Metal leachability from coal combustion residuals under different pHs and liquid/solid ratios

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HIGHLIGHTS

• Comprehensive characterization of metal concentrations in coal combustion residues.
• First study to test the new USEPA LEAF Method 1313 and 1316 in fly ash.
• Ni, Zn and Pb were the highest with Pb being close to Florida industrial Soil Cleanup Target level.
• All metals except Cd showed amphoteric behaviors with increasing solution pH.
• All metal leaching excluding Ba and Pb decreased with increasing liquid:solid ratios.

ARTICLE INFO

Article history:
Received 30 March 2017
Received in revised form 24 June 2017
Accepted 5 July 2017
Available online 13 July 2017

Keywords:
Coal combustion residuals
Fly ash
Trace metals
LEAF
SPLP
Metal leachability

ABSTRACT

Coal combustion residuals (CCRs) contain variable amounts of trace metals, which can negatively impact the environment. We analyzed metal concentrations and leachability of CCRs from seven coal-fired power plants from Florida. The purpose of this study was to characterize and assess metal leachability in representative CCRs samples from coal-fired power plants, including As, Ba, Cd, Cr, Pb, and Se. The specific objectives were to: (1) measure metal leachability under different pH conditions and liquid-to-solid ratios using USEPA Leaching Environmental Assessment Framework (LEAF) Methods 1313 and 1316, and (2) compare their leachability with those obtained by the Synthetic Precipitation Leaching Procedure (SPLP). All metals excluding Cd showed amphoteric behavior, presenting higher concentrations at low and high pH using LEAF Method 1313. The highest Cd leaching was observed at pH 2–4 and decreased at pH > 7. SPLP results were highly variable when compared to the LEAF data. All metals except Ba exceeded the Florida Groundwater Cleanup Target Levels at all pH levels, however, metal leaching was low at typical soil pH of 4–9. Metal concentrations in fly ash decreased in most cases with increasing LS ratio. Therefore, due to potential leaching of some metals, evaluation is needed before beneficial use of CCRs.

Published by Elsevier B.V.
1. Introduction

Coal combustion residuals (CCRs) are one of the largest waste streams generated in the USA [1]. They are byproducts of coal combustion during electricity generation and consist of fly ash, bottom ash and flue gas desulfurization (FGD) residue [2]. In 2013, over 115 million tons of CCRs were produced in the USA, with ~51.4 tons being beneficially used for mine waste treatment, cement and concrete mixture, fill materials and metal recovery [3,4]. Due to updated Clean Air Act [5], CCRs production reached 140 million tons in 2015 [1,5].

Fly ash is fine in size (0.5–100 μm), which is generated during coal combustion and carried up with flue gas. To minimize its release into the atmosphere, emission control devices are used to separate fly ash in the flue gas from the air stream [6]. Bottom ash is the remaining residue in the boiler after fly ash removal and is formed in dry-bottom boilers and stokers [7]. FGD residues are produced by air-emission control devices, which contain lime-based materials to trap SO₂ as CaS or CaSO₄ to reduce its atmospheric concentrations [8]. In some cases, a selective catalytic reduction process is used to reduce NOₓ emissions by spraying ammonia into the flue gas [9].

CCRs contain variable amounts of soluble salts and trace metals that may leach out and cause environmental problems [1,10]. Depending on the combustion process, CCRs can be enriched with trace metals such as As, Cu, Pb, Se and Zn [8,11,12]. Coal source impacts trace metal concentrations in CCRs [13]. For example, Appalachian and Illinois Basin coals have higher Pb, Cr, Ni, and As concentrations than coals from the Rocky Mountains and Northern Plains, while Gulf Coast coals show the highest Hg concentration [1,14]. Because different coals contain different metal concentrations and pH values, metal leachability from CCRs can vary widely.

Metal concentrations in CCRs are generally low, rarely reaching the hazardous levels based on USEPA’s Toxicity Characteristic Leaching Procedure (TCLP) [15]. However, if not managed properly, CCRs have the potential to cause environmental contamination due to leaching of trace metals [11]. For example, trace metals including As, Se, B, Sr and Ba were detected in water from the impacted area 18 months after the collapse of the Kingston facility [12]. The collapse of another facility in 2014 released ~39,000 tons of ash into the Dan River, causing As, Se and Ba contamination in Duke river sediment [15,16]. Therefore, it is important to assess the potential risk associated with CCRs to minimize their impact on the environment.

The Synthetic Precipitation Leaching Procedure (SPLP) has been used to determine metal leachability under controlled laboratory conditions [17]. However, it does not consider site-specific conditions or leaching behavior over different time [1]. Leaching Environmental Assessment Framework (LEAF) methods were developed to examine metal leaching over a range of pHs (2–13; USEPA Method 1313) and liquid/solid ratios (0.5–10 mL/g; USEPA Method 1316), which help to assess metal leaching behavior in landfills or surface impoundments [15]. Combined with geochemical speciation modeling, LEAF methods can estimate metal leachability under different environmental conditions and land disposal characteristics [8,18]. Even though tests with wild range of pHs and L/S has been done in the past, they used different protocols and some report are incomplete, thus limited information is available regarding metal leachability of CCRs [19,20].

The purpose of this study was to characterize and assess metal leachability in representative CCRs samples from coal-fired power plants in Florida, including As, Ba, Cd, Cr, Pb, and Se. The specific objectives were to: (1) measure fly ash metal leachability under different pH conditions using LEAF Method 1313 (pH 2–13); (2) evaluate their leachability under different liquid-solid ratios using LEAF Method 1316 (0.5–10 mL/g); and (3) compare the LEAF results with those from SPLP.

2. Materials and methods

2.1. Chemicals, reagents and CCR samples

All chemicals were of analytical grade or better. Nitric acid (trace metal grade), H₂O₂, HCl and KOH were obtained from Fisher Scientific (Waltham, MA). Before use, all labware was washed and soaked in 1 M nitric acid for 24 h and rinsed several times with DI water.

Twenty four CCRs samples including 12 fly ash, 8 bottom ash, and 4 FGD residues were obtained from 7 representative coal-power plants in Florida. Composite samples were obtained following the in-stream and storage area methods. The in-stream method allowed collection of CCRs samples from transitory storage areas or conveyance systems. The storage area method allowed collection of CCRs samples from storage areas such as storage piles. All CCRs samples were subjected to total and SPLP analysis. Among those samples, 12 fly ash samples were analyzed using both LEAF methods (USEPA 1313 and 1316). All samples were derived from Bituminous type coal (Eastern, Central Appalachian and Illinois basin coal).

2.2. SPLP and LEAF tests

The pH was measured after shaking at a solid/liquid ratio of 1:10 (w/v) for 1 h and passing through 0.45 μm membrane filters. CCR samples were digested by USEPA Method 3050B for total concentrations [7]. Briefly, 1 g of sample was suspended in 15 mL 1:1 nitric acid and heated at 105 °C for 6 h. After cooling, 1 mL 30% H₂O₂ was added and digested for an additional 30 min before bringing samples to a 50 mL volume with double DI water. Concentrations were analyzed by inductively coupled plasma mass spectrometry (ICP-MS NexIon 300, PerkinElmer Corp., Norwalk, CT). The SPLP was used to measure metal leaching behavior in CCRs samples. The SPLP was shaken at 1:20 solid/extractant ratio for 20 h in a rotary shaker. The resulting solutions were filtered (0.45 μm), acidified with concentrated HNO₃, and pH was measured before and after acid addition. The total content of As, Cd, Co, Cr, Cu, Ni, Pb and Se was analyzed by USEPA Method 6020 using ICP-MS [21].

LEAF Method 1313 uses dilute HNO₃ or KOH to adjust pH in nine parallel batch tests at a liquid/solid ratio of 10 mL/g, with the final pH values at 2, 4, 5.5, 7, 8, 9, 10.5, 12, or 13. The pH measurement was done within 30 min to avoid neutralization of the solution. An extraction with no acid/base addition was done to assess the pH of CCRs. LEAF Method 1316 is a five parallel batch extraction as a function of liquid/solid ratios. Water was added to 20 g of ash samples to reach 0.5, 1.0, 2.0, 5.0, or 10.0 mL/g. All samples were shaken for 24 h, followed by filtration and analyzed using ICP-MS. For LEAF methods, metals of most environment concern (As, Ba, Cr, Cd, Pb and Se) were chosen. All analyses were performed in triplicate.

2.3. Quality assurance

The QA/QC in SPLP and LEAF analyses included blanks, spikes and triplicates for every 20 samples. Recovery was determined using spikes (80–120%), and relative standard deviations of triplicate analysis were obtained. The performance of the ICP-MS was checked by running an intermediate calibration standard for every 20 samples. All calibration standard checks were within the acceptable range (80–120%).
Table 1
Total concentrations of trace metals in 24 coal combustion residual samples from 7 representative power plants in Florida (mg/kg).

<table>
<thead>
<tr>
<th></th>
<th>As</th>
<th>Cd</th>
<th>Co</th>
<th>Cr</th>
<th>Cu</th>
<th>Ni</th>
<th>Pb</th>
<th>Se</th>
<th>Zn</th>
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<td>Max</td>
<td>73.0</td>
<td>4.80</td>
<td>398</td>
<td>398</td>
<td>692</td>
<td>9768</td>
<td>1018</td>
<td>58.0</td>
<td>3212</td>
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<tr>
<td>Min</td>
<td>36.8</td>
<td>0.20</td>
<td>2.62</td>
<td>6.94</td>
<td>23.8</td>
<td>13.0</td>
<td>21.0</td>
<td>3.83</td>
<td>10.7</td>
</tr>
<tr>
<td>Mean</td>
<td>52.6</td>
<td>2.13</td>
<td>44.5</td>
<td>63.7</td>
<td>103</td>
<td>916</td>
<td>156</td>
<td>21.6</td>
<td>376</td>
</tr>
<tr>
<td>St dev</td>
<td>15.3</td>
<td>1.46</td>
<td>117</td>
<td>114</td>
<td>196</td>
<td>2936</td>
<td>310</td>
<td>14.5</td>
<td>942</td>
</tr>
<tr>
<td>Median</td>
<td>46.0</td>
<td>2.55</td>
<td>8.44</td>
<td>16.0</td>
<td>37.3</td>
<td>32.0</td>
<td>32.0</td>
<td>21.0</td>
<td>113</td>
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Bottom ash (n=8) 

<table>
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<tr>
<th></th>
<th>As</th>
<th>Cd</th>
<th>Co</th>
<th>Cr</th>
<th>Cu</th>
<th>Ni</th>
<th>Pb</th>
<th>Se</th>
<th>Zn</th>
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<tr>
<td>Max</td>
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<td>1.24</td>
<td>249</td>
<td>72.8</td>
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<td>5992</td>
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<td>39.0</td>
<td>524</td>
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<tr>
<td>Min</td>
<td>1.55</td>
<td>0.12</td>
<td>2.03</td>
<td>1.67</td>
<td>6.98</td>
<td>5.97</td>
<td>0.54</td>
<td>0.80</td>
<td>6.20</td>
</tr>
<tr>
<td>Mean</td>
<td>11.3</td>
<td>0.57</td>
<td>32.3</td>
<td>22.9</td>
<td>52.4</td>
<td>7.67</td>
<td>50.5</td>
<td>7.68</td>
<td>101</td>
</tr>
<tr>
<td>St dev</td>
<td>17.1</td>
<td>0.50</td>
<td>81.2</td>
<td>26.6</td>
<td>100</td>
<td>2111</td>
<td>129</td>
<td>13.3</td>
<td>178</td>
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<tr>
<td>Median</td>
<td>5.76</td>
<td>0.38</td>
<td>5.55</td>
<td>10.7</td>
<td>14.5</td>
<td>12.5</td>
<td>3.87</td>
<td>1.71</td>
<td>28.0</td>
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FGD (n=4) 

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<tr>
<th></th>
<th>As</th>
<th>Cd</th>
<th>Co</th>
<th>Cr</th>
<th>Cu</th>
<th>Ni</th>
<th>Pb</th>
<th>Se</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Max</td>
<td>1.37</td>
<td>0.39</td>
<td>0.29</td>
<td>13.7</td>
<td>3.87</td>
<td>11.1</td>
<td>11.1</td>
<td>17.0</td>
<td>66.4</td>
</tr>
<tr>
<td>Min</td>
<td>0.40</td>
<td>0.01</td>
<td>0.19</td>
<td>1.99</td>
<td>1.74</td>
<td>0.37</td>
<td>0.37</td>
<td>0.00</td>
<td>4.69</td>
</tr>
<tr>
<td>Mean</td>
<td>0.81</td>
<td>0.13</td>
<td>0.22</td>
<td>6.47</td>
<td>2.64</td>
<td>3.34</td>
<td>3.34</td>
<td>7.09</td>
<td>22.1</td>
</tr>
<tr>
<td>St dev</td>
<td>0.42</td>
<td>0.18</td>
<td>0.05</td>
<td>7.29</td>
<td>1.00</td>
<td>5.18</td>
<td>5.18</td>
<td>7.13</td>
<td>29.6</td>
</tr>
<tr>
<td>Median</td>
<td>0.74</td>
<td>0.06</td>
<td>0.20</td>
<td>6.00</td>
<td>2.47</td>
<td>0.94</td>
<td>0.94</td>
<td>5.68</td>
<td>8.62</td>
</tr>
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Table 2
Concentration range of trace metals in coal combustion residuals based on literature (mg/kg).

<table>
<thead>
<tr>
<th></th>
<th>As</th>
<th>Cd</th>
<th>Co</th>
<th>Cr</th>
<th>Cu</th>
<th>Pb</th>
<th>Ni</th>
<th>Se</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fly ash</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Max</td>
<td>1385</td>
<td>17</td>
<td>180</td>
<td>1452</td>
<td>651</td>
<td>2120</td>
<td>353</td>
<td>47</td>
<td>2880</td>
</tr>
<tr>
<td>Min</td>
<td>1.1</td>
<td>&lt;0.11</td>
<td>7.3</td>
<td>45</td>
<td>11</td>
<td>&lt;1.40</td>
<td>23</td>
<td>&lt;1.40</td>
<td>25</td>
</tr>
<tr>
<td>St dev</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Median</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bottom ash</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Max</td>
<td>56.0</td>
<td>&lt;5.50</td>
<td>NA</td>
<td>146</td>
<td>4710</td>
<td>843</td>
<td>1267</td>
<td>8.20</td>
<td>717</td>
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<tr>
<td>Min</td>
<td>0.36</td>
<td>NA</td>
<td>NA</td>
<td>20.0</td>
<td>20.0</td>
<td>1.40</td>
<td>&lt;12</td>
<td>&lt;1.25</td>
<td>3.80</td>
</tr>
<tr>
<td>Mean</td>
<td>11.0</td>
<td>0.37</td>
<td>&lt;1.00</td>
<td>3.20</td>
<td>24.0</td>
<td>2.00</td>
<td>2.40</td>
<td>32.0</td>
<td>23.0</td>
</tr>
<tr>
<td>St dev</td>
<td>&lt;1.00</td>
<td>&lt;0.02</td>
<td>&lt;1.00</td>
<td>&lt;0.40</td>
<td>0.60</td>
<td>&lt;1.00</td>
<td>&lt;0.20</td>
<td>&lt;2.50</td>
<td>&lt;1.25</td>
</tr>
<tr>
<td>Median</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3
pH of 24 coal combustion residual samples from 7 representative power plants before and after SLP test.

<table>
<thead>
<tr>
<th></th>
<th>Fly ash (n=12)</th>
<th>Bottom ash (n=8)</th>
<th>FGD (n=4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>Before</td>
<td>After</td>
<td>Before</td>
</tr>
<tr>
<td>Mean</td>
<td>8.61</td>
<td>8.89</td>
<td>7.23</td>
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<tr>
<td>Max</td>
<td>11.9</td>
<td>12.2</td>
<td>10.8</td>
</tr>
<tr>
<td>Min</td>
<td>1.74</td>
<td>1.83</td>
<td>1.74</td>
</tr>
<tr>
<td>St dev</td>
<td>3.53</td>
<td>3.58</td>
<td>2.00</td>
</tr>
<tr>
<td>Median</td>
<td>9.57</td>
<td>10.2</td>
<td>8.44</td>
</tr>
<tr>
<td>25th Percentile</td>
<td>6.37</td>
<td>6.89</td>
<td>7.53</td>
</tr>
</tbody>
</table>

3. Results and discussion

3.1. Total metal concentrations in CCRs

Trace metal concentrations in CCRs varied widely (Fig. 1 and Table 1). Nickel, Zn and Pb were the highest, with some CCRs exceeding the Florida residential Soil Cleanup Target Levels (SCTLs) for Ni and Pb (340 and 400 mg kg\(^{-1}\)) and one sample was close to Florida industrial SCTL for Pb at 1400 mg kg\(^{-1}\). All As concentrations and some Cr and Cu also exceeded the Florida residential SCTLs (2.1, 210 and 150 mg kg\(^{-1}\)). Among metals, As and Cu are more toxic due to As’ carcinogenicity and Cu’s adverse impacts on aquatic biota [22,23]. Compared to CCRs in the US and other countries (Table 2), some concentrations of Co, Ni, Se and Zn in the fly ash, and As, Ni and Se in the bottom ash were higher. In fact, the highest Ni concentration was up to 27 times greater than those in previous studies [24–26].

All metals were enriched in fly ash samples compared to bottom ash and FGD. Among them, As, Cd and Pb have the highest vapor pressures and the lowest boiling points, resulting in higher accumulation in fly ash [27,28]. On the other hand, Cu and Cr have relatively low vapor pressures and higher boiling points so they are retained in slag or bottom ash. However, some samples presented higher concentrations of Cu and Cr in fly ash than bottom ash [29,30], which might be related to the use of a filtration device in pulverized coal boilers, such as an electrostatic precipitator [29]. Total concentrations of As, Ba, Cd, Cr, Hg, Pb and Se for all CCRs can be found in Table S1 (Supporting information).

3.2. Metal concentrations in fly ash based on SLP

SLP metal concentrations in FGD were the lowest while fly ash had the highest, especially for As, Cr, Ni and Pb (Fig. 2). The final SLP pH values were close to the sample pH values (Table 3), indicating a high buffering capacity of fly ash. Buffering capacity of CCRs is correlated to their CaO concentration [31].

SLP concentration of trace metals is related to its total concentration in CCRs samples, with pH playing an important role. For example, Ni concentration is the lowest at pH 8–10, while Cd concentration decreases at pH > 6 [32,33], which is consistent with our results where SLP data were the greatest in samples exhibiting pH < 6 (Fig. 2 and Table 3). In this study, Pb concentration was the highest in fly ash, being ~750 times the Florida Groundwater Cleanup Target Levels (FGCTL) at 15 µg L\(^{-1}\). Besides, As concentration was also high, being up to 5 times the FGCTL at 10 µg L\(^{-1}\). These results are different from McNally et al. [25] who tested fly ash in Pennsylvania using SLP, and reported a much lower
Fig. 1. Total concentrations of trace metals in 24 fly ash, bottom ash and FGD from 7 power plants. The Box-and-Whisker plots show the following: the minimum value (the lower whisker), the 25th quartile, the median, the 75th quartile, the maximum value (the upper whisker) and outlier (●). (n = 12, 8 and 4 for fly ash, bottom ash, and FGD).

Pb concentration at 0.09 mg L\(^{-1}\) but similar As concentration at 0.71 mg L\(^{-1}\). In case of FGD, even though total concentration was low compared to bottom and fly ash, some SPLP concentrations of As, Cd, Ni and Pb exceeded FGCTL (10, 5, 100 and 15 µg L\(^{-1}\)) (Fig. 2). The highest Ni concentration was up to 4 times of FGCTL of 100 µg L\(^{-1}\) Ni. Metal solubilization in FGD might be related to dis-
Fig. 2. SPLP concentrations of trace metals in 24 fly ash, bottom ash and FGD samples from 7 representative power plants. The Box-and-Whisker plots show the following: the minimum value (the lower whisker), the 25th quartile, the median, the 75th quartile, the maximum value (the upper whisker) and outlier (●); (n = 12, 8 and 4 for fly ash, bottom ash, and FGD).
solution of metal-containing carbonates by H$_2$SO$_4$ and HNO$_3$ used in the SPLP [34].

As noticed in this study, pH controls metal solubility, therefore, it is important to measure CCRs buffering capacity and final solution pH. For example, lower Cr concentration is obtained at pH < 4 compared to pH 5–7 [35]. Besides, Ni solubility is controlled by pH [36]. The disadvantage of SPLP is that it simulates the effect of acid rain on metal leaching in a single test condition [37], which is insufficient to describe metal leaching behavior under different environmental scenarios and over time [19,38]. Concentrations of As, Ba, Cd, Cr, Hg, Pb and Se for all CCRs based on SPLP can be found in Table S2.

3.3. Metal concentrations in fly ash based on USEPA LEAF Method 1313

The parallel batch test under different pHs (USEPA Method 1313) can be used to determine metal leachability over a broad range of environmental conditions. Fig. 3 presents the results for As, Ba, Cd, Cr, Pb and Se, showing significant leaching in fly ash. Concentrations of As, Ba, Cd, Cr, Hg, Pb and Se based on EPA Method 1313 for all CCRs can be found in Table S3. All metals excluding Cd showed amphoteric behavior, presenting higher solubility at low and high pH values (Fig. 3). Cadmium concentration decreased at pH > 7, with the highest being at pH < 4. pH is a master variable that can affect element speciation, therefore solubility [39]. In addition, low pH affects Ca-containing compounds, causing disturbance in the ash matrix and releasing associated metals [40].

Besides pH, metal leaching from CCRs is also influenced by solid to liquid ratio and other chemicals in CCRs matrix [41]. For example, Cu leaching is affected by ash mineralogy (presence of crystalline or amorphous minerals) and presence of organic compounds [40]. Moreover, Cd, Cu and Pb sorption is usually low at pH < 4 [42]. Tang and Steenari [41] also noticed that metals present as chlorides are released in high concentrations from CCRs.
3.3.1. As and Se concentrations

Arsenic and Se showed typical oxyanionic behavior with increasing concentrations as pH decreased (Fig. 3). Arsenic concentrations (0.70–6497 μg L⁻¹, 25th percentile = 7.8) in most fly ash samples were higher than the FGCTL at 10 μg L⁻¹. Nevertheless, at typical environmental pHs (4–8), As concentration was the lowest (0.70–204 μg L⁻¹, 25th percentile = 7.8), with more than 30% being below the FGCTL. For Se, lowest leaching occurred at pH 5.5–7 (Fig. 3). When compared to SPLP results, Se LEAF concentrations (0.00–2740 μg L⁻¹, 25th percentile = 49) were similar, with most samples exceeding the FGCTL at 35 μg L⁻¹ while As SPLP results were lower than the LEAF results. This is likely due to difference in the extraction solution, i.e., different acids used to adjust the pHs. Kosson et al. [37] also noticed similar behavior, though their concentrations were much lower than those in this study (Figs. 2 and 3). However, for As, those results are only relevant under aerobic environments where As is predominantly arsenite (As(V)). Under anaerobic conditions, As tends to exist as arsenic (As(III)), which is more mobile due to its neutral charge.

During combustion, arsenic associated with pyrite in coal is decomposed, releasing soluble AsV species in the ash [43]. They are characterized by a pH-dependent leaching. In acidic fly ash, leaching increases with pH; whereas, in alkaline fly ash, this trend is reversed, displaying a plateau of maximum solubility at pH 7–11 [33]. Other substances in fly ash may also play a role in arsenic leaching, including Ca, Fe oxyhydroxides, and Al and Mn oxides [33]. For Se, its solubility is controlled by redox potential and pH. In addition, the presence of Ca and Mg also affects Se speciation [32].

3.3.2. Ba, Cr, Pb and Cd concentrations

All barium concentrations at all pHs were lower than the FGCTL of 2000 μg L⁻¹. Conversely, Kosson et al. [37] noticed concentrations higher than the FGCTL in pH > 5.5. Different from Ba, Cr concentration was the greatest at extreme pH (>8), with the lowest being at pH 4–5.5 (0.00–563 μg L⁻¹) and with 75% of the samples being lower than the FGCTL of 100 μg L⁻¹ (Fig. 3). In a previous study, hexavalent Cr (CrVI) was the main form of Cr at pH > 7 [8]. USEPA’s study also found that post-combustion NOx controls
enhanced Cr concentration in fly ash [8]. As an oxyanion, CrVI is mobile in the environment and it is a strong oxidizer, being toxic to biological systems and a human carcinogen [44].

Similar to Cr, Pb leaching was the highest at pH < 5.5 (0.46–49.09 mg L−1, median = 57.1 mg L−1) and pH > 10.5 (0.00–81 mg L−1, median = 16.0 mg L−1) (Fig. 3). Most of the SPLP results were higher than those using LEAF 1313 method. At pH 4–10, Pb concentrations were low (0.00–732 mg L−1), with only two samples exceeding the FGCTL of 15 mg L−1. Amphoteric behavior of Pb was noted by Kosson et al. [8]. In high pH (>7), Pb can precipitate as carbonate or phosphate, which are more stable [32].

Cadmium had a typical leaching behavior of decreasing concentration with increasing pH (Fig. 3). However, all samples exceeded the FGCTL for Cd at 5 mg L−1. In USEPA’s CCRs characterization, Cd also exceeded the limit [8]. As pH increases (pH > 7.5), Cd starts to precipitate as CdCO3 and/or Cd3(PO4)2, which play an important role in controlling Cd solubility [32]. Most studies reported low Cd concentration for fly ash based on SPLP or TCLP [8, 35]. The difference might be in the final pH because neither SPLP nor TCLP controls final solution pH. Due to the buffering capacity of fly ashes, pH tends to be >7, leading to low Cd leaching. Therefore, Cd may be a limiting factor in reusing fly ash due to its high toxicity and concentration if pH is not properly managed.

Metal leachability under different pHs can be used to predict their fate and transport in risk assessment. However, metal leaching depends on site conditions, ash type, and solution pH [18]. Likewise, other factors such as sorption and/or co-precipitation with metal oxides also determine their fate in the environment [45–46]. Kosson et al. [37] studied metal leaching from fly ash-based concrete (up to 45% fly ash) and reported As leaching up to 10 mg L−1 using LEAF Method 1313. On the other hand, another study reported that hot-mix asphalt could facilitate metal leaching and mobility in the environment [18]. Thus, it is recommended that determination of maximum solubility capacity and pH are needed prior to beneficial use of these CCRs.

3.4. Metal concentrations in fly ash based on LEAF Method 1316

Metal leaching in CCRs is impacted by pH as well as liquid to solid ratio (LS). Therefore, it is important to understand how LS influences metal release. When the LS ratio was increased from 0.5 to 10, metal concentrations decreased in most samples except for Ba and Pb (Fig. 4). Concentrations of As, Ba, Cd, Cr, Hg, Pb and Se based on EPA Method 1316 for all CCRs can be found in Table S4. This might indicate that all elements reached their maximum leaching at low LS of 0.5 [47]. For Ba and Pb, its precipitation with sulfates, phosphate and carbonates might be responsible for its lower concentration [32]. The highest Pb concentration of 1889 mg L−1 was observed at pH < 2 and the highest Ba concentration of 1501 mg L−1 was observed at pH > 11. Those data are in agreement with Ba and Pb LEAF 1313 behavior and with Kosson et al. [37].

Concentrations of As, Cd, Cr, and Se in most samples exceeded the FGCTL even at LS ratio of 0.5. Compared to the SPLP data at LS ratio of 20, no trend was observed. For some samples, the SPLP followed the same trend, but for others, the SPLP data were higher. Lead concentration was low in most samples, possibly due to PbSO4 precipitation from Pb reaction with CaSO4 [41].

4. Conclusion

This work characterized CCRs samples from Florida and applied the new USEPA LEAF Method 1313 and 1316 to test metal leachability. All metals showed wide concentration ranges, with most lower than Florida industrial SCTLs. Cobalt and Ni exceeded Florida residential SCTLs in some cases while As, Cr, Cu, Cd and Pb were enriched in fly ash. SPLP data were higher in fly ash and bottom ash compared to FGD. All samples showed high buffering capacity with final SPLP pH close to the initial pH.

Most of the metals in fly ash showed amphoteric behavior with higher concentrations at very low and high pH values based on LEAF Method 1313 except Cd. Barium was the only element that did not exceed the FGCTL at all pHs. Concentrations for all metals in fly ash was low at typical soil pH levels. When the LS ratio was increased, metal concentrations in fly ash decreased in most cases. However, Ba and Pb showed an opposite trend, probably due to possible precipitation as sulfates, phosphates and carbonates. Comparison between the SPLP and LEAF data for As, Cd, Cr, Pb and Se in fly ash showed different methods produced different results.

As pH and LS ratio were the major variables that controlled metal release from CCRs, therefore, assessing wide range of those variables is possible to predict metal behavior in the environment. Thus, it is important to use appropriate method to predict metal solubility characteristics prior to beneficial use. It is also important to note that metal solubility in fly ash also depends on other factors in the environment. Beneficial use should be engineered to isolate CCRs from either rainfall infiltration or contact with groundwater to reduce metal leachability, thereby minimizing potential adverse impacts on the environment.

Acknowledgements

This research is supported in part by the University of Florida and the Hinckley Center for Solid and Hazardous Waste Management. The senior author is supported by the Brazilian National Council for Scientific and Technological Development (CNpq project 246758/2012-0).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jhazmat.2017.07.010.

References


