Effects of Fly Ash on the Properties of Calcium Aluminate Binders

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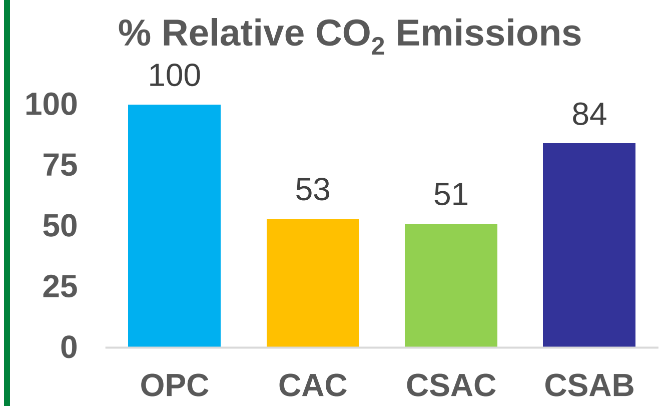
Calcium Aluminate Cement

- Ordinary portland cement production accounts for CO_2 emissions ~8% globally
- Urgent need for alternative binders is required
- Calcium Aluminate Cement (CAC) also known as high alumina cement (HAC)–originally developed by LaFarge in 1909
- Raw materials necessary for the manufacture of CACs are limestone and bauxite
- Calcination temperature is 1200 ºC
- Major Phases – Monocalcium aluminate (CA), Di-calcium aluminate (CA_2)
- Minor Phases – Mayenite ($C_{12}A_7$), and Ferrite (C_4AF)



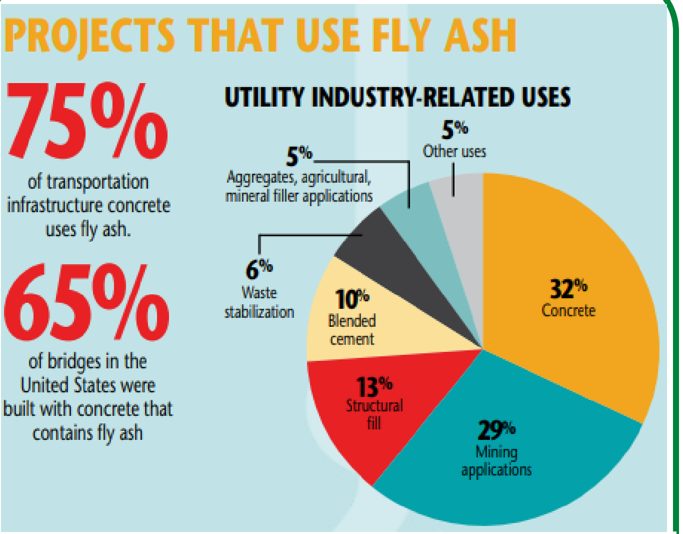
Relative CO_2 emissions for alternative cements on a gram-per-gram of material basis compared to ordinary portland cement

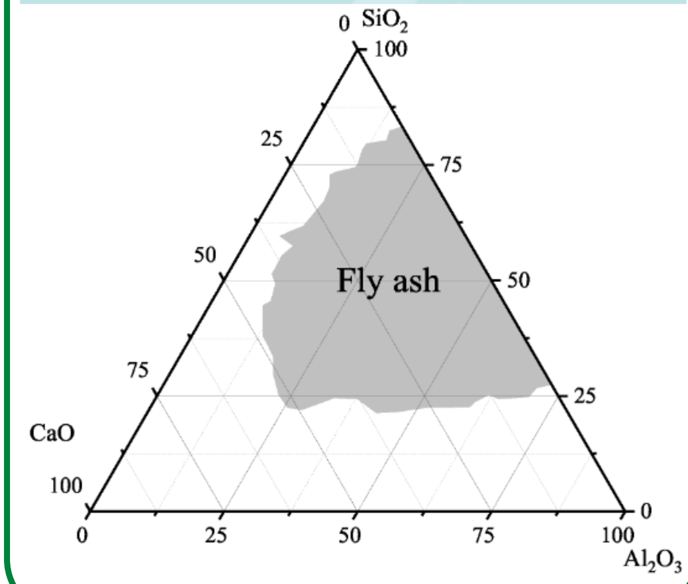
K.E. Kurtis et al, MRS Bulletin. 40 (2015)

CaO – C; SiO_2 – S; Al_2O_3 – A; Fe_2O_3 – F; SO_3 - $; H_2O – H

Research Significance : Fly Ash

- Fly ash (FA) is a -
  - Coal combustion byproduct
  - Widely used as a supplementary cementitious material (SCM)
  - Classified as
    - Class C and Class F
- The chemistry of FAs significantly impacts the hydration kinetics and compressive strength of the binders
  - Pozzolanic Reaction
  - The Filler Effect
  - Effect of Sulfur Content
- Batch-to-batch variation in chemical compositions
- No standardized method to estimate the reactivity of FA

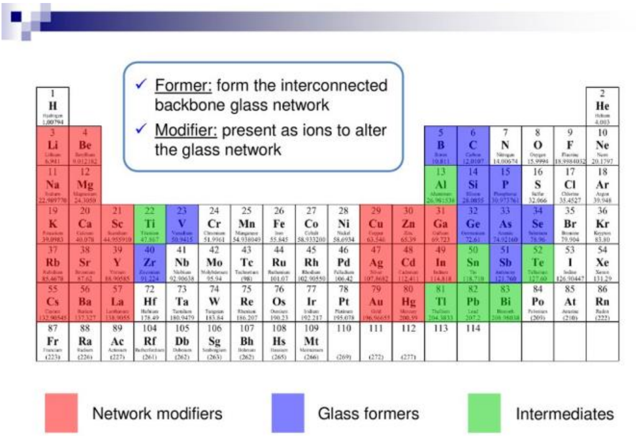


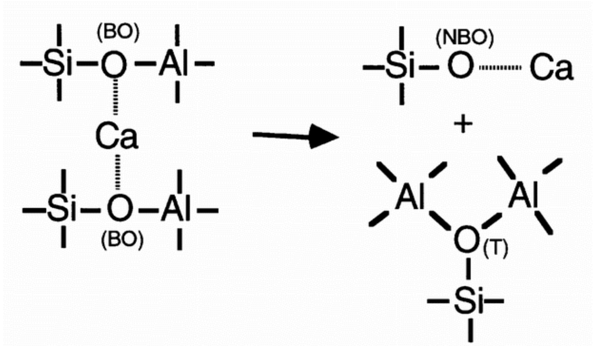


M. Amran et al, Materials 2021, 14, 4264.

Topological Constraint Theory (TCT)

- Popular tool to help
  - Better understand the link between the structure and properties of disordered materials
  - Simplify a complex material into a simple number
    - Based on the chemical bonds between atoms
- TCT consists of
  - Network formers and network modifiers
- Can be applicable to calcium aluminosilicates
  - Especially fly ashes
- Reduces the complexity of fly ashes to a single number called “*number of constraints (n_c)*”
- Proxy for reactivity of fly ashes
  - Higher n_c, higher rigidity, lower reactivity
  - Lower n_c, lower rigidity, higher reactivity





J.F. Stebbins et al, Nature. 390 (1997) 60–62

Materials and Methods

- 13 unique FAs with–
  - varying chemical compositions
  - Replace CAC at 10-50%$_{mass}$
  - Constant l/s ratio of 0.5
- Isothermal microcalorimeter was used to measure the heat release of [CAC+FA] binders
- Compressive strength of [CAC+FA] binders was tested based on ASTM C109
- X-ray diffraction and thermodynamic modelling were used to investigate phase assemblage in [CAC+FA] binders
- Thermodynamic Phase Assemblage – Gibbs Energy Minimization Software (GEMS)

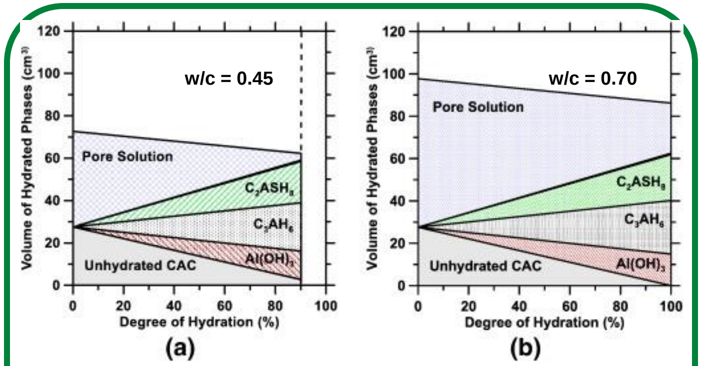
TAM IV Microcalorimeter

Instron-5881

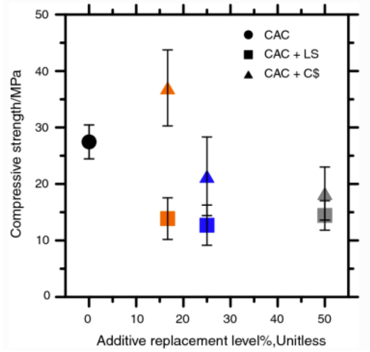
Panalytical X-pert PRO

CAC Hydration

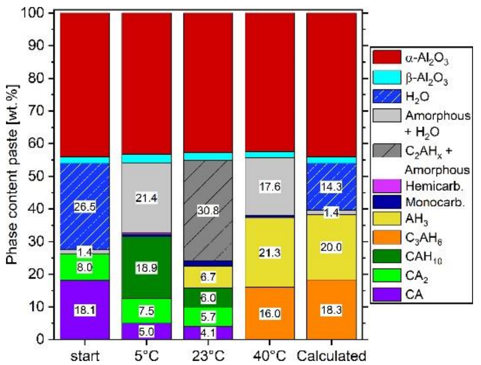
- Calcium aluminate hydrates (CAHs) and calcium aluminate silicates (CAS)
- CACs hydration
  - Composition
    - Anhydrous phases presence affects the hydrated phases
  - Water-to-cement ratio (w/c)
    - Formation of meta stable and stable phases
  - Additives
    - Formation of different hydrates affects the strength
  - Temperature dependent
    - Higher temperatures, T > 40 ^{o}C, Hydrogarnet formation
    - Moderate temperatures, 20 ^{o}C < T < 35 ^{o}C, C_2AH_8 formation
    - Lower temperatures, T < 20 ^{o}C, CAH_{10} formation



Falzone. G, et al., CCR, Vol 72, 2015



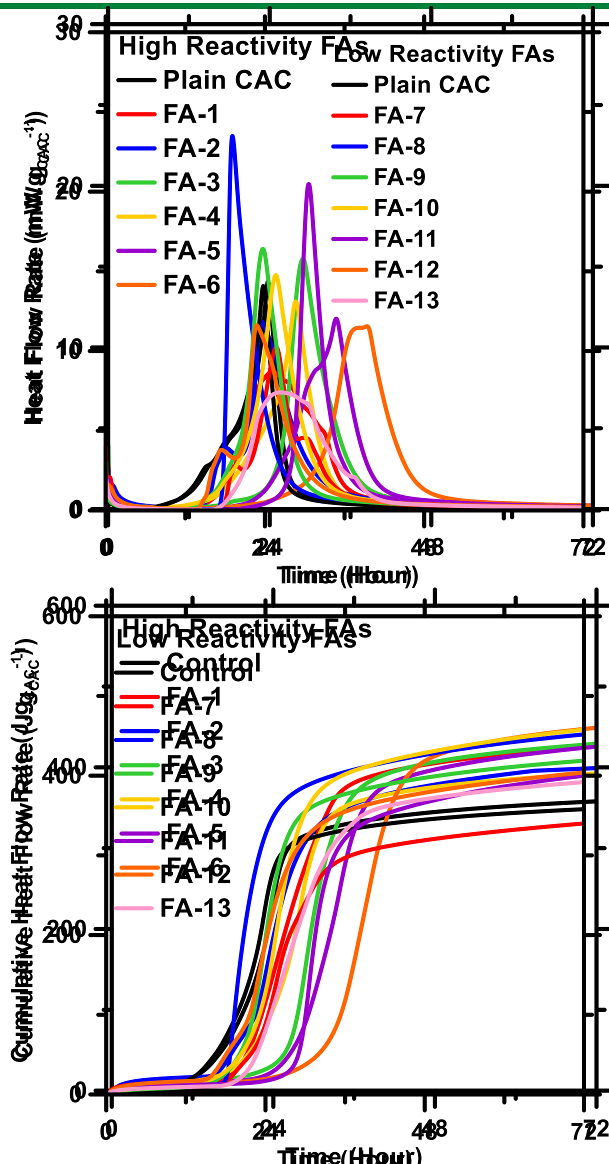
Lapeyre. J, et al., J Therm Anal Calorim, Vol 147, 2022



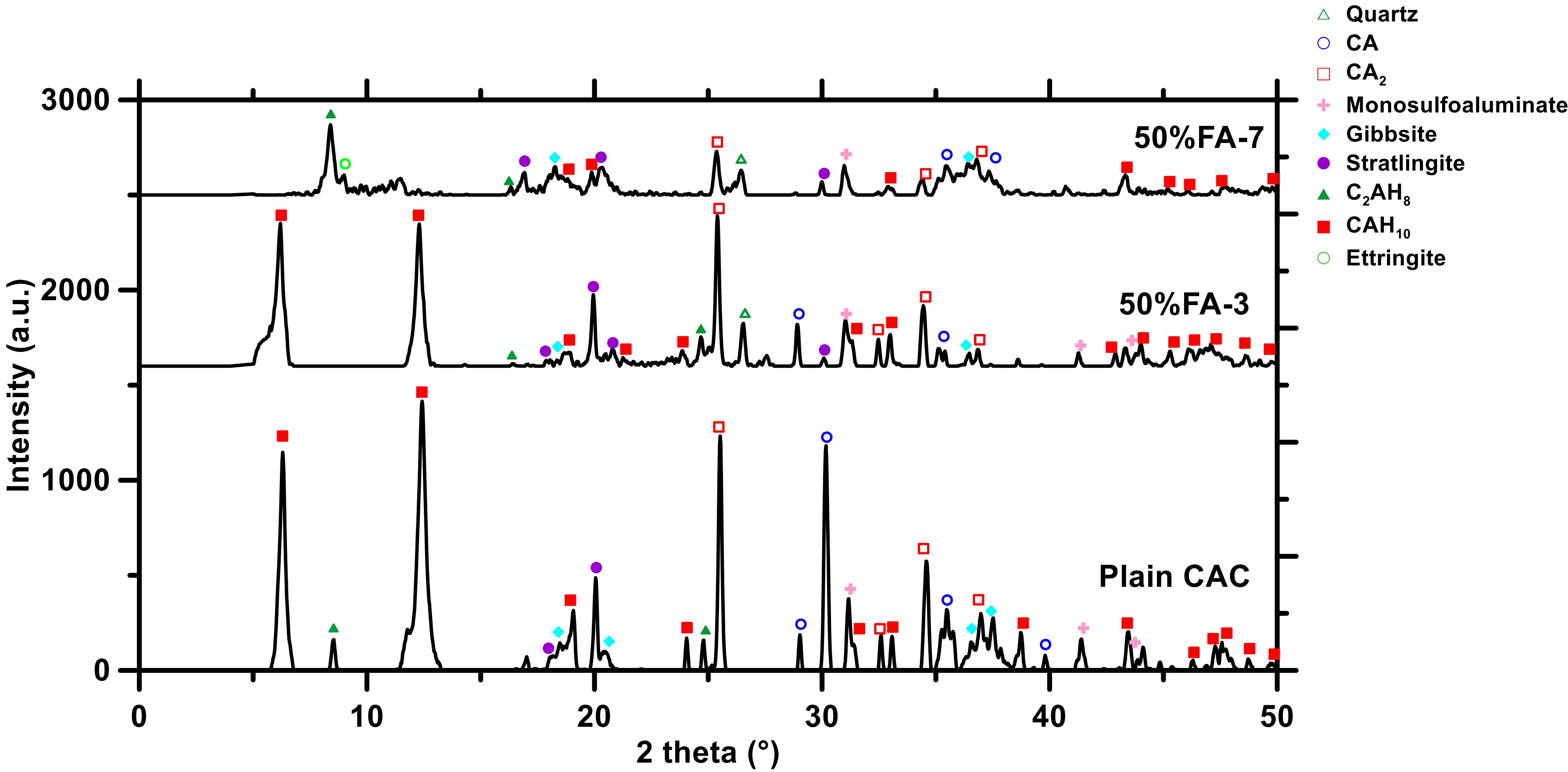
A. Koehler et al., Ceramics International, Vol. 49(3), 2023

Results : Hydration Kinetics

- High Reactivity FAs
  - Decelerate early-age hydration of CAC
  - High reactivity causes greater cumulative heat release
  - The magnitude of filler effect is less influential than higher reactivity of FAs
- Low Reactivity FAs
  - Shorten induction period of CAC
  - High volume of crystalline content
  - FAs act as fillers
  - FA-8 and FA-11 filler effect
  - FA-7 has low cumulative heat



X-Ray Diffraction Analysis

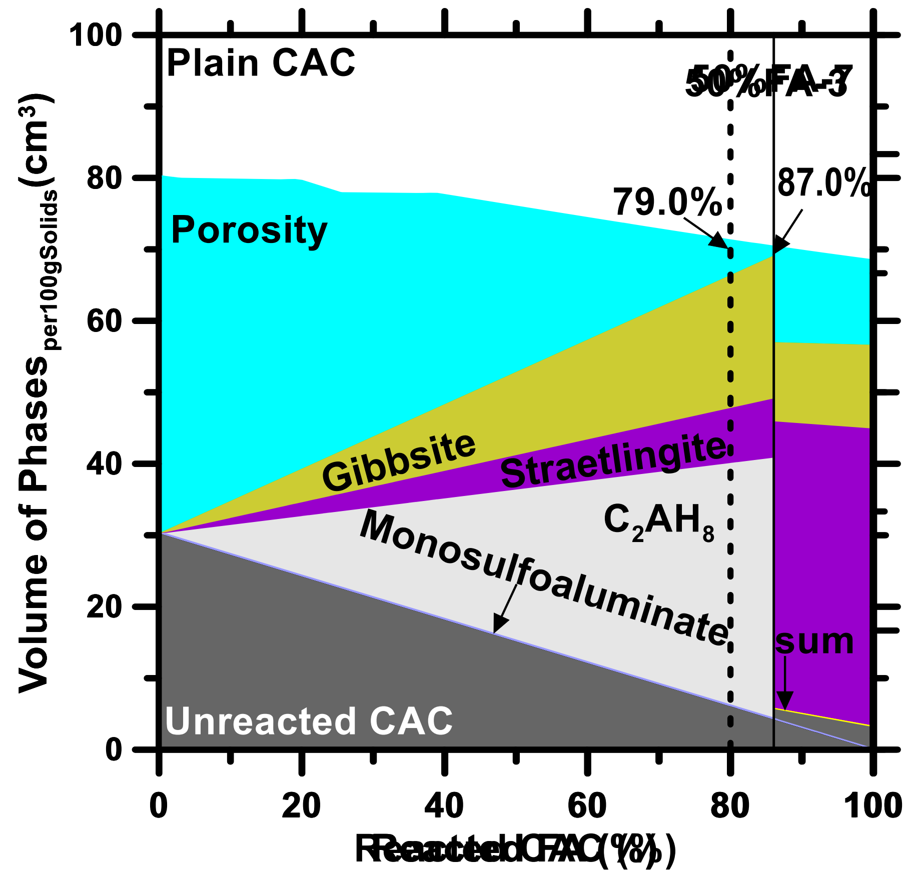


Comparison between Plain CAC, [CAC + high reactivity FA], and [CAC + low reactivity FA]

Thermodynamic Phase Assemblage

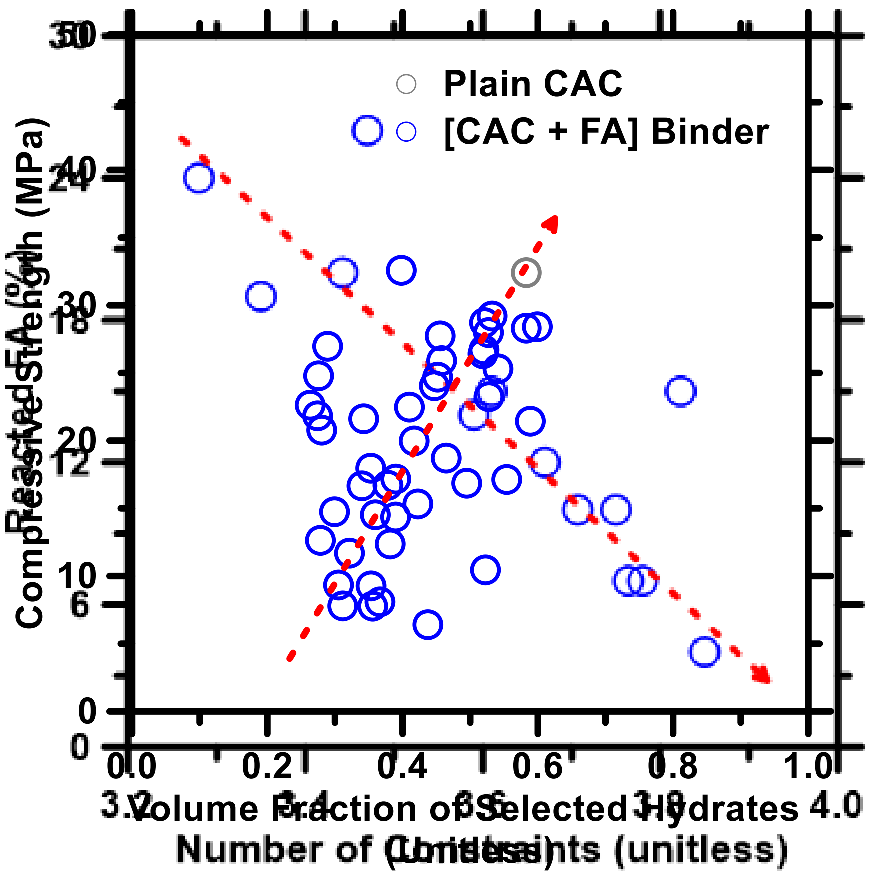
Phase assemblage at 3 days

- Degree of hydration of CAC at 3 days was 79.0%
- The hydration is arrested in plain CAC at 87% reaction of CAC
- C_2AH_8 instead of CAH_{10}
- [CAC + 50% FA-3] contains more amount of straetlingite
- [CAC + 50% FA-7] contains less amount of Straetlingite



Reactivity of FAs

- Correlation between
  - Volume fraction of hydrates vs compressive strength
  - Selected hydrates are: CAH_{10}, C_2AH_8, and Sträetlingite
- Degree of reaction of FA was determined
  - Independent of the replacement level
  - Monotonically decreases with an increase in n_c
  - Reactivities of FAs are between 4-to-26%



Conclusions

- High n_c exhibit
  - low intrinsic dissolution rate
  - lower potential to react with CAC phases
  - lower cumulative heat and compressive strength
- Low n_c exhibit
  - higher intrinsic dissolution rate
  - higher potential to react with CAC phases
  - higher cumulative heat and compressive strength
- XRD and thermodynamic simulations show
  - Good correlation with the TCT
- Degree of reaction of a given FA—is independent of its content ($\%_{mass}$) in the binder — decreases with an increase in *number of constraints*

Thank You!

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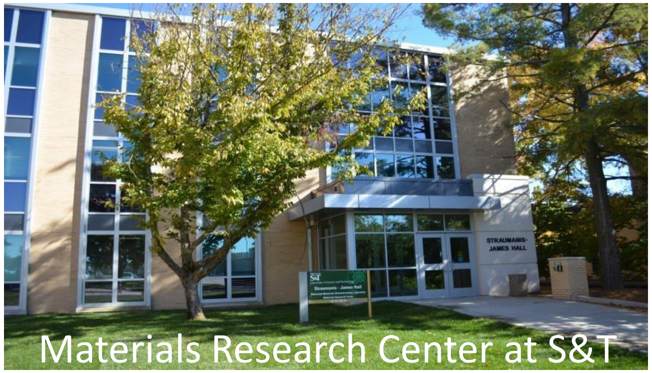

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Questions ?