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OXIDATION OF CHROMIUM IN CCA-C TREATED WOOD UNDER ALKALINE CONDITIONS

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Abstract

Information on oxidation states of chromium from CCA treated wood is of critical importance for the assessment of environmental and health hazards during all life-cycle stages of CCA treated wood, because of differences in toxicity and availability between trivalent and hexavalent chromium compounds. This work presents results of extractions of CCA-C treated aspen and red pine sawdust aimed toward removal of different forms of Cr(VI) from CCA treated wood. Significant oxidation of Cr(III) from CCA treated wood was found to occur under alkaline pH conditions, to the extent determined likely by the rate of dissolution of inert Cr(III) forms. These results imply that extraction protocols using high pH are not appropriate for determination of Cr(VI) in treated wood. Exposures, recycling and waste management options of CCA treated wood should be evaluated to understand the implications of exposure at pH conditions above 8 which are shown to lead to oxidation of water-insoluble Cr(III) to highly toxic and soluble Cr(VI) forms.

1. Introduction

Use of CCA (chromated copper arsenate) wood preservative has been restricted worldwide because of potential health and environmental risks posed by intrinsically toxic arsenic and chromium. However, information on availability and speciation of CCA components during the handling, treatment, service, waste management and recycling of CCA treated wood, remains critically important in evaluating associated environmental and human health hazards.

Chromium speciation is especially important because of the remarkable differences in toxicity and availability between Cr(III) and Cr(VI) compounds. Trivalent chromium is considered an essential human micronutrient (Nieboer and Jusys 1988), whereas Cr(VI) is a skin irritant and human carcinogen, with variable toxicity depending on the species (U.S. EPA 1998). Cr(VI) toxicity to plants and animals has also been reported, and reviewed by Kimbrough *et al*. (1999).

Highly reactive and water soluble Cr(VI) anions, present in the CCA treating solution, are however, readily reduced to Cr(III) forms by organic compounds, under the low pH prevailing in wood during the fixation reactions. In addition to having low toxicity, Cr(III) fixation products are only sparingly soluble in water, and are the least soluble CCA components in treated wood.

The question of whether, and in which forms Cr(VI) remains as a constituent of final fixation products, has been a subject of numerous studies. In early studies on CCA fixation, Dahlgren and Hartford (1972, 1972a) presented a theoretical concept which proposes a number of

intermediate Cr(VI) fixation products, but concluded that fixation proceeds until chromium is completely reduced and precipitated as Cr(III) compounds. Based on a comprehensive study of CCA fixation in wood using model compounds, Pizzi (1980, 1981, 1990) put forward a significantly different proposal, suggesting various Cr(VI) species to be persistent in wood following the fixation. Proposed polymeric Cr(VI) complexes with lignin model compounds were later characterized by Schmalzl *et al.* (1995, 2003), and based on magnetic susceptibility measurements they demonstrated that chromium in these complexes is present in trivalent, and not hexavalent form as anticipated by Pizzi (1980).

Experimental approaches to speciation of Cr in CCA treated wood have been based on solid state spectroscopic techniques, or extractions with Cr(VI) targeting extractants followed by qualitative analysis of extracts. X-Ray Photoelectron Spectroscopy (XPS) studies suggested that Cr(III) is the predominant form of chromium in CCA treated wood (Kaldas *et al*. 1998), although presence of higher oxidation states, in particular Cr(V), was not ruled out (Hughes *et al*. 1992, Yamamoto and Ruddick 1994). Other non-destructive techniques, in particular X-ray Absorption Near Edge Structure (XANES), which detects both Cr(III) and Cr(VI) oxidation states, indicate that chromium is present solely in trivalent form in CCA treated wood (Illman *et al*. 1996, Nico *et al*. 2004).

Indirect methods of quantification and speciation of chromium, involve its extraction from CCA treated wood and subsequent chemical analysis of extracts. Speciation of chromium from CCA treated wood has been traditionally performed following water extraction, under the assumption that any Cr(VI) compounds theoretically present in treated wood, are ultimately water soluble. These studies show that the leaching of Cr(VI) from properly and fully fixed CCA treated wood into water is negligible, since Cr(VI) levels were below 1ppb in leachates containing 200 to 2700 ppb of total Cr (Cooper *et al*. 2004).

The presence of hypothesized water insoluble Cr(VI) forms have been investigated by extractions with more aggressive extractants. Alkaline extraction has been reported as a selective method for extraction of "weak alkali soluble Cr(VI)" from CCA treated wood by Nygren and Nylsson (1993) who used 7% Na_2CO_3 as extractant and reported 22% of Cr(VI) in carbonate extracts. Solo-Gabriele *et al*. (2004) applied alkaline extraction for isolation of Cr(VI) from CCA treated wood and wastes according to EPA Method 3060A (U.S. EPA 1996). This method recommends alkaline digestion using Na_2CO_3 / NaOH at 90-95^oC, for extraction of Cr(VI) from "soluble, adsorbed, and precipitated forms of chromium compounds in soils, sludges, sediments and similar waste materials". Other selective extraction protocols have been well developed and described for various Cr(VI) forms in soil, geological samples and cement matrices (Table 1).

During its life cycle, CCA treated wood might be exposed to environmental conditions that could be very different with regard to pH, presence of other chemical compounds and temperatures, inducing new chemical pathways for transformations of otherwise stable CCA fixation products. Because of pronounced differences in availability and intrinsic toxicity between Cr(VI) and Cr(III), it is important to understand the fate of Cr under various conditions that could prevail in landfills or that could be encountered during the service life, recycling and recuperating of CCA treated wood (Pasek and McIntyre 1993). Some exposures such as use of deck washing solutions are suspected to favor oxidation of Cr(III) to more toxic Cr(VI) (Taylor *et al*. 1999).

Two key issues are addressed in this work regarding the speciation of Cr in CCA treated wood. First, the suitability of extraction techniques for assessment of oxidation states of chromium *in situ* is evaluated, especially those extraction protocols involving alkaline conditions targeting inert Cr(VI) compounds. Second, the possible oxidation of Cr from stable trivalent to toxic and soluble hexavalent form at alkaline conditions is addressed.

In this work we examine and discuss the results of attempts to extract Cr(VI) from unfixed and fixed CCA treated wood with a range of extractants recommended for extraction of Cr(VI) from soils and other solid matrices. Method induced oxidation of Cr(III) in alkaline conditions has been observed and is investigated in the presence of wood, holocellulose and cellulose. In addition, EPA method 3060A (U.S. EPA 1996) for extraction of Cr(VI) from soils, sludges, sediments and similar wastes is evaluated for its applicability for CCA treated wood, since it is the standard method for analysis of a wide range of solid matrices, possibly including CCA treated wood waste.

Table 1. Specific Chromium Extractants

Target species	Extractant	Protocol	Original reference
Soluble Cr^{VI}	H_2O (pH 5.7)	extraction	James *et al.* 1995, Grove and Ellis 1980, Vitale et al. 1997
Exchangable Cr^{VI} / Adsorbed Cr^{VI}	K_2HPO_4/KH_2PO_4 (5mM/5mM, pH7.0)	extraction	James *et al*. 1995, Vitale et al. 1997
Exchangeable Cr^{III}/Cr^{VI}	NH_4Cl, 1*M*	extraction	Grove and Ellis 1980
Total Cr^{VI}	$Na_2CO_3/NaOH$ (0.28M/0.5M pH 12)	cold extraction or digestion at 90-95°C	James *et al*. 1995, Vitale et al. 1997, Solano et al. 1994
	NaOH, 0.1*M* (pH 13)	sonication	James *et al*. 1995, Vitale et al. 1997
	Na_2CO_3, 0.1*M*	digestion	Potgieter and Potgieter 2003
Total Cr^{VI} / Soluble Cr^{III}	$Na_2CO_3/NaOH$ (0.25%/0.40%)	digestion at 70°C	Coedo *et al*. 2000

2. Materials and Methods

2.1 Materials

Wood sawdust was prepared from trembling aspen (*Populus tremuloides* Michx.) and red pine (*Pinus resinosa* Ait.) sapwood, milled in a Wiley mill, and sieved. The fraction passing

25-mesh and retained by 40-mesh screens was collected for the experiments. Holocellulose was isolated from extractive free aspen sawdust (TAPPI Standard T208 om-84) by the "acid chlorite" procedure (Wise *et al.* 1946). Cellulose used in the experiments was ashless Whatman filter paper 541 (Whatman International Ltd.).

2.2 Methods

2.2.1 CCA Treatment:

Sawdust was treated with commercial CCA type C preservative at retention levels of 6.4 (aspen and red pine) and 30.0 kg/m^3 (red pine). Concentrations of CCA treating solutions were adjusted for each retention level as to ensure target preservative retention after mixing solution with sawdust at 2:1 (w/w) ratio. Fixation was conducted under controlled temperature of 30^{o}C and high relative humidity. Concentrations of Cr, Cu and As in treating solutions were verified by Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-AES), according to AWPA Standard A21-93 (AWPA 1996), and the content of hexavalent chromium by spectrophotometry using diphenylcarbazide as color developing reagent (Coggins and Hiscocks 1978).

2.2.2 Extractions of CCA treated sawdust:

The presence of water insoluble Cr(VI) compounds in CCA treated sawdust was investigated by extraction with a number of extractants, reported to be specific for Cr(VI) (Table 1). In addition, some arsenic- and copper-specific extractants were shown to efficiently solubilize chromium, and are therefore included in this work. These extractants include 1M solutions of CH_3COONH_4, NH_4HCO_3, $NaHCO_3$, and NH_4OH.

Extractions with phosphate buffer, which was chosen to target H_2CrO_4 adsorbed or exchanged on wood chemical constituents, were conducted only during early fixation stages when adsorption of H_2CrO_4 is expected to be a prominent intermediate fixation mechanism (Dahlgren and Hartford 1972). Other extractions were applied during different fixation stages in aspen sawdust treated to the retention of 30kg/m^3, and on completely fixed CCA treated aspen (6.4 and 30 kg/m^3) and red pine (6.4 kg/m^3).

Extractions were conducted at different times of fixation reactions between CCA components and the wood, or after their completion (as determined by the absence of water soluble Cr(VI)). Approximately 1-2 g of treated sawdust were extracted with water, or extracting solution on an oscillatory shaker with extractant to solid ratio of about 50:1 (w/w). All extractions were performed on two replicate samples. Water extraction was applied as a first step to remove unfixed Cr(VI) and other poorly stabilized CCA components. The duration and number of extraction steps varied, depending on the extraction efficiencies. Extractions were performed in two stages, the first one being water extraction, and second stage being comprised of one or few consecutive extraction steps with individual extracting solutions. After each extraction step, the sample was filtered and fresh solution was added for the subsequent extraction step. After extractions were complete, samples were transferred to crucibles, filtered, and washed with deionized water. The solid residue was dried at 105 ± 3^{o}C and subjected to acid digestion using peroxide-nitric acid, according to AWPA A7-93 Standard (AWPA 1996). All the extractions were conducted at ambient temperature. Extracts were analyzed for the content of CCA components on ICP-AES, and for Cr(VI) either by spectrophotometry or by Ion Chromatography (IC).

All reagents used for preparation of extractants were analytical grade, and their respective concentrations are given in Table 1.

2.2.3 $CrCl_3$ Treatment and Extraction:

Oxidation of Cr(III) in the presence of wood was investigated by extraction of aspen sawdust treated with $CrCl_3$ solution. Three replicate samples of about 1.0 g sawdust, which was treated with $CrCl_3$ solution (1126 ppm) at 2:1 (w/w) solution to wood ratio, were extracted with 50 ml of 1M NH_4HCO_3; 1M $NaHCO_3$; 1M NH_4OH; or 0.5M NaOH/0.28M Na_2CO_3 for 48 hours. A control experiment was carried in the absence of wood, (1ml of $CrCl_3$ mixed with 20 ml of extractant). The pH of the solution was observed to change considerably after addition of extractant to $CrCl_3$ treated wood. In order to investigate the effect of pH on the level of chromium oxidation, a similar experiment was done using buffer solutions in pH range of 7 to 12.6 as extractants. In this case, $CrCl_3$ solution used for sawdust treatment had Cr concentration of 9323 ppm, which provides Cr content corresponding to CCA treatment of 30 kg/m^3. Buffer solutions used for investigation of the pH effect on the level of oxidation of Cr from $CrCl_3$ were: pH 7 (KH_2PO_4/K_2HPO_4), pH 8.5 (borax/HCl), pH 9.5 (Borax/NaOH), pH 10.5 ($NaHCO_3$/NaOH) (CRC 1973), pH 11.5 (0.1M Na_2CO_3), and pH 12.6 (0.1M NaOH).

In addition, oxidation of Cr(III) in the presence of oxidizing agent was verified by addition of 30% H_2O_2 (4ml) into the mixture of $CrCl_3$ and 0.1M NaOH extractant.

2.2.4 Alkaline digestion (U.S. EPA 1996)

Samples extracted according to Method 3060A (U.S. EPA 1996), were CCA treated aspen sawdust (6.4 and 30 kg/m^3), $CrCl_3$ treated aspen sawdust, aspen holocellulose, cellulose and lignin model compounds. Extracting solution consisted of 0.28 M Na_2CO_3/0.5 M NaOH. The pH was monitored during the use of the solution, and was on the average 13.25. Phosphate buffer was 0.5 M KH_2PO_4/0.5 M K_2HPO_4 (pH 7). $MgCl_2$ additions were made with $MgCl_2 \cdot 6H_2O$ instead of anhydrous $MgCl_2$, in amounts corrected for the hydrate content. Approximately 0.5-1 g of wood sample was placed in 250 Erlenmeyer flasks, and after addition of 50 ml of extracting solution and 0.5 ml of phosphate buffer, covered with 50 ml Erlenmeyer flasks and placed in a water bath at the constant temperature of 93°C. Samples were manually stirred every 3-5 min during the course of digestion. Alkaline digestion was conducted for 1 h from the time that samples reached the temperature of 90-95°C. After digestion, Erlenmeyer flasks were cooled in ice water, filtered through 0.45 μm membrane filter, and analyzed for the Cr(VI) content within one hour by IC, and for total Cr, Cu and As by ICP-AES within one week.

Preliminary determination of Cr content in uniformly treated sawdust, from which samples were taken for alkaline digestion, was performed by acid digestion and ICP-AES analysis. Cr concentrations of $CrCl_3$ solutions were also determined with ICP-AES. Extraction blanks were prepared for $CrCl_3$ in the absence of wood, as well as with wood in the absence of Cr, and analyzed along with other samples. Spike solutions of Cr(VI)/Cr(III) (100 ppm) were prepared from 1000 ppm ICP-AES certified standards (Inorganic Ventures, Inc.).

2.2.3. Instrumentation

ICP-AES analyses were performed on Perkin Elmer Optima 3000 instrument equipped with the conventional nebulizer. Matrix effect was investigated for all extractants, and when observed, standard solutions were prepared to account for matrix effects.

Ion Chromatography Determination of Cr(VI) was performed by IC (Dionex DX-600), equipped with GP 40 Gradient Pump, AD25 absorbance detector, and PC10 Postcolumn Pneumatic Delivery Package, Dionex IonPac AS7 analytical and Dionex IonPac NG1 guard column, according to Method 7199 (U.S. EPA 1996).

Standard solutions for ICP-AES, IC and spectrophotometry were prepared from 1000 ppm Cr(VI), Cr(III), As and Cu standards (Inorganic Ventures, Inc.).

3. Results

The presence of hypothesized intermediate Cr(VI) compounds formed as transition products during the fixation process (Dahlgren and Hartford 1972, 1972a) was investigated by extraction with phosphate buffer (targeting adsorbed H_2CrO_4 and Cr(VI) anions exchanged on wood constituents), and Na_2CO_3 and NaOH (targeting prospective water insoluble chromates). Amounts of Cr(VI) extracted with phosphate buffer (Table 2) are close to those obtained by water, suggesting that no water-insoluble forms of Cr(VI) are available for extraction with more aggressive extractant such as KH_2PO_4 /K_2HPO_4. Extractions with Na_2CO_3 and NaOH yielded higher amounts of Cr(VI) during the one-hour extraction sequence, in comparison to water or phosphate buffer at all chosen times during CCA fixation.

Results on extraction of Cr(VI) species with a range of other selected extractants in completely fixed CCA treated aspen (6.4 kg/m^3) are presented in Table 3 on the basis of total Cr in CCA treated samples, as cumulative values for five consecutive extraction steps lasting 6, 22, 141, 220, and 238 h respectively. Hexavalent chromium was present in three extracts with pH higher then 8, and no detectable Cr(VI) was found in NH_4Cl, NH_4Ac or water extracts. Large cumulative amounts of extracted Cr(VI) ranging from 9.7 to 63.6 %, suggest that these extractants are oxidizing Cr(III) rather then removing low solubility Cr(VI) hypothesized to be present in the wood. NH_4HCO_3 extractant was superior in oxidizing Cr(III) (63.6% of total Cr) at pH 8, in comparison to $NaHCO_3$ or NH_4OH. It is important to note that alkaline extractants were also more successful in extracting total chromium, especially NH_4HCO_3, which extracted around 86% of chromium.

Table 2. Sequential extraction of aspen (CCA retention 30 kg/m^3) with H_2O/H_2O and H_2O/extractant at different stages of CCA fixation.

Fixation time (h)	Extraction step	Extractant	Average Cr(VI) (%)
0	1st	H_2O	**81.4**
	2nd	H_2O	**0.09**
		KH_2PO_4/K_2HPO_4	**0.08**
6	1st	H_2O	**54.5**
	2nd	H_2O	**0.08**
		KH_2PO_4/K_2HPO_4	**0.08**
6	1st	H_2O	**55.0**
	2nd	H_2O	**0.12**
		Na_2CO_3	**0.27**
46	1st	H_2O	**24.7**
	2nd	H_2O	**0.70**
		Na_2CO_3	**1.65**
46	1st	H_2O	**24.1**
	2nd	H_2O	**0.60**
		NaOH	**2.23**

* - Cr(VI) analysis - Spectrophotometry

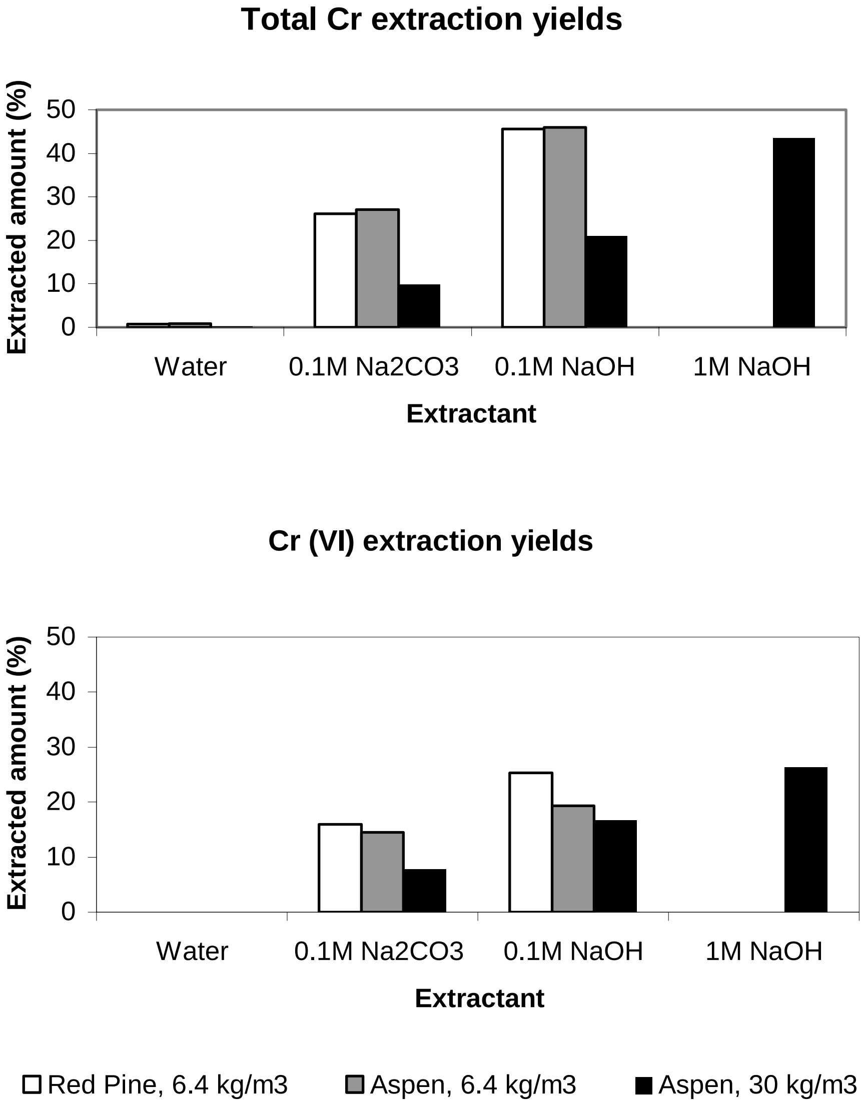
Table 3. Cr (VI)* extraction from CCA treated aspen (6.4 kg/m^3) after completed fixation.

Extraction step	Extractants	pH	Cr(VI) (%)	Cr (%)
1st	H_2O		b.d.l	3.3
2nd-5th	NH_4Cl	4.6	b.d.l	1.9
1st	H_2O		b.d.l	2.7
2nd-5th	CH_3COONH_4	7.1	b.d.l	11.9
1st	H_2O		b.d.l	2.4
2nd-5th	NH_4HCO_3	8.0	63.6	85.7
1st	H_2O		b.d.l	2.8
2nd-5th	$NaHCO_3$	8.7	9.7	23.8
1st	H_2O		b.d.l	2.8
2nd-5th	NH_4OH	11.4	13.7	43.3

* - Cr(VI) analysis – IC
b.d.l. – below analytical detection limit

Extractions of total and hexavalent Cr with water, Na_2CO_3 and NaOH, from CCA treated red pine and aspen for two retention treatments (6.4 and 30 kg/m^3) are presented in Fig. 1 as cumulative values of eight extraction steps lasting approximately 0.50, 6, 23, 22, 26, 48, 66 and 264 h. Extraction yields of total Cr are comparable between aspen and red pine treated to the retention of 6.4 kg/m^3. However, amounts of hexavalent Cr are slightly, but consistently lower in aspen than in red pine extracts. Extraction efficiency follows the order: 1M NaOH > 0.1M NaOH > 0.1M Na_2CO_3, as can be seen from results for aspen treated to 30kg/m^3.

Figure 1. Cumulative extraction yields of total Cr and Cr(VI) from CCA treated red pine (6.4 kg/m^3) and aspen (6.4 and 30 kg/m^3).



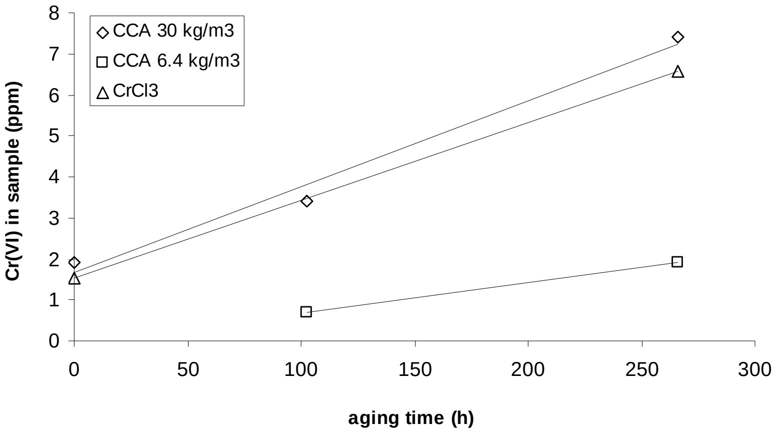
Extraction yields for total and hexavalent chromium according to EPA Method 3060A (U.S. EPA 1996) are presented in Table 4. Following the alkaline digestion of fully fixed CCA treated aspen (30 kg/m^3), 1.4% of Cr was found in hexavalent form. However, $CrCl_3$ treated aspen sawdust, aspen holocellulose and cellulose also yielded considerable amounts of Cr(VI) in alkaline extracts, confirming oxidation of Cr(III) to Cr(VI) during alkaline digestion. Addition of $MgCl_2$, suggested by EPA Method 3060A (U.S. EPA 1996) for prevention of method induced oxidation in soil and like matrices, does decrease the level of Cr(III) oxidation but does not prevent it completely. Our results (Table 4) demonstrated lower overall solubility of chromium in the presence of $MgCl_2$, moreover, it was predominantly in hexavalent form. It has also been shown that oxidation of soluble Cr(III) does proceed in unfiltered samples at room temperature (Figure 2). No Cr(VI) peak was detected by IC in control samples containing extracting solution and $CrCl_3$, or those containing wood and extracting solution. Thus, possible interference in IC analysis or spontaneous Cr(III) oxidation in the absence of wood is ruled out.

Table 4. Extraction of Cr(VI) and total Cr according to EPA Method 3060A.

Sample	Treatment	$MgCl_2$ addition	CrVI* (%)	Cr total (%)
Aspen	CCA 30 kg/m^3	N	1.4	4.0
		Y	0.6	0.5
Aspen	$CrCl_3$	N	3.0	9.3
		Y	0.3	0.2
Holocellulose	$CrCl_3$	N	6.6	n.a.
		Y	0.3	0.3
Cellulose	$CrCl_3$	N	9.6	11.5
		Y	0.7	0.5
Blank	$CrCl_3$	N	b.d.l.	n.a.
		Y	b.d.l.	n.a.

* - Cr(VI) analysis - IC

Figure 2. Cr(VI) monitoring in aged extracts following extraction according to EPA Method 3060A. No $MgCl_2$ was added



* - Cr(VI) analysis - IC

Oxidation of Cr(III) from $CrCl_3$ in presence and absence of wood sawdust was investigated at room temperature for all extractants which extracted detectable Cr(VI) from CCA treated wood, including the solution used by EPA Method 3060A (Table 5). Oxidation of Cr(III) by alkaline extractants was confirmed for all extractants used for extraction of CCA treated aspen (Table 3). The extent of oxidation in CCA treated wood was higher in comparison to $CrCl_3$ treated wood due to longer duration of extraction. With respect to efficiency of individual extractants, oxidation of Cr(III) in $CrCl_3$ treated wood was more pronounced in presence of NH_4OH and less in presence of NH_4HCO_3 in contrast to corresponding CCA treated wood samples. In general, fraction of oxidized Cr (% of Cr(VI) of total soluble Cr) from $CrCl_3$, was found to increase with pH, while oxidation of Cr in CCA treated wood was dependant on the choice of extractant, and may be related to the ability of the extractant to solubilize Cr(III).

Table 5. Cr extraction yields in $CrCl_3$ treated aspen at 23°C. Extraction time 48h. (based on amount in the sample)

Extraction	pH	Cr(VI) (%)	Cr total (%)	Cr(VI) / soluble Cr (%)
0.5M NaOH / 0.28M Na_2CO_3	13.5	7.8	16.1	48.7
1M NH_4OH	11.4	15.2	40.6	37.0
1M $NaHCO_3$	8.7	1.7	12.3	13.4
1M NH_4HCO_3	8.0	1.1	33.9	3.3

* - Cr(VI) analysis – IC

The effect of temperature on the solubility and stability of Cr in wood exposed to conditions of EPA protocol were investigated on aspen sawdust spiked with a mixture of Cr(VI) and Cr(III) (Table 6). Low recoveries of Cr(VI) of 15.2 and 52.5 % in absence and presence of $MgCl_2$ respectively verify the reduction of Cr during alkaline digestion. The extent of reduction was lower in the presence of $MgCl_2$, as previously observed in experiments with CCA treated wood. Cr solubility was profoundly decreased in the presence of $MgCl_2$, to such a extent that all trivalent chromium was rendered insoluble in its presence.

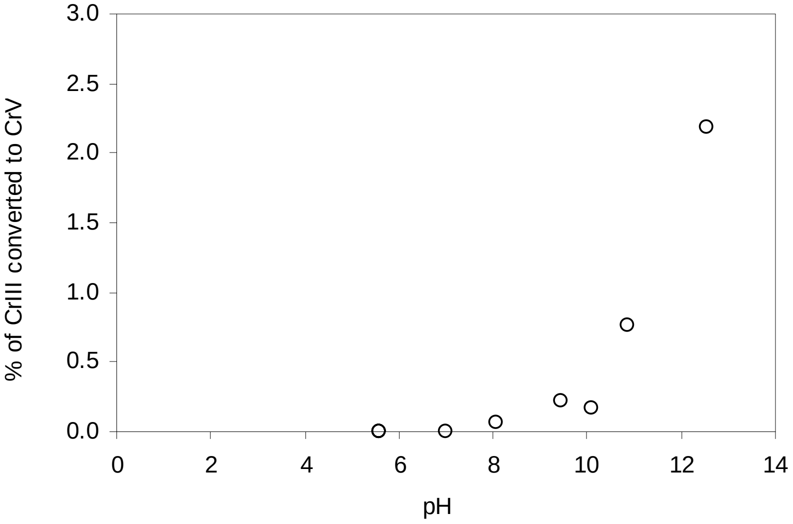
Table 6. Recovery of spike additions of Cr(VI) and Cr(III)

Analyte recovery (%)		$MgCl_2$ addition
Cr(VI)	Cr, total	
15.2	25.5	N
52.5	21.5	Y

* - Cr(VI) analysis - IC

Extractions conducted in buffer solutions indicate that oxidative transformations are pH dependant, and can be observed at pH above 8 (Fig. 3).

Figure 3. Chromium oxidation in $CrCl_3$ treated aspen during extraction with buffer solutions.



4. Discussion

CCA fixation and reduction of chromium in investigated samples, was considered complete prior to extraction, on the basis of absence of Cr(VI) in water extract. Consecutive extractions of fixed sawdust with water or other Cr(VI)-targeting extractants also did not yield any detectable Cr(VI). Analyses of Cr(VI) in completely fixed wood by solid state techniques usually do not give evidence of insoluble Cr(VI) forms (Nico *et al.* 2004). Elevated Cr(VI) extraction yields from the samples extracted with alkaline extractants, as reported here, can therefore most likely be explained by method induced oxidation of Cr(III) during extractions.

Fixation of Cr from CCA in wood is governed by the reduction of Cr(VI) to Cr(III) by wood chemical constituents at low pH, resulting in precipitation of Cr(III) in forms of different stable compounds of low-solubility. On the basis of previous research, oxidation of Cr(III) from these compounds is known to occur only upon the action of strong oxidizing agents such as sodium hypochlorite on CCA sludges (Kazi and Cooper 2002), and hydrogen peroxide on treated sawdust (Kazi and Cooper, 2005) or sodium percarbonate (Taylor *et al.* 1999) on CCA treated wood. These oxidation pathways prevail when treated wood is exposed to acidic conditions. In contrast, under alkaline conditions, the standard reduction potential for the Cr(VI)/Cr(III) redox couple has a negative value (Nieboer and Jusys 1988):

$$(CrO_4)^{2-} + 4H_2O + 3e^- = Cr(OH)^{2+} + 6OH^- \qquad (Eo=-0.13V, pH=14)$$

This indicates that Cr(VI) is the stable form of Cr under alkaline and oxidizing conditions. However, only a few oxidants are known to be capable of oxidizing Cr(III) to Cr(VI), and the oxidation kinetics are very slow. Conversion of labile (including colloidal and dissolved) forms of Cr (III) to Cr(VI) have been reported to occur by strong oxidants such as H_2O_2 at high pH (Vogel 1996) or in the presence of manganese compounds (Bartlett and James 1979, Zhang and Bartlett 1999).

Here we report on spontaneous oxidation of Cr(III), in the presence of wood, under alkaline conditions. Oxidation of Cr(III) is observed at pH 8 and above, in the presence of wood, holocellulose, and cellulose, and was detected in CCA treated samples, as well as in wood samples treated with $CrCl_3$ only. Control experiments show that in the absence of wood, Cr(VI) was not detected in alkaline solutions of $CrCl_3$ even after prolonged reaction times, except at low levels in the EPA protocol. This negligible oxidation was most likely caused by dissolved oxygen, previously reported to occur in the absence of other intermediate species at pH above 9 (Schroeder and Lee 1975). It was therefore concluded that wood chemical constituents act as oxidizing agents or catalysts for oxidation of Cr(III), under alkaline conditions.

Surplus Cr(III) was observed in instances when Cr(VI) was present in alkaline solutions, suggesting that dissolution of Cr(III) is a necessary requirement for oxidation reactions to proceed. Similarly, the extent and rate of chromium oxidation with manganese oxides was shown to be highly dependant on the rate of dissolution of Cr(III) compounds in soil (Bartlett and James, 1979, Fendorf 1995). In CCA treated wood, final chromium fixation products include chromium hydroxide, chromium arsenates and their associations with the wood matrix, according to recent revised proposals (Bull 2001, Nico *et al.* 2004). Cr(III) originating from these fixation products exist as negatively charged $Cr(OH)^{4-}$ and $Cr_2(OH)_2{}^{4-}$ soluble species in the pH range of 8 to 13.5 (Rai *et al.* 1989; Fendorf 1995). Results of our experiments show consistently higher amounts of total soluble Cr in comparison to Cr(VI), indicating that . Although dissolution of Cr(III) compounds might be recognized as a critical step preceding Cr oxidation, no clear relationship between oxidized and soluble fraction could be established based on our data. Fraction of oxidized chromium in the solution (% of Cr(VI) of total soluble Cr) increased proportionally to pH of the extractant when aspen was treated with $CrCl_3$ (Table 5). However, corresponding relationship was not found in extracts of CCA treated wood, and instead ratios of Cr(VI) to Cr(III) varied considerably, which can be explained by comparatively more complex effect of individual extractants on the rate and extent of dissolution of Cr fixation products, combined with different oxidation rates.

The kinetics of oxidation likely depends on the amounts and availability of oxidizing agents from wood. James *et al.* (1995) suggested that oxidation potential of Cr(III) compounds in soil depends on the Cr(III) form, the oxidizing potential of the matrix for Cr(III), its reduction potential for Cr(VI), and pH. The results of our experiments show that Cr(III) is oxidized in the presence of wood, holocellulose and cellulose. Under the same experimental conditions, oxidation was more rapid in the presence of carbohydrates than wood, and more rapid in cellulose than in holocellulose. It indicates an active role of carbohydrates, in particular cellulose, in the mechanism of Cr(III) oxidation. Polysaccharides and lignin undergo complex reactions in alkaline medium, resulting in degradation and dissolution of most hemicelluloses and severe cleavage of linkages in lignin. The composition and reactivity of these degradation products, especially after chemical modification of wood during CCA treatment, and their particular role in oxidation of chromium are not understood. Chemical differenced between wood species, reflected in difference between investigated red pine and aspen seem to have little effect on the extent of chromium oxidation. Initial preservative retention does affect the extent of oxidation, resulting in higher contents of Cr(VI) in the solution and higher Cr(VI) fraction when compared to total dissolved Cr.

Most prominent chromium oxidation pathways in soil include oxidation in the presence of manganese oxides and hydroxides (Bartlett and James, 1979) and photo induced oxidation by free hydroxyl radicals (·OH) in the presence of Fe(II) (Zhang and Bartlett 1999, Zhang 2000). Manganese is intrinsically present in wood *in situ*, probably in Mn(IV) and Mn(III) forms at very low levels. It can be reduced to Mn(II) only under acidic conditions, and thus this mechanism can be eliminated as responsible for Cr(III) oxidation described here. However, Cr oxidation in wood involving free radicals might be a feasible pathway. Zhao *et al.* (1995) showed that oxidation of Cr(III) by free radicals does occur in alkaline medium such as 0.5 M NaOH. Hydroxyl radicals (·OH) are believed to affect Cr redox chemistry even at lower alkalinity such as in surface waters, (Lin 2002). Phenoxy radicals are found in alkaline solutions of lignin (Clare and Steelink 1973) and free radical intermediates are formed in the cellulose by low and high-energy radiation, upon the treatment with alkali and during thermal and enzymatic treatments. However, the actual mechanism of Cr(III) oxidation by wood components cannot be elucidated on the basis of experimental approach and data presented in this work.

Results presented here strongly suggest that determination of Cr(VI) in wood according to EPA Method 3060A for soil and like matrices is not appropriate for determination of Cr(VI) in CCA treated wood samples, because this method does not preserve the Cr oxidation state. Recovery of spike additions of Cr(VI) is at most around 50%, and even lower for CCA treated wood. Method induced oxidation of native Cr(III) has been confirmed to be low but ubiquitous regardless of the source of Cr(III). Addition of $MgCl_2$ to extraction mixture did inhibit oxidation of chromium considerably, although not to an extent that would allow recommendation of this method for determination of Cr(VI) in CCA treated wood. In particular, it decreases the solubility of Cr(III), which is an essential step for Cr(III) oxidation, and in that way does decrease the level of Cr(III) oxidation. In all samples extracted in the presence of $MgCl_2$, amounts of total extractable Cr and Cr(VI) were very similar, with differences within experimental errors, suggesting that all soluble Cr existed in hexavalent state, while all trivalent chromium was precipitated. Solubility of chromium hydroxide is known to decrease in alkali upon boiling the solution (Vogel 1996), in comparison to its solubility at the room temperature. In samples that were left unfiltered, following one hour extraction at 90-95°C, solubility of Cr increased and oxidation of Cr proceeded at the room temperature. A similar observation was made for filtered samples suggesting that wood chemical components that are dissolved prior to filtering and are retained in filtrate do have considerable oxidizing capacity and promote the oxidation. EPA Method 3060A suggest that Cr(VI) should be stable in soil samples for 168 hours following the extraction, which cannot be proposed in this case.

Our results suggest that other protocols employing alkaline conditions for selective extraction of Cr are not suitable due to concomitant Cr oxidation. Nygren and Nilsson (1993) suggested that diluted alkalis are selective extractants for Cr(VI) from CCA treated wood, and that following removal of water soluble Cr(III) and Cr(VI) by water extraction, only alkali-soluble Cr(VI) would be extracted with alkali solutions. Under this assumption, they ascribed all Cr in the solution to hexavalent form, without conducting speciation studies. However, solubility of Cr(III) in alkalis has been shown to be higher than in water, so even if alkaline extraction is applied after water extraction, Cr(III) will be extracted together with any Cr(VI). Only those analytical methods that allow for the speciation of Cr(VI) such as IC can be recommended for speciation of Cr in these extracts

Conclusions

Oxidation of Cr(III) in wood was observed in all investigated extractants that had pH of around 8 and above, which indicates an important route for the conversion of chromium from inert form to mobile and highly toxic Cr(VI). In the light of significant hazards posed by Cr(VI), exposures and recycling options for CCA treated wood involving high pH, such as use of alkaline deck washing solutions, cement-wood composites, or high pH leaching media, should be carefully evaluated with regard to possible Cr(III) oxidation.

The extraction with alkaline extractants does not preserve the oxidation state of Cr and therefore cannot be recommended as a valid approach for qualitative and quantitative investigation of insoluble forms of Cr(VI). In particular, EPA Method 3060A (US EPA 1996) does not meet criteria for determination of Cr(VI) in CCA treated wood. No recommendations for modification of alkaline extractions to avoid method induced Cr(III) oxidation can be made before this oxidation mechanism is fully understood.

Nondestructive techniques such as XANES and magnetic susceptibility are considered more appropriate methods for Cr speciation than extractions, particularly for assessment of Cr(VI) in CCA treated wood.

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