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NREL's e-Ca Test: A Scalable, High-Sensitivity Water Permeation Measurement Methodology

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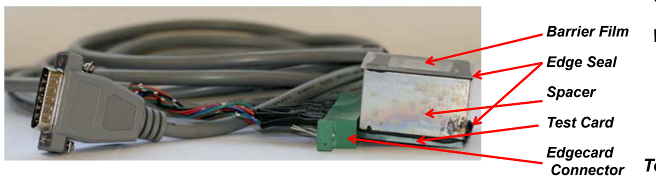
Motivation:

Barriers to oxygen and moisture are critical packaging components for a wide variety of industries. The requirements of each application vary significantly, with differing needs for cost, flexibility, transparency, and permeation rates. It is believed that for next generation technologies like OLEDs and organic PV (OPV) modules, extremely low (10^{-6} to 10^{-8} g/m²/day) water vapor transmission rates (WVTR) may be required. To aid in the research and development of such barriers, a quantitative high-throughput technique that can measure many barriers in parallel under a series of conditions is necessary. NREL's e-Ca Test is this technique!



NREL's e-Ca Test Assembly. *Components are fabricated separately and assembled in a module design, so that the test can be scaled to many simultaneous measurements, while retaining high quantitative sensitivity.*

Common Water Vapor Transport Testing Methods

Test Method	Standards and References	Description	Range (g/m²/day)	Advantages	Disadvantages
Cup Test	ASTM E96	Scavenger method using gravimetric evaluation	0.1 - 1000	• ASTM Standard • Commercially available • High throughput • Wide range of environmental control possible • Inexpensive	• Very low sensitivity • Can not monitor transients • Prone to user error
Isostatic (MOCON)	ASTM F1249	Diffusion cell with coulometric moisture sensor	0.05 - 100 (Permatron) $5x10^{-4}$ - 5 (Aquatron)	• ASTM Standard • Commercially available • Can monitor transients • Intermediate sensitivity	• Temperature (5-50C) • Limited throughput • Sensitivity • Intermediate cost
HTO/ Radioactive Tracer	Dameron; Dunkel	Diffusion cell with detection of water doped with tritium either by ionization chamber or indirectly by hygroscopic salt and scintillation method	10^{-8} - 10	• Extremely good sensitivity • Potentially high throughput (indirect)	• Expensive • Radiation • Not commercially available • Multiplexing difficult for ionization chamber method • Limited environmental control
Optical Ca Test	Nisato	Scavenger method monitoring Ca oxide formation optically	10^{-6} - 10	• Good sensitivity • Potentially high throughput • Wide range of environmental control possible • Can monitor transients	• High capital investment • Not commercially available • No standard - potential for inaccurate numbers
Mass Spectroscopy	Zhang; Renade; Obrien; Hulsmann	Diffusion cell with residual gas analyzer, sometimes paired with programmed valving system to increase sensitivity	10^{-7} - >10	• Very good sensitivity • Can monitor other species than moisture	• High capital investment • Not commercially available • Limited throughput • Limited environmental control
Electrical Ca Test	Paetzold; Choi; NREL	Scavenger method monitoring Ca oxide formation electrically	10^{-7} - 10	• Good sensitivity • Potentially high throughput • Low capital investment • Wide range of environmental control possible	• Not commercially available yet • Moderate level of accuracy.

Ca Test Basics:

The generic electrical Ca Test method uses the resistance of a Ca metal trace or pad as a sensor element to detect water permeation. The premise of the test is that as water permeates through the barrier on test, it will react with the conductive Ca metal to form resistive $Ca(OH)_2$. If the Ca test area and geometry is known, then by measuring the resistance of the Ca as a function of time, the amount of Ca consumed by water that has permeated through the barrier can be determined and, thus, the rate of permeation is obtained.

Assumption:

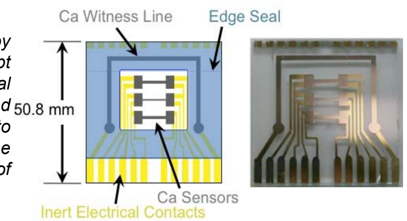
$Ca + 2H_2O(g) \rightarrow Ca(OH)_2 + H_2$ n=2 ΔG^0_{rxn}=-441 (kJ/mol)

Working Equation:

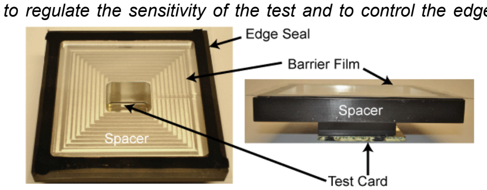
$$WVTR = n\delta\rho_{Ca}\left(\frac{l_{eff}}{w}\right)\left(\frac{A_{Ca}}{A_B}\right)\left(\frac{M_w}{M_{Ca}}\right)\left[\frac{d\left(1/R\right)}{dt}\right]$$

E-Ca Test Components:

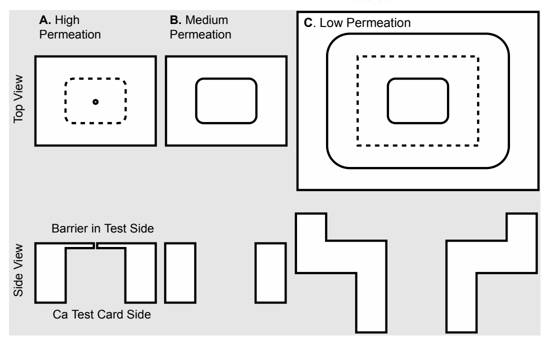
Test Card: *Evaporated Ca traces are contacted by evaporated Ti/Au contacts in a 4-pt configuration. Multiple lines allow several measurements of the WVTR to be made and averaged. A "witness line" is integrated into the test structure to examine failure of the edge seal and to provide an estimate of background noise.*



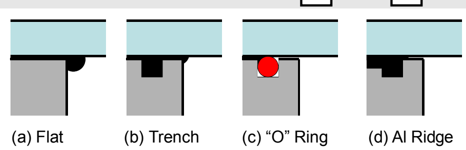
Spacer: *Pinholes and other defects can create localized and/or nonuniform oxidation of Ca, which would give spurious results (see simulation below). In addition to mitigating the effects of pinholes, the spacer serves to regulate the sensitivity of the test and to control the edge seal position and flow.*



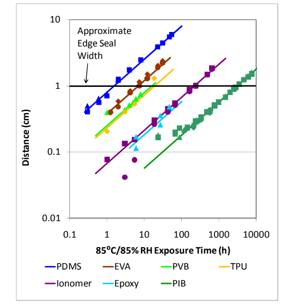
Spacer Designs. *By adjusting the ratio of barrier area to exposed Ca area the sensitivity of the test can be optimized.*



Spacer Surface Design. *The sealing surface of the spacer dictates the edgeseal flow and the exposure of the edgeseal to the inside of the assembly.*

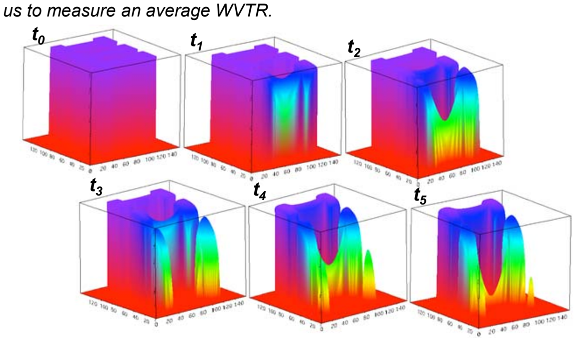


Edgeseal: *Several Commercial edgeseals were tested for moisture ingress and overall durability, documenting the distance moisture moved into the edge seal as a function of time. A desiccated PIB material was best for both overall performance and ease of use.*



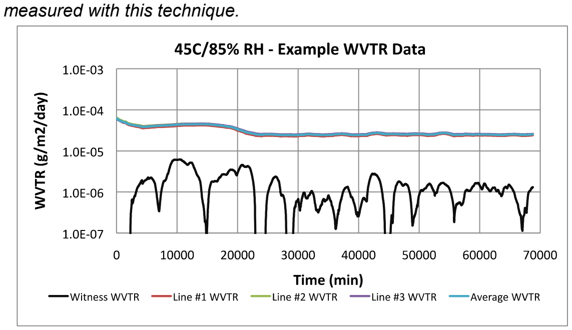
Simulation of Ca Degradation for No Spacer:

In this simulation, we examine the effect of a defect in the barrier near the edge of the aperture. This time-lapse simulation is for the case of ~3 mm separation between the barrier and the test card. This demonstrates the difficulty of introducing redundancy and patterned Ca sensors in traditional Ca test geometries, which place the sensor in contact with the barrier. In NREL's standard spacer designs, such simulations are boring, because each Ca sensor degrades uniformly. This is because of sufficient separation between the barrier and the test card such that diffusion allows us to measure an average WVTR.



Ultimate Sensitivity:

We have demonstrated measurement in the 10^{-5} g/m²/day range and have confidence that 10^{-6} g/m²/day and possibly 10^{-7} g/m²/day can be measured with this technique.



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NREL PV Module Reliability Workshop
Golden, Colorado
February 25-27, 2014
NREL/PO-5K00-61542