium species; this methodology was developed for soils, sludges and similar waste materials, it was not developed specifically for wood. The alkaline digestion methodology acknowledges that some conversion of Cr(III) to Cr(VI) during the digestion may be possible in certain matrices. The alkaline digestates were analyzed for Cr(VI) using ion chromatography (IC, Method 7199, Dionex AS7 column [20]). Detailed experimental procedures can be found elsewhere [17]. Laboratory blanks were consistently below detection limits. Duplicate analyses were typically within 5% and sample recovery from spike analyses were 95-100% on average.

Leachable Cr and Cr(VI) concentrations were assessed in several manners. First, the leaching of Cr from CCA-treated wood as a function of leaching solution pH was examined by extracting wood samples (one new wood sample and one weathered wood sample) in solutions of deionized water to which an acid (1N nitric acid) or a base (1N sodium hydroxide) was added to achieve a desired pH (pH 1–13). Second, many wood and ash samples were subjected to a US EPA regulatory leaching test known as the synthetic precipitation leaching procedure (SPLP, Method 1312). The SPLP extraction fluid simulates a slightly acidic rainfall and contains diluted sulfuric and nitric acid in a 3:2 ratio (pH 4.20 ± 0.05). The SPLP is frequently used by regulatory agencies in the US to assess potential leaching of pollutants from wastes or contaminated soils that are land applied or otherwise subjected to leaching from rainfall. The SPLP was selected over a related test, the toxicity characteristic leaching procedure (TCLP, Method 1311), because the leaching solution is less likely to impact Cr speciation. The TCLP simulates acid-forming conditions that can occur in municipal waste landfills and consists of a 0.1 M acetic acid solution (buffered with sodium hydroxide to a pH of 4.93 ± 0.05) [20]. The organic content and buffered nature of the TCLP can result in a reduction of Cr(VI) to Cr(III) during the course of the leaching procedure. The TCLP was performed on several ash samples to illustrate this point. Finally, several wood samples were also leached with an alkaline solution created by leaching 100 g of crushed portland cement concrete in 2 L of reagent water for 18 h (pH 11.0); the purpose was to examine the disposal scenario, where wood was co-disposed with debris containing large amounts of concrete rubble.

All leaching experiments were performed at a liquid to solid ratio of 20:1 and were rotated end-over-end for 18 ± 2 h. With the exception of the experiment using the alkaline concrete solution, 100 g of each sample were leached with 2 L of leaching solution. The alkaline leachate experiment was conducted using 10 g of sample and 0.2 L of leaching solution. After the rotation, the final pH of the leachate was recorded, and the leachate sample was filtered through a 0.7 μ m borosilicate glass fiber filter. A portion of the filtered leachate was digested following Method 3010A [20]. The acid digestate was analyzed for Cr using the ICP–AES following Method 6010B [20]. A second portion of the filtered leachate was analyzed for Cr(VI) concentrations using the IC method as mentioned previously; samples were analyzed for Cr(VI) within 24 h of collection.

3. Results and discussion

3.1. Total and hexavalent chromium in unburned wood samples

Total Cr concentrations in the new CCA-treated wood samples ranged from 1310 to 15,800 mg/kg (Table 1). These concentrations fell within the range expected based on the amount of chemical added to the wood product and the composition of CCA (Type-C) [1]. Type-C, CCA-treated wood, the most common formulation used in the US, nominally contains 1870 mg-Cr/kg-wood for wood treated to

4 kg-CCA/m³-wood and 18,710 mg-Cr/kg-wood for wood treated to 40 kg-CCA/m³-wood [18]. As described earlier, the CCA-treatment reaction is driven by the reduction of Cr(VI) to Cr(III). The Cr(VI) concentrations measured in the new CCA-treated wood samples ranged from 22 to 248 mg/kg. This corresponds to 0.7–4.0% of the Cr in the samples. Cruz et al. [21] reported the amount of Cr(VI) in CCA-treated building timbers to be less than 2% of the Cr. Hingston et al. [3] reported that approximately 10% of the Cr in CCA-treated (Type-C) wood remains as Cr(VI). Other studies, such as Nico et al. [22] and Wright and Banks [23], have reported undetectable levels of Cr(VI) in CCA-treated wood samples.

Small amounts of Cr(VI) were also measured in the weathered wood samples. The weathered utility pole contained less than 0.8% of the Cr as Cr(VI), while the playground sample contained 0.7% of the Cr as Cr(VI) (Table 1). The fraction of Cr in the Cr(VI) from the two samples of mulched wood from C&D debris recycling operations were 2.5% and 7.1%, respectively (Table 1). The total Cr concentrations were much less in these samples because most of the C&D debris wood was comprised of untreated wood. The CCA-treated wood contained in the C&D debris wood was considered to be primarily represented by weathered material, though it is possible that some new product was present in the form of cutoffs from construction sites.

3.2. Chromium leaching from CCA-treated wood

Fig. 1 illustrates the impact of extraction solution pH on leaching of total Cr and Cr(VI) from an unweathered (or new) CCA-treated wood sample and a weathered sample. The concentrations presented in Fig. 1 represent an average of duplicate measurements. The highest Cr concentrations were observed at pH 1 with 27 and 32 mg/L of Cr leaching from the new CCA-treated wood and from the weathered wood sample, respectively. Total Cr concentrations were also elevated at high pH values though not as high as the acidic pH range (3.4 mg/L for unweathered wood and 20 mg/L for weathered wood). Total Cr concentrations were encountered in the range of 1-2 mg/L for the unweathered sample and in the range of 5-6 mg/L in the weathered wood sample in the near neutral pH range of 4-8. All of the chromium in the acidic and neutral regions was present as Cr(III). Cr(VI) was observed at pH values greater than 9. Although the amount of Cr(VI) at the alkaline pH extreme was substantial, a majority of the chromium leached existed in the form of Cr(III).

Leachable total Cr was found at relatively low levels in the SPLP leachates, ranging from 0.1 to 2.9 mg/L (Fig. 2a). This falls within the range reported previously [7]. Sample-I leached the highest total Cr. No trends were observed between SPLP leachate concentrations and retention values with the exception that untreated wood leached considerably less than treated wood. Cr(VI) was below the detection limit (0.04 mg/L) for all SPLP leachates from CCA-treated wood. The final pH of the SPLP leachates varied with a range of 4.37–6.64, a range typical of leachates from CCA-treated wood. None of the sample pH values exceeded the pH of 9, the threshold pH, after which Cr(VI) was detected in the pH experiment (Fig. 1).

Leachable Cr measurements from the three samples leached using the concrete-derived solution (final pH 10–12) indicated that more than 50% of total Cr leached was in the form of Cr(VI) (Fig. 2b). These results are consistent with those of Munson and Kamdem [24] who reported that 60-70% of the total chromium that leached from wood cement-bonded particleboard containing recycled CCA-treated wood was in the Cr(VI) form. The total Cr and Cr(VI) leached were not greater in samples containing higher retention values. Rather, more total Cr was leached for samples containing the lower retention level. This may have resulted from the lower pH conditions in samples with higher retention levels. As observed from Fig. 1, an increase in pH in the high pH range resulted in more Cr and Cr(VI) leaching. Also of interest, is that the total chromium concentrations in the leachates from the concrete leaching solution were lower than those from the SPLP solution. This cannot be explained based on pH effects alone (see Fig. 1) and thus, some other

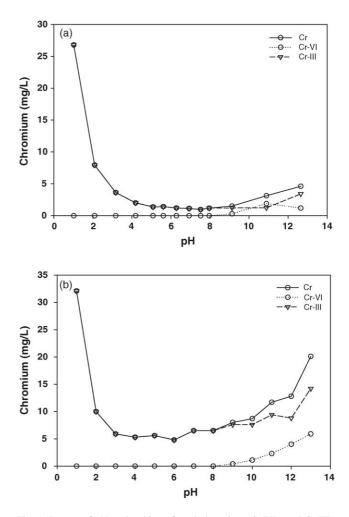


Fig. 1. Impact of pH on leaching of total chromium, Cr(VI), and Cr(III): (a) unweathered CCA-treated wood (pH-N) and (b) weathered CCA-treated wood (pH-W).

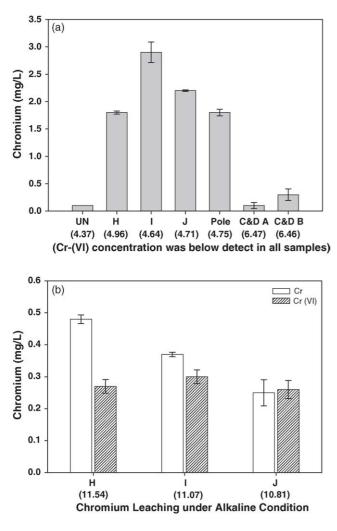


Fig. 2. Total chromium and Cr(VI) concentrations in leachate produced from unburned CCA-treated wood samples: (a) SPLP and (b) alkaline condition. The value in parenthesis represents final pH of extraction solution.

chemical factor must have played a role. The alkaline concrete solution contained additional elements and compounds, such as calcium, potassium, and carbonates, and these may have impacted Cr leaching by competing with Cr for oxyanions.

3.3. Total and leachable chromium and chromium(VI) in ash samples

The concentration of Cr in the ash samples increased with higher retention value of CCA-treated wood (Table 2). The ash sample produced from the combustion of 4.0 kg/m³ CCA-treated wood contained approximately 15,000 mg-Cr/kg and the sample from the 40 kg/m³ CCA-treated wood contained over 100,000 mg-Cr/kg. The concentration of Cr(VI) in the ashes also increased as retention value of the original wood samples increased. Cr(VI) represented between 4 and 7% of the total chromium concentration. When compared to untreated wood, the combustion process resulted in both the

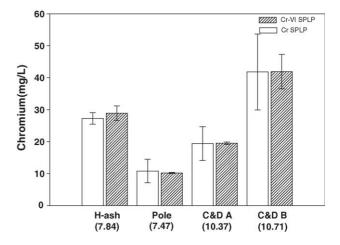


Fig. 3. Total chromium and Cr(VI) concentrations in leachate produced from CCA-treated wood ash samples using SPLP (untreated wood ash, sample I-ash and J-ash were below the detection limit (Cr < 0.016 mg/L) and Cr(VI) < 0.04 mg/L)). The value in parenthesis represents final pH of extraction solution.

conversion of chromium towards Cr(VI) and an increase in the total concentration.

As expected, lower concentrations of total Cr were detected in ash samples produced from the combustion of the two samples originating from C&D debris recycling facilities. These samples were a mixture of untreated wood and treated wood. The C&D debris wood ash samples contained approximately 2000 mg-Cr/kg. The fraction of Cr existing as Cr(VI) was much greater in these samples relative to the ash sample created from the combustion of pure CCA-treated wood. Cr(VI) in C&D B-ash represented 43% of the total Cr, whereas Cr(VI) in the C&D A-ash sample represented 29% of the total Cr. Clearly, a larger fraction of the Cr(III) contained in these samples was oxidized to Cr(VI) during the combustion process. Oxidation of Cr(III) to Cr(VI) in combustion systems has been reported previously [19] and difference in the degree of oxidation may result from several factors. One possible explanation for the differences noted in this study is discussed in the following presentation on leaching results.

Cr was detected in SPLP leachates from four of the six ash samples tested; Fig. 3 presents the Cr and Cr(VI) concentrations for the four samples. Cr concentrations were below the detection limit in ash from the combustion of CCA-treated wood treated to 9.6 and the 40 kg/m³ retention values (samples I and J, respectively), but were relatively high (>10 mg/L) in samples treated to lower CCA retention values. As noted previously, the ash samples were a subset of samples described in an earlier study [19]. The earlier study only looked at total Cr, and the results are for the most part consistent between the studies (though a small amount Cr was measured in the SPLP leachate from sample J in the previous study that was not detected here). The previous study concluded that such dramatic differences were possibly a result of different chromium species.

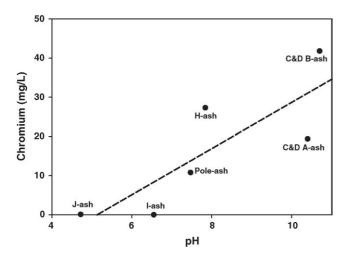


Fig. 4. Total chromium concentration vs. final pH of leaching solution for SPLP leachates from CCA-treated wood ash.

SPLP leachate Cr(VI) concentrations in the four detected ash samples ranged from 11 to 42 mg/L (Fig. 3). The Cr(VI) detected in these leachates represented nearly all of the total Cr (94–100%). Fig. 4 plots the total Cr concentration (which is represented in nearly entirety by Cr(VI)) as function of the pH measured in the SPLP solution after the 18 h extraction. The results suggest that the pH of the ash and the resulting pH of the leaching solution during the leaching test were primary factors controlling how much Cr(VI) is measured in the solution at the end of the experiment. Several reasons may account for differences in pH among the ash samples. First, the pH of the ash is likely influenced by the amount of CCA in the original wood sample. CCA is an acidic solution of arsenic acid and chromic acid, and as the concentration of CCA in a wood sample increases with higher retention levels, one may expect lower pH values in leachates from ash. This pH effect resulted in the leaching of greater quantities of chromium for samples containing lower retention levels of CCA and corresponding higher pH values. This could explain why the pH was greater in the H ash sample relative to the I and J ash samples, and thus, why Cr(VI) leached to a greater extent.

Secondly, the presence of other materials in the wood mix may help increase the pH. C&D debris wood is often accompanied by small amounts of soil or concrete that could result in an increase in ash pH. In this study, the fraction of Cr(VI) to the total Cr concentration was the highest (29–43%) for the C&D samples. As seen in Fig. 4, these samples had the highest pH values. Thus, despite having much smaller amounts of Cr and Cr(VI) relative to other samples, the C&D debris wood samples leached among the highest Cr and Cr(VI) concentrations. The high pH of the ash may have contributed to the relatively high fraction of Cr(VI) in the ash samples, and it may have allowed leached Cr(VI) to remain in solution as Cr(VI) as opposed to being reduced to Cr(III) as may have occurred in the lower pH ash samples.

In the methodology it was noted that the SPLP was selected as a preferential leaching test for the wood and ash samples because of the possible reduction of Cr(VI) by the organic, buffered TCLP leaching solution. To examine this, several ash samples were leached using the TCLP and the results were compared to results using the SPLP. Samples H–J were all leached using the TCLP. As was the case with the SPLP, Cr, and Cr(VI) were only detected in H sample. The TCLP Cr and Cr(VI) concentrations were lower than the SPLP concentrations. The SPLP leaching contained 29 mg/L of Cr(VI), while the TCLP contained 6.4 mg/L. These results corroborate the results from the previous study [19], where TCLP Cr concentrations were lower than SPLP Cr concentrations. The results suggest that as Cr(VI) is leached into solution, some fraction of the Cr(VI) is reduced to Cr(III), which precipitates or sorbs and is removed from solution.

4. Waste-management issues

4.1. Hazardous waste status

A primary question that must be addressed when assessing the management of a solid waste is whether it is classified as a hazardous waste; such a classification greatly increases the regulatory compliance and costs for managing a solid waste. CCA-treated wood is exempt from the definition of hazardous waste under RCRA when discarded after its intended end use [25]. As has been reported elsewhere, CCA-treated wood often leaches arsenic above the toxicity characteristic (TC) limit (5 mg/L); less frequently, it leaches chromium above its respective TC limit (5 mg/L). When 13 new CCA-treated wood samples were tested by Townsend et al. [7], 11 samples exceeded the US EPA's TC threshold for arsenic, while none of the samples exceeded the TC limit for chromium. When weathered CCA-treated wood samples were tested [26], 60 out of 100 samples exceeded the TC limit for arsenic, while 20 samples exceeded the limit for chromium.

As discussed in detail elsewhere [26], if the only reason a waste is a TC hazardous waste is because of Cr, the waste generator may petition the US EPA (or authorized state program) to exclude the waste from characterization as hazardous. The generator must demonstrate that the discarded wood contains chromium in exclusively or nearly exclusively the Cr(III) form and that the wood will not be managed in a manner, where the Cr(III) will be oxidized to Cr(VI). The results obtained in this study indicate that the majority of the Cr in CCA-treated wood will be in the Cr(III) form. Since arsenic is the most likely cause for CCA-treated wood to be hazardous, this point becomes somewhat moot. It may be an important observation for other wood preservatives that contain chromium but not arsenic (see Section 5).

While CCA-treated wood may be exempt from the definition of a hazardous waste, the same is not true for ash produced from burning CCA-treated wood. The research presented here and as well in a previous study [19] found that the Cr may in some cases leach from wood ash at concentrations greater than the 5 mg/L TC limit and thus, might have to be managed as a hazardous waste. This may impact reuse and disposal operations and is discussed in greater detail in subsequent sections.

4.2. Impact on recycling

Since CCA-treated wood is most often excluded from being a hazardous waste, it is normally managed in the same fashion as other municipal wastes, most frequently as part of the C&D debris stream. Reuse and recycling options for source-separated CCA-treated wood are somewhat limited; this material will most often be landfilled or combusted in a waste-to-energy (WTE) facility. CCA-treated wood that is co-mingled with the other components in the C&D debris stream is either disposed in a landfill or sent to a C&D debris processing facility. The processing facilities separate components from one another for subsequent recycling, and a major recovered C&D debris component is wood. Because of difficulties encountered in separating preserved wood from other wood sources, CCA-treated wood often becomes mixed in with the rest of the recovered wood stream [18,27,28]. The two primary markets for processed C&D debris wood are boiler fuel and landscape mulch.

Concerns with respect to land application of mulch containing CCA-treated wood relate to direct human exposure to the mulch and possible contamination of underlying groundwater (see [27] for a more detailed explanation). Risk from direct exposure is typically evaluated by comparing the total concentration of an element to a risk-derived screening level. In Florida, for example, the Florida Department of Environment Protection (FDEP) has published a soil cleanup target level (SCTL) for residential settings of 210 mg/kg for Cr. This level was derived assuming that the Cr in the soil exists as Cr(VI). Given that CCA-treated wood will only be a fraction of the recovered C&D debris wood stream and that the percentage of Cr(VI) in CCA-treated wood is small, land applied mulch appears to pose minimal concern with respect to direct human exposure to Cr. For example, in the unlikely event that a mulch product contained 100% CCA-treated wood (with an average concentration of 3000 mg/kg of Cr) and that 4% of the total chromium in the wood was Cr(VI) (the highest percentage observed in this study), the resulting Cr(VI) concentration in the mulch (120 mg/kg) would still be less than the Florida residential SCTL. With respect to leaching from land applied mulch, total Cr concentrations in SPLP leachates from C&D debris wood in this study did not leach Cr(VI) above the detection limit.

If the recovered wood from C&D debris recycling were combusted as fuel, the results of this study do indicate that Cr(VI) could be a potentially limiting issue. CCA-treated wood ash contained both a greater concentration and relative percentage of Cr(VI) when compared to the wood before combustion. The results found that conversion of Cr(III) to Cr(VI) did occur in many samples, most notably in those samples, where the ash was more alkaline. Ash from the combustion of C&D debris wood was found to be more alkaline than ash from the combustion of CCA-treated wood alone (refer back to Fig. 4). Thus, while the amount of CCA-treated wood in a commingled C&D debris wood stream may be smaller compared to source separated CCA-treated wood, a greater fraction of the ash will be converted to Cr(VI). Since the results indicate that nearly all of the Cr(VI) is leachable, ash from the combustion of C&D debris wood containing even moderate amounts may be a TC hazardous waste.

4.3. Landfill disposal

In terms of landfill disposal, the reducing environments that occur in most landfills suggest the Cr(VI) conversion would not be a problem. The typical pH of MSW landfill leachate is in the range of 6-8. Leaching experiments conducted here did not find Cr(VI) in CCA-treated wood leachates at this pH range. If CCA-treated wood were disposed in an alkaline environment, Cr(VI) might pose a problem. An example of such an environment would be a monofill, where alkaline ashes were disposed. A scenario that was tested in this study was leaching in an environment, where CCA-treated wood was co-disposed along with large amounts of concrete. Cr(VI) was observed in these alkaline leachates. This is not a very likely scenario, however, as most CCAtreated wood disposed by landfilling is co-disposed with other materials in addition to concrete that result in neutral pH conditions.

5. Implications for other wood preservatives

The results described here suggest that the biggest concern with Cr in discarded CCA-treated wood is combustion. CCA-treated wood is currently exempt from the definition of hazardous waste and issues regarding arsenic would be of greatest concern with regard to land applied mulch and disposal in landfills. The results may, however, lend themselves to assessing potential risk resulting from other treated wood chemicals that do not contain As but do contain Cr. The wood preservative acid copper chromate (ACC) has been receiving renewed interested as a result of the 2004 voluntary withdrawal of CCA-treated wood (for most residential applications) by the treated wood industry. In an effort to begin marketing, this wood preservative again, the US EPA has been petitioned by a manufacturer for re-registration of the chemical. The ACC wood preservative contains chromium in the same form as CCA (CrO₃), and one might expect it to form similar complexes when exposed to wood. The Cr concentrations are typically higher than CCA, in the range of 3400–13,450 mg/kg depending upon the application [29].

Assuming that the Cr in ACC behaves in a similar fashion as CCA, one would again expect that impact on combustion systems would be the biggest concern. The primary difference to be considered is that ACC is not exempt from the definition of hazardous waste like CCA, since the exemption applies only to arsenical-treated wood. The generator of discarded

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ACC waste might be able to demonstrate that the Cr in the wood exists exclusively or nearly exclusively in the Cr(III), but unless they could guarantee that it would never be burned (which would be almost impossible to do), it would not meet the requirement of the exclusion that says the waste will not be managed in a oxidizing environment. Additional testing similar to what was reported in the current study for CCA-treated wood would be advised for ACC-treated wood if it were to seriously be pursued as a replacement to CCA.

6. Conclusion

The potential impact of Cr(VI) on the management of discarded CCA-treated wood was examined. The results indicate that although a great majority of the Cr(VI) in the CCA preservative solution becomes fixed in the wood product, a small fraction of the total Cr in new and weathered CCA-treated wood may exist as Cr(VI). Cr(VI) was only observed to leach from unburned CCA-treated wood at pH values greater than 9. When chipped CCA-treated wood and C&D debris wood containing CCA-treated wood were leached using the US EPA's SPLP, no Cr(VI) was observed above the detection limit. Since the pH of most landfills is near neutral, conversion of Cr(III) to Cr(VI) is unlikely under this disposal option. An evaluation of the potential Cr(VI) in land applied mulch suggests that direct human exposure to such mulch should not be a problem with respect to chromium.

The waste-management scenario where Cr from discarded CCA-treated wood is combusted might increase risks to the environment and human health due to conversion of chromium to Cr(VI) and concentration of Cr within the ash. Combustion in a WTE facility would not be an uncommon management option for source separated CCA-treated wood. CCA-treated wood also commonly occurs mixed with recycled C&D debris wood, and a large market for the material is boiler fuel. This study found that some Cr(III) in combusted CCA-treated wood did convert to Cr(VI), and that this Cr was readily leachable. The conversion of Cr(III) to Cr(VI) during combustion was not found to be strongly tied to the original amount of Cr present, but rather more strongly related to the alkalinity of the ash. Ash samples with higher pH values leached greater concentrations of Cr(VI). This is a concern because mixed wood from C&D debris facilities had the highest pH and because many WTE facilities add lime to scrub the exhaust gas, resulting in a very alkaline residual. These factors should be considered when considering the combustion of CCA-treated wood, as well as the combustion of other preserved wood products containing Cr.

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