The Stability of Air-Void Systems in Fresh Concrete

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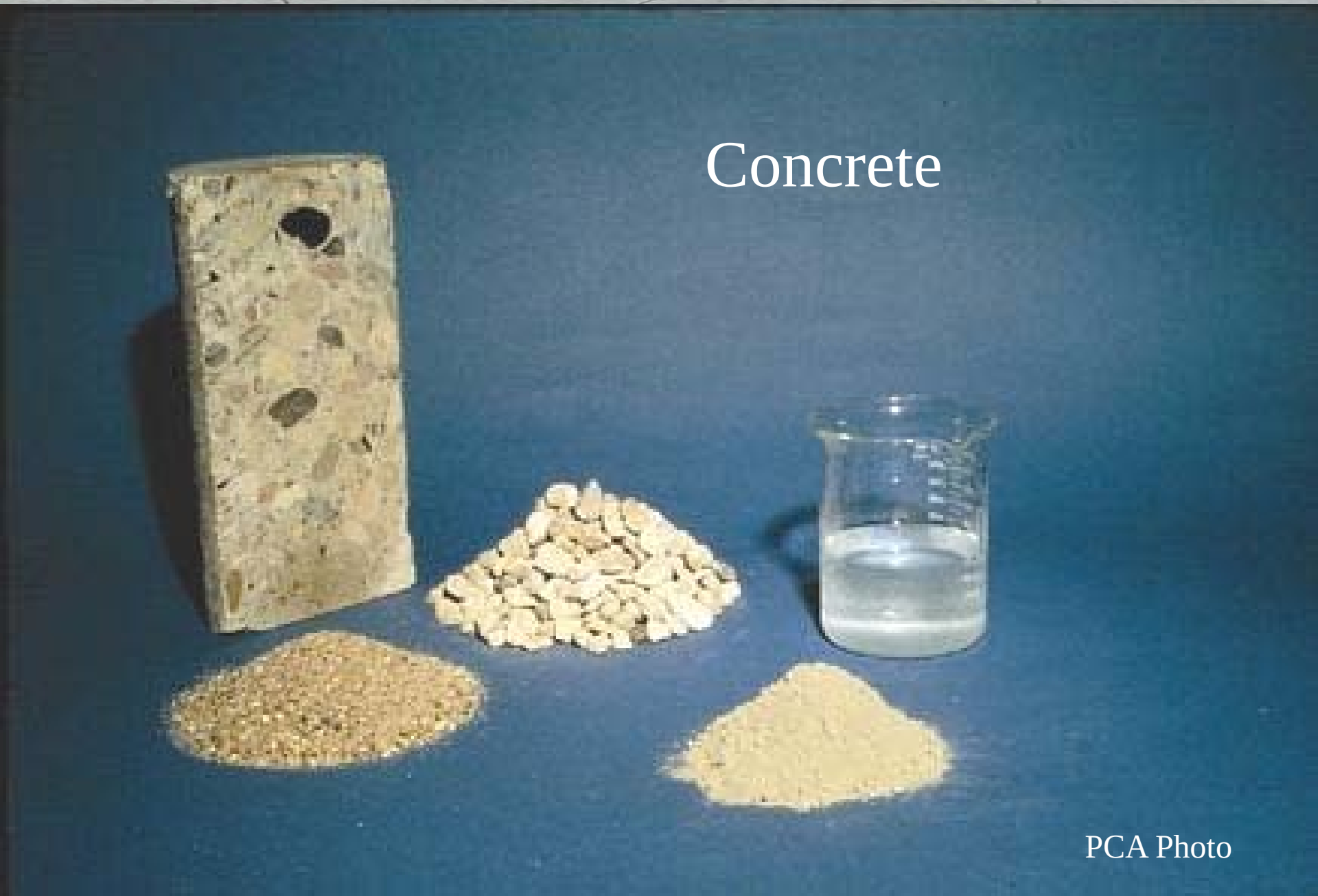
Acknowledgements

- Texas Department of Transportation
- Portland Cement Association
- Oklahoma Transportation Center
- W.R. Grace
- CP Tech Center

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…



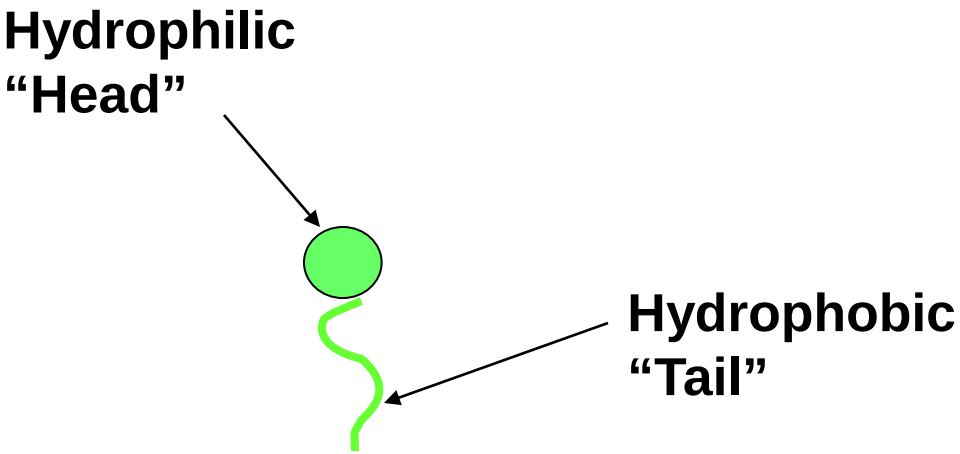
What is…

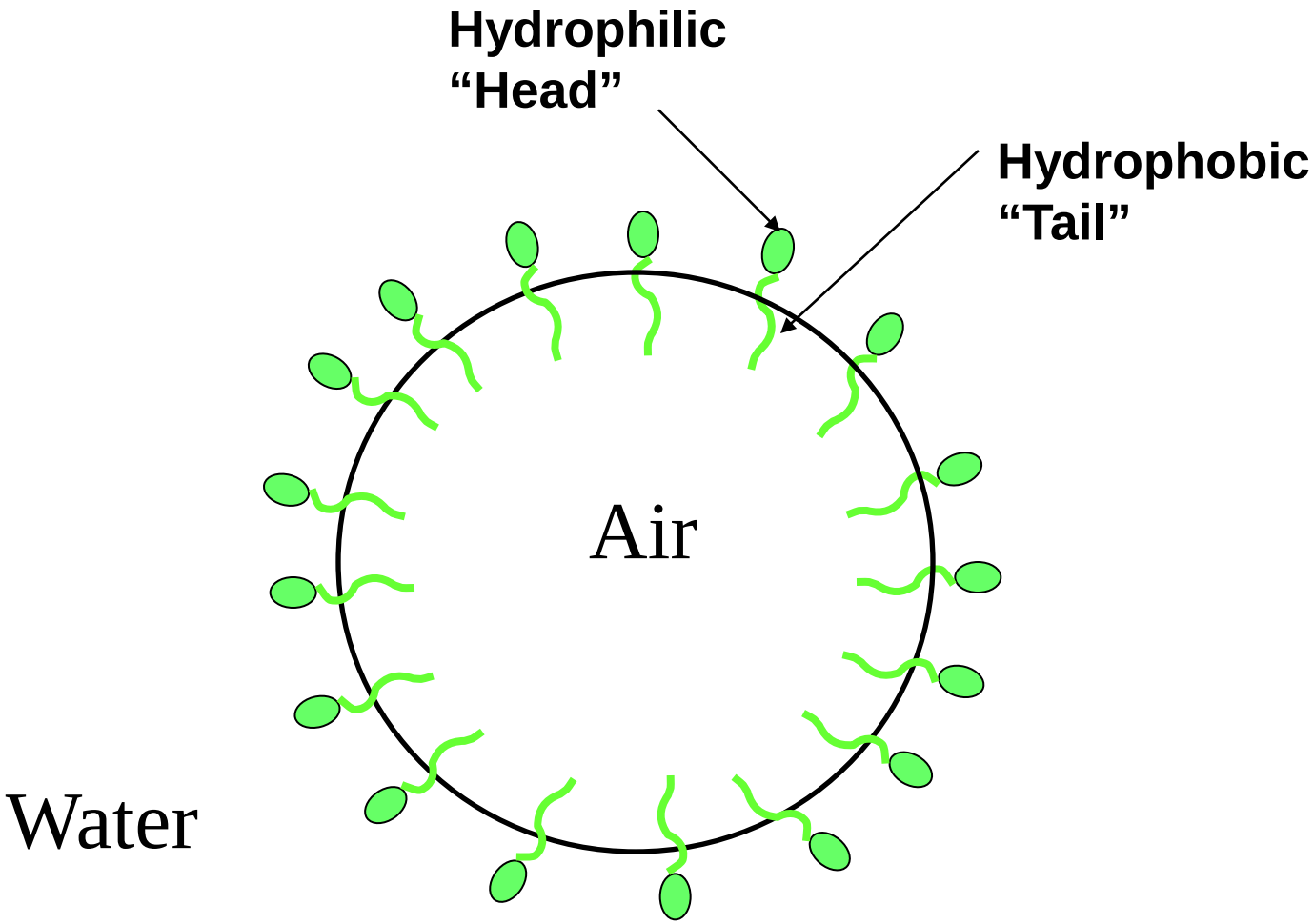
Air-entrained concrete

+

What is Air-Entrained Concrete?

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



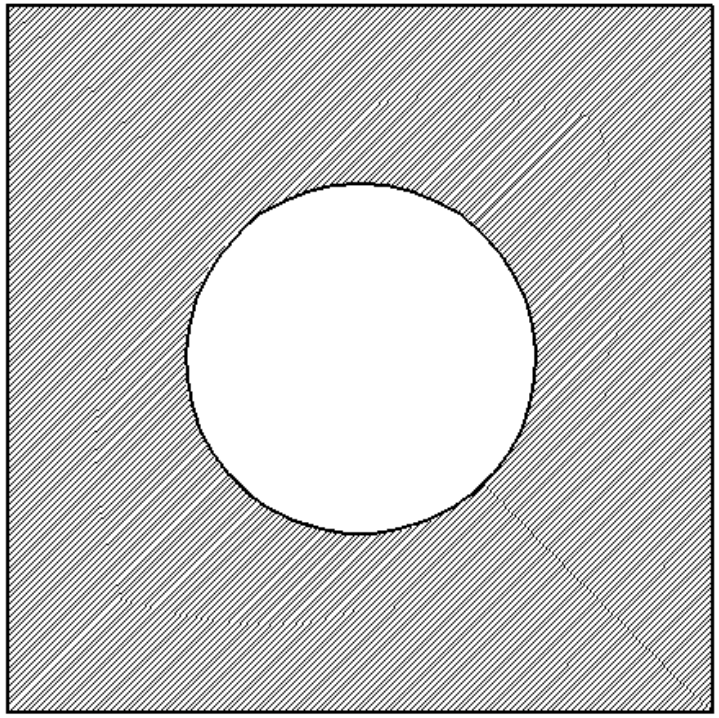

Hydrophilic
“Head”
Hydrophobic
“Tail”
Air
Water

Why…

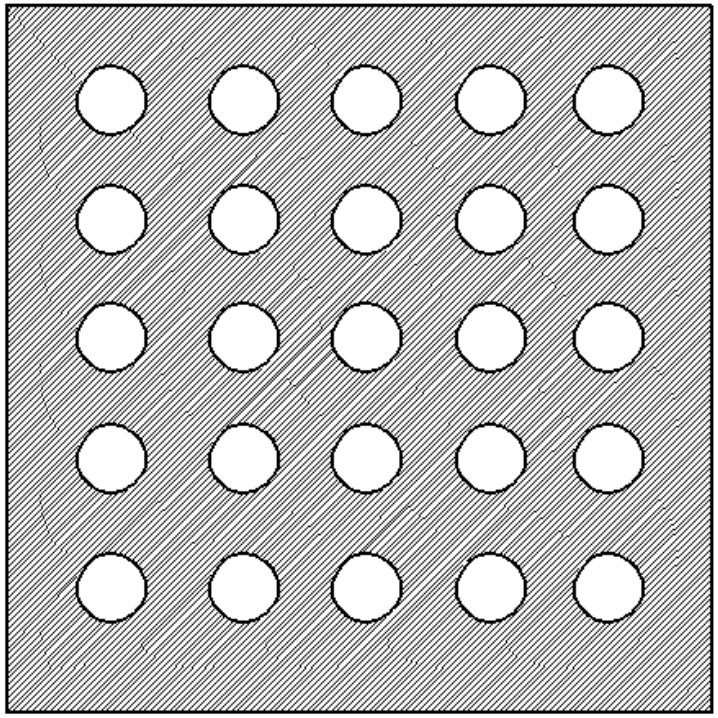
- These bubbles are key in the freeze-thaw resistance of the concrete
- Smaller bubbles are more effective in providing freeze-thaw resistance than larger bubbles

What do you want in an Air-Void System?

A



B



- 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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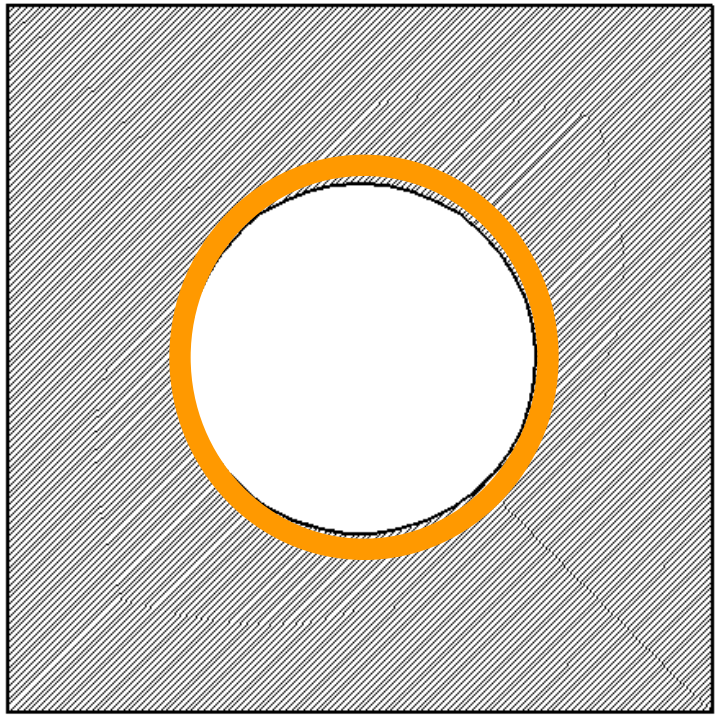
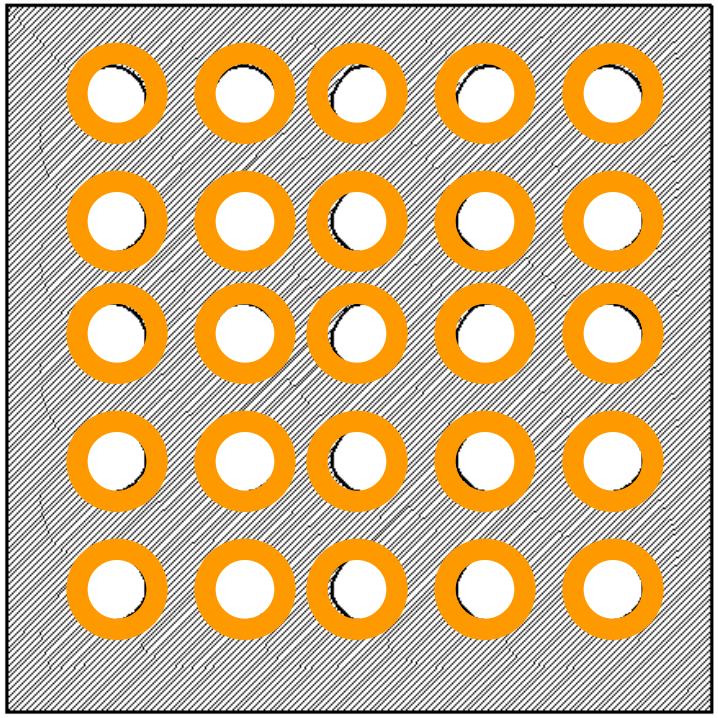
A



B



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- Case B though has a lower spacing factor and a higher specific surface.

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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- Everything!

- Research has reported that air-entrained bubbles in concrete under no outside influence change in diameter with time

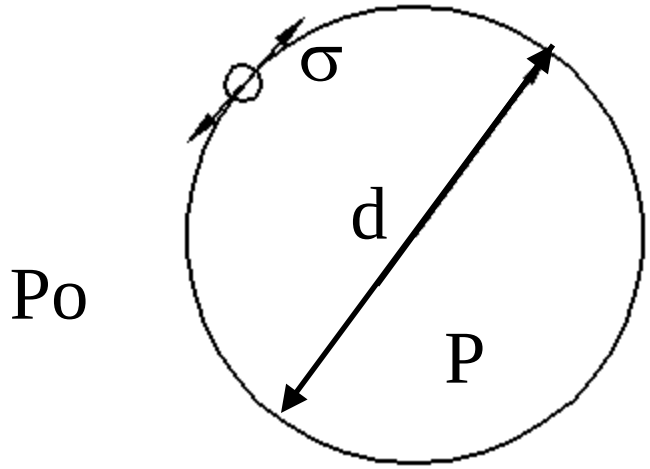
YIKES!

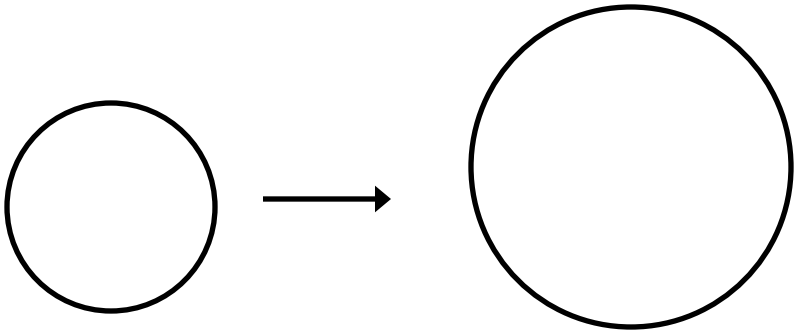
Change in Bubble Systems

- Do bubble systems change in undisturbed concrete with time?
- Mielenz et al. 1958 – Yes!
- Bruere 1962 – No!
- Powers 1968 – Maybe

Mielenz et al. 1958

$$P = Po + 4\sigma/d$$





Mielenz et al. 1958

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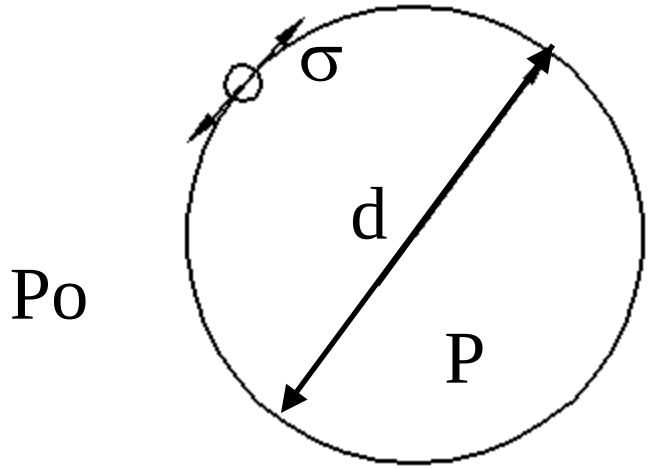

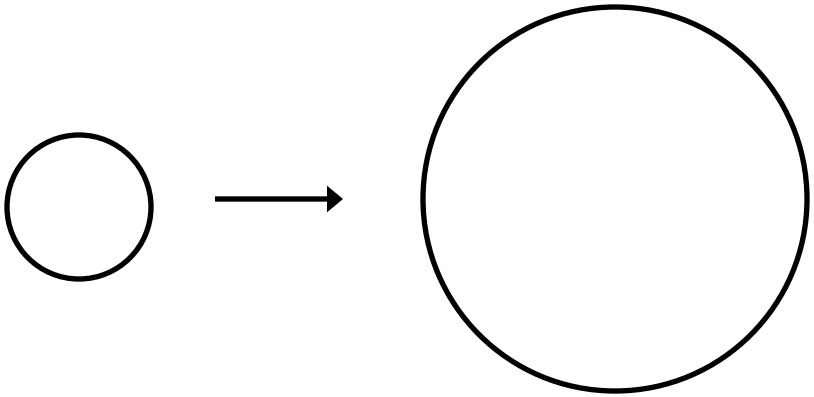

Mielenz et al. 1958

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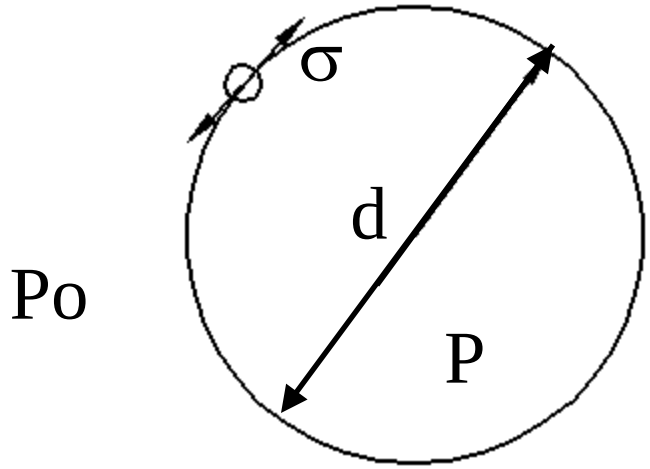
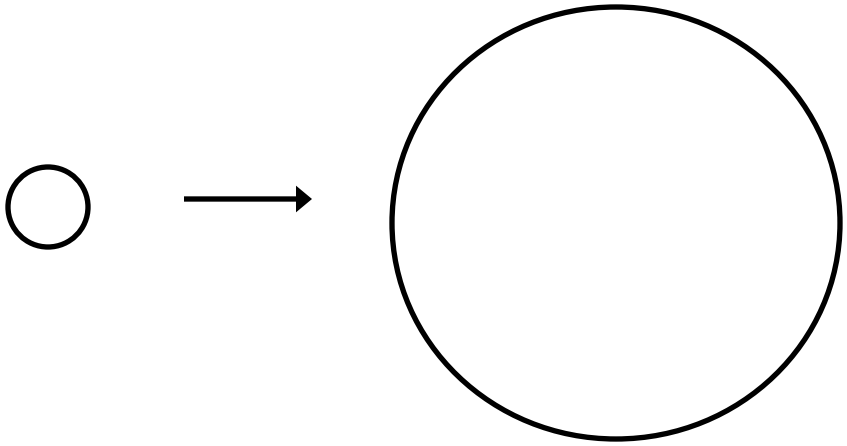
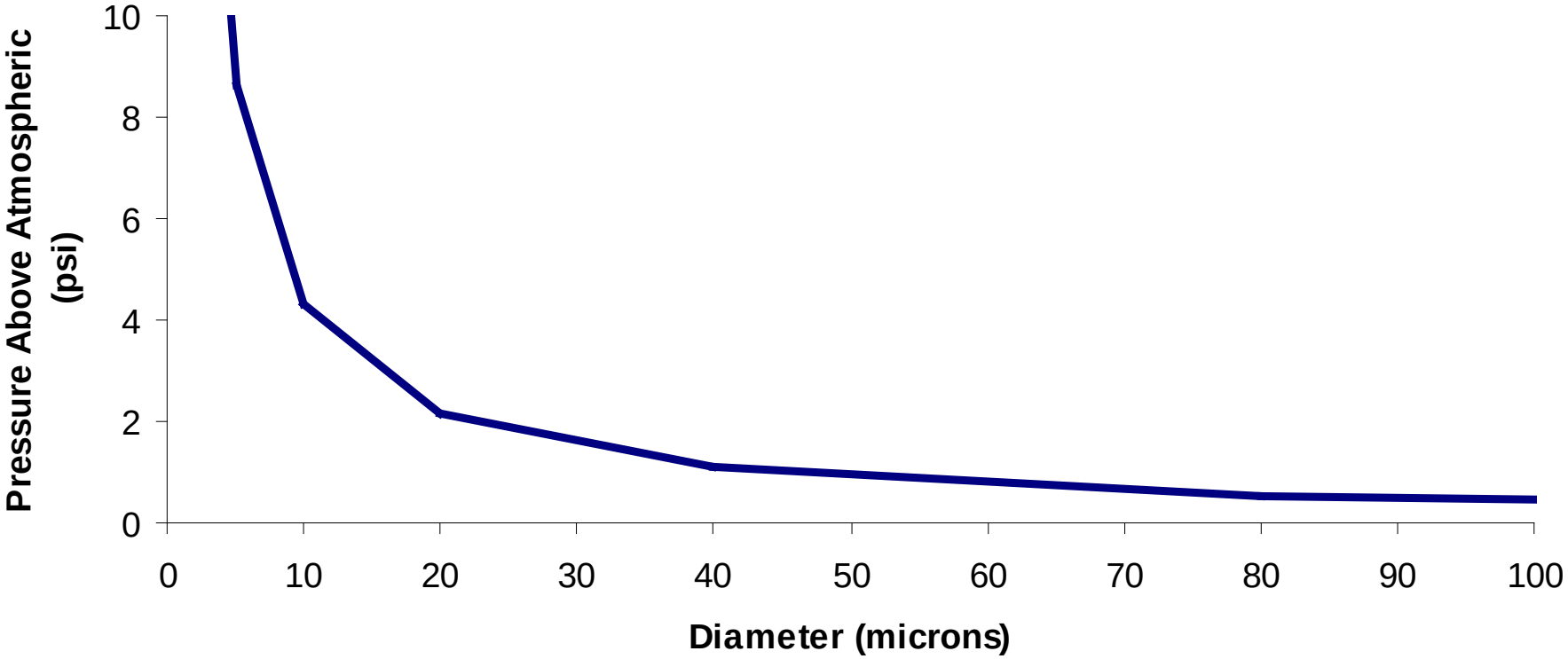






Assumes σ = 72 dynes/cm

Mielenz et al. 1958

- Cement Paste

Fresh Air < Hardened Air

- Concrete

Fresh Air > Hardened Air

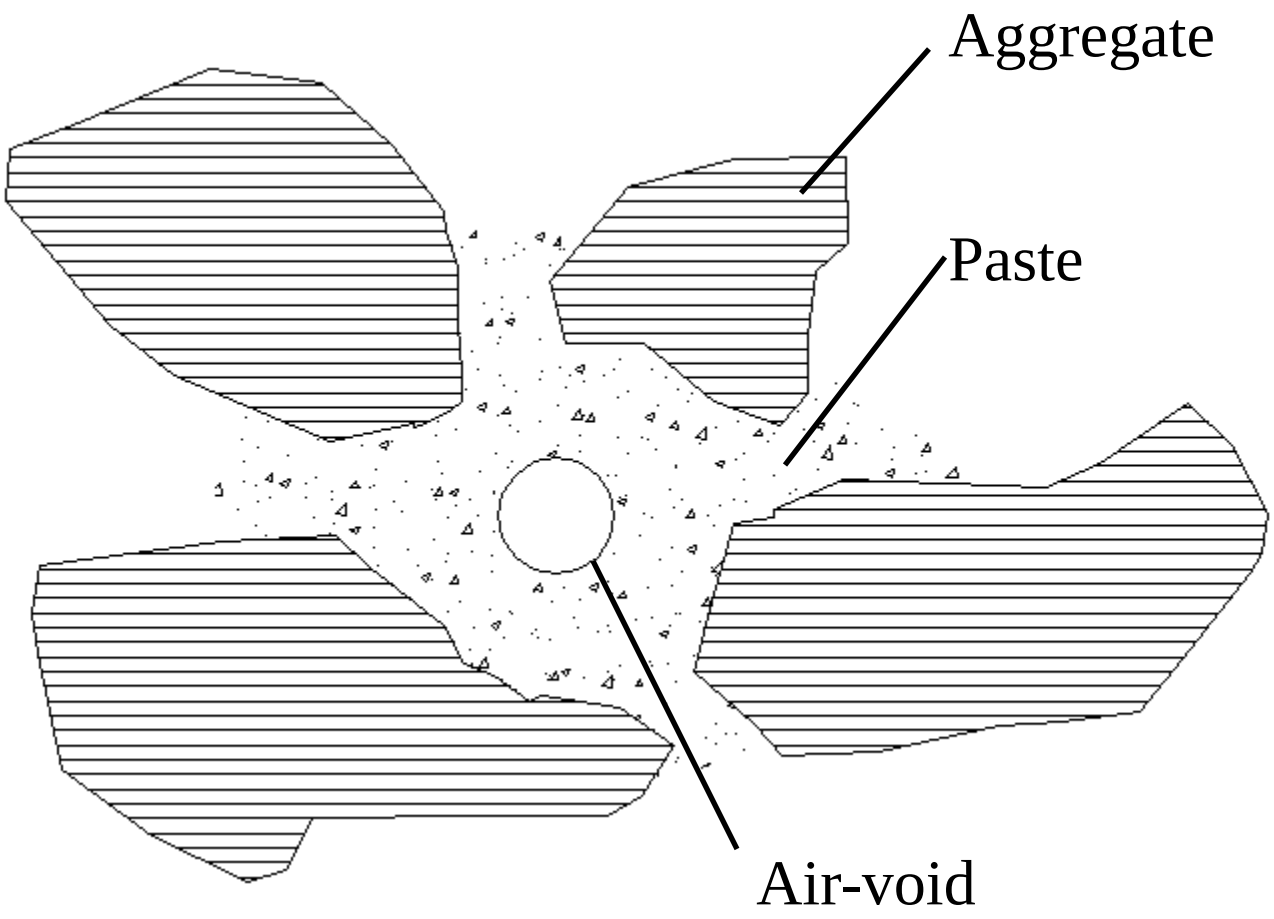
- Anything that extends set time increases the loss of small air-entrained bubbles

Bruere 1962

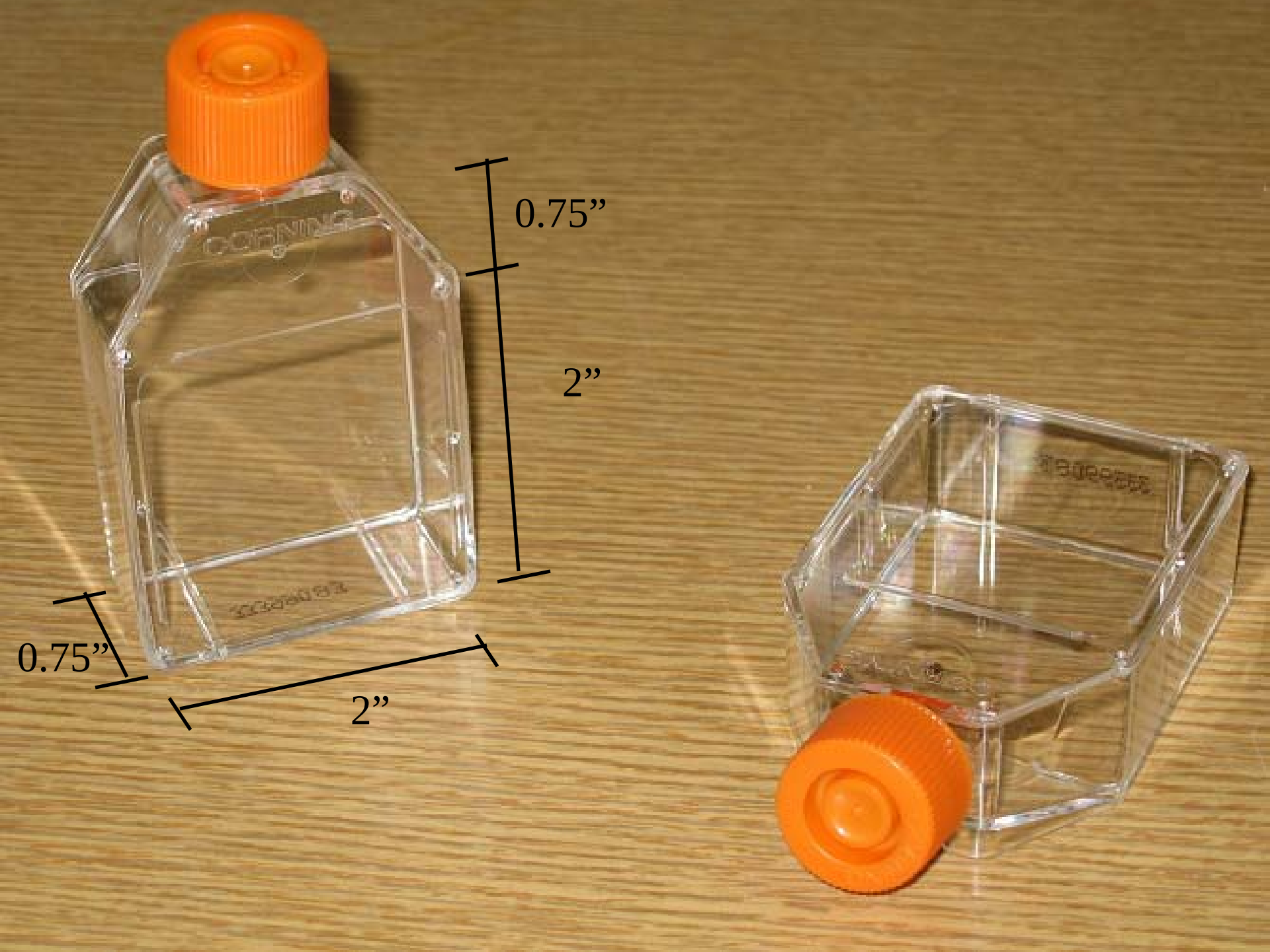
- Made air-entrained paste and used admixtures to accelerate and retard set time
- Also made specimens with out the admixtures
- In hardened concrete the air void content and systems of all three were the same

Powers 1968

Powers 1968

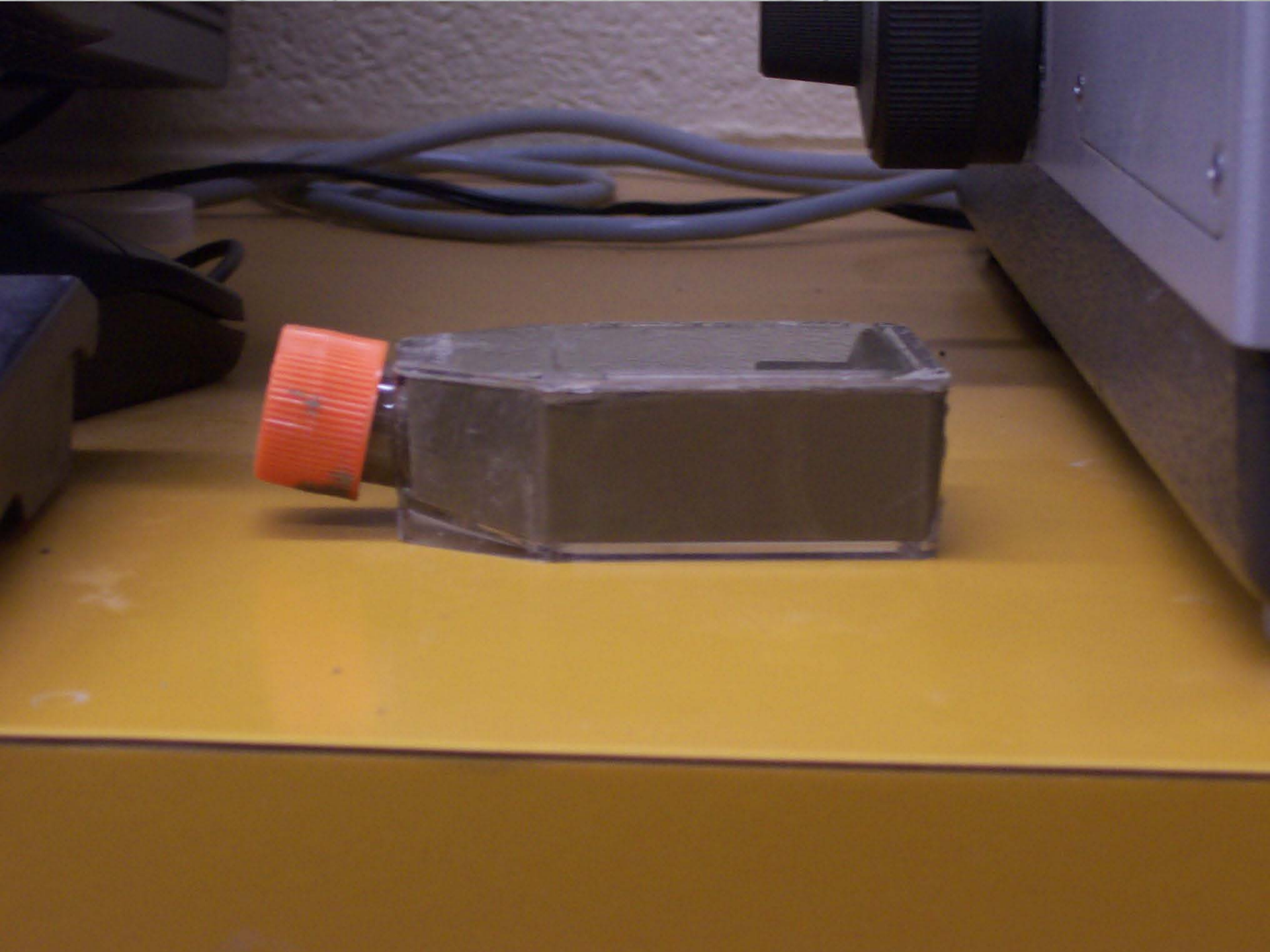


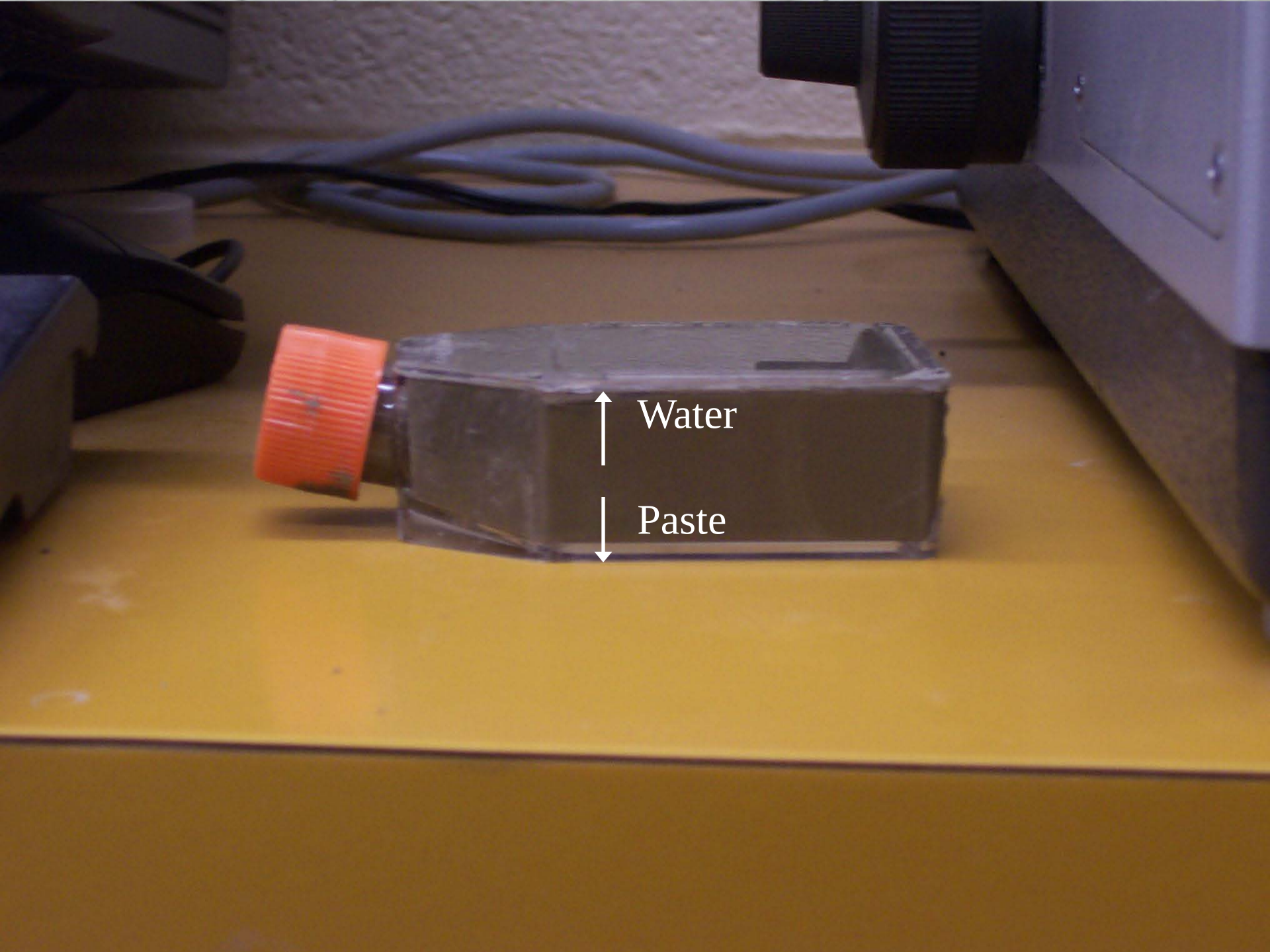
Experimental Work


0.75”
2”
0.75”
2”
CORNING

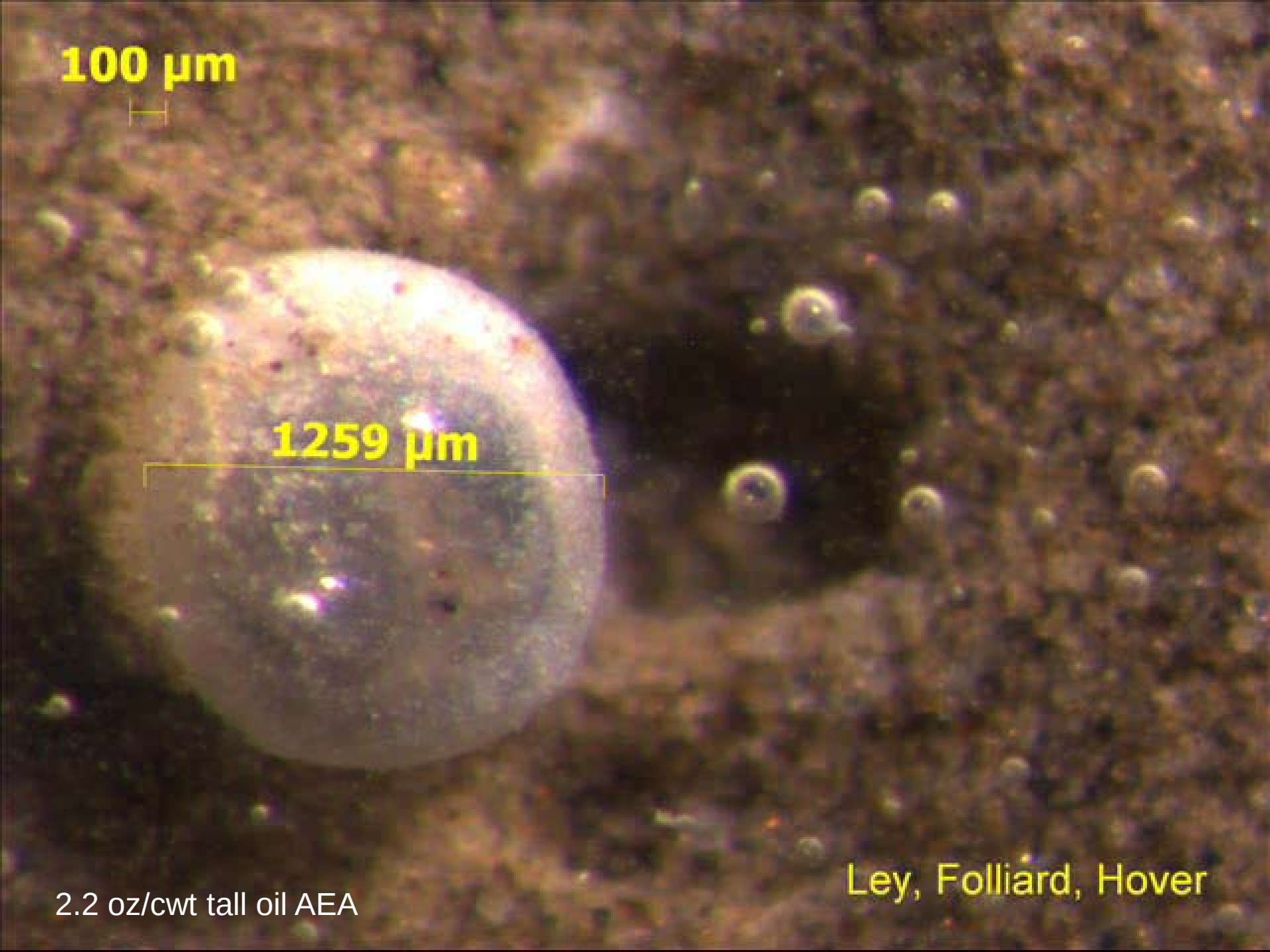
- Paste Mixture
  - 0.45 w/cm
  - 2.2 oz/cwt of a tall-oil AEA
  - Cement 0.53 alkali content (Na_2O eq)
  - Mixed in a Hobart Mixer according to ASTM C 305


CORNING




Water
Paste


AxioCam MRc 5
ZEISS
VAIO



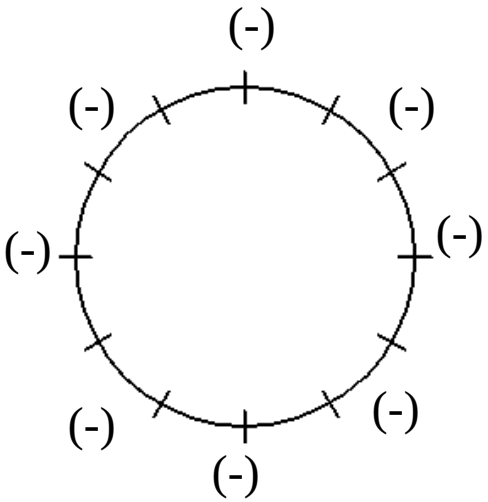
2.2 oz/cwt tall oil AEA

Observations

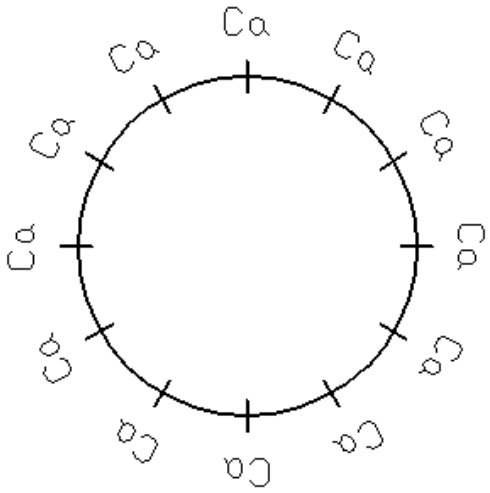
- Air Entrained Paste
  - Paste seems to push on large bubble
  - Bubble diameters do not change unless pushed on by the paste
  - Bubbles seems to have a “shell” surrounding them
  - Bubbles do not coalesce

Nature of AEA Film

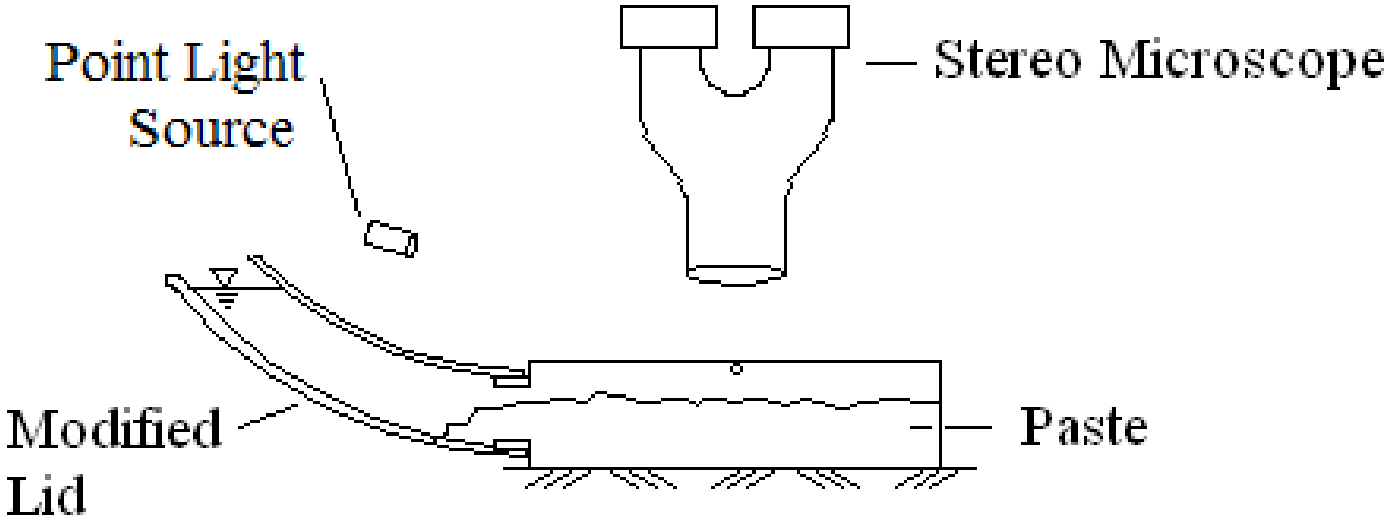
- AEAs used commercially in concrete are anionic
- Calcium has been hypothesized to be attracted to the negative surface charge of air entrained bubbles (Mielenz et al. 1958, Powers 1968, Dodson 1990, Corr 2003)



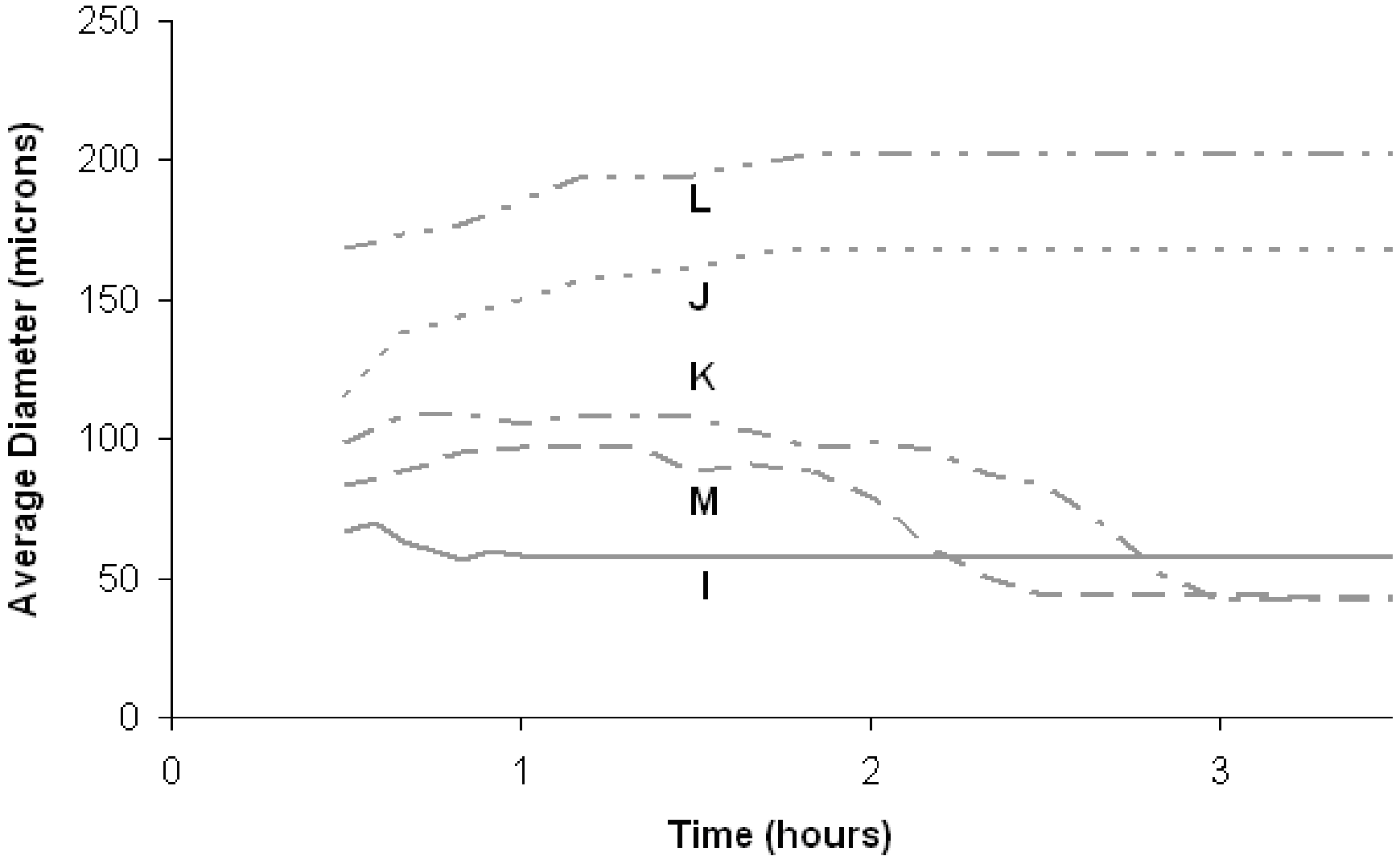
Initial



After 5 minutes

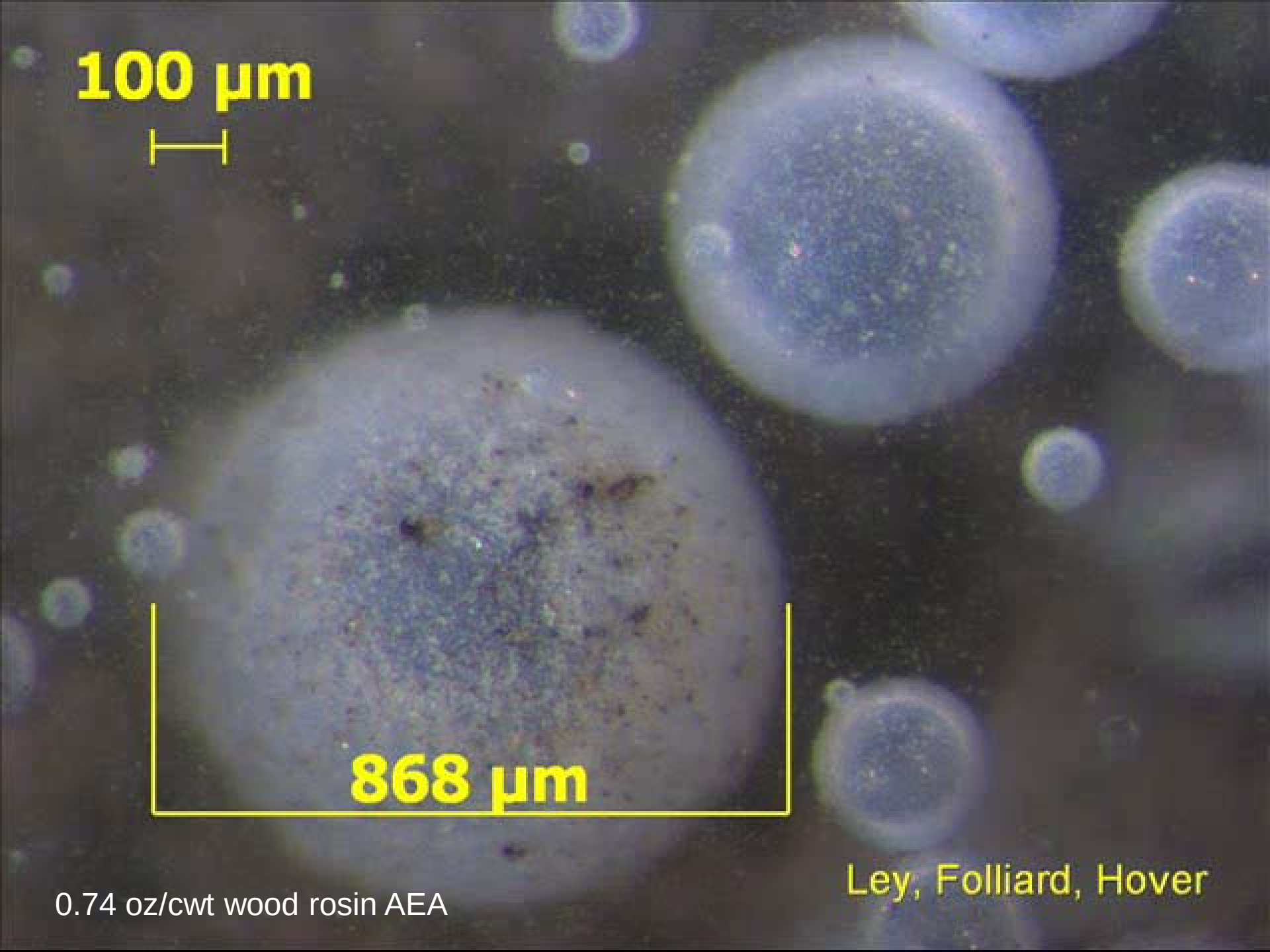

Point Light Source
Stereo Microscope
Modified Lid
Paste

no AEA


250
200
150
100
50
0
Average Diameter (microns)
L
J
K
M
I
0
1
2
3
Time (hours)

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
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  - The bubbles appear to be covered in a shell
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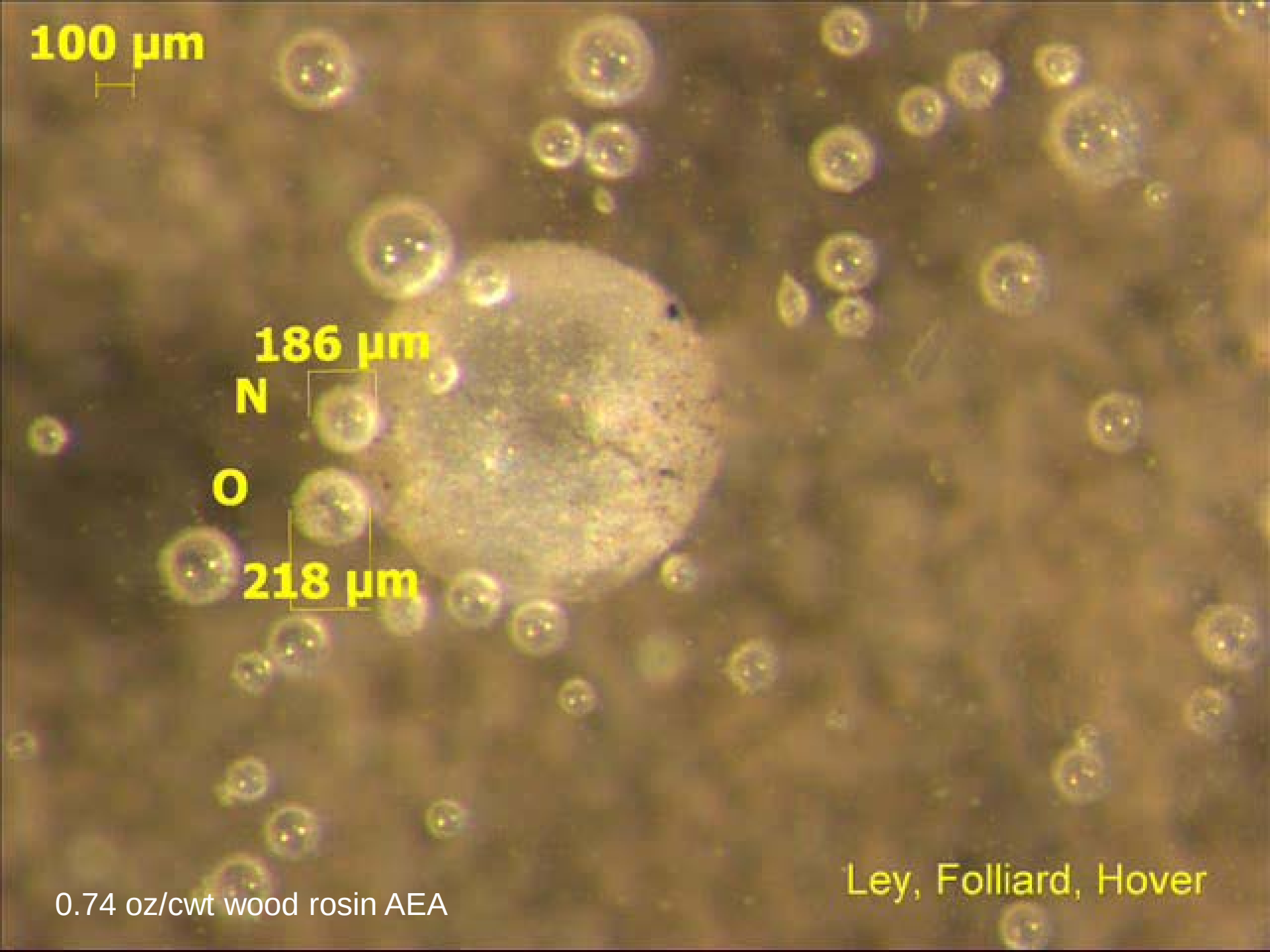


0.74 oz/cwt wood rosin AEA

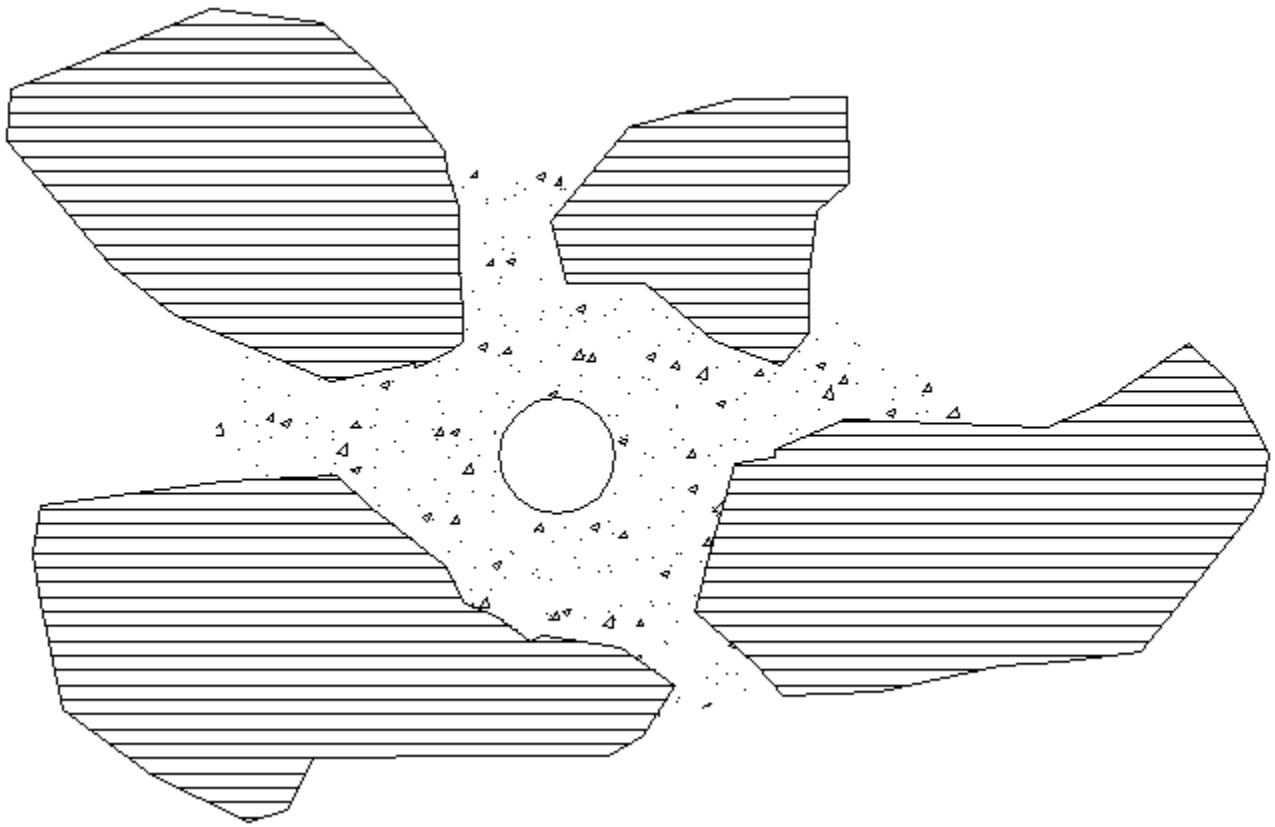
Observations

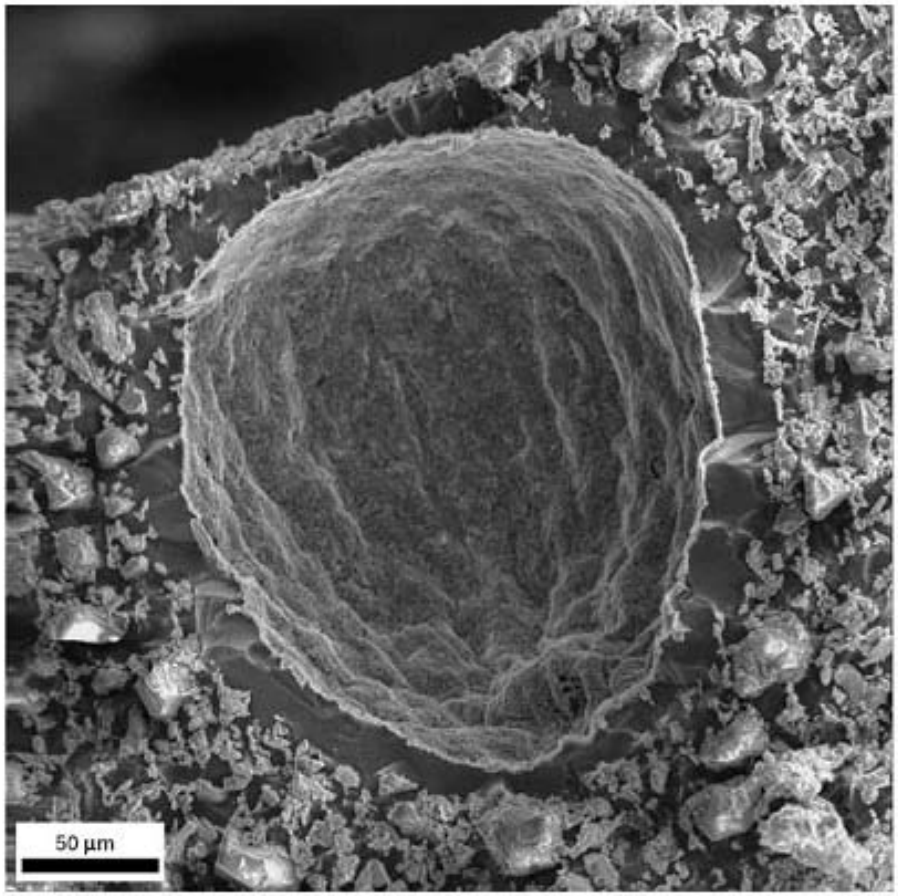
- Air-entrained paste that had been pressured
  - The shell of the large air void is damaged
  - Smaller bubbles decrease in diameter and larger bubbles increase in diameter

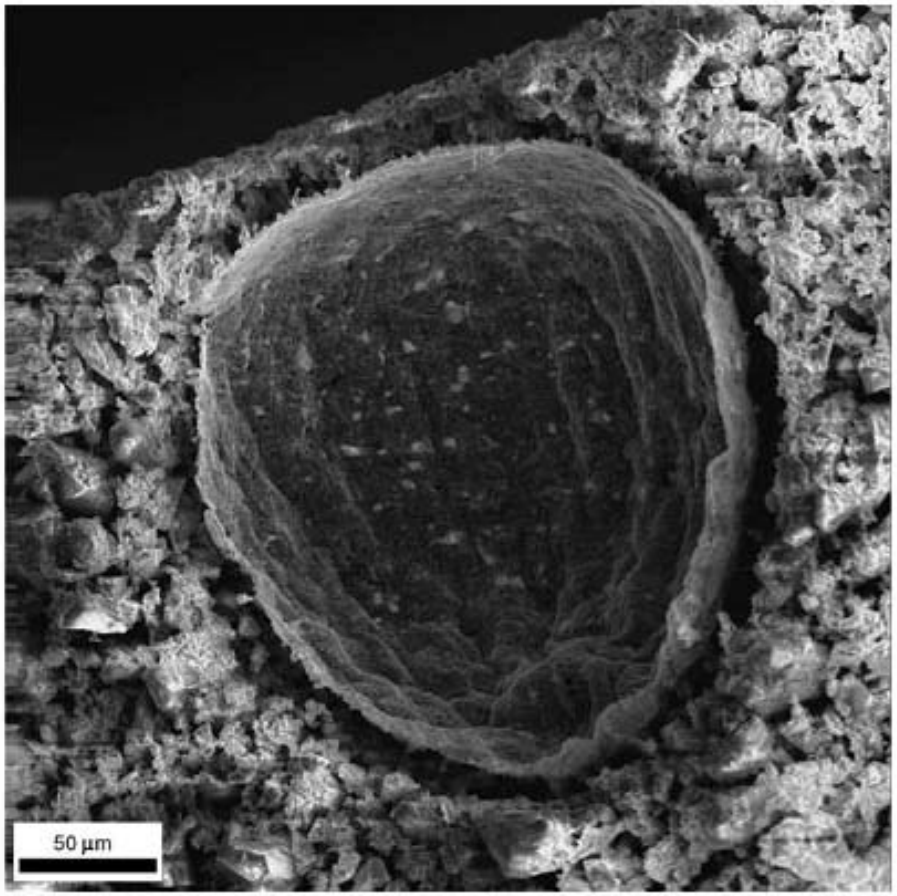
Findings

- 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!

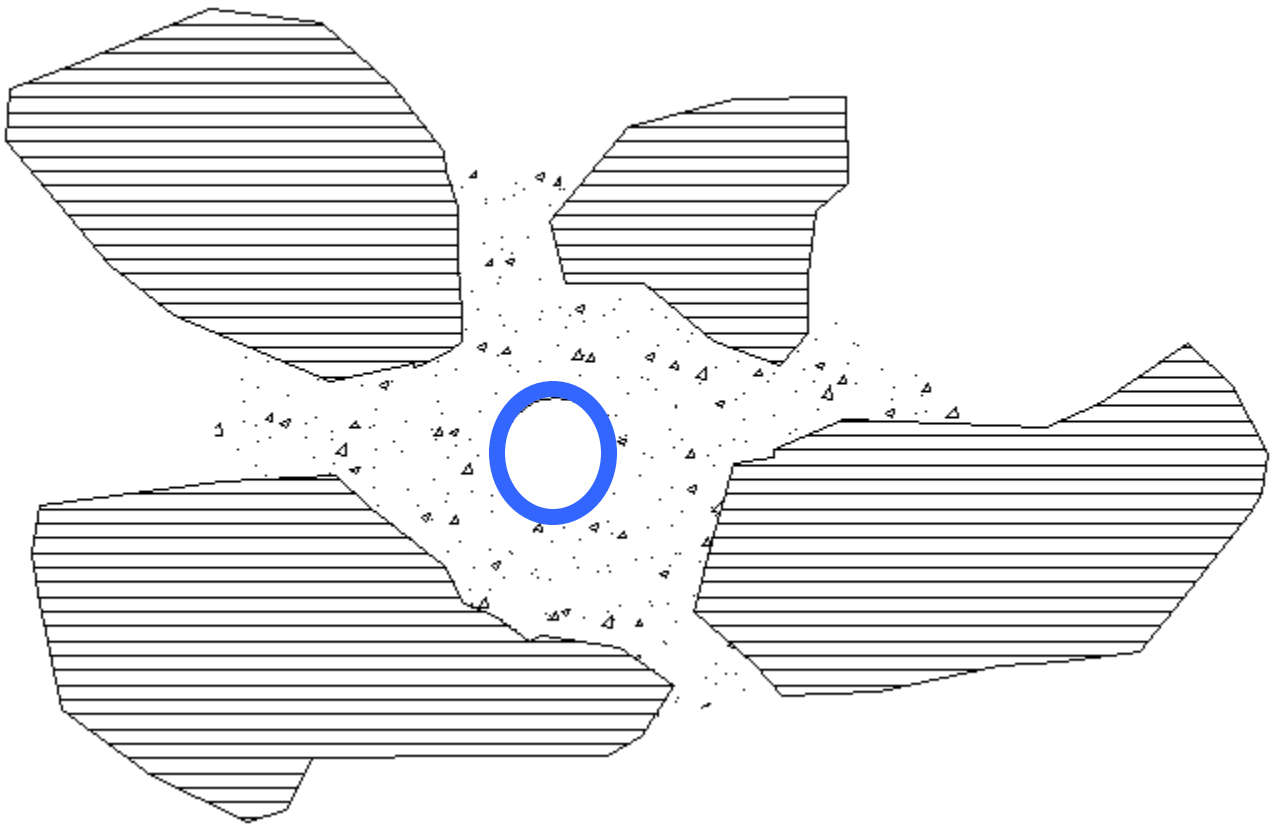






0.4 w/cm – frozen 5 minutes after mixing (Corr, 2003)

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

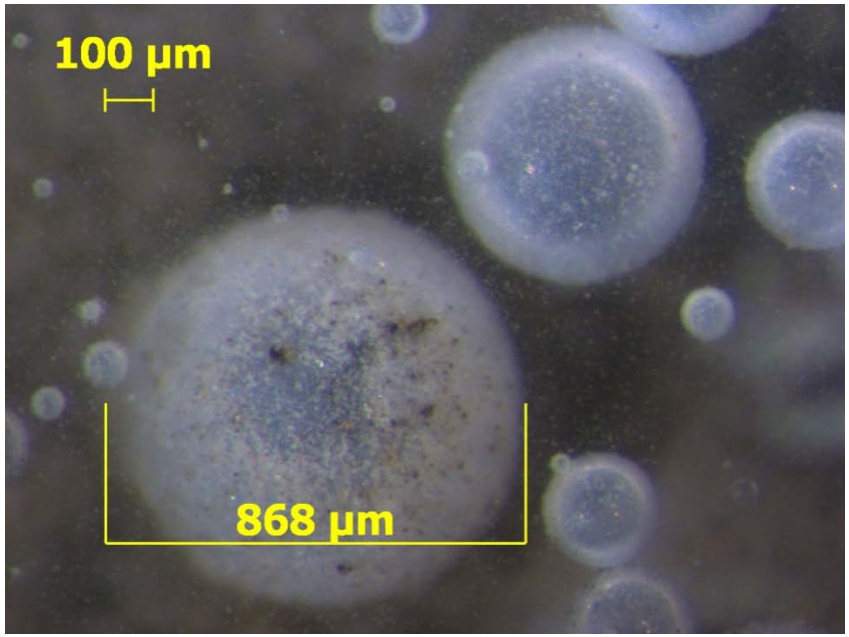
Properties of Bubble Shells

- Physical Properties
- Chemical Properties

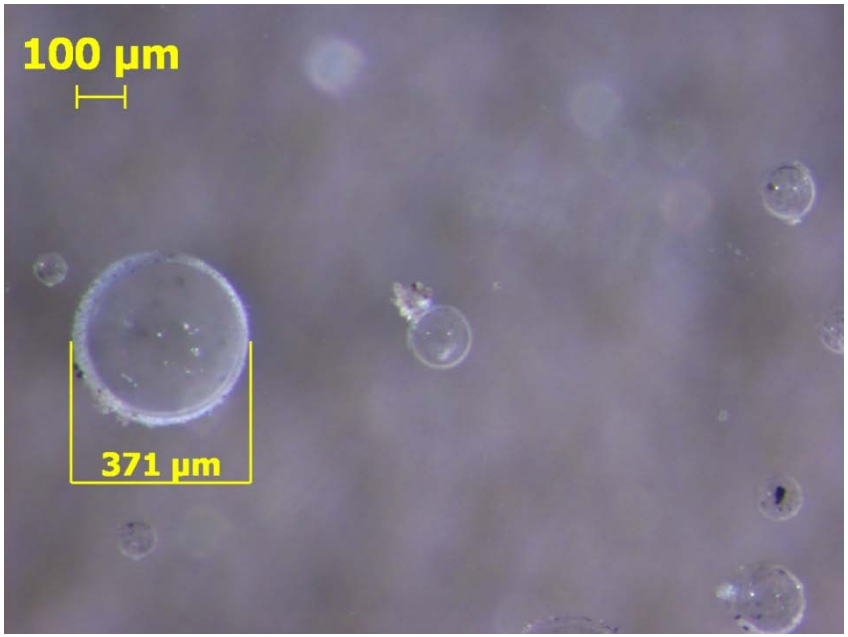
Physical Properties

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

Transparency

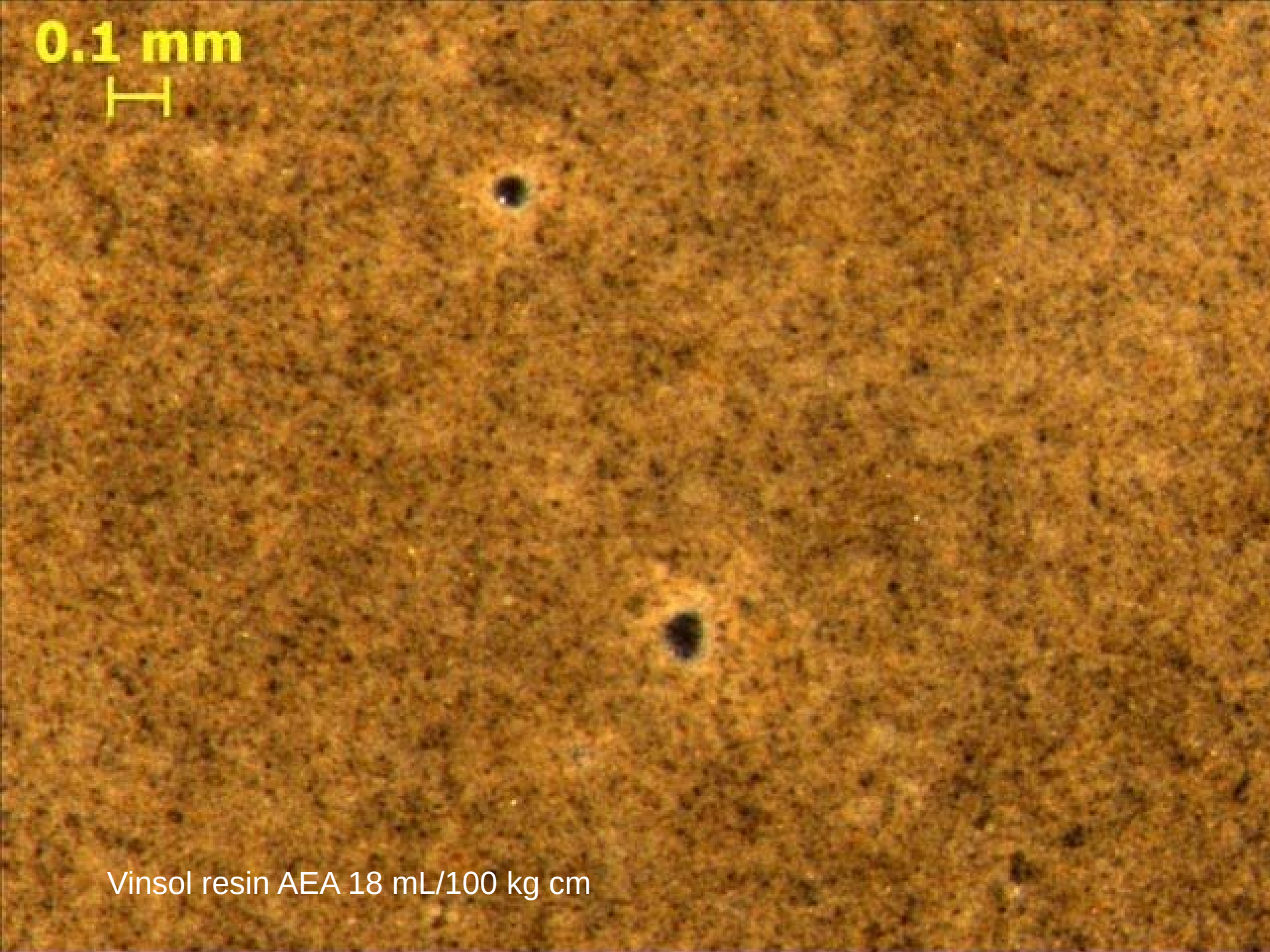


wood rosin AEA 48 mL/100 kg cm



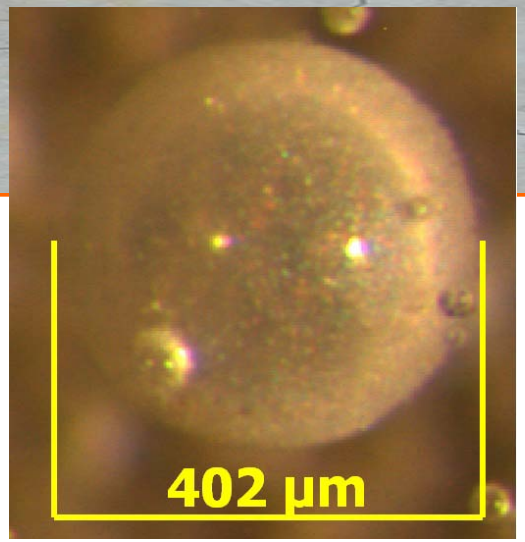
no AEA

Adhesion of Cement Particles

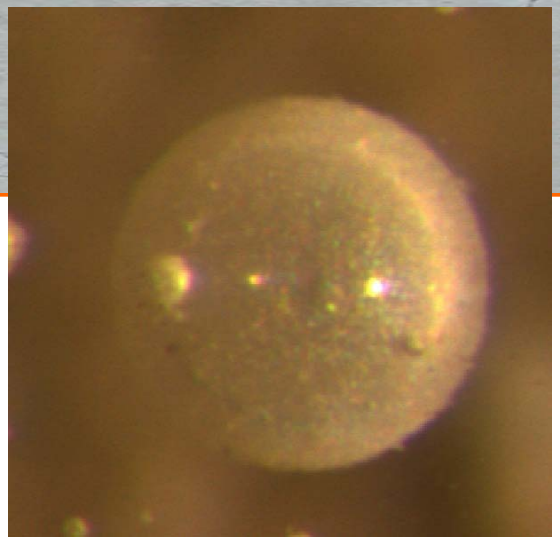


Vinsol resin AEA 18 mL/100 kg cm

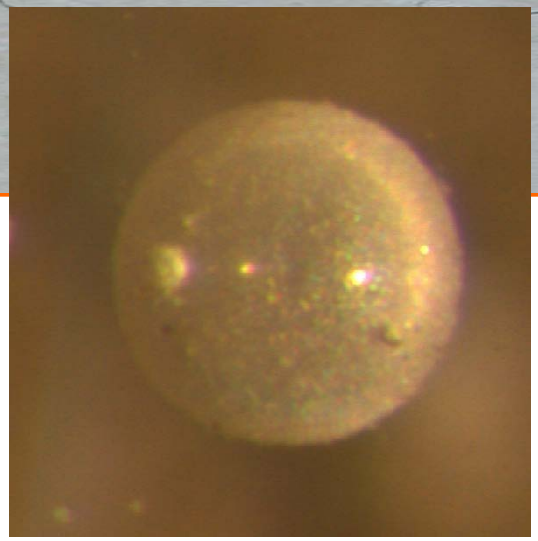
Air-Void Shell Response to Pressure



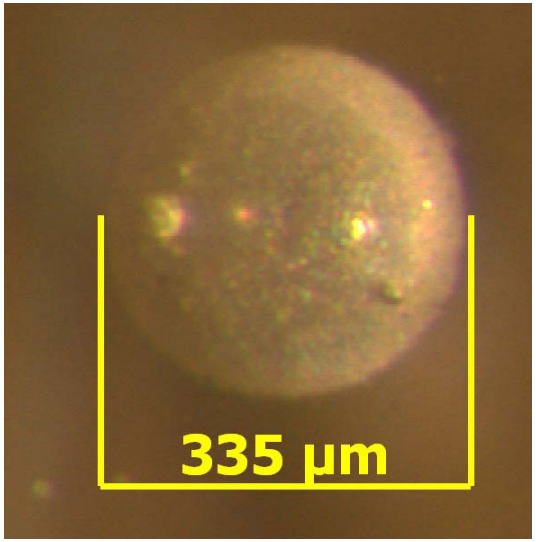
0 bar



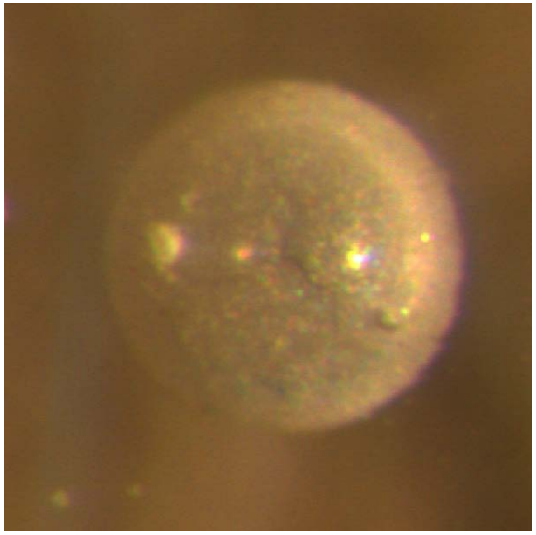
0.2 bar



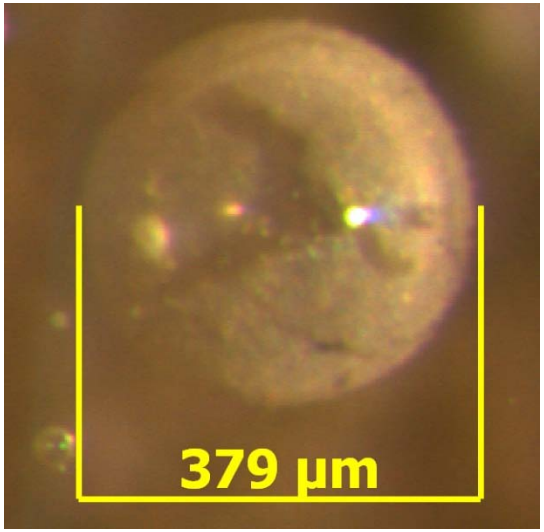
0.5 bar



0.7 bar

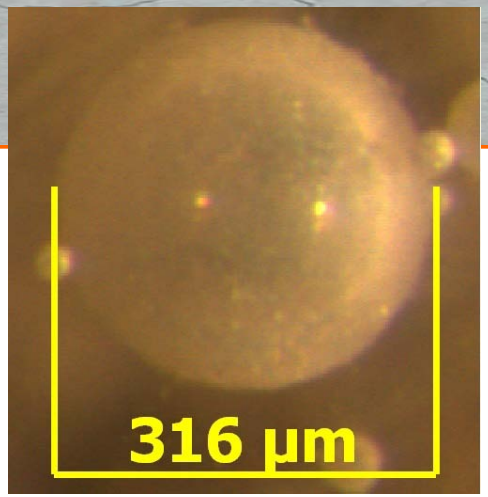


0.3 bar



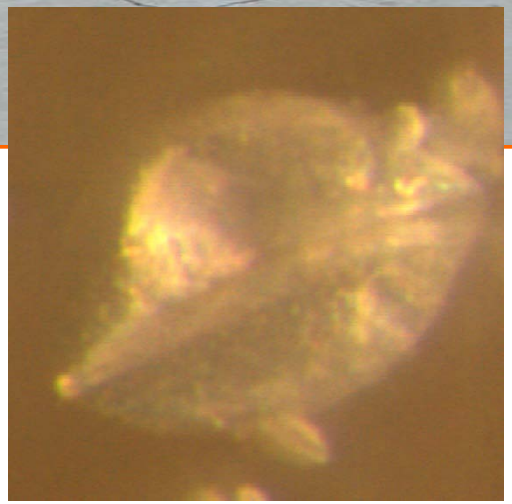
0 bar

Vinsol resin 26 mL/100 kg cm WR 81 mL/100 kg cm

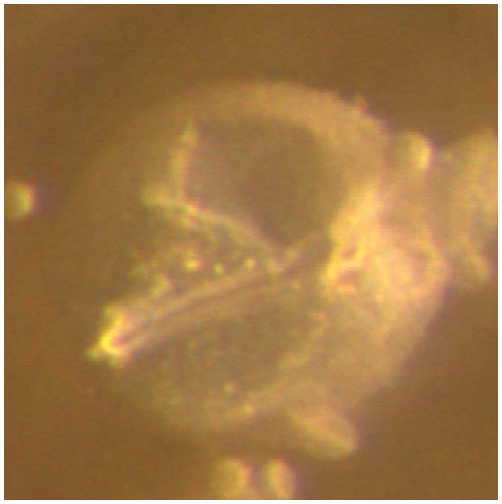


0 bar

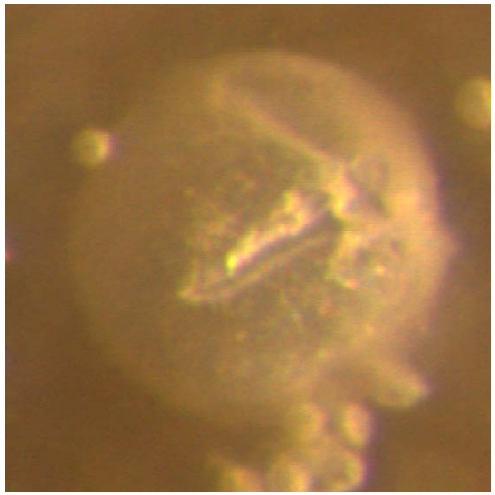
0.3 bar



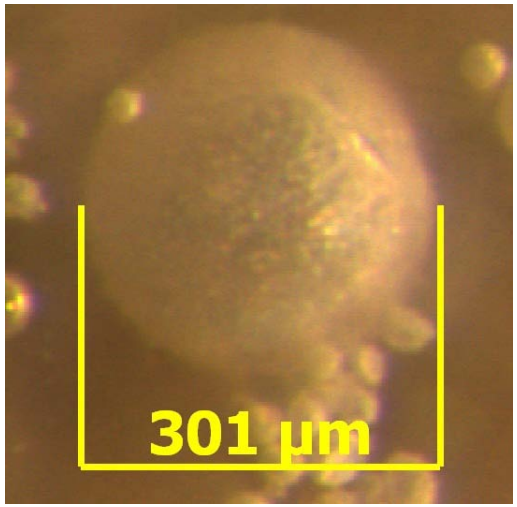
0.7 bar



0.2 bar



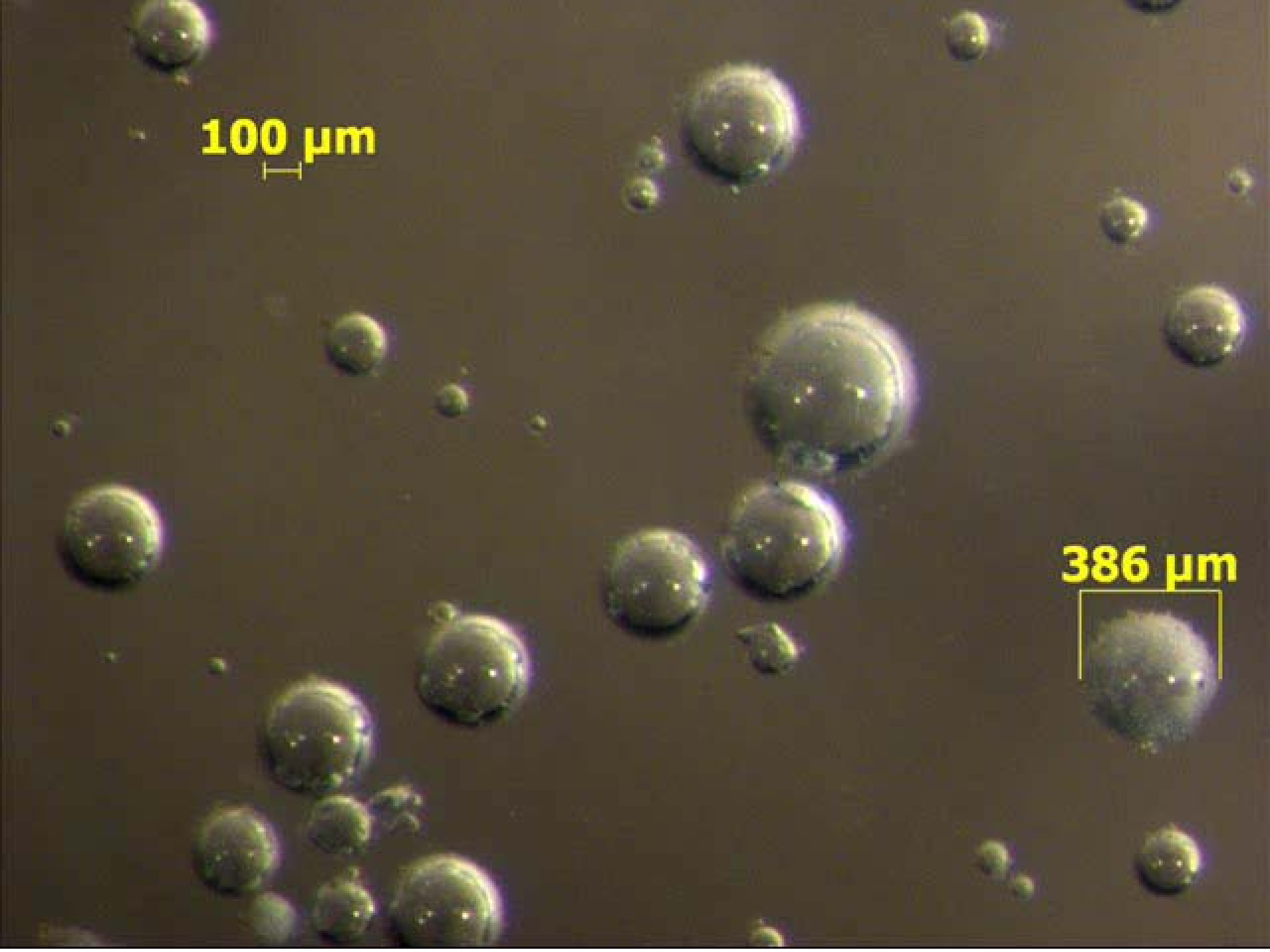
0.1 bar

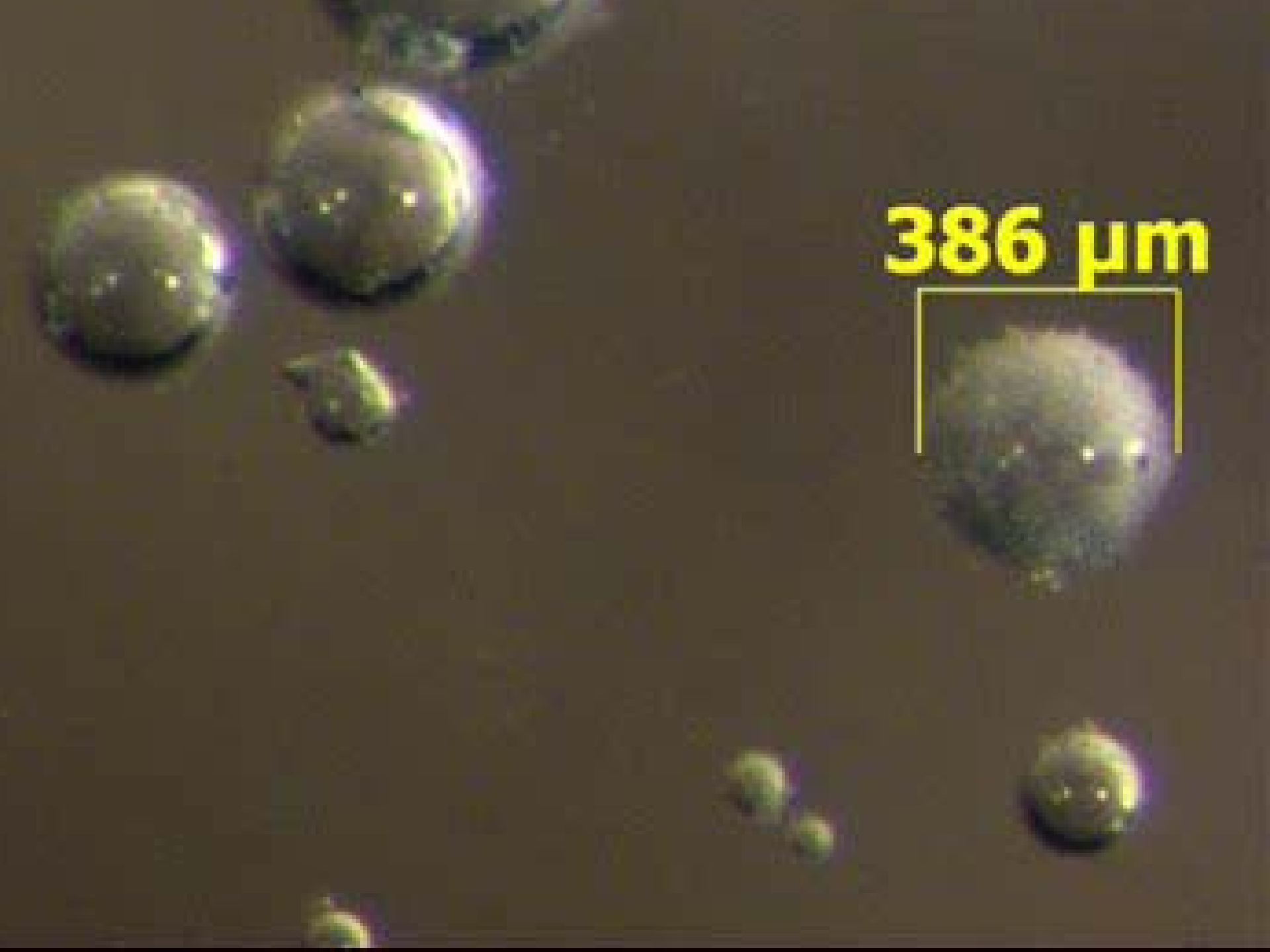


0 bar

synthetic AEA 47 mL/100 kg cm WR 81 mL/100 kg cm

Self Healing


100 µm
386 µm


386 µm

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

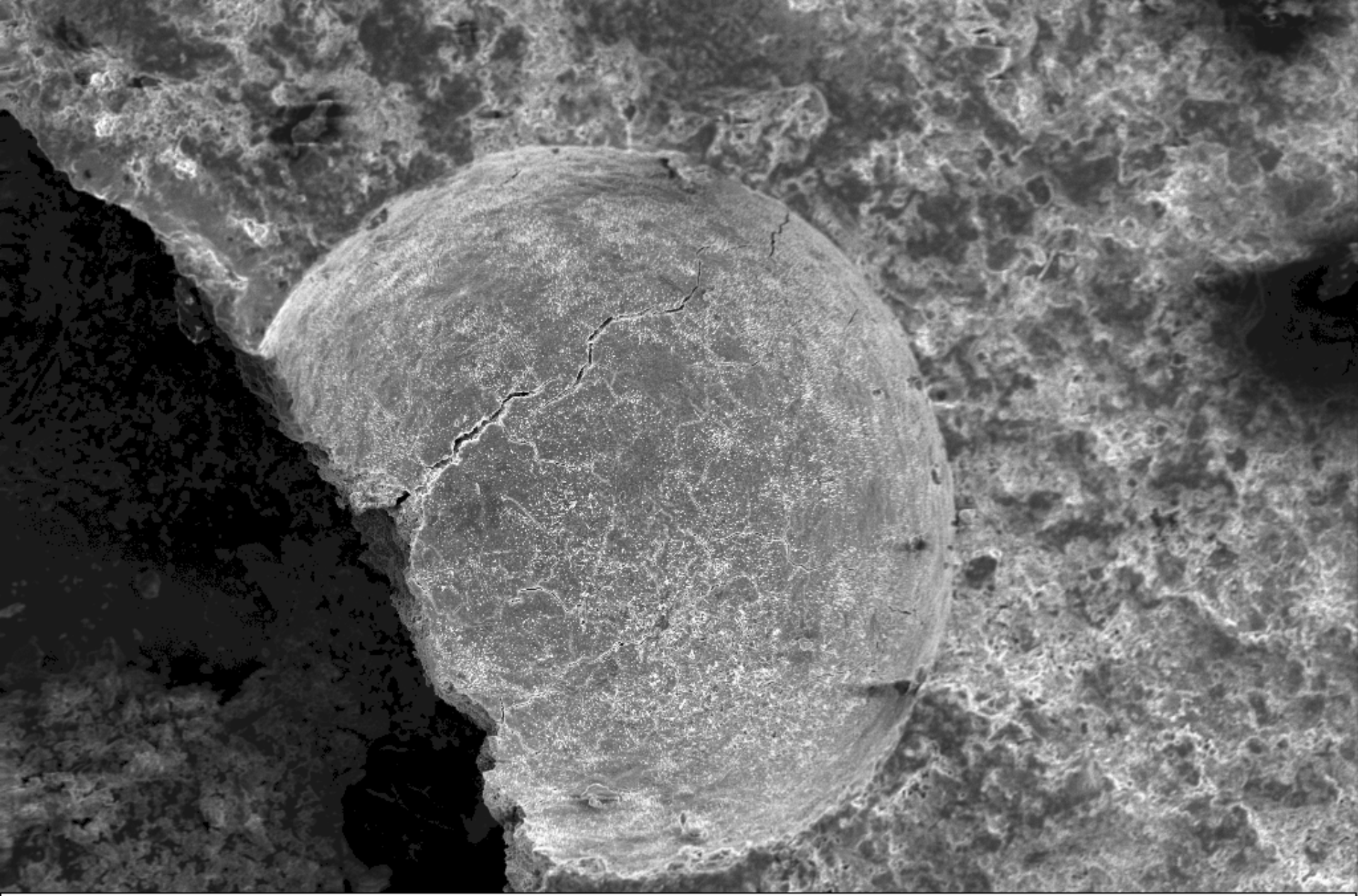
Chemical Properties

- 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



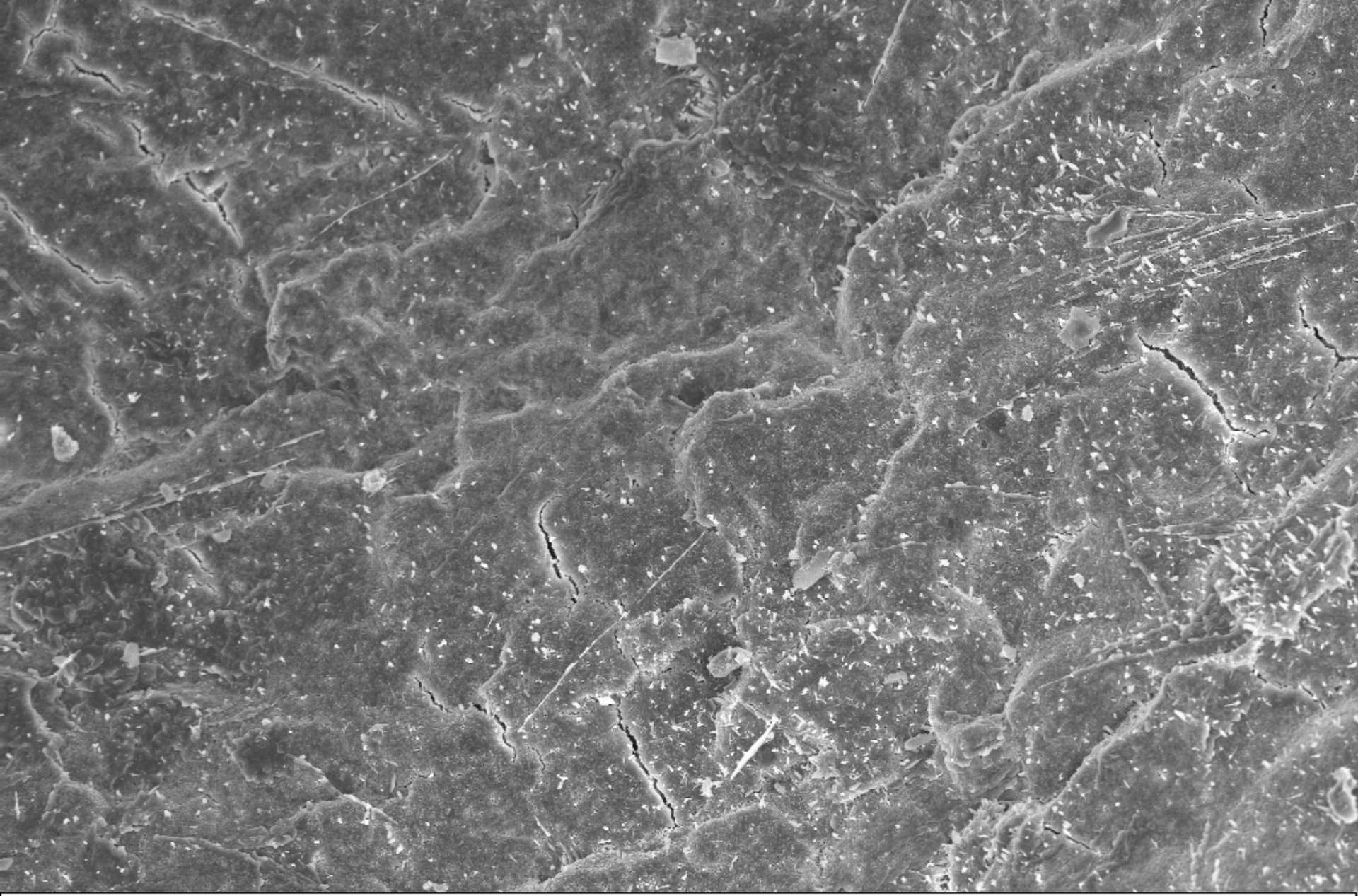
Mag = 375 X

100µm

EHT = 10.00 kV
WD = 12 mm

Signal A = InLens
Photo No. = 3103

Date :7 Mar 2007
Time :17:31



Mag = 2.05 K X

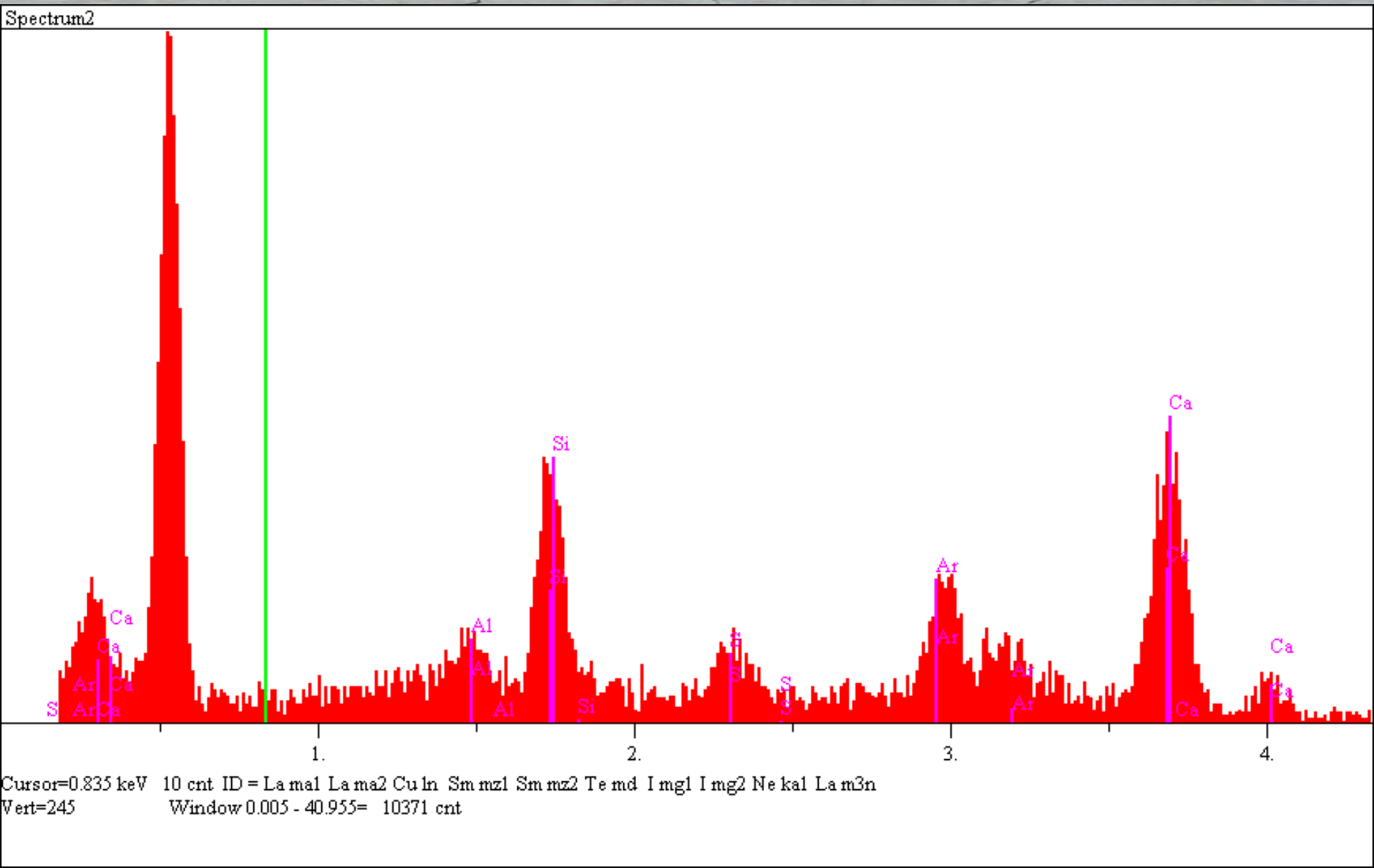
10µm

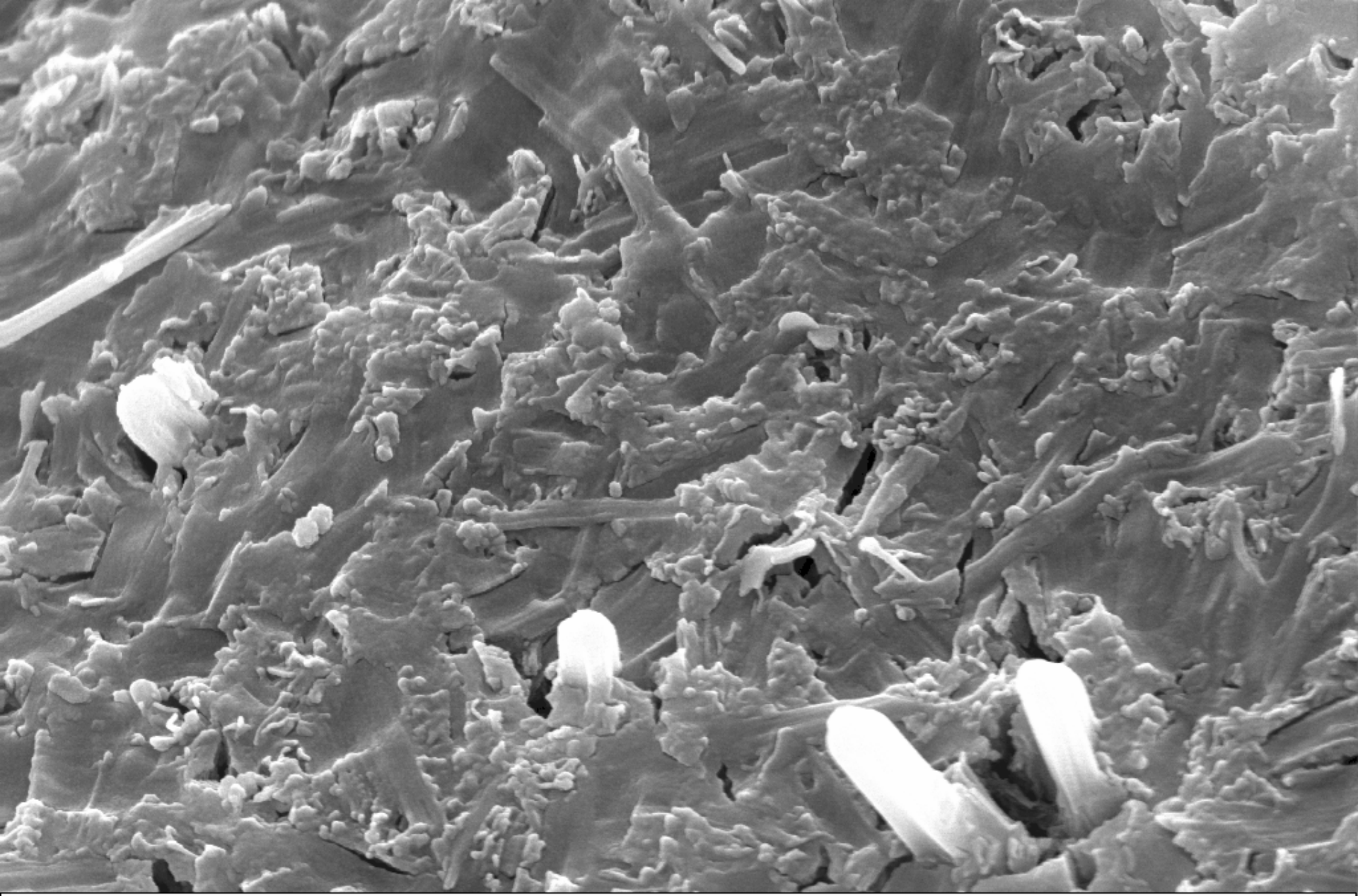
EHT = 10.00 kV
WD = 11 mm

Signal A = InLens
Photo No. = 3090

Date :7 Mar 2007
Time :16:17

Air-Void Shell





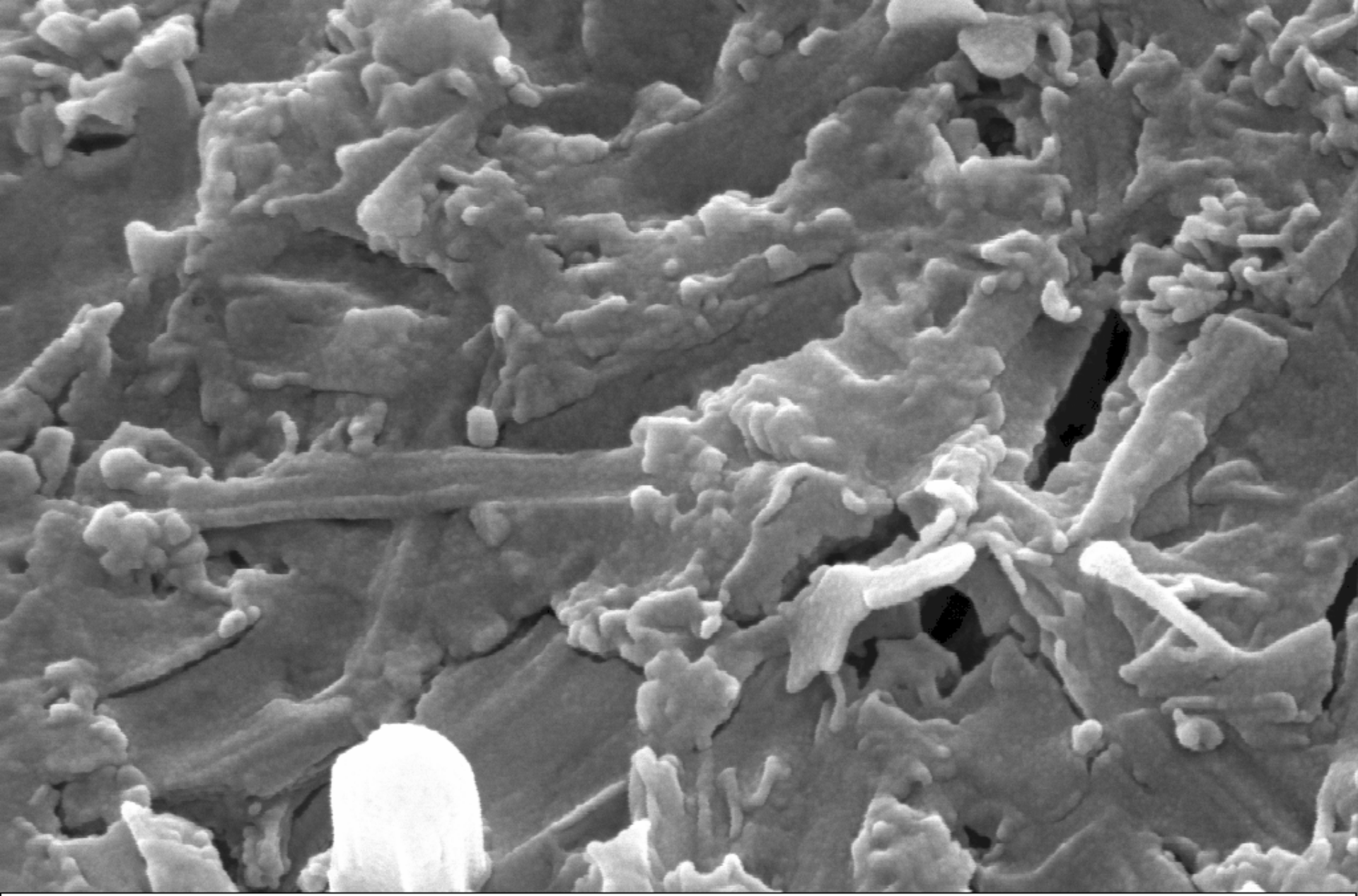
Mag = 60.29 K X

1µm

EHT = 10.00 kV
WD = 6 mm

Signal A = InLens
Photo No. = 3086

Date :7 Mar 2007
Time :16:02



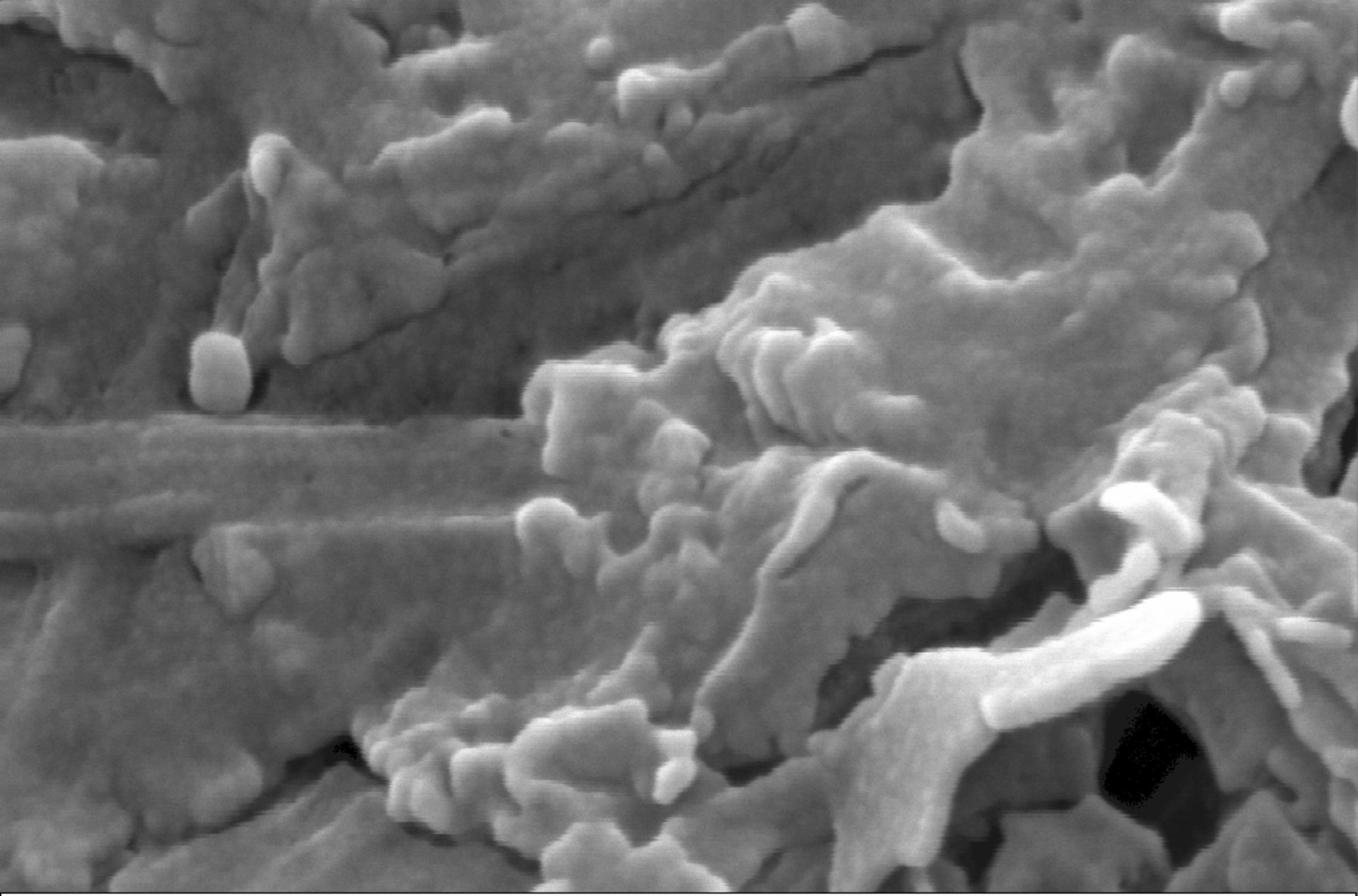
Mag = 150.00 K X

200nm

EHT = 10.00 kV
WD = 6 mm

Signal A = InLens
Photo No. = 3087

Date :7 Mar 2007
Time :16:04



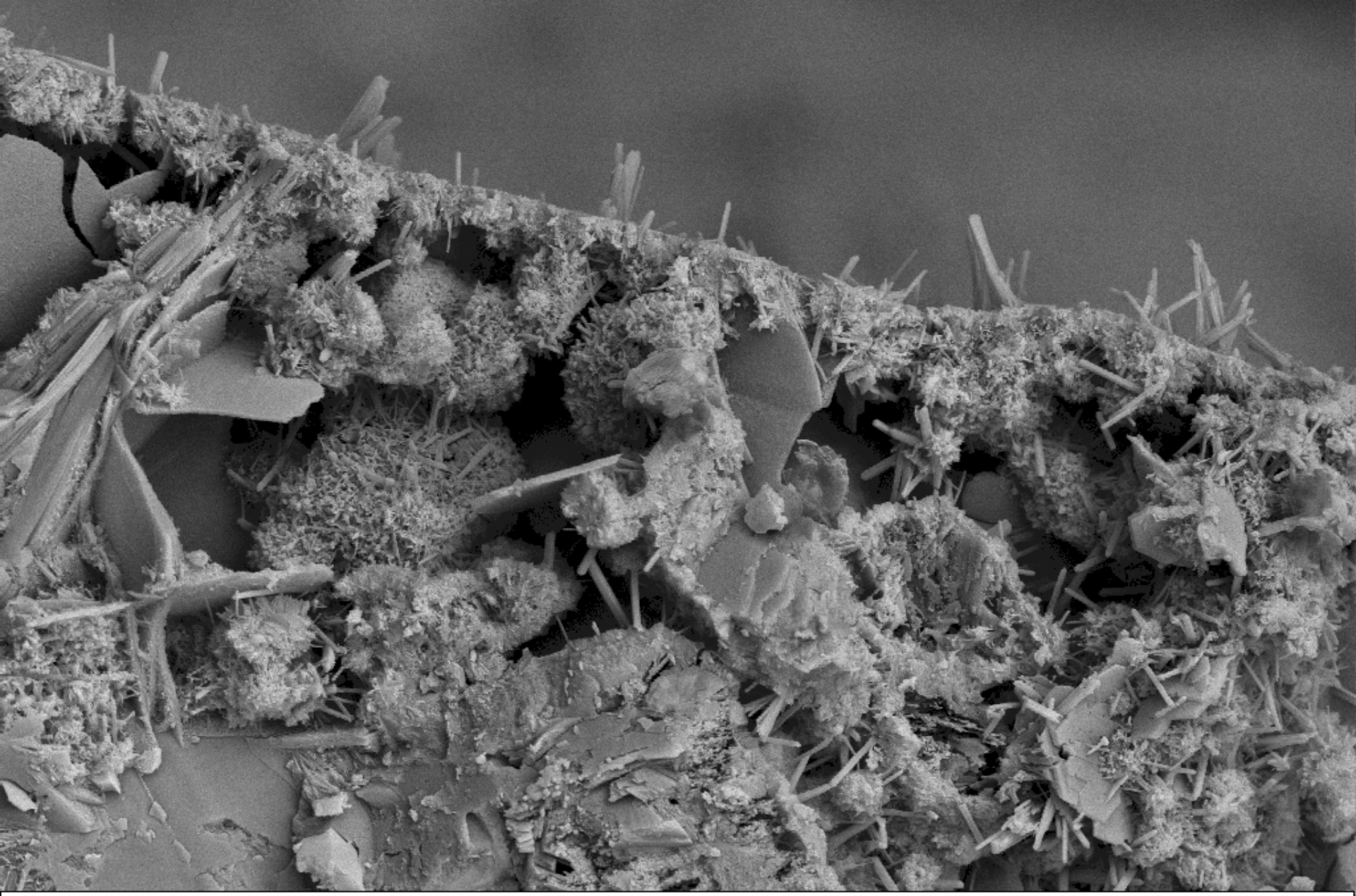
Mag = 300.00 K X

200nm

EHT = 10.00 kV
WD = 6 mm

Signal A = InLens
Photo No. = 3088

Date :7 Mar 2007
Time :16:05



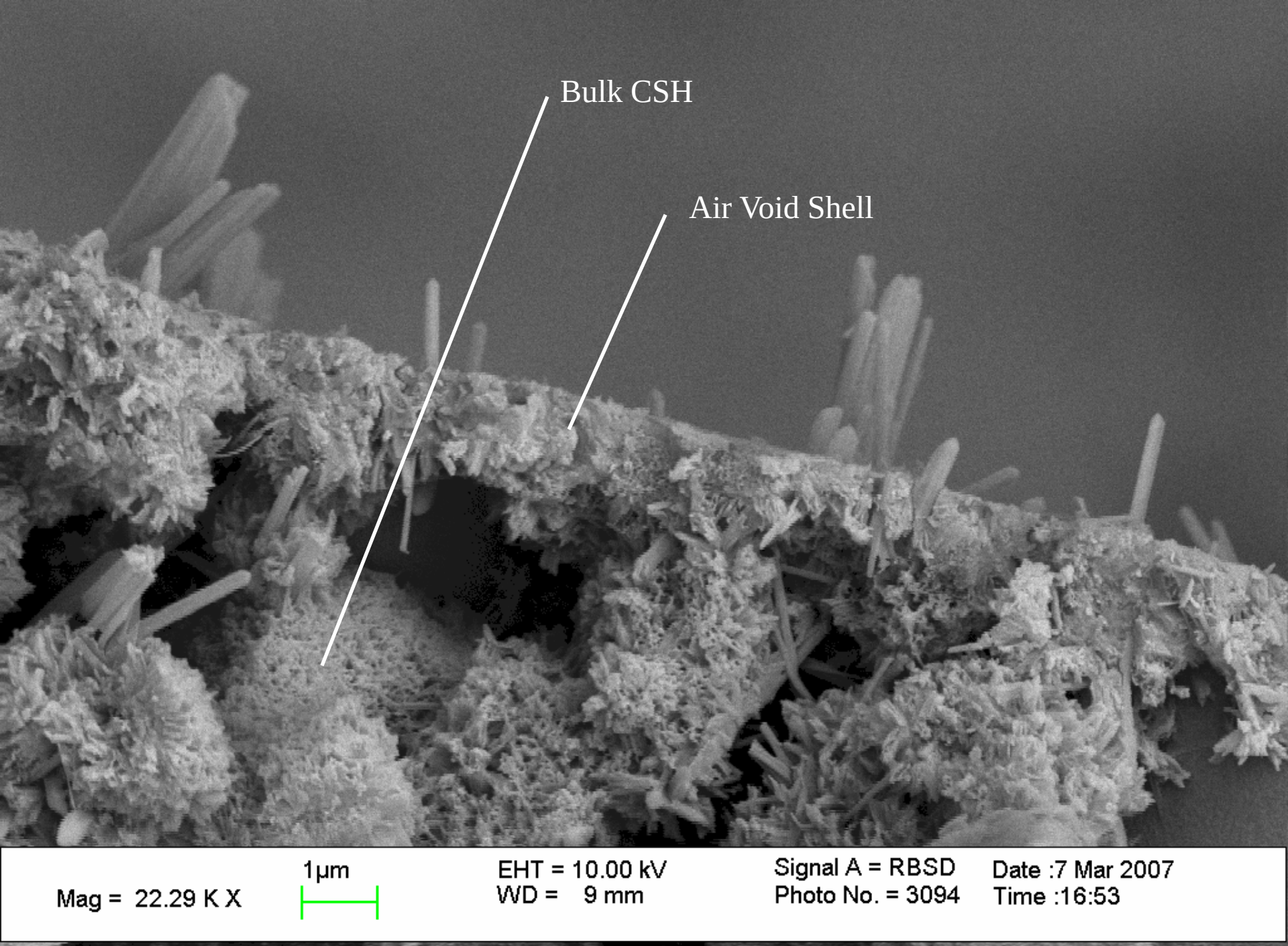
Mag = 7.85 K X

2µm

EHT = 10.00 kV
WD = 9 mm

Signal A = RBSD
Photo No. = 3096

Date :7 Mar 2007
Time :16:55


Bulk CSH
Air Void Shell
Mag = 22.29 K X
1µm
EHT = 10.00 kV
WD = 9 mm
Signal A = RBSD
Photo No. = 3094
Date :7 Mar 2007
Time :16:53

Conclusions

- The air-void shell appears to be made up of a calcium silicate with a different density/morphology then bulk paste C-S-H

What Do We Know?

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- A shell is formed around air entrained bubbles and not around non air entrained bubbles

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- 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

The What if Game…

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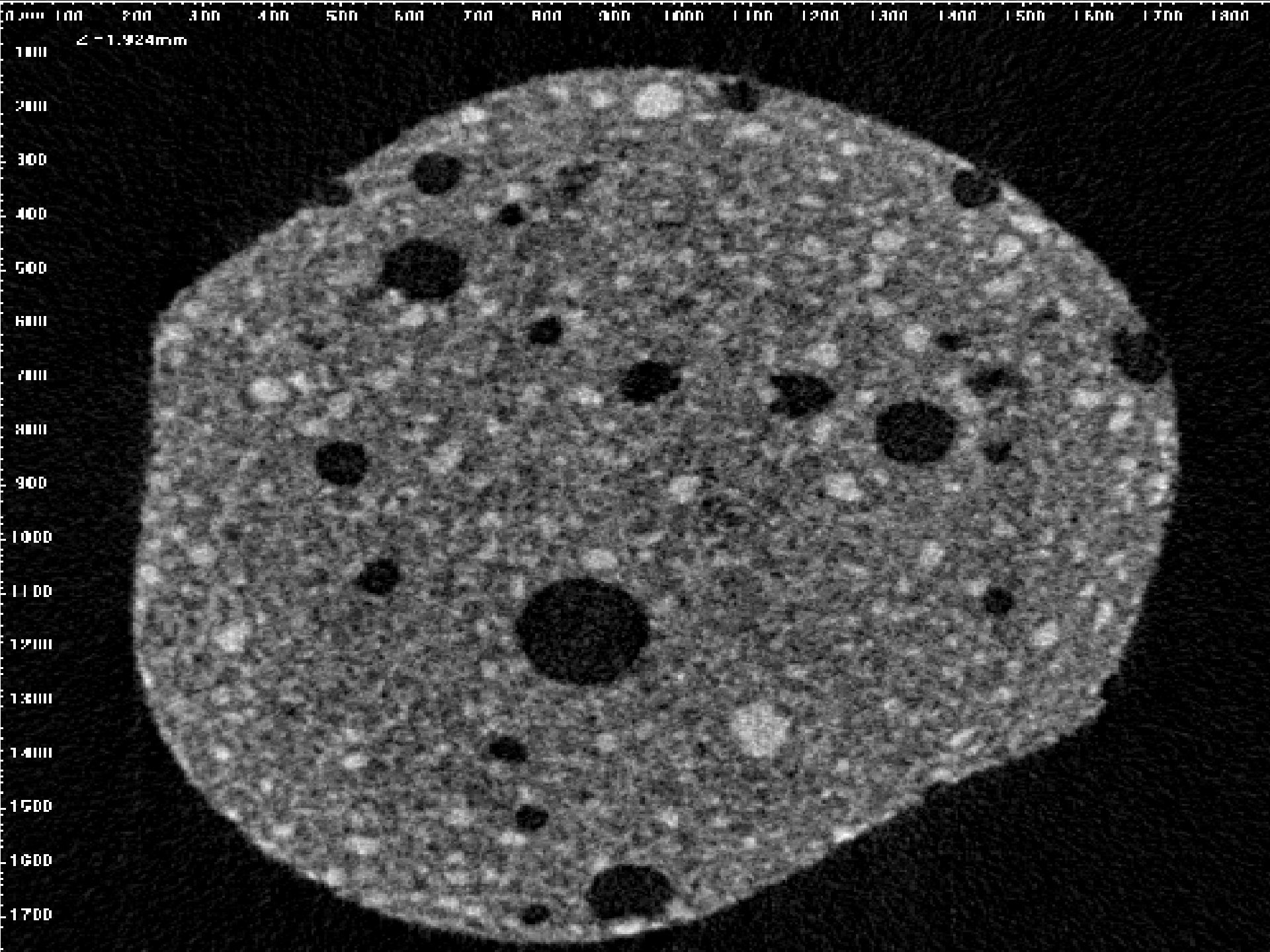
  - If the large air-voids get too large then they will escape from the paste and the air volume decreases
  - If the large air-voids don’t escape then the air volume increases
  - Either way we lose small air-voids and this is bad for frost durability

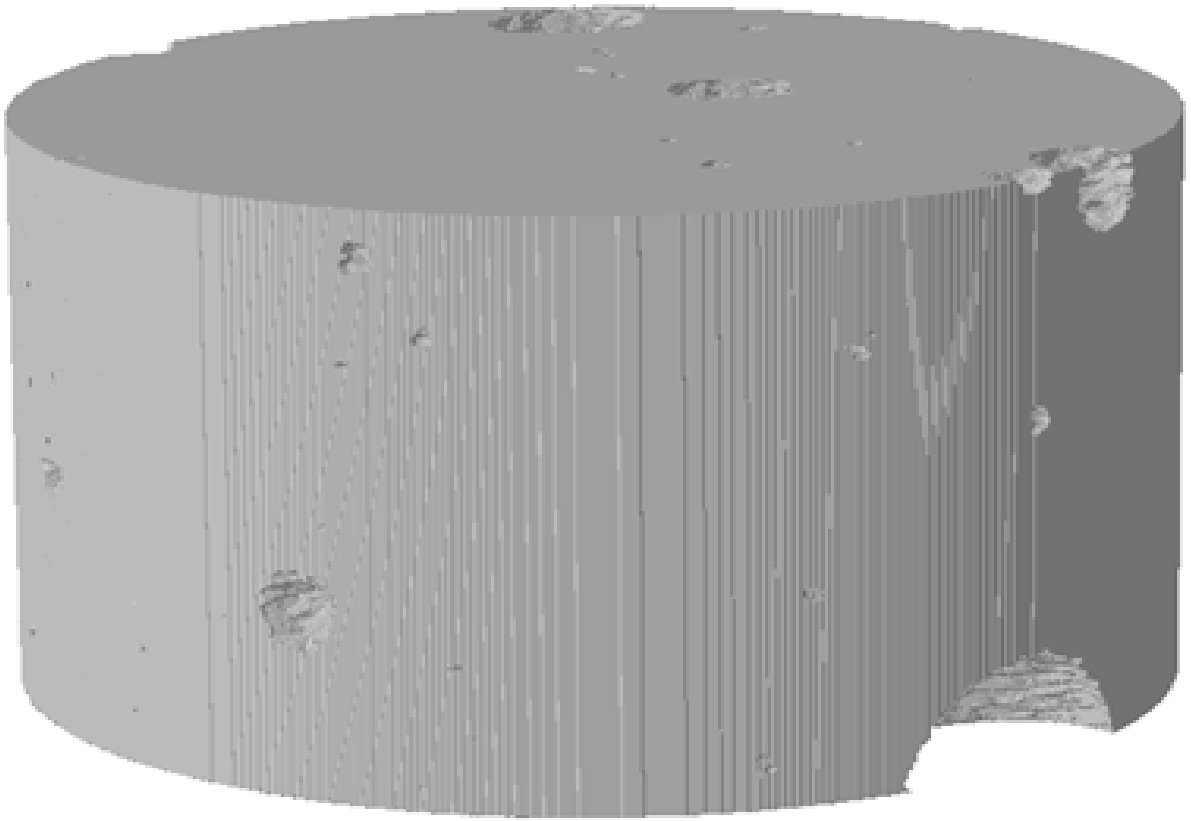
Current Research

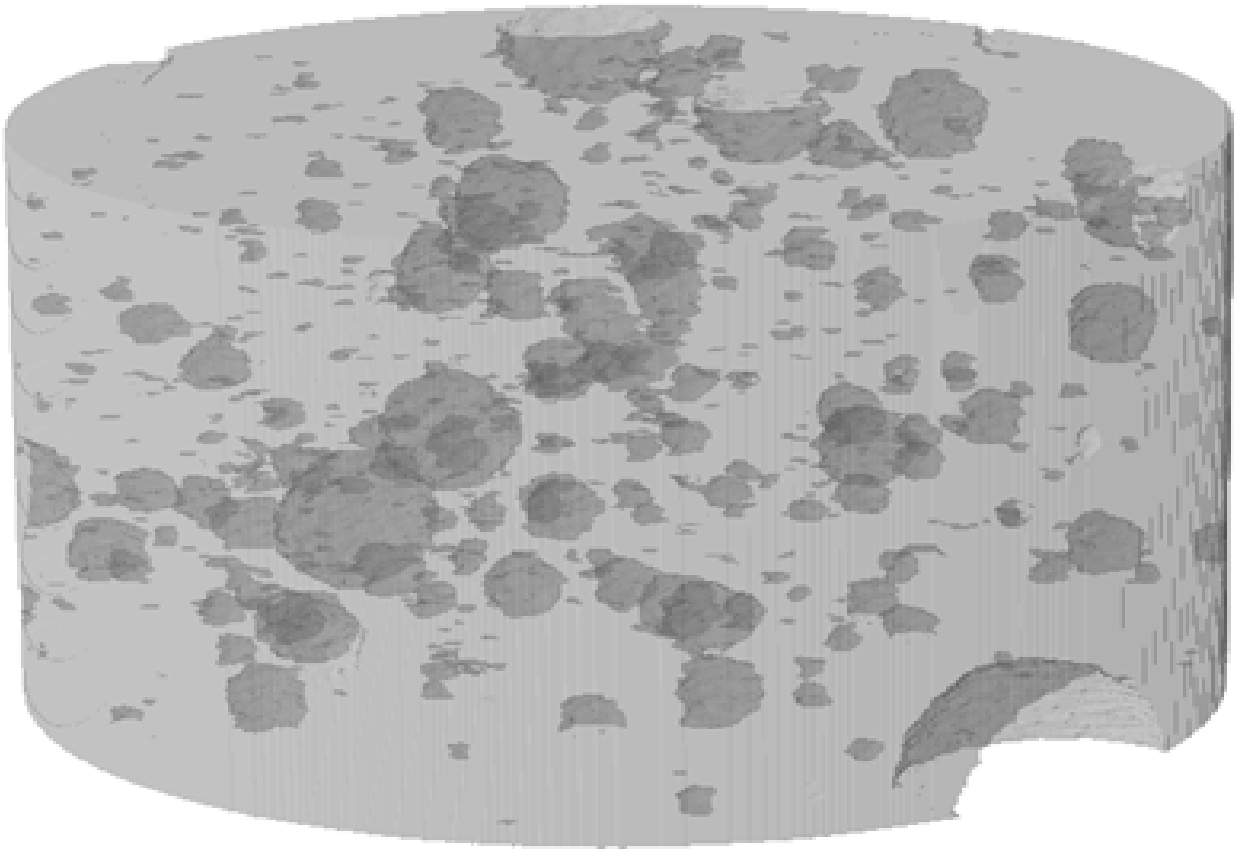
- A more detailed chemical characterization of the hydration shell is being completed
- Interactions between AEAs and other admixtures are being examined

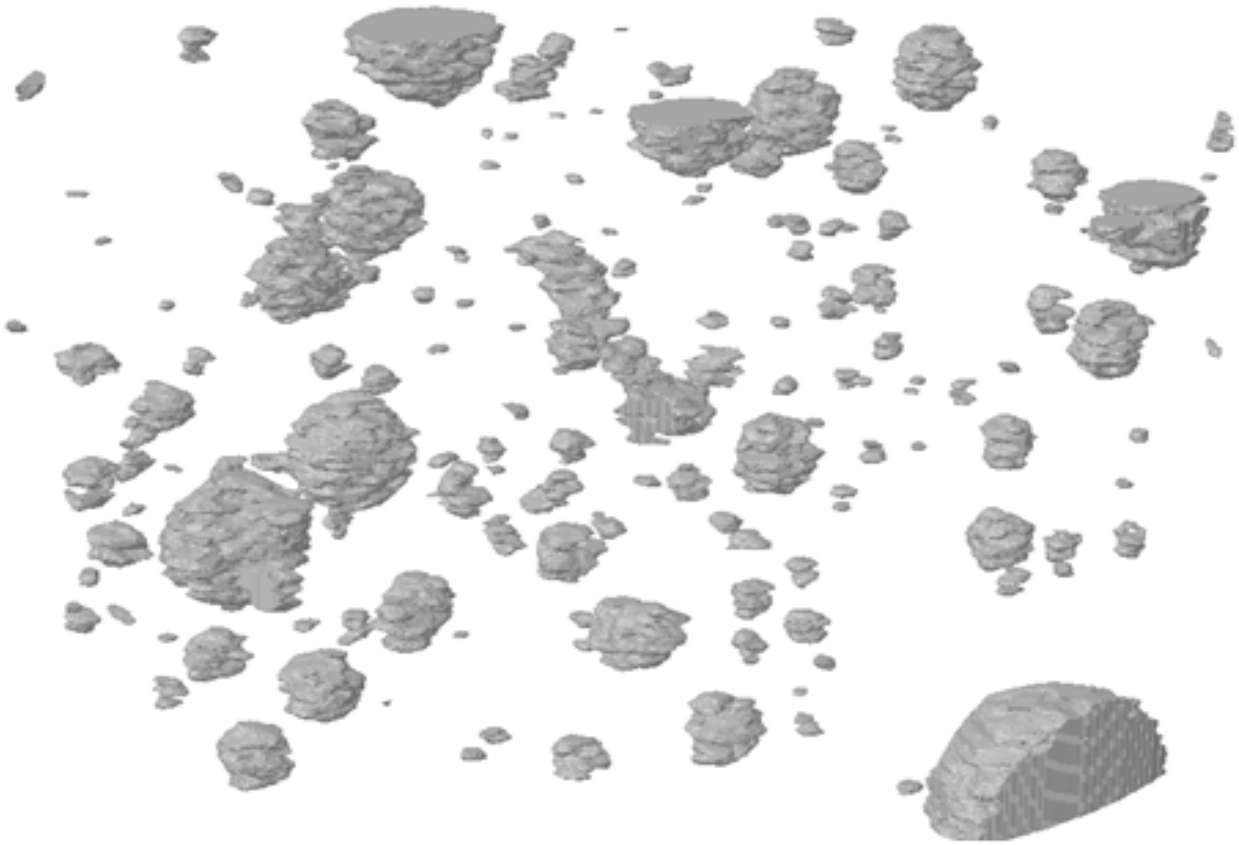
Current Research

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


z = 1.924mm
0 mm 100 200 300 400 500 600 700 800 900 1000 1100 1200 1300 1400 1500 1600 1700 1800
100 200 300 400 500 600 700 800 900 1000 1100 1200 1300 1400 1500 1600 1700







Questions???

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