

Alternative Cementitious Materials for the Precast Industry

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With thanks to:

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 Tyler Ley

 Neal Berke



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Much of this presentation's data was produced as part of the FHWA Exploratory Advanced Research Program



U.S. Department of Transportation
Federal Highway Administration

- Georgia Institute of Technology
 - Kimberly Kurtis
 - Lisa Burris (me)
 - Prasanth Alapati
- Oklahoma State University
 - Tyler Ley
- Temple University
 - Mehdi Khazadeh
- Tourney Consulting Group
 - Neal Berke
- US Army ERDC
 - Robert Moser





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What are Alternative Cements?

- Hardening systems with different chemistries than portland cement (OPC)
- Often lower CaO content → less Raw materials-derived CO_{2e}
- Often lower production temperatures → less Fuel-derived CO_{2e}
- Often radically different behavior/properties from OPC
- Many produced for decades (at least)



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What are Alternative Cements?

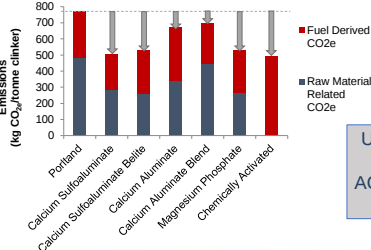


OPC ACMs



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Why use ACM?



■ Fuel Derived CO_{2e}
■ Raw Material Related CO_{2e}

Up to 40% reduction in CO_{2e} by using ACMs instead of OPC (1:1)

Gartner, E., "Industrially interesting approaches to 'low-CO2' cements," Cement and Concrete Research, 2004, 1489-1498.



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Why use ACMs?

In addition to sustainability benefits...

- Very rapid setting and strength gain: +5000 psi in 2 hrs possible
- Resistance to cold temperatures
- Reduced shrinkage (reduced cracking and prestress losses)
- Currently used for repairs and full-scale structures (typ. bridge decks)
- Established supply chain (Multiple U.S. suppliers including in VA, MO, and OK)
- Improved durability (in some cases)



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Why use ACMs?

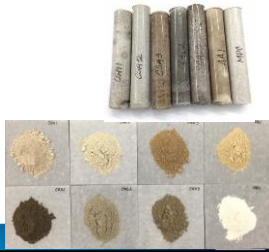
ACMs will never replace OPC/PLC but they instead provide some specialized tools for accomplishing different tasks and goals



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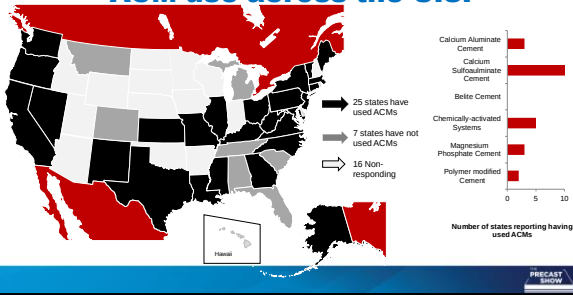
6 Primary Types of Alternative Cements:

- Calcium Sulfoaluminate Cement (CSA1)
- Calcium Sulfoaluminate Belite Cement (CSAB, CSA2)
- Calcium Aluminate Cement (CAC)
- Portland-Calcium Aluminate-Calcium Sulfate Ternary Blend Cement Blend (CACB)
- Chemically/Alkali Activated Binder ('geopolymer') (AA1)
- Magnesium-based Cement (phosphate, oxychloride) (MPC)



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ACM use across the U.S.



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Basics of ACM Production, Reaction, and Composition

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Calcium Sulfoaluminate (CSA)
Calcium Sulfoaluminate Belite (CSAB)

- Raw materials:
 - Limestone
 - Bauxite
 - Gypsum
- Fabrication:
 - Rotary kiln
 - 1350°C
 - Large quantities of anhydrite are added to help control set time
- Mineral components:
 - Ye'elmitte – (C₄A₃S), also called Klein's compound
 - Dicalcium silicate – belite (C₂S)
 - Calcium sulfate

CSA Type	Ye'elmitte C ₄ A ₃ S (%)	Belite C ₂ S (%)	Calcium Sulfate CS (%)	Other (%)
Type A – Accelerating Additive	35-45	0-20	10-30	5-55
Type B – Belitic CSA (BCSA)	20-30	30-60	5-25	0-35
Type C – Expansive Additive	10-20	10-30	40-60	0-40
Type K – Shrinkage Compensating Cement	1-10	30-50	1-20	20-70

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How are CSAs different from OPC?

- Hydration process: **OPC**
 $2C_3S + 6H \rightarrow C - S - H + 3CH$

C = CaO
S = SiO₂
H = H₂O
A = Al₂O₃
S = SO₃

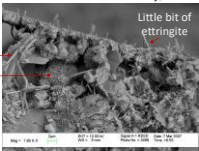
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How are CSAs different from OPC?

Hydration process: **OPC**

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

Image credit: Tyler Ley, OkState



CH
C-S-H
Concrete's strength-giving phase

Little bit of ettringite

3-5 hr lag between mixing and hardening

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How are CSAs different from OPC?

Hydration process: **OPC**

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

3-5 hr lag between mixing and hardening

CSA

$$C_4A_3\bar{S} + 2C\bar{S} + 38H \rightarrow C_6\bar{A}\bar{S}_3H_{32} + 2AH_3$$

ye'elimitite anhydrite Lots of water ettringite aluminum hydroxide

Hydrates and hardens rapidly → early and high strength gain
Can set in 10-15 min at w/c=0.40

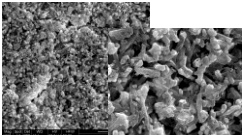
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How are CSAs different from OPC?

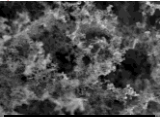
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CSA microstructure at 7 days

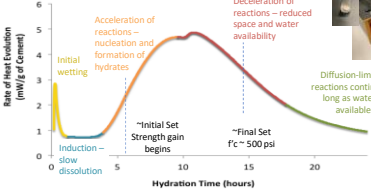


CSA microstructure at 5 min

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How are CSAs different from OPC?

Hydration Kinetics

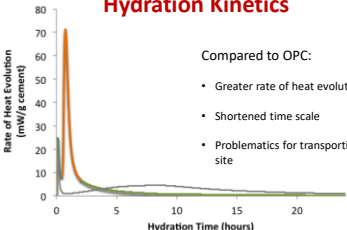


Initial wetting
Induction – slow dissolution
Acceleration of reactions – nucleation and formation of hydrates
Initial Set
Strength gain begins
Deceleration of reactions – reduced space and water availability
Final Set
f'c ~ 5000 psi
Diffusion-limited reactions continue as long as water is available

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How are CSAs different from OPC?

Hydration Kinetics



Compared to OPC:

- Greater rate of heat evolution
- Shortened time scale
- Problematics for transporting materials to the site

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Calcium Sulfoaluminate (CSA) Calcium Sulfoaluminate Belite (CSAB)

Advantages:

- HIGH early strengths (as high as 5000 psi @ 2 hrs)
- Very low shrinkage, and expansive formulas available
- Freeze-resistant
- Many examples of in-place performance
- Long-term strength development
- Two U.S. suppliers

Disadvantages:

- VERY fast set (5-35 min)
- Rapid heat release

CTS
Rapid Set
Buzzi Unicem USA

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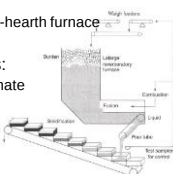
Calcium Aluminate Cement (CAC)

- Raw materials:
 - Limestone
 - Bauxite
- Fabrication:
 - Reverberatory open-hearth furnace
 - >1450°C
- Mineral components:
 - Monocalcium Aluminate
 - Ferrite

	Calcium Aluminates (%)	Belite C ₂ S (%)	Gehlenite (%)	Ferrite (%)	Other (%)
Calcium aluminate cement (ciment Fondu)	56	7	4	24	9

Two major types of CAC:

- Ciment Fondu ("pure" CAC)
- Ternal (Ternary blend: OPC + CAC + Calcium Sulfate)



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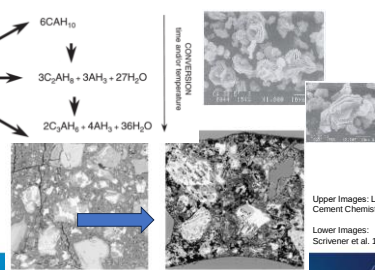
How are CACs different from OPC? Conversion

$6\text{CA} + 6\text{H}_2\text{O} \xrightarrow{T < 15^\circ\text{C}} 6\text{CAH}_{10}$

$6\text{CA} + 6\text{H}_2\text{O} \xrightarrow{T > 70^\circ\text{C}} 3\text{C}_2\text{AH}_8 + 3\text{AH}_3 + 27\text{H}_2\text{O}$

$6\text{CA} + 6\text{H}_2\text{O} \xrightarrow{T > 70^\circ\text{C}} 2\text{C}_2\text{AH}_4 + 4\text{AH}_3 + 36\text{H}_2\text{O}$

CONVERSION
time and/or temperature



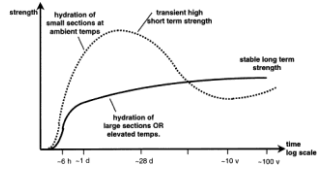
Upper Images: Lea's Cement Chemistry
Lower Images: Scrivener et al. 1999

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How are CACs different from OPC? Conversion

- Initial CAC hydrates are very strong
- Exposure to higher temperatures cause "conversion"
- New phases is denser, resulting in increased porosity and a drop in strength (40% of max)

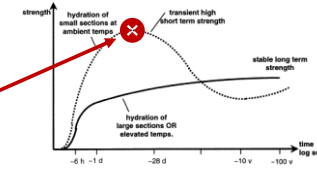


PRECAST SHOW

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- Failure can be prevented by:
 - Designing based on the converted strength

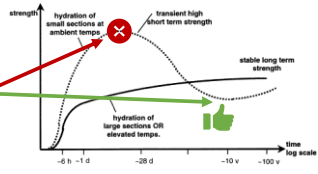


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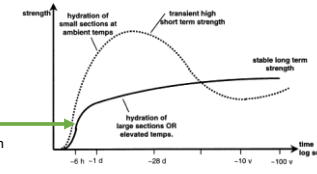


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How are CACs different from OPC? Conversion

- Initial CAC hydrates are very strong
- Exposure to higher temperatures cause "conversion"
- New phases is denser, resulting in increased porosity and a drop in strength (40% of max)
- Failure can be prevented by:
 - Designing based on the converted strength
 - Utilizing heat during curing
- No need to be afraid of conversion
- Possible use to accelerate precast construction?



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Calcium Aluminate Cement (CAC)

- Advantages:
 - HIGH early strengths
 - Multiple formulations available depending on needs
 - Very high heat resistance – often used in refractory applications
 - High corrosion and abrasion resistance
 - 2 U.S. Suppliers
- Disadvantages:
 - VERY fast set (5-35 min)
 - Very high initial heat release
 - Must use proprietary chemical admixtures
 - Must have understanding of conversion process and methods of estimating long term strength

Table 2. Strength Gain of CAC Versus RHPC

Temperature (°C)	Concrete	0.5	1.0	1 day	3 days
64.4 (16)	CAC	1480 (24)	1605 (26)	1800 (30)	4520 (75)
64.4 (16)	RHPC	0 (0)	0 (0)	1740 (23)	3335 (53)
53.4 (12)	CAC	2040 (37)	3220 (54)	3405 (59)	3945 (67)
53.4 (12)	RHPC	0 (0)	145 (2)	425 (5)	4235 (69)
42.8 (10)	CAC	2750 (51)	3220 (54)	3405 (59)	3465 (59)
42.8 (10)	RHPC	0 (0)	145 (2)	145 (2)	1015 (17)
32 (9)	CAC	725 (13)	4780 (83)	3075 (53)	3465 (59)
32 (9)	RHPC	0 (0)	0 (0)	145 (2)	290 (5)

* Concrete placed 2.75 x 2.75 x 11 in (70 x 70 x 280 mm) cement content
890 kg/m³ (250 kg/m³, w/c = 0.3)
Source: Scherer and Gustin (1998)

ACI Tech Note on CAC:
<https://ftp.dot.state.tx.us/pub/txdot/info/cac/cac-concrete.pdf>

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Magnesia Cements

- Raw materials:
 - Magnesium-bearing rocks (MgCO₃)
 - Phosphate activator solution
- Fabrication:
 - Magnesia ground, then calcined in a kiln (sometimes twice).
 - Reactivity is increased with longer burn time and hotter burn temperatures.
- Very very fast setting time (my experience)
- Very white binder
- Very low w/c required

Mag Cement Types	Hydration Process
Sorel (Magnesium Oxychloride) cement	3MgO + MgCl ₂ + 11 H ₂ O → 3Mg(OH) ₂ ·8H ₂ O
Magnesium Phosphate	MgO + NH ₄ H ₂ PO ₄ + 5H ₂ O → NH ₄ MgPO ₄ ·6H ₂ O
Magnesium Silicate Hydrate (M-S-H)	C-S-H + MgSO ₄ → CaSO ₄ + SiO ₂ + Mg(OH) ₂ → CaSO ₄ + M-S-H
Magnesium Oxy sulfate	3MgO + MgSO ₄ + 11 H ₂ O → 3Mg(OH) ₂ ·MgSO ₄ ·8H ₂ O

Image: Qiao et al. 2010

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Magnesium Phosphate Cement

- Advantages:
 - HIGH strengths (as high as 7250 psi @ 3 hrs!!!)
 - VERY heat resistant
 - No shrinkage
 - Low water requirement
 - Beautiful concrete
- Disadvantages:
 - VERY fast set (5-35 min)
 - VERY high retarder dosing requirements
 - Currently primarily available from China
 - Shipping costs
 - Availability issues (phosphate is in high demand at the beginning of the growing season)
 - Weird material consistency
 - Very different materials and microstructure

12.0kV 5.9mm x500 BSE3D 20µm

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Alkali Activated Materials (Geopolymers)

- Developed first in the 1940s?
- Refined by Joseph Davidovits (1979) – coined the term “Geopolymer”
- Raw materials:
 - Aluminosiliceous materials (most commonly metakaolin, slag, fly ash)
 - Alkali hydroxide or alkali silicate solutions, for example: NaOH
- Fabrication:
 - No real “fabrication” process besides mixing and placing the materials.

Water, Aggregates, Activators, GGBS, PFA, Geopolymer Concrete

<https://idasco.co/en/geopolymer-concrete/>

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Alkali Activated Cement Reactions

Si or Al based material: kaolinite-based clay, slag, natural pozzolan, fly ash

Mixed with alkaline solution: sodium hydroxide, sodium silicate

Solution dissolves the starting material and reforms into solid binder matrix

12.0kV 5.9mm x500 BSE3D 20µm

PRECAST SHOW

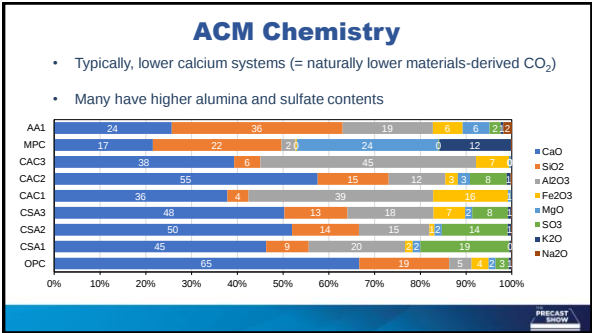
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Alkali Activated Cements

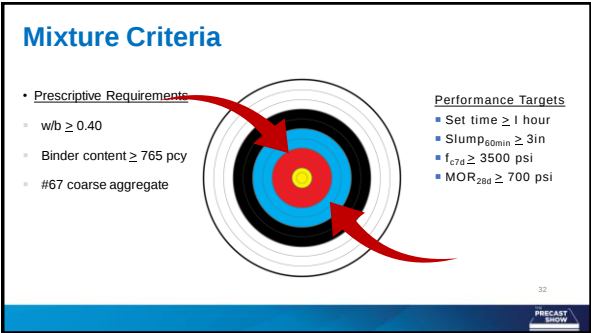
- Advantages:
 - Heat resistant
 - Low shrinkage
 - No risk of prehydration during storage
 - Can achieve very high strengths
 - Several U.S. suppliers established recently
- Disadvantages:
 - Requires use of either a proprietary activation formula or caustic solution
 - Many formulations require heat curing (autoclave or steam cure)
 - No consistent dosing requirement – activation formula dosage varies with materials
 - No current supplier in the U.S.

PRECAST SHOW

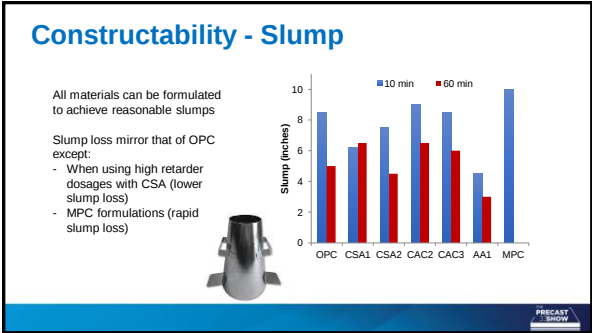
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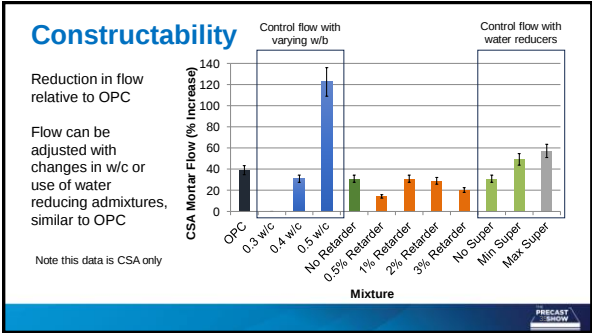
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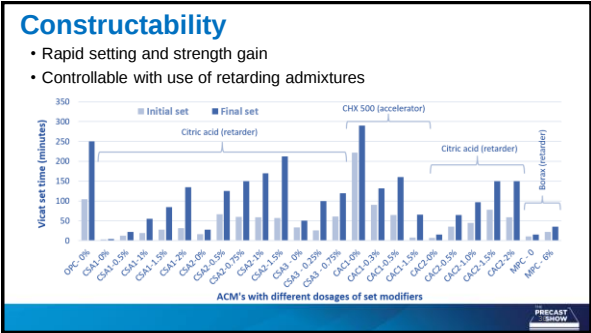
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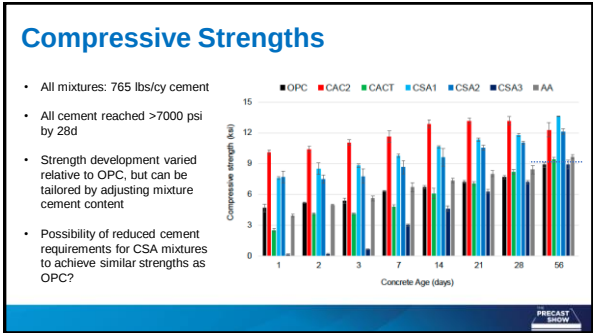
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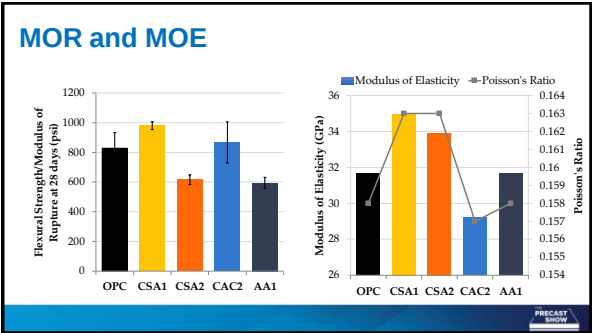
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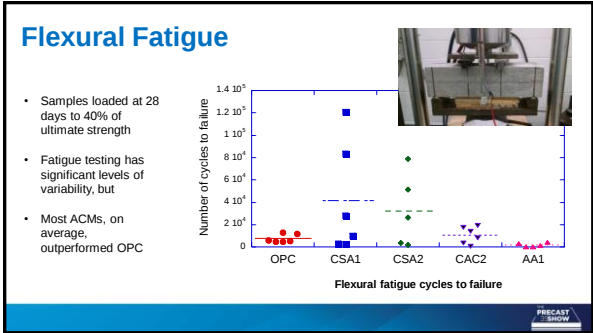
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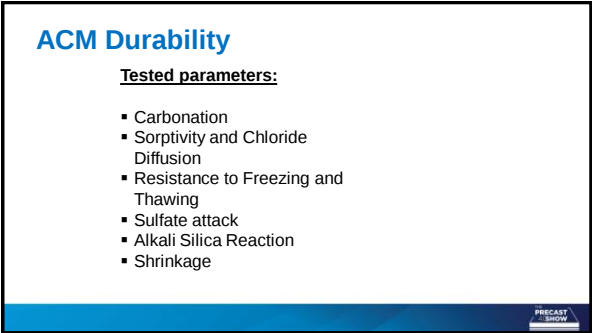
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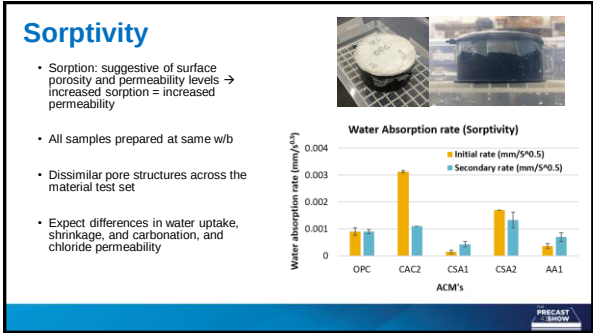
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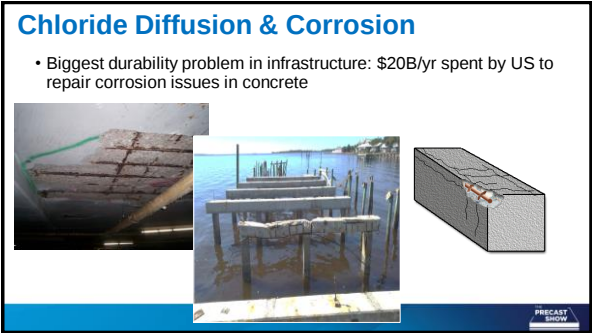
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Chloride Diffusion

- Controls time to initiation of corrosion

When enough chlorides reach the surface of the steel, concrete's protective 'passivating layer' will fail and corrosion will initiate.

6 years from corrosion initiation to spalling of concrete

Chloride movement

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Chloride Diffusion

- Lower diffusivity in CSA materials compared to OPC

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Chloride Diffusion

- Most ACMS:
 - Similar chloride binding
 - Lower chloride infiltration levels than OPC

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Chloride Diffusion

- Most ACMS:
 - Higher diffusion coefficients (faster infiltration rate) ☹
 - Use of a polymeric sealant SIGNIFICANTLY improved diffusivity

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Corrosion

- Varying results for corrosion testing, but generally similar to OPC performance

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Corrosion

- In cracked section tests CSA showed the greatest bar corrosion

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Carbonation

- CO₂ from the atmosphere consumes CH and lowers concrete pH
- Lower pH leads to initiation of corrosion
- After CH is consumed C-S-H can be decalcified – leading to strength reduction
- Carbonation sequesters CO₂ from the atmosphere...
- Use of phenolphthalein solution can be sprayed onto broken samples to ID areas with pH >10 → pink = not carbonated

Possan et al (2017) Case Studies in Construction Materials

Reinforcement
Covering
Concrete surface
CO₂
CH
C-S-H
pH
Time
Non-carbonated zone
Semi-carbonated zone
Carbonated zone

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Carbonation

CSA1 – 84 days
OPC – 84 days
CSA2 – 84 days
CAC2 – 84 days
CAC3 – 84 days
AA1 – 84 days

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Carbonation

- All ACMs carbonated MUCH faster than OPC
- Accelerated carbonation was likely related to lower calcium content and lack of CH

Carbonation Rate – in./yr^{0.5} Carbonated pH

OPC	0.08
CSA	1.72
CAC	1.16
CACT	0.35
AA1	1.54

Accelerated Carbonation
Temperature: 30 °C
Relative humidity: 55% to 60%
CO₂ concentration: 7%

Carzana et al (2018) Cement and Concrete Composites

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Carbonation – pH Change

- Greater reduction in pH in ACMs compared to OPC
- Increased likelihood of carbonation-driven corrosion

From FHWA project:

	Uncarbonated pH	Carbonated pH
OPC	>13	< 13
CSA	>13	9 - 11
CAC	9 - 11	< 9
AA1	> 13	< 9

LPC = PLC
SL03 = 60/40 CSA/OPC
SL05 = 60/40 CSA/PLC

Carzana et al (2018) Cement and Concrete Composites

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Carbonation

Corrosion Rates Without Carbonation:

LPC = PLC
SL03 = 60/40 CSA/OPC
SL05 = 60/40 CSA/PLC

Corrosion Rates With Carbonation:

Carbonation depth (mm)

Carbonation SIGNIFICANTLY increases likelihood of corrosion in ACM systems

Carzana et al (2018) Cement and Concrete Composites

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Freezing and Thawing

"Dry concrete (generally below ~ 75 to 80% internal relative humidity) is normally immune to damage from freezing." ACI 201

Mechanism of Frost Damage in Concrete

- Water expands 9% as it freezes
- Water will move from paste to pores to provide space for this expansion
- When concrete is at a critical saturation level (91%) or does not have enough entrained air, expansion results in cracking of the concrete

32°F

Non Air-entrained

courtesy of M. Thomas

Saturation < 91.7%

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Mechanism of Frost Damage in Concrete

Non Air-entrained

32°F
23°F

courtesy of M. Thomas

Saturation > 91.7%

56

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Mechanism of Frost Damage in Concrete

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32°F
23°F

courtesy of M. Thomas

Saturation > 91.7%

57

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Mechanism of Protection by Air Voids

Air-entrained

32°F
23°F

courtesy of M. Thomas

Saturation > 91.7%

58

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Mechanism of Protection by Air Voids

Air-entrained

32°F
23°F

courtesy of M. Thomas

Freezing, Saturation > 91.7%

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Freezing and Thawing

- Entrained air in concrete provides:
 - Extra pore space for expansion of water
 - Reduced distance for water to travel to reach the voids
- Does this phenomenon work similarly with ACMs?
- Testing was performed with ACMs using systematic dosages of synthetic AEA (e.g., 3%, 4%, 5% air)

Good durability above 80

Poor durability below 20

courtesy of M. Thomas

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Freezing and Thawing

- Reduced uptake of water in CSA samples compared to PC
- Longer time to reach critical saturation levels in CSA concretes

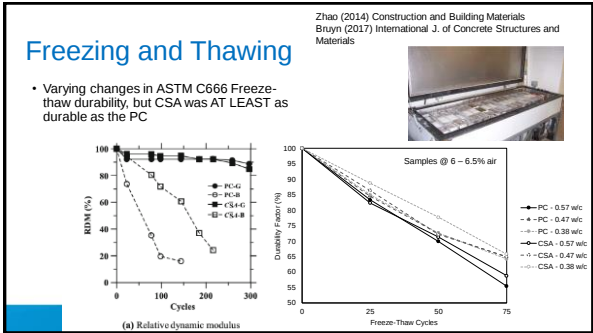
Bruyn (2017) International J. of Concrete Structures and Materials

(a) Drying percentage weight change

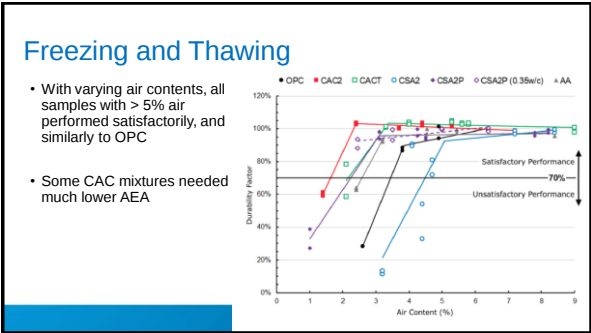
(b) Weight change per day

Fig. 1 Percent weight change and rate of weight change of the portland and CSA cement pastes.

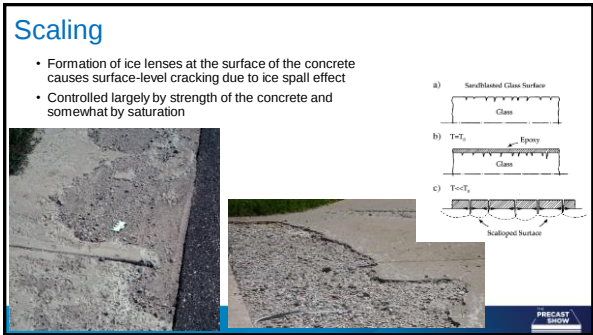
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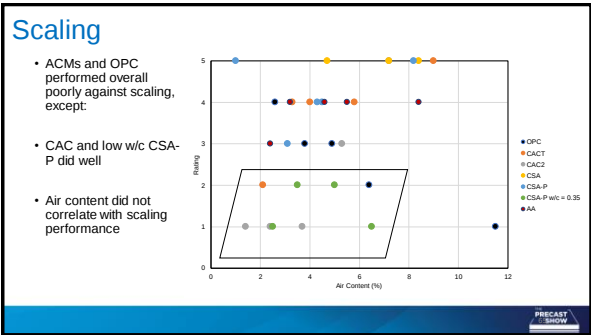
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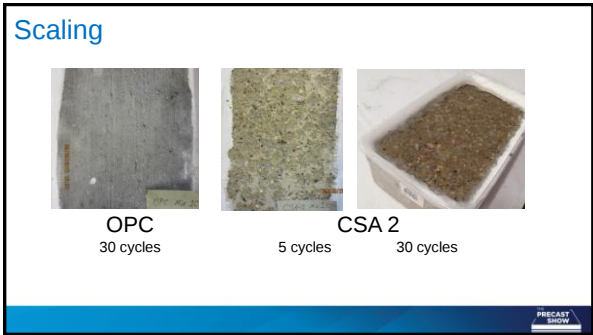
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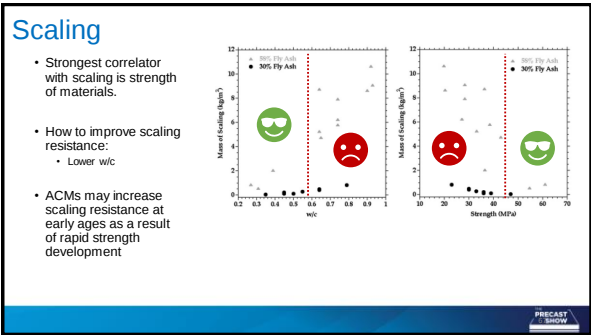
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Alkali Silica Reaction

- Some silica aggregates dissolve when in contact with alkaline concrete pore solution and form a gel
- Higher alkali content in the pore solution and higher presence of calcium lead to increased risk of reaction
- Exposure to water and humidity lead to expansion of the gel and cracking in concrete structures

Reactive silica in aggregate reacts with alkali to form a gel.

When gel is exposed to water, swelling takes place. Swelling of gel causes internal pressure, causing concrete to crack.

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Alkali Silica Reaction – AMBT Results:

- No ACMs found to CAUSE ASR
- CAC and CSA found to control reactive aggregate better than OPC

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Alkali Silica Reaction – CPT Results:

- All ACMs, except the ternary-blend CAC improved ASR resistance

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Sulfate Attack – Where is this an issue?

Sulfates in soil attack concrete resulting in decalcification, strength loss, and expansive compound formation

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Sulfate Attack – Types

Two types :

Chemical – sulfate reacts with calcium in samples, converts to ettringite (causes expansion) or gypsum (results in section loss)

Physical – salts build up in pores of concrete, create stress – when that stress exceeds the tensile stress of the concrete, concrete spalls

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Sulfate Attack Mechanisms

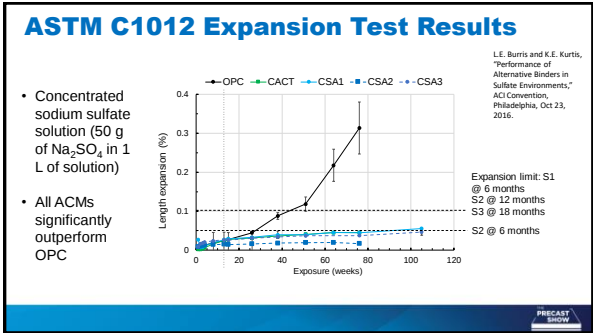
In OPC, chemical sulfate attack typically occurs through:

- (1) reaction of sulfate with monosulfate hydrate, calcium aluminate hydrate, and/or unhydrated C_3A , producing ettringite
- (2) through reaction of sulfate with CH , producing gypsum, lowers pore solution alkalinity and results in a destabilization of $C-S-H$

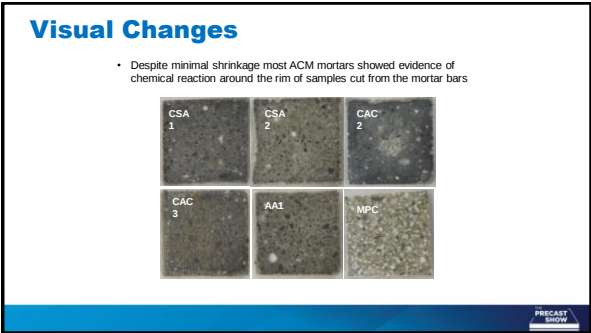
- Most ACMs do not have CH as a hydration product → Less susceptible to sulfate attack?
- However, many do have calcium aluminate monosulfate hydrates and → Susceptible to sulfate attack?

ARE ACMS SUSCEPTIBLE TO SULFATE ATTACK?

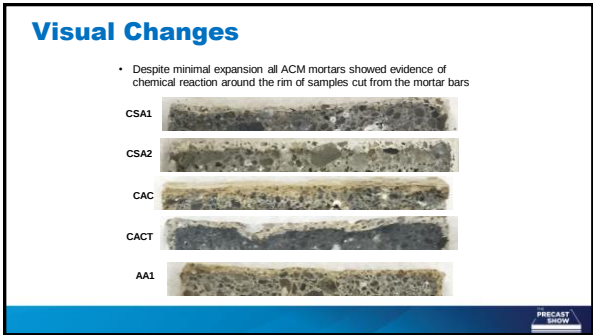
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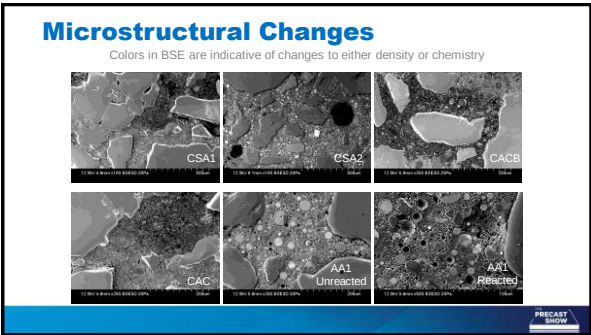
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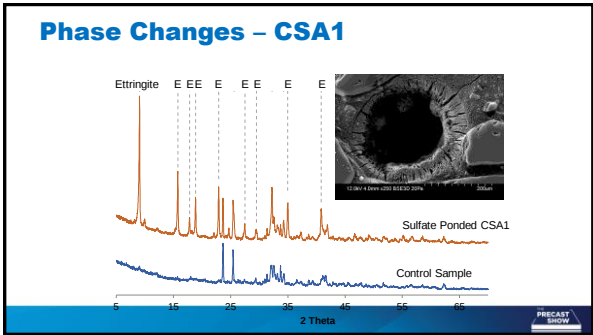
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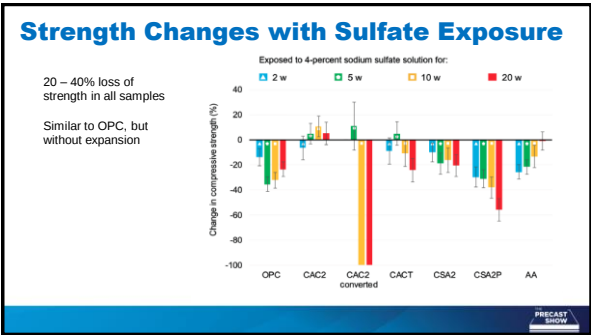
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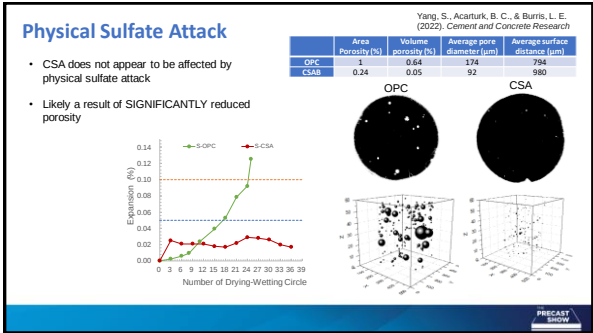
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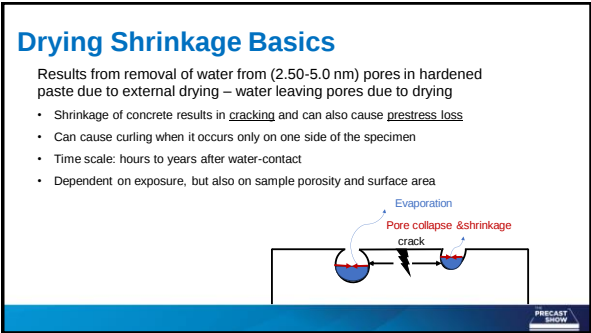
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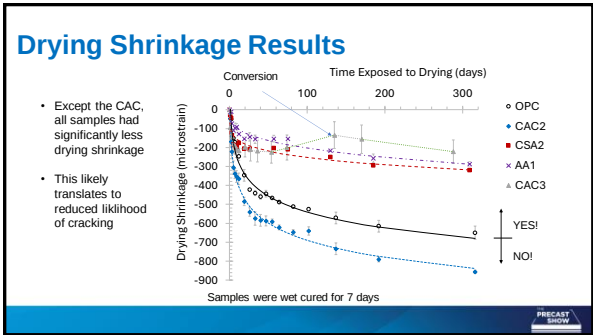
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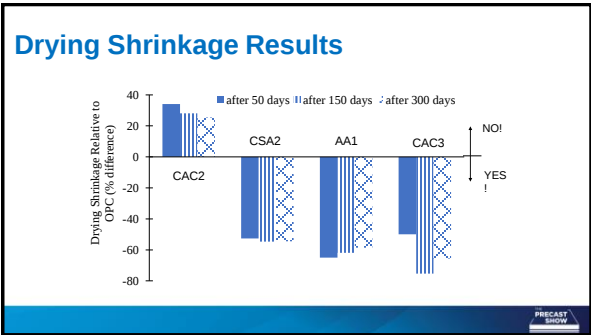
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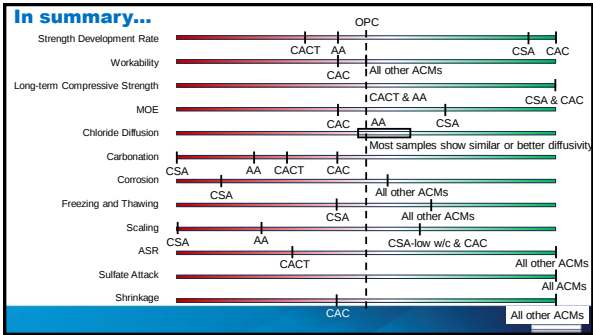
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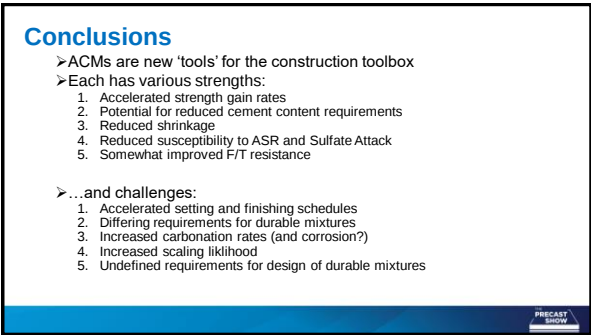
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For more Information...

- Dr. Burris' contact information: burris.189@osu.edu or:
- Two FHWA technotes:
<http://www.fhwa.dot.gov/advancedresearch/pubs/16017/index.cfm>
<https://highways.dot.gov/sites/fhwa.dot.gov/files/FHWA-HRT-24-012.pdf>



The Experimental Research Program

Novel Alternative Cementitious Materials for Development of the Next Generation of Sustainable Transportation Infrastructure

Technote

TECHNOTE

Novel Alternative Cementitious Materials for Development of the Next Generation of Sustainable Transportation Infrastructure

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FHWA Contract: Federal Highway Administration
Research Team: Robert W. Burris, PhD, et al.

RESEARCH DESCRIPTION
The research and the results of research information presented herein are intended for the general public and are not intended for use in any other way.

PRECAST SHOW

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Questions?



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