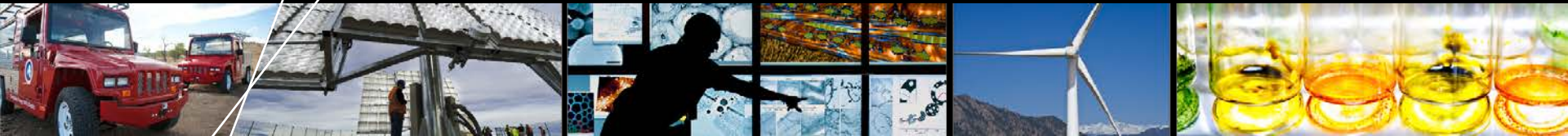


NREL's e-Ca Test



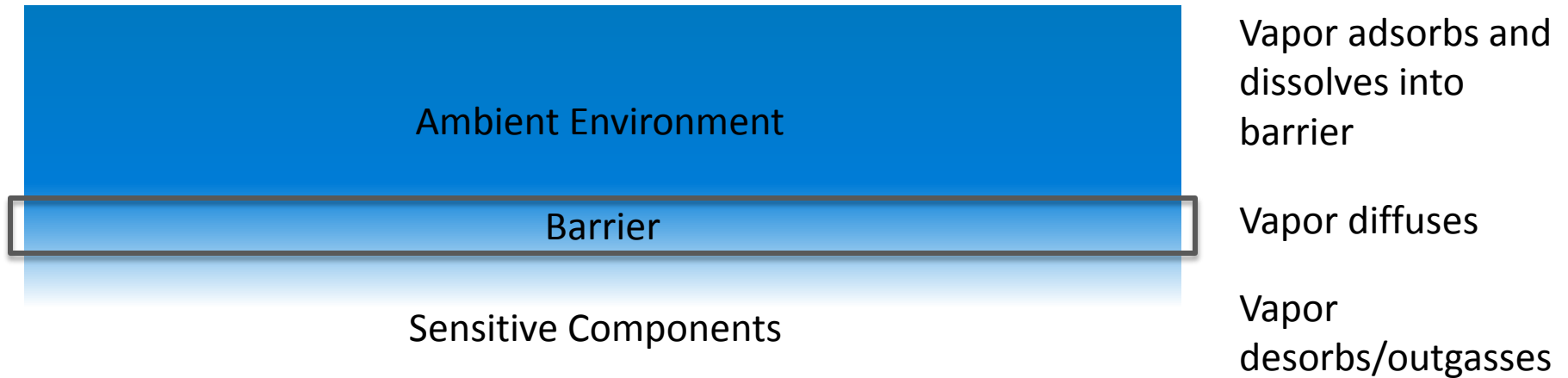
Barrier Technologies Workshop

Arrelaine A. Dameron

September 19, 2012

NREL/PR-5200-56665

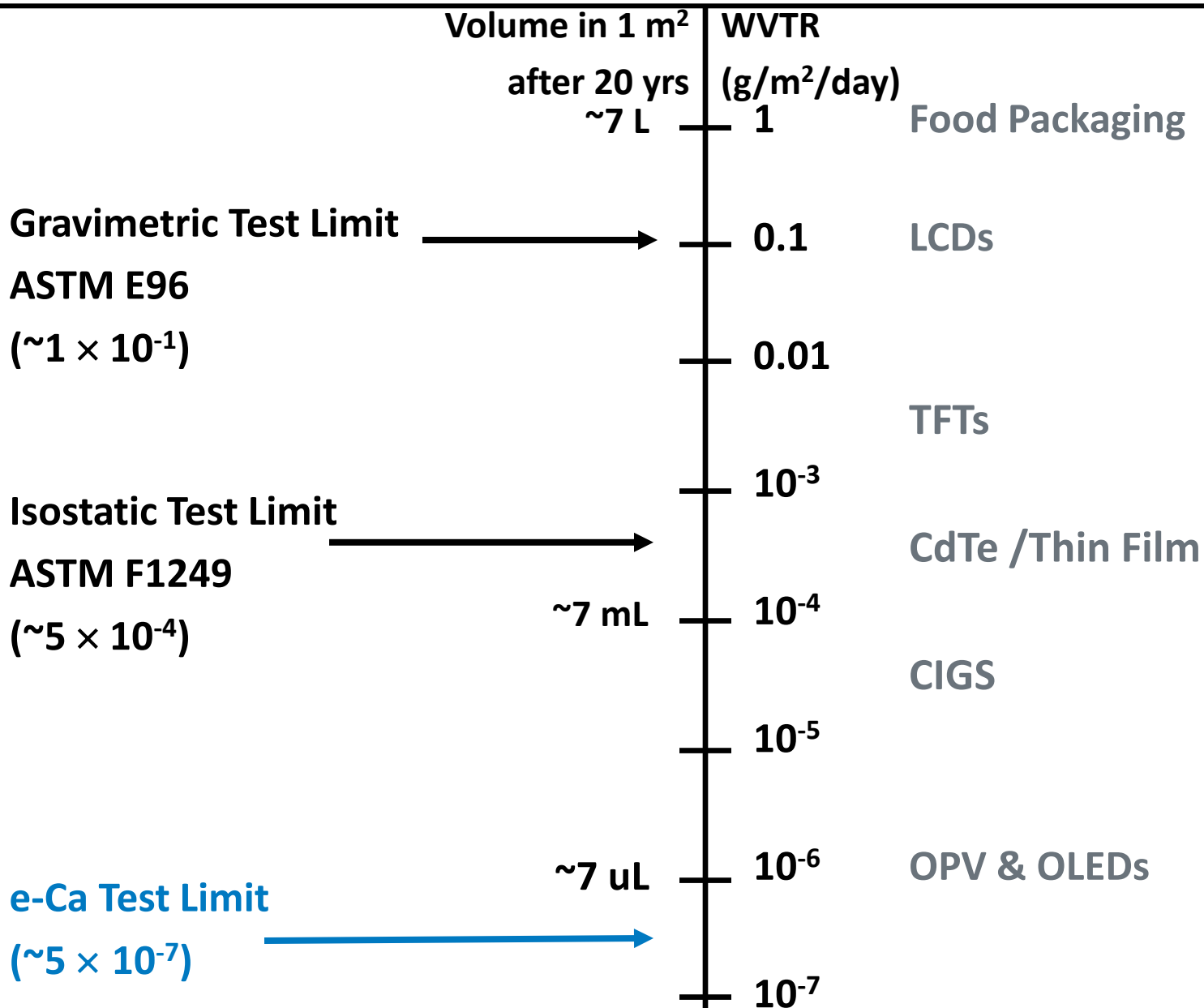
Characterization of Water Permeation Barriers



Desire a characterization method that is:

- Reproducible
- Highly sensitive
- Easy to use
- Scalable

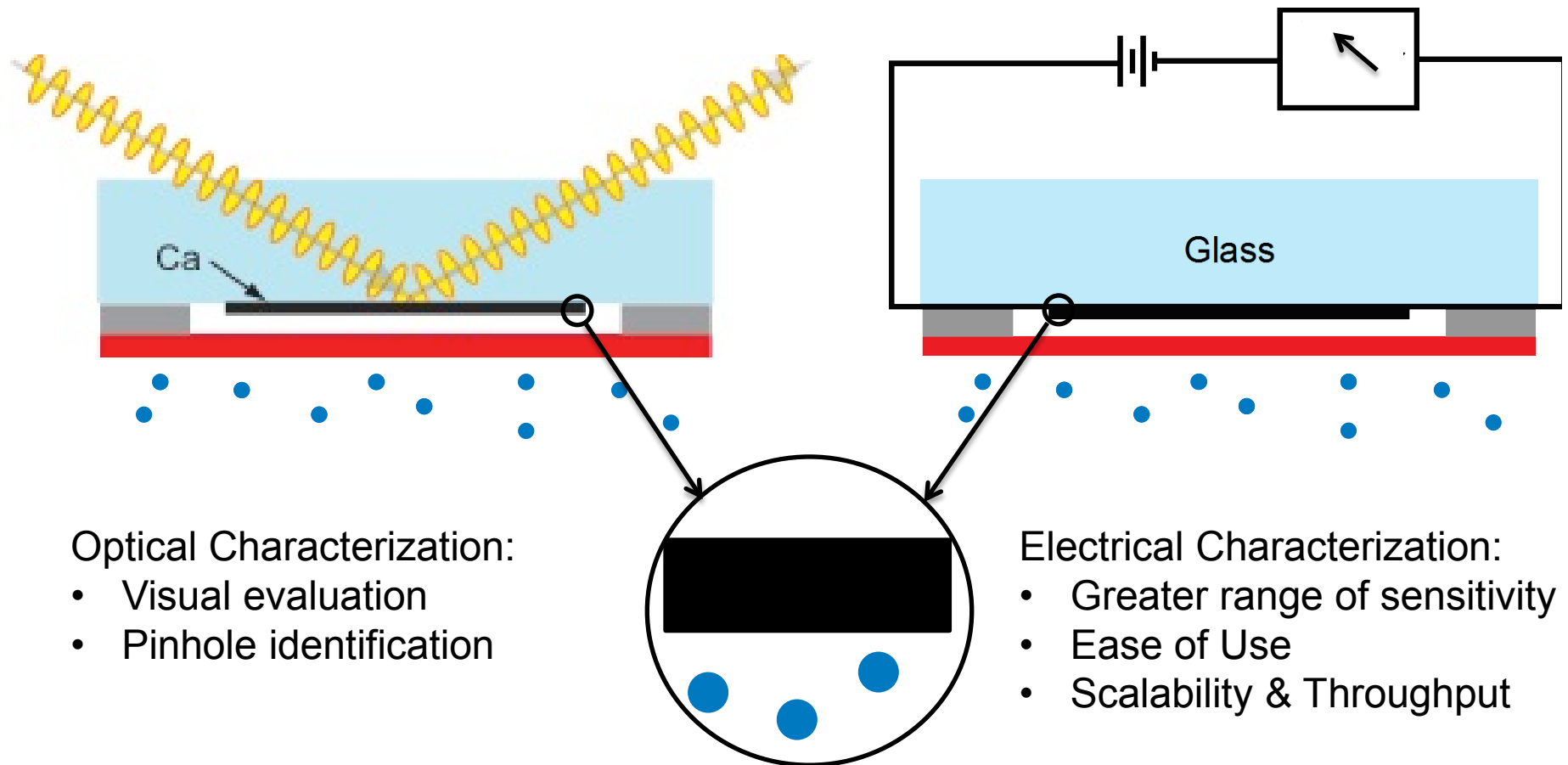
Application Specific Tolerable Water Permeation



Ca Test Basics



Opaque and Conductive \rightarrow Transparent and Insulating



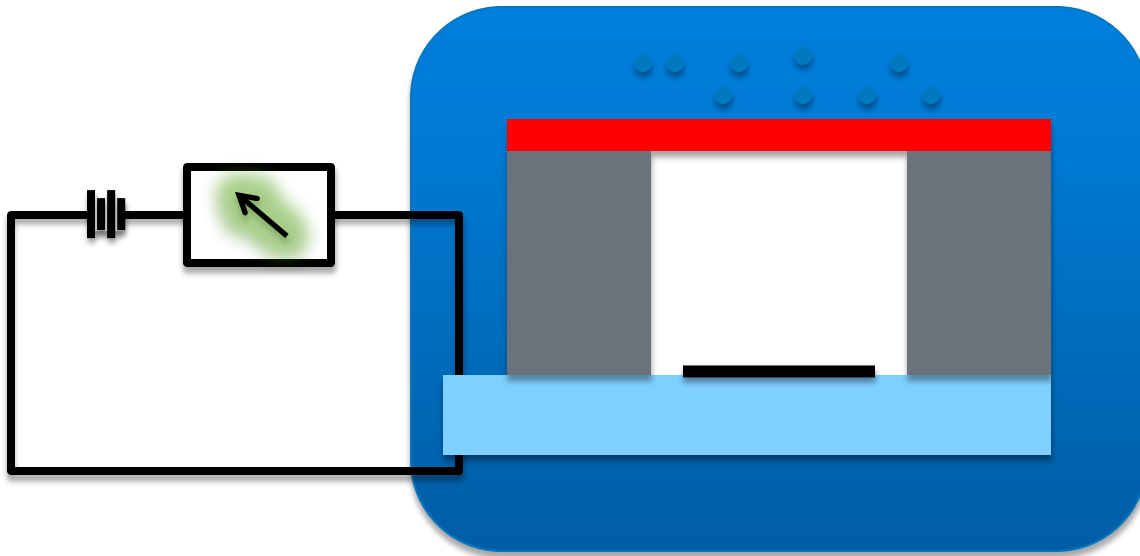
Optical Characterization:

- Visual evaluation
- Pinhole identification

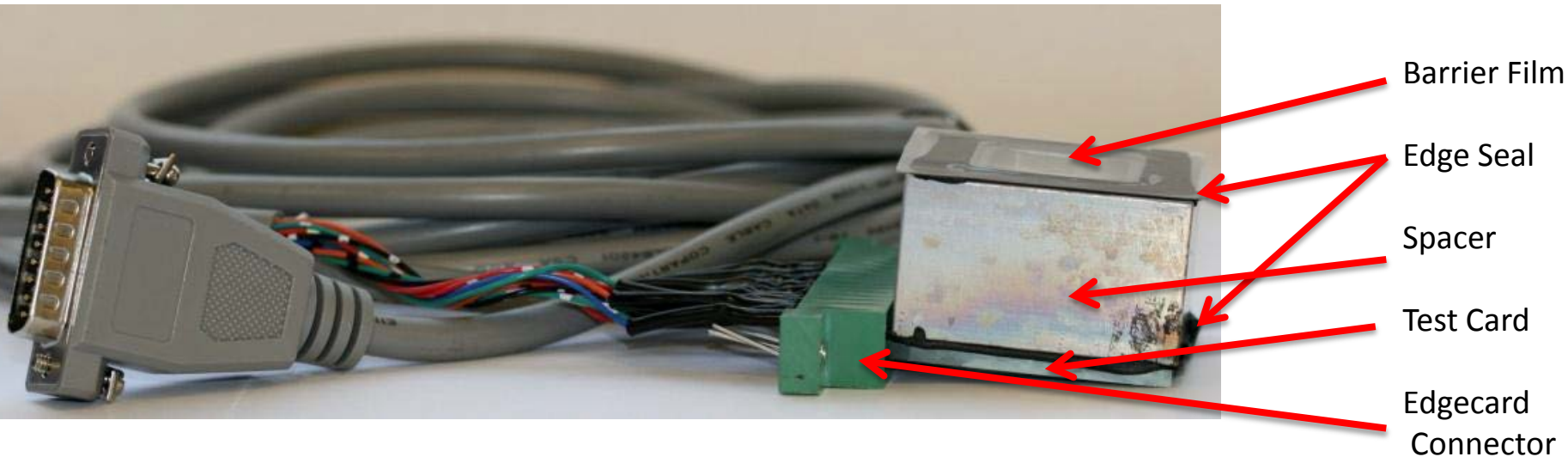
Electrical Characterization:

- Greater range of sensitivity
- Ease of Use
- Scalability & Throughput

NREL's e-Ca Test



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



WVTR Equation

Reaction Ratio:
 $\text{Ca} + 2\text{H}_2\text{O}(\text{g}) \rightarrow \text{Ca}(\text{OH})_2 + \text{H}_2$
 $n=2$

Ca Density:
 1.55 g/cm^3

Ratio of Apertures

Measured Resistance

Ca Resistivity:
 $4.02 \times 10^{-6} (\Omega \cdot \text{cm})$ at 23°C

$$WVTR = n \delta \rho_{Ca} \left(\frac{l_{eff}}{w} \right) \left(\frac{A_{Ca}}{A_B} \right) \left(\frac{M_w}{M_{Ca}} \right) \left[\frac{d\left(\frac{1}{R}\right)}{dt} \right]$$

Trace Dimensions

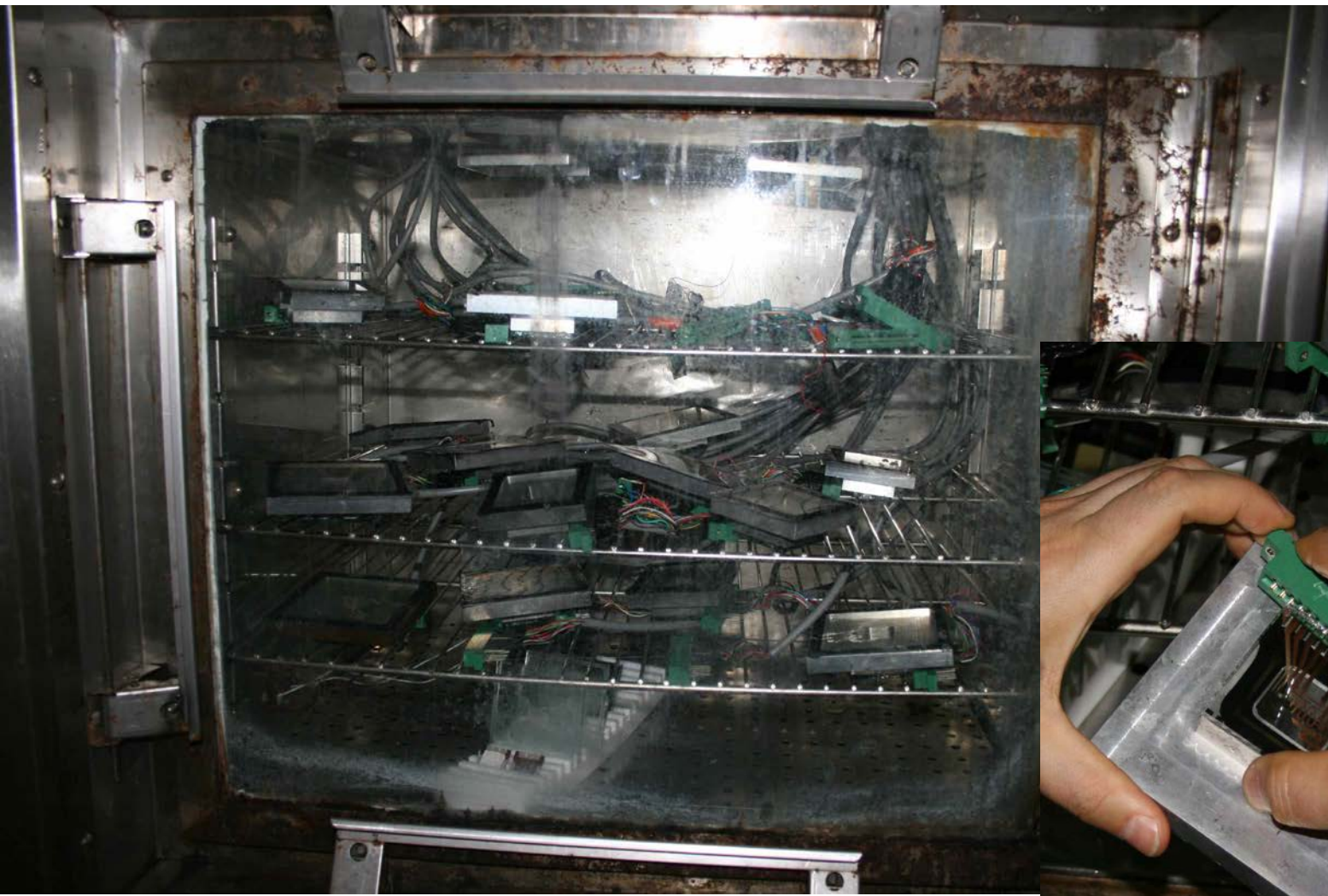
Ratio of Molecular Weights

Time

$$R_0 = \frac{R}{1 + \alpha(T - T_o)}$$

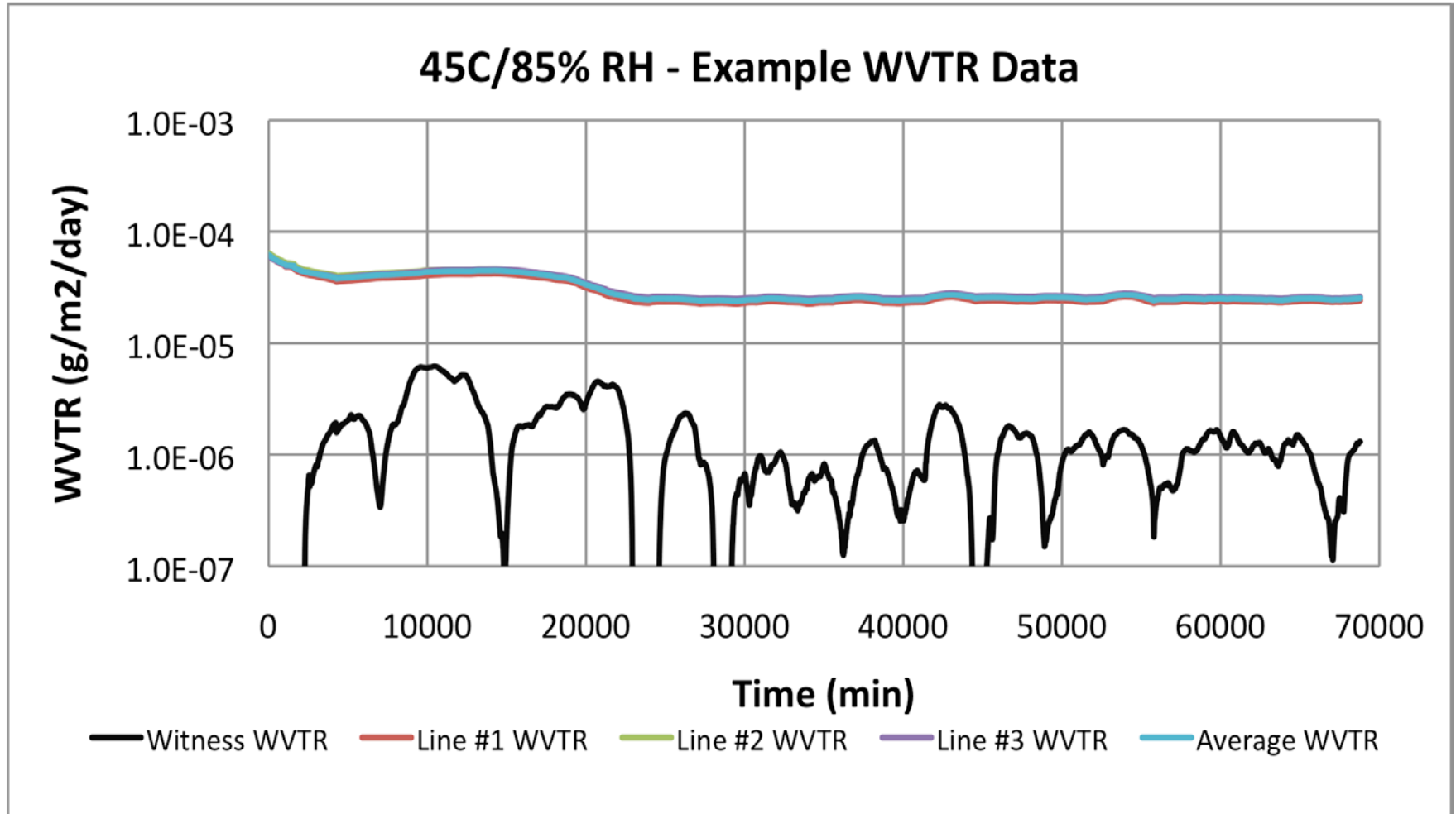
We measure the resistance with respect to time to calculate the WVTR.

Samples on test



Measured e-Ca Test Data

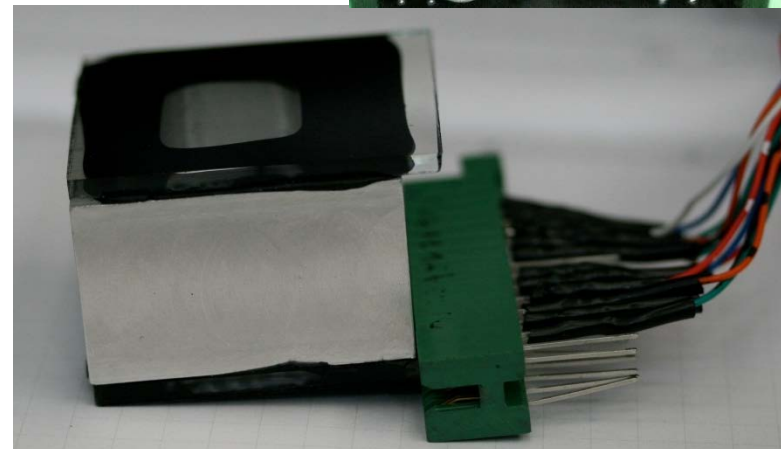
Actual measured data from a barrier film provided by a commercial partner shows steady state permeation at $\sim 3 \times 10^{-5} \text{ g/m}^2/\text{day}$.



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

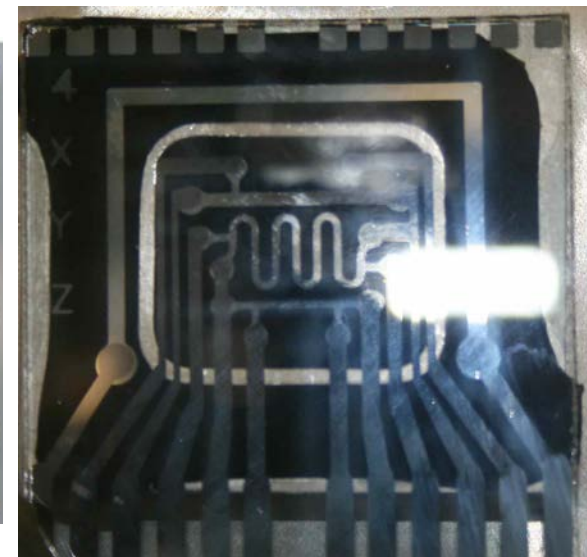
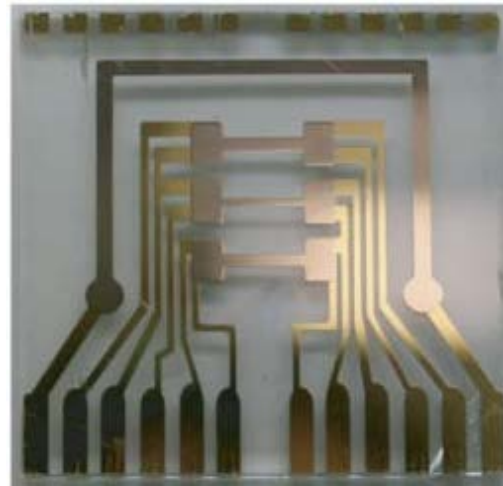
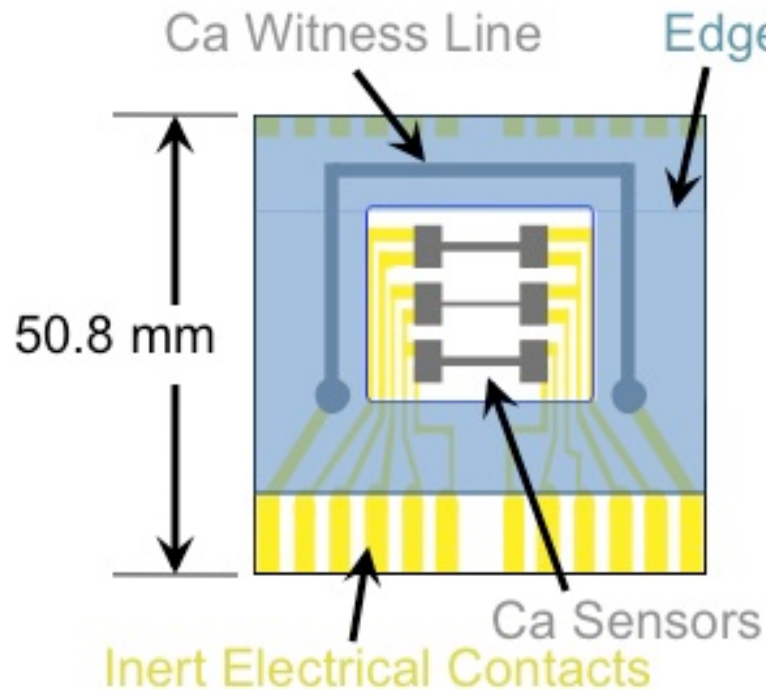
Ca Test Components

- **Computer for Data collection**
 - Custom software
 - Data collection, averaging and calculations, and WVTR display
- **Commercial digital multimeter**
 - 6.5 digit accuracy => $\pm 0.1 \text{ m}\Omega$
- **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 edgecard
 - **Custom diffusion spacer element**
 - Machined aluminum block
 - Barrier Film

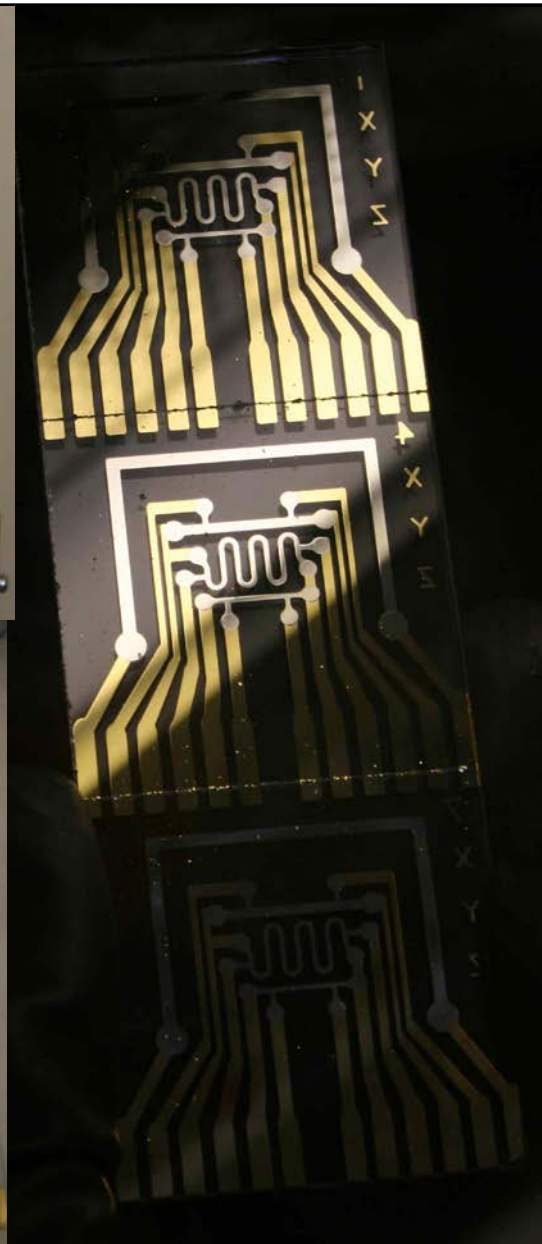
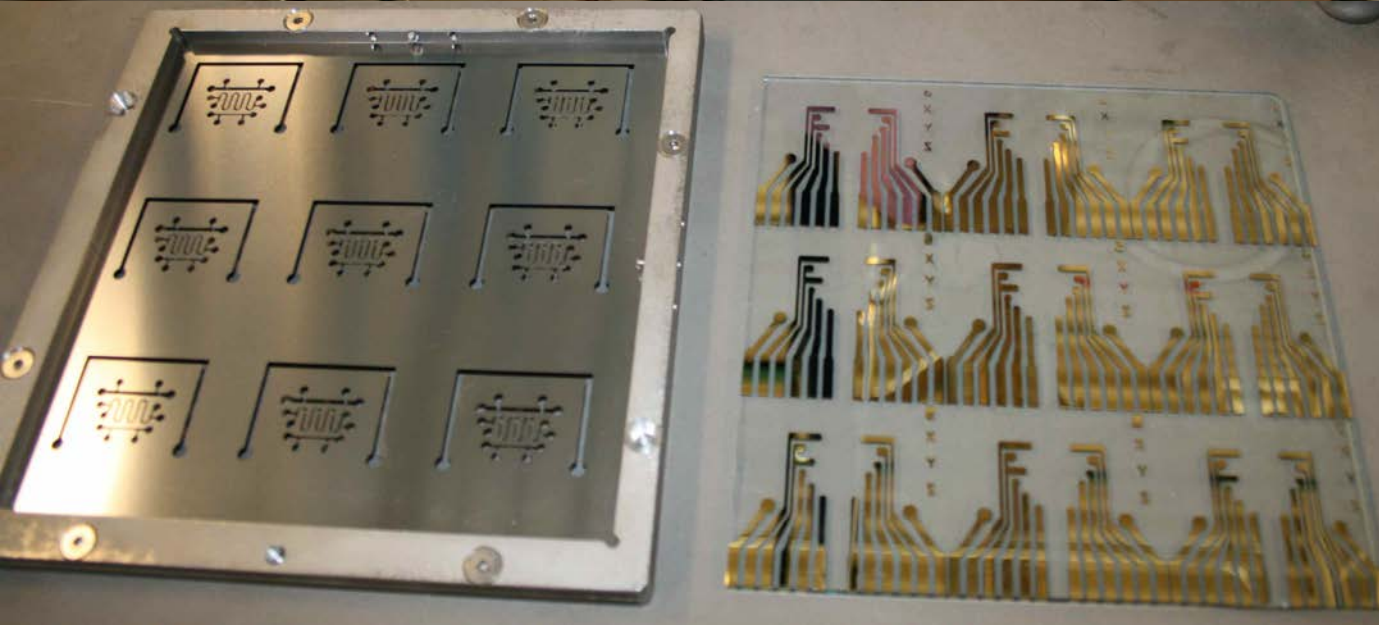
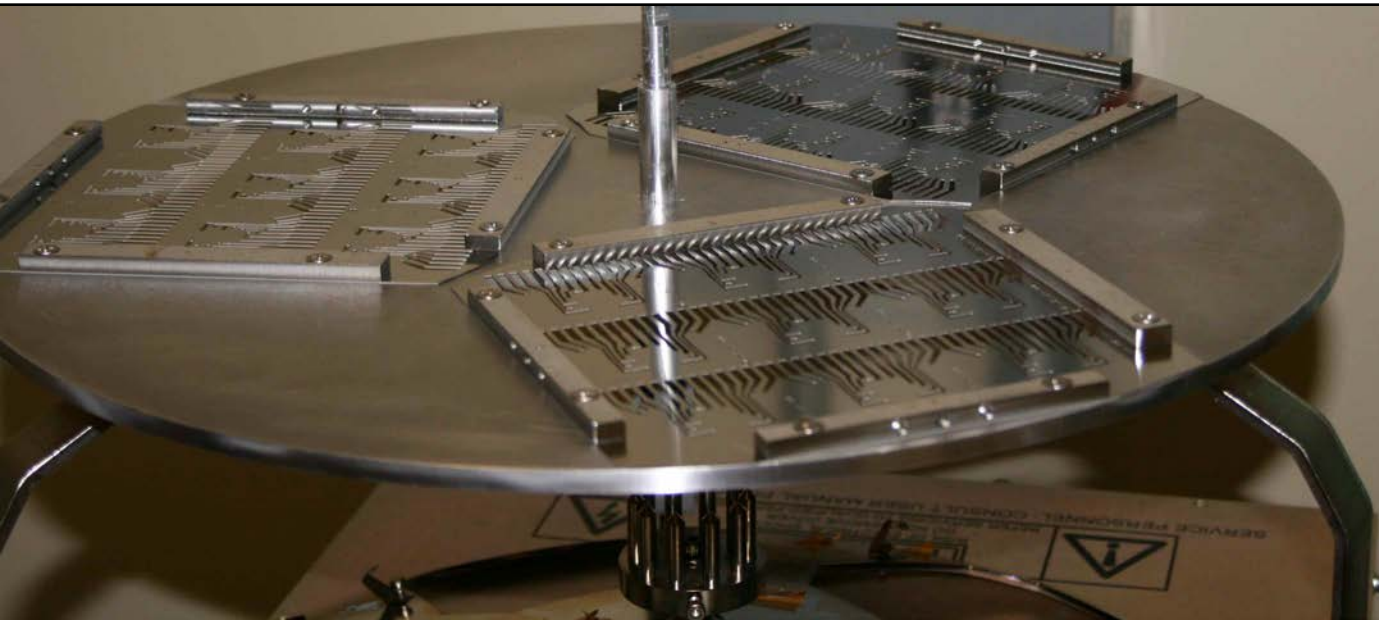


Test Card

- 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



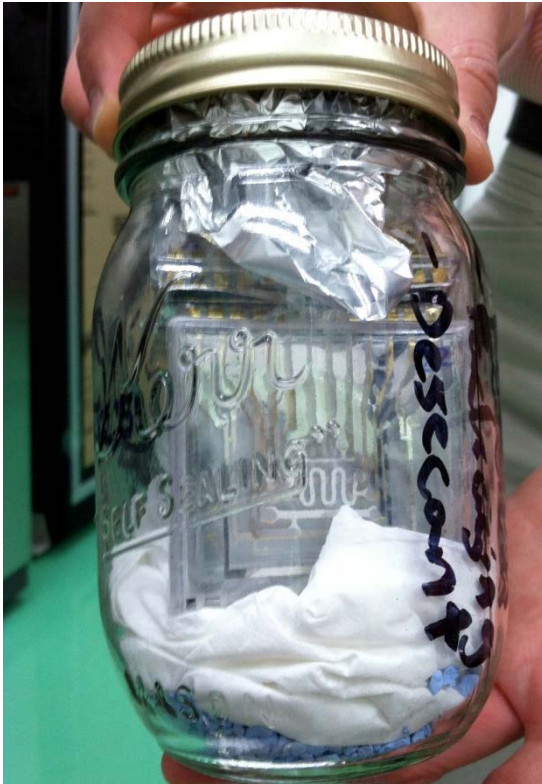
Test Card Fabrication



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 $<1\text{\AA}/\text{day}$ or WVTR of $\sim 10^{-9}\text{g}/\text{m}^2/\text{day}$



We even shipped them to Japan!

Edge Seal Evaluation

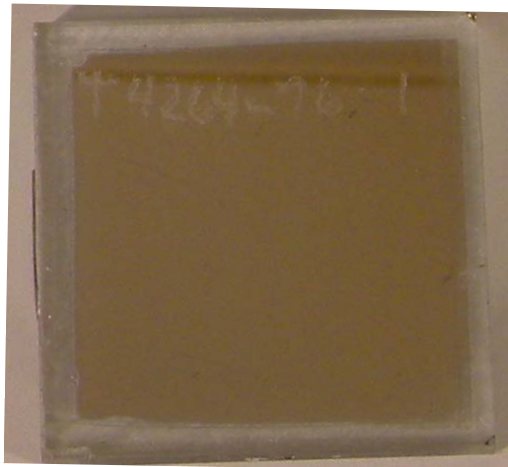
Using the Optical Ca Test concept as an effective means of evaluating edge seal materials similar to applied environment



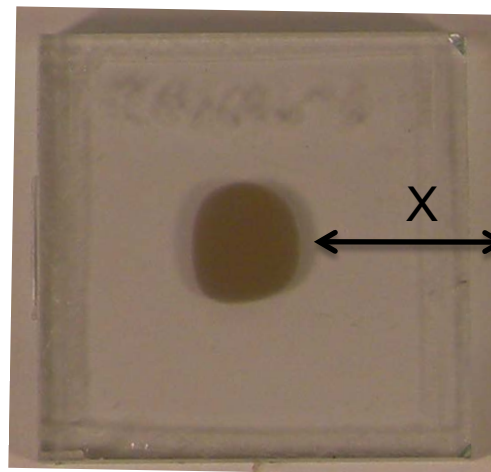
$$X = K\sqrt{t}$$

PDMS

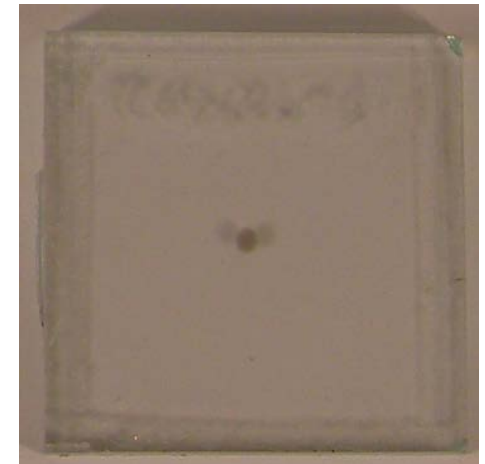
85C/
85 %RH



0 h

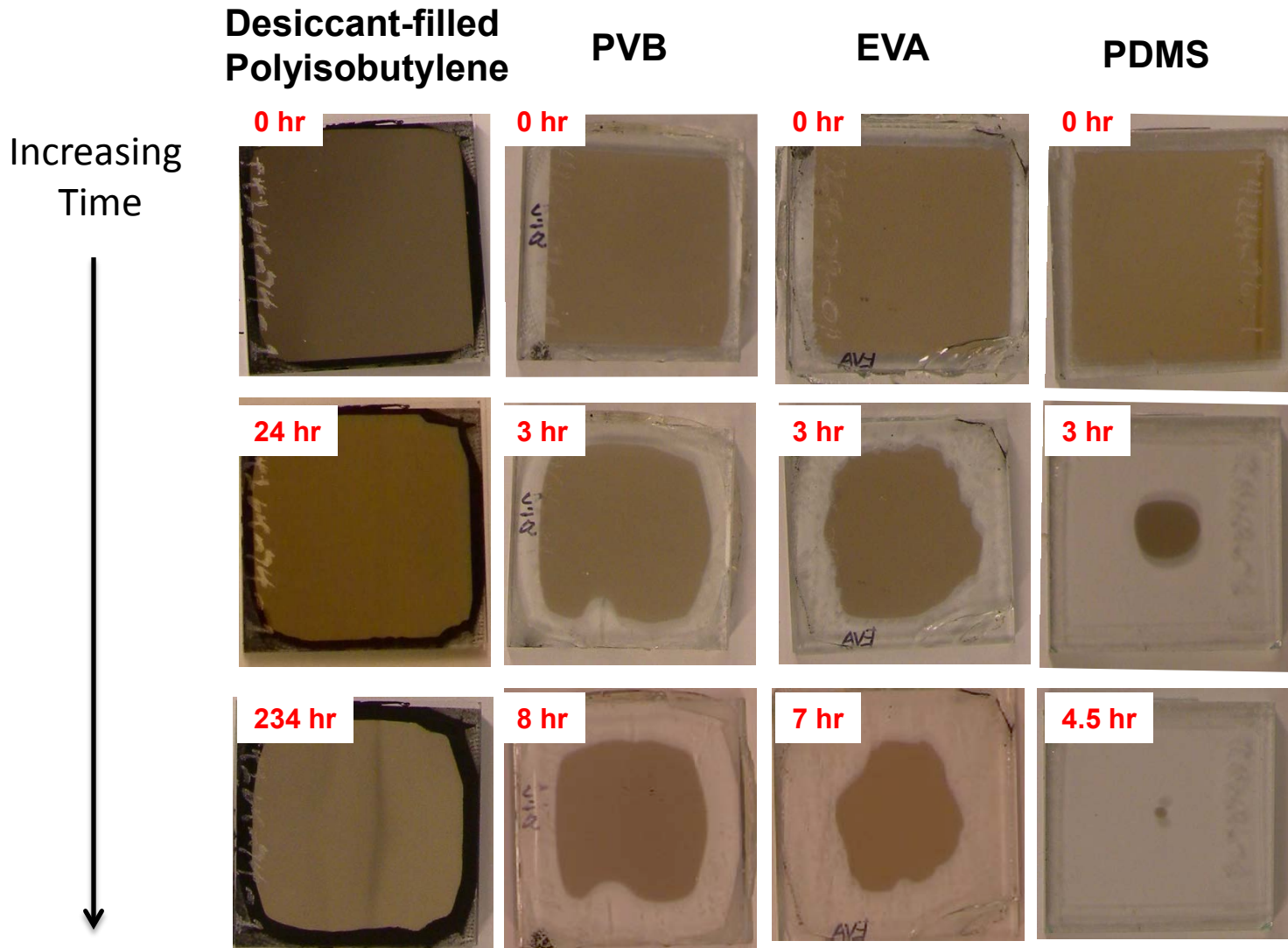


3 h



4.5 h

Typical Edgeseal Results

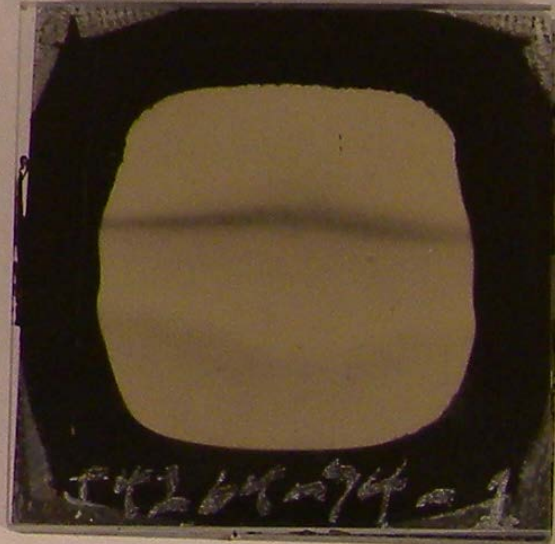


We tested for hundreds of hours....

Desiccant Filled PIB Edgeseal



115 h



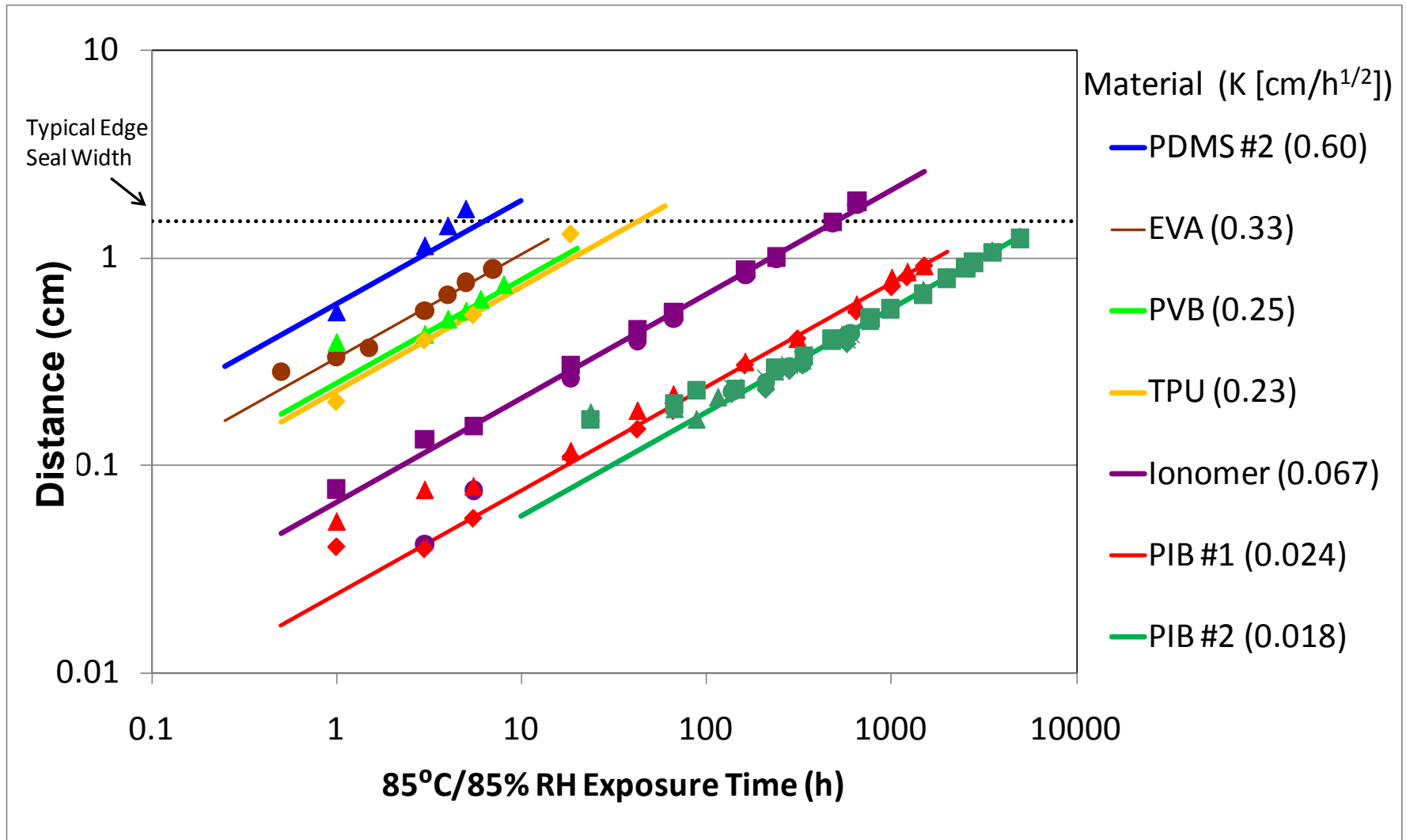
1488 h



3509 h

We tested for thousands of hours....

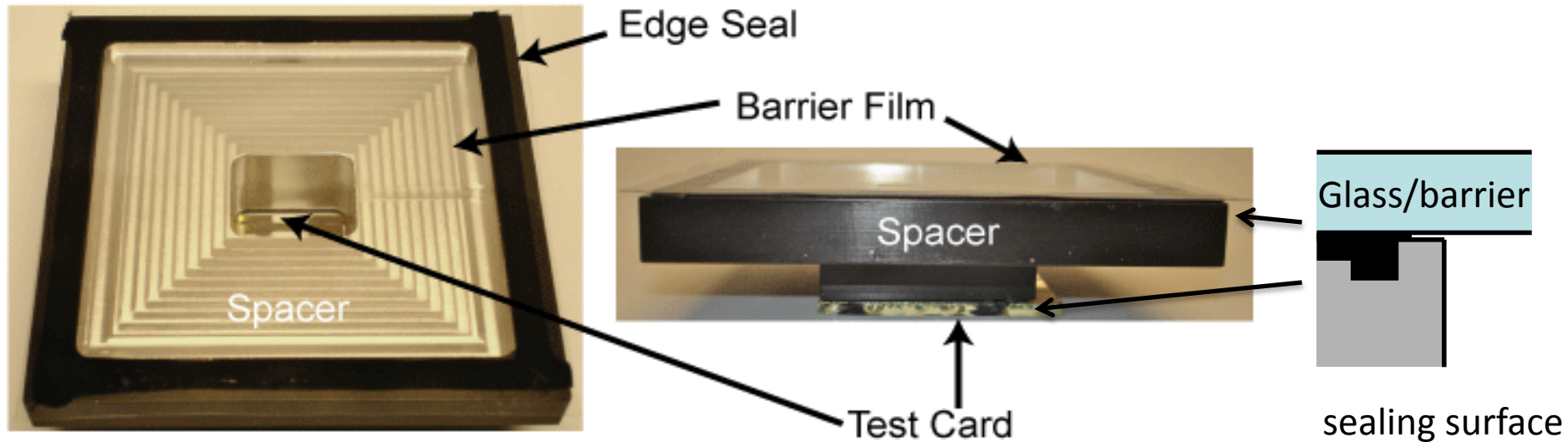
Relative Comparison of Materials



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

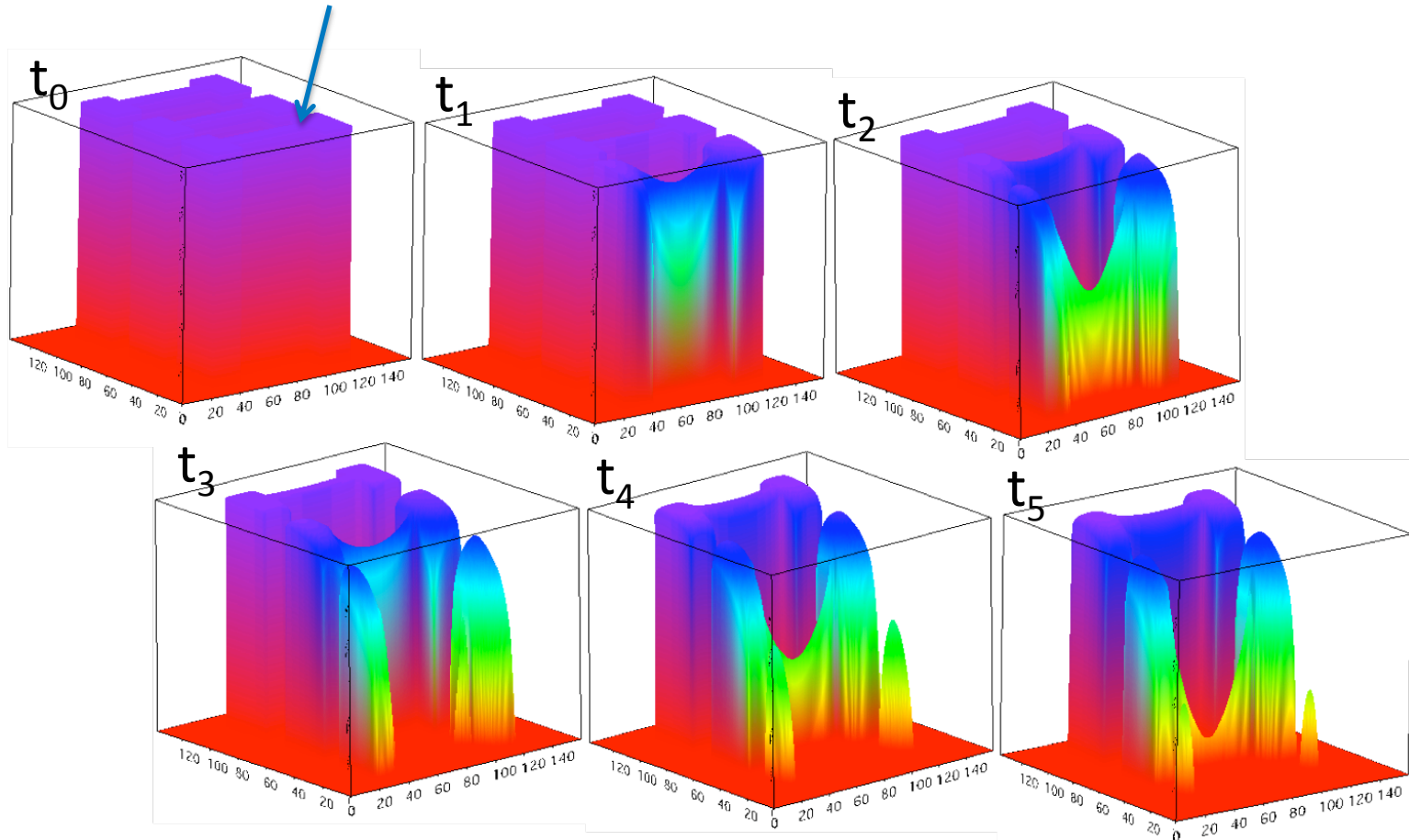


The ratio of apertures controls the sensitivity range by adjusting the barrier area relative to the Ca area

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

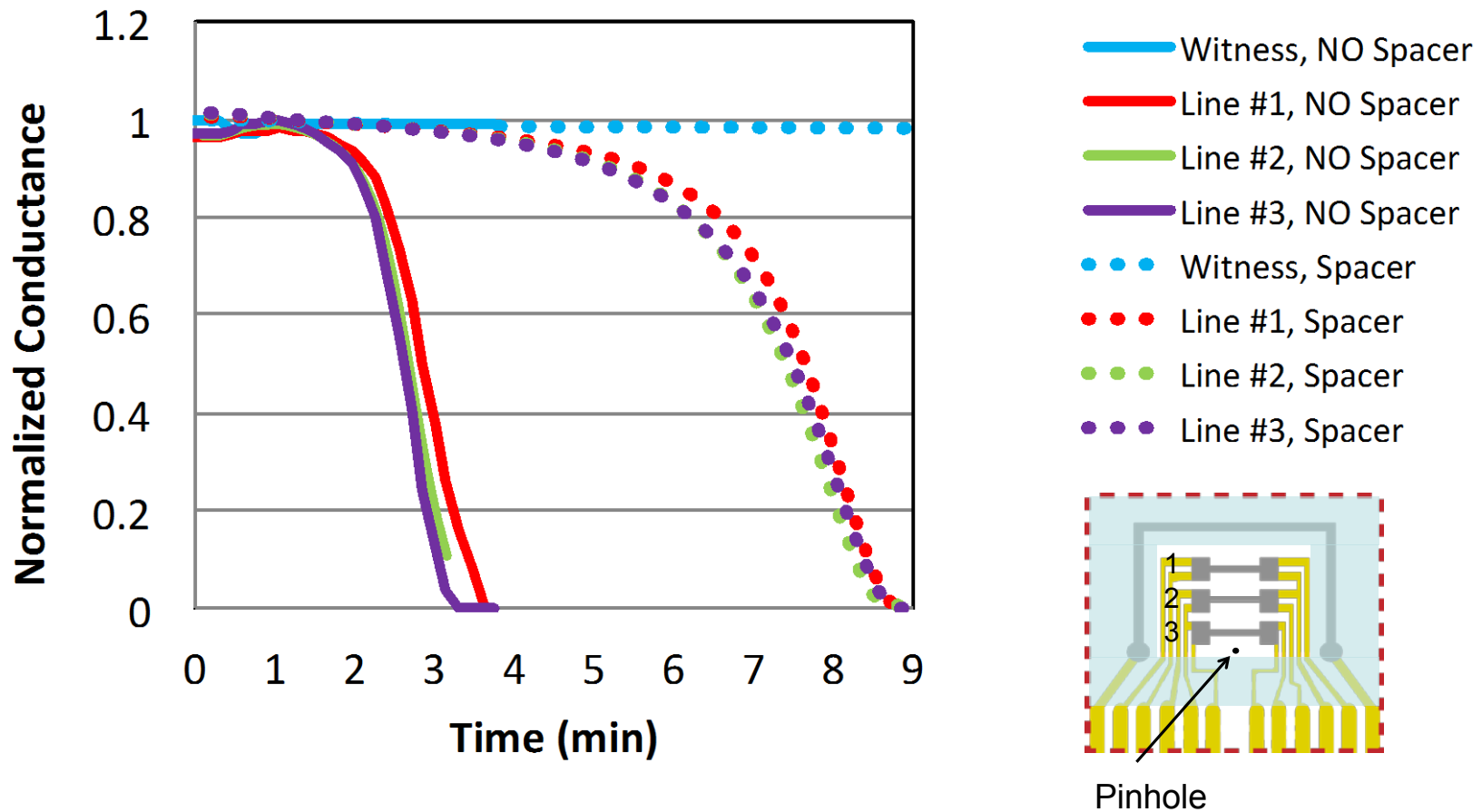
Advantage #2: Diffusion compensation

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



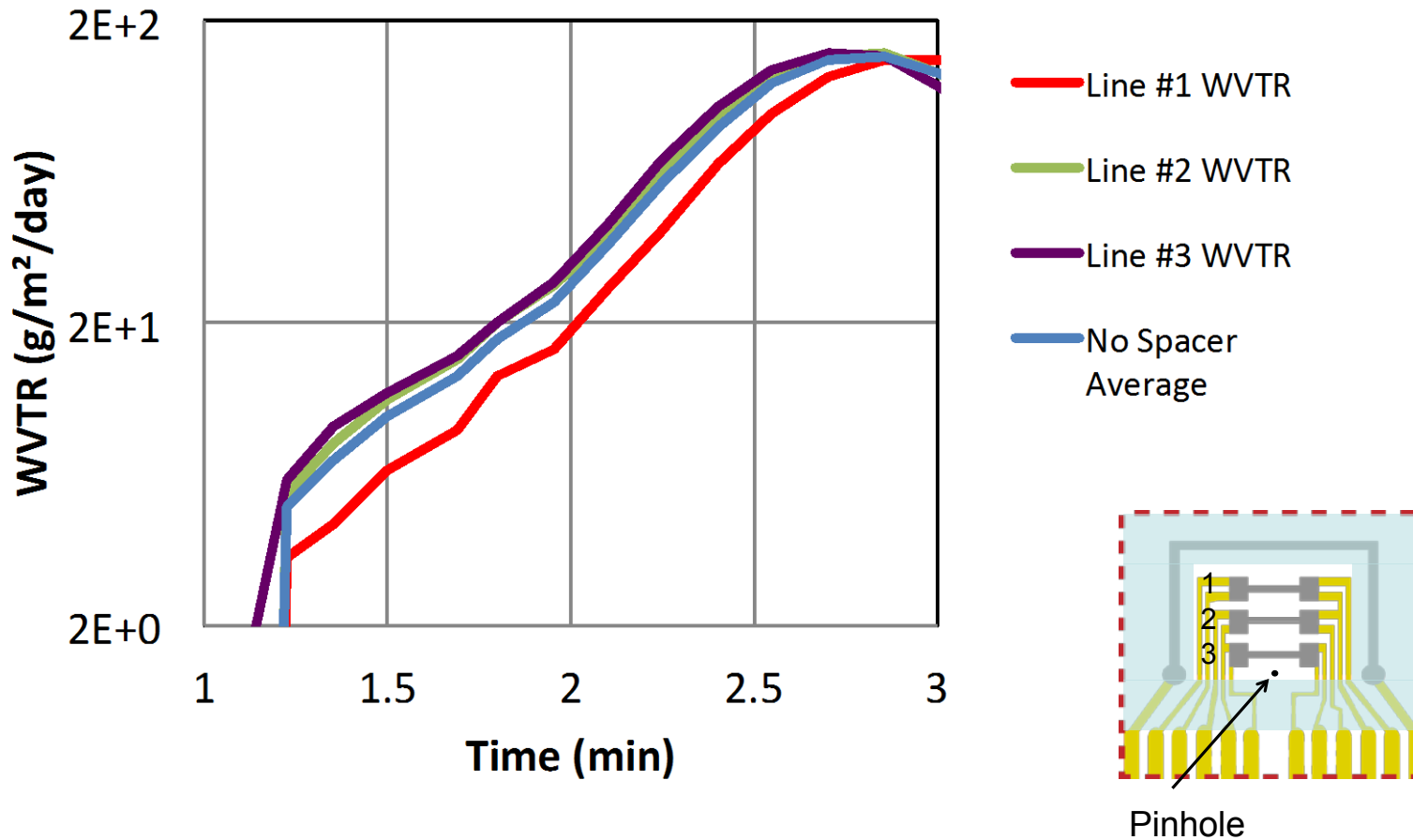
- **Resultant measurement is NOT reflective of the average WVTR!**

Advantage #2: Accounting for defects



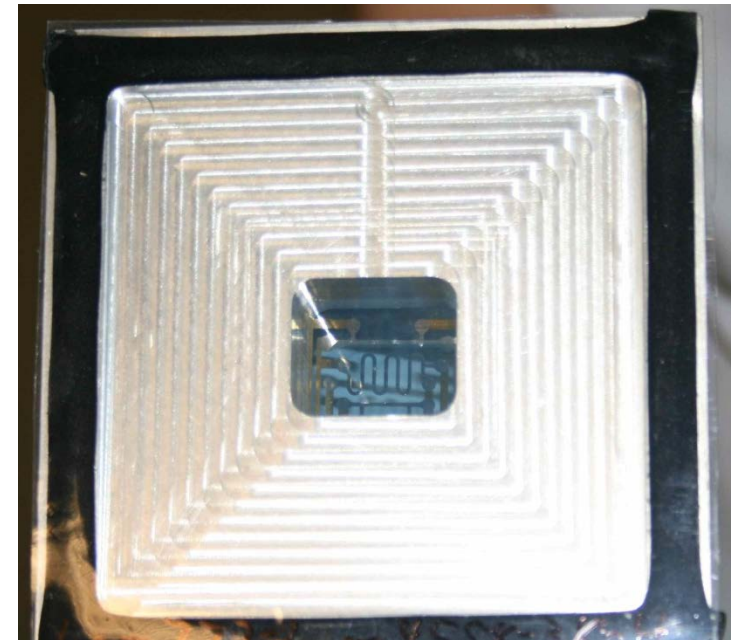
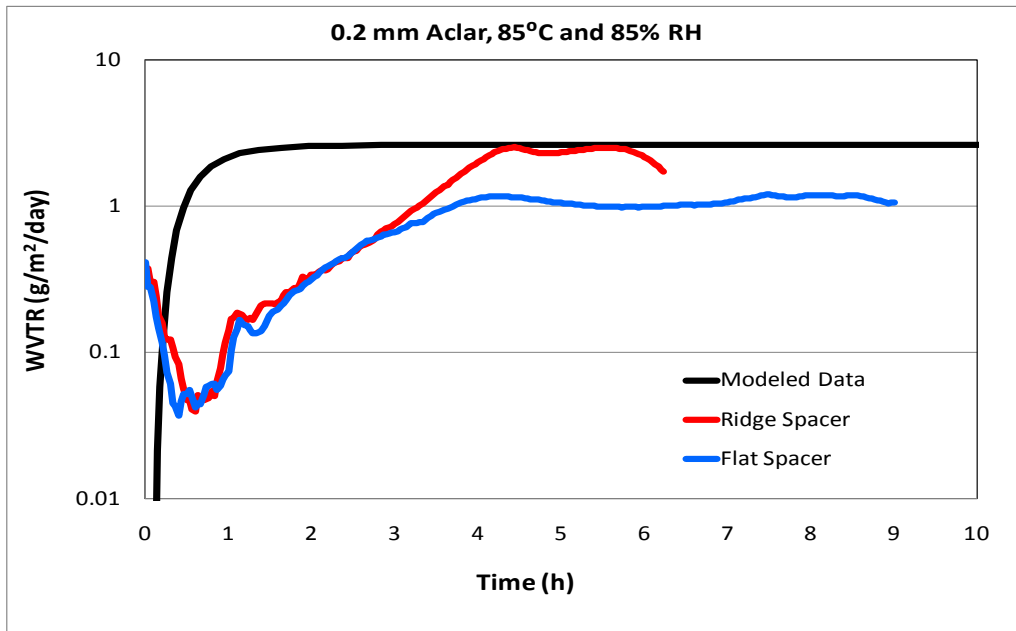
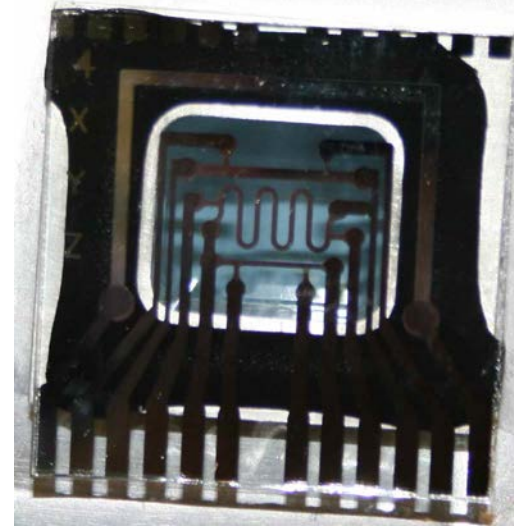
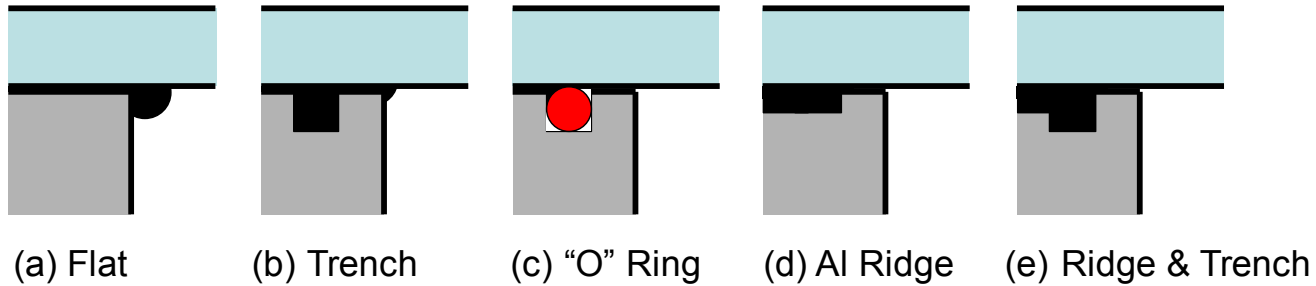
Without a spacer, the trace closest to the pinhole defect produced the highest WVTR

Advantage #2: Accounting for defects



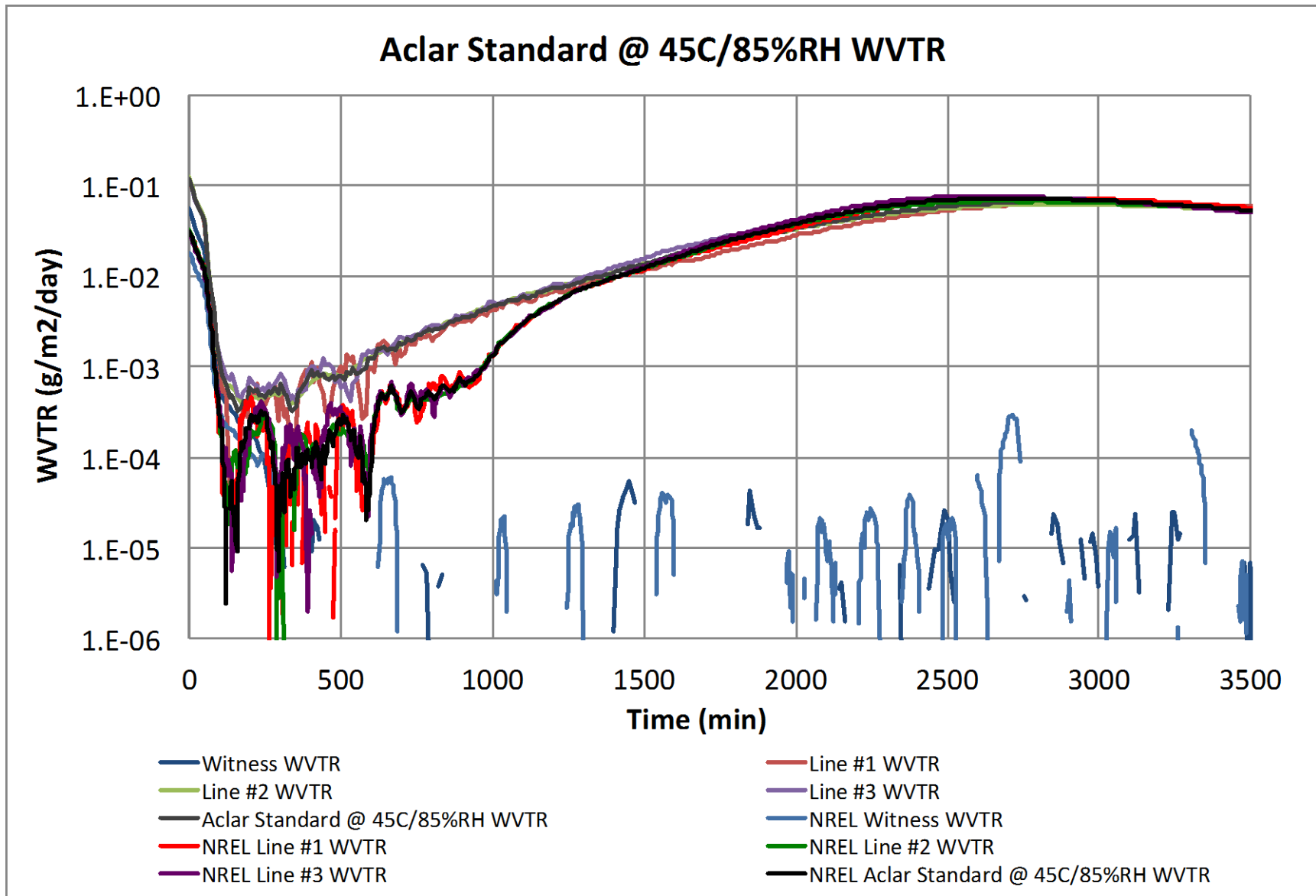
Without a spacer, the trace closest to the pinhole defect produced the highest WVTR.

Advantage #3: Edgeseal Control

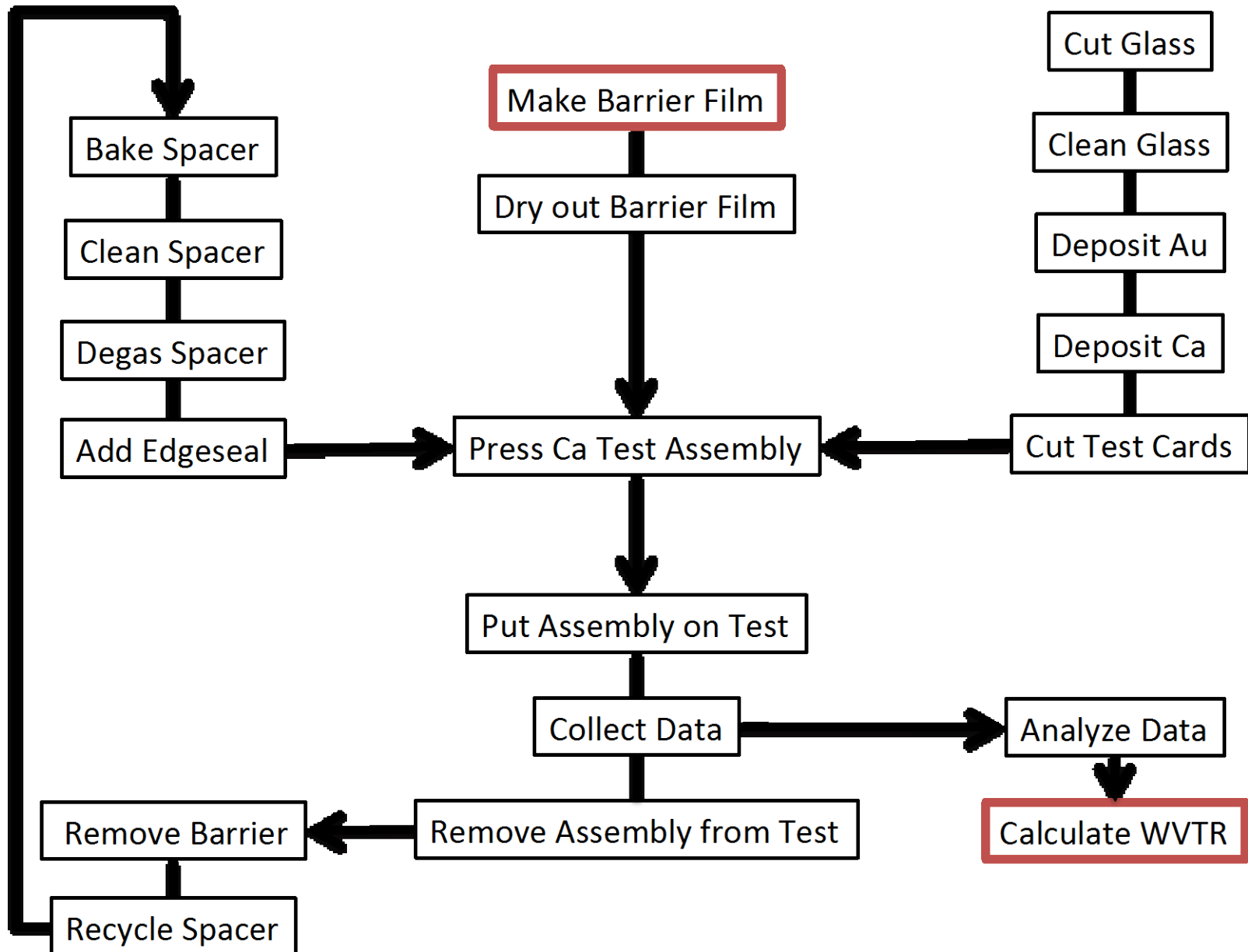


- **Spacer sealing surface design**
 - allows for reproducible testing areas
 - limits the influence of the edgeseal materials on the measurement

Device to Device reproducibility

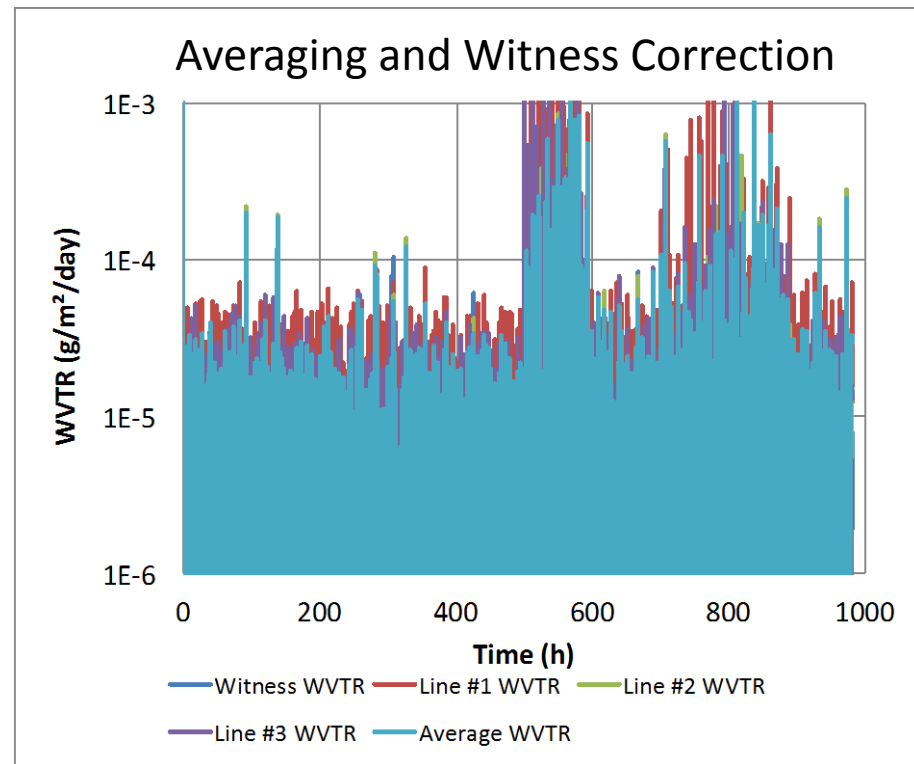
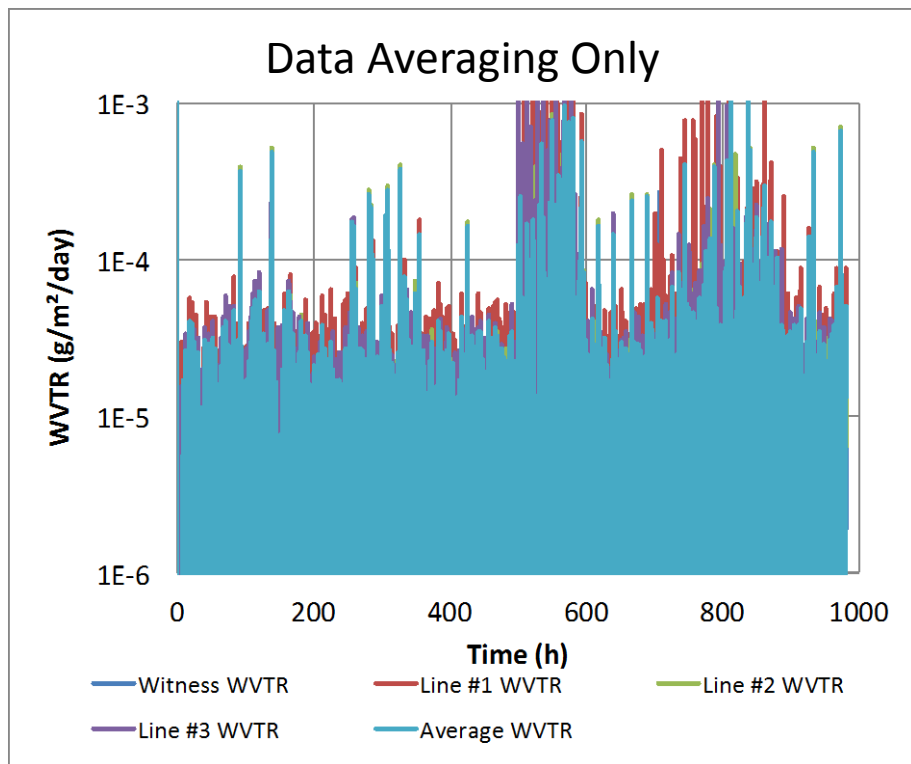


e-Ca Process Flowchart



Witness Correction and Data Averaging

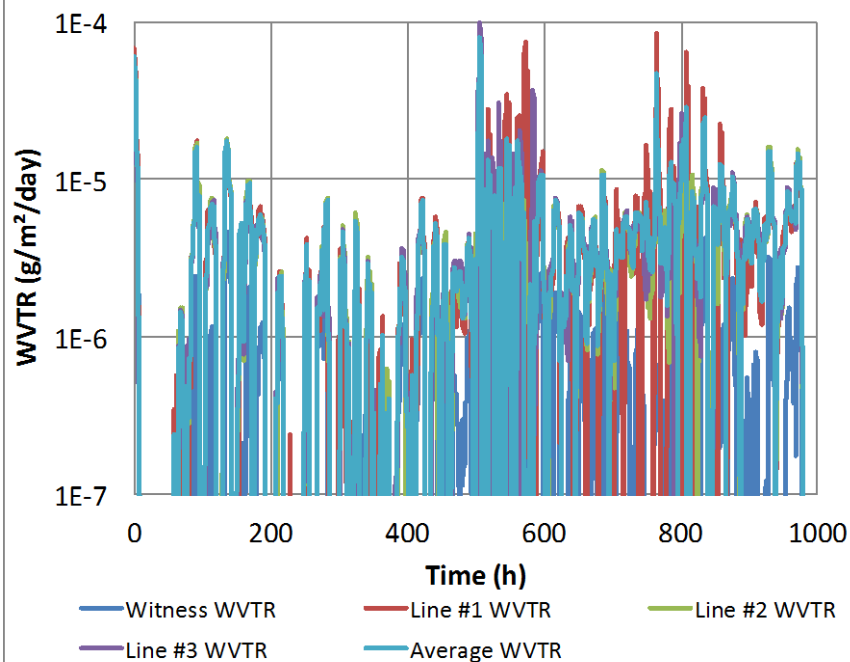
Averaging over 1 hrs



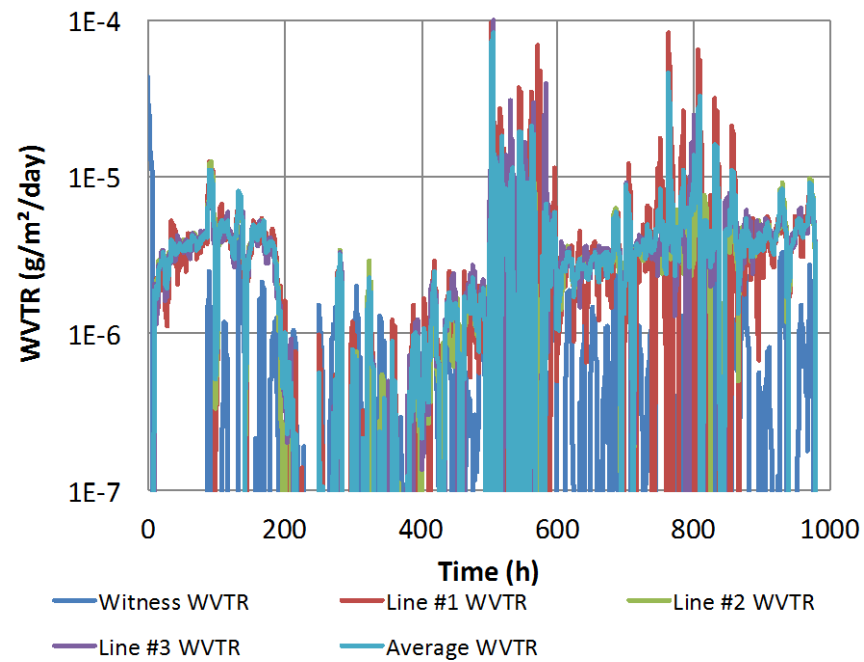
Witness Correction and Data Averaging

Averaging over 12 hrs

Data Averaging Only

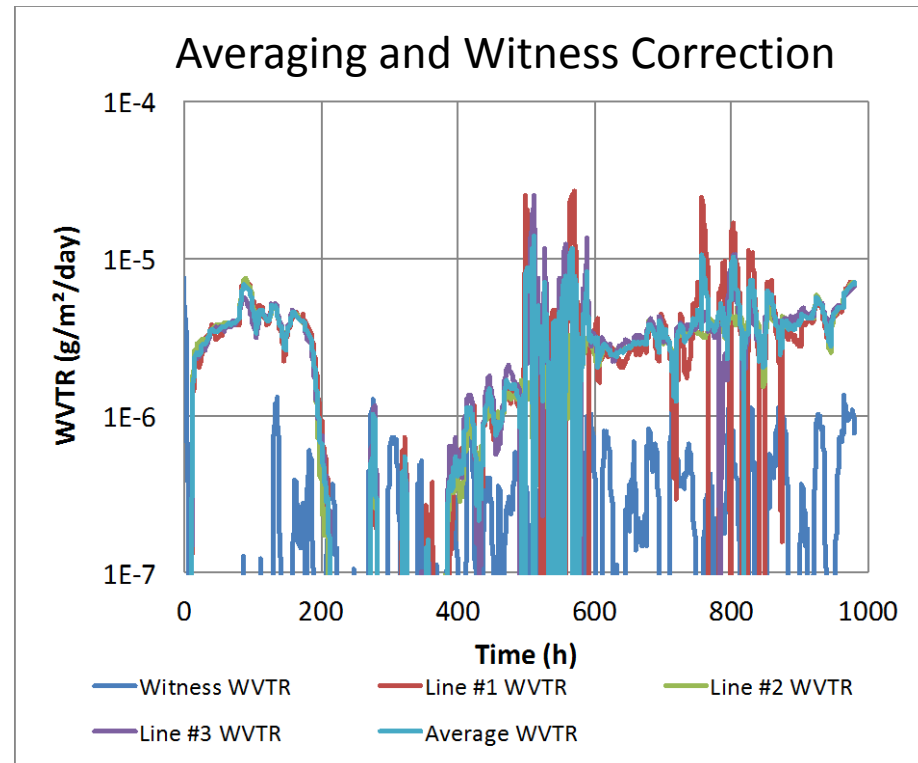
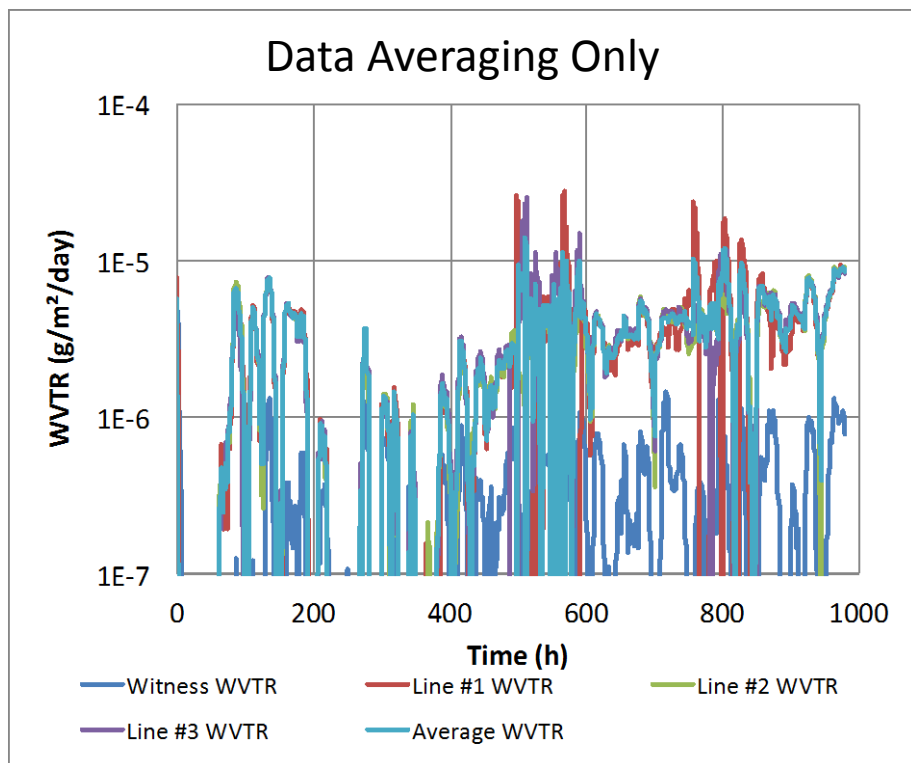


Averaging and Witness Correction



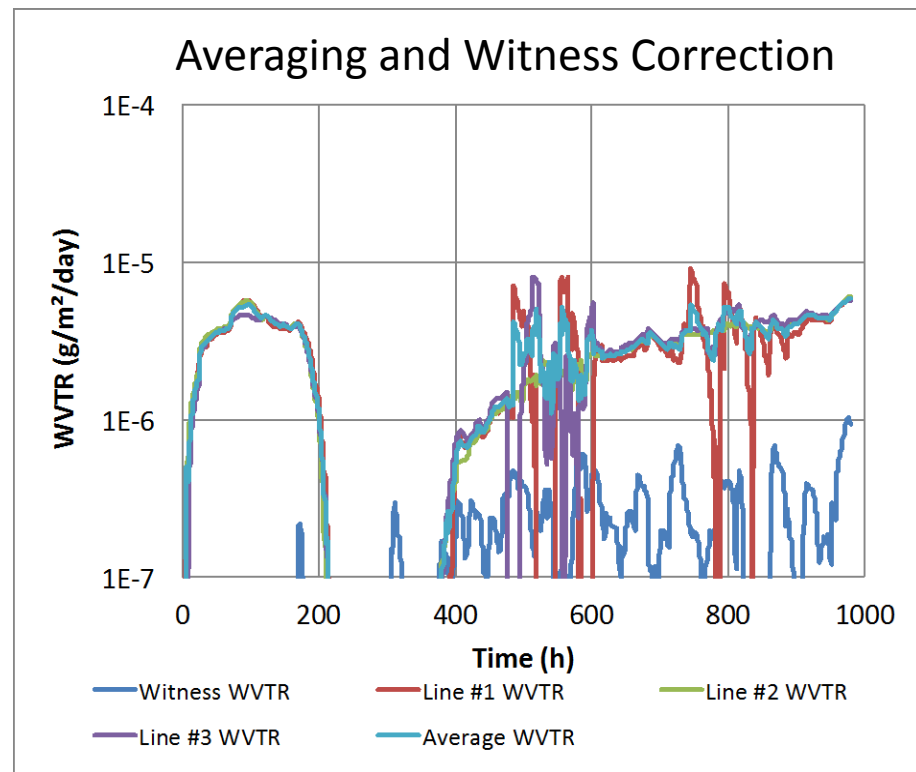
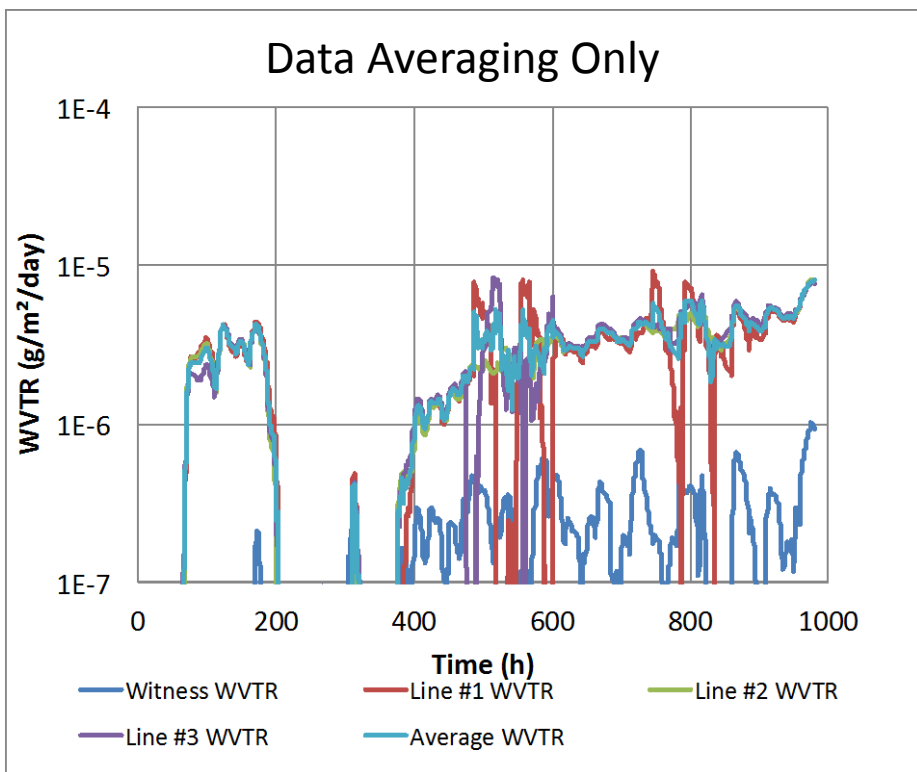
Witness Correction and Data Averaging

Averaging over 24 hrs



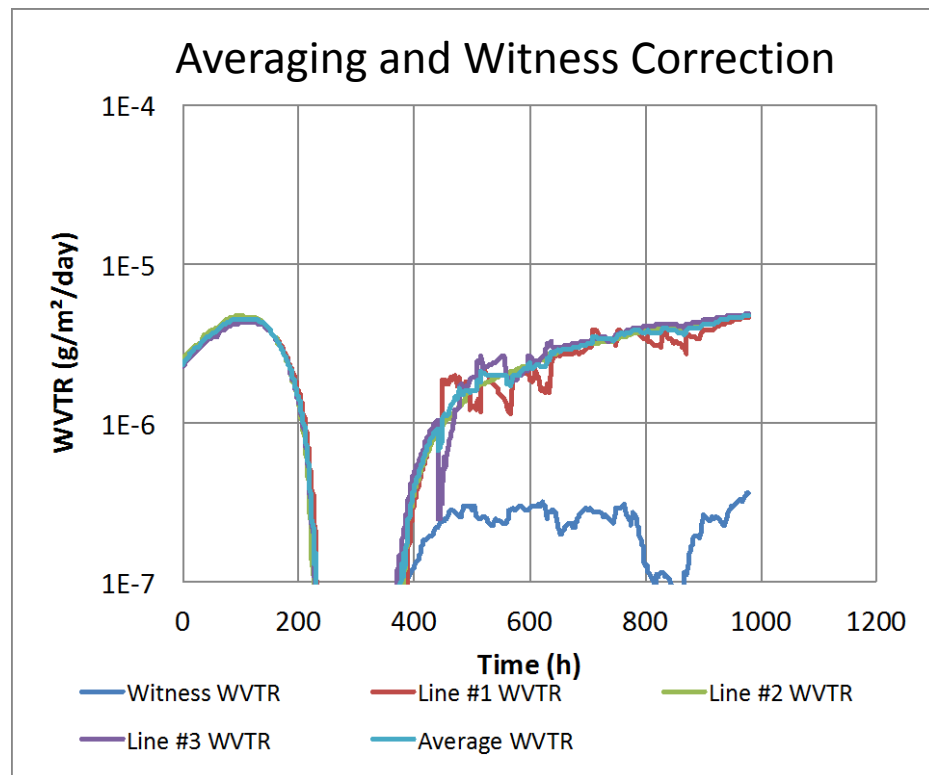
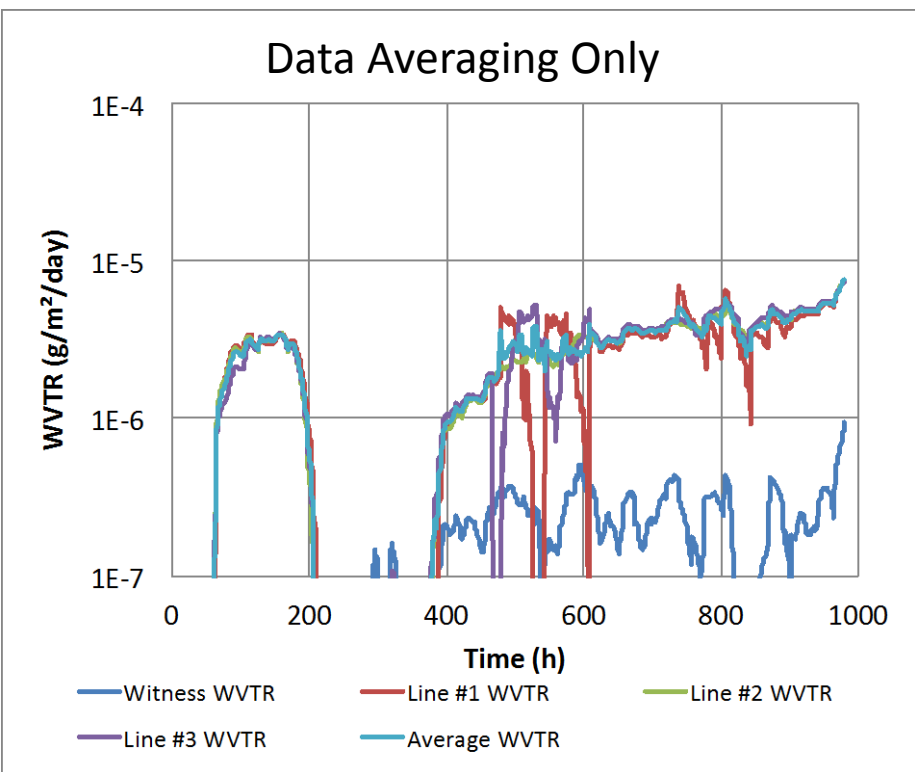
Witness Correction and Data Averaging

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/m²/day range and have confidence that 10^{-7} g/m²/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.**