PONDED COAL ASH AS A SUPPLEMENTARY CEMENTITIOUS MATERIAL: PRODUCTIVE REUSE INCLUDING CHEMI-MECHANICAL BENEFICIATION

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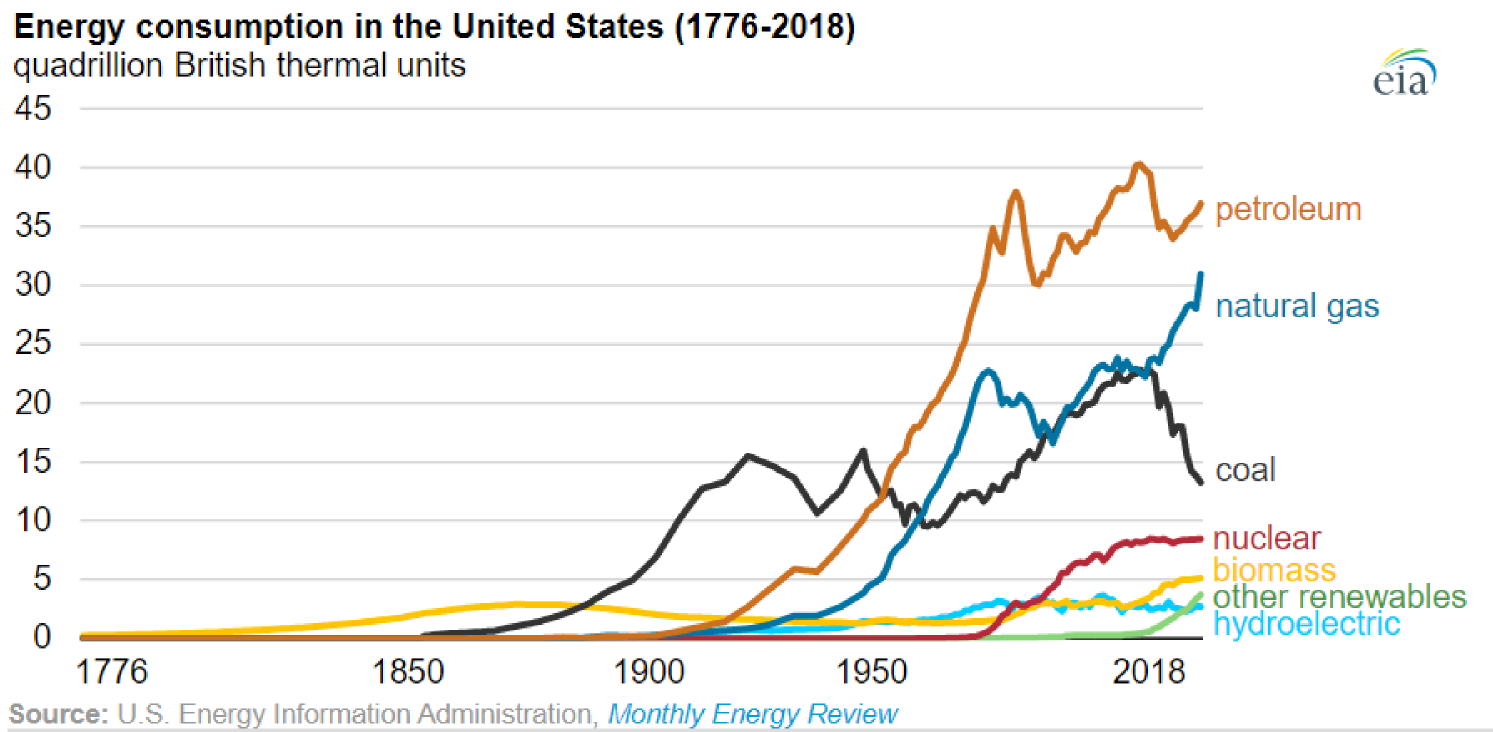
THE BENEFITS OF FLY ASH

- Fly ash is a byproduct of coal combustion and is currently the most widely utilized supplementary cementitious material in the world
- Provides improvements to compressive strength, workability, heat of hydration, and resistance to chemical/weather damage
- Based on its status as an industrial byproduct blending fly ash provide improvements to embodied CO_2 emissions and cost

Chou MI.M. (2012) Fly Ash. In: Meyers R.A. (eds) Encyclopedia of Sustainability Science and Technology. Springer, New York, NY. https://doi.org/10.1007/978-1-4419-0851-3_121

FLY ASH SHORTAGES

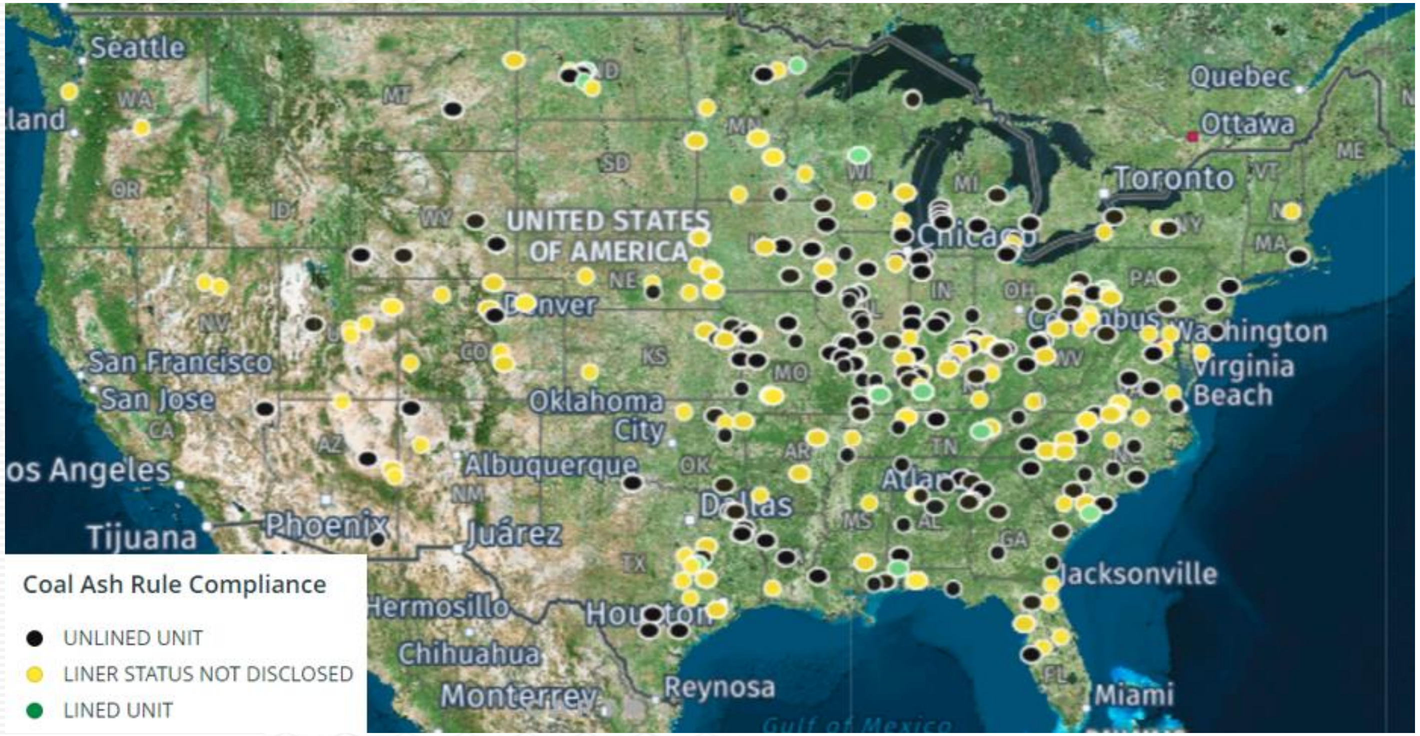
- An industry wide shift away from coal combustion as a source of power (in favor of Natural gas and renewables) is leading to shortages in fly ash supply
- The construction Industry highly depends on fly ash in order to reduce cost and improve quality
- A new, large supply of supplementary cementitious materials is needed in order to compensate for this drop in supply



https://www.eia.gov/todayinenergy/detail.php?id=40013

WHAT IS THE SOLUTION?

- Only approximately half of all fly ash produced is beneficially utilized
- Waste coal ash is placed in wet storage (ponds) or in dry storage (landfills)
- The ACAA estimates that there is >2 billions tons of ponded ash stored around the country
- The majority of coal ash ponds are unlined (~95%) and contaminate groundwater sources exceeding federal levels (~90%)
- 2015 EPA regulations require the relocation or closure of the majority of these ponds
- May utilize the material as an SCM instead of relocating it



Liner status of 738 coal ash ponds in 43 states

Coal Ash = Fly Ash + Bottom Ash + Flue Gas Gypsum

https://earthjustice.org/features/map-coal-ash-contaminated-sites

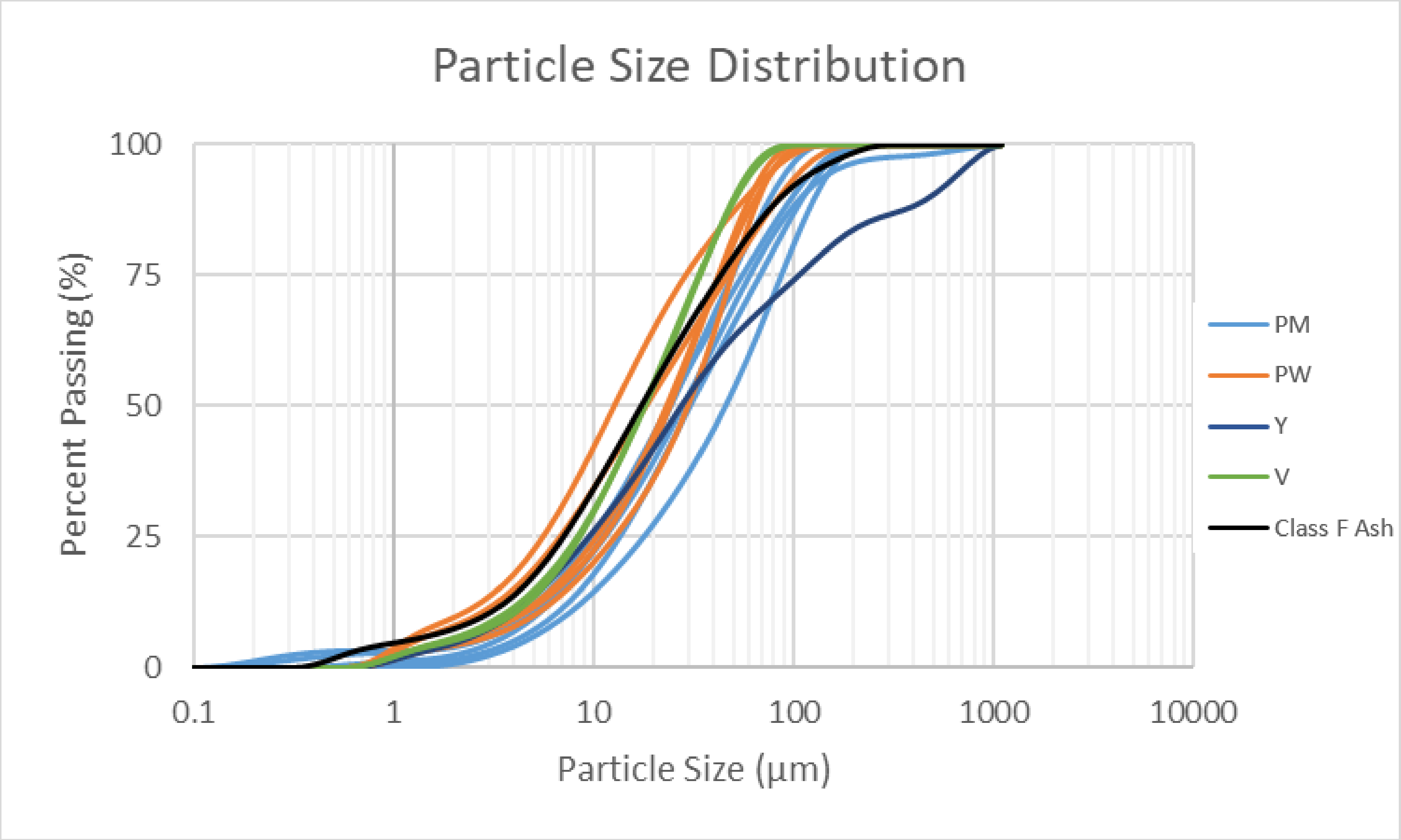
COLLECTED ASHES

- 13 Ashes were collected from 4 power plants
- All ashes were derived from eastern bituminous coal
- PM ashes were taken from depths: 0.5 – 5 ft and are less than 10 years old
  - PM ashes historically do not consistently meet ASTM C618 standards
- PW ashes were taken from depths: 0.5 – 3 ft
  - PW ashes are typically stored due to a lack of market demand
- V ashes were collected from depths: 10 – 15 ft and are less than 20 years old
- Y ash was collected at shallow depths below phreatic surface using a hydraulic excavator
  - Plant Y possesses no dry collection capacity

RECLAIMED ASH OXIDE COMPOSITION: XRF

Wt.%	Class F Ash	PM1	PM2	PM3	PM4	PM5	PW3	PW6	PW8	PW9	PW10	Y1	V1	V2
SiO_2	55.3	54.5	52.4	52.4	53.7	54.8	46.6	38.5	55.6	54.4	40.1	49.6	47.0	46.8
Al_2O_3	27.2	28.9	30.5	28.3	30.1	28.9	21.2	17.4	26.0	24.5	17.9	27.6	18.7	18.8
Fe_2O_3	8.0	8.7	8.6	11.8	8.0	8.1	23.8	36.9	10.2	12.3	34.7	12.4	24.1	24.6
Sum of Oxides	90.5	92.0	91.5	92.5	91.7	91.8	91.7	92.7	91.8	91.3	92.6	89.7	89.8	90.3
SO_3	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.3	0.9	0.6	0.5
CaO	1.3	1.1	1.6	1.1	1.4	1.3	1.6	1.6	1.6	1.9	1.4	1.0	3.2	3.2
Na_2O	0.5	0.4	0.4	0.3	0.3	0.4	0.6	0.5	0.7	0.8	0.4	0.5	0.6	0.6
MgO	1.2	1.0	1.0	0.8	0.9	0.9	0.8	0.7	1.0	1.0	0.7	1.0	0.9	0.9
K_2O	3.0	2.8	2.6	2.4	2.5	2.5	2.3	1.8	2.9	2.8	1.9	2.5	2.5	2.5
P_2O_5	0.2	0.5	0.9	0.3	0.8	0.6	0.2	0.2	0.3	0.2	0.2	1.0	0.2	0.2
Na_2O_e	2.5	2.2	2.1	1.9	2.0	2.0	2.1	1.7	2.6	2.6	1.7	2.1	2.2	2.2
LOI (%)	1.4	9.8	18.4	4.3	8.9	6.3	1.4	1.8	4.4	2.6	9.0	12.5	5.9	5.2
TOC (%)	-	5.1	11.6	3.6	7.5	5.4	0.1	0.2	3.0	0.9	5.1	3.7	3.8	3.6
D_{50} (μm)	17.37	45.7	28.2	24.5	23.8	30.5	24.3	29.7	18.3	12.7	23.4	27.6	18.2	17.9
Fineness (%)	23.7	50.1	34.0	28.0	30.4	37.3	23.0	29.2	25.7	14.7	21.8	38.6	13.6	14.0

PARTICLE SIZE DISTRIBUTIONS: LASER PSA

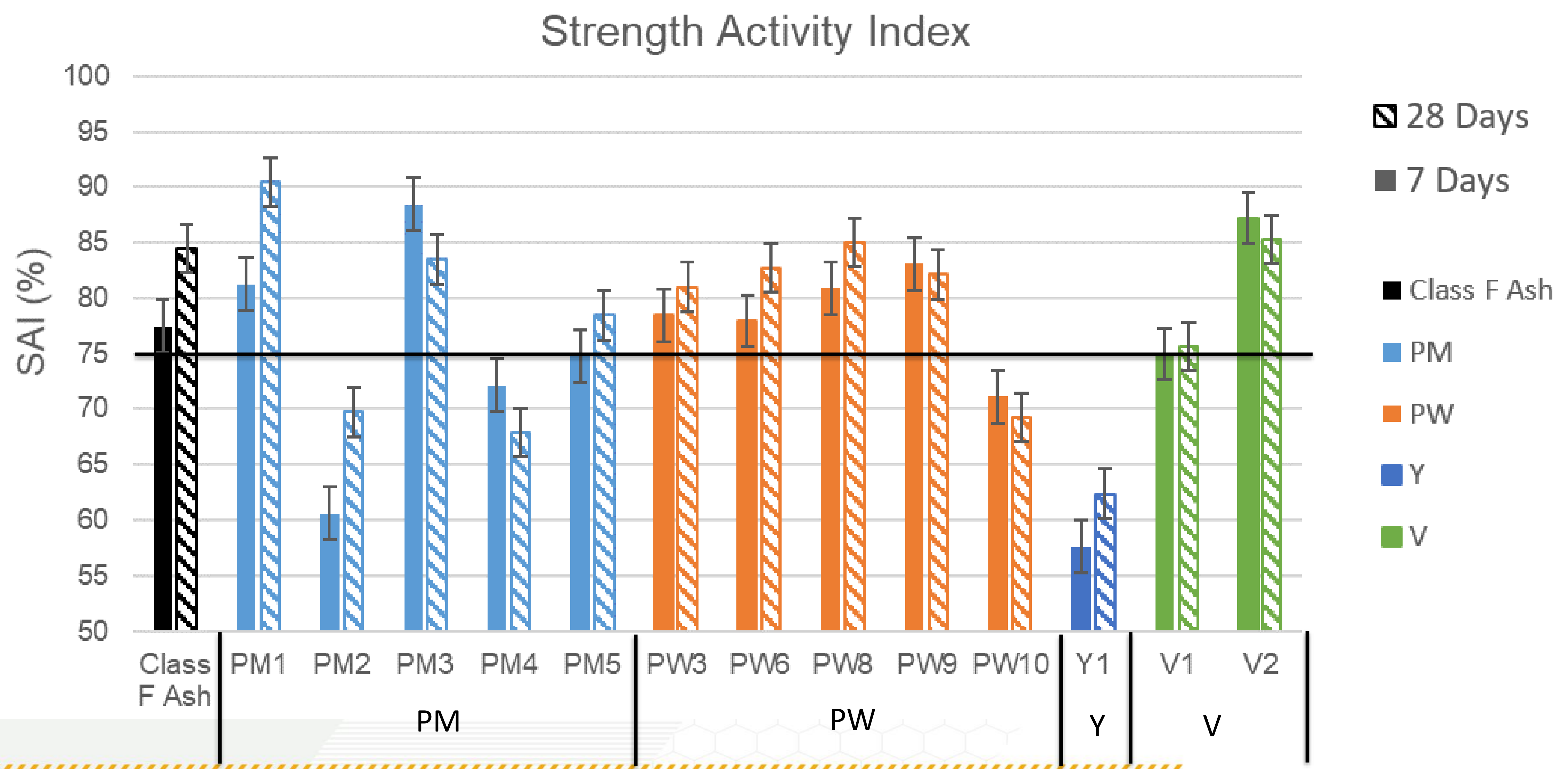


https://civilarc.com/compressive-strength-mortar-cubes/
https://www.globalgilson.com/1x1x10inch-single-prism-mold

TESTING PLAN

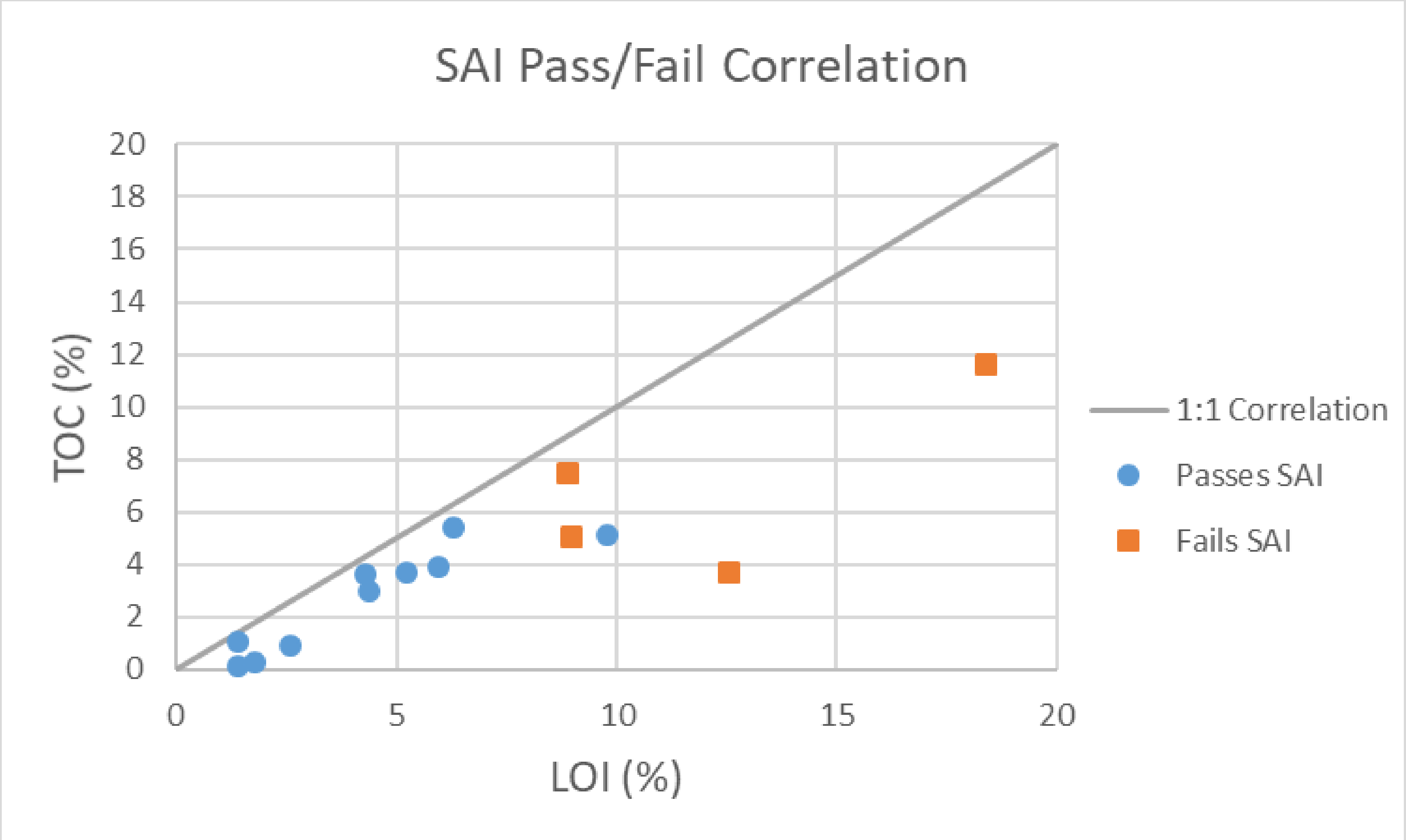
- Compressive Strength 2” Mortar Cubes (Strength Activity Index)
  - In accordance with ASTM C109
  - 20% replacement at a constant W/B ratio 0.48
- Isothermal Calorimetry
  - 20% replacement at a W/B Ratio of 0.4
  - Held at 25 °C for 48 hours
- ASR Expansion
  - ASTM C1567 measured up to 14 days
  - 20% Replacement and a W/B = 0.47

STRENGTH ACTIVITY INDEX



CAUSE OF RECLAIMED ASH FAILURE

- Ashes possessing an LOI greater than 8% frequently fail SAI requirements
- Failing ashes also possess larger quantities of hydrated phases

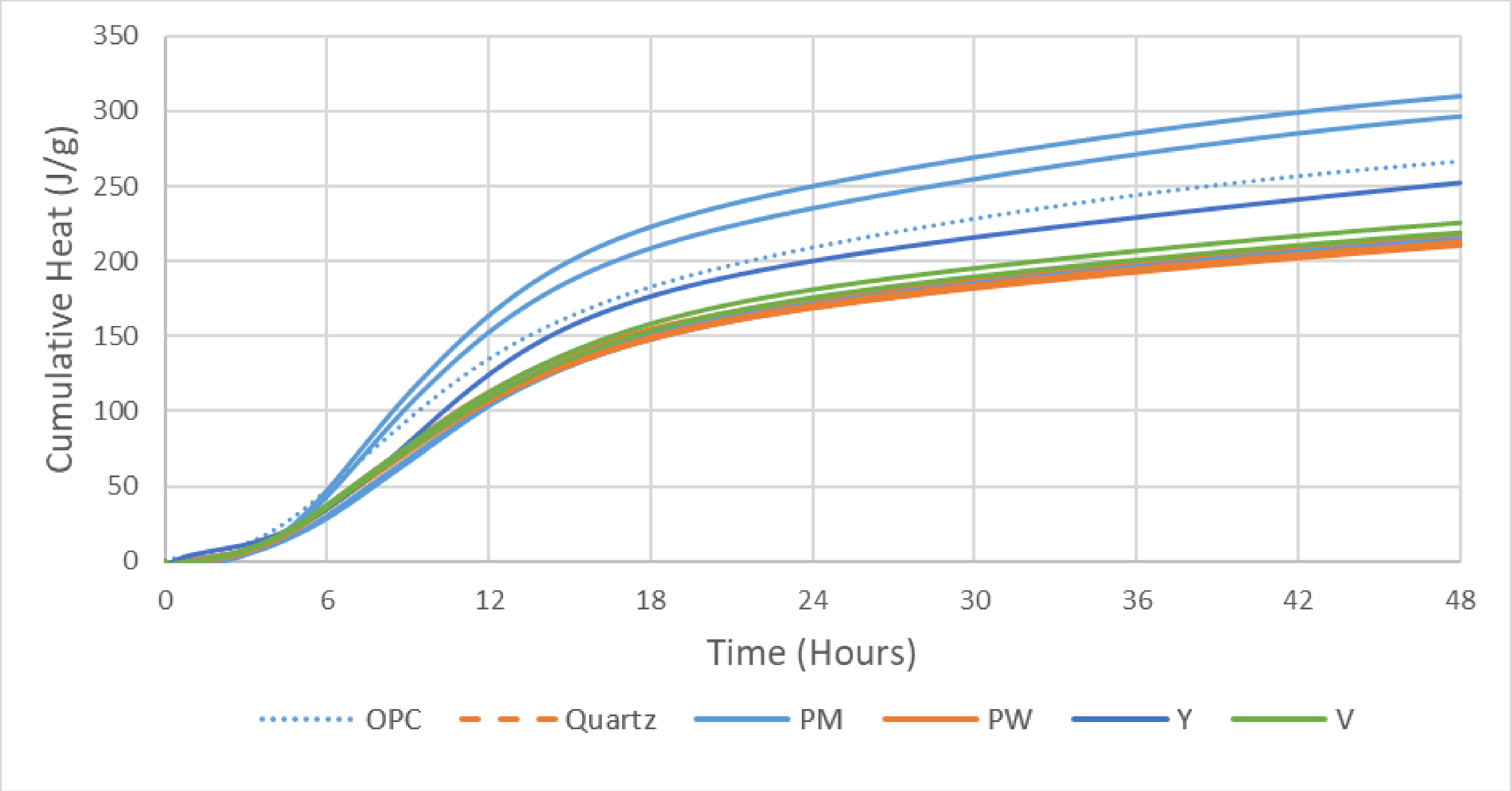


ASTM C618

- Four of the 13 ashes fail compressive strength Requirements
- Two additional ashes fail requirements for LOI and fineness
- A total of six ashes fail ASTM C618 Requirements

	ASTM C618 Class F	PM1	PM2	PM3	PM4	PM5	PW3	PW6	PW8	PW9	PW10	Y1	V1	V2
$SiO_2 + Al_2O_3 + Fe_2O_3$ (%)	>50%	92	91	93	92	92	92	93	92	91	93	90	90	90
CaO (Report)	<18%	1	2	1	1	1	2	2	2	2	1	1	3	3
SO_3 (%)	<5%	0	0	0	0	0	0	0	0	0	0	1	1	1
LOI (%)	<6%	10	18	4	9	6	1	2	4	3	9	13	6	5
Fineness (%)	<34%	50	34	28	30	37	23	29	26	15	22	39	14	14
SAI 7 Days (%)	≥75%	81	61	88	72	75	78	78	81	83	71	58	75	87
SAI 28 Days (%)	≥75%	90	70	83	68	78	81	83	85	82	69	62	76	85
Passes C618 (Y/N)		N	N	Y	N	N	Y	Y	Y	Y	N	N	Y	Y

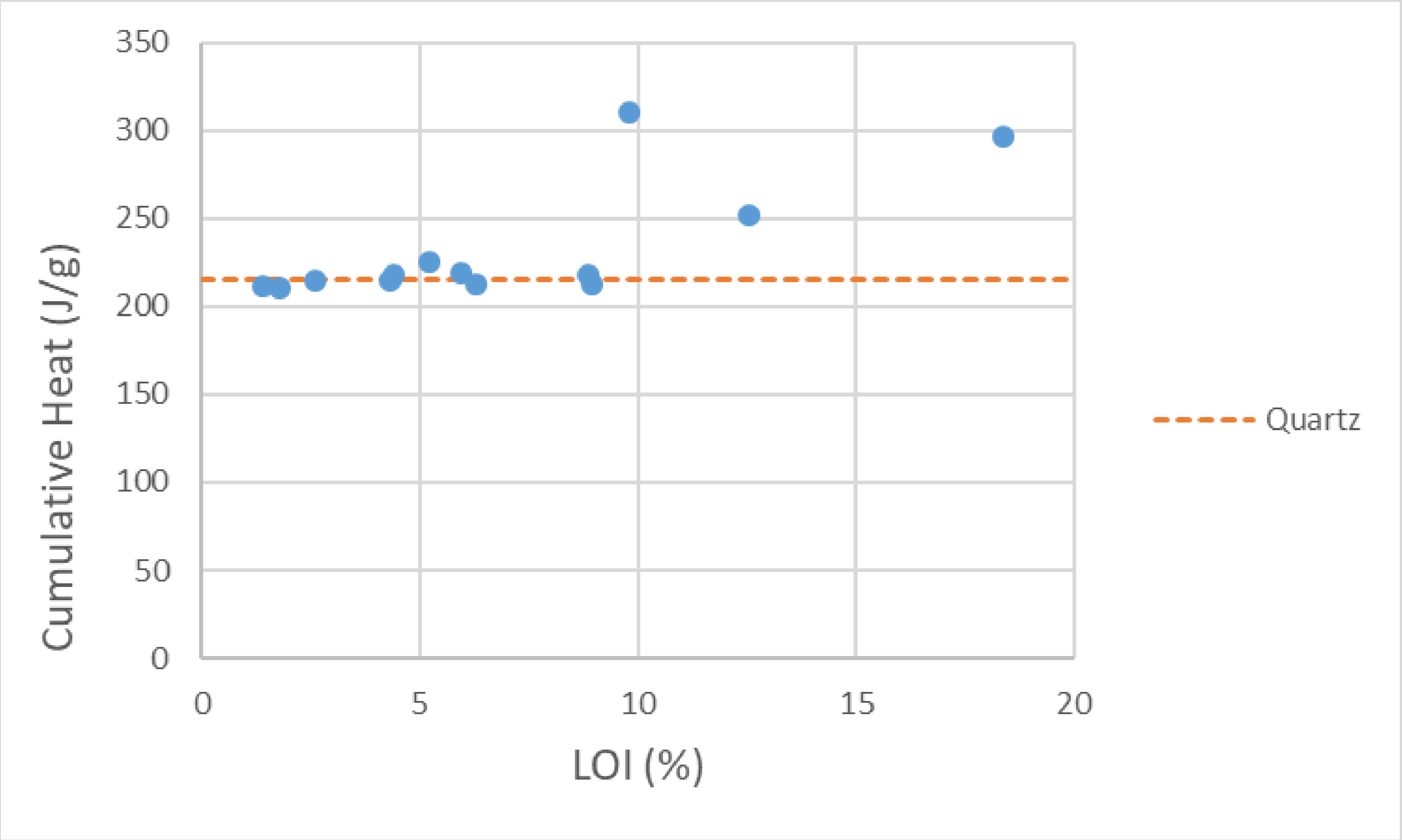
ISOTHERMAL CALORIMETRY



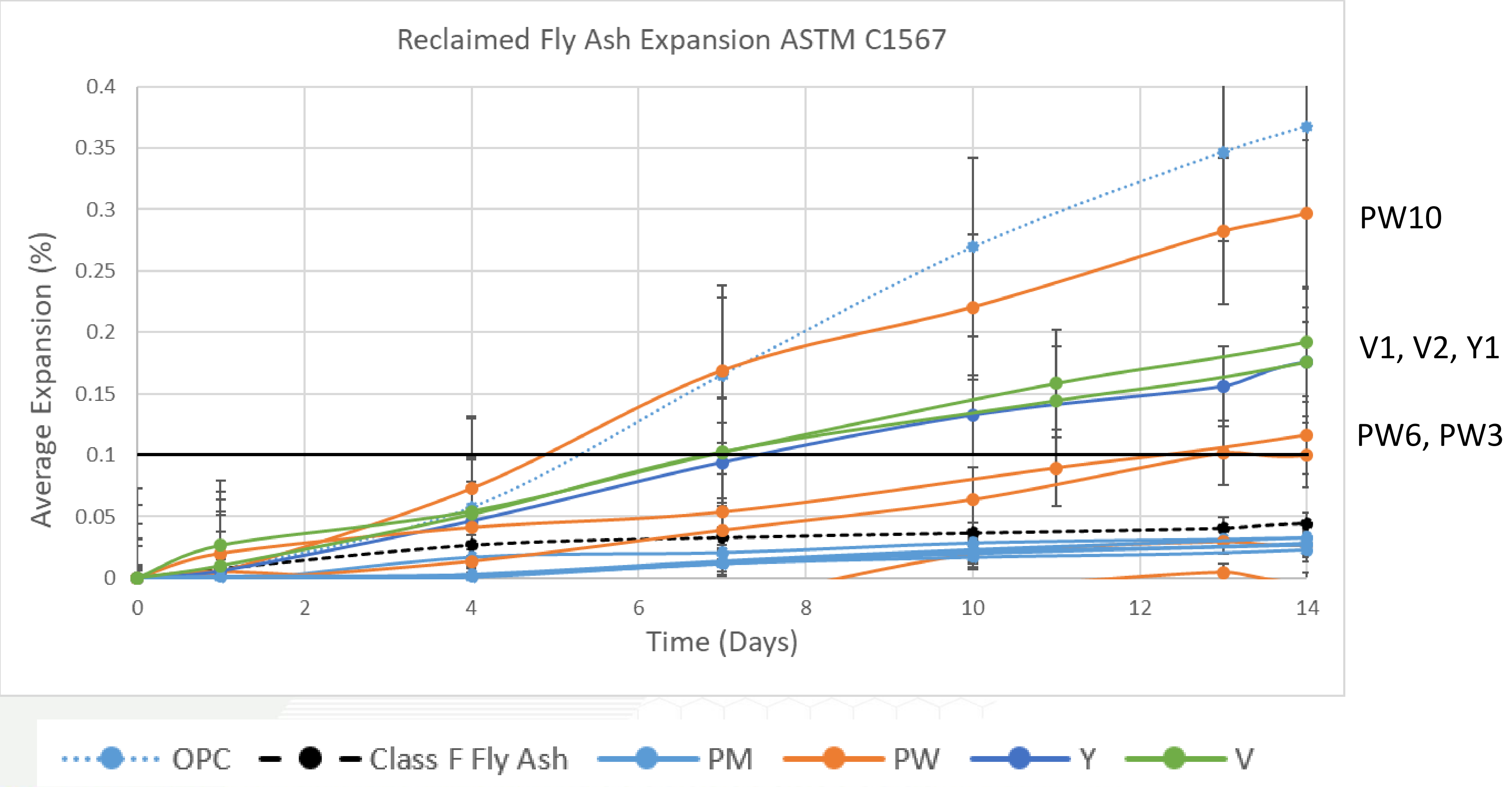
PM1,
PM2,
Y1

CAUSE FOR ELEVATED HYDRATION HEAT

- Ashes possessing elevated hydration heats universally possess larger LOI compared to ashes behaving conventionally

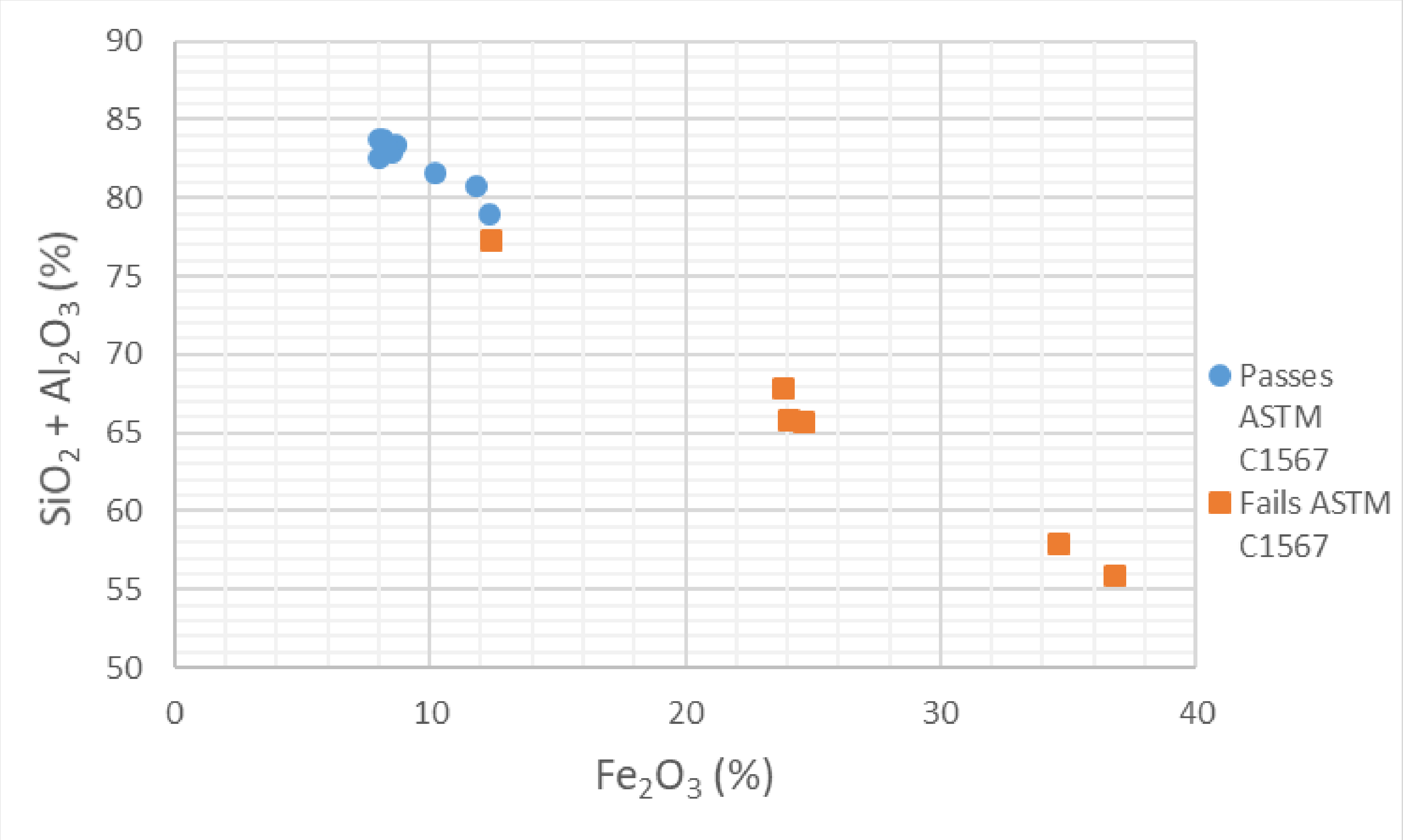


ASR EXPANSION



CAUSE OF ASR FAILURE

- For low CaO content ashes the ASR mitigation depends on the ratio of primary oxides, With high iron contents aggravating the ASR reaction



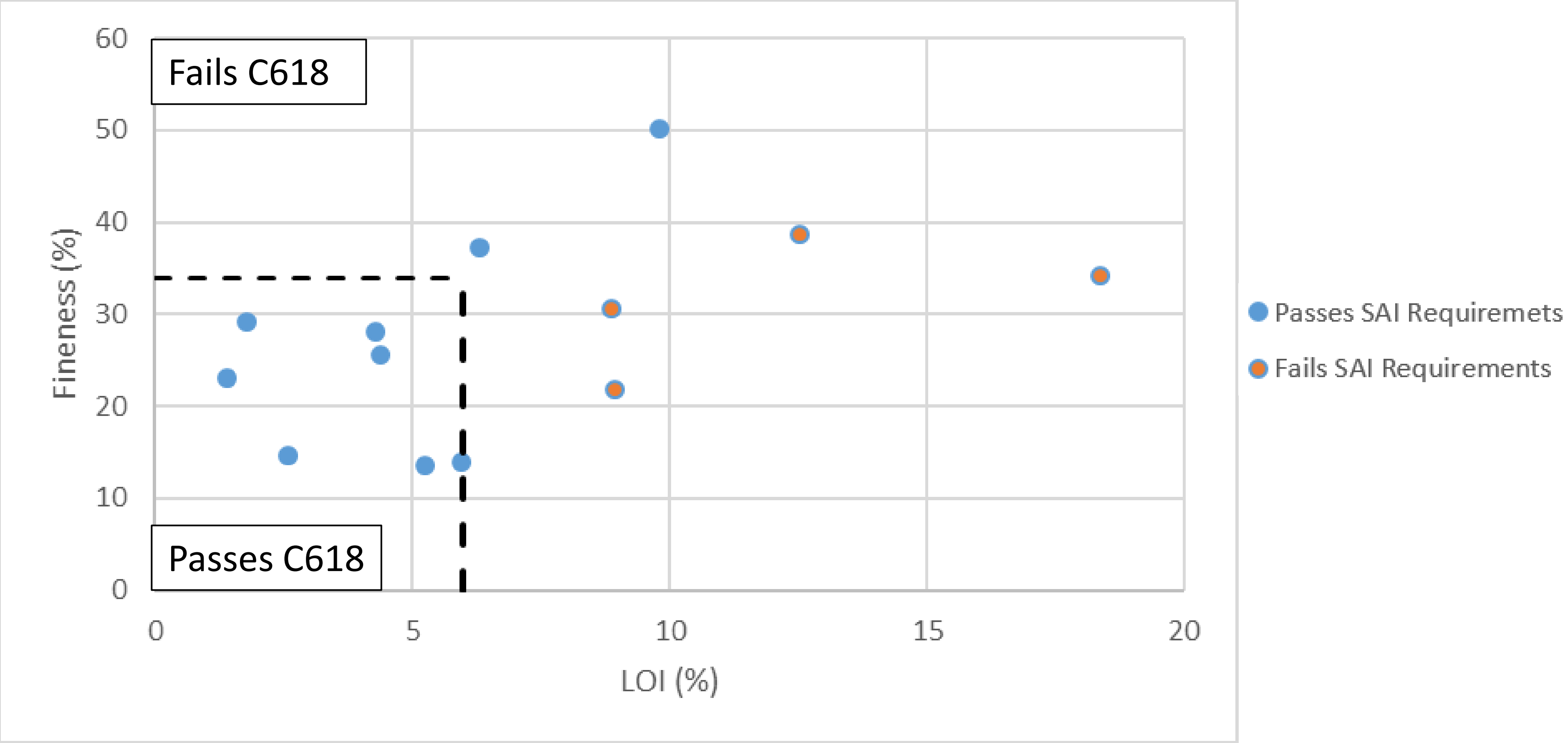
THOUGHTS

Common problems with ponded ashes:

- High LOI
- Large Iron Contents
- Large PSD
- Low reactivity
- Dewatering

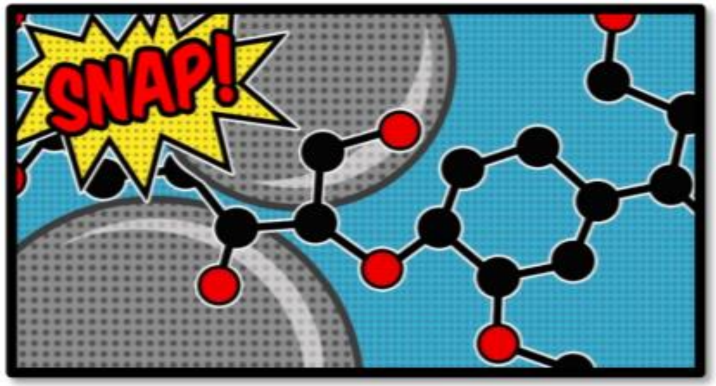
Potential Problem:

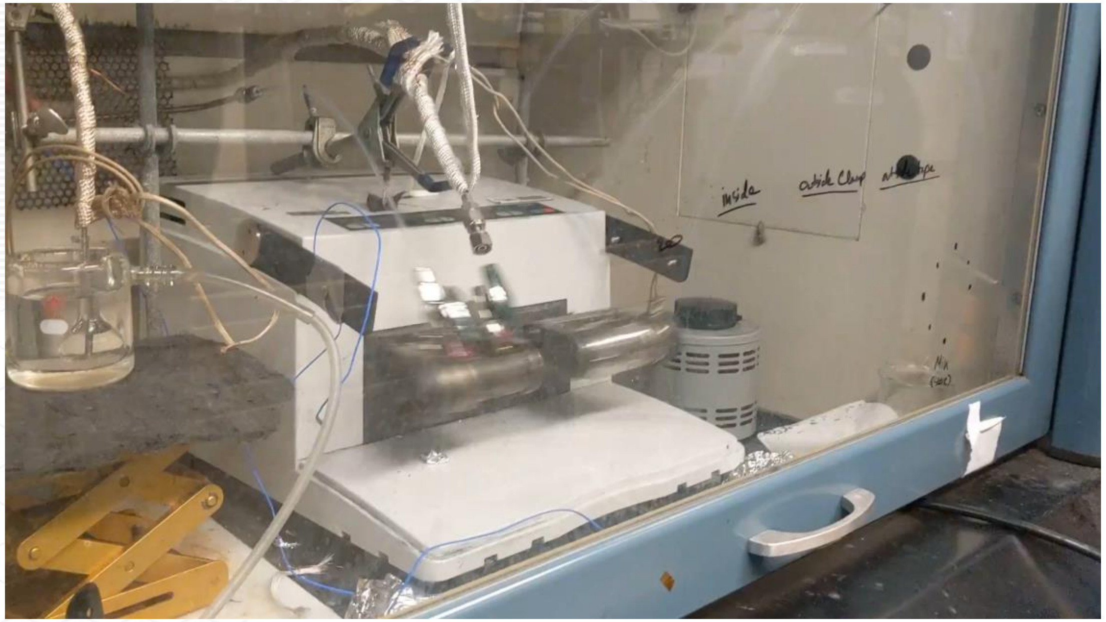
- Flue Gas Gypsum



BENEFICIATION POTENTIAL: CHEMI - MECHANICAL GRINDING

- Utilizing chemi - mechanical grinding via ball mill possesses the potential to mitigate a number of these problems
- Mechanical grinding is typically utilized to lower the particle size of a material
- Each impact possesses the potential to create hot spots with high temperature/pressure of up to ~800 °C
- This process destroys crystalline structures increasing quantity of reactive phases
- High water content ashes may provide additional benefits

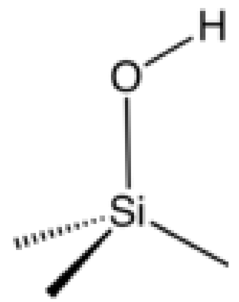




* A Short communication on this topic is currently under review by Fuel

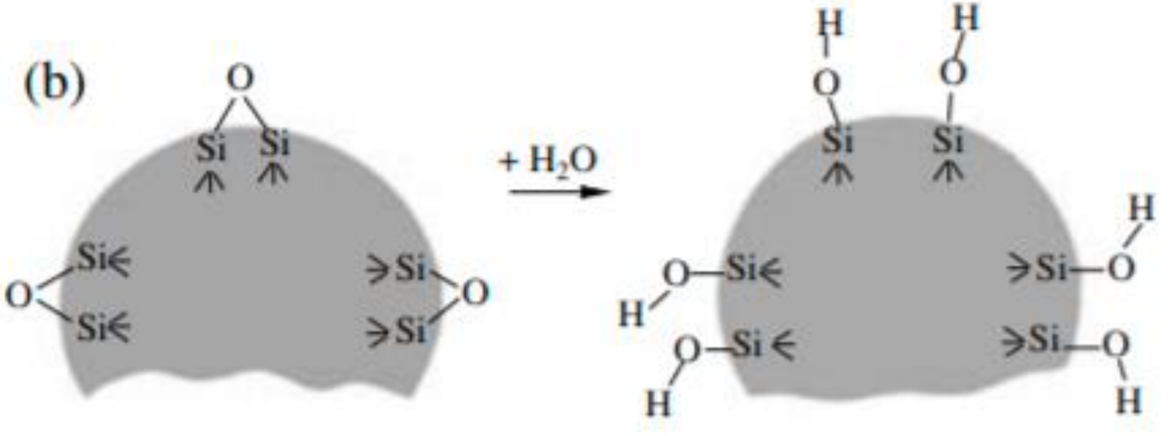
Sievers, Carsten. *Mechanocatalytic Lignin Conversion. Powerpoint Presentations*

FORMATION OF SILANOL GROUPS

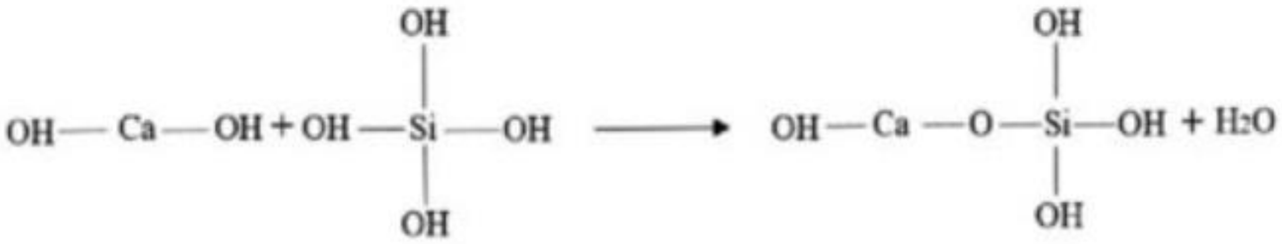


- The high heat/pressure creates an environment ideal for forming silanol groups
- Silanol groups form on the surface of siliceous materials via hydrolysis, a chemical reaction with water:

$$Si_2O + H_2O \rightarrow 2\, Si - O - H$$



- Silanol groups behave as reactive sites for the induction of the pozzolanic reaction
- Possess the capability of reacting quickly with $Ca(OH)_2$
- Speeds up the pozzolanic reaction



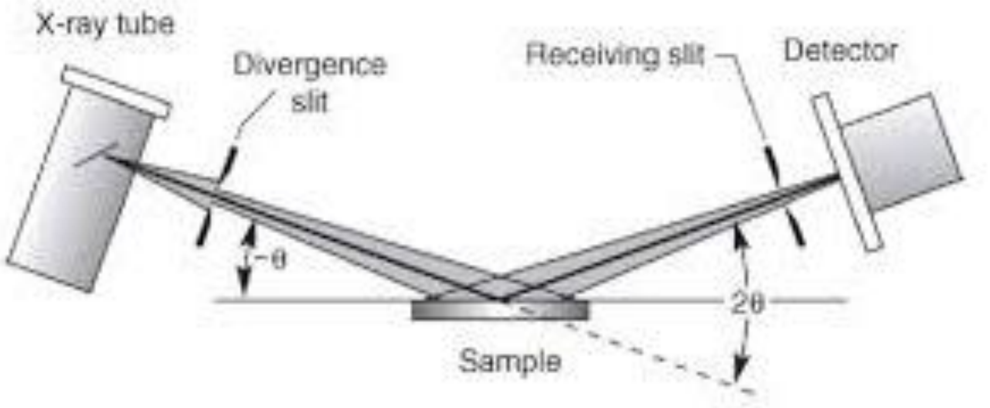
Pozzolanic reaction between silanols and calcium hydroxide

https://www.researchgate.net/publication/320042386_Effect_of_silane_admixtures_on_mechanical_and_microstructural_properties_of_cementitious_matrices_containing_tailings

https://www.researchgate.net/publication/239046276_Density_of_silanol_groups_on_the_surface_of_silica_precipitated_from_a_hydrothermal_solution

BENEFICIATION PROCESS

- Ashes which failed compressive strength requirements were beneficiated: PM2, PM4, PW10, and Y1
- These ashes were mixed with H_2O until they reached a "muddy" consistency
- Ashes were grinded in a Mixer Mill MM400 by Retsch for 1 hr at 25 Hz
- Resulting ashes were analyzed utilizing x-ray diffraction (XRD), scanning electron microscopy (SEM), and attenuated total reflectance (ATR)



X-Ray Diffraction

https://research.ntu.edu.sg/facts/Training%20Courses/Documents/Short%20Course%20Thin%20film%20XRD%20GIXRD%20RSA%20Buenconsejo%202019.pdf

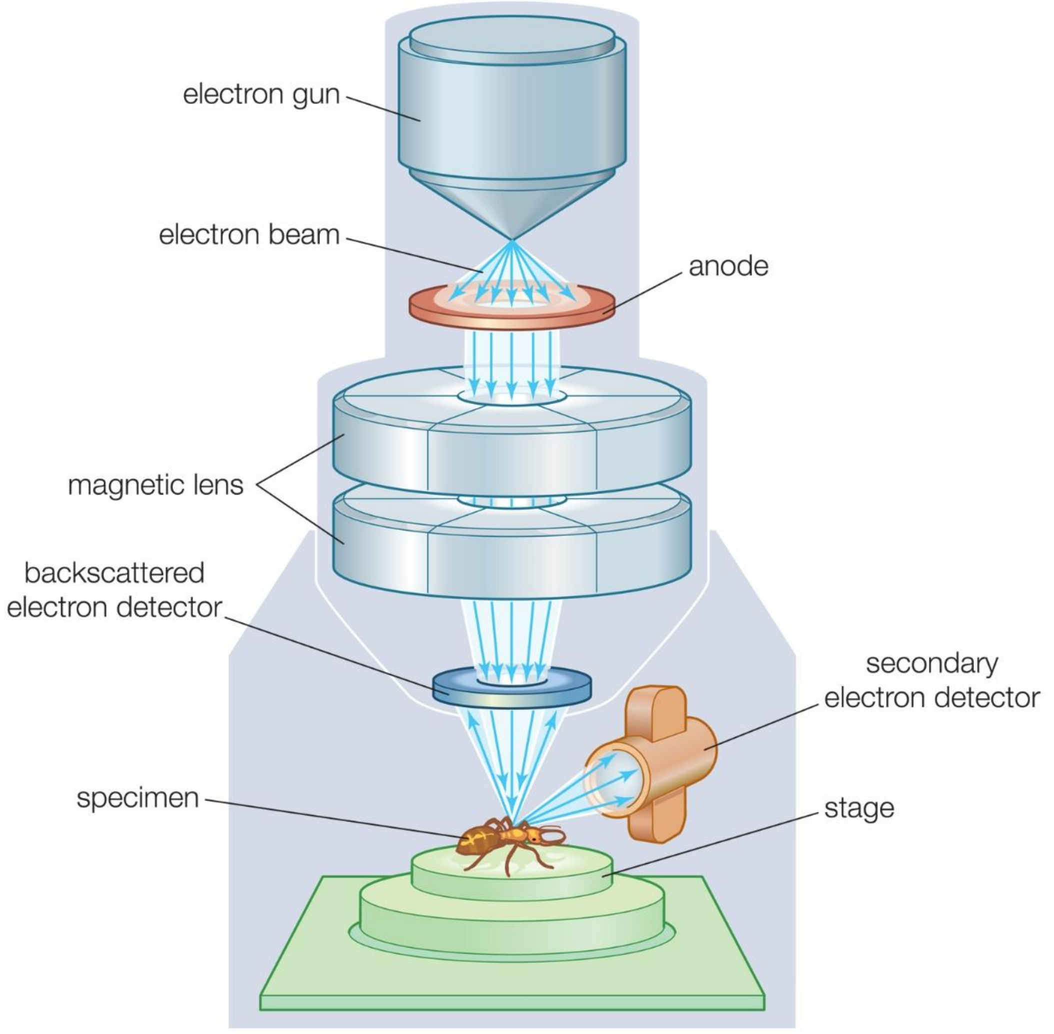
X-RAY DIFFRACTION

- Quantified using 10% LaB_6 as a reference material
- Shows an increase in amorphous content of between 5 – 36 percentage points

Wt. %	Before Milling				After Milling			
	PM2	PM4	PW10	Y1	ML PM2	ML PM4	ML PW10	ML Y1
Quartz	12.9	13.7	10.9	14.0	5.9	3.7	5.1	9.3
Hematite	0.4	0.4	3.1	0.3	0.0	0.0	0.4	0.0
Magnetite	0.4	0.4	9.1	0.4	0.0	0.0	12.3	0.0
Mullite	27.2	33.9	8.0	17.4	10.8	8.7	8.4	9.3
Calcite	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Ettringite	0.0	0.0	0.0	0.1	0.3	0.0	0.0	0.0
Amorphous	59.2	51.6	68.8	67.8	83.0	87.7	73.7	81.3

SCANNING ELECTRON MICROSCOPY

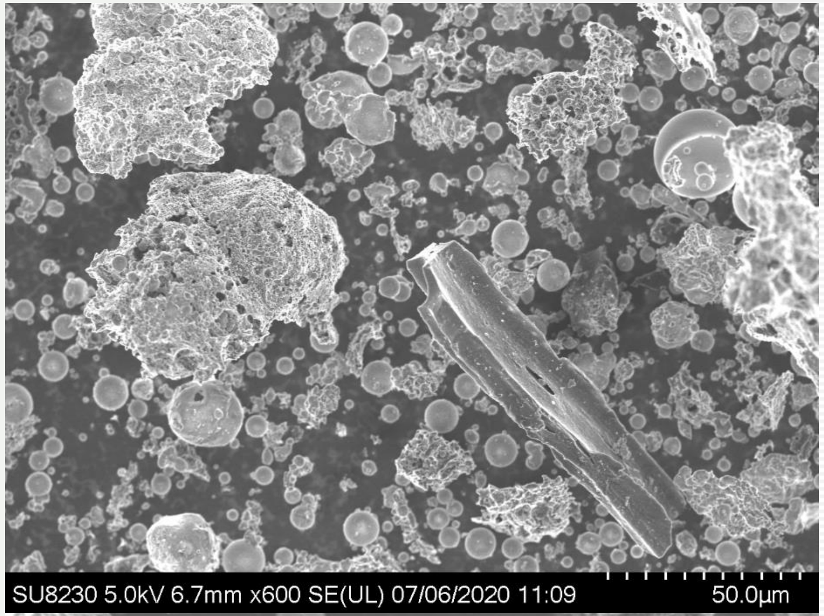
- Scanning electron microscopy was conducted on samples PM2 before and after grinding
- Hitachi SU 8230 with a 5 kV acceleration voltage
- Samples were observed between 20 – 50 µm magnification range



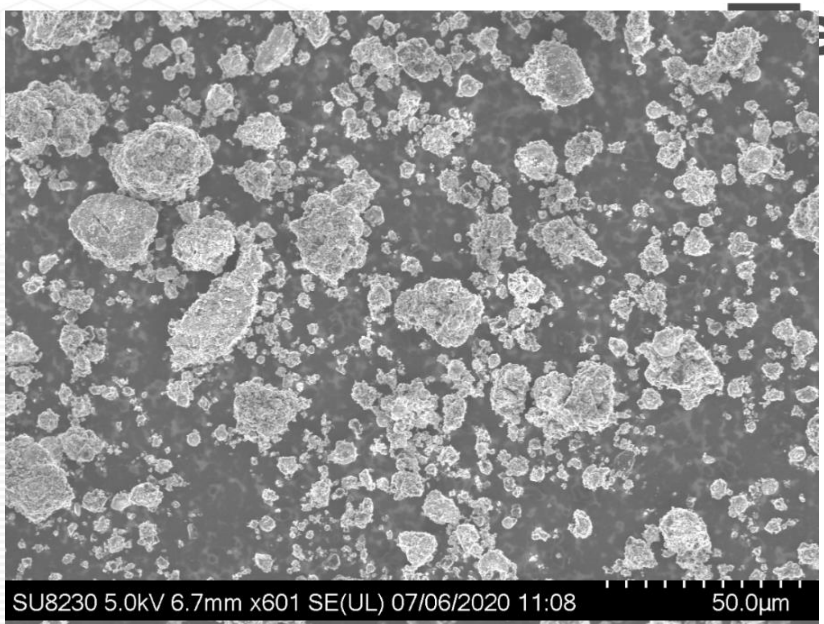
https://www.britannica.com/technology/scanning-electron-microscope

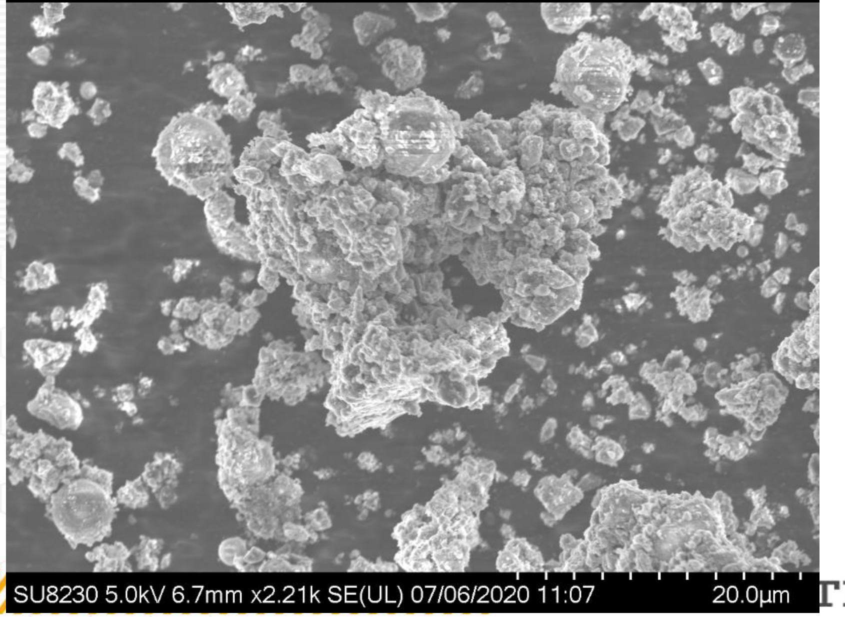
SCANNING ELECTRON MICROSCOPY

Before Milling



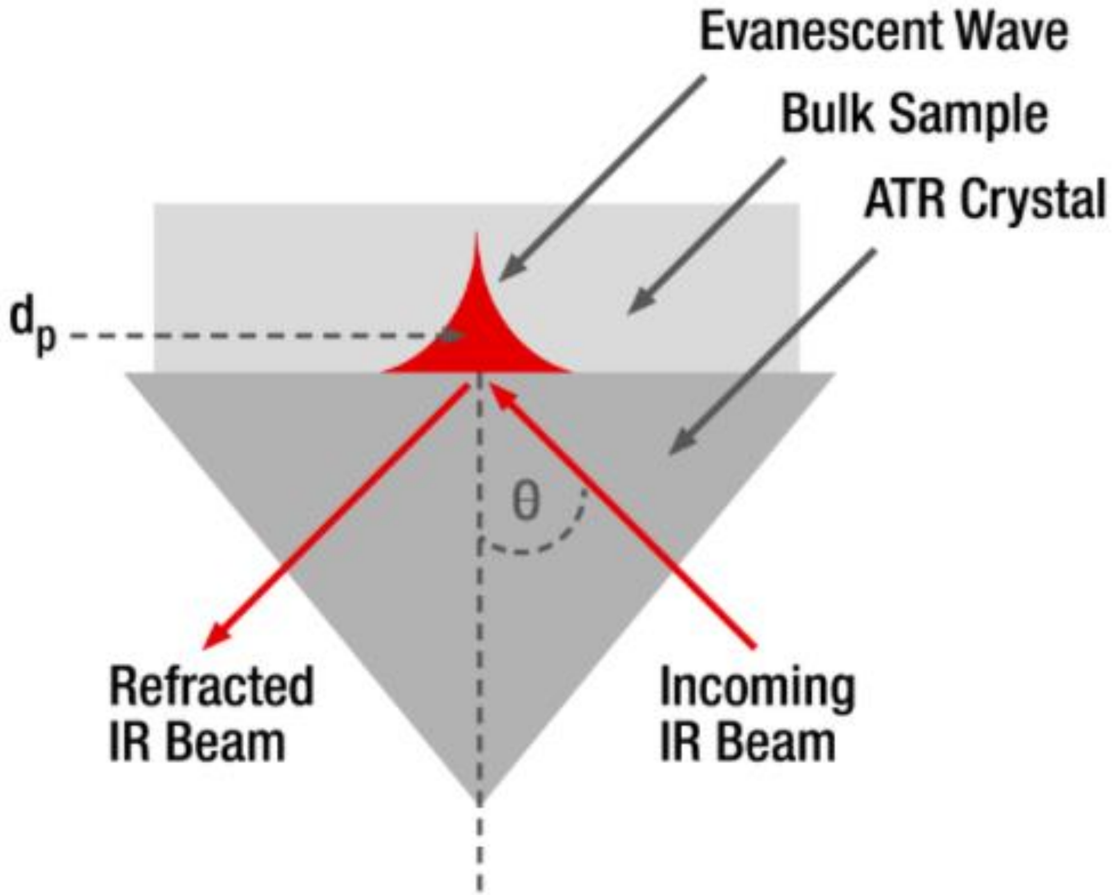
After Milling





ATR

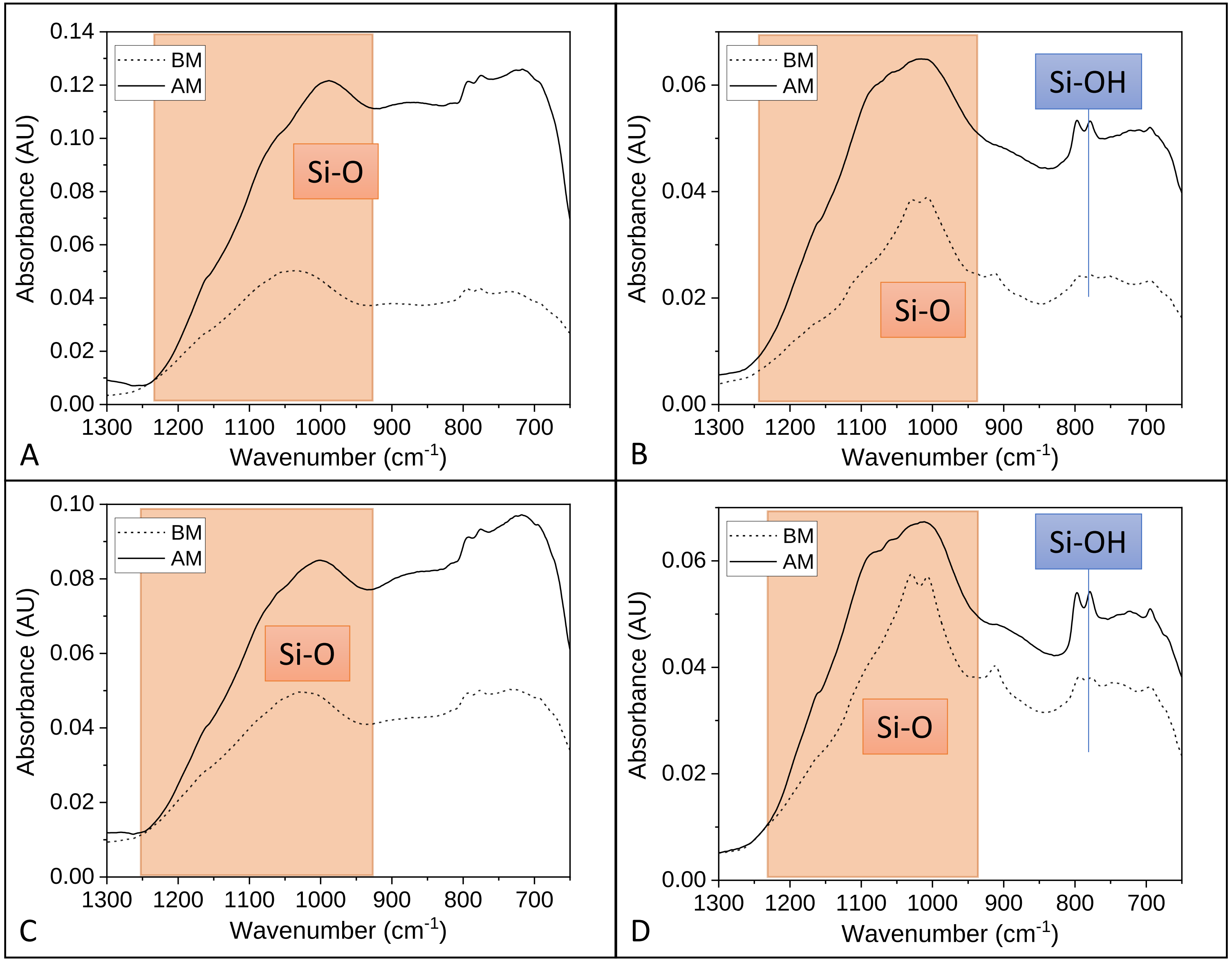
- Attenuated total reflectance were collected for each sample before and after milling
- Nicolet 8700 equipped with a Smart iTR Attenuated Total Reflectance sample accessory
- 64 scans with a resolution of 4 cm^{-1}



Work performed by Giada Innocenti

https://wiki.anton-paar.com/en/attenuated-total-reflectance-atr/

ATR (CONT.)



A) PM2

B) PM4

C) PW10

D) Y1

BENEFICIATION THOUGHTS

Fixes:

- Particle size/fineness Issues
- Increases Reactivity (Change amorphous content and silanol groups)
- Can be performed with a high water content/ reduces dewatering cost
- Resulting product will perform more consistently

Other:

- Workability will not improve
- May not affect LOI