Carbonation in OPC and Alternative Cement Concrete: Impact of Real Climate versus Accelerated Testing and Implications on Service Life

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ConCarb2019

ENPC, Champs sur Marne

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Exploratory Advanced Research (EAR)

U.S. Department of Transportation
Federal Highway Administration

Georgia Institute of Technology

What are ACMs?

Defining alternative binders (or alternative cements) has been an *evolutionary* process:

- Alternative (non-Portland) cements
- Per ACI ITG-10R-18:

alternative cement–an inorganic cement that can be used as a complete replacement for portland or blended hydraulic cements, and that is not covered by applicable specifications for portland or blended hydraulic cements.

NEW!
ACI Committee 242: Alternative Cements

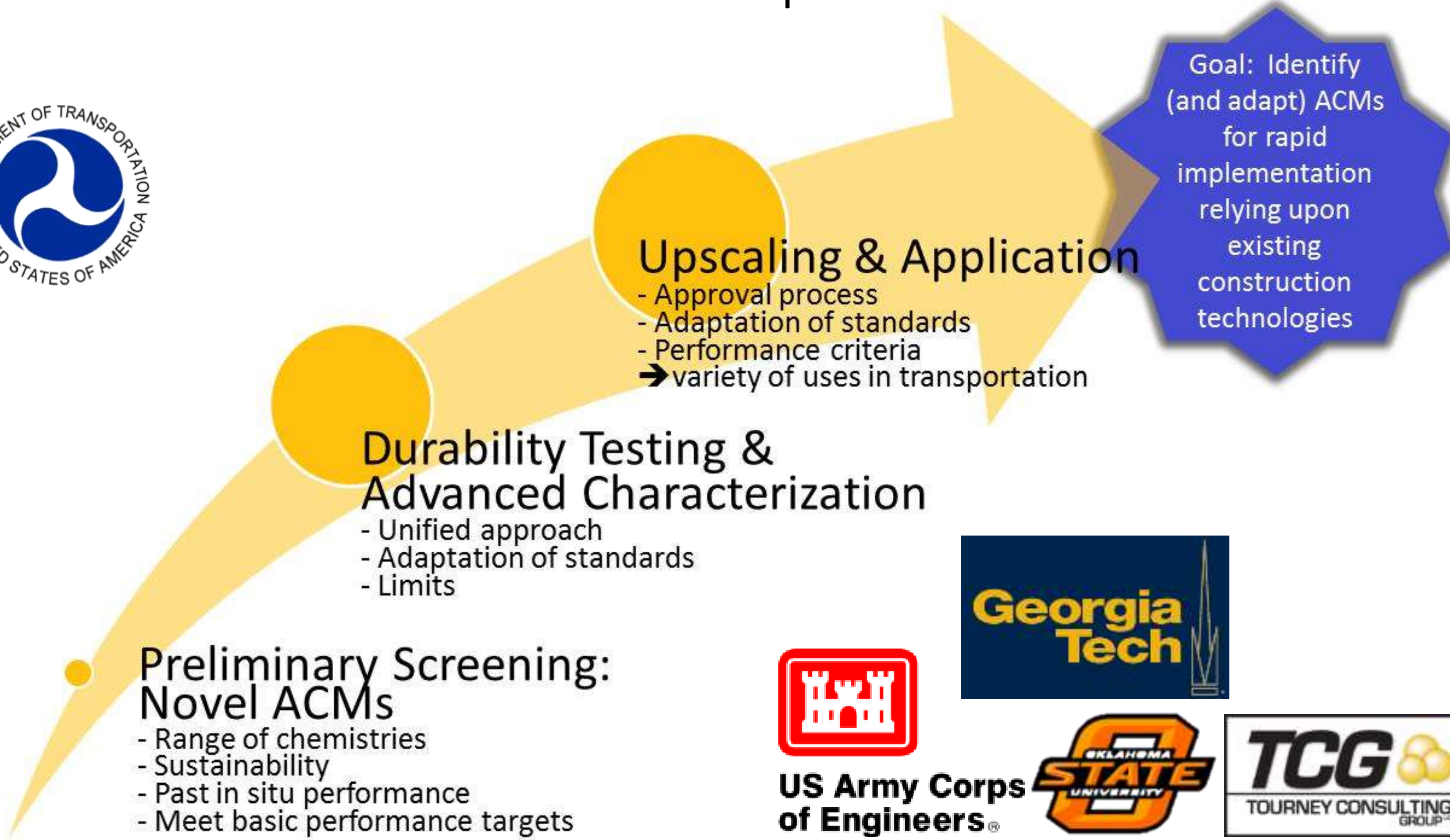
What are ACMs?

ACI ITG-10 classification of commercially available and emerging alternative cement technologies.

Clinkered alternative cements - ACM produced using technologies similar to portland cement production, with process changes that preclude production of portland cement but positively affect the environmental impact of production.	• Calcium aluminate (CAC) • Reactive belite • Calcium sulfoaluminate (CSA) • Carbonated calcium silicate
Calcined alternative cements - ACM produced by calcining a raw material only, without further pyroprocessing, to produce additional mineral phases within the material.	• Magnesium oxychloride • Magnesium phosphate (MPC) • Magnesium ammonium phosphate • Magnesium potassium phosphate
Nonclinkered alternative cements - ACM produced using precursors that require no pyroprocessing and set after addition of an activating solution to cause reactions that are not hydration or acid-base.	• Alkali-activated (AA) • Fly ash • Slag • Recycled glass • Supersulfated cement

PROJECT OVERVIEW

- FHWA Exploratory Advanced Research (EAR) project 2014-2019
- Novel Alternative Cementitious Materials for Development of the Next Generation of Sustainable Transportation Infrastructure



US Army Corps of Engineers

Georgia Tech

Oklahoma State University

TCG Tourney Consulting Group

RESEARCH TEAM

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Tourney Consulting Group

- Neal Berke

US Army ERDC

- Robert Moser
- Sarah Williams
- Stephanie Wood

US Army Corps of Engineers®

PROJECT OVERVIEW

- Phase 1: 12+ ACMs considered, 9 ACMs evaluated
- Phase 2, 3: 5 ACMs evaluated
- Many, many mix designs evaluated against performance criteria, benchmarked against companion OPC

Constructability
- Mixture Design
- Fresh Properties
- Adequate Working Time
- Material Consistency

Hydration
- Phase Development
- Effect of Admixtures
- Setting Time
- Shrinkage

Mechanical properties
- Compressive Strength
- Flexural Strength
- Flexural Fatigue

Durability
- Corrosion
- Transport properties
- Carbonation
- Durability in Freezing and Thawing Environments
- Sulfate and ASR Resistance

Life Cycle Analysis

→ Viability for Use in Transportation Infrastructure **(Tier 3)**

Why are we interested in ACMs?

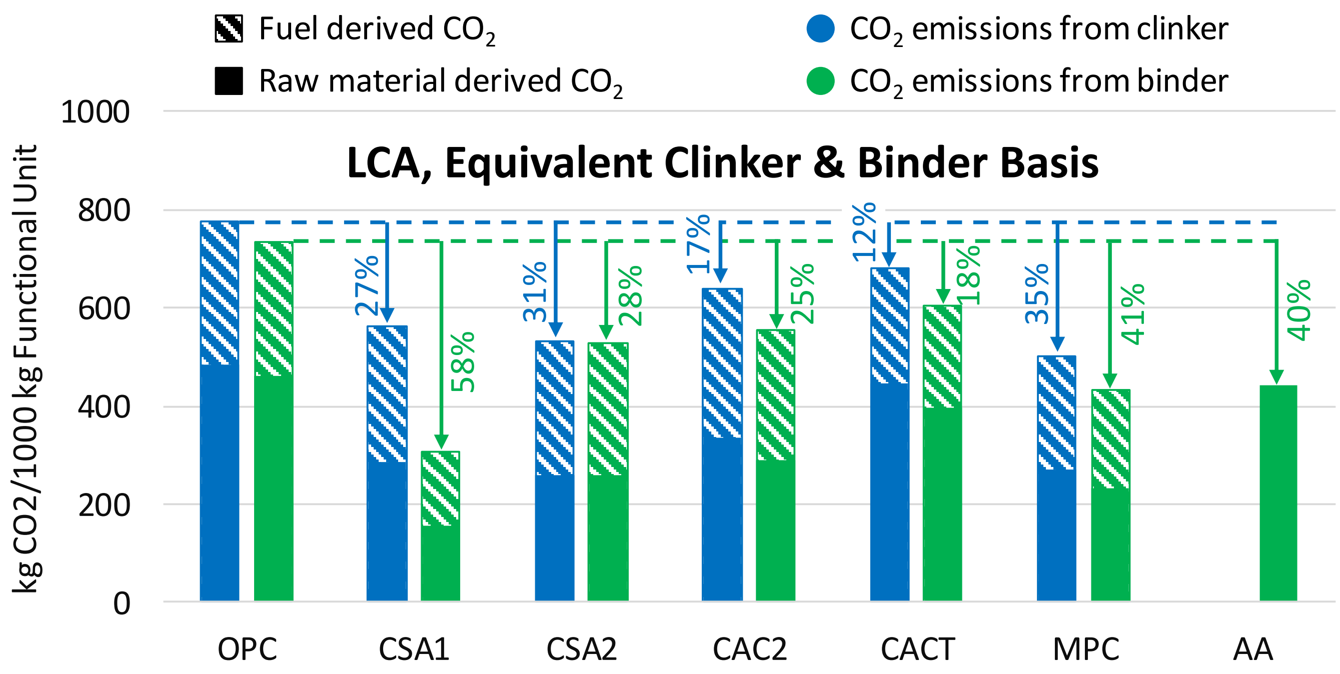
Unique properties appropriate for specialty applications could benefit larger scale transportation infrastructure construction

- Repair (fast set)
- Shrinkage compensation
- High early strength
- Low heat of hydration
- Enhanced durability
- New construction methods

Why are we interested in ACMs?

Sustainable construction materials

- Lower embodied CO_2
- Lower embodied energy
- Higher strength → smaller dimensions
- Enhanced durability → longer service life



Kurtis, Burris, Alapati, *Proc. IGCMat*, 2016
http://www.igcmat.com/papers/Kurtis_igcmat_2016.pdf.

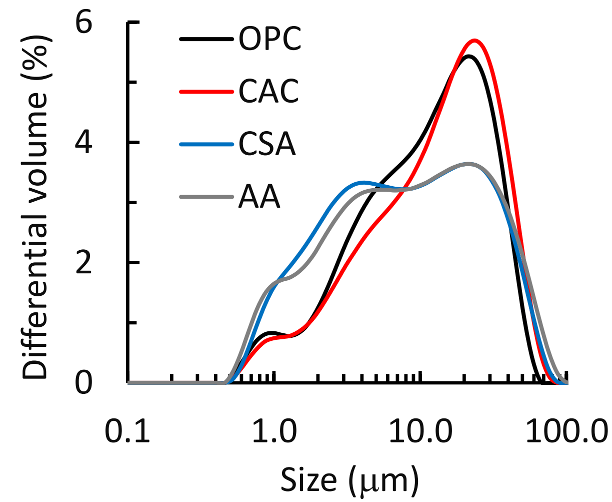
Burris et. Al., Novel Alternative Cementitious Materials for Development of the Next Generation of Sustainable Transportation Infrastructure, FHWA TechBrief – 2015.

Agenda

- Carbonation in ACM vs OPC concrete
  - Reaction mechanisms
  - Effects on porosity, performance
  - Carbonation rates
- Influence of CO_2 concentration
  - Atmospheric levels vs accelerated testing
- Conclusions & Recommendations

Materials: 3 ACMs (out of 9)

Binder		Specific gravity	SSA (m^2/g)
Calcium Aluminate cement	CAC	2.97	306.4
Calcium SulfoAluminate cement	CSA	2.81	501.3
Alkali-Activated binder (C-ash)	AA	2.58	550.7
Type I/II Ordinary Portland cement	OPC	3.05	333.3

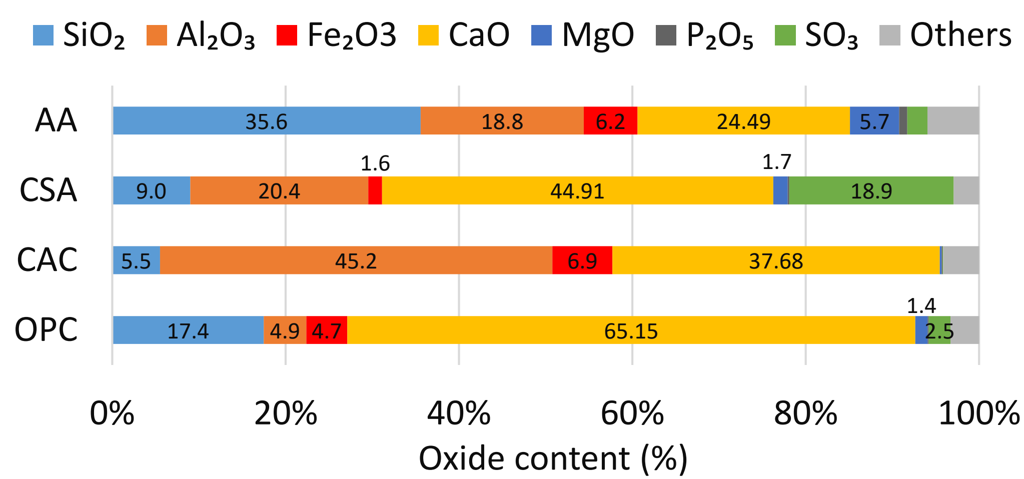



CAC


CSA

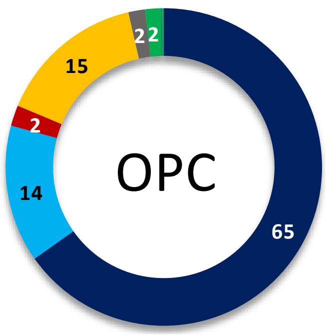

AA


OPC



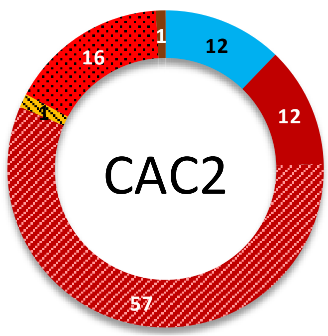
Varied Phase Composition

9 ACMs evaluated (Phase 1); 5 ACMs evaluated (Phase 2, 3)



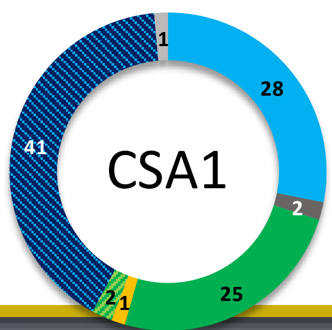
Common phases in OPC

C_3S C_2S C_3A C_4AF $CaCO_3$ $CaSO_4$ Other



Common phases in CAC

CA $C_{12}A_7$ C_2AS Fe_2O_3



Common phases in CSA

C_2S $CaSO_4.(H_2O)_{0.5}$ $C_4A_3\bar{S}$

Different hydration products

OPC

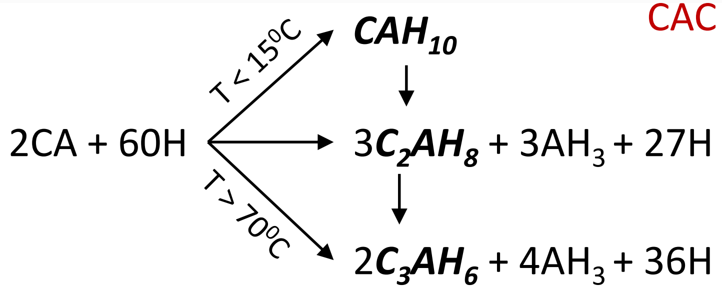
$$2C_3S + 6H \rightarrow \boldsymbol{C\text{-}S\text{-}H} + 3CH$$

$$C_2S + 4H \rightarrow \boldsymbol{C\text{-}S\text{-}H} + CH$$

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

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

CAC



CSA

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

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

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

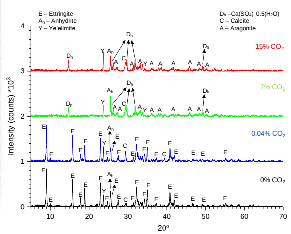
AA

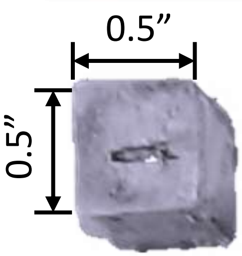
$$(Ca + Si) + H \rightarrow \boldsymbol{C\text{-}S\text{-}H}$$

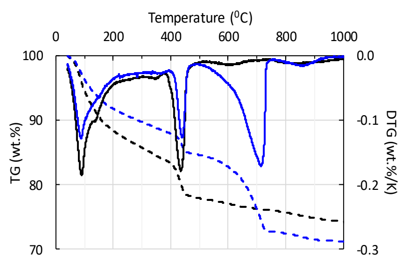
$$(Si + Al) + \text{Alkaline sol} \rightarrow \textbf{\textit{(alkali cation)-A-S-H}}$$

Understanding Carbonation in ACMs vs OPC: 3 Objectives

1. Reaction mechanisms (hydration and carbonation products)

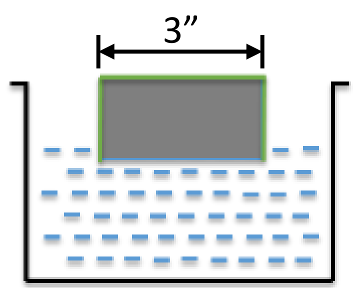






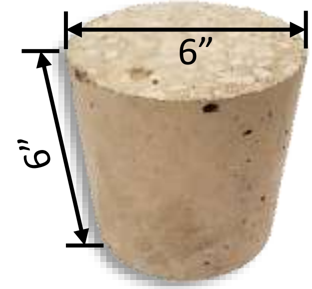
Cement paste cubes at w/c : 0.45 (0.25–*AA)*

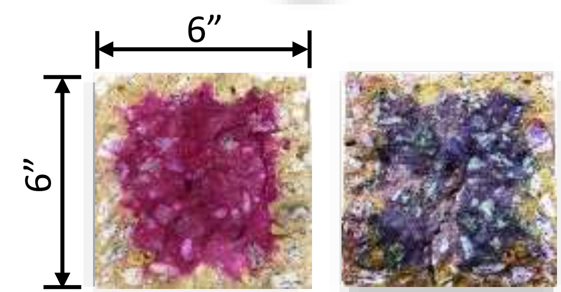
2. Effects on porosity



Cement mortar discs at w/c : 0.45 (0.25–*AA)*

3. Effects on pH, and rate of carbonation





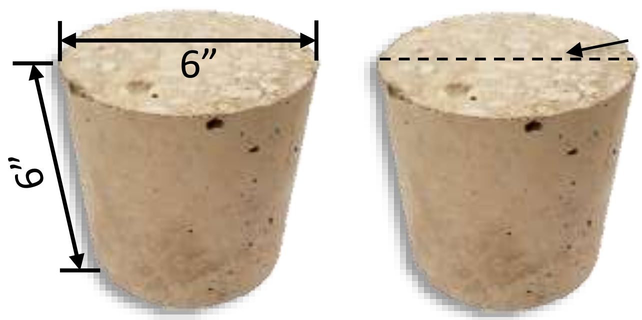
Concrete cylinders at w/c : 0.4 (0.205–*AA)*

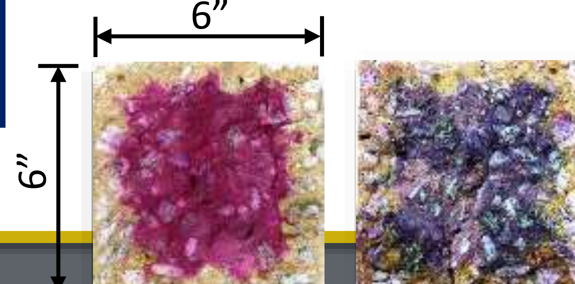
ACM Durability - Approach

Laboratory testing of ACM concrete durability

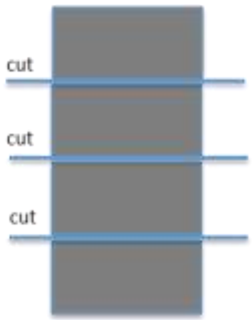
- Rely, as much as possible, on established accelerated test methods
- Compare against OPC
- Relate to materials characterization to understand factors governing performance
- Validate against field performance

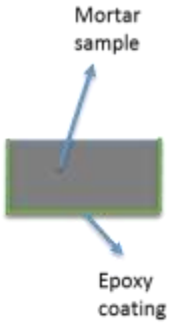
Exposed to **7% CO_2** at 30C and 55%RH for 56 days (84 days – concrete)

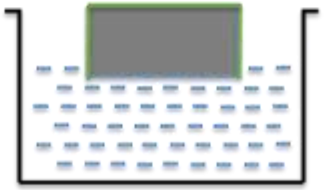


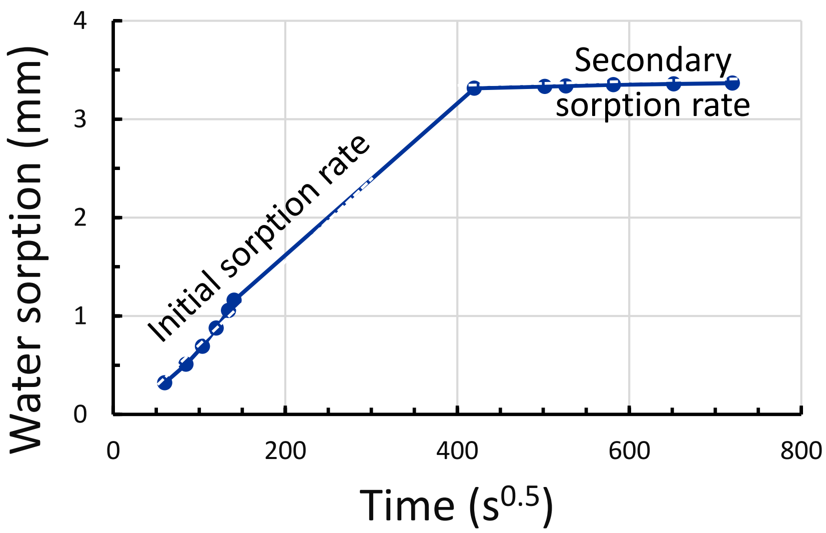


Sorptivity Test – ASTM C1585



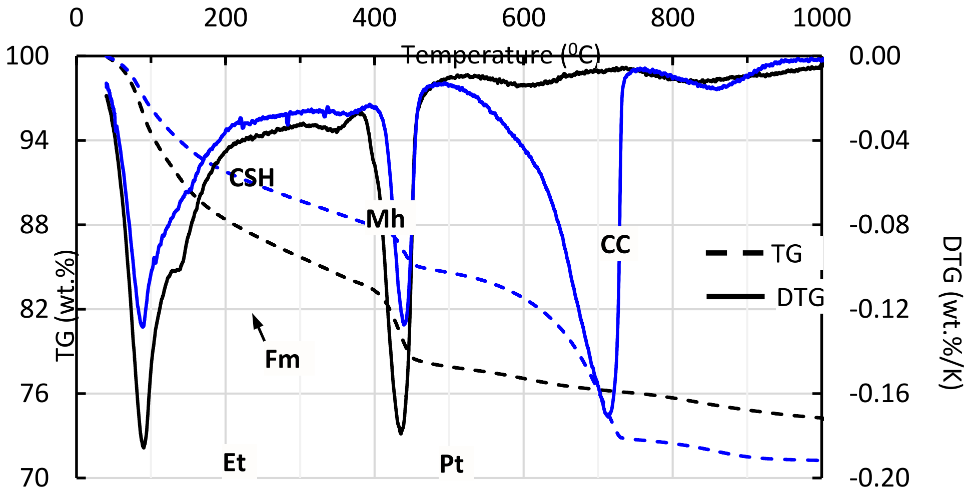




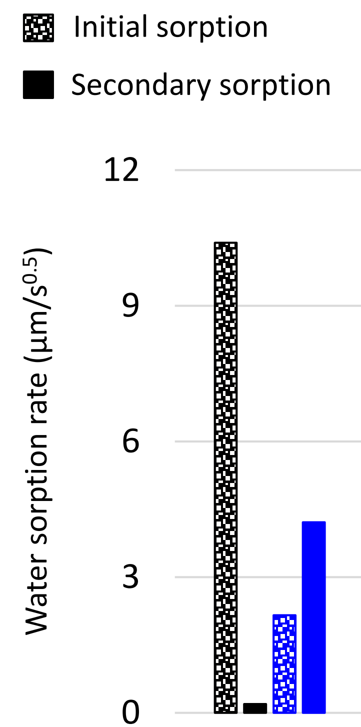


Carbonation in OPC

CO_2 exposure level: 0, 7% for 56 days



Et – Ettringite, Pt – Portlandite, CSH – (C-S-H), CC – $CaCO_3$
Fm – Monosulfo aluminate, Mh – $Mg(OH)_2$



$$CH + CO_2 \rightarrow CaCO_3 + H$$

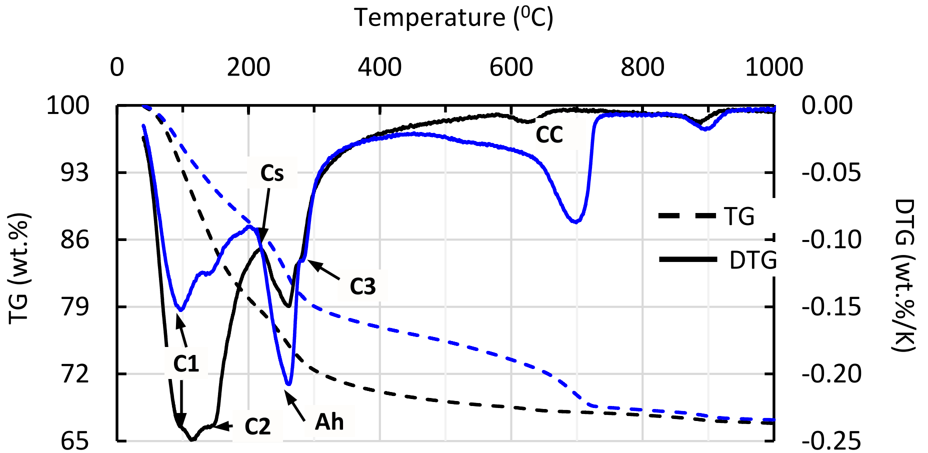
- Decomposition of secondary phases – might not significantly affect the strength
- Initial sorption ↓, secondary sorption ↑

  Dissolution of phases (CH) into pore water -> precipitating as $CaCO_3$ in capillary pores

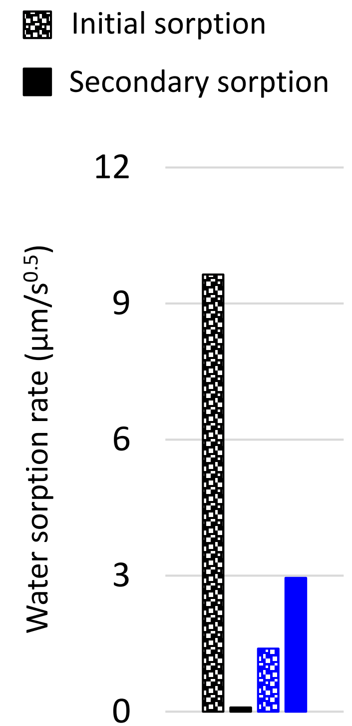
- CH buffers the pore solution --> carbonation might reduce the pH

Carbonation in CAC

CO_2 exposure level: 0, 7% for 56 days



Ah – AH_3, C1 – CAH_{10}, C2 – C_2AH_8, C3 – C_3AH_6
Cs – C_2ASH_8, CC – $CaCO_3$



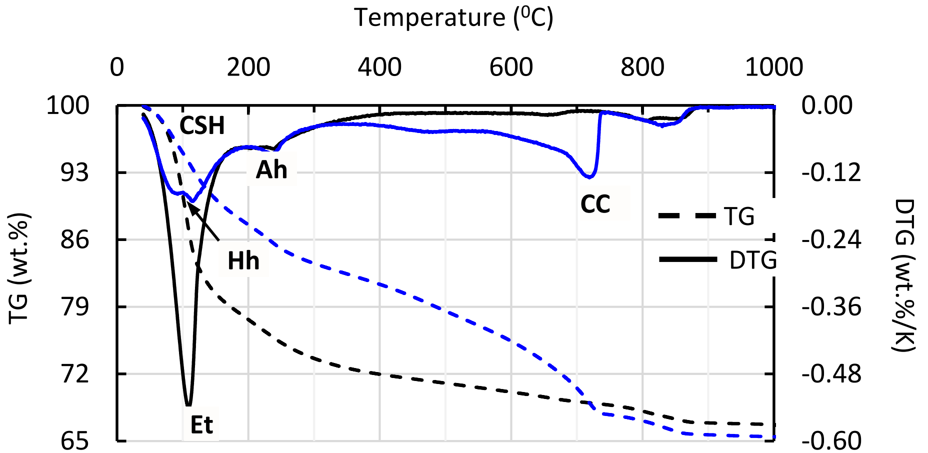
$$CO_2 + CAH_{10} \rightarrow CaCO_3 + 2AH_3 + 7H$$

- Decomposition of primary phases – might significantly affect the strength
- Initial sorption ↓, secondary sorption ↑

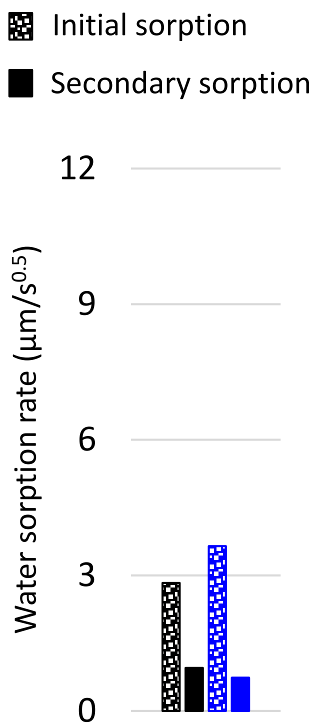
  Dissolution of CAH_{10} phase into pore water -> precipitating as $CaCO_3$ in capillary pores
- CAH_{10} buffers the pore solution --> carbonation might significantly reduce the pH

Carbonation in CSA

CO_2 exposure level: 0, 7% for 56 days



Et – Ettringite, CSH – (C-S-H), CC – $CaCO_3$, Ah – AH_3
Hh – $CaSO_4.(H_2O)_{0.5}$



$$\text{Ettringite} + CO_2 \rightarrow 3CaCO_3 + 3C\bar{S}H_x + AH_3 + (29-x)H$$

- Complete decomposition of primary phases – might significantly affect the strength

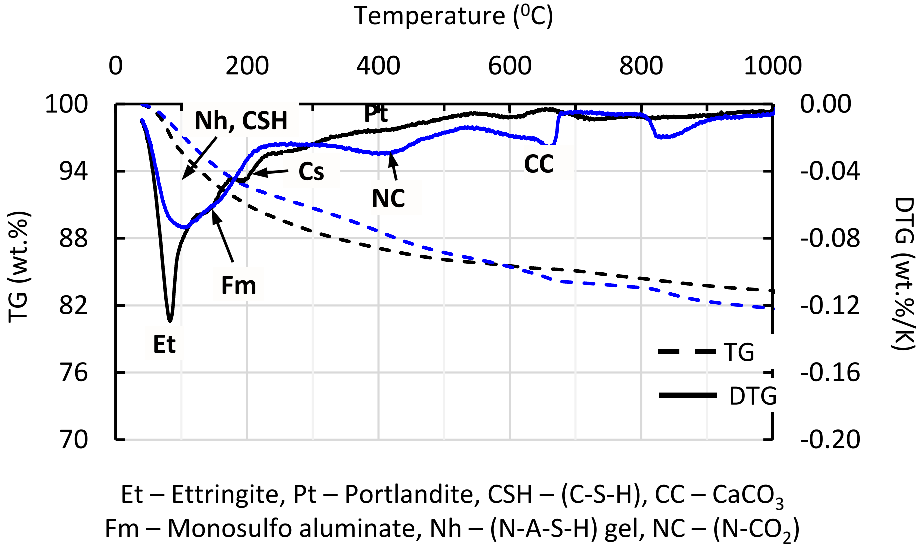
- Initial sorption ↑, secondary sorption ↓

  Carbonation of ettringite --> $CaCO_3$, and release of significant amounts of water

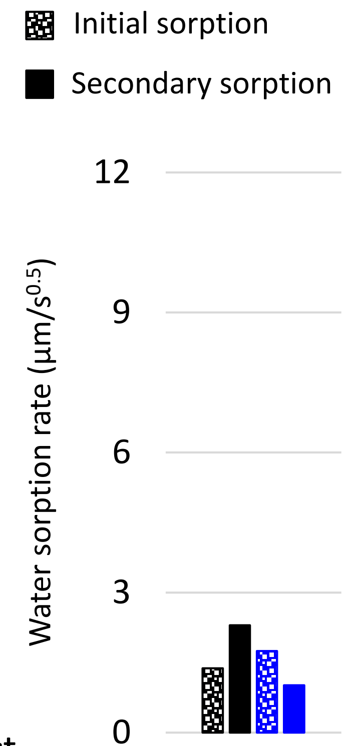
- Acidification of pore water with CO_2--> carbonation might reduce the pH

Carbonation in AA

CO_2 exposure level: 0, 7% for 56 days



Et – Ettringite, Pt – Portlandite, CSH – (C-S-H), CC – $CaCO_3$
Fm – Monosulfo aluminate, Nh – (N-A-S-H) gel, NC – (N-CO_2)

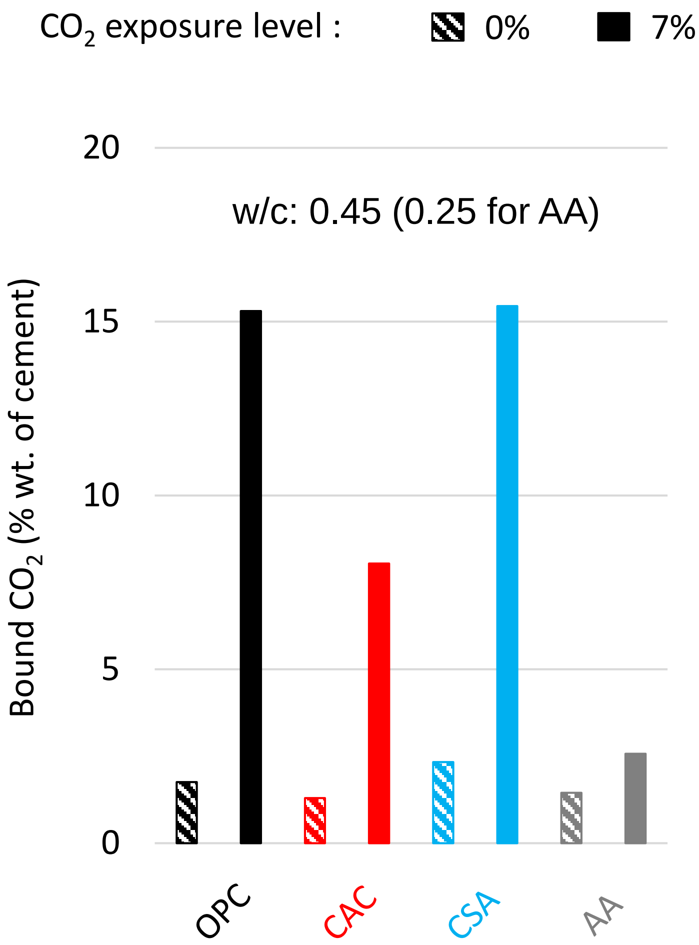


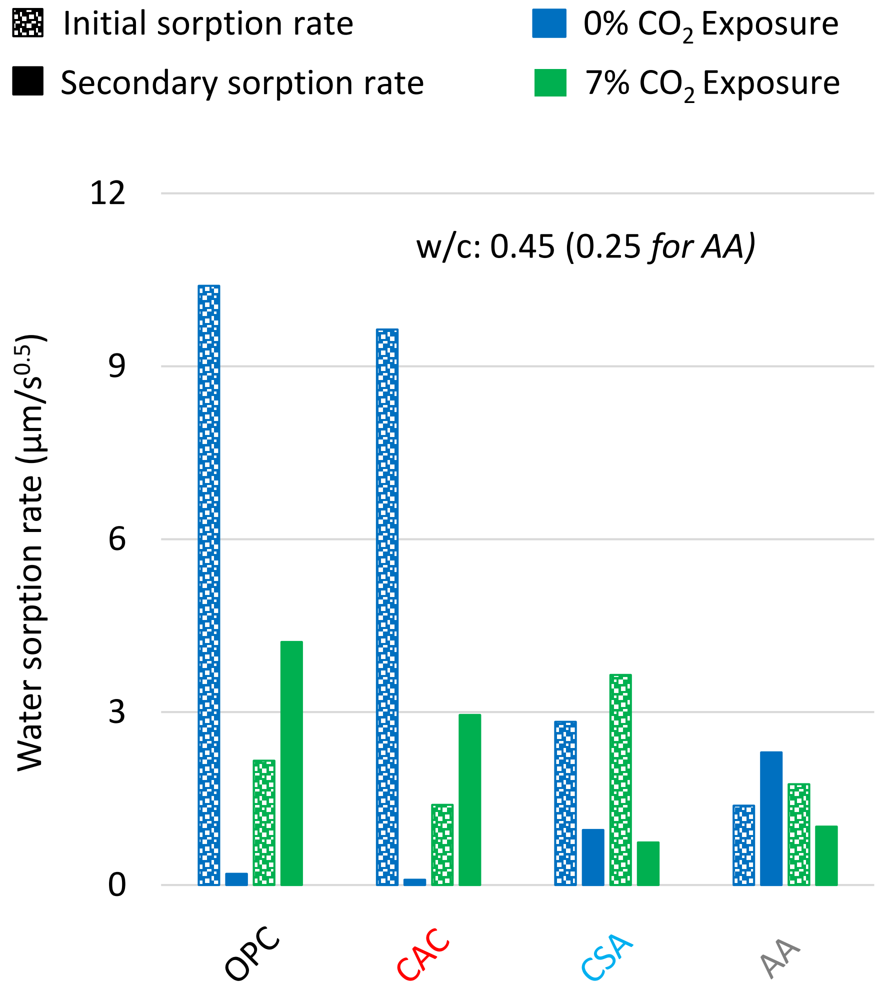
- Decomposition of secondary phases – might not significantly affect the strength
- Initial sorption ↑, secondary sorption ↓

  Carbonation of ettringite -> $CaCO_3$, and release of significant amounts of water

- Carbonation of alkalis --> might significantly reduce the pH

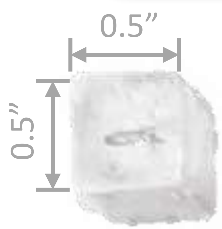
CO_2 Binding, Effects on Porosity

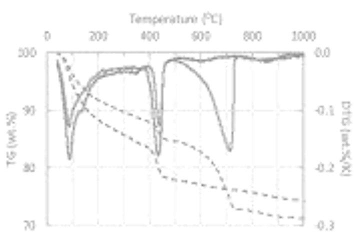




Carbonation Rates for ACMs vs OPC

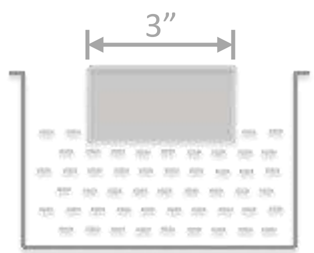
1. Reaction mechanisms (hydration and carbonation products)





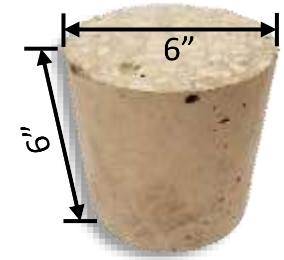
Cement paste cubes at
w/c : 0.45 (0.25–*AA)*

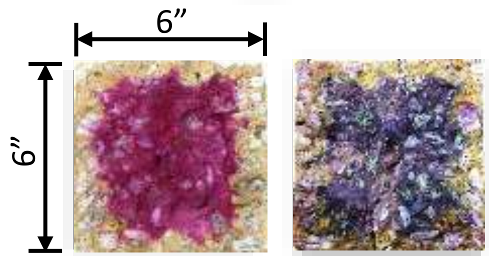
2. Effects on porosity



Cement mortar discs
at
w/c : 0.45 (0.25–*AA)*

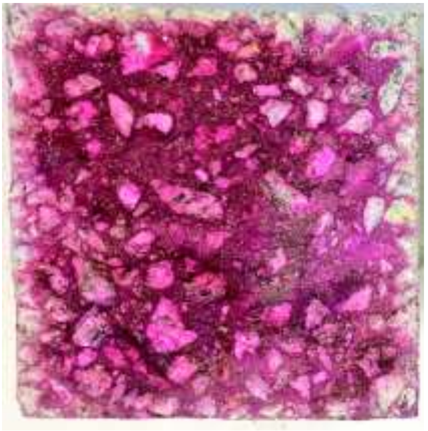
3. Effects on pH, and rate of carbonation



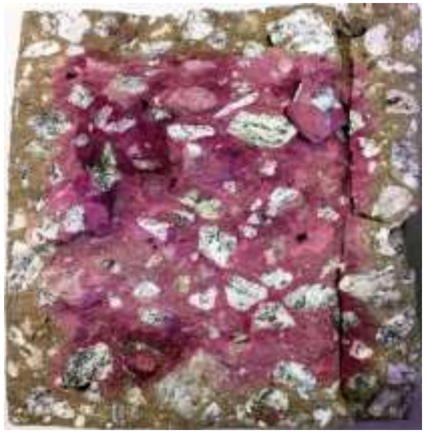


Concrete cylinders at
w/c : 0.4 (0.205–*AA)*

Carbonation in Concrete

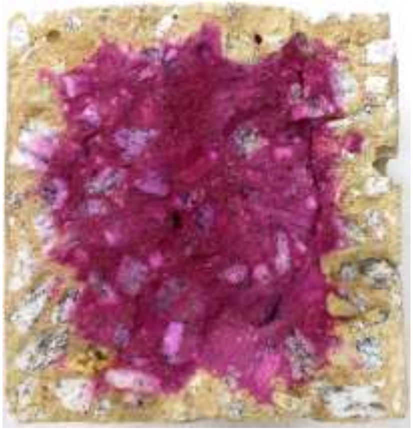


OPC



CAC2

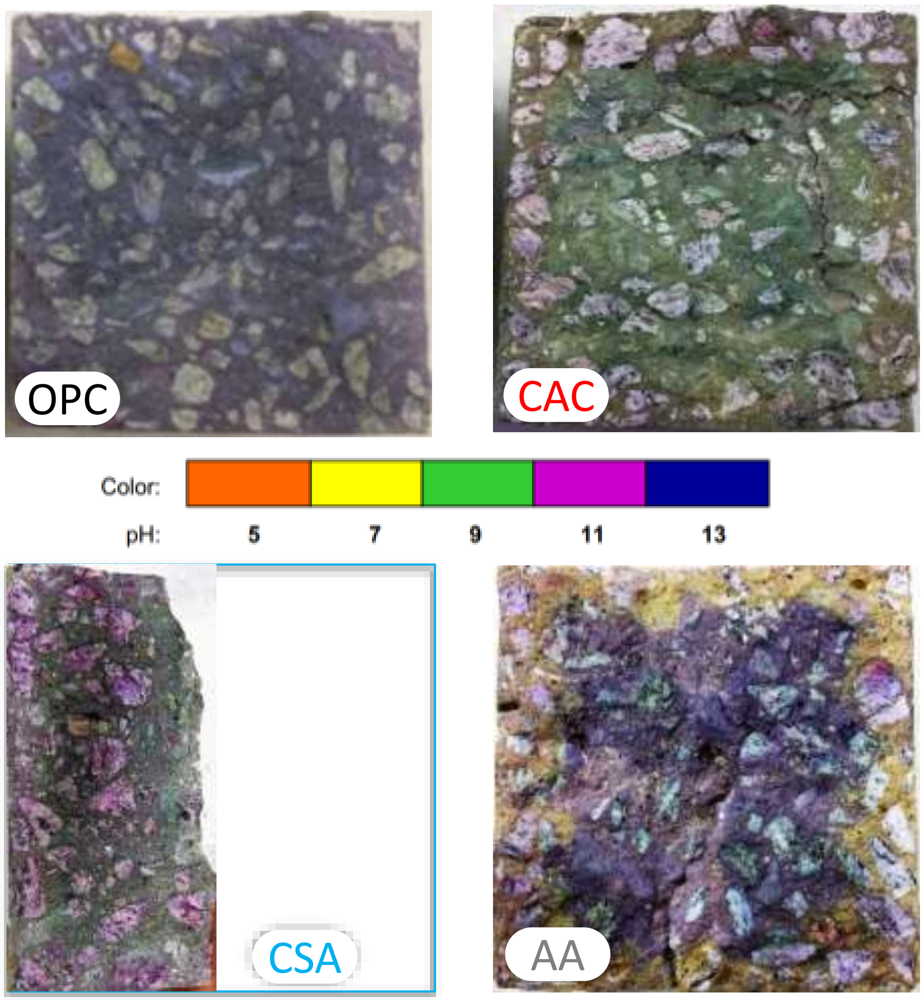
CSA2



AA

Phenolphthalein indicator

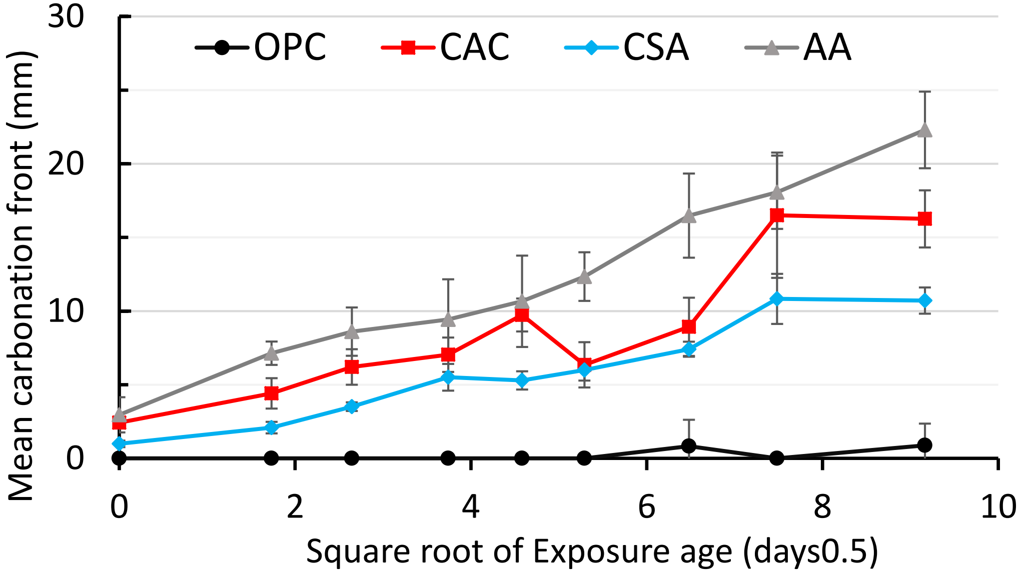
Effects of carbonation on pH



- Exposed to 7% CO_2 for **84 days** @ 30C & 55%RH
- Split into 2 halves -> sprayed with “rainbow” indicator

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

Carbonation rate in ACMs compared to OPC

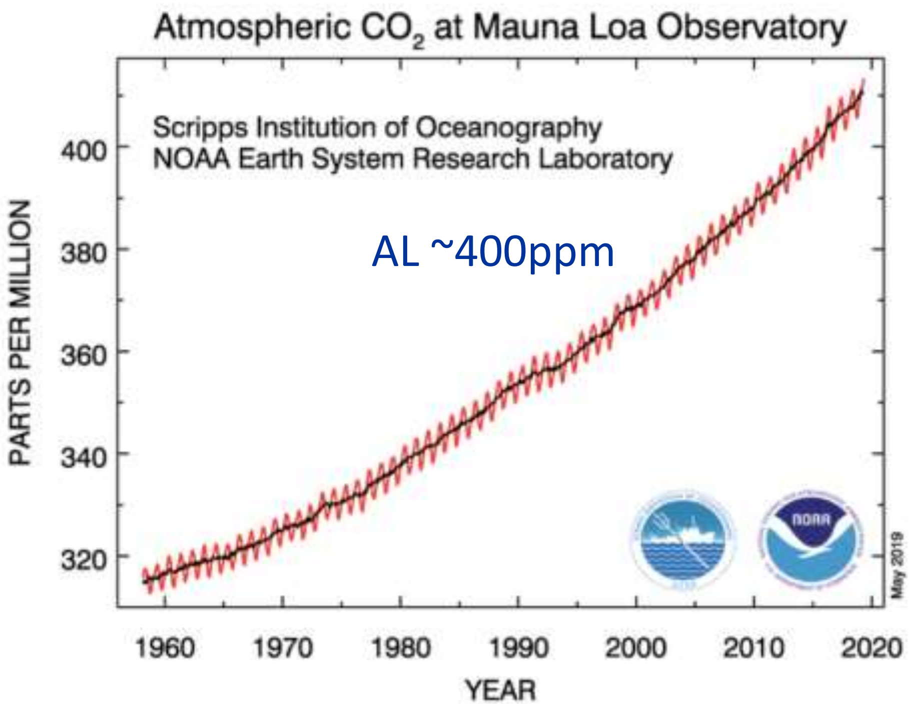


	Carbonation rate ($mm/yr^{0.5}$)
OPC	2
CAC	29
CSA	30
AA	39

- Even though AA has low porosity and higher pH, the amount of CO_2 required to carbonate is significantly lower compared to CSA and OPC
- In CAC, reduction in capillary porosity with carbonation
- OPC has higher amounts of CH – good buffering capacity (compared to ACMs) even at higher levels of carbonation

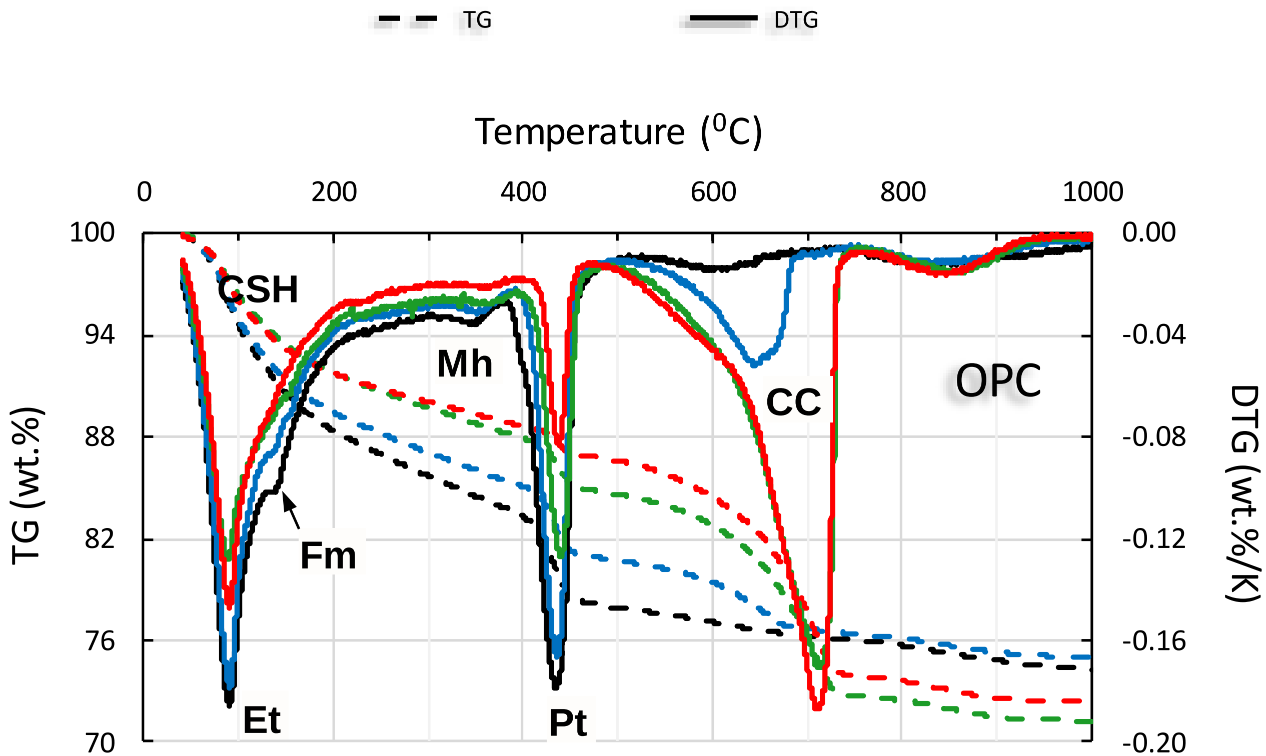
Agenda

- Carbonation in ACM vs OPC concrete
  - Reaction mechanisms
  - Effects on porosity, performance
  - Carbonation rates
- Influence of CO_2 concentration
  - Atmospheric levels vs accelerated testing
- Conclusions & Recommendations



OPC: Effect of [CO_2]

CO_2 exposure level: **0**, **0.04**, **7**, **15%** for 56 days



Et – Ettringite, Pt – Portlandite, CSH – (C-S-H), CC – $CaCO_3$
Fm – Monosulfo aluminate, Mh – $Mg(OH)_2$

$$CH + CO_2 \rightarrow CaCO_3 + H$$

Conclusions: ACM vs OPC Carbonation

- CAC, CSA and AA concretes carbonated at a much faster rate compared to OPC concrete.
- Carbonation in CAC and CSA --> significant decomposition of main hydration products.
- Carbonation in OPC and CAC mortar mixtures resulted in significant reduction in near-surface capillary porosity.
- pH levels in the carbonated region of ACM concrete dropped below 9.
  - Effects on steel passivation and corrosion must be examined.

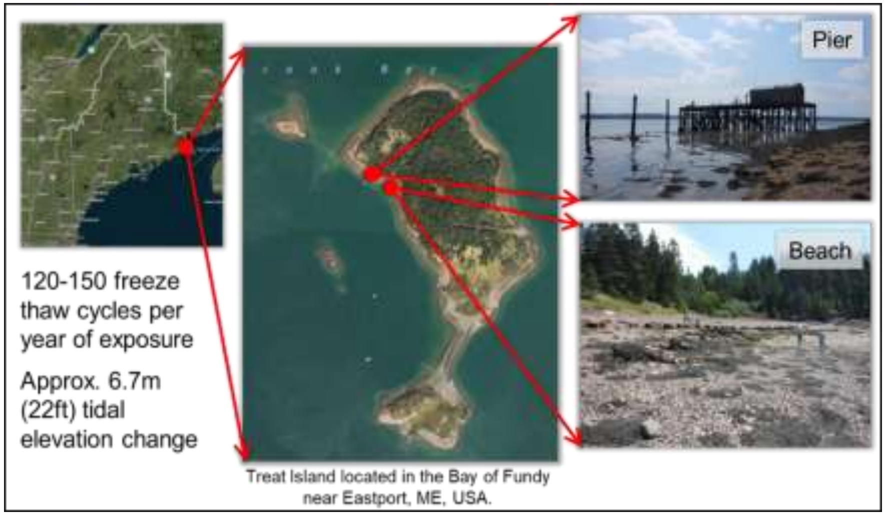
More detailed presentation of these results: Alapati and Kurtis, Sixth International Conference on the Durability of Concrete Structures, 18-20 July 2018, University of Leeds.

Conclusions: Carbonation Testing

- Increased [CO_2] produced more rapid rates of carbonation, but with mechanisms relatively consistent with exposure to atmospheric levels, *except for AA*
  - → Higher concentrations likely not appropriate for AA systems
  - → Carbonation appears to facilitate conversion
  - → Relevant for test method design
  - → Provides some insight into potential effects of increasing global GHG emissions
- Need to establish consistent accelerated exposure test, considering sample preparation (w/c, curing, age at testing) and exposure (duration, CO_2 concentration, temperature, RH)
- Correlation with other performance metrics (e.g.,sorptivity, diffusivity, corrosion onset, compressive strength) necessary
- Validation against field performance necessary

Field Durability Studies

- Treat Island, Maine: wet/dry, freeze/thaw, corrosion
- Biscayne Bay, Florida: wet/dry, corrosion
- Yearly monitoring during site inspections:
  - Visual and NDE
- Retrieval for lab testing:
  - Petrographic analysis
  - Chloride diffusion
  - Mechanical properties



Treat Island – Coastal Maine Exposure

Biscayne Bay – Coastal Florida Exposure

Field Durability Studies

- Photos after 3yr of severe exposure at Treat Island:

OPC

CSA

CAC

AA

Field Durability Studies

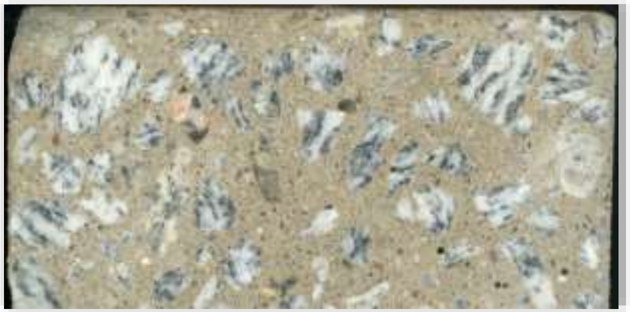
- Petro after 2yr of severe exposure at Treat Island:

OPC

CSA

CAC1

AA



ACMs have faired remarkably well in this severe environment, with as good or better performance than OPC concrete – no freeze/thaw damage, no scaling, edge retention – NO DAMAGE

Recommendations: Carbonation

- Carbonation may be a concern for all ACMs used in low-cover reinforced concrete subject to moderate humidity conditions.
  - Of all ACMs considered, a blend of CAC and OPC performed best (not presented here)
  - OPC out-performed all ACMs, including CAC/OPC blend

- Further studies are needed to assess the influence of carbonation on passivation behavior in reinforced ACM concrete.

Electrochemical tests on carbonated systems are being performed

Questions?

Discussion

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