Trends in the Mechanical and Chemical Behavior of Fly Ash Produced During 130 Years of Power Generation

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Waste Materials: Defining the Problem

- Waste stream in the US is increasingly complex
- Trends in fly ash production
  - Properties
  - Disposal
- Mixtures with different physical and chemical properties
- What have we learned?

(Ash spill at TVA - www.nytimes.com)

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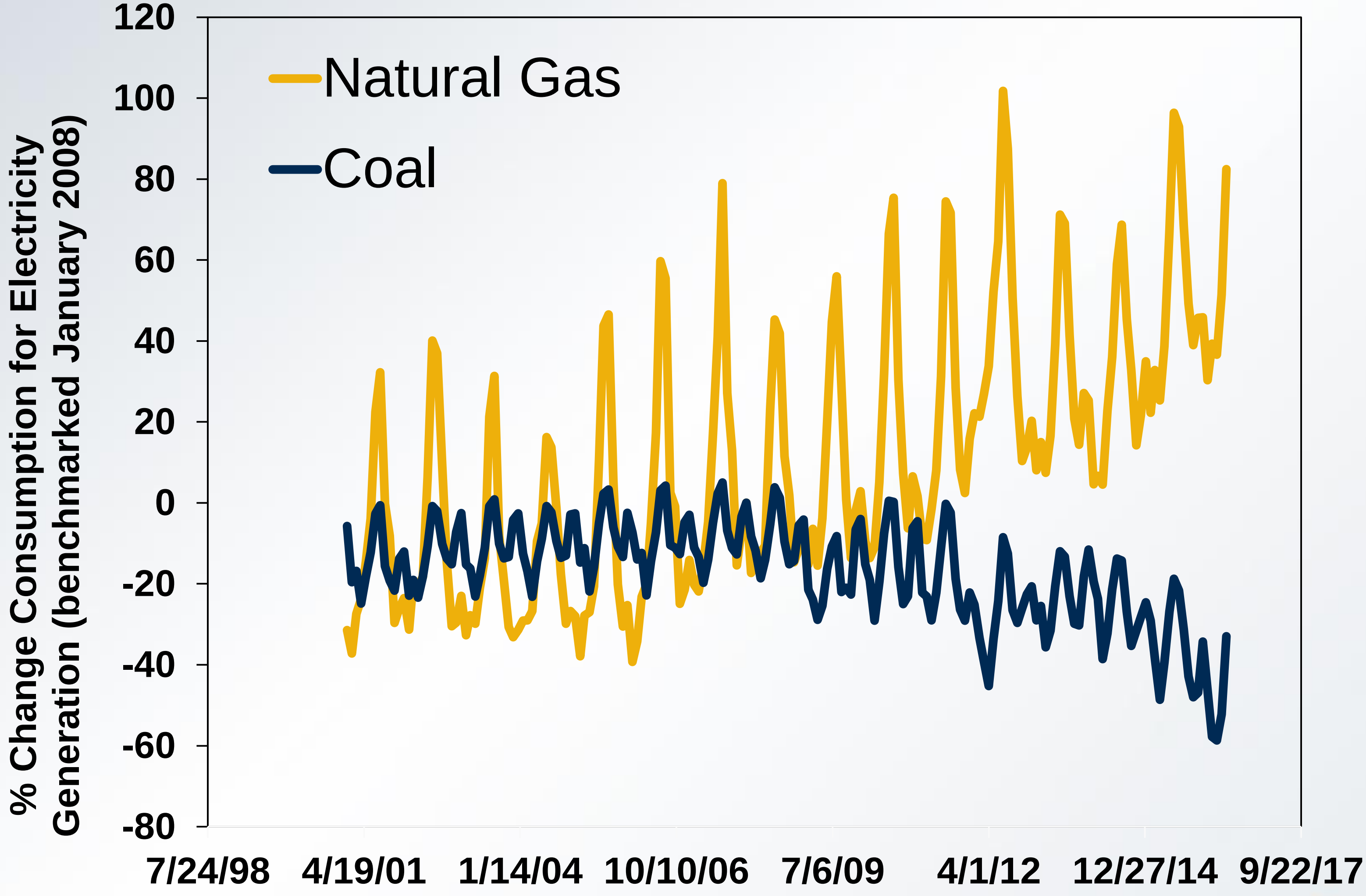
Sustainable Materials Management

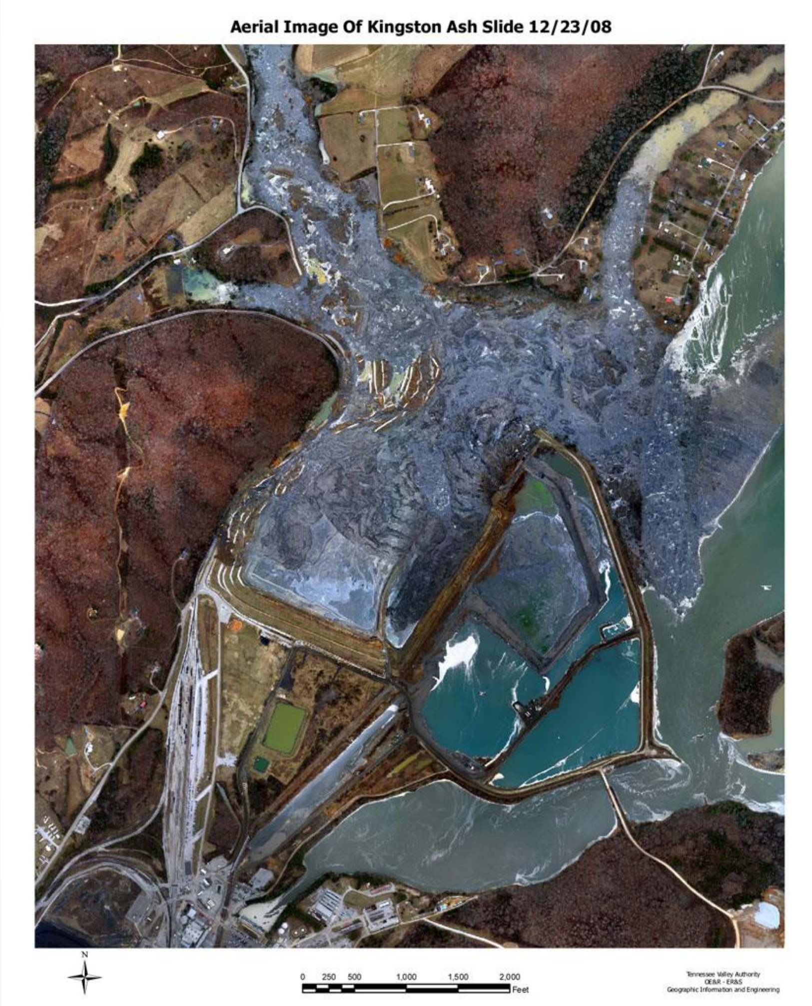
- ASCE defines sustainability as:
  - Set of environmental, economic, and social conditions - in which all of society has the capacity and opportunity to maintain and improve its quality of life indefinitely,
  - Without degrading the quantity, quality or the availability of natural, economic, and social resources
  - "Triple Bottom Line" model of development

Evolving Energy Sources and Associated Concerns



Coal Combustion Residuals: Beneficial Use

- CCR must provide functional benefit
- CCR must substitute for virgin material
- Use of the CCR must meet relevant product specifications, regulatory/design standards
- Comparable to or lower environmental releases than those from analogous products made without CCR



http://upload.wikimedia.org/wikipedia/commons/4/45/Aerial_view_of_ash_slide_site_Dec_23_2008_TVA.gov_123002.jpg

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Reusing the Waste: Coal Combustion Products

- Coal combustion products (131 million tons)
  - Fly ash
    - Cement replacement (1 ton FA reduces ~ 0.8 tons CO_2 from cement manufacture)
    - Coal only (ASTM)
    - Biomass (sustainability life cycle problems)
    - Embankments
  - Flue gas desulfurization
    - Gypsum
    - Agricultural
  - Bottom ash
    - Aggregate replacement
  - Boiler slag
- ~43% utilization

http://www.acaa-usa.org/

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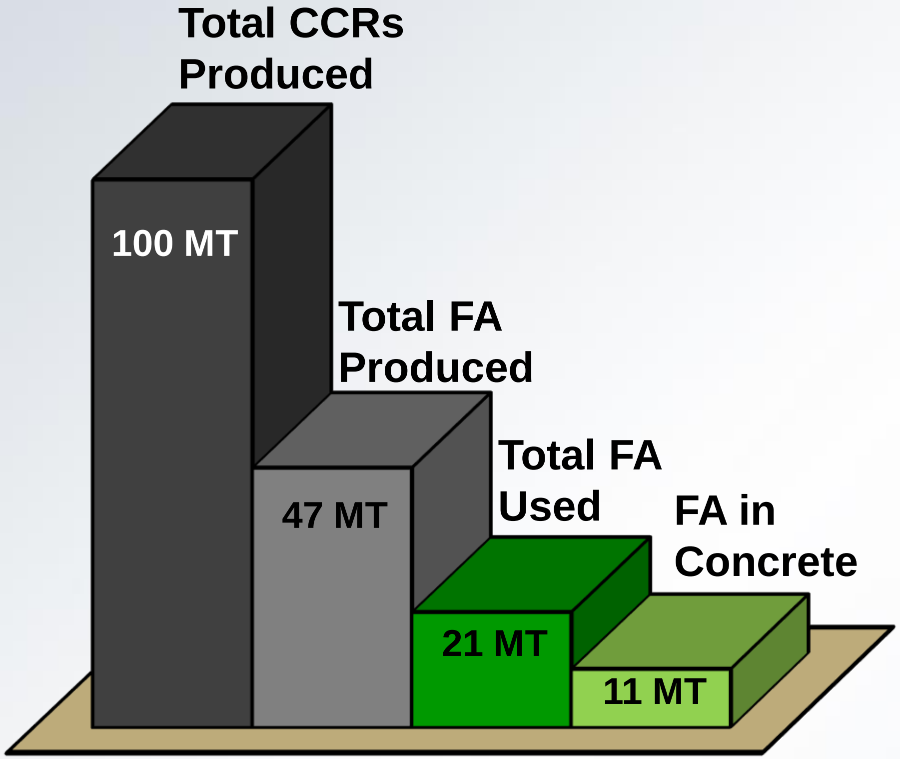
Annual CCR / Fly Ash Production And Reuse

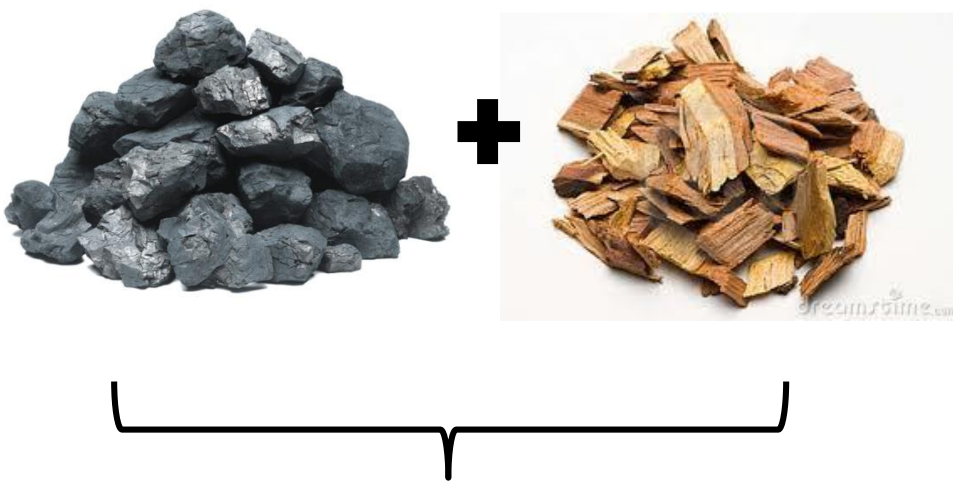


2012 CCR & Fly Ash Statistics (ACAA, 2012)

- **45% of fly ash (FA) is productively reused**
- **Concrete industry - largest reuse sector for fly ash - 51% of FA reuse**
- **26 MT of FA disposed in on-site settlement ponds or landfills**

Sustainability: Carbon Cycling

- **Direct combustion/co-combustion biomass with coal - attractive option for renewable energy , reducing CO_2 emissions.**
  - **ASTM C618 allows only fly ash from 100% coal combustion for use in concrete.**



Coal and biomass co-fired fly ash

Coal: http://www.baylorfans.com/forums/showthread.php?t=256299
Wood chips: http://www.heb.com/page/recipes-cooking/cooking-tips/wood-chips

Pure biomass ash

http://www.heb.com/page/recipes-cooking/cooking-tips/wood-chips
http://www.pelletstoves.ie/page26.php
http://www.jetmulch.com/mulch.php

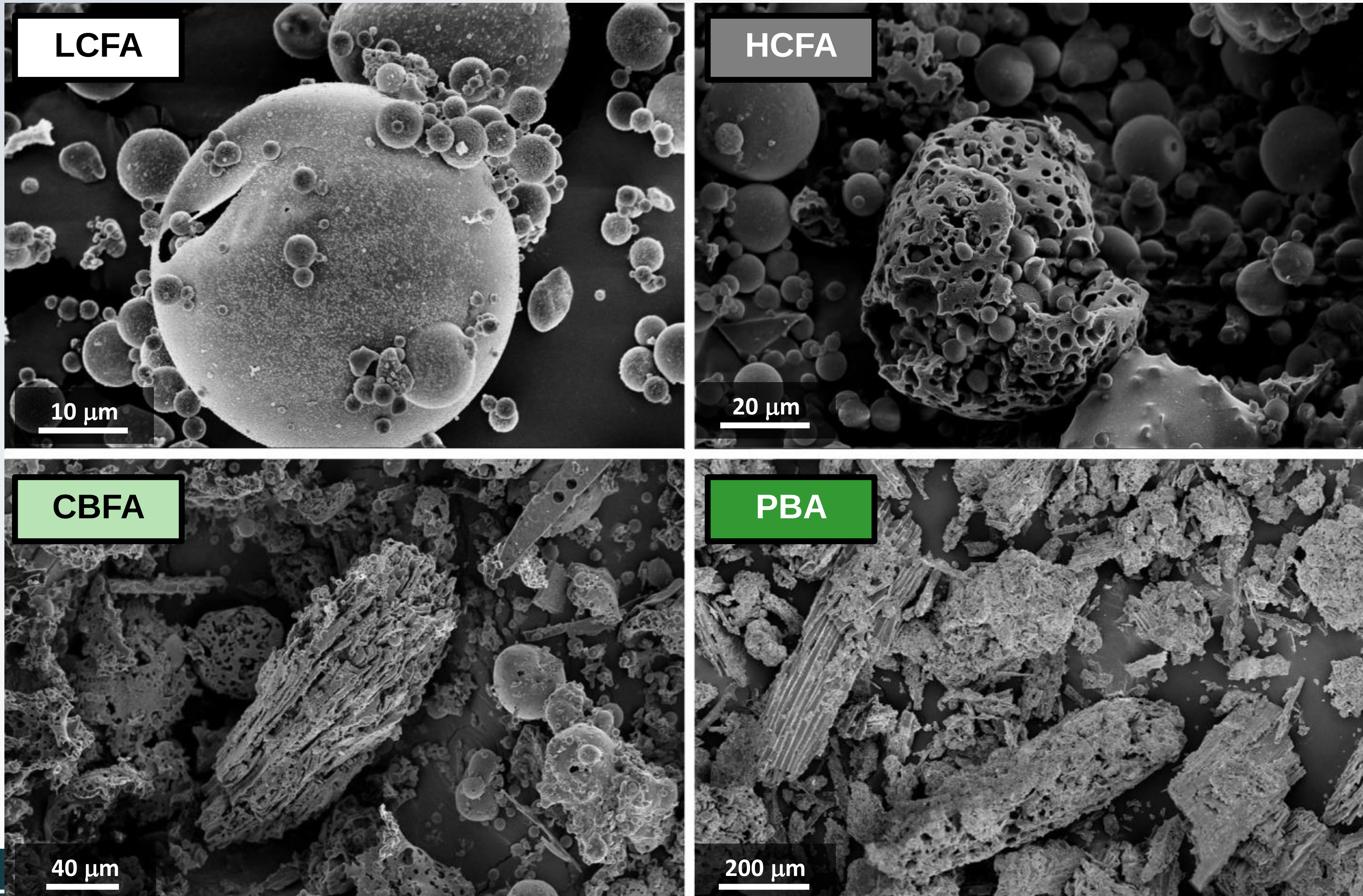
What are the questions?

- Can we effectively use high organic content fly ash in construction materials?
  - High carbon content fly ash
  - Coal and biomass co-fired fly ash
  - Pure biomass ash

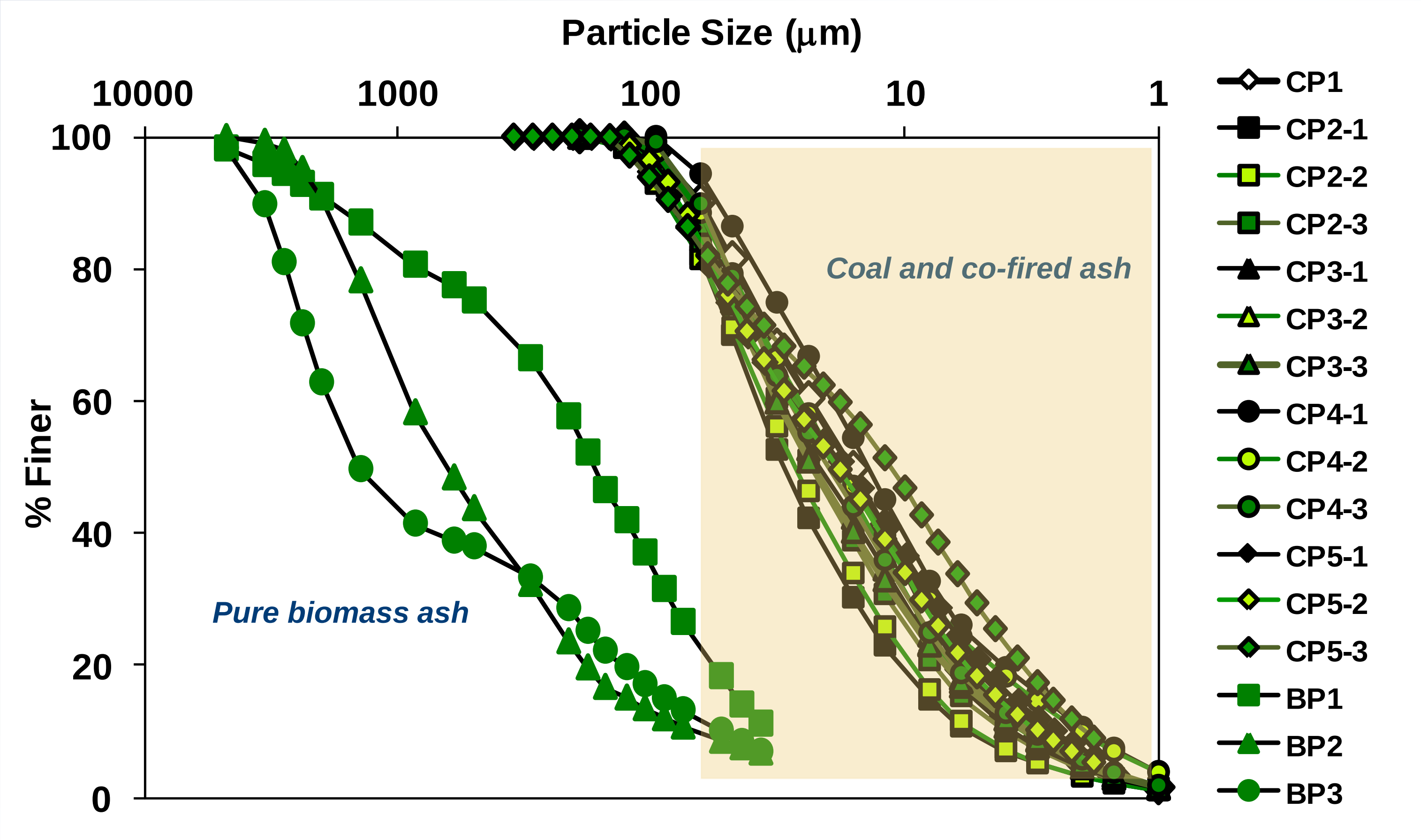
- Are there physical properties we can exploit for better characterization and reuse of the waste?

FLY ASH CHARACTERISTICS: WHAT DO WE KNOW?

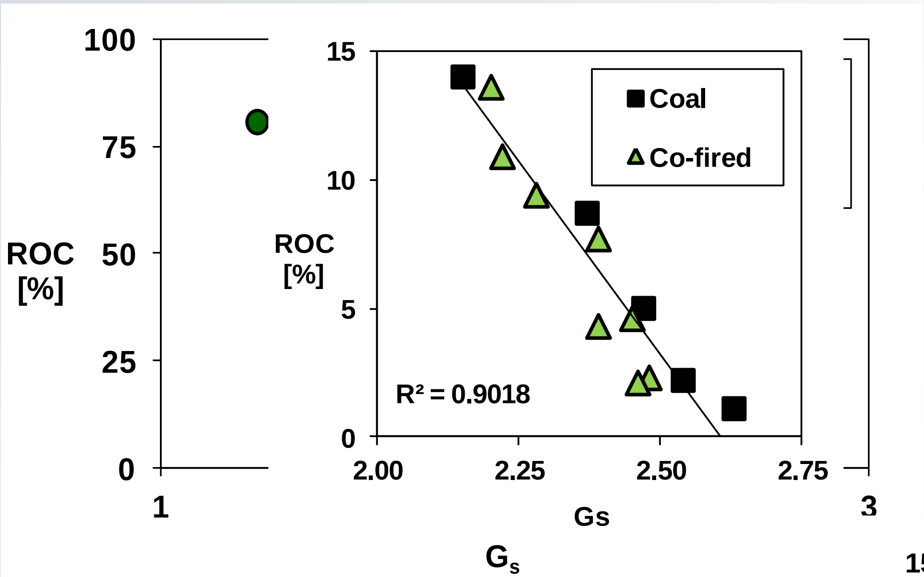
Morphology: What is in fly ash today?



Particle Size Distribution: Comparison to soil

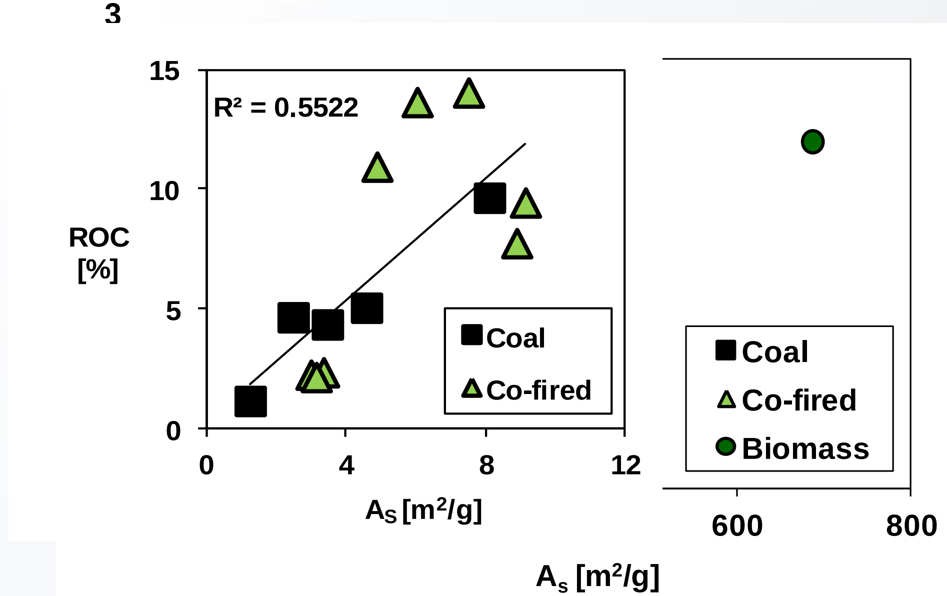


Physical Characteristics: Specific gravity and surface area

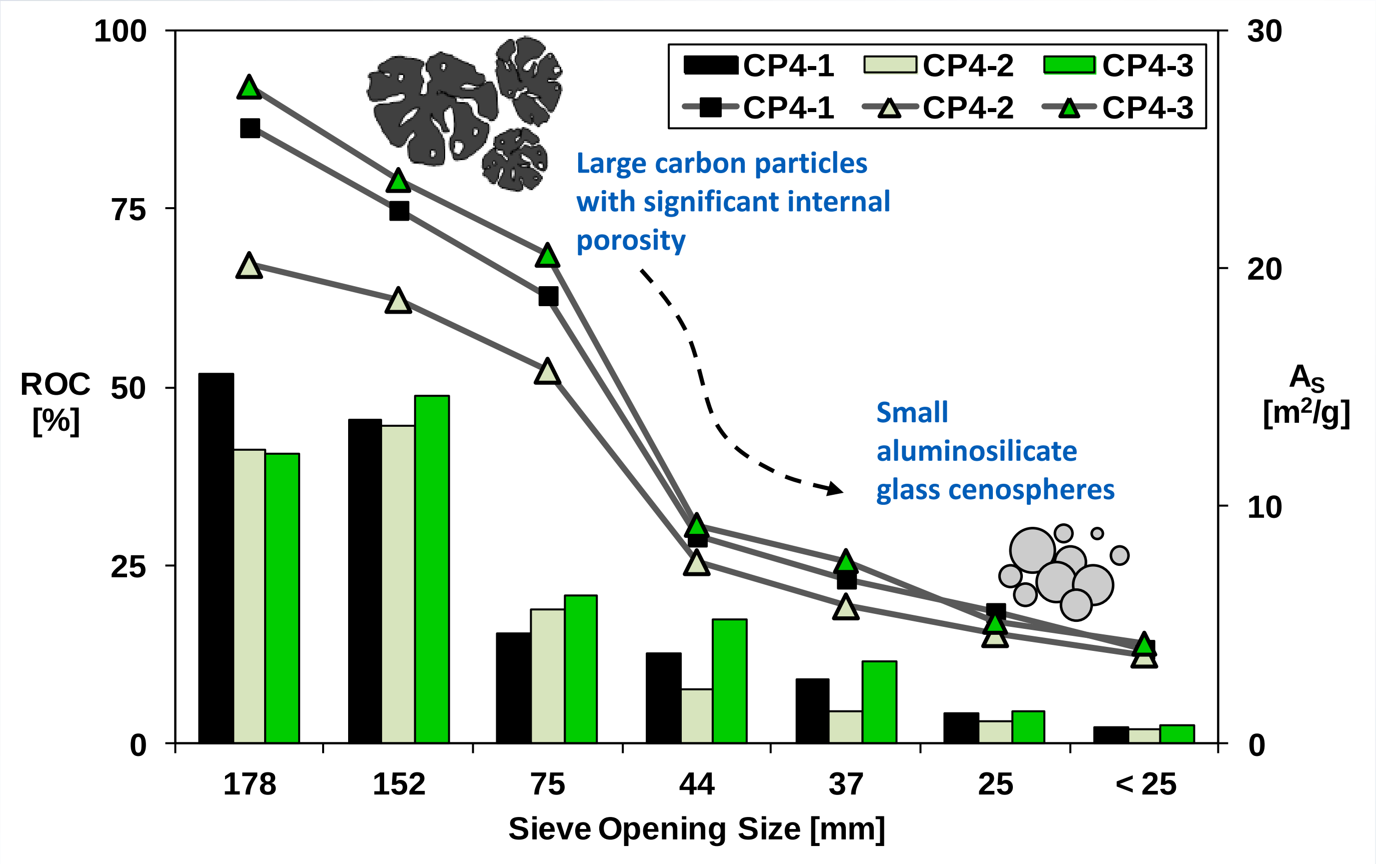


G_s decreases with increasing residual carbon content

A_s increases with increasing residual carbon content



Particle Size, Carbon Content, and Surface Area



Carbon content is more important in determining fly ash surface area than particle size.

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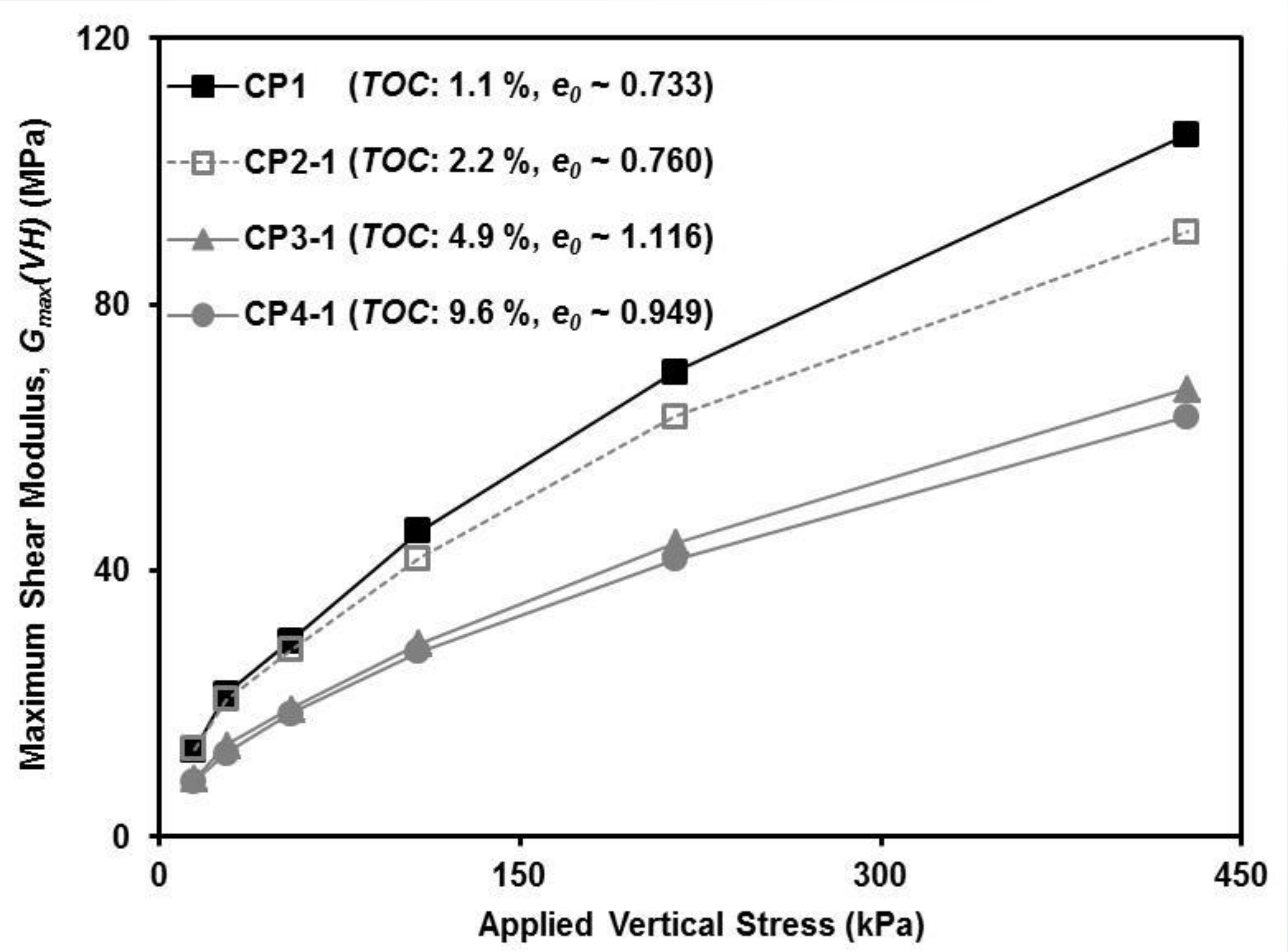
Fly Ash Stiffness: G_{max} = f(Organic Content)



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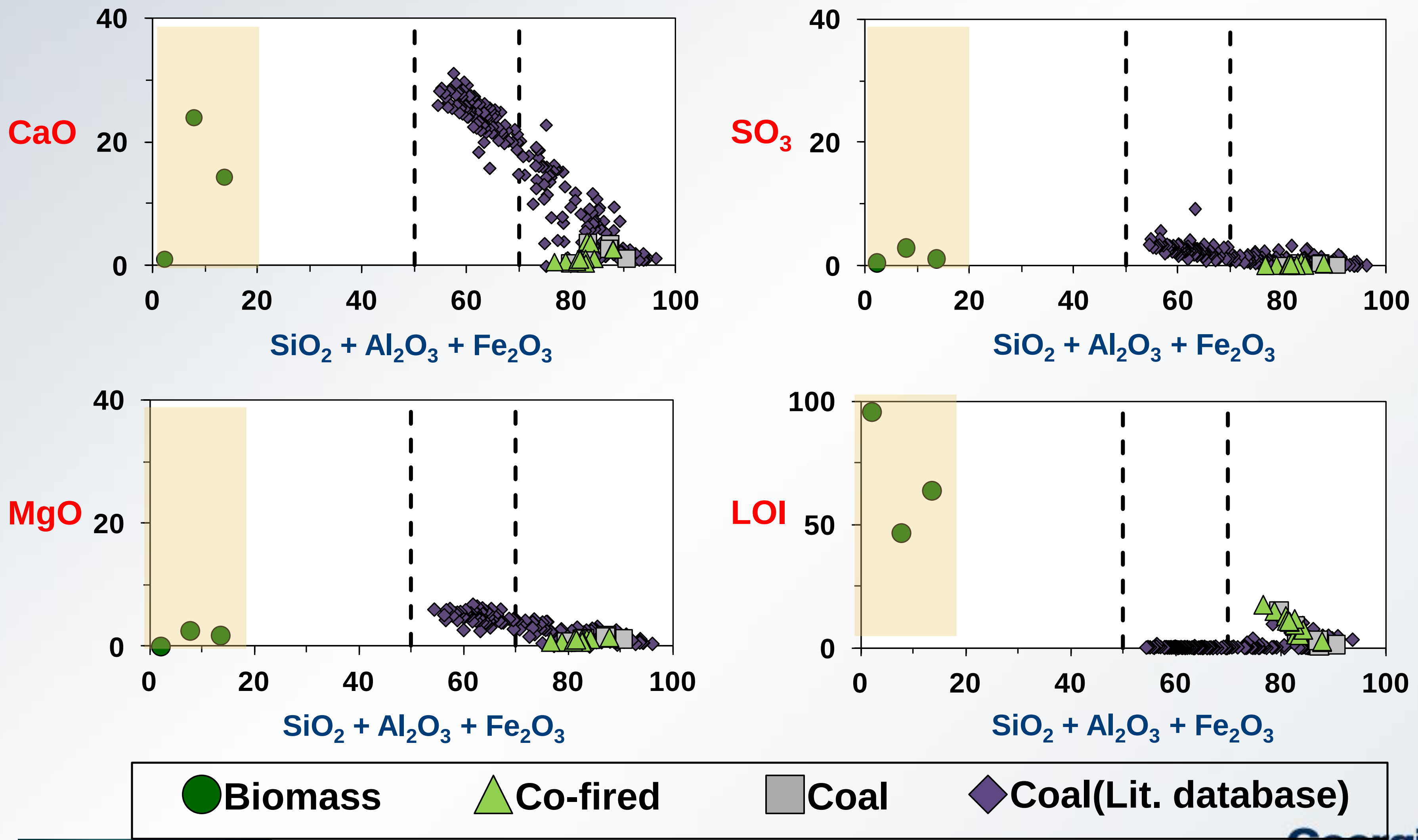
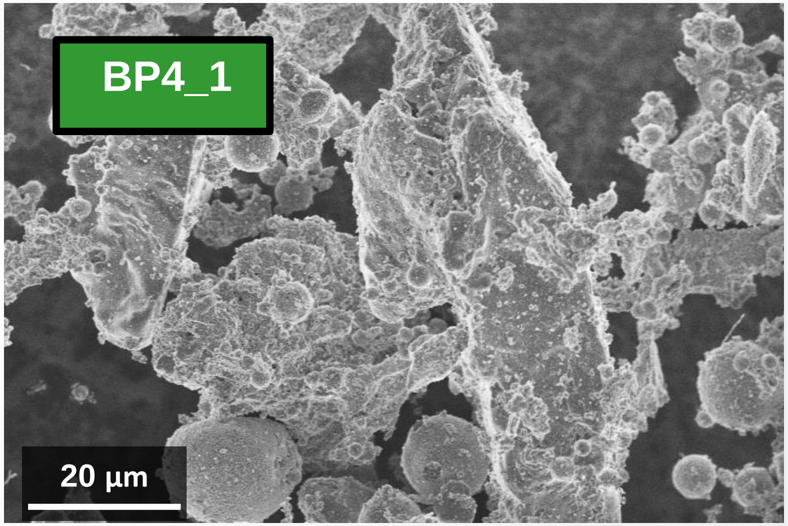
Chemical Composition: ASTM C618 Criteria

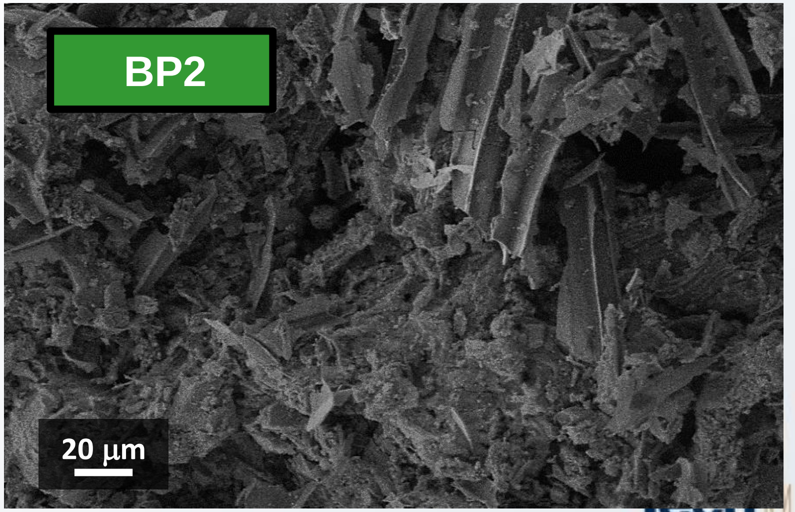


Physical Characterization: Biomass Ash – Full Scale Comparison

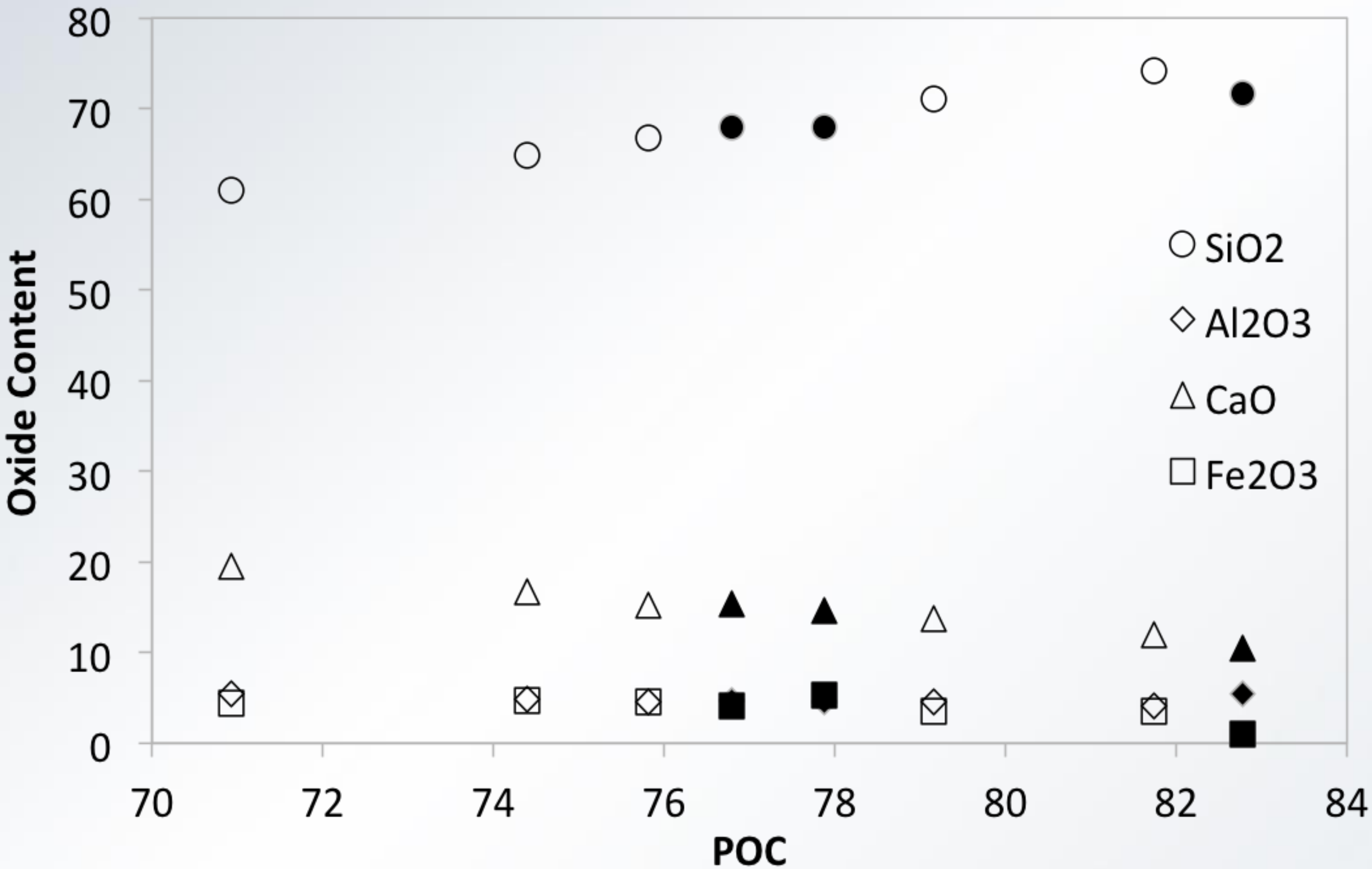
Ash	BP1	BP2	BP3	BP4_1
D_{50} (µm)	168	640	1440	**5.27**
C_u	6.6	13.4	35.5	**0.99**
LOI (%)	46.7	63.9	95.9	**1.59**
G_s	1.87	1.62	1.27	**2.68**
A_s (m^2/g)	116	180	387	**1.50**

Yeboah, N. N. N. (2013)

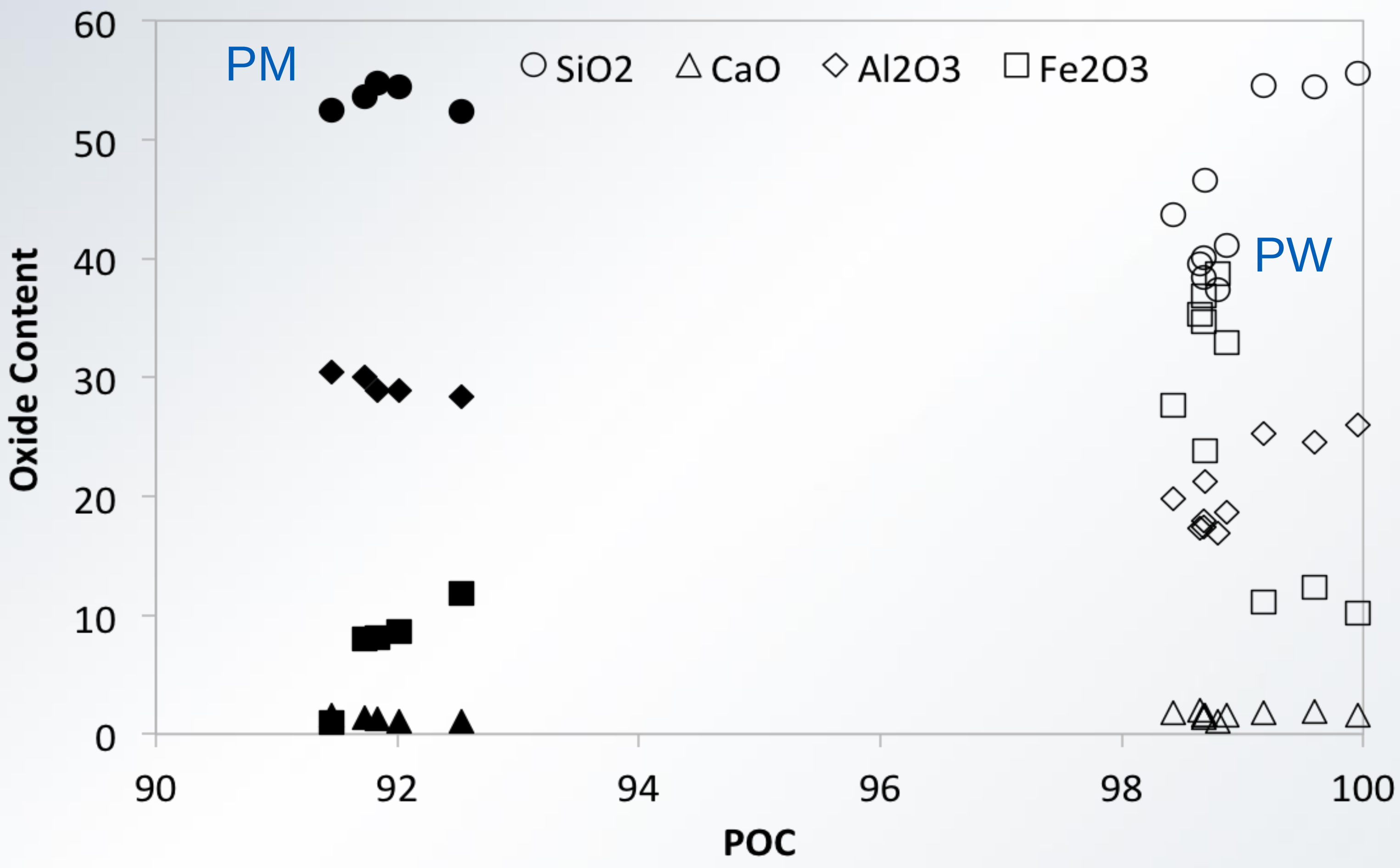




Biomass Ash Oxide Characterization: Full Scale Power Plant



Ponded Ash: Oxide Characterization



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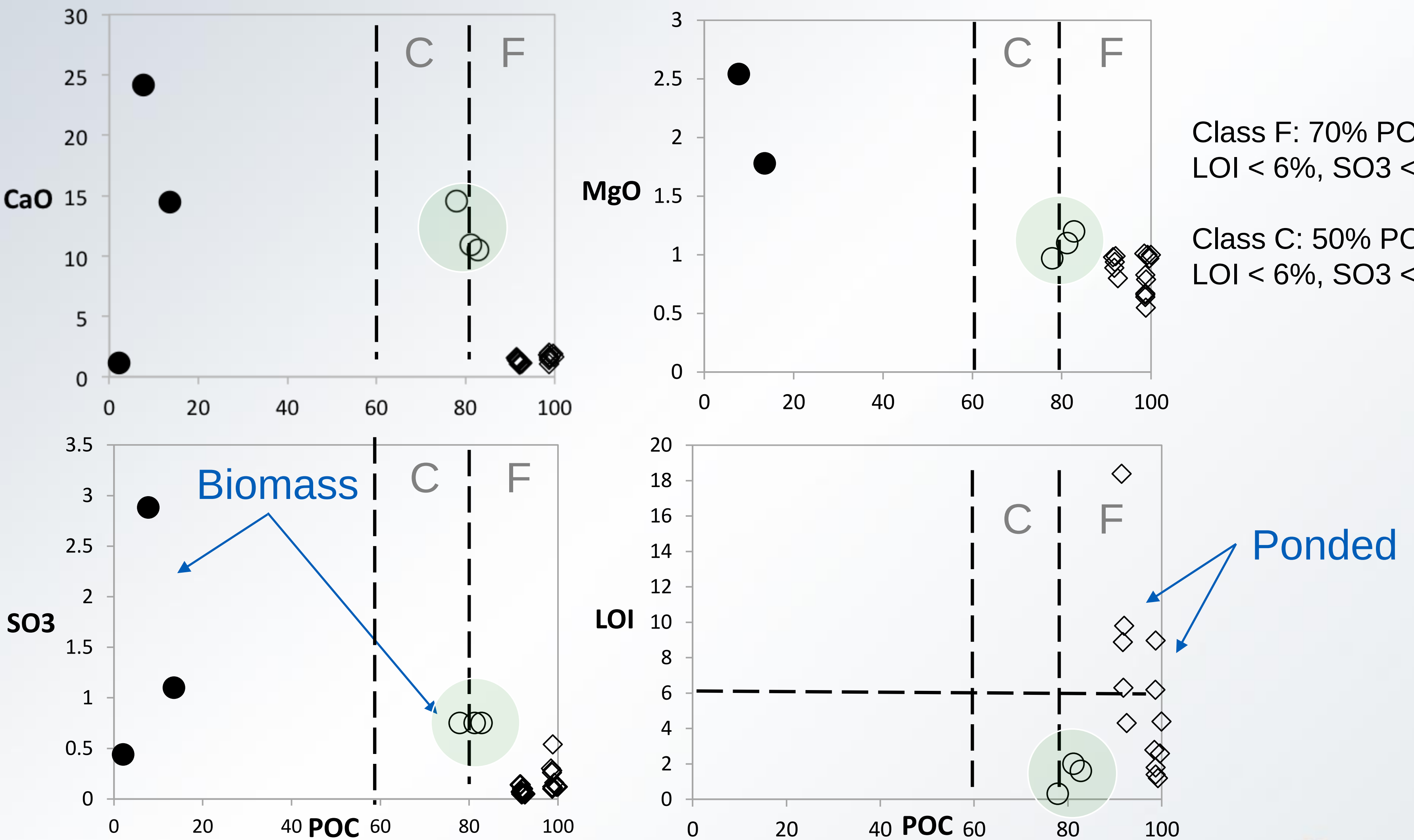
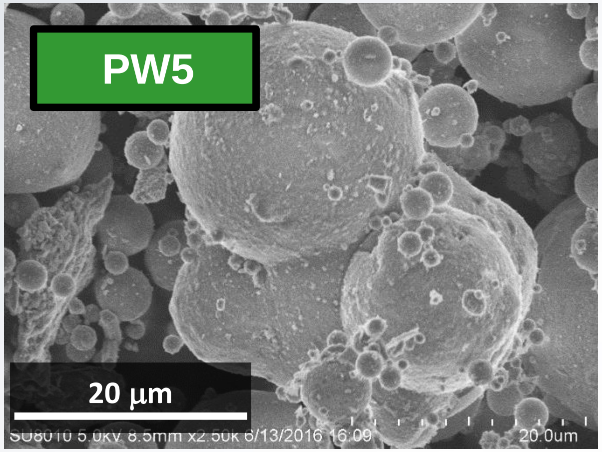
ASTM C618 Requirements:
Ponded and Biomass Classification

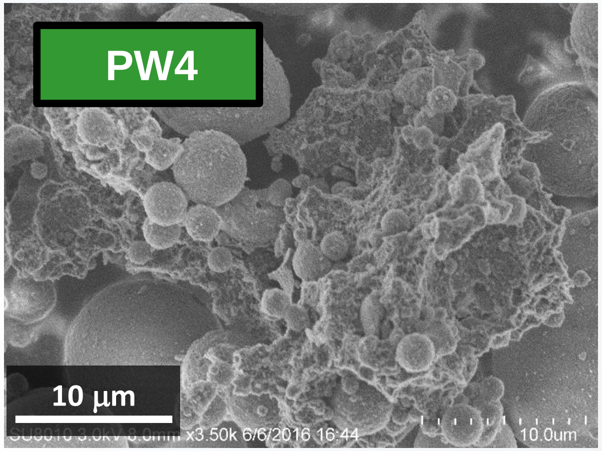


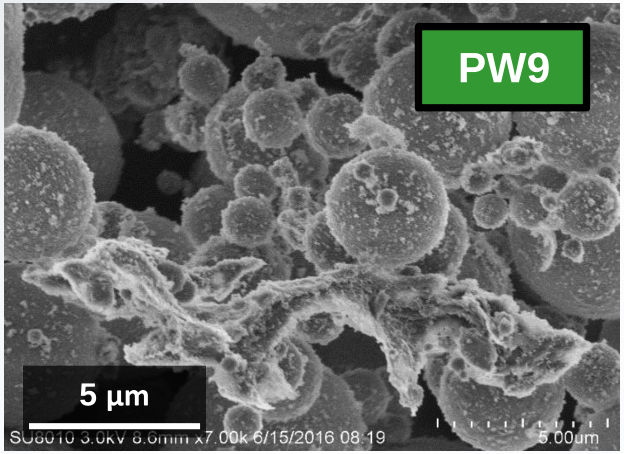
Class F: 70% POC, LOI < 6%, SO3 < 5%

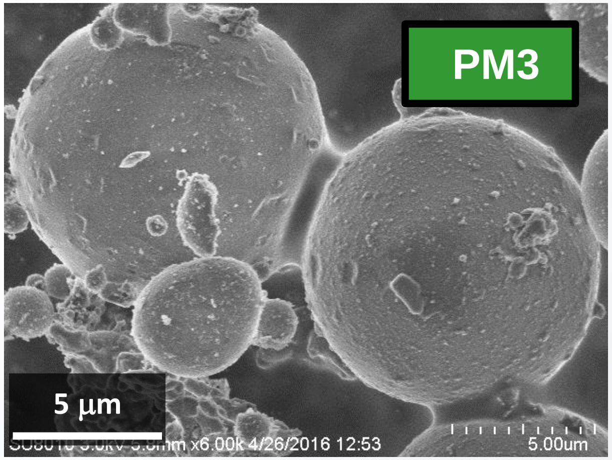
Class C: 50% POC, LOI < 6%, SO3 < 5%

Ponded Ash: Ageing/In-situ Cementation



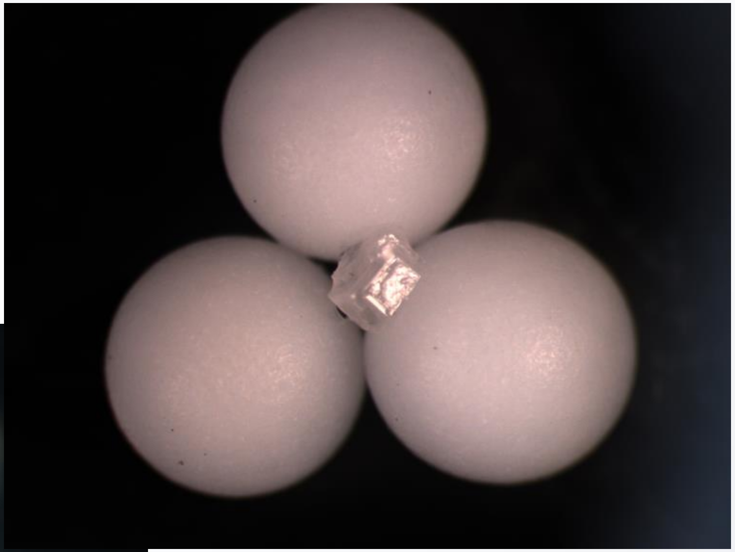


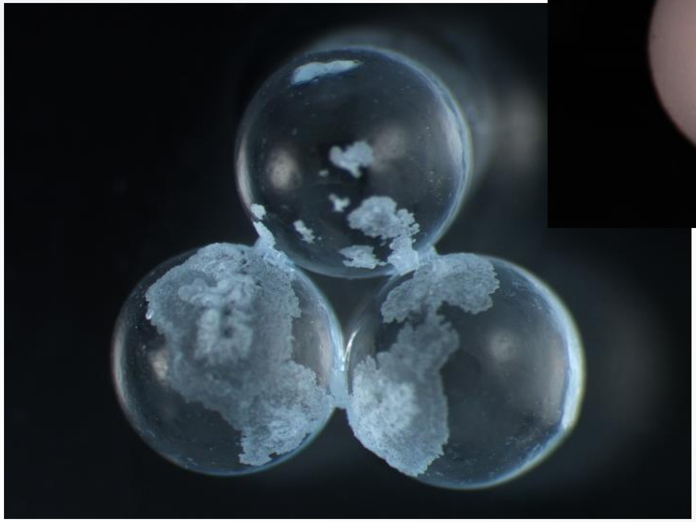




Lessons Learned: Properties

- Organic carbon content
- Physical properties
- Ageing



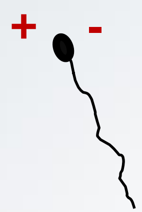


Images by Ross Cutts

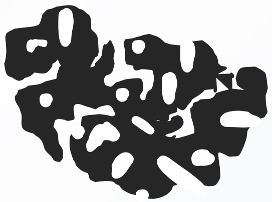
BENEFICIAL USE APPLICATIONS

Beneficial Use Challenges

Conversion to low NO_X, SO_X and CO_2 operations have resulted in residual material with <u>increased carbon content,</u> which is detrimental for reuse in concrete.

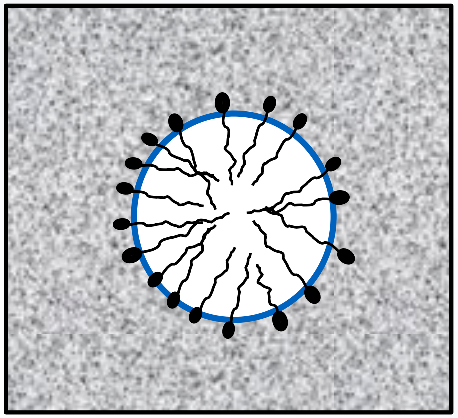


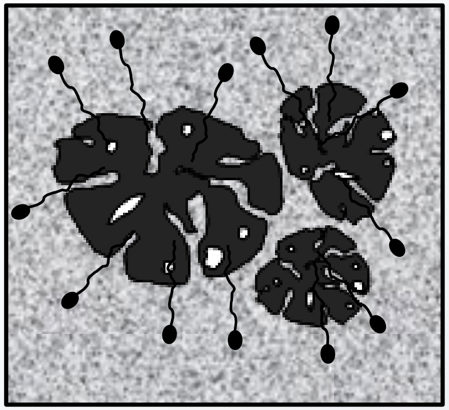
AEA: cationic or anionic surfactant with hydrophobic hydrocarbon chain



Porous residual carbon particle

Air entraining agents (AEA) surround air bubbles, creating stable air voids in concrete.





AEA adsorbed by organic carbon in fly ash, resulting in concrete with reduced entrained air.

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Beneficial Use

PRODUCTIVE REUSE

- ❑ **Fired brick production (bench-scale)**
  - Partial replacement of fire-brick clay (Boral Bricks, Smyrna GA) with:
    - HCFA
    - CBFA
    - Savannah Harbor dredged
    - Sediments
- ❑ **Alkali-activated geopolymer solidification/stabilization**
  - Ash samples mixed with activator solution and allow to cure under varying conditions.

Fired-brick pug mill and extruder

Mixing fly ash geopolymers

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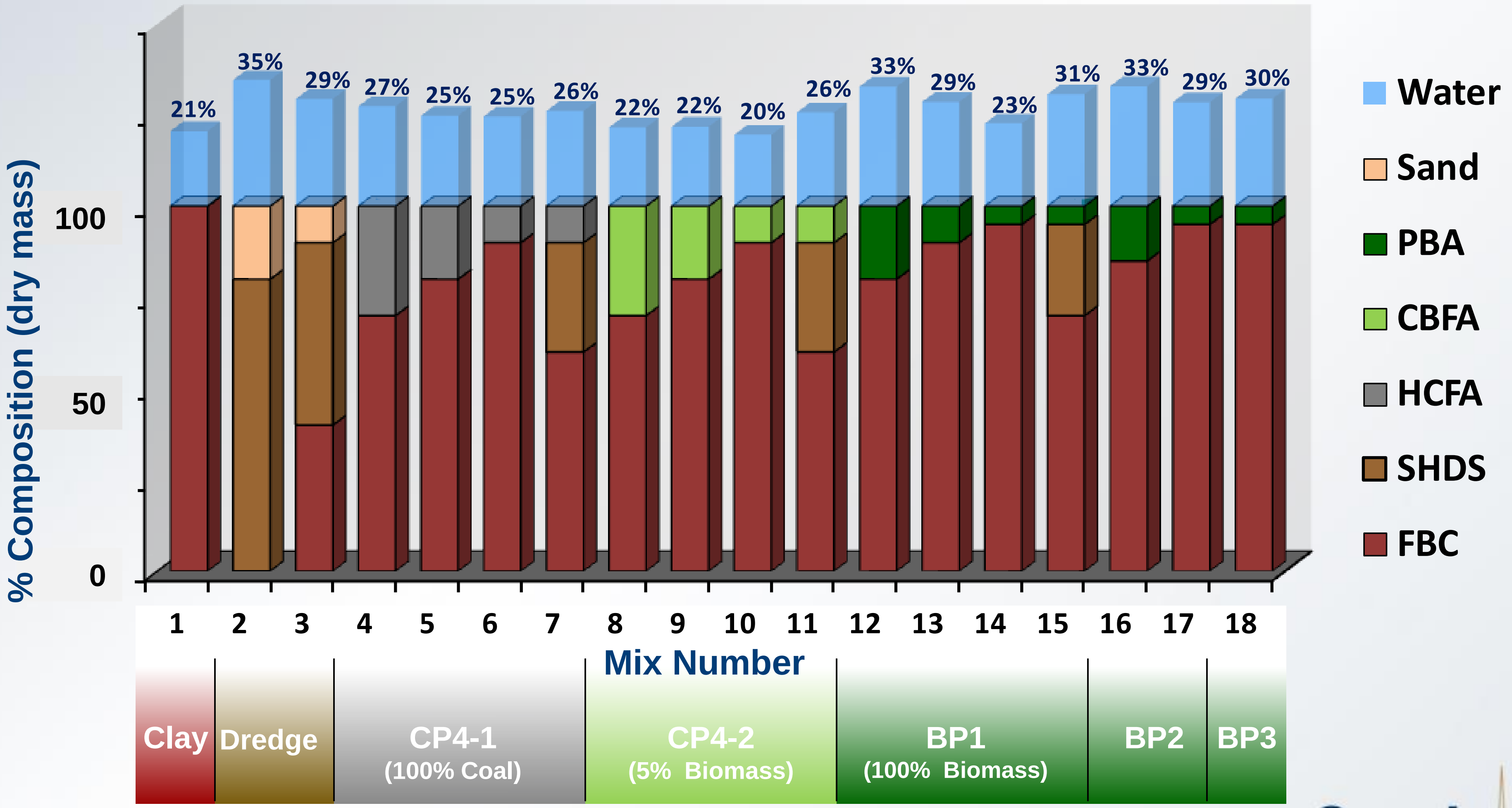
Fired Brick Production: Materials

Materials	Description
CP4-1	High carbon fly ash (HCFA)
CP4-2	Coal, biomass co-fired (CBFA)
BP1	Pure biomass ash (PBA)
BP2	
BP3	
Dredge	Savannah Harbor dredged sediment (SHDS)
Clay	Commercial fired-brick clay – Boral Bricks (FBC)






Fired Brick Production: Mix Designs



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Fired Bricks

Mix 3

50% Dredge
10% Sand
40% Clay

Mix 7

30% Dredge
10% HCFA
60% Clay

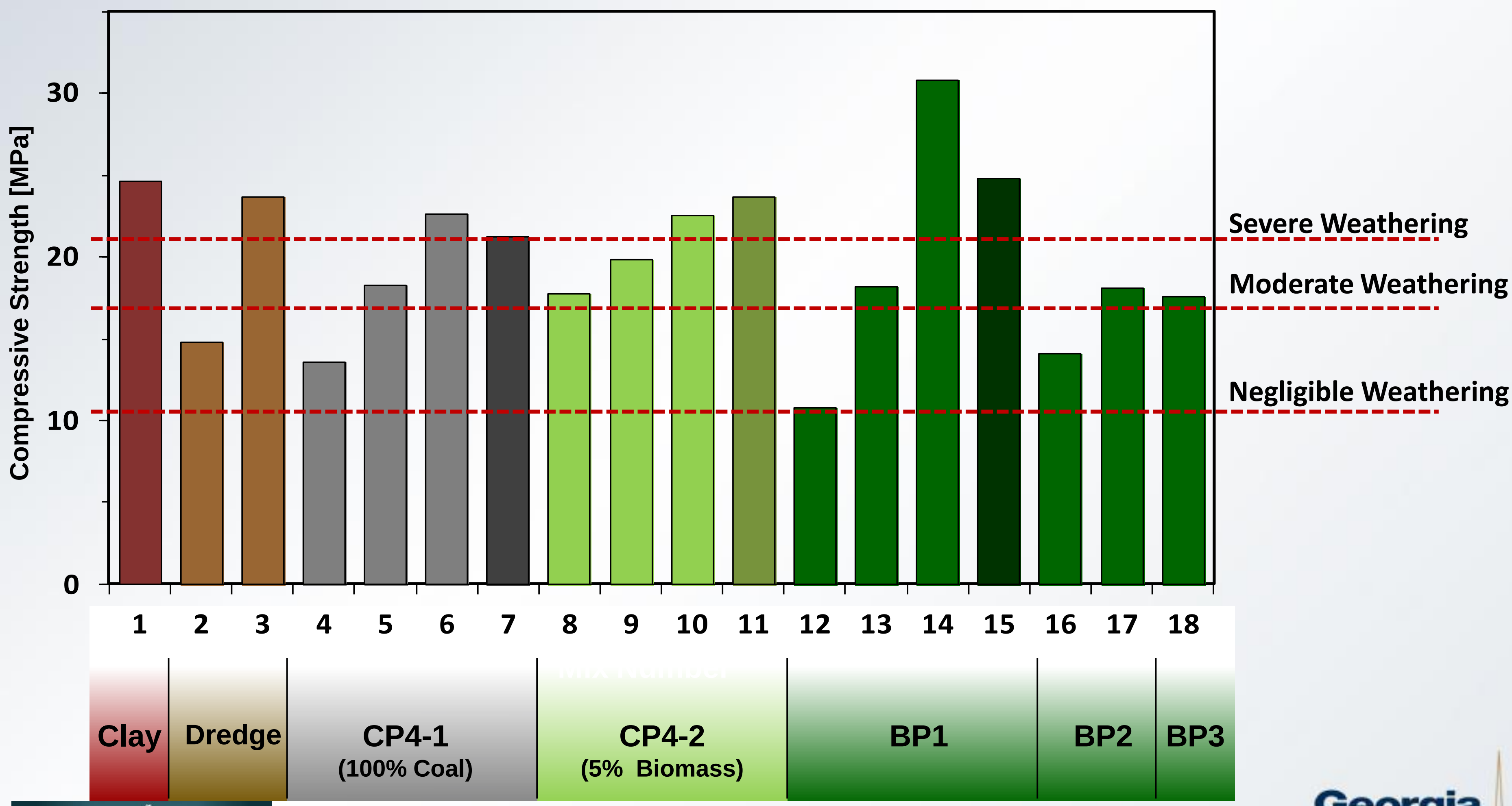
Mix 11

30% Dredge
10% CBFA
60% Clay

Mix 15

35% Dredge
5% PBA
60% Clay

Fired Bricks: Compressive Strength



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Toxicity Characteristic Leaching Procedure: TCLP

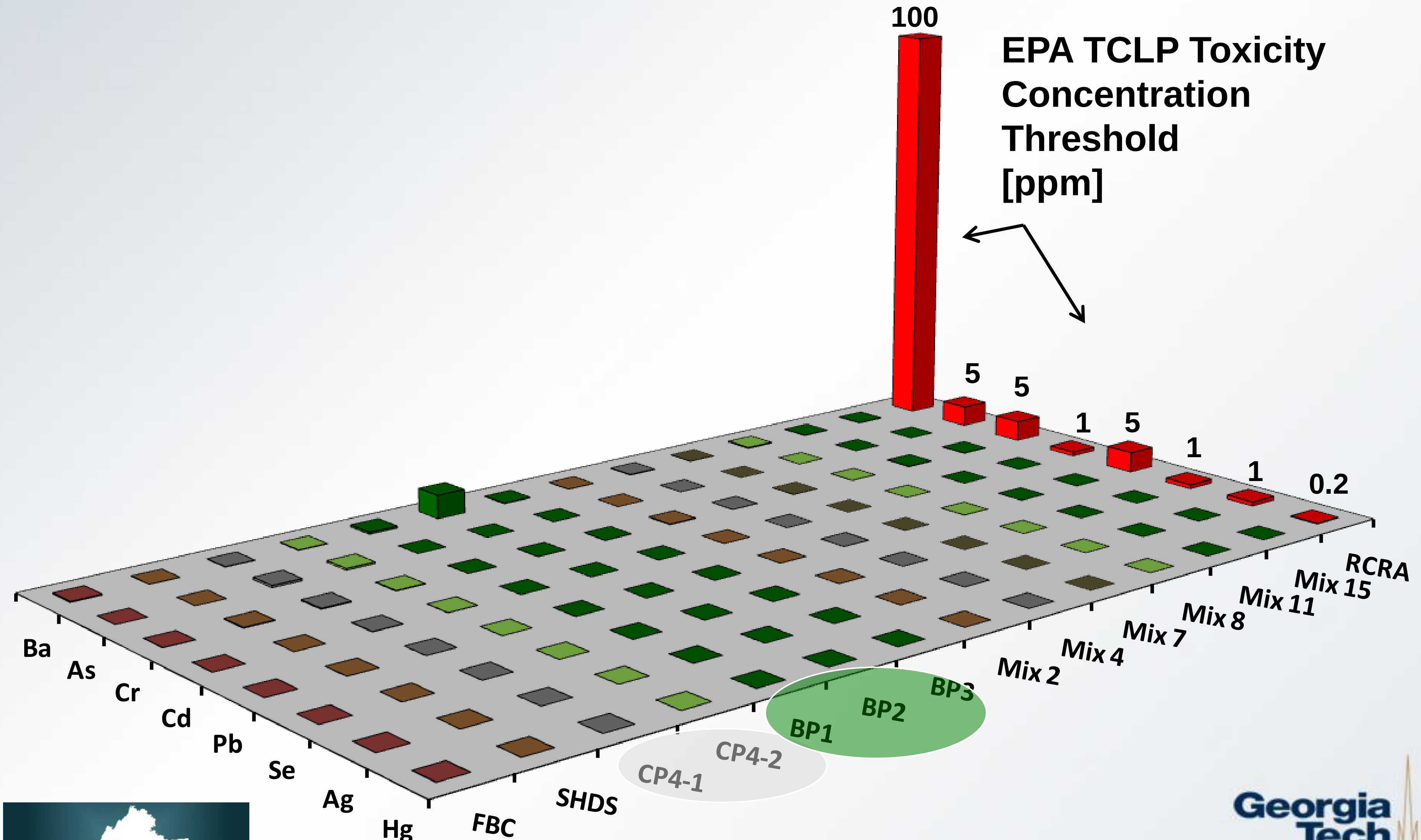
- **TCLP standard test (EPA Method 1311) used to characterize waste as either hazardous or non-hazardous for the purpose of disposal.**

- **RCRA outlines 40 contaminants the TCLP tests for.**

- **Any solid waste that fails the test for any one of these contaminants is considered "toxic", and must be handled accordingly.**

- **8 heavy metal contaminants on the list of 40 contaminants**
  - **Ag, As, Ba, Cr, Cd, Pb, Se and Hg**

TCLP: Results Compared With EPA Limits



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Geopolymerization

- **Geopolymerization: polycondensation reaction, when naturally occurring aluminosilicates or silicates are mixed with highly alkaline solution (activator).**

- **2 stage reaction process, aluminosilicate material dissolves and then precipitates into a solid binder.**

- **Typically synthesized from clay-based materials like metakaolin, for use as substitute for Portland Cement in concrete.**

- **<u>40 – 100 MPa</u> compressive strength (28 MPa typical specification for concrete)**

- **Low carbon coal fly ash is becoming a common aluminosilicate material for geopolymer synthesis as Portland cement substitute.**

- **This study focused on geopolymer synthesis with <u>biomass co-fired</u> ash with <u>high residual carbon content</u>.**

Materials

ASH SAMPLES

LCFA	CBFA
CP1	CP4-2
100% Coal	5.5% Biomass
1.1% ROC	7.7% ROC

REAGENTS

- Sodium hydroxide (NaOH) pellets
- Sodium silicate ($Na_2Si_3O_7$) in aqueous solution

ACTIVATOR SOLUTION

NaOH dissolved in deionized H_2O
(typically 12 – 13 Molar)

+

Aqueous $Na_2Si_3O_7$

Mixed and allowed to homogenize over night

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Alkali Activated Geopolymers

$$n(Si_2O_5,Al_2O_2) + 2nSiO_2 + 4nH_2O + NaOH \text{ (or KOH)}$$

(Si-Al materials)

↓

$$Na^+,K^+ + n(OH)_3\text{–}Si\text{–}O\text{–}Al^-\text{–}O\text{–}Si\text{–}(OH)_3$$

$(OH)_2$

(Geopolymer precursor gel)

Stage 1

Dissolution of aluminosilicates in parent material and subsequent, reorientation.

$$n(OH)_3\text{–}Si\text{–}O\text{–}Al^-\text{–}O\text{–}Si\text{–}(OH)_3 + NaOH \text{ (or KOH)}$$

$(OH)_2$

↓

$$(Na^+,K^+)\text{-}(\text{–}Si\text{–}O\text{–}Al^-\text{–}O\text{–}Si\text{–}O\text{–}) + 4nH_2O$$

O O O

(Geopolymer backbone)

Stage 2

Polycondensation and hardening.

(Davidovits,1979)

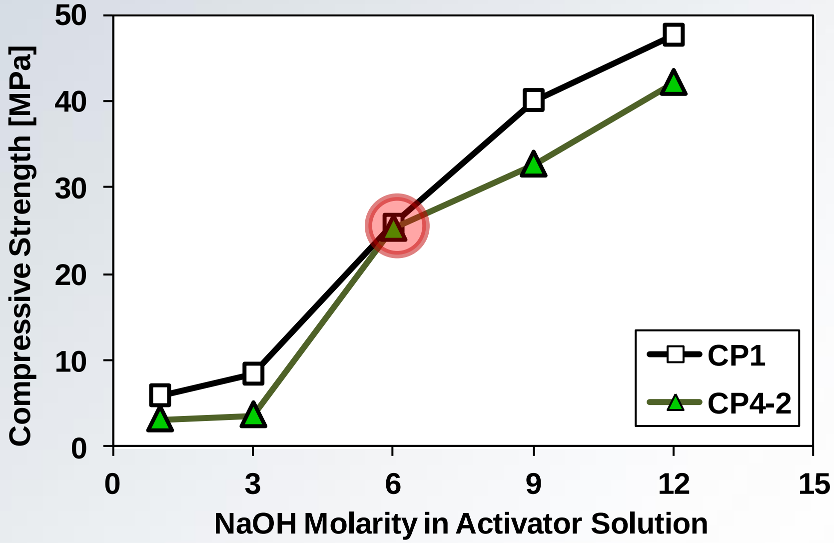
Ash + activator solution mixed for 15 minutes

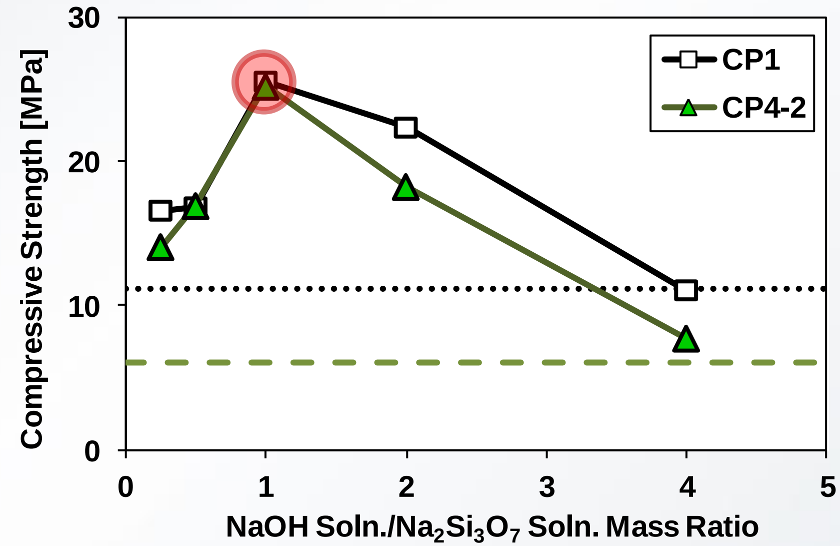
Mixture poured into 2-inch molds. Left to cure for 1 hr.

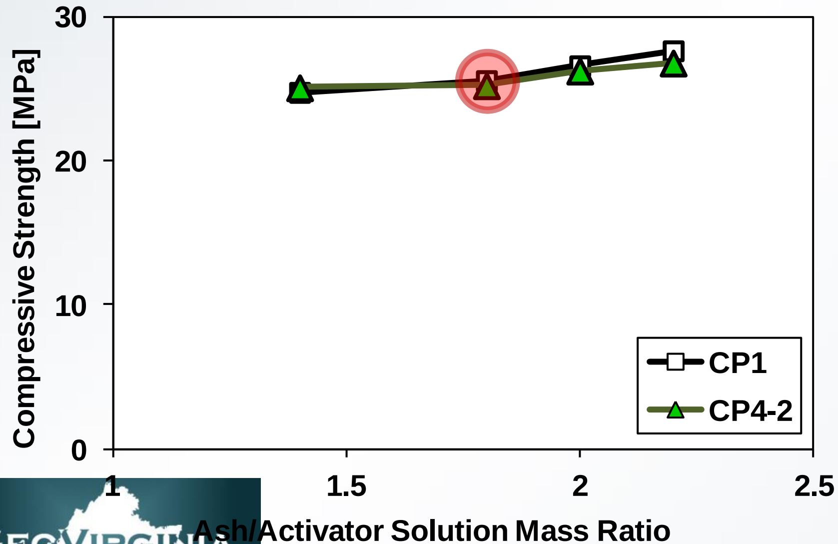
Molds placed in preheated oven and cured at a given temp for 48 hrs.

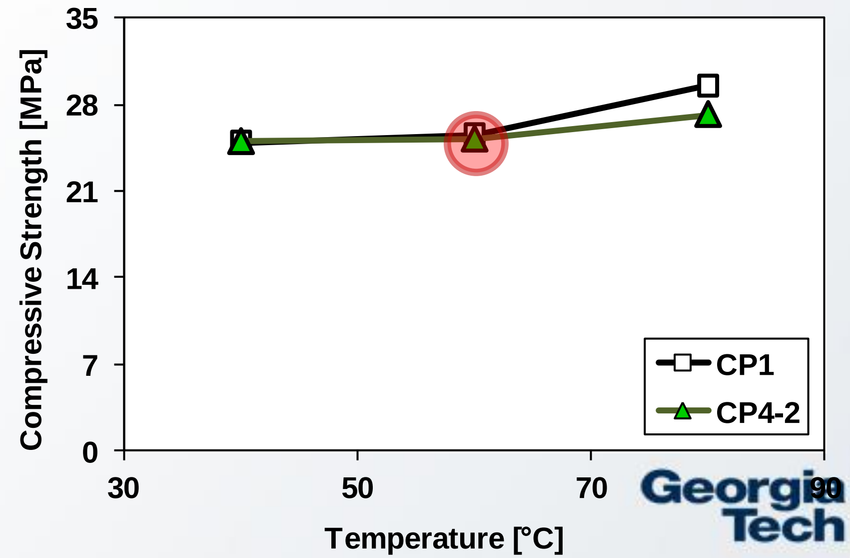
After curing, blocks are tested for compressive strength.

Alkali Activated Geopolymers:
Compressive Strength Results









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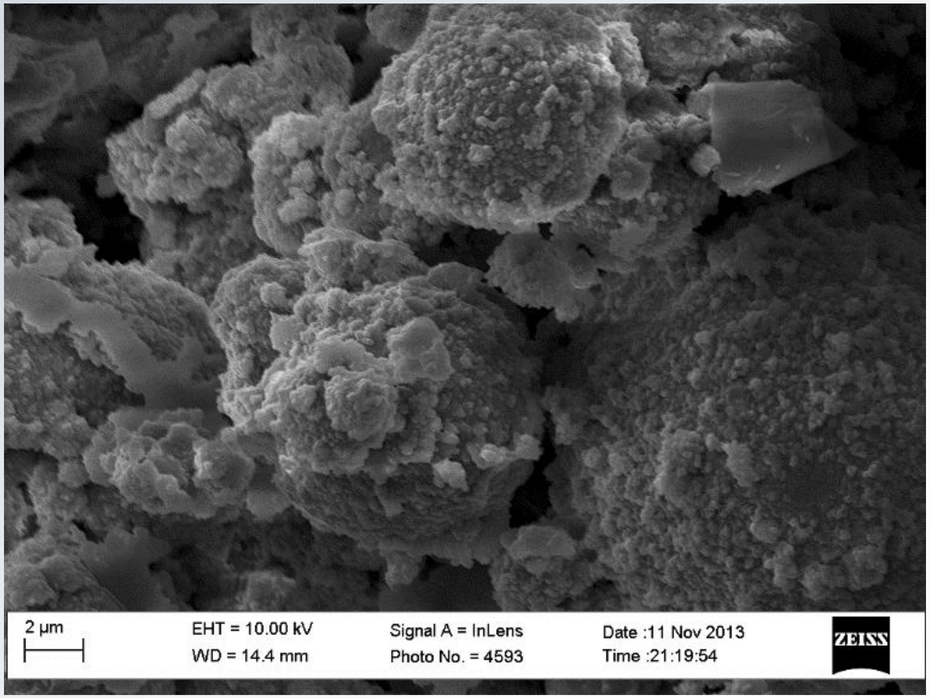
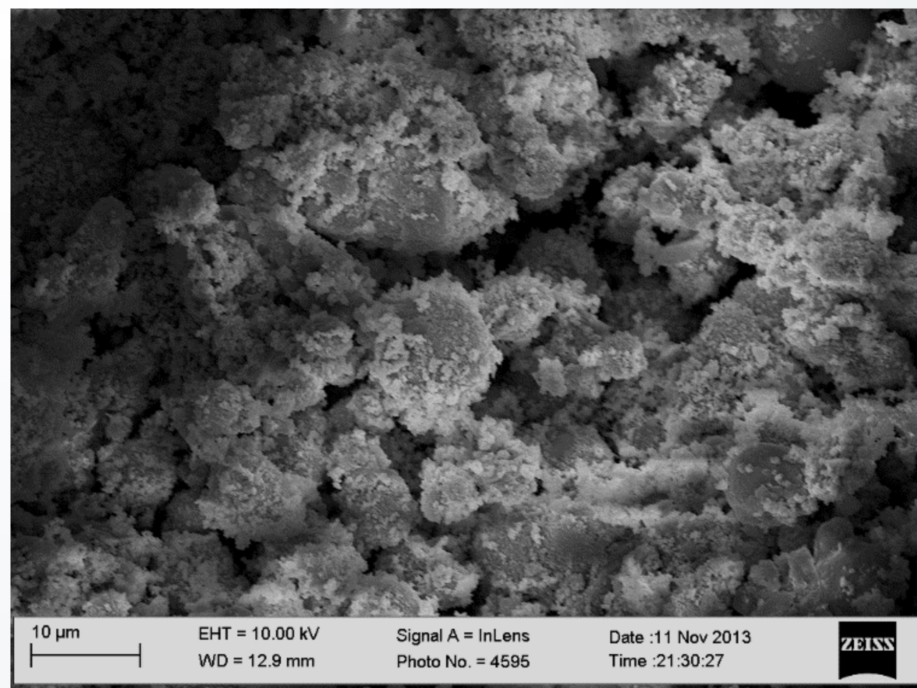
Alkali Activated Geopolymers:

Microstructure - SEM



1 Mol. NaOH

3 Mol. NaOH



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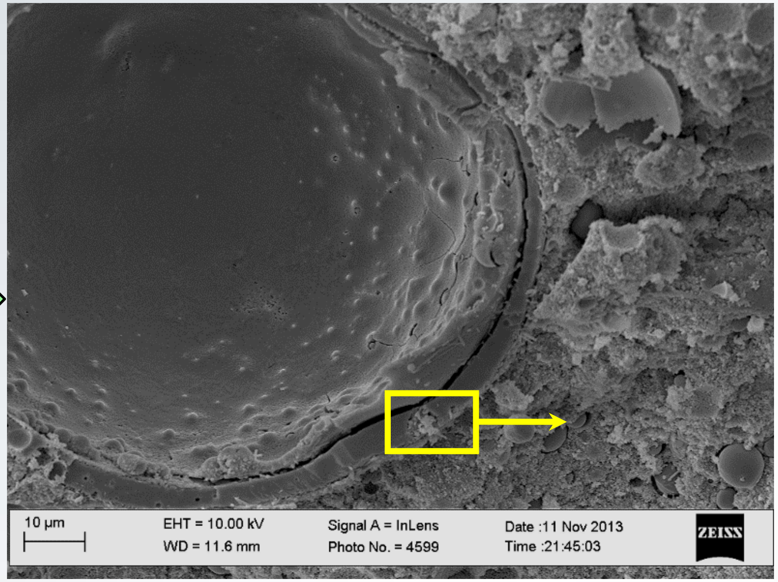
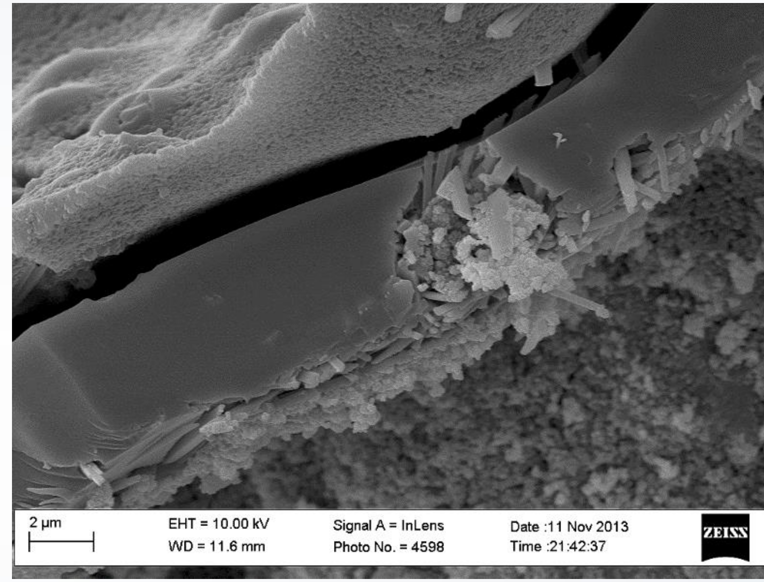
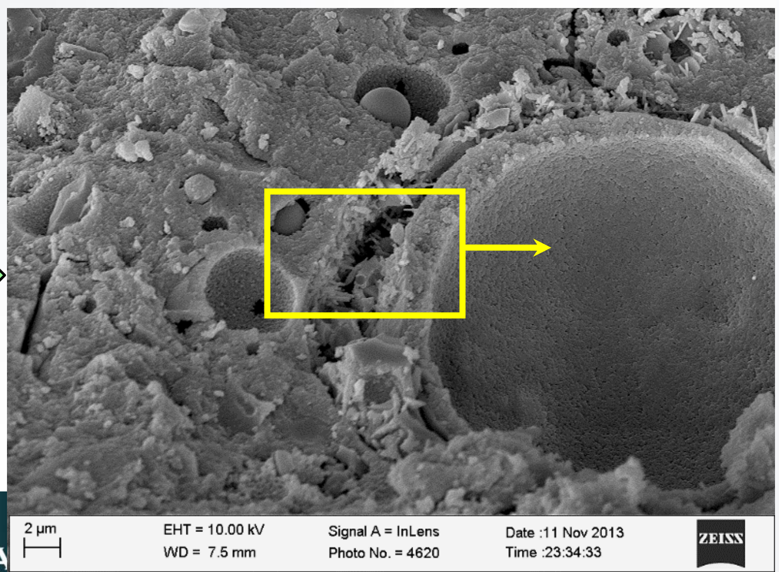
Alkali Activated Geopolymers:
Microstructure - SEM

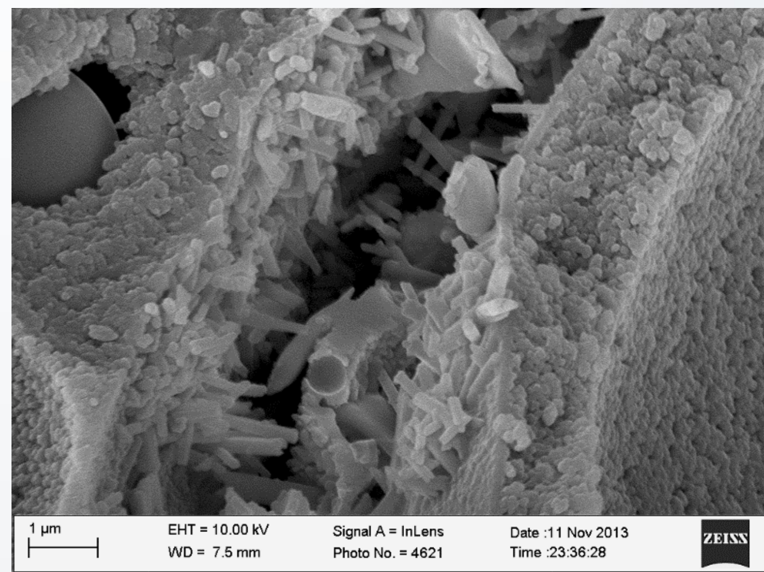
6 Mol. NaOH





12 Mol. NaOH





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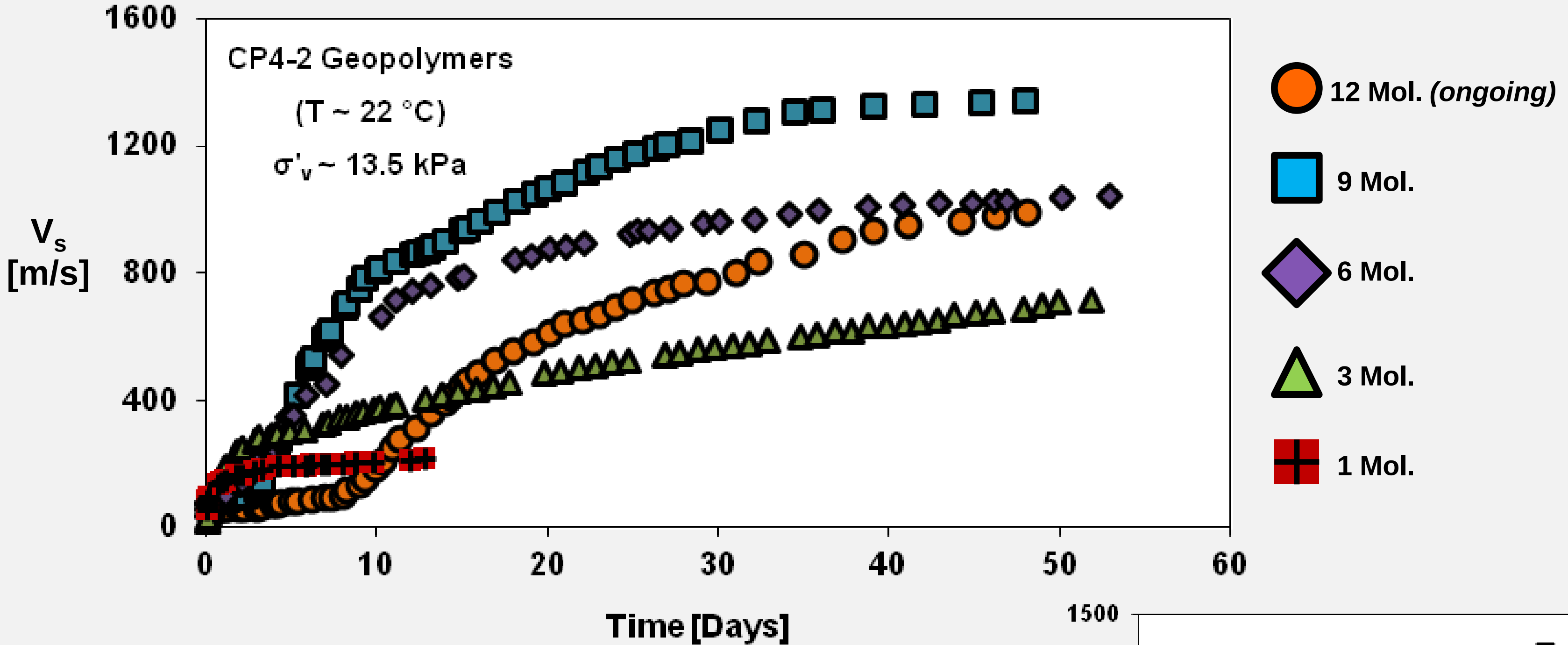
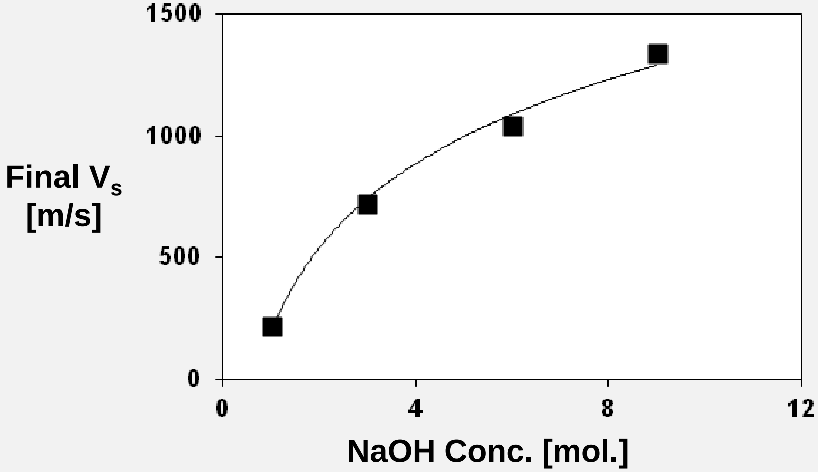
Alkali Activated Geopolymers:

V_s(VH) evolution at room temperature.





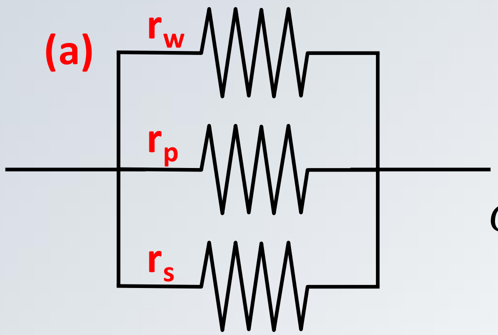
Lessons Learned: Beneficial Reuse

- Brick materials
  - High organic carbon content
  - Other wastes, such as dredge
- Geopolymerization

Fly Ash Emerging Properties: Electrical & Thermal

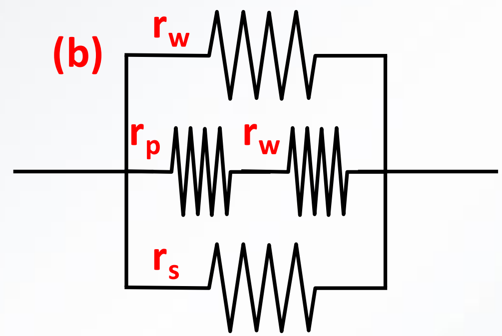
- Electrical conductivity
  - ASTM C618: regulation of reuse of fly ash with TOC > 6%
  - Estimation of in-situ carbon content: important challenge
  - No proper method determining carbon content after disposal
  - High e (or w): contribute to stability issues
- Thermal conductivity
-

Conductivity – f(particle, water, and organic)



$$\frac{1}{r_{mix}} = \frac{1}{r_p} + \frac{1}{r_w} + \frac{1}{r_s}$$

$$G_{mix} = G_p + G_w + G_s$$

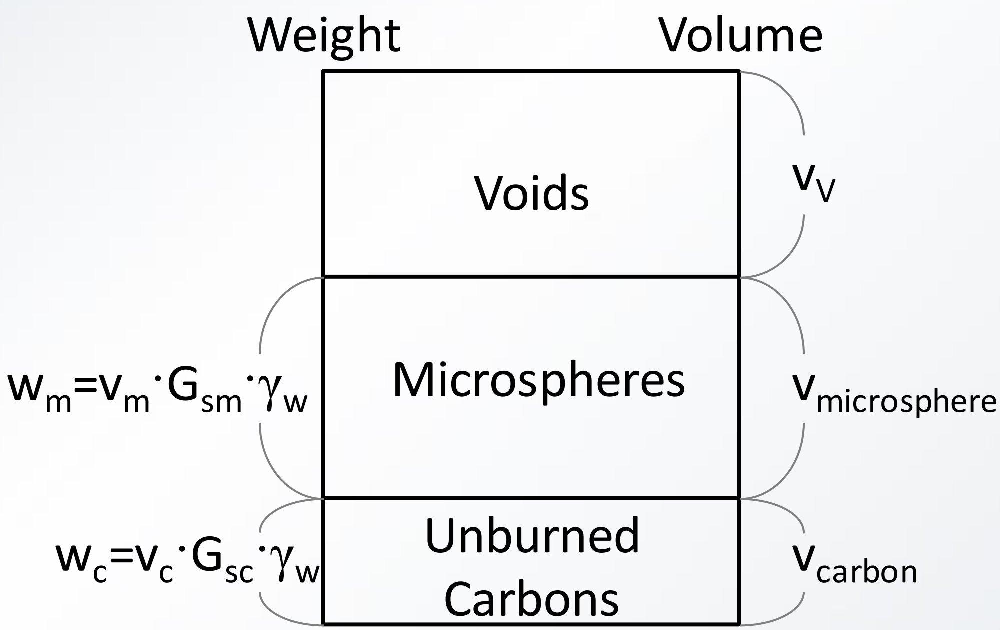


TOC < TOC*

$$\frac{1}{r_{mix}} = \frac{1}{r_p + r_w} + \frac{1}{r_w} + \frac{1}{r_s}$$

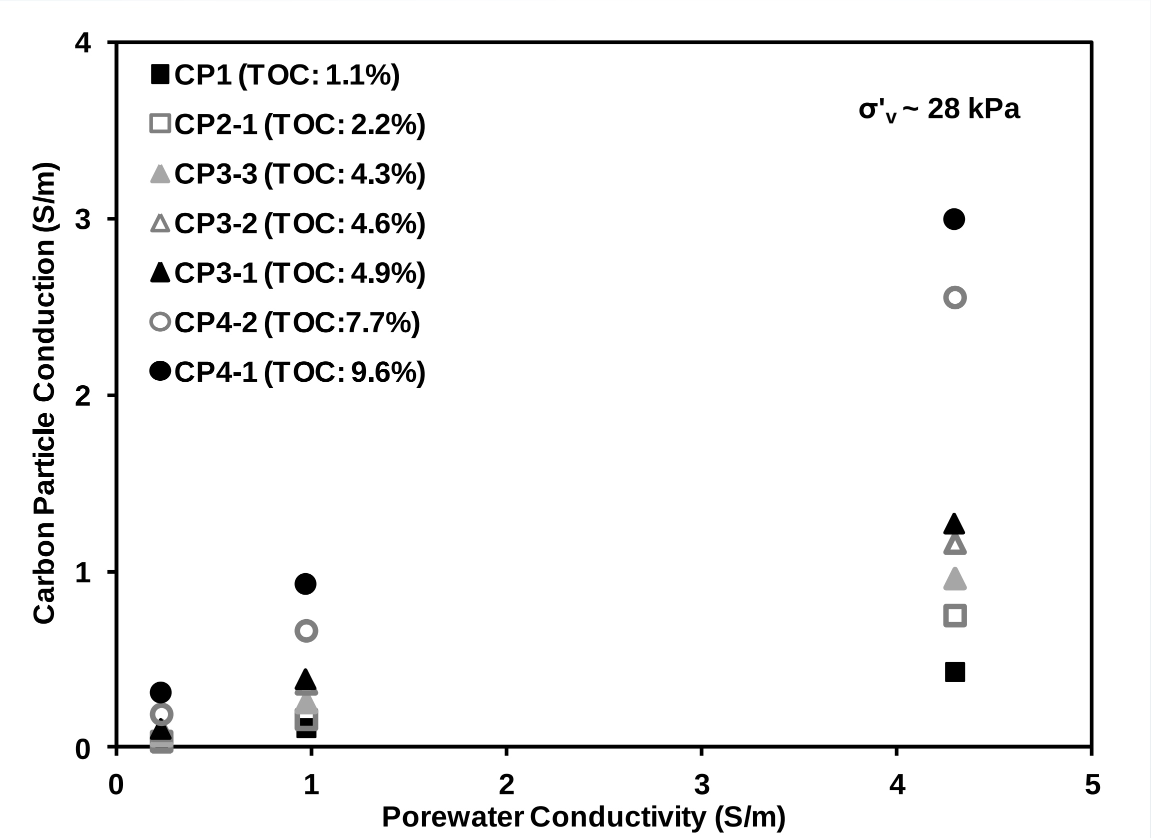
$$G_{mix} = G_{cp} + G_w + G_s$$

$$G_{cp} = \frac{G_p \times G_w}{G_p + G_w}$$



Conductivity – f(Pore fluid conductivity)

- TOC < TOC*
  → Conductive Carbon particles: generally dispersed
  → Pore water: act as an electron carrier b/w carbon particles
- TOC > TOC* → Carbon particles: continuous contact b/w them ≠ $f(\sigma_w)$
- σ_{cp} ~linear increase with an increase in σ_w



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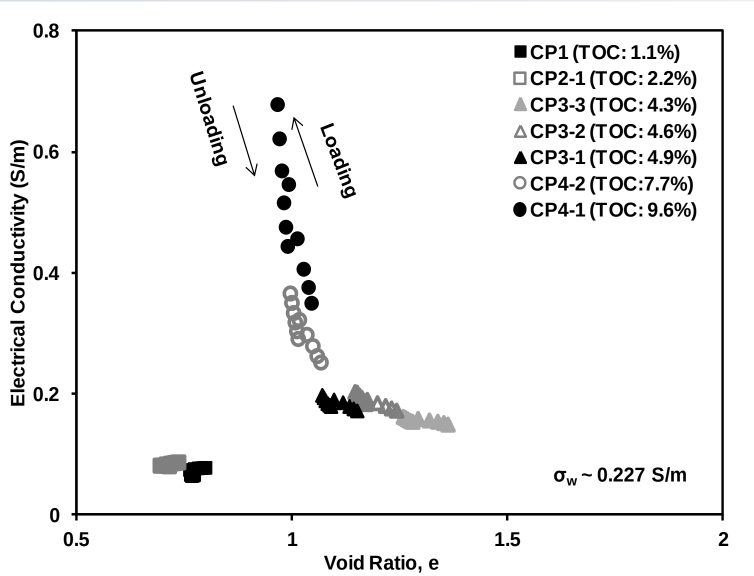
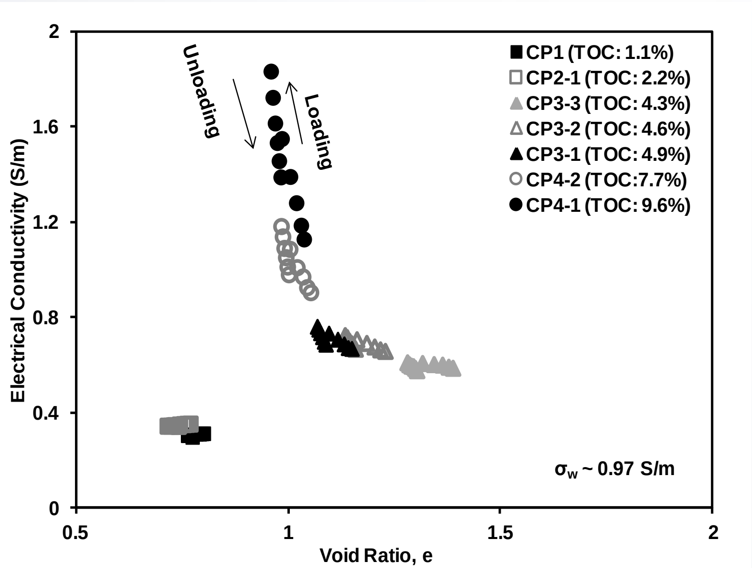
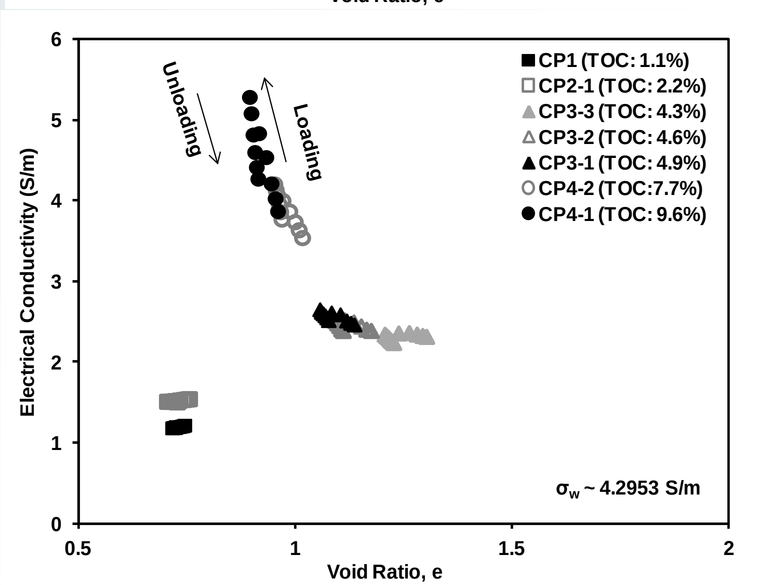
Electrical Conductivity = f(Organic Content)





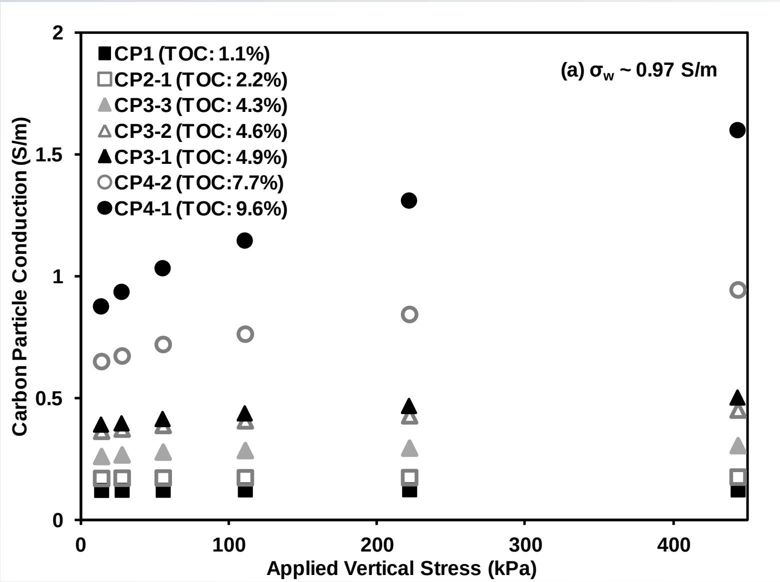


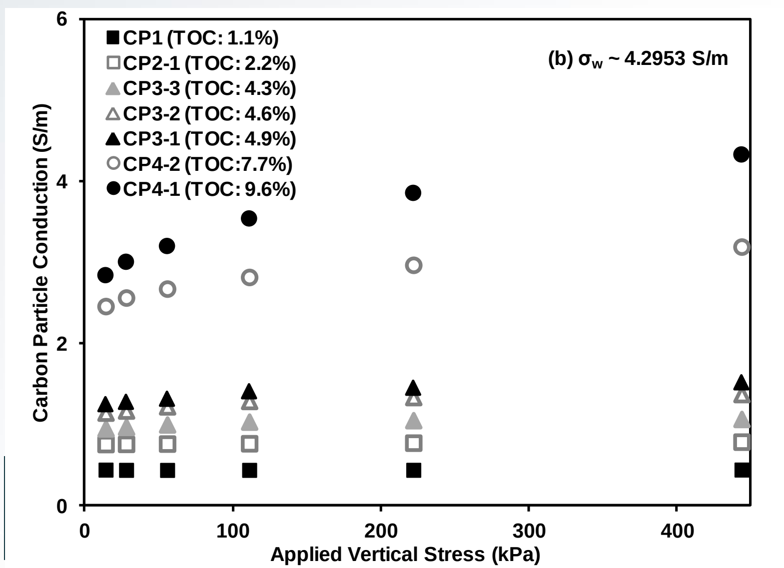
- Most soil particles are non-conducting.

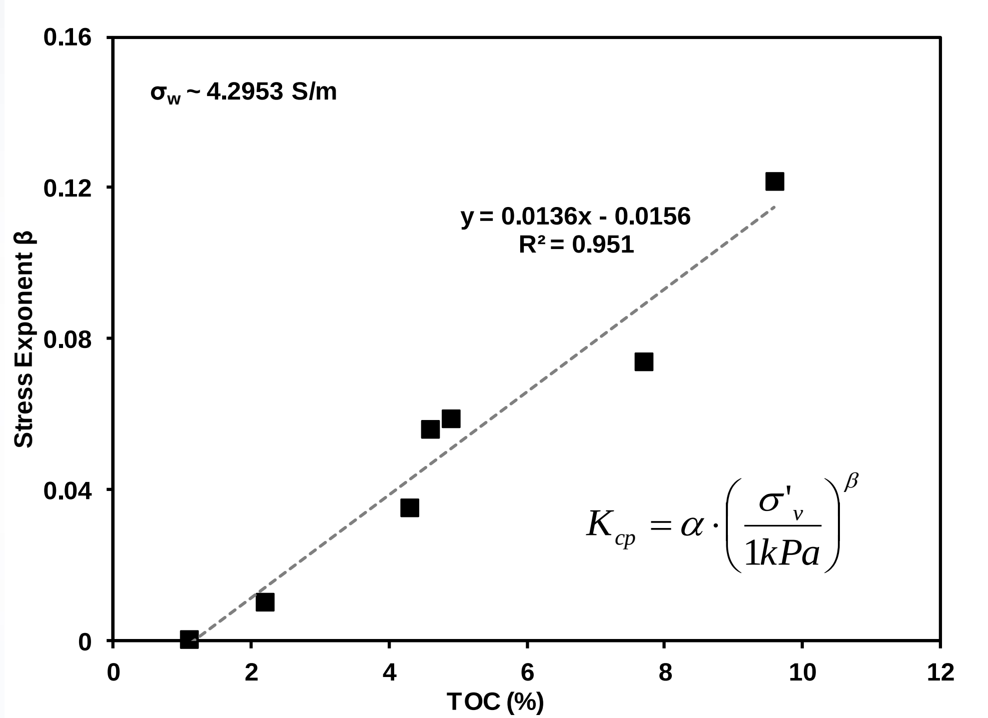
→ Conductivity of a soil media ~ f(pore water conductivity, surface conductivity)

- With decrease in void ratio, conductivity ↓
- Carbon particles are highly electrically conductive
- Conductive materials are affected by stress due to the change in contact area

Electrical Conductivity = f(Stress)





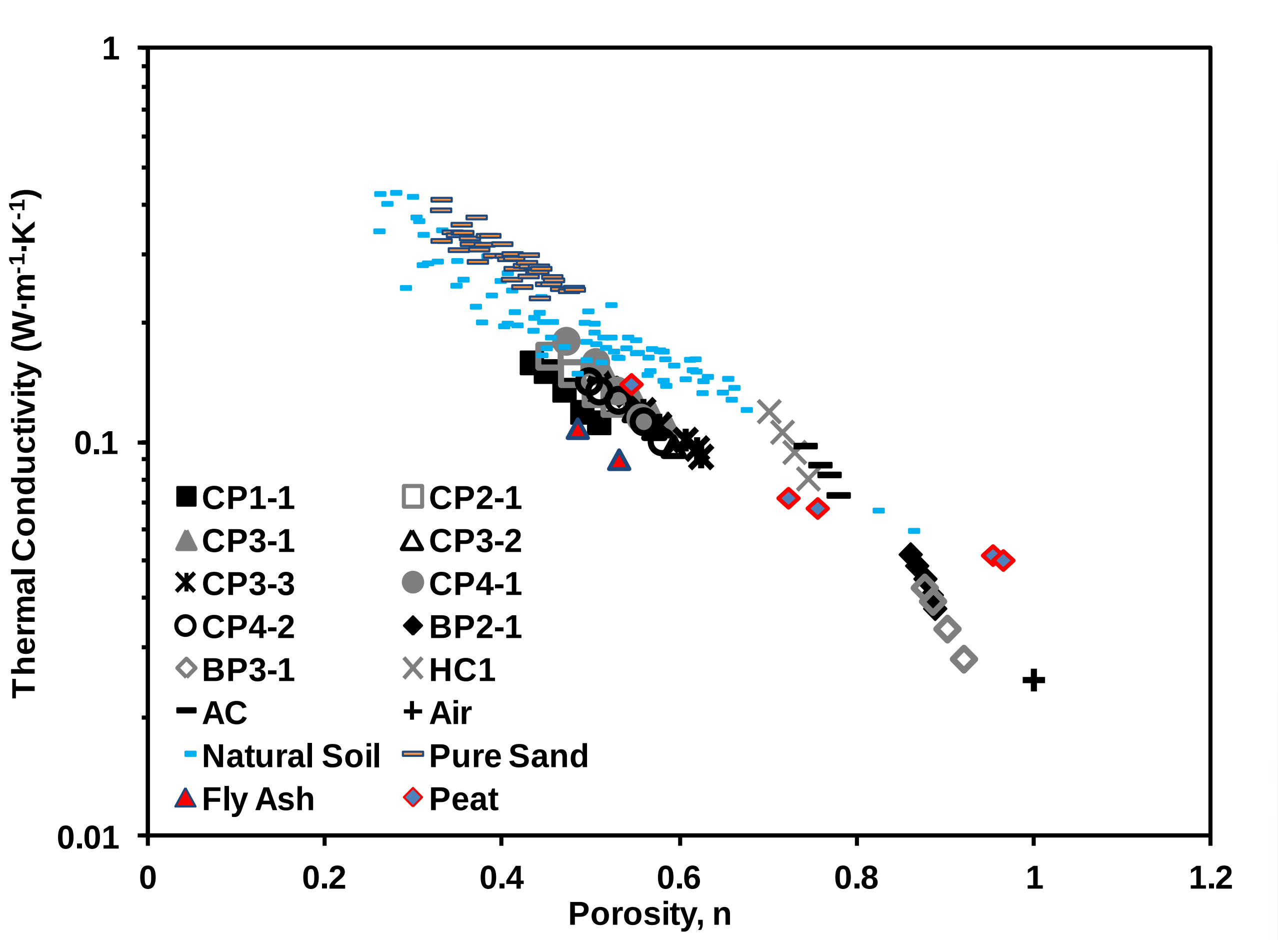


Georgia Tech

Comparison with Dry Natural Soils: Thermal Conductivity

- Comparison in terms of porosity:
  - K_t of fly ashes < K_t of natural soils
  - G_s of fly ash < G_s of natural soils (hollow microspheres)
  - Retained air = additional thermal conduction barrier
- Comparison in terms of dry density:
  - Comparable K_t

Comparison with Dry Natural Soils: Thermal



Data- pure sand: Yun and Santamarina (2008); natural soil: Johansen (1975) & Smith and Byers (1938); peat: Smith and Byers (1938) & Gavriliev (2004); fly ash: Rao and Singh (1999)

Conclusions

- Lessons learned
  - Properties
  - Beneficial use
  - Emerging properties

http://i2.cdn.turner.com/cnnnext/dam/assets/140209142735-04-nc-coal-ash-ap647727992116-horizontal-large-gallery.jpg

Acknowledgements

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