The Stability of Air-Void Systems in Fresh Concrete

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Overview

• Introduction
• Do bubble systems change in undisturbed concrete with time?
• What are some of the physical and chemical properties of bubble hydration shells?
• Conclusions
What is... Concrete
What is Air-entrained concrete +
What is Air-Entrained Concrete?

- Concrete made with a specialized surfactant which stabilizes air bubbles created from the mixing action.
Water

Air

Water

Hydrophilic “Head”

Hydrophobic “Tail”
Why…

• These bubbles are key in the freeze-thaw resistance of the concrete
• Smaller bubbles are more effective in providing freeze-thaw resistance than larger bubbles
What do you want in an Air-Void System?

- Volume of air provided is the same for both circumstances.
- Case B though has a lower spacing factor and a higher specific surface.
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What Affects Air-Entrainment...
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• Everything!
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• Research has reported that air-entrained bubbles in concrete under no outside influence change in diameter with time.
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YIKES!
Change in Bubble Systems

- Do bubble systems change in undisturbed concrete with time?
- Mielenz et al. 1958 – Yes!
- Bruere 1962 – No!
- Powers 1968 – Maybe
P = P₀ + 4σ/d
\[ P = P_0 + 4\sigma/d \]
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Assumes $\sigma = 72$ dynes/cm
• Cement Paste
  Fresh Air < Hardened Air

• Concrete
  Fresh Air > Hardened Air

• Anything that extends set time increases the loss of small air-entrained bubbles
• Made air-entrained paste and used admixtures to accelerate and retard set time
• Also made specimens with out the admixtures
• In hardened concrete the air void content and systems of all three were the same
Powers 1968

Diagram showing the components of concrete:
- Aggregate
- Paste
- Air-void
Experimental Work
• Paste Mixture
  – 0.45 w/cm
  – 2.2 oz/cwt of a tall-oil AEA
  – Cement 0.53 alkali content (Na₂O eq)
  – Mixed in a Hobart Mixer according to ASTM C 305
2.2 oz/cwt tall oil AEA

Ley, Folliard, Hover
Observations

• Air Entrained Paste
  – Paste seems to push on large bubble
  – Bubble diameters do not change unless pushed on by the paste
  – Bubbles seems to have a “shell” surrounding them
  – Bubbles do not coalesce
• AEAs used commercially in concrete are anionic
• Calcium has been hypothesized to be attracted to the negative surface charge of air entrained bubbles (Mielenz et al. 1958, Powers 1968, Dodson 1990, Corr 2003)
Observations

• Non air-entrained paste
  – The air-voids were not effected by the paste
  – The bubbles appear to be transparent and not covered in a shell
  – The bubbles change size with time
0.74 oz/cwt wood rosin AEA
Observations

• Air-entrained paste
  – The air-voids were not effected by the paste
  – The bubbles appear to be covered in a shell
  – The bubbles do not change size with time
Observations

• Air-entrained paste that had been pressured
  – The shell of the large air void is damaged
  – Smaller bubbles decrease in diameter and larger bubbles increase in diameter
Findings

• It appears that a shell is created around a bubble when an AEA is used
• This shell seems to be important in resisting the transfer of gas from the surrounding fluid
• If this shell becomes damaged then it is possible that a transfer of gas could occur

• Powers was right!
0.4 w/cm – frozen 5 minutes after mixing (Corr, 2003)
w/cm = 0.3 – sublimated 3 hr after mixing (Rashad and Williamson, 1991)
Conclusion

• If this water filled gap does exist around an air-void then it seems possible that the interchange of air previously witnessed could occur in concrete
Properties of Bubble Shells

- Physical Properties
- Chemical Properties
Physical Properties

- Transparency
- Adhesion of cement particles
- Air-void shell response to pressure
- Self Healing
Transparency

wood rosin AEA 48 mL/100 kg cm

no AEA
Adhesion of Cement Particles
Vinsol resin AEA 18 mL/100 kg cm
Air-Void Shell Response to Pressure
Vinsol resin 26 mL/100 kg cm WR 81 mL/100 kg cm cm
0 bar 0.3 bar 0.7 bar
0.2 bar 0.1 bar 0 bar

synthetic AEA 47 mL/100 kg cm WR 81 mL/100 kg cm
Self Healing
Conclusions

• Differences in transparency between air-entrained and non air-entrained
• Cement particles adhere to air-entrained bubbles
• Different AEA respond differently to outside stresses
• The bubble shells have been observed to repair themselves
Chemical Properties

- Chemical properties at 60 days of hydration
Chemical Properties

• Chemical properties at 60 days of hydration

• What the heck is that shell anyway?
Properties at 60 days of hydration
Air-Void Shell

Spectrum2

Cursor=0.835 keV  10 cnt  ID = La m1 La m2 Cu l1 Sm m11 Sm m22 Te m61 I m1 I m2 Ne k1 La m3n
Vert=245  Window 0.005 - 40.955= 10371 cnt
Conclusions

• The air-void shell appears to be made up of a calcium silicate with a different density/morphology than bulk paste C-S-H
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What Do We Know?

- A shell is formed around air entrained bubbles and not around non-air entrained bubbles.
- The shell is important to resist gas transfer.
- Different surfactants cause the shells to have different physical properties.
- The bubble shell is a calcium silicate.
- Rapid shell formation is possible.
Why Do We Care?
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- Discrepancies between fresh and hardened air-void measurements are likely caused by air interchange between the voids
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  – If the large air-voids get too large then they will escape from the paste and the air volume decreases
  – If the large air-voids don’t escape then the air volume increases
  – Either way we lose small air-voids and this is bad for frost durability
Current Research

• A more detailed chemical characterization of the hydration shell is being completed
• Interactions between AEAs and other admixtures are being examined
Current Research

• A μCT scanner is being used to monitor the changes of the air-void systems in fresh cement paste.
Questions???

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