

Impact on Leaching & Retention of Metals from High Temperature Reaction of CCA Metals with Alumino-Silicate Sorbents

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Abstract

Past studies have shown that many alumino-silicate mineral sorbents are effective in controlling heavy metal emission during incineration. The objective of this study was to identify Al-Si based mineral sorbents that can minimize leaching of heavy metals from the incinerator ash of Chromated Copper Arsenate (CCA-) treated wood. Experiments were carried out using CCA metal spikes combined with Al-Si sorbents, heated to 700 °C, 900 °C and 1100 °C for 30 minutes. The residual ash was leached using the toxicity characteristic leaching procedure (TCLP). X-Ray Diffraction (XRD) analysis was conducted to determine the crystalline speciation of the products. Results showed that low leaching was observed for chromium, below the 5 mg/L TC limit, by alumina and silica at all temperatures, and kaolin at higher temperatures (900 °C and 1100 °C). For copper, all sorbents displayed low leaching values (< 51 mg/l) as compared to the baseline. For arsenic, all sorbents exceeded the TC limit. Speciation characterization results revealed the formation of several metal-metal and metal-mineral compounds that might have resulted in different leaching behaviors of each metal-sorbent pair under different combustion conditions. The results suggest that a combination of sorbents at different stages of the combustion process can be effective to control the leaching of CCA metals.

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Keywords: Source Modification; Chromium; Copper; Wood Preservative; Incineration; Adsorption; Leachate Management.

1. Introduction

Chromated copper arsenate (CCA) has a history of use as a popular wood preservative for pressure treated wood, and was widely used for decks, mailbox and light posts, swing sets, playscapes, picnic tables, landscape ties, underwater dock pilings, ocean-side boardwalks, telephone utility poles and residential building foundations [1]. Up until 2004, CCA-treated wood represented 90% of the U.S. waterborne preservative market [2, 3, 4]. Although the use of CCA chemical for residential purposes was phased out in 2004, CCA-treated wood still had a market share of about 30% in the waterborne treated wood market [5]. The peak disposal quantities of CCA-treated wood in the U.S. occurred in 2008 at 660 thousand cubic meters, but it is estimated that the disposal volume will still remain at 290 thousand cubic meters in 2040 [6]. Unless managed properly, these large volumes can have a significant impact on the environment [7].

Recycling of wood from construction and demolition debris, along with other wood wastes is common [8, 9]. Energy recovery is the primary disposal pathway for recycled wood waste as it leads to significant volume reduction as well as provides a way to convert waste to energy [8, 10]. It is estimated that more than 50% of CCA-treated wood waste is burned in waste-to-energy plants in the state of Florida [11,12]. However, incineration can pose serious health and environmental problems due to potential volatilization of metals at high temperature as well as leaching of metals in ash; arsenic and chromium leaching from wood ash, beyond TC limits, has been reported in the past [3,13].

Research studies have shown the potential of injecting alumino-silicate based mineral sorbents in combustion systems for controlling heavy metals [14, 15, 16, 17]. These studies have focused on coal combustion processes; however, not much work has been done on CCA wood combustion using these sorbents. Little is known about the characteristics of Al-Si sorbent-CCA metals mixture ash in combustion systems and the reason for the variation in leaching behavior with different alumino-silicate sorbents.

The objective of this study was to evaluate the utility of alumino-silicate sorbents for CCA-treated wood disposal by investigating CCA metals and alumino-silicate sorbent interaction at high temperatures, the results of which may be applicable to several thermal processes. A series of alumino-silicate sorbents were tested with CCA metals, and the leaching and speciation characteristics of the products were studied. The goal was to determine the most suitable alumino-silicate sorbents and optimal operating conditions for controlling metal leaching in high-temperature conditions simulating CCA-treated wood incineration, to guide their safe disposal.

2. Experimental

2.1 Materials

Three main criteria were identified to shortlist sorbents for these experiments: i) ability to reduce leaching and enhance gas phase capture against CCA metals based on past studies, ii) low cost, and iii) readily available so that they can be used on an industrial scale. Out of the wide array of sorbents in the Al-Si sorbent spectrum, the sorbents shown in Table 1 were shortlisted for further investigation based on a comparison of their relative performance in retaining CCA metals [15, 16, 17]. The sorbent materials chosen belong to two categories: i) pure chemicals like alumina and silica, in order to understand the pure metal-chemical interaction, and ii) minerals like attapulgite clay, diatomaceous earth, and kaolin, in order to evaluate readily available minerals for practical applications.

Table 1: List of Al-Si Sorbents Used in Experiments

Name of Sorbent	Chemical formula	Molecular Weight (g)	CAS #
Alumina	Al_2O_3	102.0	1344-28-1
Attapulgite Clay*	$\text{Si}_{16}\text{MgH}_{3.6}\text{O}_{5.9}$	167.7	–
Diatomaceous Earth*	$\text{Si}_{106}\text{Al}_{4.6}\text{Ca}_{0.3}\text{Mg}_{0.5}\text{Fe}_2\text{O}_{229.5}$	7119.7	61790-53-2
Kaolin	$\text{H}_2\text{Al}_2\text{Si}_2\text{O}_8\text{-H}_2\text{O}$	258.2	1332-58-7
Silica	SiO_2	60.1	7631-86-9

* The formula and molecular weight are approximates based on % composition. Varies according to mineral composition

In this study, pure chemicals containing CCA metals were used to provide a fundamental baseline to understand the nature of interaction between sorbents and CCA metals as well as obtain data regarding leachability and speciation of CCA metals on application of sorbents. A metal spike was prepared containing all the three CCA metals in the same mass ratio as the CCA Type C chemical [18]. Arsenic oxide (As_2O_5), chromium nitrate nonahydrate ($\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) and copper nitrate hydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$) were used as they are readily soluble in water. Metal concentration in the spike sample was: 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

First, various sorbents of 20 g each were mixed with 50 mL metal spike in 75 mL porcelain crucibles. This quantity was chosen because completing the various analyses such as leaching and digestion tests requires a minimum of 15 g of materials. Each sorbent-spike sample was prepared in triplicate. The samples were first heated in a muffle furnace (Fisher Isotemp Programmable Forced Draft Furnace, Models # 10-750-58 and 10-

750-126) at ~90 °C (below water's boiling point) for 14 hours to evaporate the water so as to minimize losses due to boiling. The furnace was then raised to the designated temperature of 700, 900 or 1100 °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 combustion facilities in industrial boilers. Herein, the capacity of the furnace (maximum possible temperature of 1125 °C) determined the upper limit for temperatures that were tested. It should be noted that many prior studies have already reported the effectiveness of sorbents in capturing metals in high-temperature combustion systems, and therefore the focus of this study was to examine the impact of the metal-sorbent interaction on leachability. As such, the system was not designed to minimize volatilization during heating. XRD analysis was performed to obtain information regarding possible product speciation in the residue. Amongst the large variety of compounds identified, information regarding solubility was available for a few. Such information is of interest as soluble compounds are likely to leach out during TCLP tests.

2.3 Analyses

The residue was extracted from crucibles and was ground to powdered form using a coffee grinder (Kitchen Aid BCG1000B Onyx Black Coffee Grinder). A portion of the residue was leached following the TCLP procedure as described in EPA SW 846 Method 1311 [19]. After each sample was thoroughly mixed, 10 g of the sample were transferred to a 250 mL polyethylene container using an acid-rinsed spoon, wherein 200 mL of the appropriate extraction fluid were added to the container resulting in the 20:1 liquid/solid ratio consistent with the standard method. 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 and stored below 4 °C until analysis. Two different types of extraction fluids were used in the TCLP procedure. Extraction fluid 1 (pH= 4.93 ± 0.05) was used when the pH of the product was less than 5. For samples that had a pH > 5, extraction fluid 2 (pH= 2.88 ± 0.05) was used. For each sample, 50 mL of TCLP leachate was liquid digested following the procedures described in EPA SW 846 Method 3010 A [19].

A portion of the metal spike residue was digested for the total metal content analysis following the solid digestion method as described in EPA SW 846 Method 3050 B [19]. All digested samples were analyzed using Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-AES) as described in EPA SW 846 Method 6010B to determine the metal content in the two digestates. The % spike recovery from digested samples was between 80-120% of the original samples.

X-Ray Diffraction (XRD, Phillips APD 3720) analysis of the residue was conducted to determine the crystalline speciation of the products. The operating conditions of the XRD were: 2θ - 10-70 degrees; sample rotation step size - 0.02 degree; time step - 0.5 s or 1 s. *PC Identify* software was used to determine the compounds corresponding to the peaks observed in the XRD pattern. 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. Equilibrium between the electrode and sample was established by gently stirring the probe in the leachate sample. Readings were obtained with a resolution of 0.001 pH.

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

$$VR = \frac{\text{mass of CCA metal in 'sorberent - spike' ash}}{\text{mass of CCA metal in spike}} \times 100\% \quad (1)$$

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

$$LR = \frac{\text{mass of CCA metal in ash} - \text{mass of CCA metal in leachate}}{\text{mass of CCA metal in ash}} \times 100\% \quad (2)$$

3. Results

3.1. TCLP Leaching Results

Results of TCLP leaching for each metal are illustrated in Figure 1. The baseline leaching of chromium from pure metal spike ash was very high, at around 730 mg/L at 700 °C and 900 °C and ~58 mg/L at 1100 °C (Fig. 1). All the sorbents showed reduction in leaching level for chromium. Alumina and silica leached less than the TC limit of 5 mg/L of chromium at all three temperatures. Kaolin and diatomaceous earth leached less than the TC limit for chromium at 900 °C and 1100 °C. All sorbents exhibited an inverse temperature relationship with respect to leaching, i.e., leaching decreased with an increase in reaction temperature.

For arsenic, the baseline leaching was at around 750 mg/L at 700 °C, ~640 mg/L at 900 °C and ~600 mg/L at 1100 °C (Fig. 1). All the sorbents showed some reduction in leaching level for arsenic, but they still leached more than the TC limit of arsenic (5 mg/L) at all three temperatures. For 700 °C and 900 °C batches, arsenic leaching broadly followed the following trend: alumina, silica < diatomaceous earth < kaolin < attapulgite clay. Except diatomaceous earth, all sorbents exhibited lower arsenic leaching at 1100 °C.

For copper, the baseline leaching was around 570 mg/L at 700 °C, 490 mg/L at 900 °C and ~470 mg/L at 1100 °C (Fig 1c). Since copper is not considered hazardous for its toxicity characteristic, there is no TC limit for it. However, its excessive leaching can harm aquatic ecosystems and therefore warrants monitoring [20]. All the sorbents showed low leaching (< ~50 mg/L) for copper. Alumina exhibited a decrease in leaching with an increase in temperature. No specific temperature dependence trend was exhibited by other sorbents.

3.2. Volatilization Retention

The baseline VR for chromium was very low, at around 6.3% at 700 °C, ~4.8% at 900 °C and ~4.7% at 1100 °C (Figures 2(a), 2(b) & 2(c)). With sorbents, VR ranged from 0 – 33%. All sorbents had a very low VR at 1100 °C. All alumino-silicate sorbents exhibited inverse temperature dependence, i.e., VR decreased with an increase in temperature. The baseline VR for arsenic was also very low, at around 6.3% at 700 °C, ~4.8% at 900 °C and ~4.7% at 1100 °C. With sorbents, the retention ranged from 20 – 40%. No specific temperature dependence

trends were observed. The baseline VR for copper was low, but higher than arsenic and chromium. VR for copper was at 17% for 700 °C, ~13% at 900 °C and ~12% at 1100 °C. With sorbents, all tests showed moderate to good VR for copper, 20-60%, across all temperatures. No specific temperature dependence trend was observed for any sorbent or group of sorbents.

Since LR was our primary focus, our experimental system wasn't optimized to maximize VR. Therefore, some volatilization losses might have occurred during heating, before reaching the high temperature required for chemical reaction. Hence, relatively low VR was observed in the current study as compared to other sorbent injection studies [21] wherein the time taken to reach the designated temperature was very short. The values, therefore, should be used to examine the trend only.

3.3. Leaching Retention

Figure 3 shows the LR results for these sorbents. The baseline LR for arsenic, chromium and copper was around 80%, 80% and 90%, respectively at all three temperatures. All sorbents exhibited a high LR at all the three temperatures for arsenic (80-100%), chromium (80-100%) and copper (90-100%). Here, it should be kept in mind that very high LR, over ~98%, is required to leach metals below permissible levels. Lower LR may be possible than those observed here for more realistic scenarios involving prolonged leaching. Alumina, kaolin and silica showed excellent LR for chromium, close to 100% in some cases. However, no specific temperature dependence was observed for all metals. Copper's strong affinity for formation of bi-metallic and metal-sorbent compounds, as evidenced from speciation results (Table 2), could be a possible reason for such a high LR. This illustrates that in all the leaching scenarios encountered, a significant portion of the CCA metals still remained in the ash.

Table 2: Summary of Speciation Characterization Results for CCA Spike-Sorbent Products from High-Temperature Reaction

Sorbent	700 °C	900 °C	1100 °C
Alumina	CuAlO ₂ , Cu₃(AsO₄)₂ , CuCr₂O₄ , Cr ₂ (AsO ₃) ₄ , Cr ₅ O ₁₂ , Cr₂O₃	Cu ₄ (As ₂ O ₇)O ₂ , CuAlO ₂ , Cu₃(AsO₄)₂ , CuCr₂O₄ , CuCrO₄ , Cr ₂ (AsO ₃) ₄ , CuAs ₂ O ₄ , AlAsO₄ , Cr₂O₃ , Cu ₃ As	CuAlO ₂ , Cu₃(AsO₄)₂ , CuCr₂O₄ , Cr₂O₃ , Cr ₄ As ₃ , As₂O₅ , AlAsO₄ , CuAs ₂ O ₄ , Cu ₃ As
Attapulgite Clay	Cu ₃ (AsO ₄) ₂ ·(OH) ₃ , Cu ₃ (AsO ₄) ₂ ·(OH), MgCrO₄ , Mg(H ₂ AsO ₄) ₂ ·H ₂ O, CrO(OH) , Mg ₃ Cr ₂ (SiO ₄) ₃	Cu₃(AsO₄)₂ , Cr ₂ (AsO ₃) ₄ , CrO(OH) , Cu ₅ (AsO ₄) ₂ ·(OH) ₄ , Cr₂O₃ , Cu ₅ As ₂ , Cu ₂ (AsO ₄)OH, Mg ₃ (AsO ₄) ₂	Cu ₅ (AsO ₄) ₂ ·(OH) ₄ , Cu₃(AsO₄)₂ , Cu ₂ MgO ₃ , As₂O₅ , CuMgSi ₂ O ₆ , Cu ₂ (AsO ₄)OH, MgCrO₄ , Cr₂O₃
Diatomaceous Earth	Cr₂O₃ , CuCrO ₂ , Cu₃(AsO₄)₂ , CrFeAs ₂ , Cr ₂ SiO ₄ , Cu ₃ As, CuFe ₂ O ₄ , AsCu ₉	Fe ₃ AsO ₇ , CuCr₂O₄ , Cu ₂ As ₃	Fe ₃ AsO ₇ , Cr₂O₃ , As₂O₅ , CuCrO ₂ , Cu ₂ As ₃ , Cu₃(AsO₄)₂ , CrFeAs ₂ , AsCu

Kaolin	Cr₂O₃ , CrO(OH), Cu ₅ (AsO ₄) ₂ ·(OH) ₄ , Cu ₂ (AsO ₄)OH, Cu ₂ (OH) ₂ (CrO ₄)	As ₂ O ₄ , AlAs, CuCr₂O₄ , Cu ₄ (As ₂ O ₇)O ₂ , Al(H ₂ AsO ₄)·H ₂ O, Cu ₅ (AsO ₄) ₂ ·(OH) ₄ , Cr(OH)₃	Cu ₅ (AsO ₄) ₂ ·(OH) ₄ , Cr₂O₃ , CrO(OH) , CrO₃ , Cr ₅ O ₁₂ , Cu ₂ (AsO ₄)OH
Silica	As₂O₅ , Cu ₅ As ₂ , Cu _{9.5} As ₄ , Cu₃(AsO₄)₂ , Cr₂O₃ , Cr ₂ (AsO ₃) ₄ , CuAs ₂ O ₄	SiAs ₂ , Cu₂As₂O₇ , CuCr₂O₄ , Cr₂O₃ , Cr ₂ (AsO ₃) ₄ , CuAs ₂ O ₄	Cu ₅ As ₂ , Cr₂O₃ , CrO₃ , Cr ₂ (AsO ₃) ₄ , CuAs ₂ O ₄
Spike	Cr₂O₃ , CrO₃ , CuAs ₂ O ₄ , Cu₃(AsO₄)₂ , Cr ₄ As ₃ , As₂O₅ , Cu ₂ As ₃ , CrAs ₂ , Cu₂As₂O₇	Cu₂As₂O₇ , Cu₃(AsO₄)₂ , Cr ₂ O ₅ , CrO₃ , Cu ₂ As ₃ , Cr ₂ (AsO ₃) ₄ , CuAs ₂ O ₄ , CuCrO ₂ , CuCrO₄ , CuCr₂O₄ , Cu ₉ As ₄ , Cu ₅ As ₂ , Cu ₃ As, Cr ₅ As ₃ , Cr ₂ (AsO ₄) ₃	CrO₃ , Cr ₂ (AsO ₄) ₃ , Cr ₂ (AsO ₃) ₄ , CuAs ₂ O ₄ , Cu₃(AsO₄)₂ , CrAs ₂ , As₂O₅ , Cu ₅ As ₂ , CuO, CuCrO₄ , Cu ₃ As

Acid-Solubility data is available for compounds marked in bold. All acid-solubility data has been taken from *The Handbook of Chemistry and Physics*, 64th Edition, 1983-1984, CRC Press

Mass balance calculations showed that the leaching fraction was typically less than 1%. Metal in ash varied from 1% - 40% in most cases and the remaining metal was in the form of volatiles. No trends were observed except for chromium with alumina and silica at 1100 °C, where almost all of chromium was in the volatile fraction. This may have led to a low availability of Cr for leaching at that temperature, hence explaining the leaching trends for that case.

3.4. Speciation of Residual Ash

Metal-mineral compounds whose presence has been indicated by XRD are shown in Table 2. For chromium, compounds like CuCr₂O₄, Cr₂O₃, etc. were formed, which are insoluble (chromium is present as Cr(III)). They may not leach out of the TCLP solution, thereby contributing to the low leachability of chromium from alumino-silicates (e.g. alumina at 700 °C). On the other hand, in compounds like MgCrO₄, CrO₃ and CuCrO₄, chromium is present as Cr(VI), which is highly mobile and may have contributed to high chromium leaching [22] for some sorbent cases, e.g. attapulgite clay at 700 °C and baseline at 900 °C.

For arsenic, compounds like Cu₃(AsO₄)₂, As₂O₅, Cu₂As₂O₇, etc. were formed, which are soluble, and hence may have contributed to the high leaching of arsenic and copper in the system (e.g. baseline and attapulgite clay at 900 °C). Although insoluble compounds like AlAsO₄ was identified, all aluminum-based sorbents exhibited high arsenic leaching; hence, these insoluble compounds were likely to have been minor reaction products.

For copper, a large variety of metal-metal and metal-mineral compounds were formed. Solubility information is available regarding only a few. Some of them like Cu₃(AsO₄)₂, Cu₂As₂O₇, Cu₃CrO₆, CuCr₂O₇·2H₂O, and CuCrO₄ may be soluble while others like CuCr₂O₄ may be insoluble. It is likely that the formation of a mixture of both soluble (e.g. Cu₃(AsO₄)₂) and insoluble compounds (e.g. CuCr₂O₄) may have contributed to the moderate leaching of copper upon application of alumino-silicate sorbents. The metal spike exhibited excessive

leaching for all three CCA metals. This might have resulted from the dominance of soluble compounds in the product (e.g. CuCrO_4 , $\text{Cu}_3(\text{AsO}_4)_2$).

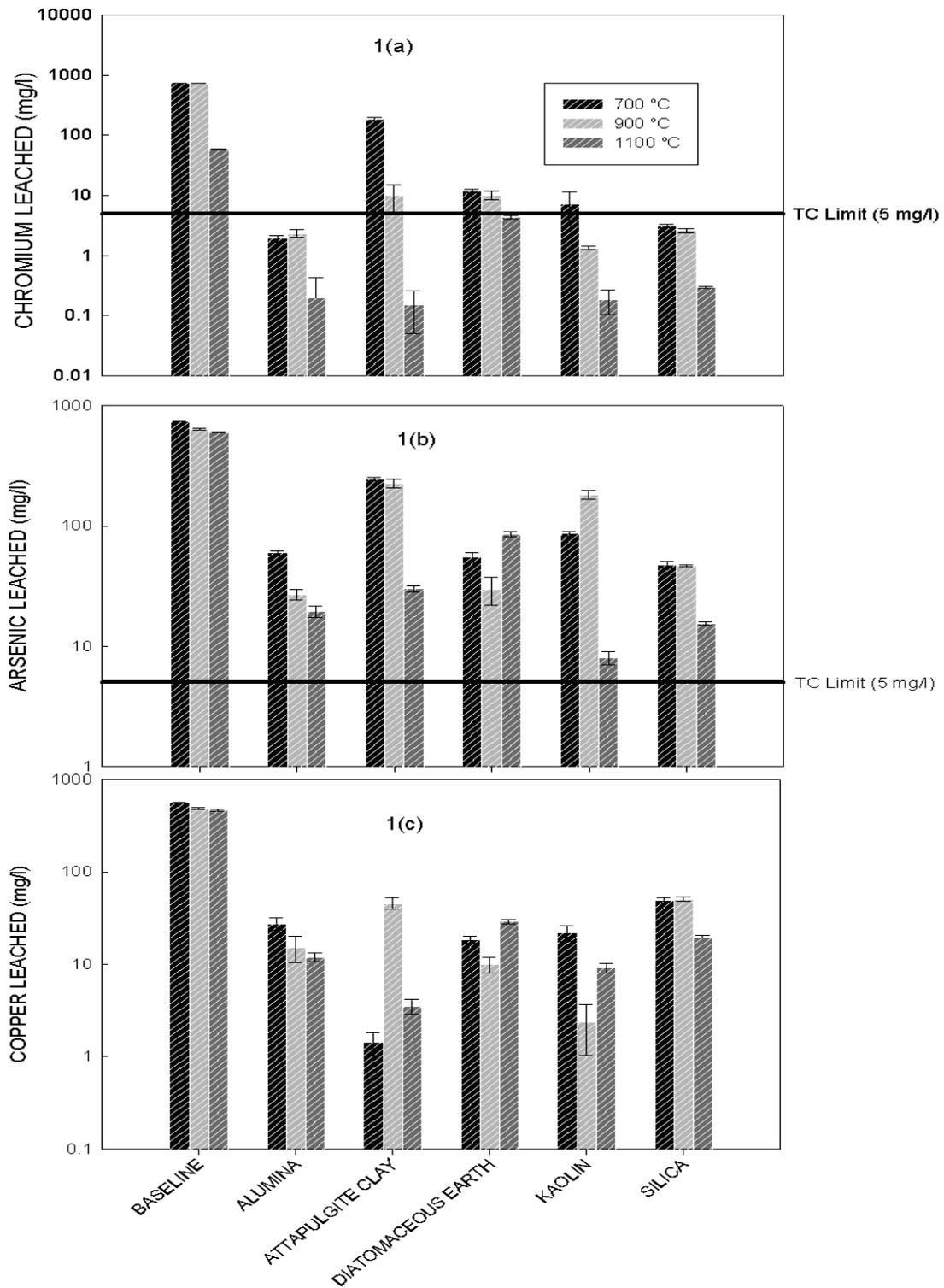


Figure 1: Leaching from sorbent-spike samples at different temperatures: (a) arsenic, (b) chromium, and (c) copper

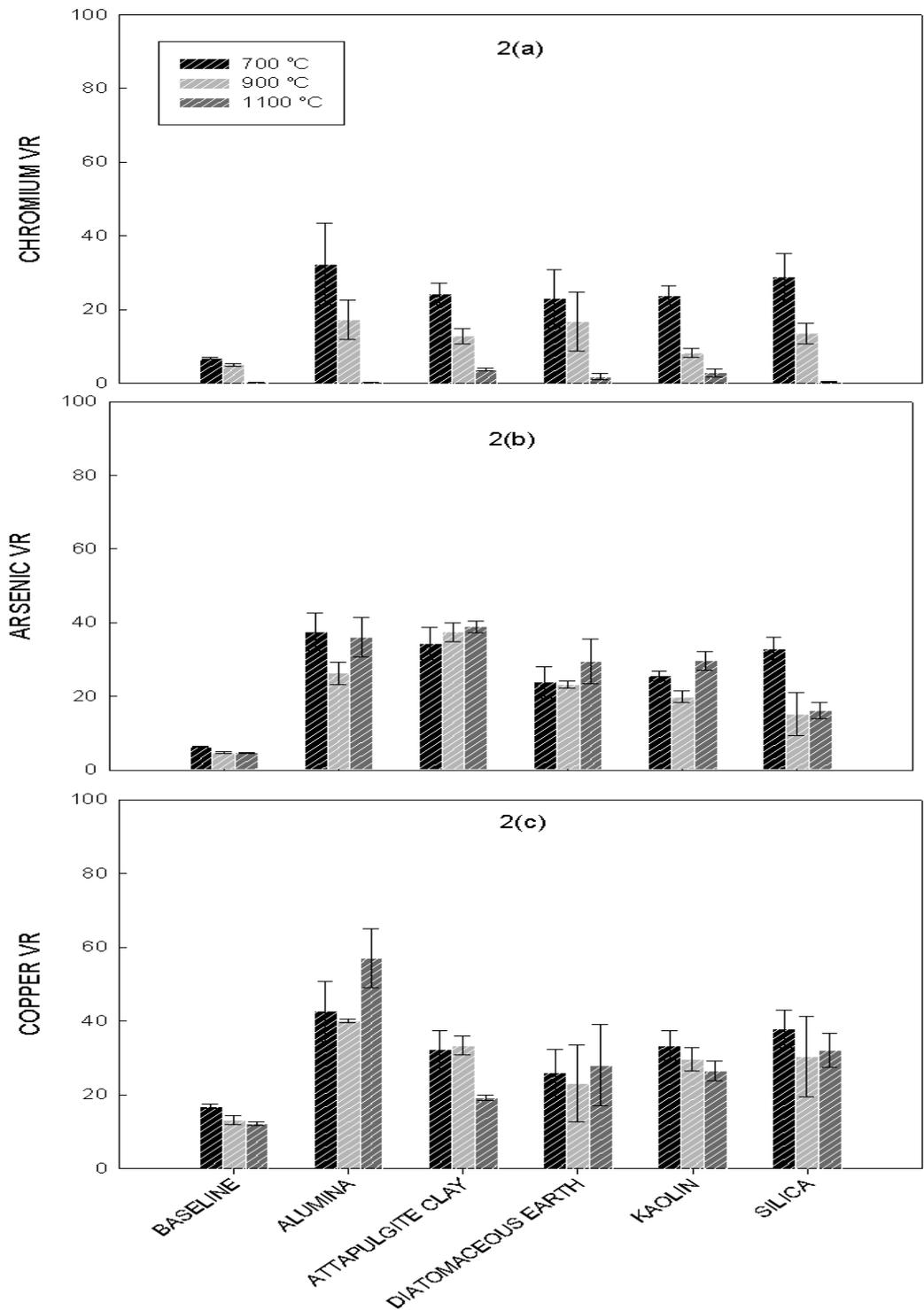


Figure 2: Volatilization retention of sorbent-spike samples at different temperatures: (a) arsenic, (b) chromium, and (c) copper

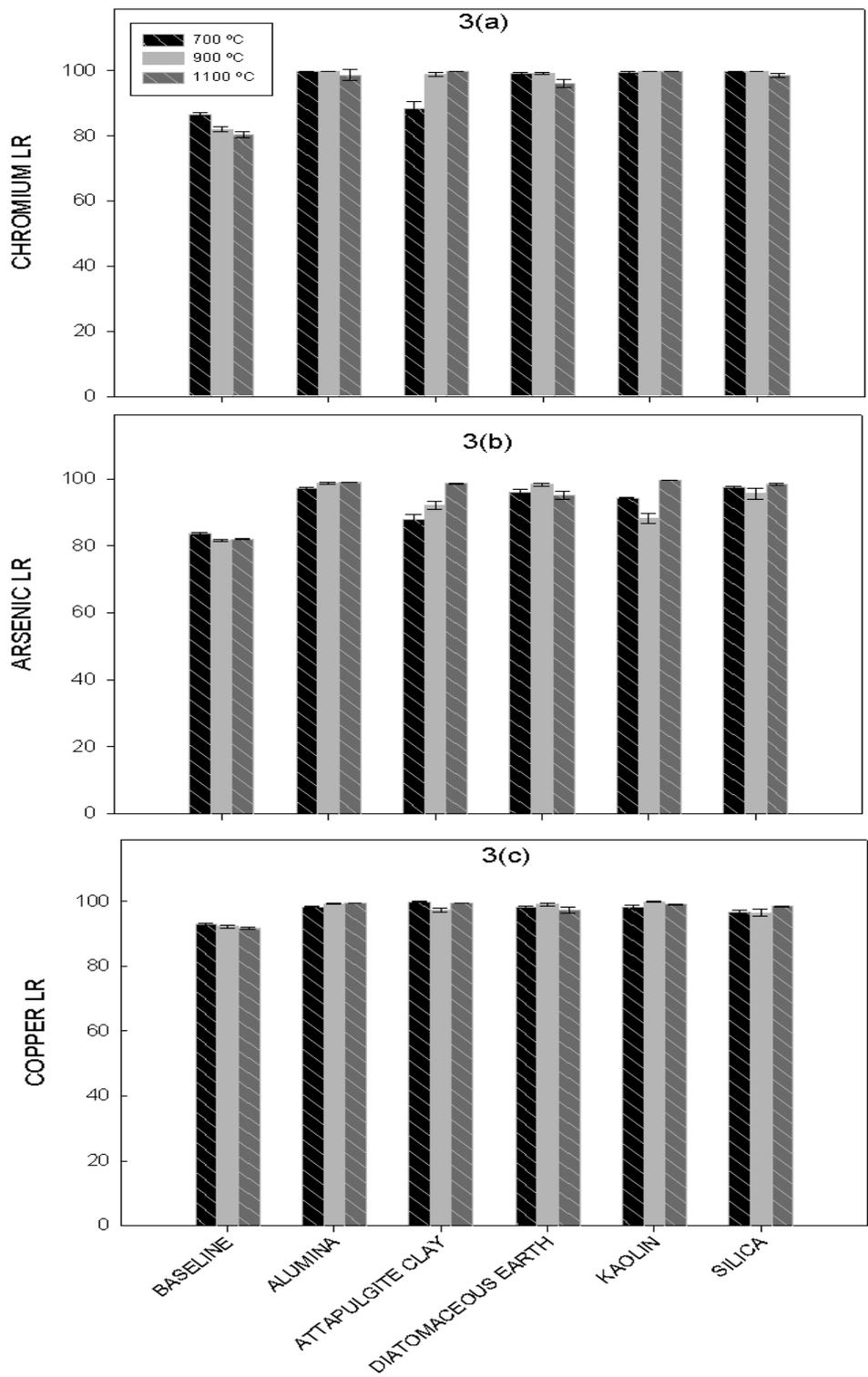


Figure 3: Leaching retention from sorbent-spike samples at different temperatures: (a) arsenic, (b) chromium, and (c) copper

3.5. pH Effects

Past studies have identified leachate pH as a contributing factor for metal leaching, with high leaching observed at low (< 4) and high (> 11) pH values, and the least leaching at neutral/near neutral pH values [4, 13, 23]. In these experiments, leachate pH was measured for all samples to assess the impact of pH on metal leaching. Figure 4(a) shows the leachate pH for various sorbent-spike samples and Fig. 4(b) plots the concentrations of arsenic, copper and chromium as a function of leachate pH. In general, alumino-silicate sorbent leachate pH was typically in the range of 4-6. Kaolin exhibited an unusually high pH at 900 °C and the reason for it couldn't be ascertained. For chromium, leaching was less than 15 mg/L at lower pH (< 6) in most cases with the exception of Kaolin at 900 °C (high pH, low leaching) and Attapulgitic Clay at 1100 °C (low pH, high leaching). Leaching greater than 15 mg/L was observed for arsenic, regardless of the leachate pH, with the exception of Kaolin at 700 °C (< 10 mg/L). For copper, leaching ranged between 1 – 55 mg/L, with the bulk of the data points between 10 – 55 mg/L, at low pH values (4 – 6), with the exception of Kaolin at 900 °C (high pH, low leaching).

The relationship between pH and leachate concentrations helps explain some of the previous observations and can serve as an indicator for the leaching behavior. For example, in alkaline environments (high pH environment), there is a greater possibility of leaching of chromium due to the hypothesized conversion of Cr(III) to Cr(VI) at a pH > 9 [24]. As previously discussed, other factors like speciation and complexation affect leaching besides pH. Thus while a pH relationship such as that shown in Fig. 4(b) can be helpful for assessing potential leachability, other factors impacting leachability should not be neglected.

3.6. Leaching and Volatilization Retention Correlation

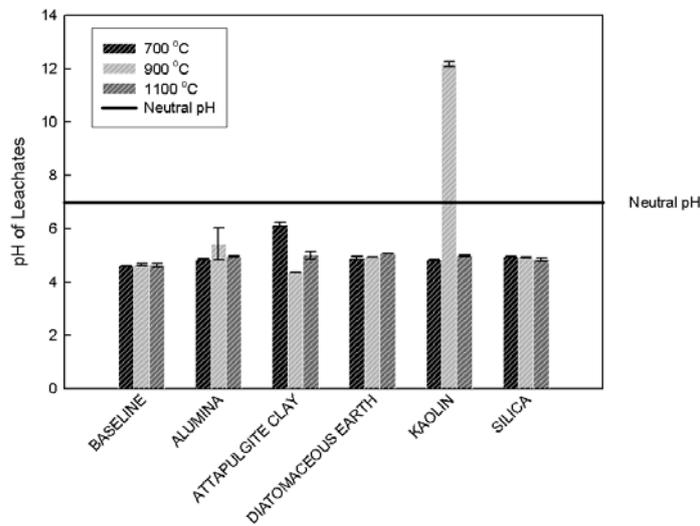
Correlation plots were drawn for molar leaching and volatilization retention of As-Cr, As-Cu and Cr-Cu pairs to gain insights of possible relation between speciation and leaching. Only As-Cu pair showed any significant correlation. Figure 5(a) shows a strong molar leaching correlation between the arsenic and copper leaching from alumina, diatomaceous earth, silica and kaolin (except for 900 °C samples). A possible reason for this strong correlation could be the formation of $Cu_3(AsO_4)_2$, Cu_xAs_y type of compounds (which are soluble) as key products. Figure 5(b) shows strong volatilization retention correlation between arsenic and copper from almost all sorbents, especially alumina, silica and kaolin.

4. Discussion

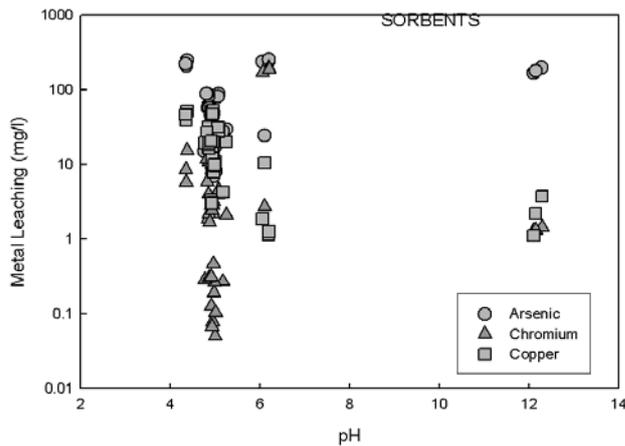
Baseline (spike): Results for all three metals showed high leaching and conversely low LR for all temperatures as expected. As indicated in speciation and Cu-As leaching correlation results, preferential formation of soluble hexavalent chromium compounds (e.g. CrO_3), and soluble Cu-As compounds (e.g. $Cu_3(AsO_4)_2$ and $Cu_2As_2O_7$) may have contributed to the excessive Cr, As and Cu leaching.

Alumina, Silica & Kaolin: Both alumina and silica exhibited low leaching for Cr (below TC limit) and lower As leaching (though still above TC limit) at all three temperatures. Kaolin too exhibited similar leaching behavior except for slightly higher Cr leaching (~ 7 mg/l) at 700 °C. All three sorbents exhibited lower Cu leaching (< 100 mg/L) at all three temperatures as compared to the baseline. The low leaching of Cr could be due to the

formation of trivalent chromium compounds like Cr_2O_3 , $\text{Cr}(\text{OH})_3$, $\text{CrO}(\text{OH})$, etc., which are insoluble and hence result in low leachability. It appears that Al and Si didn't bind themselves to Cr present in the system, although they facilitated the formation of trivalent Cr compounds (probably by keeping the pH acidic), and therefore resulted in low leaching of Cr. Although some Al-Cu & Al-As compounds were formed, several Cu-As compounds were observed in the XRD results and are suspected to be predominant, therefore resulting in high leaching for As & Cu. This is also supported by strong leaching correlation between As and Cu for alumina and silica.

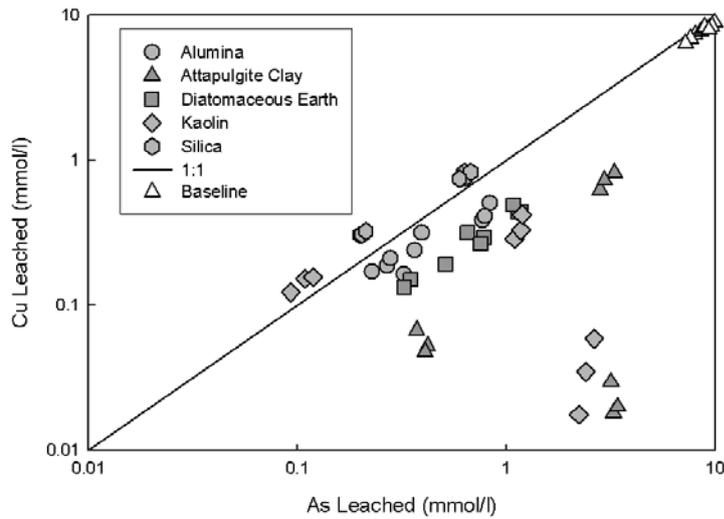


4(a) Leachate pH for Different Sorbent-Spike Combustion Products

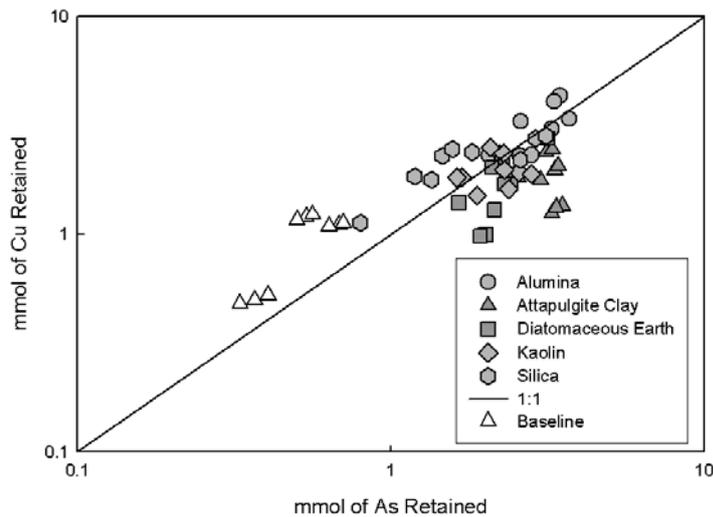


4(b) Correlation between leachate pH and metal concentration in leachate for different Sorbent-Spike Combustion Products

Figure 4(a): Leachate pH for different sorbent-spike products from high-temperature reaction; **(b)** Correlation between leachate pH and metal concentration in leachate



5(a) Leaching Correlation for As & Cu based on their concentration in leachate



5(b) Volatilization Retention Correlation between As & Cu based on the concentration of metals in the spike-sorbent combustion product

Figure 5: (a) Correlation of leaching between arsenic and copper concentrations in leachate; (b) Correlation of volatilization retention between arsenic and copper concentrations in ash

Attapulgite Clay & Diatomaceous Earth: These sorbents exhibited low leaching for Cr (below TC limit) only at 1100 °C and high As leaching (above TC limit) at all temperatures. While speciation results show the formation of a wide spectrum of metal-sorbent compounds, a possible reason for low Cr leaching at 1100 °C may have been the excessive volatilization of chromium at that temperature leaving very little chromium available for leaching. It is suspected that the high Cr leaching at 700 °C and 900 °C may have been due to the presence of alkaline earth metals like Ca and Mg, that are known to leach Cr [10], in these minerals. Solo-Gabriele et al. [22] reported chromium leaching from various wood ash samples between 0.2-25 mg/L with the highest leaching

observed for samples characterized by low level of CCA treatment. Cu leaching is typically high, but low for Attapulgite Clay at 700 °C and 1100 °C, possibly due to sorbent-Cu binding, but the exact compounds couldn't be conclusively identified due to experimental limitations. For all other cases, reasons for As-Cu leaching trends are expected to be similar to those for alumina.

5. Conclusions and Implication

Lab experiments were conducted to evaluate the capability of alumino-silicate sorbent materials in reducing leachability of CCA metals from residual ash as well as to characterize the retention of these metals. Alumino-silicate based sorbents were demonstrated to be very effective in reducing the leaching of chromium during incineration conditions likely by forming thermally stable and insoluble compounds and also significantly improved VR of the CCA metals in the ash. Product speciation, as identified by XRD, plays a critical role in leaching and volatilization characteristics of metals by formation of a variety of bimetallic compounds and a few sorbent-metals compounds. Formation of soluble As-Cu compounds may have contributed to higher leaching of both metals. Low leachate pH, facilitated by alumino-silicate sorbents, appears to have resulted in low chromium leaching for these tests. Results indicate that a few alumino-silicate sorbents showed good chromium retention, with alumina and silica exhibiting very low chromium leaching (below TC limit) at all three temperatures. Kaolin too exhibited low chromium retention, close to the TC limit in the entire temperature range and hence could potentially be used in practical applications.

The knowledge learned from this study can help develop effective strategies for implementing an effective technology for safe disposal of CCA wood. Since co-incineration is the preferred thermal process for the treatment of CCA-treated wood [8], choosing a suitable sorbent, based on the knowledge of metal-sorbent interactions can result in effective control of the leaching and volatilization of CCA metals. This study reveals alumino-silicates being good for chromium retention, whereas Misra et al. [25] and Iida et al. [10] reported alkaline earth based sorbents having great capabilities in reducing As and Cu leaching. Thus, a suitable co-fuel for CCA-treated wood would have both alkaline-earth sorbents (for As and Cu control) and alumino-silicate sorbents (for Cr control). Municipal solid waste has constituents similar to the test sorbent materials and can be evaluated as a suitable co-fuel for CCA-treated wood.

Acknowledgements

This research was sponsored by the Hinkley Center for Solid & Hazardous Waste Management (FCSHWM), Grant No. 00050891. The authors also acknowledge the Major Analytical Instrumentation Center (MAIC), University of Florida, for the use of XRD in its facilities. The authors also thank Mr. Chih-Hsiang Chien at the University of Florida for preparing the graphical work.

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