

Characteristics of chromated copper arsenate-treated wood ash

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Abstract

The combustion of recovered wood from construction and demolition waste as biomass fuel is a common practice. When chromated copper arsenate (CCA)-treated wood is present as part of the wood fuel mix, concentrations of arsenic, chromium, and copper become elevated in the ash. The objectives of this study were to estimate the fraction of CCA-treated wood needed to cause the ash to fail regulatory guidelines and to test a series of solvents for the purpose of extracting the metals from the ash. Ash samples were prepared in an industrial furnace using samples of CCA-treated wood, mixtures of CCA-treated wood and untreated wood, and recycled wood waste collected at construction and demolition recycling facilities. Regulatory guidelines were evaluated by measuring total metals concentrations (using neutron activation analysis) and by conducting standardized leaching tests (toxicity characteristic leaching procedure (TCLP) and synthetic precipitation leaching procedure (SPLP)) on the ash. Ten different solvents, ranging from distilled water to strong acids, were also tested for their ability to extract metals. Results of this study indicate that metal concentrations (chromium plus copper plus arsenic) can be as high as 36% of the ash by weight for treated wood samples containing high retention levels (40 kg/m^3) of CCA. All ash samples from the combustion of 100% CCA-treated wood and mixtures containing 5% CCA-treated wood leached enough arsenic (and sometimes chromium) to be characterized as a hazardous waste under US regulations. Concentrated nitric acid, which was the most effective solvent tested, was capable of removing between 70 and 100% of the copper, between 20 and 60% of the chromium, and 60 and 100% of the arsenic for samples characterized by low retention levels. A particular finding of interest was the efficiency of distilled water and other weak solvents to extract measurable amounts of chromium, especially for ash samples containing low retention levels of CCA. Citric acid was

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particularly effective at removing arsenic (between 40 and 100%) for ash samples produced from wood containing low CCA retention levels. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

The combustion of wood waste has the benefits of producing energy within a cogeneration plant, reducing the waste volume, and the production of ash with beneficial properties for agricultural purposes [1–3]. The quality of the ash is compromised, however, when the wood fuel contains treated wood, in particular wood treated with chromated copper arsenate (CCA) [4–8]. One potential source of CCA-treated wood within biomass fuel is from treated wood products entering through the construction and demolition (C&D) debris wood stream [9–11].

The presence of CCA-treated wood in biomass fuel has been recognized to increase the concentrations of arsenic, copper, and chromium in the ash, often to the point that it may no longer be land applied and may possibly have to be managed as a hazardous waste [12]. This issue is likely to be magnified in the near future because of two factors. First, the mass of C&D debris generated is growing and this waste stream is increasingly being recycled. The US Environmental Protection Agency (EPA) [13] estimates that 123 million tonnes of building-related C&D debris were generated in the US in 1996. McKeever [14] estimates that 29 million tonnes of wood entered the waste stream in 1996 from C&D debris. Second, the amount of CCA-treated wood being disposed, largely through C&D debris, is expected to increase dramatically in the near future. It has been estimated that the amount of CCA-treated wood disposed in Florida, USA, will quadruple by 2006 from the estimated 3.7 million ft³ that were disposed statewide in 1996 [15].

The presence of large amounts of CCA-treated wood in C&D debris wood recycled as fuel creates concern from several perspectives. Experience indicates that much of the CCA-treated wood is indistinguishable from the untreated wood, and separation is extremely difficult. In the short term, it appears that facilities experiencing CCA contamination within their recycled wood stream will continue to generate contaminated wood. One option for addressing this issue would be to burn recycled wood waste from C&D operations as long as the contamination does not result in a hazardous material as defined by regulatory criteria. An alternative would be to treat the ash by removing the metals.

To address these alternatives, research was conducted to characterize ash from the combustion of CCA-treated wood and wood mixtures containing CCA-treated wood. The characteristics of the ash were examined with respect to required regulatory criteria and to evaluate a series of solvents for the removal of the metals from the ash. Although a considerable amount of research has been conducted evaluating characteristics and leaching of unburned CCA-treated wood [16,17], limited information is available concerning the characteristics of the ash produced from burning CCA-treated wood. This paper is intended

to provide information that would be useful in developing ash disposal strategies for wood fuel systems that may experience contamination from CCA-treated wood.

2. Background

Various formulations of CCA-treated wood have been developed, incorporating different concentrations of chromium, copper, and arsenic. The American Wood Preservers' Association (AWPA) [18] has designated these formulations as CCA Types A–C. The most widely used of the three is CCA Type C, containing 47.5% chromium as CrO_3 , 18.5% copper as CuO , and 34.0% arsenic as As_2O_5 . Another difference in the types of CCA-treated wood products is their retention value, or mass of CCA chemical used to treat a volume of wood (kg CCA/m^3 wood). Retention values range from 4 to 40 kg/m^3 . Lower retention values are suitable for aboveground applications but higher retention levels are necessary for wood foundations, structural poles, piling foundations, and immersion in saltwater.

Regulatory requirements for the disposal of wastes differ somewhat depending on the country, but in general solid wastes such as ash must be tested to determine whether they display toxic or hazardous properties sufficient to require special management. In the US the first determination that must be made is whether the ash is hazardous by establishing its toxicity characteristic (TC) which is assessed using the toxicity characteristic leaching procedure (TCLP) [19]. The TCLP involves leaching the ash in a leaching fluid that simulates a domestic waste landfill, and analyzing the leachate for designated constituents. If the leachate concentration of a designated constituent is greater than the TC concentration, the waste is hazardous by the TC. Arsenic and chromium are both designated TC constituents with regulatory limits of 5 mg/l each. Copper is not a designated TC constituent.

Wastes that are not hazardous, but contain toxic constituents must still be managed properly. Disposal in a lined sanitary landfill is an available option for most non-hazardous solid wastes, but other options include disposal in unlined landfills and land application. For example, in the case of ash from the combustion of wood, land application as a soil amendment is commonly practiced. The determination of appropriate management options for non-hazardous solid wastes is less well defined, but a risk assessment approach is typically employed. A site-specific risk assessment may be conducted, but more commonly, leaching tests are performed and the results are compared to default risk-based target levels. For conditions where direct exposure of a heavy metal is of concern (e.g. disposal through land application), an aggressive acid digestion is used to leach the heavy metals into solution or a total metals analysis is conducted. The resulting concentration of the metal is compared to appropriate direct exposure target concentrations. For Florida, for example, there are two regulatory target levels, one for residential areas and another for industrial areas. Arsenic has the strictest criteria with target levels of 0.8 mg/kg for residential areas and 3.7 mg/kg for industrial areas. For conditions where leaching to groundwater is a concern (e.g. disposal in an unlined landfill or through land application), a common practice is to perform the synthetic precipitation leaching procedure (SPLP) [20] and to compare SPLP leachate concentrations to appropriate groundwater cleanup target levels (GWCTLs). The SPLP is similar in nature to the TCLP, but a simulated rainfall is used as the leaching fluid. The GWCTLs for Florida, for example, are 0.05 mg/l for arsenic, 0.1 mg/l for chromium, and 1 mg/l for copper.

3. Objectives

During this study, CCA-treated wood ash was analyzed for total metals concentrations and was subjected to a set of leaching tests. The primary objectives of these experiments were to estimate the fraction of CCA-treated in a mixture of CCA-treated wood and untreated wood that would cause the ash to fail regulatory guidelines for land application, disposal within an unlined landfill, or criteria for classification as a hazardous waste. Additional leaching tests were conducted with a series of solvents for the purpose of extracting the metals from the ash.

4. Methods

Sample preparation included collection, processing, and incineration of the wood samples. Appropriate laboratory analysis followed for the purpose of determining total metals concentrations and leaching characteristics of the ash.

4.1. Sample preparation

A total of 10 batches of wood at 54 kg each were processed for experimentation (Fig. 1). Seven of these 10 batches were controls of known composition (batches 1–5, 9 and 10). These batches consisted of untreated southern yellow pine (batch 1), treated wood at 4, 9.6 and 40 kg/m³ retention levels (batches 2–4), weathered wood (batch 5), and two mixtures designed to mimic C&D waste wood (batches 9 and 10). Both sets of mixtures consisted of 5% CCA-treated wood (4 kg/m³ retention level) mixed with 95% untreated southern yellow pine. The remaining three batches (6–8) were collected from C&D recycling facilities.

The control samples (batches 1–5, 9 and 10) were purchased as 3.8 cm × 8.9 cm × 3 m lumber from a local retail outlet. The weathered wood sample (batch 5) consisted of two 18-year-old utility poles. Slices were cut from the top, center, and butt-end of the poles to obtain a representative sample. Batches 6–8 were composite grab samples of chipped wood from three different C&D facilities located within Florida, USA. All control samples were shredded utilizing an industrial shredder.

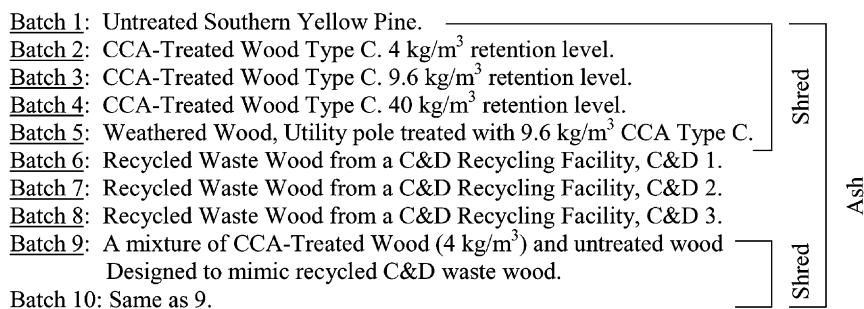


Fig. 1. Samples processed for experimentation.

Samples were incinerated using an industrial furnace (Al-Jon/United Inc.). The dimensions of the furnace were roughly 3.3 m × 3.3 m × 2.5 m. Grates and catch pans were specially constructed for this experiment to capture the ash. Prior to the incineration process, the industrial furnace was broomed clean. In order to minimize carryover of the CCA chemical, the samples considered to contain the least amount of CCA were incinerated first followed by samples that contained progressively higher amounts of CCA. The samples were incinerated for approximately 1.5 h at a temperature that varied between 650°C at the beginning of the burn to 425°C toward the end of the burn. Following incineration, the ash sample (approximately 1 kg) was collected from the catch pan. Between samples the grate and catch pan were rinsed with water.

4.2. Laboratory analysis

Laboratory analysis included measurements for the total amount of metal within each sample as well as measurements of the extractable fractions. Two series of experiments were conducted to determine the extractable fractions. The first set focused on standard leaching tests (TCLP and SPLP) used for regulating the disposal of solid wastes. The second set focused on evaluating different solvents for their ability to extract the metals from the ash. The solvents chosen included (a) those found to remove metals from unburned wood, such as citric acid and a combination of sodium hydroxide and citric acid [21–23], and (b) those typically used in sequential extraction procedures for soils, such as distilled water, magnesium chloride, hydrogen peroxide, hydroxylamine hydrochloride, acetic acid, nitric acid, and hydrochloric acid [24–26]. A total recoverable metals analysis which consisted of a sequence of strong acid and hydrogen peroxide additions was also performed as per US EPA guidelines [20].

4.2.1. Total metals analyses

Total metals analyses were conducted on the ash samples and on the unburned wood samples. Total metals concentrations of the ash were needed to evaluate allowable disposal methods for the ash given regulatory criteria and to estimate the percentage of metals extracted using different solvents. The purpose of analyzing the unburned wood samples was to confirm that the wood controls used in this study (untreated, 4, 9.6, 40 kg/m³, and weathered wood) were in fact treated to their rated level.

Two sets of ash samples were analyzed for total metals concentrations using neutron activation analysis. One set was analyzed by the University of Florida's Nuclear Reactor Facility located in Gainesville, FL. The second set was analyzed by the Massachusetts Institute of Technology's Nuclear Reactor Facility located in Cambridge, MA. The retention levels of the unburned wood samples were measured in quintuplicate through two different laboratories (Langdale Forest Products, Valdosta, GA and Hickson Corp., Conley, GA) using ASOMA X-ray spectrometers (Models 111 and 200).

4.2.2. TCLP and SPLP

Ash collected contained a mixture of fine powdery material that averaged less than 2 mm in diameter and larger black cinders that averaged in size from 5 to 10 mm in diameter. Given this variability, each sample was separated into a large (>4.75 mm) and small

(<4.75 mm) fraction. Sample sizes were generally 100 g. In the few cases where insufficient quantities of ash were available smaller samples were used and the leaching fluid was adjusted accordingly to provide the recommended 20:1 liquid:solid ratio (by mass), as described by standard US leaching protocols [20]. Results for each size fraction for a given sample were weighted and combined to report the concentration from that sample as a whole.

TCLP analysis followed standard US regulatory protocols (Method 1311 in [20]). The TCLP's extraction fluid consists of an acetic acid buffer system designed to simulate the environment in a municipal waste landfill that results from anaerobic decomposition of organic wastes. The TCLP prescribes that one of two fluids be used, depending on the initial alkalinity of the waste. Both extraction fluids contain the same amount of acetic acid, but one fluid also contains sodium hydroxide. The pH of fluid one is 4.93 and the pH of the second fluid is 2.88. Each sample was thoroughly mixed with the appropriate fluid on a rotary extractor for 18 ± 2 h. After rotation, the sample was pressure filtered, the pH was measured, and concentrated nitric acid was added as a preservative. Next a liquid acid digestion was conducted according to Method 3010A [20] for Cr and Cu analysis and Method 3020A [20] for As analysis. A Perkin-Elmer atomic absorption spectrophotometer (Model 5100) equipped with a flame atomizer was used for the analysis of chromium and copper. Arsenic was also analyzed on the Perkin-Elmer 5100 but sample atomization was accomplished with a graphite furnace (HGA 600). The SPLP test (Method 1312 in [20]) is essentially the same as the TCLP test, with the exception that a different extraction fluid was used. The extraction fluid is a poorly buffered acidic solution of sulfuric and nitric acids (pH = 4.20) that simulates the characteristics of rainfall. The results are determined in units of mg of metal (As, Cu, or Cr) per liter of leachate. Analyses were conducted in duplicate. Greater than 90% recovery was obtained from matrix spike analysis [27].

4.2.3. *Solvent extraction study*

A total of 10 extractions (Table 1) were conducted for eight ash samples (batches 1–8). The first two extractions, distilled water (DW) and magnesium chloride (MC), were designed to determine the water soluble and ion-exchangeable fractions of the metals in the ash samples, respectively. The next two solvents, hydrogen peroxide (Pero) and hydroxylamine hydrochloride (HH) are strong oxidants and reductants, respectively. The remaining six extractions (SHC, Acetic, Citric, HCl, Nitric, TRM) utilized either weak or strong acids to remove the metals from the ash. The last of these six extractions was a total recoverable metals (TRM) test which employed a combination of concentrated acids and hydrogen peroxide to extract metals. An amount between 1 and 2 g of ash were used for each extraction. After extraction, the leachates were analyzed for chromium and copper on an atomic absorption spectrophotometer fitted with a flame atomizer (Perkin-Elmer 372). Arsenic was analyzed using a colorimetric method (Method 3500C in [28]). Analyses were conducted in triplicate. Reproducibility of the metal's results for a given leachate were excellent with replicates within 5% of one another. More variability ($\pm 25\%$) was observed between different sub-samples which originated from the same batch. This variability was attributed primarily to sample heterogeneity within a given batch. Results from sample spike analysis indicate sample recoveries greater than 70%. All results are provided in terms of milligram

Table 1
Summary of solvent extraction procedures

Extraction procedure	Description ^a	Reference
Distilled water (DW)	Add 10 ml of distilled water, soak for 1 h. Shake for 20 min in shaker.	[25]
Magnesium chloride (MC)	Add 10 ml of 1 M MgCl ₂ (pH 7.0), shake and wait for 1 h. Then add 10 ml of 1 M ammonium acetate.	[24]
Hydrogen peroxide (Pero)	Add 4 ml of 30% H ₂ O ₂ . Heat to 60°C until the initial reaction has ceased. Add some more H ₂ O ₂ in 0.5 ml lots until the initial reaction has ceased.	[25]
Hydroxylamine hydrochloride (HH)	Add 10 ml of a 1 M hydroxylamine hydrochloride/1 M ammonium acetate solution. Shake for 20 min. Repeat twice.	[25]
Sodium hydroxide plus citric acid (SHC)	Prepare a solution with 1 g NaOH and 1.50 g citric acid in 1 l of distilled water. Add 50 ml of the leaching solution to the ash. Shake for 10 min and leave overnight.	[22]
Acetic acid (Acetic)	Soak ash in 60 ml concentrated glacial acetic acid. Shake for 30 min and soak the sample for an additional 24 h.	[23]
Citric acid (Citric)	Soak ash in 60 ml of 1 M citric acid. Shake for 30 min and soak the sample for an additional 24 h.	[23]
Hydrochloric acid (HCl)	Soak ash in 60 ml of concentrated hydrochloric acid. Shake for 30 min and soak the sample for an additional 24 h.	[26]
Nitric acid (Nitric)	Soak ash in 60 ml of concentrated nitric acid. Shake for 30 min and soak the sample for an additional 24 h.	[23]
Total recoverable metals, EPA Method 3050B (TRM)	Soak ash in 10 ml of 1:1 HNO ₃ and heat to 95°C for 10–15 min. Allow sample to cool, add 5 ml of conc. HNO ₃ , and reflux for 30 min. Repeat previous step until no brown fumes are given off, heat sample to 95°C for 2 h and then cool the sample. Add 3 ml of 30% H ₂ O ₂ and heat for 2 h then cool the sample. Add 10 ml of conc. HCl and reflux for 15 min.	[20]

^a The description corresponds to the point after 1–2 g of ash was transferred to a 125 ml beaker. At the end of the extraction all samples were filtered and brought to a 100 ml volume with deionized distilled water.

of metal extracted per kilogram of ash, as a percent of the total amount of metal present in the sample, or as milligram per liter within the leachates produced.

5. Results

Results are presented for total metals analysis, TCLP and SPLP tests, and the solvent extraction study.

5.1. Results from total metals analyses

Results from neutron activation analysis (Table 2) indicate that metal concentrations of the untreated wood ash samples were on the order of a 100 mg/kg for each metal. Metal concentrations for the ash prepared from C&D wood were on the order of 1000–4000 mg/kg for each metal. For the 4, 9.6 kg/m³, and weathered wood samples, Cr, Cu, and As concentrations were on the order of tens of thousands of mg/kg, whereas for the 40 kg/m³ wood ash sample, concentrations were on the order of hundreds of thousands of mg/kg. For the 40 kg/m³ sample, data show that the metals, Cr, Cu, and As, account for 36% of the ash by weight.

The measured values of the unburned wood samples were between 30 and 50% higher than their rated value. The measured values of the untreated, 4, 9.6, 40 kg/m³, and weathered wood samples were <0.3, 4.8, 13.1, 48.7, and 12.7 kg/m³, respectively, with a standard deviation less than 6% of the measured values.

5.2. Results from TCLP and SPLP analysis

Results (Table 3 and Fig. 2) show that the TCLP and SPLP leachate concentrations for arsenic and copper generally increased for samples characterized by higher retention

Table 2
Total metals concentrations of ash samples

Sample description	Average metals concentration from neutron activation analysis (mg/kg)		
	Cr	Cu	As
Untreated wood ash	106 (22) ^a	330 (192)	31 (7)
Ash from wood treated at 4 kg/m ³	21300 (7700)	10520 (3800)	11080 (3100)
Ash from wood treated at 9.6 kg/m ³	49150 (19100)	32950 (11900)	37950 (20500)
Ash from wood treated at 40 kg/m ³	165000 (3000)	98450 (4500)	99300 (5700)
Ash from weathered wood	52250 (13000)	39250 (15600)	30550 (12100)
Ash from recycled wood waste, C&D 1	1100	1400	730
Ash from recycled wood waste, C&D 2	1860	2090	1310
Ash from recycled wood waste, C&D 3	3530	1900	2250
Ash from laboratory mixture of untreated wood (95%) and CCA-treated wood at 4 kg/m ³ (5%)	–	–	–

^a Standard deviation of the analysis between the University of Florida and Massachusetts Institute of Technology reactor given in parenthesis.

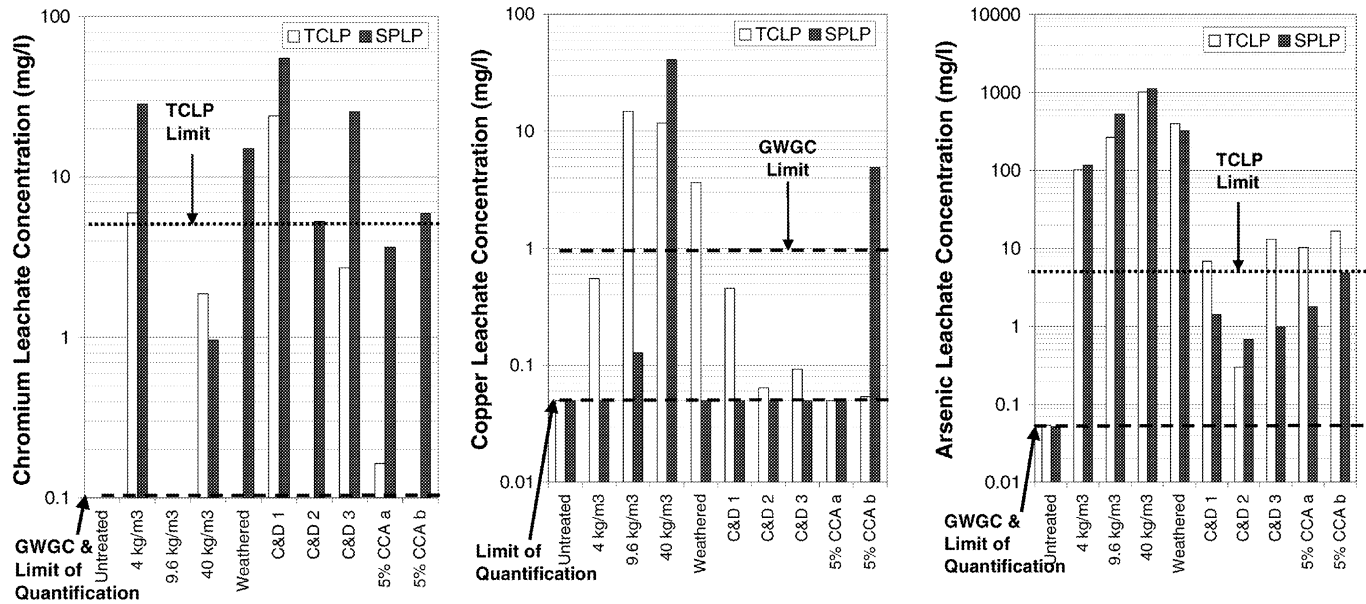


Fig. 2. TCLP and SPLP results for chromium, copper, and arsenic.

Table 3
Summary of TCLP and SPLP results conducted on CCA-treated wood ash^a

Sample ID	Arsenic concentration (mg/l)		Chromium concentration (mg/l)		Copper concentration (mg/l)	
	TCLP	SPLP	TCLP	SPLP	TCLP	SPLP
Untreated	<0.05	<0.05	<0.1	<0.1	<0.05	<0.05
4 kg/m ³	50.7	58.6	5.98	28.6	0.55	<0.05
9.6 kg/m ³	133	265	<0.1	<0.1	14.8	0.13
40 kg/m ³	511	561	1.88	0.96	11.8	40.8
Weathered	199	162	<0.1	15.0	3.63	<0.05
C&D 1	3.46	0.79	24.1	55.0	0.45	<0.05
C&D 2	0.21	0.29	<0.1	5.29	0.064	<0.05
C&D 3	6.74	0.54	2.72	25.5	0.093	<0.05
5% CCA	5.16	1.09	0.16	3.66	<0.05	<0.05
	8.39	2.42	<0.1	5.92	0.054	<0.05
Regulatory limit ^b	5.0	0.05	5.0	0.10	NA	1.0

^a NA: not available.

^b TCLP limits from 40CFR 261.24, Florida GWGC criteria from FAC 62-777 and GWGC criteria listed under SPLP column.

levels. The leachable concentration for these metals was greatest in the CCA-treated wood samples with the highest standard retention values (9.6 and 40 kg/m³). The samples from the C&D recycling facilities and the premixed wood displayed measurable, but lower values. The results for chromium were more variable. The greatest concentrations of leachable chromium were observed in the 4 kg/m³ and C&D samples, while the 40 kg/m³ sample had much smaller concentrations of chromium in the leachate. These results, although not as anticipated, were consistent with the results of the solvent extraction portion of this study (Section 5.3) for the acetic acid extraction, an entirely independent analysis (see Table 5). The consistency between the two independent methods supports the validity of the results which indicate that chromium in the ash produced from samples containing lower CCA retention levels is apparently more mobile using an acetic acid solution. This difference in mobility is potentially due to differences in the pH of the ash samples and the presence of different chromium species. Hexavalent chromium is typically much more mobile in the environment than trivalent chromium, it thus appears that the incineration conditions in certain test runs (e.g. the 4 kg/m³) resulted in the conversion of the Cr(III) present in the wood to Cr(VI), while incineration conditions in other test runs (e.g. the 40 kg/m³) did not. It should be noted that only the concentrations of total chromium, and not Cr(VI) or Cr(III), were measured. The species of chromium occurring in similar test conditions warrants further study.

In comparing the results of the TCLP and SPLP tests on the ash samples, it is observed that there is no substantial difference in the arsenic concentrations. In fact, only one sample displayed a difference of arsenic concentration of more than one order of magnitude. The similarity in leaching of arsenic between the TCLP and SPLP tests can likely be attributed to a similarity in the solubility of arsenic over the pH range encountered in these tests. The concentration of copper was substantially higher in the TCLP leachate than in the SPLP leachate for the 4, 9.6 kg/m³, and weathered wood sample. The TCLP test was slightly more

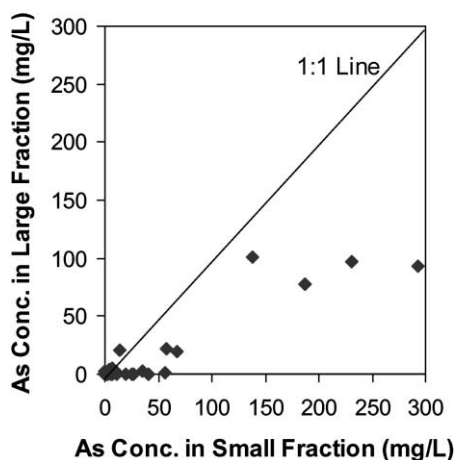


Fig. 3. TCLP and SPLP arsenic concentration for small and large fraction of ash.

aggressive for the C&D samples. It is of interest to note that the 40 kg/m³ sample displayed higher concentrations in the SPLP leachate than in the TCLP leachate. But this was the only sample that exhibited a lower final pH for the SPLP solution than for the TCLP solution and this difference is likely due to the lower pH values associated with that particular sample. The SPLP leachates displayed greater concentrations of chromium in the majority of the samples. The primary exception corresponded to the 40 kg/m³ sample. Whereas this sample leached more copper with the SPLP solution, the TCLP solution was more aggressive at leaching chromium.

Leachability of the samples was also a function of particle size. It was found that the majority of the mass was associated with the fine ash, and thus this fraction would control the average properties of an ash sample. In the case of arsenic (Fig. 3) more arsenic was leached per unit mass from the finer ash relative to the larger ash particles as can be observed by the majority of the points falling significantly below the 1-to-1 line. For chromium, the same trend was observed. The opposite relationship was observed for a few of the copper data points where more copper was leached from the larger particles relative to the small particles.

5.3. Results from the solvent extraction study

A summary of the results in tabular format are provided in Tables 4 and 5. Figs. 4 and 5 are representative of the results from this portion of the study.

5.3.1. Chromium

Chromium was characterized by two fractions. One fraction was readily leached by weak solvents and another fraction that could not be leached. Overall, less than 65% of the chromium could be extracted. In general, the percent removal was generally less for the samples containing more CCA chemical (e.g. Table 4). In other words, the smallest percent

Table 4
Percentage of copper, chromium, and arsenic removals for various solvents^a

Sample ID	Total concentration (mg/kg)	Solvent									
		DW	MC	Pero	HH	SHC	Acetic	Citric	HCl	Nitric	TRM
Chromium removal (%)											
Untreated	106	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
4 kg/m ³	21300	7.5	4.6	0.2	2.9	1.6	4.7	5.7	14	23	24
9.6 kg/m ³	4920	BD	BD	BD	0.1	1.6	0.6	2.0	15	18	30
40 kg/m ³	165000	BD	BD	BD	BD	2.2	0.3	0.5	5.1	7.2	32
Weathered	52300	BD	BD	BD	0.1	1.3	BD	1.9	13	15	28
C&D 1	1100	2.5	0.9	0.4	0.9	8.3	1.5	BD	11	1.2	11
C&D 2	1860	30	16	29	15	41	8.5	41	39	56	15
C&D 3	3530	52	29	48	26	55	10	55	53	63	17
Copper removal (%)											
Untreated	330	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
4 kg/m ³	10500	0.1	0.9	0.6	4.6	3.9	9.5	21	57	71	62
9.6 kg/m ³	33000	BD	1.8	1.7	9.9	5.5	5.8	21	57	75	60
40 kg/m ³	98500	0.2	0.7	1.2	5.0	3.0	3.7	16	27	48	49
Weathered	39300	BD	0.9	1.1	4.5	3.2	2.9	16	46	56	50
C&D 1	1400	BD	0.5	0.3	BD	2.8	0.6	18	47	26	27
C&D 2	2090	0.5	3.0	1.6	2.2	13	16	27	63	107	56
C&D 3	1900	BD	2.3	4.5	1.8	13	16	25	54	84	61
Arsenic removal (%)											
Untreated	31	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
4 kg/m ³	11100	4.1	6.4	9.8	67	8.4	20	42	41	90	52
9.6 kg/m ³	38000	5.9	5.2	5.4	24	6.0	7.8	22	73	46	8.4
40 kg/m ³	99300	17	7.5	4.8	7.9	8.8	1.2	18	16	31	38
Weathered	30600	12	5.4	14	29	15	8.7	60	51	115	110
C&D 1	730	1.3	7.2	13	23	16	3.2	54	6.6	108	33
C&D 2	1310	1.4	15	19	31	11	3.1	102	70	125	116
C&D 3	2250	0.5	5.2	6.6	15	2.0	1.6	69	31	59	91

^a NA: not available; BD: below detection.

Table 5
Chromium, copper, and arsenic leachate concentrations for various solvents

Sample ID	Solvent									
	DW	MC	Pero	HH	SHC	Acetic	Citric	HCl	Nitric	TRM
Chromium leachate concentration (mg/l)										
Untreated	BD ^a	BD	BD	BD	BD	BD	BD	BD	BD	BD
4 kg/m ³	32	9.8	0.8	6.0	7.0	20	25	59	98	58
9.6 kg/m ³	BD	BD	0.2	0.3	16	5.8	20	151	179	172
40 kg/m ³	BD	0.2	BD	0.2	71	10	15	169	234	608
Weathered	0.4	BD	0.2	0.3	14	BD	BD	136	155	170
C&D 1	2.4	0.4	0.4	0.4	8.0	1.5	20	10	1.2	5.4
C&D 2	12	3.2	11	2.8	16	3.3	16	15	22	8.2
C&D 3	19	5.3	18	4.8	21	3.9	21	20	23	11
Copper leachate concentration (mg/l)										
Untreated	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD
4 kg/m ³	0.1	1.0	1.4	6.8	8.3	20	45	121	149	73
9.6 kg/m ³	0.2	5.9	11	43	36	38	135	379	496	227
40 kg/m ³	3.0	6.8	24	49	59	73	314	538	943	594
Weathered	0.2	3.5	8.6	21	25	23	9.3	362	441	240
C&D 1	BD	0.1	0.2	BD	1.4	0.3	125	24	14	7.6
C&D 2	0.1	0.4	0.4	0.3	3.1	3.8	6.6	15	26	8.8
C&D 3	BD	0.3	1.1	0.2	3.1	4.0	6.1	13	21	9.7
Arsenic leachate concentration (mg/l)										
Untreated	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD
4 kg/m ³	9.2	7.1	22	75	19	45	97	91	199	132
9.6 kg/m ³	45	20	41	92	46	59	170	553	349	64
40 kg/m ³	331	75	96	79	176	23	349	313	605	746
Weathered	75	17	86	88	92	53	373	313	704	674
C&D 1	0.2	0.5	1.9	1.7	2.3	0.5	8.0	1.0	16	4.8
C&D 2	0.4	2.0	4.8	4.0	2.8	0.8	27	18	33	30
C&D 3	0.2	1.2	3.0	3.3	0.9	0.7	31	14	27	41

^a NA: not available; BD: below detection (0.1 mg/l).

removals were generally obtained for the 40 kg/m³ sample, followed by the 9.6 kg/m³ and weathered wood samples, which were then followed by the 4 kg/m³ sample. The greatest percent removals were obtained from the C&D 2 and C&D 3 samples. Solvents utilized on the C&D 2 sample, for example, extracted between 8 and 60% of the chromium (Table 4). Of interest is the finding that even weak solvents, such as distilled water, were capable of extracting significant quantities of chromium. For the C&D 2 sample, 30% of the chromium was extracted by distilled water, whereas for the C&D 3 sample 52% was extracted. A significant fraction of chromium (7.5%) was also removed from the 4 kg/m³ sample using distilled water. A peculiar observation is associated with the mass of chromium removed by the weaker solvents. For samples characterized by high retention levels, quantities of chromium (in mg/l) were below detection limits, whereas for samples containing lower retention levels (C&D 2, and 4 kg/m³) weaker solvents were capable of removing several milligrams of chromium per liter of solvent (Table 5). Only the very strong acids (such as nitric acid) were capable of extracting several hundred mg/l of chromium from samples

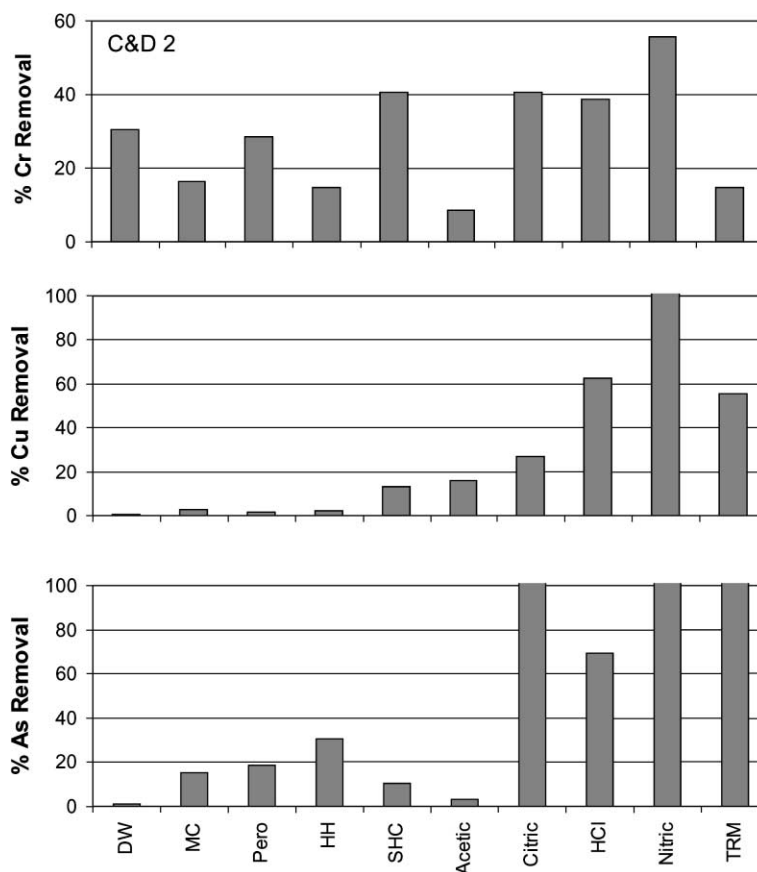


Fig. 4. Percentage of Cr, Cu, and As removals for each solvent for the field sample C&D 2.

characterized by high retention levels (Fig. 5). The reason for these trends are not entirely understood. One possible hypothesis that can explain these trends is the formation of different chromium species within the combustion process. Cr(VI) is generally more mobile than Cr(III). Cr(VI) is generally found in more alkaline environments. It is possible for a larger proportion of the chromium to exist in the +6 valence for lower retention levels. Samples containing less CCA chemical produce more wood ash relative to the amount of chemical present. Wood ash is generally alkaline. If a higher proportion of wood ash is present in the sample then that sample would be characterized by a higher pH. If more Cr(VI) is present at higher pH levels then higher percent removals would be expected for samples of lower retention values as observed in the data. The larger mass (mg/l) of chromium removed with strong acids for samples characterized by high retention levels is likely due to the mobilization of some Cr(III). The observed trends, nevertheless, are consistent with the results from the TCLP and SPLP tests described in Section 5.2 which found that leachate con-

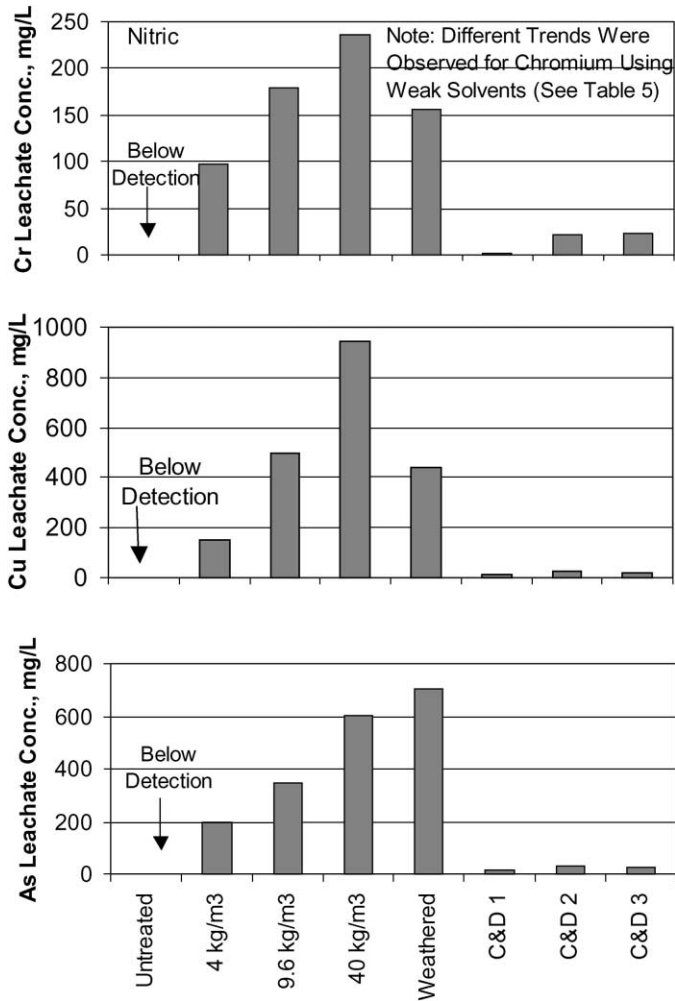


Fig. 5. Chromium, copper, and arsenic concentrations for nitric acid extraction.

centrations (mg/l) were lower for ash produced from samples containing higher retention levels of CCA. Again the formation of acetic acid insoluble chromium species (e.g. Cr(III)) in samples produced from high CCA retention levels, as described earlier, may explain this finding.

5.3.2. Copper

Less than 16% of the total copper was extracted with the following six solvents, distilled water, magnesium chloride, hydrogen peroxide, hydroxylamine hydrochloride, citric acid with sodium hydroxide, and acetic acid (Table 4 and Fig. 4). Slightly better performance was obtained from the citric acid which extracted between 16 and 27% of the total copper. The

best results were obtained from the total recoverable metals extraction and from hydrochloric and nitric acids. The highest percent extractions (between 75 and 100% in three cases) were obtained using nitric acid on the ash produced from the 9.6 kg/m³ sample and ash samples from wood collected at C&D recycling facilities. It is interesting to note that the nitric acid extraction and in some cases the hydrochloric acid extraction performed better than the TRM extraction. Recall that the TRM extraction is conducted with hydrogen peroxide and concentrated hydrochloric and nitric acids under heated conditions. The entire procedure takes roughly 4–6 h, whereas the nitric and hydrochloric acid extractions require a 24 h contact time with the ash. This increased contact time is one likely reason for the enhanced removal using either nitric or hydrochloric acid alone.

The percent removals using nitric acid for all samples (Table 4) varied from 26 to 100%, with the lowest removals corresponding to the 40 kg/m³ and C&D 1 samples. The greatest removals were associated with the remaining C&D samples and the 4 and 9.6 kg/m³ samples. Although percent removals were generally small for the 40 kg/m³ sample, the total mass of metal leached from this sample was the highest among those tested. This observation is evident in Fig. 5 where the leachate concentration for the 40 kg/m³ sample was over 900 mg/l as Cu, whereas the 9.6 kg/m³, weathered wood, and the 4 kg/m³ sample contained leachate concentrations of 500, 440 and 150 mg/l, respectively. The leachate concentrations from the C&D samples were less than 30 mg/l and the concentration of the untreated wood sample was below detection. These results are consistent with the relative amount of CCA chemical in each sample, where the lowest concentration corresponds to the untreated wood sample; the next highest are the C&D samples; the remaining concentrations proceed from 4 kg/m³, weathered, 9.6 kg/m³, to 40 kg/m³.

5.3.3. Arsenic

Among the metals analyzed, the highest percent removals were observed for arsenic. For the field samples (two of the three C&D samples and the weathered wood sample), nitric acid and TRM were capable of removing between 90 and 100% of the arsenic (Table 4). Such wood would be typically seen at recycling operations and therefore high percentage of arsenic removals would be expected from ash produced from recycled C&D wood wastes. Smaller percent removals were observed for the weaker solvents, distilled water, magnesium chloride, hydrogen peroxide, the combination of sodium hydroxide and citric acid, and acetic acid. Of particular interest is the ability of hydroxylamine hydrochloride and citric acid to extract greater than 40% of the arsenic for the 4 kg/m³ sample. In most cases, citric acid performed better than concentrated hydrochloric acid. This finding is of significance given that citric acid is easier to handle than the mineral acids and may therefore be more economically feasible to use within an ash treatment system.

The total mass of arsenic removed is readily observed from the leachate concentrations (e.g. Fig. 5) where an increase is generally observed with increasing retention levels. The lowest concentrations were observed for the untreated wood control and for the C&D samples. The leachate concentrations of the 4, 9.6, and 40 kg/m³ samples increased in that sequence. The mass of arsenic leached from the weathered wood sample was in some cases larger than the mass removed from the 40 kg/m³ samples. This observation was consistently observed among several of the solvents utilized and may indicate that the weathering process may enhance the leachability of arsenic.

6. Discussion and conclusions

In keeping with the discussion presented in Section 2 of this study, the wood ash results were compared to current regulations and guidelines for determining proper management of solid wastes. Again, this assessment was based on existing US and Florida regulations and policy, and this assessment may differ for other states or countries. Whether the ash is “hazardous” as defined by US standards was determined using the TCLP test. Results show that TCLP limits were exceeded for arsenic for all ash samples, except untreated wood and two of the three C&D samples (Table 6). For arsenic, the degree to which the limits were exceeded was strongly dependent upon the retention levels of the original wood sample. For the lowest retention level, 4 kg/m³, the TCLP limit for arsenic was exceeded by a factor of 10. Values were exceeded by a factor of 30–100 for samples containing higher retention values (9.6, 40 kg/m³, and weathered wood). For chromium, the 4 kg/m³ and one of the C&D samples exceeded TCLP limits. Of interest is that although arsenic appears to be the most problematic metal from a regulatory standpoint, the C&D 1 sample failed TCLP criteria for chromium but not for arsenic. Therefore, two of the three C&D samples tested failed TCLP criteria. One failed for arsenic and the other failed for chromium. Results therefore indicate that there is a significant likelihood that ash produced from C&D wood waste would fail TCLP criteria if the wood waste contains more than 5% CCA-treated wood by weight. It is difficult to assign one number for the percentage of CCA that can be burned with untreated wood waste that would produce a hazardous ash. Variability was observed in the data, presumably due to differences in wood waste and combustion characteristics. However, clearly the data show that the number for the percentage of CCA should be below 5%.

The results were also compared to policies used to determine when a non-hazardous waste can be land applied or disposed in an unlined landfill. The total metals analysis results were the most restrictive when compared to land application criteria. When total metals analysis results were compared to direct exposure target concentrations, it was found that no CCA-treated wood could be mixed with untreated wood and meet the state residential

Table 6
Comparison of SPLP and TCLP results to regulatory standards or policy

Sample ID	Sample exceeds TCLP limit ^a		Sample exceeds Florida GWCTL, TCLP leachate			Sample exceeds Florida GWCTL, SPLP leachate		
	As	Cr	As	Cr	Cu	As	Cr	Cu
Untreated	N	N	N	N	N	N	N	N
4 kg/m ³	Y	Y	Y	Y	N	Y	Y	N
9.6 kg/m ³	Y	N	Y	N	Y	Y	N	N
40 kg/m ³	Y	N	Y	Y	Y	Y	Y	Y
Weathered	Y	N	Y	N	Y	Y	Y	N
C&D 1	N	Y	Y	Y	N	Y	Y	N
C&D 2	N	N	Y	N	N	Y	Y	N
C&D 3	Y	N	Y	Y	N	Y	Y	N
5% CCA	Y	N	Y	Y	N	Y	Y	N
	Y	N	Y	N	N	Y	Y	N

^a N: no; Y: yes.

(0.8 mg/kg) or industrial guidelines (3.7 mg/kg). The fact that even ash from untreated wood does not meet the direct exposure guidelines for arsenic demonstrates that the risk-based concentration for arsenic is low and many wastes will have difficulty meeting this limit. Results of the SPLP tests were used to assess potential risk of ash leaching to groundwater (e.g. disposal in unlined landfills) and showed that only ash from untreated wood passed the GWCTLs for all metals (Table 6). All of the remaining samples, including the C&D samples and mixtures of CCA-treated wood exceeded the GWCTL for at least one metal. Ash from wood waste should be therefore free of CCA if it is to be considered for disposal in unlined landfills in Florida. Thus, even if C&D wood were mixed with other wood sources so that the resulting ash is not hazardous (as is the current practice in Florida), the ash must be managed in a lined landfill.

Results from the solvent extraction study show that maximum metals removals were 70–100% for copper, 20–60% for chromium, and 60–100% for arsenic for samples characterized by low retention levels. These maximum removals were observed for the nitric acid or TRM extractions. Also of significance is the ability of citric acid to extract most of the arsenic from the samples characterized by low retention levels. Forty-two percent of the arsenic was removed for the 4 kg/m³ sample, 60% for the weathered wood sample, and between 70 and 100% was removed for two of the three C&D samples. Such results indicate that solvent extraction is technically feasible for removing the arsenic but not necessarily feasible for removing the chromium. For example, it was found that one of the ash samples produced from C&D wood waste exceeded TCLP criteria for arsenic by 26% (TCLP leachate concentration of 6.7 mg/l) and another sample exceeded TCLP criteria for chromium by almost a factor of 5 (TCLP leachate concentration of 24.1 mg/l). In order to treat the ash so that enough arsenic and chromium are removed, the solvent extract utilized must be capable of extracting over 30% of the TCLP-extractable arsenic and greater than 80% of the TCLP-extractable chromium. The fraction removed for arsenic was readily met by at least one of the solvents tested; however, the chromium removals did not achieve the levels needed in order for the ash to pass TCLP on a consistent basis.

It is also important to note that although a fraction of the chromium was difficult to leach, a portion of the chromium was readily mobilized by relatively weak solvents (e.g. distilled water). The lower the retention level the higher the percent, and in some cases mass, that was leached. Results therefore indicate that there is enough mobile chromium to be of environmental concern, even if the ash is exposed to weak solvents.

7. Recommendations

Given the results of this study, it is concluded that solvent extraction methods merit further evaluation for potentially removing CCA from the ash so that the ash from the combustion of wood containing small quantities of CCA can be classified as a non-hazardous waste. Future research should focus on evaluating the impacts of pH and speciation on the mobility of chromium from the ash. There is also a need to evaluate other solvents, such as organic solvents and surfactants, for removing CCA from the ash. An ideal scenario would be the use of the solvent extract, containing the CCA chemical, within the CCA manufacturing process. Such a recycling option would require further research in purifying the

solvent extract and converting the metals to their proper valence needed for wood treatment purposes.

Results also indicate that a wood mixture containing more than 5% CCA-treated wood will exceed TCLP limits. Research has shown that for Florida, for example, recycled wood from C&D recycling facilities located within the state is composed of 6% CCA-treated wood on average [11]. During 1996, most wood burning facilities in Florida also accepted wood from additional sources thereby diluting the fraction of CCA-treated wood to approximately 2–3%. Given that the quantities of CCA-treated wood disposed are forecasted to increase significantly [15], it is likely that C&D wood waste will contain a higher fraction of CCA-treated wood thereby making recycling of C&D wood for cogeneration purposes in Florida and potentially in other states unfeasible due to the production of a hazardous ash. In the absence of a good ash treatment method, removal of CCA-treated wood from the remaining wood stream prior to incineration is the only viable alternative that will minimize the amount of metals within the ash. Research should be conducted to determine the feasibility of sorting technologies. If the purpose of sorting is to produce a non-hazardous ash in the event that the wood is burned, then the sorting technology should be efficient enough to provide a fuel product containing less than 5% CCA-treated wood.

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