3M Science. Applied to Life.™

Membrane Defect Analysis

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US DOE, NRC Canada & Fraunhofer ISE
Fuel Cell/Electrolyzer Quality Control Workshop (virtual)

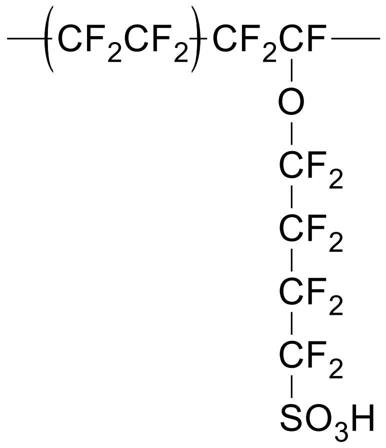
5/6/21

Outline

- What's the Goal?
- The early days – Dryer lint experiment
- Manual inspection - Representative images
- Automated Inspection- What does it mean?
- So, you see something now what? – Accelerated durability testing
- What's the conclusion?

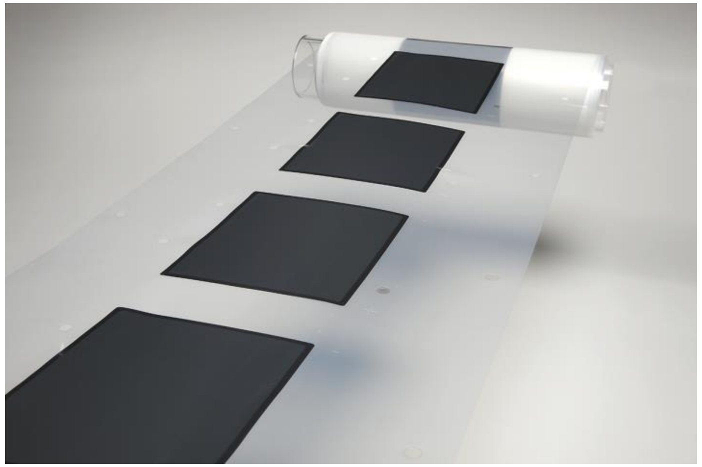
3M

3M Fuel Cell Focus

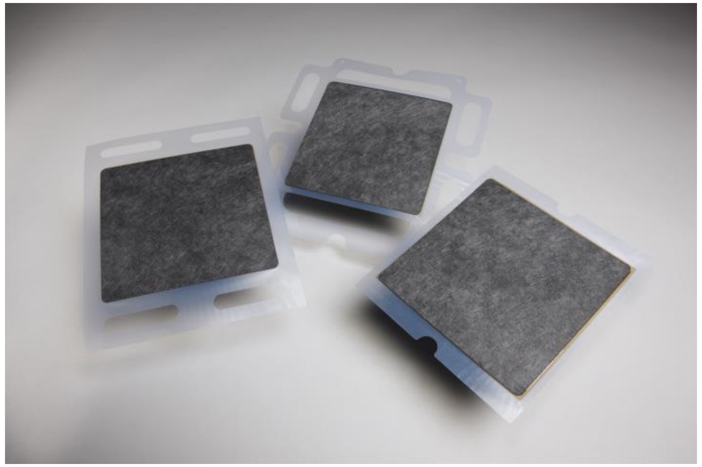


3M Ionomer

2016 - Present



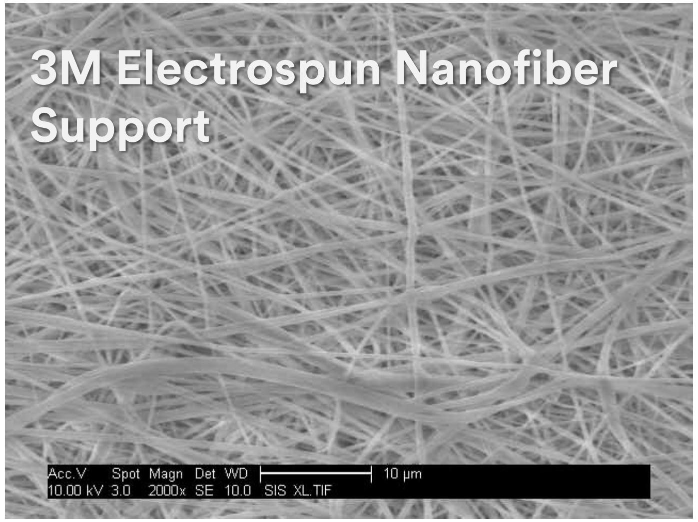
Subgasketed
CCM

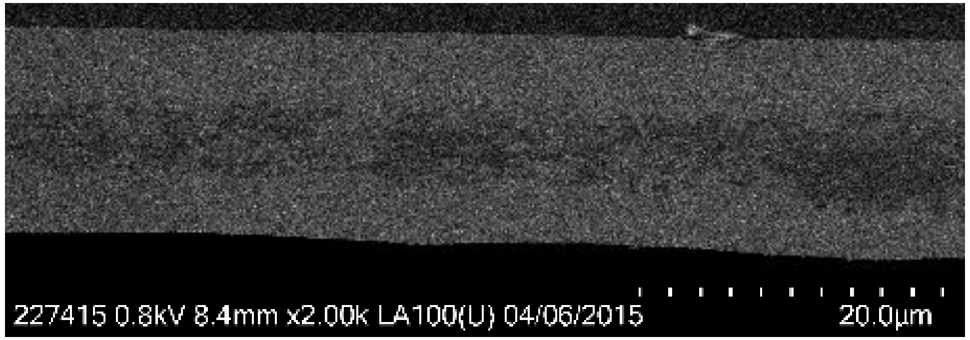


MEAs

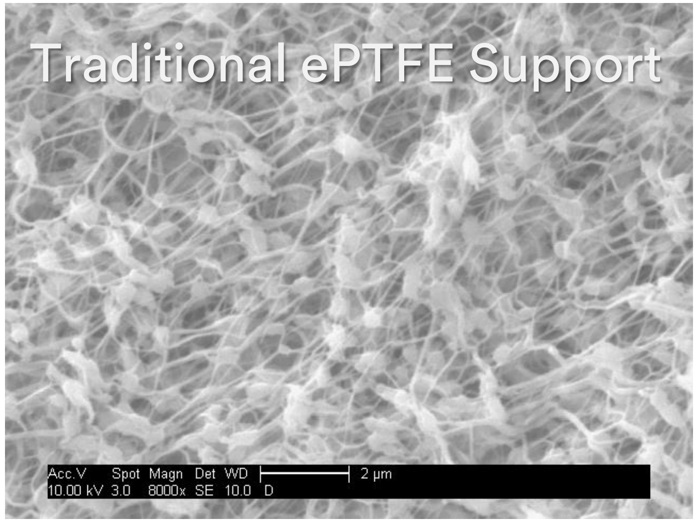
~2000 - 2018

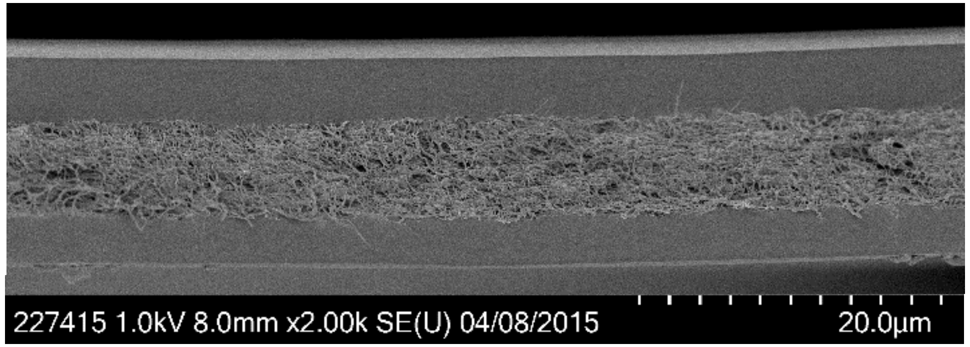
Fiber Support or Reinforcement





Nanofiber support





ePTFE support

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What's the Goal?

To identify defects* and eliminate those that result in premature cell failure

*observation, foreign material, anomaly, feature, etc.

$P_{detection}$ = defect is detected
$P_{failure}$ = defect results in premature failure
$N_{detection}$ = defect is not detected
$N_{failure}$ = defect does not result in premature failure

P= Positive, N= Negative

P_f, P_d Successful Intervention	N_f, P_d Increased membrane cost (lower yield)
P_f, N_d Increased ownership cost (premature failure)	N_f, N_d No consequence

Apply Baye's Theorem?

$$P(P_f|N_d) = \frac{P(P_f|P_d) \cdot (P_d)}{P(P_f)}$$

$P(P_f|N_d)$ = prob. failure given no detection

$P(P_f|P_d)$ = prob. of failure given detection

$P(P_d)$ = prob. detection

$P(P_f)$ = prob. of failure

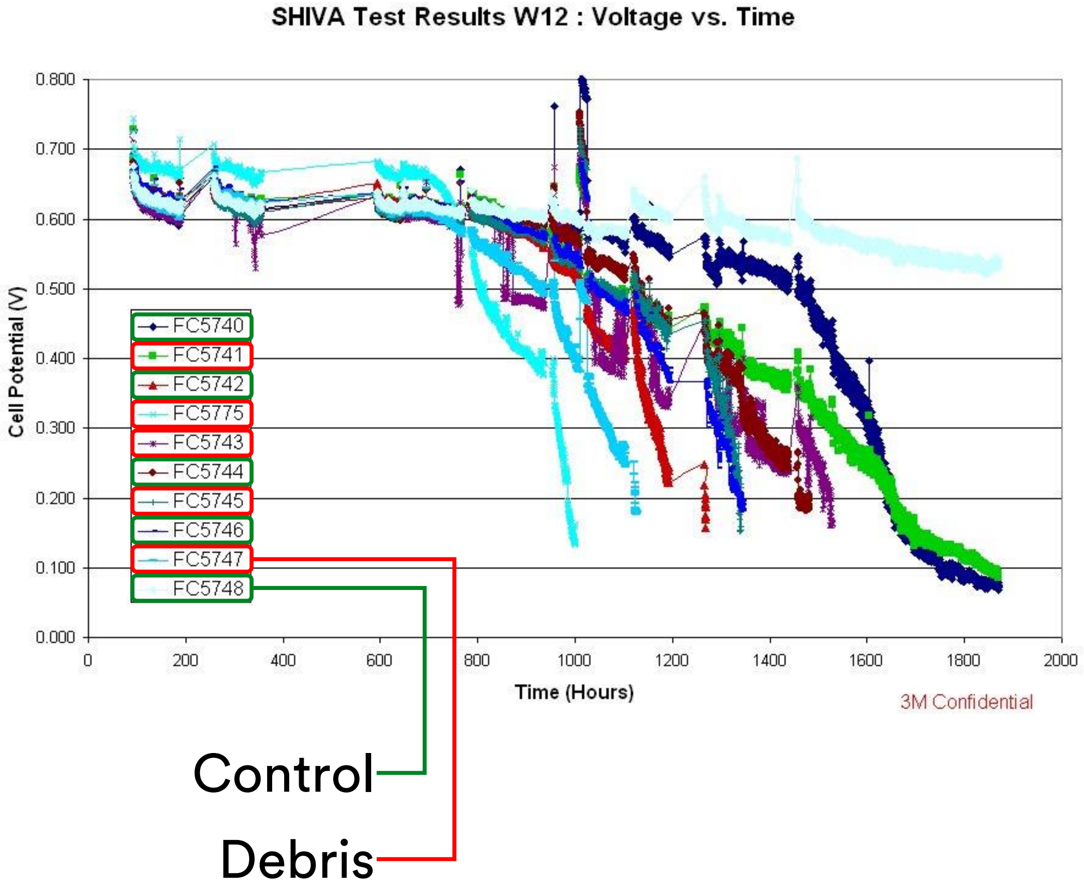
Check my math!

The Early Days

2002

- Garment fibers observed in or on membrane surface
- Membrane deliberately contaminated with dryer lint (mixed into ionomer dispersion)
- Fiber debris – Odd cells
- Control – Even cells

10 cell accelerated durability station (load cycle protocol)



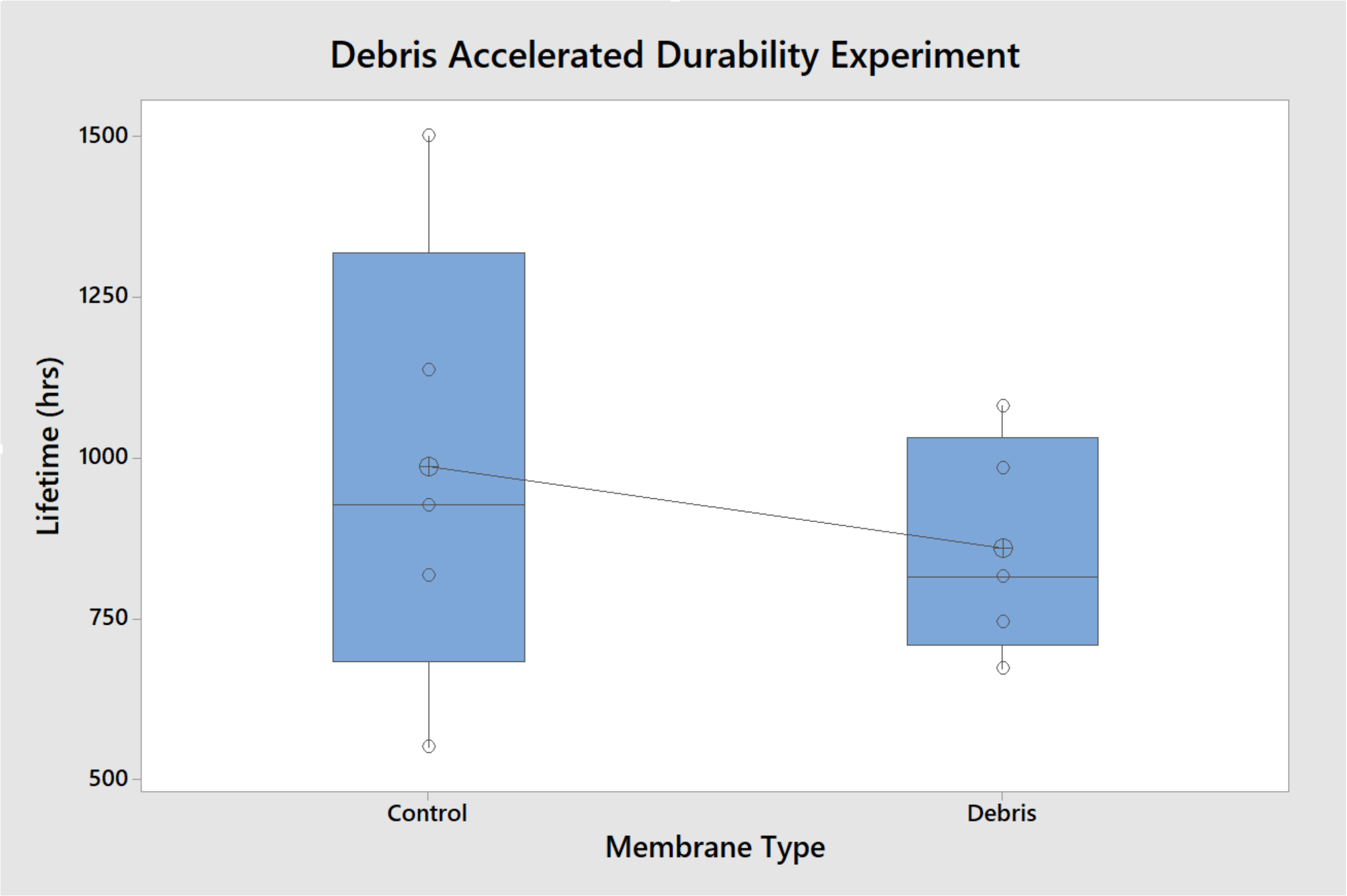
Shiva 1 Debris Study

Two Sample T-Test

Null hypothesis	$H_0: \mu_1 - \mu_2 = 0$
Alternative hypothesis	$H_1: \mu_1 - \mu_2 \neq 0$

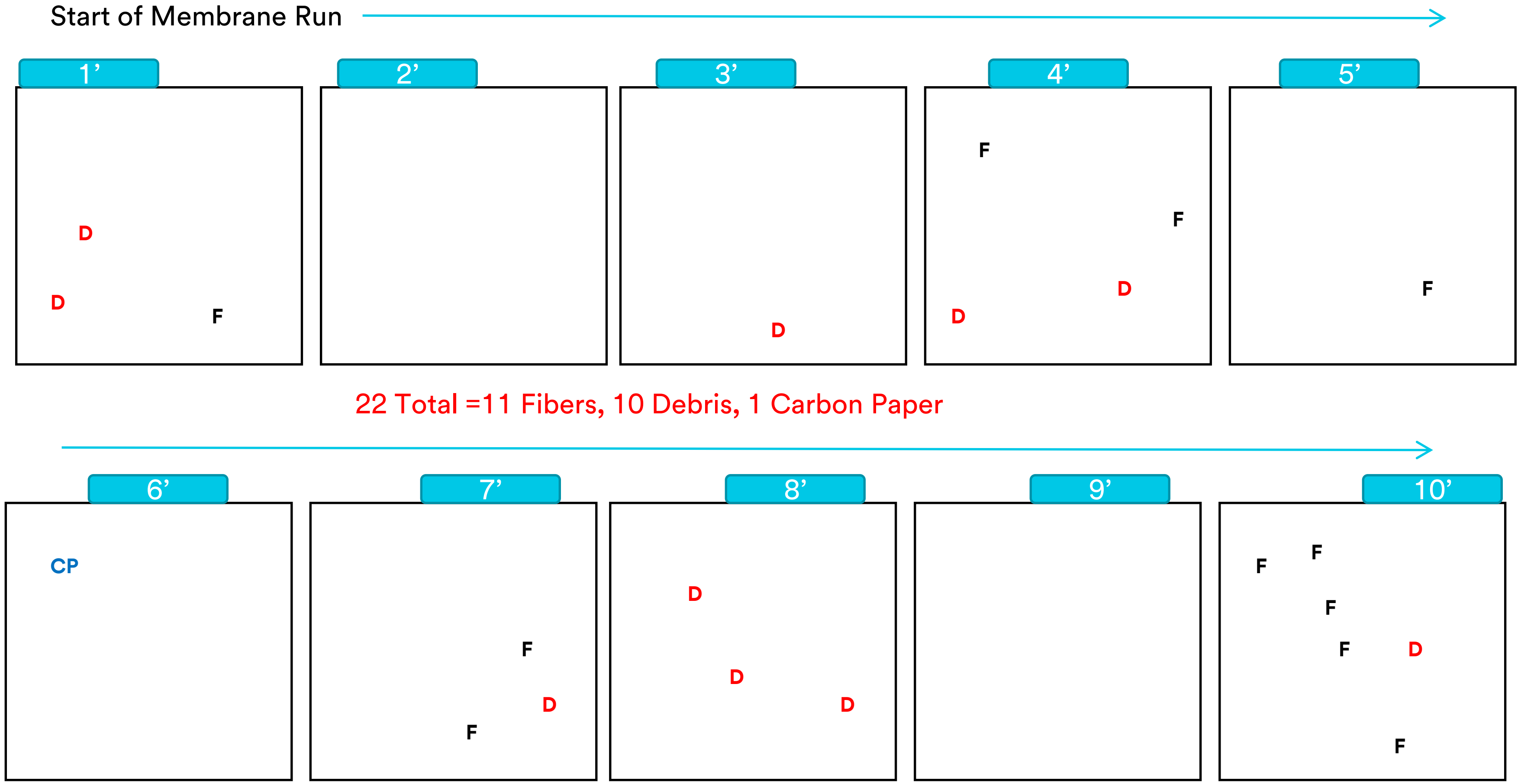
T-Value	DF	P-Value
0.72	5	0.504

P > 0.05 therefore null hypothesis accepted



Manual Inspection

Membrane divided into 1-foot sections

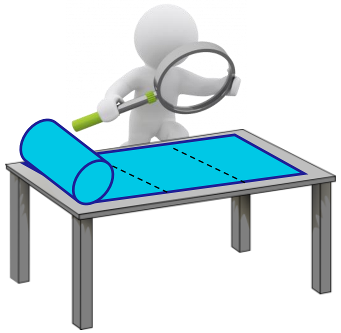


Key:

CP= Carbon Paper

D=Debris

F=Fiber

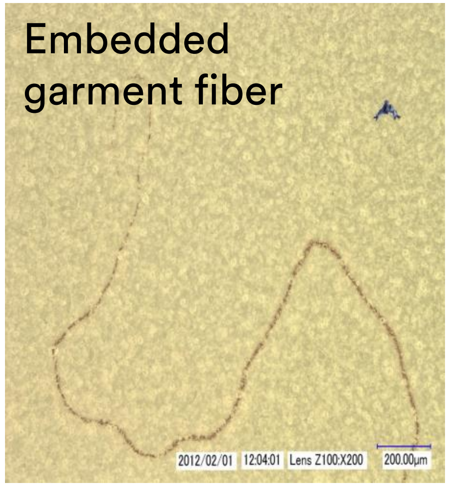


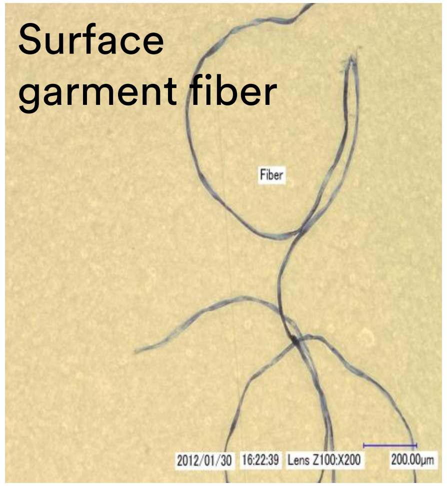
Deliverable 2: Debris After S6 Run

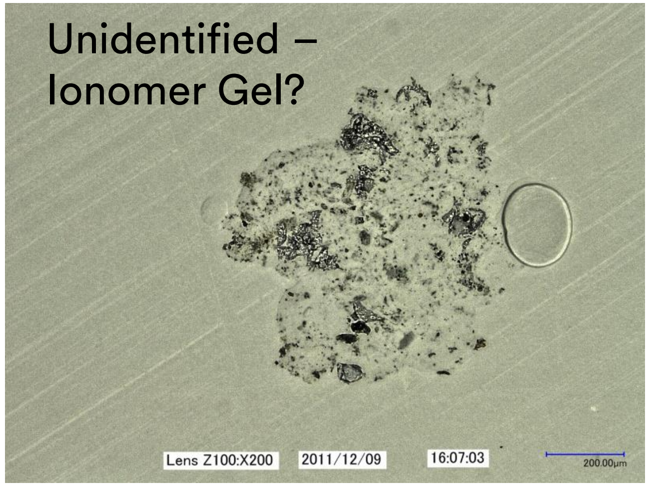
8

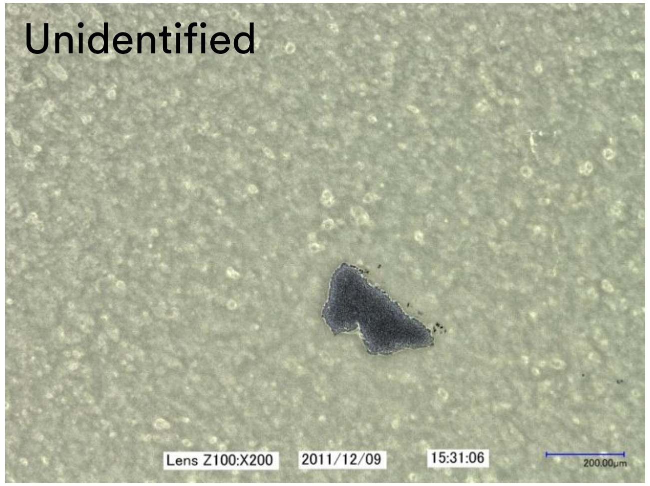
Representative Debris

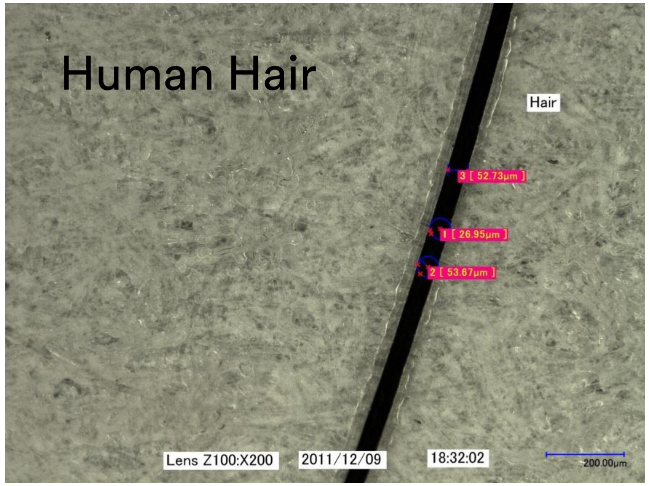
Fibers

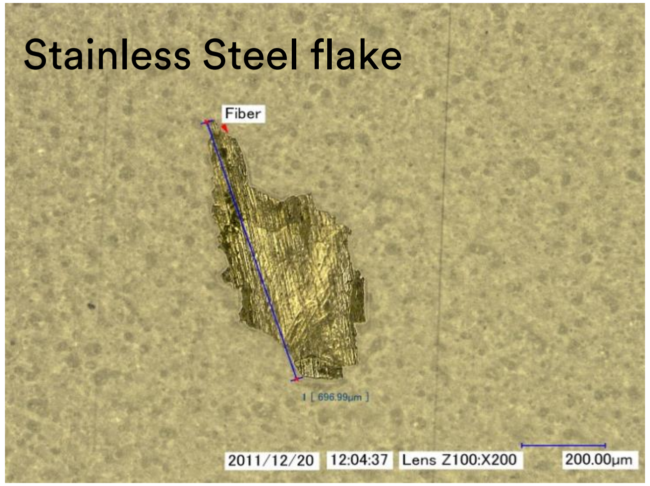






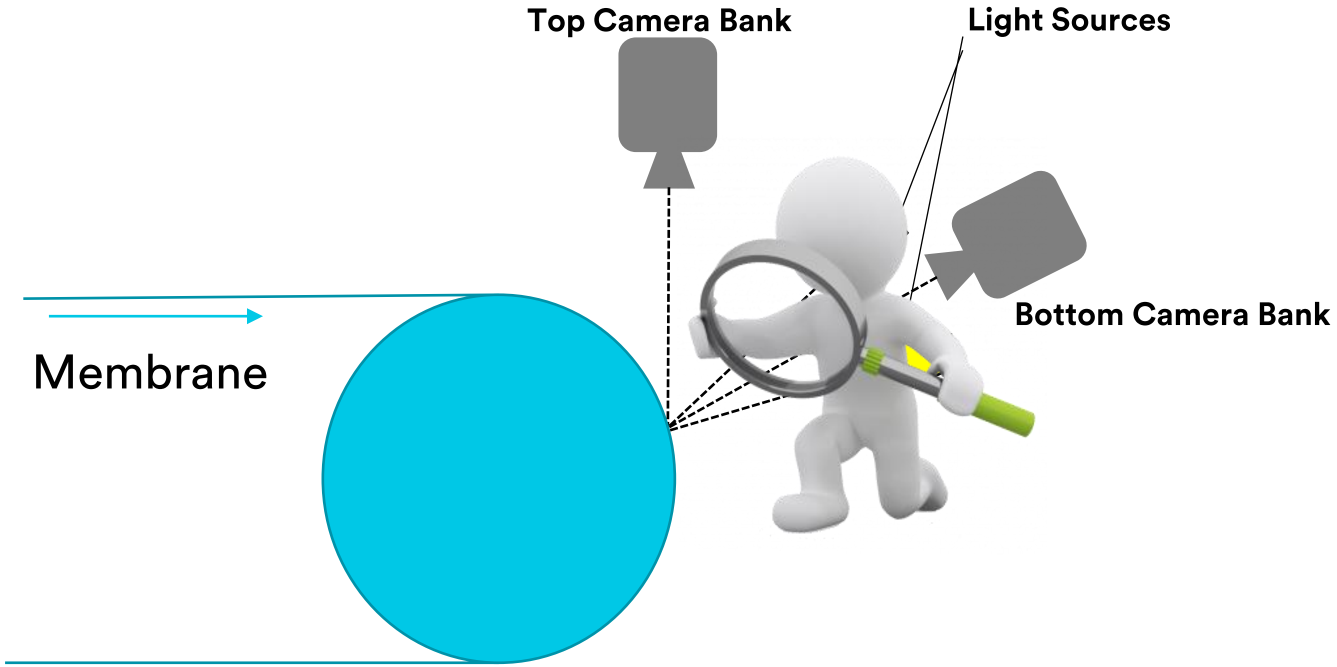






Automated Inspection

2012



Initial inspection

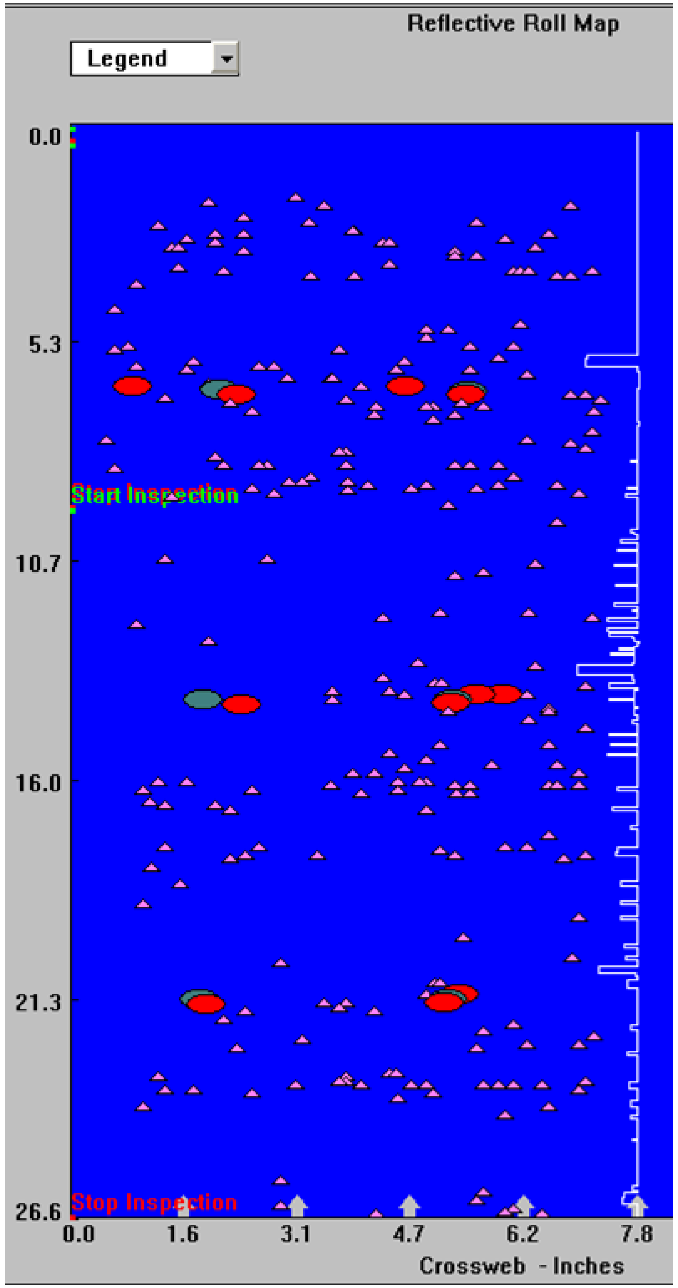
- 20 m of good-looking membrane
- No constraints on detection
  - 14,000 detections.
- With size, and roundness constraints
  - ~1,000 (~500 per camera)

- Ran same roll tested 3 times:
  - Run 1- Most sensitive 26.6'
  - Run 2- Least sensitive 27.4'
  - Run 3- Moderate sensitivity 27.1'

Run 1

Observations sorted into different buckets:

Legend*
- Fibers
- Hash/Small Fibers
- Dark spots

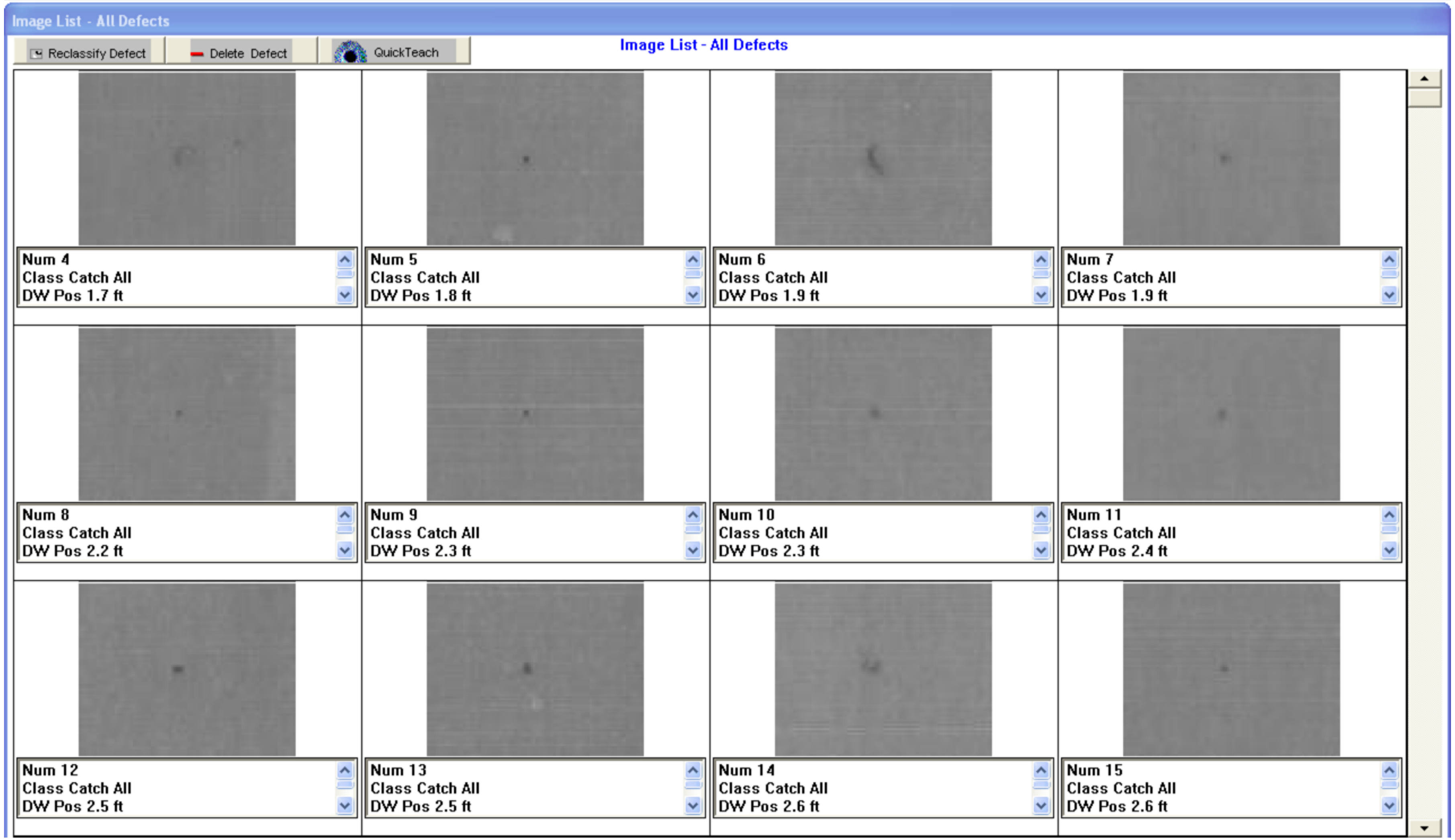


Run 1 - Sensitive Width and Length Settings

- 271 defects in 26.6ft

Typical Detection Images

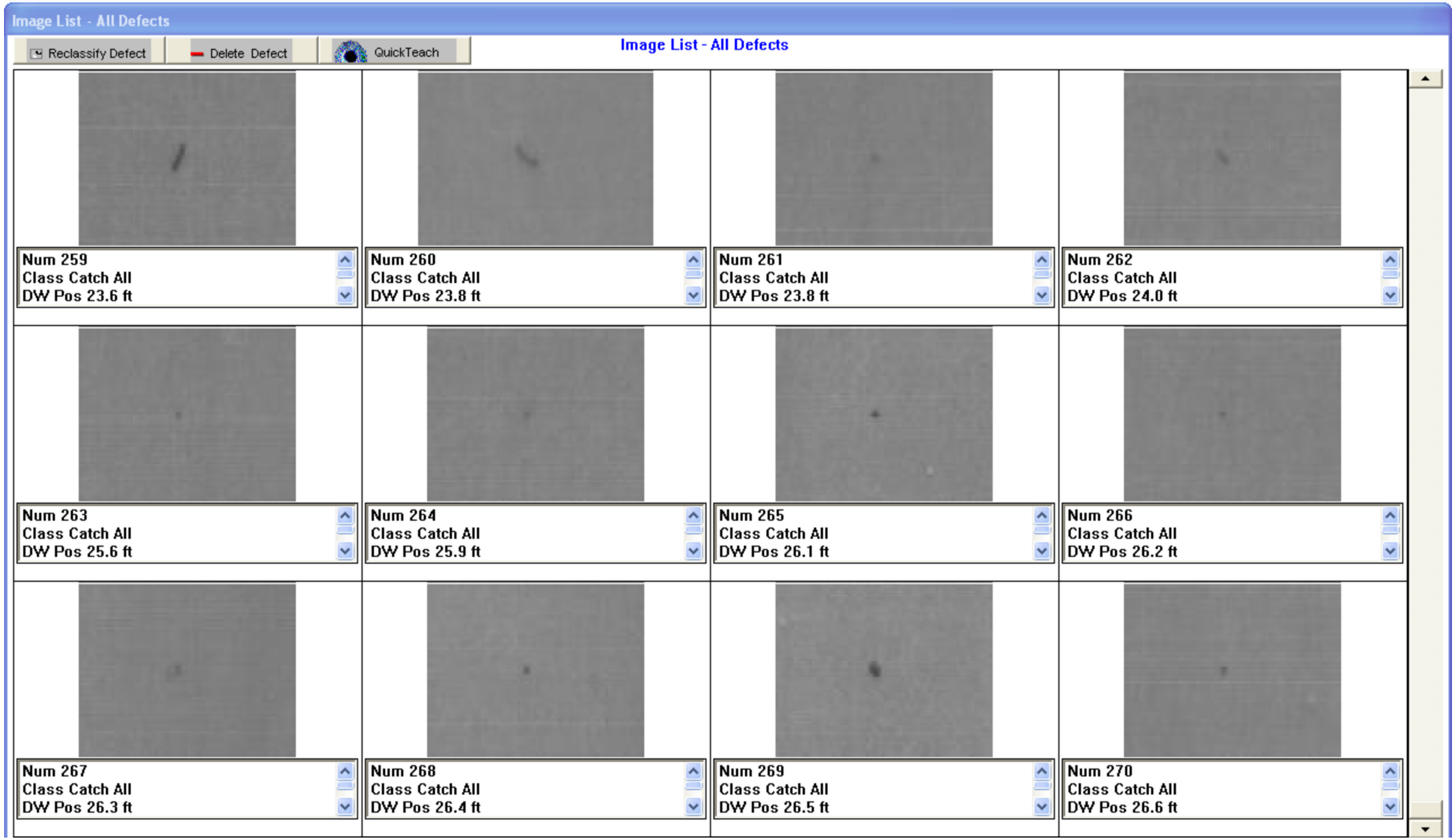
Run 1 – Most sensitive settings



More Images

Run 1 – Most sensitive settings

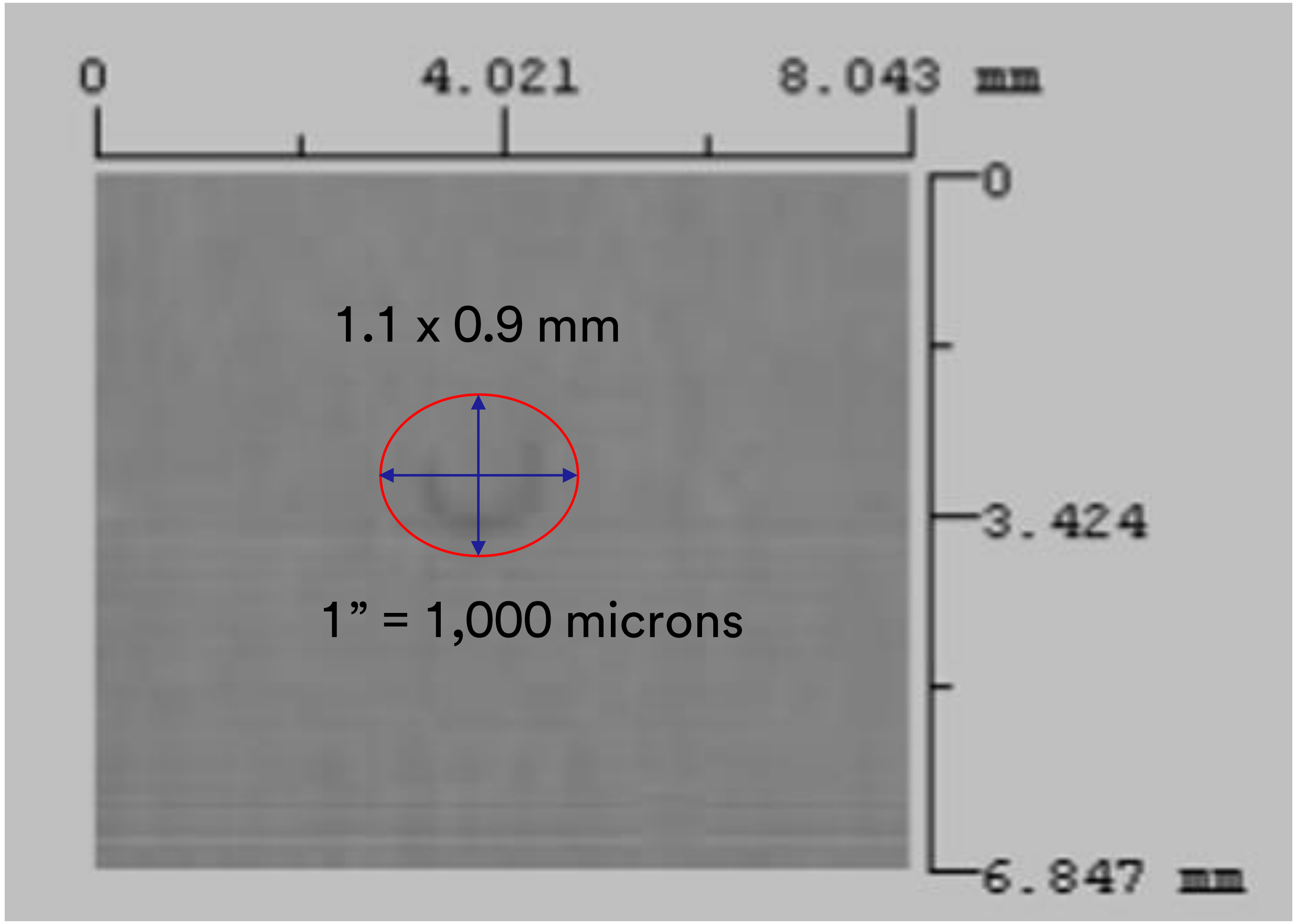
Dark spots suspected to originate from electrospun nanofiber support



Some Perspective

14 micron membrane
(0.14” in image)

Single pixel
size 20 micron

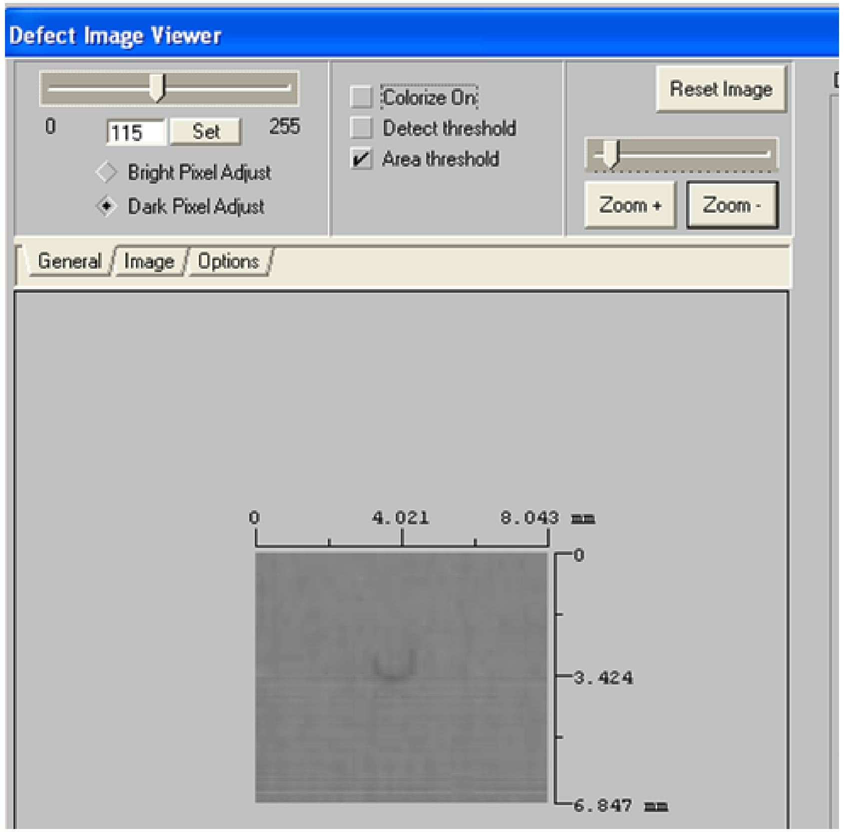


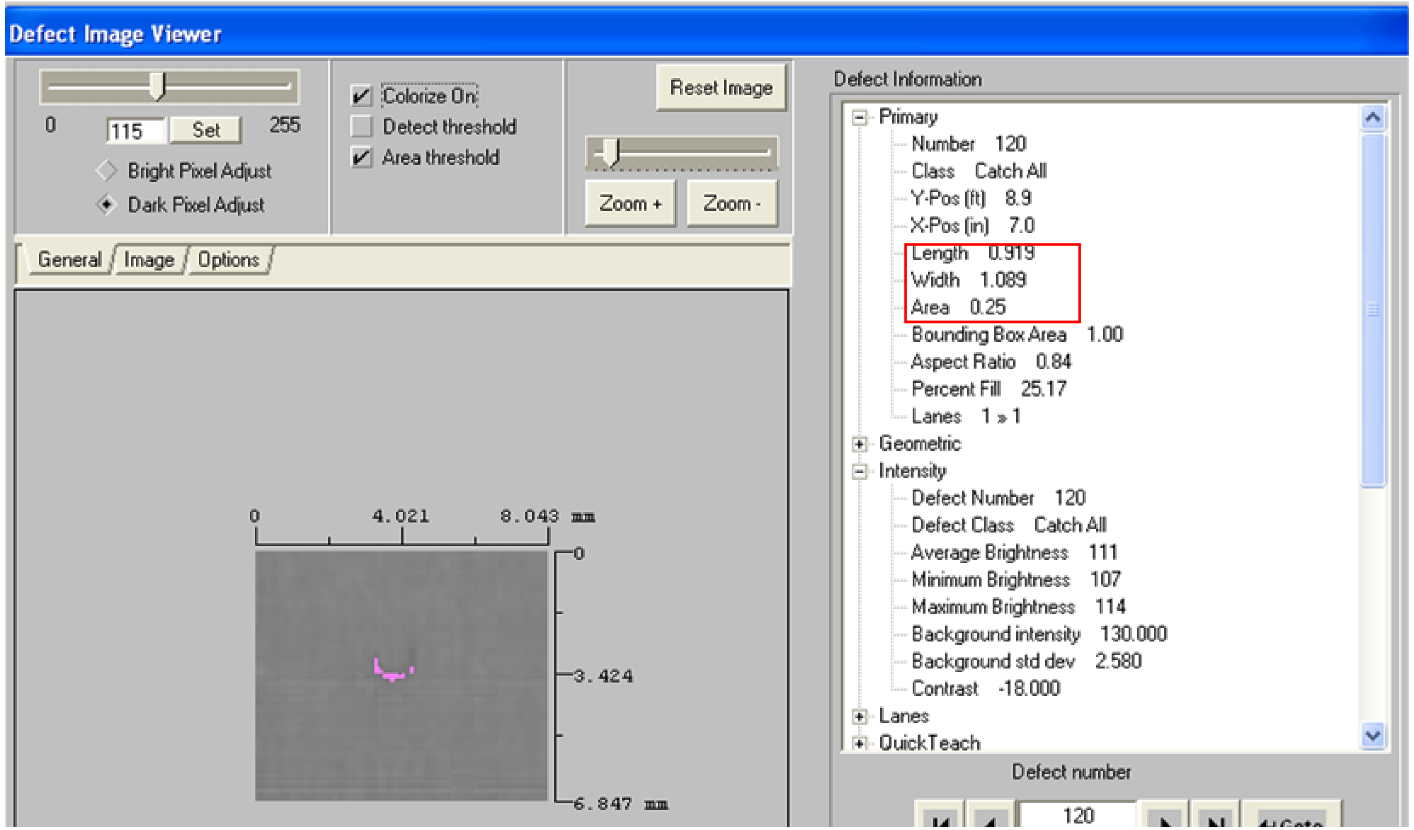
Threshold Settings

Defect #120, Run 1

Pink is what software classified as “Defect”

•Did not pick up all parts of defect

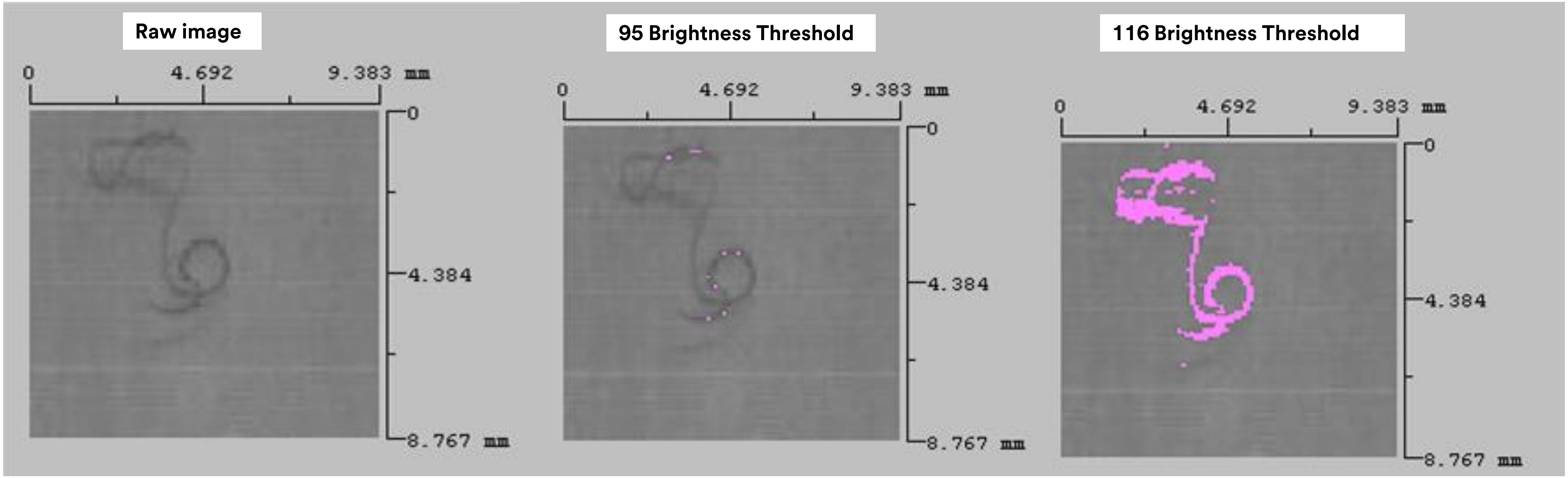




Threshold Settings

Run 1: Defect #145

- Fiber might be classified differently based on threshold setting
- Brightness threshold of 116 seems reasonable in this case

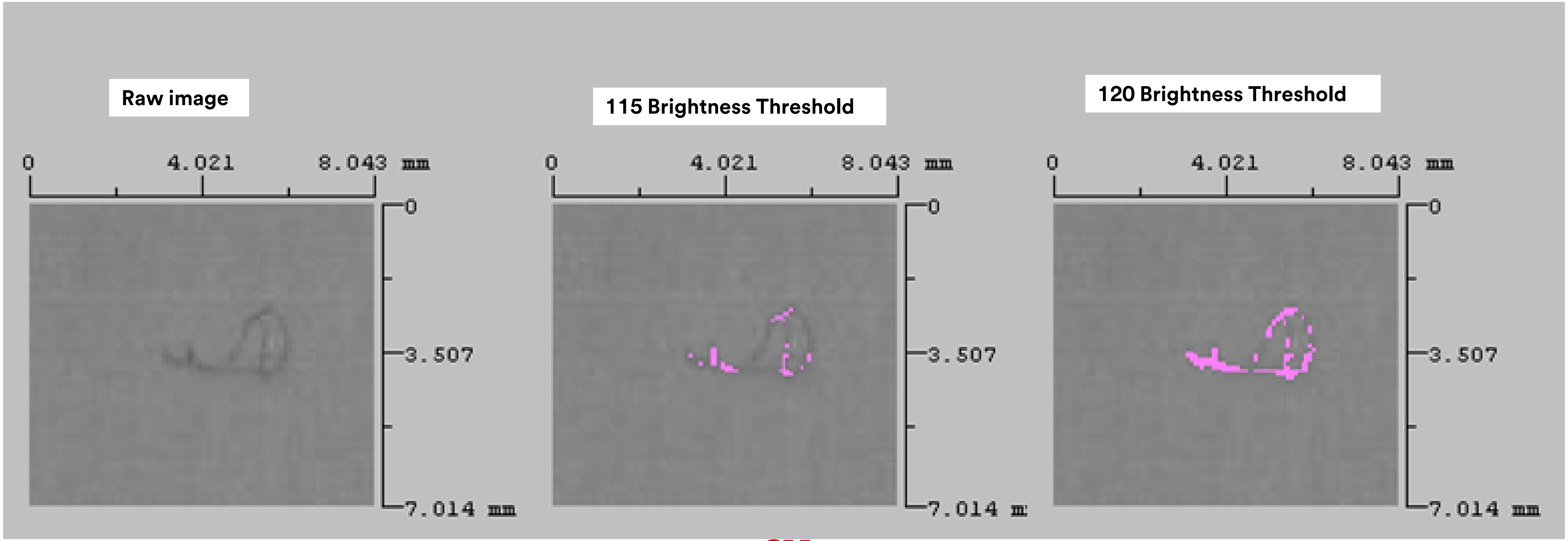


Threshold Settings

Run 1: Defect #215

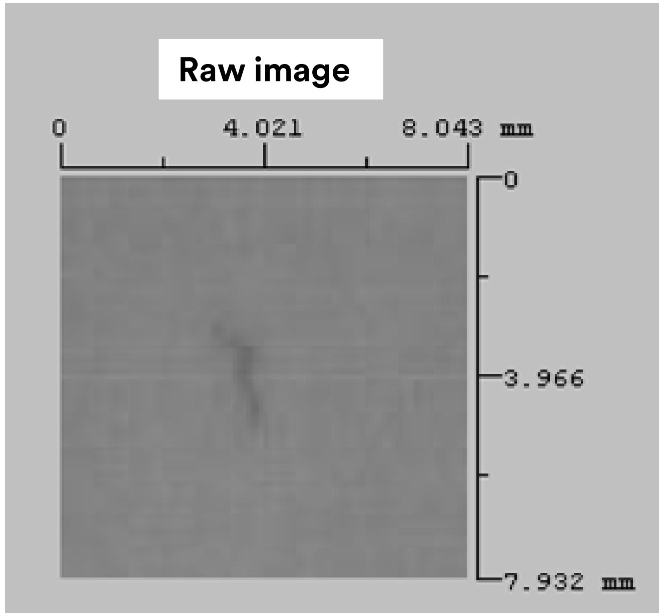
Another example

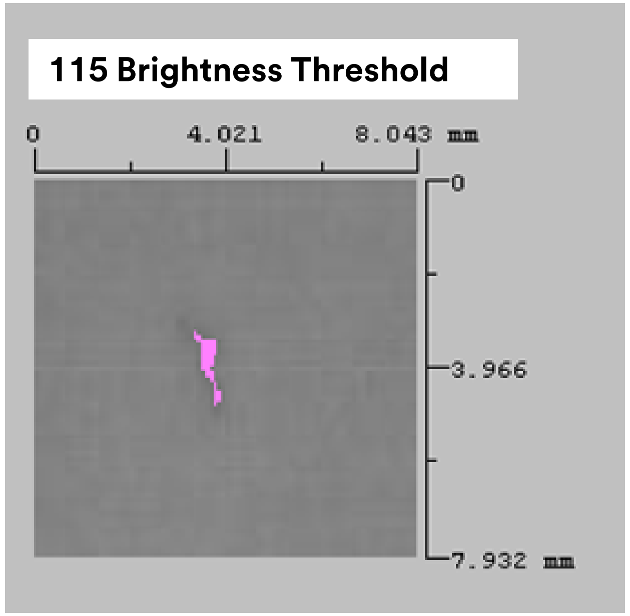
- Brightness threshold of 115 may not accurately capture this defect

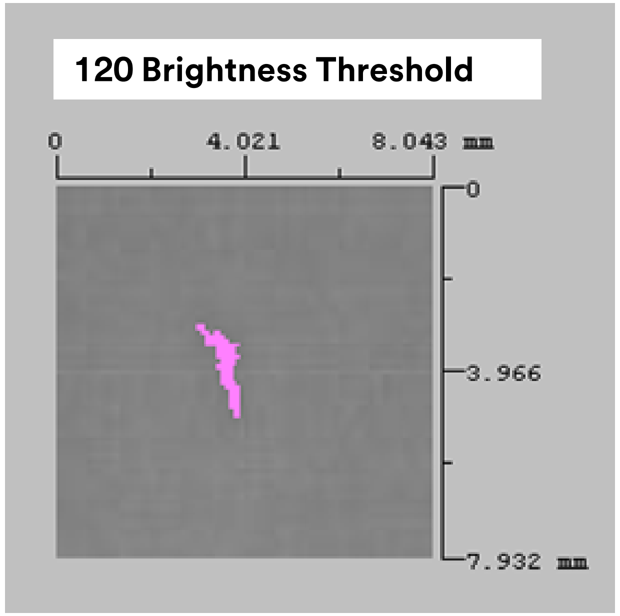


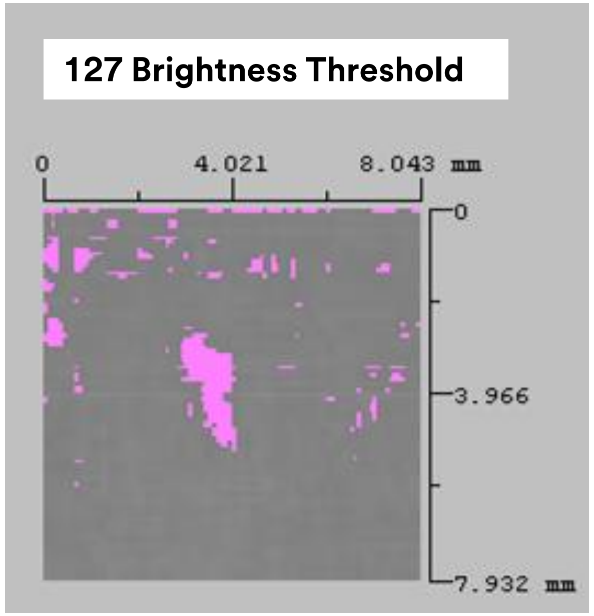
Detection Threshold – too much of a good thing

Run 1: Defect #129



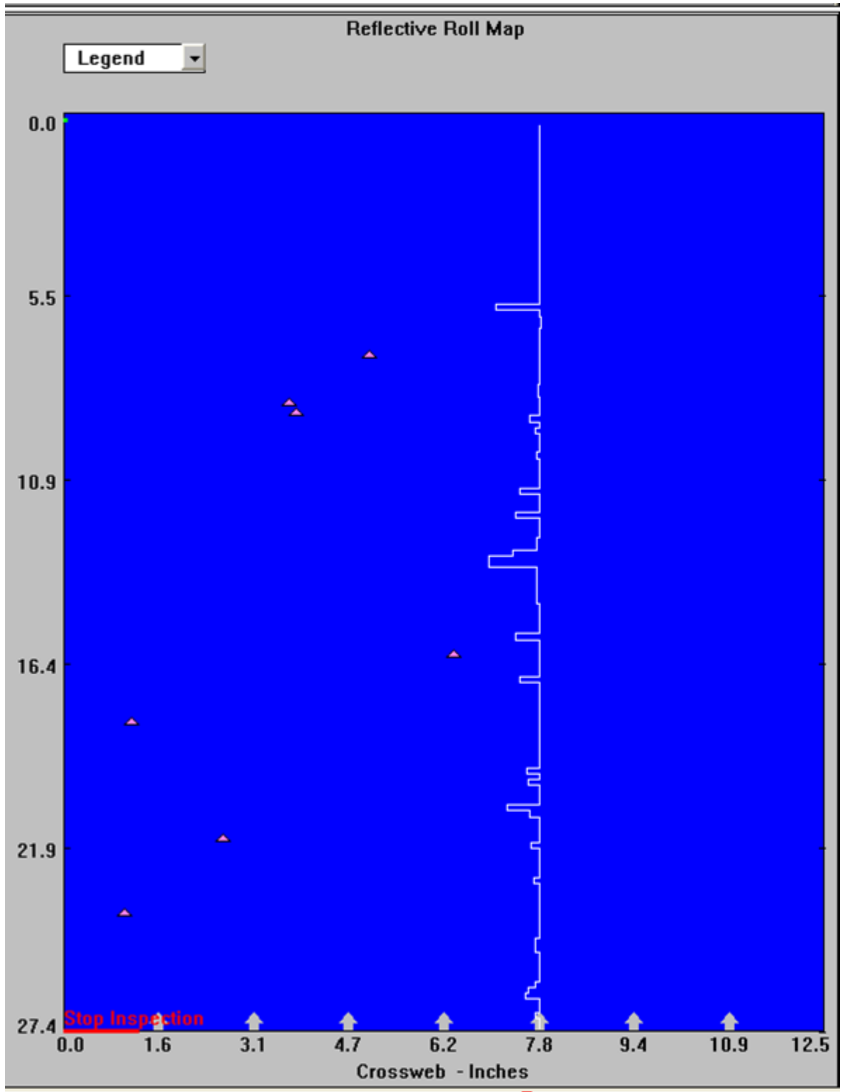






Run 2

Least sensitive settings



Run 2-Increased width and length criteria

9 defects in 27.4ft

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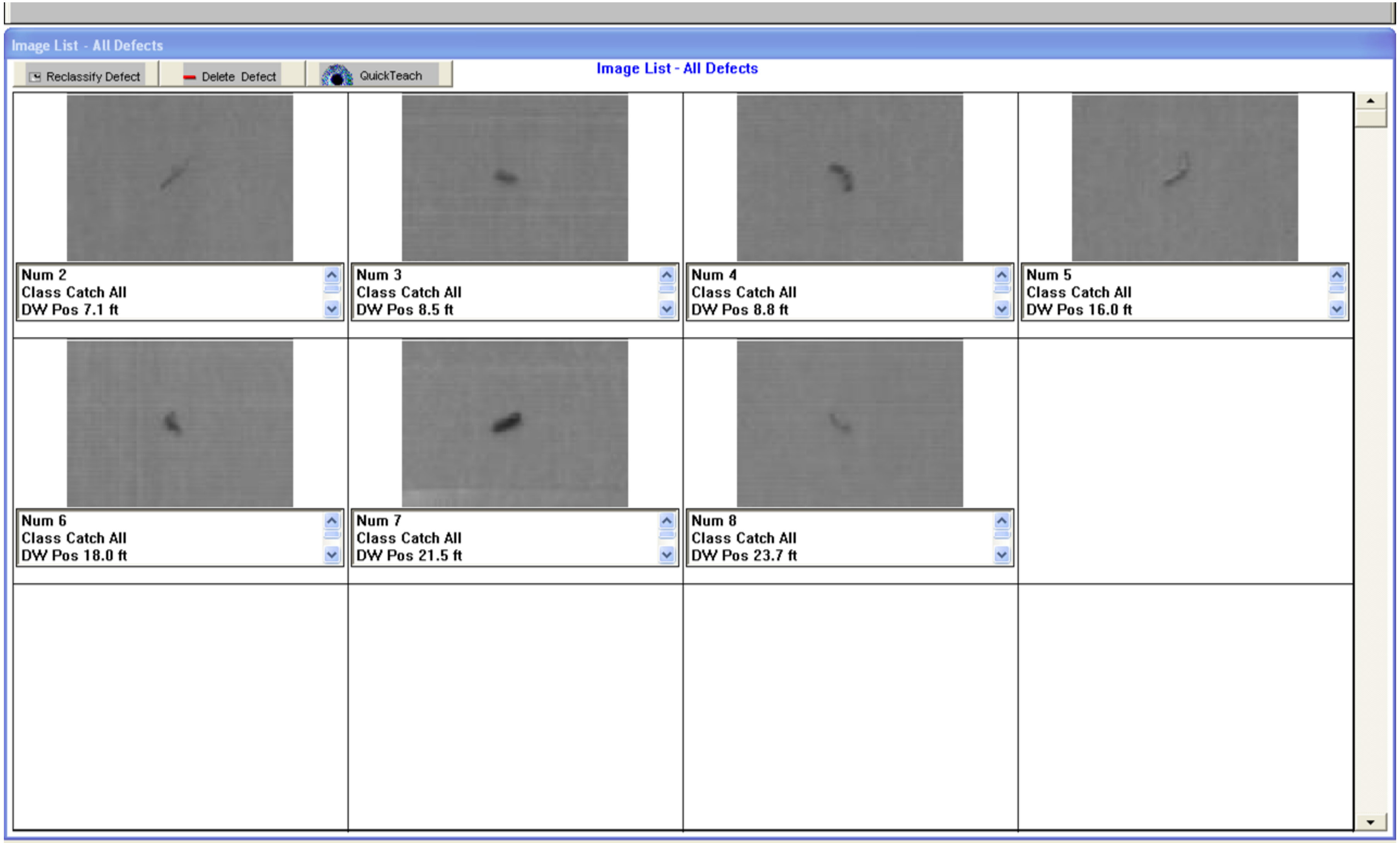
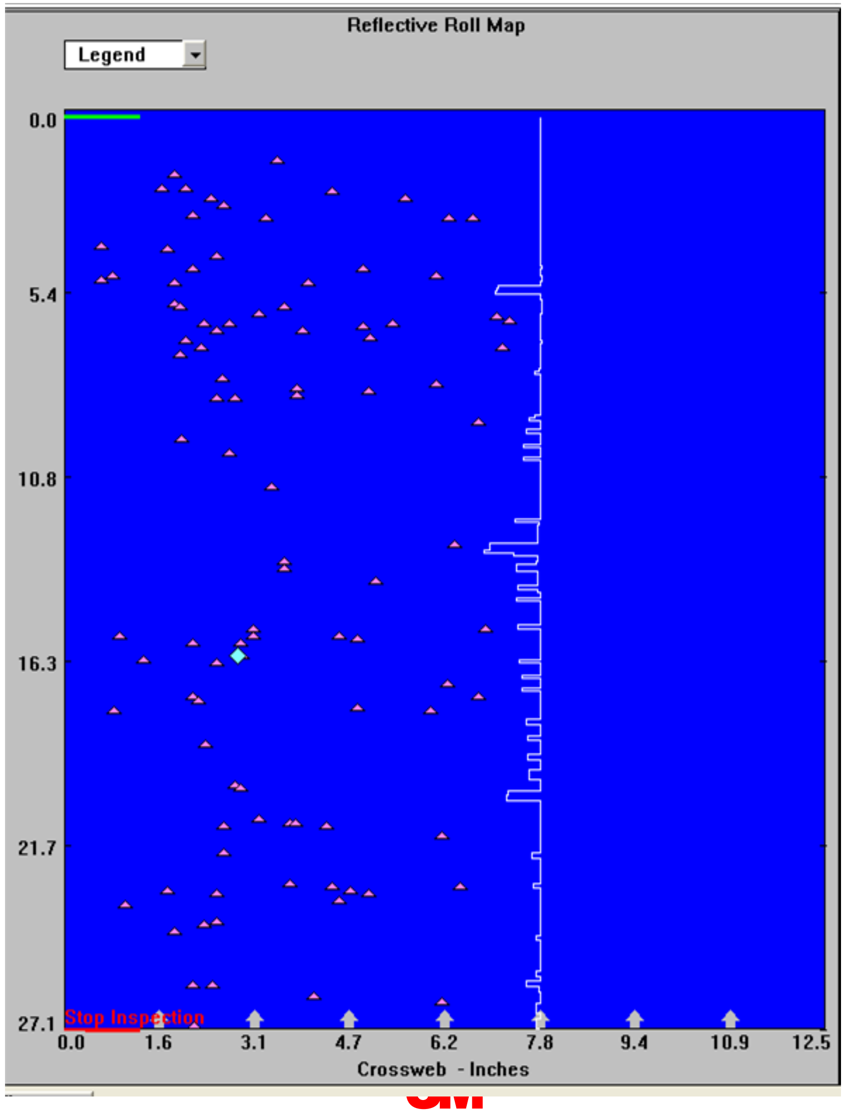
Typical Detection Images

Run 2 – Least sensitive settings



Run 3

Moderate sensitivity settings

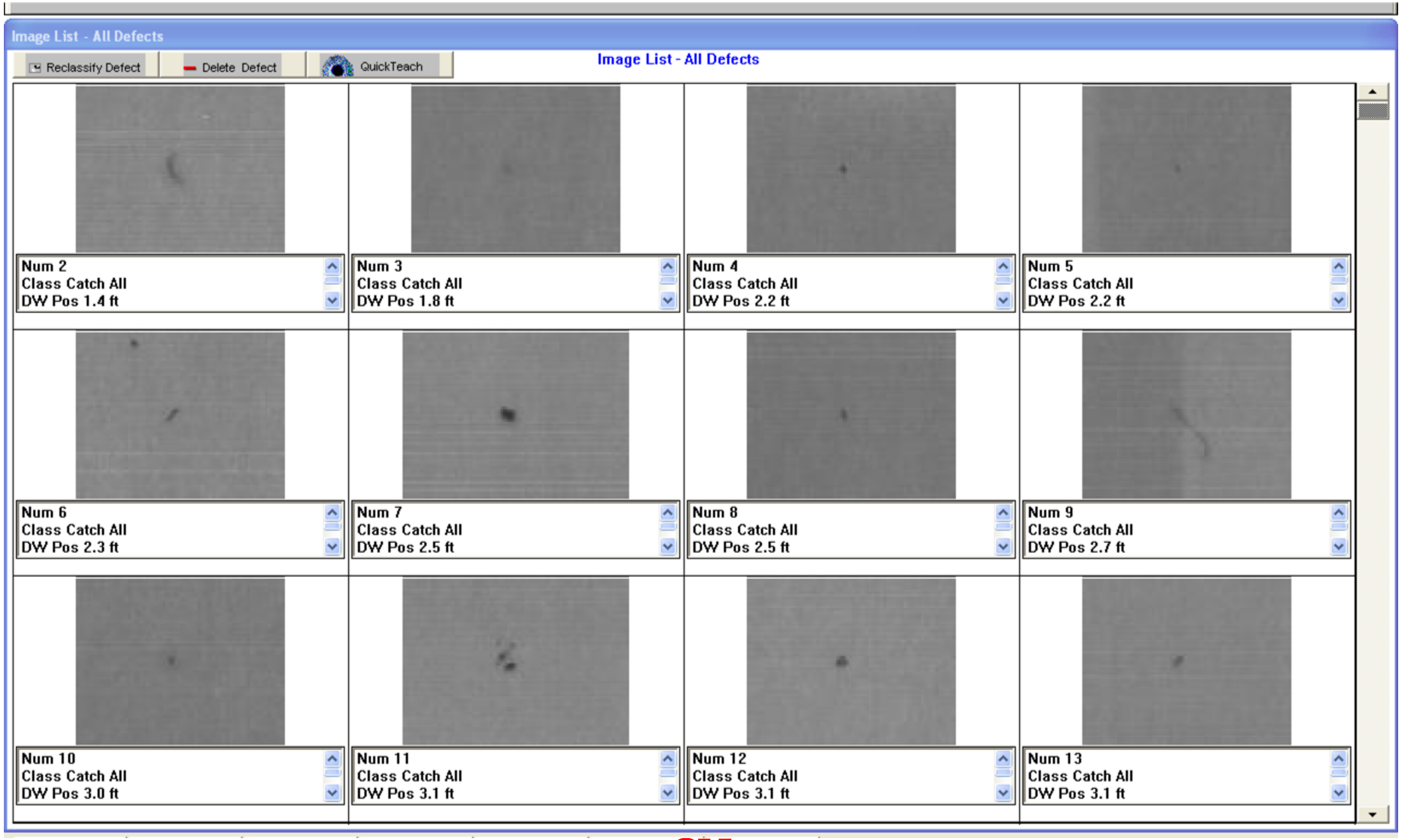


Run 3- Length and width criteria between Run 1 and Run 2

- 103 defects in 27.1ft

Typical Defect Images

Run 3 – Moderate sensitivity settings

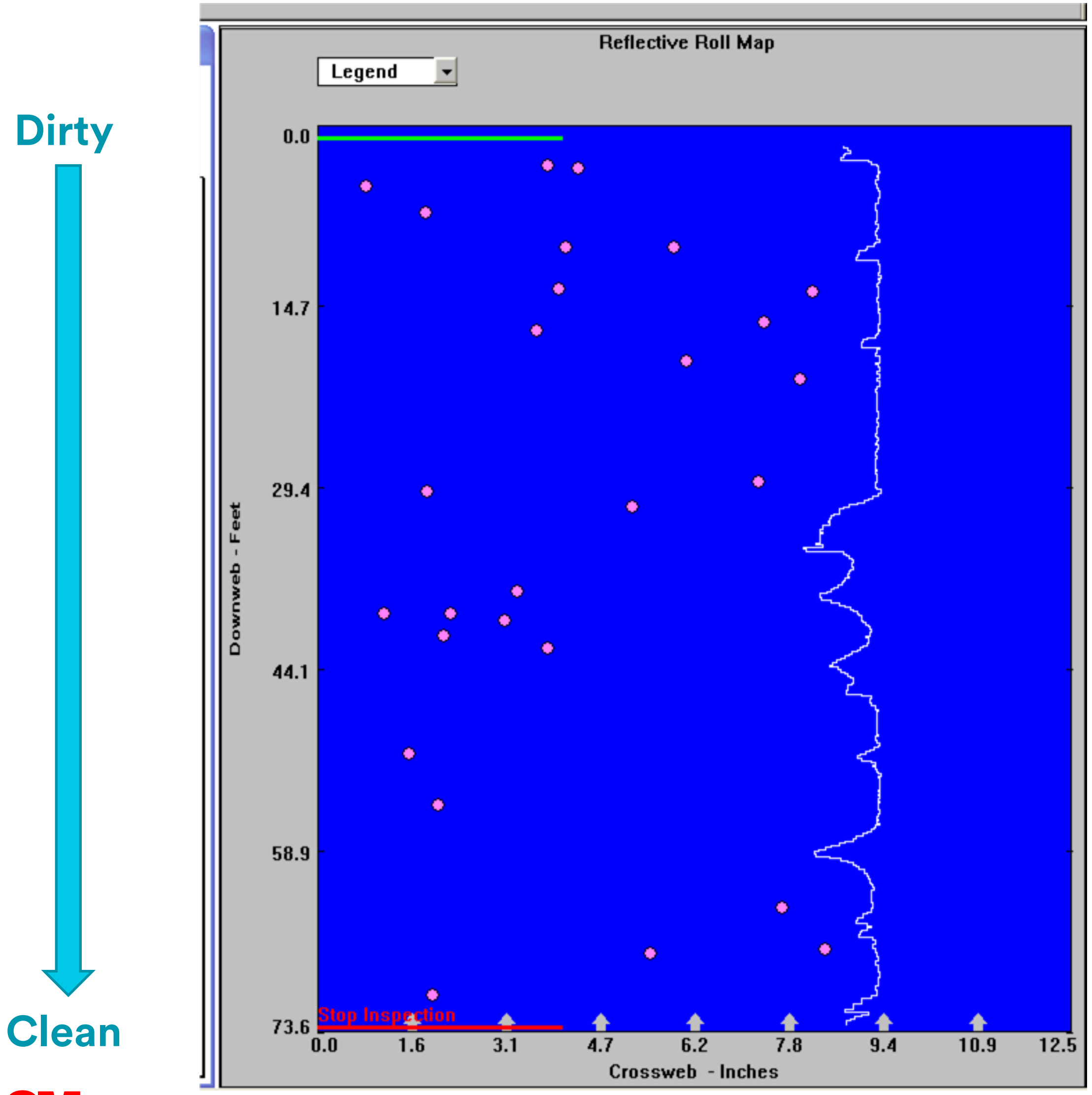


“Clean” *vs.* “Dirty” coating environment

75 foot Membrane Run (~25 minutes)

- Beginning of the run was under “Dirty” Conditions.
  - Operators in the area working, doors open, moving around.
- Throughout the run, cleanliness measures were put in place.
  - Coating enclosure closed
  - Operators left the area
  - Ion bar neutralizing peeled substrate, etc.

29 Defects Total
73 ft analyzed



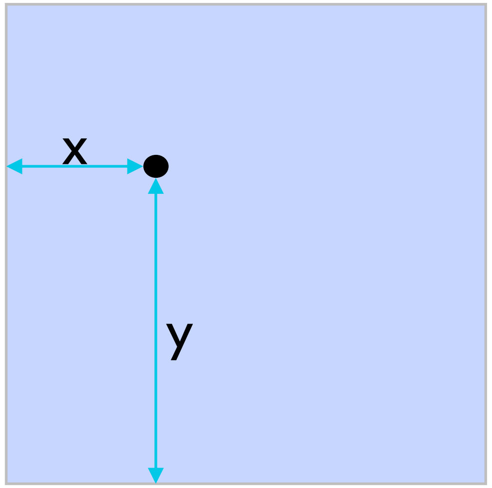
So, we see something, now what?

- Automated inspection equipment will find something
- “Generous” set points still yield one defect every 3 feet or less
- Rejecting all defects is functionally impossible

Test Plan

Accelerated Durability Testing followed by postmortem analysis

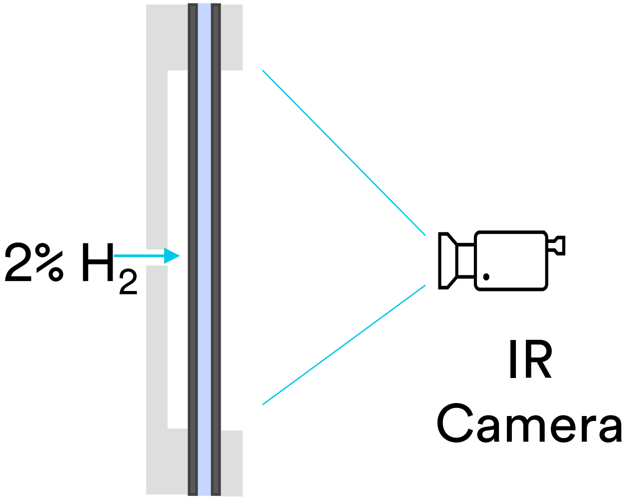
1) Locate know debris prior to fabricating CCM



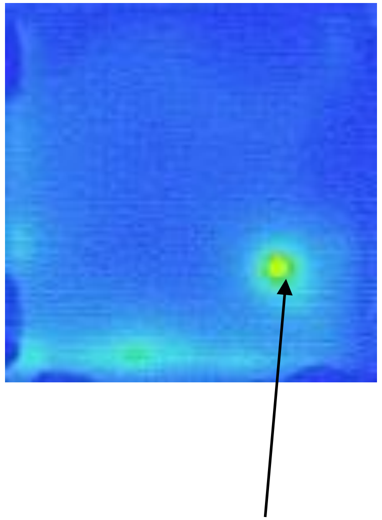
MEAs:
- Anode: 0.05 Pt/C
- Cathode: 0.25 PtCo/C
- Membrane: 14-micron 3M 800EW
  - nanofiber
  - peroxide scavenging additives

2) Run in accelerated (OCV) test

3) Identify Failure locations at EOL



Side view of CCM in fixture



Hot spot indicates breach in membrane

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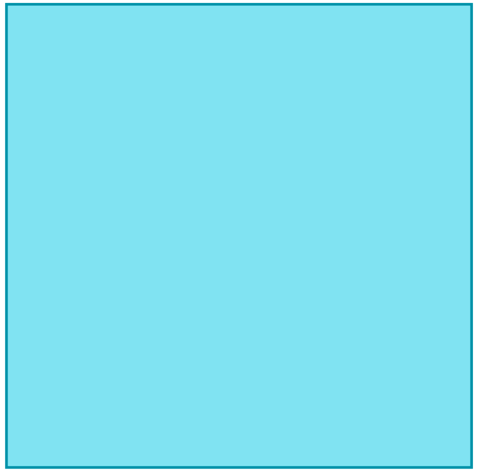
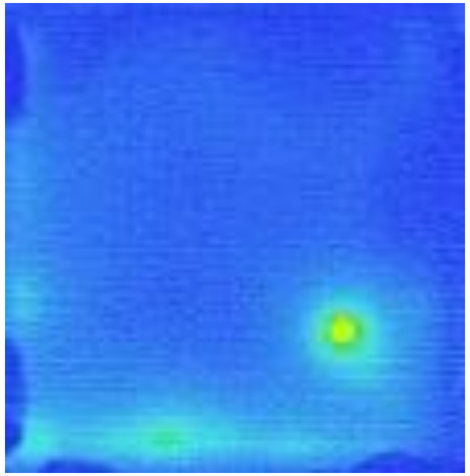
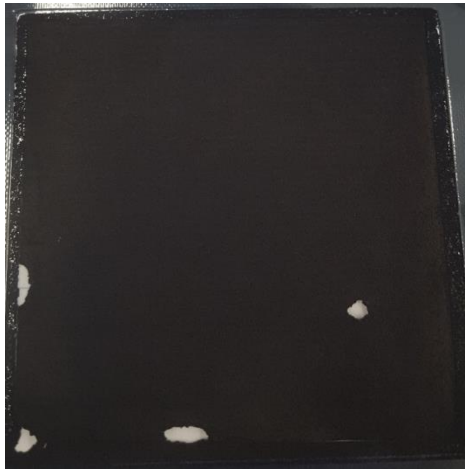
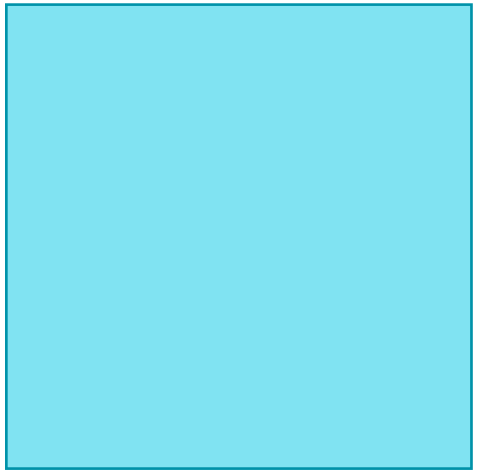
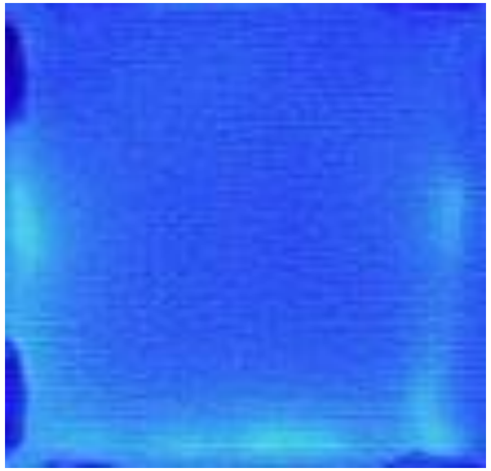
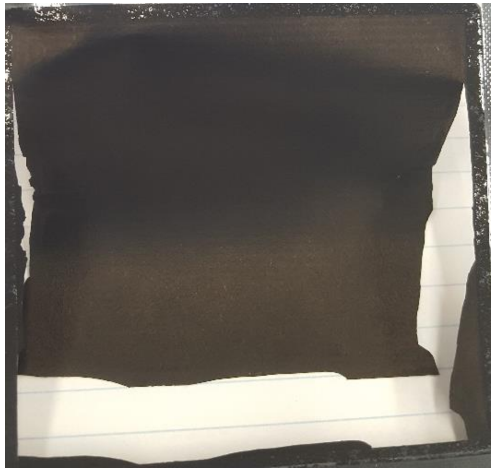
Postmortem – Control membranes

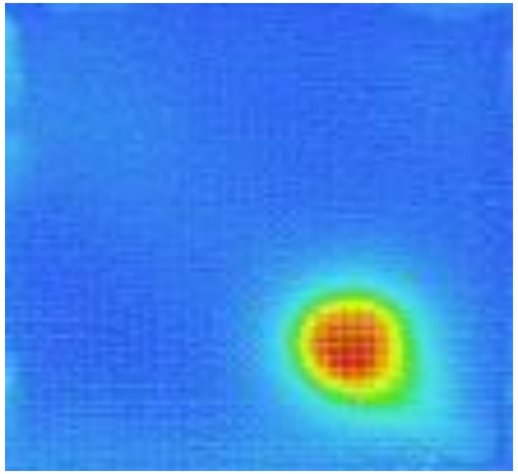
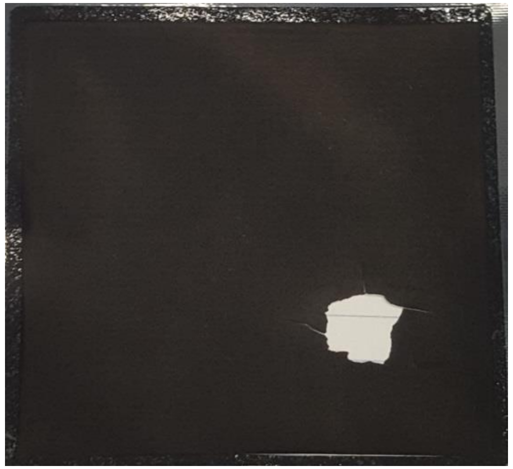
Defect Map | IR Image | GDLs removed

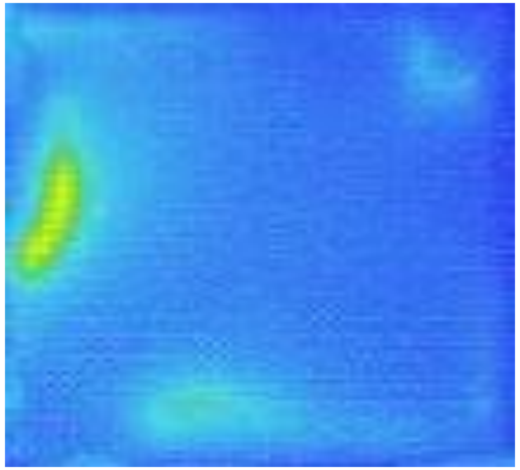
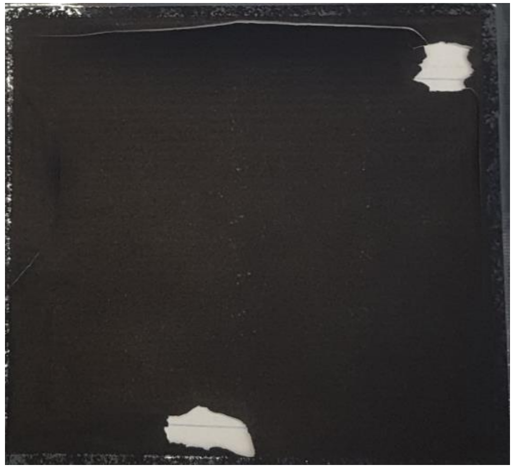
Control
FC029875
OCV lifetime =1634 h
FRR = 1.84 $\mu g/cm^2/day$

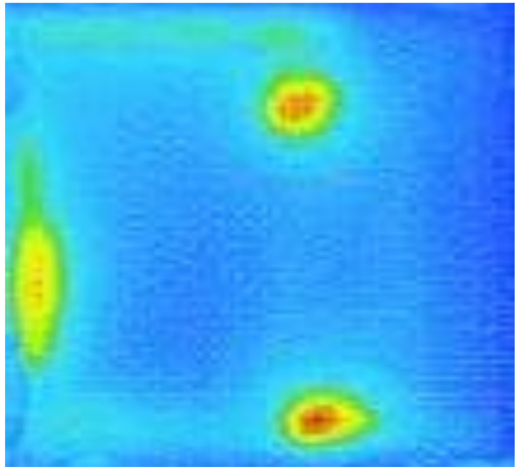
Control
FC029876
OCV lifetime =1403 h
FRR = 2.26 $\mu g/cm^2/day$

Control
FC029877
OCV lifetime =1303 hrs
FRR= 3.44 μmg/cm^2/day

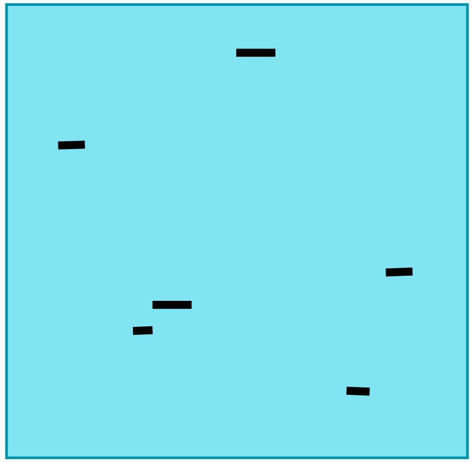
Control
FC029878
OCV lifetime =1192 hrs
FRR= 3.29 μmg/cm^2/day

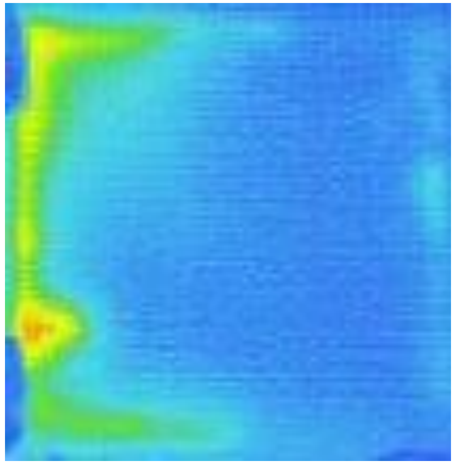


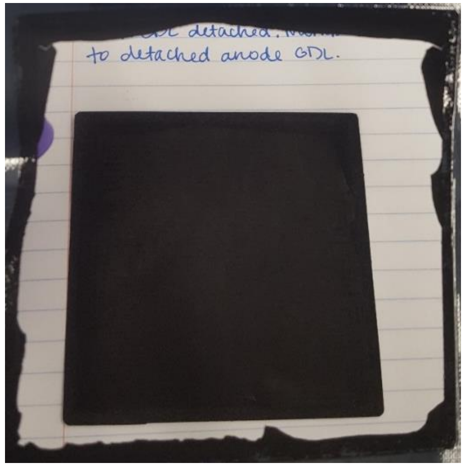

Control
FC029879
OCV lifetime =1482 hrs
FRR= 1.10 μmg/cm^2/day

Postmortem – Debris membranes

Defect Map | IR Image | GDLs removed

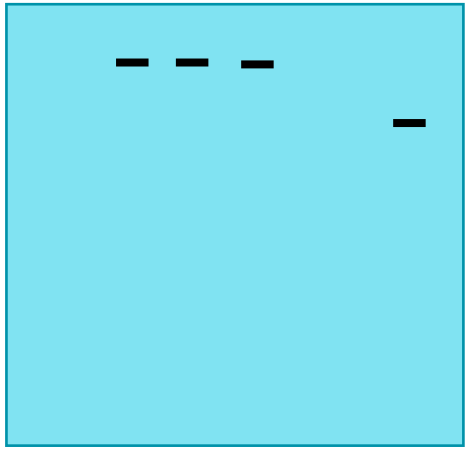


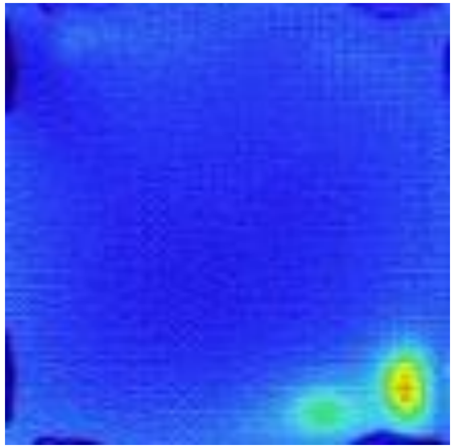




Membrane Defects
FC029163
OCV lifetime = 2336 hrs
FRR= 0.94 μmg/cm^2/day

No obvious relationship



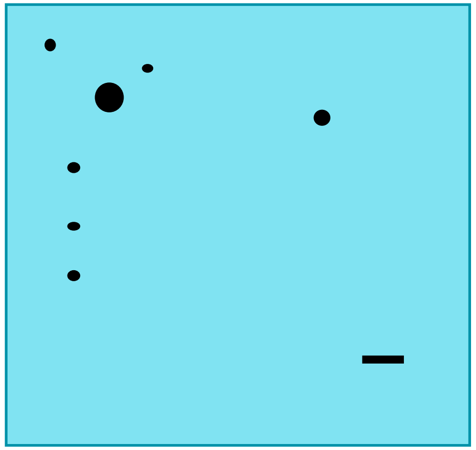


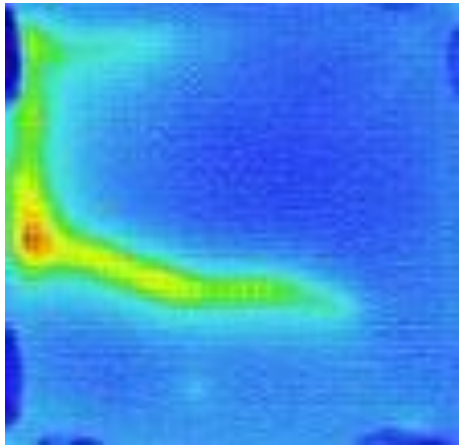
Membrane Defects
FC029165
OCV lifetime = 1062 hrs
FRR= n/a

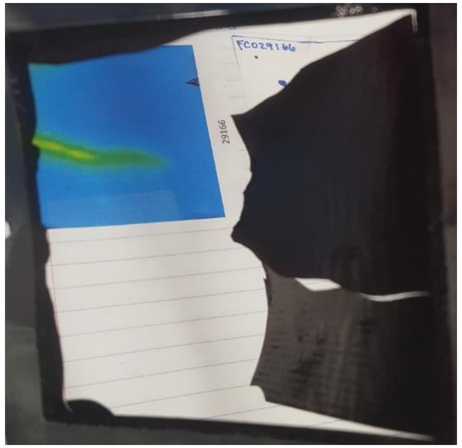
No obvious relationship

Postmortem – Debris membranes

Defect Map | IR Image | GDLs removed

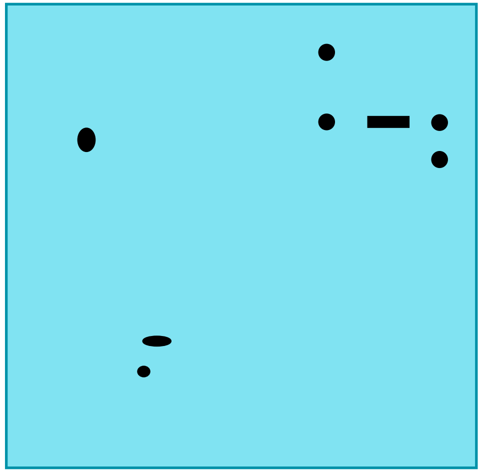


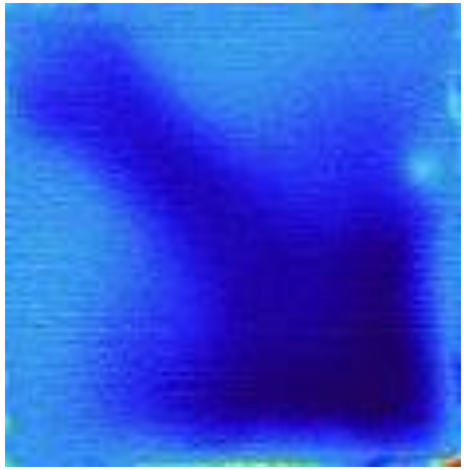




Membrane Defects
FC029166
OCV lifetime = 1467 hrs
FRR= 1.76 μmg/cm^2/day

Possible relationship with one debris location



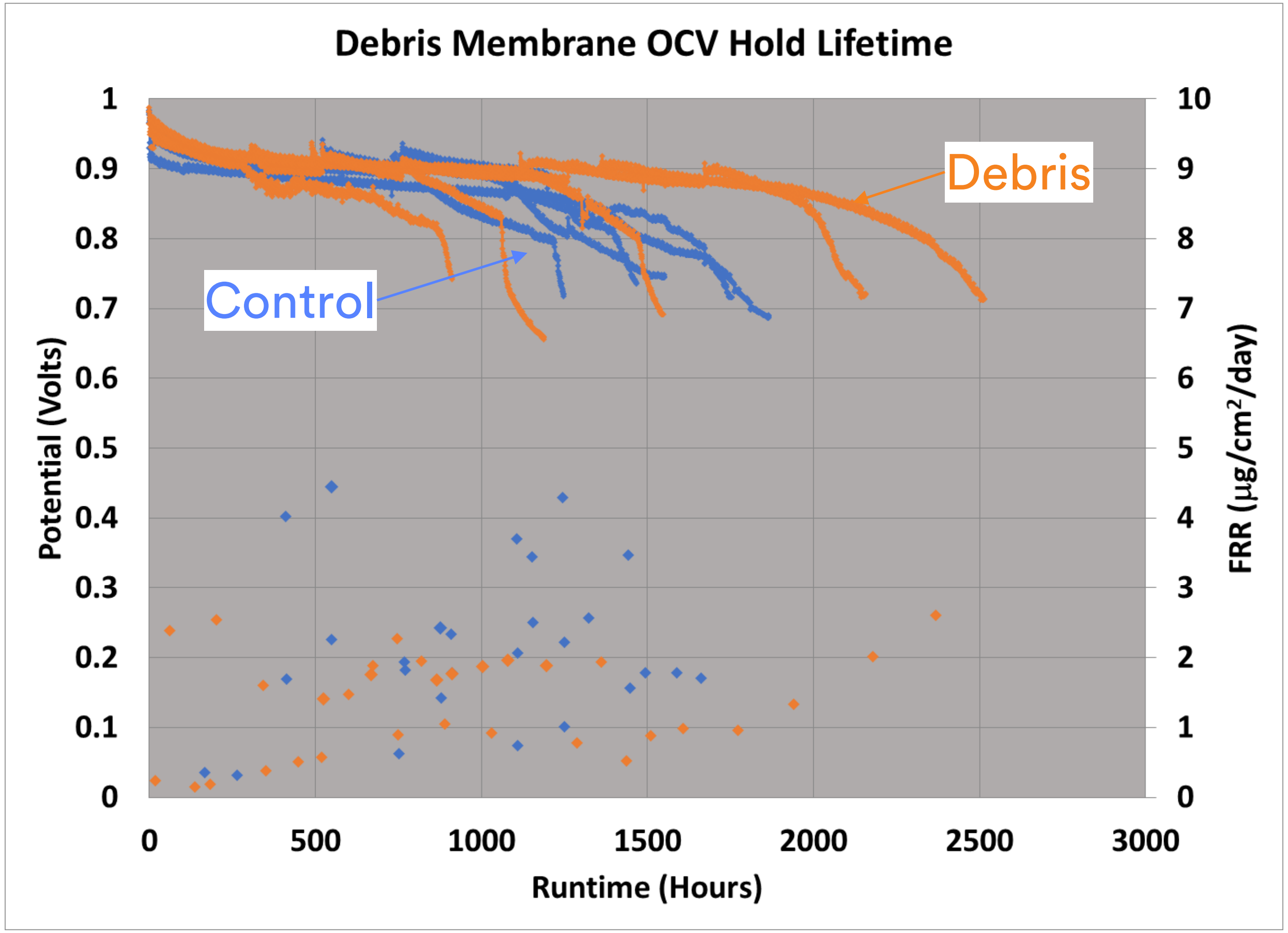


Membrane Defects
FC029167
OCV lifetime = 2044 hrs
FRR= n/a

Possible relationship with one debris location

Known debris OCV testing

All Cells

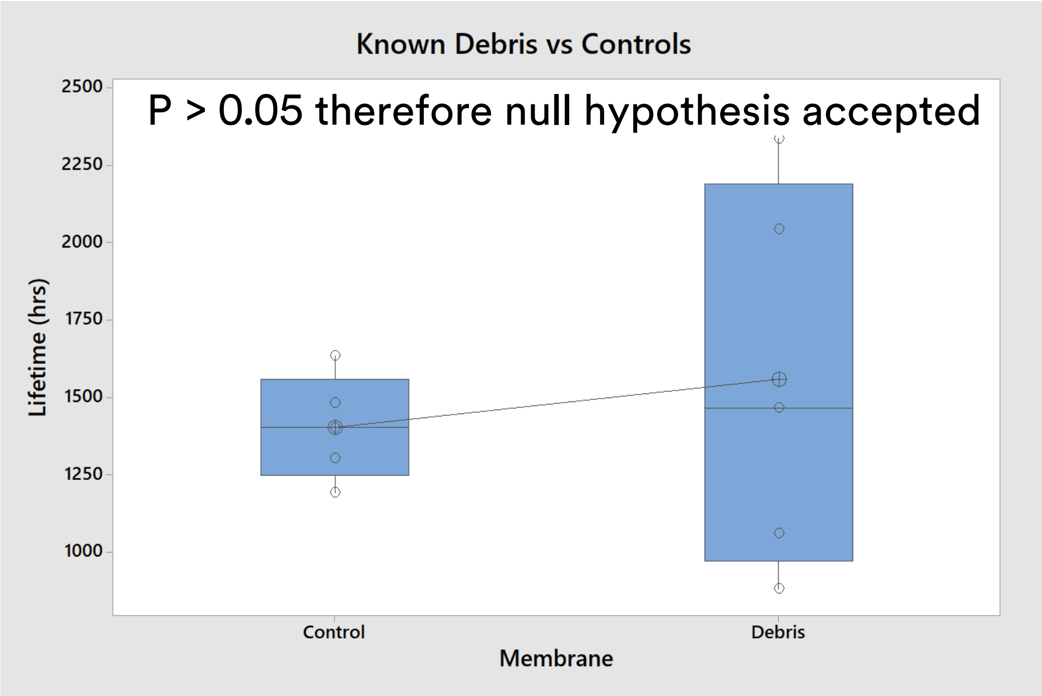


Known debris OCV testing

OCV Lifetime and Fluoride Release Rate (FRR) Two Sample T-Test

Null hypothesis $H_0: \mu_1 - \mu_2 = 0$
Alternative hypothesis $H_1: \mu_1 - \mu_2 \neq 0$

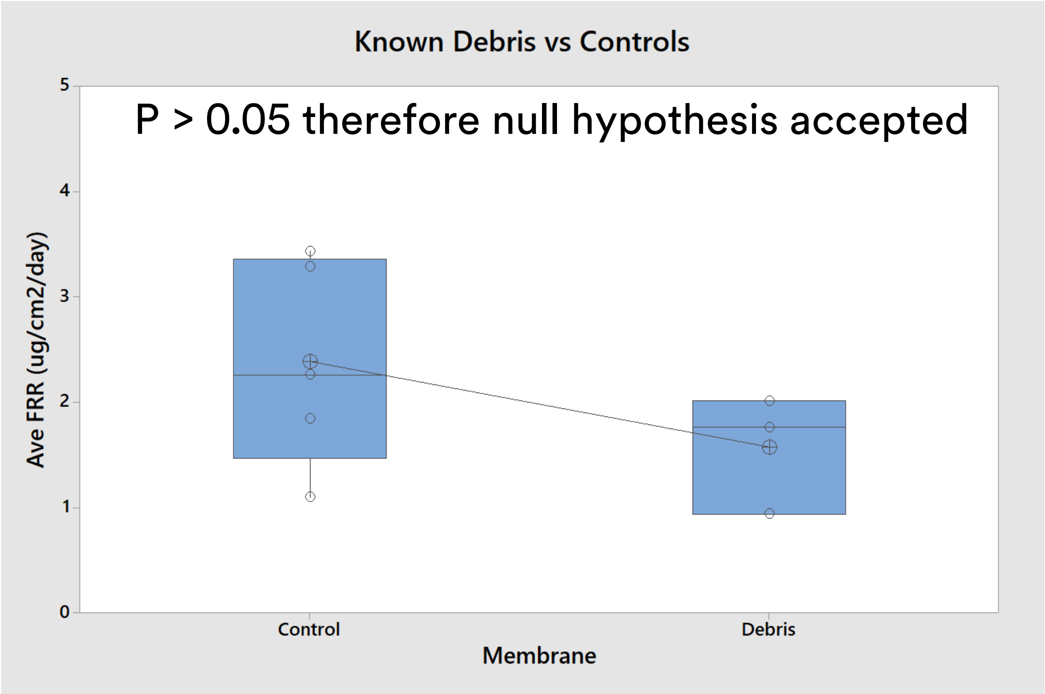
OCV Lifetimes



T-Value	DF	P-Value
-0.54	4	0.619

Null hypothesis $H_0: \mu_1 - \mu_2 = 0$
Alternative hypothesis $H_1: \mu_1 - \mu_2 \neq 0$

OCV F^- Release Rate



T-Value	DF	P-Value
1.48	5	0.198

3M

What we didn't talk about

- Electrode defects
- Casting liner will have scratches, debris, defects, etc.
- Support material (nanofiber or ePTFE) will have defects and irregularities.
- Repeating defects can often be traced to the circumference of a process roll.
- Camera placement (on angle, off angle, reflection, transmission)
- Line speed
- Data management
- Reject strategy (Mark? Skip? Defect per meter threshold?)
- 100% inspection *vs.* sampling plan
- Inspection location – (Membrane production or CCM or MEA converting)
- Operating conditions and the impact on failure mode.
- Electrolyzers and other applications

3M

What’s the Conclusion?

1. Inspection is hard. A super small pixel size is 20 um which is still 2X the membrane thickness.
2. If you look, you will see something.
3. Equipment parameters (off-angle or on-angle camera location, light angle, etc.) matter.
4. Data analysis parameters matter (threshold settings)
5. Liner, support, and membrane coating all bring their own optical features to the party.
6. “Zero defects” is irrational (see item 2 above).
7. At first glance, many defects appear to have no immediate effect in simple accelerated testing.
8. Accelerated durability testing may not provide the full answer.
9. Reducing debris (garment fibers, gels, etc.) should be done anyway.
10. ***Best way to manage all these issues for reliable, high volume manufacturing is not clear.***

What would Mike do with unlimited time and money?

1. Expand accelerated and non-accelerated testing with known or exaggerated defects.
   a) RH Cycle
   b) Soft shorts[1]
   c) Highly Accelerated Stress Test (HAST)[2,3] or other analysis of chemical and mechanical stressors[4]
2. Hire a statistician/quality engineer
3. Explore machine learning to analyze mountain of inspection and testing data.
4. Learn from experts in other fields that have wrestled with similar issues (optics, Si wafers, battery, etc.)
5. Get comfortable with the idea that most observations might be benign.

[1] Mittelsteadt and Liu, Handbook of Fuel Cells, Wiley, 15 December 2010
[2] Lai and Fry, *J. Power Sources* 274 (15) January 2015, 1162-1172
[3] Lai et. al. *J. .Electrochem. Soc.*, 165 (6) F3217-F3229 (2018)
[4] Singh et. al., *J. Electrochem. Soc.*, 164 (13) F1331-F1341 (2017)

Thank you