Modeling of entrained air dissolution and long-term saturation:

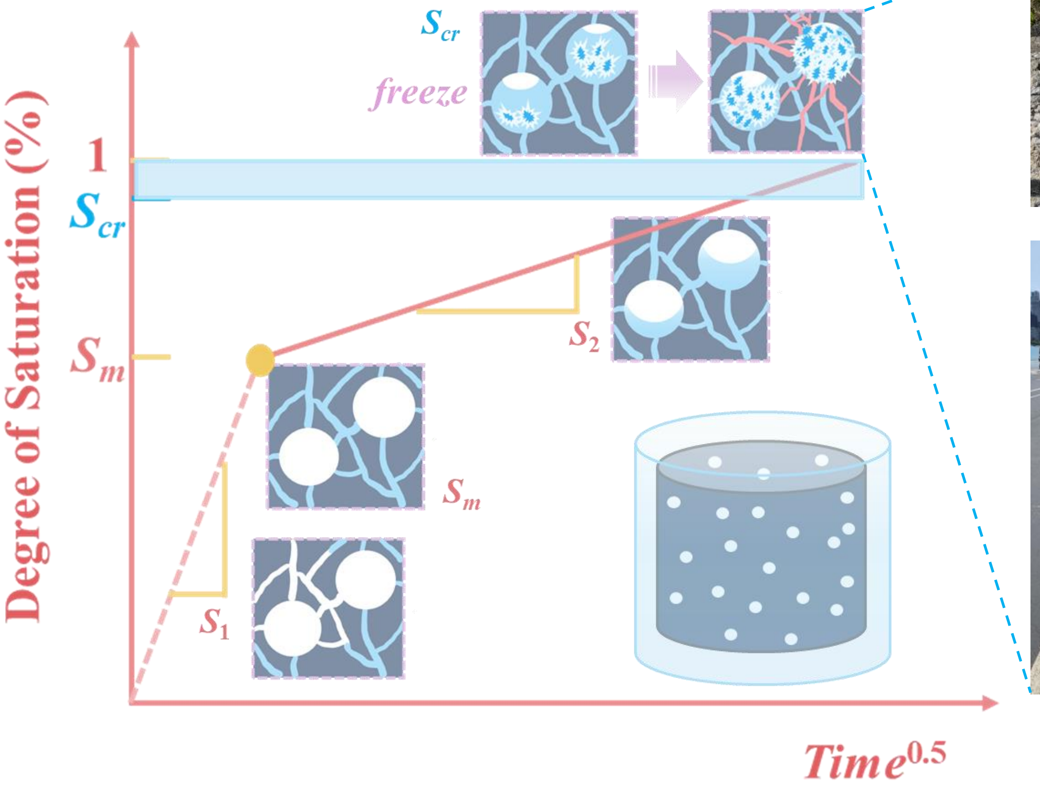
Role of microstructure in emerging cementitious materials

Aiqing "Felix" Xu, Postdoctoral Fellow

Kimberly Kurtis, Professor, Associate Dean

Georgia Institute of Technology

1. Introduction & motivation



(Photo credit: Dr. Kurtis)

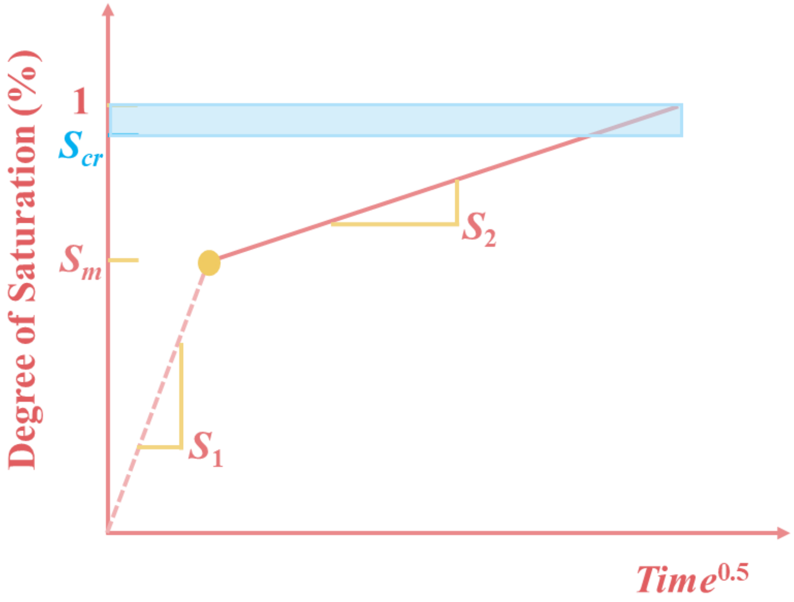
- Background
  - Water saturation governs **freeze-thaw resistance** and **long-term durability** in cementitious materials.
  - Saturation = Stage 1 (S_1) + Stage 2 (S_2) :
    - S_1: Rapid capillary suction
    - S_2: Slow air dissolution → controls S_{cr} (~86%)
  - Once $S \geq S_{cr}$, freeze-thaw damage occurs even with enough air content.

Longer S_2 → delayed S_{cr} → higher freeze-thaw durability

1. Introduction & motivation

- Knowledge gaps
  - Focus mainly on **OPC** systems.
  - Prior work: **Air-void optimization**, but lacks **long-term saturation kinetics (S_2)**.
  - ➢ Research on **emerging cementitious materials** (LC^3, CSA, geopolymers) is limited.

- Research gaps
  - No unified framework to **quantify the timescale of S_2** in different cementitious systems.
  - Current models insufficiently capture saturation behavior of **emerging low-carbon cements**.

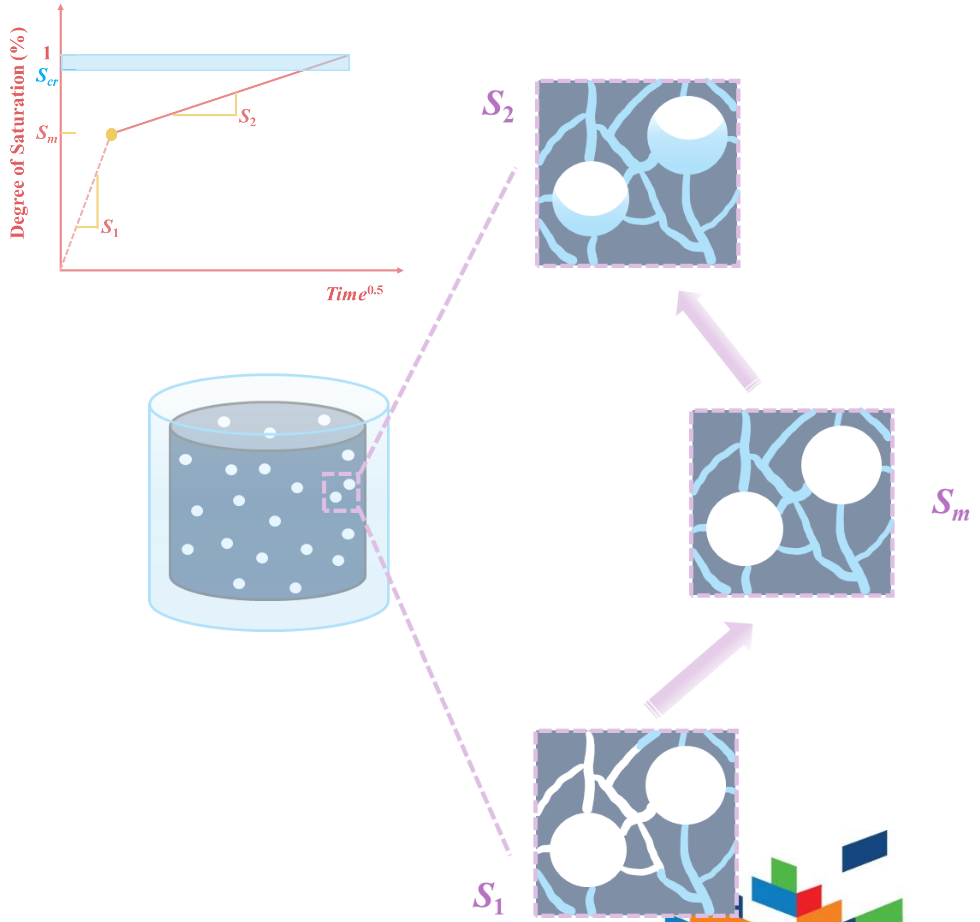


(Photo credit: Dr. Kurtis)

1. Introduction & motivation

- Significance
  - Describe dissolution, diffusion, and advective filling in cementitious materials.
  - Link **microstructural parameters** to **saturation kinetics**.
  - Enable reliable prediction of **freeze-thaw**.

- Objective
  - Provide a **generalizable modeling framework** that applies across OPC and emerging systems.
  - Advance predictive understanding of long-term saturation.
  - Support the design of durable, sustainable cementitious systems.



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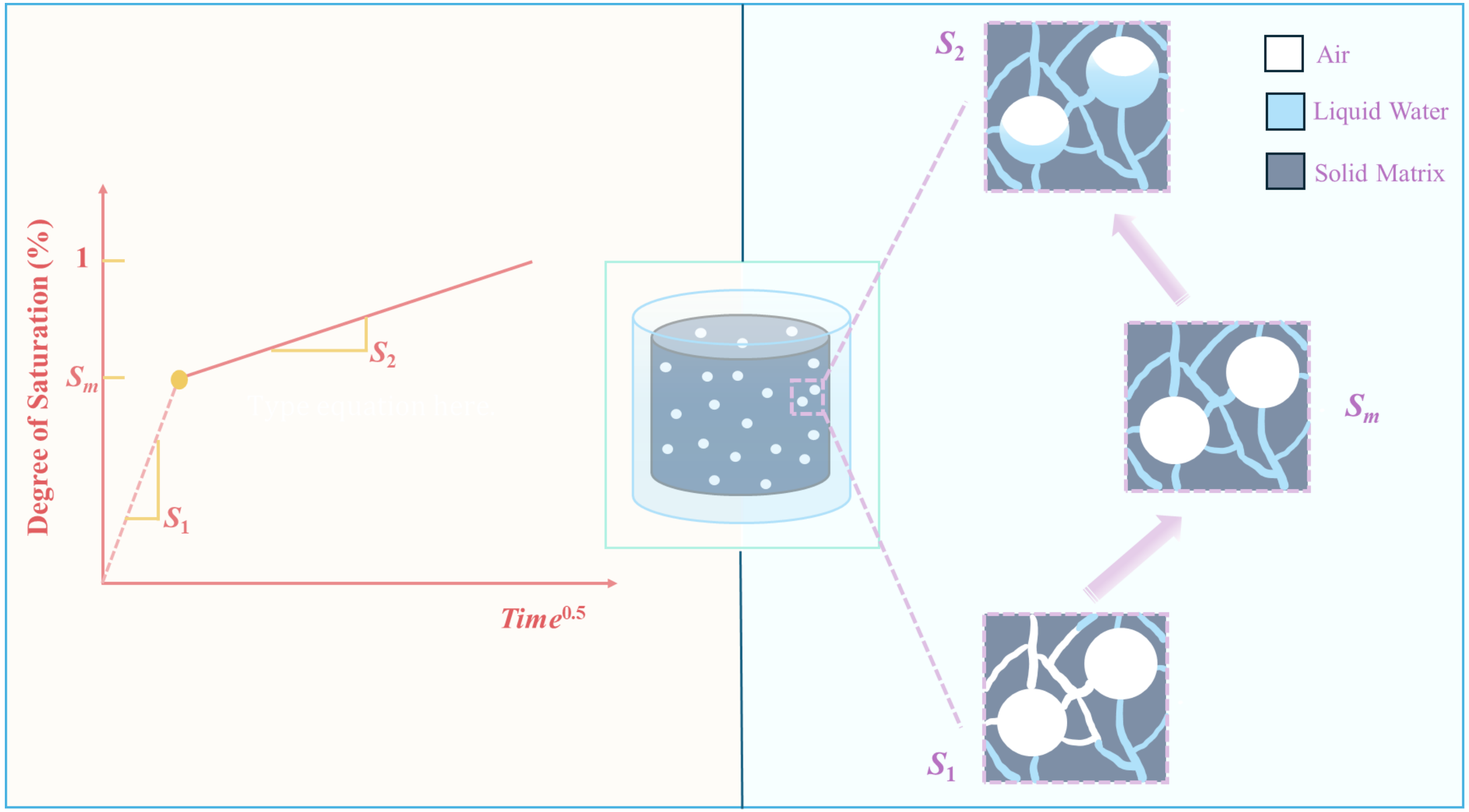
2. Air dissolution and long-term saturation in cementitious materials

- Air voids and water saturation in cementitious materials



S_1: Capillary absorption
- Rapid process
- Capillary suction-driven

S_2: Air dissolution-diffusion
- Slow, long-term process
- Laplace pressure

$$P_g = P_0 + \frac{2\sigma}{R}$$

- Henry's Law

$$C_g = P_g \cdot k_H$$

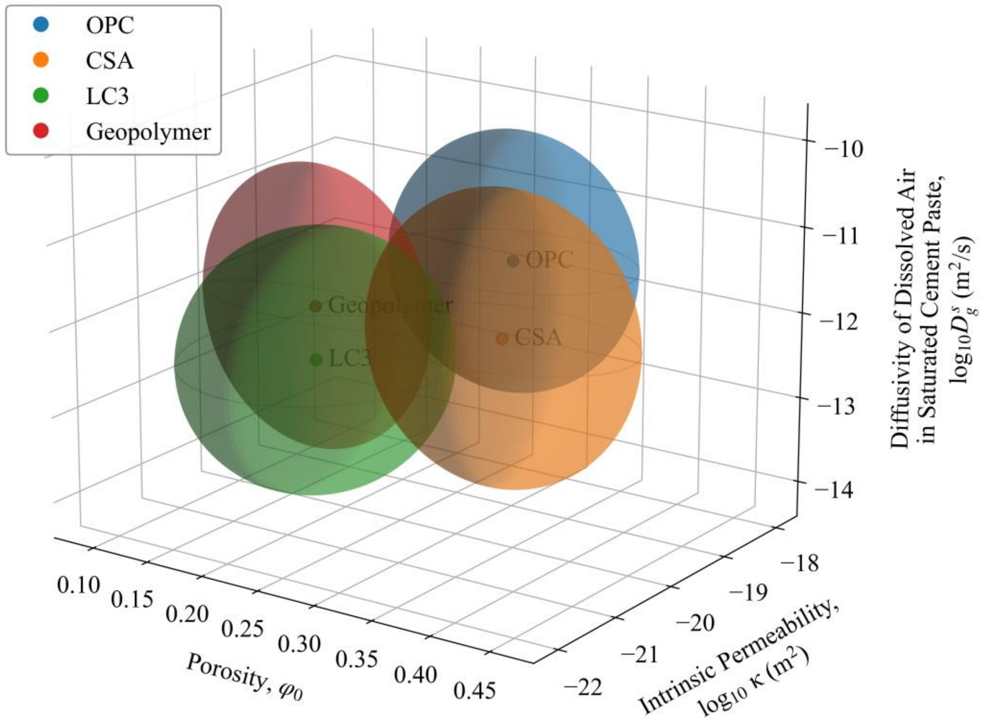
- Diffusion flux

$$J(R,t) = -D \left.\frac{\partial C_g}{\partial r}\right|_{r=R(t)}$$

2. Air dissolution and long-term saturation in cementitious materials

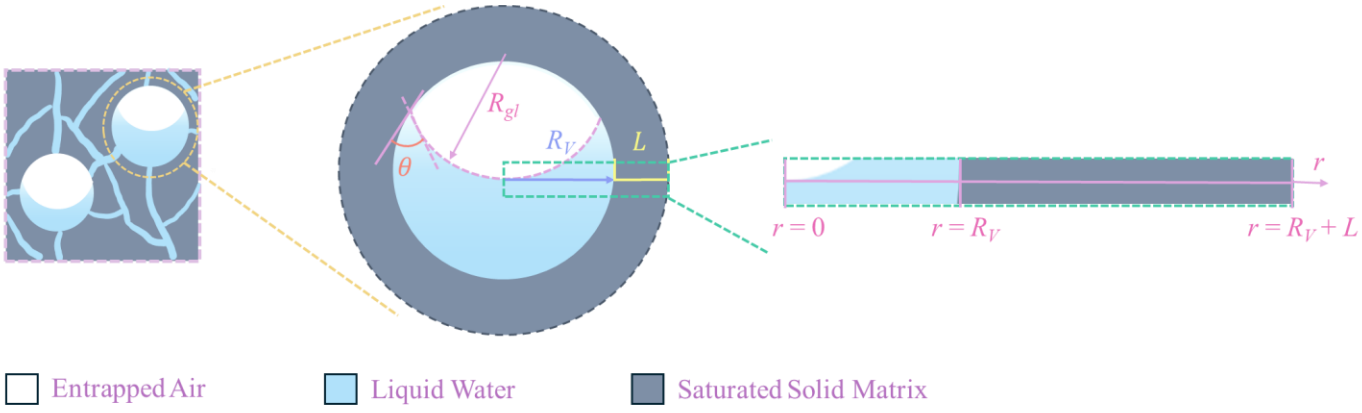
- Variations in physical and microstructural properties across cementitious systems

Parameters	OPC System (Baseline)	CSA Cement System	LC^3 System	Geopolymer System
Bulk porosity, φ_{bulk}	0.2–0.4	~0.23–0.45	~0.1–0.3	0.1–0.3
Intrinsic permeability, κ (m^2)	10^{-18}–10^{-20}	10^{-19}–10^{-21}	10^{-19}–10^{-22}	10^{-20}–10^{-21}
Diffusivity of dissolved air in saturated hydrated cement paste, D_g^s (m^2/s)	10^{-10}–10^{-13}	~10^{-11}–10^{-14}	10^{-11}–10^{-14}	~10^{-11}–10^{-14}
Tortuosity, τ	$\tau = \varphi_{eff} \cdot \varphi_{seg}^{-3.15}$	1.5 × OPC	3–4 × OPC	1.2–2 × OPC
Air void-paste ITZ thickness, δ (μm)	~30	~0.65 × OPC	~0.67 × OPC	No distinct porous ITZ observed
ITZ porosity, φ_{ITZ}	~2–3 × bulk paste	~0.8 × OPC	~0.75 × OPC	Comparable to bulk paste



3. Mechanism and modeling of air dissolution and water filling

- Physical description of the process



- Governing equations -- Single void dissolution kinetics (SVDK) model (Smith et al., 2020)
  - Gas mass in the spherical void

$$\frac{\partial m_g}{\partial t} = 4\pi R_V{}^2 \left(D_g^s \frac{\partial C_g}{\partial r}\bigg|_{r=R_V^+} + \frac{\kappa}{\eta} C_g \frac{\partial P_l}{\partial r}\bigg|_{r=R_V^+} \right)$$

  - Liquid water mass in the spherical void

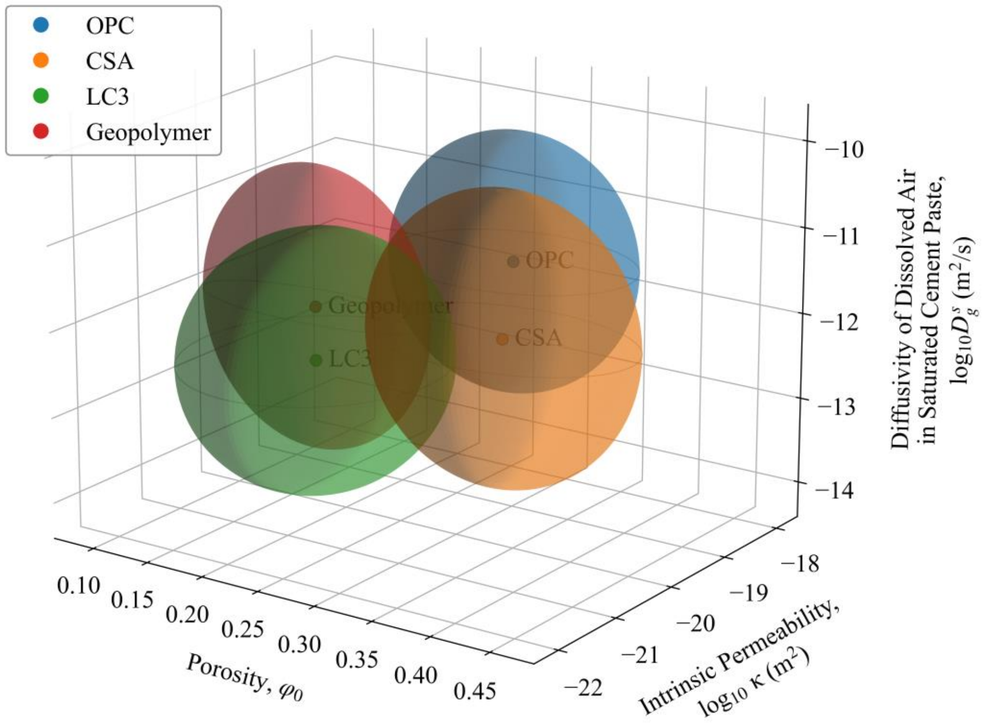
$$\frac{\partial m_l}{\partial t} = 4\pi R_V{}^2 \left(-D_g^s \frac{\partial C_g}{\partial r}\bigg|_{r=R_V^+} + \frac{\kappa}{\eta} \left(\rho_l - C_g\right) \frac{\partial P_l}{\partial r}\bigg|_{r=R_V^+} \right)$$

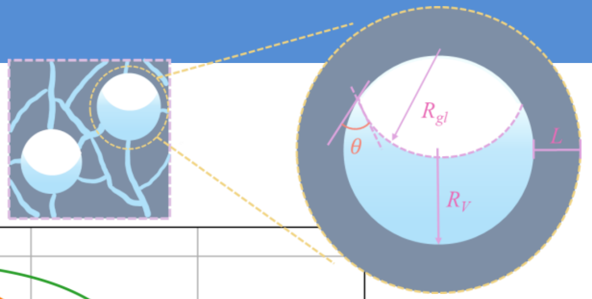
  - The concentration of dissolved gas in the liquid

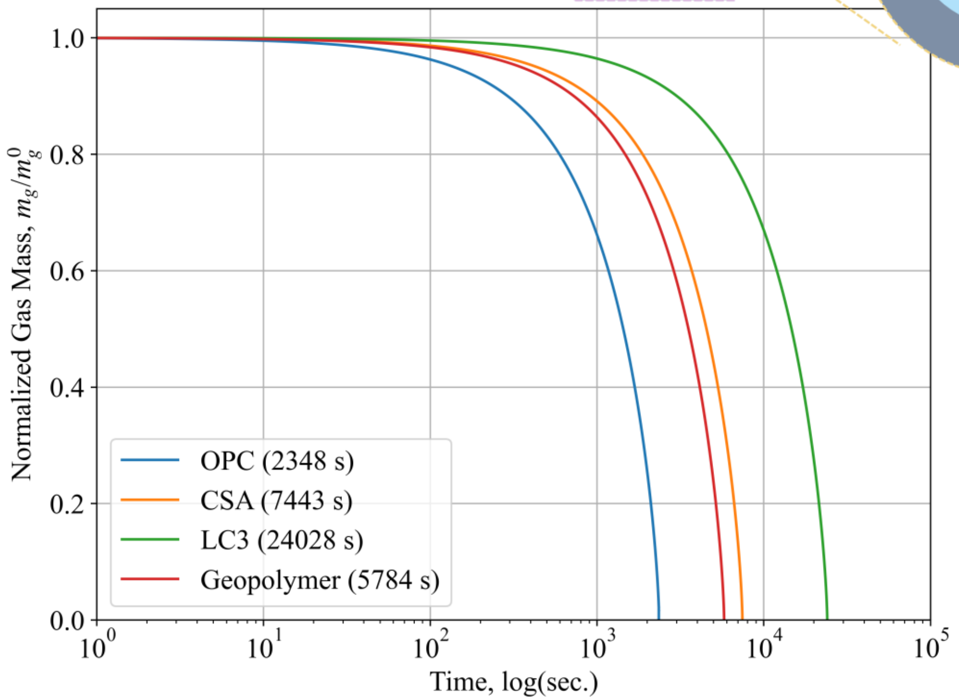
$$\frac{\partial C_g}{\partial t} = \underbrace{\frac{D_g^s}{\varphi_0} \frac{1}{r^2} \frac{\partial}{\partial r}\left(r^2 \frac{\partial C_g}{\partial r} \right)}_{\text{diffusion}} + \underbrace{\frac{\kappa R_V \left(R_V + L\right)}{\varphi_0 \eta} \frac{\left[P_l\left(R_V + L, t\right) - P_l\left(R_V, t\right)\right]}{r^2 L} \frac{\partial C_g}{\partial r}}_{\text{advection}}$$

4. Parametric analysis of saturation kinetics

- Comparison across different cementitious systems







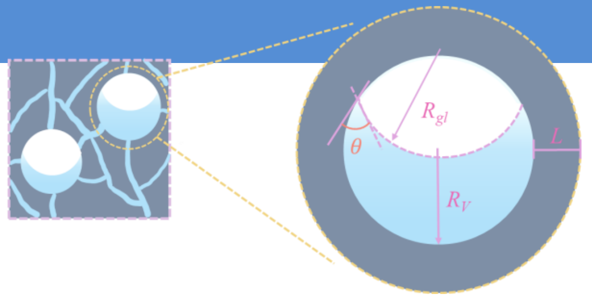
Physical Parameters	OPC	CSA	LC³	Geopolymer
φ_0	0.3	0.34	0.2	0.2
κ, (m^2)	1×10^{-19}	1×10^{-20}	3.16×10^{-21}	3.16×10^{-21}
D_g^s, (m^2/s)	3.16×10^{-12}	1×10^{-12}	3.16×10^{-13}	1.34×10^{-12}

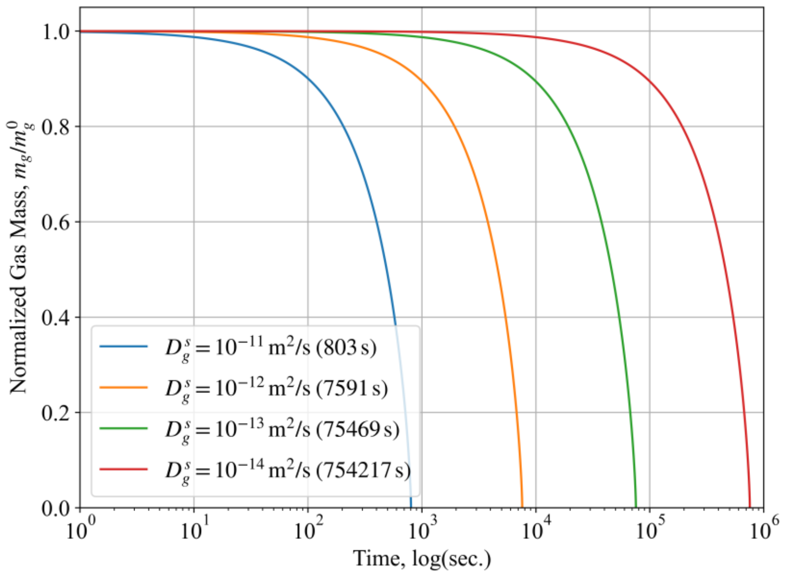
$R_V = 10\ \mu m$ $\quad L = 1\ mm$

$\theta = 20°$ $\quad m_t = 0.5$

4. Parametric analysis of saturation kinetics

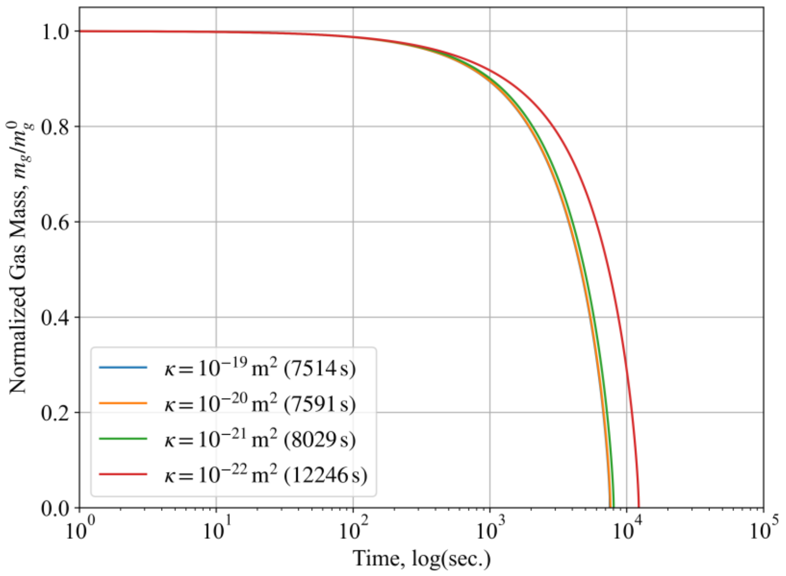
- Transport-related physical properties





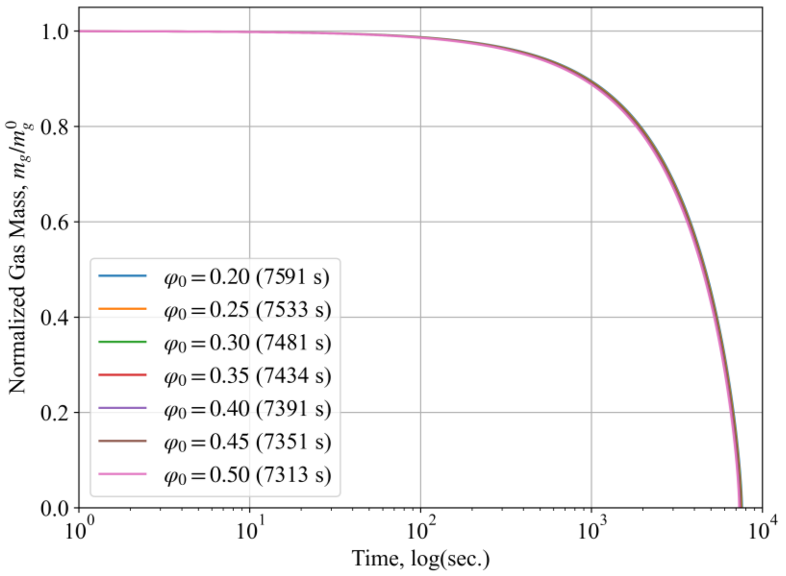
Diffusivity of dissolved air in saturated cement paste, D_g^s

$\kappa = 1 \times 10^{-20}$, $\varphi_0 = 0.2$, R_V = 10 μm, L = 1 mm, θ = 20°



Intrinsic permeability of cement paste, κ

$D_g^s = 1 \times 10^{-12}$, $\varphi_0 = 0.2$, R_V = 10 μm, L = 1 mm, θ = 20°

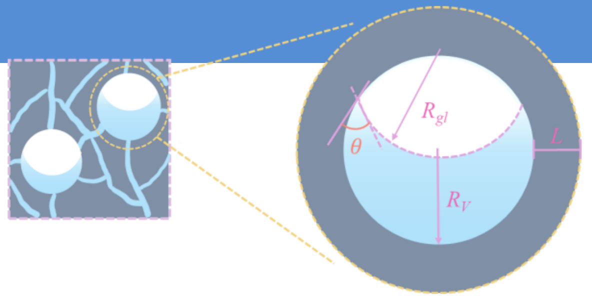


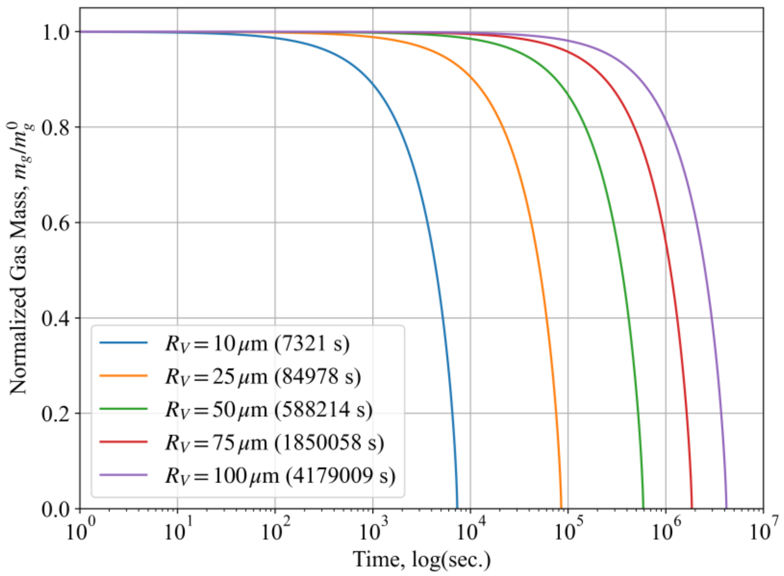
Porosity of cement paste matrix, φ_0

$D_g^s = 1 \times 10^{-12}$, $\kappa = 1 \times 10^{-20}$, R_V = 10 μm, L = 1 mm, θ = 20°

4. Parametric analysis of saturation kinetics

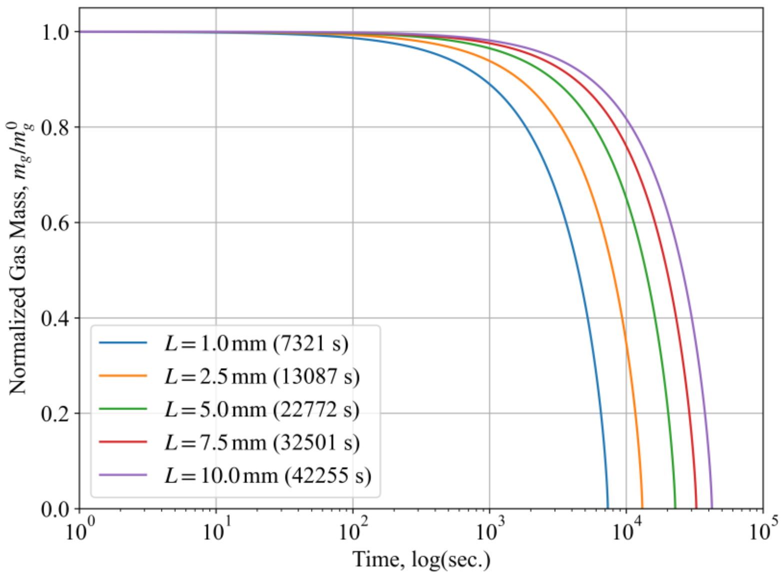
- Microstructure-related geometrical properties





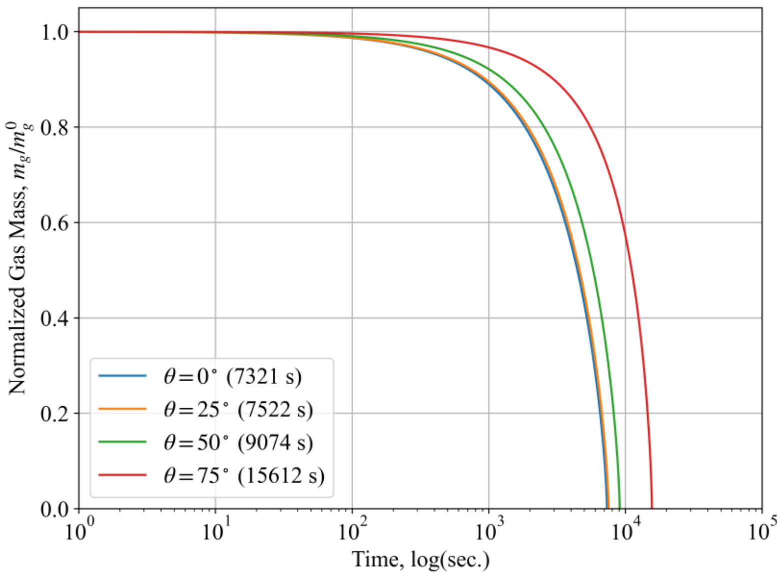
Spherical air void radius, R_V

L = 1 mm, θ = 0°, $D_g^s = 1 \times 10^{-12}$, $\kappa = 1 \times 10^{-20}$, $\varphi_0 = 0.2$



Saturated cement paste shell thickness, L

R_V = 10 µm, θ = 0°, $D_g^s = 1 \times 10^{-12}$, $\kappa = 1 \times 10^{-20}$, $\varphi_0 = 0.2$

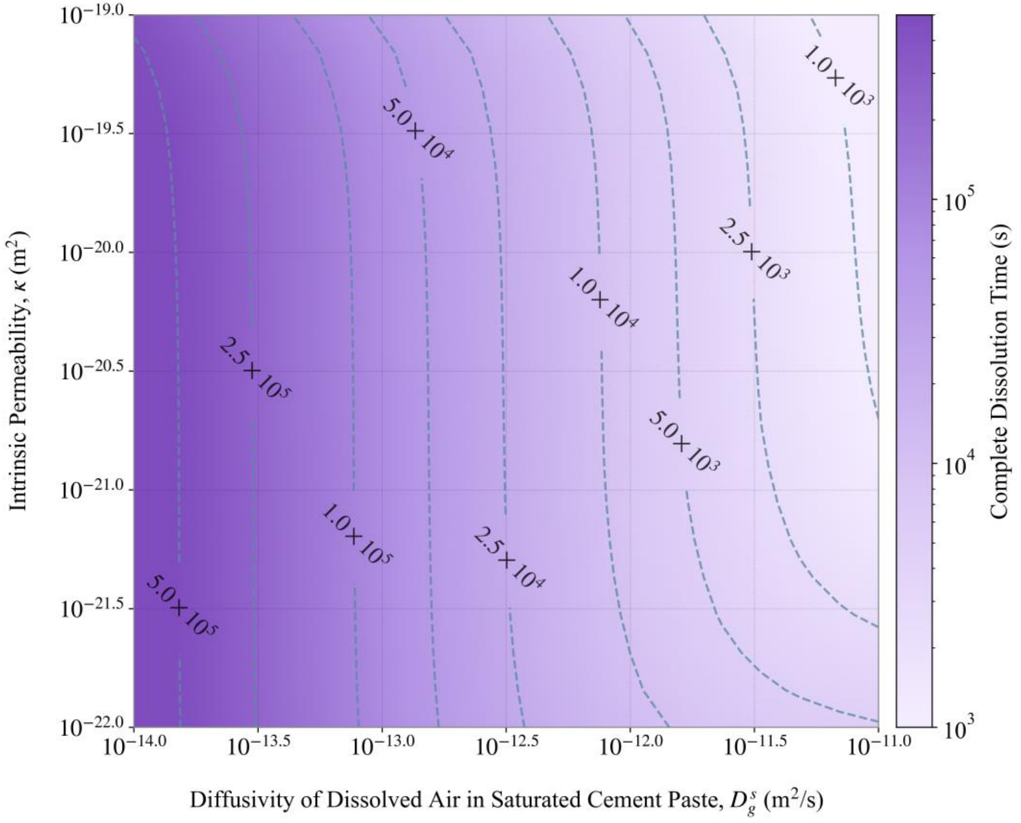


Air-liquid interface contact angle, θ

R_V = 10 µm, L = 1 mm, $D_g^s = 1 \times 10^{-12}$, $\kappa = 1 \times 10^{-20}$, $\varphi_0 = 0.2$

5. Microstructure-informed optimization for freeze-thaw durability

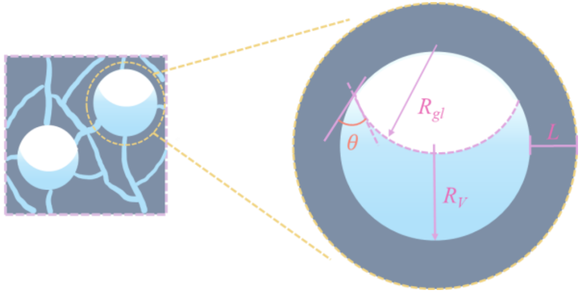
- Transport-related physical properties



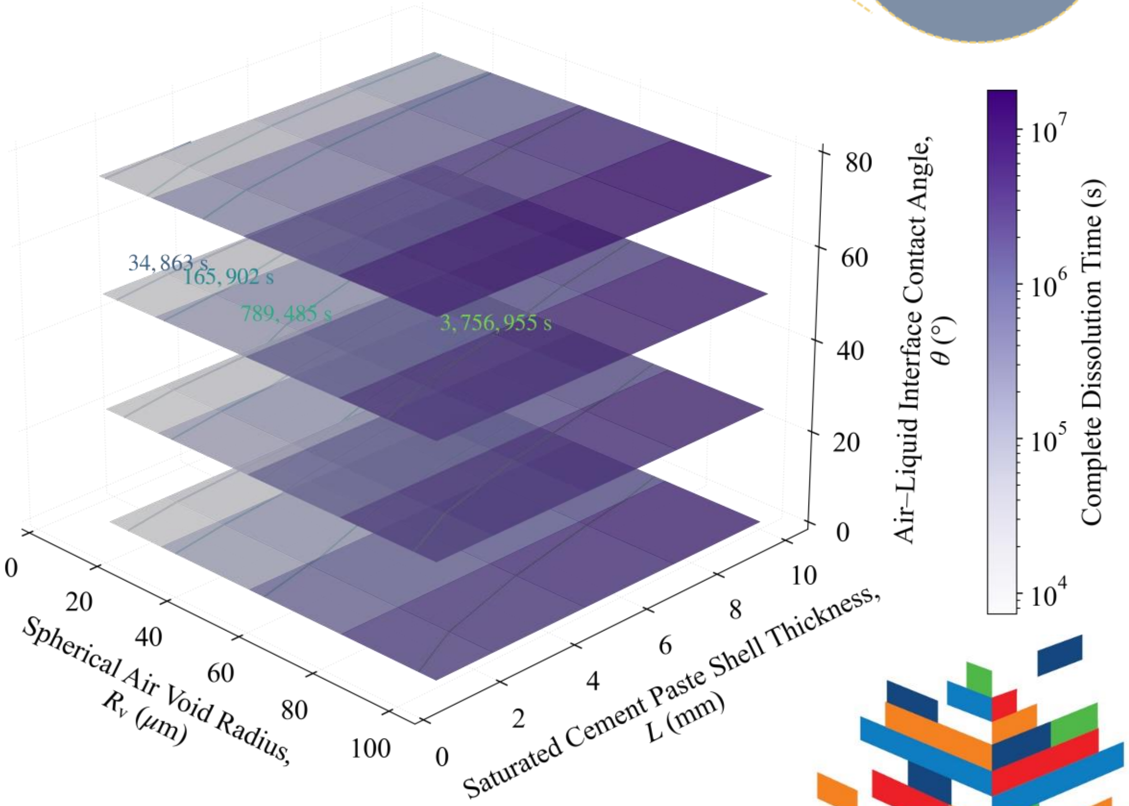
- Refining diffusion pathways (e.g., increasing tortuosity, reducing D_g^s) is more effective than altering porosity.
- Combining low D_g^s and low κ yields better long-term air retention and freeze-thaw durability.
- **System-specific insights:**
  - OPC requires stronger densification and air control.
  - CSA focuses on cracking and setting control.
  - LC^3 should preserve its low-transport dense matrix.
  - Geopolymers need to reduce shrinkage and ensure compatibility with air-entraining agents.

5. Microstructure-informed optimization for freeze-thaw durability

- Microstructure-related geometrical properties



  - Create a controlled amount of stable, larger entrained voids (e.g., R_V~50–100μm) mixed with abundant small voids to keep spacing factor.
  - Increase interfacial hydrophobicity to enlarge contact angle and initial gas volume to slow dissolution.
  - Increase the effective path from void to free surface, e.g., add SCMs to densify paste to raise tortuosity.



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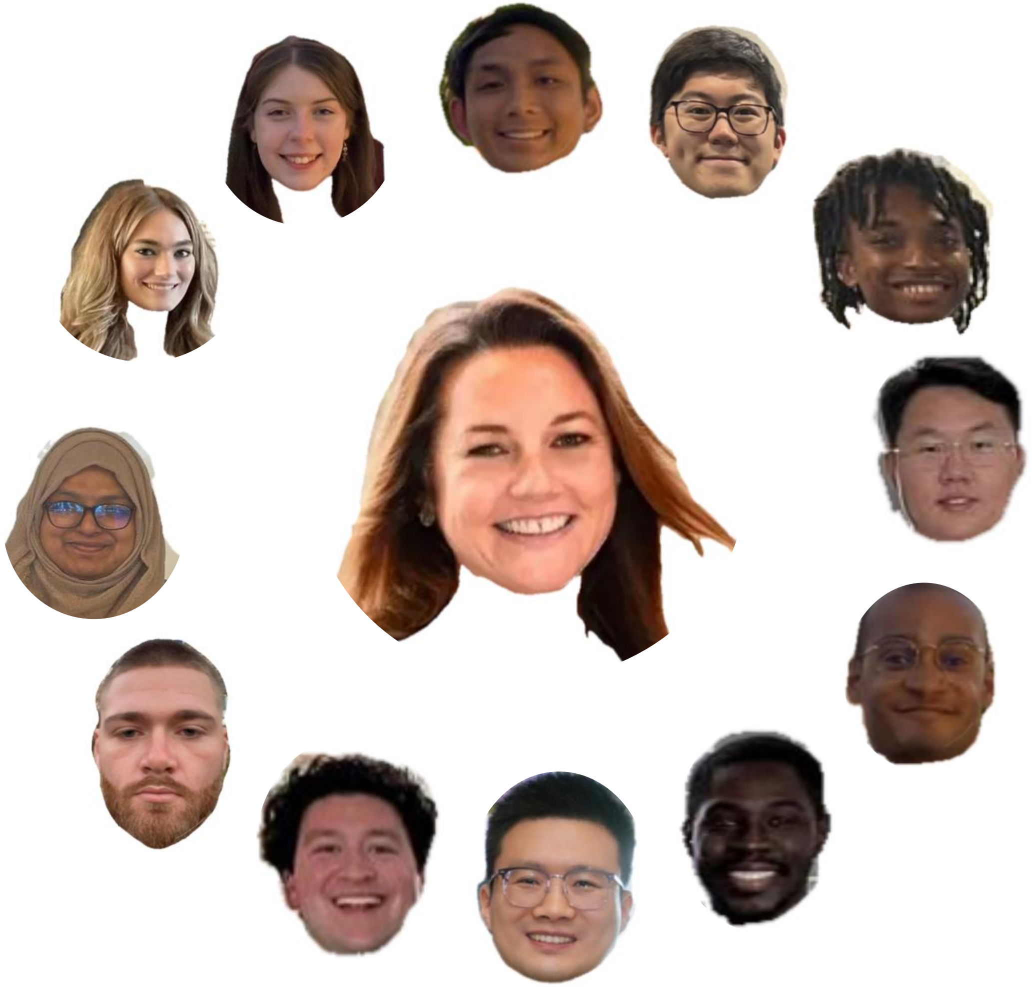
6. Summary

- **Comparison across different cementitious systems:**
  - From OPC to emerging systems, the transition from conventional to low-carbon, dense microstructures corresponds to progressively improved freeze-thaw durability.
- **Transport parameters dominate the kinetics of air void saturation:**
  - Diffusivity is the most critical factor, permeability plays a secondary role, and porosity shows limited impact in the typical range of cement paste.
- **Geometrical parameters provide additional ways for durability design:**
  - Air void radius provides the strongest geometrical control, shell thickness increases the diffusion path, and contact angle moderately affects dissolution.

6. Summary

- **Design implications for freeze-thaw durability.**
  - Optimizing void systems through a bi-modal or multi-modal distribution (many small voids for spacing, stable larger ones for air retention).
  - Refining transport pathways by reducing diffusivity and permeability via low w/b, SCMs, densified ITZ, and improved curing.
  - Modifying interfacial chemistry to increase contact angle and delay void dissolution.
  - **System-specific insights:** OPC needs densification and air stability; CSA should control cracking and setting; LC^3 should maintain its dense, low-transport microstructure; and geopolymers should limit shrinkage and ensure AEA compatibility.

Acknowledgements



Thank you!
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Questions?

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Aiqing "Felix" Xu
aqxu@gatech.edu

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