Modeling Hydration Kinetics of Sustainable Cementitious Binders Using a Data Informed Nucleation and Growth Approach

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U.S. Department of Transportation
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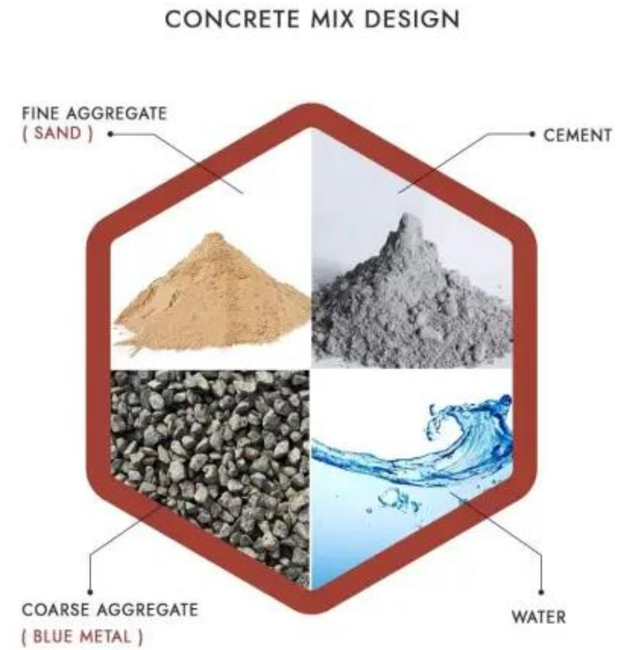
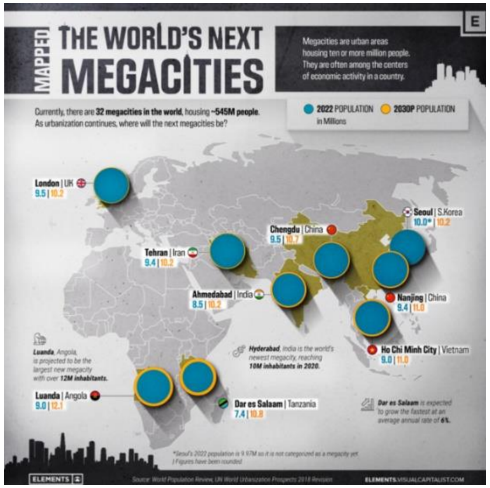
arpa·e CHANGING WHAT'S POSSIBLE

Missouri S&T

Concrete: Overview

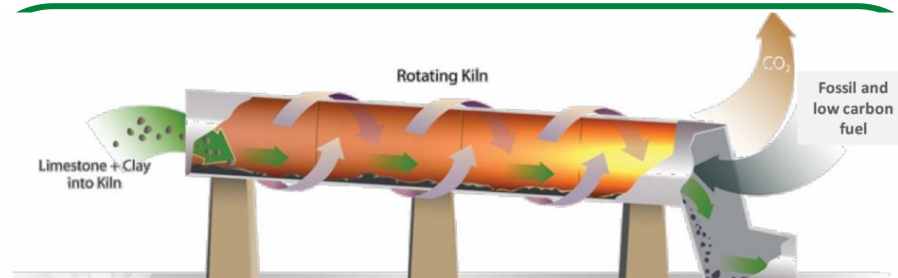
- Concrete: The principal material for construction of (nearly all) infrastructure
- Concrete = Portland cement + water + sand + stones + chemicals (to regulate properties)
- Production-and-use: 40 billion tons/year
  - Employs 10 million Americans
  - Creates $1.3 trillion worth of engineered systems
- 2050 projections
  - Global population: 10 billion
  - (Sub)urbanites: 6.6 billion
  - Rise of >50 megacities
  - Concrete production: ~60 billion tons/year

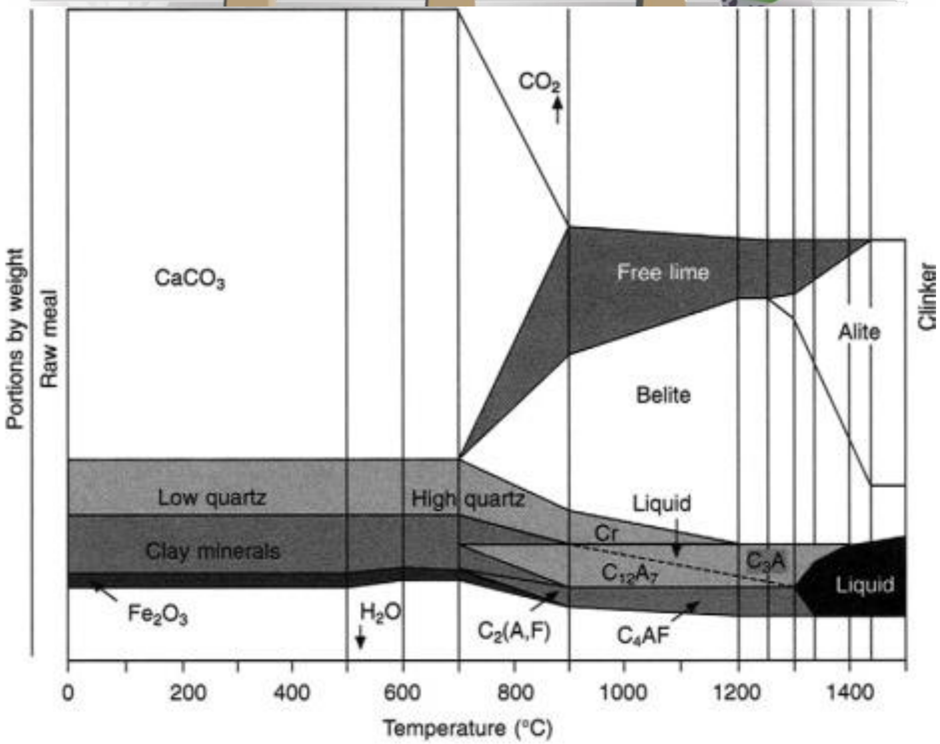


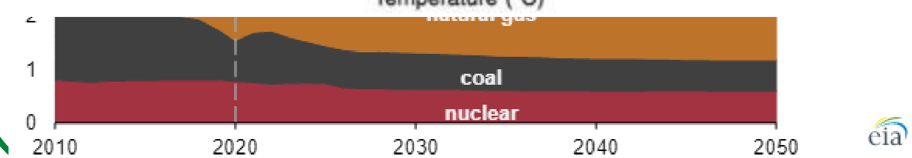


Concrete: The ugly

- The **carbon-footprint** problem
- Limestone ($CaCO_3$) is needed to produce cement: 70%$_{mass}$
  - CO_2 released at ~800 °C
- Clinkering temperature: 1450°C
  - Achieved using fossil fuels
  - Switching to electricity doesn't help (68% of electricity is generated from fossil fuels)
- 0.85 tons of CO_2 emitted for every ton of cement produced
- Cement production: 8% of all anthropogenic CO_2 emissions
- IPCC: "Essential field of action"



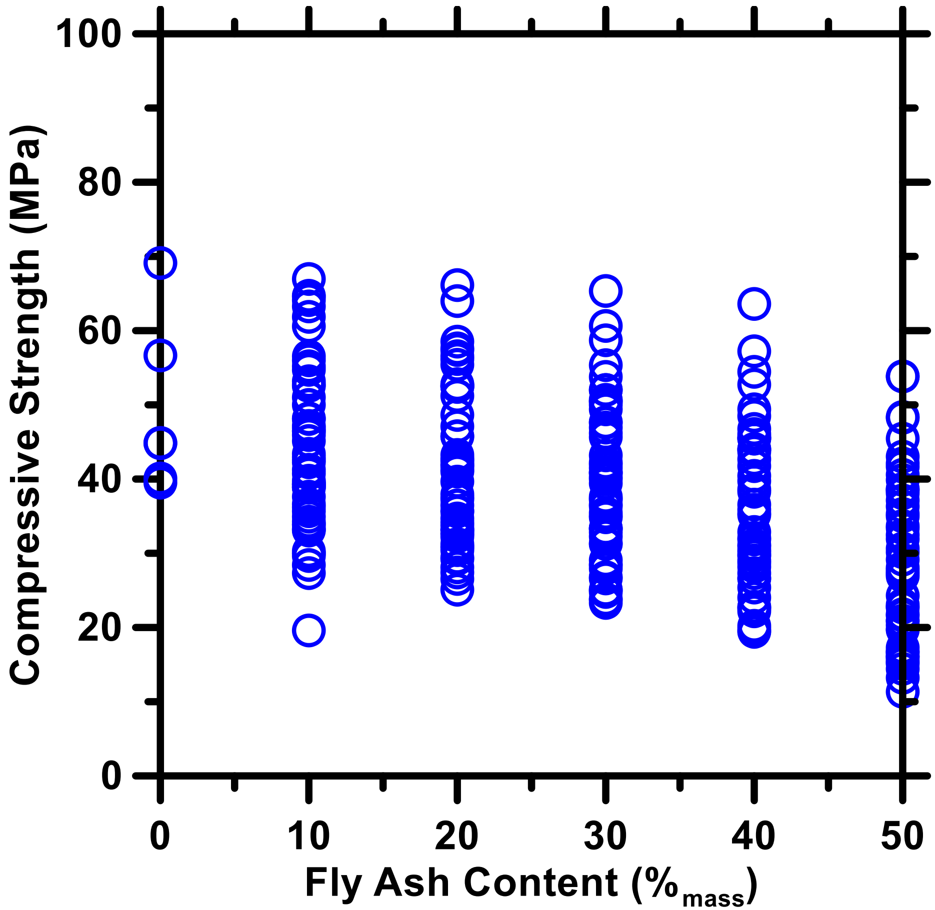




Using supplementary cementitious materials

- Use supplementary cementitious materials (SCMs) to partially replace cement in concrete
  - Coal fly ash; slags; waste glass
  - Geological materials (e.g., clay)
- SCMs are not as reactive as cement: Cannot replace >50%
- Feature substantial batch-to-batch variations in composition
- Affect chemical reactions (cement hydration); microstructural evolution; property development in unpredictable ways.

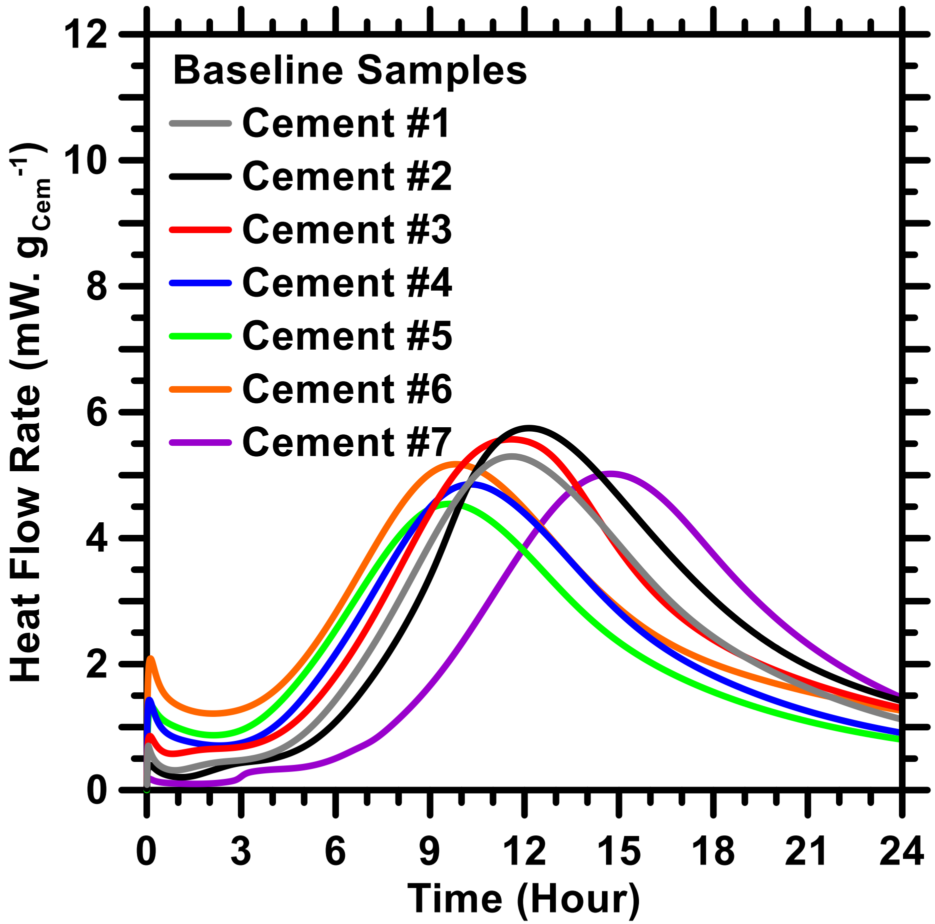
Snellings, RILEM Tech. Report 2016



Lapeyre et al., Sci. Reports 2021
Cook et al. Mat. & Des. 2021
Han et al. Front. Mat. 2022

Cement Hydration: Plain Paste

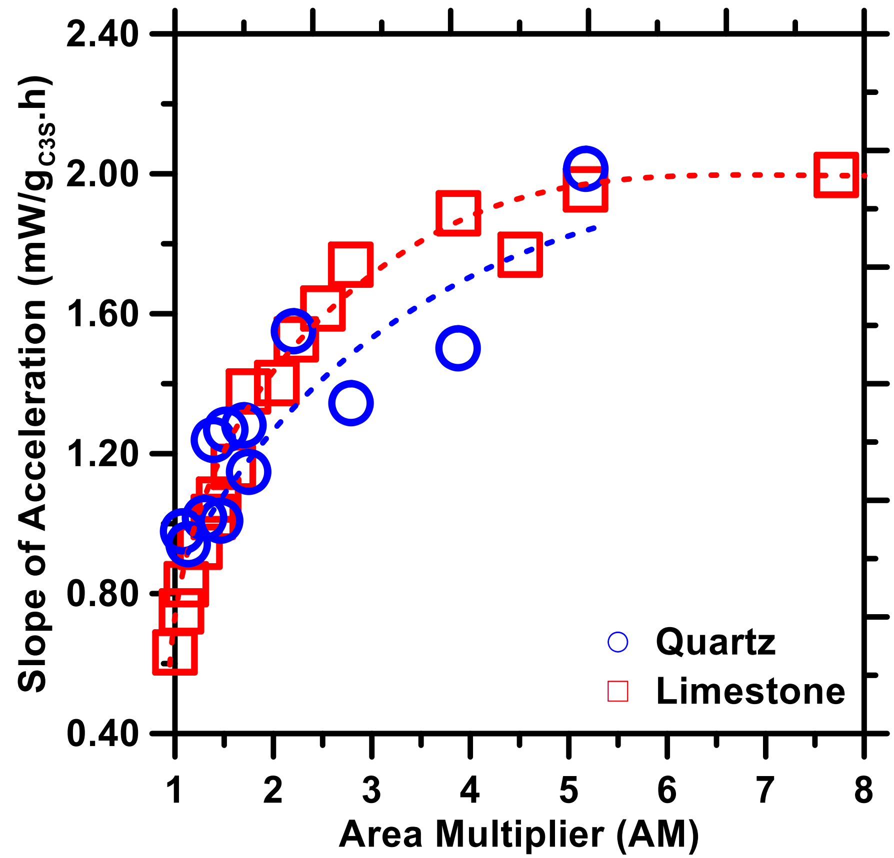
- Cement reacts with water to form products: "**hydration**"
- **Isothermal calorimetry** is typically used to monitor hydration kinetics
  - Heat evolution linked to rate/extent of cement hydration
- Anhydrous phases dissolve; products (C-S-H) nucleate and grow; microstructure evolves; and properties develop
- Different phases; disparate kinetics; disparate mechanisms
- Modeling challenges:
  - Account for hydration mechanisms of all anhydrous phases



Lapeyre et al. J. Am. Ceram. Soc. 2018; 2019

Cement Hydration: Binary Paste

- SCMs: fillers (limestone and quartz)
- In general, filler addition increases reaction rates
- Extent of acceleration is strongly dependent on:
  - Filler fineness (surface area)
  - Cement replacement (%)
- Limestone *superior* than quartz at equivalent surface area
- Modeling challenges:
  - Not all fillers are the same
  - Acceleration does NOT linearly increase with surface area

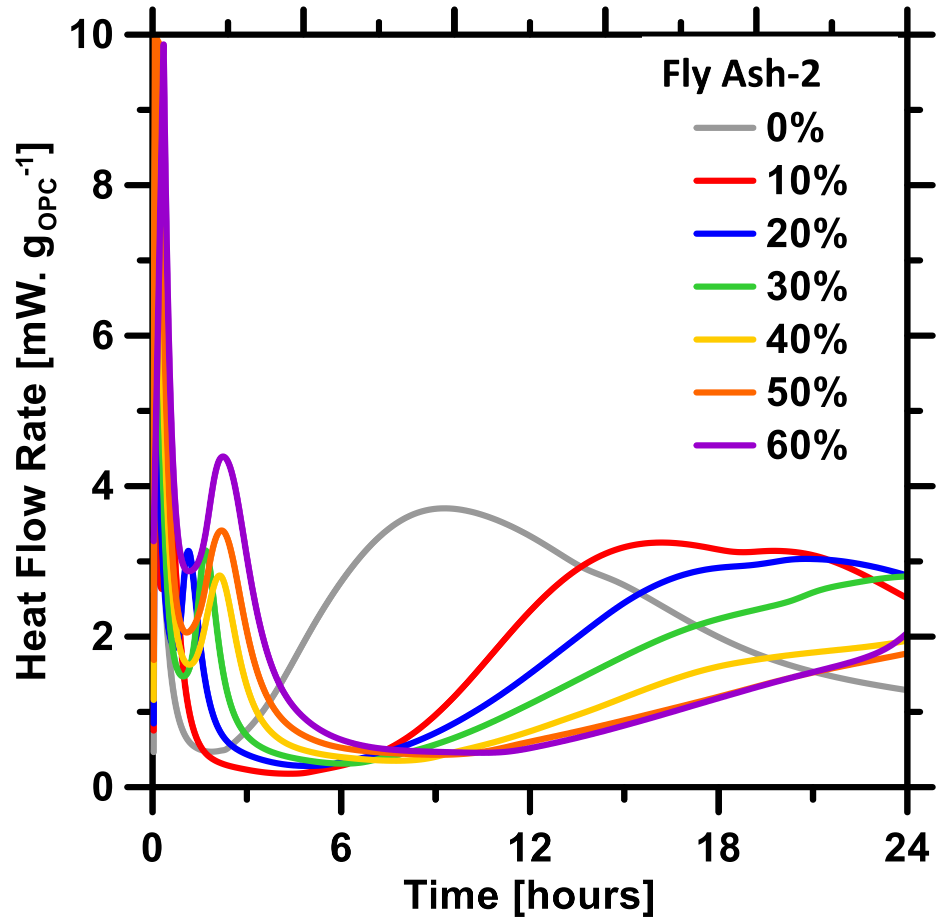


Area Multiplier: Factor increase in surface area

Oey et al.; Kumar et al. J. Am. Ceram. Soc. 2013; 2017

Cement Hydration: Binary Paste

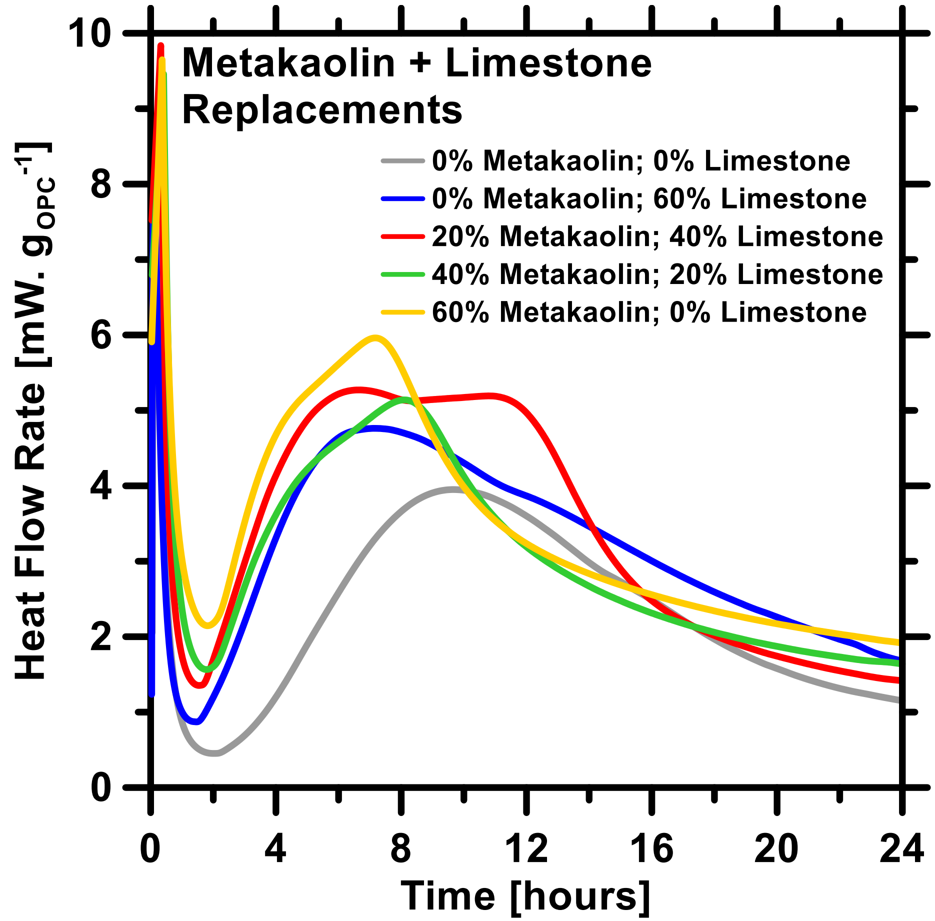
- SCMs: silica or aluminosilicates
- Silica fume and metakaolin – at least in the first 24 h – accelerate cement hydration kinetics
  - Later on, they may react with calcium hydroxide; alter hydration
- Fly ash – a highly heterogeneous material – alters hydration kinetics in myriad ways
- Modeling challenges:
  - Changes in hydration kinetics strongly dependent on PSD and **chemistry** of the SCM
  - Multiple mechanisms (filler effect; pozzolanic reaction; etc.) at play at any given time



Han et al. CBM 2023

Cement Hydration: Ternary Paste

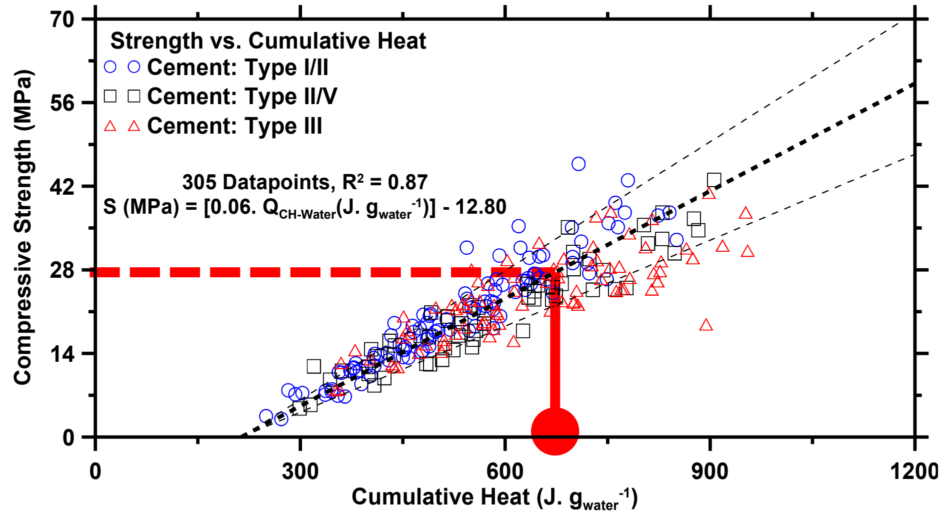
- Interactions between SCMs and paste components are complex
  - Filler effect; pozzolanic effect; secondary reactions; etc.
- E.g., Cement-limestone-metakaolin reaction to form hemi- and mon—carboaluminate
- E.g., SO_3/Al_2O_3 of the binder could be altered, thereby affecting hydration of the C_3A phase
- Modeling challenges:
  - Multiple concurrent reaction mechanisms need to be considered to model the overall progression of reaction

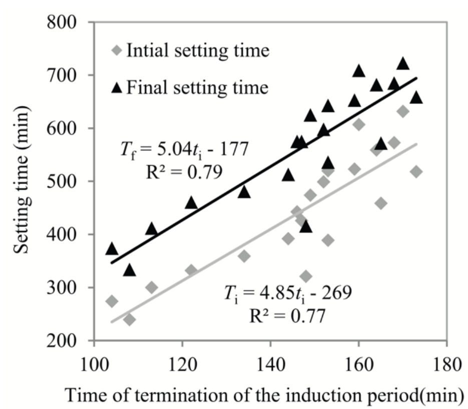


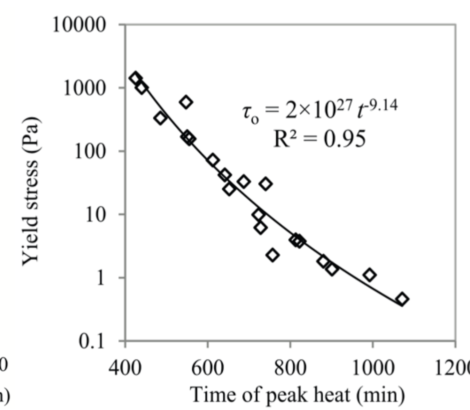
Han et al. (Unpublished)

Why model hydration kinetics?

- *Apriori* prediction of hydration kinetics (calorimetry profile) is very useful
- If we know what % of cement has reacted, thermodynamic models can predict phase assemblage
- More heat = greater extent of cement hydration = more products = less porosity; more solid-to-solid phase connectivity; more strength
- Cumulative heat is linked to properties
  - strength; set time; rheology; etc.
- If hydration can be predicted, performance can be estimated
- Useful for cement design, mixture proportioning, etc.



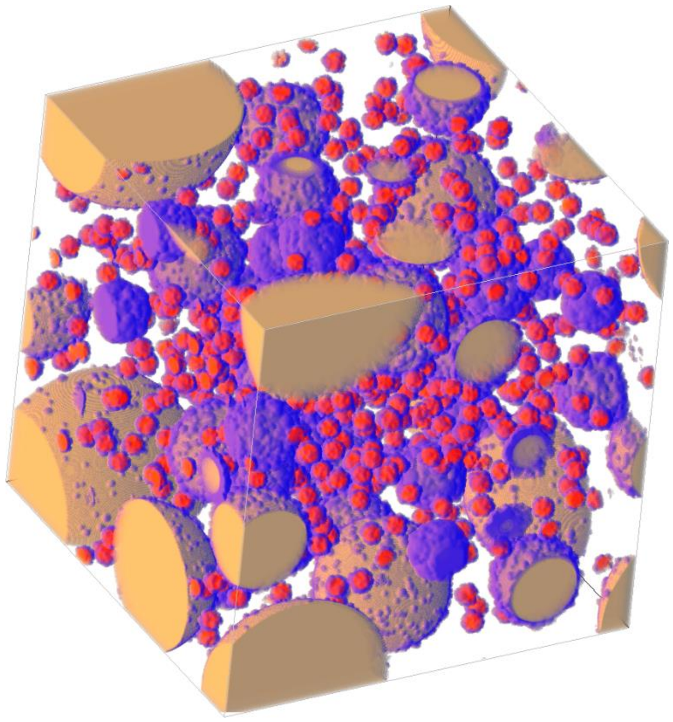




Kumar et al. Cem. Conc. Compos. 2013
Meng et al. Cem. Conc. Compos. 2019

Nucleation-and-Growth Mechanism

- Classical phase boundary (heterogenous) nucleation-and-growth models
  - substrate: cement and/or SCM surfaces
  - A **single product** with constant density forms heterogeneously at nucleation event
  - Product **grows** (usually in **isotropic** fashion) at **constant rate**
- Inputs
  - cement, SCM, water contents; SSA of solids
  - **cement/SCM chemistry not considered**
- Parameters need to be optimized **using calorimetry profiles**
  - Nucleation density; growth rate; morphology of the product; etc.



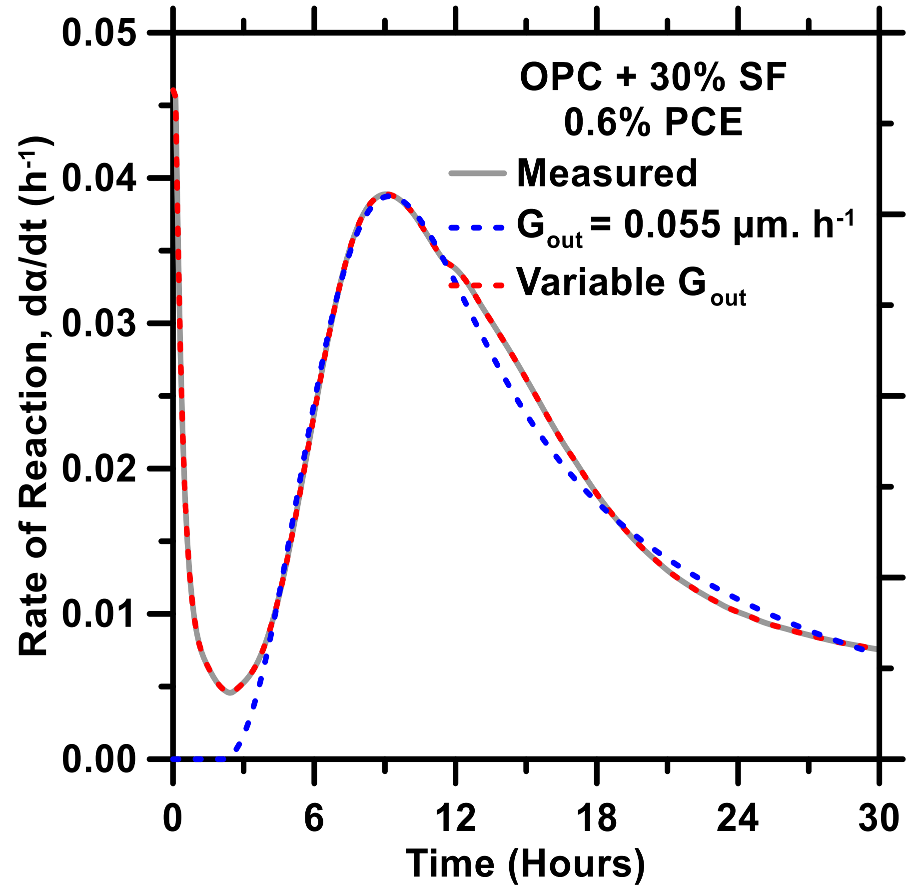
Cement

SCM

C-S-H (single product)

Nucleation-and-Growth Mechanism

- Modified phase boundary nucleation-and-growth models
  - Product morphology is acicular
  - Product does not grow freely into capillary pore space
  - Density of product not constant
  - Product growth rate varies with time (or supersaturation)
- Excellent fits can be obtained
- But, calorimetry profiles still needed to optimize parameters

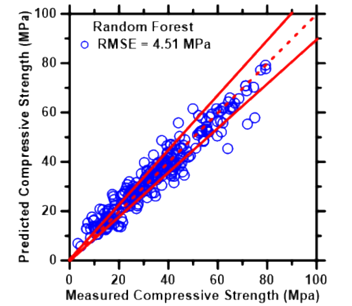


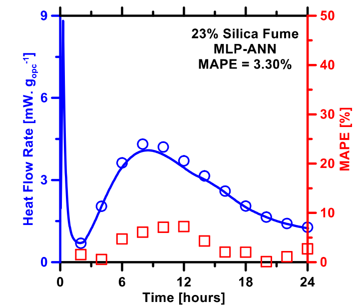
Meng et al. J. Phys. Chem. C 2016

Supervised machine learning

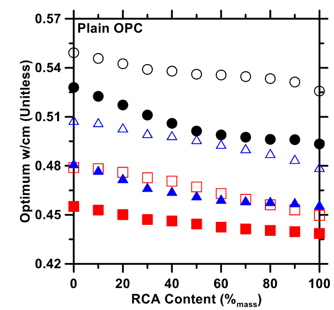
- Machine learning (ML) is a form of artificial intelligence: unsupervised and supervised
- **Supervised ML model** is first trained using a database
- The ML model develops patterns, input-output correlations in the data
  - Correlations may or may not be known from theory
- Once trained, the ML model can leverage input-output correlations to predict in new data-domains
- In the case of cement pastes/concretes
  - **Training**: ML model learns correlations between inputs (physiochemical properties of precursors) and output (heat evolution; elastic modulus; strength; etc.)
  - **Testing**: Predicts properties (heat evolution) of new pastes/concretes, using their mix design as input

Predict properties of new systems



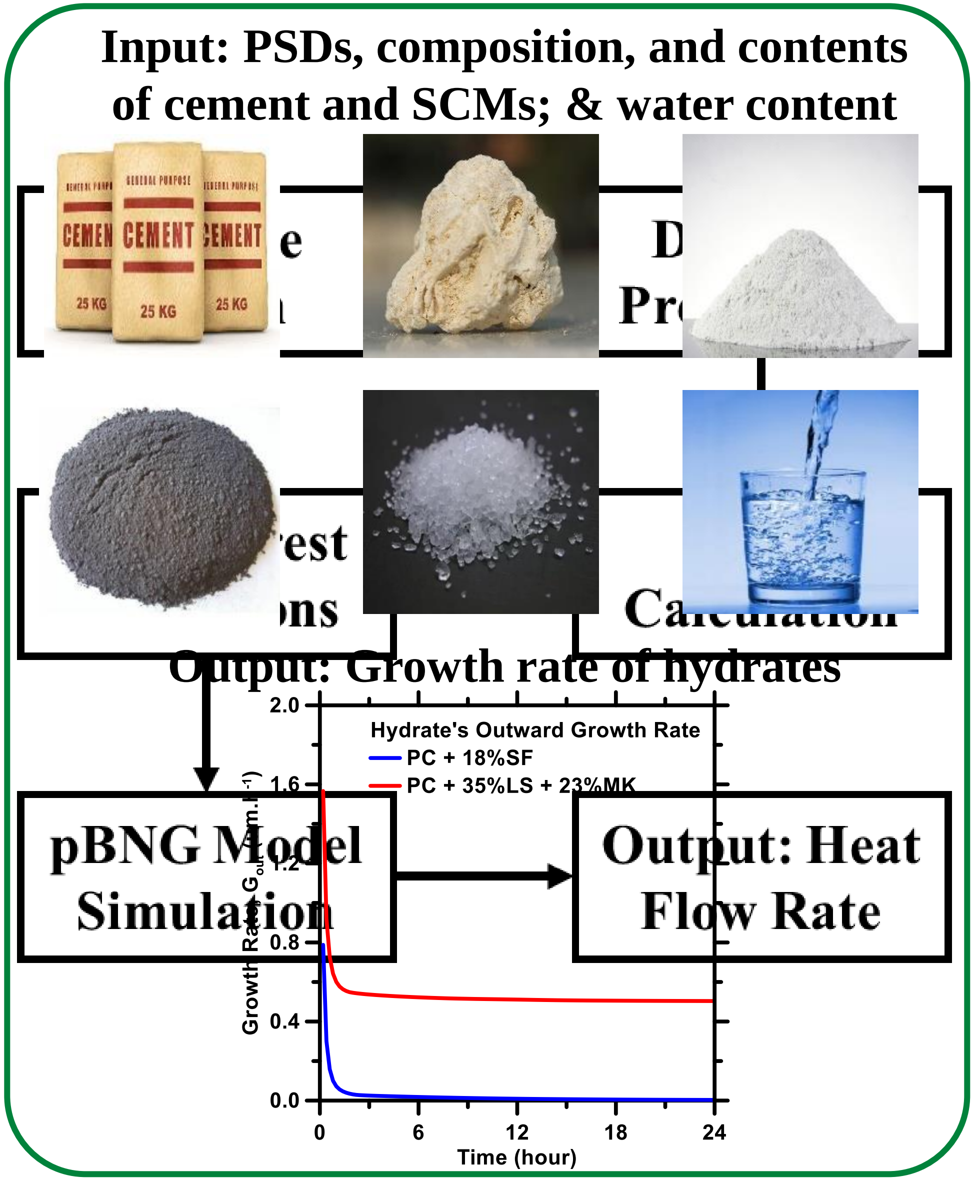


Optimize mixture design of systems



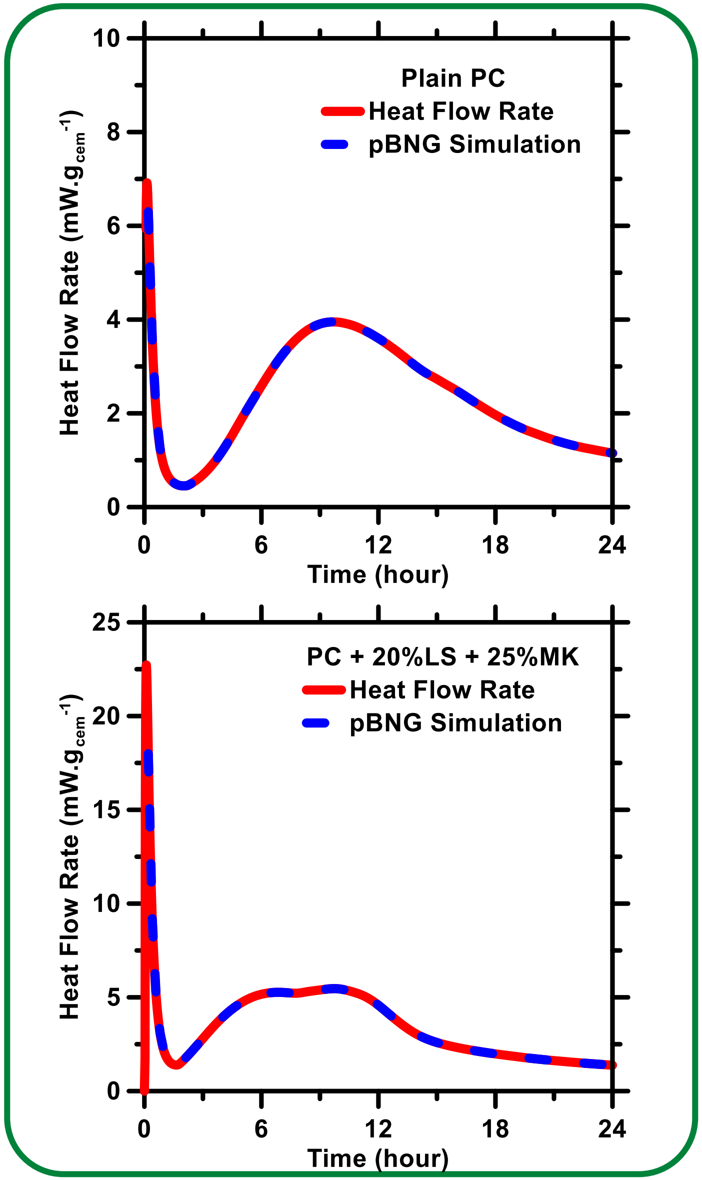
Database used for machine learning

- **Training:** hundreds of unique pastes
  - Plain, binary, and ternary pastes
- Cement: Commercial and synthetic
- SCMs
  - Different types: limestone; quartz; calcined clay; silica fume; fly ash; etc.
  - 0-to-60%$_{mass}$ cement replacement
- **Inputs:** Physiochemical properties (composition, PSD) of pastes at t = 0 h
- **Outputs:** growth rate of hydrates
- **Blind-testing:** Pastes, with new PSDs and replacement levels of SCMs; different cement compositions



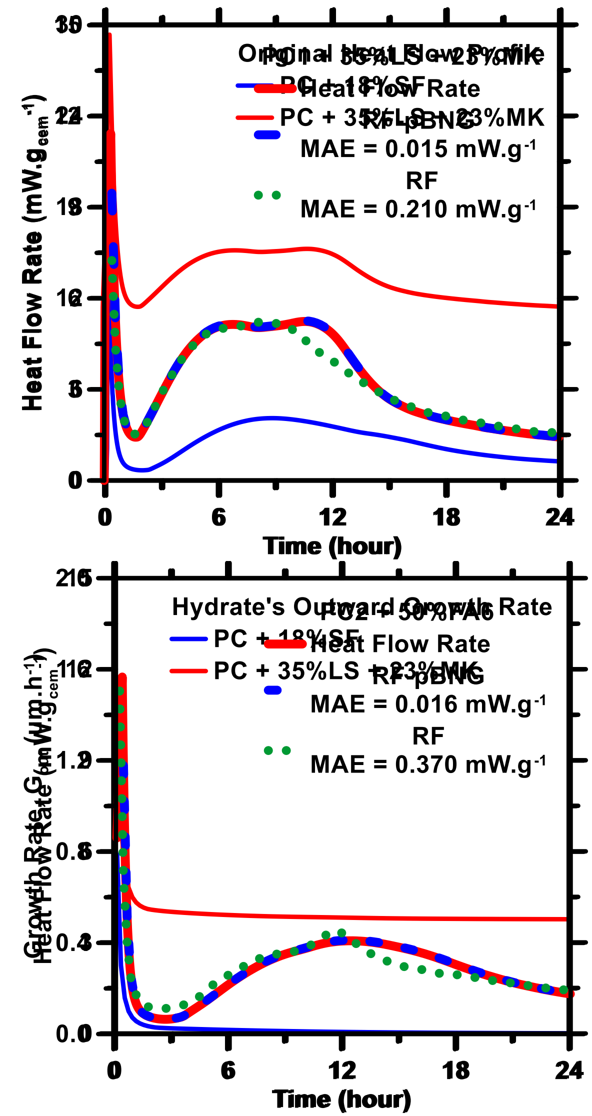
Advanced Nucleation-and-Growth Model

- $\alpha(t) = B \cdot X(t)$ Degree of hydration obtained from calorimetry profiles
- $X(t) = 1 - \exp\left(-2r_G \cdot \boxed{G_{out}(t)} \cdot a_{BV} \cdot t \cdot \left(1 - \frac{F_D\left(G_{out}(t)\cdot\sqrt{\pi\cdot g\cdot I_{density}}\cdot t\right)}{G_{out}(t)\cdot\sqrt{\pi\cdot g\cdot I_{density}}\cdot t}\right)\right)$ Calculate the growth rate of hydrates using Cahn's euqation
- $SSA_{binder} = SSA_{cement} + a_{scm1}SSA_{scm1}\frac{z_{scm1}}{100-z_{scm1}} + a_{scm1}SSA_{scm2}\frac{z_{scm2}}{100-z_{scm2}}$
- Effective surface area (a_{scm}) is used to account for pozzolanic reaction, sulfate effect, $Al(OH)^-$, amalgamation and filler effect.
- This model can be used to simulate hydration kinetics of cement replaced by common SCMs



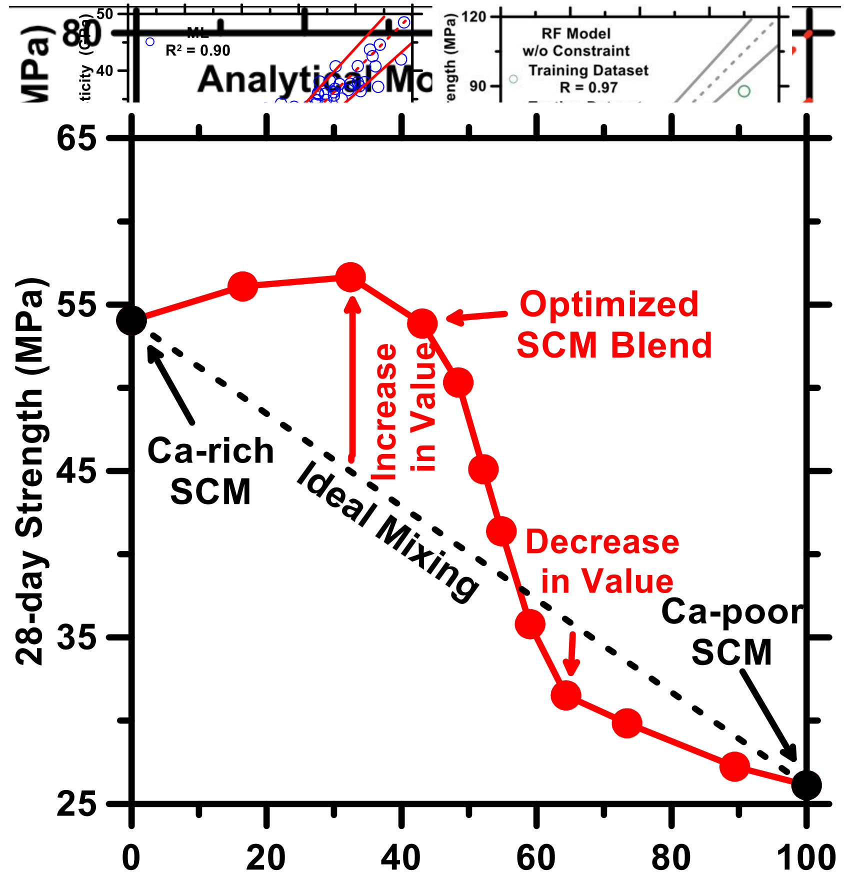
Advanced Nucleation-and-Growth Model

- Phase boundary nucleation and growth models require hydrate's growth rate (G_{out}) to reproduce heat flow profiles
- G_{out} profile showed simpler structure and trend
- ML optimized parameters for pBNG model, which allowed it to reproduce the heat flow rate profiles
- ML integrated with pBNG model produced superior predictions to standalone ML
- Nucleation and growth model regulate final output to avoid violation of material laws.

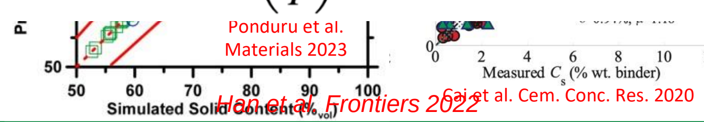


Other applications of machine learning

- Combine with ***game theory*** to develop simple, closed-form analytical models
  - (1) Quantify "importance" of each input parameter
  - (2) Construct a function using only "consequential" parameters
  - (3) Optimize the coefficients
- Predict constructability and compliance metrics of concrete
  - set time; rheology; steel rebar corrosion potential; strength
- Material design to **optimize performance**



$$CS = C_1 X_{C3S}^2 + C_2 X_{C2S} + C_3 X_{C3A} + C_4 X_{C4AF}^2 + C_5 \left(X_{gypsum} + X_{FA} x_{SO3}\right) + C_6 X_{FA} N_c + C_7 exp\left(\frac{C_8}{T}\right) + C_9$$



Conclusions

- Using SCMs to partially replace cement become an emerging solution for reducing the carbon emission in the cement industry
- Nucleation and growth model is the promising tool to reproduce hydration kinetics of [cement + SCMs] systems
- It cannot produce hydration kinetics for new systems without knowing growth rate of hydrates
- Harness the power of machine learning to predict necessary parameters for the nucleation and growth model
- The advanced nucleation and growth model can predict the hydration kinetics of [cement + SCMs] systems without the violation of material laws

Questions?