HYDRATION AND PERCOLATION

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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

\[ \text{w/c} = 0.38 \quad \text{w/c} = 0.70 \]
Percolation & Setting

- If setting corresponds to a percolation threshold, it should occur at fixed DOH w/c = 0.38 and w/c = 0.70.
Acoustic Velocity

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

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

![Diagram of equipment setup]

- Pressure sensor & Thermocouple
- Capillary tube
- Thermal jacket
- Water
- Cement
Measuring Chemical Shrinkage

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Measuring Chemical Shrinkage

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

cement

Pressure sensor & Thermocouple

Capillary tube

Thermal jacket

water
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,

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

\[ k_B \propto \frac{1}{t_{set}} \]
Modeling Shrinkage

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

![Graph showing setting time vs. $k_B$ for Class H, w/c=0.35.](image)

- All T, with & without additives

- $t_{set} = \frac{0.622}{k_B}$

- $R^2 = 0.9898$
Measuring DOH

- Solvent quenching yields artificially high DOH
- Best solvents are i-PrOH & THF
- Best method is freeze-drying
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![TGA weight loss derivative vs Temperature graph](image-url)
DOH vs Age

- At initial set, DOH ≈ 4% (w/c = 0.35)
DOH at Initial Set

- For Class H cement, $w/c = 0.35$, DOH at initial set is $\sim 0.04$ for all $T$
**DOH at Initial Set**

- For Class H cement, $w/c = 0.35$, DOH at initial set is $\sim 0.04$ for all $T$.
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 $\lambda$
  
  $$\lambda = \frac{r_c}{r_s}$$

- Shell is hydration product

- Percolation is setting point

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?

Cherry Pit & Hydration

- Layer thickness vs Degree of hydration, $\alpha$
- Core shrinks as hydration proceeds

\[ \lambda = r_c / r_s \]

\[ \lambda = \sqrt{1 - \alpha} \]
Model Prediction

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

![Graph showing DOH at percolation threshold vs w/c ratio with model and data points.](image-url)
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
• \( \text{DOH at initial set} \propto \frac{1}{t_{\text{set}}} \)
• \( \text{DOH at initial set} \approx 4\% \) 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
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