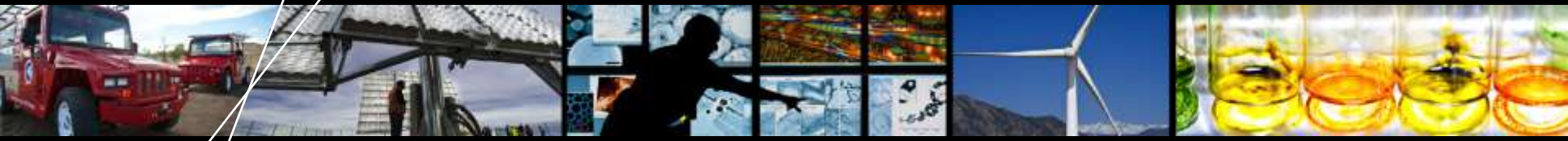
NREL
NATIONAL RENEWABLE ENERGY LABORATORY

NREL's e-Ca Test

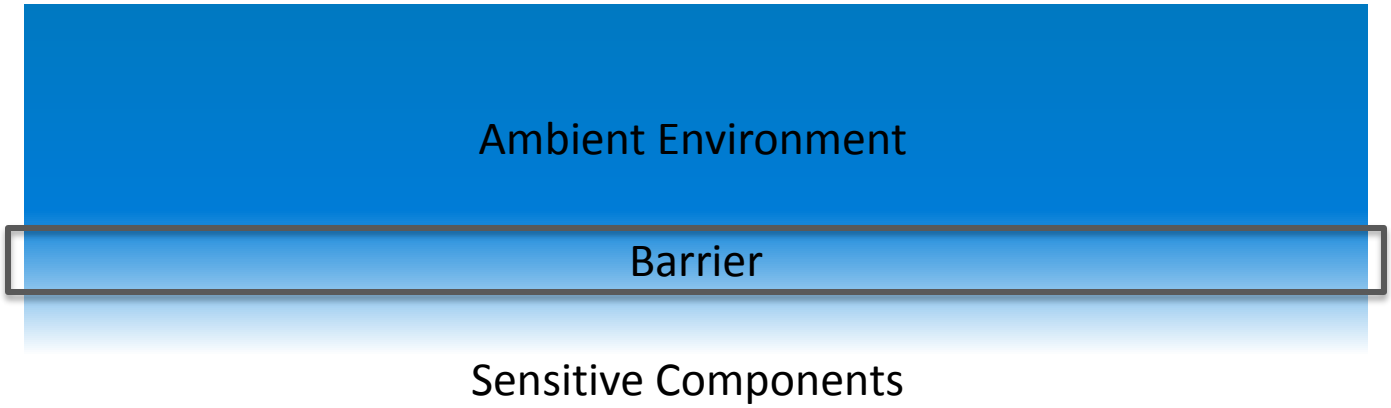


Barrier Technologies Workshop

Arrelaine A. Dameron

September 19, 2012

Characterization of Water Permeation Barriers



Vapor adsorbs and dissolves into barrier

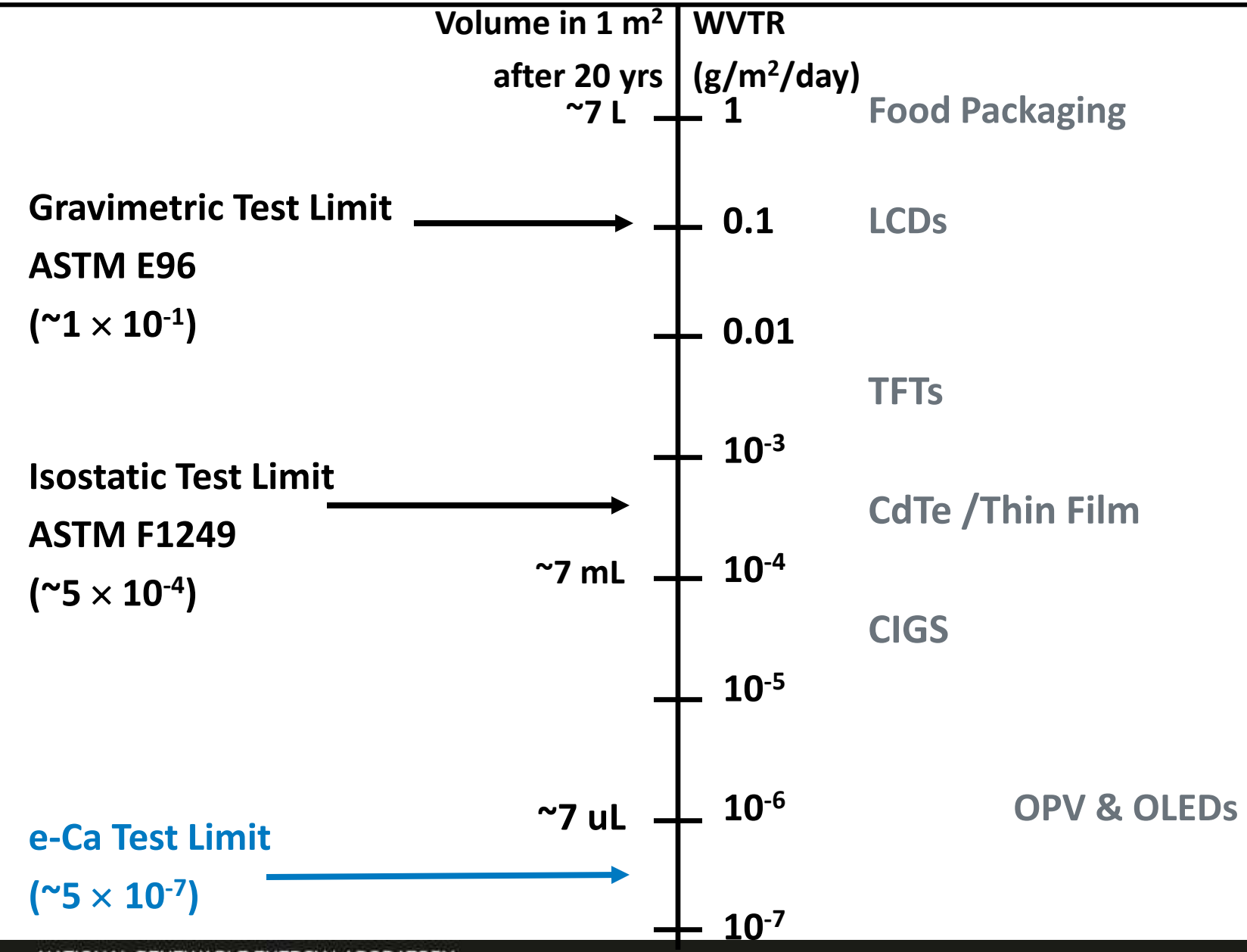
Vapor diffuses

Vapor desorbs/outgasses

Desire a characterization method that is:

- Reproducible
- Highly sensitive
- Easy to use
- Scalable

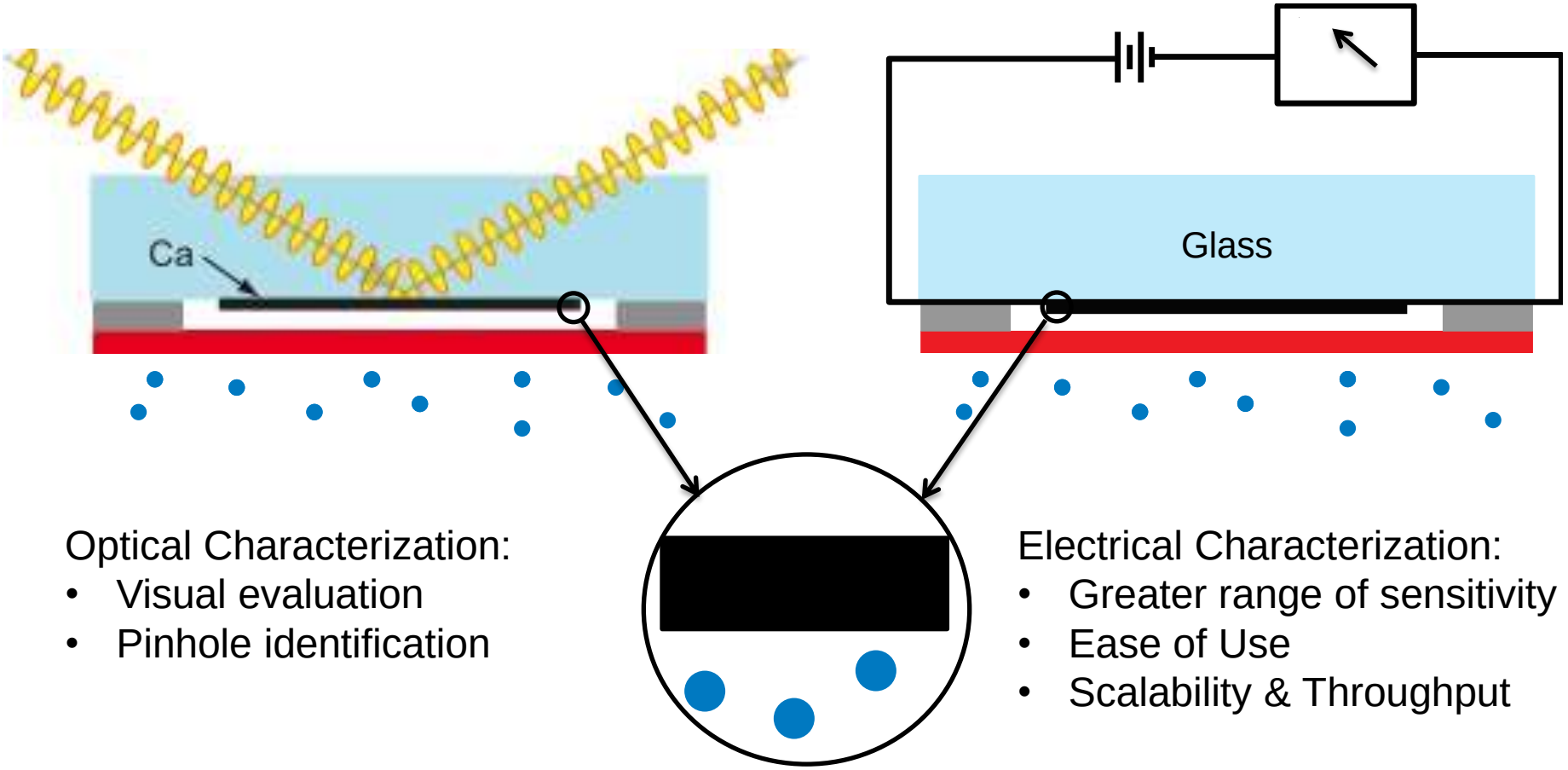
Application Specific Tolerable Water Permeation



Ca Test Basics

$Ca + 2H_2O \rightarrow Ca(OH)_2 + H_2$

Opaque and Conductive → Transparent and Insulating



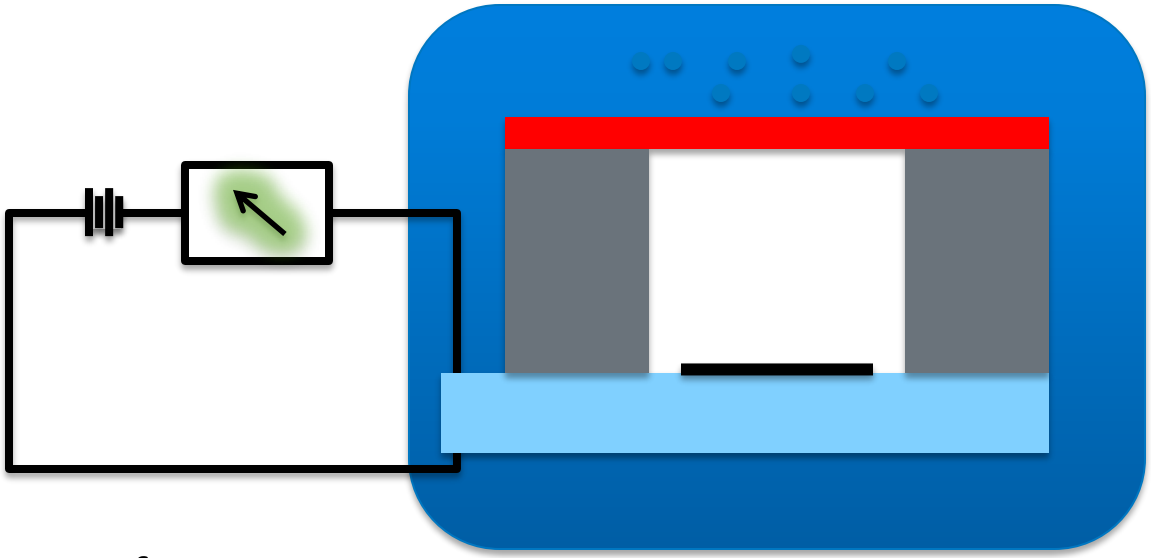
Optical Characterization:
- Visual evaluation
- Pinhole identification

Electrical Characterization:
- Greater range of sensitivity
- Ease of Use
- Scalability & Throughput

G.Nisato *et al.*, *Proceedings Asia Display/IDW* pp. 1435, 2001.

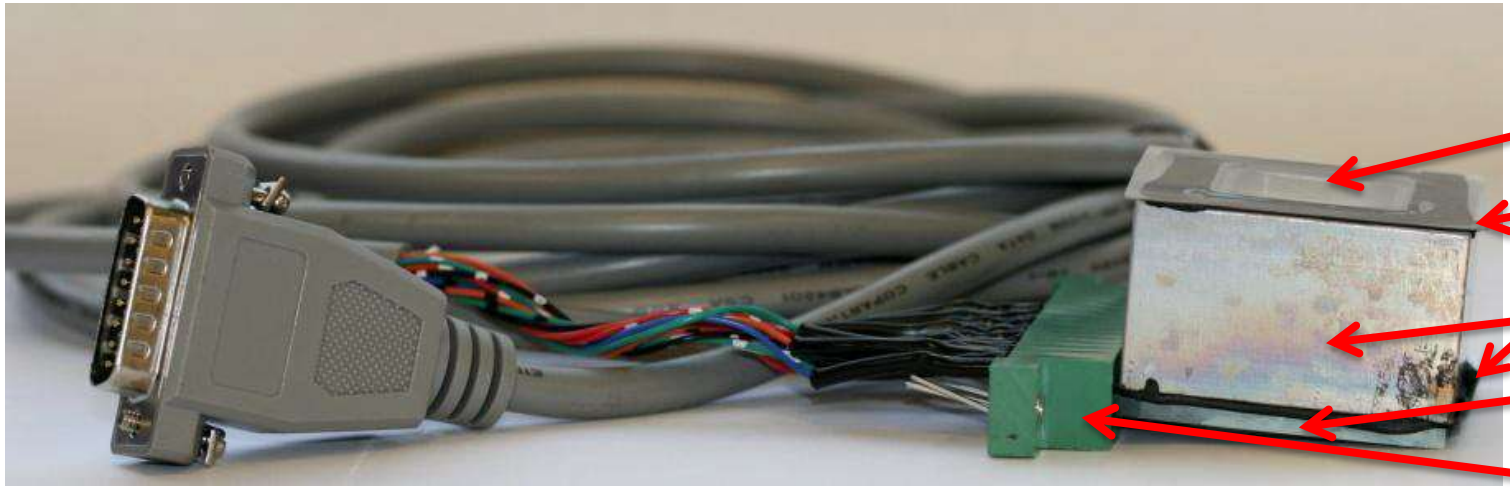
R. Paetzold *et al.*, *Review of Scientific Instruments*, vol. 74, pp. 5147, 2003.

NREL's e-Ca Test

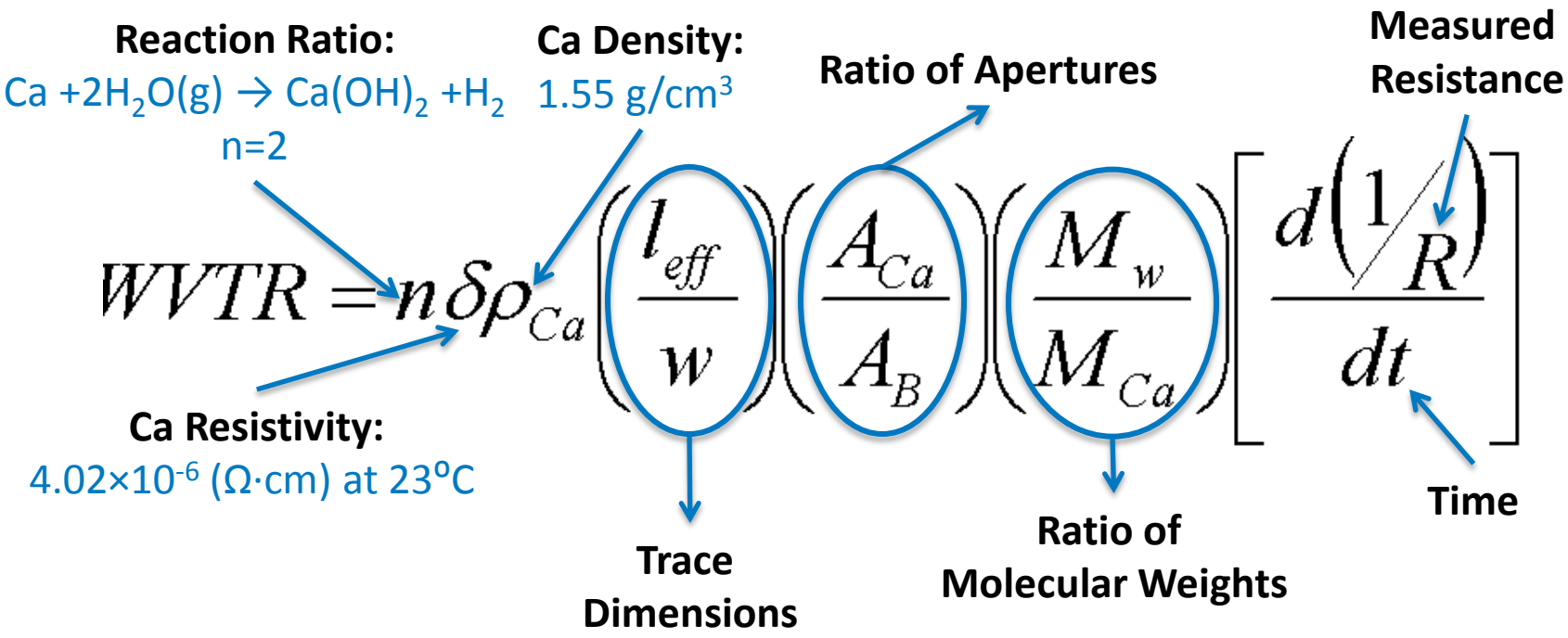


$$Ca + 2H_2O(g) \rightarrow Ca(OH)_2 + H_2$$

Ca transforms from opaque, conductive metal to transparent, resistive oxide upon exposure to water



WVTR Equation



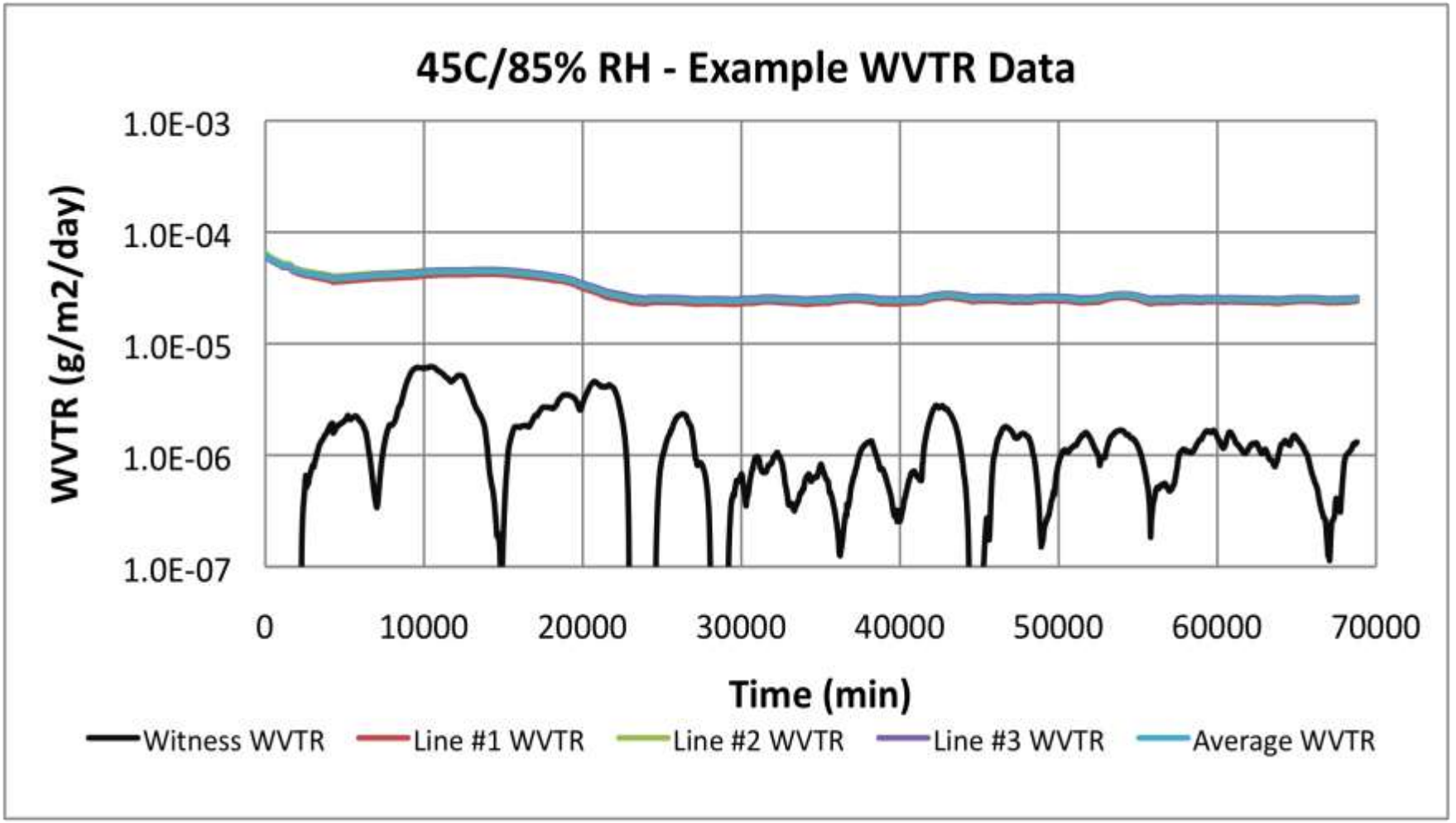
$$R_0 = \frac{R}{1 + a\left(T - T_o\right)}$$

We measure the resistance with respect to time to calculate the WVTR.

Samples on test

Measured e-Ca Test Data

Actual measured data from a barrier film provided by a commercial partner shows steady state permeation at ~3 ⍰ 10^{-5} g/m^2/day.



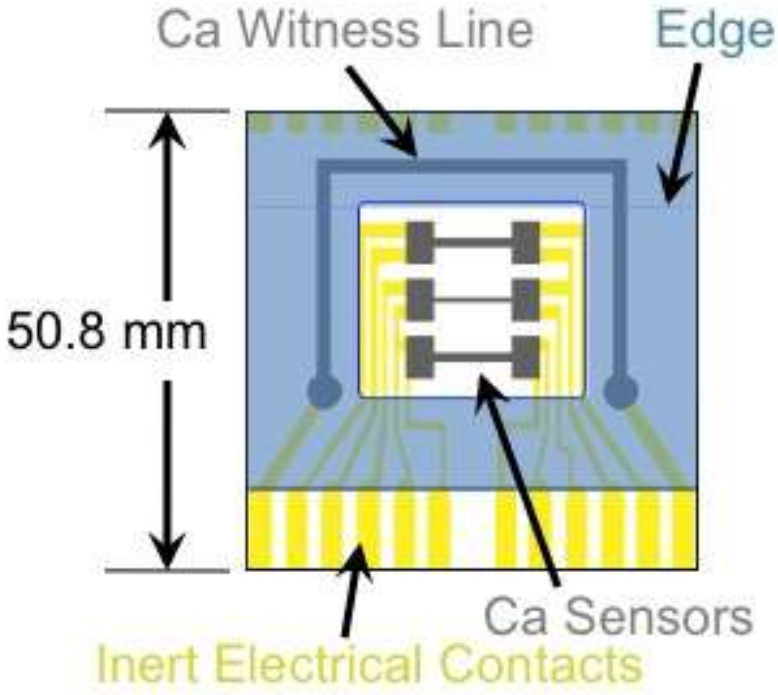
This data is well above the sensitivity limits of NREL's e-Ca test.

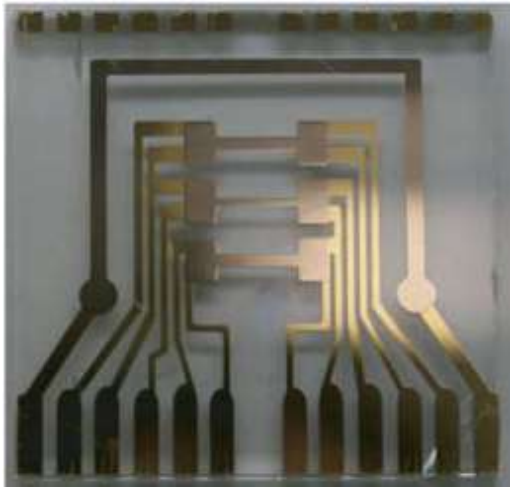
Ca Test Components

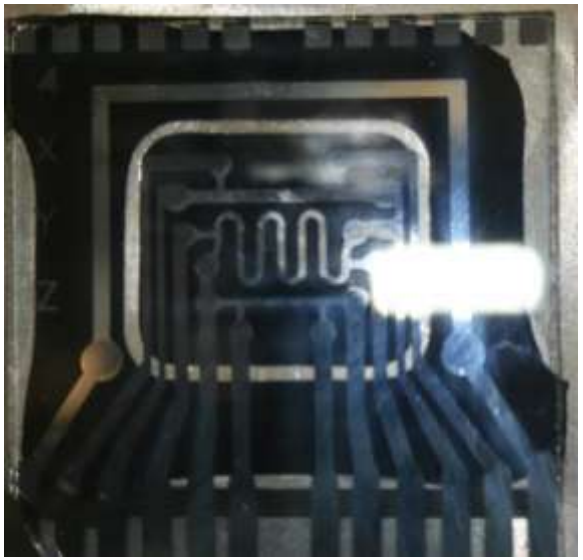
- **Computer for Data collection**
  - Custom software
    - Data collection, averaging and calculations, and WVTR display
- **Commercial digital multimeter**
  - 6.5 digit accuracy => ±0.1 mΩ
- **Multiplexing Distribution Hardware**
  - Combination of commercially available and custom assembled instrumentation
  - Current configuration can measure up to 128 samples
- **Ca Test Assembly**
  - Cables between electronics and Ca assembly
  - Commercial edgecard connector for easy/fast connect/disconnect
  - ***Custom Test Card with Ca and Au traces***
    - Evaporated contacts using shadow mask onto glass substrate
  - Commercial edgeseal
  - ***Custom diffusion spacer element***
    - Machined aluminum block
  - Barrier Film

Test Card

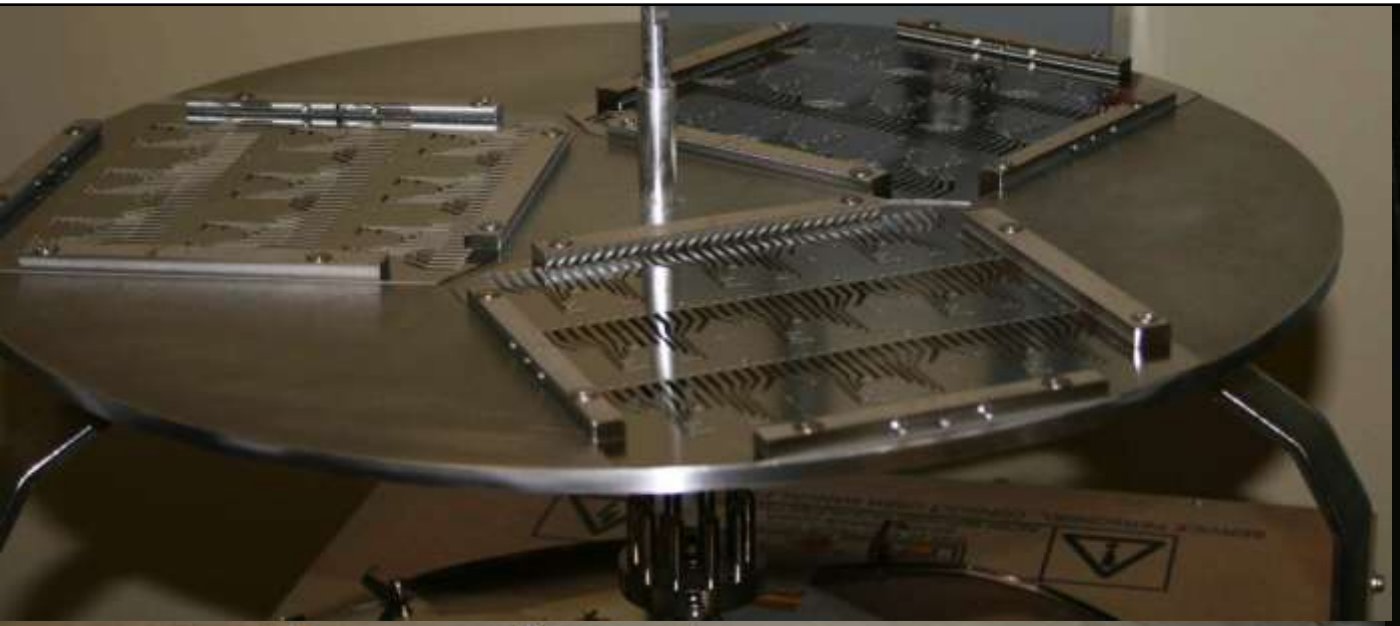
- Ca Traces are fabricated separate from the barrier film
- 3 redundant 4-pt measurements of Ca resistance as a function of time
- Witness line monitors edgeseal integrity and provides internal standard of sensitivity limits
- Inert contacts pass signal to the outside of the assembly and fit into standard edgecard connector

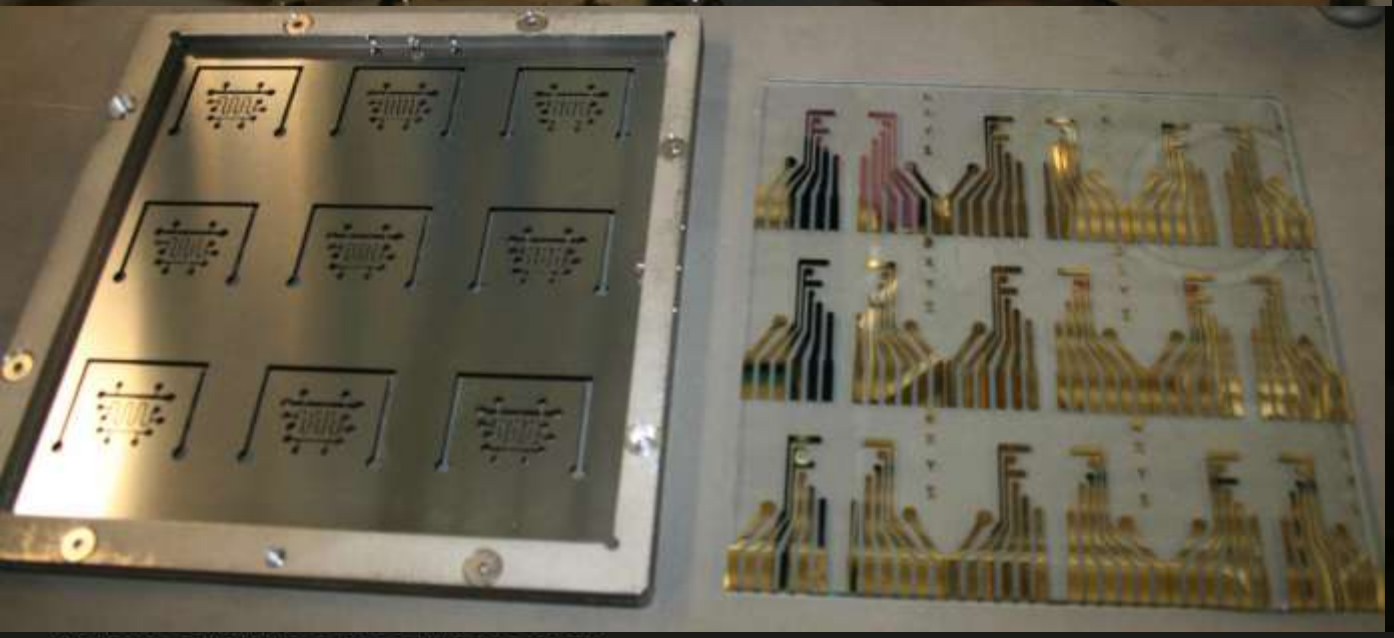


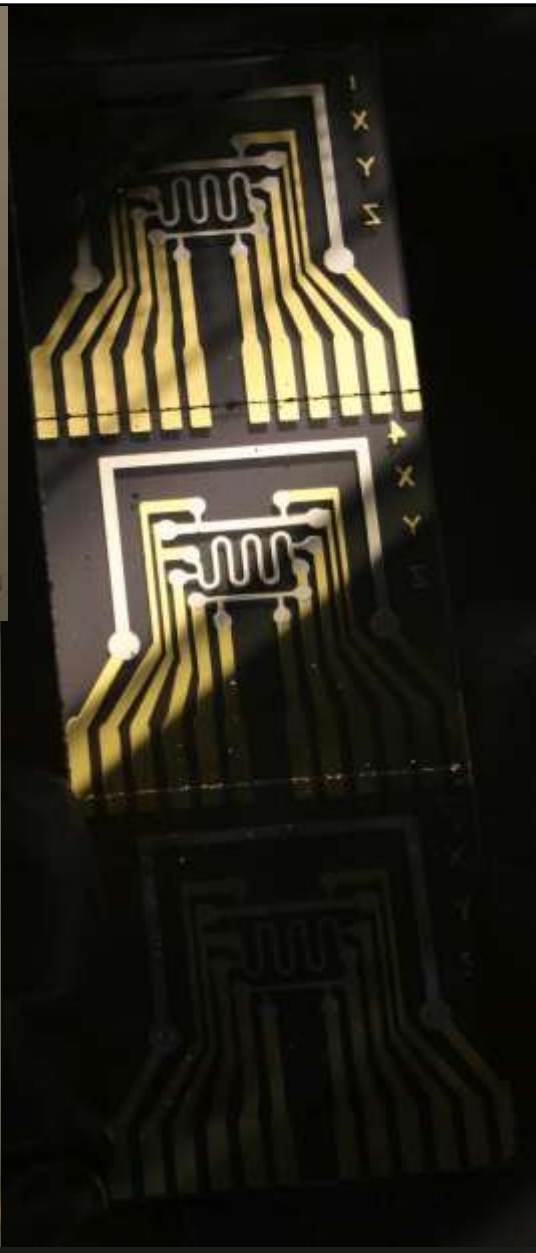




Test Card Fabrication







Test card stability and packaging

- Test cards can be produced in bulk (and stored in inert environment) prior to obtaining barriers to be tested
- Storage in ambient conditions for 2 months using simple packaging methods resulted in <1% change (worst).

Equivalent to <1Å/day or WVTR of ~10^{-9}g/m^2/day

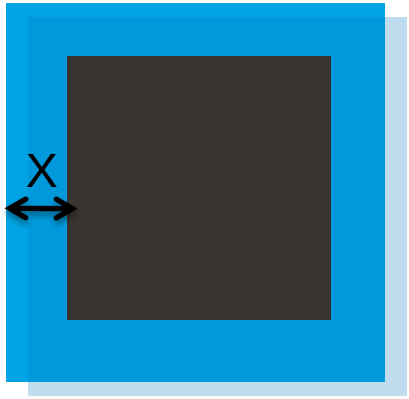
We even shipped them to Japan!

Edge Seal Evaluation

Using the Optical Ca Test concept as an effective means of evaluating edge seal materials similar to applied environment

Glass
100nm Ca
Edge Seal
Glass

$$X = K\sqrt{t}$$

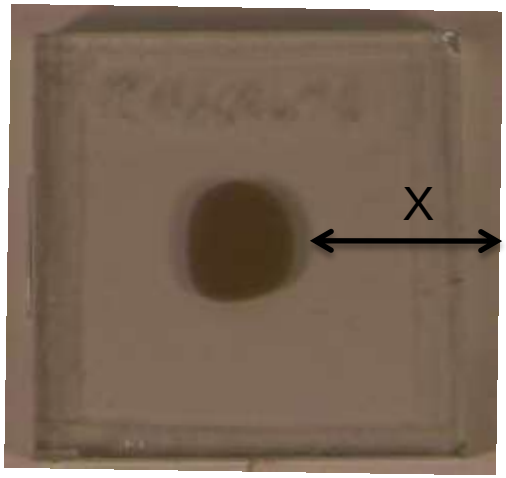


Ca turns transparent appearing to shrink toward center

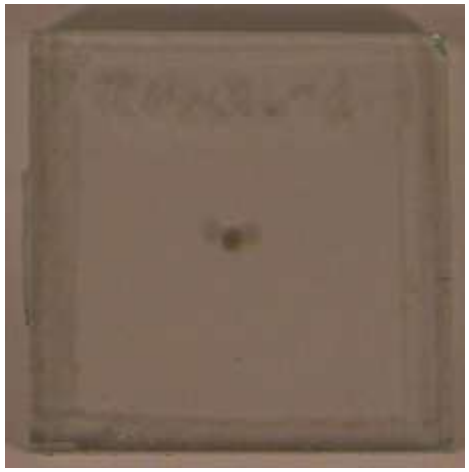
PDMS

85C/
85 %RH

0 h

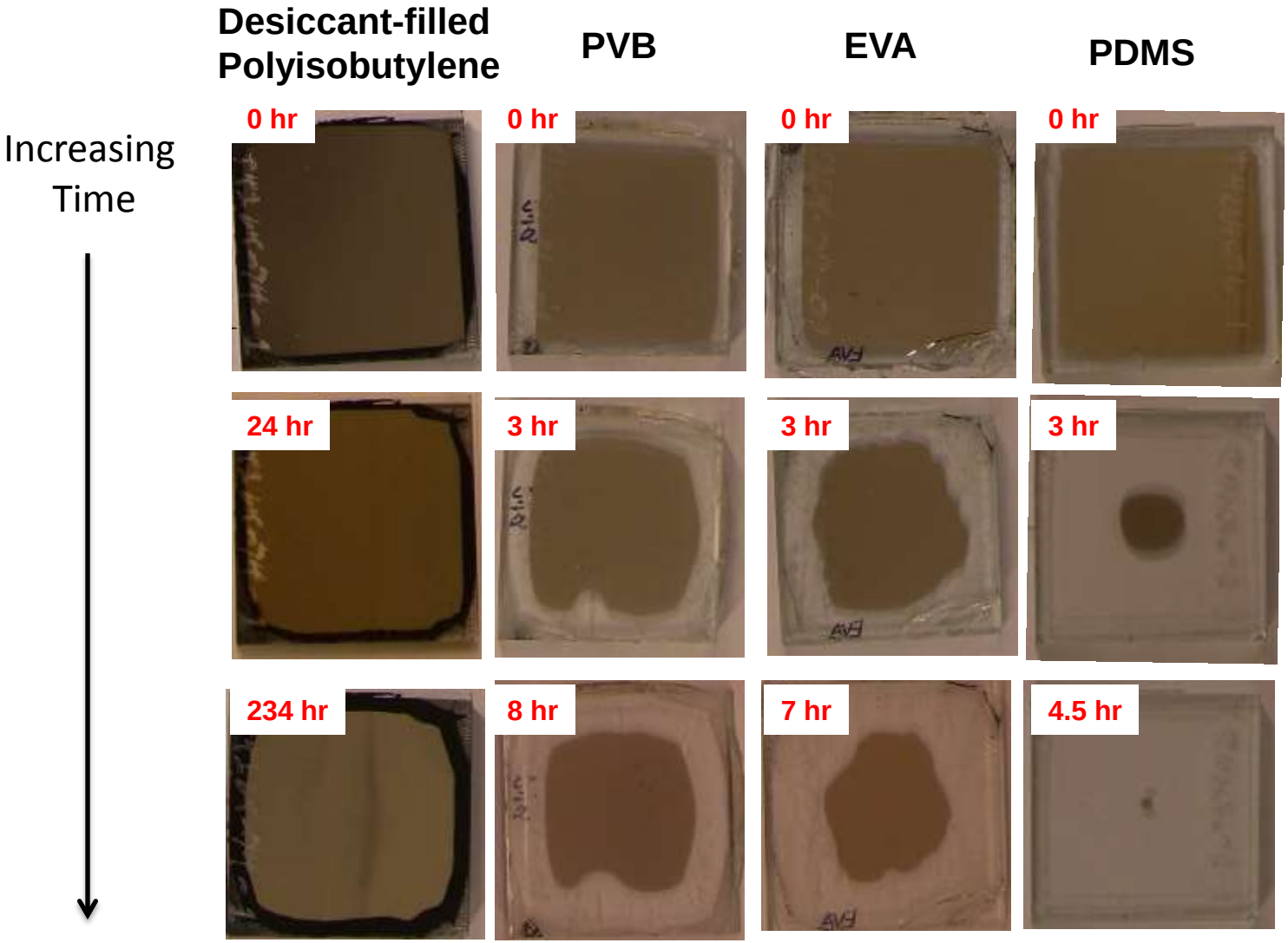


3 h



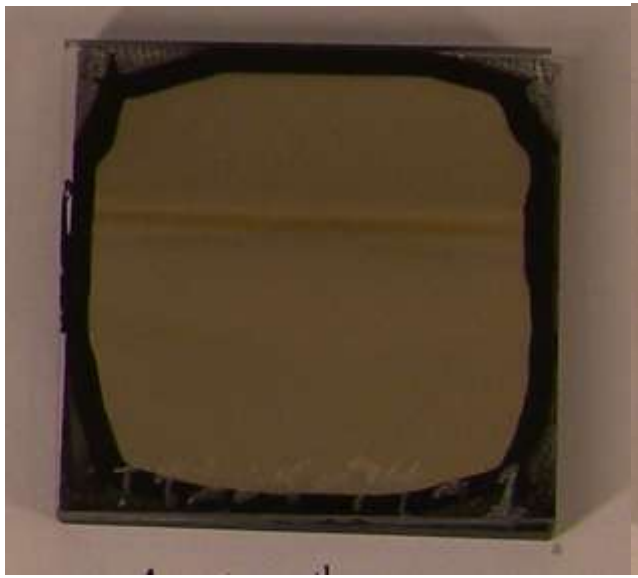
4.5 h

Typical Edgeseal Results



We tested for hundreds of hours….

Desiccant Filled PIB Edgeseal



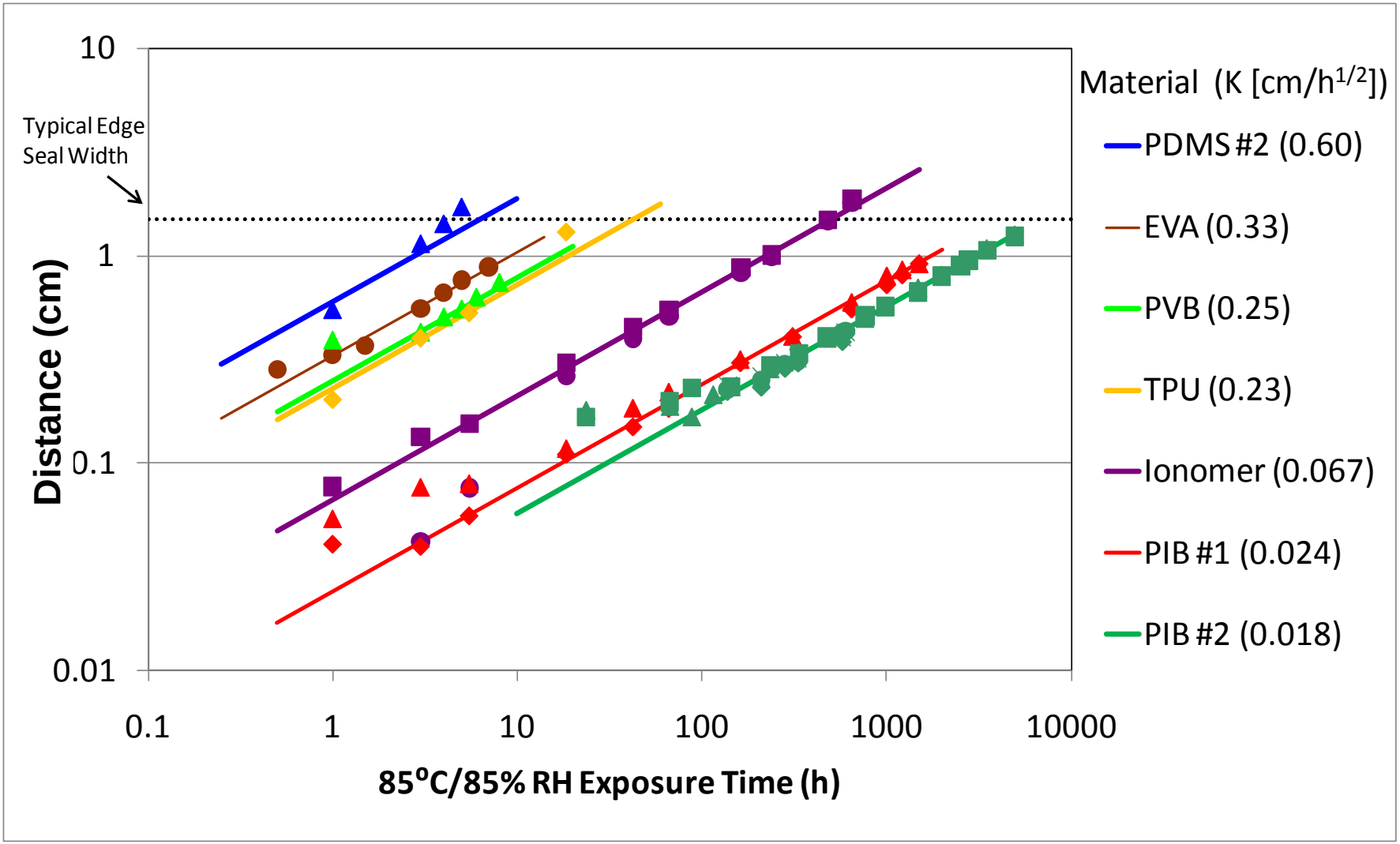
115 h

1488 h

3509 h

We tested for thousands of hours….

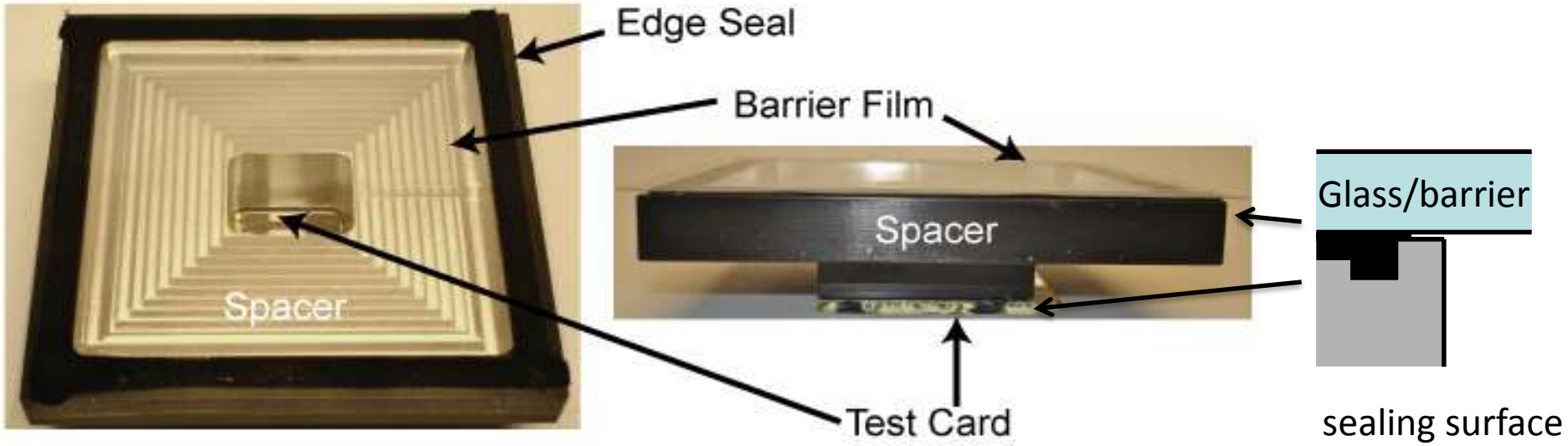
Relative Comparison of Materials



Finally we picked one!

PIB#2 material performed the best and was the easiest to use for this application.

The ‘Spacer’



The spacer element is a non-absorbing mechanically fabricated cavity with apertures on the barrier side and on the test card side and sealing surfaces between the spacer to barrier film and spacer to the test card.

The spacer provides a means to assemble the test quickly with a mechanical press.

Addition of the spacer provides several advantages...

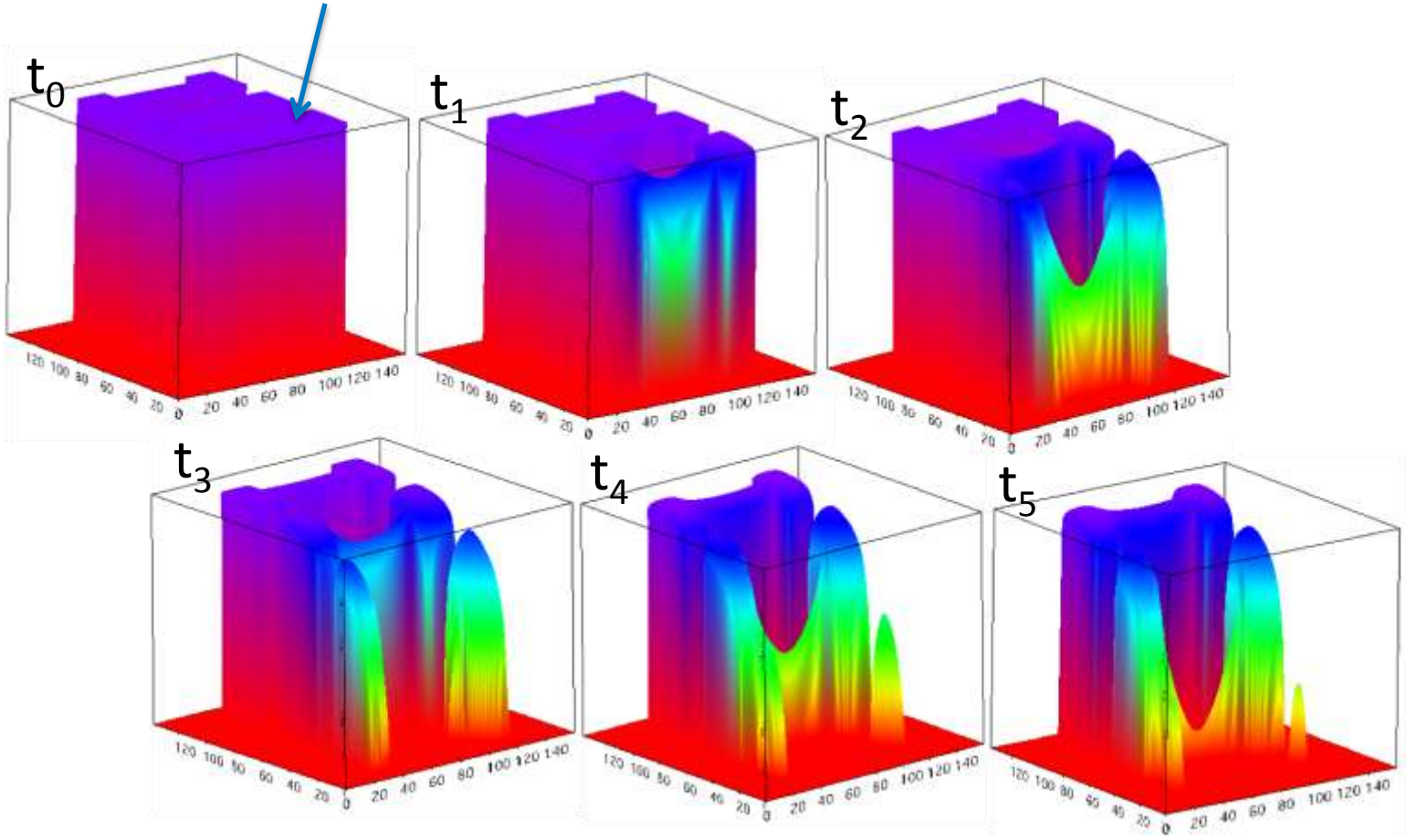
Spacer Advantage #1: Aperture Ratioing

The ratio of apertures controls the sensitivity range by adjusting the barrier area relative to the Ca area

- Some ratios (barrier area : Ca area) that we can use presently are 9:1, 30:1, 60:1, 700:1

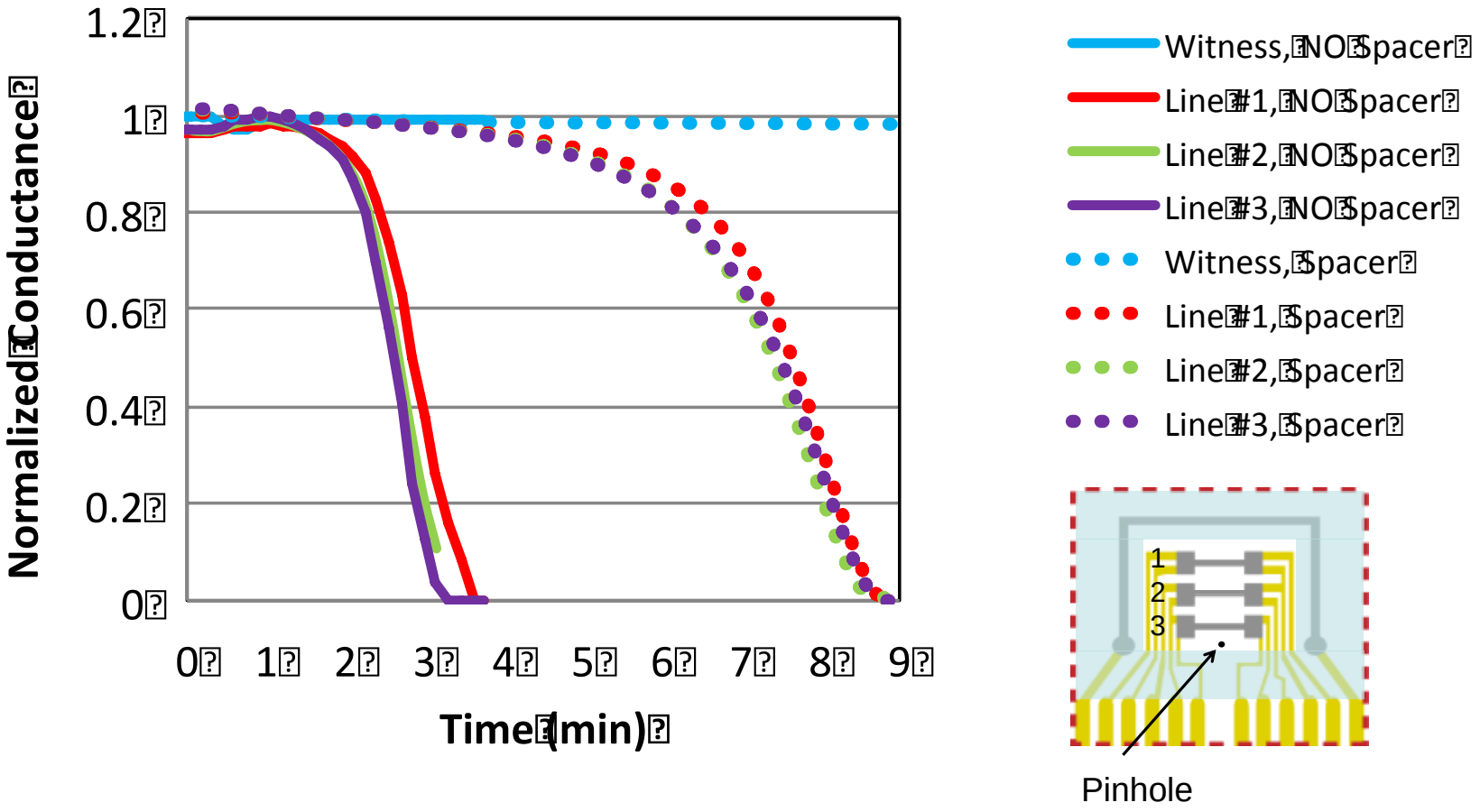
Advantage #2: Diffusion compensation

- **Worst Case Scenario:** **Ca traces are deposited onto the barrier but the barrier has a pinhole defect:**



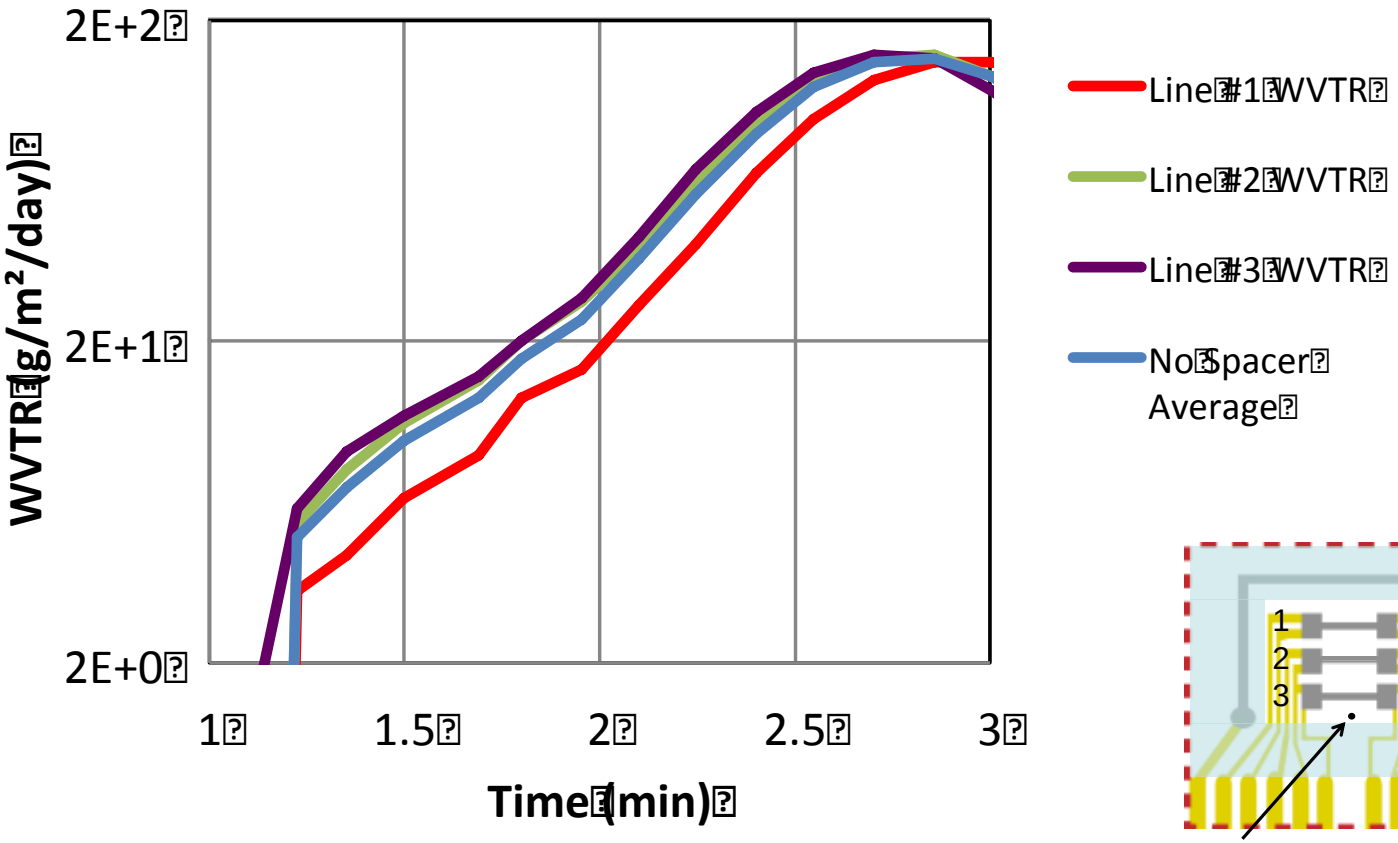
- **Resultant measurement is NOT reflective of the average WVTR!**

Advantage #2: Accounting for defects



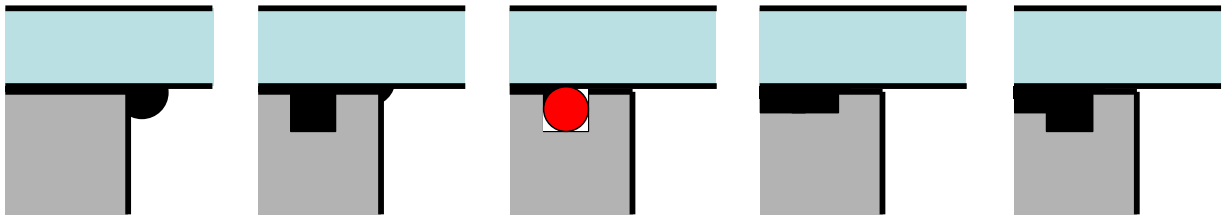
Without a spacer, the trace closest to the pinhole defect produced the highest WVTR

Advantage #2: Accounting for defects

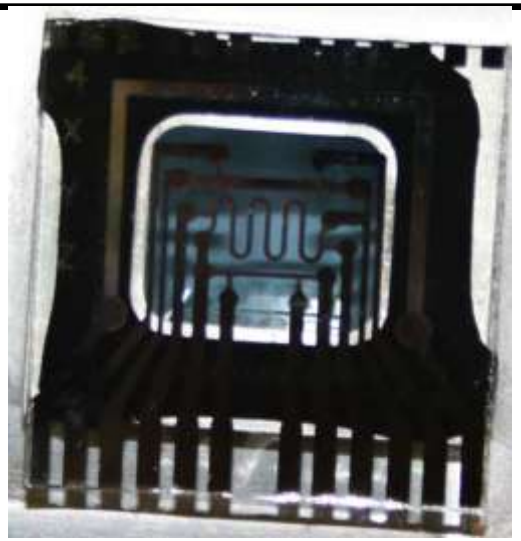


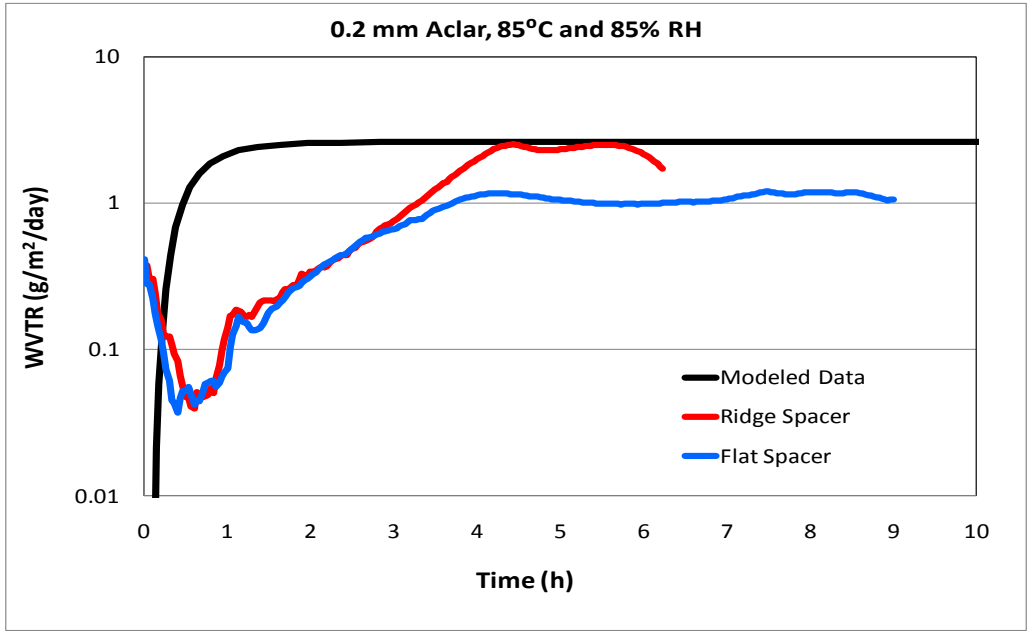
Without a spacer, the trace closest to the pinhole defect produced the highest WVTR.

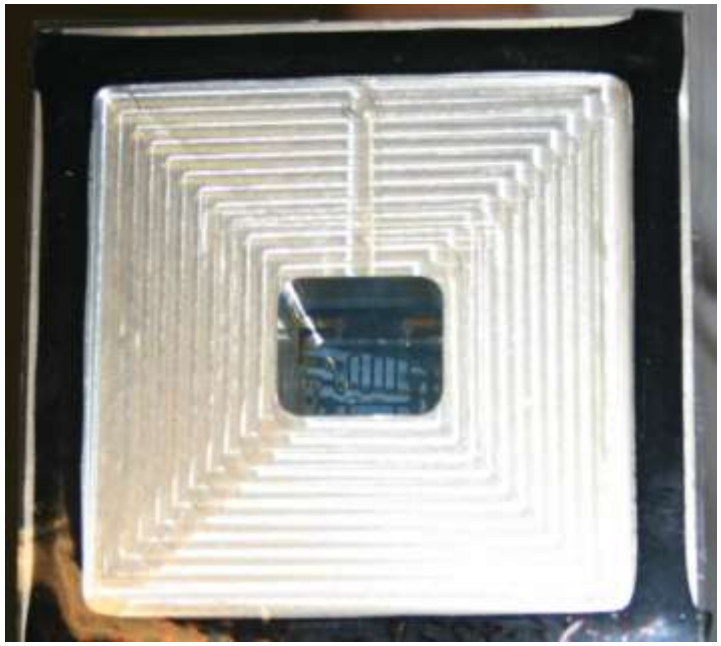
Advantage #3: Edgeseal Control



(a) Flat (b) Trench (c) “O” Ring (d) Al Ridge (e) Ridge & Trench

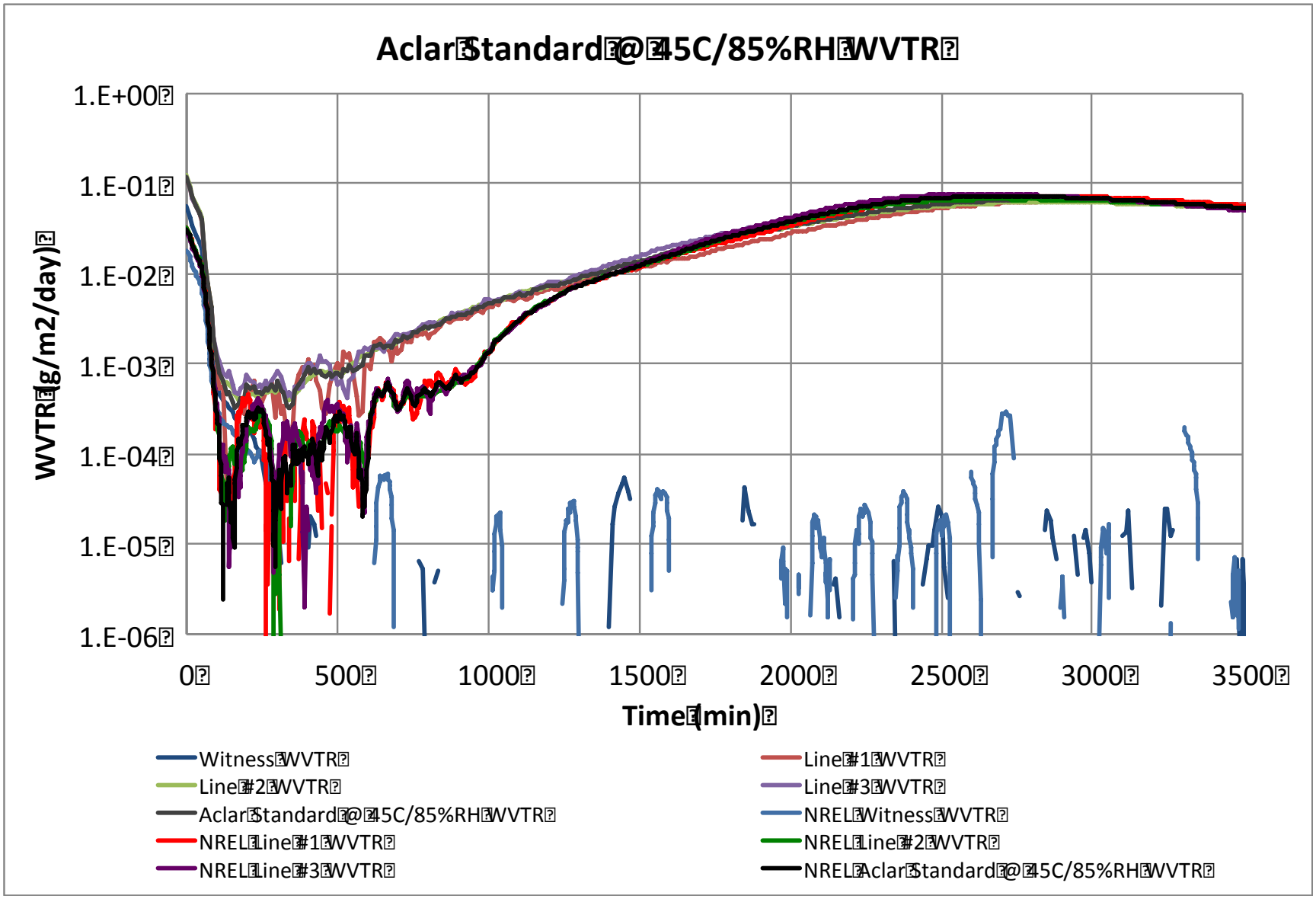




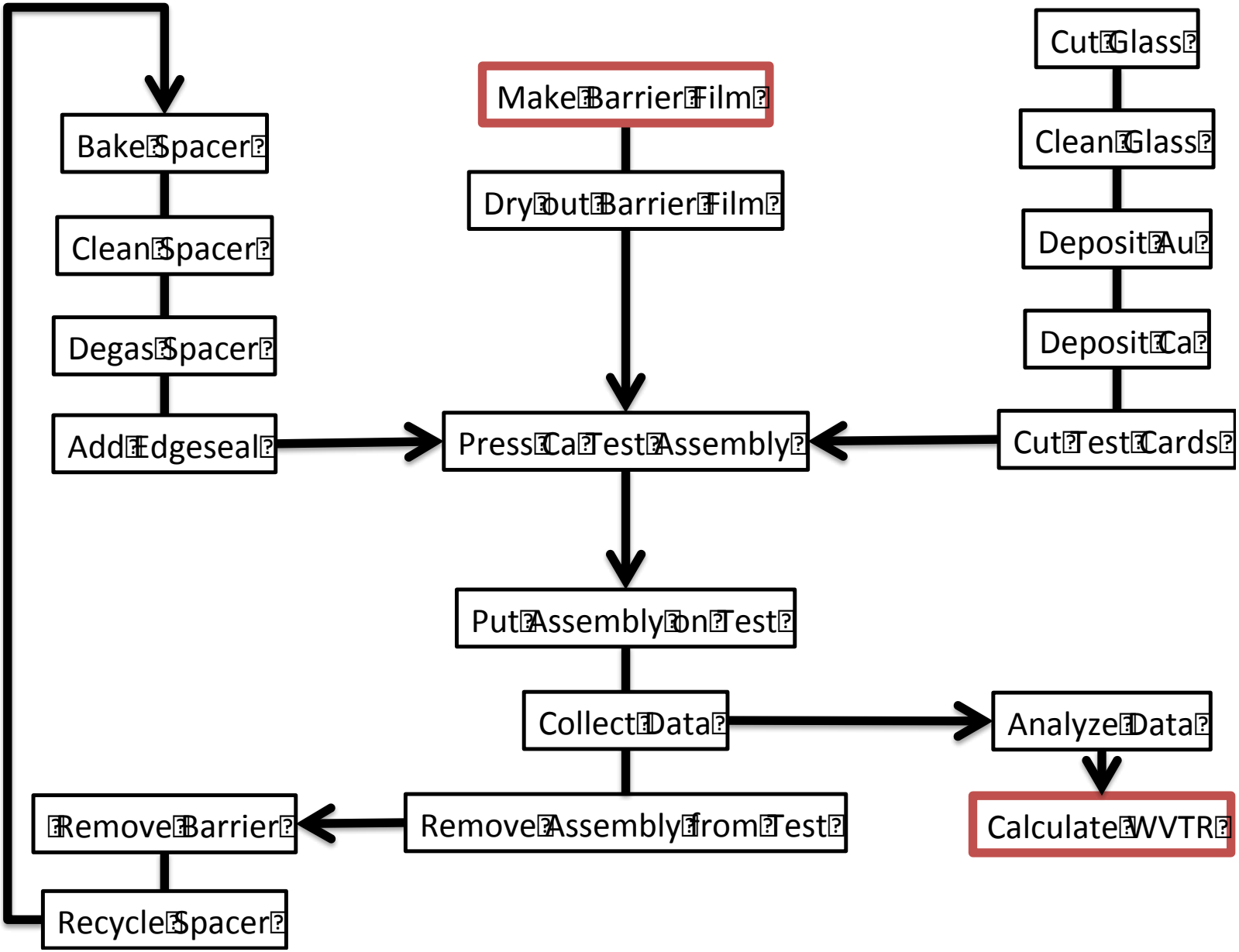


- **Spacer sealing surface design**
  - allows for reproducible testing areas
  - limits the influence of the edgeseal materials on the measurement

Device to Device reproducibility

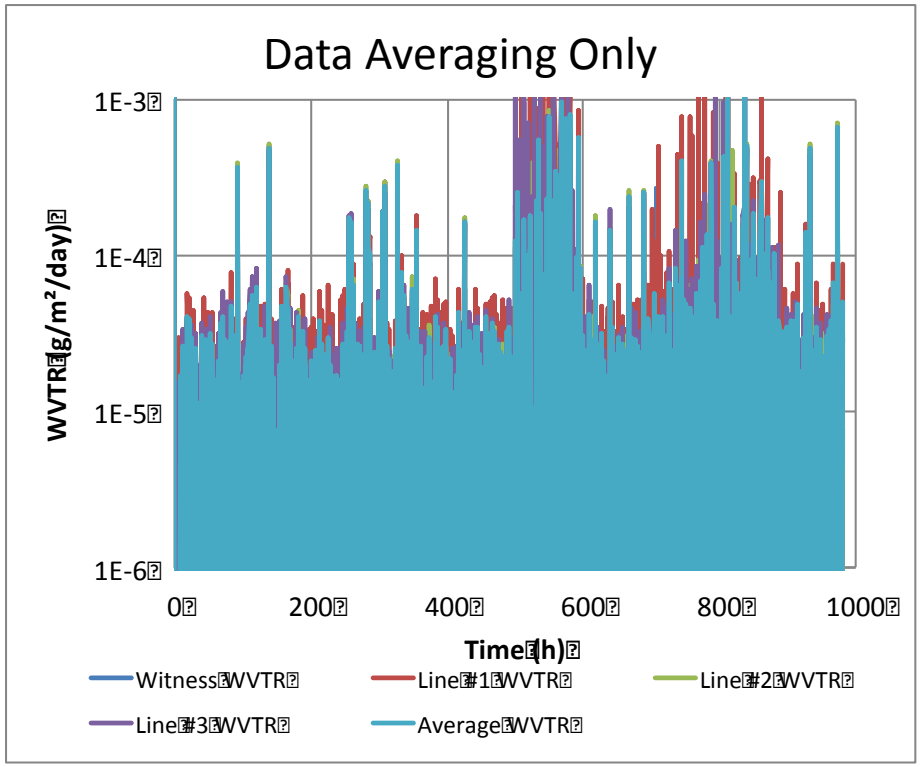


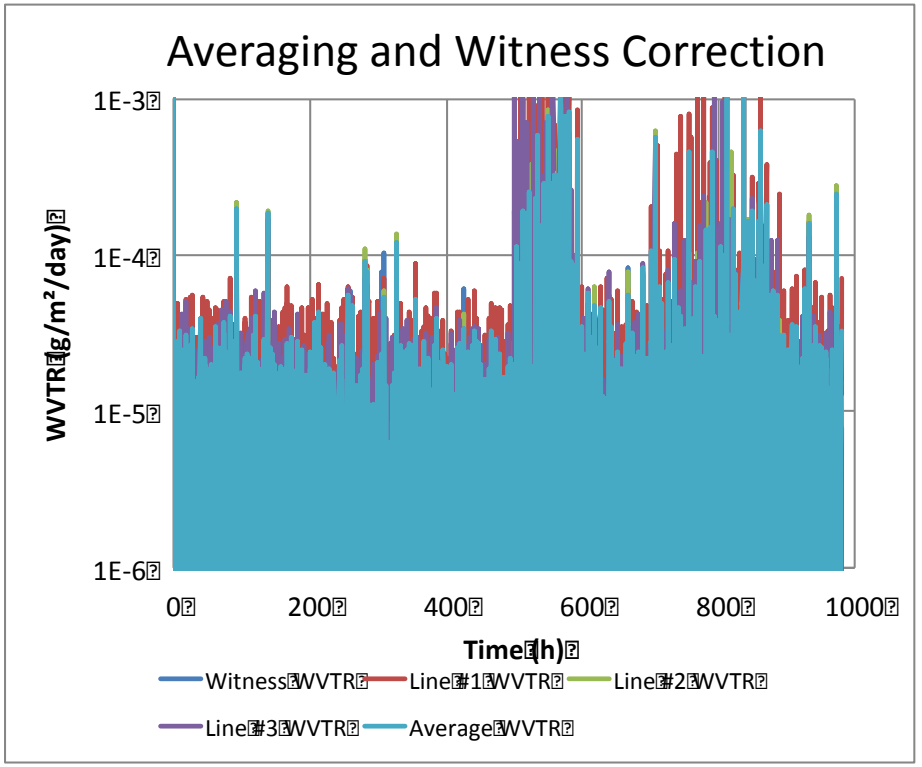
e-Ca Process Flowchart



Witness Correction and Data Averaging

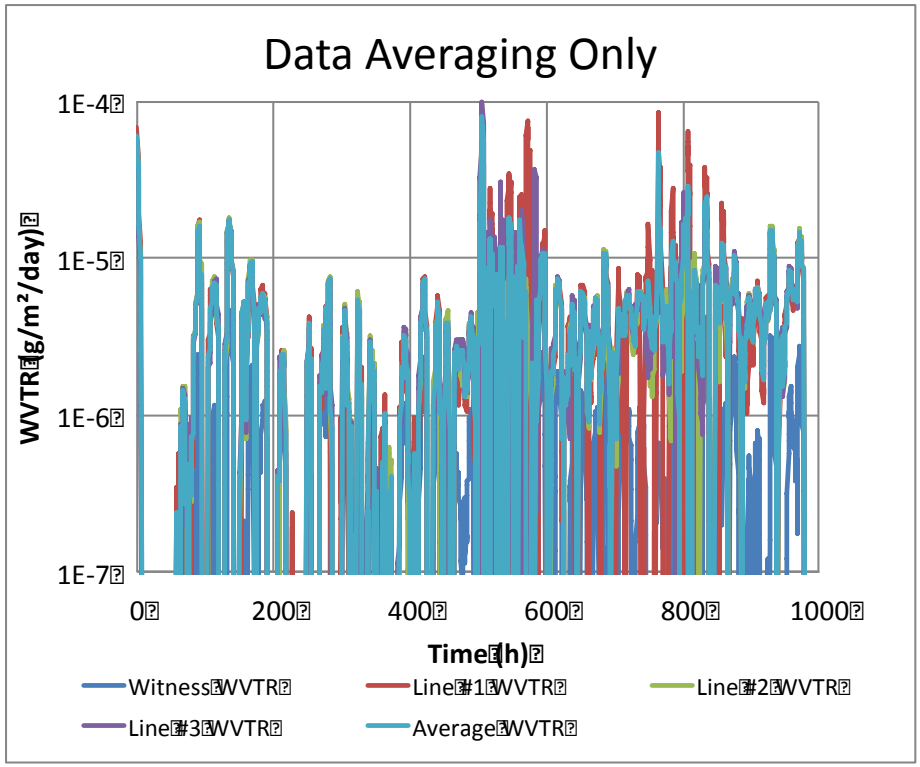
Averaging over 1 hrs

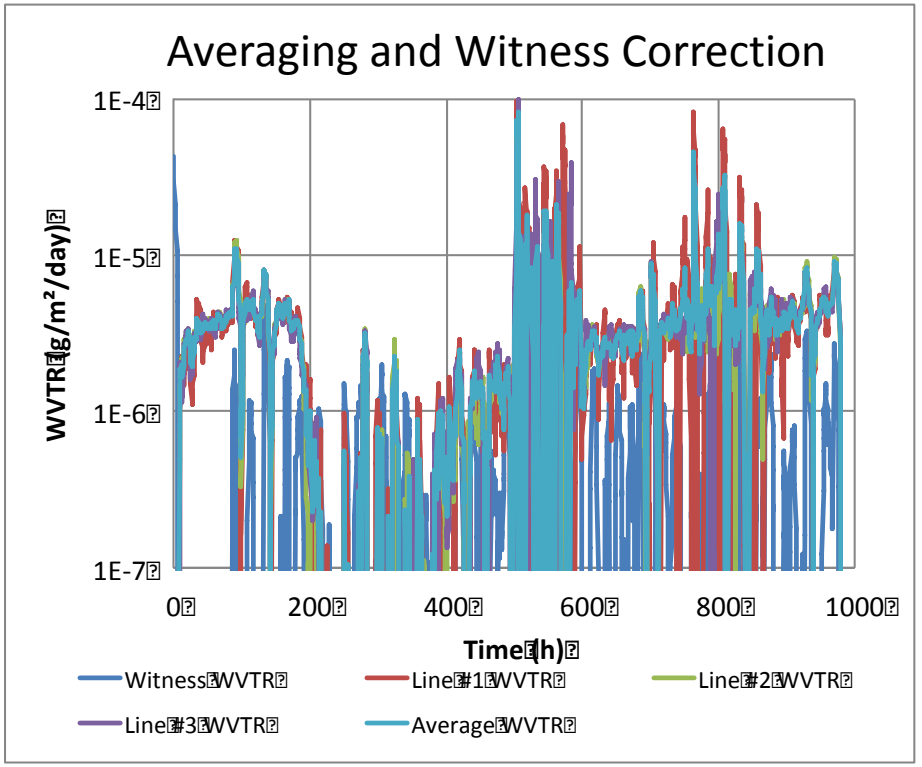




Witness Correction and Data Averaging

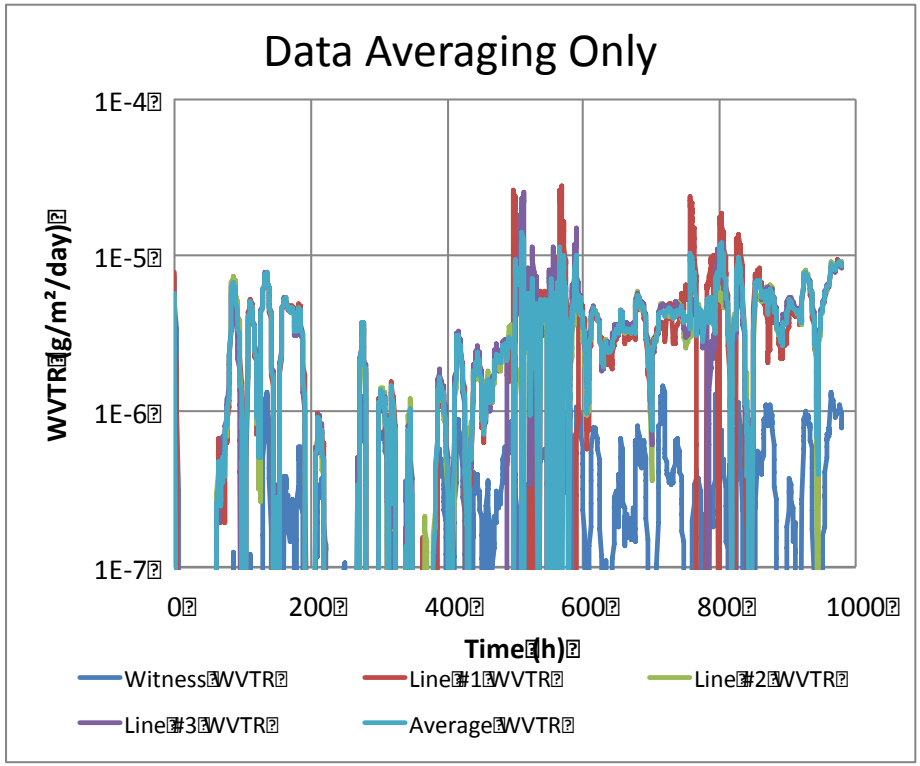
Averaging over 12 hrs

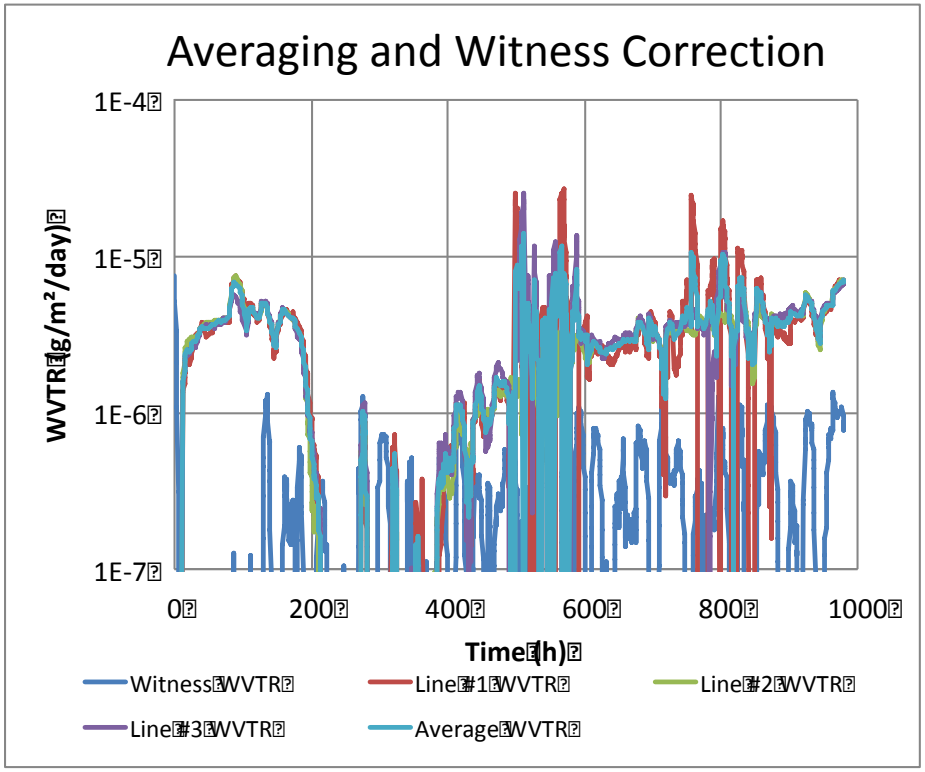




Witness Correction and Data Averaging

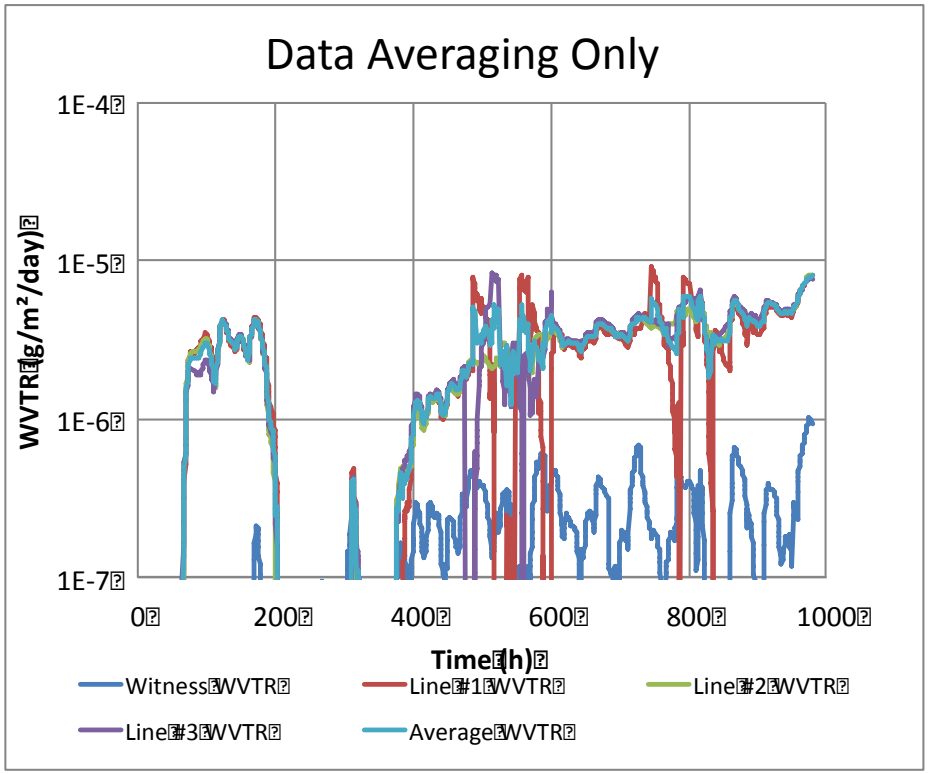
Averaging over 24 hrs

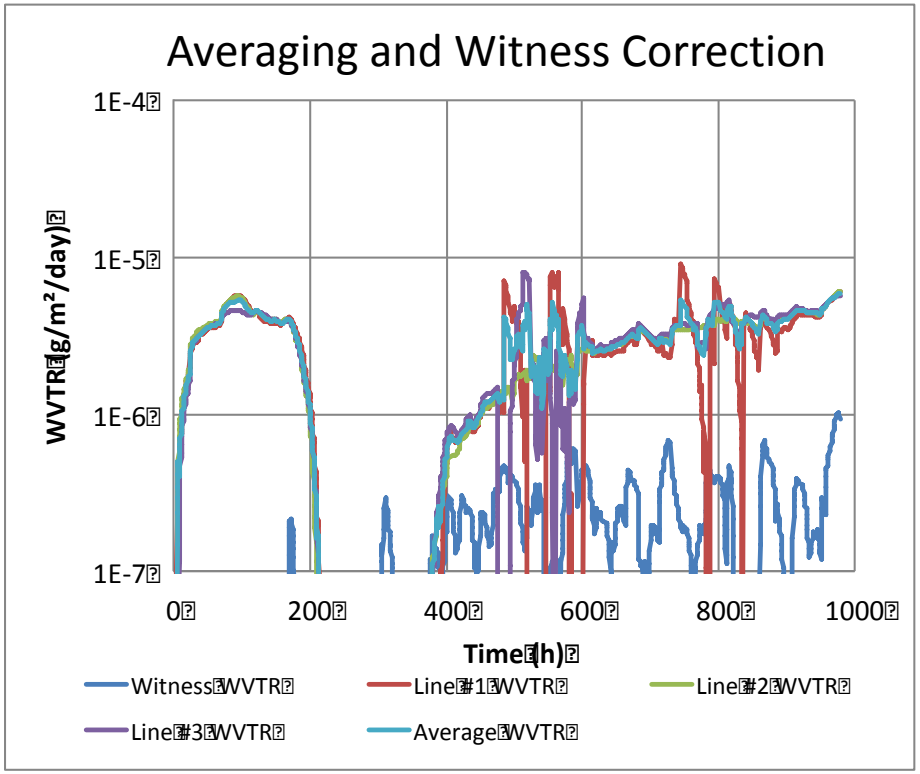




Witness Correction and Data Averaging

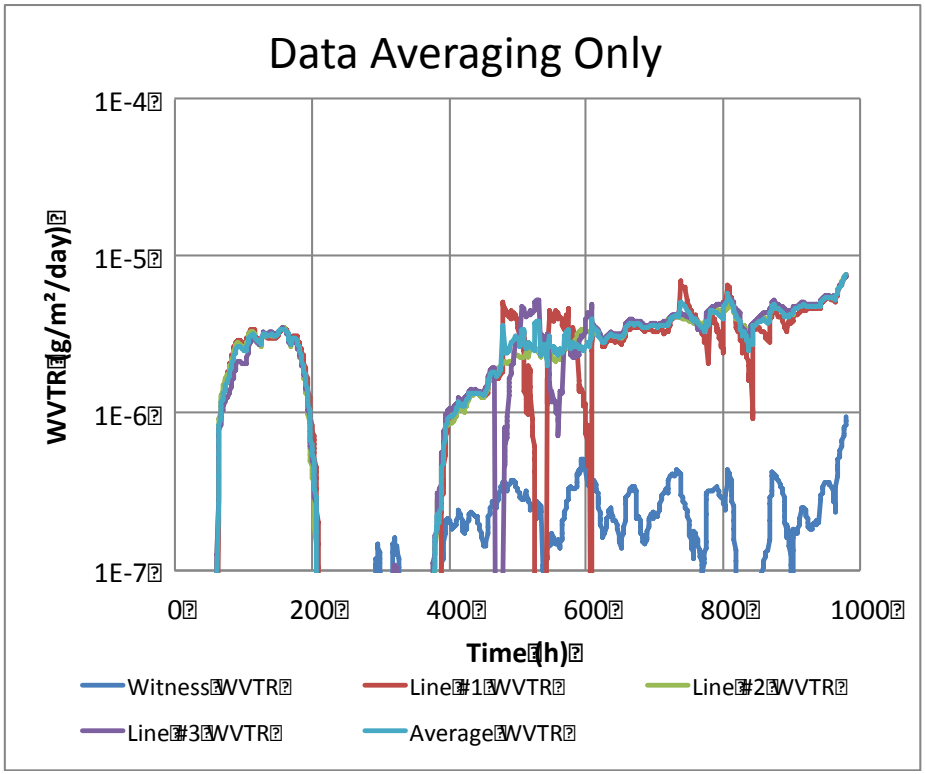
Averaging over 48 hrs

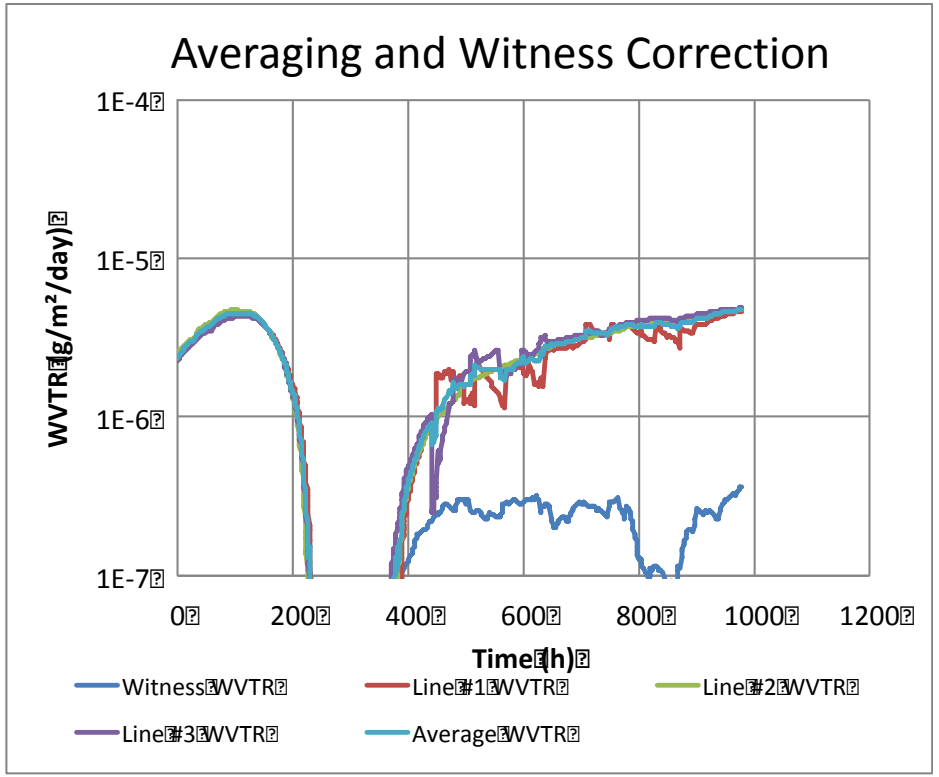




Witness Correction and Data Averaging

Averaging over 120 hrs





What we still need to do…

- **Understanding Ca Test breakthrough and lag times**
  - Ca degradation effects?
  - Spacer adsorption effects
  - Contact compatibility
  - Annealing effects
- **Develop usable standards**

Conclusions

- **e-Ca Test can be used *reproducibly* for a scalable *steady state* WVTR characterization method**
- **We have demonstrated measurement in the $<10^{-5}$ g/m^2/day range and have confidence that 10^{-7} g/m^2/day can be qualitatively analyzed with this technique.**
- **Sensitivity can be modulated by:**
  - Varying aperture area
  - Temperature correction
  - Witness correction
  - Data Averaging
- **For accurate reproducible results, control of the spillover of edge seal material, and gas diffusion lengths are important.**