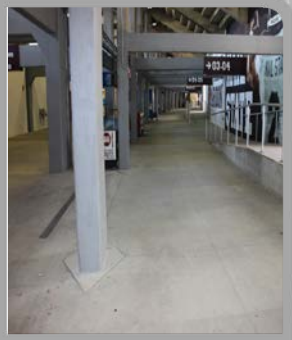
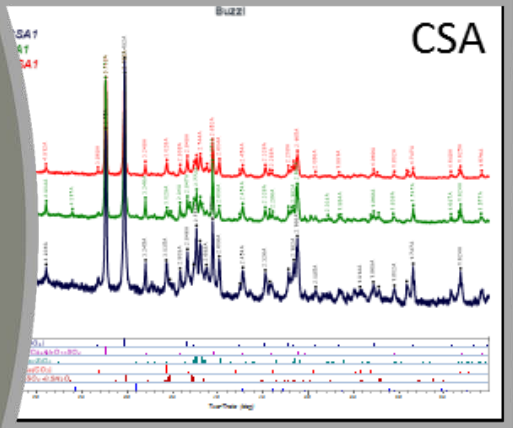
Increasing Material Sustainability Using Emerging Materials Technology and Design

ARPA-E Workshop





Jay Shannon, PhD

Research Civil Engineer

Concrete and Materials Branch, Geotechnical and Structures Laboratory

US Army Engineer Research and Development Center (ERDC)

10-11 April 2018

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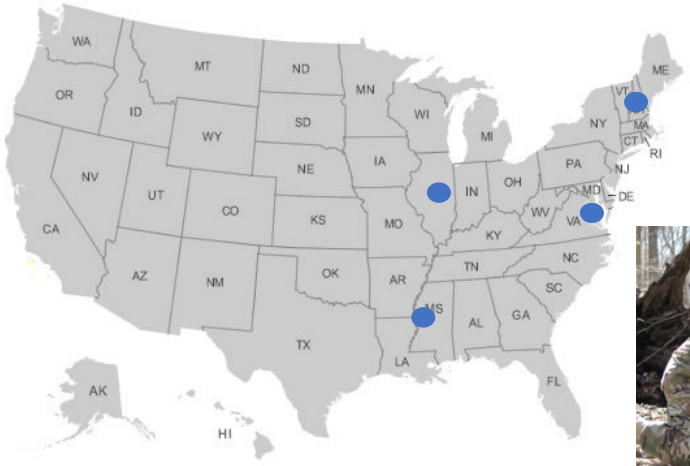

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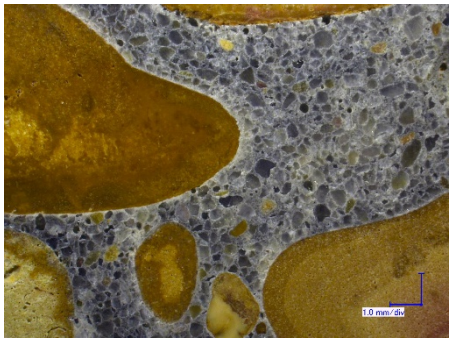
Outline and Topics

- Laboratory and Field Research Results
  - Emerging Cement Types – Portland Limestone Cement (PLC)
  - High Replacement of Cement with Supplementary Cementitious Materials (SCM)
  - Synergistic Effects of PLC with SCMs
- Ongoing ERDC Involved Programs
  - Alternative Cements
  - Geopolymers
- Design Considerations



OPC

$2C_3S + 6H \rightarrow$ ***C-S-H*** $+ 3CH$

$C_2S + 4H \rightarrow$ ***C-S-H*** $+ CH$

$C_3A + 3C\bar{S}H_2 + 26H \rightarrow C_6A\bar{S}_3H_{32}$ ***(Ettringite)***

$2C_3A + C_6A\bar{S}_3H_{32} + 4H \rightarrow 3C_4A\bar{S}H_{12}$ ***(Afm)***

CSA

$C_4A_3\bar{S} + 2C\bar{S} + 38H \rightarrow$ ***Ettringite*** $+ 2AH_3$

$3CA + 3C\bar{S} + 38H \rightarrow$ ***Ettringite*** $+ 2AH_3$

$C_4A_3\bar{S} + 18H \rightarrow$ ***Afm*** $+ 2AH_3$

$C_4A_3\bar{S} + 8C\bar{S} + 6CH + 90H \rightarrow 3$***Ettringite***

CAC

$2CA + 60H \xrightarrow{T < 15^{\circ}C} CAH_{10}$

$2CA + 60H \rightarrow 3C_2AH_8 + 3AH_3 + 27H$

$2CA + 60H \xrightarrow{T > 70^{\circ}C} 2C_3AH_6 + 4AH_3 + 36H$

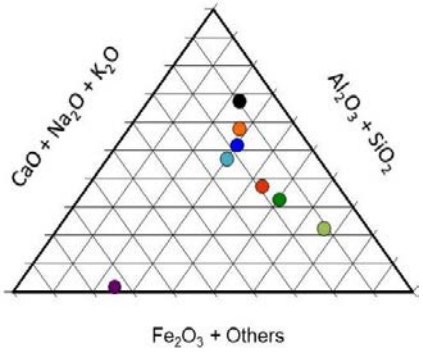
AA

(Ca + Si) + H $\rightarrow$ ***C-S-H***

(Si + Al) + Alkaline sol $\rightarrow$ ***(alkali cation)-A-S-H***

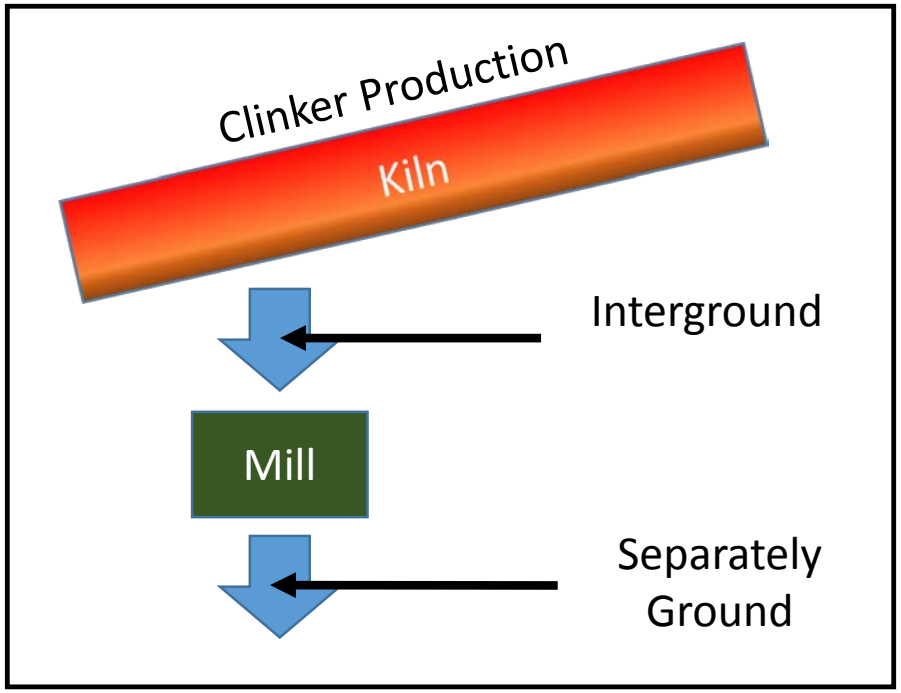
MPC

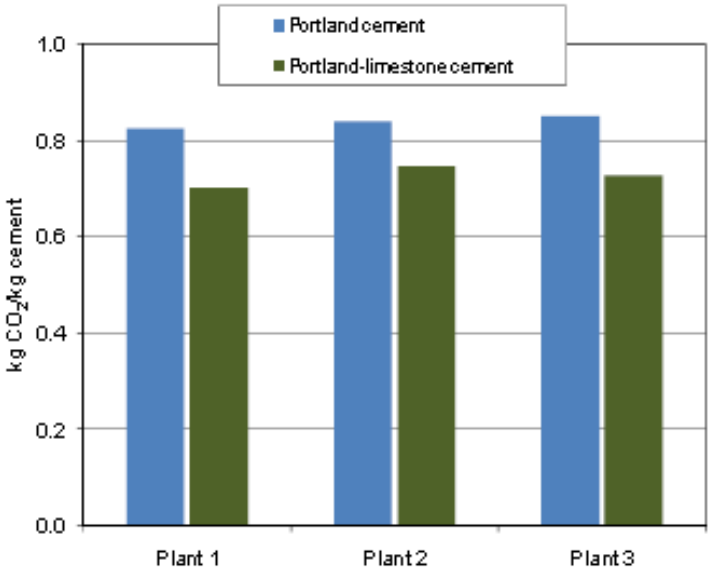
(Mg + P + K) + H $\rightarrow$ ***K-M-P-H***



Portland Limestone Cement (PLC)

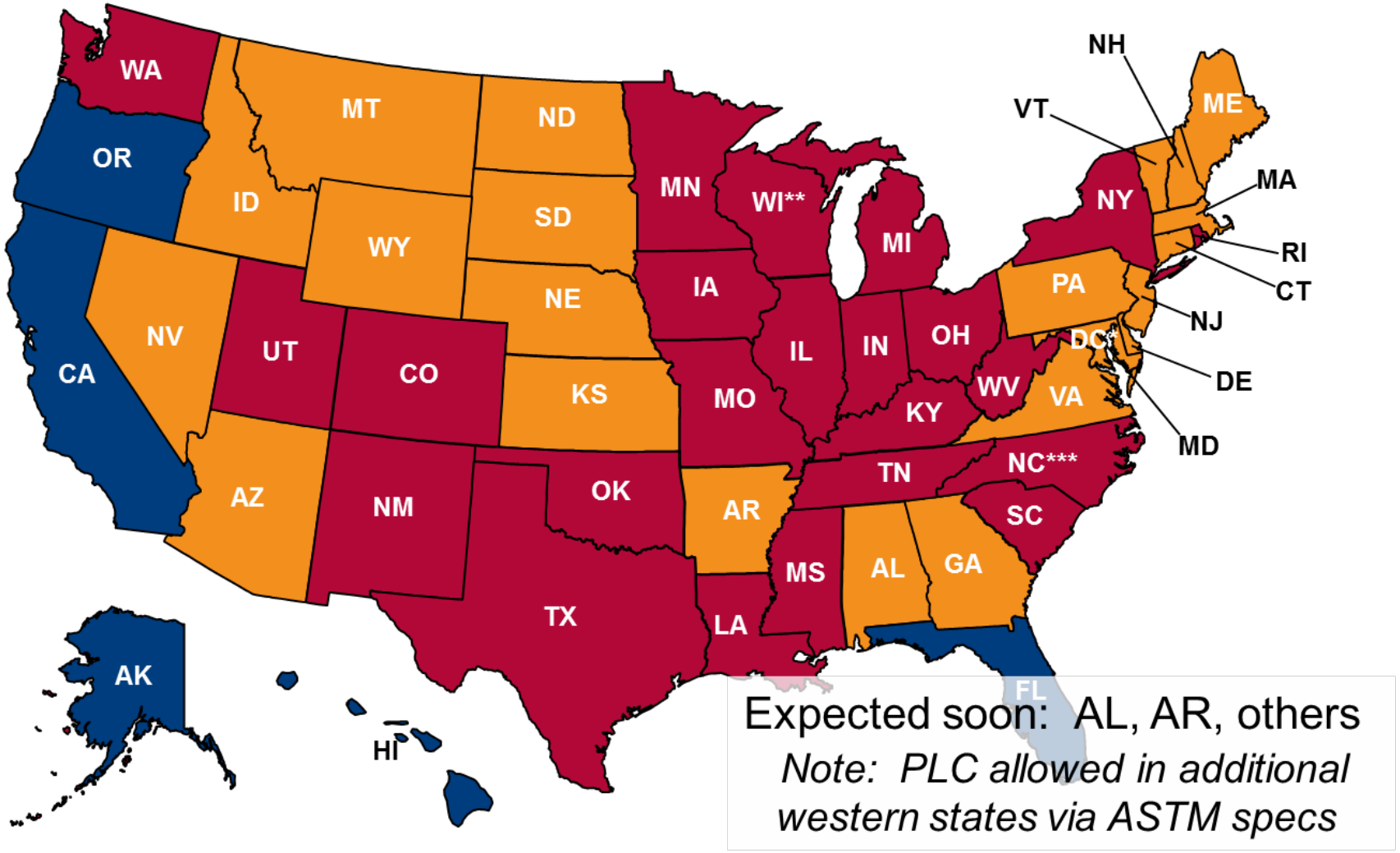
- Manufacture – 2 Main Methods
- Specifications
  - ASTM C1157
    - Type GU or MS
  - ASTM C595 or AASHTO M240
    - Type IL
- Limestone Content Measurement





	10% limestone (per million tons of cement)	15% limestone (per million tons of cement)
Energy Reduction		
Fuel (million BTU)	443,000	664,000
Electricity (kWh)	6,970,000	10,440,000
Emissions Reduction		
SO_2 (lbs)	581,000	870,000
NO_X (lbs)	580,000	870,000
CO (lbs)	104,000	155,000
CO_2 (tons)	189,000	283,000
Total Hydrocarbon, THC (lbs)	14,300	21,400

State DOTs now allowing Type IL in concrete

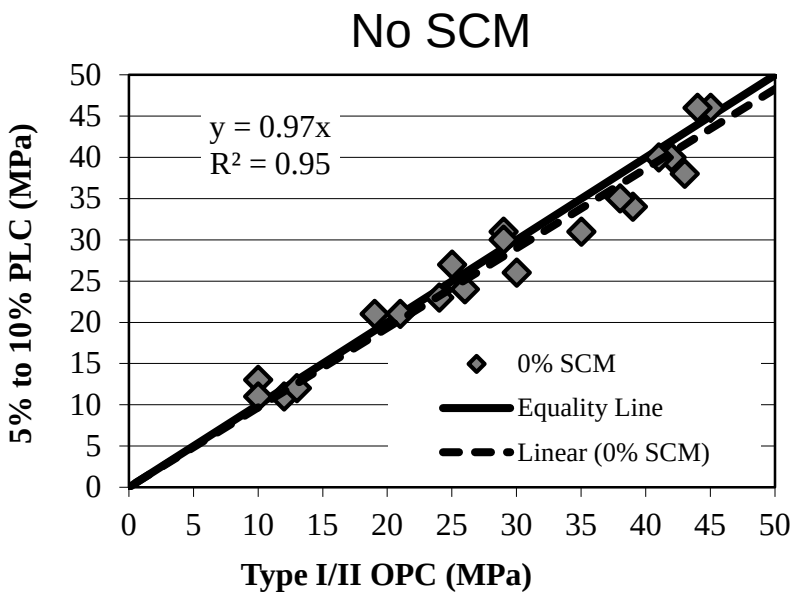


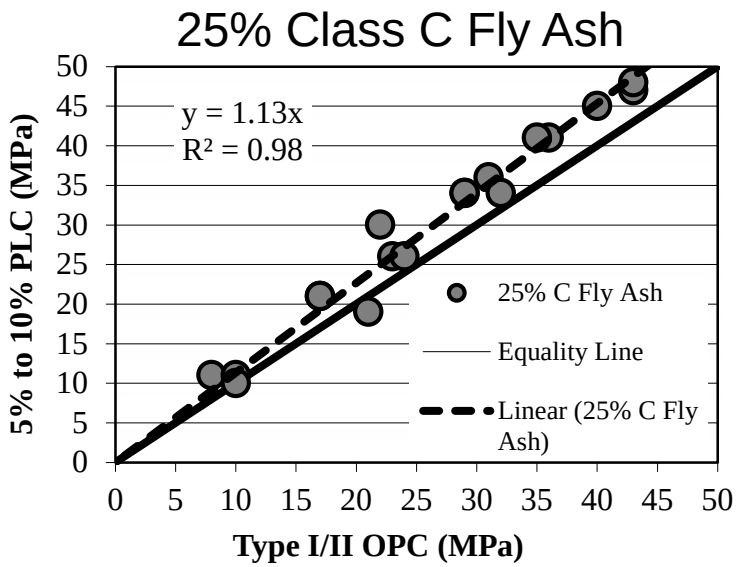
** Limestone percent (%) not to exceed 10% nominal
*** Limestone percent (%) not to exceed 12%

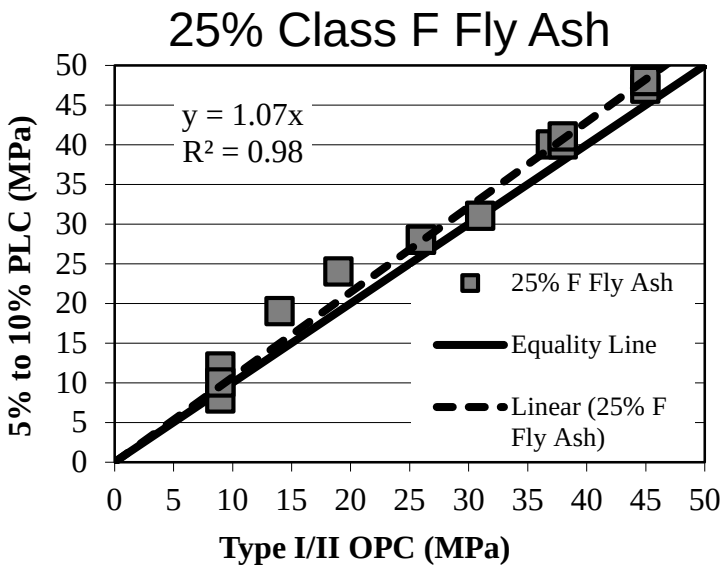
Approved · Not approved · Unknown

	A1	A2	C1	C2	C3	C4	C5	D1	D2	D3	E1	E2
Cement Type	OPC	PLC	OPC	PLC	PLC	OPC	PLC	OPC	PLC	PLC	OPC	PLC
Al_2O_3 (%)	5.5	5.3	5.0	4.5	4.3	4.9	4.2	4.4	4.2	4.0	4.6	4.0
Cl (%)	0.023	0.021	0.008	0.018	0.011	0.011	0.015	0.007	0.008	0.010	0.010	0.009
CaO (%)	63.9	63.4	64.2	64.3	64.5	63.8	64.9	63.1	63.1	63.1	63.1	63.9
Fe_2O_3 (%)	3.4	3.4	3.5	3.3	3.3	3.5	3.1	3.3	3.2	3.2	3.2	2.9
K_2O (%)	0.65	0.61	0.35	0.43	0.33	0.34	0.34	0.67	0.64	0.71	0.52	0.44
MgO (%)	0.8	0.8	1.0	1.1	1.0	1.1	1.0	2.8	2.7	2.7	3.1	3.1
Na_2O (%)	0.13	0.12	0.18	0.16	0.17	0.18	0.15	0.09	0.09	0.07	0.07	0.07
SiO_2 (%)	19.1	17.8	20.3	19.1	18.5	20.1	17.9	20.3	19.3	17.9	19.0	16.7
SO_3 (%)	3.2	3.9	3.1	3.2	3.3	3.5	3.2	3.2	3.3	3.4	3.3	3.3
C_3S (%)	60.67	---	59.39	---	---	58.25	---	59.10	---	---	58.98	---
C_2S (%)	8.63	---	13.29	---	---	13.74	---	13.55	---	---	9.93	---
C_3A (%)	8.78	---	7.42	---	---	7.01	---	5.91	---	---	6.84	---
C_4AF (%)	10.42	---	10.71	---	---	10.74	---	10.13	---	---	9.60	---
Na eq (%)	0.56	0.52	0.41	0.44	0.39	0.40	0.38	0.52	0.52	0.54	0.41	0.36
Limestone (%)	2.19	8.83	0.10	8.46	10.30	0.35	13.01	0.27	5.23	14.02	4.07	15.69
LOI (%)	2.37	4.71	1.18	4.2	5.08	1.45	6.25	1.54	3.78	6.95	2.63	7.29
Blaine (m^2/kg)	422	522	403	549	482	424	579	421	440	556	407	681
Vicat Initial (min)	95	95	115	105	115	125	95	140	165	100	105	90
Vicat Final (min)	170	160	190	170	220	215	155	250	270	225	205	175
1 Day Strength (MPa)	18.2	19.9	18.0	20.9	16.5	18.0	18.7	15.2	13.7	17.1	15.0	20.1
3 Day Strength (MPa)	29.7	31.8	25.9	30.7	28.1	26.8	29.5	27.0	23.8	27.4	25.8	29.2
7 Day Strength (MPa)	34.6	38.0	31.6	37.9	35.6	34.2	34.1	30.2	28.6	32.3	31.8	35.6
28 Day Strength (MPa)	41.4	42.8	44.0	45.3	42.5	46.1	42.8	39.3	34.8	39.7	42.1	41.2

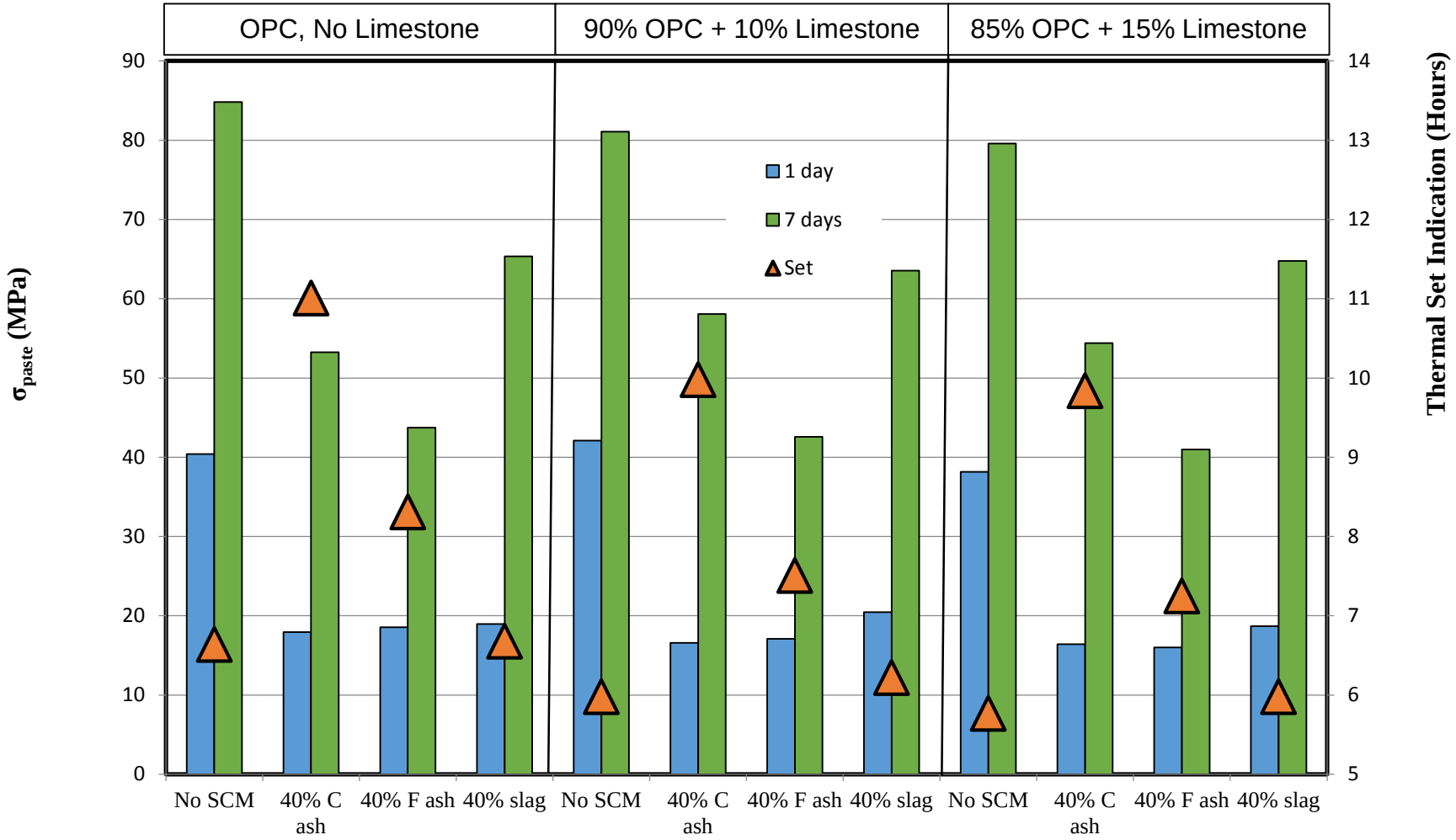
OPC to PLC Trends – Single Manufacturer



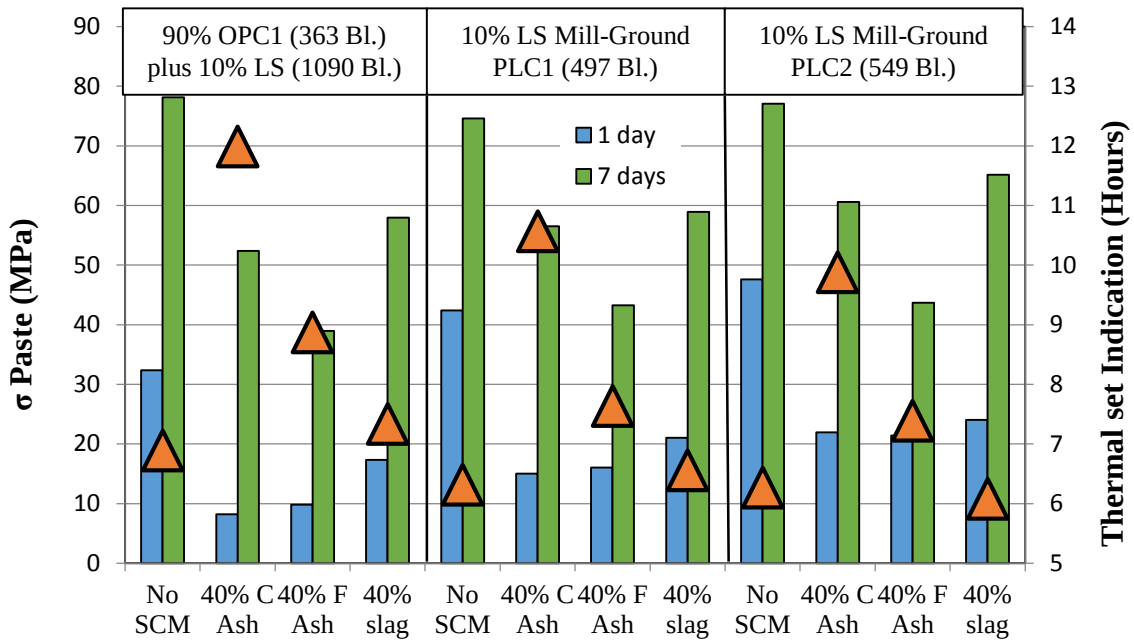


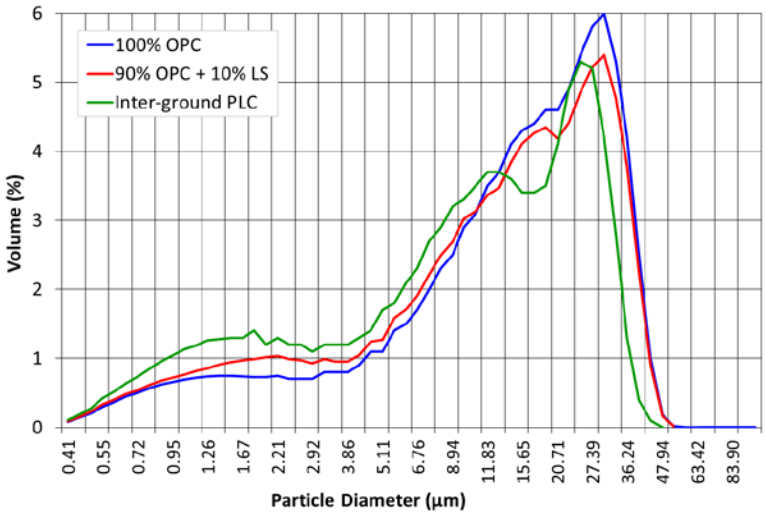


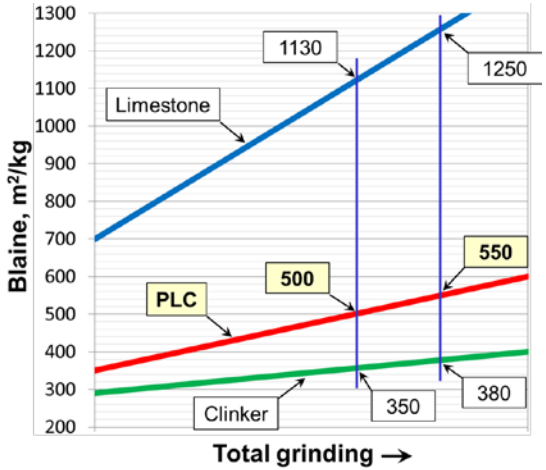
OPC to PLC Trends – Single Manufacturer



OPC to PLC Trends – Grinding Effects

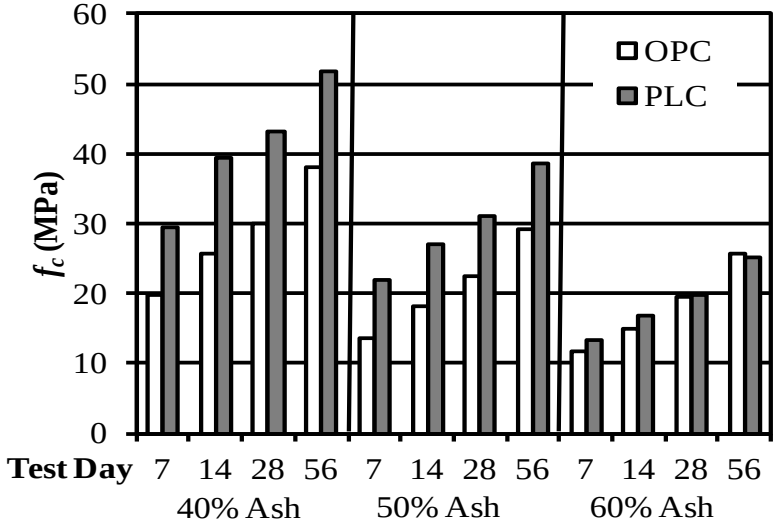


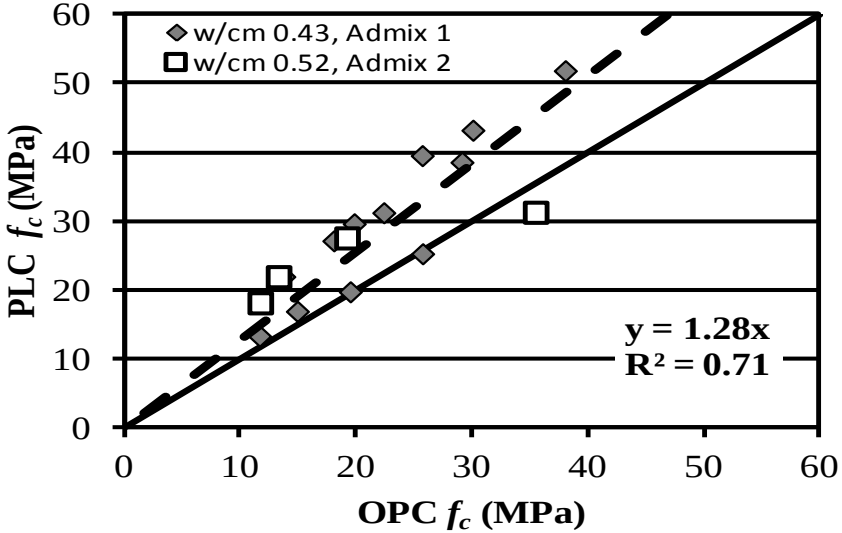




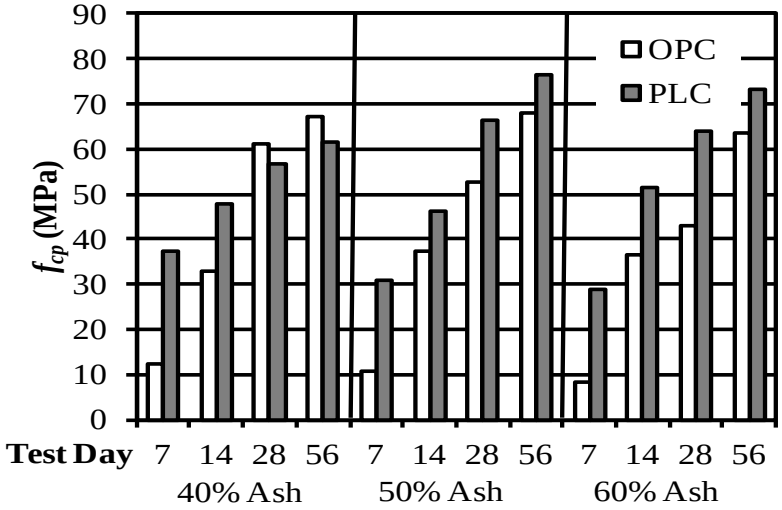
OPC to PLC Trends – Single Manufacturer

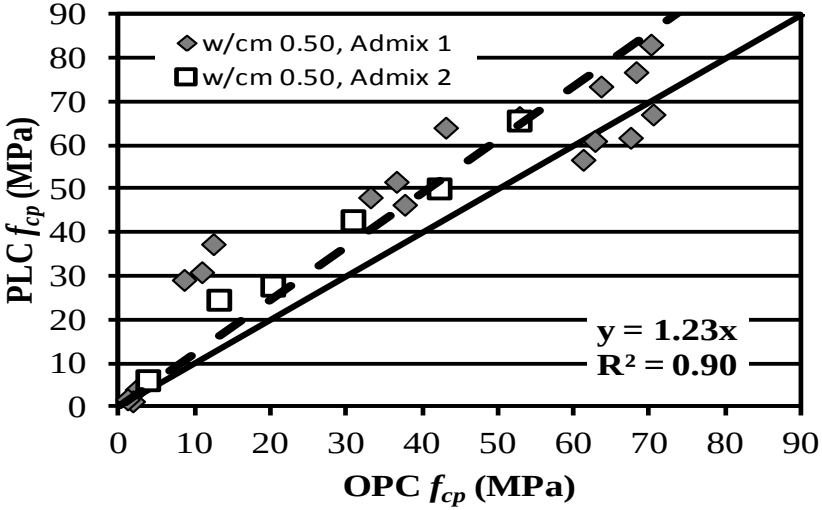
Concrete



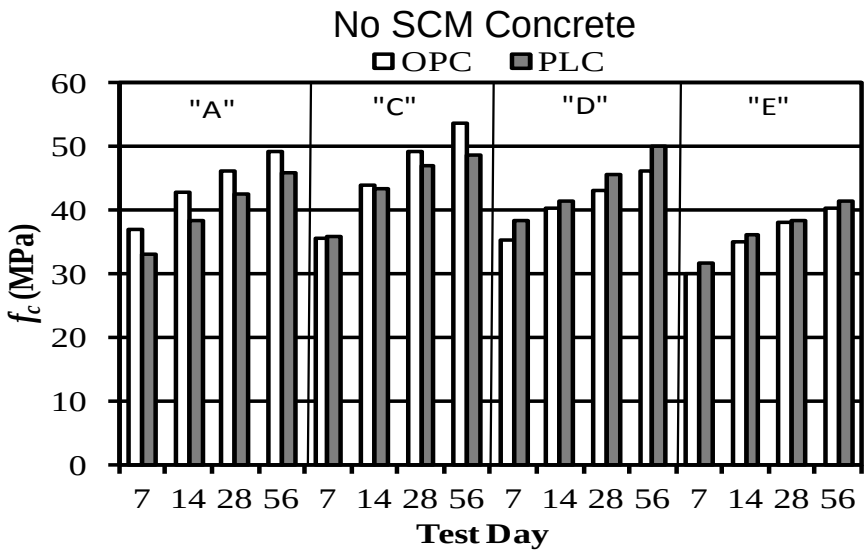


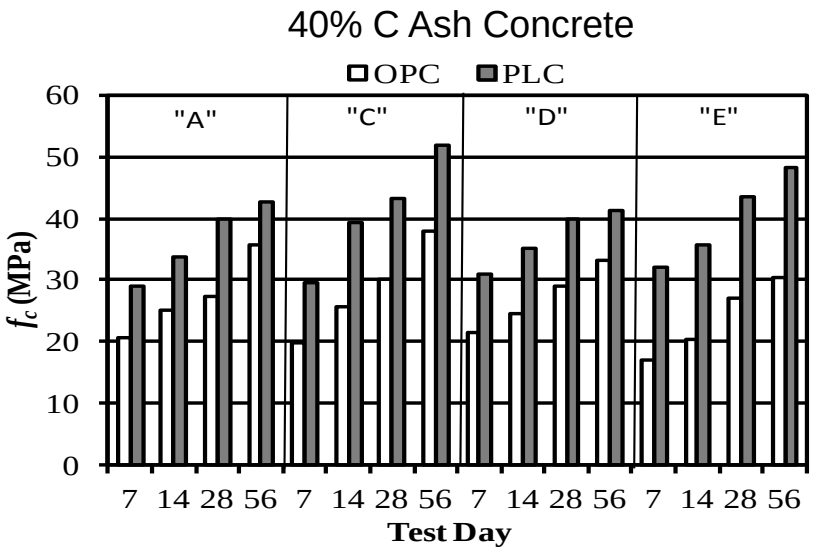
Cement Paste

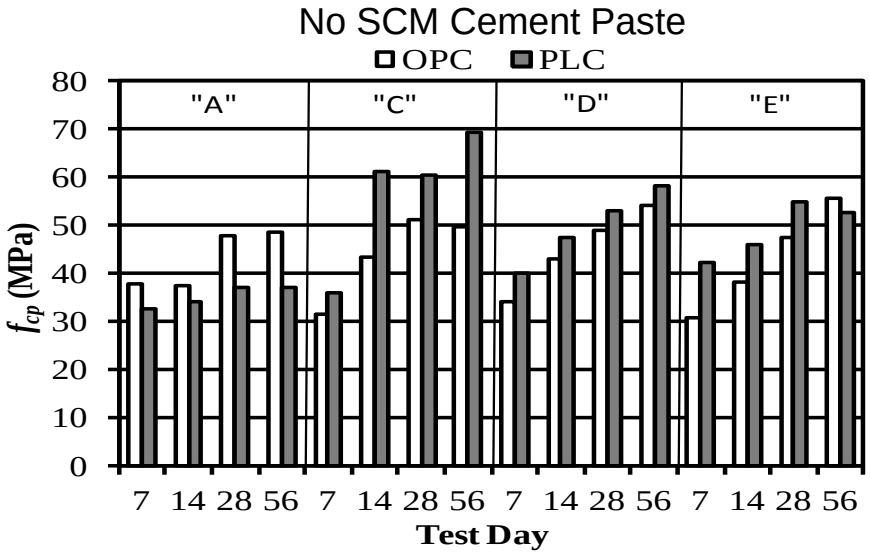


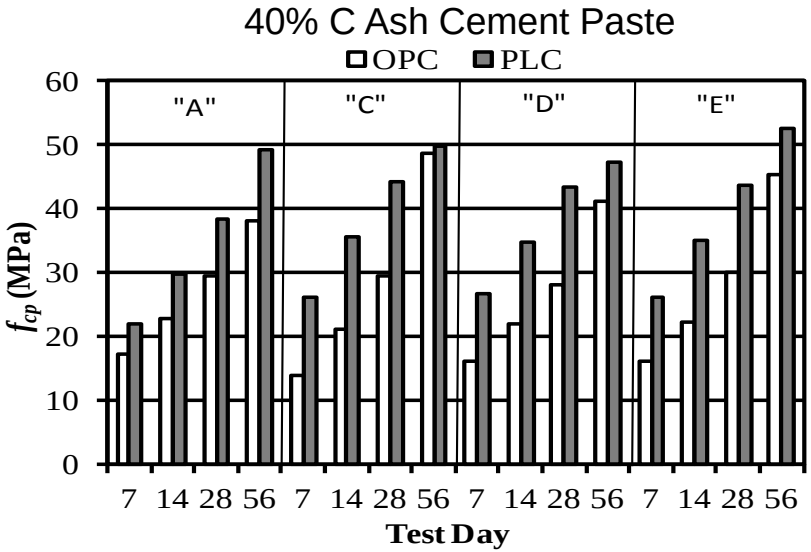


OPC to PLC Trends – Multiple Manufacturer

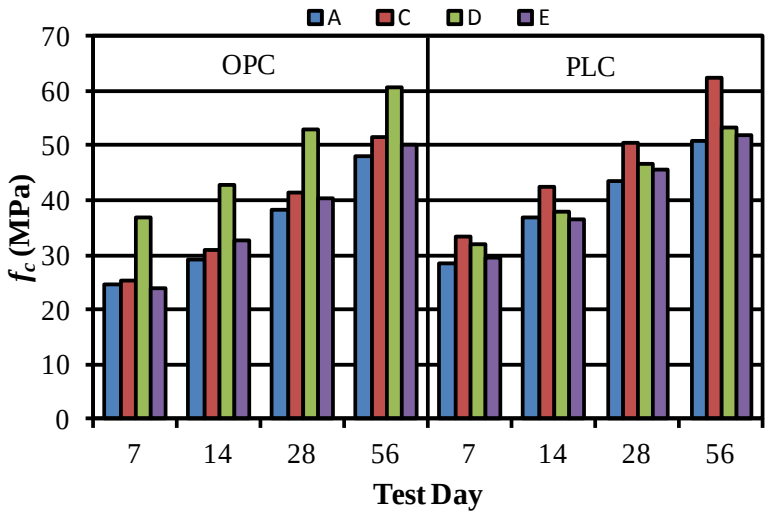


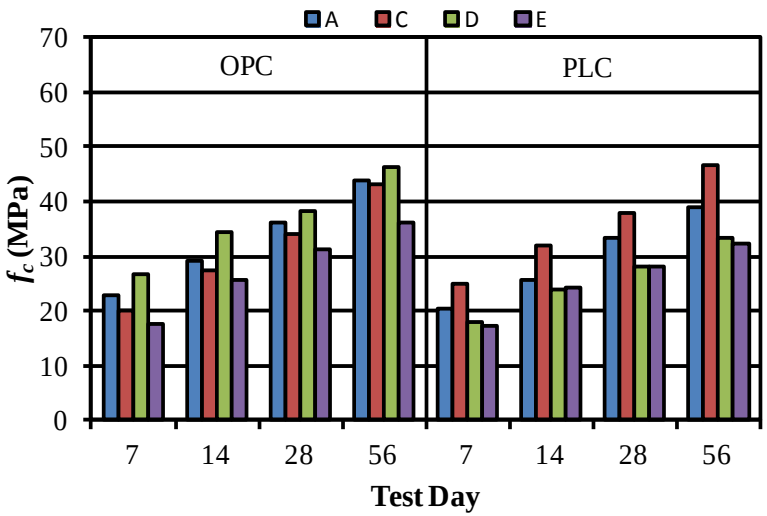




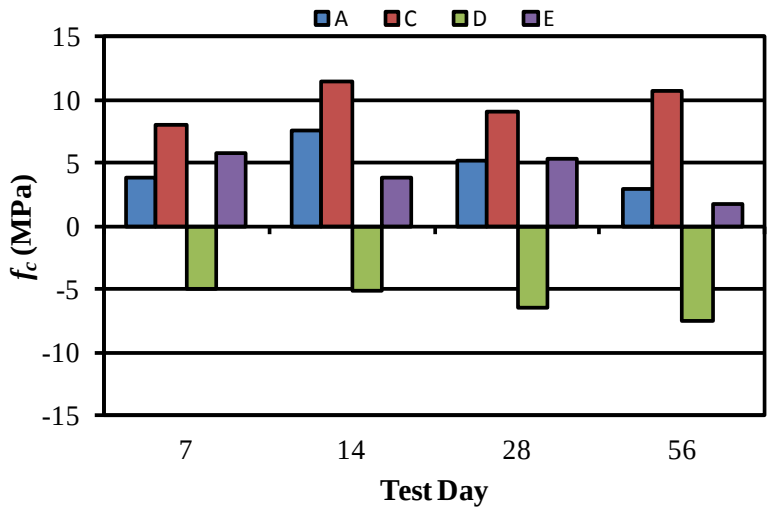


OPC to PLC Trends – Multiple Manufacturer

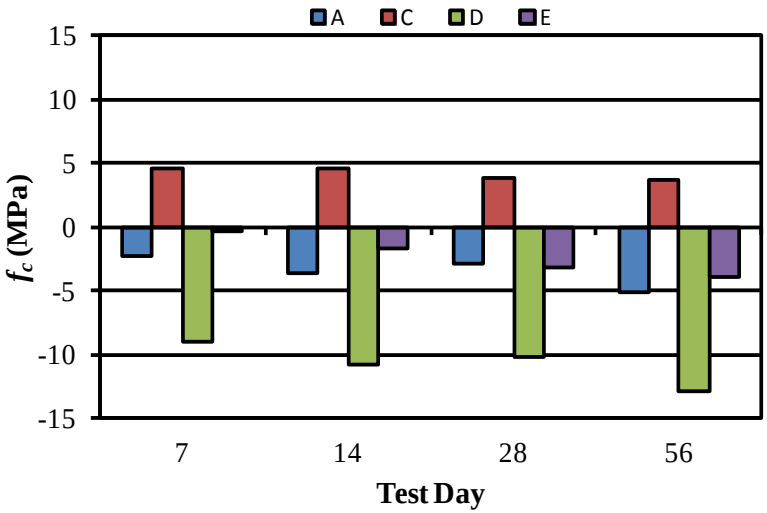




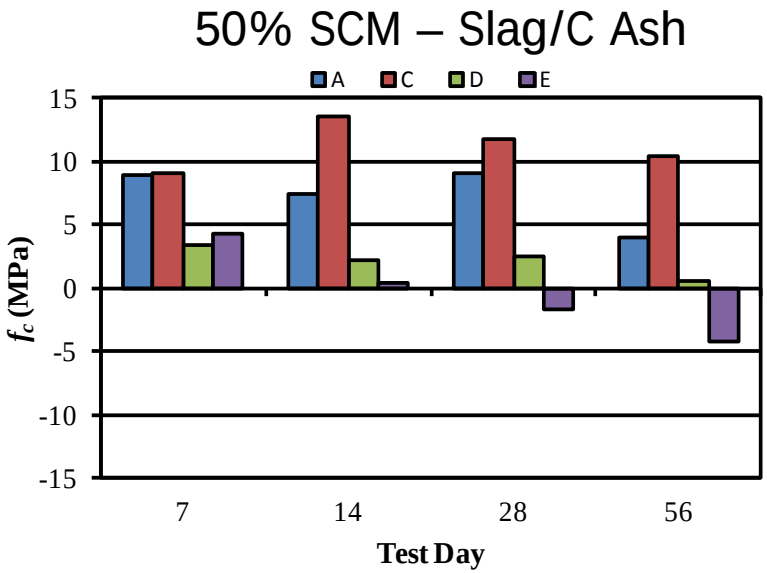
40% SCM - C Ash
> 20% CaO

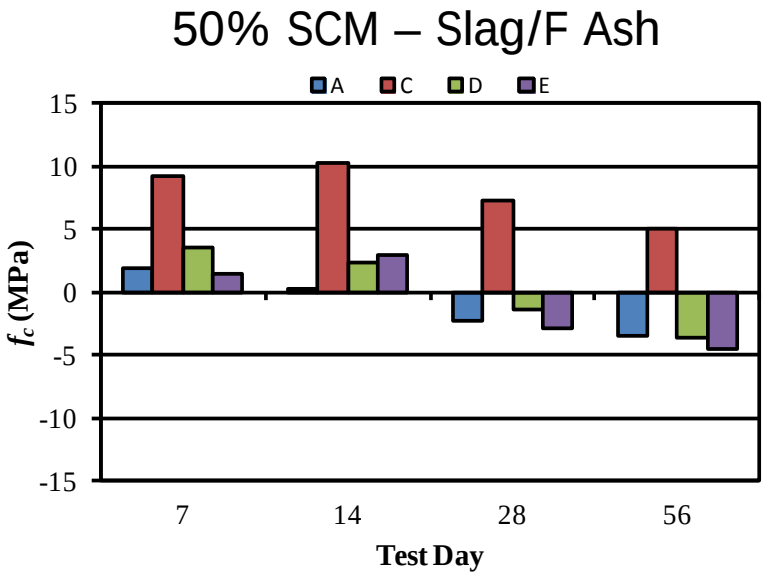


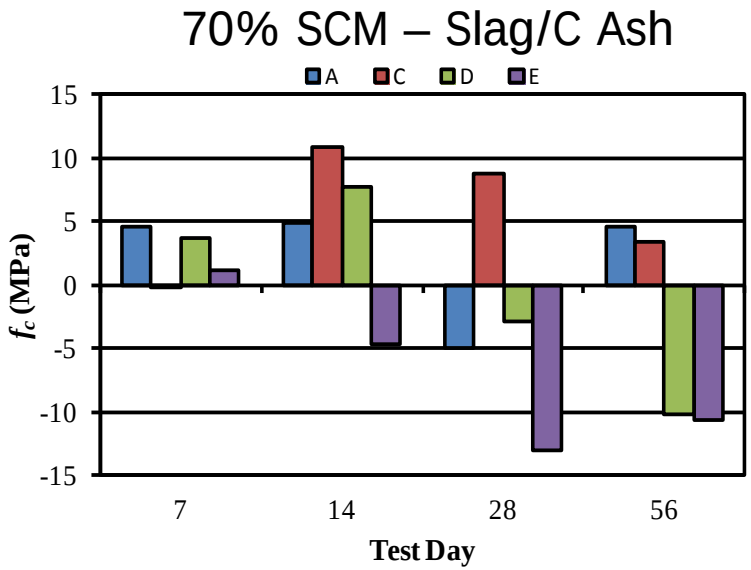
40% SCM - F Ash
< 7% Cao

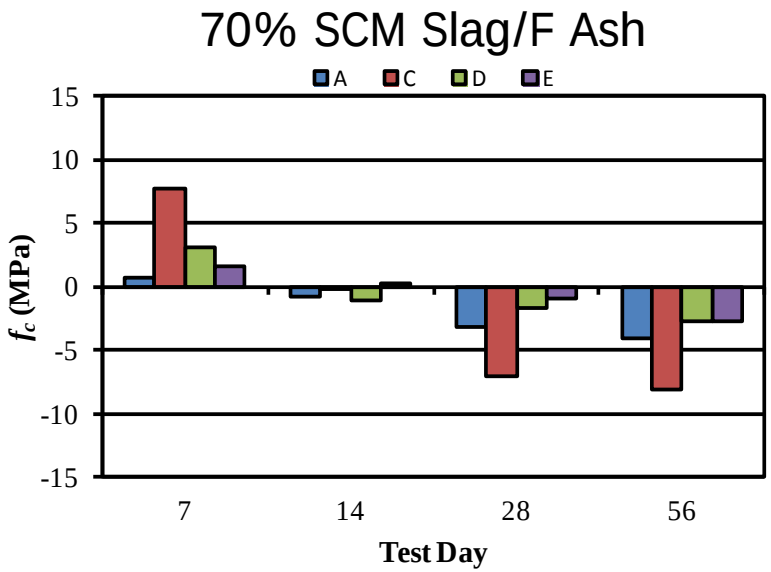


OPC to PLC Trends – Multiple Manufacturer



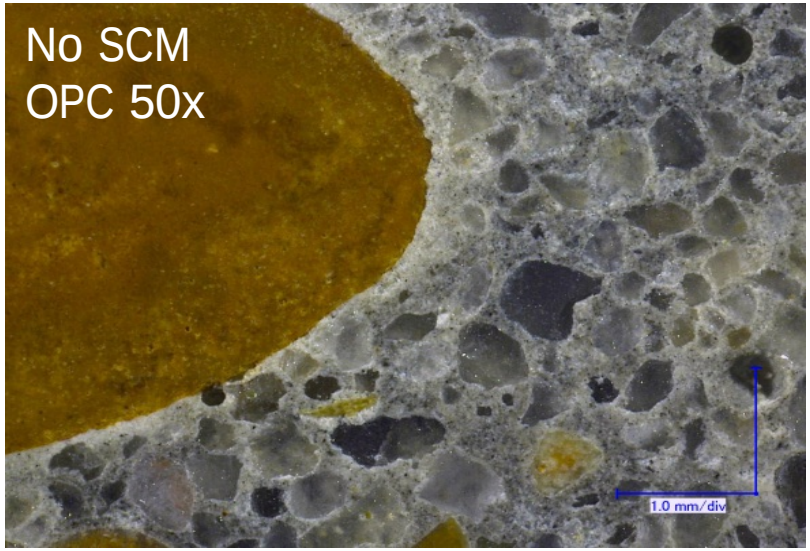


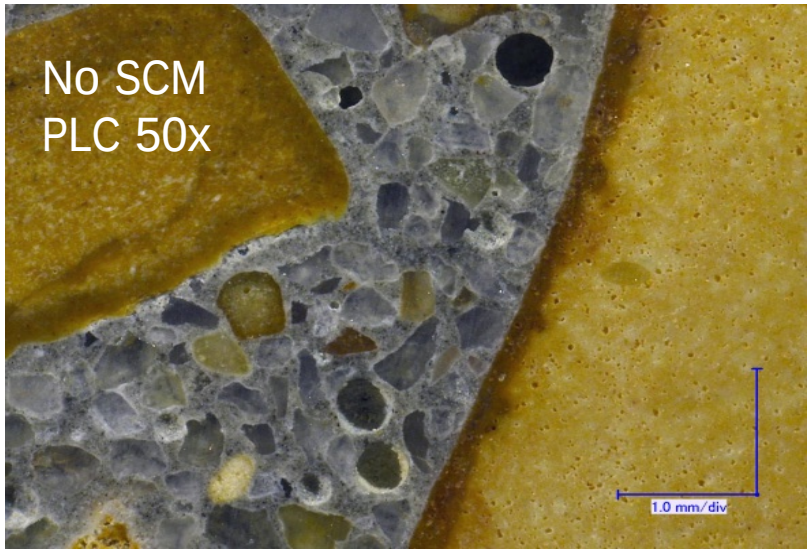




Summary of Results

- Fresh mix properties not significantly different
- 50% replacement generally PLC better than OPC
- 40% replacement C ash better with PLC, F ash better with OPC
- 60% replacement may be upper limit
- Time of set up to 0.7 hr faster
- >5 MPa higher PLC to OPC difference with limestone aggregates
- Large variability between sources
- Perceived effects of ITZ and hydration on concrete properties





Field Study – Davis Wade Stadium

- $75M expansion & renovation
- Design focus on sustainable attributes of materials
- Most concrete using 50% replacement (30% slag + 20% Class C fly ash), some with OPC, some with PLC
- 1900 m^3 (2485 yd^3)
- Data showed benefits in compressive strength and durability
- Mitigation of setting delay
- Ready mix supplier and contractor would use product again
- Completed 2014

Field Study – Davis Wade Stadium

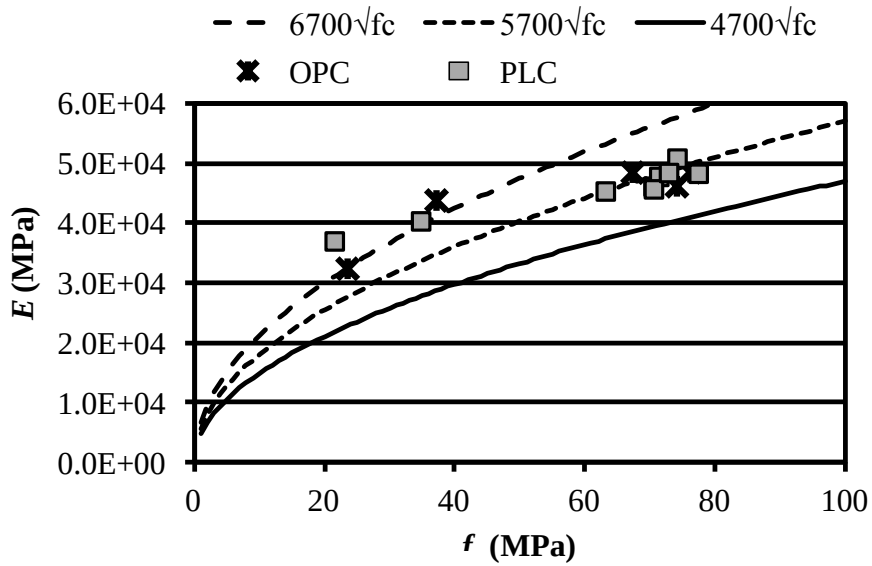
Group	1	2	3	4	5	6
n_{trucks}	3	1	10	5	1	1
Trucks Included	TM 5-7	TM 17	TM 9-16, 18, 19	TM 1-4, 8	TM 20	TM 21
Mix and Cement	F (*OPC #1*)	G (*PLC #1*)	G (*PLC #1*)	G (*PLC #1*)	F (*OPC #2*)	G (*PLC #1*)
w/cm	0.41-0.42	0.41	0.43-0.44	0.44-0.45	0.39	0.42
Cementitious content (kg/m^3)	361-362	349	339-350	340-348	348	339
Age	*Shown: Average Compressive Strength in MPa (Standard Deviation) [n]*					
1 day	6.1 (1.2) [9]	10.0 (0.4) [3]	7.7 (1.0) [30]	10.4 (1.5) [12]	---	---
3 day	18.0 (2.4) [9]	19.6 (0.2) [3]	19.3 (2.7) [30]	21.7 (2.3) [15]	25.8 (1.2) [5]	22.6 (1.1) [5]
7 day	28.0 (4.8) [9]	32.7 (0.9) [3]	29.0 (2.8) [30]	35.5 (4.0) [15]	38.5 (1.8) [5]	33.9 (2.0) [5]
14 day	42.0 (3.7) [9]	---	41.5 (3.9) [24]	46.6 (4.2) [15]	---	---
28 day	55.8 (4.5) [9]	60.7 (1.4) [3]	54.3 (5.1) [30]	60.0 (5.6) [15]	66.7 (2.3) [6]	63.6 (2.2) [6]
56 day	66.9 (3.3) [9]	68.0 (0.9) [3]	62.5 (7.1) [30]	66.6 (4.8) [15]	77.6 (2.6) [5]	73.5 (1.8) [5]
90 day	70.4 (4.6) [3]	71.3 (1.4) [3]	70.2 (5.0) [21]	69.6 (4.9) [7]	---	---
180 day	74.0 (3.0) [8]	74.0 (2.7) [3]	70.2 (6.6) [31]	73.4 (4.6) [14]	---	---

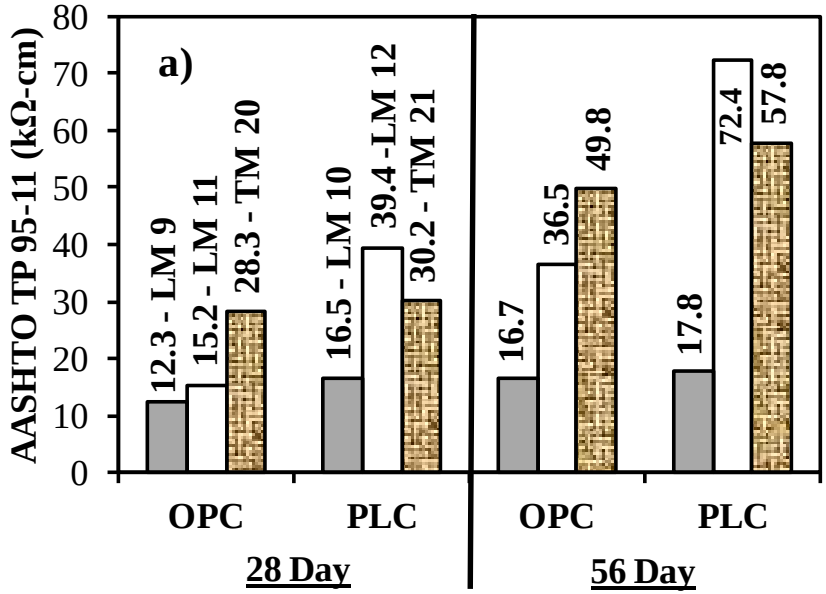
-- 1 to 7 day data shown are the equivalent test day strengths for specimens cured at 23 ^{o}C, where measured values were adjusted using maturity relationships. Actual equivalent 23 ^{o}C ages prior to adjustment were 0.8 to 1.6, 2.6 to 3.5, and 6.4 to 7.8 days.

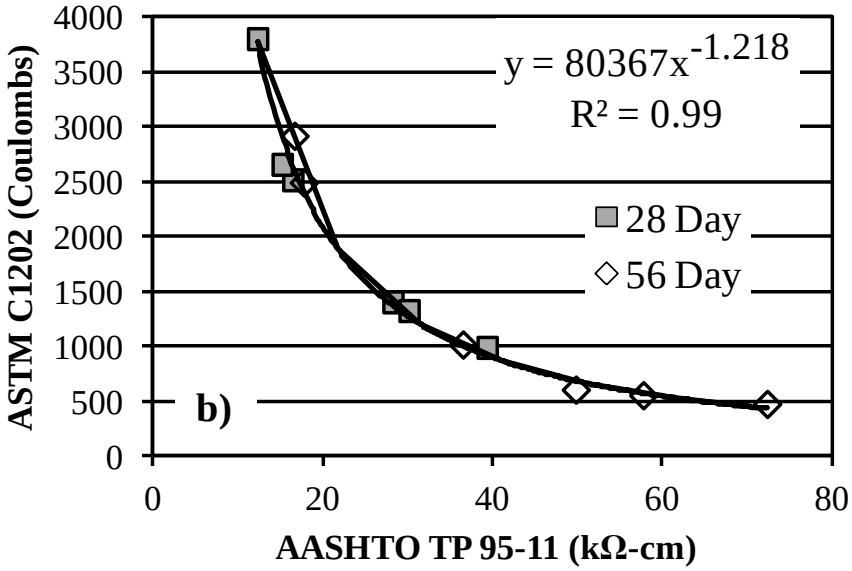
-- 14 to 180 day strength data are measured values according to C39, without adjustment.

-- n_{trucks} = number of trucks sampled, n = number of cylinders tested

Field Study – Davis Wade Stadium







Alternative Cementitious Materials

- FHWA Exploratory Advanced Research (EAR) project 2014 – 2018
- Novel ACM for development of the next generation of sustainable transportation infrastructure

Goal: Identify (and adapt) ACMs for rapid implementation relying upon existing construction technologies

Upscaling & Application
- Approval process
- Adaptation of standards
- Performance criteria
- ➔ variety of uses in transportation

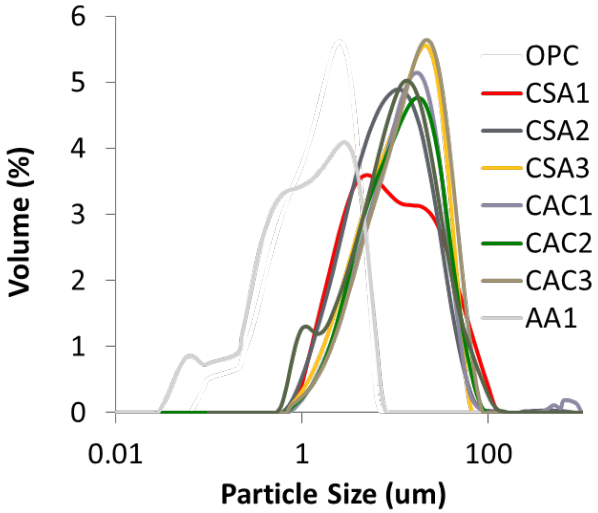
Durability Testing & Advanced Characterization
- Unified approach
- Adaptation of standards
- Limits

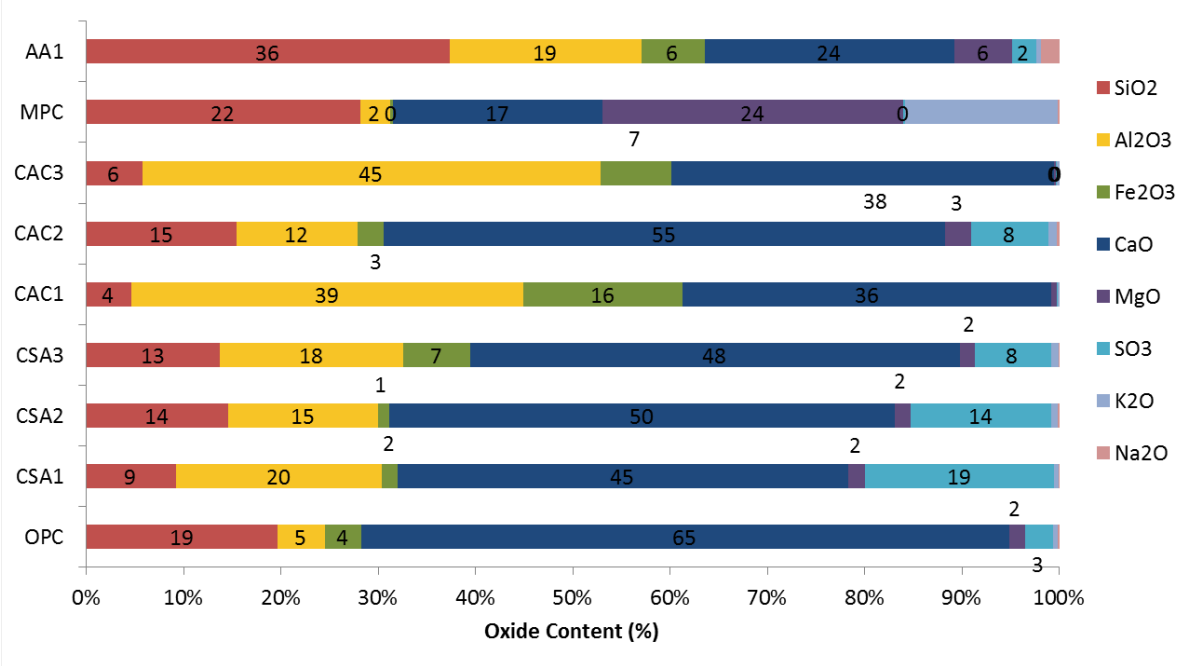
Preliminary Screening: Novel ACMs
- Range of chemistries
- Sustainability
- Past in situ performance
- Meet basic performance targets

US Army Corps of Engineers

Alternative Cementitious Materials

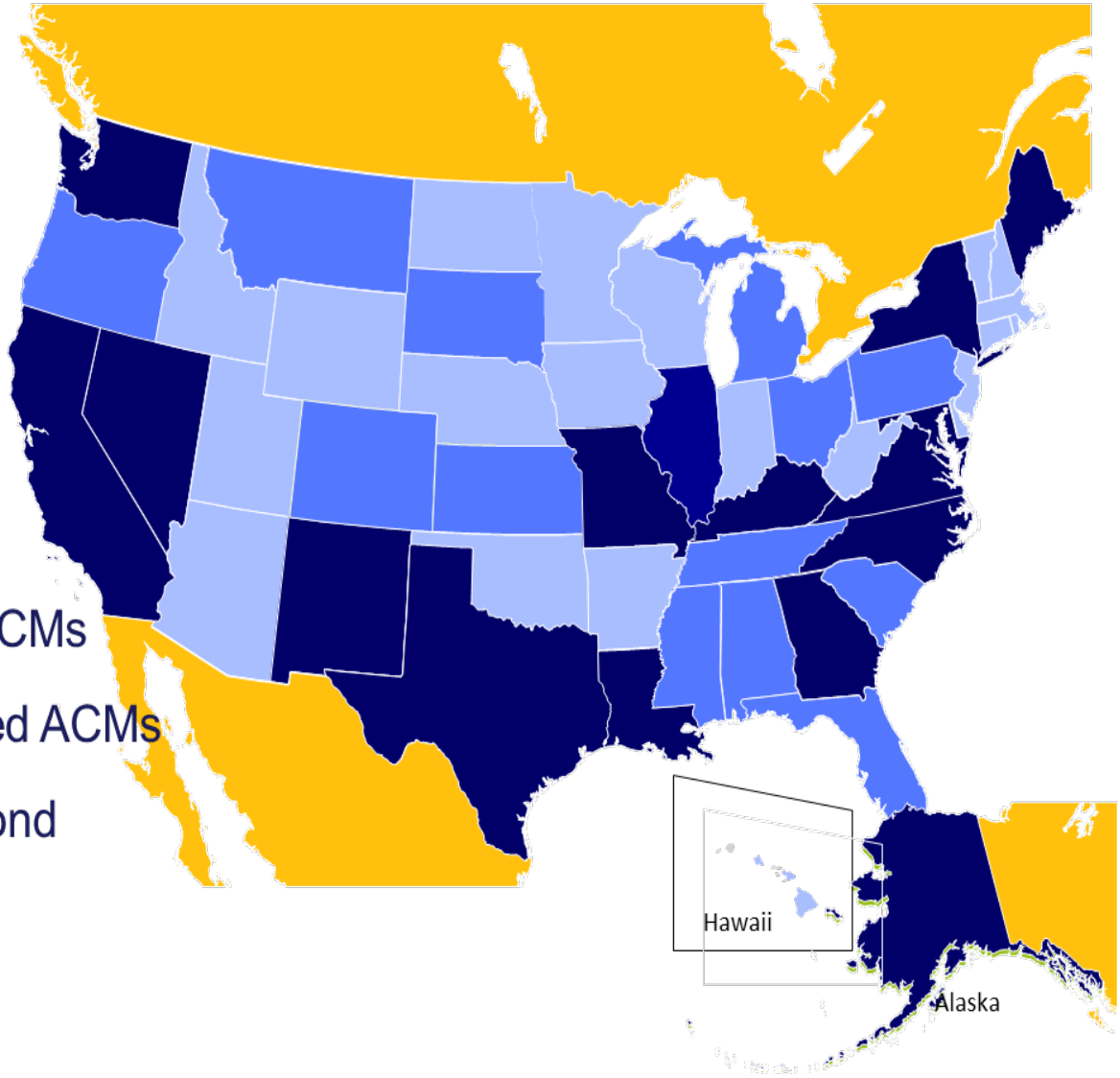
- Typically have lower CaO content
- Usually more coarse
- Require ACM specific mixture designs and methodology
    - Lower w/cm
    - Different admixtures





Alternative Cementitious Materials

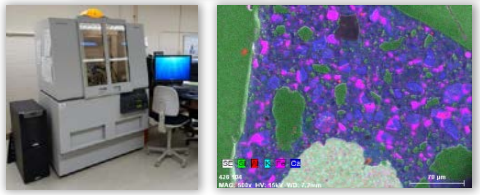
ACM usage determined from respondent answers to a 2014 poll sent to U.S. State DOT representatives in the AASHTO Subcommittee on Materials (SOM) and through discussions with TWG.



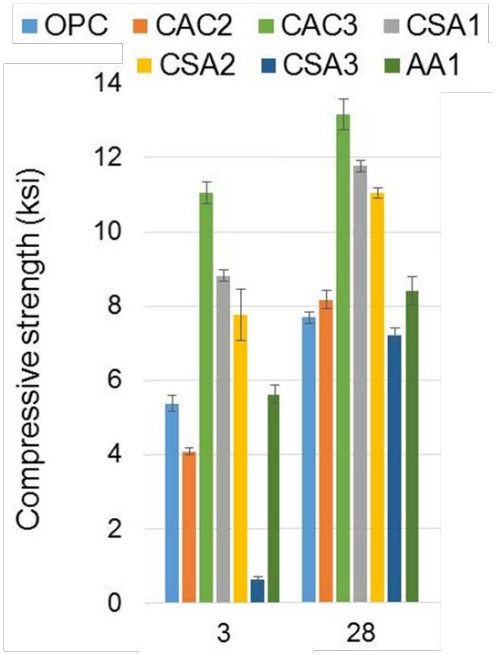
- 15 states have used ACMs
- 13 states have not used ACMs
- 22 states did not respond

Challenges with ACMs

- Research to practice transitions
  - Academia often has different focus than industry
- Business models
  - Proprietary blends
  - Focus on specialty products of general use
- Long term consistency
  - Variability of products
  - Pre-approved source issues
- Sole sourcing
  - Difficult of government to sole source
  - Difficult to specify in contracts
- Specifications
  - Lack of prescriptive specifications
  - Difficult to develop performance based specifications

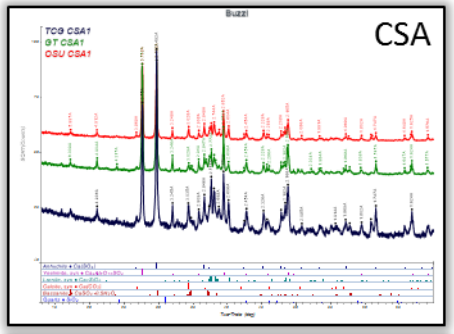


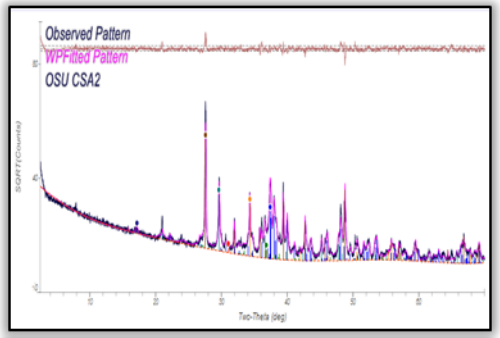
Compressive strength

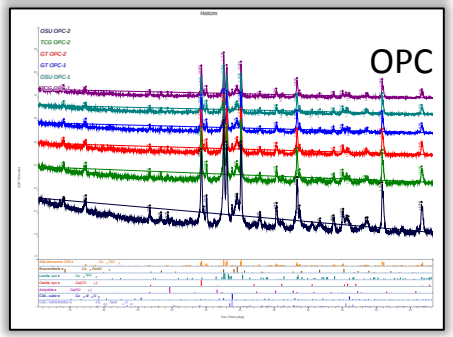


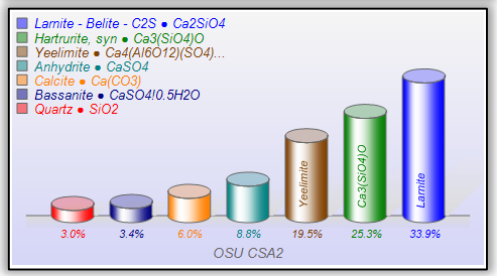
Path Forward for ACMs

Characterization of material properties

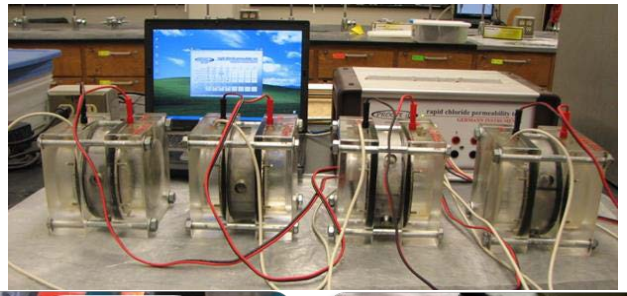


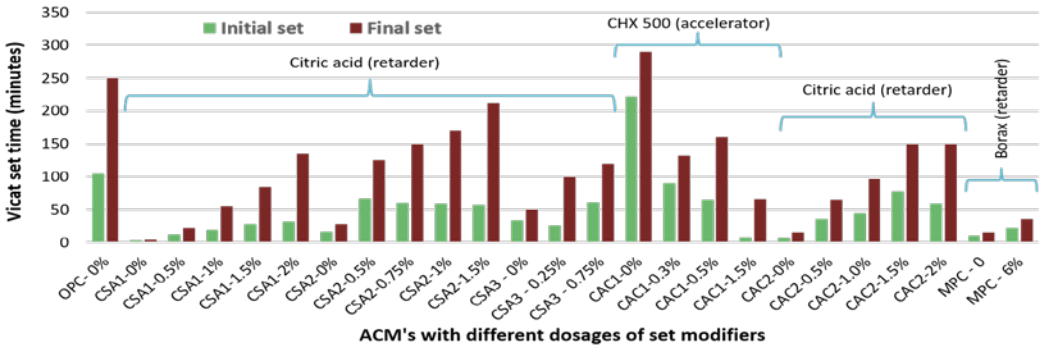


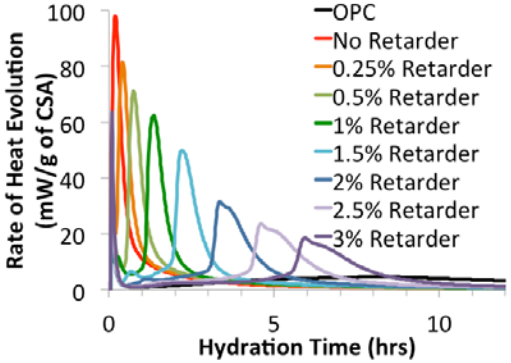




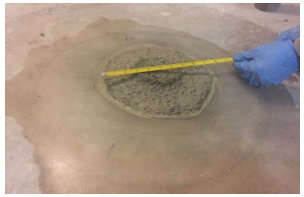
Constructability and Field Performance







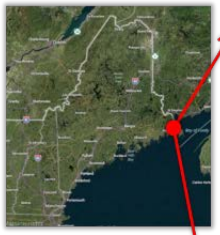
Path Forward for ACMs



Tier 1 Test Requirements			
Test Property	Test Method	Test Age	Test Criteria
Compressive Strength	ASTM C39	2 hr.	≥ 2,500 psi
		3 hr.	≥ 3,000 psi
		1 day	≥ 4,000 psi
		7 day	≥ 5,000 psi
		28 day	≥ 5,000 psi
Flexural Strength	ASTM C78	2 hr.	≥ 350 psi
		7 day	≥ 500 psi
		28 day	≥ 600 psi
Bond Strength (RS/RS)	ASTM C882	1 day	≥ 1,000 psi
		7 day	≥ 1,500 psi
Bond Strength (OPC/RS)		1 day	≥ 1,000 psi
		7 day	≥ 1,250 psi
Modulus of Elasticity	ASTM C469	2 hr.	2 ≤ x ≤ 6 Mpsi
		28 day	2 ≤ x ≤ 6 Mpsi
Time of Setting Penetrometer Method	ASTM C403	Initial Set	≥ 15 min
		Final Set	15-90 min
Slump	ASTM C143	Within 5 min of added water	3-9 inches if > 9 in. perform slump flow
Slump Flow	ASTM C1611	Within 5 min of added water	≥ 9 inches
Tier 2 Test Requirements			
Test Property	Test Method	Test Age	Test Criteria
Length Change	ASTM C157	28 Day Stored in air	-0.04% ≤ x ≤ +0.03% at 28 day
		28 Day Stored in water	Continue testing and report length change until 64 weeks
Coefficient of Thermal Expansion	ASTM C531	-	≤ 7 (in./in./°F × 10^{-6})
Shrinkage Potential	ASTM C1581	14 day	Record microstrain but no pass/fail limits at this time
		28 day	Record microstrain and fail if any ring cracked

Path Forward for ACMs

- Field durability testing of large scale mixtures – Treat Island weathering station



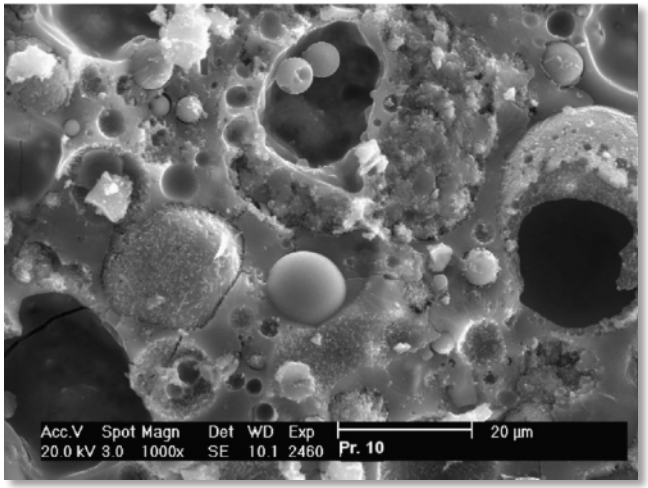
100-160 freeze thaw cycles per year of exposure

Approx. 6.7m (22ft) tidal elevation change

Treat Island located in the Bay of Fundy near Eastport, ME, USA.

Geopolymers

- Alkali-activated geopolymers are special cements formed by mixing a concentrated alkaline solution with a finely-divided reactive aluminosilicate (sometimes with Ca too)
- Alkali-activated geopolymeric cements are strong, fast-setting, inexpensive, and very versatile
- Manufactured from glassy silicates like slag, fly ash, metakaolin, and volcanic ash
- Can use waste alkalis from manufacturing operations
- No Portland cement is involved!



Skvara et al, 2006

Soil solidified with alkali-activated mixture using slag

Geopolymer Advantages

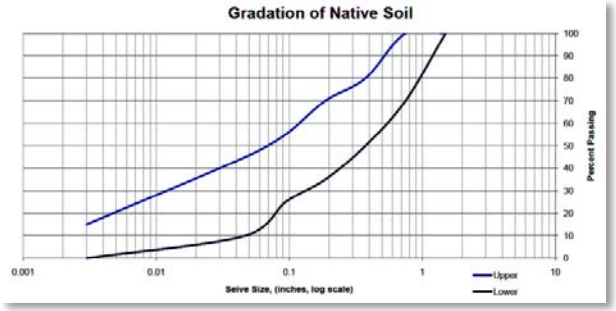
- Fast: mixture sets in hours and gets ultimate strength in days
- Easy to Obtain Materials: suitable raw materials are available almost everywhere (eg, fly ash, slag)
- Economical: uses waste/local materials or low-fired clay soils
- Versatile: basic chemistry adapts from a wide variety of glassy aluminosilicates
- Variation of natural weathering process that occurs in volcanic ash deposits

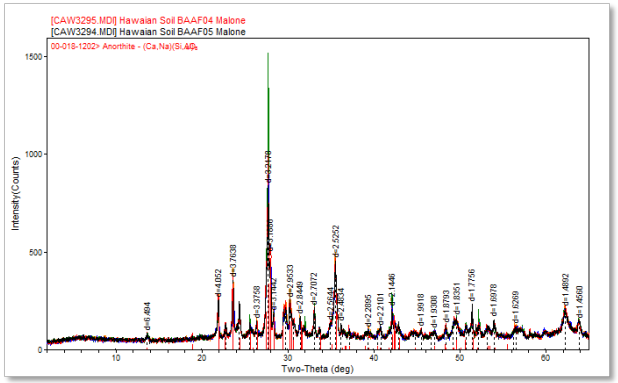
Exchange Reaction
- Initial: $Na_2CO_3 + Ca(OH)_2$
- Final: $NaOH$ and $CaCO_3$

Geopolymerization Rxn: Aggregates
- NaOH breaks down reactive surface of aggregates
- Forms A-S-H gel phase

Geopolymerization Rxn: Supplementary Cementing Materials
- Alkalis down fly ash and slag
- For C-A-S-H gel phase

Pohakuloa Training Area (PTA)



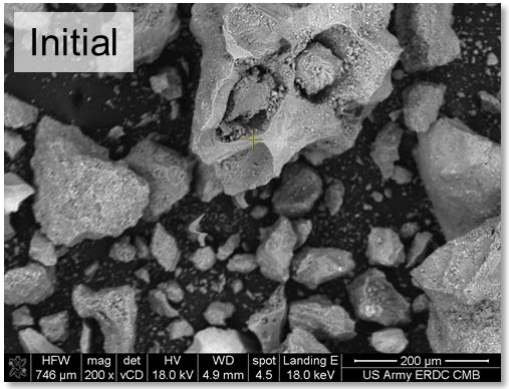


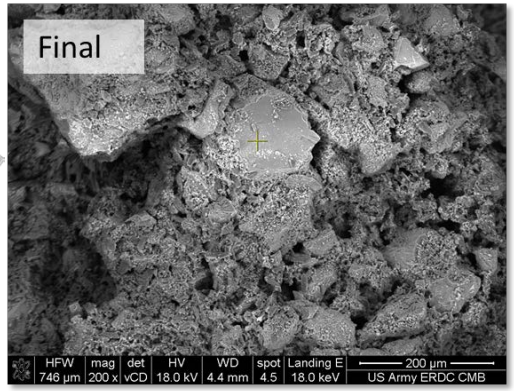
Mixture Components

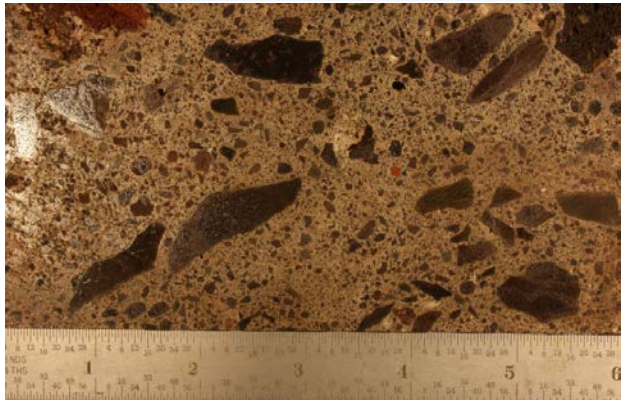
Blend Dry Components

Add Activator Solution

Blend Until Balling Occurs

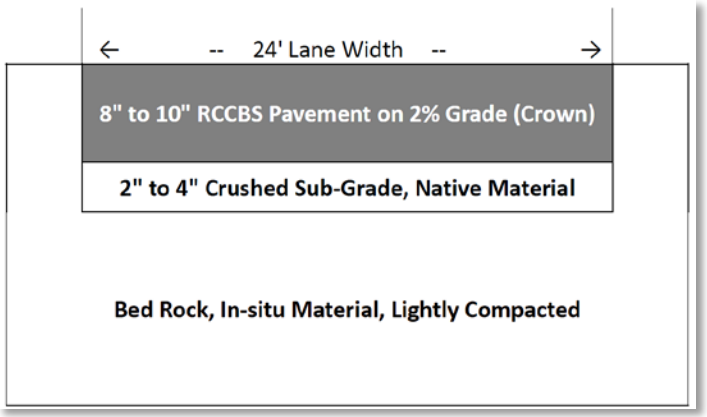






Field Placement

- Placement at the PTA test site
- Photos from the field provided by Chris Moore and Samuel Craig (US Army ERDC – CMB)



Design Considerations

- Overdesign directly leads to decreased sustainability
  - Better understanding of safety factors and design could lead to more efficient mixtures
- Contractor/Ready Mix Supplier
  - Contractor and ready mix supplier faster set times, lower chances of delays
  - May be preferential add cement to mixture than to wait for warmer temperatures
- Quality Control
  - Low quality control can cause increases in overdesign to account for variability in mixtures

Design Requires
4500 psi at 28 days

↓

Safety Factor of 1.2
5400 psi at 28 days

↓

Contractor Request
6000 psi at 14 days

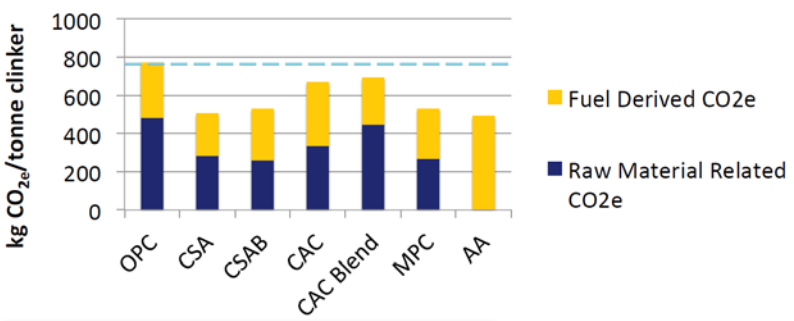
↓

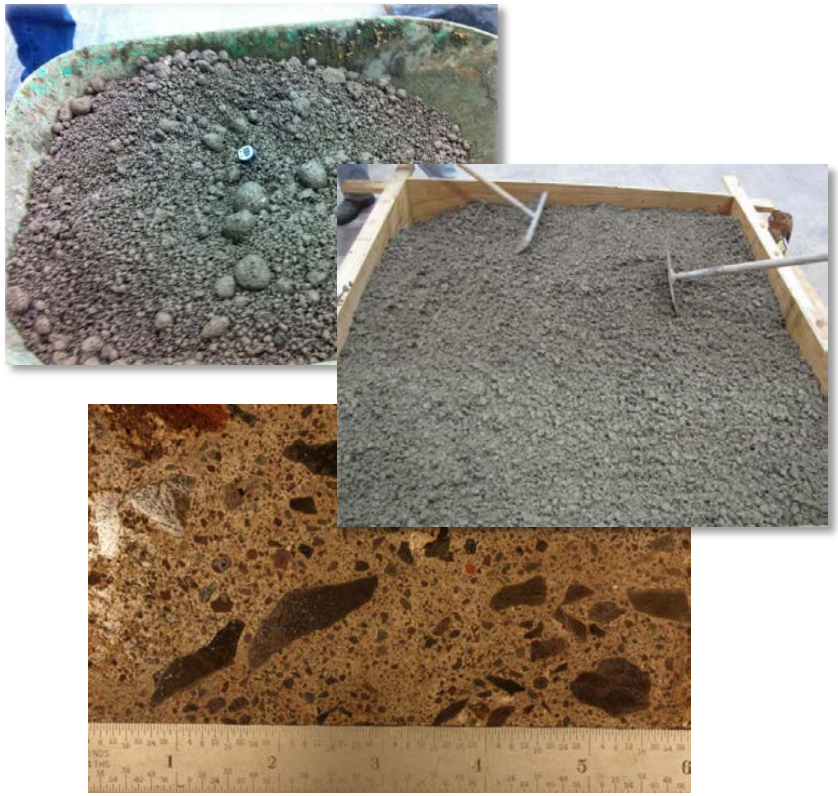
RMC Supplier
Targets 6500 psi

Can Add > 1/3
Excess Cement

Summary

- Positive environmental effects
- Challenges on equivalent or improved performance and durability
- Multiple options for alternative cementitious materials, clinker reduction, geo-materials, etc.
- Project variables likely to influence advantageous alternatives





PLC – Jay Shannon, ERDC
ACM – Kimberly Kurtis, GA Tech / Monica Ramsey, ERDC
Geopolymers – Chris Moore, ERDC / Chuck Weiss, ERDC