Minimization of Metals Leaching from CCA-Treated 
Wood Ash through High Temperature Reaction with 
Mineral Sorbents 

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Abstract 

Chromated copper arsenate (CCA) treated wood is the popular treated wood found in the wood waste disposal sector. Incineration has been a key disposal pathway for CCA-treated wood waste; however, the potential for emissions of toxic metals from combustion, and their accumulation and subsequent leaching from ash has raised public concerns. Earlier studies by our group focused on evaluating combinations of CCA chemical with sorbents for their ability to minimize leaching of ash. The objective of this study was to evaluate the ability of sorbents to minimize the leaching of CCA-treated wood and to compare the results to evaluate the influence of the wood matrix on the effectiveness of sorbents to minimize leaching. Experiments were carried out using CCA wood with alkaline earth, alumino-silicate and iron-based sorbents combusted at 700 °C and 1100 °C. A portion of the residual was leached using the toxicity characteristic leaching procedure (TCLP).
Alkaline earth sorbents (cement and Mg(OH)₂) successfully reduced the leaching of arsenic from the ash to below the TCLP limit. Fe₂O₃ (iron-based sorbent) and kaolin (alumino-silicate sorbent) were able to achieve low leaching (below TCLP limit) of chromium. For copper, low leaching from baseline CCA wood ash was observed, and alkaline earth sorbents demonstrated the best potential to further lower copper leaching. When the leachate pH was high, low leaching for As and Cu occurred, whereas a lower leachate pH correlated with low chromium leaching. These results are broadly consistent with prior studies using CCA chemicals that showed alkaline-earth sorbents to be effective for As and Cu and Fe₂O₃ to be effective for Cr. Therefore, a combination of sorbents (like cement and Fe₂O₃) used at different stages of high-temperature processes involving CCA wood, or burning CCA wood in industrial processes containing these minerals, may effectively control the leaching of CCA metals from CCA-treated wood waste.

**Keywords:** Arsenic; Chromium; Cement; Kaolin; Ferric Oxide; Leaching Retention.

1. **Introduction**

Chromated copper arsenate (CCA) was a popular wood preservative in the United States, applied to wood products to prevent structural decay during outdoor use. The wood waste was often disposed in unlined landfills [1, 2] and was inadvertently recycled into mulch and fuel [3, 4, 5]. Such disposal options are not recommended because of the leaching of arsenic, chromium, and copper from the wood or ash [6, 7, 8, 9]. Therefore, phase down of CCA-treated wood began from 2004 for residential applications; however, CCA production still represented over 90% of the U.S. waterborne preservative market through 2004 [10], and CCA-treated wood waste still represents about 30% of the waterborne treated wood market [11]. It is estimated that by 2040, the disposal volume for CCA wood will remain at 290,000 cubic meters [12] and can significantly impact the ecosystem [13].

Historical estimates indicate that over half of the CCA-treated wood waste in Florida is burned to produce energy [14, 15]; however, incineration may result in volatilization of metals during combustion and accumulation of metals in ash [16]. Among trace metals, chromium is considered least volatile and arsenic is classified as semi-volatile. Therefore, chromium is typically found in both the bottom ash and fly ash, and arsenic is typically enriched in fly ash in an incineration process [17]. CCA wood ash has been reported to leach arsenic and in some cases chromium, beyond TCLP limits [7, 8] and therefore may be required to be managed as a hazardous waste. When incinerator ash is disposed of in landfills, the heavy metals contained in the ash may leach out and contaminate landfill leachate and if the leachate is not managed properly it can also contaminate soil and groundwater [18, 19].

Past research studies have shown the potential of injecting mineral sorbents into combustion systems for controlling emissions of arsenic and other heavy metals [20, 21, 22, 23]. Metals and sorbents react in the vapor phase at high temperature to form metal-sorbent compounds that have relatively larger particle sizes and hence are very efficiently captured by electrostatic precipitators and baghouses. Another major advantage is that these toxic metals are transformed into stable, non-toxic and non-leachable compounds [16, 24, 25] that become suitable for landfill disposal. Sorbents like lime have been used in flue gas treatment for removing SO₂ [26, 27].
and in other industries such as power plants and waste incinerators. Alumina and silica based sorbents were found to be effective in capturing Pb& Cd under incineration conditions [28, 29, 30].

Based on the same principle, our research team, as documented by [31, 32] evaluated the efficacy of alkaline-earth, Al, Si, Fe-based mineral sorbents, combusted with pure chemicals containing CCA metals for reducing leaching of CCA metals. Results showed that alkaline earth sorbents such as cement, calcium hydroxide and Mg(OH)₂ were the most promising for reducing the leaching of arsenic from ash below the 5 mg/L TCLP limit and retaining copper at concentrations below detection limits at temperatures between 700°C and 1100°C. For chromium, leaching below the 5mg/L TC limit was achieved by the introduction of alumino-silicate sorbents like alumina and silica at temperatures between 700°C and 1100°C and kaolin and Fe₂O₃ at 1100°C. Since pure CCA chemicals were used for that study, it was not known if the wood matrix portion of CCA wood would interfere with the interactions identified from those studies. The wood matrix contains carbon, nitrogen, hydrogen, oxygen, sulphur and other trace elements that could potentially impact the interactions between the CCA chemicals and the sorbents.

Therefore, the objective of this study was to evaluate the utility of sorbent technology for CCA-treated wood disposal by investigating CCA wood-sorbent interaction in high-temperature conditions. The results of this study may be applicable to various thermal processes for minimizing the environmental impacts from the disposal of CCA-treated wood through combustion processes. A series of these sorbents were combusted with CCA wood, and the leaching of their products was examined. The most suitable sorbent candidates and the optimal operating conditions for controlling metal leaching were identified.

2. Experimental

2.1 Materials

A good sorbent should reduce leaching, facilitate gas phase capture of metals, and be low cost and easy to procure, so that it can be used on an industrial scale. Previous studies using pure chemicals containing CCA metals examined leachability and speciation of CCA metals upon application of sorbents, and included alkaline earth metal-based sorbents, alumino-silicate based sorbents and iron-based sorbents [31, 32]. Based on the results of those studies, the following sorbents were chosen for this present study: Cement (Florida Rock Industries, Inc.), magnesium hydroxide (Mg(OH)₂, CAS # 1309-42-8), ferric oxide (Fe₂O₃, CAS # 1309-37-1) and kaolin. CCA wood sawdust (henceforth referred to as CCA wood) and CCA wood ash, obtained by incineration of CCA wood, were used for baseline readings. Particle size was not considered as a criterion in this study for comparing the leaching behavior of these sorbents. Although particle size is known to be an important parameter in chemically adsorbing metal vapors, it is more economically viable to use the sorbent material available in the market without controlling its particle size.

2.2 Experimental Conditions

Forty gram of CCA wood was added to 16 g of chosen sorbent in a porcelain crucible. This quantity of sorbent was used because a minimum of 15 g of residue is required to complete the various analyses such as leaching.
and digestion tests. Each sorbent-wood sample was prepared in triplicate. The samples were heated in a muffle furnace (Fisher Isotemp Programmable Forced Draft Furnace, Model # 10-750-58) to 700°C or 1100 °C and stayed at that temperature for 30 minutes to replicate high temperature conditions commonly encountered at combustion facilities in industrial boilers. Since many prior studies already reported the feasibility of sorbents in capturing metals in combustion flue gas, this system focused on the impact of the metal-sorbent interaction on leachability and was not specifically designed to minimize volatilization.

2.3 Analyses

On an average, 5.6% of ash (by mass) was obtained on combustion of CCA wood at 700 °C and ~1% of ash at 1100 °C. The residue was extracted from crucibles and ground to powdered form using a coffee grinder (Kitchen Aid BCG100OB Onyx Black Coffee Grinder).

For the TCLP procedure as described in EPA SW 846 Method 1311 [33], a 10g portion of the sample was transferred to a 250 mL polyethylene container using an acid-rinsed spoon. Two types of extraction fluids were used in the TCLP procedure. Extraction fluid 1 (pH = 4.93 ± 0.05) was used for residues with pH < 5, while extraction fluid 2 (pH = 2.88 ± 0.05) was used for the rest. Two hundred mL of the appropriate extraction fluid was added to the container resulting in the 20:1 liquid/solid ratio that the method required. Subsequently, the container was placed on a rotary extractor and tumbled for 18±2 hours at 30 rpm. This was followed by pressure filtering of the samples through an acid-rinsed 0.7 µm glass fiber filter paper. The solid phase was discarded and the filtered leachate was placed in an acid-rinsed polyethylene or glass bottle. All samples were stored below 4 °C until analysis.

Fifty mL of the TCLP leachate for each sample was liquid digested as described in EPA SW 846 Method 3010 A [33]. A portion of the residue was digested for the total metal content analysis following the solid digestion method as described in EPA SW 846 Method 3050 B [33]. All digested samples were analyzed using Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-AES) as described in EPA SW 846 Method 6010B [33] to determine the metal content in the two digestates. The % spike recovery from digested samples was between 80-120% of the original samples.

Leachate pH was measured for all samples to assess the impact of pH on metal leaching. Accumet AP62 portable pH meter equipped with a pH electrode was used for measuring pH. Prior to each sampling, the meter was calibrated using three buffering solution standards. The probe in the leachate sample was gently stirred to establish equilibrium between the electrode and sample. Readings were obtained with a resolution of 0.001 pH.

3. Results and Discussions

3.1. TCLP Leaching Results

Figure 1 shows the leaching results. The baseline leaching of arsenic from CCA wood was at ~11 mg/L, exceeding the TC limit for arsenic of 5 mg/L, whereas the baseline leaching from CCA wood ash was ~220
mg/L at 700 °C, and ~350 mg/L at 1100 °C. For chromium, the baseline leaching from CCA wood was at ~5.2 mg/L, whereas the baseline leaching from CCA wood ash was ~ 0.2 mg/L at 700 °C, and ~0.4 mg/L at 1100 °C. For copper, the baseline leaching from CCA wood was at ~7.3 mg/L, whereas the baseline leaching from CCA wood ash was ~0.4 mg/L at 700 °C, and ~1 mg/L at 1100 °C. As noted above, chromium leaching from CCA wood was 5.2 mg/L whereas for the ash it goes down to 0.2 to 0.4 mg/L.

Past studies have identified pH as one of the contributing factors for this result [6, 7, 9]. However, since the pH for CCA wood and CCA wood ash is in the range of 4-6, it is suspected that a change in speciation may have resulted in these differences in leachability. The conversion of Cr(VI) in CCA chemical to Cr(III) in the wood matrix during treatment is considered as fixation of the chemical and is a measure of treatment efficiency [34]. Therefore, in the CCA wood sample, we would expect most of Cr as Cr(III) if the fixation of CCA chemical is proper with the wood matrix. For CCA wood ash, it is likely that most of Cr would be present as Cr(VI) as wood burning is an oxidation process.

The baseline leaching values for CCA wood are consistent with those observed in the current study. Prior leaching studies have shown that arsenic leaching from CCA wood averages ~ 7 mg/L, ~2.6 mg/L for chromium and ~9.9 mg/L for copper. For ash, prior studies have generally shown that these numbers go up. TCLP results for CCA wood ash show arsenic leaching between 51-511 mg/L, chromium leaching between 0.1-78 mg/L, and copper leaching between 0.5-100 mg/L. The higher level of leaching from CCA wood ash is due to the vaporization of biomass during combustion, resulting in an increase in concentration of heavy metals in the ash. The range of leaching depends upon the type of CCA wood used and the corresponding treatment level [7, 16, 19, 35].

**Arsenic:** All sorbents showed some reduction in leaching for arsenic compared to CCA wood ash. Cement and Mg(OH)₂ leached significantly less than the TC limit of 5 mg/L at both temperatures and Fe₂O₃ leached more than the TC limit at 700 °C (~ 55 mg/L) but < 5 mg/L at 1100 °C. Kaolin leached significantly higher than the TC limit at both temperatures, at around ~55 mg/L.

Results from previous studies [20, 31, 32, 36, 37, 38] indicate that the formation of insoluble metal mineral compounds such as Ca₂As₂O₇, Ca₃(AsO₄)₂, MgHAsO₄, etc. may have resulted in the low leaching of arsenic. Mahuli et al. [36] and Jadhav et al. [37] demonstrated that the formation of calcium arsenate as a dominant reaction product through the reactions between arsenic oxide (As₂O₃) and lime (CaO) at high temperatures, unlike physical adsorption, results in improved capture of arsenic at high temperatures. Based on metal-sorbent speciation results, Misra et al. [31, 32] have theorized that the propensity of formation of Fe-Cu & Fe-As compounds such as CuFe₂O₄ and Fe₂(AsO₃)₃ increases with temperature and may have resulted in low As and Cu leaching using Fe₂O₃ sorbent at 1100 °C. Similarly, the lack of appreciable Al/Si – As/Cu binding resulted in relatively higher leaching of As and Cu from Kaolin.

**Chromium:** Fe₂O₃ and kaolin leached significantly below the TC limit (5 mg/l) for Cr at both temperatures. However, the trend for the two alkali-earth sorbents was just the opposite. Cement leached ~40 mg/L of Cr 700°C but only ~0.4 mg/L of Cr at 1100°C, whereas Mg(OH)₂ leached only 0.2 mg/L of Cr 700°C but 7mg/L of
Cr at 1100°C.

Past studies indicate that the formation of trivalent chromium compounds like CuCr₂O₄, Cr₂O₃, Cr(OH)₃, CrO(OH), FeCr₂O₄, FeCr₂O₃ under the presence of kaolin and Fe₂O₃ results in low chromium leaching. Therefore, it is possible that the formation of Fe-Cr compounds is the likely reason for low Cr leaching in these experiments. Similarly, due to the absence of significant Al/Si – Cr compounds in past speciation studies, it has been theorized that Kaolin most likely facilitated the formation of trivalent Cr compounds by keeping the pH acidic and therefore resulted in low leaching of Cr in our experiments [19, 31, 32, 36, 37].

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**Figure 1:** Leaching from sorbent-wood samples for arsenic, chromium and copper at different temperatures: (a) 700°C, (b) 1100°C
On the other hand, the high Cr leachability from alkaline-earth sorbents is consistent with past studies that demonstrated high Cr leaching (> 5 mg/l) using alkali-earth sorbents and may be explained by the formation of hexavalent chromium compounds like MgCrO₄, Cu₃CrO₆, CuCr₂O₇·2H₂O, CaCrO₄, CrO₃ and CuCrO₄. It is not clear why these trends were not observed for cement at 1100°C and Mg(OH)₂ at 700°C. It is likely that the formation of trivalent compounds like MgCr₂O₄ as dominant product may have resulted in low Cr leaching with Mg(OH)₂ at 700 °C. For cement, it is suspected that cement-biomass-Cr interactions may have resulted in the formation of trivalent Cr compounds that led to low leaching from cement at 1100 °C [19, 31, 32, 36, 37].

**Copper:** Since copper is not considered hazardous for its toxicity characteristic, there is no TC limit for it. Both cement and Mg(OH)₂ leached less than 0.1 mg/L Cu at both 700 °C and 1100 °C. Leaching with Fe₂O₃ was < 1mg/L for higher temperatures whereas kaolin leached ~ 5 mg/L and higher at both temperatures.

Copper leaching was likely controlled by the solubility characteristics of a large variety of Cu-As/Cr and Cu-sorbent compounds that were formed, as indicated in past speciation studies. Since the Cu-As compounds are more soluble while As-alkaline earth compounds are insoluble, the provision of alkaline earth sorbents into combustion system takes arsenic away from copper, thus reducing the leaching. As shown in speciation results in past studies, the lack of appreciable Al/Si – As/Cu binding resulted in relatively higher leaching of As and Cu from kaolin [31, 32].

### 3.2. pH Effects

Past studies have shown that leachate pH can be used as an indicator to assess the potential leachability of a sample [6, 7, 9]. Figure 2(a) shows the leachate pH for various sorbent-wood samples. A high leachate pH (>9) was exhibited by alkaline earth based sorbents, whereas leachate pH for Fe₂O₃ and kaolin was typically in the range of 4-6, which is similar to the baseline. Fig. 2(b) displays the concentrations (mg/L) of arsenic, copper and chromium as a function of leachate pH. It can be observed that for arsenic and copper, the leaching was higher at lower pH values (pH = 4-6) and very low leaching at high pH (9-12).

A possible reason for similarity in As-Cu leaching trend at lower pH could be the formation of leachable bimetallic As-Cu species in the products as identified in prior studies with sorbent-CCA metals [31, 32]. For chromium, generally, there was lower leaching at low pH (4-6) and high chromium leaching in the high pH range (pH = 10-12) possibly due to the presence of chromium as Cr(VI) at these pH levels, which is consistent with past studies [18]. However, there were exceptions to this trend, as evidenced by low Cr leaching at high pH by Mg(OH)₂ at 700°C and by cement at 1100°C as explained above.

### 4. Conclusions and Implications

Laboratory scale experiments were conducted to evaluate select sorbent materials for their capability in reducing ash leachability of CCA wood by the formation of thermally stable and insoluble compounds. Results indicate that alkaline earth based sorbents are very effective in reducing the leaching of arsenic and copper. Kaolin and Fe₂O₃ were the most suitable for chromium, whereas Fe₂O₃ was very effective for all three metals at 1100 °C. Product speciation plays an important role in determining the fate of the metals and leachate pH can serve as a
good indicator for predicting the leaching behavior of these metals.

![Graph showing leachate pH for different sorbent-wood combustion products and correlation between leachate pH and metal concentration in leachate.

Figure 2: (a) Leachate pH for different sorbent-wood combustion products; (b) Correlation between leachate pH and metal concentration in leachate.

These results can be used to design and implement effective strategies for preventing CCA metals from impacting the environment by using sorbent(s) at high combustion temperatures. Figure 3 shows a conceptual diagram of a proposed thermal system for incineration of CCA-treated wood with sorbent injection. Since
arsenic is mostly found in gas phase at high temperatures while chromium and copper remain in the feed, sorbents can be injected in both feed and gas phase to effectively capture the heavy metals. Since our results show that all sorbents that work with As and Cr also work well with Cu, it is expected that injecting Cr-specific sorbents in feed and As-specific sorbent in gas phase will control Cu leaching and vaporization as well. Possible strategies could include using a single sorbent like Mg(OH)\textsubscript{2} at low temperatures (~700 °C) and Fe\textsubscript{2}O\textsubscript{3} at high temperatures (~1100 °C), or a combination of sorbents (depending on capture efficiency requirements) such as cement in the flue gas to capture arsenic and Fe\textsubscript{2}O\textsubscript{3} in the feed to capture chromium and copper.

Since wood wastes are often co-incinerated with municipal solid wastes [39], choosing a suitable co-fuel or sorbent that exhibits the behavior as described above, can successfully control the leaching and volatilization of CCA metals. For instance, most coal combustion units are equipped with lime scrubbers (for sulfur dioxide capture), which can effectively scavenge arsenic in the gas phase. Similarly, in the cement making process, cement dust is present in the system that can scavenge the arsenic in gas phase. Steel mills, which use iron ores, coke (a byproduct of coal) and lime in their manufacturing process, could be another possible option for burning CCA-treated wood with a few modifications. All these facilities are usually equipped with particulate control devices like electrostatic precipitators and baghouses; therefore, no additional devices are required.

There has been a gradual shift to copper based preservatives like ACQ (Alkaline Copper Quaternary) and CBA (Copper Boron Azole) for wood treatment since the phase-down of CCA-treated wood. However, wood treated with these preservatives leaches high amounts of copper, higher than in CCA-treated wood [40, 41, 42]. Most of the sorbents examined in this study exhibit low leaching for copper (esp. alkaline-earth), suggesting that they may be applicable to other treated wood wastes for minimizing losses through leaching.

![Figure 3: Conceptual Diagram of Proposed Thermal System for incineration of CCA-treated wood with Sorbent Injection](image)

**Figure 3:** Conceptual Diagram of Proposed Thermal System for incineration of CCA-treated wood with Sorbent Injection

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