Mechanochemical Activation of Basaltic Fines

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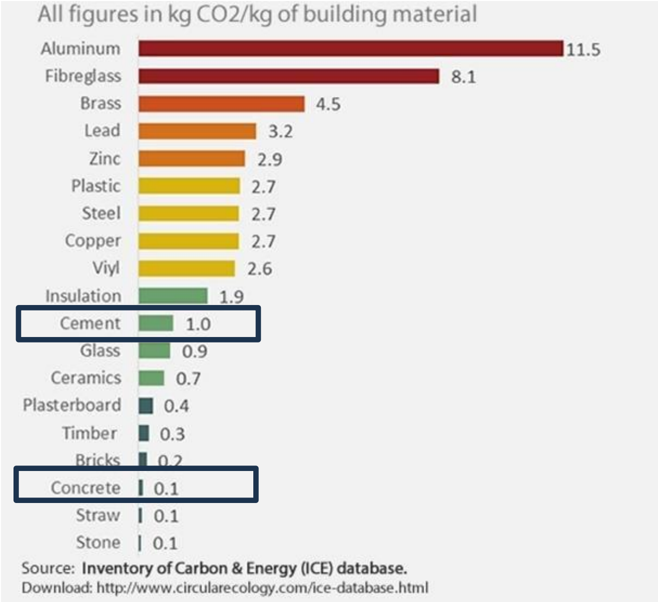
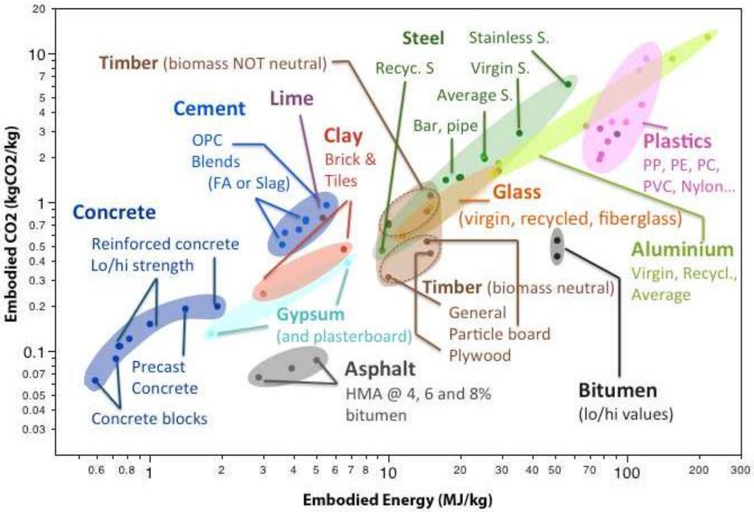
ACCESS LAB

CO_2 in Concrete

- Concrete contributes 6-8% global CO_2 emissions
- Not possible to replace concrete with any other material
- Cement, which is 15% of concrete by mass, is responsible for 90% of concrete emissions
- We must reduce cement CO_2 emissions



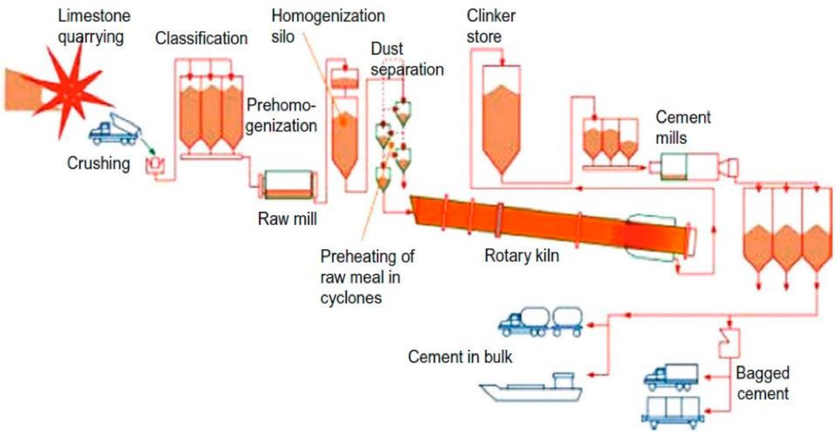


ICE database; Barcelo et al. MS 2014

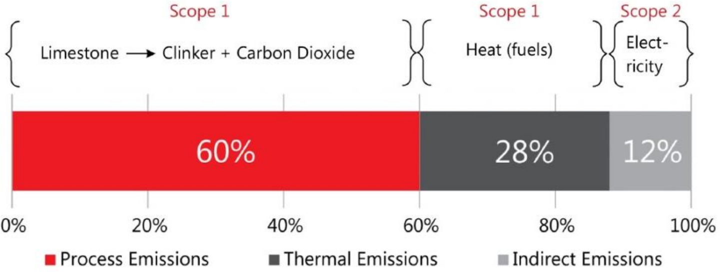
- Roadmaps to reduce emissions by 40% by 2030 and go carbon neutral by 2050

Cement CO_2 Emissions

- Limestone, clay, and other materials heated to 1450 °C to produce OPC
- Limestone decomposition reaction causes about 60% emissions $CaCO_3 \rightarrow CaO + CO_2$
- Reduce limestone in cement production
  - Portland limestone cement (PLC) with 5-15% limestone added post-heating



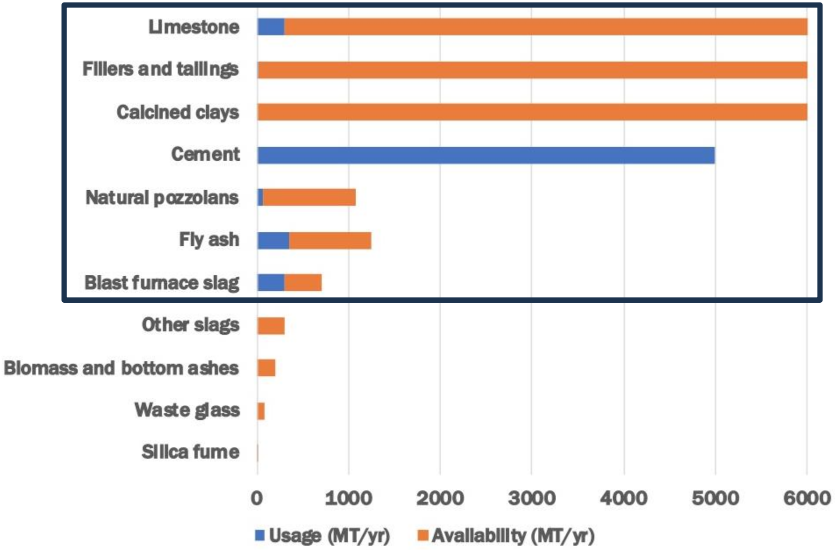
Cement Industry Federation; Rahman et al. Energies 2017



- Most conventional way to reduce concrete emissions is to reduce cement content in concrete
- Many novel methods that have not seen much testing at the concrete scale (scaling)
- Can we replace limestone with another Ca-source?

Supplementary Cementitious Materials (SCMs)

- SCMs, finely ground amorphous calcium aluminosilicates, critical to reduce CO_2 emissions
- SCMs provide significant benefits to concrete
  - Improve sustainability, fresh properties, later-age strength, and **durability**
- Fly ash, slag, and silica fume most commonly used
  - Often industrial byproducts
  - Increasing shortfalls being reported locally
  - How to identify novel SCMs?

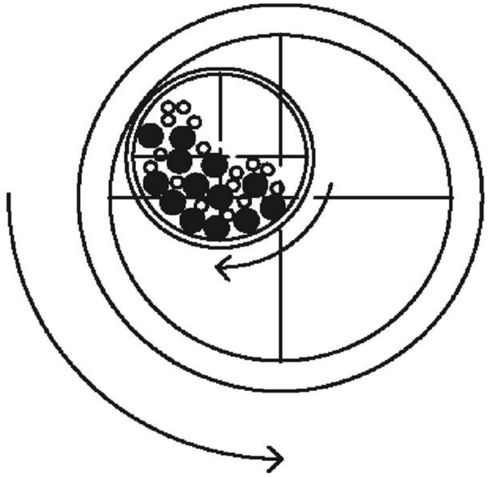


- Novel SCMs must be identified, characterized, and used for continued concrete CO_2 reductions
- Calcined clays, natural pozzolans, reclaimed fly ashes
- Manufactured SCMs: Thermal activation, **mechanochemical activation**, CO_2 mineralization

PCA Design and Control of Concrete Mixtures; Snellings RILEM TL 2016; Juenger et al. CCR 2019; Scrivener et al. CCR 2018; Snellings et al. CCR 2023

Mechanochemical Activation of Fillers

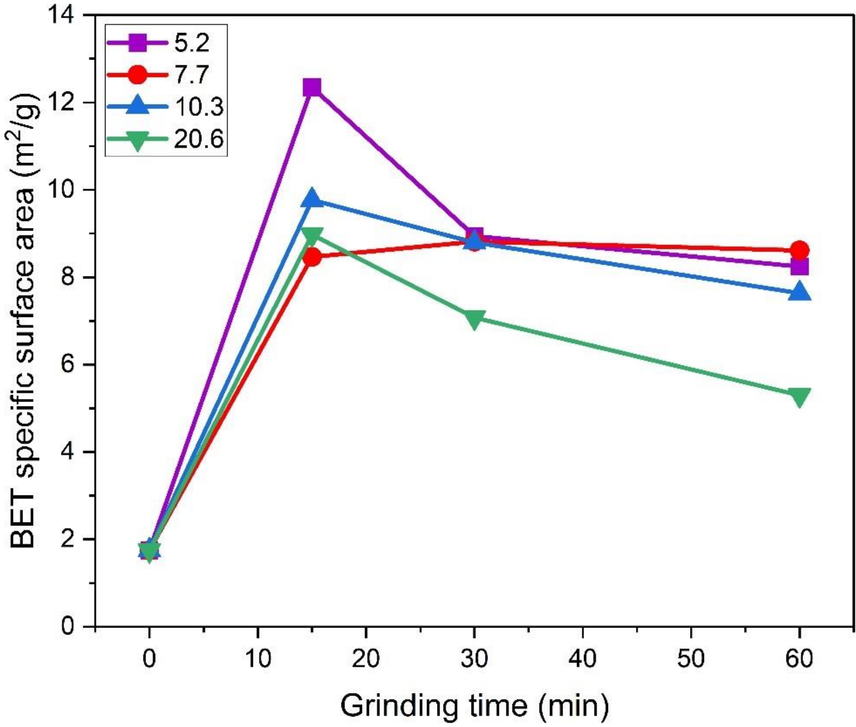
- Fillers can be activated by high-energy grinding (planetary ball mill)
- Our work has focused on basaltic fines, mine tailings, clays
- Others are doing this at scale: Carbon Upcycling, Polysius
- Generally the focus has been on clays
- Possibility of combining with CO_2 exposure for high Ca/Mg fillers
- Focusing on basaltic fines in this talk



Tole et al. MP 2019

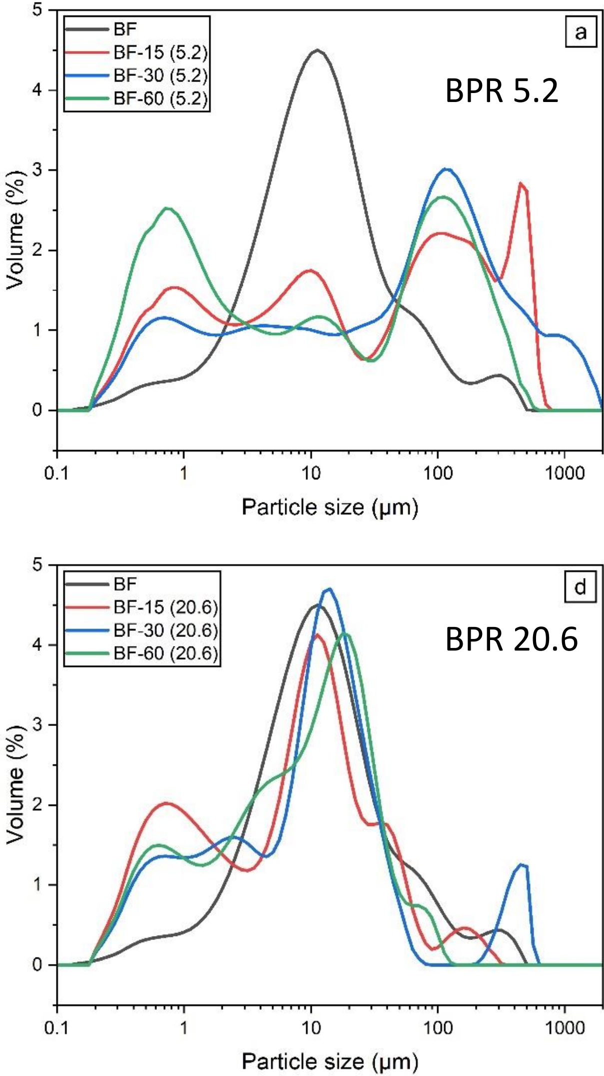
BET SSA

- BET SSA increases from 1.8 m^2/g between 5.3 and 12.4 m^2/g
- BET SSA decreases or levels off after 15 min grinding
- Agglomeration causes reduced BET SSA
- BET SSA reduces as ball-to-powder ratio (BPR) increases
- S. Amroun, M. Tahlaiti, P. Suraneni, Mechanochemical activation of basaltic fines for enhanced reactivity, PrePrint (2024)



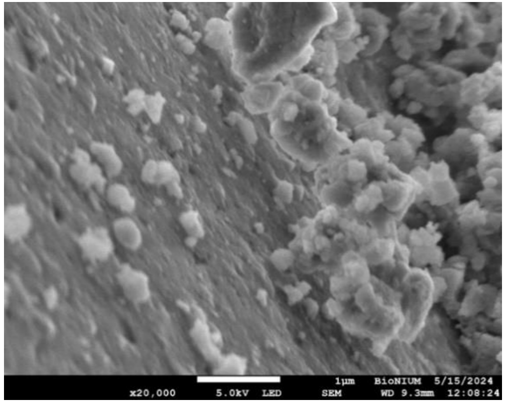
Particle Size Distribution

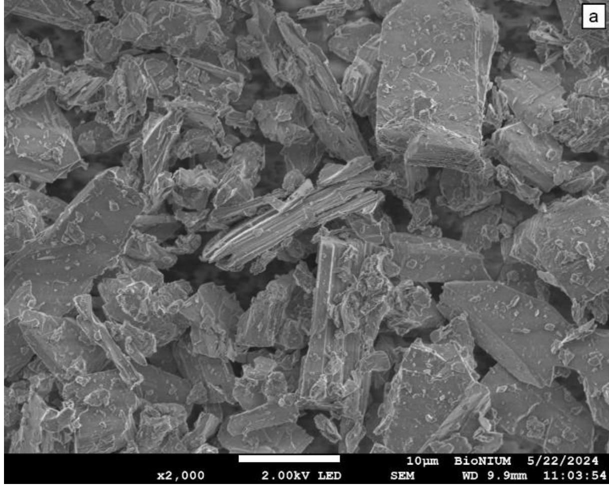
- Near normal distribution changes to bi- or tri-modal distribution
- Fines < 1 µm: Fracture
- Normal ~ 10 µm: Unaffected particles or fracture
- Coarse ~ 100 µm: Aggregates



SEM

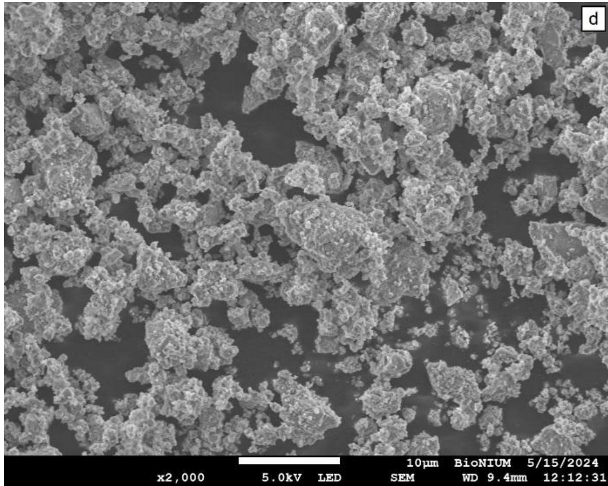
- BF shows angular particles, around 10 µm in size, consistent with PSD
- After MCA, particle distribution broader
  - Fines, normal, and coarse
  - Consistent with PSD
- Aggregates clearly seen
- Morphology changes towards spherical particles





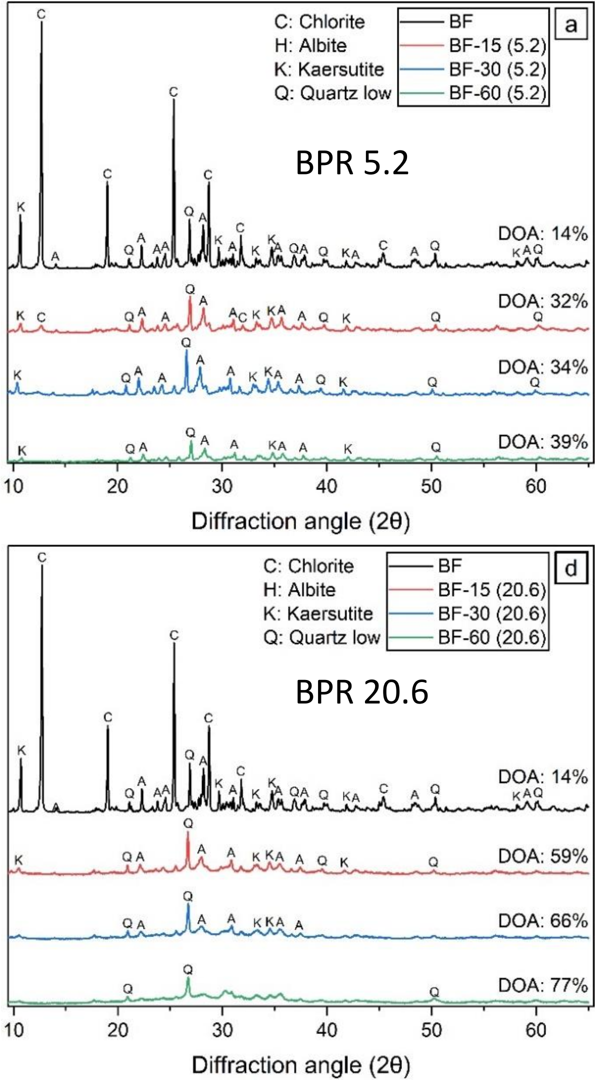
BF

BPR-60 (20.6)



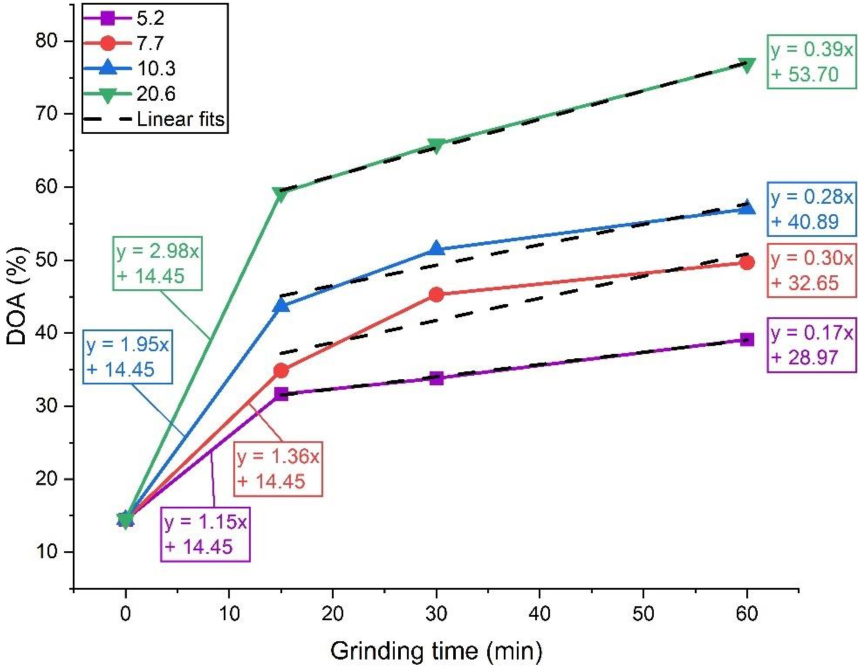
XRD

- BF is very crystalline
- After MCA, clear amorphization
- But amorphization phase dependent
- Ease of amorphization follows hardness: chlorite, MH = 2 > kaersutite, MH = 5 > albite, MH = 6 > quartz, MH = 7
- DOA is just an estimate



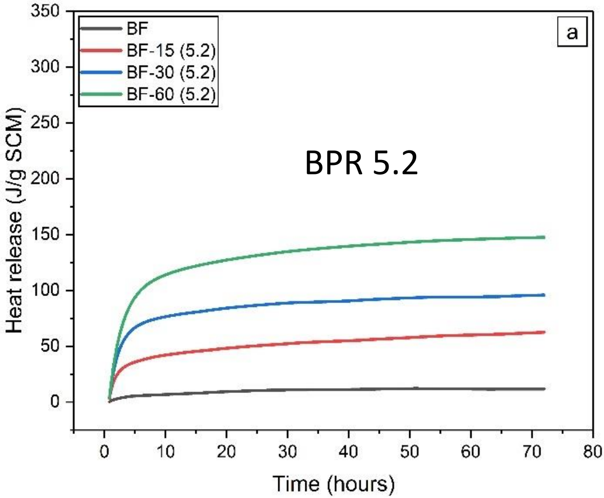
XRD

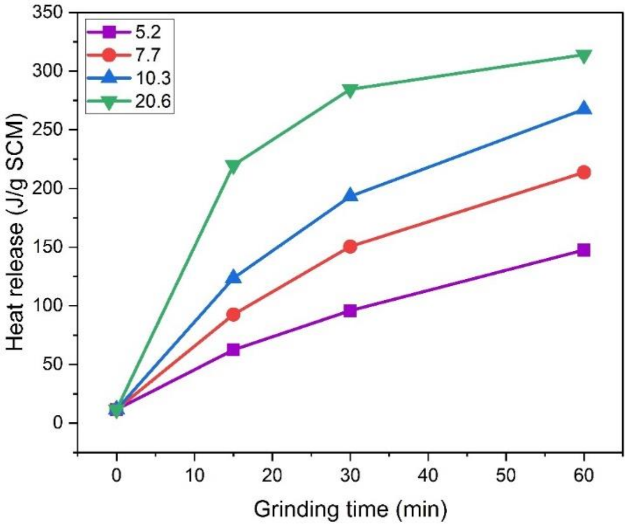
- Amorphization increases with grinding time and BPR
- Limited number of points but data seems bilinear

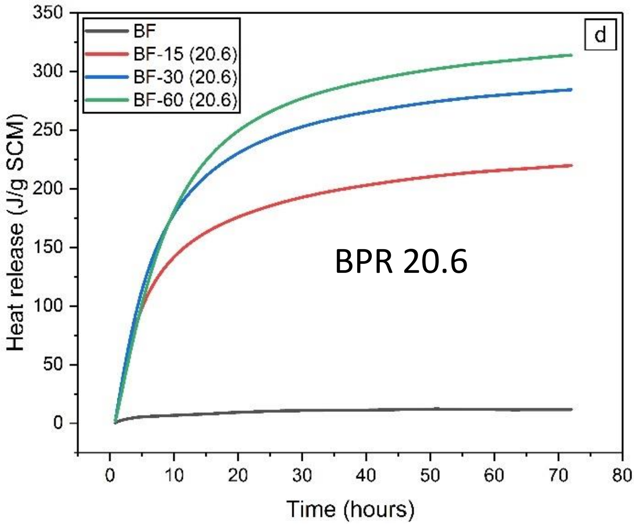


Modified R^3 Test

- Reactivity increases with grinding time and BPR
- We get materials well beyond the inert threshold especially at high BPR/grinding time
- The increase in reactivity with grinding time decreases with an increase in BPR

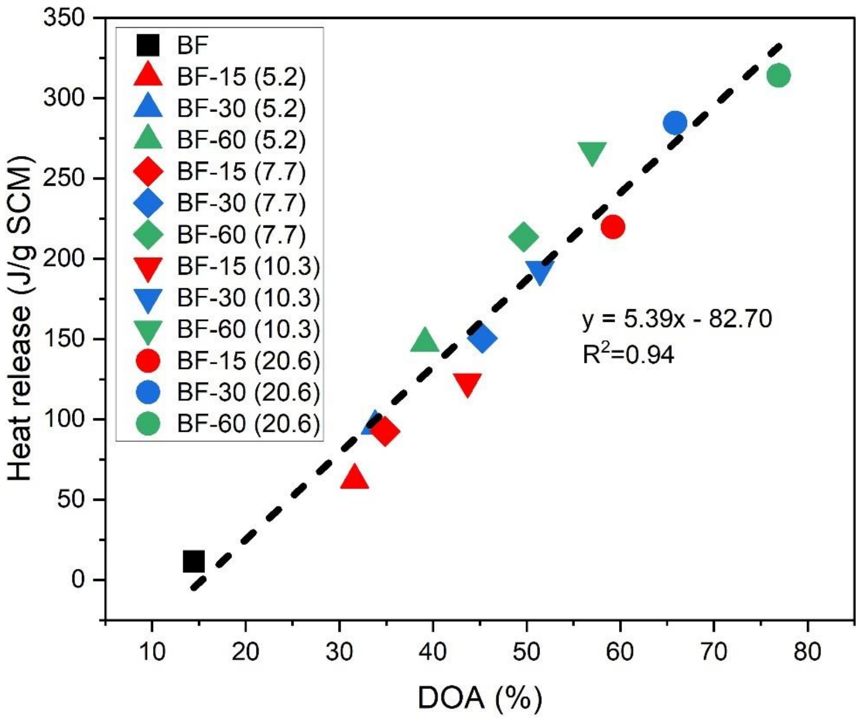






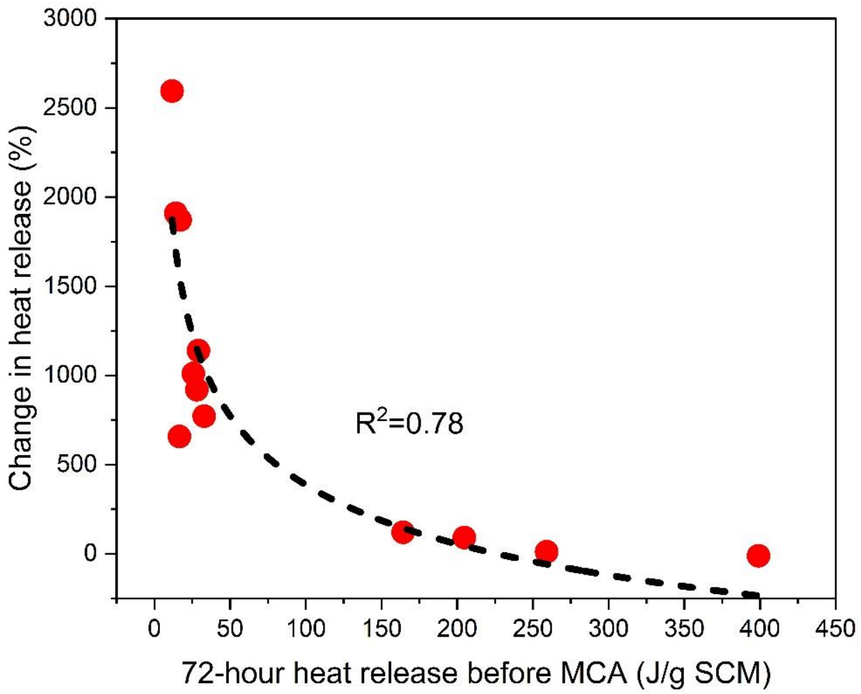
Amorphization Drives Reactivity

- Strong linear relationship between estimated DOA and reactivity
- No relationship with SSA and related parameters
- Over a wide range, amorphous content controls reactivity
- Do you get same results if you ball mill for long durations?



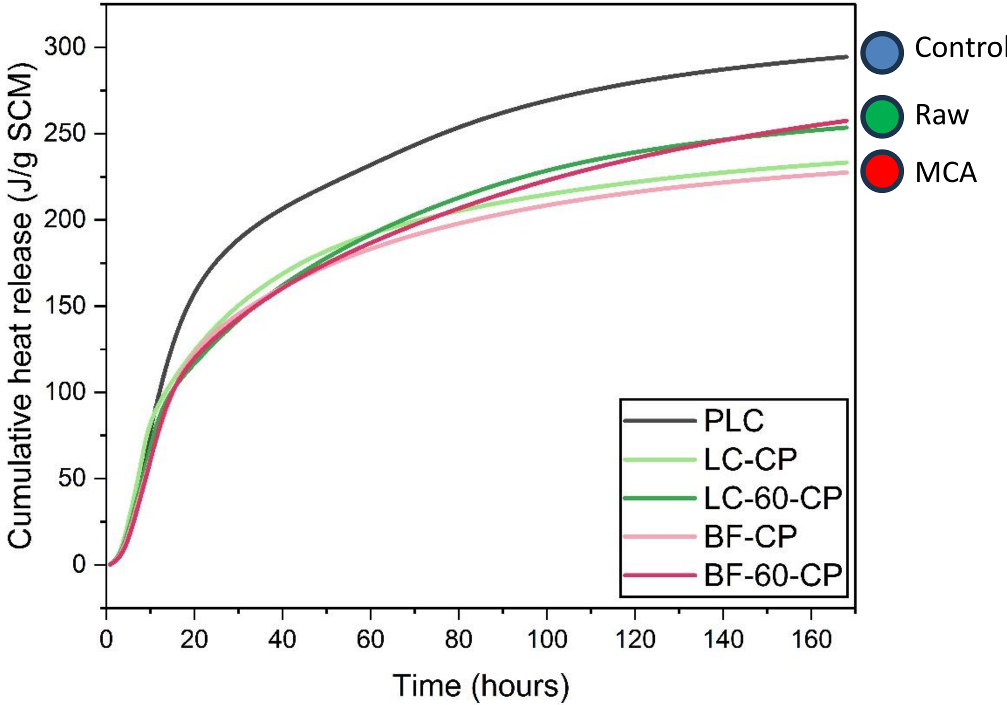
What About Other Materials?

- Many other materials tested
- Results shown for 12 materials
- MCA generally works, but does not always make sense
- Reactivity increase shows strong negative correlation with initial heat release
- Highly amorphous materials -> High initial heat release -> Limited further amorphization -> Limited increase in heat release



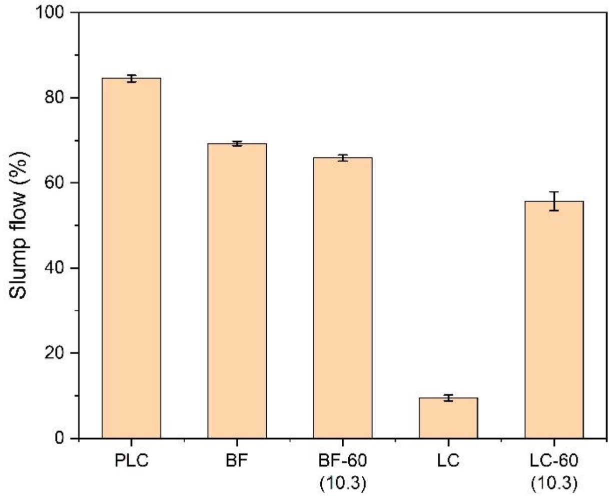
Cement Pastes

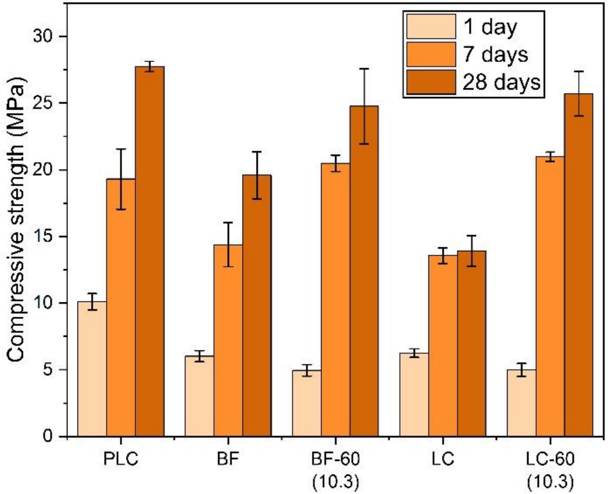
- At 30% replacement, pastes with MCA SCMs show increased heat release
- Shown for basaltic fines and a low kaolinitic clay

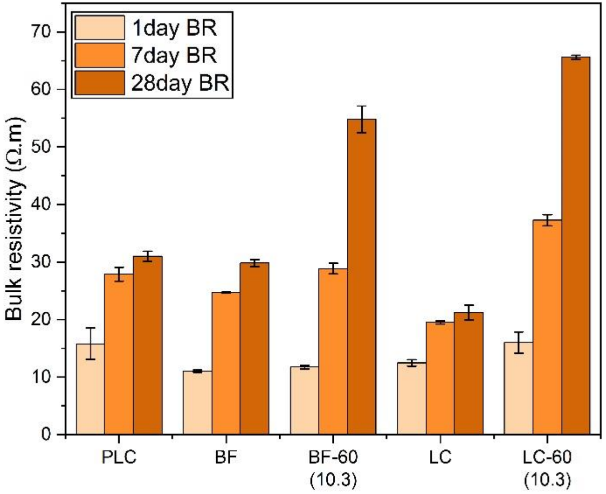


Cement Mortars

- Improved/similar flow despite high SSA due to spherical particles
- Strength significantly improved over raw SCMs at 7 days and beyond
- Bulk resistivity increases at 28 days confirm generation of reactive SCMs







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Conclusions

- Mechanochemical activation studied in lab for basaltic fines and other materials
- SSA increases, complex particle size distribution, agglomeration, and spherical particles
- Amorphization, with extent depending on phase hardness
- Reactivity increases with BPR and grinding time
- Amorphization drives reactivity, strong linear effect
- MCA shown for many materials, increase in reactivity depends on initial reactivity
- Improved heat release, mortar flow, strength, bulk resistivity seen in cement pastes and mortars

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