Comprehensive Investigation of Biomass Fly Ash in Concrete: Strength, Microscopy, Quantitative Kinetics and Durability

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ACERC annual conference
February 28, 2007

Outline

- Introduction
- Strength, Microscopy and Kinetics
  - Strength and Microscopy of ash concrete
  - Strength and kinetics (fly ash/$Ca(OH)_2$)
- Durability (ASR expansion Mitigation)

Story about Pozzolan

- When: 1st century
- What: (volcanic ash + lime) = cement
- Who: ancient Romans and Greeks
- Where: best materials near Mount Vesuvius, Bay of Naples, Italy
- Why: named after the village- Pozzuoli

Note: Modern Portland cement has a history of only 180 years.

Sears Tower-
A Fly Ash Concrete Building

Note: 1) 1450 feet and 110 stories high

2) No. 1 tallest building in the world until 1998

Background

- Non-compliant coal fly ash becoming common:
  - Emissions control
  - Opportunity fuels such as biomass-coal cofiring
- ASTM C 618
  - Allows Class C Class F (coal-derived) fly ash
  - Excludes all non-coal-derived material in fly ash

Chemistry

- Cementitious reaction

  $2Ca_3SiO_5 + 7H_2O \rightarrow 3CaO{\bullet}2SiO_2{\bullet}4H_2O + 3Ca(OH)_2$ ***Eq. 1***

- Pozzolanic reaction

  $3Ca(OH)_2 + 2SiO_2 + H_2O \rightarrow 3CaO{\bullet}2SiO_2{\bullet}4H_2O$ ***Eq. 2***

- Alkali silica reaction (ASR)
  - $4SiO_2 + 2NaOH = Na_2Si_4O_9 + H_2O$ ***Eq. 3***
  - $SiO_2 + 2NaOH = Na_2SiO_3 + H_2O$ ***Eq. 4***
  - Expansion → cracks → failure
  - "Cancer" of concrete

- Fly ash addition will depress or even eliminate ASR, mainly depending on properties and replacement ratio of fly ash.

Fly Ash

- Coal: class C and class F
- Wood: fly ash from pure wood combustion
- Five cofired fly ashes (coal/biomass):

<table>
<tr><th>Name</th><th>Coal</th><th>(%)</th><th rowspan="6">Cofired With…</th><th>Biomass</th><th>(%)</th></tr>
<tr><td>SW1</td><td rowspan="2">Galatia coal</td><td>80</td><td rowspan="4">Switch Grass</td><td>20</td></tr>
<tr><td>SW2</td><td>90</td><td>10</td></tr>
<tr><td>10P</td><td rowspan="3">Powder River Basin</td><td>90</td><td>10</td></tr>
<tr><td>20P</td><td>80</td><td>20</td></tr>
<tr><td>SAW</td><td>80</td><td>Sawdust</td><td>20</td></tr>
</table>

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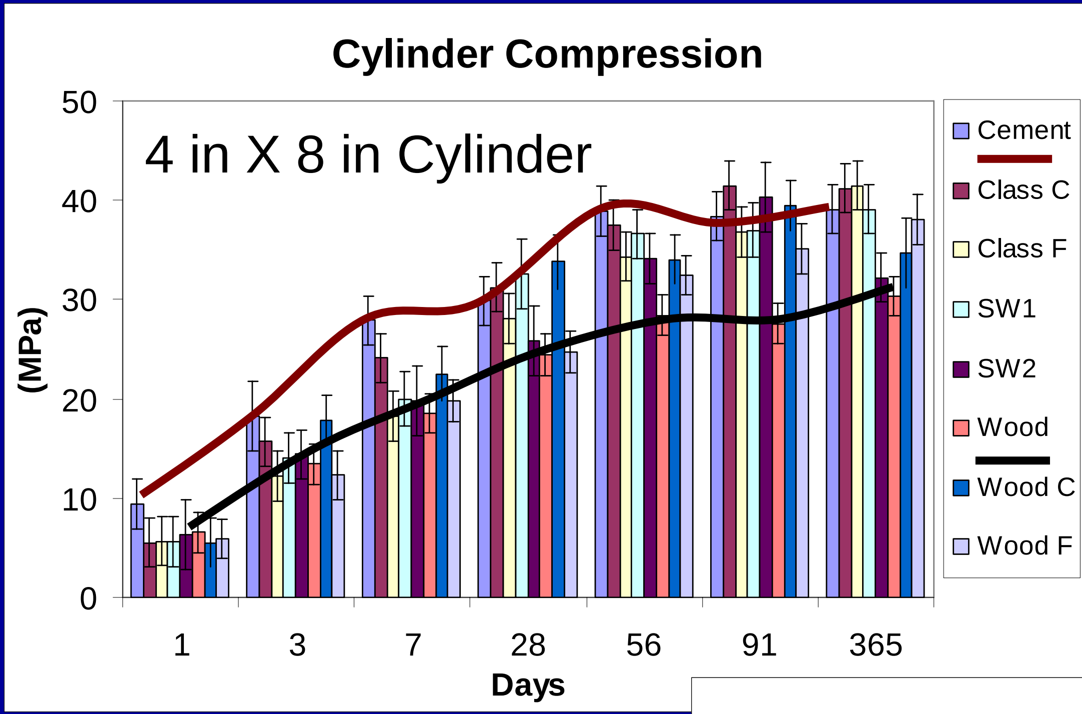
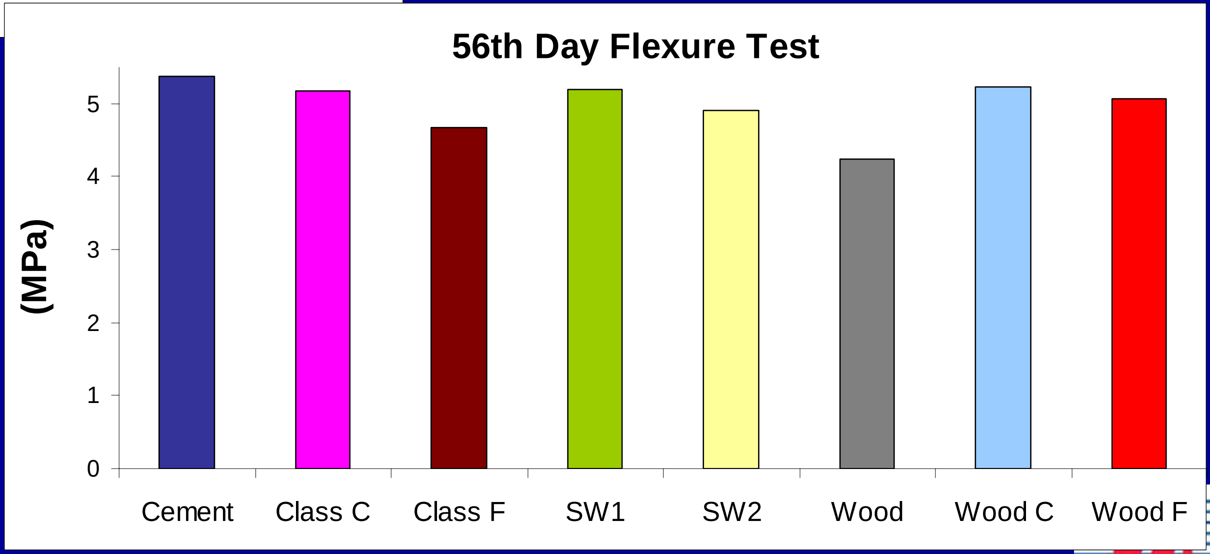
Strength

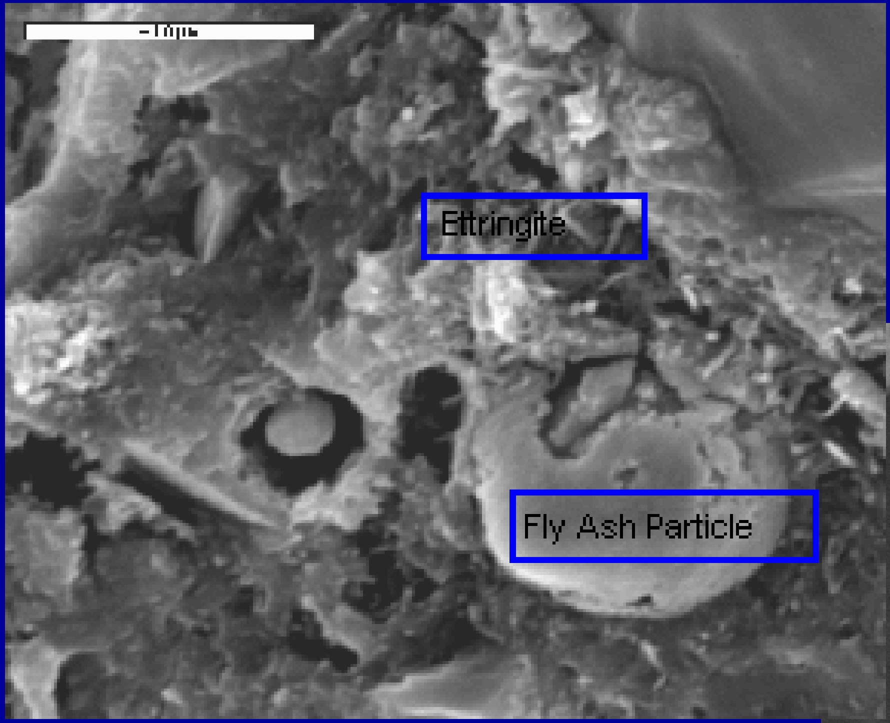


Fly ash/cement =1/3(wt)

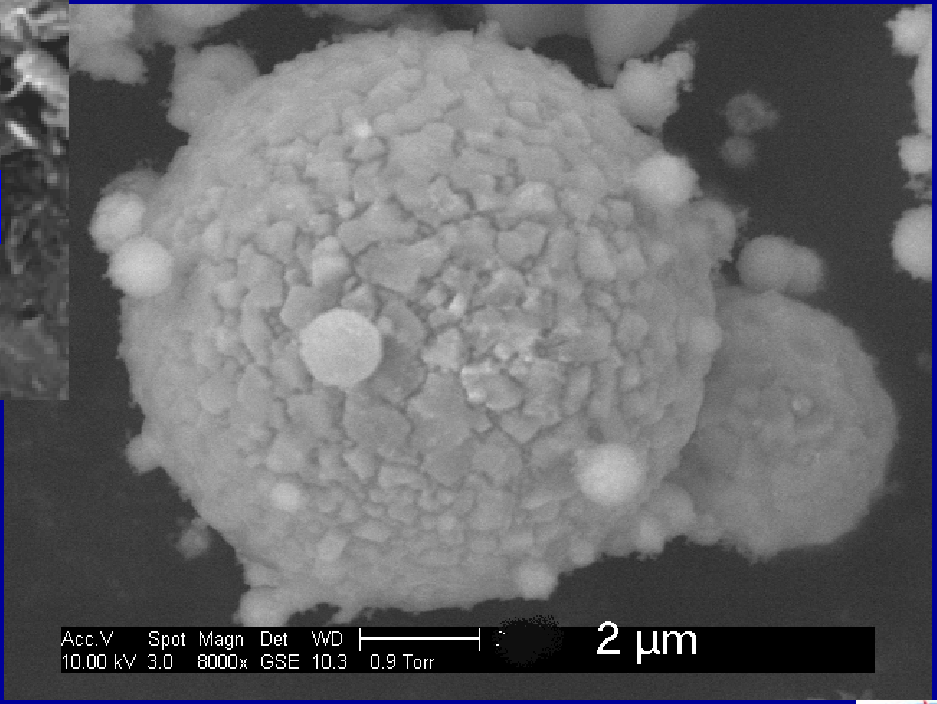
6 X 6 x 20 in beam



SEM (reacted/raw) SW1 Fly Ash

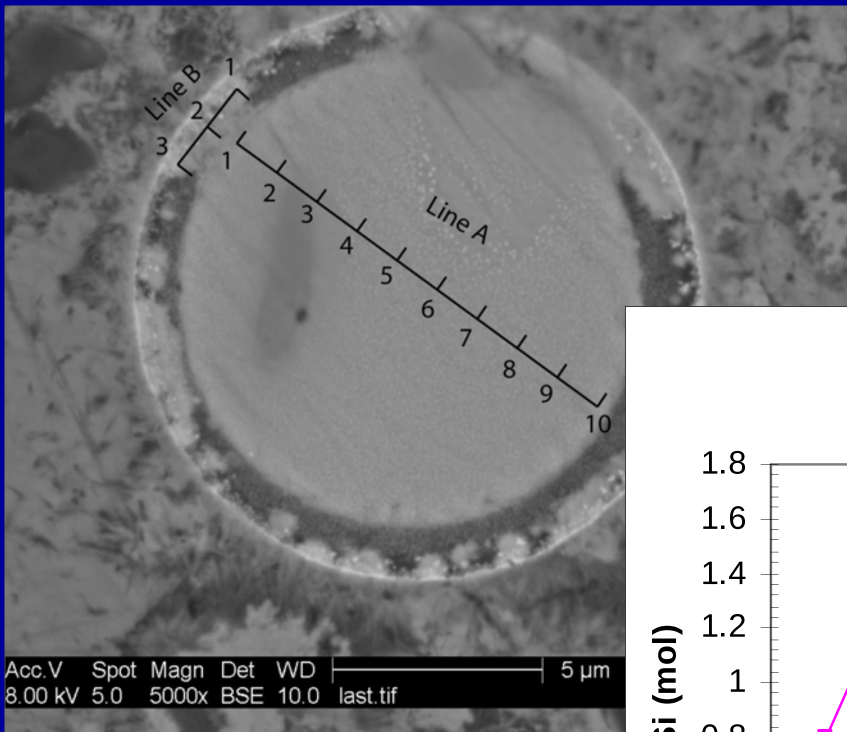


365-day in concrete

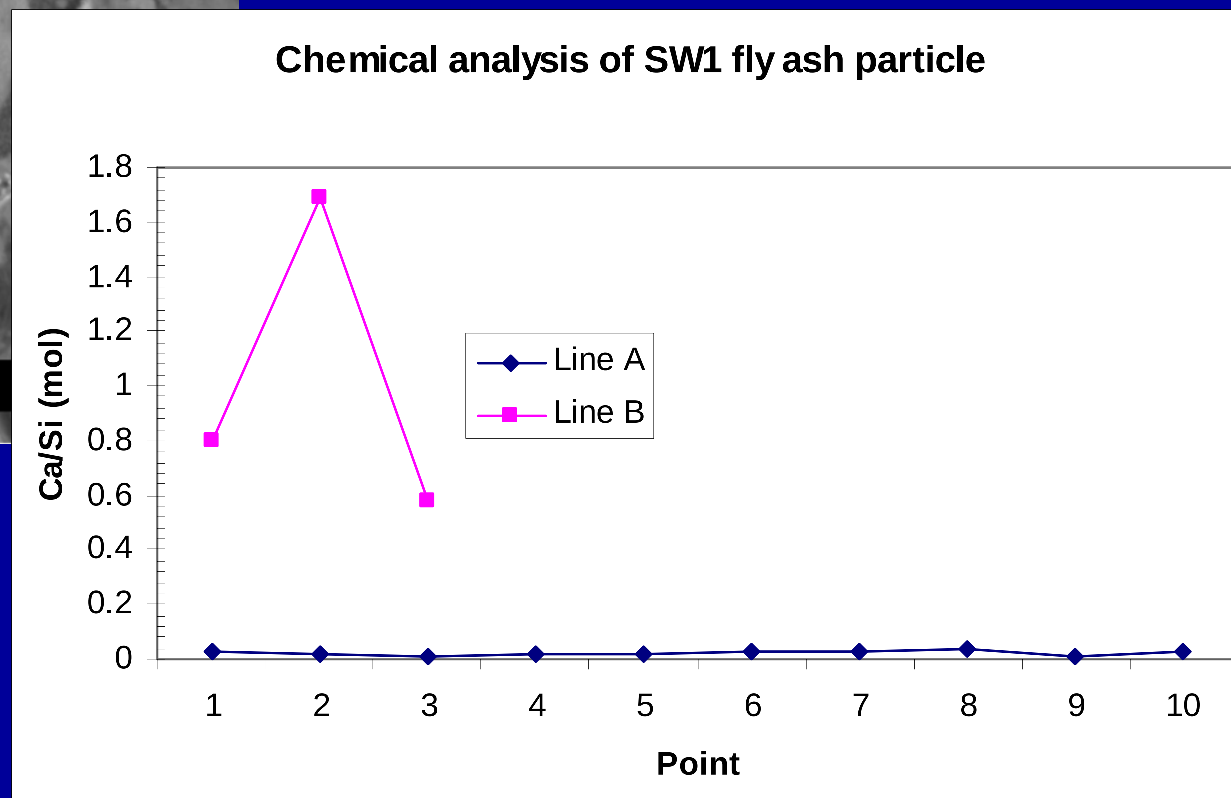


Raw particle

EMPA Chemical Analysis



One year in Concrete



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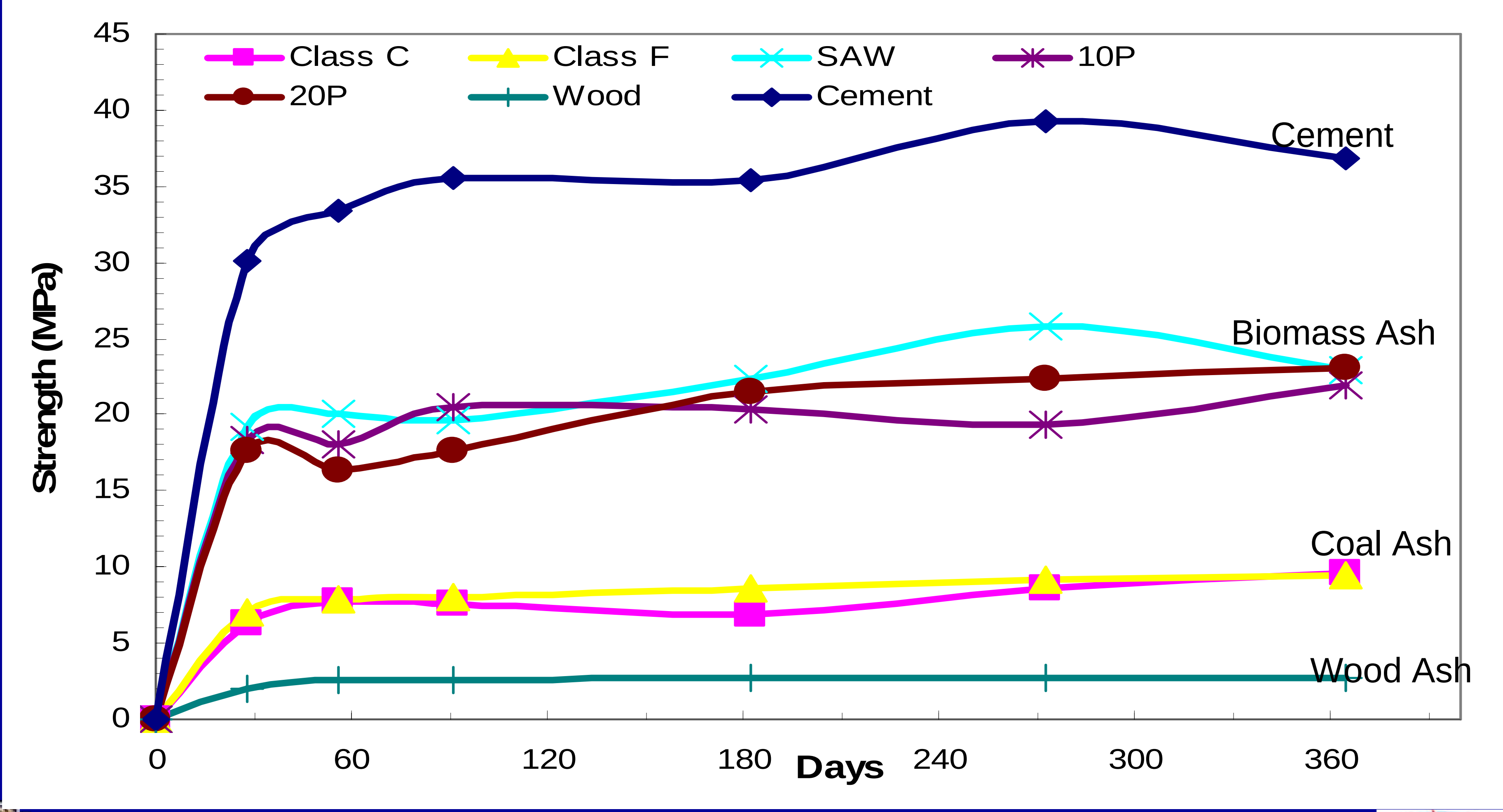
Experimental Setup

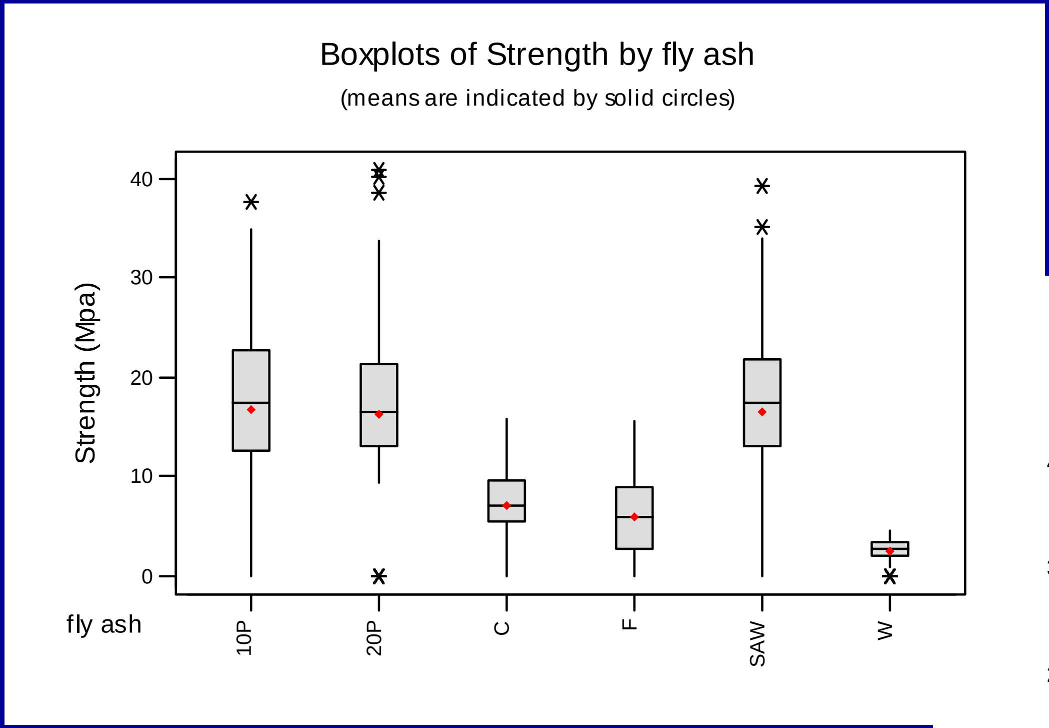
Variable	Description
Fly ash(6)	C, F, Wood, SAW, 10P and 20P
Fly ash / $Ca(OH)_2$ (3)	80 / 20, 70 / 30, 60 / 40
Temperatures (3)	23ºC, 43ºC, 63ºC
Testing Dates (6)	1, 2, 3, 6, 9 and 12 months
Replicates	2
Reaction extent of $Ca(OH)_2$	TGA
Samples Curing	Vacuum sealed in Mason Jars
Strength test of 2 in cube	Compression

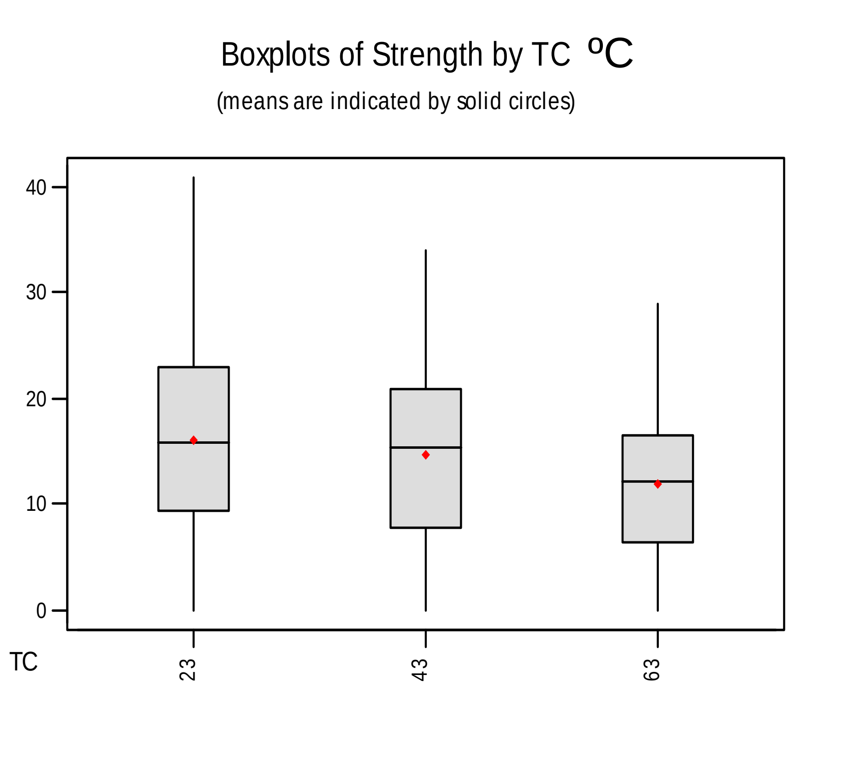
Compression Strength

70/30 mixing ratio, 23ºC (as examples)



Statistical Strength Analysis





Quantitative Kinetics

- Parabolic diffusion

$$\alpha^2 = kt$$

- First order (CH)

$$-\ln(1-\alpha) = kt$$

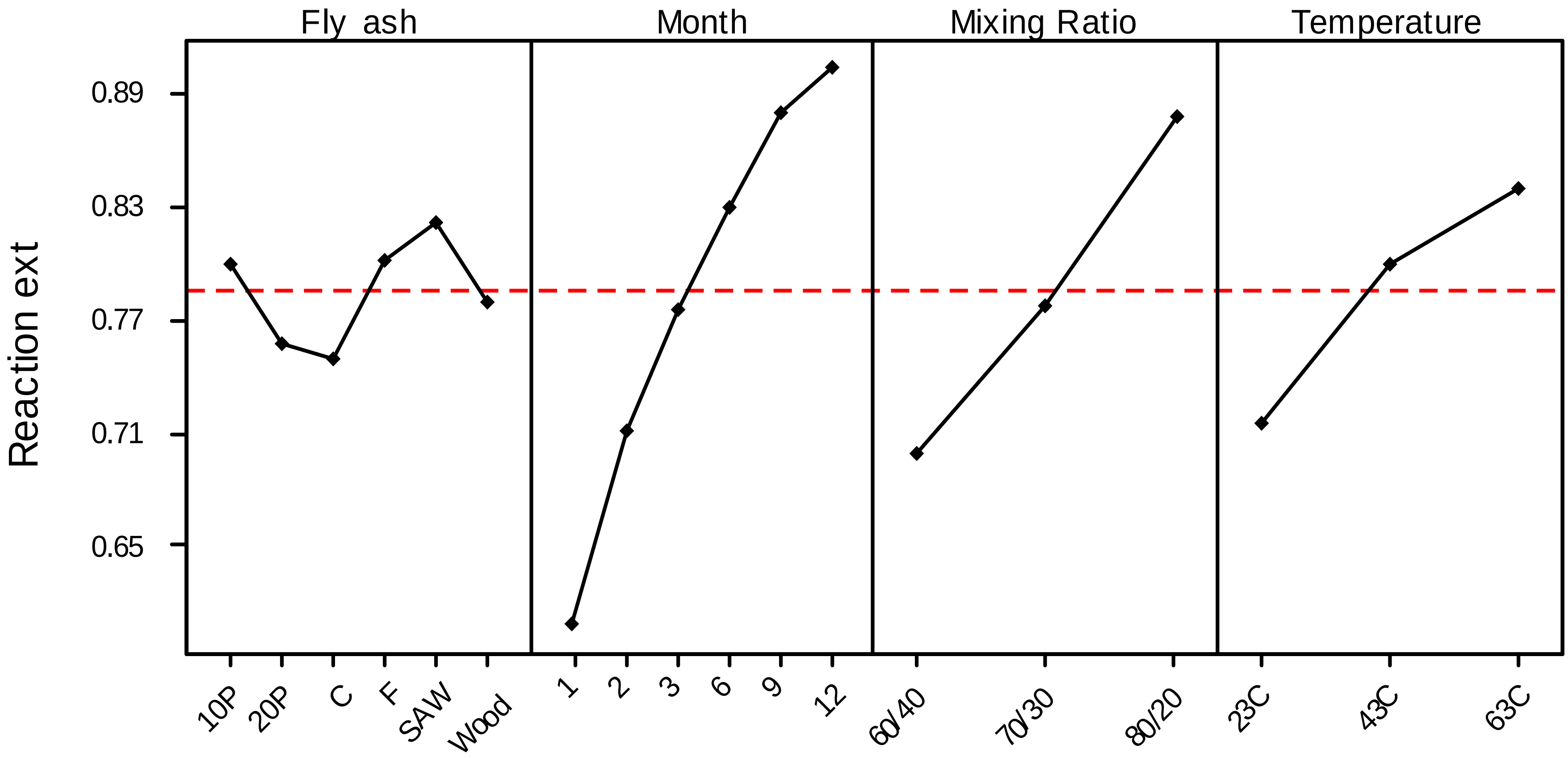
- First order to CH & ash, respectively

$$\frac{d\alpha_{CH}}{dt} = k(1-\alpha_{CH})(1-\alpha_{ash})$$

Where

$$k = k_0 * \exp(-E_{act}/RT)$$

Quantitative Kinetics (continued-1)



Therefore, first order of CH and parabolic diffusion mechanisms are not appropriate.

Quantitative Kinetics (Continued-2)

	Kinetics Parameters				Excess amount of ash		
	k^0 ($Month^{-1}$)	Ea/R (K)	b	R^2	80/20	70/30	60/40
F	199453	3639	1.875	0.95	0.425	0.1375	-0.15
C	38.71	986.2	2.28	0.94	0.344	0.016	-0.312
Wood	5.05	191.1	2.99	0.93	0.202	-0.197	-0.596
10P	2408	2316	1.74	0.94	0.452	0.178	-0.096
20P	2535	2391	1.86	0.93	0.428	0.142	-0.144
SAW	245700	3688	1.71	0.96	0.458	0.187	-0.084

Note: b is the stoichiometric coefficient, one gram of fly ash chemically combines with b grams of $Ca(OH)_2$

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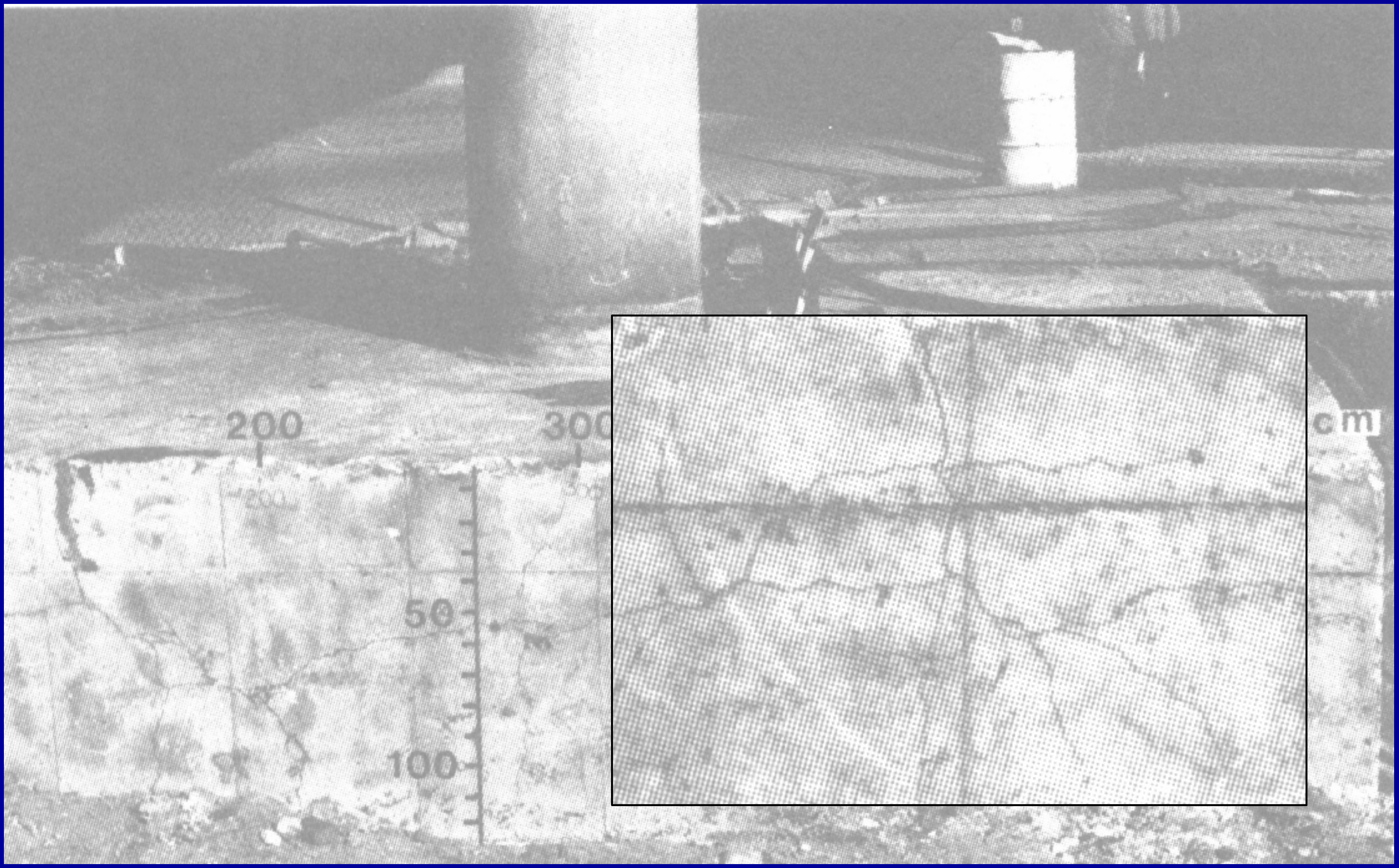
ASR Cracks



ASR cracks within field concrete

ASR Experimental Setup (Expansion)

❖ Materials:
- High alkali cement (1.15% Equiv. Na_2O)
- Reactive aggregate: wood opal Virgin Valley, Nevada
- 6 fly ashes C , F , wood, SAW, 10P and 20P
- 3 ratios of fly ash/cement: 15/85, 25/75 and 35/65

❖ Curing container: ASTM containers

❖ Sample dimensions: 1 X 1 X 10 inches

❖ Expansion:
- 1, 14, 28, 56, 84, 126, 182 and 364 days after mixing
- Digital length comparator (precision ±0.0001 in)

Note 1: Observe ASTM C 227 and 441

Note 2: Equiv. $Na_2O\%=(Na_2O + 0.658\ K_2O)\%$

ASR Experimental Setup (Pore solution)

- Specimens: 2 (D) X 4 (H) inches cylinder
- High pressure extrusion (up to 240 thousand lbs)
- Pore solution analysis
  - Test days: up to 6 months after mixing
  - Ions analyzed: OH^-, Na^+, K^+ and et al
  - Test instrument: 1) Atomic absorption, 2) Ion Chromatography and 3) Acid-base titration.

Expansion and Pore Solution Extrusion

Expansion Measurement (± 0.0001in)

Piston

N_2 Purge

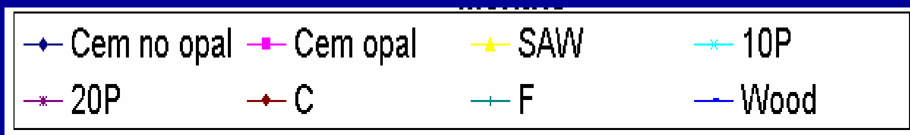
Pore solution

Double-layered prestressed cylinder

Base

Max operation Load of 240 thousand pounds with 100 cycles finished

ASR Expansion and Pore Solution Analysis

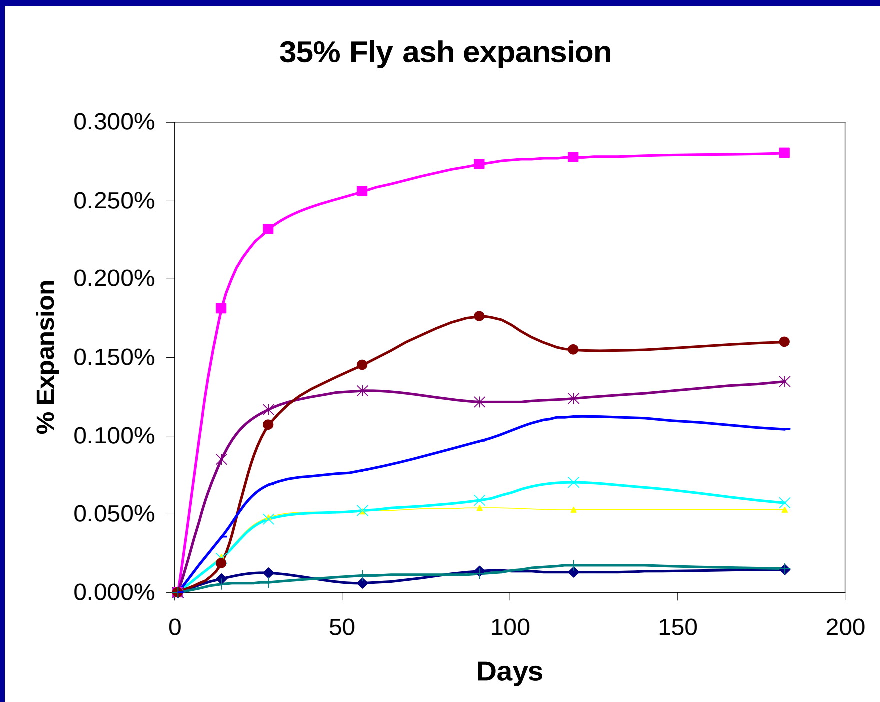


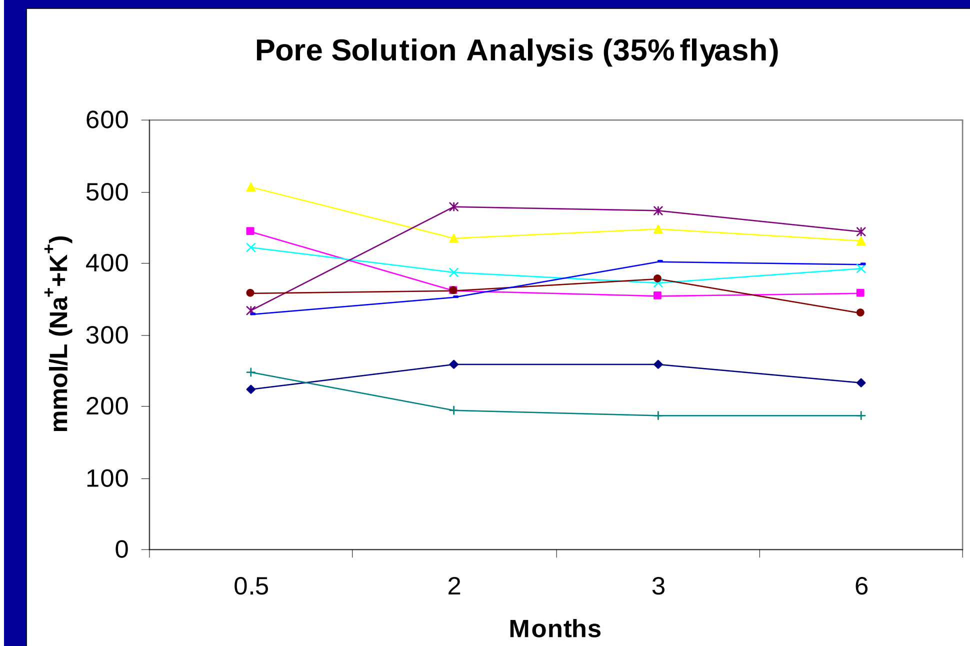
Soluble alkali (%):

C (1.03), F (0.53), wood (1.78)

SAW (2.88) 10P (2.71) 20P (2.46)

Cement (1.15) (ASTM limit<0.6)





Conclusions

Biomass Fly ash has

- Equal strength to that of pure cement concrete from 1 month to 1 year after mixing.
- Significant pozzolanic reaction up to one year in concrete.
- 3-6 times the strength of coal ash samples with $Ca(OH)_2$.
- Comparable strength with $Ca(OH)_2$ even to pure cement.
- Quantitative kinetics has been derived.
- Mitigates ASR expansion to within ASTM limits.
- Matches or outperforms coal ash in reducing ASR expansion.

Acknowledgement

Thanks

- ❖ Dr. Baxter for his consistent academic and financial support.
- ❖ Undergraduates Sharon Bragonje, Justin Tullis, Rick Dalton, Emilio Llamazos and Amber Miller for their hard work.