Interactions of Calcium Sulfoaluminate Belite Cement with Alkanolamines as Admixtures

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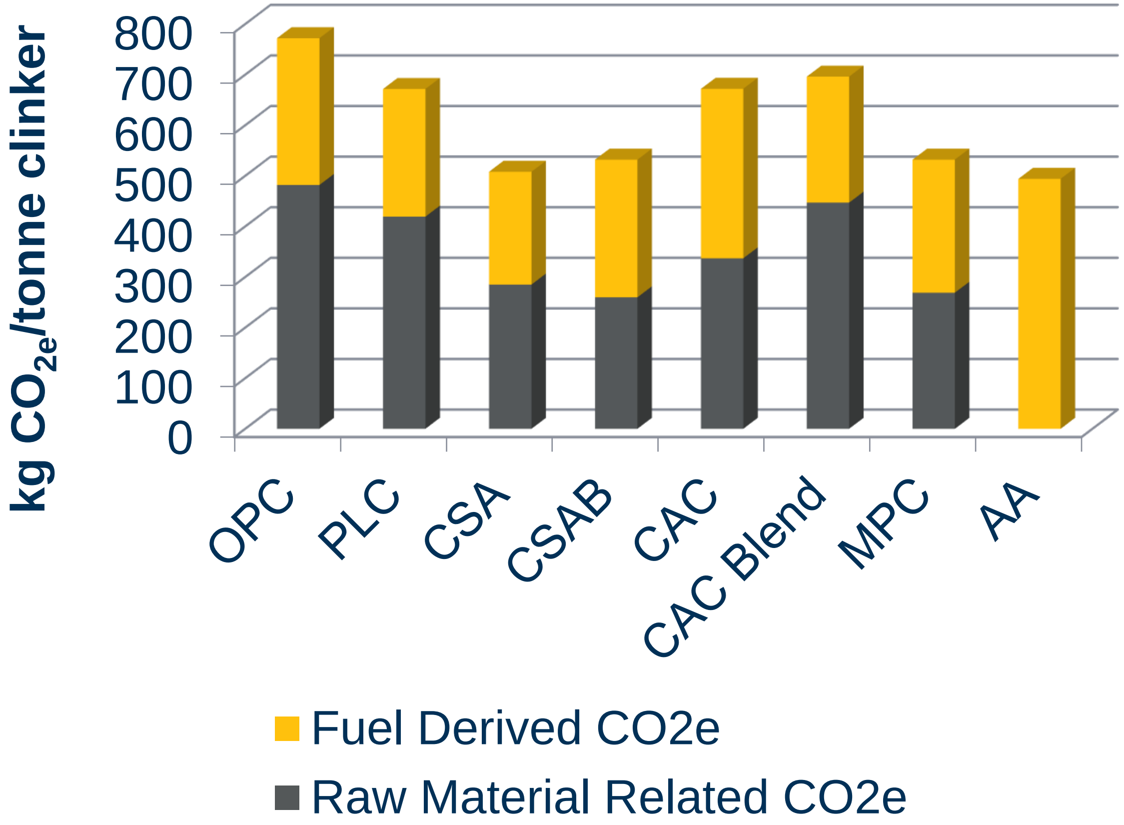
Motivation

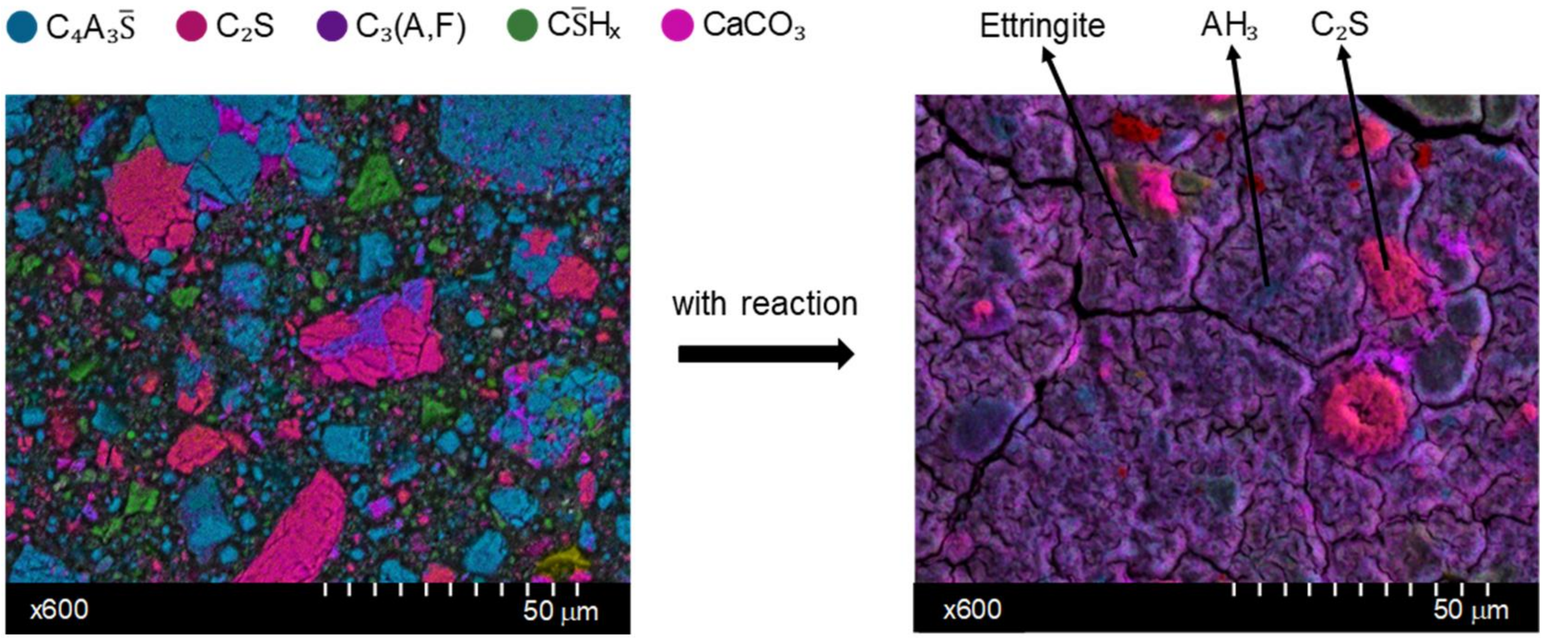
- Lower embodied-carbon cements
  - Portland limestone cement (Type IL)
  - Blended cements (fly ash, slag, silica fume)
  - Limestone calcined clay cement (LC3)
  - Calcium sulfoaluminate cement (CSA)
- Can we use admixtures to tailor lower embodied-carbon cement performance?
  - Commonly used admixtures in PC
    - Dispersants
    - Set controllers



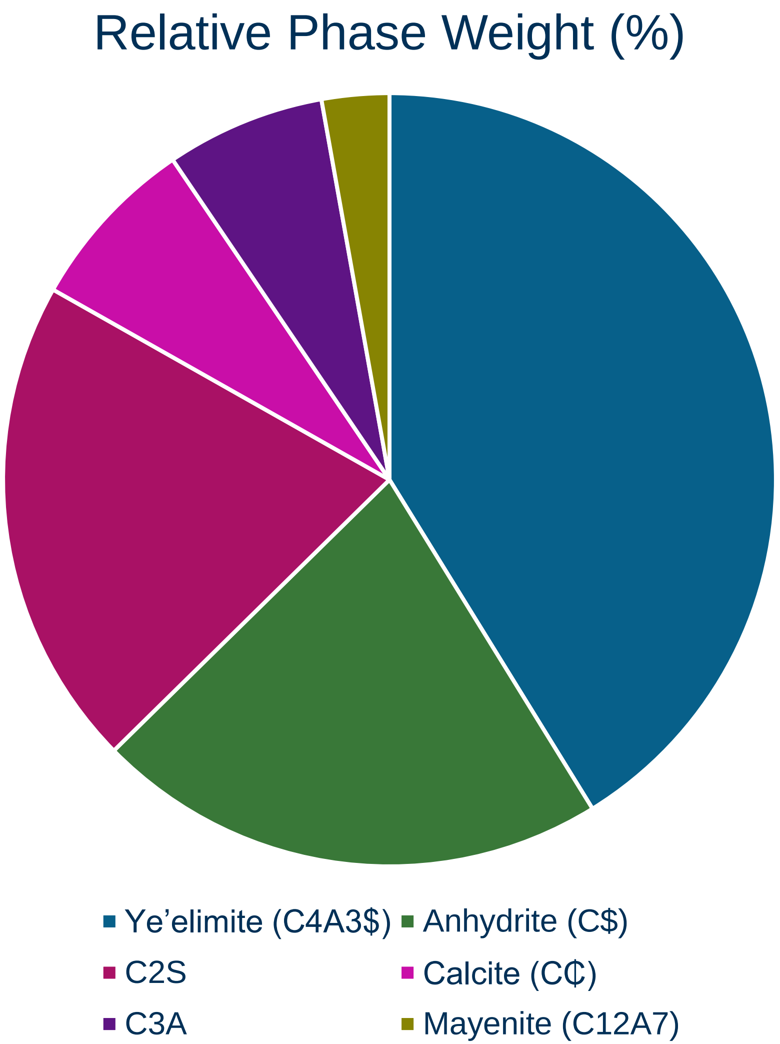
Burris, Lisa, Kimberly Kurtis, and Tom Morton. *Novel Alternative Cementitious Materials for Development of the Next Generation of Sustainable Transportation Infrastructure* [Tech Brief]. Georgia Institute of Technology, 1 Oct. 2015. United States Federal Highway Administration, Office of Infrastructure Research and Development, Report No. FHWA-HRT-16-017, https://rosap.ntl.bts.gov/view/dot/35928.

What is CSAB?

- CSA
  - Ye'elimite + anhydrite + water → ettringite + AH_3
- B(elite)
  - C_2S + water → CH + C-S-H
- Applications similar to Type III PC
- Shrinkage compensating

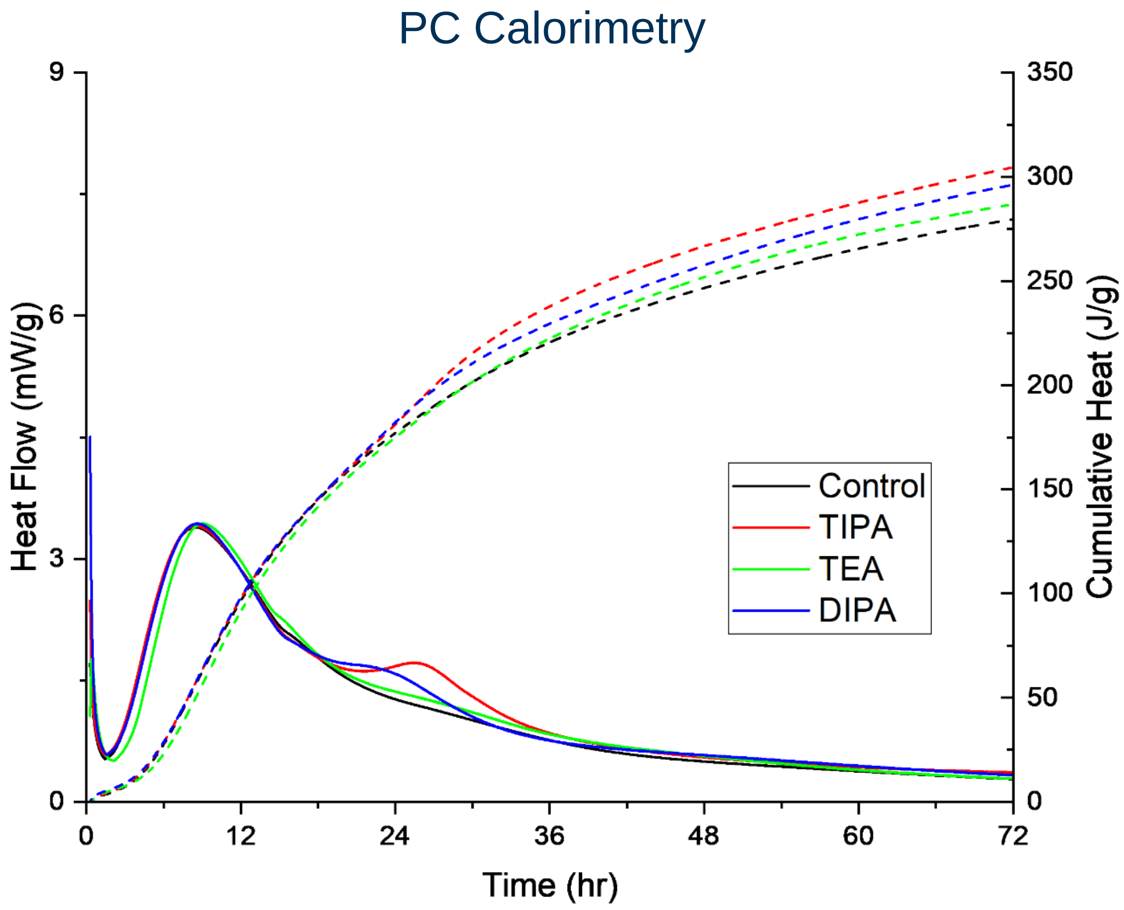


Courtesy of Prasanth Alapati



Objective

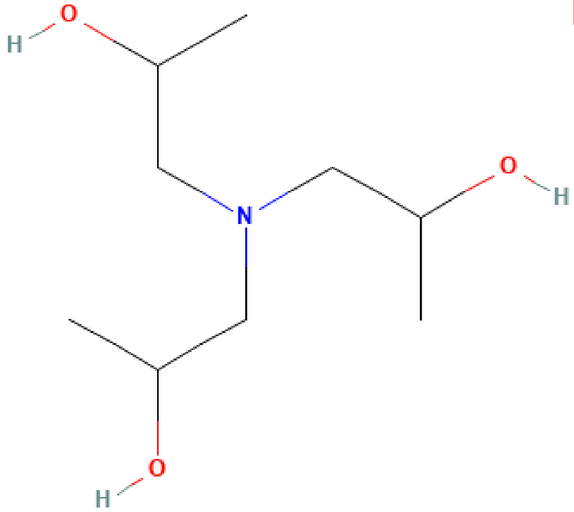
- How do alkanolamines (as an admixture) affect CSAB hydration in early ages?
  - Phase formation
  - Structural build-up
  - Microstructure
- Why alkanolamines?
  - Commonly used in PC
  - Increases compressive strength
  - Increases degree of hydration



What are Alkanolamines?

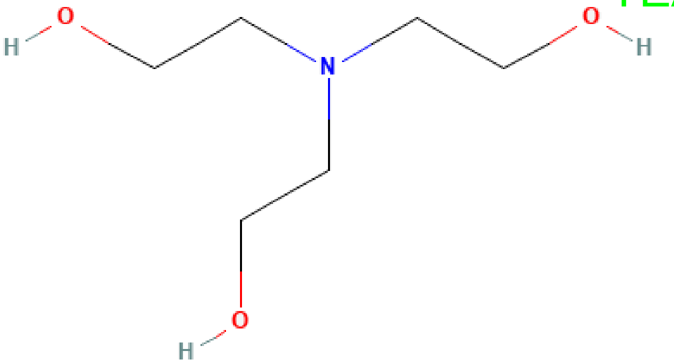
- Ethylene/propylene oxide + ammonia
- Two most common:
  - Triisopropanolamine (TIPA, $C_9H_{21}NO_3$)
  - Triethanolamine (TEA, $C_6H_{15}NO_3$)
- Also in this study:
  - Diisopropanolamine (DIPA, $C_6H_{15}NO_2$)
- Uses in cement:
  - Grinding aids
    - Improve particle fineness and size distribution
    - Prevent agglomeration
    - Improve grinding efficiency
  - Set controller
    - Reduce/elongate setting time
    - Accelerate/decelerate hardening

TIPA



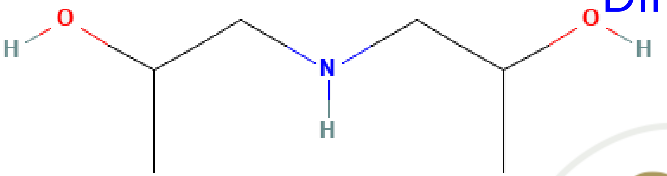
https://pubchem.ncbi.nlm.nih.gov/compound/triisopropanolamine#section=2D-Structure

TEA



https://pubchem.ncbi.nlm.nih.gov/compound/triethanolamine#section=2D-Structure

DIPA



https://pubchem.ncbi.nlm.nih.gov/compound/diisopropanolamine#section=2D-Structure

Materials and Methods

- Commercial CSAB from Netherlands
- Commercial alkanolamines (>99%)
- 0.45 w/c
- 0.02% alkanolamine by weight of cement

- Isothermal calorimetry

https://www.tainstruments.com/new-tam-air/

https://rigaku.com/products/x-ray-diffraction-and-scattering/xrd/miniflex

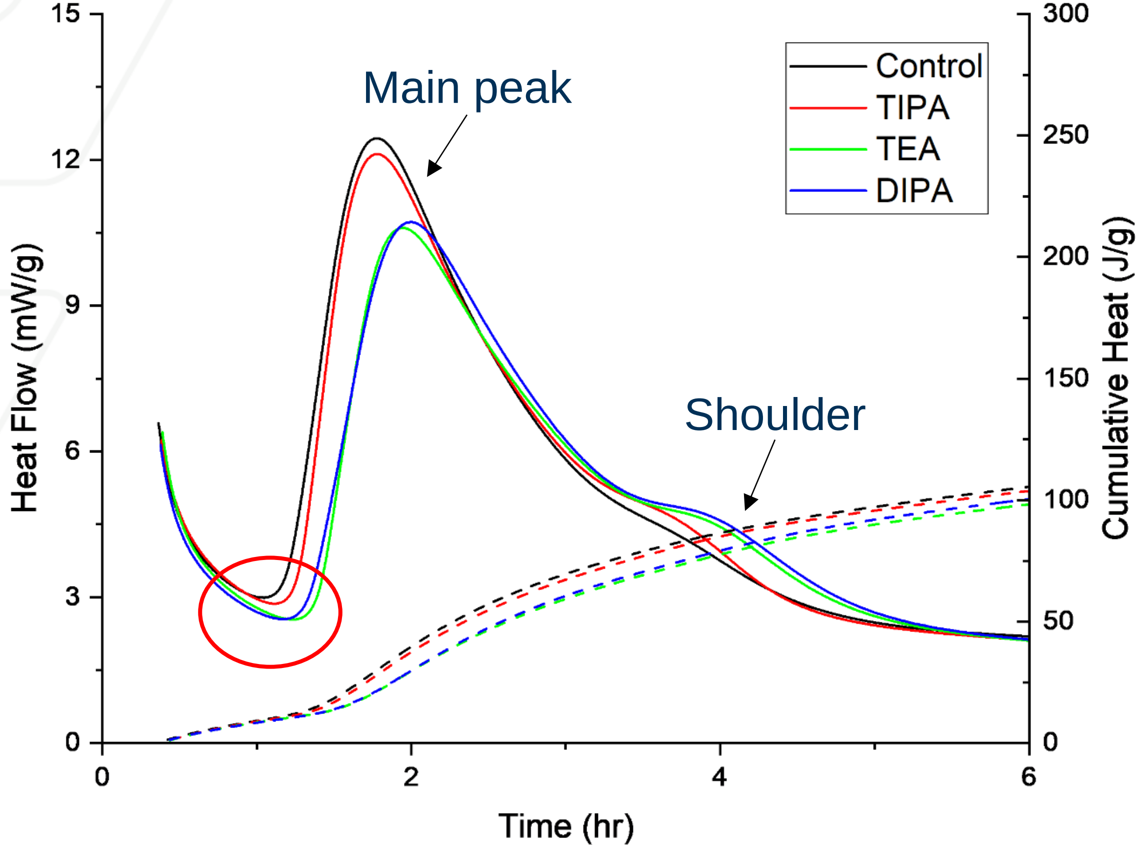
https://www.labwrench.com/equipment/15975/exstar-tg-dta7000-series

https://www.anton-paar.com/corp-en/products/details/rheometer-mcr-102-302-502/

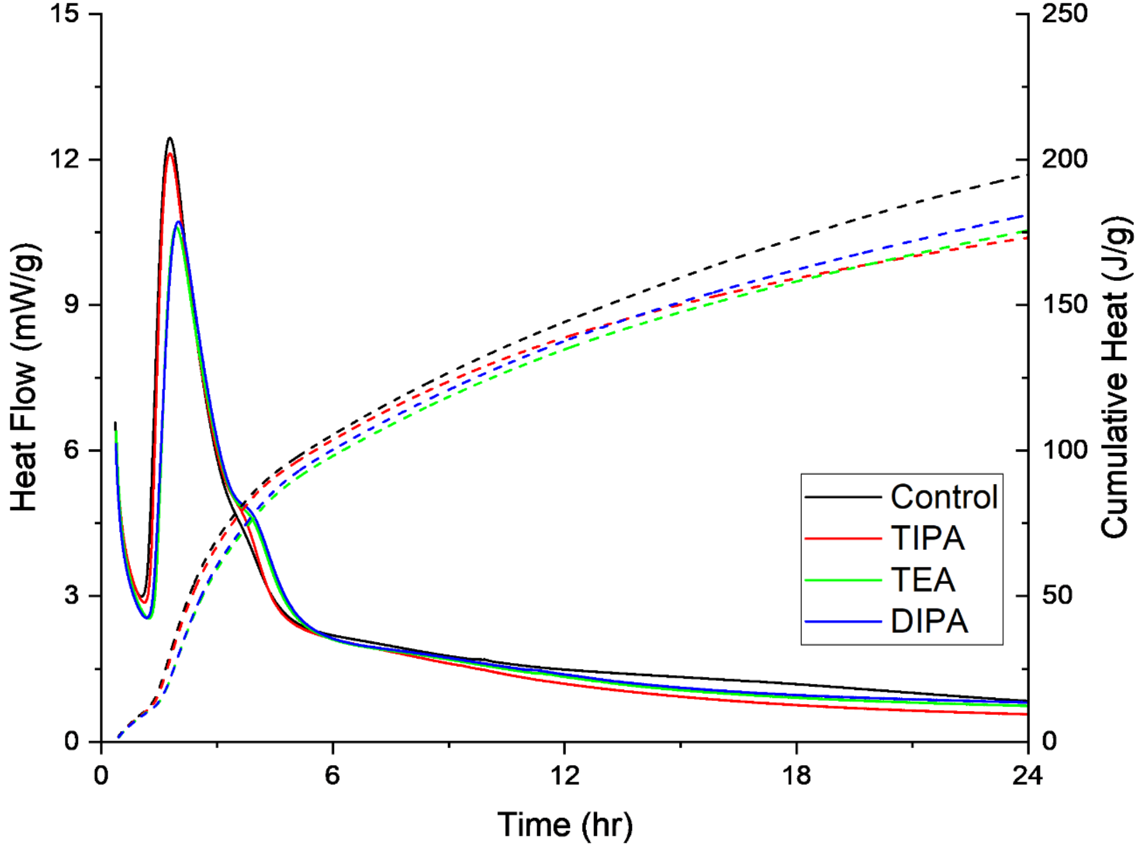
https://mcf.gatech.edu/tools/hitachi-su-8230-sem/

Rate of Reaction by Calorimetry

0 – 6 hours of hydration



0 – 24 hours of hydration

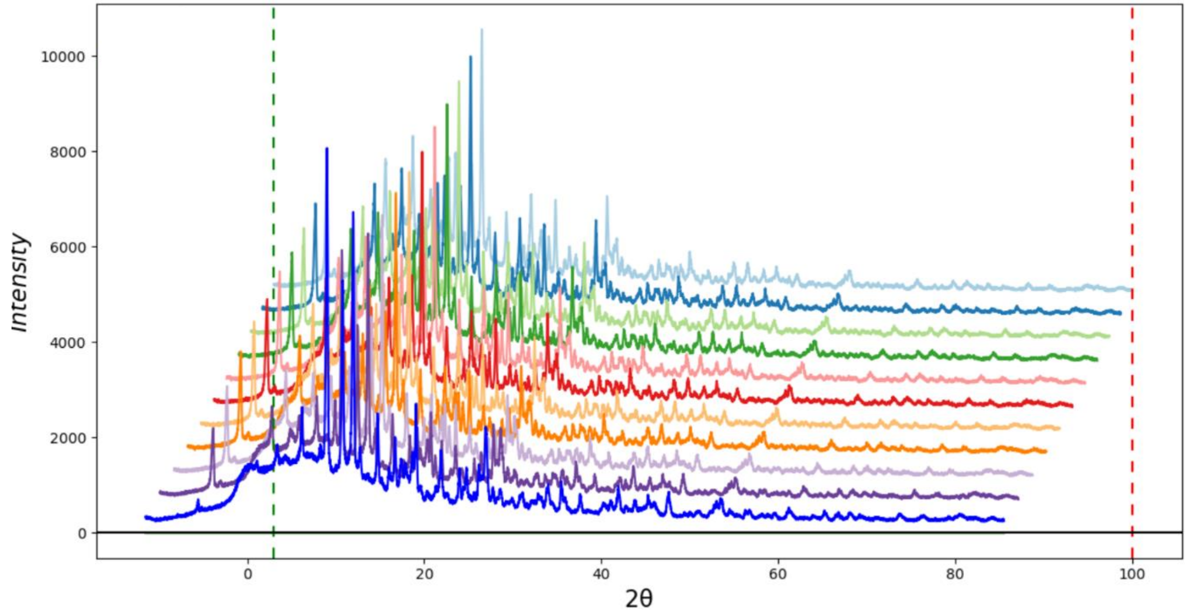


- Similar behavior between:
  - Control and TIPA
  - TEA and DIPA
- Longer latent period with alkanolamine samples

- All alkanolamines
  - Enhance shoulder
  - Decrease heat between ~9 - 24 hours
  - Decrease cumulative heat

In-situ XRD Method

- Internal standard
  - 15% quartz
  - Mixed for 5 minutes
- Sample holder
  - Standard 2 mm deep powder sample holder
  - Custom-fabricated magnetic ring
  - 8-micron thick Kapton foil

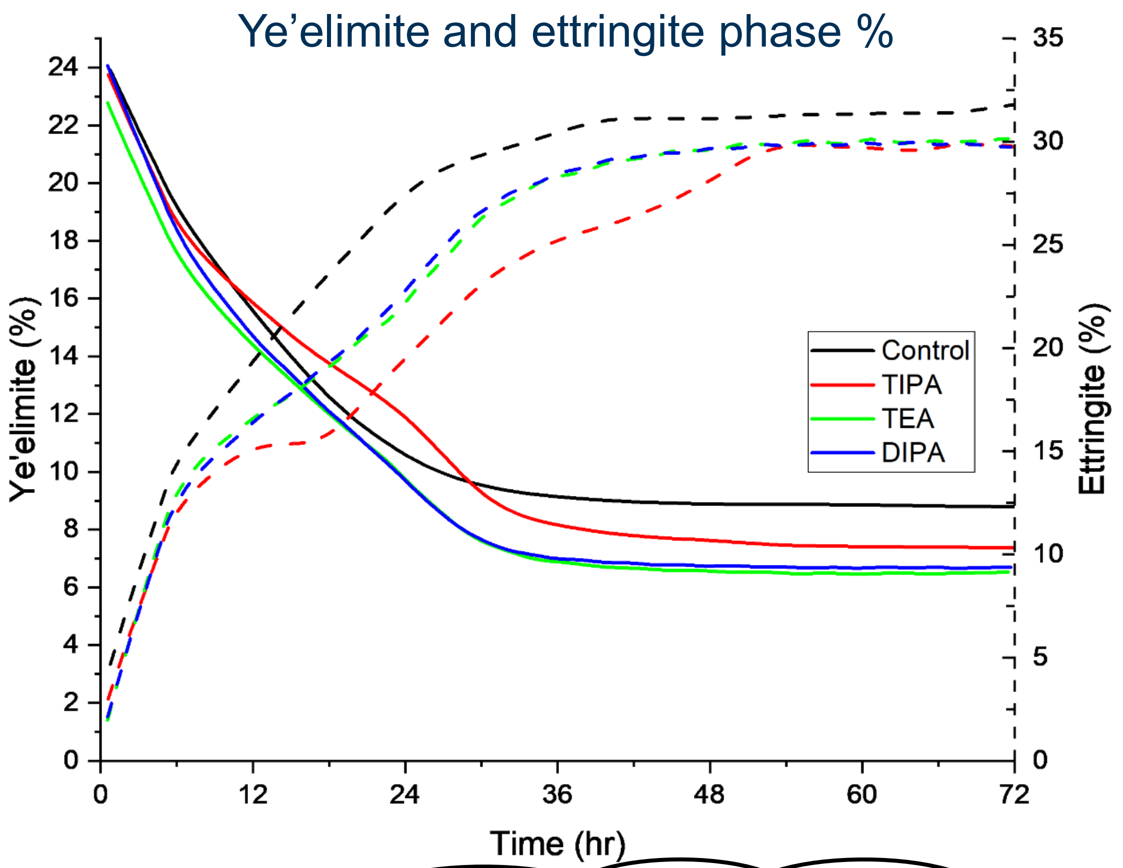


Ring and sample holder

CSAB paste sample

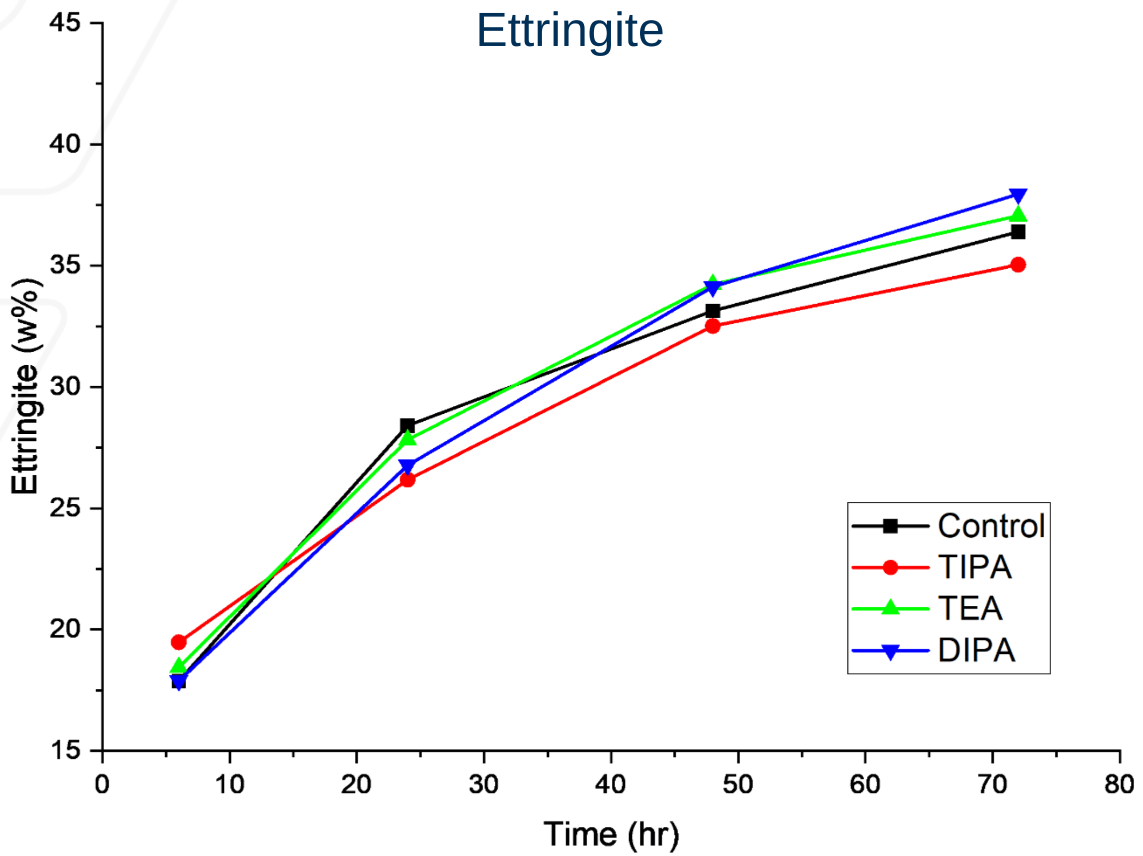
In-situ hydration by XRD

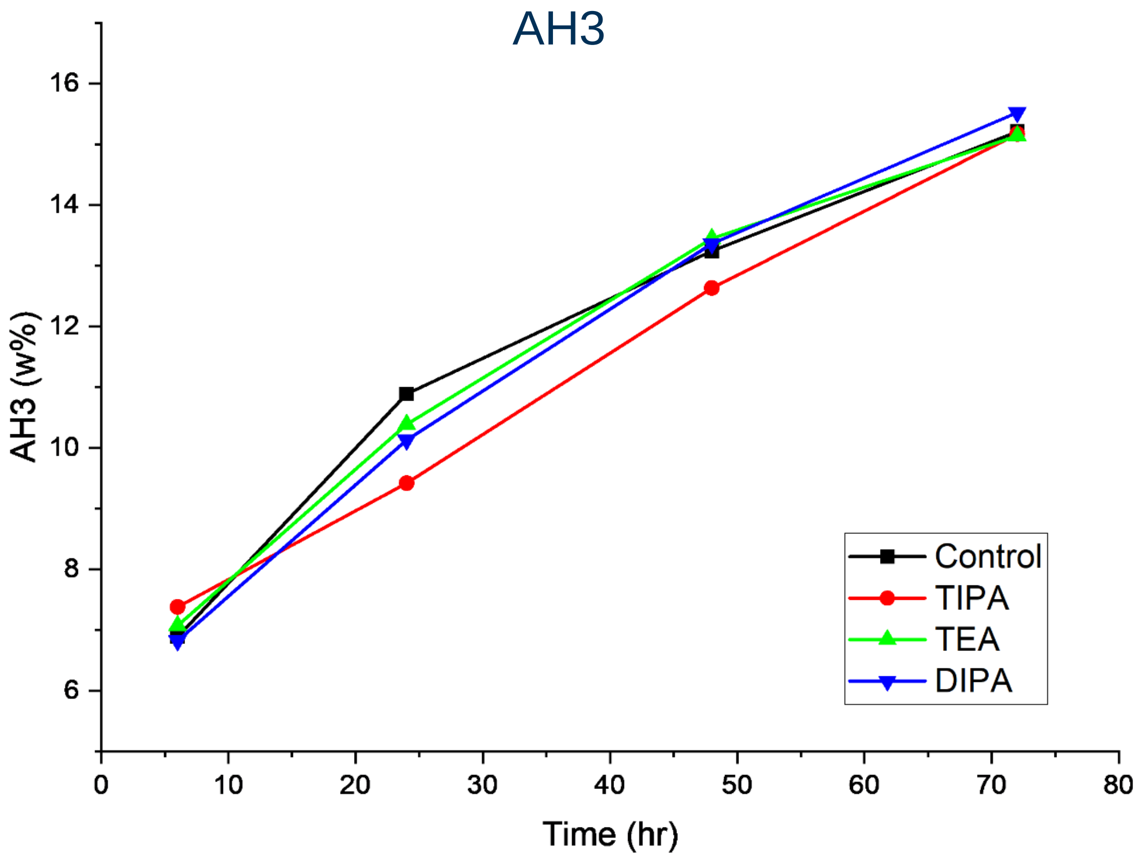
- Slower rates of ettringite formation with alkanolamines
  - Slightly 0 - ~6 hours
  - More significant ~6 - ~48 hours
- Decrease in ye'elimite dissolution rate for TIPA containing sample
- Greater ye'elimite consumption
  - Decrease in ettringite formation
- Other phases
  - Anhydrite shows similar trends as ye'elimite
    - Decrease in dissolution rate at ~6 - ~18 hours
    - Greater consumption in alkanolamine samples
  - No consumption of C2S and C3A



Ye'elimite + anhydrite + water → ettringite + AH_3

Product Formation from TGA

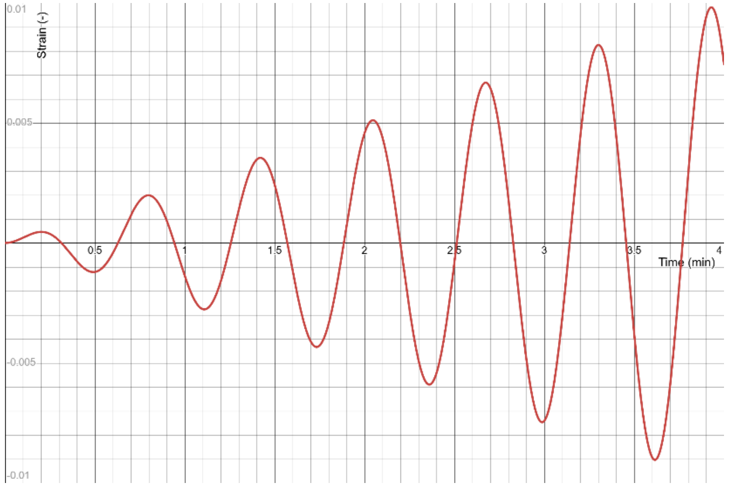




- Alkanolamines affect ettringite formation more than AH3
- TIPA has greater effect than TEA or DIPA
- Alkanolamines affect ettringite and AH3 differently at 6 hours vs. later
  - TIPA increase hydration products at 6 hours, but decreases later
  - TEA and DIPA have little affect at 6 hours, less at 24 hours, and greater ettringite later

Amplitude-sweep Oscillatory Rheometry Method

- Apparatus
  - 50 mm parallel plates
  - 80 grit sandpaper
  - 1 mm gap
  - 25 °C
- Procedure
  - Frequency: 10 rad/s
  - 24 points over 0.001% – 1% strain
- Results
  - Storage modulus, G’ (elastic behavior)
  - Loss modulus, G’’ (viscous behavior)
  - Limit of linear viscoelastic region



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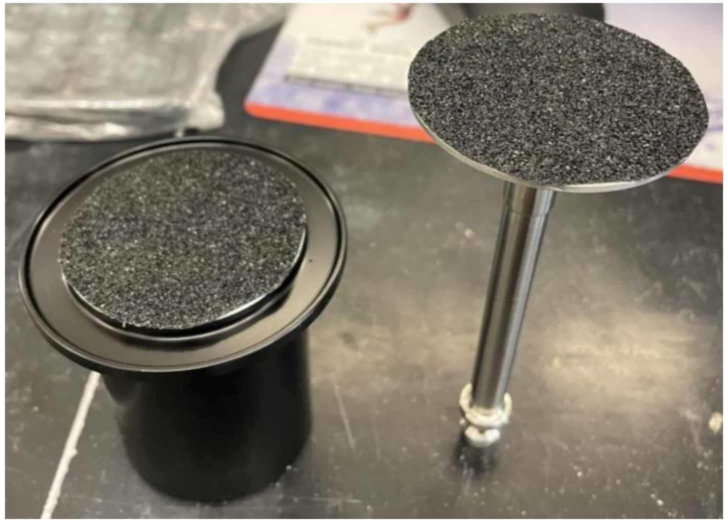
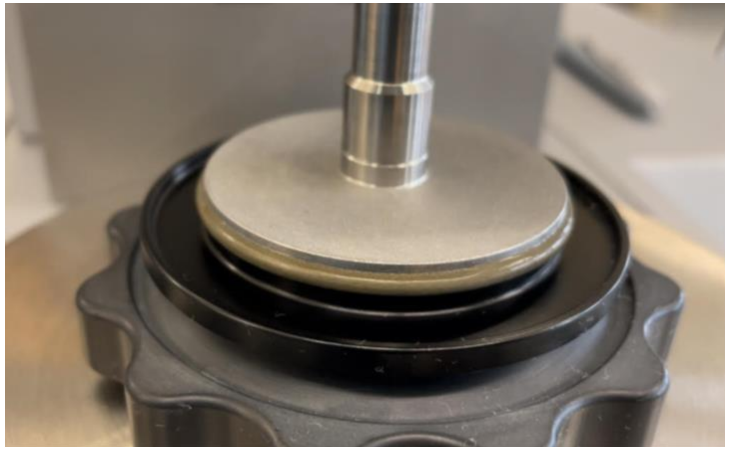


Courtesy of Prof. Burak Uzal



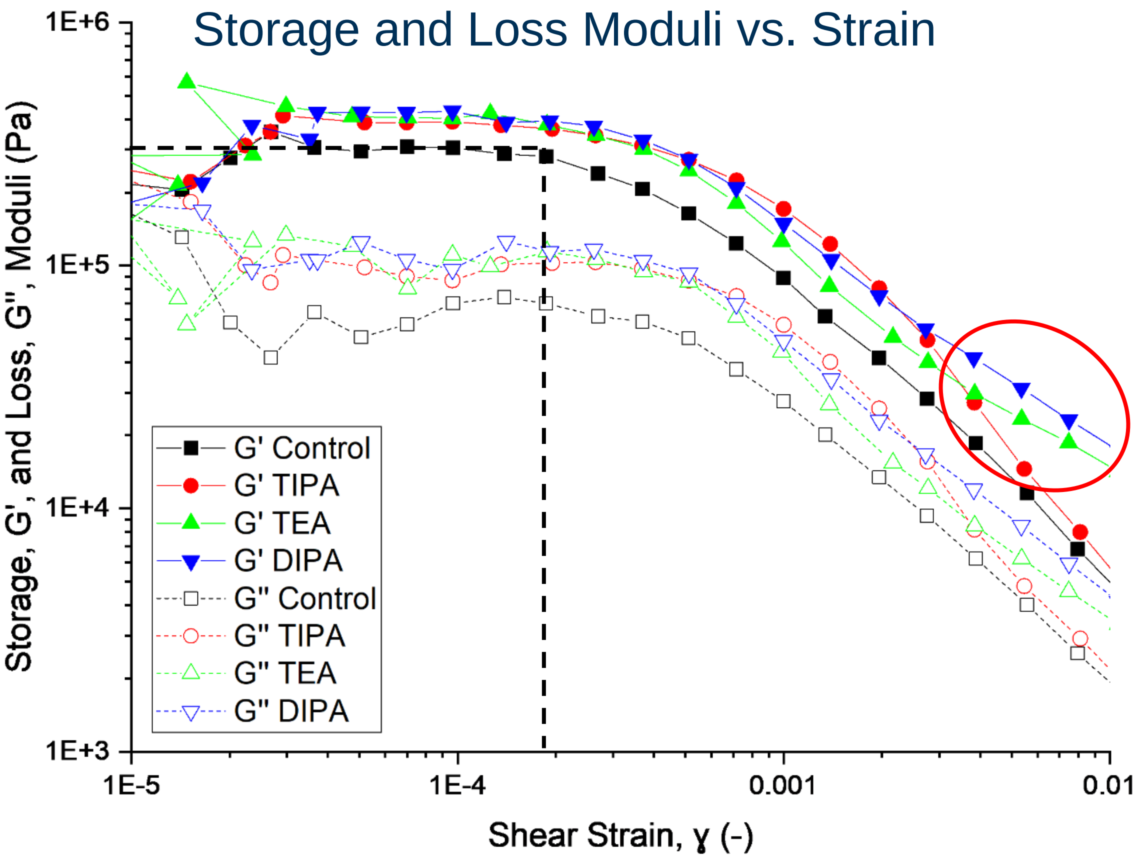
Courtesy of Prof. Burak Uzal

Rheology by Amplitude-sweep Oscillatory Rheometry

- Greater G’ and G”
  - Higher stiffness
  - Lower workability
  - Only slightly, significant differences are on orders of magnitude

- Larger linear viscoelastic region in samples with alkanolamines

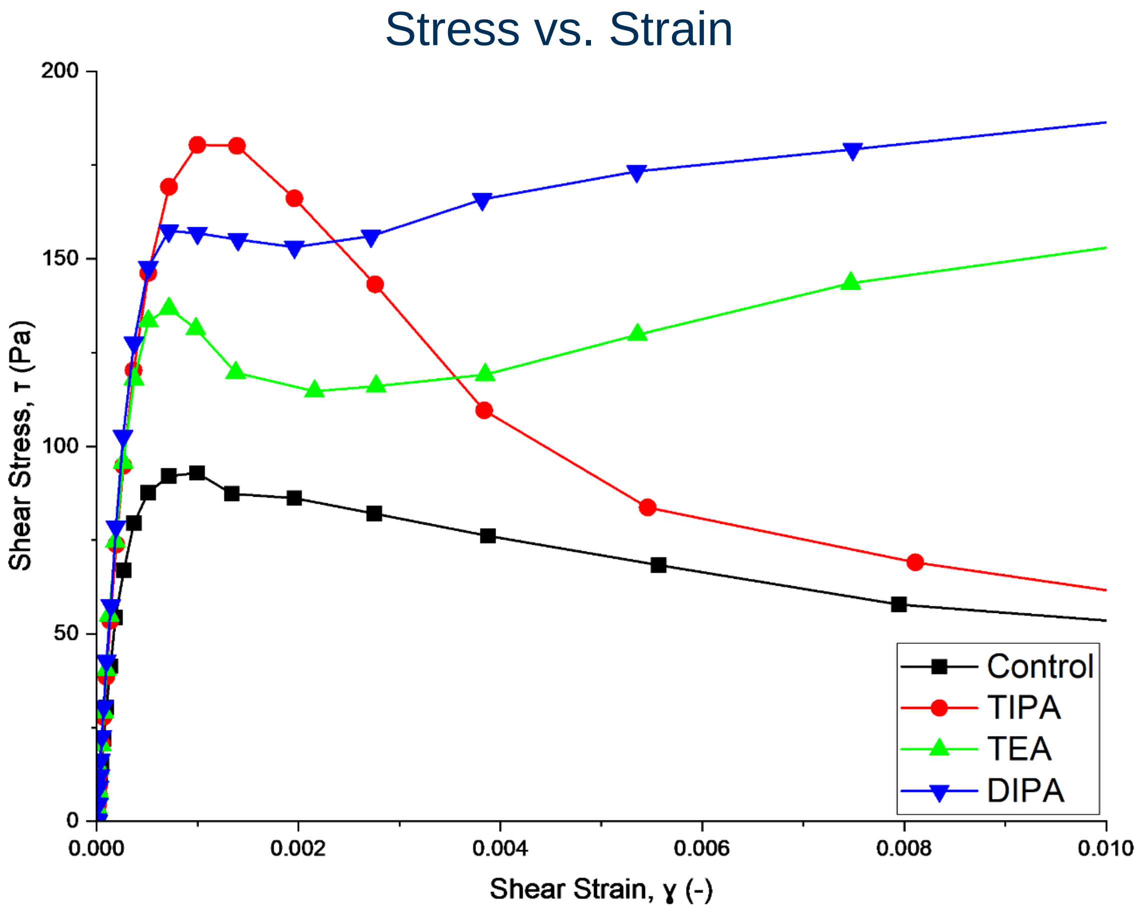
- “Curving out” behavior in TEA and DIPA



Rheology by Amplitude-sweep Oscillatory Rheometry

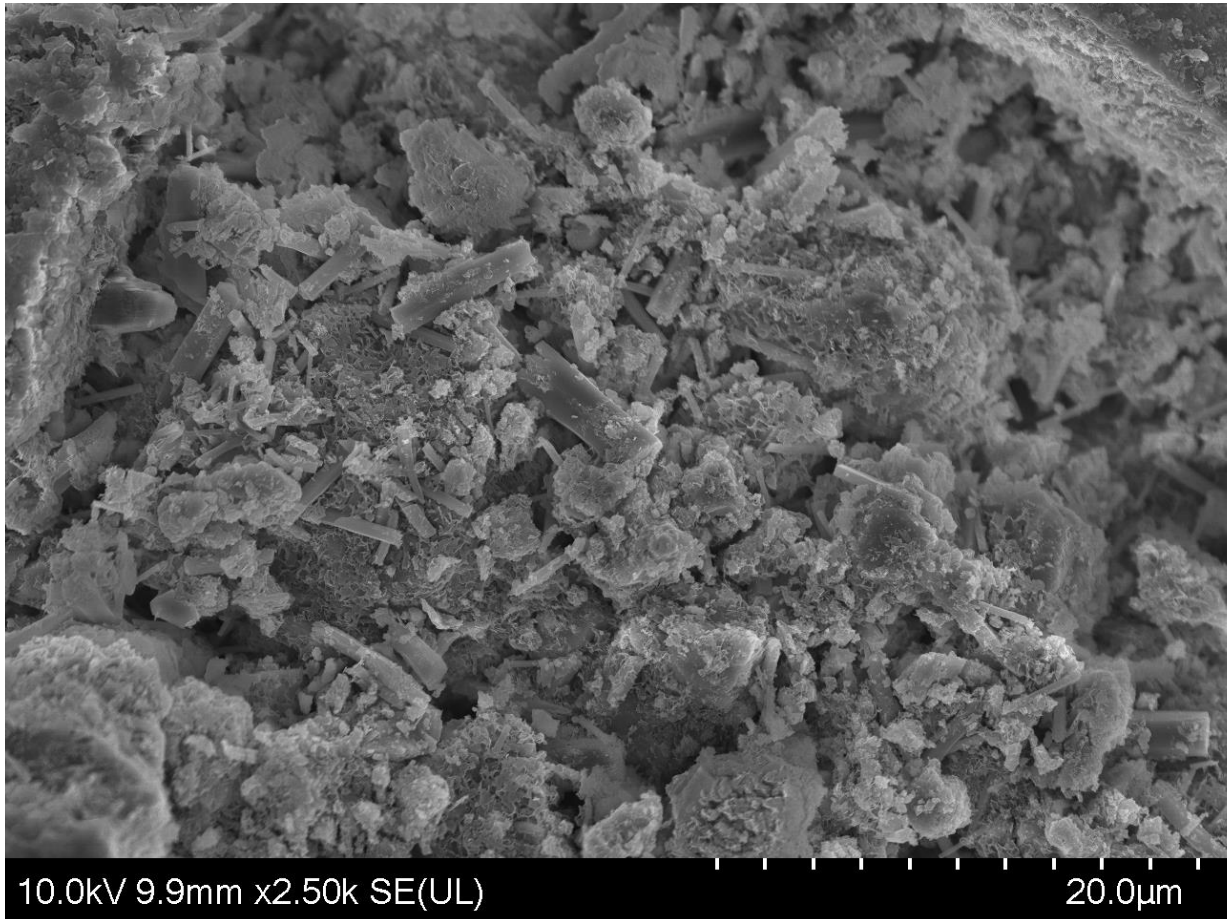
- Same data, different visualization

- Greater yield stress in samples with alkanolamines
  - TIPA > DIPA > TEA
- Behavior similar to strain hardening in TEA and DIPA containing samples
  - Also behaved similarly in calorimetry
- These properties may be beneficial in 3D printing applications



SEM

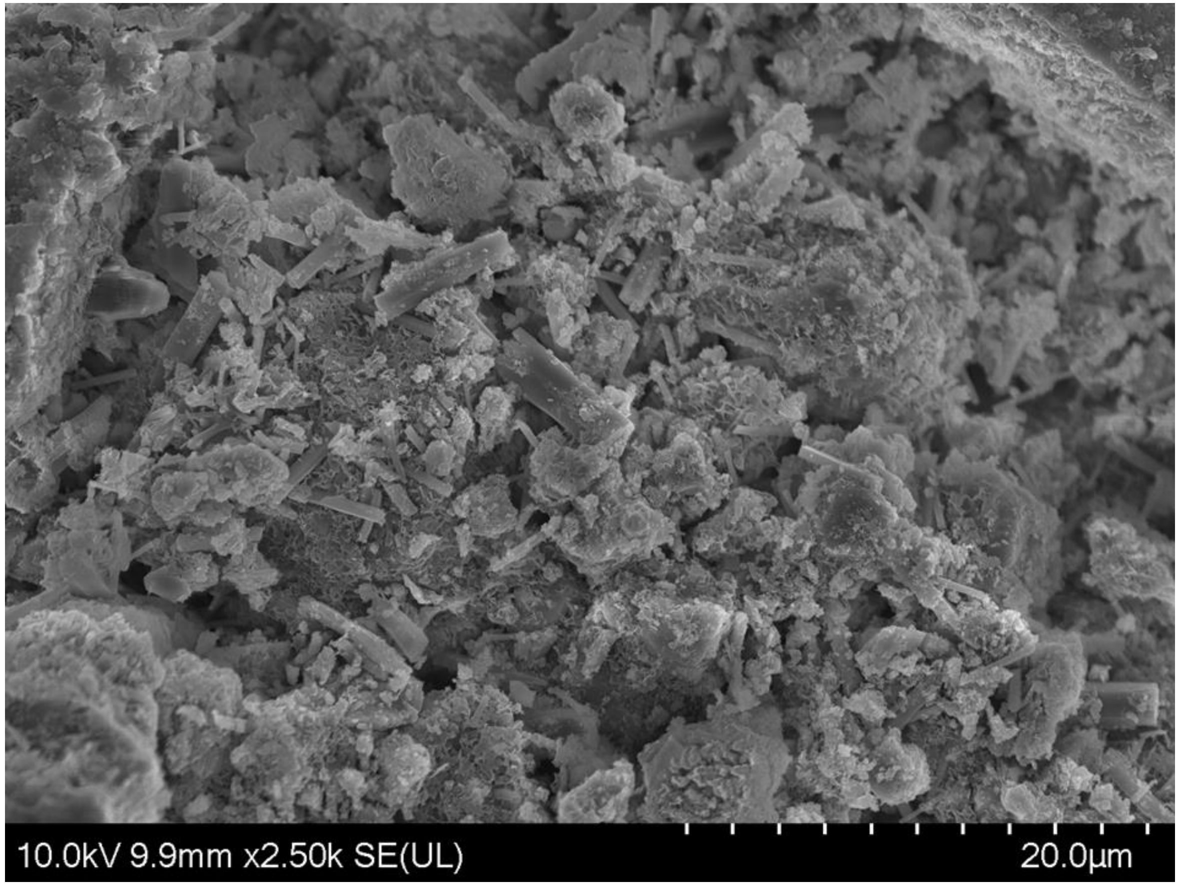
- Ongoing work
- In PC:
  - Affect C-S-H and CH morphology
  - Lack of agreement about ettringite morphology
- XRD and TGA results suggest possibility of poorly crystalline ettringite
- Could changes in rheology result from morphology?



CSAB paste at 2 hours of hydration

Summary

- Alkanolamines do affect hydration of CSAB differently than PC
  - TEA and DIPA delay hydration peaks
  - All decrease in heat of hydration
  - Changes in hydration product amount
  - All increase stiffness and decrease workability
  - Ongoing work to link those changes to morphology
- Possibility to use alkanolamines to tailor desired properties
  - Rheology
  - Set time
  - Dimensional stability
  - Strength
- Can extend to other systems that form ettringite



Acknowledgements

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Questions?

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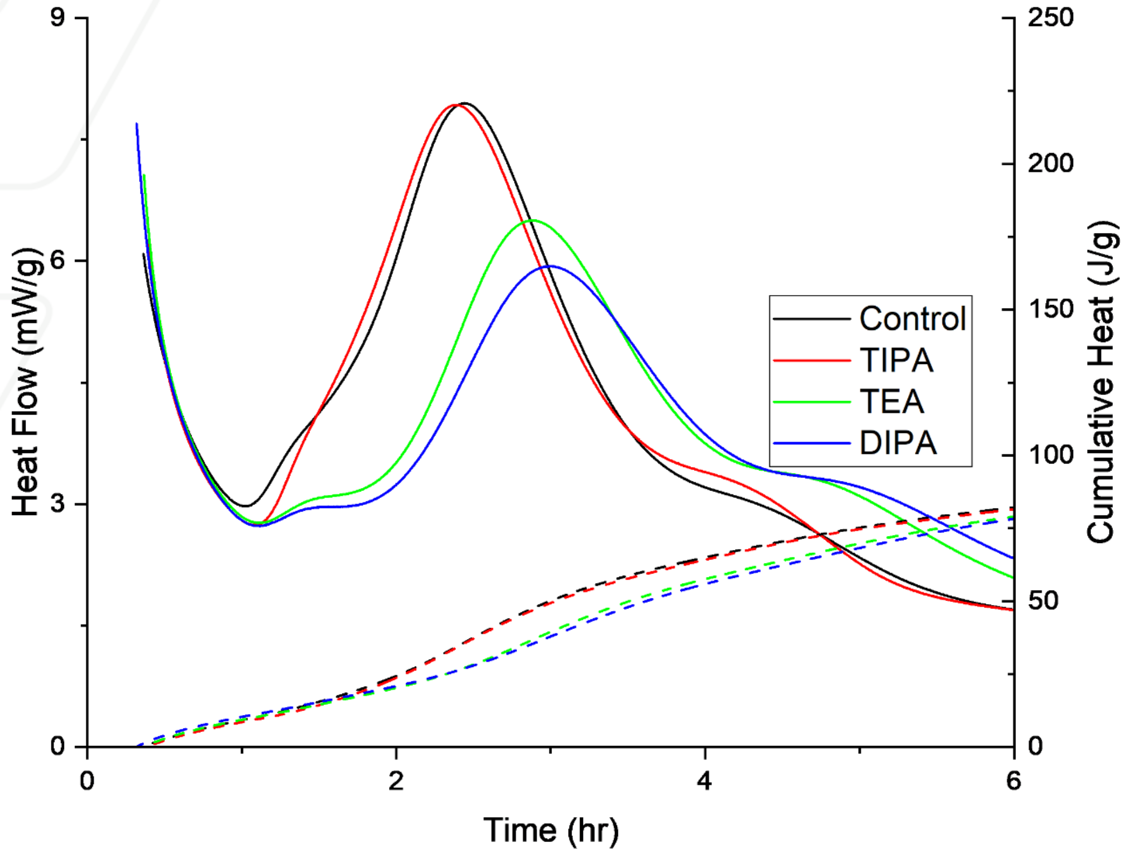
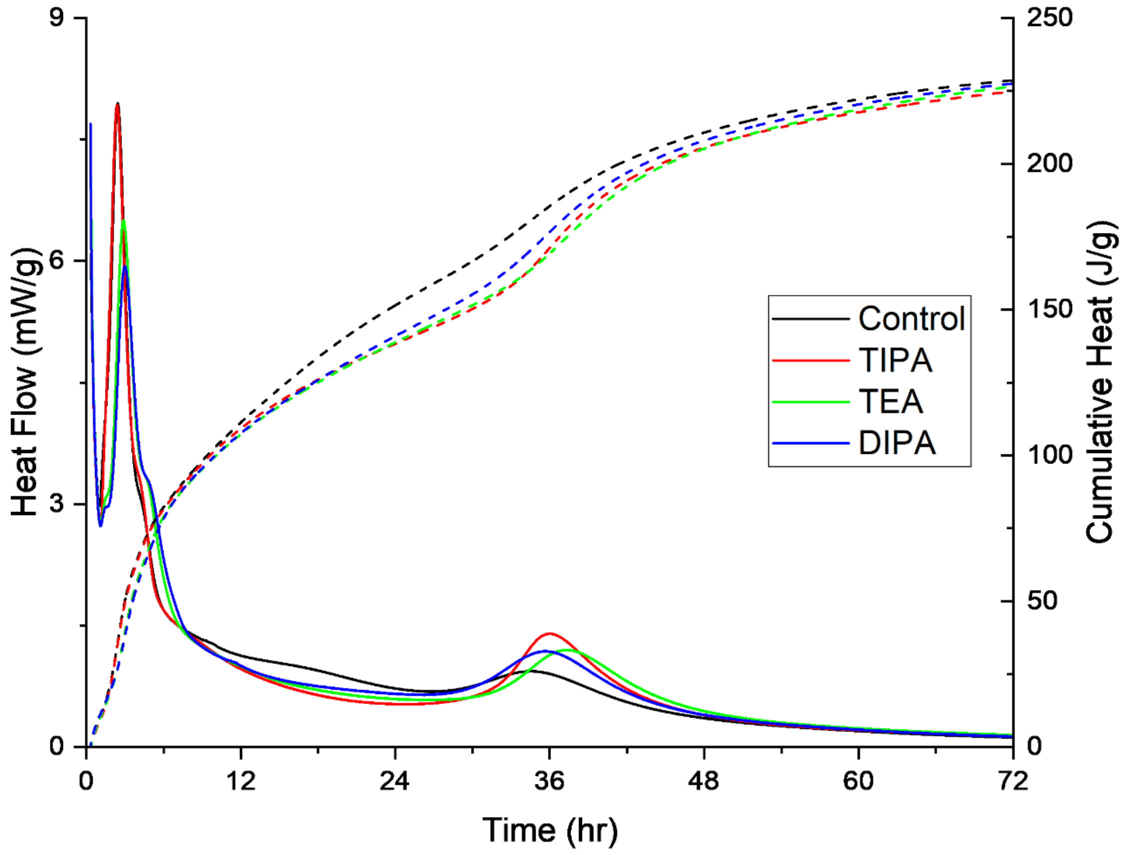
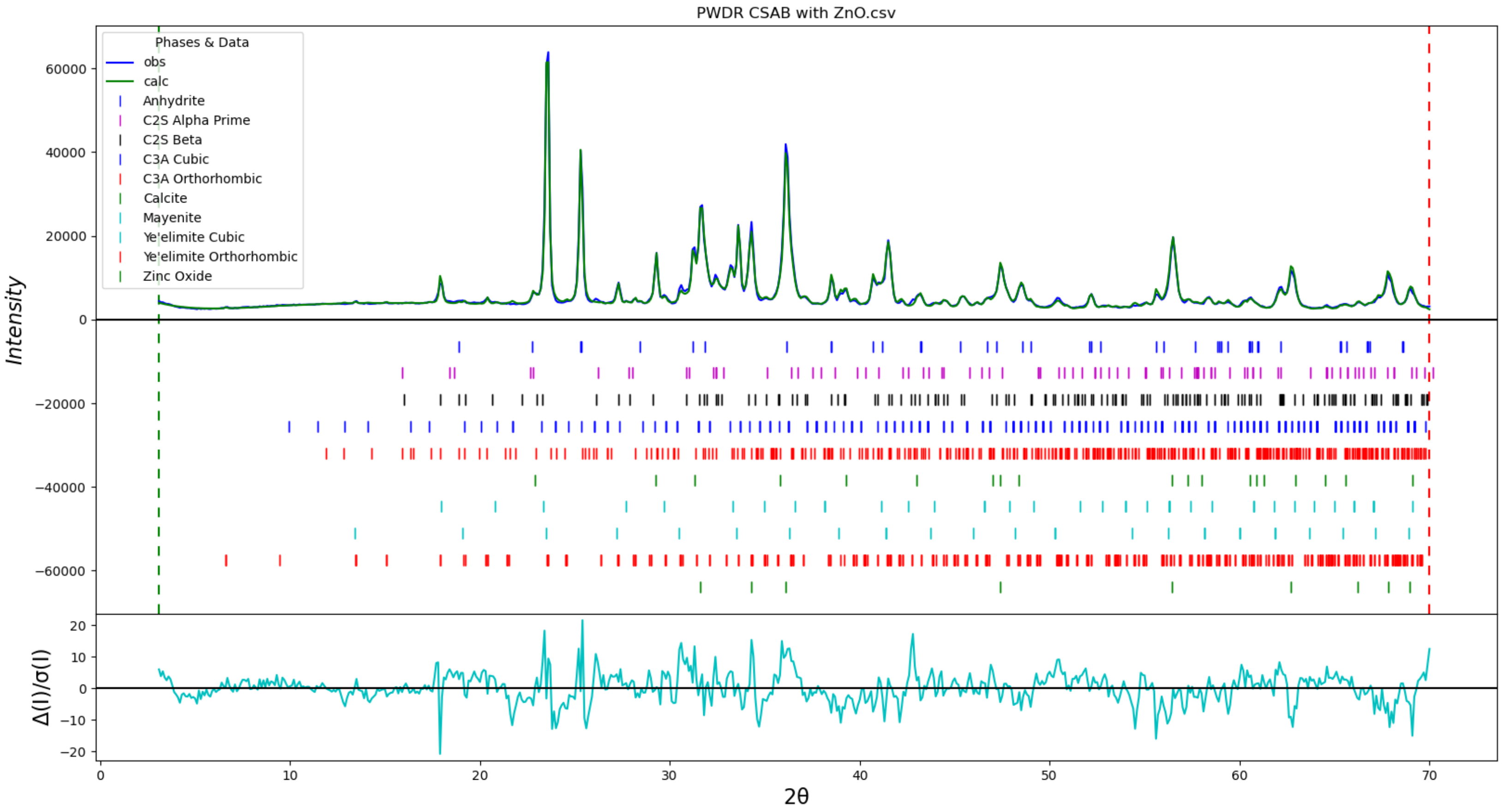
CSAB and Quartz Calorimetry



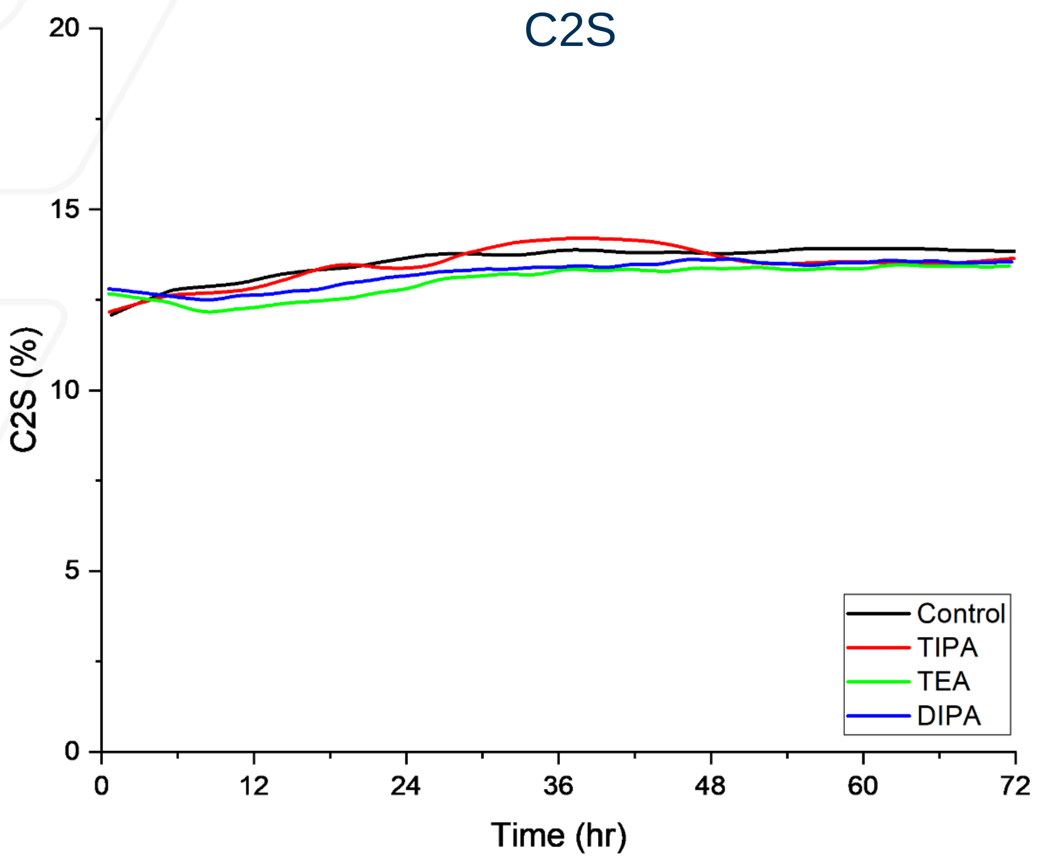


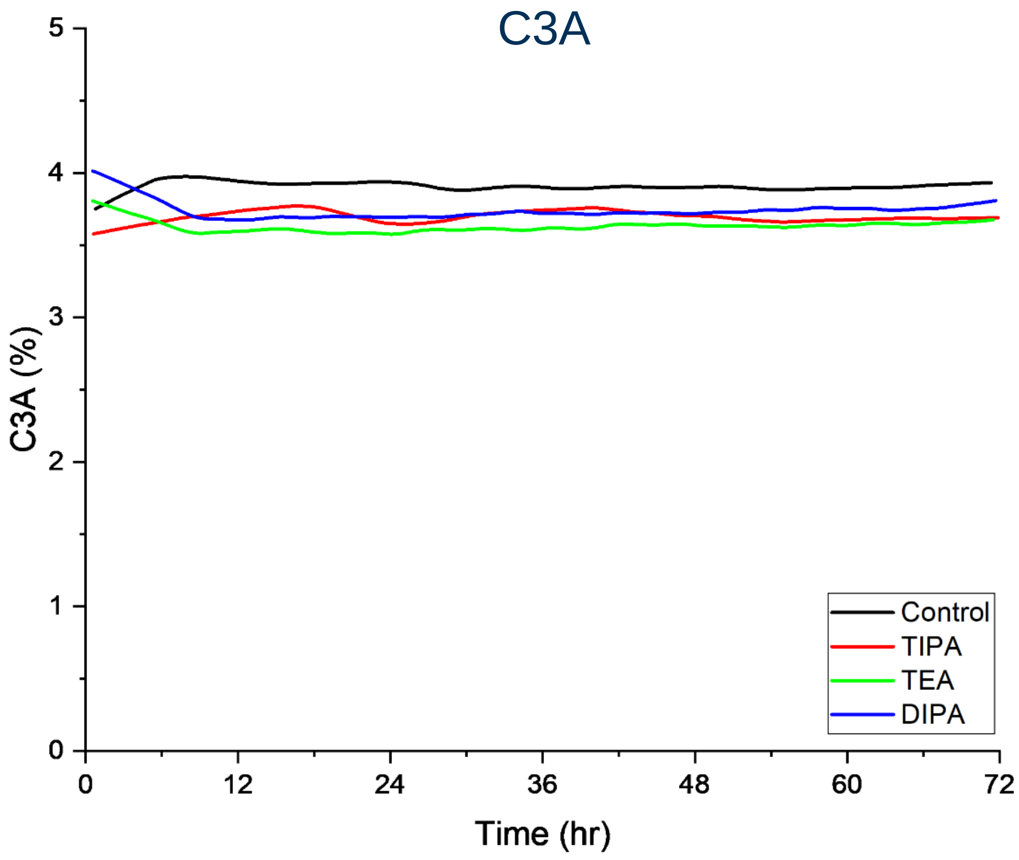
XRD Anhydrous CSAB

Phase	Weight (%)
Anhydrite	19.0
Ye'elimite	36.5
Calcite	6.5
C2S	18.2
Mayenite	2.5
C3A	5.9



In-situ XRD C2S and C3A





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Portland Cement Rheology