EREF New Project Kick-Off Meeting

MSW Combustion Ash Co-disposal with Unburned Waste: Implications for Elevated Temperature Landfills

February 13, 2019

Stephanie C. Bolyard, PhD
Research and Scholarship Program Manager
Mission & Background

- **Mission:** To fund and direct scientific research & educational initiatives for sustainable waste management practices to benefit industry participants and the communities they serve.

- Non-lobbying, independent organization

- Not a membership organization

- Fund solid waste research & educational initiatives
  - Largest source of research funding in North America
  - Largest source of graduate scholarships in North America
  - Global in scope
1) **Scholarships** – given to graduate students whose research is solid waste focused

2) **Education Program** – providing technical content to industry and non-industry personnel

3) **Data and Policy** – to aggregate industry data, analyze trends, and evaluate policy

4) **Research Grants** – primarily allocated to academic institutions
Seeking Funds/Scholarships?
Some Recommendations

1) Should be a problem/issue that is broad or has strong interest by industry/agencies (ideal if in N. America too)
   • Narrow or niched submissions are rarely successful

2) Grant request should be aligned with effort
   • Typical grant size is $160,000
   • Significant equipment expenditures should be well justified

3) Duration should be aligned with effort
   • Typical duration = 2 years
   • Underestimating duration to be competitive doesn’t work

4) Annual cash flow is important
   • $100,000 over 2 years = $50,000/year… this is better than $100,000 over 1 year = $100,000/year
Research Proposal Review & Funding Process

Submission Deadlines in December & May (2 page length)

Full proposal = 10+ page length w/ budget

RC consists of 28 experts in solid waste industry

RC ranks based on technical AND relevancy

Consideration based on available funds & interest

Preproposal Review

Technical Review

Research Council Subcommittee Review and Recommendation

Rating/Ranking by Council

Funding Consideration by Board

Review by Committee & Invitation for Full Proposals

By topical experts in academia & industry; Typically 3-5 reviewers per proposal

Subcommittees formed by topic; recommend multiple proposals

Typically recommends 4 – 8 proposals for funding

Typically funds 3 – 10 proposals per year
Yongho Sohn, PhD, FASM
Pegasus Professor
Lockheed Martin Professor of Engineering
Director for Materials Characterization Facility
University of Central Florida

Debbie Reinhart, PhD, PE, BCEE
Pegasus Professor
Associate VP for Research and Scholarship
University of Central Florida
MSW Combustion Ash Co-disposal with Unburned Waste – Implications for Elevated Temperature Landfills

Yongho Sohn\textsuperscript{1,*} and Debra Reinhart\textsuperscript{2}

\textsuperscript{1} Department of Materials Science and Engineering  
\textsuperscript{2} Department of Civil, Environmental and Construction Engineering  
University of Central Florida, Orlando, FL

* Director for Materials Characterization Facility  
University of Central Florida, Orlando, FL
Project Goal

To characterize samples of MSW ash rigorously to better understand the potential for ash exothermic reactivity
Project Objectives

● Conduct comprehensive and meticulous analyses of MSW ash by examining structural, elemental and thermal characteristics:
  ● Elemental composition
  ● Structure and phase constituents
  ● Electronic/chemical state
  ● Thermal response (weight and caloric changes)

● Develop thermodynamic model to identify and predict potential reactions and transformations as functions of environmental variables such as temperature, pressure and chemistry.
Why Ash?
A total of 27 landfills cells were studied:
- 22 of these landfill cells provided landfill gas well monitoring data.
- 5 landfill cells were evaluated using exceedance data.

Of the 27 landfill cells, 78% reported temperature exceedances greater than 131°F.
Of the 22 landfill cells that provided monthly monitoring data, 64% had elevated temperatures. 10% had >15% of wells with elevated temperatures.
Cumulative Gas Quality Data Analysis

- A CH₄:CO₂ ratio less than 1 is often used as an indicator of elevated temperatures within landfills.
- As gas well temperature increases, the percent of gas wells reporting a CH₄:CO₂ ratio < 1 increases.
- Methane generation impacted at temperatures > 145°F
ETLF cells in this study tended to be larger than non-ETLF cells both in site area and landfill depth.

<table>
<thead>
<tr>
<th></th>
<th>Site Area (acres)</th>
<th>Current Landfilled Area</th>
<th>Design Landfill Depth (feet)</th>
<th>Current Landfill Depth (feet)</th>
<th>Well Depth (feet)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-ETLF</td>
<td>195</td>
<td>82</td>
<td>130</td>
<td>112</td>
<td>73</td>
</tr>
<tr>
<td>ETLF</td>
<td>846</td>
<td>141</td>
<td>152</td>
<td>148</td>
<td>93</td>
</tr>
</tbody>
</table>

N = 8 landfill cells (no elevated temp)
N = 14 landfill cells (with elevated temp)
Cause of Elevated Temperatures - Ash Disposal?

- Data from 22 landfill cells analyzed; 14 (64%) landfills had elevated temps.
- 8 landfills reported history of accepting ash.
- 7 of these 8 landfills with ash report elevated temperatures (88%).
Effect of Ash Disposal on Maximum Temperature

N = 14 landfill cells (no ash)
N = 8 landfill cells (with ash)
Effect Of Ash Disposal On Percent Of Elevated Temperature Readings

N = 14 landfill cells (no ash)
N =8 landfill cells (with ash)
Combination of coal ash and biosolids used as landfill cover on the west side of the landfill; the four most abundant elements found through X-ray Fluorescence, excluding carbon, were calcium (48% by weight), iron (19%), silicon (10%), and aluminum (7%).
Effect of Ash Disposal on Percent of Elevated Temperature Readings

Effect of ash disposal on temperature over time: Landfill with medium ash concentration
Effect of Ash Disposal on Percent of Elevated Temperature Readings

Effect of ash disposal on temperature over time: Landfill with medium ash concentration
What Constituent Phases in MSW Ash Can Cause Elevated Temperatures?

- Elemental Aluminum: $\text{e.g., } \text{Al} + 3\text{H}_2\text{O} \rightarrow \text{Al(OH)}_3 + 3/2 \text{H}_2$

- Elemental Iron: $\text{e.g., } \text{Fe} + \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{FeCO}_3 + \text{H}_2$

- Calcium compounds: $\text{e.g., } \text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2$
  $\text{e.g., } \text{Ca(OH)}_2 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O}$
Other Possible Reactions

- Rust and hydrogen sulfide, oxidation of FeS:
  \[
  2\text{FeO(OH)} + 3\text{H}_2\text{S} = 2\text{FeS} + \text{S} + 4\text{H}_2\text{O}
  \]
  \[
  4\text{FeS} + 7\text{O}_2 \rightarrow 2\text{Fe}_2\text{O}_3 + 4\text{SO}_2
  \]

- Scrap iron and carbonates:
  \[
  2\text{H}_2\text{O} + 5\text{CO}_2 + 4\text{Fe} \rightarrow 4\text{FeCO}_3 + \text{CH}_4
  \]

- Aluminum dross:
  \[
  2\text{H}_2\text{O} + 5\text{CO}_2 + \text{Al}_4\text{C}_3 + 12\text{H}_2\text{O} = 4\text{Al(OH)}_3 + 3\text{CH}_4
  \]
  \[
  \text{AlN} + 3\text{H}_2\text{O} = \text{Al(OH)}_3 + \text{NH}_3
  \]
  \[
  \text{AlP} + 3\text{H}_2\text{O} = \text{Al(OH)}_3 + \text{PH}_3 + 4\text{Fe} \rightarrow 4\text{FeCO}_3 + \text{CH}_4
  \]

- Also other carbonation reactions, hydrolysis, and metal oxides reaction with acids
Technical Approach

● Characterization of Ash:
  ✓ Chemistry, structure (micro and atomic) and electron/chemical state of ash sample
  ✓ X-ray diffraction (XRD)
  ✓ X-ray photoelectron spectroscopy (XPS)
  ✓ X-ray fluorescence spectroscopy (XRF)
  ✓ Cross-Sectional optical/scanning electron microscopy with X-ray energy dispersive spectroscopy (OM/SEM with XEDS)
  ✓ Transmission electron microscopy with X-ray energy dispersive spectroscopy and electron energy loss spectroscopy (TEM with XEDS and EELS)

● Thermal Response Analysis:
  ✓ Oxygen or nitrogen as the gas carrier
  ✓ Thermal response (weight gain/loss and heat release/absorption) helps in characterizing the ash samples (and potentially some understanding in nature of elevated temperature)
  ✓ Effect of heating on the rate of combustion or pyrolysis of the ash samples
Technical Approach (Continued)

- Completion of rigorous ash characterization will provide foundation for further work, both by modeling and experiment for mechanistic understanding.

- Develop thermodynamic model to identify and predict potential reactions and transformations as functions of environmental variables such as temperature, pressure and chemistry.

- Identification of “critical” experiments for further understanding and mitigation.
Characterizing Ash

Determine chemistry, structure (micro and atomic) and surface electron state of Ash:

• Chemistry (or Composition) – what elements are present?

• Structure – how are these elements distributed and arranged?
  • Molecular phase identification (crystalline vs. amorphous)

• Surface electron state - how are these elements bonded and can bond (with environment)?

Examine the thermal response of Ash:

• Weight gain or loss? Heat release or absorption?
Characterization Tools

A variety of techniques to determine all characteristics of Ash:

• X-ray Diffraction (XRD)

• X-ray Fluorescence Spectroscopy (XRF)

• X-ray Photoelectron Spectroscopy (XPS)

• Cross-Sectional Optical/Scanning Electron Microscopy with X-ray Energy Dispersive Spectroscopy (OM/SEM with XEDS)

• Transmission Electron Microscopy with X-ray Energy Dispersive Spectroscopy and Electron Energy Loss Spectroscopy (TEM with XEDS and EELS)
Thermal Response

A variety of techniques to determine thermal response of Ash:

- Thermal Gravimetric Analysis (TGA)
- Differential Scanning Calorimetry (DSC)
- Simultaneous TGA/DSC
- TGA or DSC coupled with Mass Spectrometer
Characterization Technique: X-ray Diffraction

- Monochromatic X-ray particle/wave and Bragg’s Law of Diffraction
- Atomic/ionic arrangement within crystalline compound
- Approximate amount of amorphous materials

Martin et al., J Hazard Mater, 2012
Characterization Technique: X-ray Fluorescence Spectroscopy

- Monochromatic X-ray particle/wave incidence
- Emission of characteristics secondary (or fluorescence) X-ray – Energy Level Detected
- Elemental/chemical analysis
- Estimation of compound (?) amount

Gong et al., Int J Environ Res Public Health, 2017
Characterization Technique: X-ray Photoelectron Spectroscopy

- Monochromatic X-ray particle/wave incidence
- Kinetic energy of ejected electrons
- Elemental composition (ppm)
- Chemical state and electronic state of the elements

Snellings et al., Rev Mineral Geochem, 2012
https://en.wikipedia.org/wiki/Fly_ash

Wang et al., Nanotech, 2015
Characterization Technique: Example of Al Alloy Powders

Gas Atomized Al Alloy (UCF Proprietary) Powders (for 3D printing purpose)

Phase Constituent Analysis by TEM (high angle annular dark field)
- FCC $\alpha$-Al
- Other sub-micrometer dispersoid phases

Surface Scale Analysis (electron energy loss spectroscopy): ~10 nm thick $\gamma$-Al$_2$O$_3$
Thermal Response: Thermal Gravimetric Analysis (TGA)

- Mass of a sample is measured over time as the temperature changes:
  - Phase transitions
  - Absorption and desorption
  - Chemisorptions
  - Thermal decomposition
  - Solid-gas reactions (e.g., oxidation or reduction).

Requires, in most cases, prior, knowledge of reactions and reaction temperature.
Thermal Response: **Differential Scanning Calorimetry (DSC)**

- Measurement of difference in the amount of heat required to increase the temperature of a sample and reference:
- Amount of heat (exothermic or endothermic) as a function of temperature (e.g., various phase transformations and reactions).
Thermal Response: Simultaneous TGA/DSC and Connection to Mass Spectrometer

Weight gain/loss and heat content are measured simultaneously.

Simultaneous TGA/DSC with Violatile Species Identification with Temperature Increase
Details of Characterization Tools

- Melvin-Panalytical Empyrean XRD units (2)
  - ✓ High Resolution Bragg-Brentano HD Incident Optics for High Resolution
  - ✓ High temperature stage and Small Angle X-ray Scattering
- Melvin-Panalytical XRF
- Thermo Scientific ESCALAB 250Xi XPS
- Zeiss ULTRA-55 Field Emission SEM with XEDS
- FEI Tecnai F30 (300KeV) TEM with XEDS
  - ✓ HAADF/ADF/BF S-TEM Detectors
  - ✓ GIF200 EELS and EF-TEM

Project Objectives

● Conduct comprehensive and meticulous analyses of MSW ash by examining structural, elemental and thermal characteristics:
  ● Elemental composition
  ● Structure and phase constituents
  ● Electronic/chemical state
  ● Thermal response (weight and caloric changes)

● Develop thermodynamic model to identify and predict potential reactions and transformations as functions of environmental variables such as temperature, pressure and chemistry.
Questions?