Hydration and Percolation

George Scherer[A], John Quintanilla[B],
Sulapha Peethamparan[C], Jie Zhang[A],
Emily Weissinger[A], Salvatore Torquato[A]

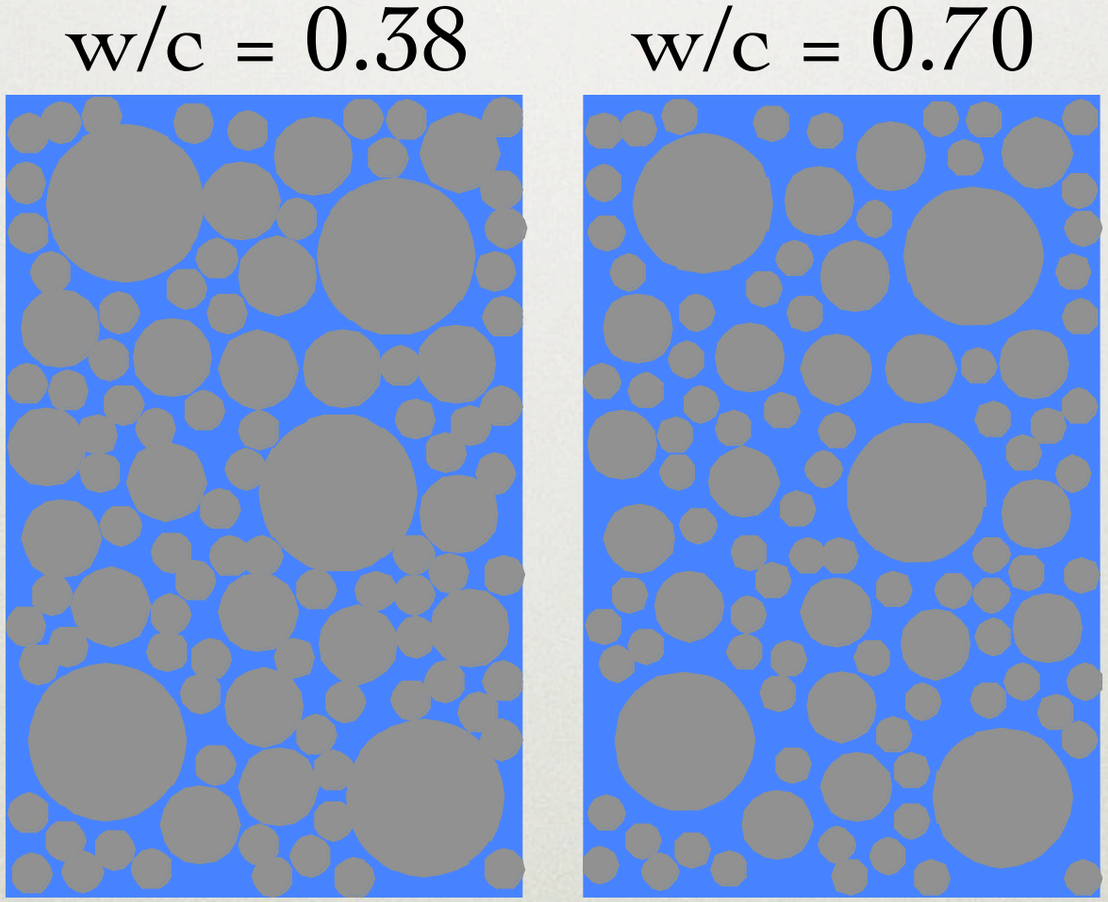
[A] Princeton University
[B] University of North Texas
[C] Clarkson University

Hydration and Percolation

- Percolation & Setting
- Characterizing the setting point
  - Vicat needle & acoustic velocity
  - Chemical shrinkage
  - DOH by TGA
- Cherry pit model

Percolation & Setting

- If setting corresponds to a percolation threshold, it should occur at fixed DOH



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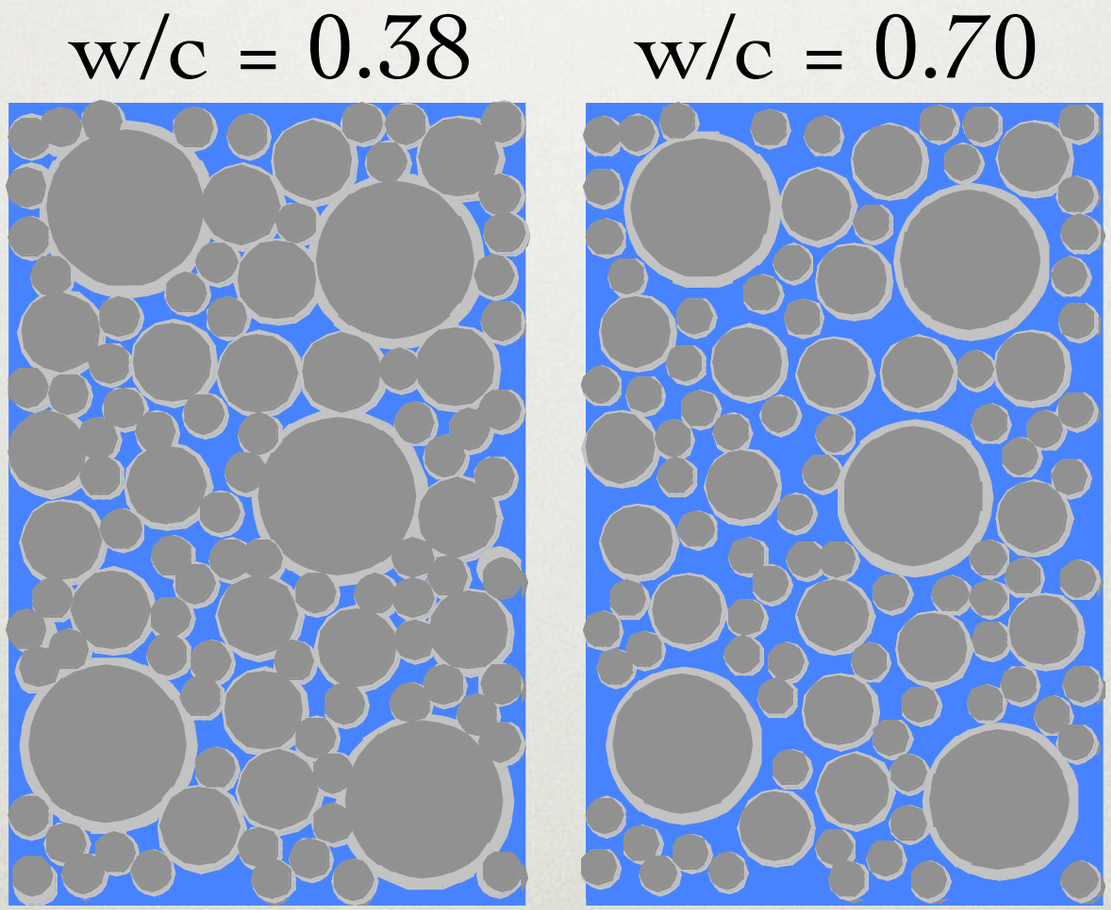
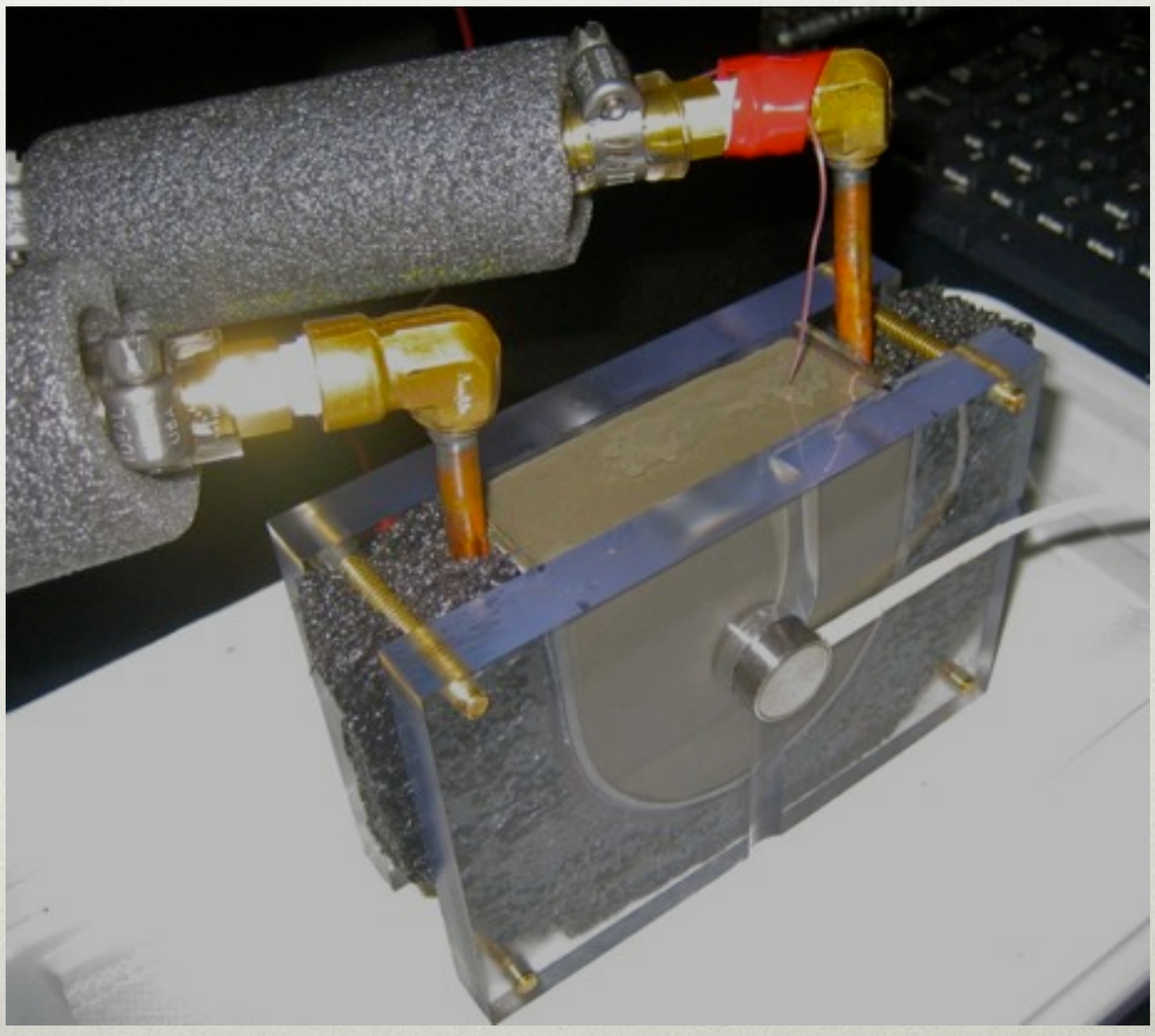


Acoustic Velocity

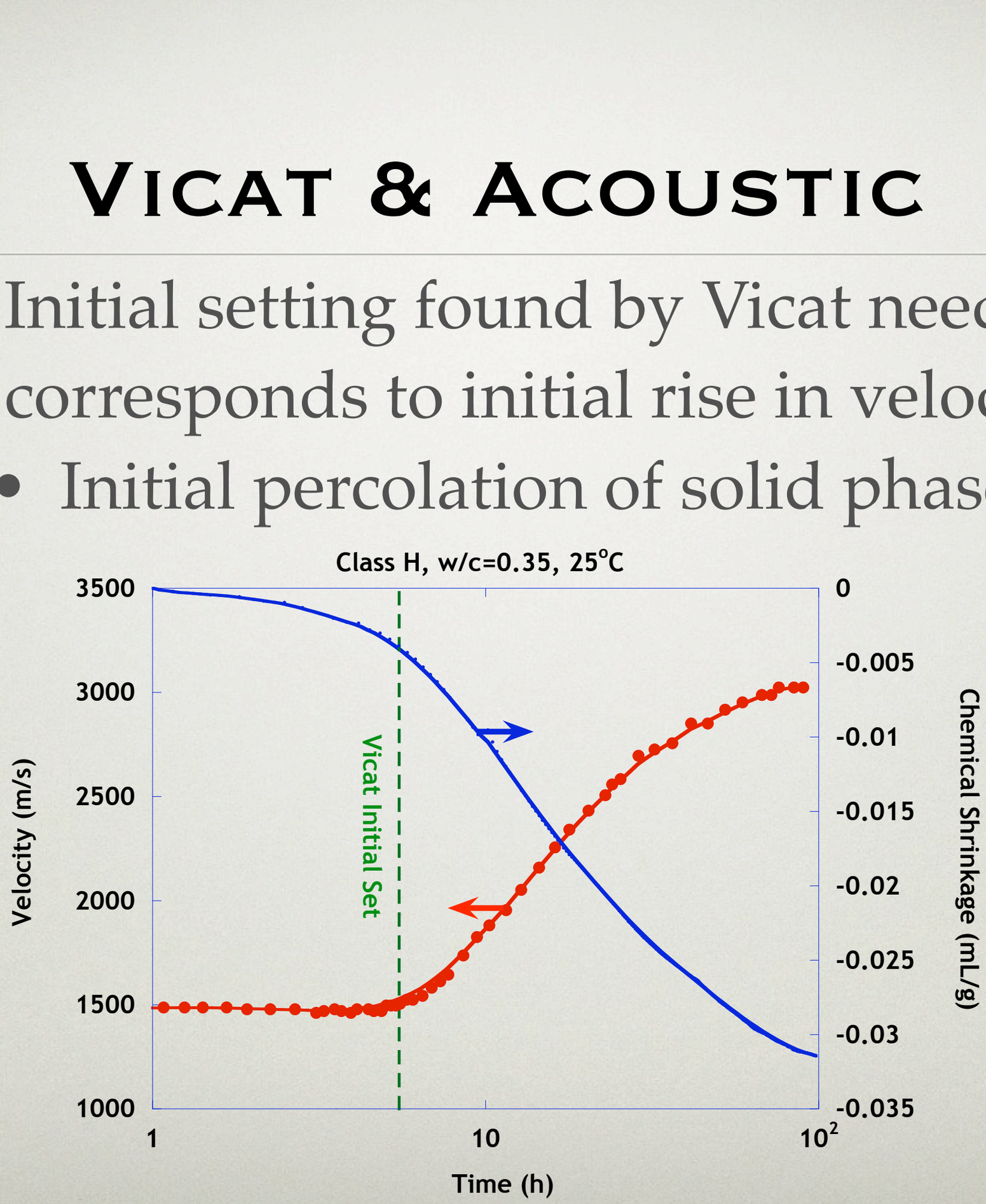
- Initial velocity ↔ compressibility of water
- Velocity rises at percolation threshold

Based on design by D.G. Aggelis & T.P. Philippidis, NDT&E International 37 (2004) 617–631



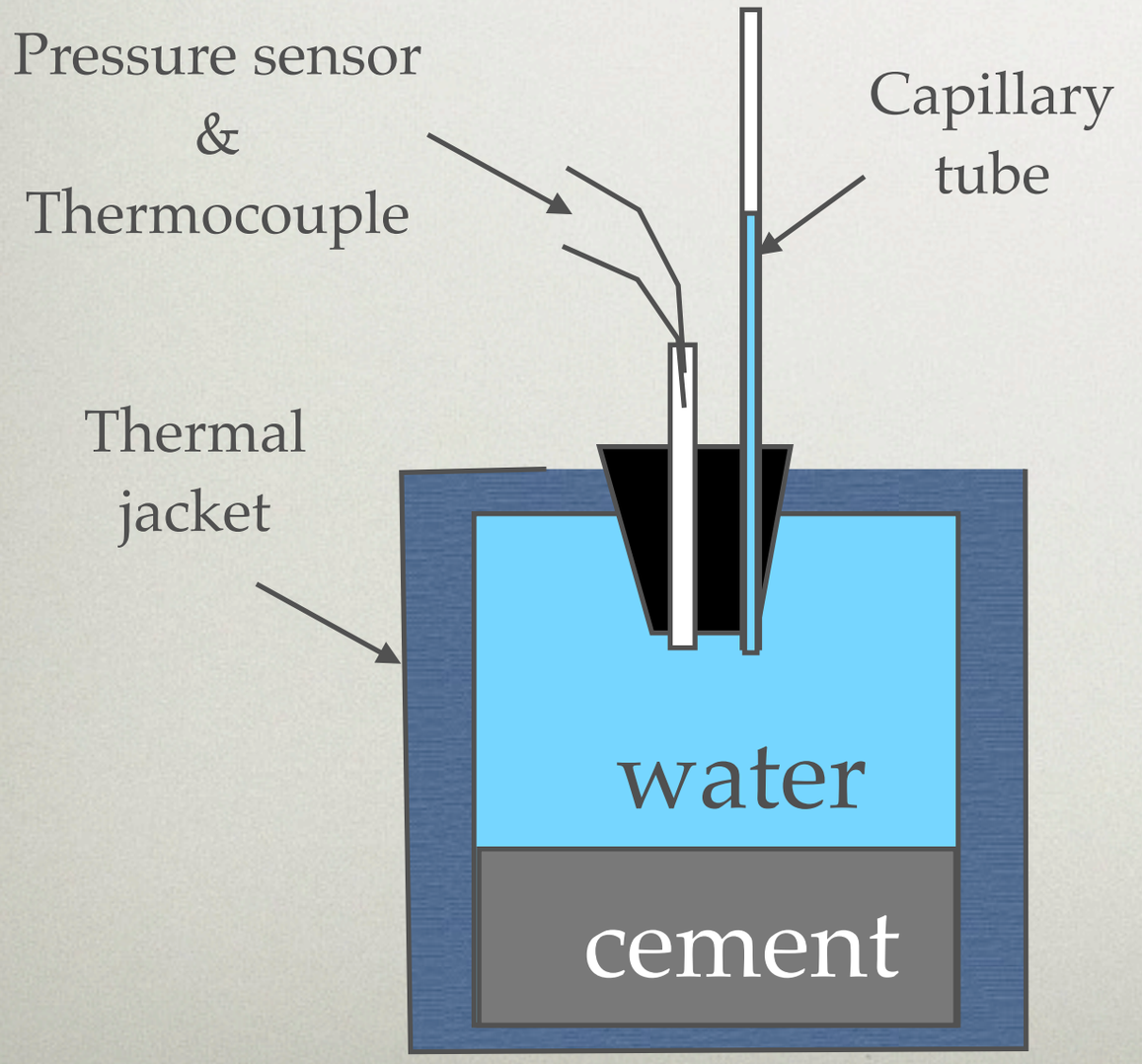
Vicat & Acoustic

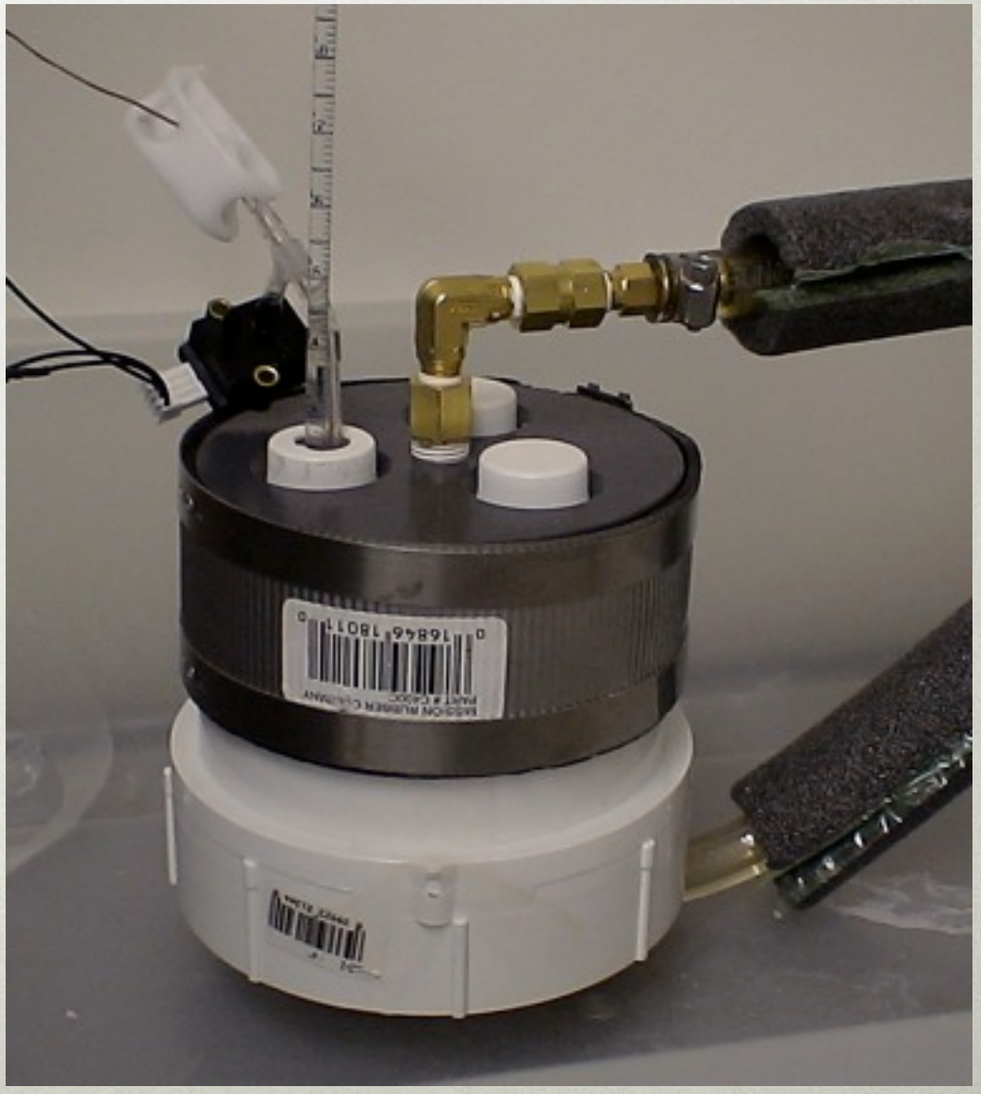
- Initial setting found by Vicat needle corresponds to initial rise in velocity
- Initial percolation of solid phase

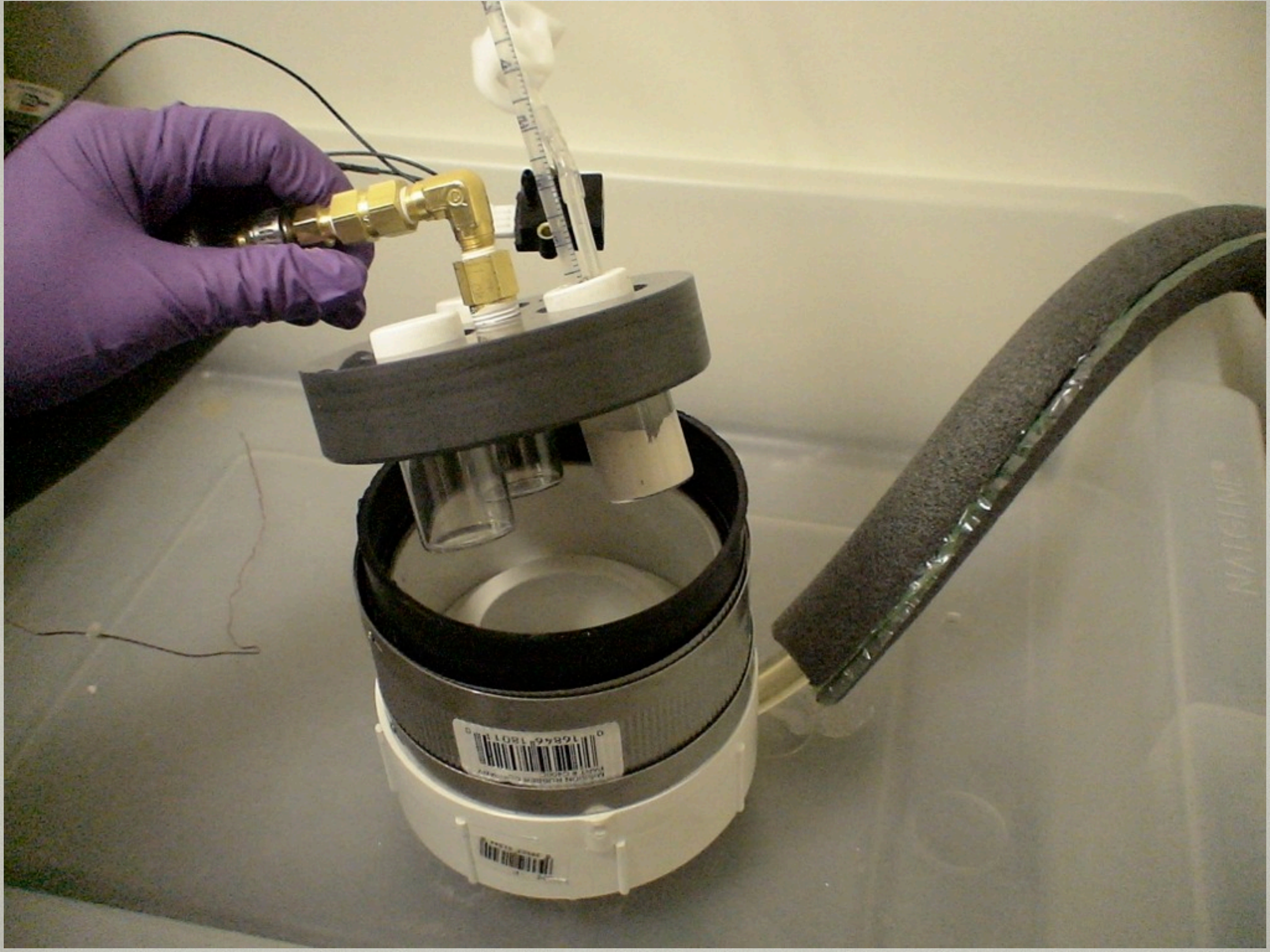


Measuring Chemical Shrinkage

- New method for quantifying volume change by measuring change in hydrostatic head







Modeling Shrinkage

- Use Avrami-Cahn model, proposed by Thomas
- Near setting point, A-C-T model reduces to

$$X \approx \frac{\pi}{3} O_v^B I_B G^3 t^4 \equiv \frac{\pi}{3} k_B^4 t^4$$

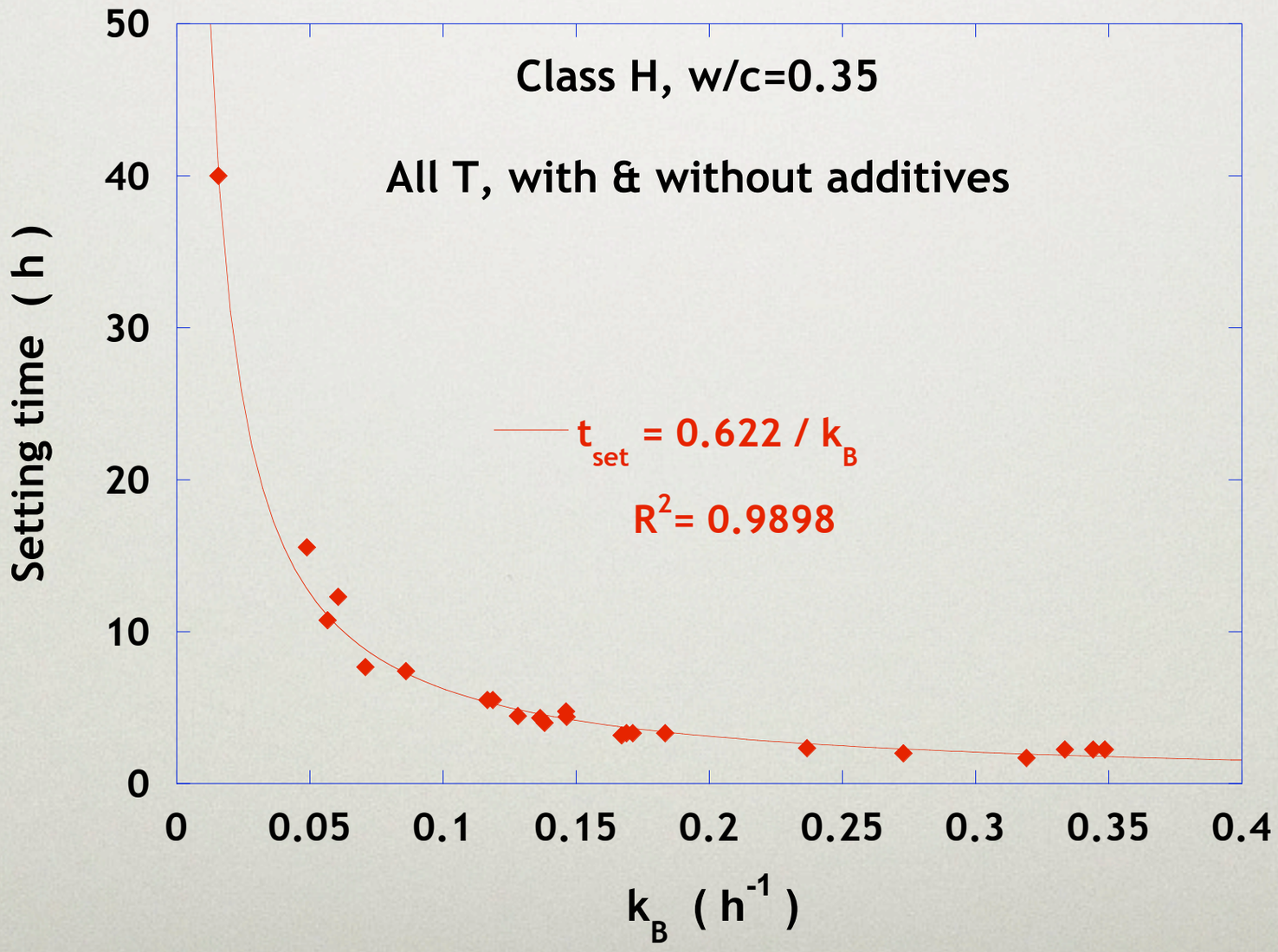
- If setting time represents percolation,

$$X_{set} \approx \frac{\pi}{3} k_B^4 t_{set}^4$$

$$k_B \propto 1 / t_{set}$$

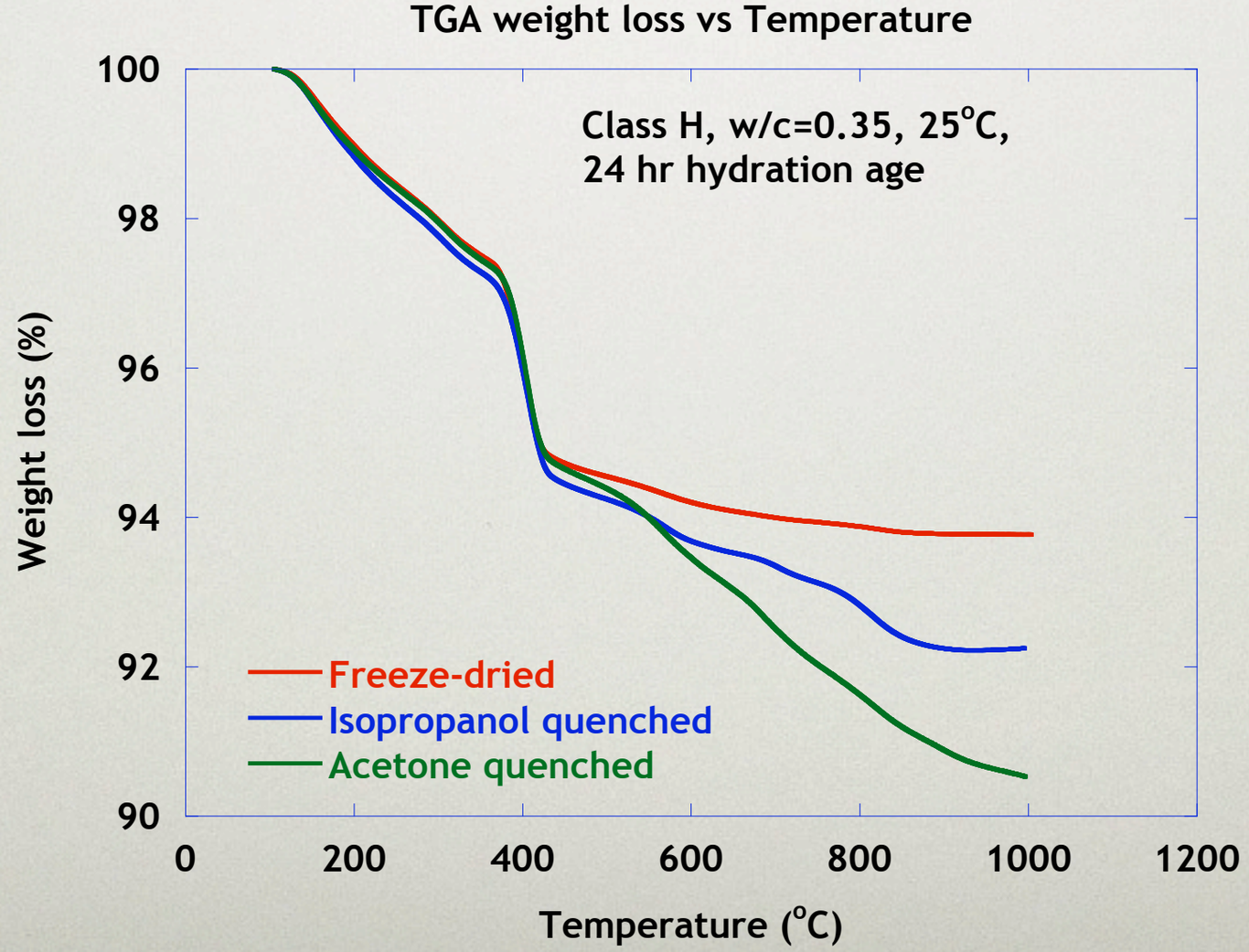
Modeling Shrinkage

- Shrinkage & setting data confirm that setting occurs at fixed DOH



Measuring DOH

- Solvent quenching yields artificially high DOH
  - Best solvents are i-PrOH & THF
  - Best method is freeze-drying



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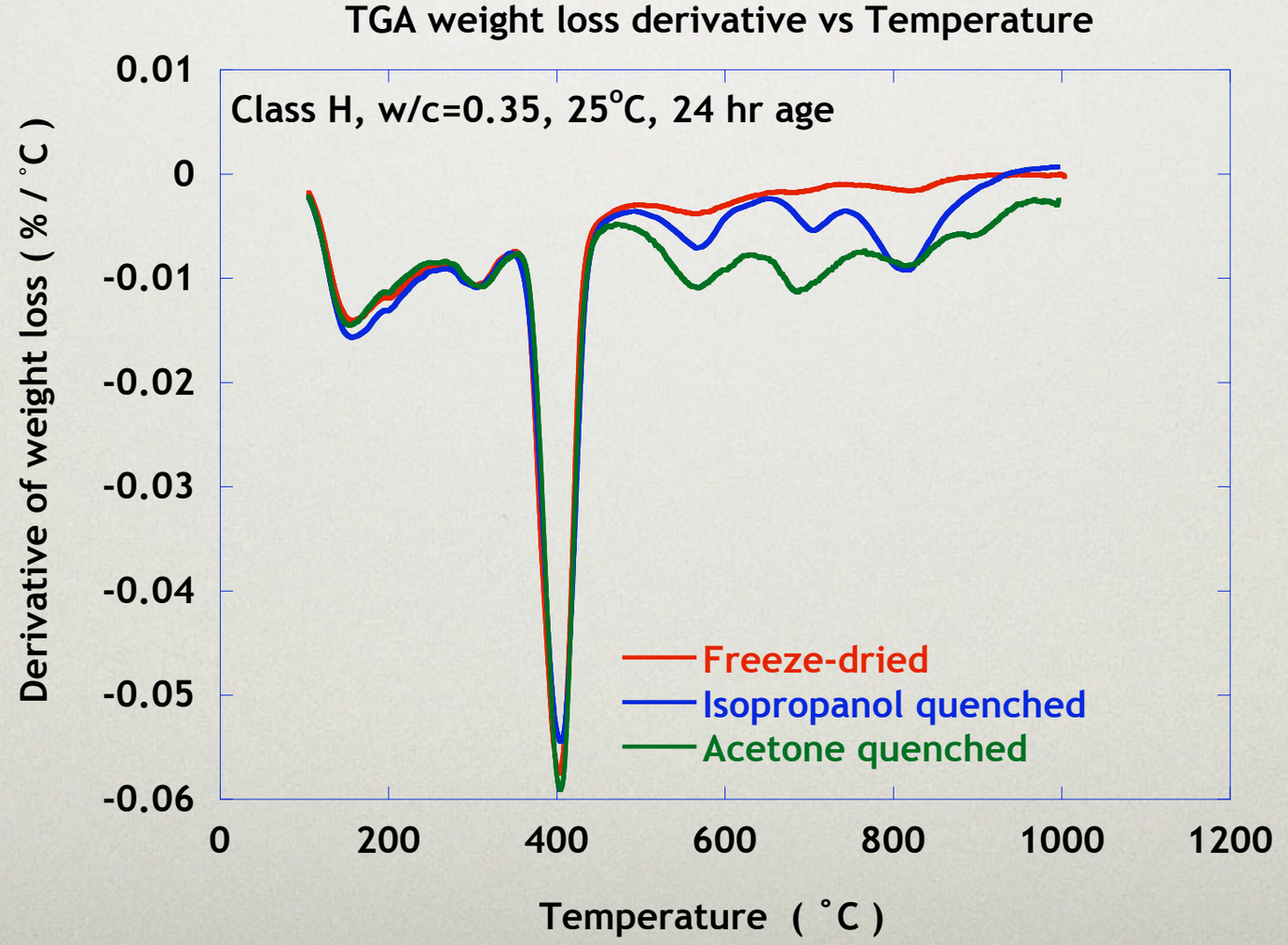
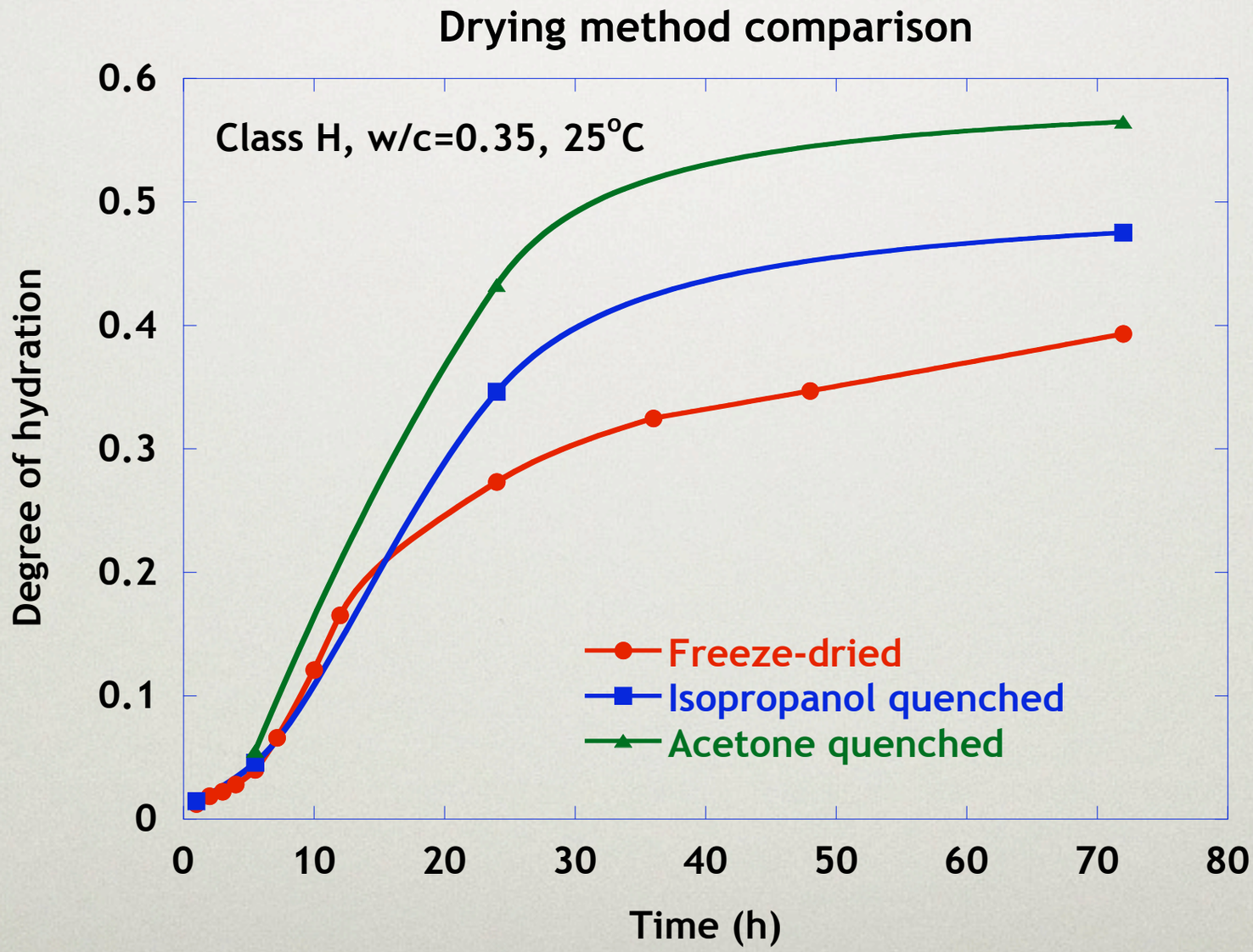


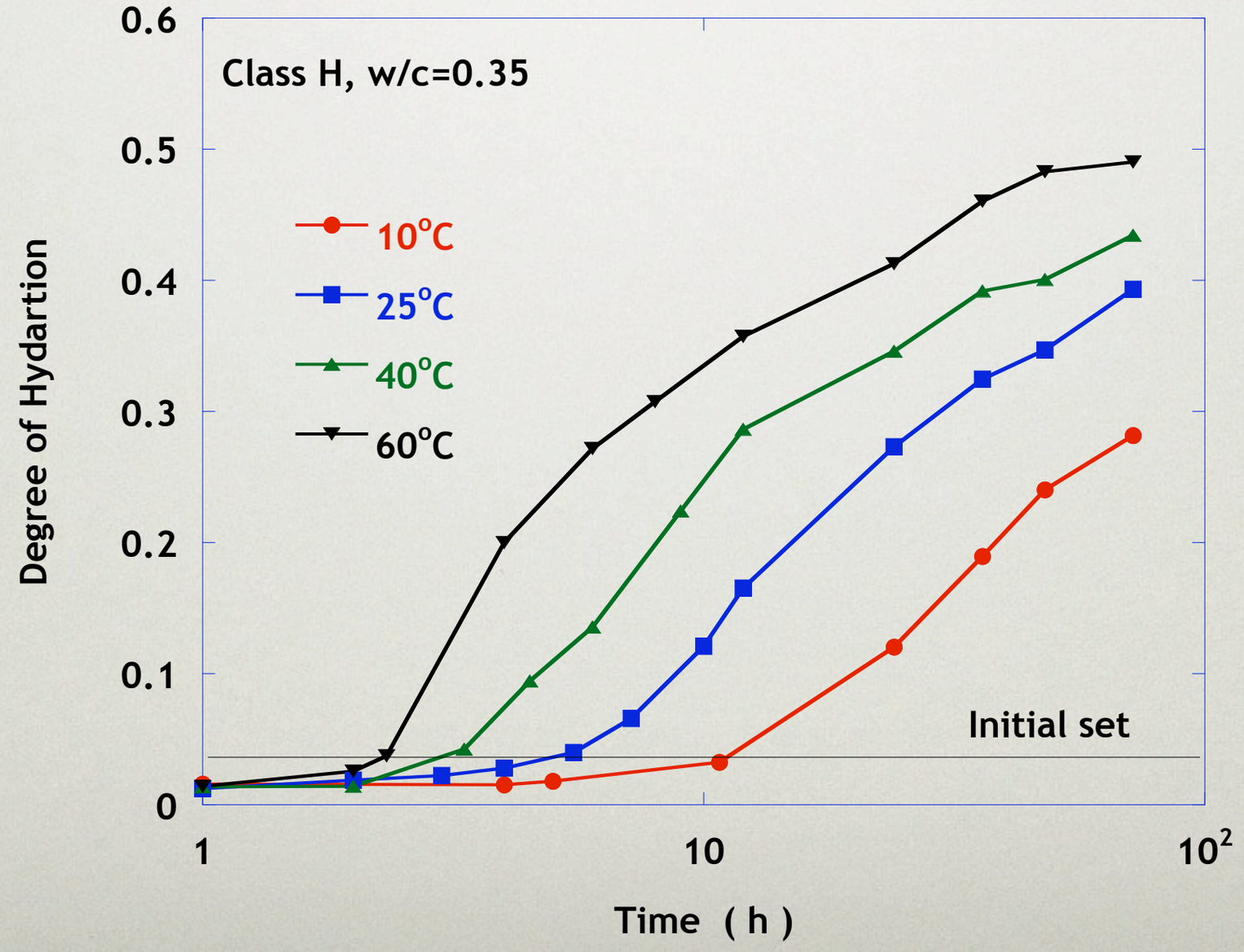
DOH vs Age

- At initial set, DOH $\approx 4\%$ (w/c = 0.35)



DOH at Initial Set

- For Class H cement, w/c = 0.35, DOH at initial set is ~0.04 for all T



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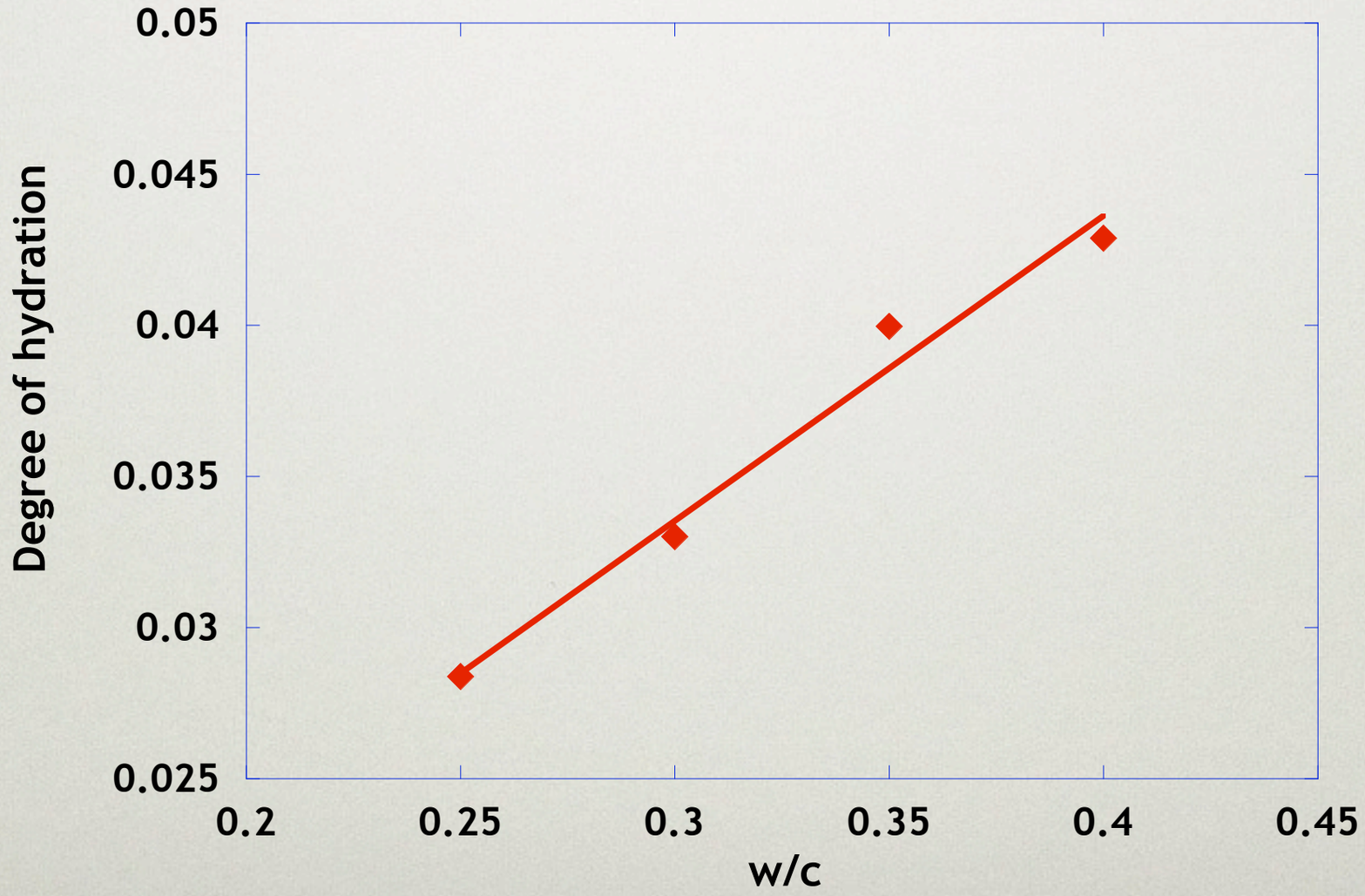


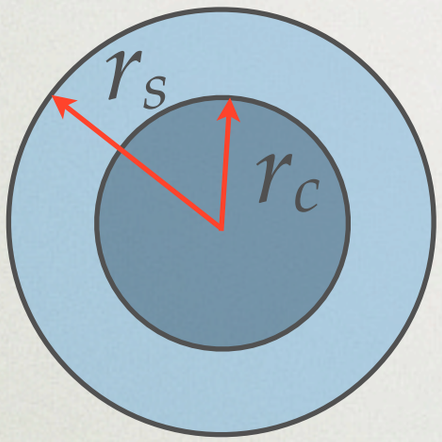
DOH versus w/c

- Satisfactory percolation model must explain DOH at initial set
- Test Cherry Pit (or, hard core-soft shell) model developed by Torquato
  - core = clinker, shell = hydrates
  - Provides *analytical expression* for DOH at percolation threshold

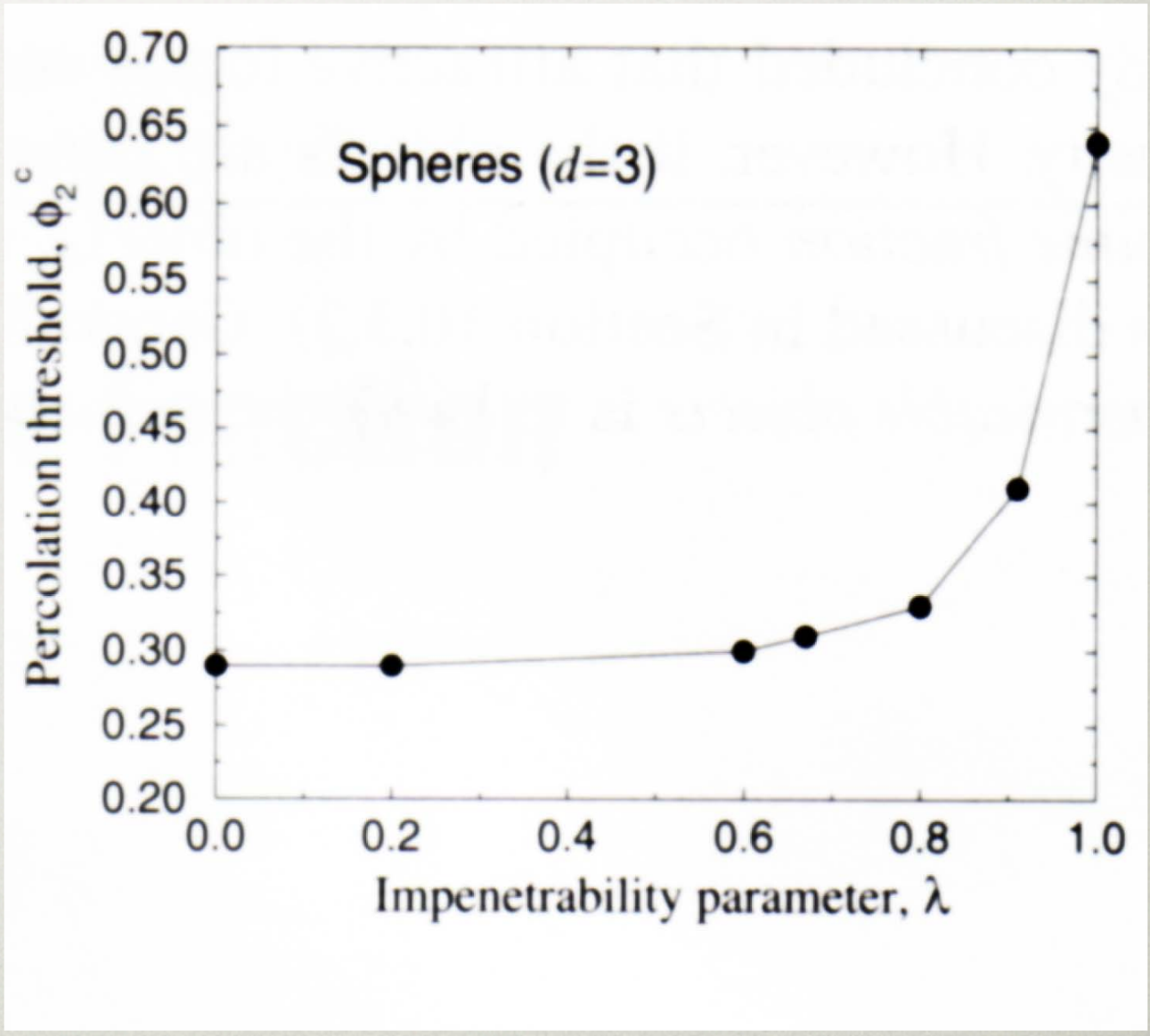
Cherry Pit Model

- Radius ratio of hard core to soft shell is λ

$$\lambda = r_c \,/\, r_s$$



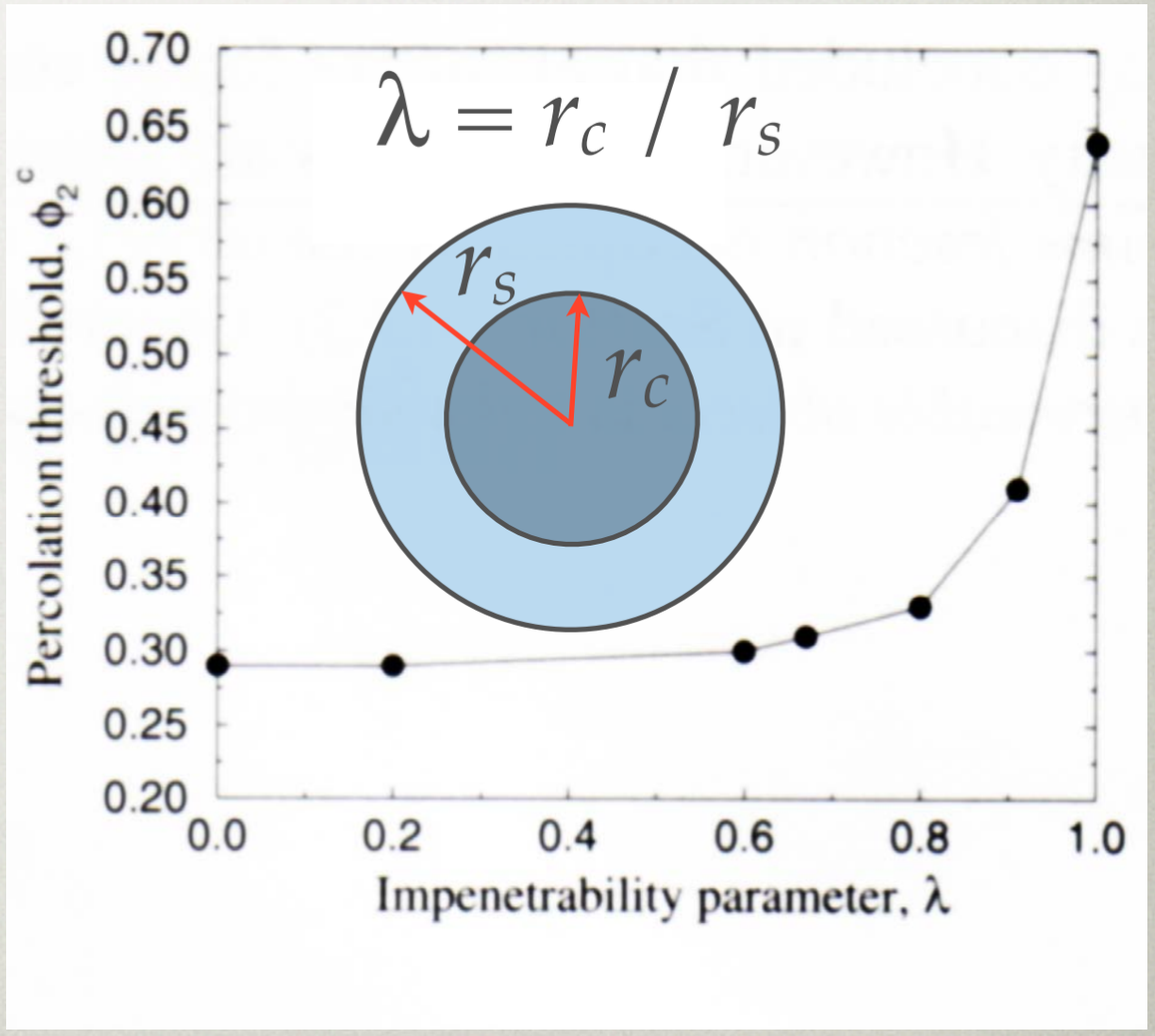
- Shell is hydration product
- Percolation is setting point



S. Torquato, *Random Heterogeneous Media*,(Springer, New York, 2002)

Cherry Pit Model

- Rigid spheres ($\lambda = 1$) form rigid packing when volume fraction reaches $v \approx 0.64$
- Overlapping spheres ($\lambda = 0$) form network at $v \approx 0.29$
- What is thickness of hydration layer at setting point?



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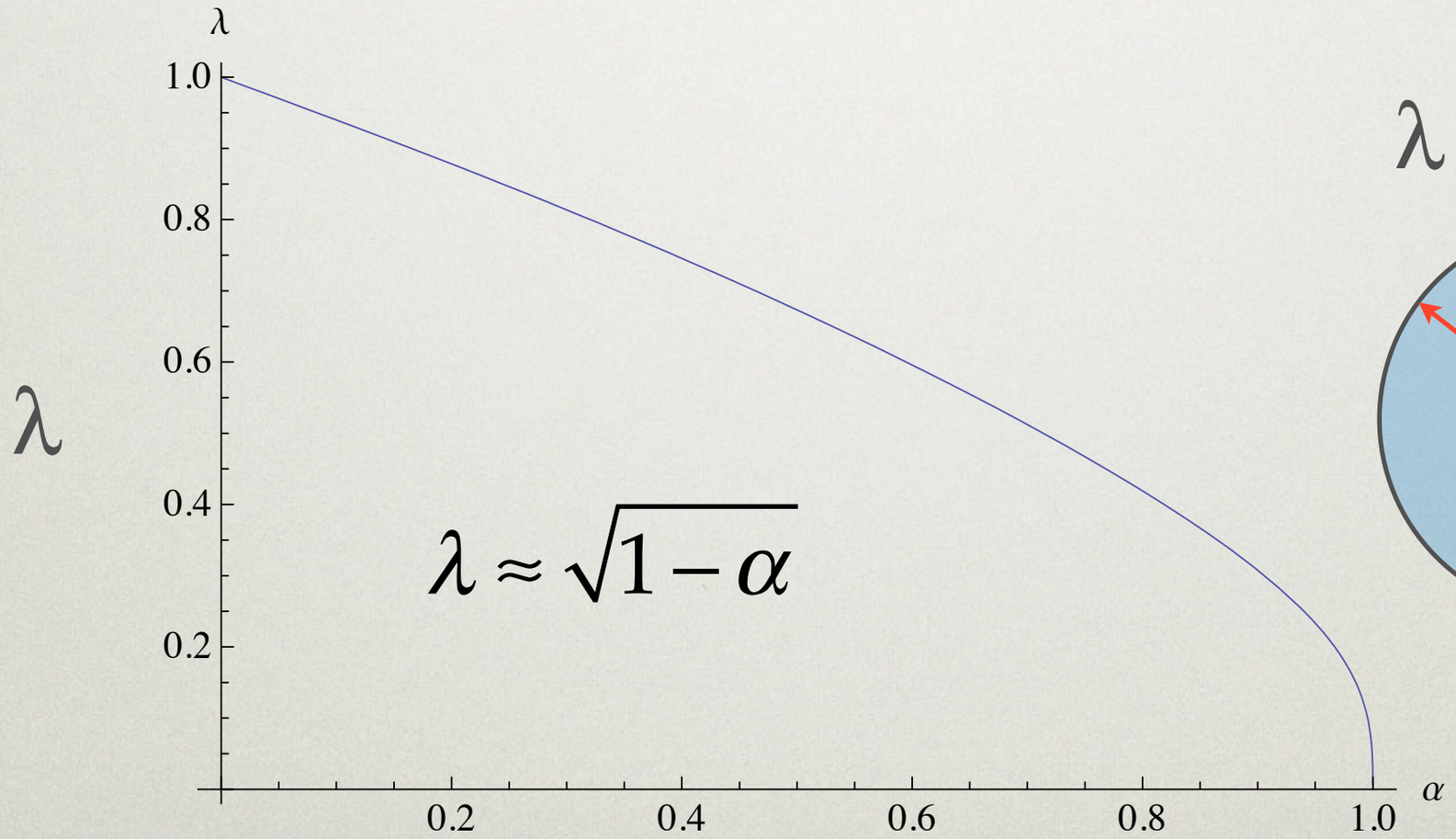
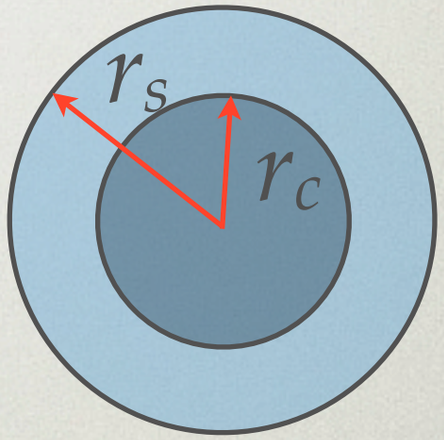
Cherry Pit & Hydration

- Layer thickness vs Degree of hydration, α
  - Core shrinks as hydration proceeds

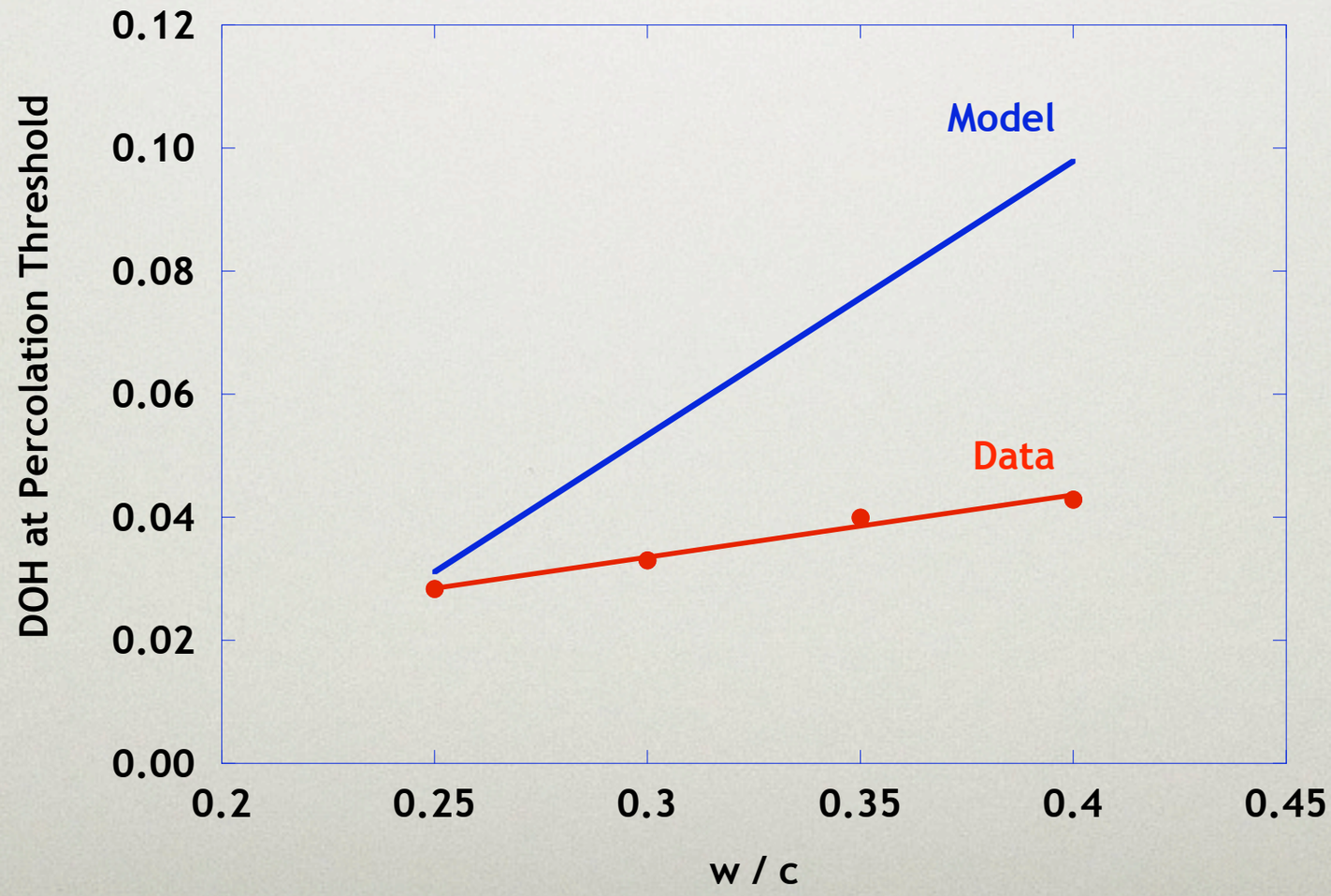


$$\lambda = r_c \,/\, r_s$$



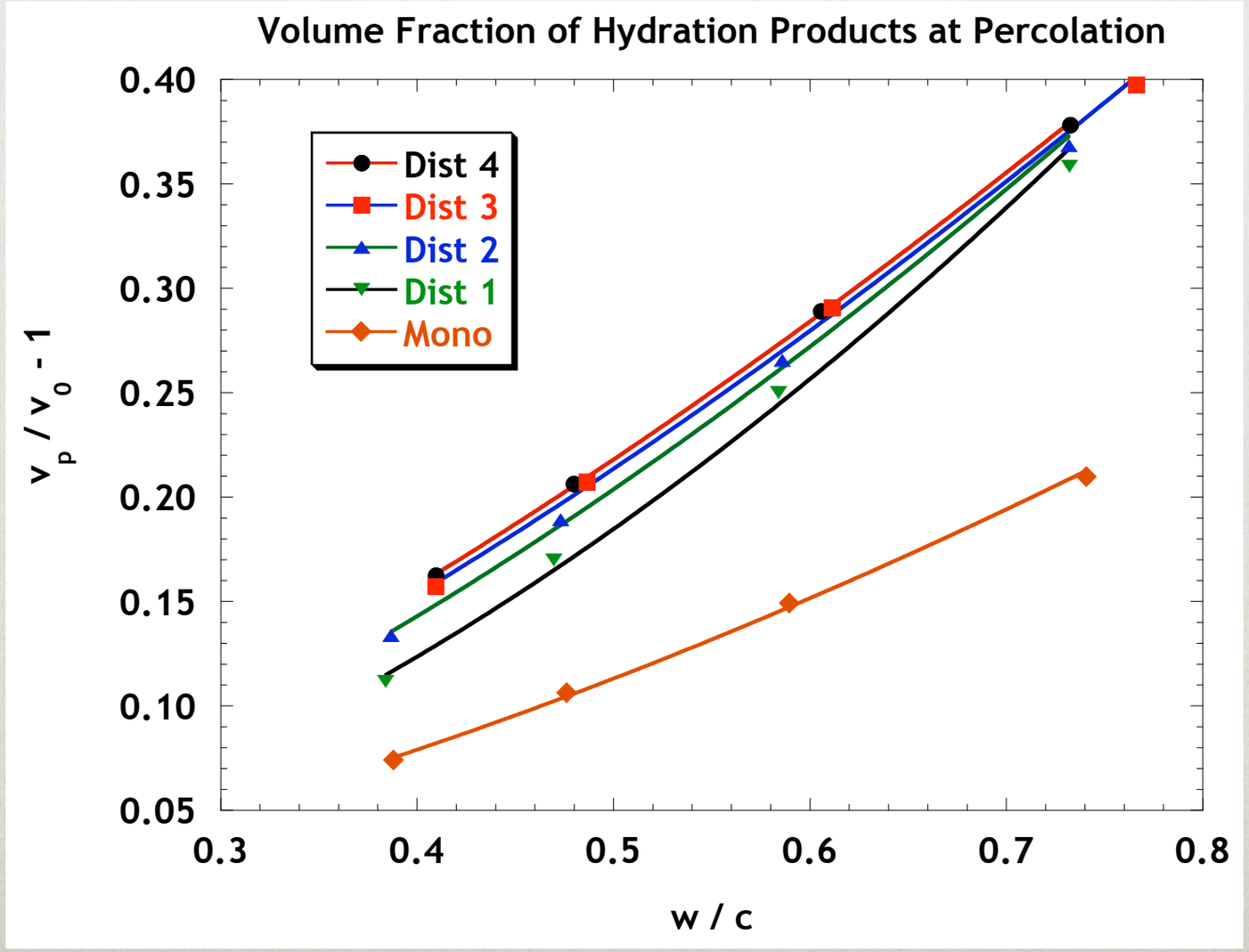
Model Prediction

- Original model assumes uniform particle size
  - Requires too much hydration for setting
  - Will fines enable earlier setting?



Size Distribution

- Introducing particle size distribution *increases* predicted DOH at percolation threshold



Role of Aggregation

- Simulations assume that particles are initially dispersed ("equilibrated")
- Particles in paste actually slightly aggregated
  - Reduces interparticle distance
  - Reduces DOH needed to percolate
  - Accounts for poorer performance at higher w/c, where aggregation more important
- Initial aggregation can be included in model

Conclusions

- Setting corresponds to percolation
  - Corresponds to increase in acoustic velocity
  - Occurs at constant DOH for given w/c
    - DOH at initial set $\propto 1/t_{set}$
- DOH at initial set $\approx 4\%$ at $w/c = 0.35$ is lower than predicted by Cherry Pit model
  - Discrepancy not from neglect of psd
  - Probably reflects neglect of agglomeration
- Next simulations will explore aggregation

Acknowledgment

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