Leaching Retention of CCA Metals from High-Temperature Reaction with Alkaline Earth and Iron Based Sorbents

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Abstract

Chromated copper arsenate (CCA) was the dominant wood preservative used for outdoor wood products to prevent structural decay prior to its phase down starting from 2004. Incineration is one key disposal alternative for CCA-treated wood; however, it results in volatilization of metals at high temperature and accumulation of metals in ash. The objective of this study was to assess alkaline earth and iron based sorbents for their capability to minimize leaching of metals from the incinerator ash. Experiments were carried out by heating CCA metal spikes combined with sorbents to temperatures of 700, 900 and 1100 ^{o}C. The residual ash was analyzed for leaching retention using the toxicity characteristic leaching procedure (TCLP) and speciation by X-ray diffraction (XRD). Results show that alkaline earth sorbents (cement, calcium hydroxide and magnesium hydroxide) were the most promising for reducing the leaching of arsenic from the ash below the 5 mg/L TCLP limit and retaining copper at concentrations below detection limits. For chromium, iron and magnesium based sorbents resulted in the highest retention with low leachate concentrations (<5 mg/L) at 1100 ^{o}C. Leaching appeared to be highly pH dependent, with As and Cu leaching more at low pH values and Cr leaching more at high pH values. Results also indicate that the formation of compounds like $Ca_3As_2O_7$, $FeCr_2O_4$ and $CuCr_2O_4$ during the reaction reduced the volatilization of metals. The results suggest that a combination of sorbents at different stages of high-temperature processes may offer effective control of the leaching of CCA metals.

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1. Introduction

Chromated copper arsenate (CCA), which is composed of oxides of chromium, copper, and arsenic, has a history of use as a popular wood preservative. In 1996, 13 million cubic meters of CCA-treated wood were produced, accounting for about 79% of all the treated wood in the United States. The production continued representing over 90% of the U.S. waterborne preservative market through 2004 [1]. The use of the chemical for residential wood products was phasedout in 2004. In spite of the phase-out, CCA-treated wood continues to represent about 30% of the waterborne treated wood market [2]. Disposal forecasts predict that the peak disposal quantities in the U.S. occurred in 2008 with a total of 660 thousand cubic meters of CCA treated wood disposed. It was estimated that disposal quantities will remain high due to the long service life of the treated wood product [3]. By 2040, the disposal volume is estimated to remain at 290 thousand cubic meters [4]. These quantities are significant and capable of impacting the environment if not managed properly [5].

The prominent disposal pathway for CCA-treated wood has traditionally been in construction and demolition (C&D) debris landfills along with other wood wastes [6, 7]. Recycling of wood from C&D debris is common, and energy recovery is the primary disposal pathway for the recycled wood waste because it results in a significant reduction in waste volume and converts waste to useful energy [8]. Historical estimates indicate that over half of the CCA-treated wood waste in Florida is burned to produce energy [9, 10]. However, disposal of CCA-treated wood via incineration may be problematic due to possible volatilization of toxic metals at high temperature. Accumulation and subsequent leaching of toxic metals in the ash are also important issues associated with its incineration. This may pose serious health and environmental problems. CCA wood ash has been reported to leach arsenic and in some cases chromium, beyond TCLP limits [11, 12] and therefore has to be managed as a hazardous waste.

Among the metals contained within CCA, arsenic is the most toxic to humans. Studies have shown that long-term exposures to CCA-treated wood may result in an increased cancer risk [13]. During high-temperature combustion of fuel containing arsenic, many arsenic compounds vaporize and subsequently recondense on fine particulate matter (typically in the submicron range) when the flue gas cools down. Existing particulate control devices such as baghouses or electrostatic precipitators (ESPs) are least efficient in controlling particulates in the submicron range. Also, arsenic leaching from ash can pose a problem for ash disposal. The form of chromium in the wood matrix is as Cr(III) [11], but combustion of CCA wood has been reported to result in oxidation of Cr(III) to Cr(VI) in some cases [10, 14], a much more toxic form for humans [15]. Copper, too, is toxic to aquatic organisms [16] and can create problems, if copper containing wastes leach into sensitive aquatic ecosystems.

Research studies have demonstrated the potential of injecting mineral sorbents into combustion systems for controlling emissions of metals [8, 17]. The metals interact with sorbents in air stream and undergo chemisorption at high temperatures. The injected particles are in the super-micron range so the metal-sorbent products are very efficiently captured by ESPs and baghouses. Another major advantage is that these toxic

metals can be transformed into non-toxic and non-leachable compounds [8, 18, 19] that become suitable for landfill disposal. Sorbent injection techniques can be easily retrofitted to existing thermal facilities, though the particle removal system may have to be upgraded to collect the relatively larger load of particles [17, 20].

The objective of this study was to evaluate the utility of sorbent technology for CCA-treated wood disposal by investigating metal-sorbent interaction in high-temperature conditions, results of which may be applicable to thermal processes using alkaline earth and iron based sorbents. Past studies [22] have focused on the control of metal emissions using sorbents in coal combustion processes, while not much work has been done on CCA-treated wood incineration systems. Limited leachability data are available on sorbent-metal interactions for CCA metals. In this study, these sorbents were combusted with CCA metals, and the leaching and speciation of the products were examined. The goal was to determine the most suitable sorbent candidates and optimal operating conditions in order to minimize impacts from the disposal of CCA-treated wood through thermal processes.

2. Experimental

2.1   Materials

The criteria for a good sorbent for this study are its ability to reduce leaching and enhance gas phase capture against CCA metals. Additionally, they should be low cost and readily available so that they can be used on an industrial scale. Various researchers [8, 21, 22, 23] have successfully used Ca-based sorbents for metal capture. Based on this, calcium hydroxide ($Ca(OH)_2$, CAS # 1305-62-0) was chosen for the experimental matrix. Magnesium hydroxide ($Mg(OH)_2$, CAS # 1309-42-8) was added to the matrix as a representative of alkaline earth metals and to test if the conclusions drawn from the performance of Ca-based sorbents could be extended to other alkaline earth metals. Cement (Florida Rock Industries, Inc.) was chosen because calcium is a major constituent in it and hence the leaching and volatilization retention properties exhibited by cement are expected to be similar to that of Ca-based sorbents. As cement kilns burn waste-derived fuels such as scrap tires, they could be a potential option for burning CCA-treated wood. Ferric oxide was added to the matrix based on its use in metallurgical processes, where formation of insoluble ferric arsenate compounds like scorodite ($FeAsO_4 \cdot 2H_2O$) is a popular method for disposal of arsenic [24]. Iron is also known to form ferrous chromite ($FeCr_2O_4$), a commonly occurring mineral, which is insoluble in water and slightly soluble in acids. Amongst Fe-based minerals, ferric oxide (Fe_2O_3, CAS # 1309-37-1) was chosen as it is inexpensive and readily available. 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, use of the sorbent materials available in the marketwithout controlling its particle size was considered to be more economically viable.

In the current study, pure chemicals containing CCA metals were used to obtain data regarding leachability and speciation of CCA metals when combusted with sorbents. While the wood composition may affect the 'sorbent–metal' interaction, pure metal compounds were used to provide a fundamental baseline for evaluating the nature of interaction between sorbents and CCA metals. A metal spike was prepared containing all the three CCA metals in the same mass ratio as the CCA Type C chemical. Arsenic oxide (As_2O_5), chromium nitrate

nonahydrate ($Cr(NO_3)_3$) and copper nitrate hydrate ($Cu(NO_3)_2 \cdot 2.5H_2O$) were used to prepare the metal spike as they are readily soluble in water. Metal concentrations in the spike sample were: As – 13 g/L, Cr – 14.6 g/L and Cu – 8.8 g/L. The spike sample had a retention level equal to 3.68 pcf of treated wood, based upon a retention level of 33 pcf for typical Type C treated wood. These high metal concentrations ensured that sufficient metals were available for reaction, despite volatilization losses.

2.2   *Experimental Conditions*

A total of 5 sets of samples were studied, including Ca $(OH)_2$ – Metal Spike, Cement – Metal Spike, $Mg(OH)_2$ – Metal Spike, Fe_2O_3 – Metal Spike and a pure metal spike sample as mentioned earlier. Samples were processed by first, mixing 50 mL of the metal spike with 20 g of various sorbents in 75 mL porcelain crucibles. This quantity of sorbent was chosen because a minimum of 15 g of residue is required to complete the various analyses. Each sorbent-spike sample was prepared in triplicate. The prepared samples were then heated in a muffle furnace (Fisher Isotemp Programmable Forced Draft Furnace, Models # 10-750-58 and 10-750-126) at ~90 ^{o}C for 14 hours to evaporate the water in the solution so as to minimize losses due to boiling. The furnace was then raised to the designated temperature of 700 ^{o}C, 900 ^{o}C and 1100 ^{o}C and kept at that temperature for 30 minutes. The time taken by the furnace to reach these temperatures ranged from 1 to 3 hours. High temperatures are commonly encountered at thermal facilities in industrial boilers. Here, the capacity of the furnace (maximum 1125 ^{o}C) determined the upper limit for temperatures that could be tested.

2.3   *Analyses*

The residue was extracted from crucibles and ground to powdered form using a coffee grinder (Kitchen Aid BCG100OB Onyx Black Coffee Grinder). This residue was thoroughly mixed and split for TCLP analysis, total metal analysis, and X-ray diffraction (XRD) analysis. For the TCLP procedure (EPA SW 846 Method 1311 [25]) a 10 g portion of the sample was transferred to a 250 mL polyethylene container using an acid-rinsed spoon. Then 200 mL of the appropriate extraction fluid were added to the container resulting in the 20:1 liquid/solid ratio that the method required. The container was then placed on a rotary extractor and tumbled for 18±2 hours at 30 rpm. After tumbling, the samples were pressure filtered 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 at temperatures below 4 ℃ until analysis. Two different types of extraction fluids were used in the TCLP procedure. For CCA spike-ferric oxide residue, extraction fluid 1 (pH = 4.93±0.05) was used because the pH of the product was less than 5. All the other samples had a pH > 5; hence, extraction fluid 2 (pH= 2.88±0.05) was used. To assess the impact of pH on metal leaching, the pH of the leachate samples upon extraction was measured (Accumet AP62 portable pH meter). A liquid digestion (EPA SW 846 Method 3010 A [25]) was then conducted on 50 mL of the TCLP extract.

For total metals analyses, a portion of the ash residue (15 g) was digested following the solid digestion method described in EPA SW 846 Method 3050 B [25]. All digested samples (TCLP and total metals digestates) were analyzed using Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-AES) as described in EPA SW 846 Method 6010B [25] to determine the metal content in the two digestates. The % spike recovery from

digested samples was between 80-120% of the original samples.

XRD analysis of the ash residue was conducted to determine the crystalline speciation of the products and then the solubility characteristics of the identified compounds were determined through property tables to better understand their leachability. Although XRD analysis is not quantitative, it provides useful qualitative information regarding possible product speciation in the residue that can shed light on the leaching behavior. Note that the sensitivity or the detection limit of the XRD technique is material and matrix dependent [26]. Therefore, the specific detection limit for the materials used in this study cannot be determined.

Two types of retention were designated: volatilization retention (VR) and leaching retention (LR). VR was calculated by the following

$$VR = \frac{\text{mass of CCA metal in 'sorbent - spike' ash}}{\text{mass of CCA metal in spike}} \times 100\%$$

(1)

LR was defined as the fraction of metal present in the ash that did not leach out and expressed as:

$$LR = \frac{\text{mass of CCA metal in ash - mass of CCA metal in leachate}}{\text{mass of CCA metal in ash}} \times 100\%$$

(2)

3. Results
3.1. TCLP Leaching Results

The baseline leaching of arsenic from pure metal spike ash was very high, at around 745 mg/L at 700 ^{o}C, ~639 mg/L at 900 ^{o}C and ~601 mg/L at 1100 ^{o}C (Fig. 1a). All sorbents showed at least an order-of-magnitude reduction in leaching for arsenic. It was observed that with cement, calcium hydroxide and magnesium hydroxide, arsenic leaching was reduced by two orders-of-magnitude to less than the TC limit of 5 mg/L at all three temperatures. Regarding ferric oxide, arsenic leached more than the TC limit at 700 and 900 ^{o}C but < 5 mg/L at 1100 ^{o}C. For chromium, the baseline leaching for the pure metal only sample was 733 mg/L at 700 ^{o}C and 900 ^{o}C and 58 mg/L at 1100 ^{o}C (Fig. 1b). All the sorbents showed some reduction in the leaching level for chromium, but only ferric oxide resulted in leaching less than the TC limit of 5 mg/L. Cement and calcium hydroxide ash leached chromium excessively (~100 mg/L) at all three temperatures. Magnesium hydroxide ash followed this trend for 700 ^{o}C and 900 ^{o}C batches, but it leached close to the TC limit of chromium at 1100 ^{o}C. For copper, the baseline leaching was 566 mg/L at 700 ^{o}C, 490 mg/L at 900 ^{o}C and 469 mg/L at 1100 ^{o}C (Fig 1c). All the sorbents showed good reduction in leaching (< 50 mg/L) of copper. Alkaline earth sorbents resulted in leaching less than 10 mg/L of copper at all three temperatures. Ferric oxide exhibited a decrease in leaching with an increase in temperature, and the leaching was < 2 mg/L at 1100 ^{o}C. Overall with respect to TCLP leachate concentrations, magnesium hydroxide appeared to be the most viable option for high temperature processing (1100 ^{o}C) of CCA metals as it reduced the As and Cr to below the TC limits and also resulted in significant decreases in Cu leaching. All sorbents exhibited an inverse temperature relationship with respect to leaching, i.e., leaching decreased with an increase in reaction temperature.

The different leaching behaviors observed with different sorbents could be due to the difference in product speciation. For example, the low leachability of arsenic might be due to the hypothesized formation of arsenic-sorbent compounds [27]. Iida et al. [8] reported arsenic leaching from wood ash samples ranging from 0.1-200 mg/L with the lower leaching values observed with $Ca(OH)_2$ sorbent and the higher ones for pure CCA ash. Chromium, on the other hand, had a high leaching level due to the formation of more soluble chromium-sorbent or chromium-copper species. Iida et al. [8] reported chromium leaching ranging from 17- ~1100 mg/L with the lower leaching values observed for pure CCA ash and higher ones observed for $Ca(OH)_2$ and Na_2CO_3 sorbents.

Low leachability of arsenic might also result from relatively lower availability of metals for leaching if the metal compounds are volatile at higher temperatures. In a CCA-treated wood ash leaching study [28], arsenic leaching varied from 0.1-1000 mg/L and copper leached between 0.07-15 mg/L with the highest leaching observed for samples characterized by high retention levels. However, the same study reported the opposite trend for chromium: leaching ranged between 0.2-25 mg/L with the highest leaching observed for samples characterized by low retention levels. Clearly, the answer is available only when it is studied together with speciation and retention level, which will be discussed in the later sections.
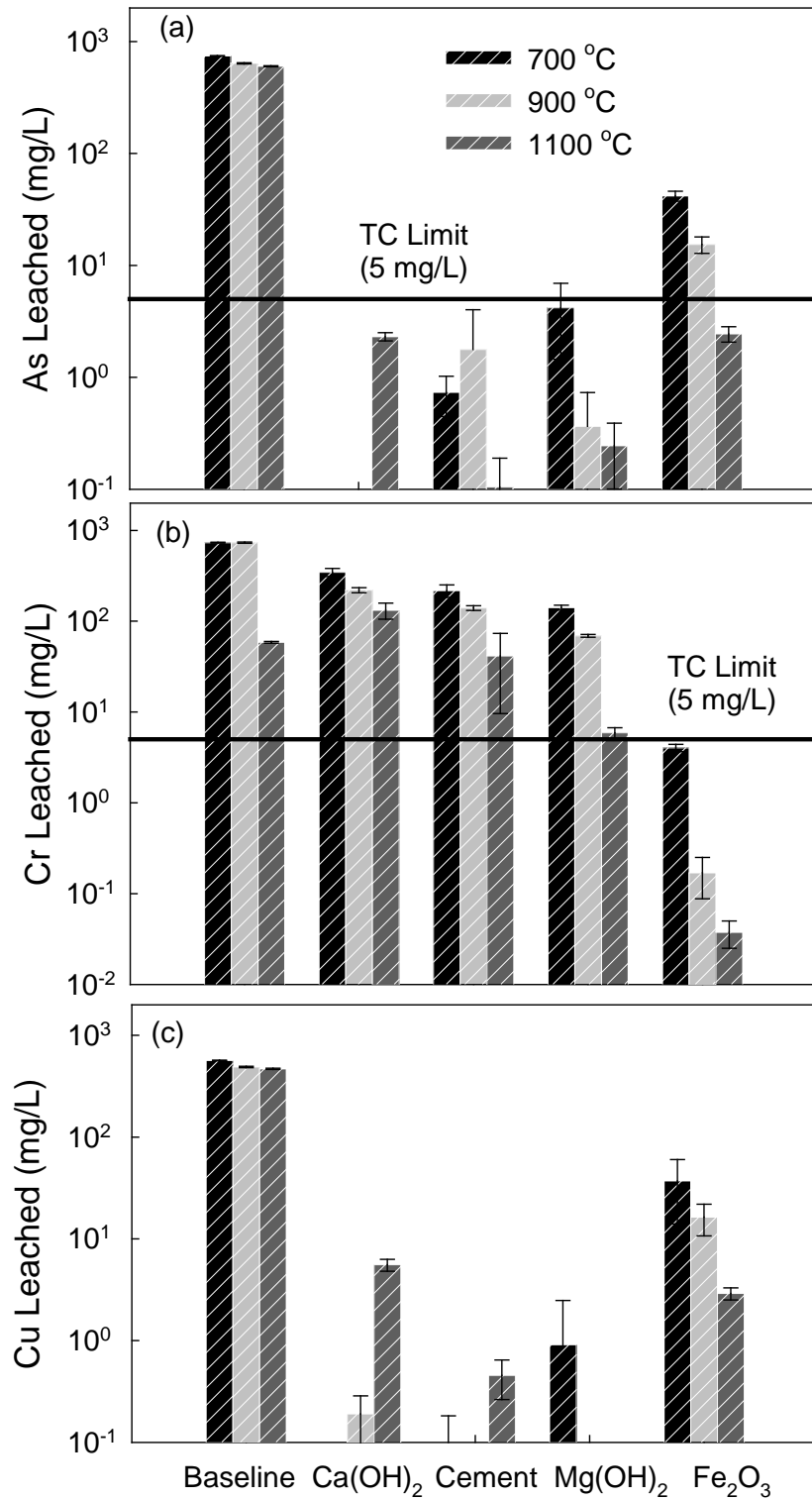
3.2. Volatilization Retention

Figure 2 shows the VR results. The baseline VR for arsenic for pure metal ash was very low, at around 6.3% at 700 ^{o}C, ~4.8% at 900 ^{o}C and ~4.7% at 1100 ^{o}C. These results are consistent with prior studies [30] that observed more volatilization of arsenic in CCA-treated wood with increasing temperatures. When sorbents were present, the retention increased to 20 – 40%. The results agree with prior studies [8] where an increase in retention was reported when $Ca(OH)_2$ was used.   For chromium, the baseline VR for pure metal ash was very low, at around 6.8% at 700 ^{o}C, 5.1% at 900 ^{o}C and 0.3% at 1100 ^{o}C. With sorbents, VR ranged from 5 – 60%. Cement, calcium hydroxide and magnesium hydroxide showed better retention than ferric oxide at 900 and 1100 ^{o}C. For copper, the baseline VR for pure metal ash was low, but higher than arsenic and chromium. For 700 ^{o}C, VR was at 16.8%; it was ~13% at 900 ^{o}C and ~12% at 1100 ^{o}C. With sorbents, retention was relatively higher at 30-60% across all temperatures. Ferric oxide showed the highest retention, above 40%, at all three temperatures.

Our experimental system wasn't optimized to maximize VR because the primary focus of the research was on retention by sorbents in the leachate. Since the temperature increase in our system was gradual, it is likely that some volatilization could have occurred during heating, before reaching the high temperature required for chemical reaction. Cuypers and Helsen [29] documented that increasing the heating rate resulted in a limited increase in arsenic retentions but resulted in greater retention for chromium. Hence, relatively low VR was observed, especially for chromium, as compared to other sorbent injection studies where the time taken to reach the designated temperature was very short. The values, thus, should be used to examine the trend only.
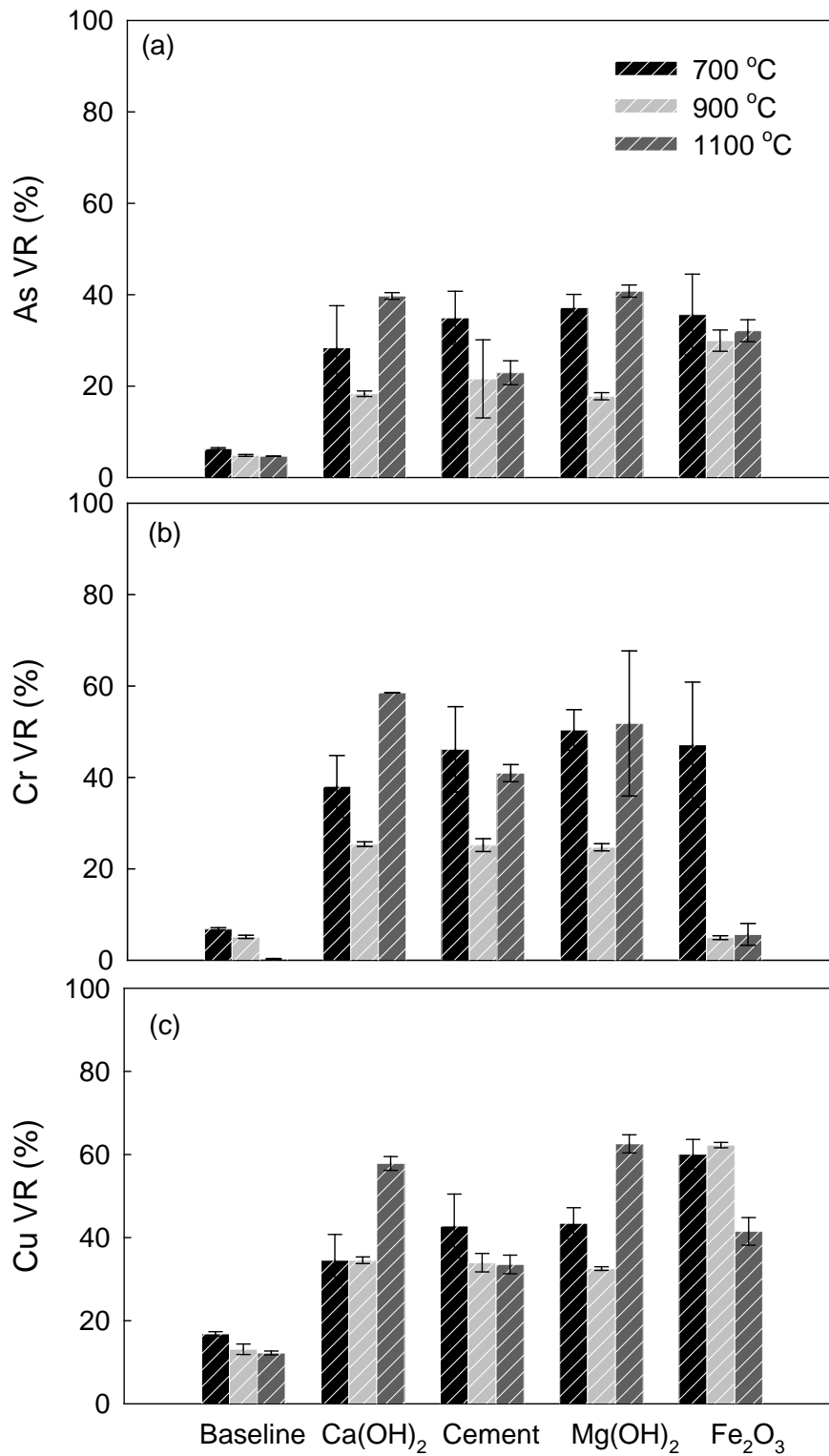
3.3. Leaching Retention

All sorbents showed a high LR, greater than 80%, at all three temperatures. In other words, in all the leaching scenarios encountered, the major portion of the CCA metals still remained in the ash. Here, very high LR, over

~98%, is required to maintain ash quality within permissible levels.

Figure 1: Leaching from sorbent-spike samples at different temperatures: (a) arsenic, (b) chromium, and (c) copper

Figure 2: Volatilization retention of sorbent-spike samples at different temperatures: (a) arsenic, (b) chromium, and (c) copper

Lower LR may be possible than those observed here for more realistic scenarios involving prolonged leaching.

Specifically, results show that for arsenic (Fig. 3a) the baseline LR was around 80% at all three temperatures. All alkali earth metal sorbents exhibited very high LR for arsenic at all temperatures, close to 100%. For chromium (Fig. 3b), the baseline LR was around 80% at all three temperatures. Ferric oxide showed excellent LR, close to 100% in most cases. No specific temperature dependence was observed for ferric oxide. For alkali earth sorbents, LR increased with an increase in temperature. For copper (Fig. 3c), the baseline LR was around 90% for all three temperatures. All sorbents exhibited excellent LR for copper at all temperatures, between 99-100% with alkali-earth sorbents exhibiting the highest LR. No specific temperature dependence was observed for any sorbent. Copper's strong affinity for formation of bi-metallic and metal-sorbent compounds could be a possible reason for such a high LR.

Mass balance calculations were performed to find out the distribution of metals between the leaching, volatilization and retention fractions for each metal-sorbent sample at different temperatures. The leaching fraction was typically much less than 1%; metal in ash varied from 5% - 40% in most cases; the remaining metal was in the form of volatiles, perhaps due to the relatively slow rate of temperature increase of the furnace system used in this study. Therefore, it can be concluded that the availability of leachable metals in the ash (the 2nd reason for leaching discussed in the previous section) is not the limiting factor for leaching for most samples. A notable exception corresponds to ferric oxide for chromium at 1100 ^{o}C where extremely low VR of CCA metals in the ash could have been the reason for the low leaching.

3.4. Speciation of Residual Ash

Since residual ash from our experiments was a complex mixture of a variety of compounds, qualitative analysis was performed as quantitative analysis was not possible. Identification of major metal-mineral compounds whose presence has been indicated by XRD (Table 1) shows that for arsenic, soluble compounds like $Cu_3(AsO_4)_2$, As_2O_5, and $Cu_2As_2O_7$ were formed, which might have contributed to the high leaching of arsenic and copper in the baseline and ferric oxide cases. On the other hand, insoluble compounds like $Ca_2As_2O_7$, $Ca_3(AsO_4)_2$, $MgHAsO_4$, etc. were formed from alkaline earth sorbents, which might have contributed to the low leaching of arsenic in those cases. Previous sorbent studies [8, 30] also reported the formation of these insoluble arsenic-alkaline earth compounds. Since the Cu-As compounds are more soluble while As-alkaline earth compounds are insoluble, the provision of alkaline earth sorbents into high-temperature system takes arsenic away from copper, thus reducing the leaching.

For chromium, compounds like $CuCr_2O_4$, Cr_2O_3, $Cr(OH)_3$, $CaCr_2O_4$, $CrO(OH)$, $FeCr_2O_4$, and $MgCr_2O_4$, were identified, which are insoluble (chromium is present as Cr(III)). They do not leach into the TCLP solution, therefore contributing to the low leachability of chromium from ferric oxide and magnesium hydroxide (for 1100 ^{o}C batch). On the other hand, in compounds like $MgCrO_4$, Cu_3CrO_6, $CuCr_2O_7 \cdot 2H_2O$, $CaCrO_4$, CrO_3 and $CuCrO_4$, chromium is present as Cr(VI) which is highly mobile. Their presence likely contributes to high chromium leaching when alkaline earth sorbents are applied.

Table 1: Summary of Speciation Characterization Results for CCA Spike-Sorbent Products from High-Temperature Reaction

Sorbent	Reaction Temperature		
	700 ^{o}C	**900 ^{o}C**	**1100 ^{o}C**
Ca(OH)$_2$	CuHAsO$_4$, **CaCrO$_4$.2H$_2$O**, Ca$_5$(AsO$_4$)$_3$.OH, **CuCrO$_4$**, CaHAsO$_4$.2H$_2$O, CaCu, CrAsO$_4$.xH$_2$O,**Ca$_3$(AsO$_4$)$_2$**	Ca$_5$(AsO$_4$)$_3$.OH, CaCu, Ca$_2$CuO$_3$, Cr$_2$O$_5$, **Ca$_3$(AsO$_4$)$_2$**, Ca$_5$(CrO$_4$)$_3$, **CaCrO$_4$**	CuHAsO$_4$, **CaCrO$_4$.2H$_2$O**, Ca$_5$(CrO$_4$)$_3$.OH, CaHAsO$_4$.2H$_2$O, CrAsO$_4$.xH$_2$O
Cement	Cu$_3$As, Cu$_4$(As$_2$O$_7$)O$_2$, **Ca$_2$As$_2$O$_7$, CaCrO$_4$, CaCr$_2$O$_4$, Cu$_3$(AsO$_4$)$_2$**	**Ca$_2$As$_2$O$_7$**, Ca$_5$(CrO$_4$)$_3$, **CuCrO$_4$**, CuAl$_2$O$_4$, CaCu$_2$O$_3$, Ca$_5$Cr$_2$SiO$_{12}$, Ca$_2$As$_3$, CaCuO$_2$	**Cu$_3$(AsO$_4$)$_2$, Ca$_2$As$_2$O$_7$**, Ca$_5$(CrO$_4$)$_3$, **CuCrO$_4$**, As$_2$O$_4$, Ca$_5$(CrO$_4$)$_3$, CaCu$_2$O$_3$, Ca$_5$CrSiO$_{12}$, Cu$_3$As, Ca$_2$As$_3$, CrO, Cu$_{9.5}$As$_4$, As$_2$O$_4$,**As$_2$O$_3$**,Al$_{13}$Cr$_2$, CaCrSi$_4$O$_{10}$
Fe$_2$O$_3$	**FeCr$_2$O$_4$**, Cr$_2$FeO$_2$, CuFe$_2$O$_4$, **Cu$_3$(AsO$_4$)$_2$**	**FeCr$_2$O$_4$**, Cr$_2$FeO$_2$, CuFe$_2$O$_4$, **Cu$_3$(AsO$_4$)$_2$**	Fe$_2$(AsO$_3$)$_4$, **FeCr$_2$O$_4$**, Cr$_2$FeO$_2$, Fe$_4$As$_2$O$_{11}$, CuFe$_2$O$_4$, **Cu$_3$(AsO$_4$)$_2$, CuCrO$_4$**
Mg(OH)$_2$	Cu$_2$MgO$_3$, CuHAsO$_4$, **MgHAsO$_4$, CuCr$_2$O$_7$.2H$_2$O**	Cu$_2$MgO$_3$, Cu$_2$O, **MgHAsO$_4$, Cu$_3$CrO$_6$**	**MgCrO$_4$, MgCr$_2$O$_4$**, Cu$_2$MgO$_3$, **MgHAsO$_4$.4H$_2$O**, Cu$_2$(AsO$_4$)OH.3H$_2$O
Spike (Baseline)	**Cr$_2$O$_3$, CrO$_3$**, CuAs$_2$O$_4$, **Cu$_3$(AsO$_4$)$_2$**, Cr$_4$As$_3$, **As$_2$O$_5$**, Cu$_2$As$_3$, CrAs$_2$, **Cu$_2$As$_2$O$_7$**	**Cu$_2$As$_2$O$_7$, Cu$_3$(AsO$_4$)$_2$**, Cr$_2$O$_5$, **CrO$_3$**, Cu$_2$As$_3$, Cr$_2$(AsO$_3$)$_4$, CuAs$_2$O$_4$, CuCrO$_2$, **CuCrO$_4$, CuCr$_2$O$_4$**, Cu$_9$As$_4$, Cu$_5$As$_2$, Cu$_3$As, Cr$_5$As$_3$, Cr$_2$(AsO$_4$)$_3$	**CrO$_3$**, Cr$_2$(AsO$_4$)$_3$, Cr$_2$(AsO$_3$)$_4$, CuAs$_2$O$_4$, **Cu$_3$(AsO$_4$)$_2$**, CrAs$_2$, **As$_2$O$_5$**, Cu$_5$As$_2$, CuO, **CuCrO$_4$**, Cu$_3$As

Note: Acid-Solubility data are available for compounds marked in bold and they are taken from The Handbook of Chemistry and Physics, 64th Edition, 1983-1984, CRC Pre

Copper leaching was likely controlled by a large variety of Cu-As/Cr and Cu-sorbent compounds that were formed. Some of them like Cu$_3$(AsO$_4$)$_2$, Cu$_2$As$_2$O$_7$, Cu$_3$CrO$_6$, CuCr$_2$O$_7$·2H$_2$O, and CuCrO$_4$ are soluble while others like CuCr$_2$O$_4$ are insoluble. Insoluble copper compounds may have dominated the products with alkaline earth sorbents, resulting in extremely low copper leaching from those sorbents. On the other hand, formation of a mixture of both soluble (e.g. Cu$_3$(AsO$_4$)$_2$) and insoluble compounds (e.g. CuCr$_2$O$_4$) may have contributed to the moderate leaching of copper from ferric oxide.

The baseline metal spike exhibited excessive leaching for all three CCA metals. This likely resulted from the

significant presence of soluble compounds in the product (e.g. $CuCrO_4$, $Cu_3(AsO_4)_2$, CrO_3). Matsumoto et al. [31] also reported the dominance of $Cu_3(AsO_4)_2$ in the ash from CCA-treated wood. Comparing the metal spike baseline with sorbent cases, an effective strategy to reduce the leaching of arsenic and copper is to provide alkaline earth sorbents that can block the binding of arsenic with copper. However, the use of alkaline earth sorbents is not beneficial if chromium is present. They take up arsenic and at the same time redirect copper to chromium for the formation of some soluble Cu-Cr compounds. Ferric oxide has strong affinity with chromium but weaker affinity with arsenic and copper. Hence, its addition results in the formation of insoluble compounds like $FeCr_2O_4$ while not affecting the binding of As-Cu compounds.

3.5. pH Effects

Several past studies [11, 12, 14, 24, 28, 32] have reported the impact of leachate pH on metal leaching in CCA sawdust samples and metal speciation has been observed to play a role in the leaching of metals from CCA-treated wood ash samples. As the relationship between pH and leachate concentrations helps explain some of these observations, the relationship was analyzed and is presented in Figure 4. In general, a high leachate pH (>9) was exhibited by alkaline earth based sorbents (Figure 4a). Ferric oxide leachate pH was typically in the range of 4-6, which is similar to the baseline results. Overall, the leaching of arsenic and copper was higher at lower pH values (pH = 4-6) and very low leaching at high pH (9-12) (Fig. 4b). A possible reason for the 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 the speciation section. At higher pH, the formation of non-leachable arsenic-alkaline earth compounds are likely responsible for the low leaching. In contrast, very high chromium leaching was encountered in the high pH range (pH = 10-12) while much lower leaching was observed at low pH (4-6). High chromium leaching at high pH could be due to the formation of Cr(VI) in alkaline conditions as reported in previous studies [14]. Townsend et al. [12] studied the impact of leachate pH on metal leaching in various CCA sawdust samples and also concluded that it was a contributing factor in metal leachability. Arsenic speciation was observed to play a role in the leaching of arsenic from CCA-treated wood ash samples, with higher ratios of arsenic (III) for ash samples exhibiting higher levels of arsenic in leachates [32].
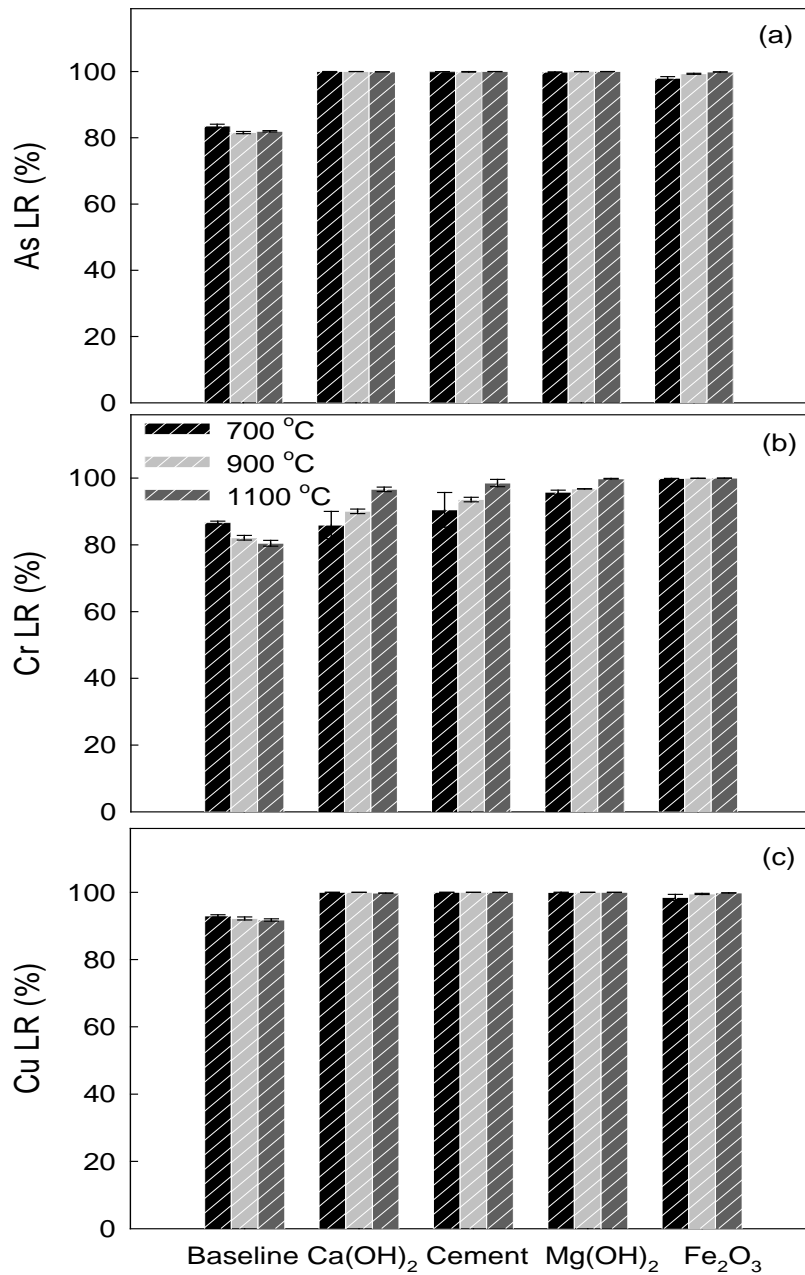
3.6. Leaching Correlation

Correlation plots of As-Cr, As-Cu, and Cr-Cu pairs show that the only observable correlation was the As-Cu pair (Figure 5) for baseline and ferric oxide cases. A possible reason for this strong correlation is the formation of compounds like $Cu_3(AsO_4)_2$ (which are soluble) as key products. When alkaline earth sorbents were present, no observable As-Cu correlation could be seen. It should be noted that data points at very low concentration, which belong to alkaline-earth sorbents, may not be reliable for correlation analysis. The results further support the previous finding that compounds like $Ca_3(AsO_4)_2$ and $Ca_2As_2O_7$ are the dominant species and the presence of alkaline earth sorbents blocks As-Cu binding.

4. Discussion

Baseline (spike): As evidenced by results for all three metals, high leaching and conversely low leaching

retention was observed at all temperatures. Speciation results indicate that the formation of soluble hexavalent chromium compounds, such as CrO_3, could have resulted in the excessive Cr leaching, whereas the formation of soluble Cu-As compounds (e.g. $Cu_3(AsO_4)_2$ and $Cu_2As_2O_7$) could have contributed to the excessive Cu and As leaching. While other compounds such as Cr_2O_3 were also identified, soluble (hexavalent Cr, Cu-As) compounds were formed under baseline conditions compared to sorbent added scenarios. This hypothesis is further reinforced by the good Cu-As leaching correlation and the poor correlation between Cr and the other two metals.


Figure 3: Leaching retention from sorbent-spike samples at different temperatures: (a) arsenic, (b) chromium, and (c) copper
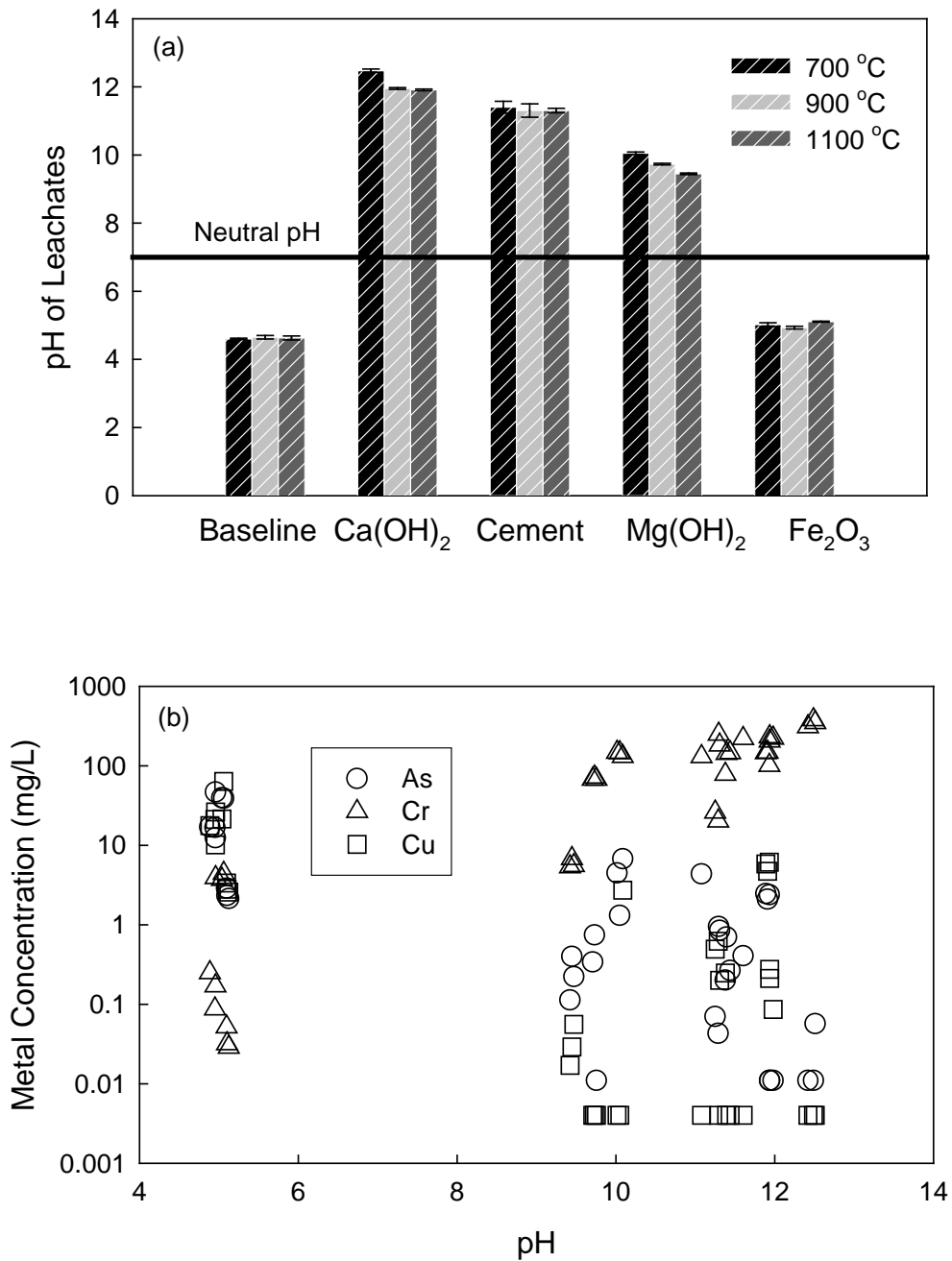
Figure 4: Leachate pH for different sorbent-spike products from high-temperature reaction; **(b)** Correlation between leachate pH and metal concentration in leachate

$\underline{Fe_2O_3}$: This sorbent manifests low leaching for Cr at all temperatures and for As and Cu at high temperatures. It appears that Fe has a relatively stronger affinity for Cr than for As and Cu. Therefore, when added to the system, it first takes up Cr before the other two metals. This is supported by the presence of $FeCr_2O_3$ and other Fe-Cr compounds in the product spectrum and the low leaching of Cr at all the three temperatures. It also appears that the propensity of forming Fe-Cu and Fe-As compounds increases with temperature. Therefore, at lower temperatures, compounds like $Cu_3(AsO_4)_2$ and $Cu_2As_2O_7$, etc. are formed due to Cu-As binding and in the

relative absence of Fe binding as explained above, resulting in the high leaching of Cu and As which is supported by a good leaching correlation between Cu-As. At 1100 °C, after combining with all the available Cr in the system, the remaining Fe binds with As and Cu forming compounds like $CuFe_2O_4$ and $Fe_2(AsO_3)_4$resulting in lower leaching of those metals at 1100 °C.
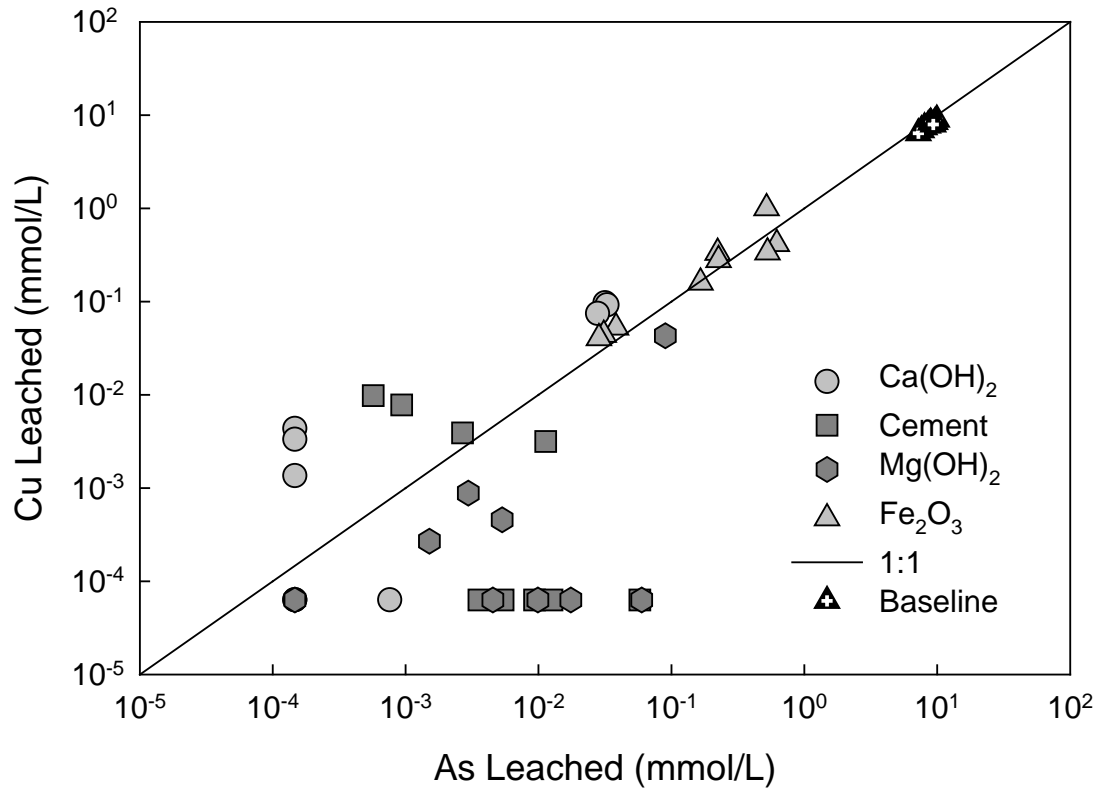
Figure 5: Leaching correlations for arsenic and copper concentrations in leachate

Ca(OH)$_2$ and Cement: Results for Ca-based sorbents were similar and exhibit very low leaching for As and Cu and very high leaching for Cr at all three temperatures. Ca has the preference to bind with As to predominantly form insoluble compounds like $Ca_3(AsO_4)_2$ explaining the low leaching and better retention for As. It appears that Ca also preferentially binds with Cr, forming hexavalent Ca-Cr compounds such as $CaCrO_4$ in abundance, which are soluble and resulted in higher Cr leaching. While several Cu-As, Cu-Cr, and Cu-Ca compounds were formed, the product spectrum for Cu compounds is likely dominated by insoluble Cu-Ca compounds like $CaCu_2O_3$ as evidenced by low Cu leaching (therefore implying that either the Cu-Cr compounds formed are insoluble or minimal) and poor As-Cu correlation (implying those compounds are not formed in abundance).

Mg(OH)$_2$: Results for Mg(OH)$_2$ were similar to the calcium based sorbents suggesting that alkaline earth metals perform comparably for volatilization and leachate retention. Results show, similar to the calcium-based sorbents, that Mg exhibits very low leaching for As and Cu at all three temperatures. For Mg, the LR of Cr at

1100°C was better than that for the calcium sorbents, bringing the leachate concentrations closer to meeting TC limits. As with Ca, the propensity for formation of Mg-As compounds such as $MgHAsO_4$ is higher, and the predominant Mg-As compounds are insoluble, resulting in low leaching of As. Similarly, formation of Cu-Mg compounds like Cu_2MgO_3 results in low leaching for Cu. For Cr, it appears that Mg has low affinity for binding with it except at 1100°C, as indicated by the absence of Mg-Cr compounds in the speciation results at low temperatures. At 1100 ^{o}C, the formation of trivalent Cr compounds like $MgCr_2O_4$ increased the retention of Cr and reduced its leaching.

5. Conclusions and Implication

Laboratory scale experiments were conducted to evaluate various sorbent materials for their capability to retain these metals in the ash by reducing leachability of CCA metals. The formation of thermally stable and insoluble compounds is the core value of the sorbent technique. Alkaline earth based sorbents were demonstrated to be very effective in reducing the leaching of arsenic and copper, while ferric oxide was better for chromium. All sorbents tested also exhibited significantly improved VR of the CCA metals in the ash. Product speciation plays an important role in determining the fate of the metals. Various sorbent-metal and bimetallic compounds were identified by XRD. As-Cu compounds contributed to higher leaching of both metals. The provision of alkaline earth sorbents was shown to block the As-Cu binding. Leachate pH served as a good indicator for predicting the leaching behavior of these metals. Chromium's leaching level was low at low pH while arsenic and copper leached less at high pH.

The knowledge learned from this study provides useful information in establishing effective strategies for implementing the technology. CCA metals are volatile and tend to stay in the gas phase at high temperatures (> 1000 ^{o}C). A combination of sorbents can be used to effectively control the leaching of CCA metals, e.g., using cement in the flue gas to capture arsenic and providing ferric oxide in the feed to bind chromium. Another possible alternative could include use of ferric oxide at low temperatures (e.g. 700 ^{o}C) or magnesium hydroxide at high temperatures (~1100 ^{o}C) to capture all three CCA metals simultaneously, both in the feed and gas phase.

Co-incineration has been identified to be one of the best available thermal processes in the short term for the treatment of CCA-treated wood [33]. Choosing a suitable co-fuel based on the knowledge of metal-sorbent interactions can result in effective control of the leaching and volatilization of CCA metals. For instance, many 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 present in the system can scavenge arsenic in the gas phase [34]. 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. Municipal solid waste, having some constituents similar to the test sorbent materials, may also be a suitable co-fuel for CCA-treated wood. All these facilities are usually equipped with particulate control devices like ESPs and baghouses. Therefore, no additional air pollution control devices would be required.

With the growing awareness regarding the hazardous effects of arsenic treated wood and the residential phase of CCA in 2004, there has been a shift to copper based preservatives like ACQ (Alkaline Copper Quaternary) and

CBA (Copper Boron Azole) for wood treatment [2]. However, leaching of copper from these alternative formulations has been reported to be much higher than that for CCA treated wood [35, 36]. Most of the sorbents examined in this study (i.e., alkaline-earth) exhibit low leaching for copper, suggesting they may be applicable to the incineration of alternative copper treated wood. More research is recommended to evaluate the effectiveness of the sorbents utilizing CCA-treated wood, as well as the new copper based alternatives. These sorbents should be evaluated individually and in combinations to confirm their ability to retain all three metals in ash generated from treated wood products.

Acknowledgements

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