Characterization of Arsenic and Selenium in Coal Fly Ash to Improve Evaluations for Disposal and Reuse Potential

Award #DE-FE0031748

DOE-NETL 2020 FE R&D Virtual Project Review Meeting – Sensors and Controls

Presenting:

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External Advisors:
SEFA Group
Santee Cooper
Motivation and Significance

Coal Combustion Residues:
~100 million tons yr\(^{-1}\) in U.S.

~60% for beneficial use
fly ash - concrete
gypsum - drywall

(American Coal Ash Association)

~40% stored/discarded
as unused solid waste
Motivation and Significance

Coal ash disposal sites

Dan River Steam Station (NC), Feb. 2014

TVA Kingston (TN), Dec. 2008

Sutton Plant at Sutton Lake (NC), Sept. 2018
Motivation and Significance

Arsenic and selenium are coal ash constituents that can pose problems near disposal sites.

TVA-Kingston coal ash spill disaster: River water and sediments

Ruhl et al., ES&T 2010
Motivation and Significance

Arsenic and selenium are coal ash constituents that can pose problems near disposal sites.

Sutton Lake, NC vs. Lake Waccamaw, NC (near coal ash pond) (reference site)

Mean Loading to Sutton Lake (O4) = 0.85 kg Se day⁻¹

Brandt et al, *ES&T*, 2017
Statement of Project Objectives

Project goal:
To improve methods to evaluate arsenic and selenium risk potential in coal fly ash

1) Arsenic and Selenium analysis methods
- **Deterministic**
  - ICP-MS
  - Synchrotron XAS (bulk and microprobe)
- **Semi-Quantitative**
  - X-ray fluorescence
  - X-ray photoelectron spectr.
  - Infrared spectr.
  - Speciation of leachable As/Se

As, Se content, valence states, mass distribution

2) Correlate material analyses with As/Se leaching

As, Se mobilization potential
TCLP, LEAF

3) Perform broad survey of fly ashes

Coal Fly Ash
- Coal feedstock
- Boiler type
- Air pollution controls (SCR)
- Operations (startup, steady state)
Today's presentation

1. Solid State XRF for arsenic and selenium content
2. Microscale speciation of As and Se in fly ash
3. Leaching and transformation potential of As and Se

**Coal Fly Ash**
- Coal feedstock
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Perform broad survey of fly ashes

**Arsenic and Selenium analysis methods**

**Deterministic**
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Correlate material analyses with As/Se leaching

As, Se mobilization potential
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As, Se content, valence states, mass distribution
1. Total Arsenic and Selenium Contents in Coal Fly Ash

- Widely variable amounts of As and Se in coal fly ash
- Depends partly on the type of feed coal

Taggart et al. 2016 ES&T
Fly ash materials representing:
- Feed coals
- Combustor types
- Post-combustion flue gas treatment

1. Total Arsenic and Selenium Contents in Coal Fly Ash

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Feed Coal</th>
<th>Year</th>
<th>Location</th>
<th>Total As (mg/kg)</th>
<th>Total Se (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KY #1</td>
<td>App</td>
<td>2015</td>
<td>storage silo</td>
<td>132</td>
<td>16</td>
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<tr>
<td>KY #3</td>
<td>App</td>
<td>2006</td>
<td>No lime</td>
<td>7150</td>
<td>208</td>
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<tr>
<td>KY #3</td>
<td>IL</td>
<td>2012</td>
<td>Lime injection</td>
<td>123</td>
<td>6</td>
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<tr>
<td></td>
<td></td>
<td>2013</td>
<td></td>
<td>70</td>
<td>44</td>
</tr>
<tr>
<td>KY #4</td>
<td>IL</td>
<td>2012</td>
<td>Startup mode w/ SCR</td>
<td>135</td>
<td>17</td>
</tr>
<tr>
<td>KY #5</td>
<td>App</td>
<td>2018</td>
<td>Baseline mode w/ SCR</td>
<td>41.5</td>
<td>13.4</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>26.1</td>
<td>6.6</td>
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<tr>
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<td>App</td>
<td>2011</td>
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<td>44</td>
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<tr>
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<tr>
<td>GA #1</td>
<td>PRB</td>
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<td></td>
<td>24</td>
<td>13</td>
</tr>
<tr>
<td>NM #1</td>
<td>San Juan</td>
<td>2013</td>
<td></td>
<td>23</td>
<td>6</td>
</tr>
</tbody>
</table>
1. Total Arsenic and Selenium Contents in Coal Fly Ash

**Analysis Parameter**
- total As/Se content
- speciation and mass distribution

**Analysis Methods**

**Deterministic**
- ICP-MS after acid digestion
- Synchrotron X-ray Absorption Spectroscopy (bulk and microprobe)

**Disadvantages:**
- Involves hazardous chemicals
- Labor intensive
- Requires advanced technical expertise
- Limited access to equipment
## 1. Total Arsenic and Selenium Contents in Coal Fly Ash

<table>
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<tr>
<th>Analysis Parameter</th>
<th>Analysis Methods</th>
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<td>Deterministic</td>
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<td>Semi-Quantitative</td>
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<td>• X-ray fluorescence</td>
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<td>• Infrared spectroscopy</td>
</tr>
<tr>
<td></td>
<td>• Synchrotron X-ray Absorption Spectroscopy</td>
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<tr>
<td></td>
<td>(bulk and microprobe)</td>
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<tr>
<td></td>
<td>• X-ray photoelectron spectroscopy</td>
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<td>• Speciation of leachable As/Se via LC-ICPMS</td>
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</table>
1. Total Arsenic and Selenium Contents in Coal Fly Ash

**X-ray Fluorescence (XRF for arsenic analysis)**

Emission energies:
- As $K_{\alpha 1}$ - 10.54 keV
- Pb $L_{\alpha 1}$ - 10.55 keV
- Pb $L_{\beta 1}$ - 12.61 keV
- Se $K_{\alpha 1}$ - 11.22 keV

As and Pb have a similar emission energy. Need to collect Pb $L_{\beta 1}$ emission to determine As.
1. Total Arsenic and Selenium Contents in Coal Fly Ash

- Consistent results for Arsenic, Lead
- Not detected for Selenium

Next steps:
- Additional samples
- Optimization for Se
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2. Microscale speciation of As and Se in fly ash
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Correlate material analyses with As/Se leaching

As, Se mobilization potential
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As, Se content, valence states, mass distribution
2. Microscale speciation of Arsenic in fly ash

Arsenic is mostly As(V) oxidation state (e.g., AsO$_4^{3-}$ anion)
2. Microscale speciation of Arsenic in fly ash

Arsenic is heterogeneously distributed within fly ash grains

Arsenic K-edge XANES (bulk fly ash)

Linear Combination Fitting of Data

Arsenic spatial distribution (μ-XRF)

Arsenite As(III) is in one grain and mixed valence As in another grain

Arsenate As(V) is in one grain and mixed valence As in another grain
2. Microscale speciation of Selenium in fly ash

Selenium is heterogeneously distributed within fly ash grains.

- Selenium K-edge XANES (bulk fly ash)
- Linear Combination Fitting of Data
- Selenium spatial distribution (μ-XRF)

Selenite Se(IV) is in one grain and mixed valence Se in another grain.
3. Leaching and transformation potential of As and Se

Toxicity Characteristic Leaching Protocol

Leachate composition:
• Deionized water
• 0.2 mM acetate/acetic acid (pH 4.9)

50 g ash per liter → Mix for 18 hr → Aqueous concentrations and speciation of As and Se

Compare with properties of fly ash
• Chemical composition
• Coal feedstock
• Combustion conditions
3. Leaching and transformation potential of As and Se

- Total elemental content is not always informative of leachable concentrations.
- Speciation of As and Se may be an important factor.

![Graph showing dissolved arsenic in TCLP (mg/L) vs. total As in ash material (mg/gdw).](image)

- $R^2 = 0.27$
- $p = 0.13$

![Graph showing dissolved selenium in TCLP (mg/L) vs. total Se in ash material (mg/gdw).](image)

- $R^2 = 0.81$
- $p = 0.0004$

Schwartz et al. 2018 *Environmental Engineering Science*
Leaching potential of selenium may be related to the amount of oxidized forms: selenite ($\text{Se}^{\text{IV}+}$) and selenite ($\text{Se}^{\text{VI}+}$).
Summary

• Total As and Se contents in fly ash: **Modified XRF analysis method**

• Arsenic is primarily As(V); Selenium is a mixture Se(0), Se(IV)

• Both elements are **heterogeneously distributed**, suggesting a distribution of reactivity and leaching potentials

• Total As and Se in fly ash **vary with feed coal type** and alone does not indicate mobilization potential

Synchrotron facilities: SSRL and NSLS-II