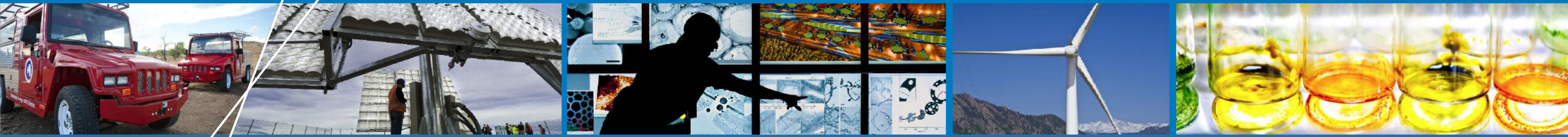
Using Indoor Component Accelerated Stress Testing to Extrapolate to Outdoor Use



2[nd] Atlas/NIST Workshop on Photovoltaic Materials Durability

Michael Kempe, John Wohlgemuth

Wednesday, November 13, 2013

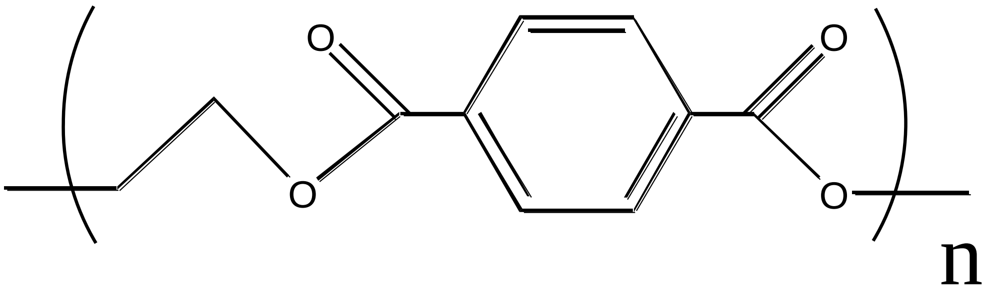
Introduction

- PV modules degrade in response to environmental stresses such as heat, humidity, UV irradiation, CTE mismatch, high voltage, and etc..
- Many degradation processes are driven by complex combinations of these stress factors.
- For some mechanisms, it is possible to quantify the governing kinetics and extrapolate long term performance.
- Getting highly predictive data is possible, but most accurate with narrow, well defined scope.

Outline

- **Look at the hydrolysis of a typical back-sheet made of PET as a case study for comparing 85 ^{o}C/85% RH to outdoor exposure.**
- **Investigate moisture ingress modeling through edge-seal materials.**
- **Look at crystalline Si corrosion model extrapolating to outdoor use.**
    - (uses data from Kent Whitfield et al. Formerly with Solaria).

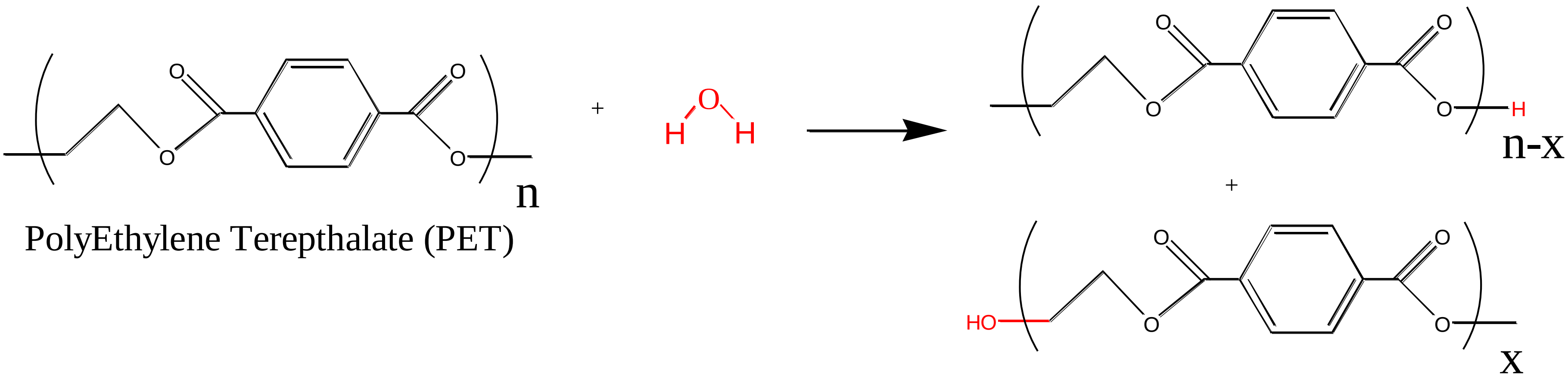
PET Hydrolysis Modeling



PolyEthylene Terepthalate (PET)

- **PET is commonly used in back-sheet materials:**
  - Low cost
  - Good electrical insulator
  - Long term track record
- **Hydrolysis results in embrittlement of PET which can lead to cracking and back-sheet failure.**
- **However, hydrolysis is only one potentially relevant failure mechanism.**

PET Hydrolysis Kinetics



PolyEthylene Terepthalate (PET)

$$\log\left(\frac{C}{C-x}\right) = A \cdot t \cdot RH^2 \cdot e^{\left(\frac{-Ea}{kT}\right)}$$

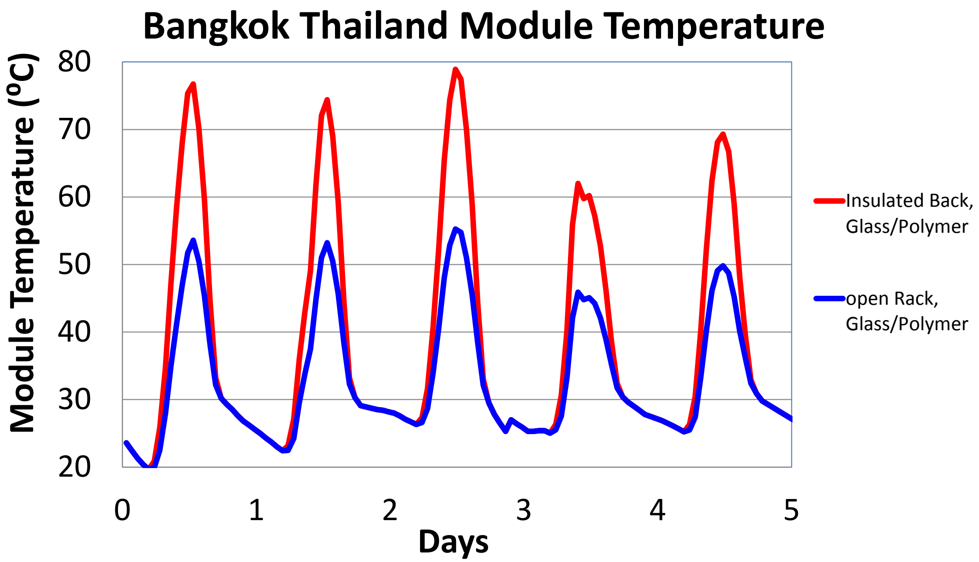
Ea=130 kJ/mol (1.34 eV), *A*=2.84·10^{10} 1/day, *RH* expressed as a percentage.

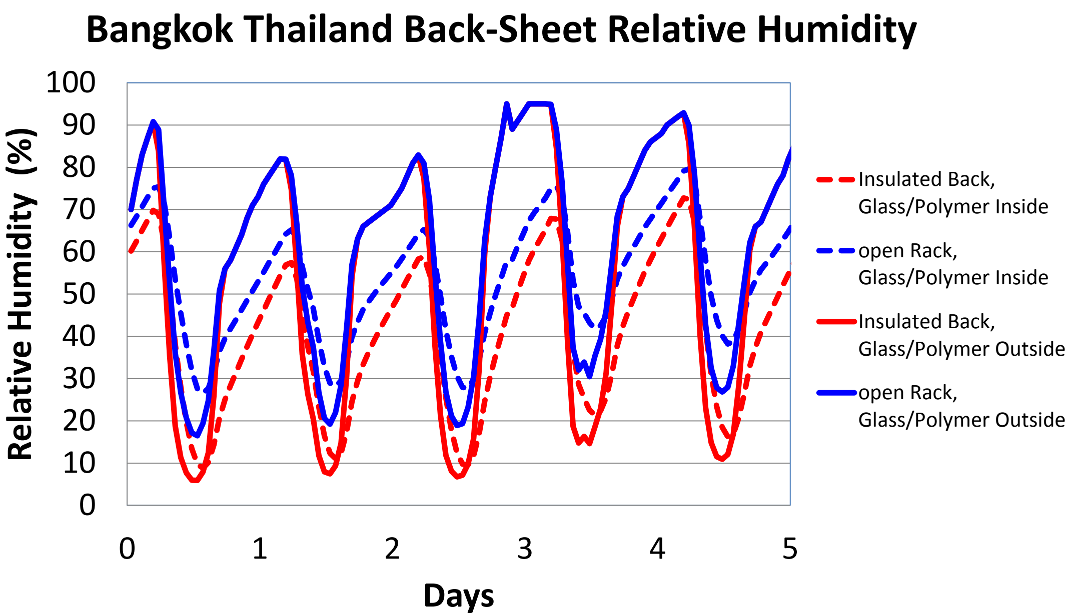
*PET becomes brittle (1/3 initial tensile strength) and “failed” when about 0.55% hydrolysis of ester bonds [log(C/C-x)=~0.0024].

*W. McMahon, H. A. Birdsall, G. R. Johnson, and C. T. Camilli, "Degradation Studies of Polyethylene Terephthalate," Journal of Chemical & Engineering Data, vol. 4, pp. 57-79, 1959.

**J. E. Pickett and D. J. Coyle, "Hydrolysis Kinetics of Condensation Polymers Under Humidity Aging Conditions," Polymer Degradation and Stability, vol. 98, pp. 1311-1320, 2013.

Back-Sheet Exposure





- The back-sheet is dry when it is hot.
- To model PET hydrolysis, we used a RH that is an average of the inside and outside humidity to estimate the degradation of PET.

PET Hydrolysis Results

$$\log\left(\frac{c}{c-x}\right) = A \cdot t \cdot RH^2 \cdot e^{\left(\frac{-Ea}{kT}\right)}$$

	Years to 0.55% degradation (i.e. Hydrolysis Service Life) (y)		1000 Hours $85^0C/85\%$ RH Years equivalent (y)	
	Open Rack	Insulated Back	Open Rack	Insulated Back
Denver, Colorado	13,000	4,900	6,500	2,400
Munich, Germany	11,000	4,400	5,100	2,100
Albuquerque, New Mexico	9,000	3,200	4,400	1,500
Riyadh, Saudi Arabia	8,200	3,000	4,000	1,500
Phoenix, Arizona	3,400	1,300	1,700	630
Miami, Florida	1,100	510	530	250
Bangkok, Thailand	700	310	320	150

PET is predicted to "fail" ($1/3^{rd}$ initial tensile strength) after 2064 h of 85 ^{0}C and 85% RH.

Site Specific Equivalent T and RH

$$R = A \cdot RH^n e^{\left(-\frac{Ea}{kT}\right)}$$

$$T_{eq} = -\frac{Ea}{k ln\left[\frac{\sum e^{\left(-\frac{Ea}{kT}\right)}}{N}\right]}$$

The equivalent temperature (T_{eq}) gives the temperature at RH_{WA} for which constant conditions will produce a degradation rate equivalent to the yearly average.

$$RH_{weighted\ average} = RH_{WA} = \left[\frac{\sum RH^n e^{\left(-\frac{Ea}{kT}\right)}}{\sum e^{\left(-\frac{Ea}{kT}\right)}}\right]^{\frac{1}{n}}$$

RH_{WA} is an average effective relative humidity weighted towards higher temperatures where most of the damage occurs.

PET Hydrolysis Equivalent T and RH

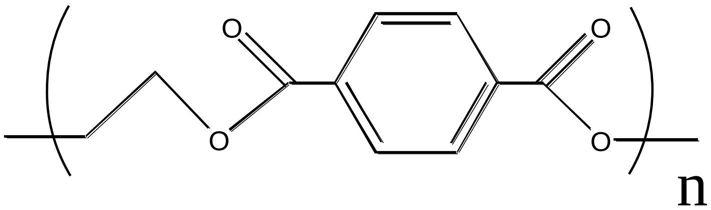
$$\log\left(\frac{c}{c-x}\right) = A \cdot t \cdot RH^2 \cdot e^{\left(\frac{-Ea}{kT}\right)}$$

	Years to 0.55% degradation (i.e. Hydrolysis Service Life) (y)		1000 Hours 85°C/85% RH Years equivalent (y)		**Teq for Ea=129.3 kJ/mol (°C)**		**RH, at Teq for 2nd order Kinetics of PET (%)**	
	Open Rack	Insulated Back	Open Rack	Insulated Back	**Open Rack**	**Insulated Back**	**Open Rack**	**Insulated Back**
Denver, Colorado	13,000	4,900	6,500	2,400	**33**	**54**	**14**	**4.6**
Munich, Germany	11,000	4,400	5,100	2,100	**28**	**46**	**25**	**8.4**
Albuquerque, New Mexico	9,000	3,200	4,400	1,500	**37**	**58**	**13**	**4.2**
Riyadh, Saudi Arabia	8,200	3,000	4,000	1,500	**48**	**70**	**5.6**	**2.0**
Phoenix, Arizona	3,400	1,300	1,700	630	**46**	**68**	**9.8**	**3.3**
Miami, Florida	1,100	510	530	250	**37**	**54**	**36**	**14**
Bangkok, Thailand	700	310	320	150	**41**	**59**	**33**	**12**

PET is predicted to "fail" (1/3rd initial tensile strength) after 2064 h of 85 °C and 85% RH.

$85^{o}C/85\%$ RH is a Large Acceleration For PET

$$log\left(\frac{c}{c-x}\right) = A \cdot t \cdot RH^{2} \cdot e^{\left(\frac{-Ea}{kT}\right)}$$



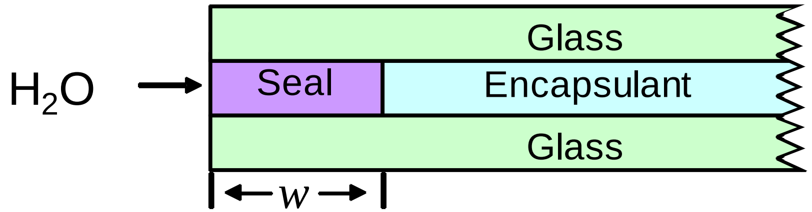
PolyEthylene Terepthalate (PET)

	Teq for Ea=129 kJ/mol (^{o}C)		RH, at Teq for 2nd order Kinetics of PET (%)		Acceleration Factor Relative to $85^{o}C/85\%$ RH	
	Open Rack	Insulated Back	Open Rack	Insulated Back	Open Rack	Insulated Back
Denver, Colorado	33	54	14	4.6	59000	22000
Munich, Germany	28	46	25	8.4	46000	19000
Albuquerque, New Mexico	37	58	13	4.2	39000	14000
Riyadh, Saudi Arabia	48	70	5.6	2.0	36000	13000
Phoenix, Arizona	46	68	9.8	3.3	15000	6000
Miami, Florida	37	54	36	14	4800	2000
Bangkok, Thailand	41	59	33	12	2900	1400

PET is predicted to "fail" (1/3rd initial tensile strength) after 2064 h of 85 ^{o}C and 85% RH.

Edge Seal Modeling

- **The use of fillers, pigments, and desiccants makes the determination of modeling parameters much more difficult.**
  - –Each inorganic component will have unique absorption/desorption and diffusion characteristics.
  - –The polymer matrix may have its own temperature and RH dependent diffusivity and solubility parameters.
  - –Thus, a complete model would involve 10 to 20 adjustable parameters.



Simplified Edge Seal Model

$$S_m = S_o e^{\left(-\frac{Ea_s}{kT}\right)} \frac{RH\%}{100\%}$$

Mobile phase water absorption is split between the polymer matrix and the mineral components. Assume linearity with relative humidity.

$$D_{eff} = D_o e^{\left(-\frac{Ea_D}{kT}\right)}$$

Mobile phase water diffusivity is an effective diffusivity. This accounts for a rapid equilibration between adsorbed and dissolved water.

$$R_{H_2O}$$

A non-reversible reaction with water that immobilizes the water.

Model Parameters: R_{H_2O}, S_o, Ea_s

R_{H_2O}

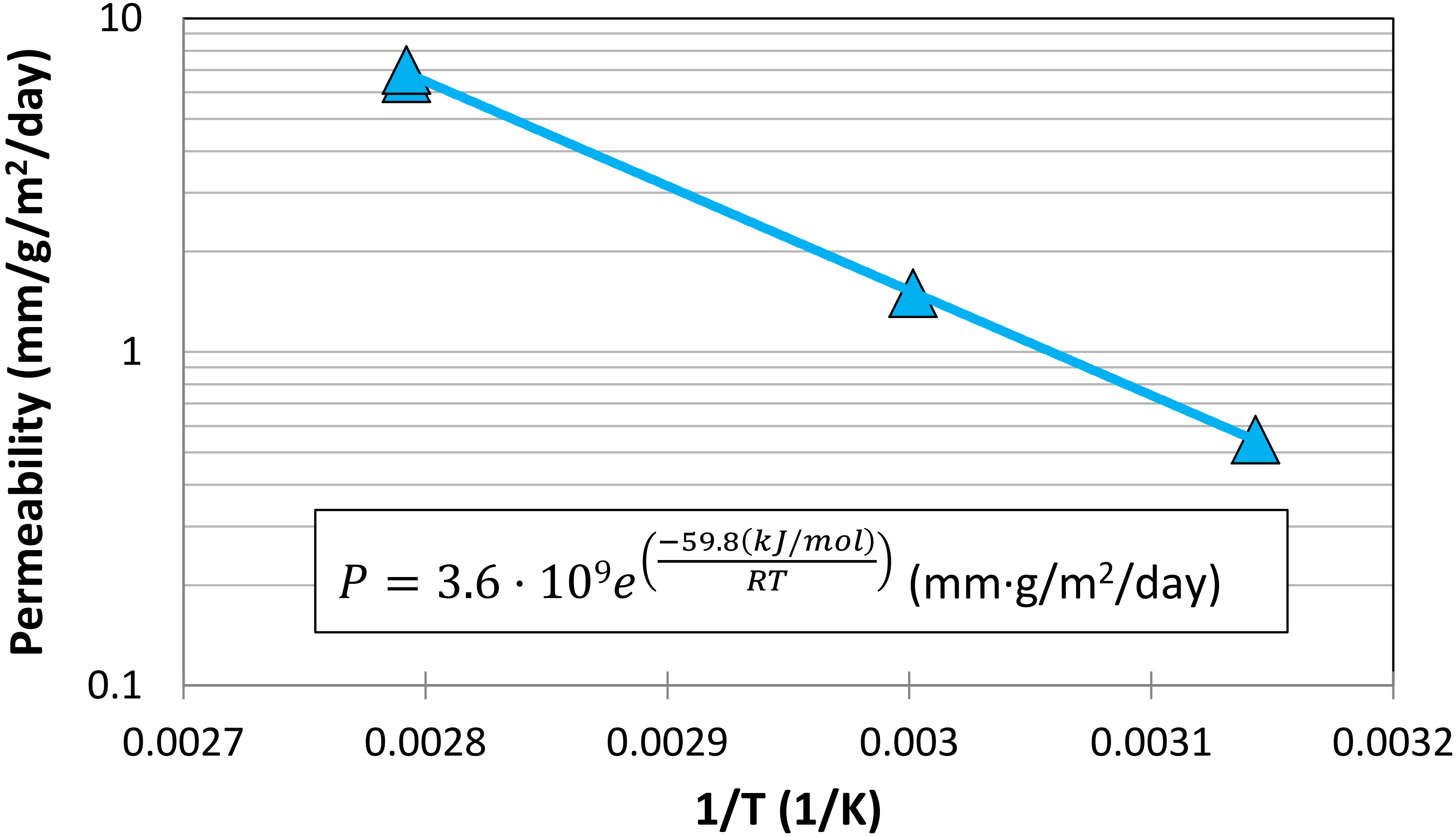
Measured by weighing samples before humidity exposure, after humidity exposure, and after drying. This gives values for both the reversible, *S*, and the irreversible moisture absorption, R_{H_2O}.

S_o, Ea_S

Measured by exposing material to controlled humidity, 85% RH at 45ºC and 85ºC, then drying in a TGA to determine reversible moisture loss. At both temperatures, values between 0.35 and 0.45% were obtained. This measurement was probably affected by adsorption on filler material and by loss of other volatile components.

A value of 5 kJ/mol was chosen as the lowest reasonable value, and S_o was set so *S* would be 0.35% at 45ºC.

Model Parameter: Ea_D

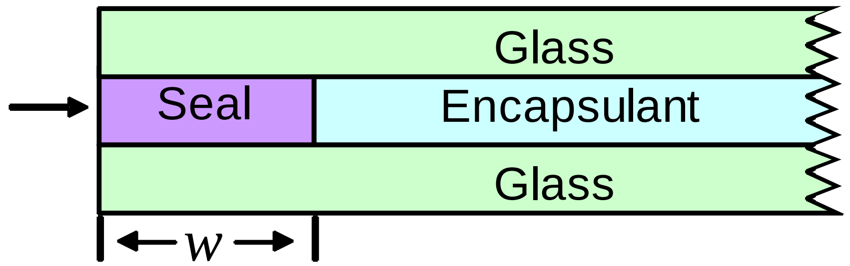


Permeability=WVTR·thickness=$D \cdot S$ for Fickian materials. Therefore, as a first order approximation $Ea_D = Ea_P - Ea_S$.

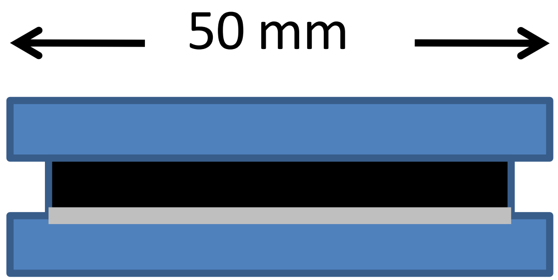
$$Ea_D = 54.8\ kJ/mol$$

Test Sample Designed to Mimic Module Edge

Module Edge H_2O →



Test Sample H_2O →



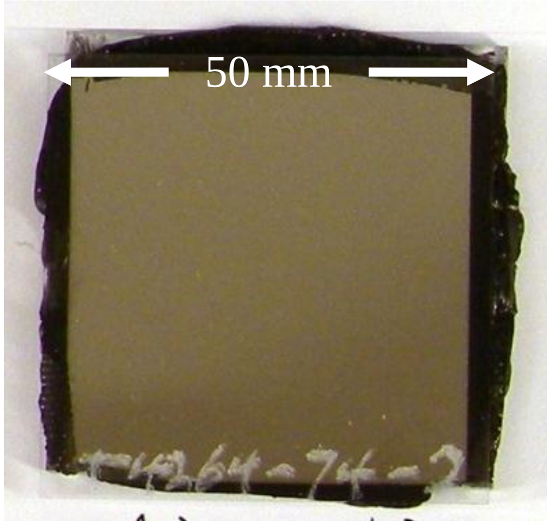
$$Ca + 2\ H_2O \rightarrow Ca(OH)_2 + H_2$$

Oxidation of Ca Indicates Moisture Ingress

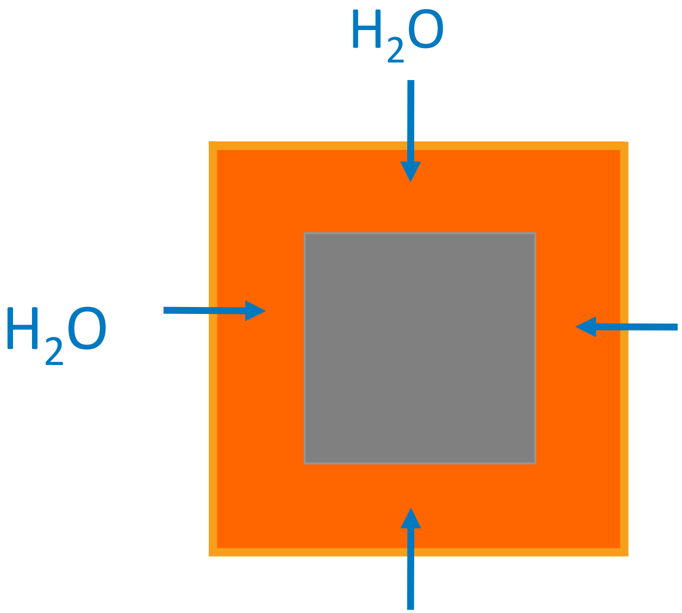
$$Ca + 2\,H_2O \rightarrow Ca(OH)_2 + H_2$$

Mirror-Like → Transparent

Unexposed



1500 h, 85°C, 85% RH

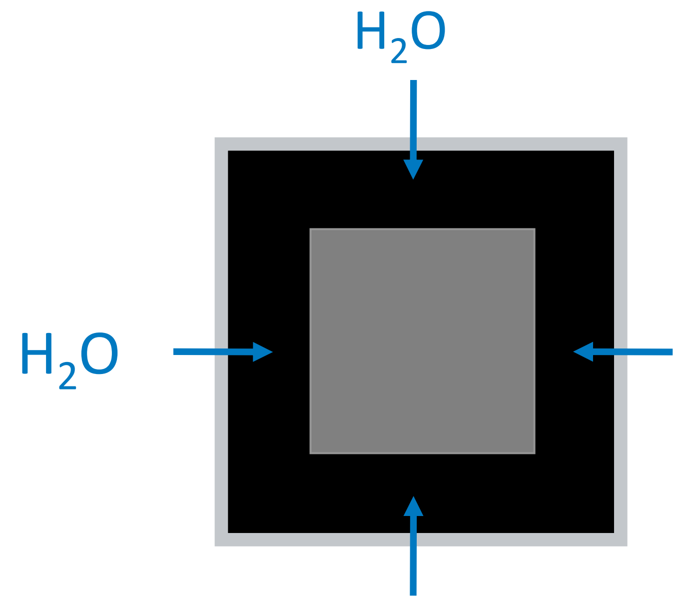


Ca test samples PIB #2 based, desiccant filled edge seal. Samples are 50 mm by 50 mm.

Moisture Ingress Rate Governed by Diffusion

$$\frac{\partial C}{\partial t} = \nabla \left(D \nabla C \right)$$

$$X \sim t^{1/2} \sim \sqrt{\frac{t \cdot D_{eff} S}{C_D}},$$

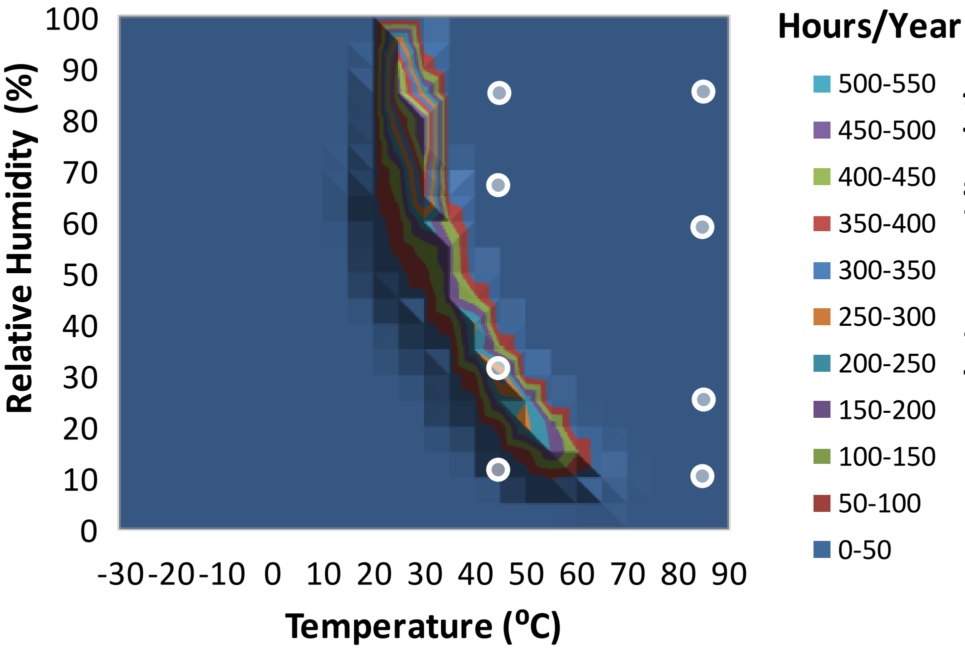


Moisture ingress measured at 45°C and 85°C, with RH held at 85%, and at lower levels using saturated salt solutions of LiCl, MgCl, or $NaNO_3$.

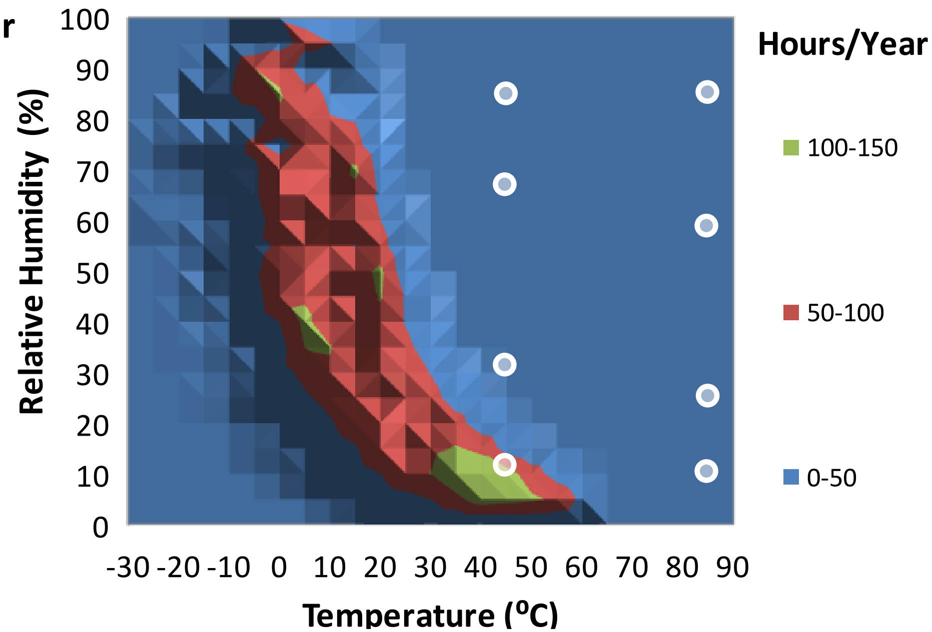
RH (%)	45 (°C)	85 (°C)
$NaNO_3$	67%	59%
MgCl	31%	25%
LiCl	11%	10%

Minimizing Extrapolation Reduces Uncertainty

Bangkok, Thailand



Denver, Colorado



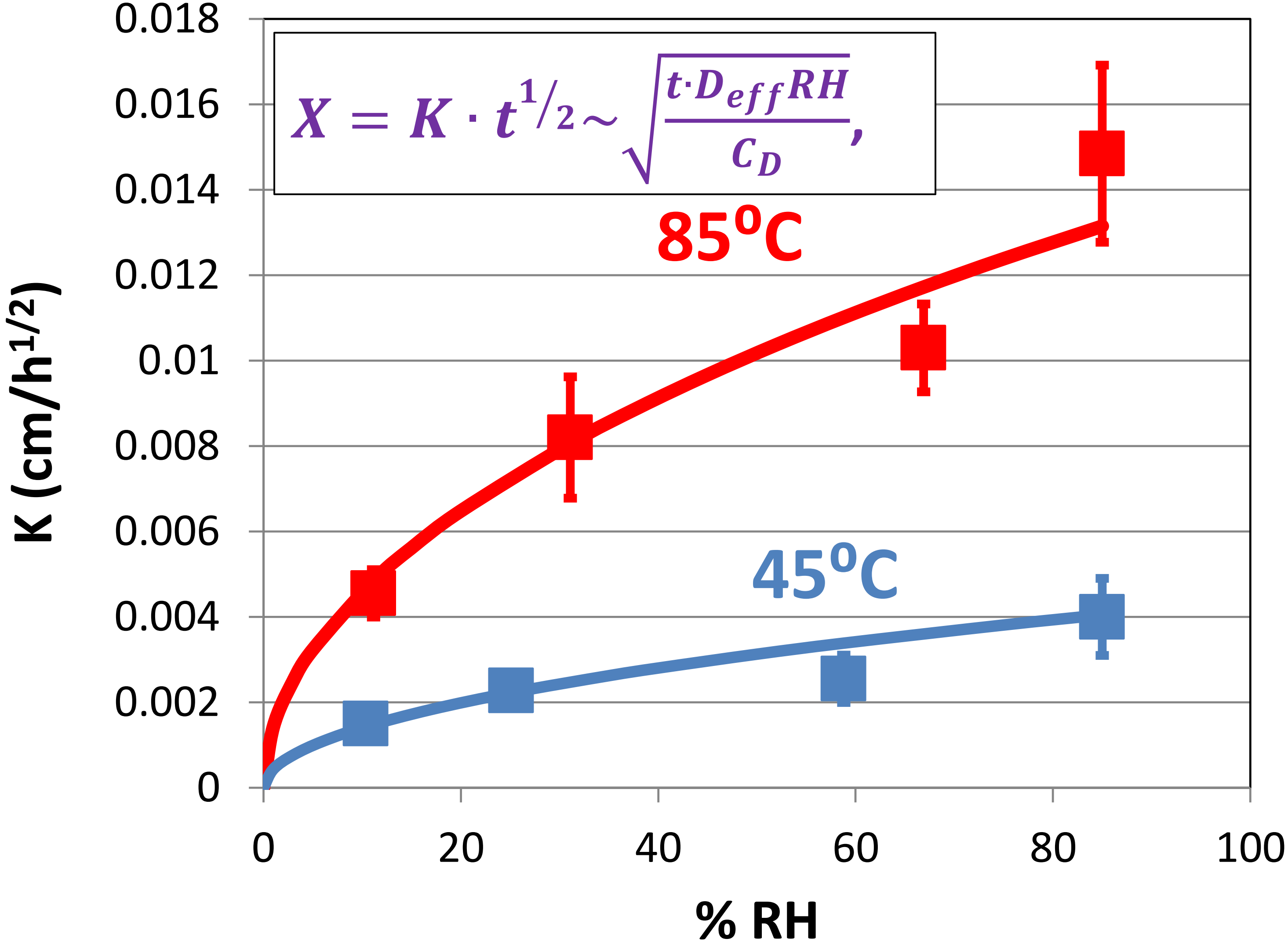
1. Conditions of 85°C and 85% RH are well beyond what will ever be seen in a deployed module.

2. Testing at low temperatures and low humidity takes an extremely long time, but it vital for reasonably minimizing extrapolation uncertainties.

RH (%)	45	85
	(°C)	(°C)
$NaNO_3$	67%	59%
MgCl	31%	25%
LiCl	11%	10%

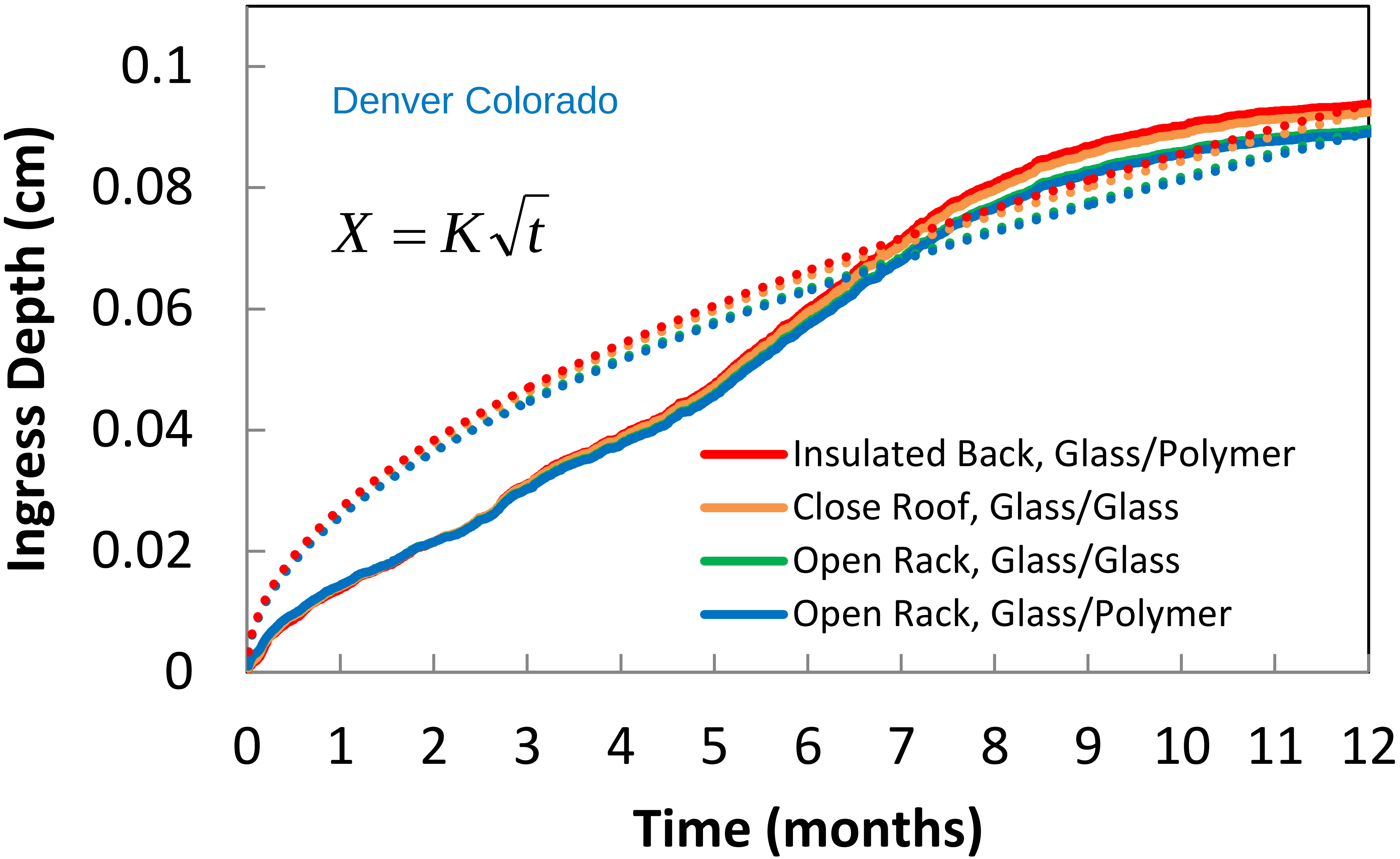
(C) Denver, Colorado

Permeation Measured at Low RH



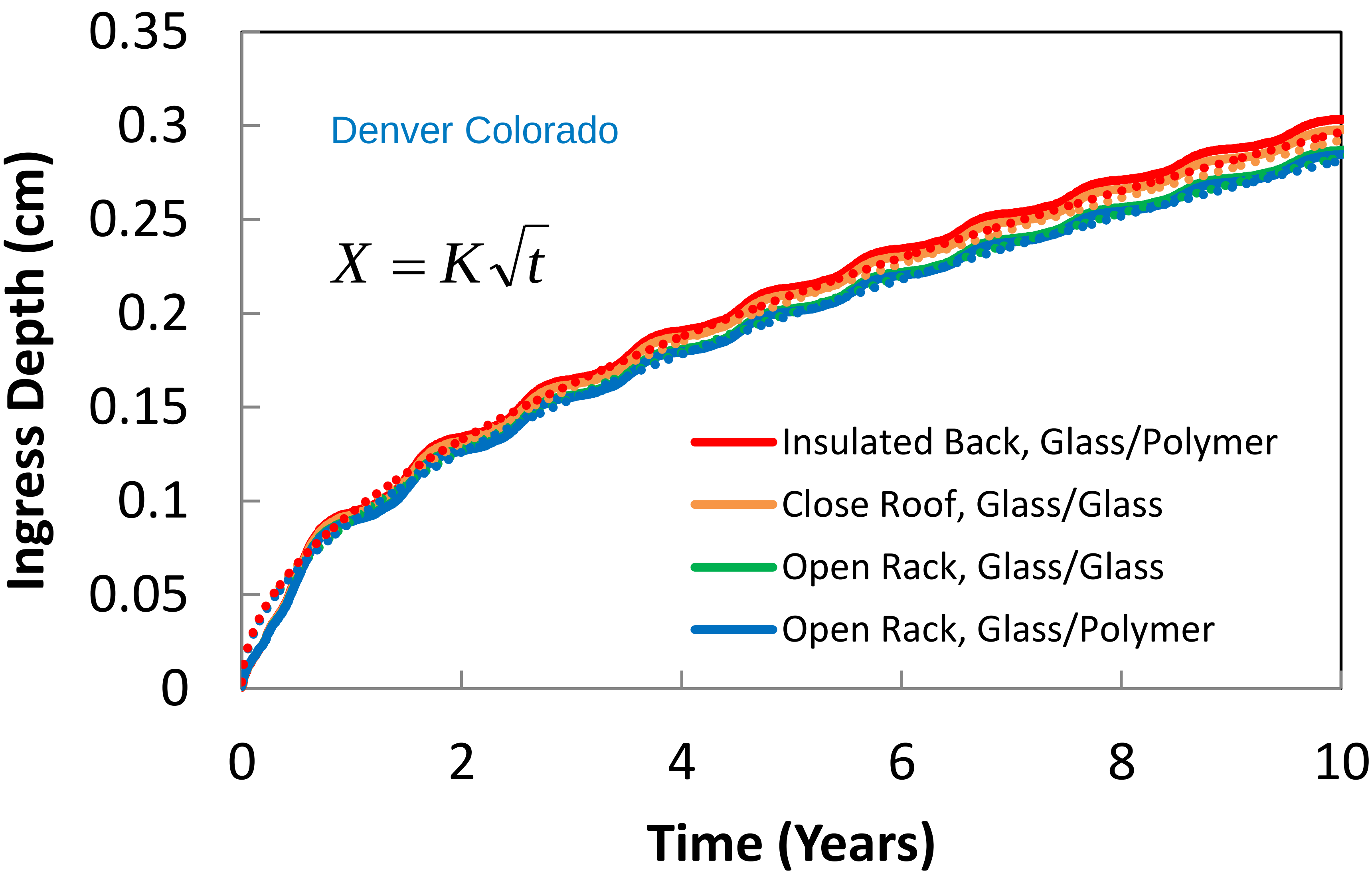
D_o Estimate from other parameters and fit to Ca data. Specifically the difference between 45 and 85°C curves.

Ingress Estimated Using Finite Element Analysis



Used TMY3 Data and Temperature estimates similar to King et al, and Kurtz et al.

Square Root Relation Works to Longer Times



Used TMY3 Data and Temperature estimates similar to King et al, and Kurtz et al.

Results for Different Climates

		Modeled K	Modeled 25 y required width	Modeled 25 y equivalent time at 85°C/85% RH	Modeled 25 y equivalent time at 45°C/85% RH
$D_o\,(cm^2/s)$=	0.33				
$Ea_D\,(kJ/mol)$=	47				
$S_o\,(g/cm^3)$=	0.16				
$Ea_S\,(kJ/mol)$=	5				
Reactive Ca absorption (g/cm^3)=	0.047	$(cm/h^{1/2})$	(cm)	(h)	(years)
Denver, Colorado	Open Rack	0.00087	0.40	900	1.2
	Insulated Back	0.00103	0.44	1,000	1.4
Munich, Germany	Open Rack	0.00096	0.45	1,100	1.5
	Insulated Back	0.00107	0.47	1,200	1.7
Riyadh, Saudi Arabia	Open Rack	0.00102	0.47	1,200	1.6
	Insulated Back	0.00124	0.51	1,400	1.9
Phoenix, Arizona	Open Rack	0.00128	0.56	1,700	2.4
	Insulated Back	0.00153	0.61	2,000	2.8
Miami, Flordia	Open Rack	0.00199	0.84	3,700	5.3
	Insulated Back	0.00225	0.90	4,300	6.1
Bangkok, Thailand	Open Rack	0.00228	0.96	4,900	6.9
	Insulated Back	0.00258	1.03	5,600	7.9

A sensitivity analysis gave about ±15% on K and Width, and ±30% on 25 yr equivalent time.

Parameters to Characterize an Environment

$$T_{eq} = \frac{-Ea}{k}\left(\frac{\sum_{i=0}^{n} e^{\left(\frac{-Ea_D}{kT_i}\right)}}{n}\right),$$

$$S_{DW} = \frac{\sum S \cdot RH \cdot D_{eff}}{\sum D_{eff}}$$

- **The ability of the edge seal to take in water and hold it is related to the equilibrium solubility at the air/polymer interface and to the diffusivity. Therefore a diffusivity weighted solubility should describe a constant equivalent external water condition.**

Simplified Equivalent Environment

D_o (cm^2/s)=		17.0	Modeled K	T_{eq} using Ea_D	Diffusivity Weighted Solubility	RH at T_{eq} and Diffusivity Weighted Solubility	K at Diffusivity Weighted Temperature and Solubility
Ea_D (kJ/mol)=		54.8					
S_o (g/cm^3)=		0.0326					
Ea_S (kJ/mol)=		5.00					
Reactive Ca absorption (g/cm^3)=		0.0320	($cm/h^{1/2}$)	(°C)	(g/cm^3)	(%)	($cm/h^{1/2}$)
Denver, Colorado	Open Rack		0.000864	23.2	0.00714	21.9	0.000874
	Insulated Back		0.000931	37.9	0.00276	8.5	0.000963
Munich, Germany	Open Rack		0.000951	17.9	0.0136	41.8	0.000966
	Insulated Back		0.00101	29.3	0.00623	19.2	0.00104
Riyadh, Saudi Arabia	Open Rack		0.00099	39.7	0.00275	8.5	0.00103
	Insulated Back		0.00108	55.7	0.00111	3.4	0.00114
Phoenix, Arizona	Open Rack		0.00120	37.9	0.00439	13.5	0.00122
	Insulated Back		0.00131	54.1	0.00174	5.3	0.00135
Miami, Florida	Open Rack		0.00179	32.2	0.0149	45.9	0.00180
	Insulated Back		0.00192	43.6	0.00753	23.1	0.00196
Bangkok, Thialand	Open Rack		0.00205	36.5	0.0140	43.1	0.00206
	Insulated Back		0.00219	48.2	0.00710	21.8	0.00224

Crystalline Silicon Metallization Corrosion

- **Whitfield et al. measured cell performance of three different cell types at a variety of Temperatures and relative humidity levels.**

Condition	Cell Type	Temp. (°C)	Rel. Humidity (%)
1	A/B/C	85	85
2	A/B/C	110	100
3	A/B/C	120	100
4	A/B/C	125	100
5	A/B/C	130	80
6	A/B/C	130	90
7	A/B/C	130	95

Table 3 Design of experiments (DOE).

K. Whitfield, A. Salomon, S. Yang, I. Suez, "Damp Heat Versus Field Reliability for Crystalline Silicon", 38th IEEE PVSC, Austin TX, 2012.

Empirical Model Forms and Parameters

Model #1

$$TF_1 = F_1 \cdot e^{c \cdot RH} e^{\frac{Ea_1}{kT}}$$

Model #2

$$TF_2 = F_2 \cdot RH^b e^{\frac{Ea_2}{kT}}$$

Exponential Corrosion Model

Cell	F1 (hr)	C (no units)	Ea1 (eV)
A	1.13E-04	-3.03	0.595
B	7.47E-05	-2.62	0.597
C	5.77E-05	-5.42	0.677

Power Law Model

Cell	F2 (hr)	b (1/%)	Ea2 (eV)
A	1.824	-2.77	0.596
B	0.320	-2.39	0.597
C	1884	-4.95	0.677

Table 4 Best fit acceleration model parameters.

K. Whitfield, A. Salomon, S. Yang, I. Suez, "Damp Heat Versus Field Reliability for Crystalline Silicon", 38th IEEE PVSC, Austin TX, 2012.

Differentiation by Extrapolation to Use Environment

	Cell Metallization Corrosion, Open Rack Glass/Polymer Module Time to Failure (y)					
	Model 1, Exponential			Model 2, Power Law		
	Cell A	Cell B	Cell C	Cell A	Cell B	Cell C
Denver	62	62	454	276.5	200	1798.4
Albuquerque	50	50	430	372.9	245	3818.1
Miami	17	17	59	27.9	23	88.8
Phoenix	27	27	237	292.9	186	2986.6
Munich	53	53	202	90.0	77	277.8
Bangkok	13	13	48	23.5	19	77.8
Riyadh	27	27	272	521.2	341	3070.6
85°C/85% RH (h)	2029	2027	1936	2010.3	1970.8	1782.4

- **The worst cell at 85°C/85% RH was predicted to be the best.**

Acceleration Factors Vary Widely

Acceleration Factors Open Rack Glass/Polymer	PET Hydrolysis	Edge Seal Moisture Ingress	Cell C Corrosion Kinetics	
			Model 1, Exponential	Model 2, Power Law
Denver, Colorado	59000	250	2057	5134
Munich, Germany	46000	200	913	793
Riyadh, Saudi Arabia	36000	180	1233	8766
Phoenix, Arizona	15000	130	1073	8526
Miami, Florida	4800	58	266	254
Bangkok, Thailand	2900	45	216	222

85/85 Stress Testing

Conclusion

- To have accurate accelerated stress tests, you must use small acceleration factors or know the kinetics very well.
- It is likely that each degradation mechanism will have different activation energies.
- Different degradation kinetics can have significantly different responses in a given environment.
- Keeping acceleration close to use conditions and at low values will decrease the associated uncertainty.

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