Surface Modified Fly Ash for Value Added Products (SuMo Fly Ash)

DE-FE0032039 - FY22 FECM Spring R&D Project Review Meeting– May 3, 2022

Sriraam R Chandrasekaran[1], PhD; Sanandam Bordoloi[2], PhD

[1]Lead Research Engineer, [2]Post Doctoral Research Associate

Prairie Research Institute, University of Illinois Urbana Champaign

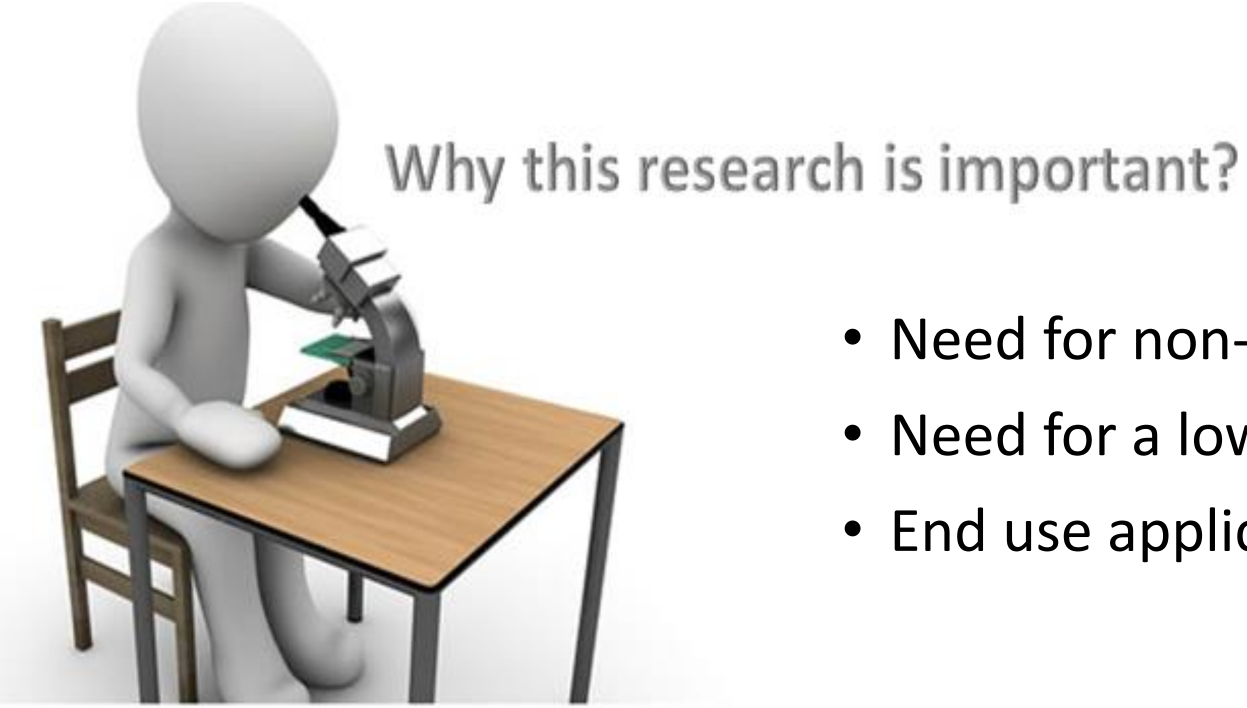
ILLINOIS SUSTAINABLE TECHNOLOGY CENTER
PRAIRIE RESEARCH INSTITUTE

THE OHIO STATE UNIVERSITY

U.S. DEPARTMENT OF ENERGY

NATIONAL ENERGY TECHNOLOGY LABORATORY

Why SuMo Fly Ash?



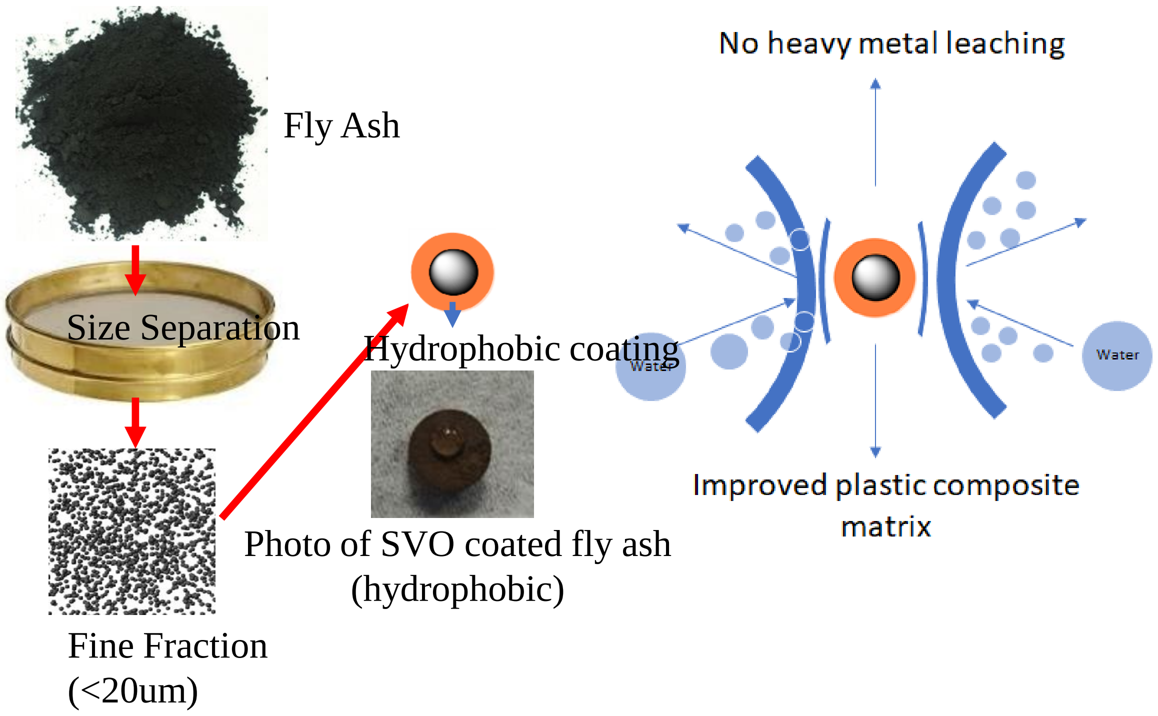
- Need for non-seasonal, high value product
- Need for a low-environmental impact product
- End use application is Fillers.

Pathway

The finer fly ash fractions is only to 10-15% of total fly ash quantity but enriched in concentration of toxic elements such as As, Se, and Hg.

- ***Thus, removing these fine fractions reduces toxic metal contaminations and potentially expands the utilization market for the residual coarse fraction.***

- ***The encapsulated fine fraction is ideally suited for use as fillers in polymer matrices due to its small particle size and improved functional properties***. <u>EPA's beneficial use goals stress the encapsulated use of fly ash in solid matrix applications</u>.



Approach

1. ***Characterization of fly ash and surface modified fly ash*** to understand fundamental ***properties relevant to their performance*** as fillers in polymers.

2. Demonstration that the new generation fly ash products ***provide functionality*** as fillers in polymers and related products.

3. Demonstration that products meet the evaluation criteria ***of EPA's 2014 encapsulated beneficial use rule*** and that products have economic value.

Project Tasks

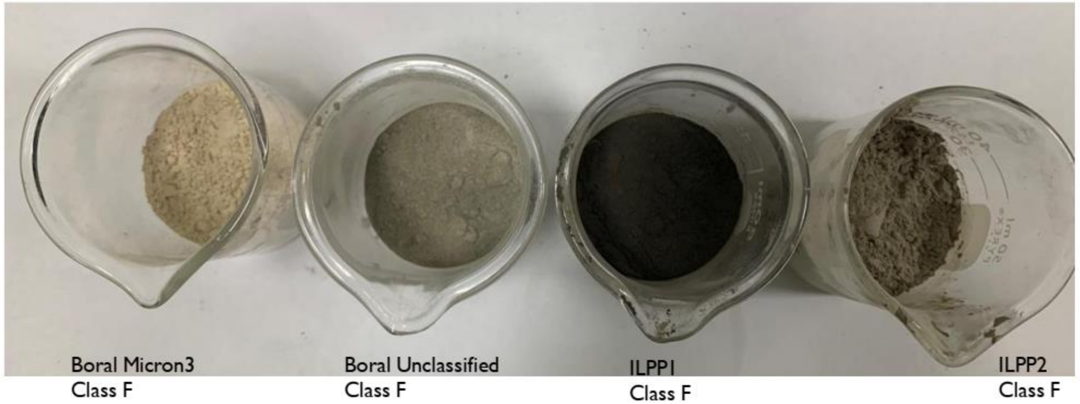
1. **Project Management and Planning**
   1.1 Updated PMP
   1.2 Completed Initial TMP
   1.3 Project Data Report and Final TMP
2. **Collection, Sizing, and Characterization of Fly Ash Material**
   2.1 Fly Ash Material Collection
   2.2 Sizing and Size Fractionation of Fly Ash
   2.3 Characterization of Fly Ash Size Fractions
3. **Development of a Surface Coating Technique to Generate Modified Fly Ash (SuMo)**
   3.1 Synthesize Sulfurized Vegetable Oil Followed by Coating
   3.2 Sulfurization of Vegetable Oil/Fatty Acids Coated Fly Ash
   3.3 Optimization of conditions to Generate SuMo Fly Ash
   3.4 Characterization of SuMo Fly Ash
4. **Suitability of SuMo Fly Ash as Filler Material in Plastics/Elastomers**
   4.1 Replacement of CaCO3 Filler in Plastics
   4.2 Replacement of Carbon Black Filler in Elastomers
5. **Environmental Characterization of SuMo Fly Ash and Final Products**
   5.1 Leaching
   5.2 Hg Volatilization
   5.3 EPA Beneficial Use Methodology

Progress to date

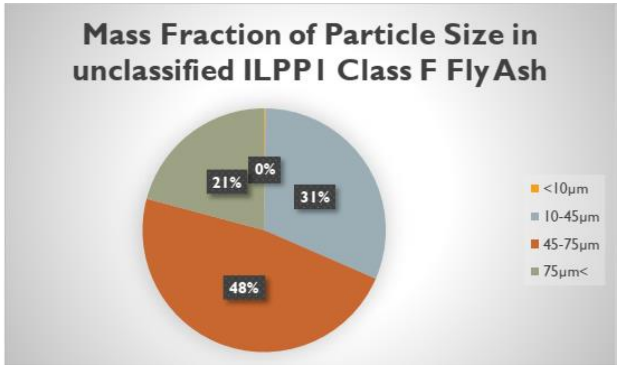
Task 2- Collection, Sizing, and Characterization of Fly Ash Material

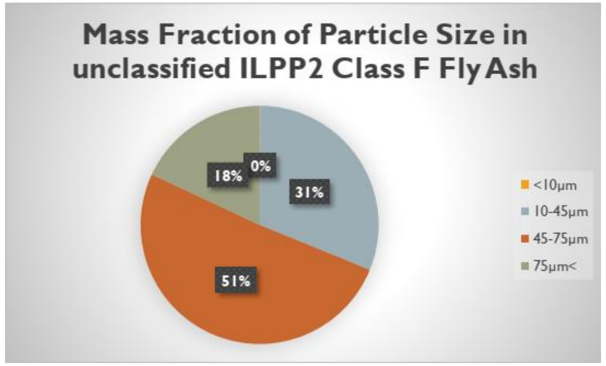
Task 2- Fly Ash Material Characterization

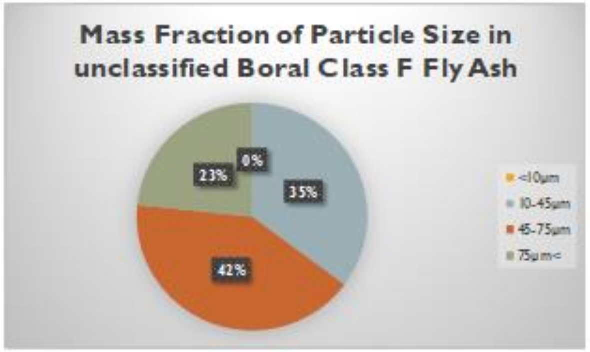
- Class F fly ash were procured from Boral Resources. A special classified Micron^3 Class F was also procured from Boral Resources. Class F fly ash was also collected from two different powerplants in Illinois.



Photos of fly ash samples procured from various sources





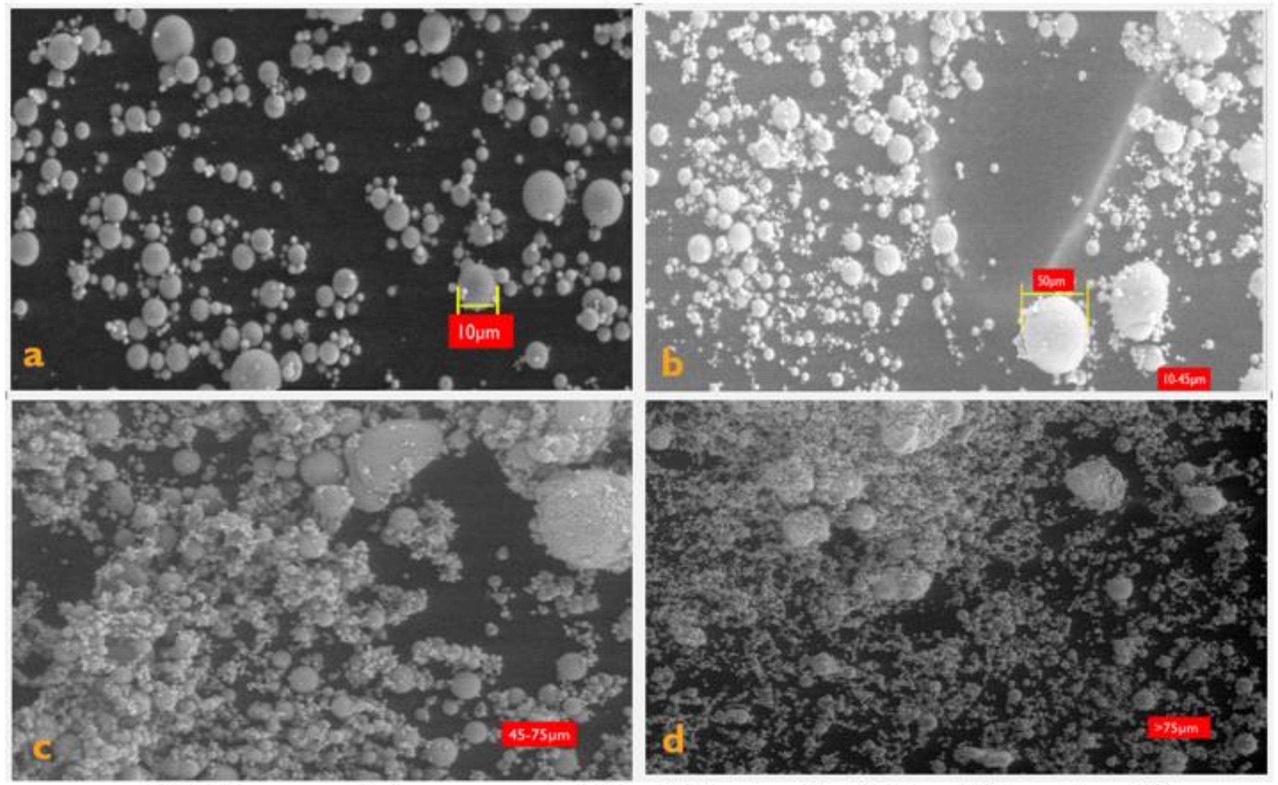


Mass fraction of selected fly ash

Task 2 - Particle Size & Morphology

- The fly ash fraction of the finest size (<10µm) was noted to consist of primarily smooth spherical particles.

- Fly ash particles in size range of 10–45µm and higher included a significant number of irregularly shaped grains.



SEM Images of size segregated Boral Unclassified Class F fly ash: a) fine fraction (<10 µm); b) fraction with particle size 10-45 µm; c) fraction with particle size 45-75 µm); d) fraction >75 µm

<u>Current task is to maintain smaller particle size as we develop coating process to maximize surface area and its functionality</u>

Task 2- Trace Metal Distribution for Leaching

- The 3-micron sample from Boral has high amounts of As, Pb, and Mn.
- In other samples, As concentrations increase slightly with a reduction in particles size but are significantly lower than Micron 3 samples.
- Boron, was found in high concentrations in all samples.

Trace metal analysis on the size segregated fly ash samples

Elements	Units	Micron 3 Boral Fly Ash	ILPP1 Fly Ash (µm)			ILPP2 Fly Ash (µm)			Boral Unclassified Class F Fly Ash (µm)		
		3 µm	>75	45-75	10-45	>75	45-75	10-45	>75	45-75	10-45
As	mg/kg	158	12	14	17	15	22	24	18	21	22
Ba	mg/kg	1630	177	172	145	306	345	287	3420	3180	3390
Be	mg/kg	3	5	5	6	BD	BD	BD	3	3	3
B	mg/kg	1040	992	1190	1720	403	548	597	522	603	616
Cd	mg/kg	2	4	4	5	3	4	5	2	2	2
Cr	mg/kg	90	56	63	78	109	145	157	60	69	70
Co	mg/kg	11	7	6	6	4	5	5	25	28	29
Cu	mg/kg	58	32	51	95	41	46	67	151	212	244
Pb	mg/kg	60	10	10	16	7	11	13	34	43	45
Mn	mg/kg	246	567	415	292	121	108	91	146	151	155
Mo	mg/kg	20	28	31	38	28	39	44	10	12	13
Ni	mg/kg	29	30	30	32	26	31	31	51	56	57
Se	mg/kg	15	20	12	10	20	29	33	8	11	12
Ag	mg/kg	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Sn	mg/kg	5	3	3	5	2	3	3	4	4	4
V	mg/kg	137	102	92	118	78	102	108	154	166	174
Zn	mg/kg	113	231	168	219	134	180	208	155	177	180
Hg	mg/kg	ND	0.84	ND	ND	ND	ND	ND	1	1.5	1.6

Task 3- Development of a Surface Coating Technique to Generate SuMo Fly Ash

Task 3- Development of a Surface Coating Technique to Generate Modified Fly Ash (SuMo)

Subtask 3.1. Synthesize Sulfurized Vegetable Oil Followed by Coating of FA – In a first step, sulfurized vegetable oil (SVO) and sulfurized fatty acid (SFA) will be synthesized by copolymerizing vegetable oils (VO)/fatty acids (FA) with elemental sulfur.

In a second step, the synthesized and characterized SVO/SFA will be dissolved in a suitable solvent. The fly ash will be slurried in a solvent-SVO/SFA mixture to promote development of a surface coating. The surface coated fly ash layer will subsequently be recovered by filtration and dried using heat.

Subtask 3.2. Sulfurization of Vegetable Oil/Fatty acids Coated Fly Ash – In another method, fly ash prewetted with VO/FA will be prepared. The VO/FA prewetted fly ash samples will then be mixed to a clear molten phase of sulfur

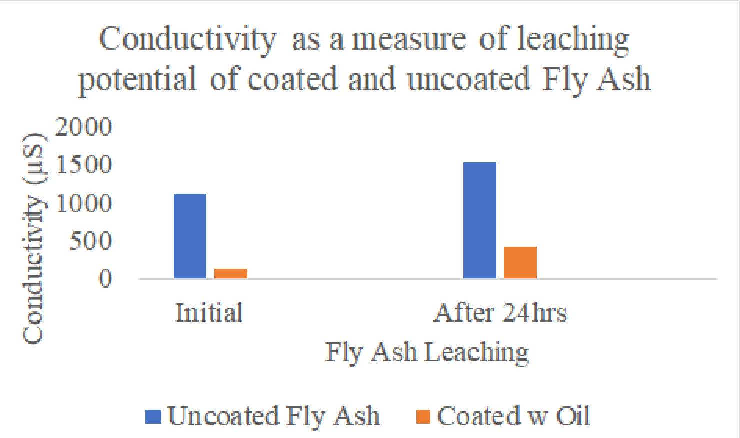
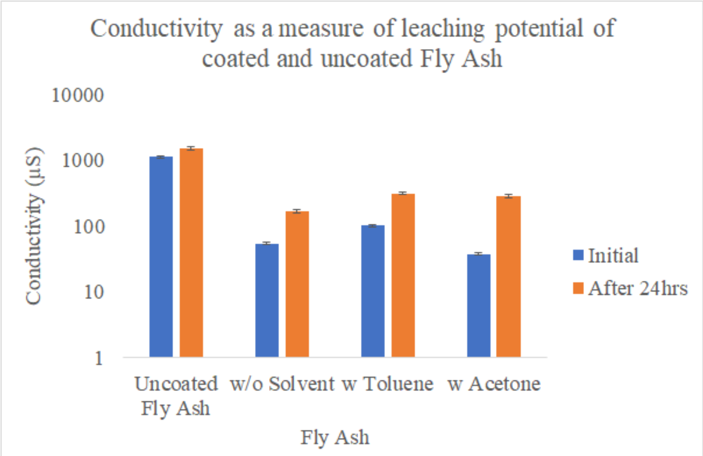
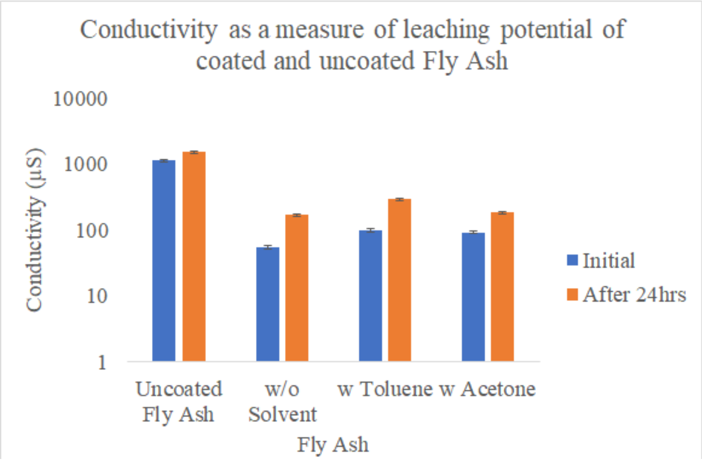
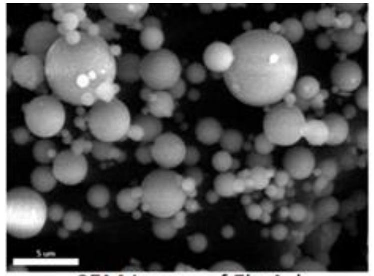
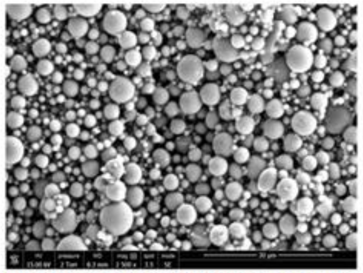
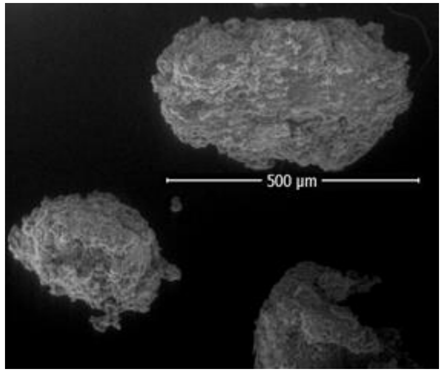
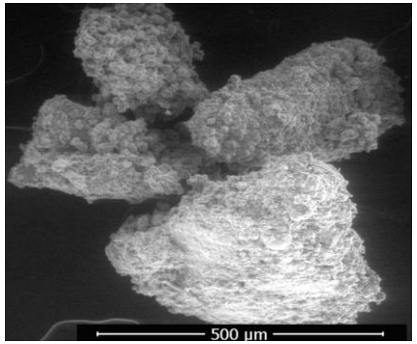
Task 3 Continued….

Conductivity and pH as Rapid Screening Tool

To rapidly screen the coating stability, we have used pH and conductivity measurements.

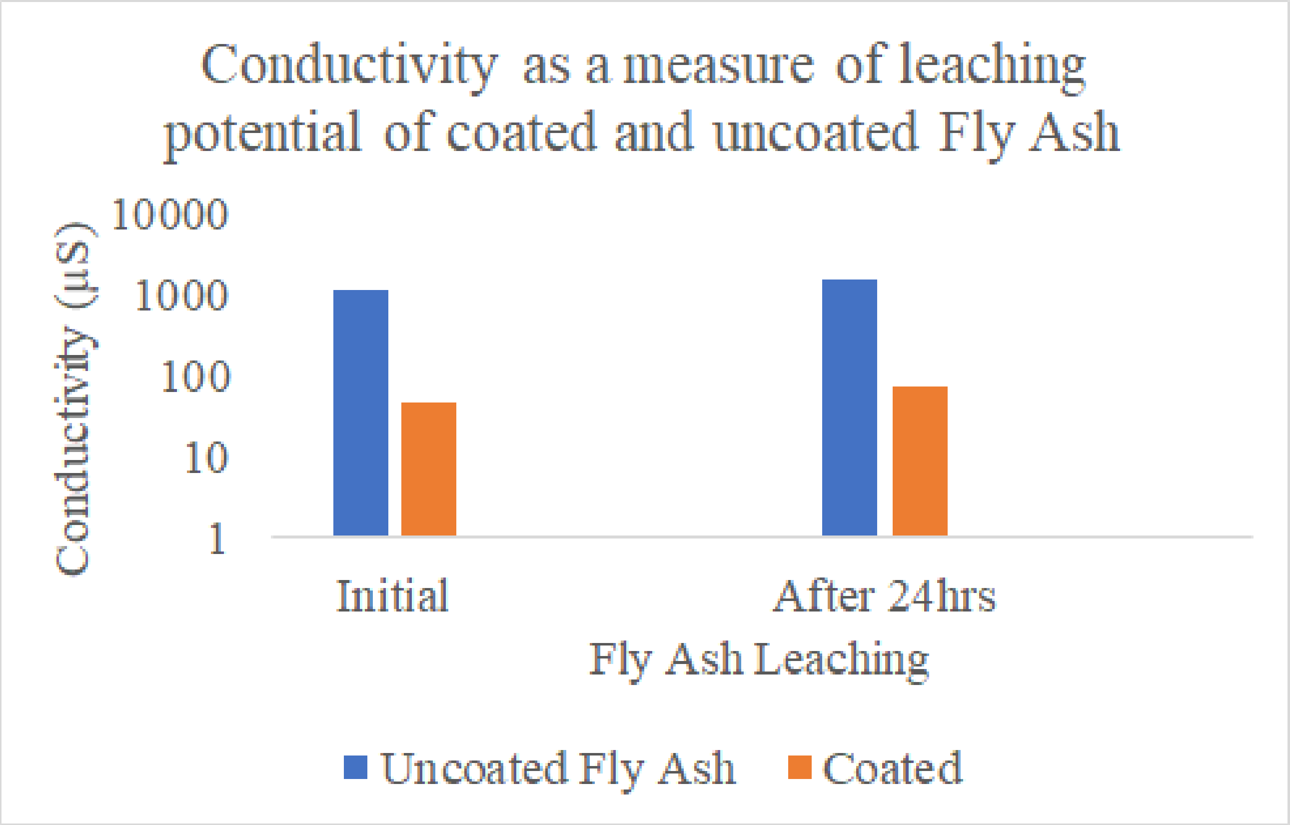
For baseline study- 1gm fly ash was added into 20mL water to look at the leaching potential. Initial pH and conductivity was measured, and the conductivity and pH after 24 hours was measured.

As the fly ash was coated, the coated fly ash (1gm) was added into 20mL water to measure the leaching potential. Initial pH and conductivity was measured, and the conductivity and pH after 24 hours was measured.

<table>
<tr><th>Methodology</th><th>Baseline Study- Fly Ash Coated with vegetable oil (VO)</th><th>3.1. Synthesize Sulfurized Vegetable Oil Followed by coating</th><th>3.2. Sulfurization of Vegetable Oil/Fatty acids Coated Fly Ash</th></tr>
<tr><td>Approach</td><td>Canola oil was dissolved in Toluene.
Fly Ash was added to the mixture and coated.
The coated material was dried in vacuum oven until all the solvent was evaporated.</td><td>Solvent used were Toluene and Acetone.
Fly Ash was mixed in the sulfurized oil and the slurry was dried</td><td>Solvent used were Toluene and Acetone.
The solvents are individually mixed with fly ash. This is followed by manual mixing with molten solvent for polymerisation.</td></tr>
<tr><td>Result</td><td>
</td><td>
</td><td>
</td></tr>
<tr><td>SEM</td><td>
SEM Image of Fly Ash

Fly Ash coated with virgin canola oil</td><td>
</td><td>
</td></tr>
</table>

Task 3 Continued…. Ongoing Work

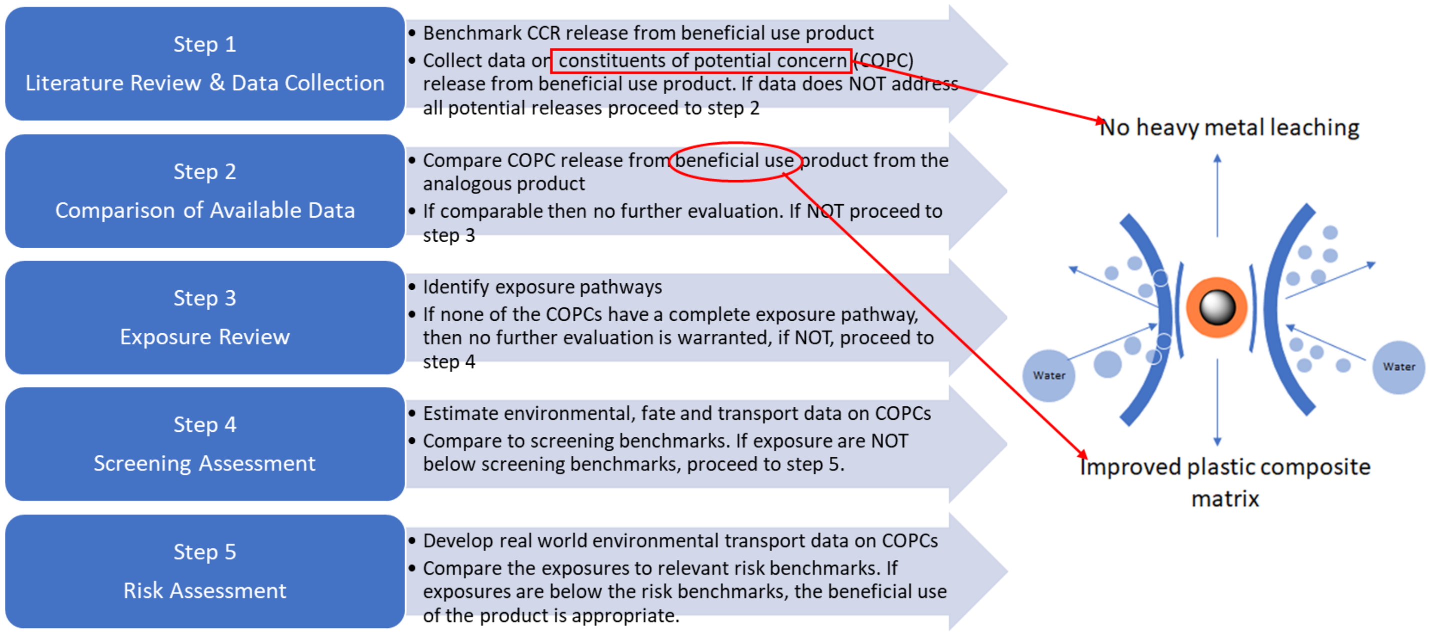
Promising results from our recent study – fly ash coated with vegetable oil reduces leaching while maintaining the particle size.



Future Work

- **Optimization of Conditions to Generate SuMo Fly Ash**
- **Characterization of SuMo fly ash**
- **Suitability of SuMo fly ash as filler materials**
- **Environmental Characterization of SuMo fly ash and final products**

Methodology to Evaluate the Beneficially Use of an Encapsulated CCR



Acknowledgements

Adam Payne, PhD (Program Manager, NETL)
Jacqueline Harden (Grants & Contracts Section Lead, UIUC)
Lisa Young (Grants & Contracts Coordinator, UIUC)

U.S. DEPARTMENT OF ENERGY

NATIONAL ENERGY TECHNOLOGY LABORATORY

THE OHIO STATE UNIVERSITY

ILLINOIS SUSTAINABLE TECHNOLOGY CENTER
PRAIRIE RESEARCH INSTITUTE

Question and Answers

Sriraam R Chandrasekaran, PhD (schandr@illinois.edu)
Sanandam Bordoloi, PhD (sanandam@illinois.edu)

U.S. DEPARTMENT OF ENERGY

NATIONAL ENERGY TECHNOLOGY LABORATORY

THE OHIO STATE UNIVERSITY

ILLINOIS SUSTAINABLE TECHNOLOGY CENTER
PRAIRIE RESEARCH INSTITUTE

Project Background

1. Existing uses for fly ash are of low value targeting applications such as concrete.

2. Transportation and beneficiation costs of off-spec materials creates barriers to low value applications.

3. The presence of elements such as As, Se, Cd, Hg, B, etc. in fly ash has led to reduction or elimination in the use of fly ash in household items such as carpets due to public health concerns.

4. EPA CCR Beneficial Use Rule regulates that the fly ash must meet relevant product specifications, and regulatory standards when used as substitute for a virgin or filler materials.