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

DE-FE0032039 – Annual Project Review Meeting – April 18-20, 2023

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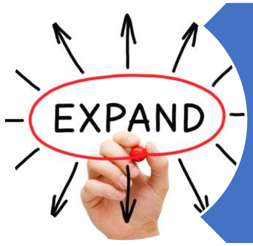
Alignment of Project with DOE mission goals

DOE mission

- ✓ Protect the environment and public health from heavy metal emanating from fly ash disposal
- ✓ Expand the beneficial use and management of fly ash



The economic viability of transportation of fly ash to greater distance to overcome regional supply demand imbalances

Technologies to size, beneficiate and store fly ash

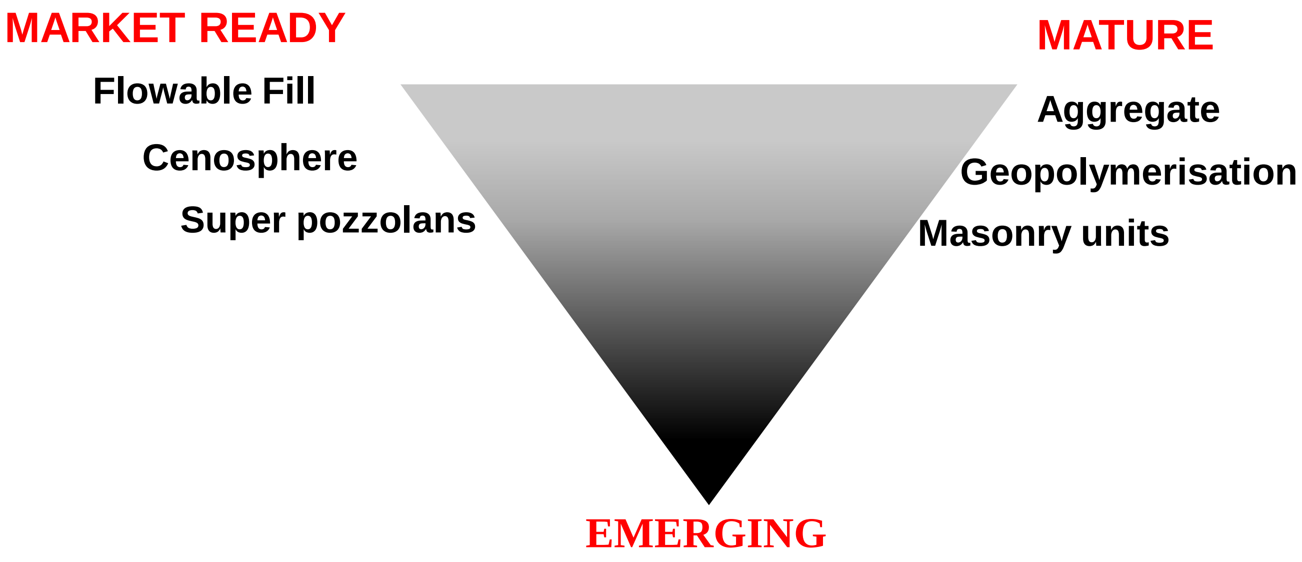
A non seasonal product demand

Fig. 1 Alignment of DOE mission with current research on fly ash utilization

<u>This research will ultimately contribute to critical operational and environmental issues negatively impacting the U.S. coal-based power generation sector</u>

Impact of Research and Development

Technology Considerations for Beneficial Usage of Fly Ash



	Waste-water brine stabilization	Polymer composites/ fillers	Proppants	Metal matrix
Product value	Low	High	High	High
Product volume	High	Moderate	Moderate	Moderate

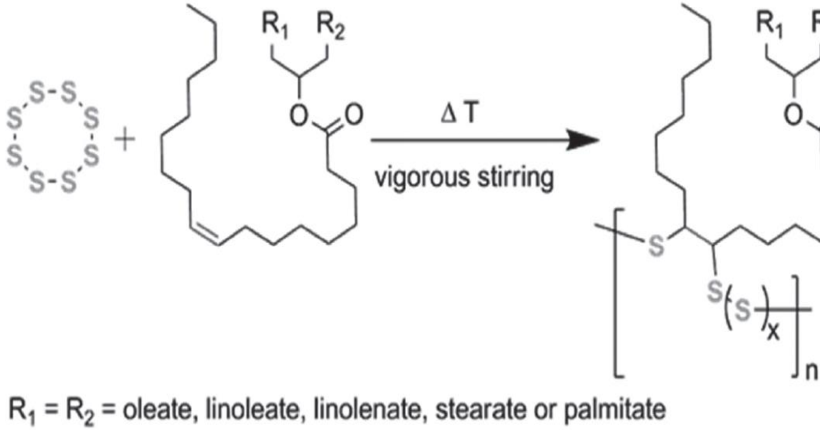
Fig. 2 Current state of potential technology of fly ash

Reference: *Duke Energy Coal Ash Beneficial Reuse Technologies Study, Raleigh, NC, November 9, 2016*

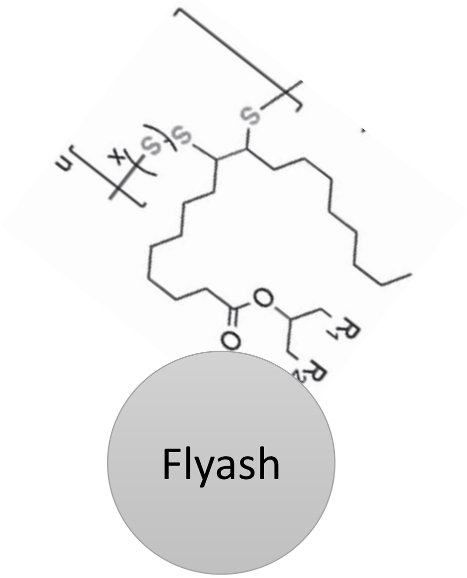
Basis of Research and Development

Background and Hypothesis

Fly ash is hydrophilic in nature. Will not blend well with hydrophobic elastomers or plastics



Hydrophobic, non-toxic, bio-based polymer



SuMo Flyash

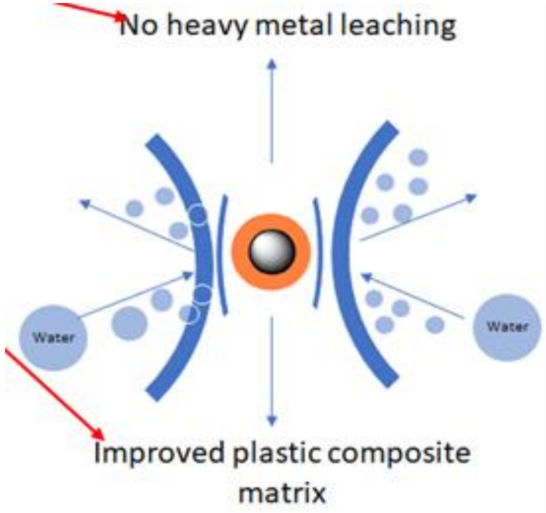
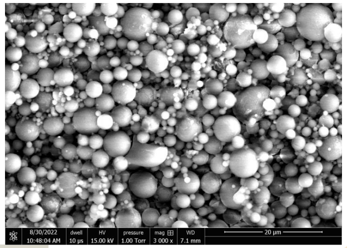
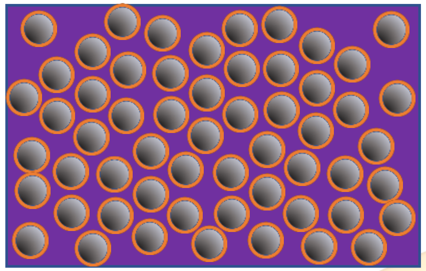


Fig. 3 Background and hypothesis of SuMo fly ash development for filler application

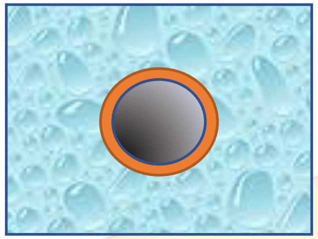
Basis of Research and Development

Develop a new generation biobased polymer coated flyash for filler application





Comprehensive characterization of the surface modified flyash (SuMo flyash)



Demonstrate the SuMo flyash in the filler applications

Demonstrate EPA's 2014 beneficial use rule with economical value

Fig. 4 Research goals of the current study

Characteristics of the Fly ash

Fig. 5 Pictures of collected fly ash

- Fly ash is texturally, physio-chemically different from source of procurement
- Boron, was found in high concentrations in all samples
- Micron[3] fly ash (Class F) is suitable for filler material as the particle size is smallest

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

The Coating Process for Producing SuMo fly ash

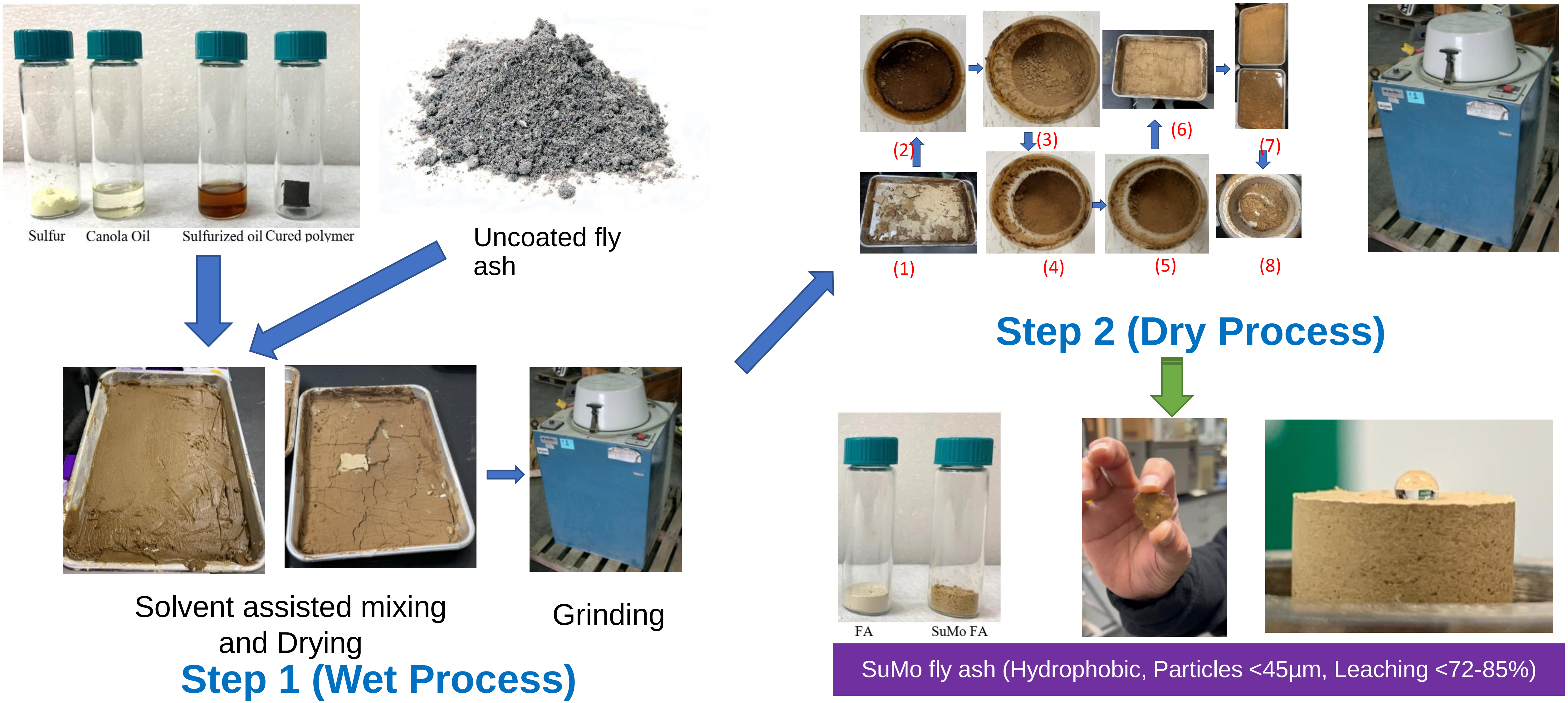


Fig. 6 Pictorial representation of steps undertaken to produce SuMo fly ash

Fast Track Leaching Test of the SuMo Fly ash

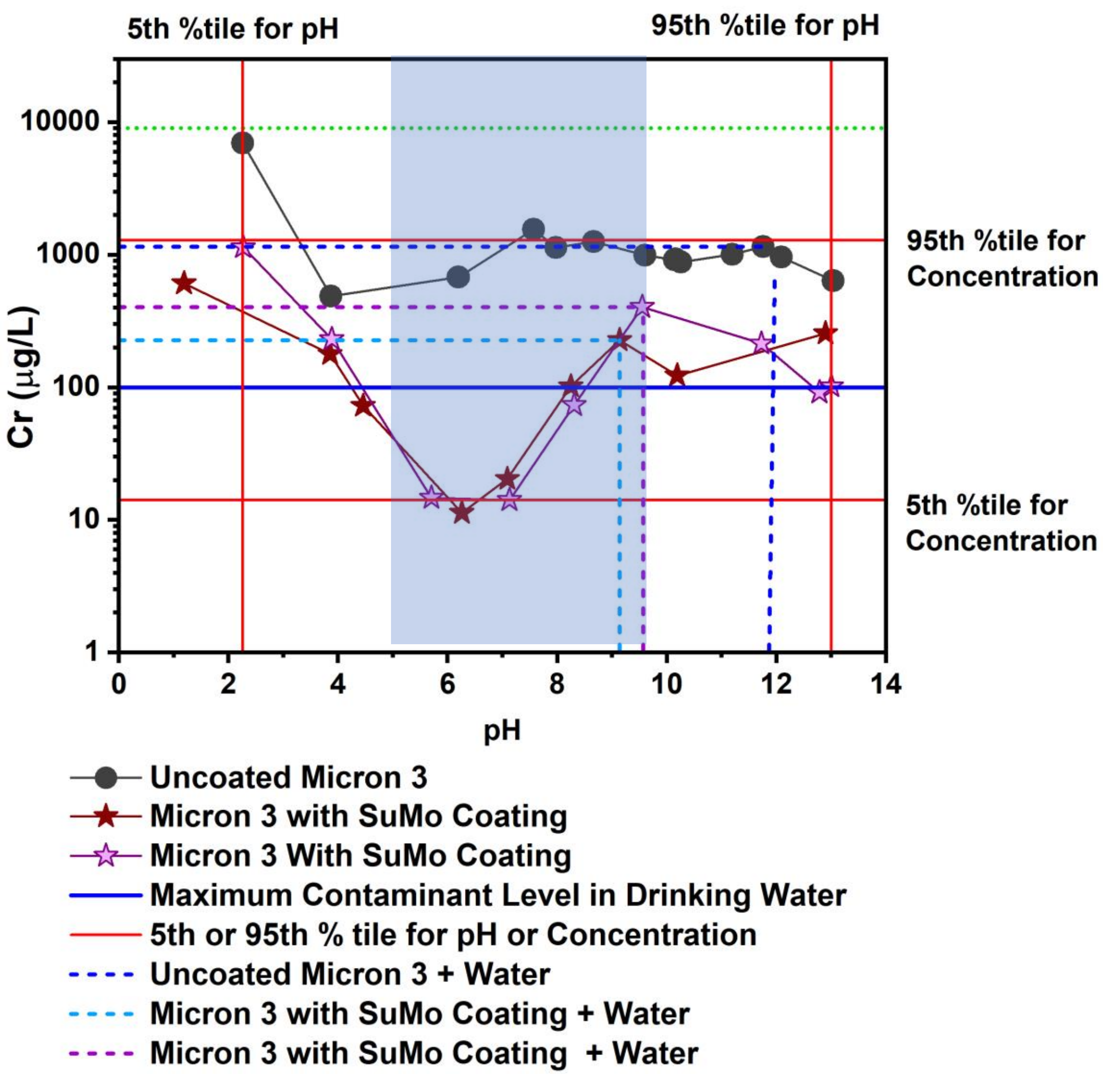
Leaching assessment by electrical conductivity and pH change in 24 hours at **L/S = 10 (EPA guidelines)**

Table. 1 Coating efficacy of SuMo fly ash against leaching based on EC and pH values

	EC (µS)-	Average range of % reduction in EC at 24h as compared to uncoated fly ash	pH	Average range of decrease in pH
SuMo Fly ash (Class F)	410-650	**74-87**	8-8.5	**3.9 - 4.4**
Uncoated Class F Fly ash	3000	NA	12.4	NA
SuMo Fly ash (Class C)	650-900	**72-81**	9-8.8	**3.8-4**
Uncoated Class C Fly ash	3400	NA	12.8	NA

- EC decreased in the range of 72-87 % for the SuMo fly ash showing coating efficacy.
- pH reduces by approximately 4 units for the SuMo fly ash showing coating efficacy.

Leaching Test of the SuMo Fly Ash following EPA protocol (LEAF)

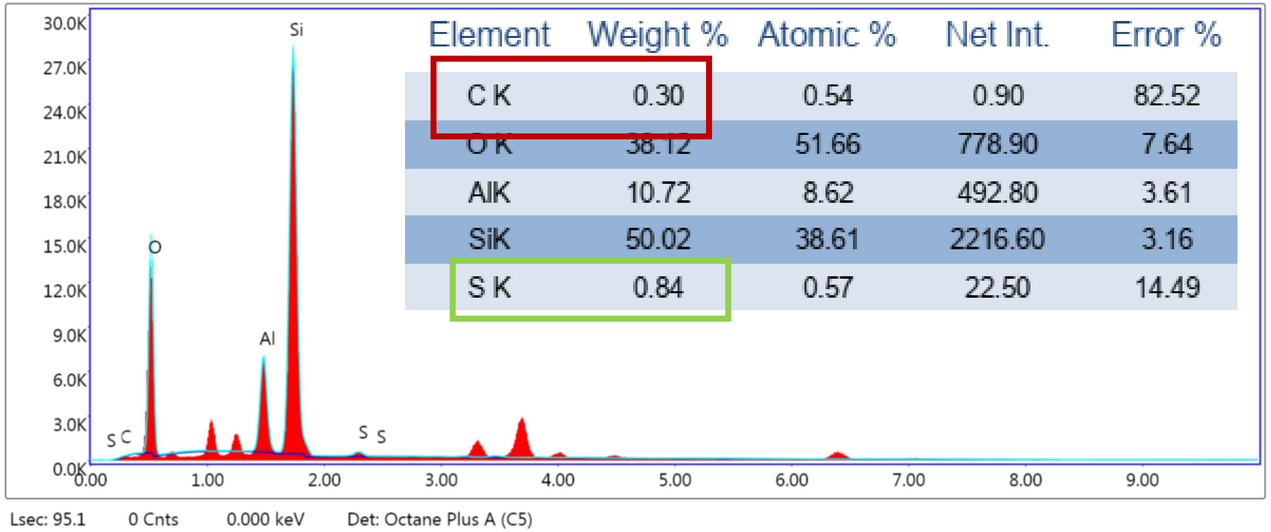


SuMo coating effectively decreased the leaching potential of B and Cr from Micron^3 fly ash.

The list of elements that have decreased leaching potential after SuMo coating include:
Ba, Be, Ca, Cd, Co, Li, Mo, Ni, Sr, and Zn.

Fig. 7 Selected ICP-MS results of leachate emanating from uncoated Class F (Micron3) and SuMo coated sample

Effect of Coating on the Surface composition of Fly Ash



Element	Weight %	Atomic %	Net Int.	Error %
C K	0.30	0.54	0.90	82.52
O K	38.12	51.66	778.90	7.64
AlK	10.72	8.62	492.80	3.61
SiK	50.02	38.61	2216.60	3.16
S K	0.84	0.57	22.50	14.49

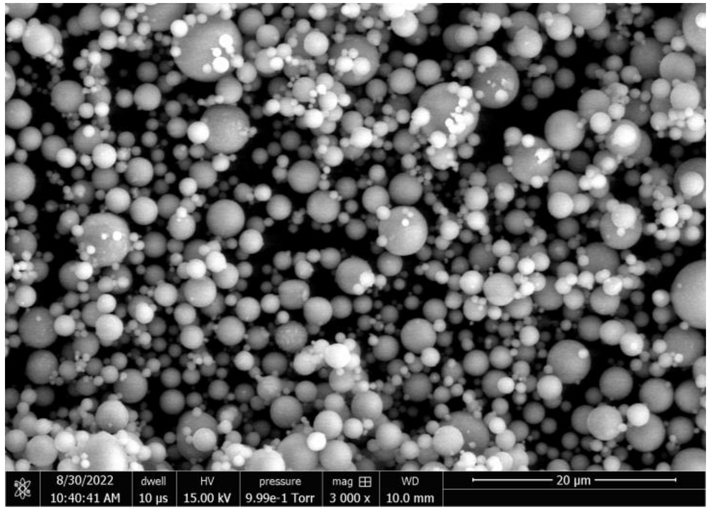
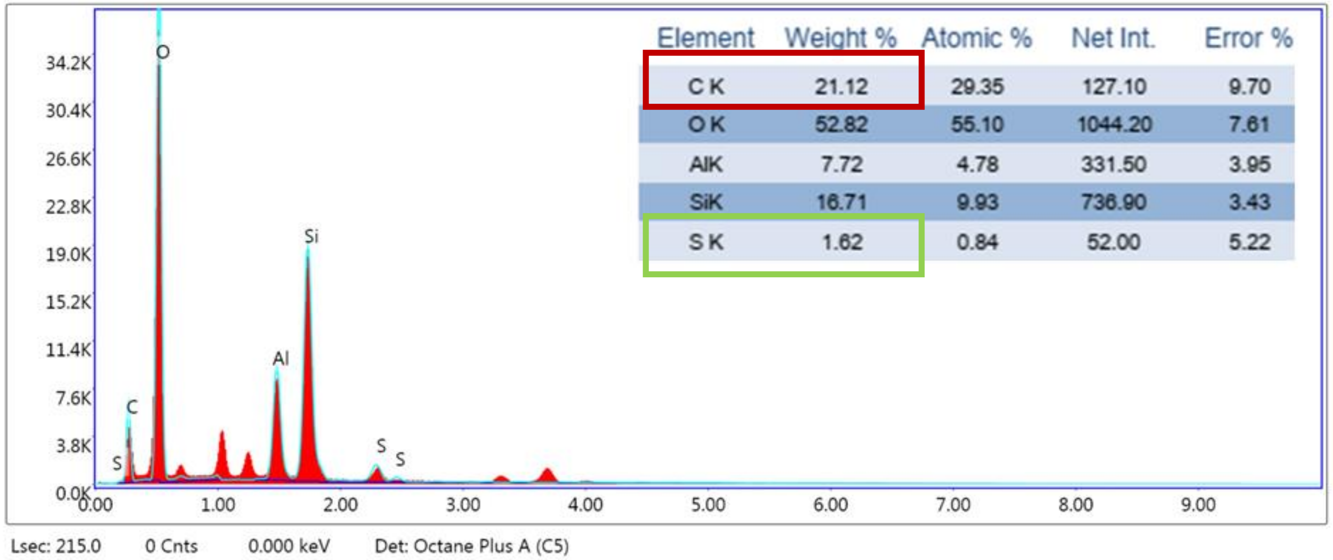


Fig.8 EDX spectra and E-SEM micrographs of uncoated fly ash



Element	Weight %	Atomic %	Net Int.	Error %
C K	21.12	29.35	127.10	9.70
O K	52.82	55.10	1044.20	7.61
AlK	7.72	4.78	331.50	3.95
SiK	16.71	9.93	736.90	3.43
S K	1.62	0.84	52.00	5.22

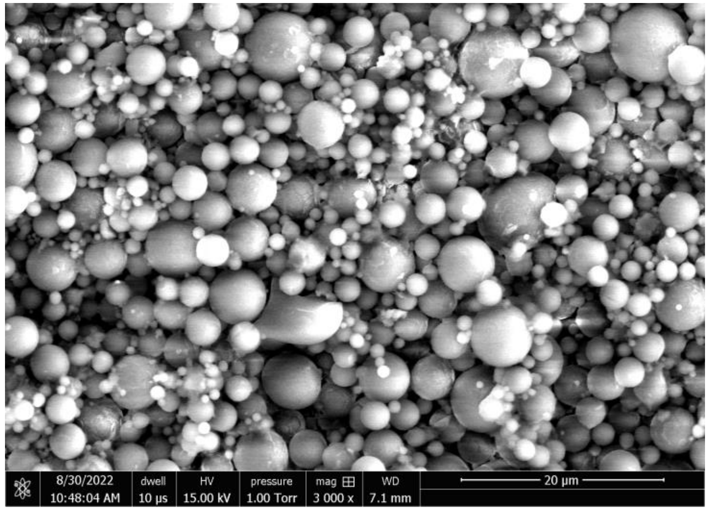


Fig. 9 EDX spectra and E-SEM micrographs of SuMo fly ash

Increase of C and S in SuMo fly ash shows coating establishment on the surface.

Optimization of the SuMo Fly Ash Manufacturing Conditions

Stage 1: Find optimum curing condition and S/Oil ratio based on polymer toughness (Durometer reading) for different oil type.

Table 2:Optimum curing condition for polymer

Oil type	S/Oil ratio	Curing temp	Curing time (h)
Canola	15/100	150	18
Soybean	15/100	180	24
Castor	15/100	150	18
Linseed	15/100	180	24
Oleic acid	NA	NA	NA
Base 44	NA	NA	NA

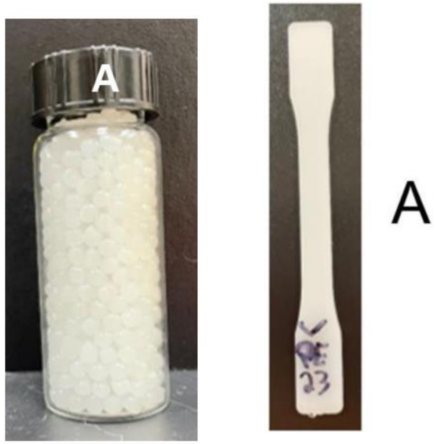
Stage 2: Find optimum ratio of sulfurized vegetable oil with respect to fly ash required to

- Minimum leaching suppression by 70 %
- Hydrophobicity with contact angle more than 110^{o}
- Particle size yield below 45 μm with 70 % yield.

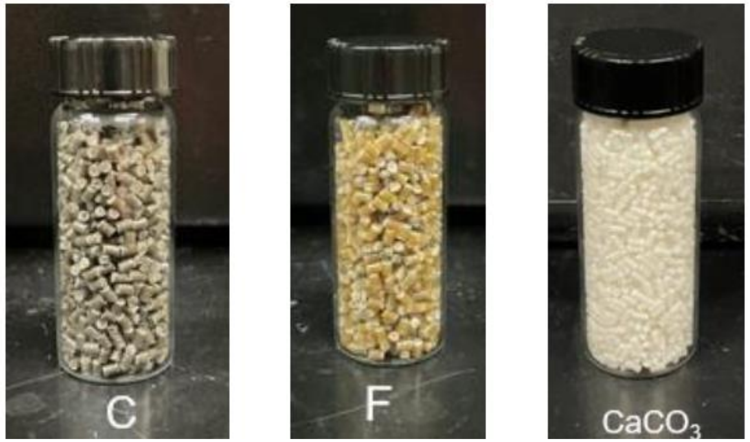
Summary

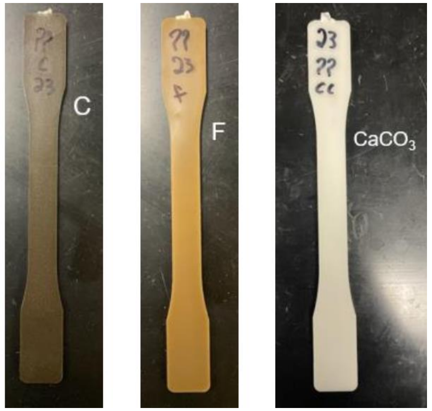
- **Class F fly ash responds better to the coating than Class C in terms of leaching suppression.**
- **The optimum ratio of sulfurized vegetable oil to fly ash coated by the two-step coating ranged between 12.5-15 %.**

Virgin Polypropylene (PP), Unmodified Fly Ash as Fillers in PP



Virgin polypropylene (PP)





Polymers with Class C, Class F and $CaCO_3$ as fillers at 20 % (by weight)

Fig. 10 Produced polymers as pellets and test bars using unmodified fly ash and $CaC0_3$ fillers

Table 3: Mechanical testing of the control material without fillers and with fillers (20%)

Samples	**Tensile Modulus (Mpa)**	**Flexural Modulus (Mpa)**	**Yield Strength (Mpa)**	**Ultimate Strength (Mpa)**	**Elongation (%)**
Virgin PP Injection-Molded Test Bar	1629 (± 64)	1708 (± 98)	12.4 (± 2.6)	17.3 (± 1.0)	59 (± 39)
Twin-Screw Pelletized PP Injection-Molded Test Bar	1464 (± 567)	1671 (± 79)	9.9 (± 5.7)	16.4 (± 6.4)	41 (± 15)
PP Test Bar Filler C	2132 (± 66)	2084 (± 96)	15.8 (± 0.8)	18.9 (± 2.4)	5.1 (± 0.2)
PP Test Bar Filler F	2233 (± 44)	1960 (±115)	17.4 (± 0.3)	18.2 (± 1.0)	5.1 (± 0.1)
PP Calcium carbonate	2106 (± 73)	2095 (± 76)	16.8 (± 1.2)	15.0 (± 5.0)	5.4 (± 0.2)

- **Uncoated Fly ash filled PP exhibited higher ultimate strength than $CaCO_3$ filler**
- **No significant change in elasticity among the three fillers in case of uncoated fly ash**

Effect of SuMo Fly Ash Fillers in PP on mechanical properties

Class F | Class C

10%

25%

Powder residue does not always adhere to surface of pellet at higher FA addition (50%)

Fig. 11 Produced polymers as pellets and test bars using SuMo fly ash

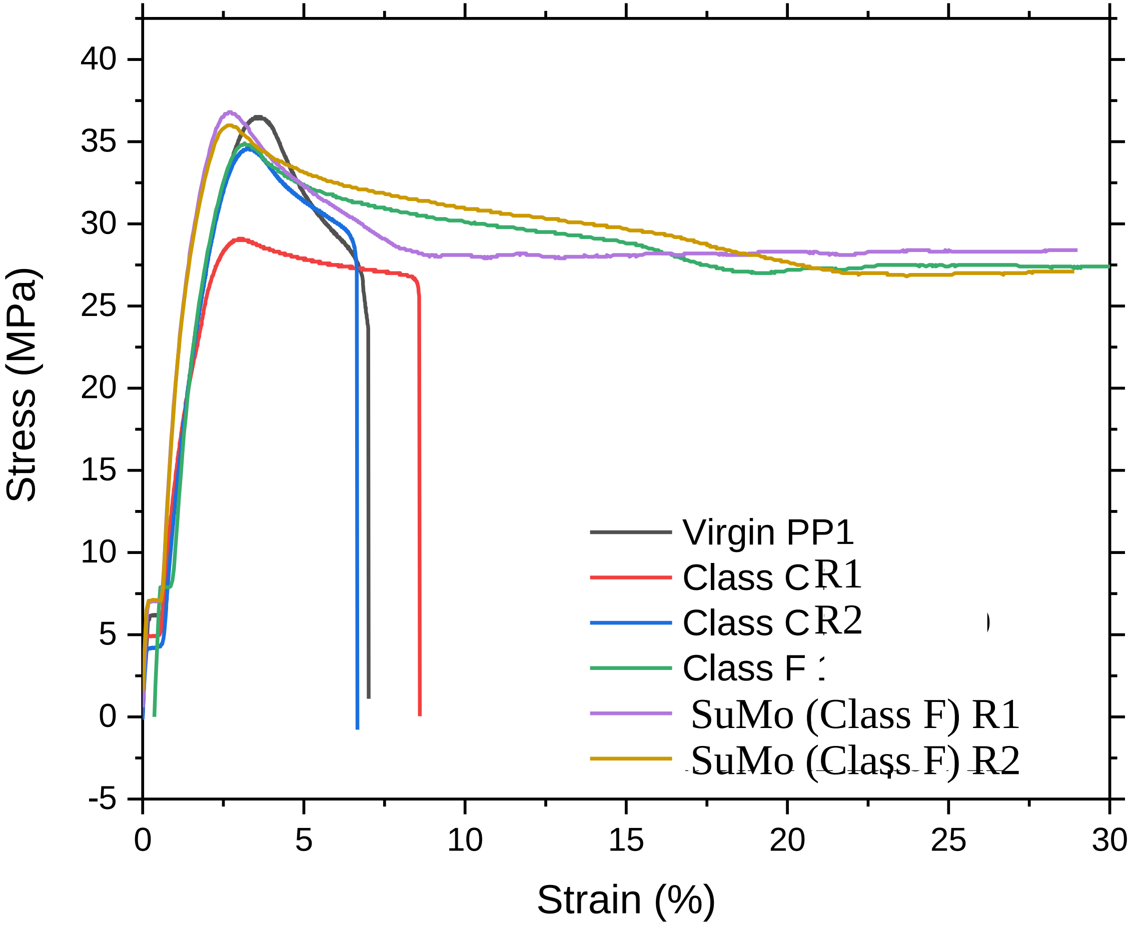


Fig. 12 Stress-strain response of SuMo fly ash as filler (10%) in PP

- **SuMo fly ash although having relatively bigger particles exhibited good tensile resistance at higher strain rates**

Effect of uncoated fly ash fillers in natural rubber

Table 4: Mechanical properties of elastomer composed with uncoated fly ash as filler in natural rubber matrix

Mechanical Properties	Unit	0	2.5	5	10
Shore hardness	NA	61	59	59	57
Tensile strength	(Mpa)	27	27	29	27.5
Elongation at break	mm	500	505	542	523
Crosslink density	Mol/cm3	0.0087	0.0089	0.0080	0.0081

- Uncoated Class F fly ash filled natural rubber did not change mechanical properties up to 10%

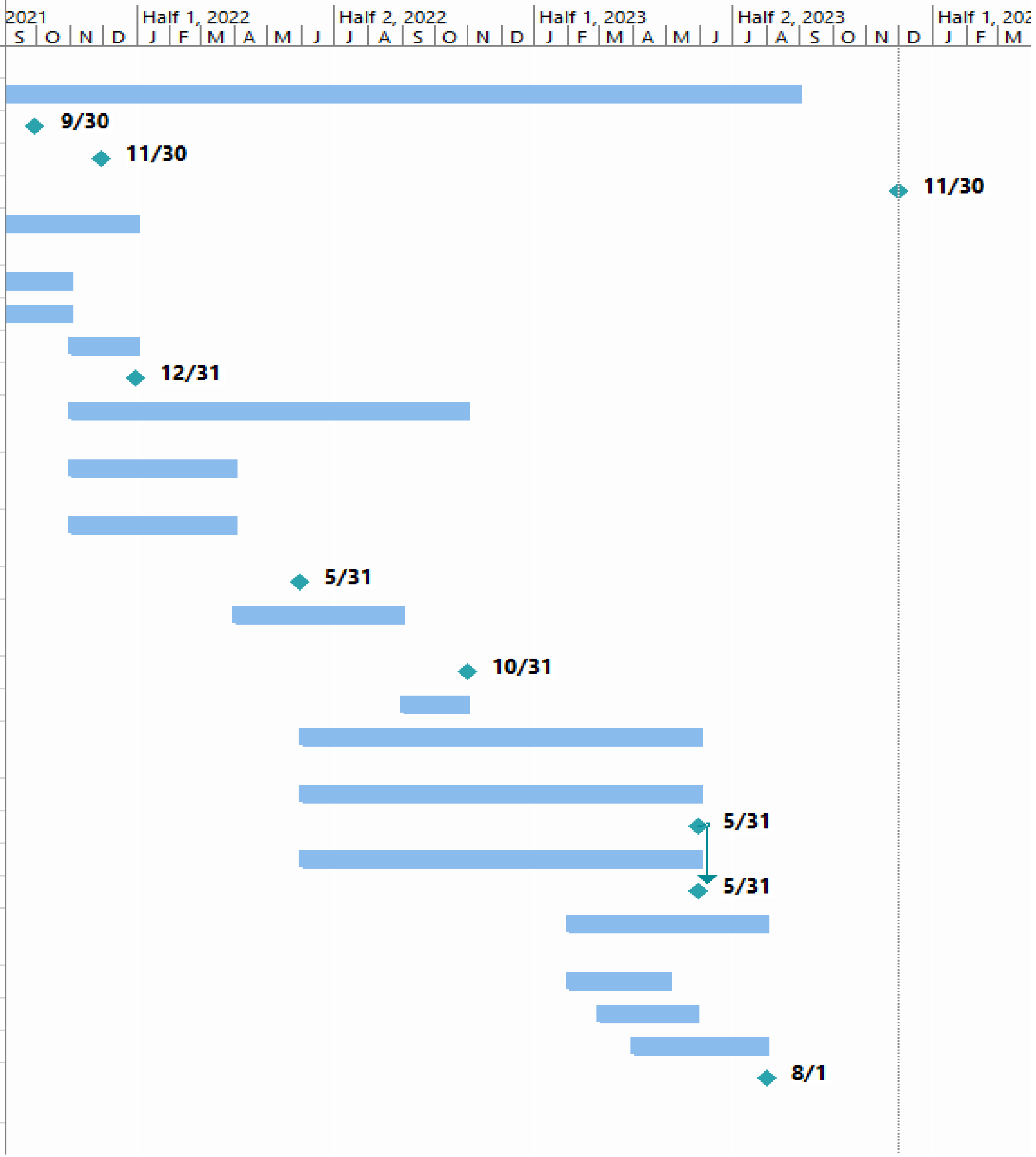
- Filler ratio will be investigated up to 30 % to see how much carbon black can be replaced by SuMo fly ash

Summary of the Research and Development

- Sulfurized Vegetable Oil coated flyash (SuMo flyash) was successfully prepared with a particle size of $\leq$ 45 micron which exhibited hydrophobicity of contact angle 120^{O}
- The coating reduces around (70-80)% leaching of metals from fly ash when exposed to water
- $Micron^3$ based SuMo fly ash filled PP exhibited higher ductility than the unfilled and Class C fly ash
- SuMo fly ash filled PE and Elastomer study is ongoing
- EPA protocol-based study on SuMo fly ash and developed composites are ongoing

Project Plan and deliverables

Task Name	Start	Finish
1. Project Management and Planning	**Wed 9/1/21**	**Thu 8/31/23**
1.1 Updated PMP	*Thu 9/30/21*	*Thu 9/30/21*
1.2 Completed Initial TMP	*Tue 11/30/21*	*Tue 11/30/21*
1.3 Project Data Report and Final TMP	*Thu 11/30/23*	*Thu 11/30/23*
2. Collection, Sizing, and Characterization of Fly Ash Material	**Wed 9/1/21**	**Fri 12/31/21**
2.1 Fly Ash Material Collection	Wed 9/1/21	Sun 10/31/21
2.2 Sizing and Size Fractationation of Fly Ash	Wed 9/1/21	Sun 10/31/21
2.3 Characterization of Fly Ash Size Fractions	Mon 11/1/21	Fri 12/31/21
Complete Characterization of the Fly Ash Size fraction	*Fri 12/31/21*	*Fri 12/31/21*
3. Development of a Surface Coating Technique to Generate Modified Fly Ash (SuMo)	**Mon 11/1/21**	**Mon 10/31/22**
3.1 Synthesize Sulfurized Vegetable Oil Followed by Coating	Mon 11/1/21	Thu 3/31/22
3.2 Sulfurization of Vegetable Oil/Fatty Acids Coated Fly ash	Mon 11/1/21	Thu 3/31/22
Complete Screening of Appropriate Coating Method	*Tue 5/31/22*	*Tue 5/31/22*
3.3 Optimization of Conditions to Generate SuMo Fly Ash	Fri 4/1/22	Wed 8/31/22
Optimized Process for Modification of Fly Ash	*Mon 10/31/22*	*Mon 10/31/22*
3.4 Characterization of SuMo Fly Ash	Thu 9/1/22	Mon 10/31/22
4. Suitabilityof SuMo Fly Ash as Filler Material in Plastics/Elestomers	**Wed 6/1/22**	**Wed 5/31/23**
4.1 Replacement of CaCO3 Filler in Plastics	Wed 6/1/22	Wed 5/31/23
Demonstrate Replacement of CaCO3 Filler in Plastics	*Wed 5/31/23*	*Wed 5/31/23*
4.2 Replacement of Carbon Black Filler in Elastomers	Wed 6/1/22	Wed 5/31/23
Demonstrate Utility of SuMo Fly Ash Filler in Elastomers	*Wed 5/31/23*	*Wed 5/31/23*
5. Environmental Characterization of SuMo Fly Ash and Final Products	**Wed 2/1/23**	**Tue 8/1/23**
5.1 Leaching	Wed 2/1/23	Wed 5/3/23
5.2 Hg Volatilization	Wed 3/1/23	Mon 5/29/23
5.3 EPA Beneficial Use Methodology	Sat 4/1/23	Mon 7/31/23
Complete Environmental Characterization of SuMo Fly Ash and Final Products	*Tue 8/1/23*	*Tue 8/1/23*



Project Team (Key Personnel)

- **University of Illinois:**
  - C. Baroi, PhD, PI
  - L. Zhao, PhD, Co-PI
  - V. Patel (Chemical Engineer)
  - S. Bordoloi (PhD, Postdoctoral Researcher)

- **Ohio State University**
  - K. Cornish (Professor, Endowed Chair and Ohio Research Scholar)

- **U.S. Department of Agriculture (USDA)**
  - B.K. Sharma (PhD, Scientist)

- **Technical Advisory Board**
  - Boral Resources, LLC
  - City Water Light and Power (CWLP)
  - Rothon Rogers (Consultant)

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Lisa Young (Grants & Contracts Coordinator, UIUC)

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Thank you

Coating homogeneity and thickness of the SuMo fly ash

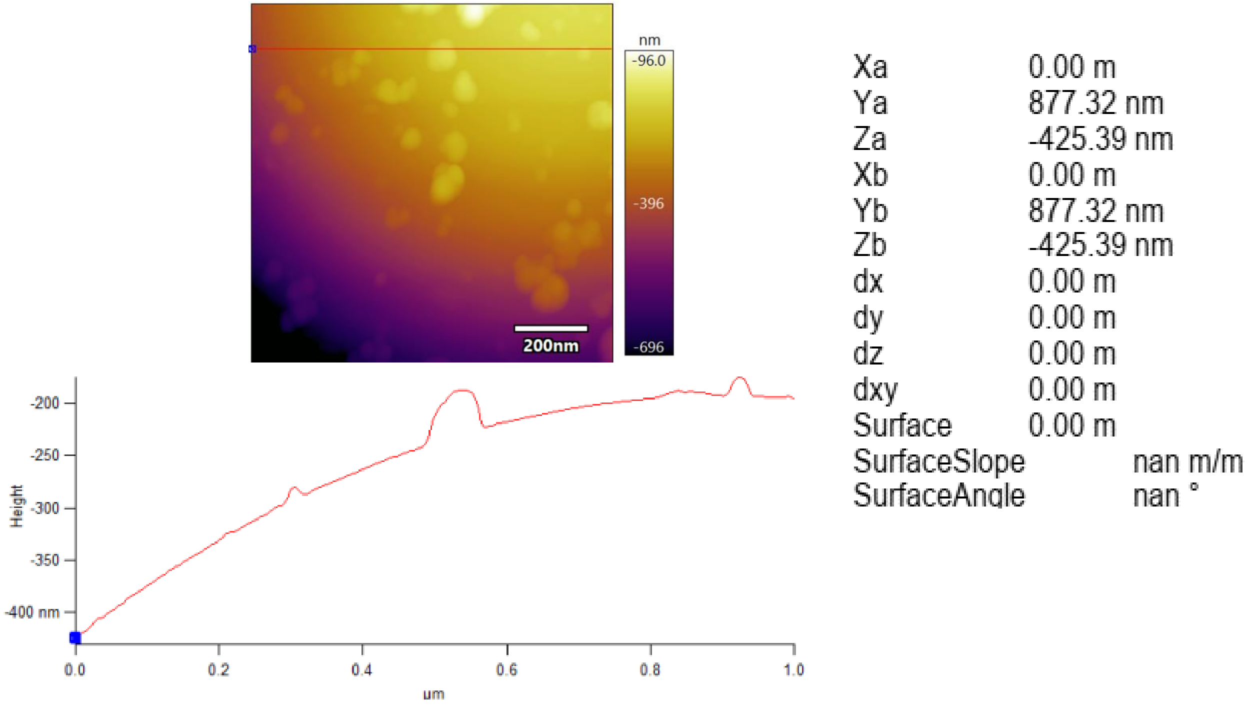

Fig.12 AFM micrographs for uncoated Class F fly ash

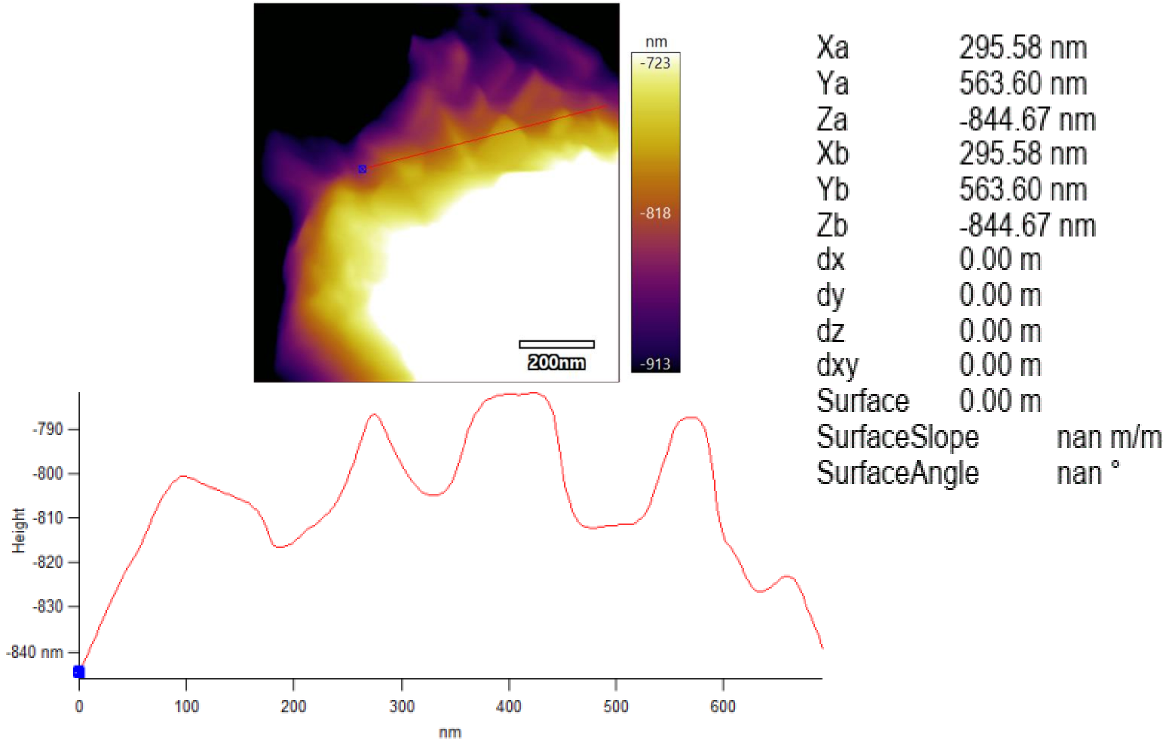

Fig.13 AFM micrographs for SuMo Class F fly ash

Relative increase in surface roughness enables higher surface area for cross linking and higher interlocking in SuMo fly ash

Outline of the Presentation

- **Background/Impact of Research and Development**
- **Basis of Research and Development**
- **Development and investigation of SuMo fly ash.**
- **Demonstrate SuMo fly ash as a replacement filler**
- **Summary and future scope**