

Polymers/Organic Materials Aging Overview

SAND2011-5864C

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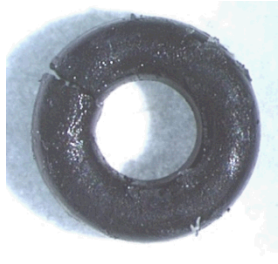
**Energy Rubber Group
2011 Educational Symposium and Technical Meeting
Sept 13-15, 2011
Galveston, Texas**

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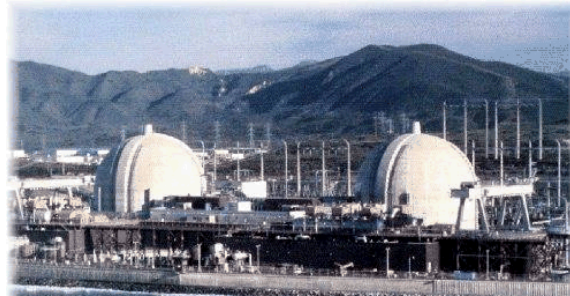


Organic Materials Problems; Organic Materials Aging and Degradation

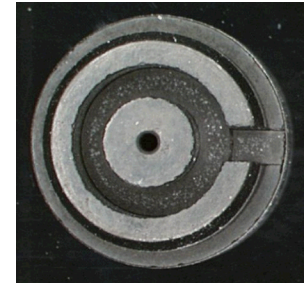
2



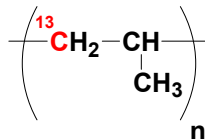
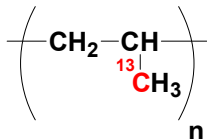
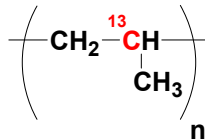
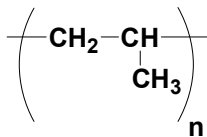
O-rings



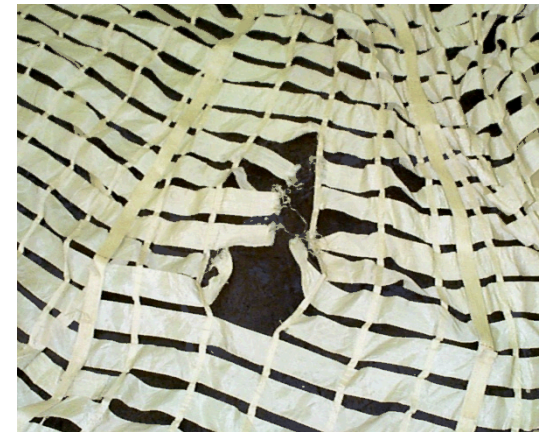
Nuclear Power Plant Cable Insulation



Shorting Plugs



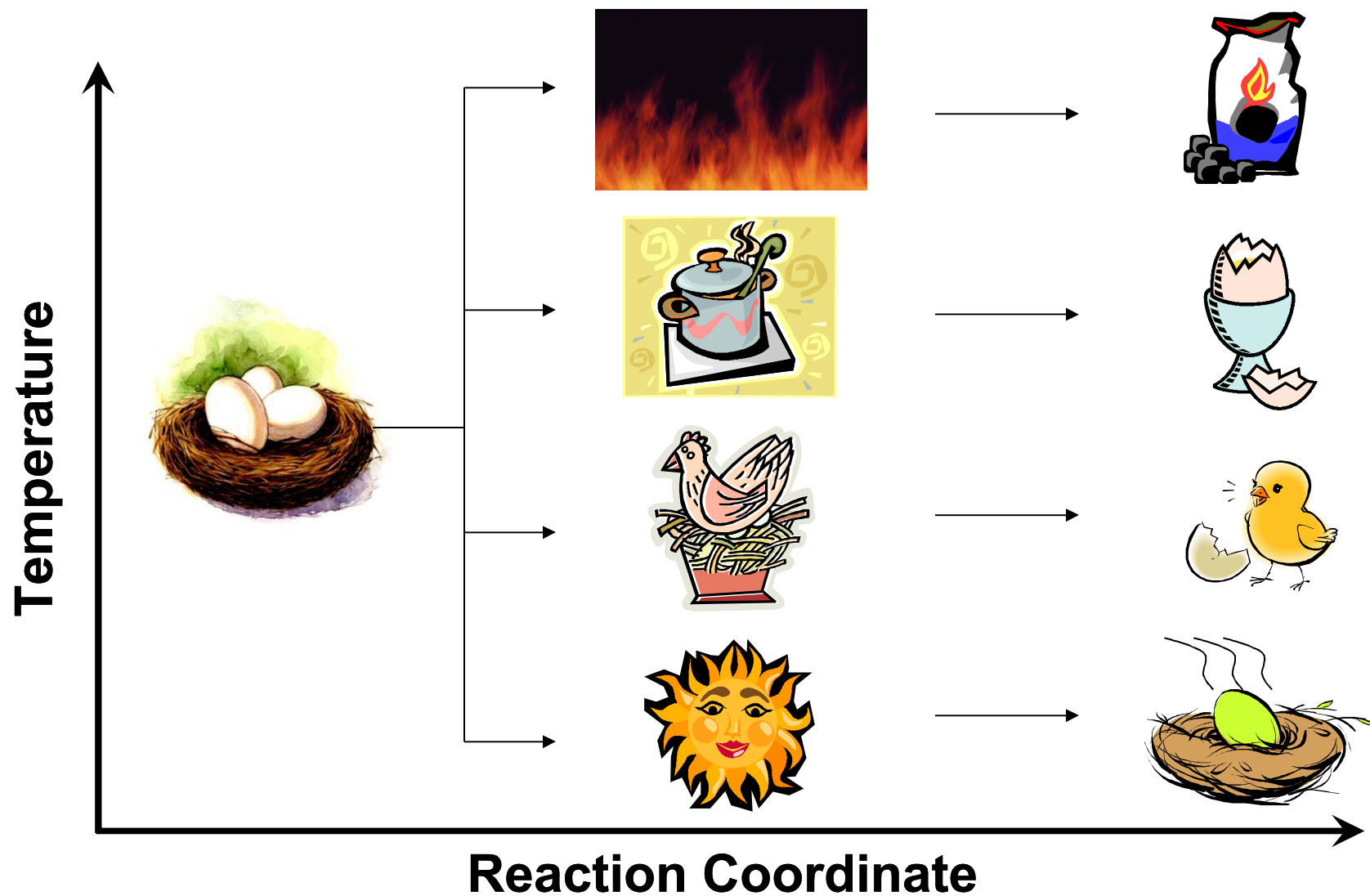
Labeled Polymers



Textiles



'Accelerated Aging'



General Approach/Goals

Macroscopic level

Physical property

Sealing Force Compression Set
Tensile Strength
Permeation Elongation
Dimensional changes

Molecular Level

Chemical Property

UV-VIS Spectroscopy
Surface Analysis
Differential Scanning Calorimetry
Additives
Molecular Weight Analysis
Density
X-Ray Analysis
Infra-red Spectroscopy
Nuclear Magnetic Resonance
GPC

Goals

- Prediction of physical properties vs. time
 - Predict remaining lifetime of field materials
- Develop condition monitoring method



Deception!

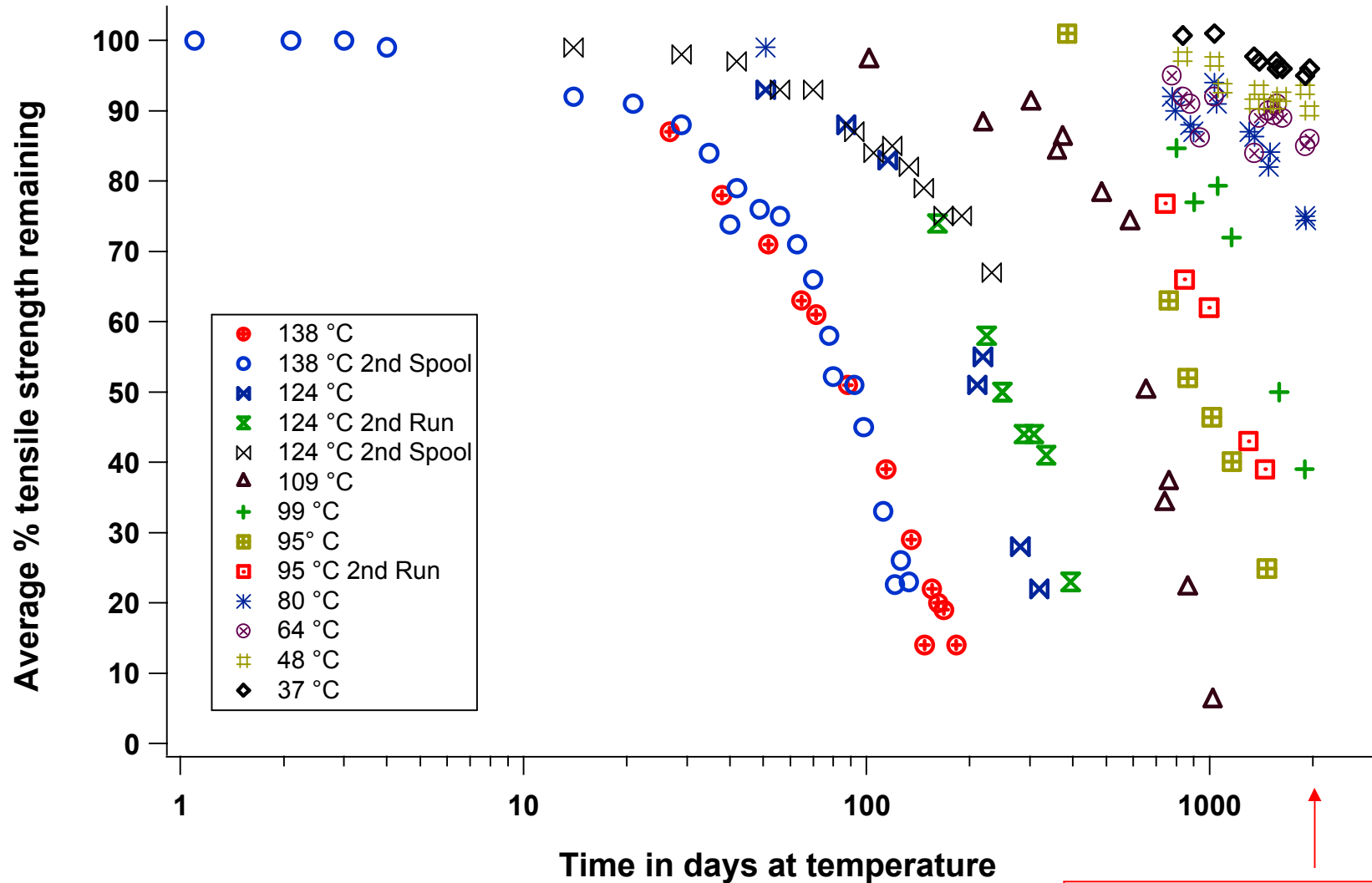
Conclusions derived from initial high temperature, short duration (even out to 1 year) accelerated aging can be misleading.

Chemistry / mechanisms must be understood.

Results must be critically analyzed to identify and understand mechanism changes



Thermal-oxidative Aging: Nylon



Arrhenius Equation

Arrhenius equation:

$$k = Ae^{-E_a/RT}$$

Old Chemist expression:

increase rate by 10 °C will double the rate



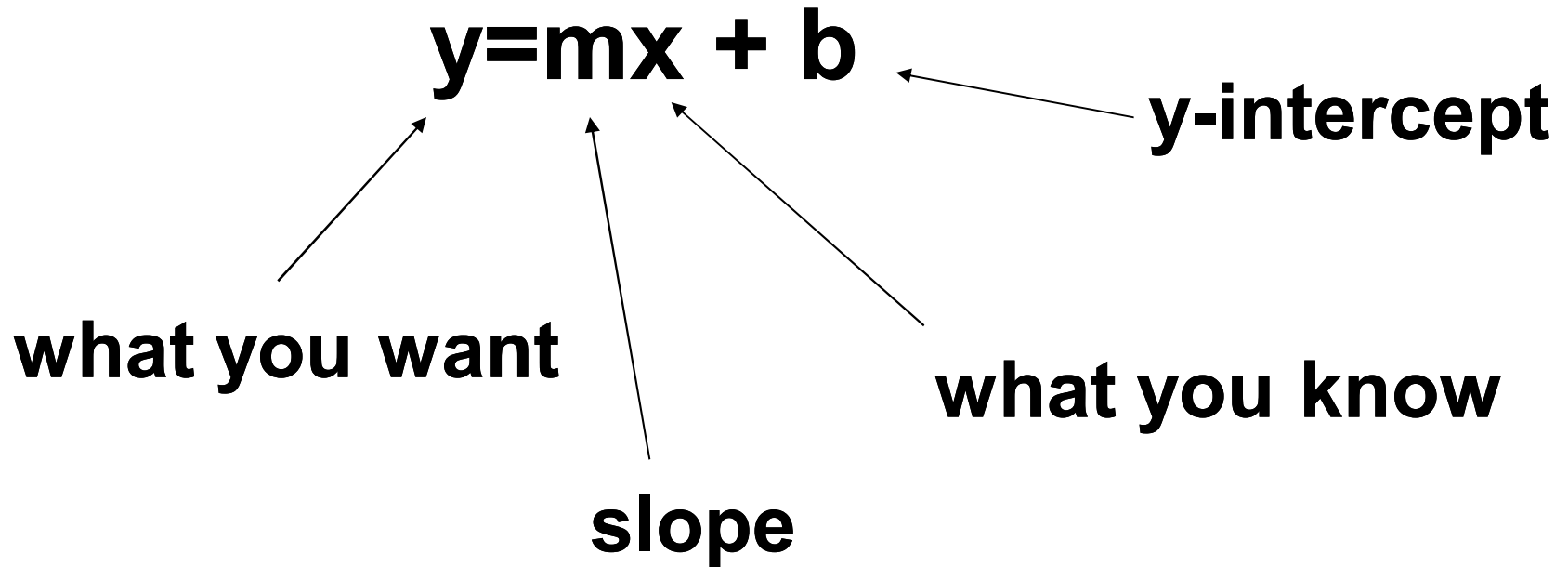
Time Warp

Back to High School....

.....but only briefly....



Equation of a Line



Function of a Line

y intercept = b

$$y = mx + b$$

slope = m

y

x



Arrhenius Equation

rate

$k = Ae^{-E_a/RT}$

Pre-exponential factor

Activation Energy

Gas constant

Temperature (Kelvin)

e

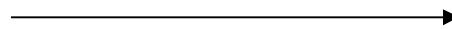
The diagram shows the Arrhenius equation $k = Ae^{-E_a/RT}$ in the center. Arrows point from labels to specific parts of the equation: 'rate' points to k ; 'Pre-exponential factor' points to A ; 'Activation Energy' points to E_a ; 'Gas constant' points to R ; 'Temperature (Kelvin)' points to T ; and ' e ' points to the exponential base.

Empirical equation



Arrhenius Equation

$$k = Ae^{-E_a/RT}$$



$$\ln(k) = \ln(A) - E_a/RT$$

$$\ln(k) = -E_a/RT + \ln(A)$$

$$\ln(k) = -(E_a/R)(1/T) + \ln(A)$$



Function of a Line

y intercept = **b**

$$y = \textcolor{blue}{m}\textcolor{red}{x} + \textcolor{green}{b}$$

slope = **m**

y

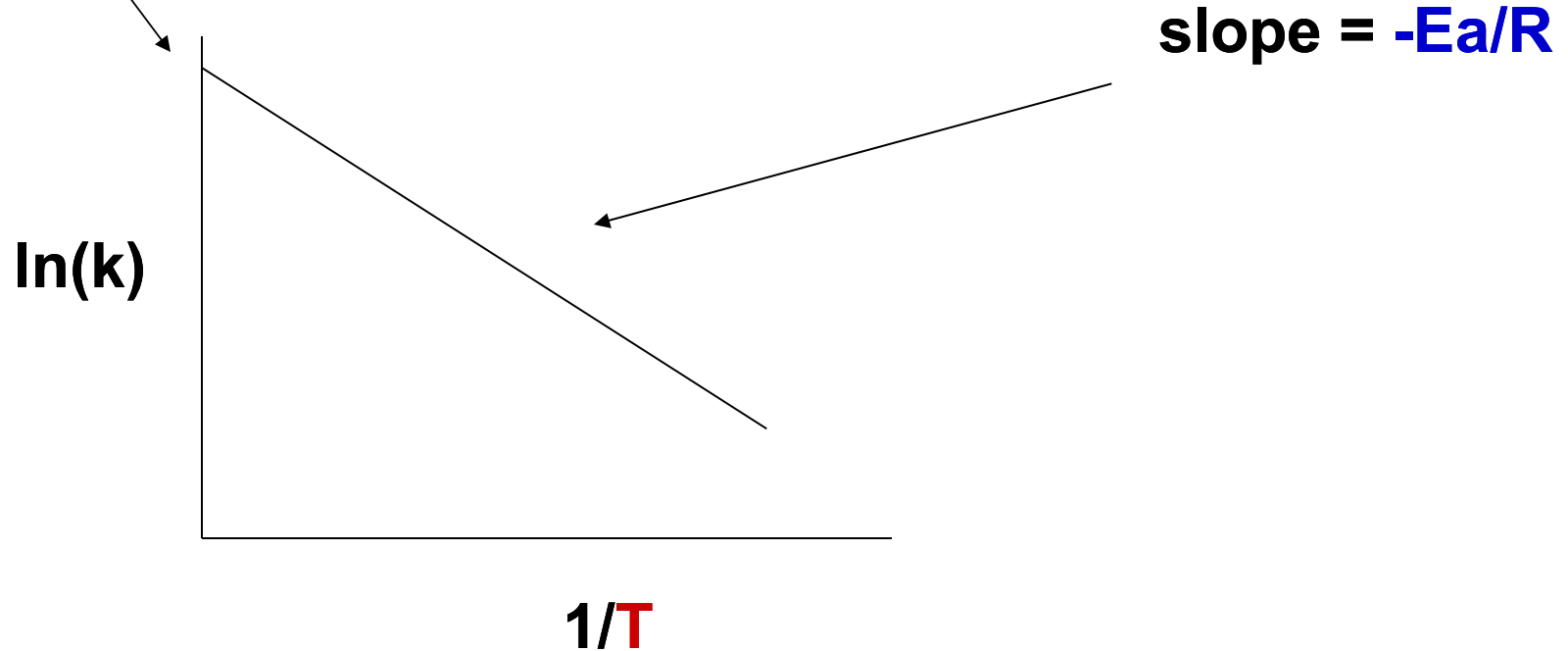
x



Function of a Line

y intercept = $\ln(A)$

$$\ln(k) = -\left(\frac{E_a}{R} \right) \left(\frac{1}{T} \right) + \ln(A)$$



Arrhenius Equation

Arrhenius equation:

$$k = Ae^{-E_a/RT}$$

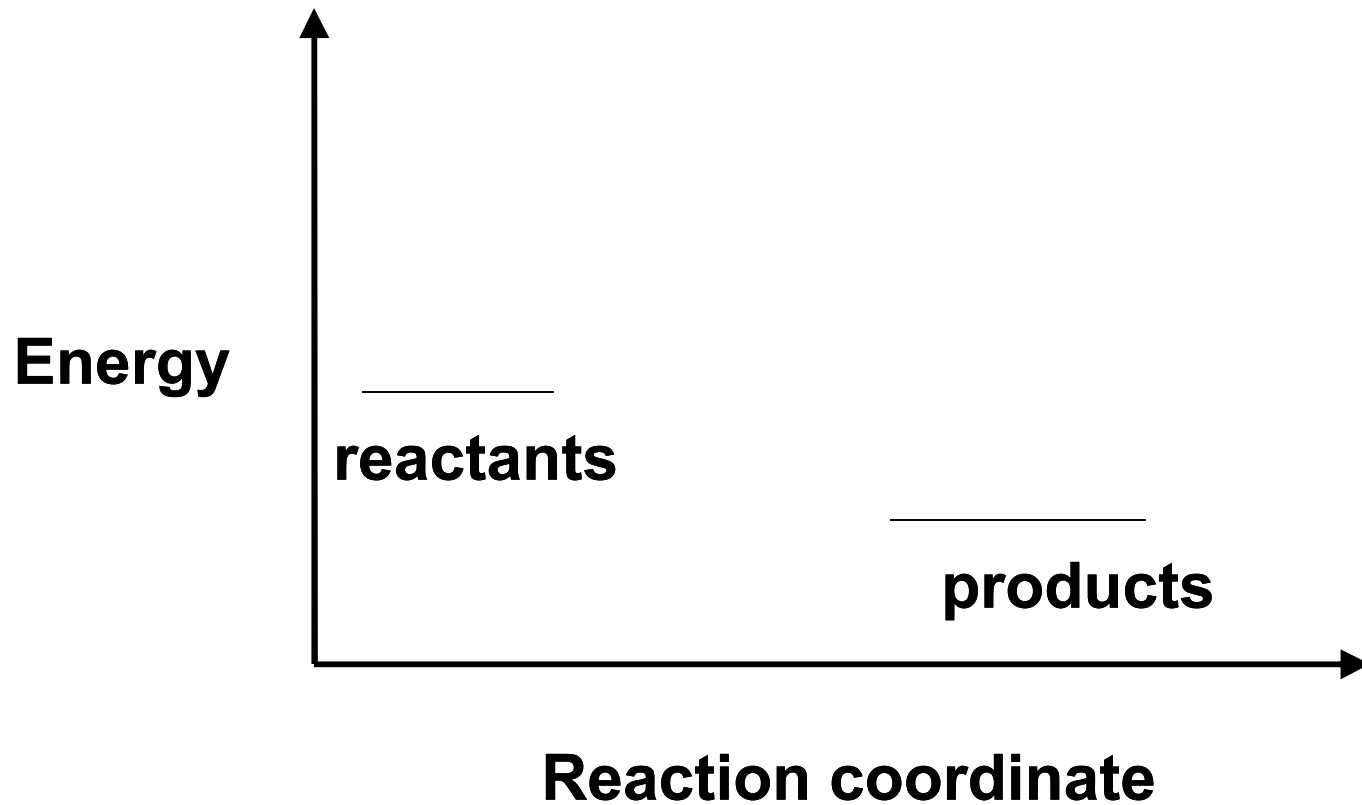
$$\ln(k) = -(E_a/R)(1/T) + \ln(A)$$

k = anything

Plot $\log(a_T)$ vs $1/T$ linear if Arrhenius

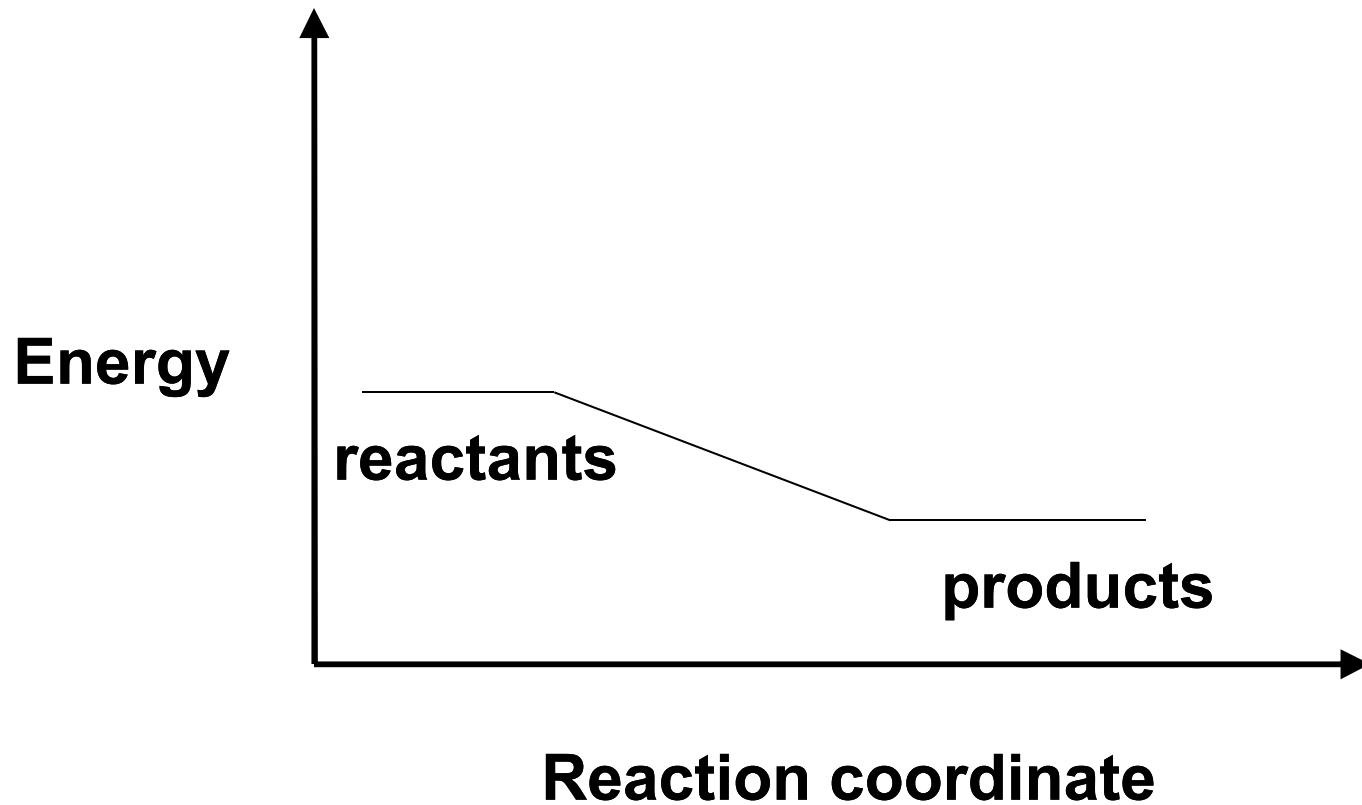
What is E_a ?

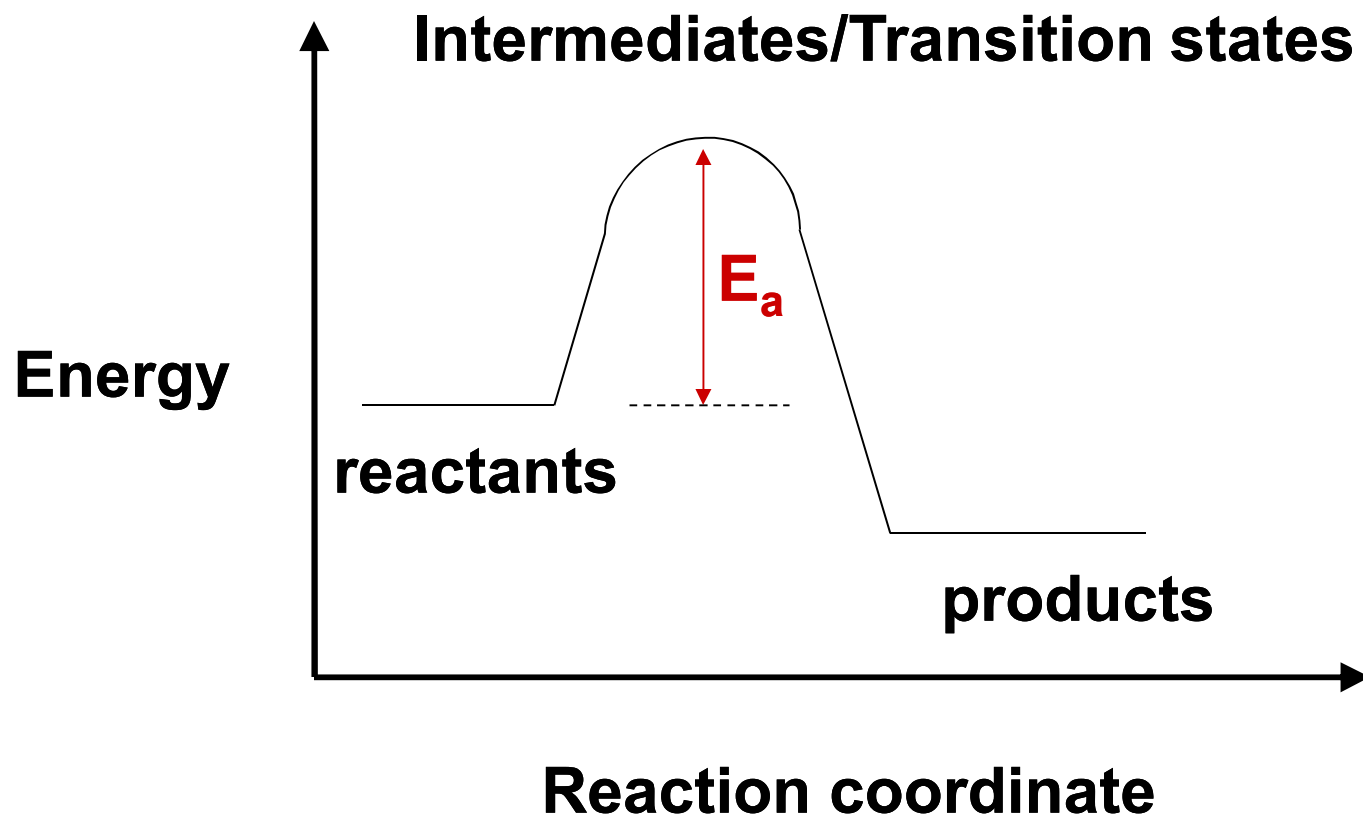


E_a 

---Imagine a marble---



E_a 

E_a 

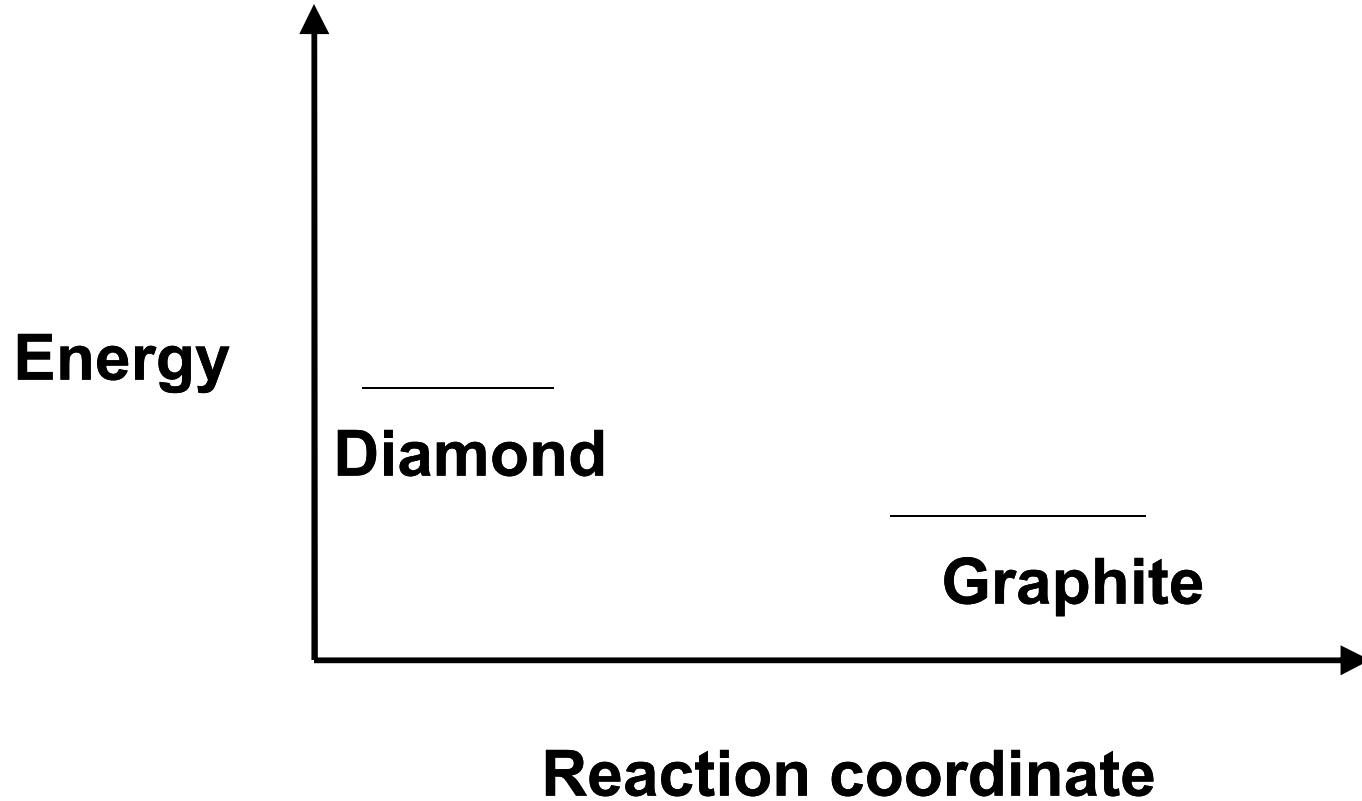
Are Diamonds *forever*?

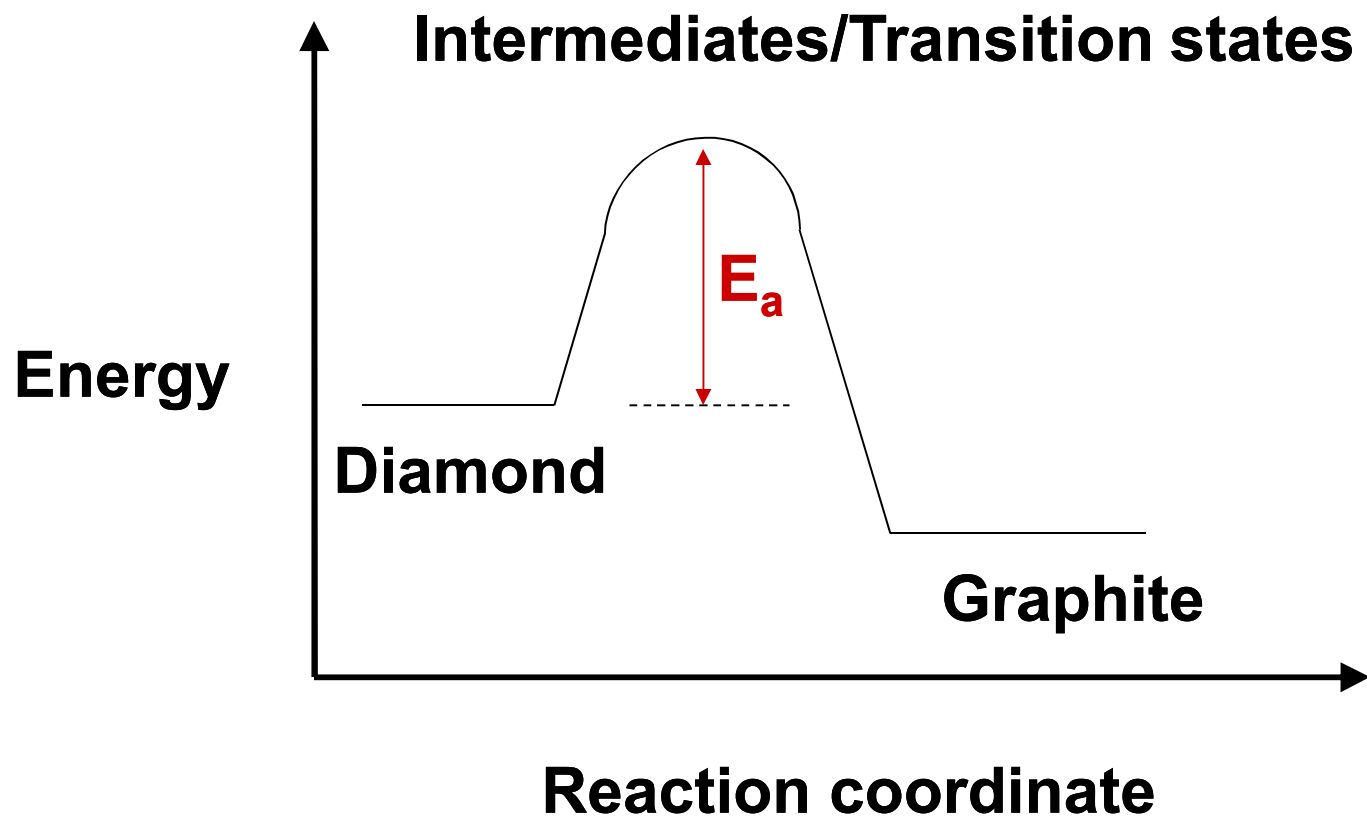


Kinetics vs. Thermodynamics

(really the same thing)

20



E_a 

Arrhenius Equation

$$k = Ae^{-E_a/RT}$$

Critical assumption is that E_a is **CONSTANT**

Assume

Ass-u-me



Time-Temperature Superposition

Does mechanism change as a function of temperature?

If same mechanism:

- same shape (log graph)
- should be constant acceleration (multiple)

1. Pick a reference temperature
2. Multiply the time at each temperature by the constant that gives the best overlap with the reference temperature data
3. Define that multiple as 'a_T' (a_T = 1 for ref. temp.)
4. Find a_T for each temperature

Plot log(a_T) vs 1/T linear if Arrhenius

Gillen, K. T.; Celina, M.; Clough, R. L.; Wise, J. *Trends in Polymer Science*, Extrapolation of Accelerated Aging Data -Arrhenius or Erroneous? 1997, 5, 250-257.

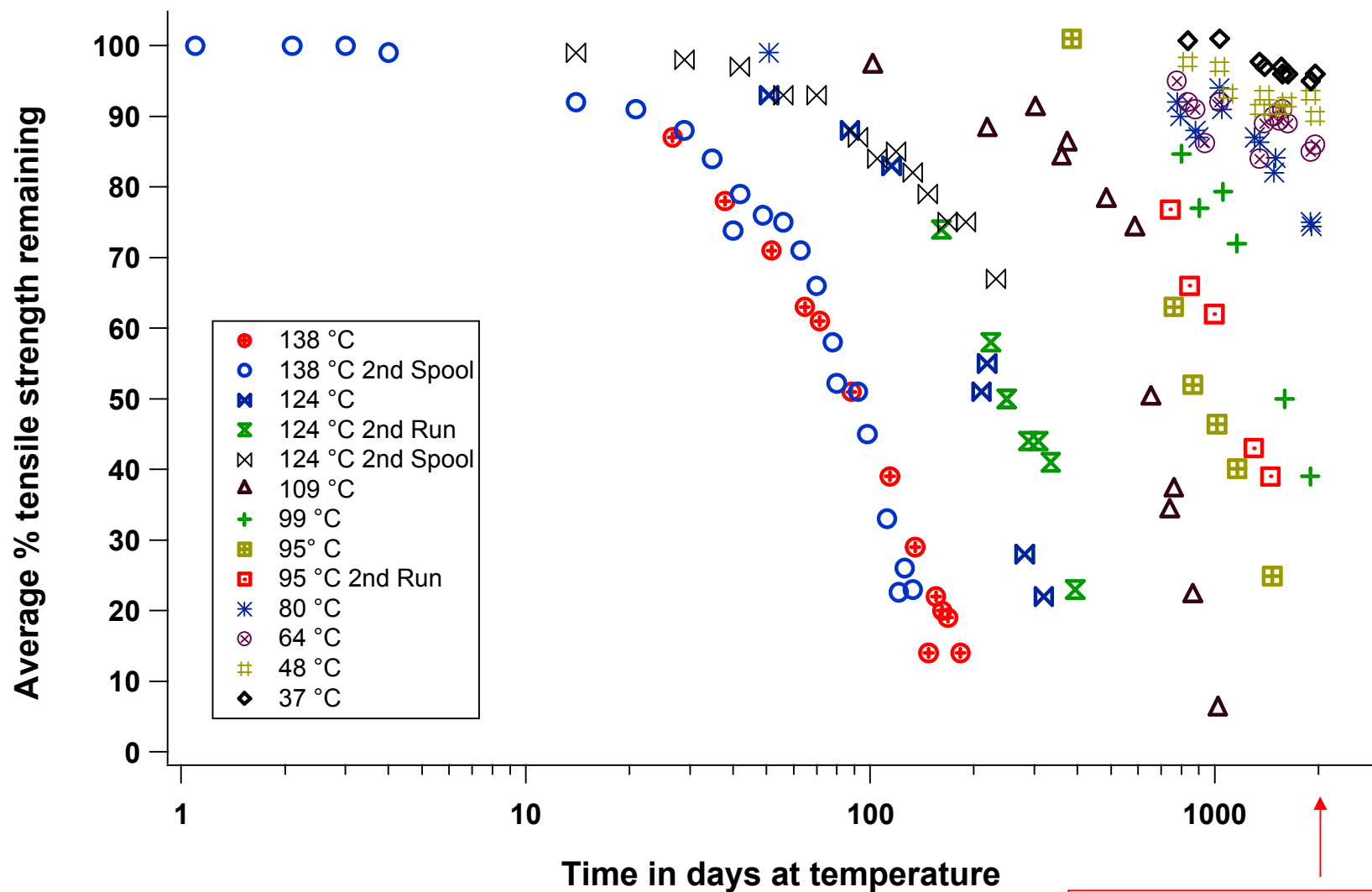
Arrhenius equation: Empirical equation

$$k = Ae^{-E_a/RT}$$

$$\ln(k) = \ln(A) - E_a/RT$$



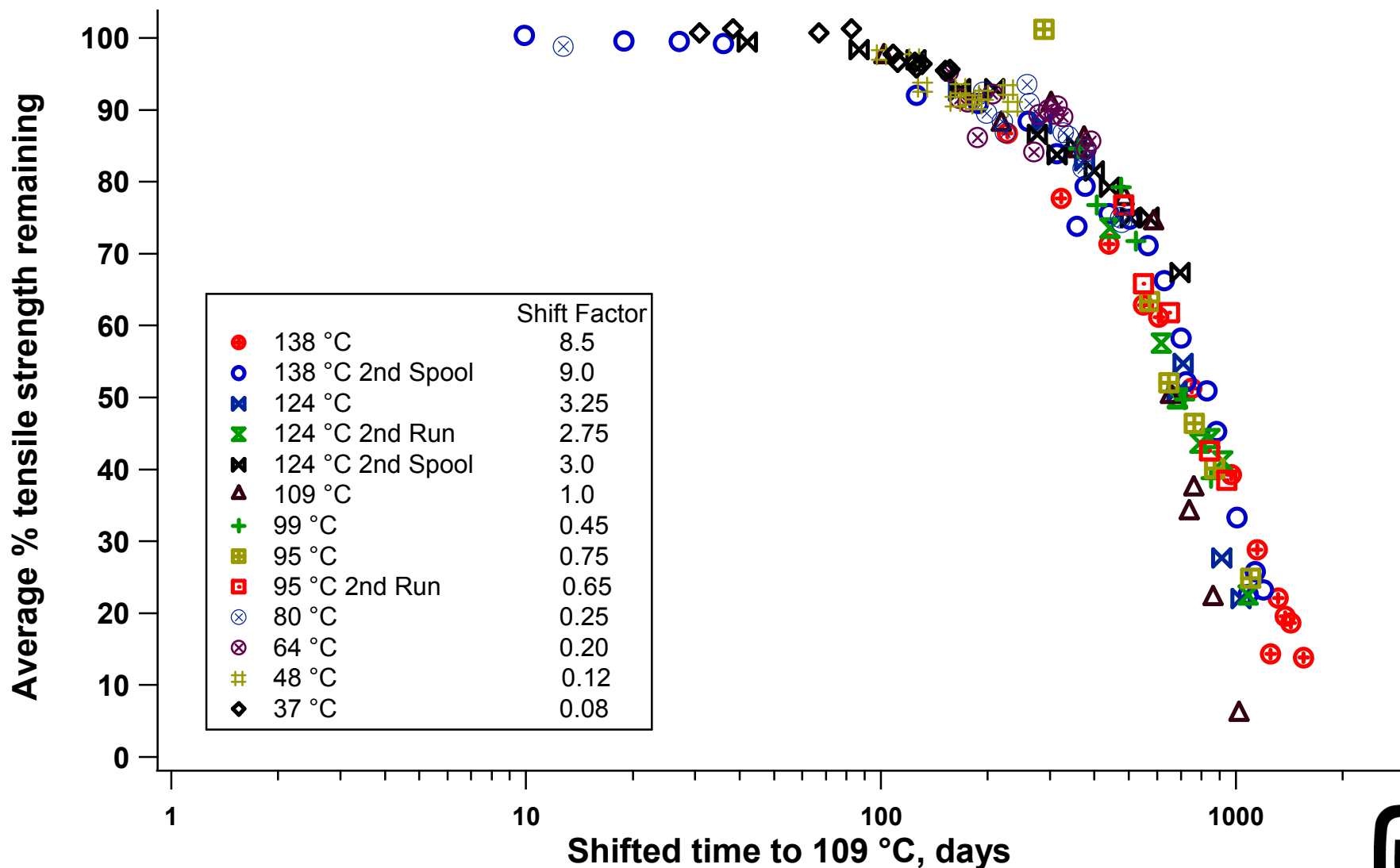
Thermal-oxidative Aging: Nylon



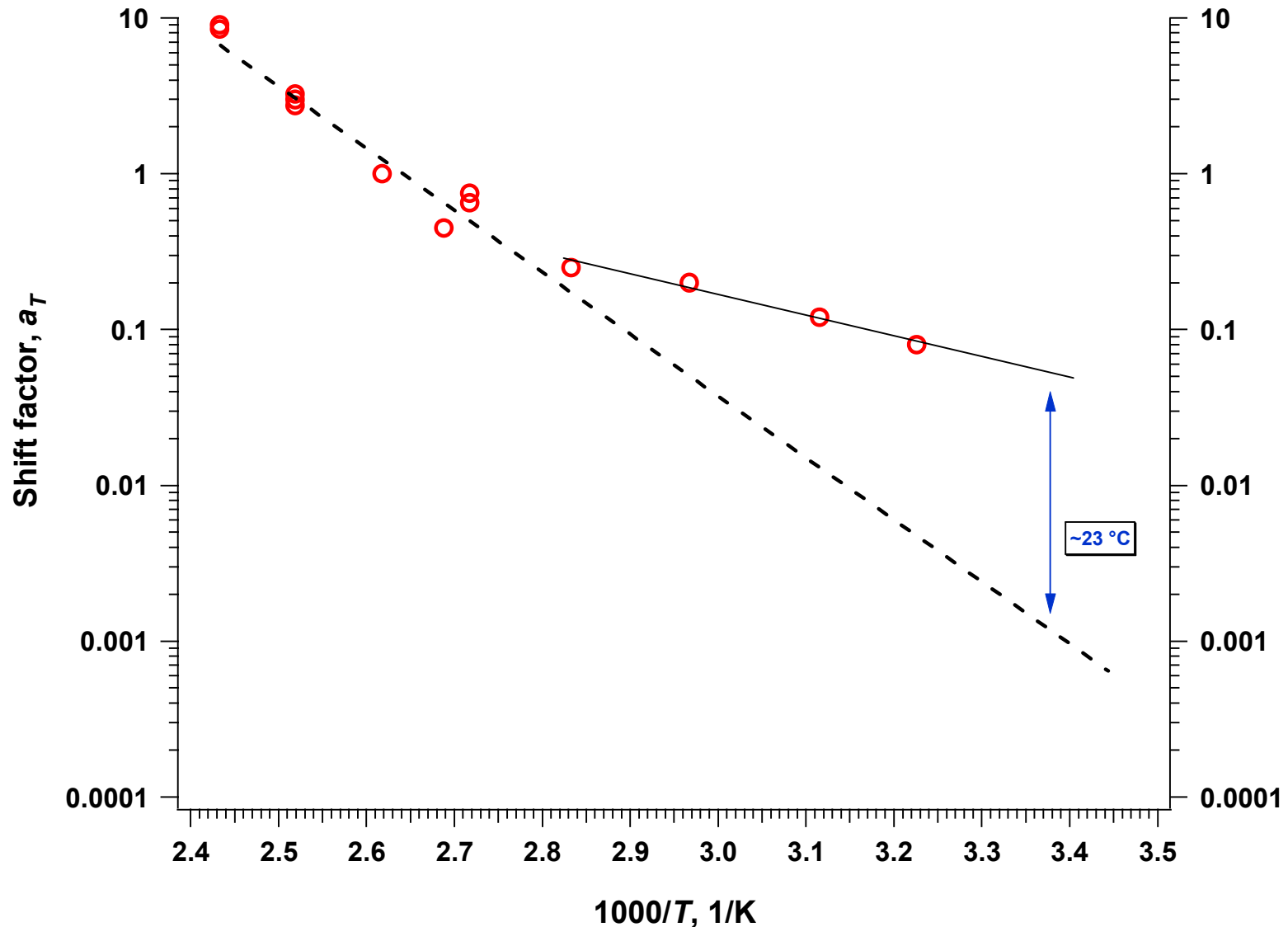
2000 days ~ 5.5 years



Thermal-oxidative Aging: Nylon Shifted Data

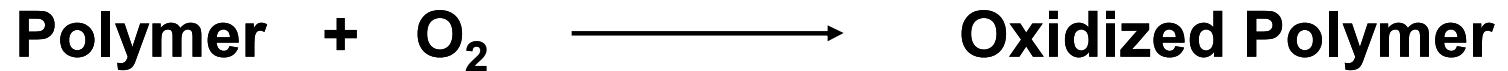


Thermal-oxidative Aging: Nylon Shift Factor Graph



Thermal Exposure

Thermal-Oxidation

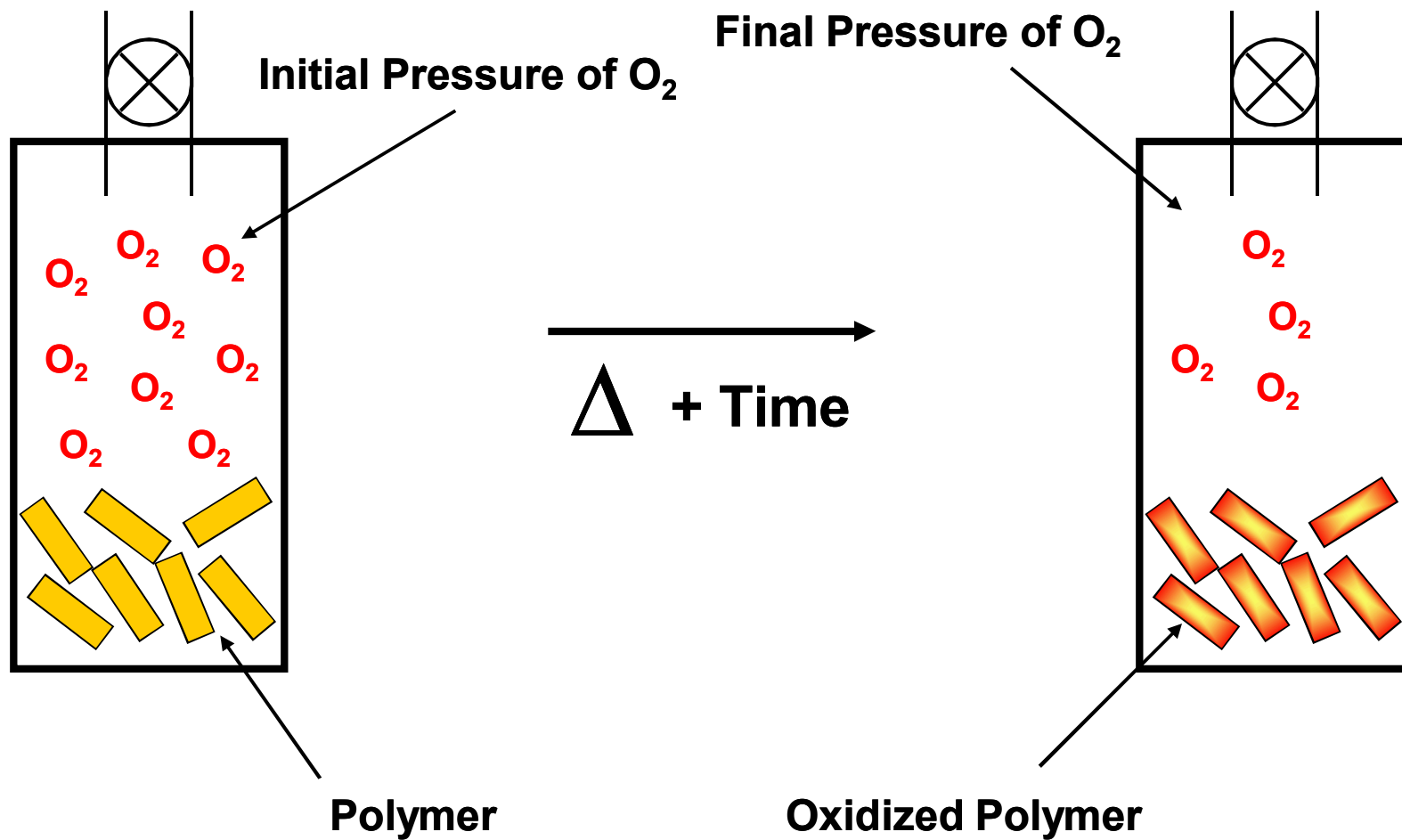


Quantify amount of oxygen consumed

- **Simple in theory**
- **Difficult in practice**
- **Amazingly sensitive**



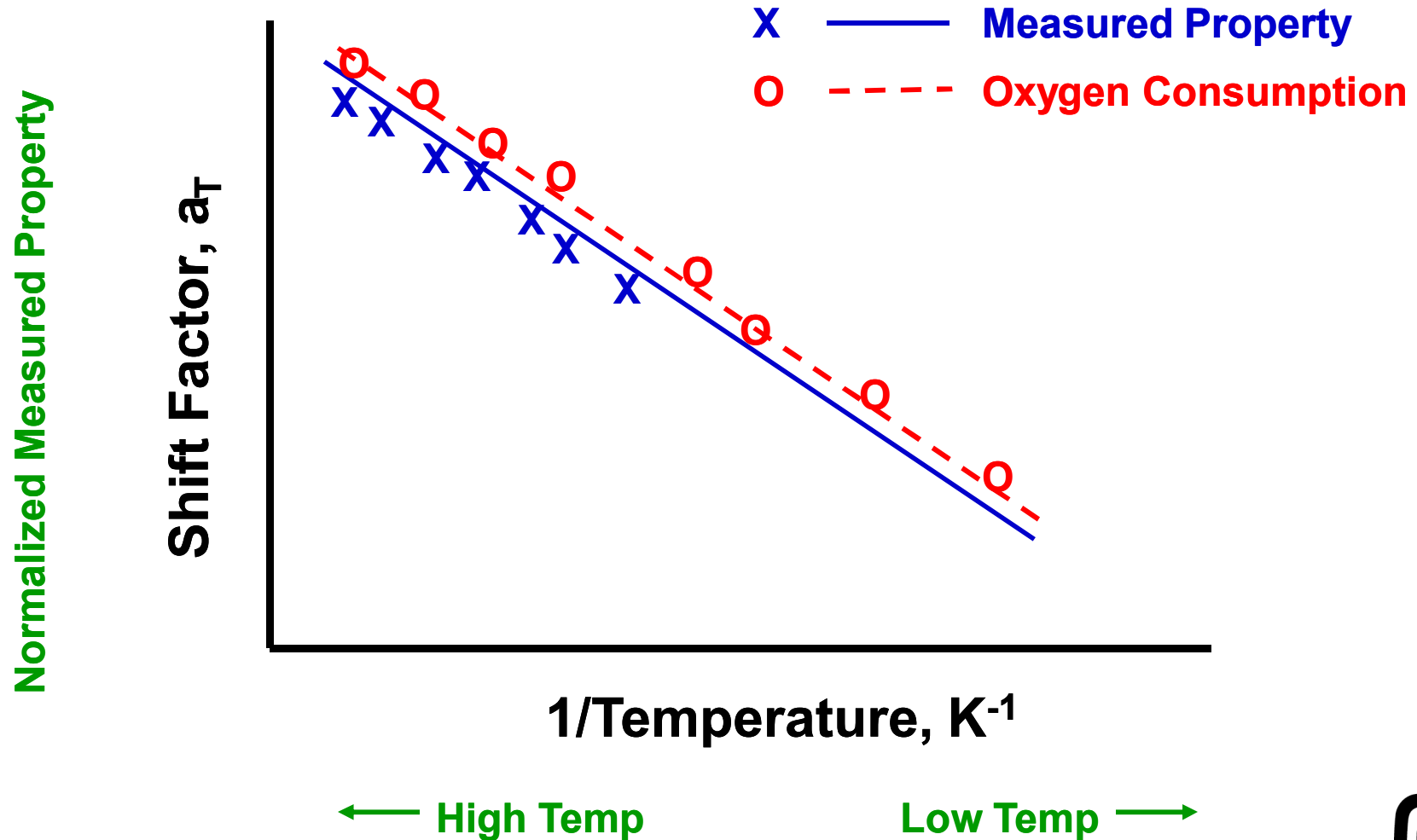
Schematic of Oxuptake



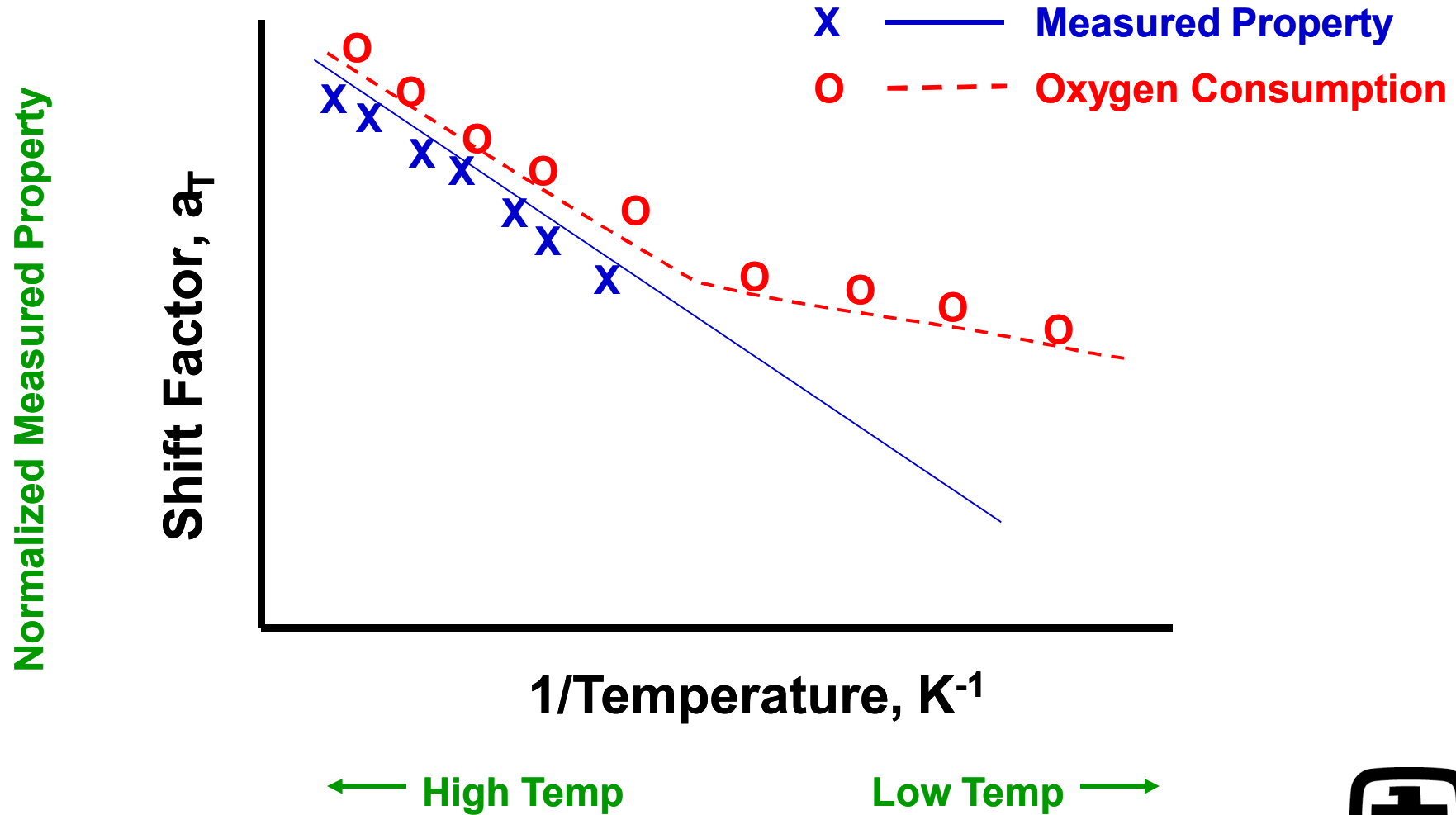
Oxygen Consumption



Enhanced Extrapolation 'Good'



Enhanced Extrapolation: 'Bad'



DLO, Need to Know

Diffusion Limited Oxidation (DLO) effects if oxygen dissolved in material used up faster by reaction than it can be replenished by diffusion from surrounding air atmosphere

Race between:

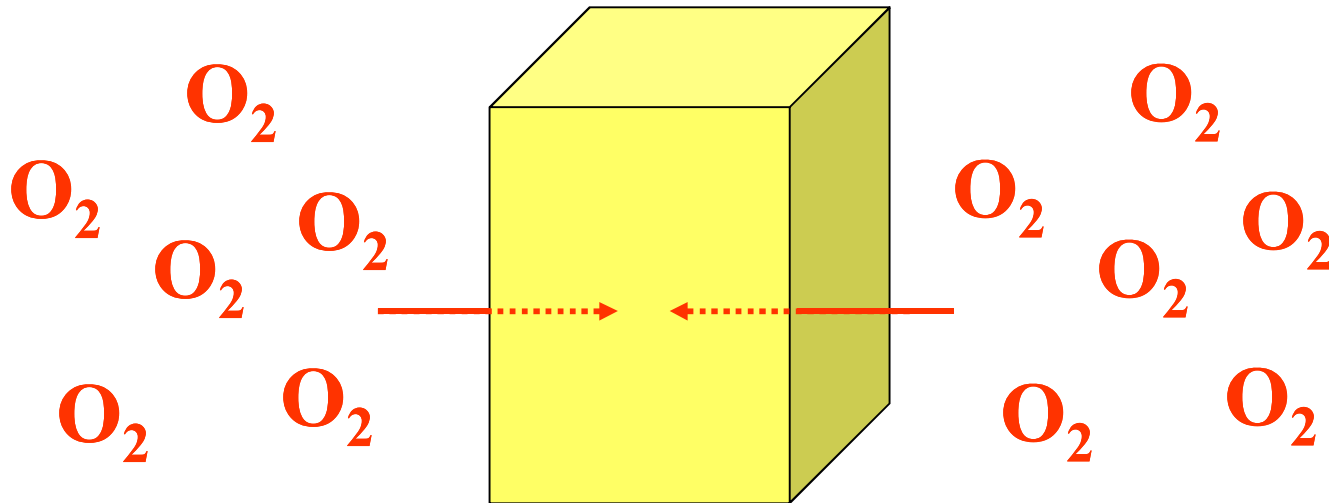
the oxygen consumption rate versus the oxygen diffusion rate

Therefore we need estimates of:

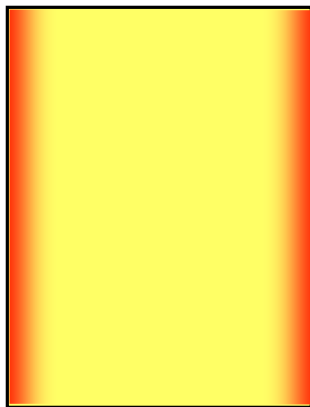
- 1. O_2 permeability versus aging temperature**
- 2. O_2 consumption versus aging temperature**



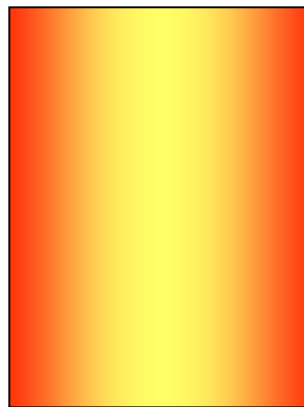
Diffusion-Limited Oxidation (DLO)



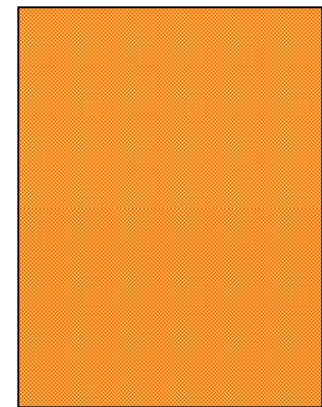
rxn rate > diffusion rate



Heterogeneous



rxn rate < diffusion rate



Homogeneous



Modulus Profiling

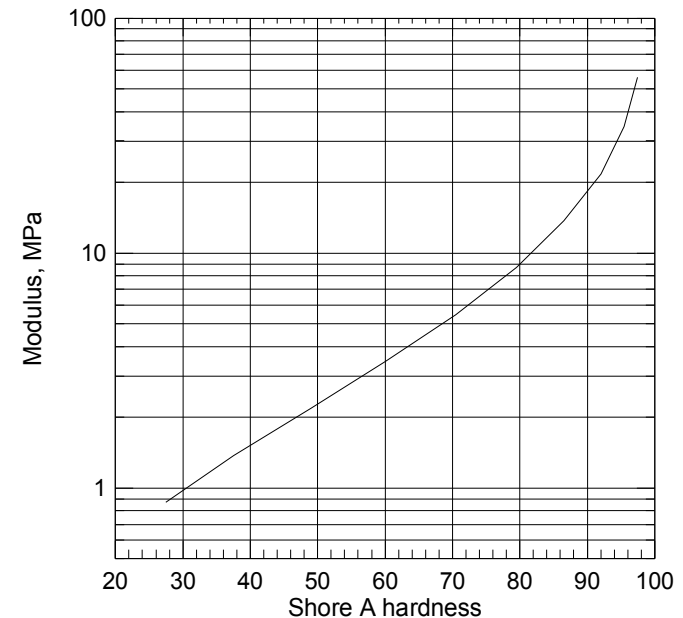
**Indentation technique
ca. 50 μ m resolution**

**Measure of Inverse tensile
compliance**

**Closely related to tensile
modulus**

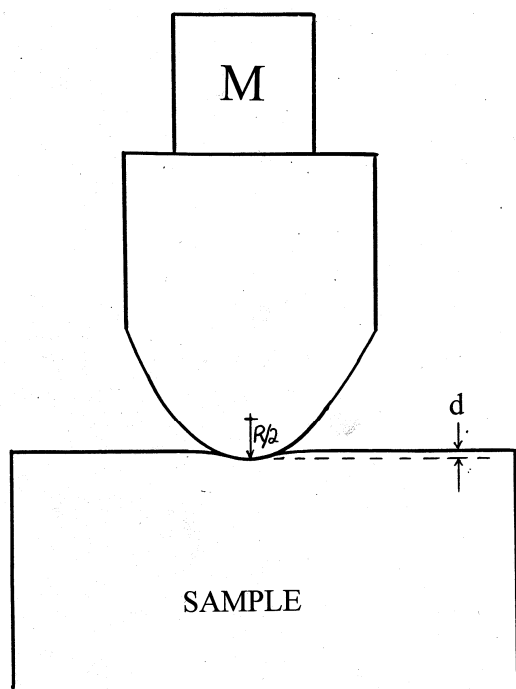
**Excellent to examine ‘geneity’ of aging
(heteo- or homo-) (DLO issues)**

Modulus vs. Shore A

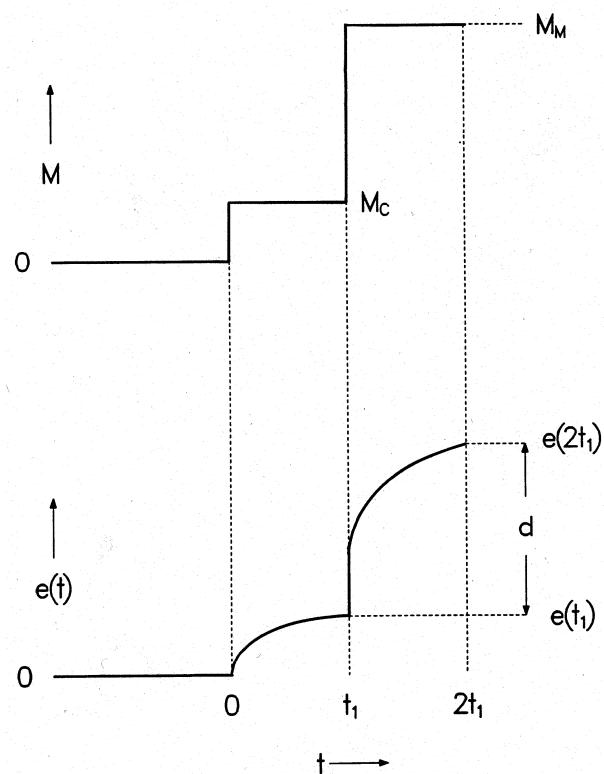


Schematic of Modulus Profile Experiment

Probe tip, sample and mass



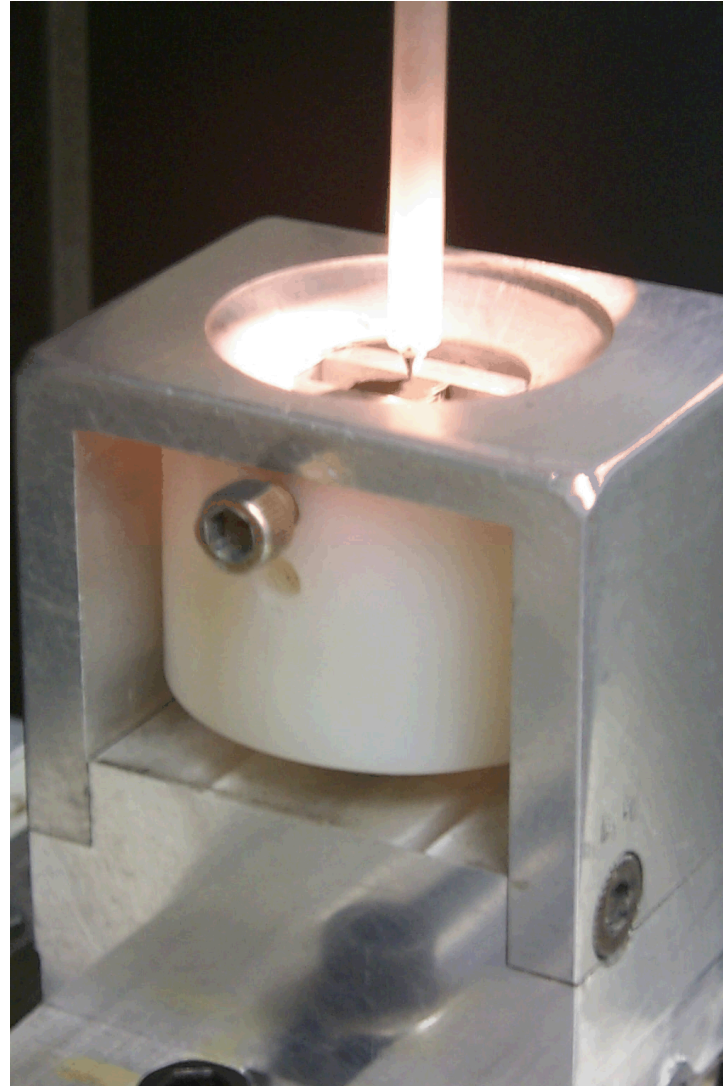
Mass is applied in two steps



Modulus Profiler

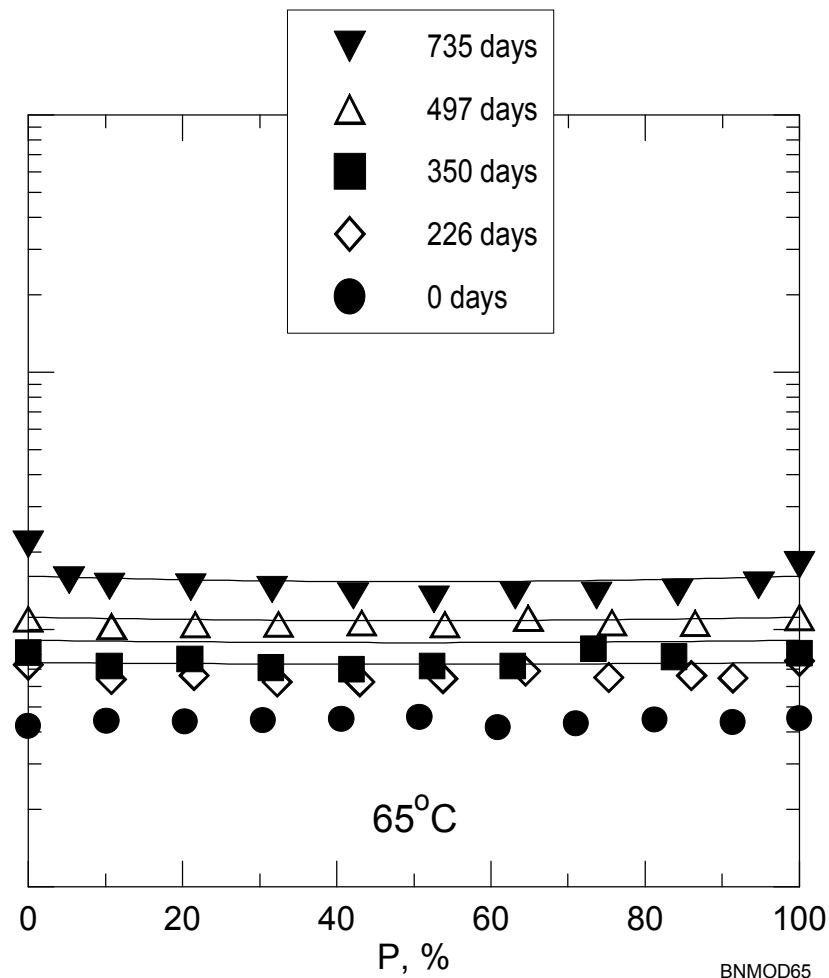


Modulus Profiler Sample



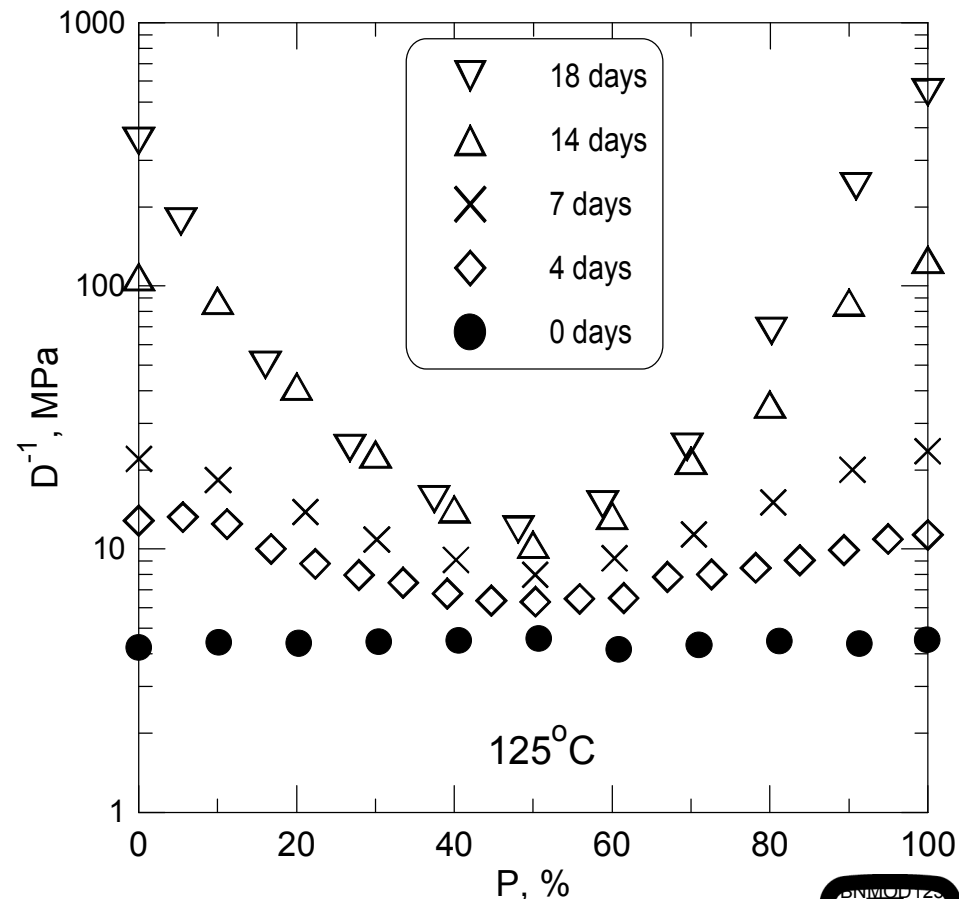
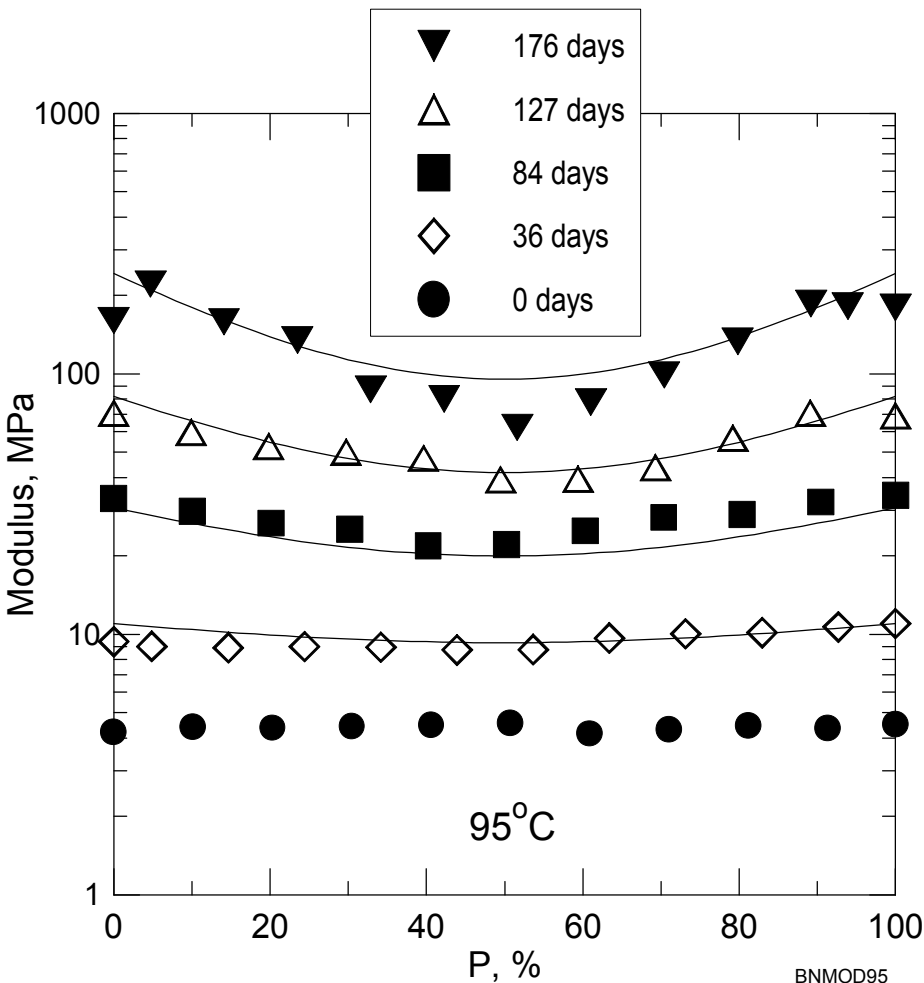
Homogeneous Aging

Modulus profiles of samples (nitrile rubber) aged at 65°C

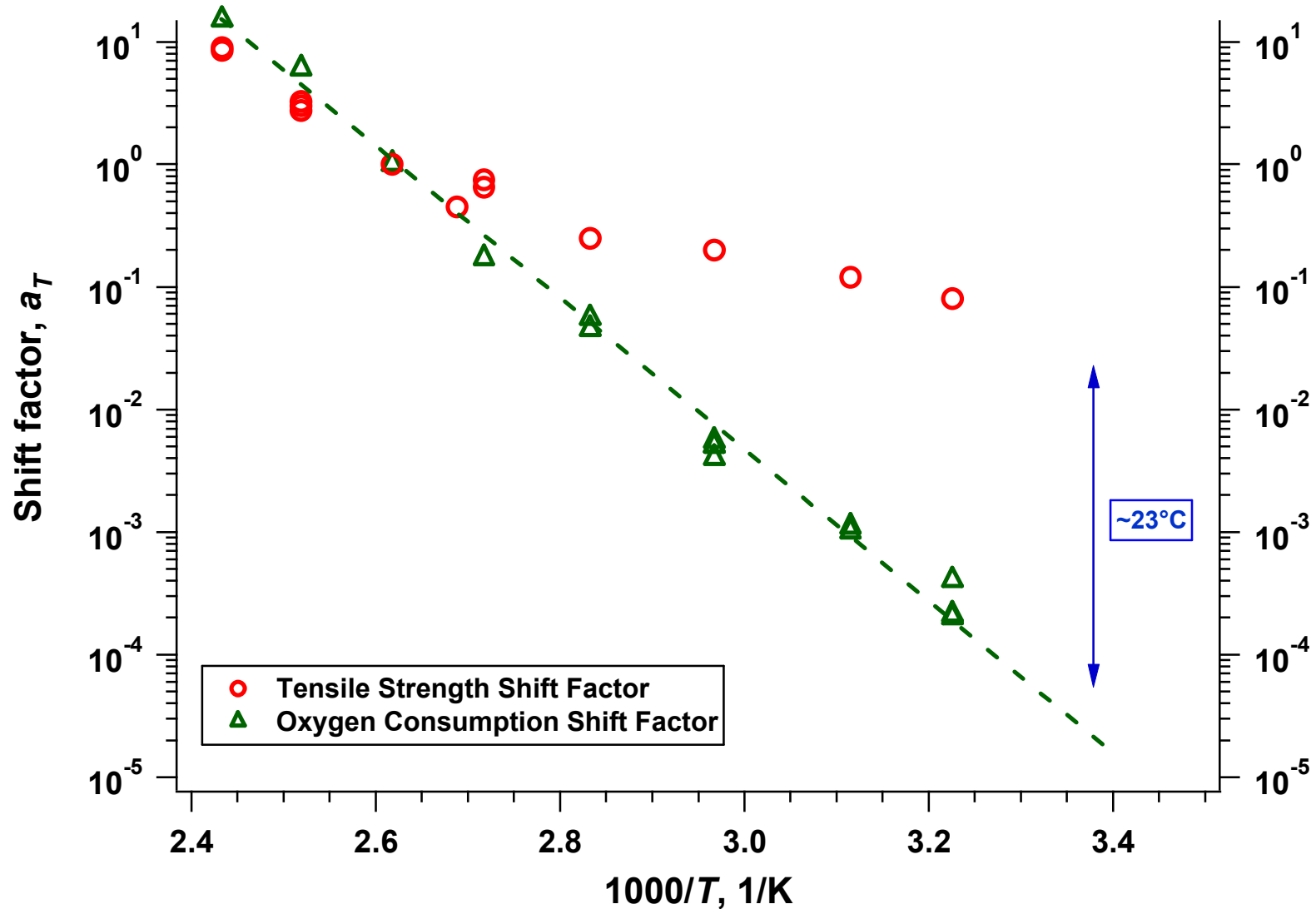


Heterogeneous Aging

Modulus profiles for samples aged at 95°C show that diffusion-limited oxidation (DLO) is becoming important; at 125°C, DLO effects are very significant



Nylon: Tensile versus Oxygen Consumption



Thermal-oxidative tensile: Prediction vs. Experimental

41

Arrhenius Predictions

64 °C Thermal-oxidative

**Arrhenius predictions severely off target
suggest change in mechanism/non-
Arrhenius behavior**

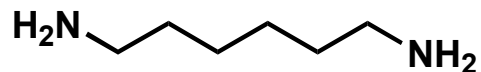
**Initial data Predicted: 92% at ca. 3700 days
Observe: 92% at ca. 835 days**

**Oxygen consumption suggests no change
in thermal-oxidative mechanism**

Possible explanation involving mechanism change?

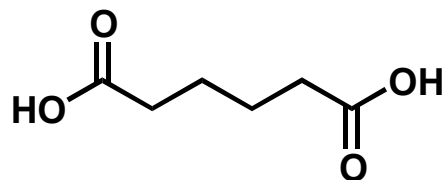


Nylon Structure

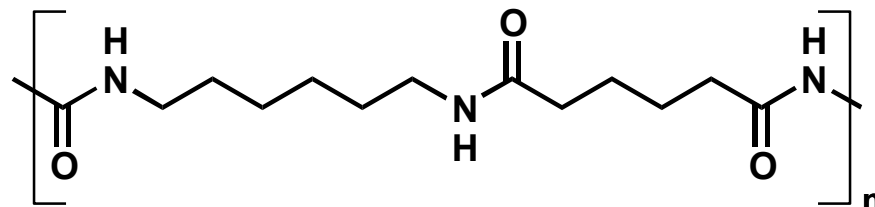
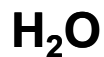
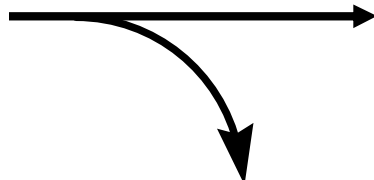


1,6 -Hexanediamine

+



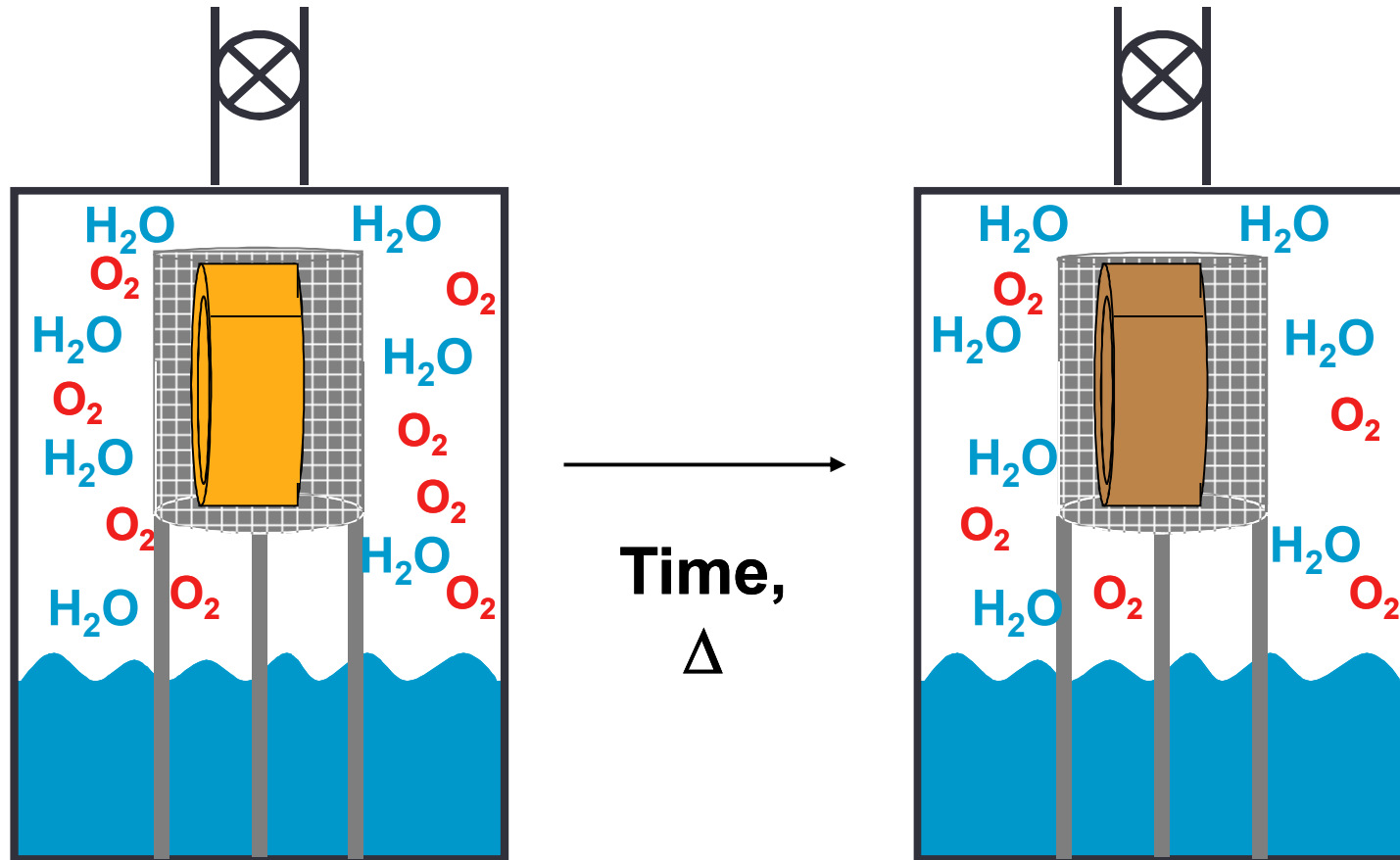
Adipic Acid



Nylon 6.6



Humidity Aging Schematic



Humidity Aging Hardware



Organic Materials Aging and Degradation

Specifics -o-rings

General path –most organic materials

This talk –details not important (all published)



O-ring Published Documentation

Bernstein, R.; Gillen, K. T. *Polymer Degradation and Stability, Predicting the Lifetime of Fluorosilicone O-rings* 2009, 94, 2107-2133.

Bernstein, R.; Gillen, K. T. "Fluorosilicone and Silicone O-Ring Aging Study," SAND2007-6781, Sandia National Laboratories, 2007.

Chavez, S. L.; Domeier, L. A. "Laboratory Component Test Program (LCTP), Stockpile O-Rings," BB1A3964, 2004.

Gillen, K. T.; Bernstein, R.; Wilson, M. H. *Polymer Degradation and Stability, Predicting and Confirming the Lifetime of O-rings* 2005, 87, 257-270.

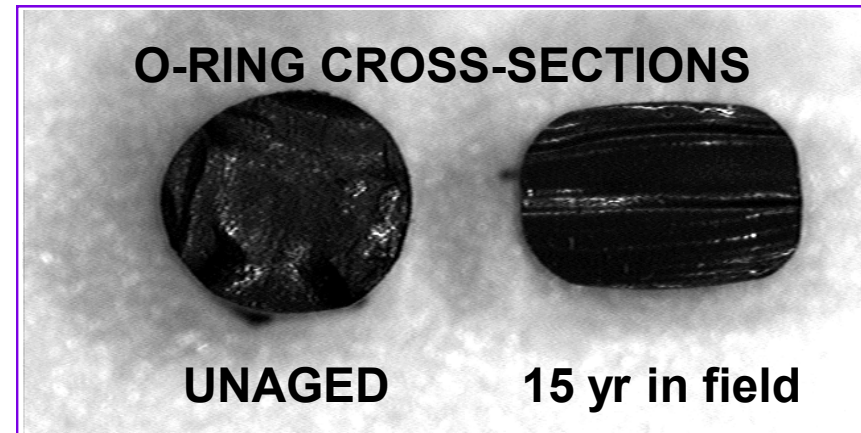
Gillen, K. T.; Celina, M.; Bernstein, R. In *Polymer Degradation and Stability Validation of Improved Methods for Predicting Long-Term Elastomeric Seal Lifetimes from Compression Stress-Relaxation and Oxygen Consumption Techniques*, 2003; Vol. 82, pp 25-35.



O-rings Background

Used as environmental seals or other seals

Most systems filled with inert gas to protect interior components from oxidation & hydrolysis



Previously:

No technique to measure equilibrium sealing force

No technique to rapidly achieve equilibrium compression set

No correlation



CSR Jigs

Gap of jig can be adjusted to any desired size

O-ring pieces cut to allow air circulation

Measurement of force involves very slow and slight compression until electrical contact is broken between the top and bottom plates

Jigs can be placed in ovens, thus providing isothermal measurements



Compression Stress Relaxation (CSR)

Shawbury-Wallace Compression Stress Relaxometer (CSR) MK II

**Commercial Instrument
Measure of Force**

-O-ring sealing force

**Can Adjust Gap Size to Approximate Actual
Compression in System**



(Wallace Test Equipment, Cryodon, England)



Accelerated aging

1) Physical force decay

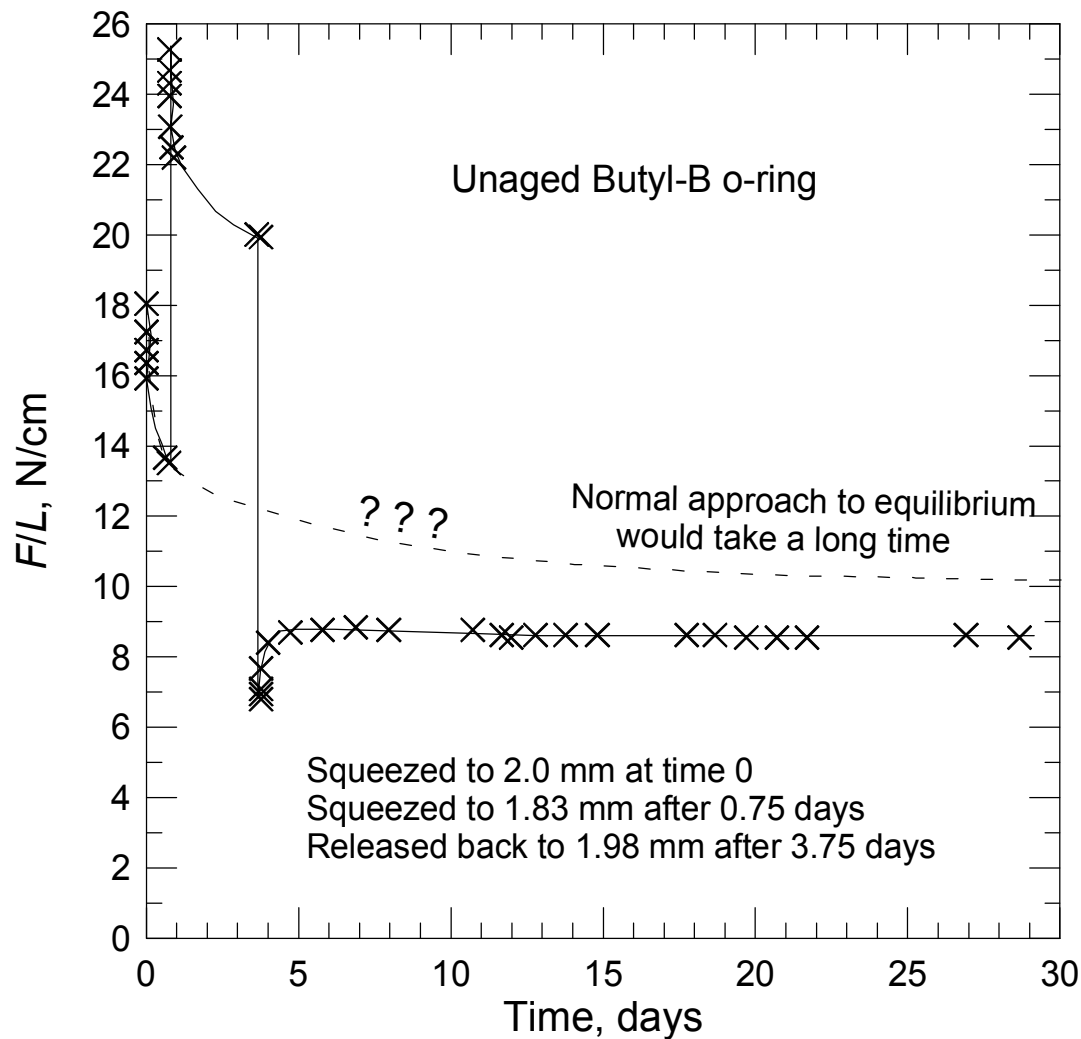
- Equilibrium values achieved –starting point
- Ability to get field returned o-ring force –ending point

2) Chemical force decay

Prediction of force changes as a function of aging



Over-compression

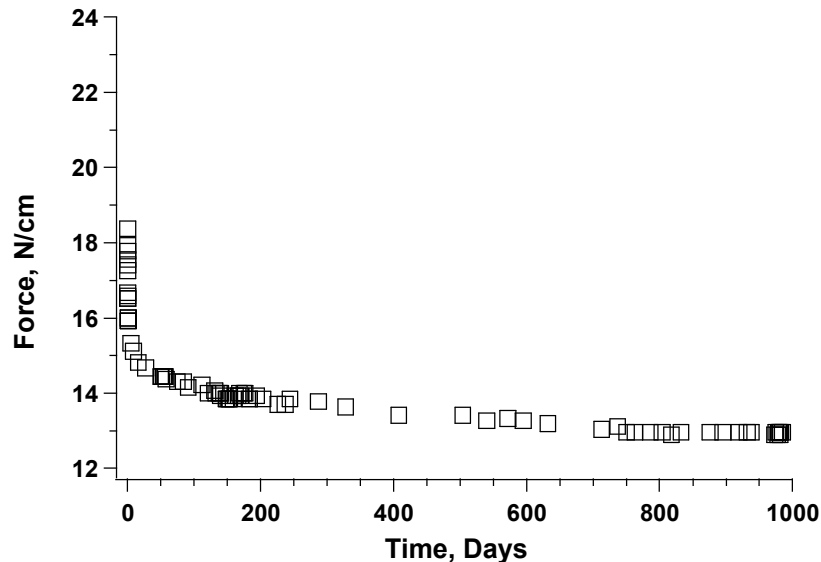


Over-compression as alternative to heating

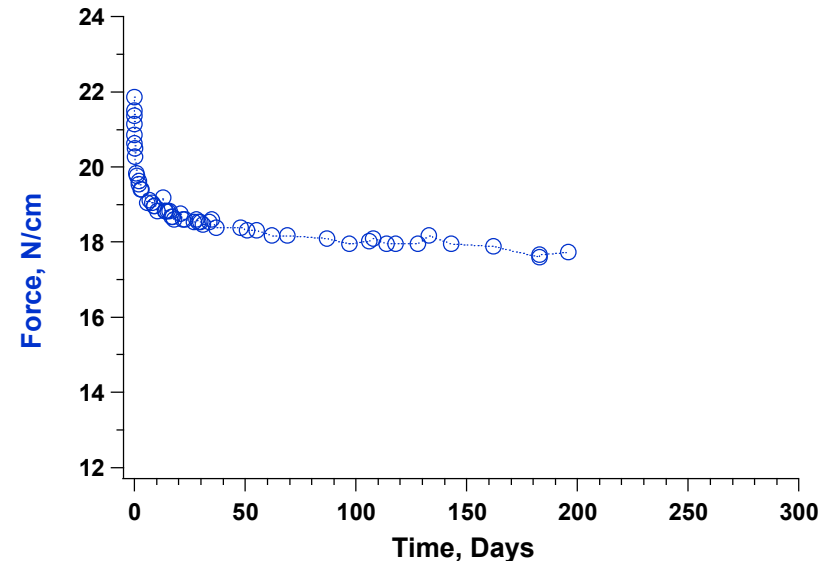


Long Term Compression Versus Force -Fluorosilicone

Simple Compression



2.65 mm (104.25 mils)

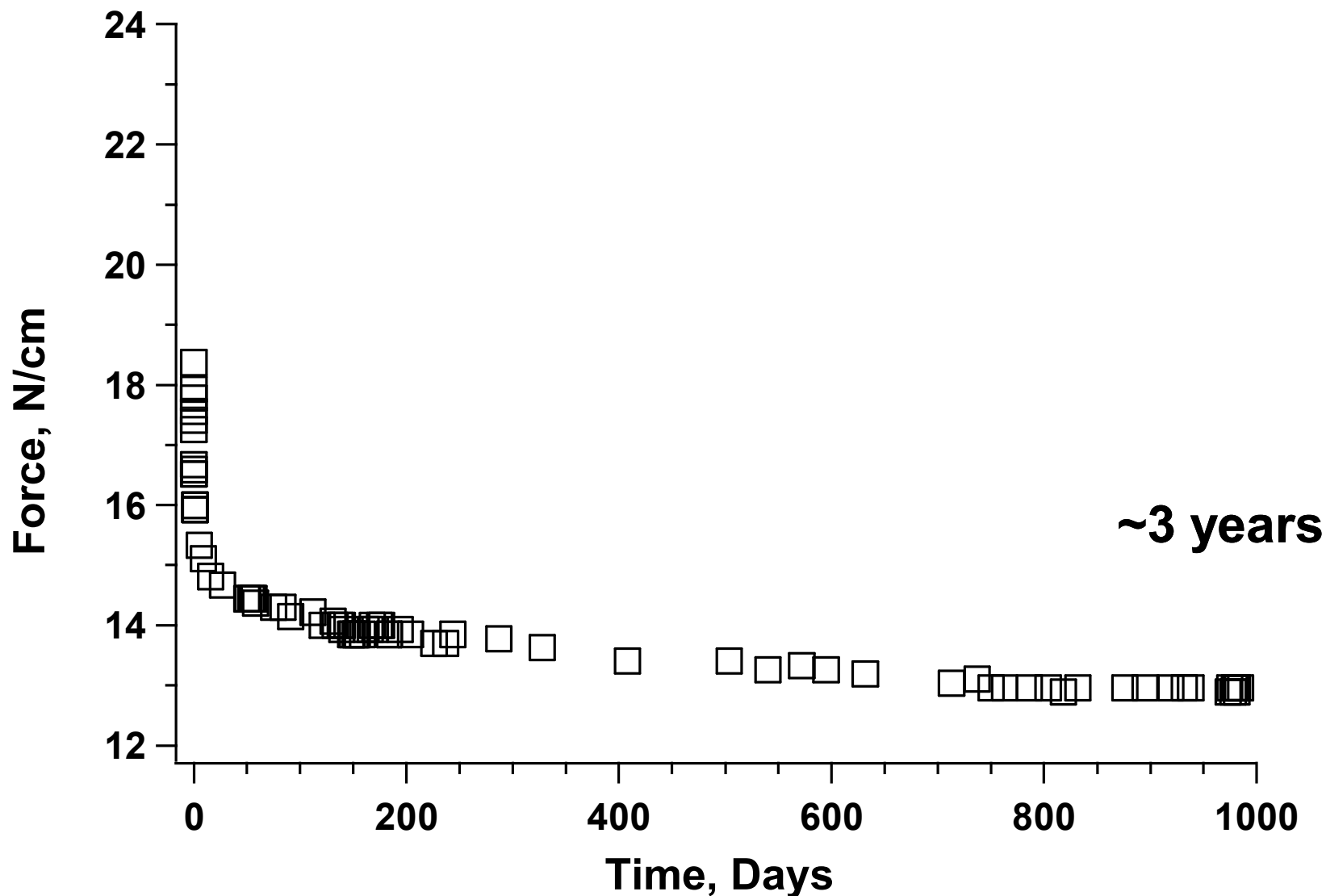


2.5 mm (98.5 mils)

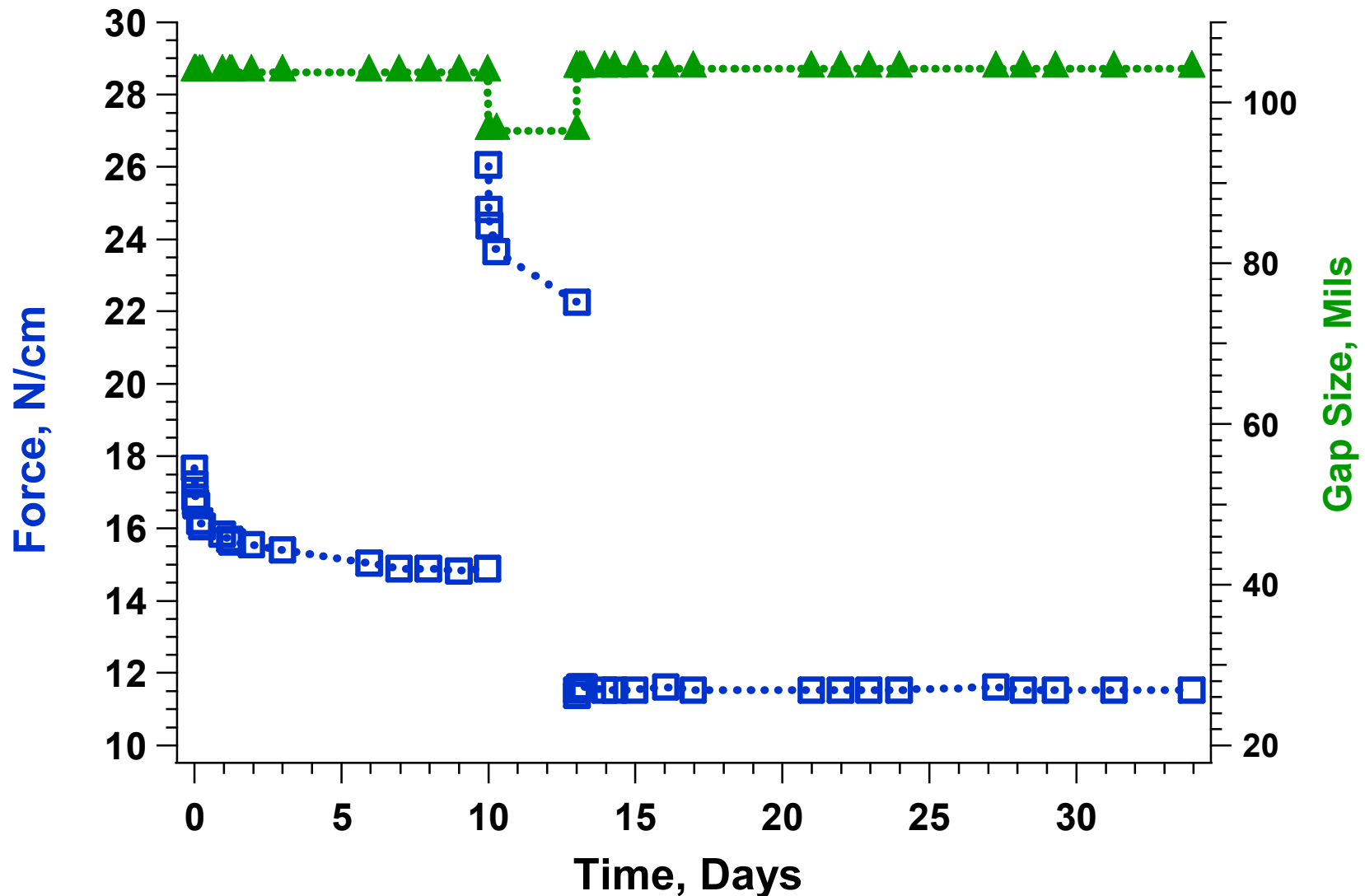
Physical relaxation is a lengthy process



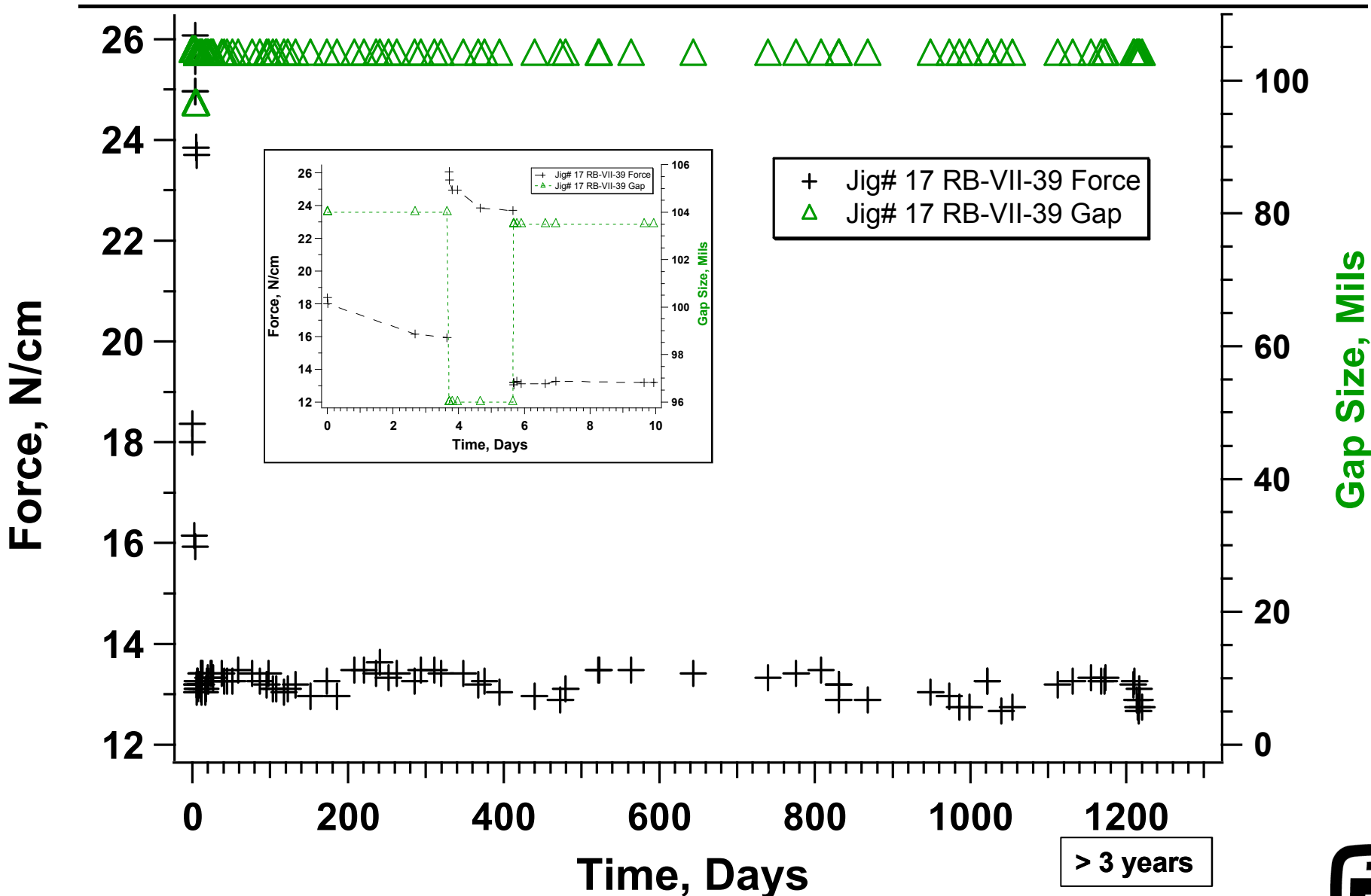
Physical relaxation at RT



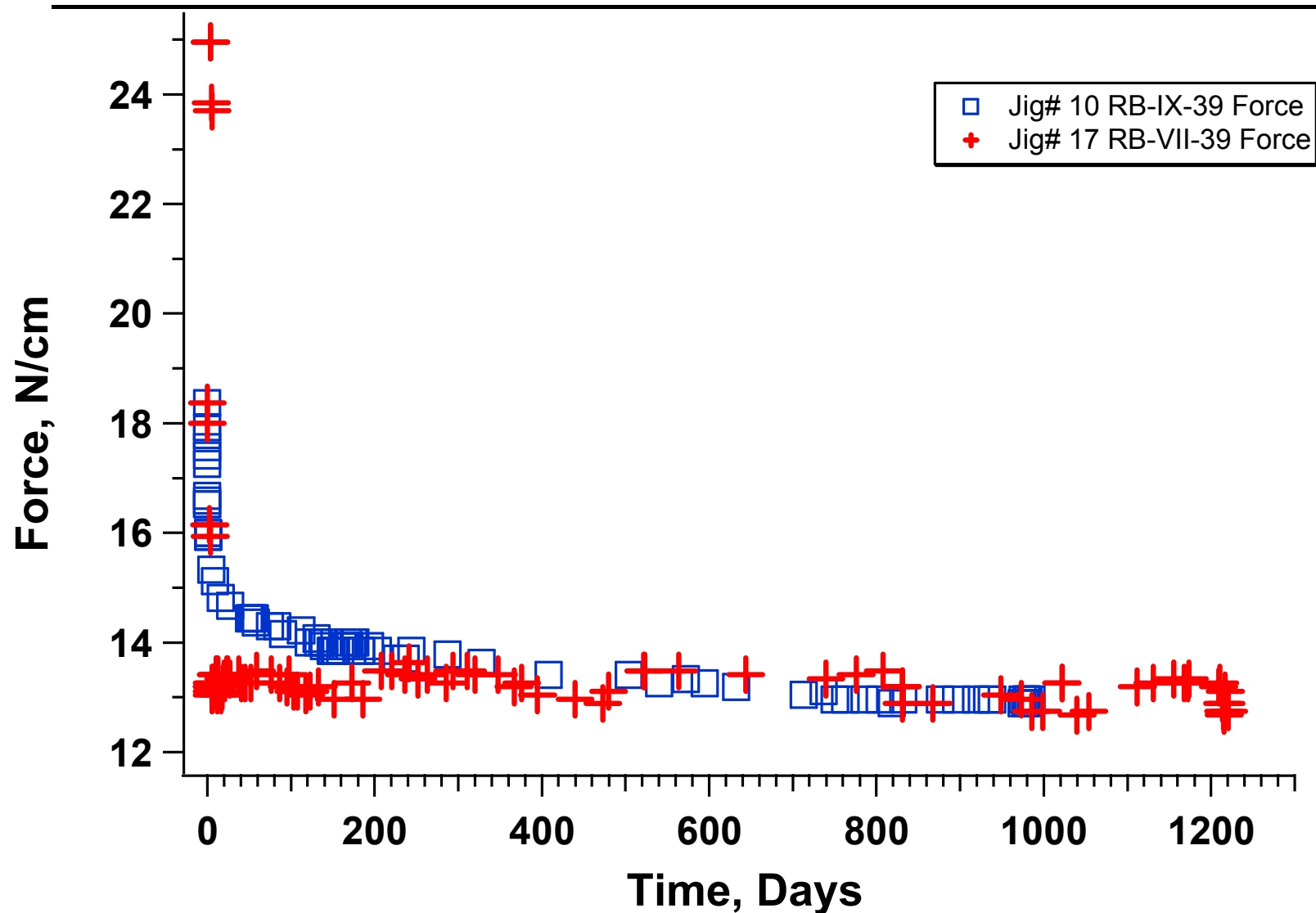
Over Compression Methodology



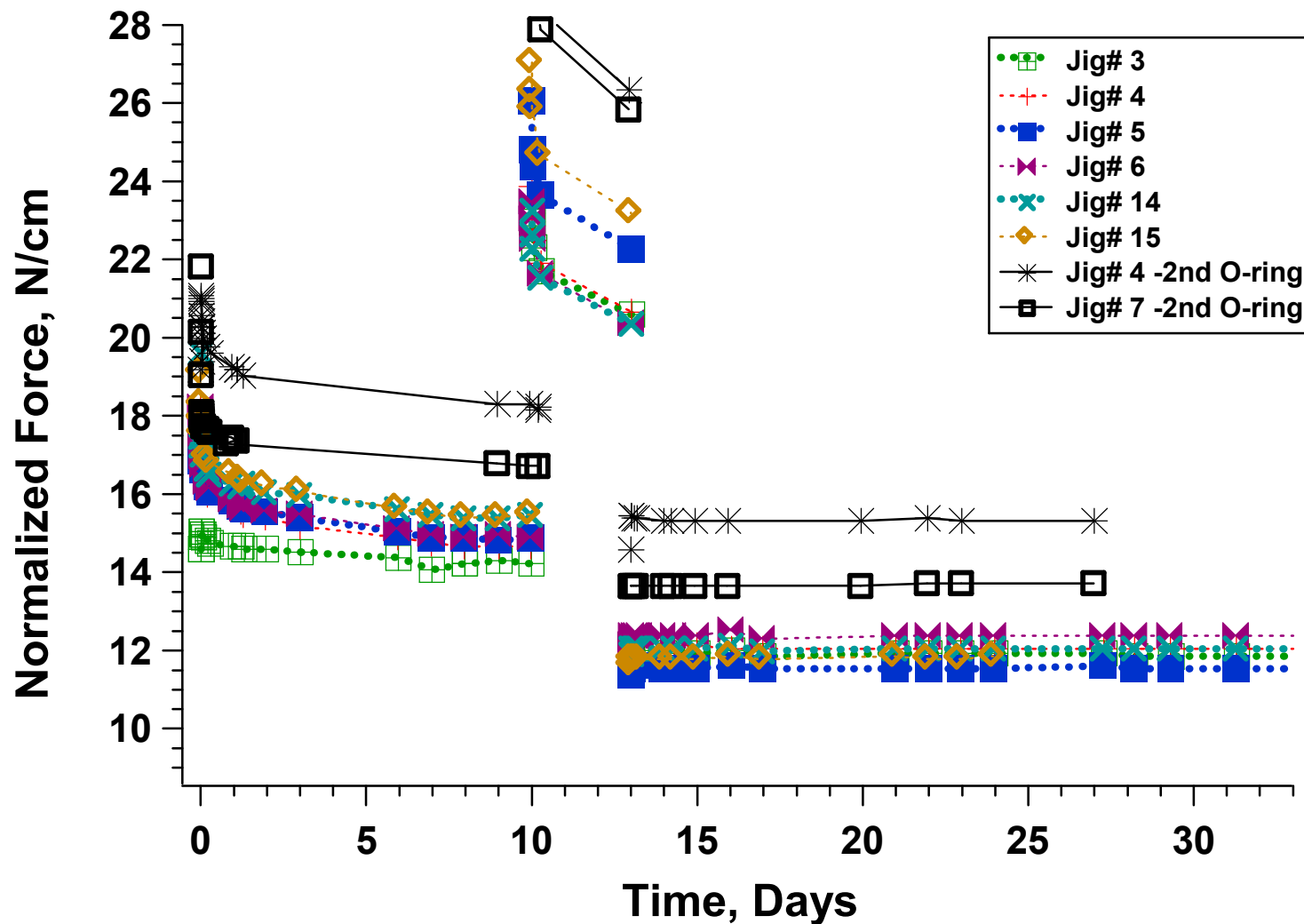
Over compression



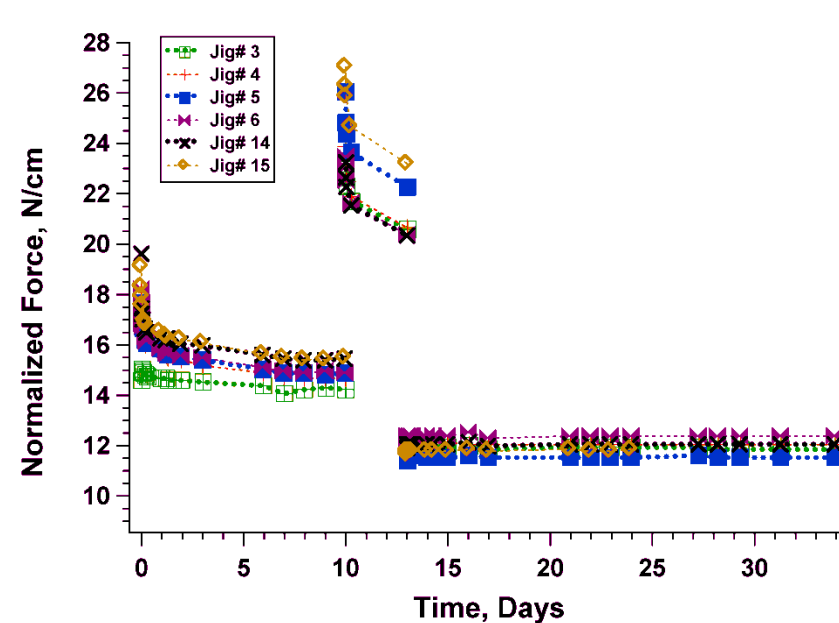
Over compression comparison



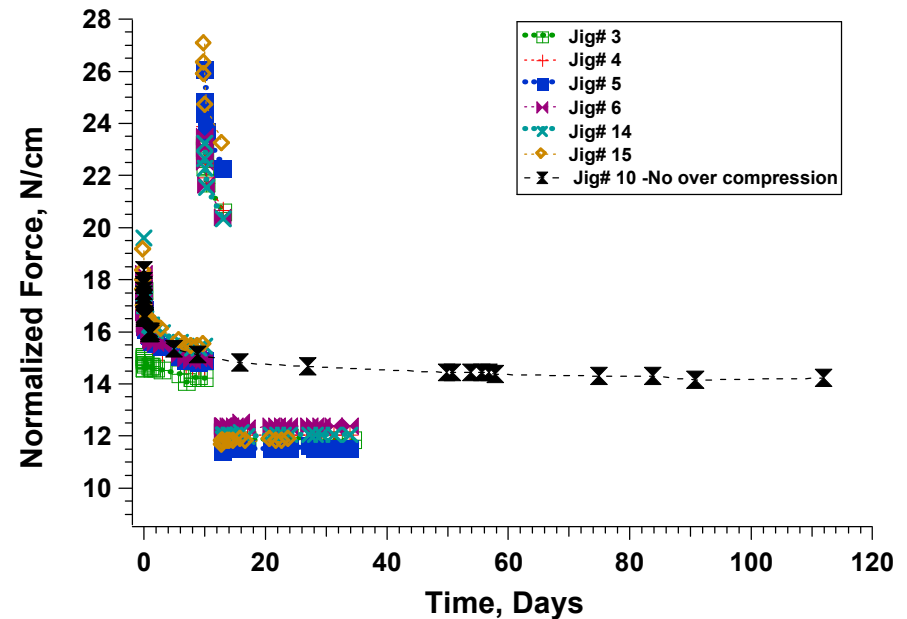
Over Compression: Multiple Jigs; Different O-rings



Over Compression: Multiple Jigs; **Same** O-ring



Good reproducibility



Much shorter equilibrium time



Over Compression: Multiple Jigs; Different O-rings

Jig#	~10 day	~After over compression	~ % drop
3	14.2	11.9	16
4	14.67	12.04	18
5	14.89	11.53	23
6	14.89	12.37	17
14	15.4	12.05	22
15	15.4	11.78	24
4	18.3	15.3	16
7	16.7	13.7	18



Accelerated aging

1) Physical force decay

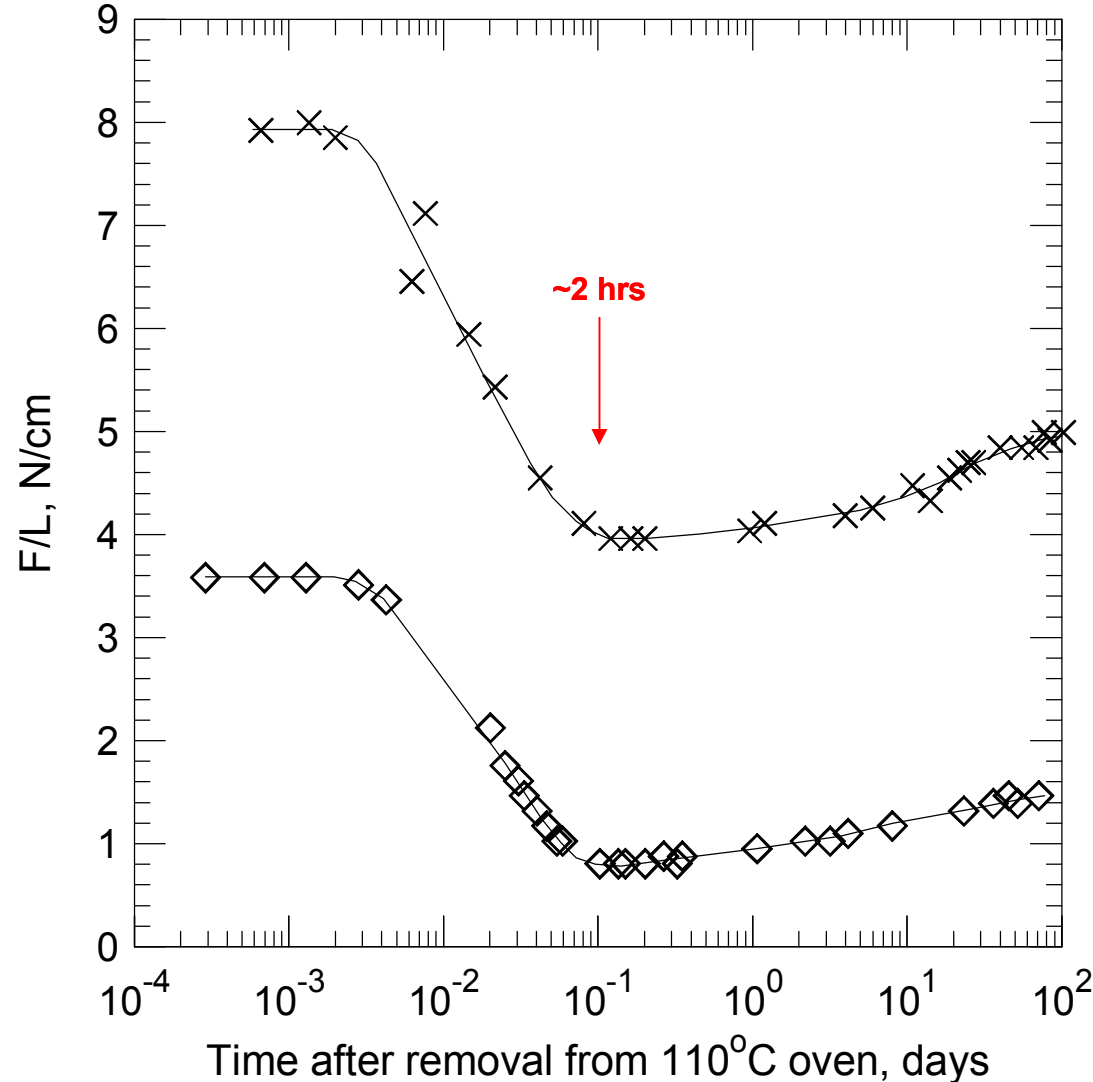
- Equilibrium values achieved –starting point
- Ability to get field returned o-ring force –ending point

2) Chemical force decay

Prediction of force changes as a function of aging



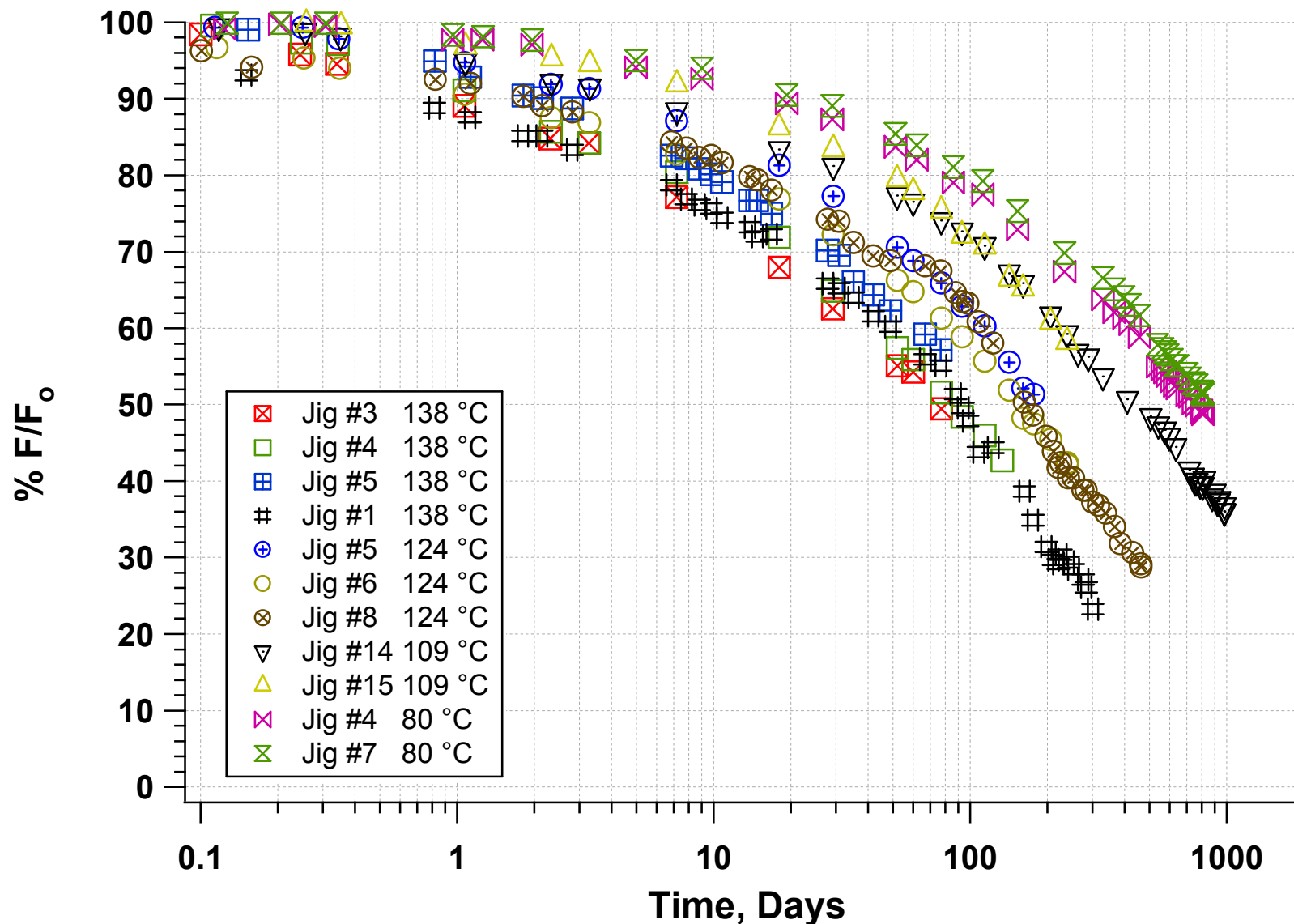
Why we do isothermal measurements...



Sealing force per unit length versus time out of a 110 °C oven for two CSR jigs containing Butyl-A o-ring segments that had aged under 25% compression until the force degraded by ~42% (top curve) and ~72% (bottom curve), respectively.



All Jigs at Temperatures -Fluorosilicone



Time-Temperature Superposition

Does mechanism change as a function of temperature?

If same mechanism:

- same shape (log graph)
- should be constant acceleration (multiple)

1. Pick a reference temperature
2. Multiply the time at each temperature by the constant that gives the best overlap with the reference temperature data
3. Define that multiple as 'a_T' (a_T = 1 for ref. temp.)
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Plot log(a_T) vs 1/T linear if Arrhenius

Gillen, K. T.; Celina, M.; Clough, R. L.; Wise, J. *Trends in Polymer Science*, Extrapolation of Accelerated Aging Data -Arrhenius or Erroneous? 1997, 5, 250-257.

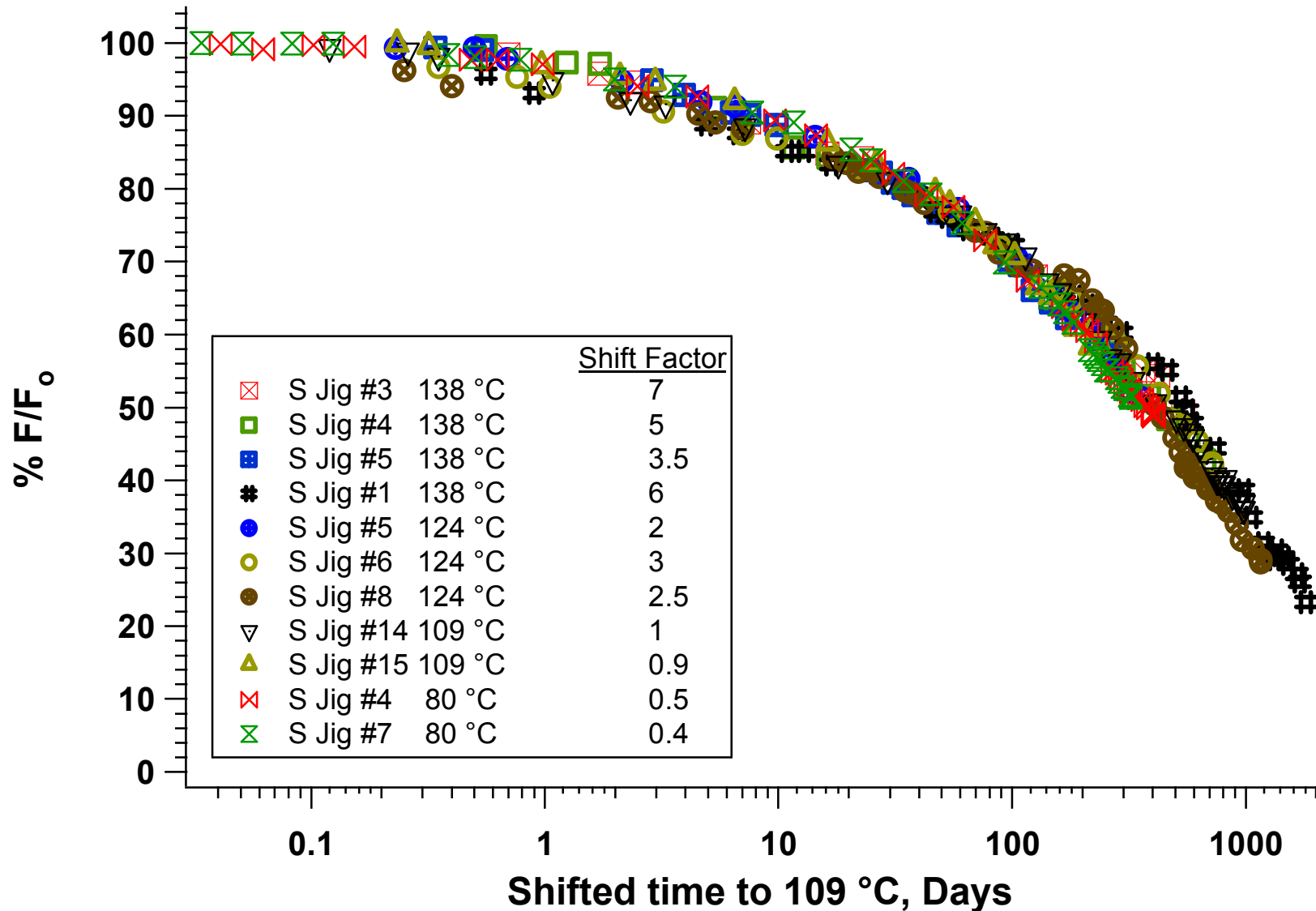
Arrhenius equation: Empirical equation

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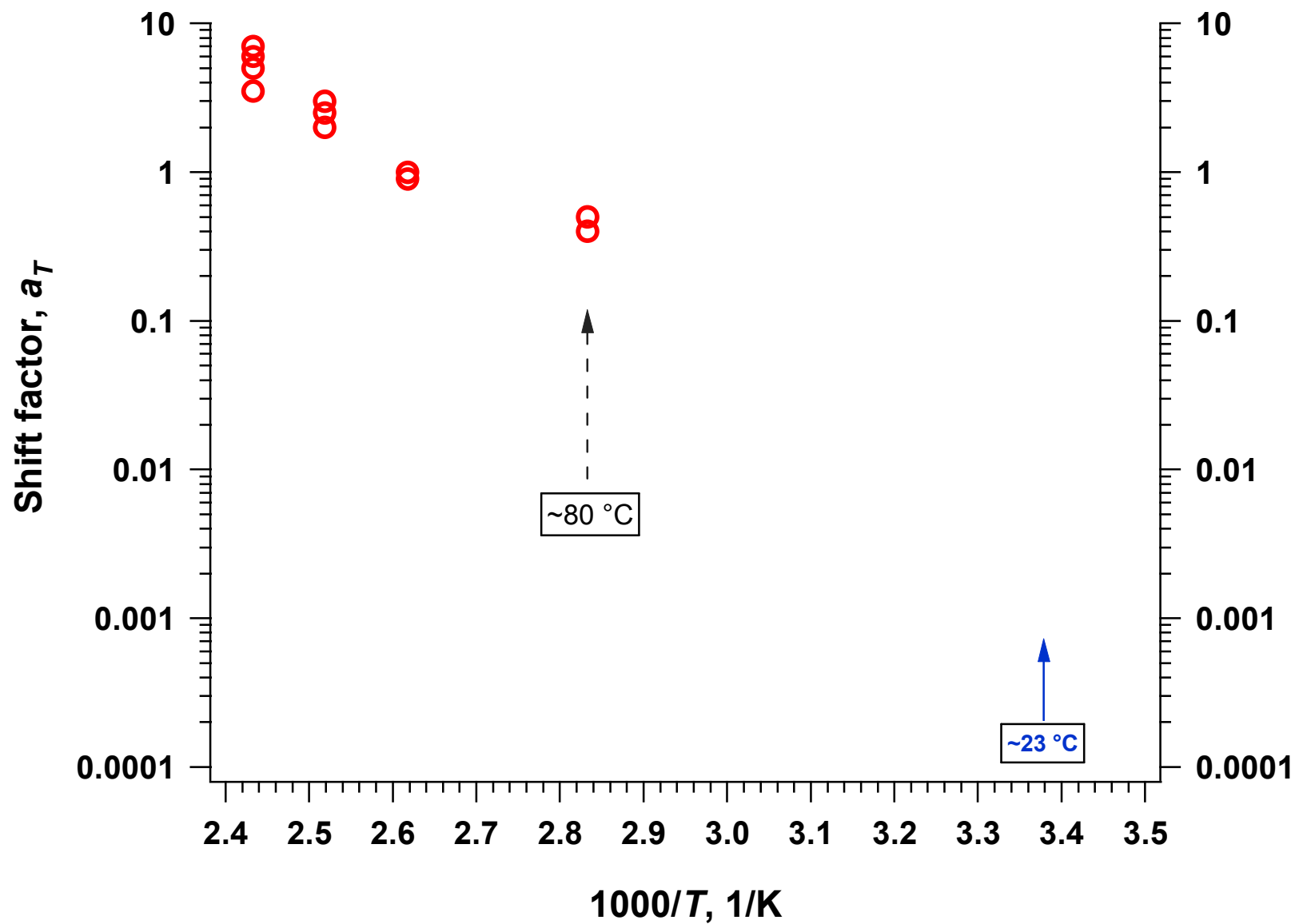
$$\ln(k) = \ln(A) - E_a/RT$$



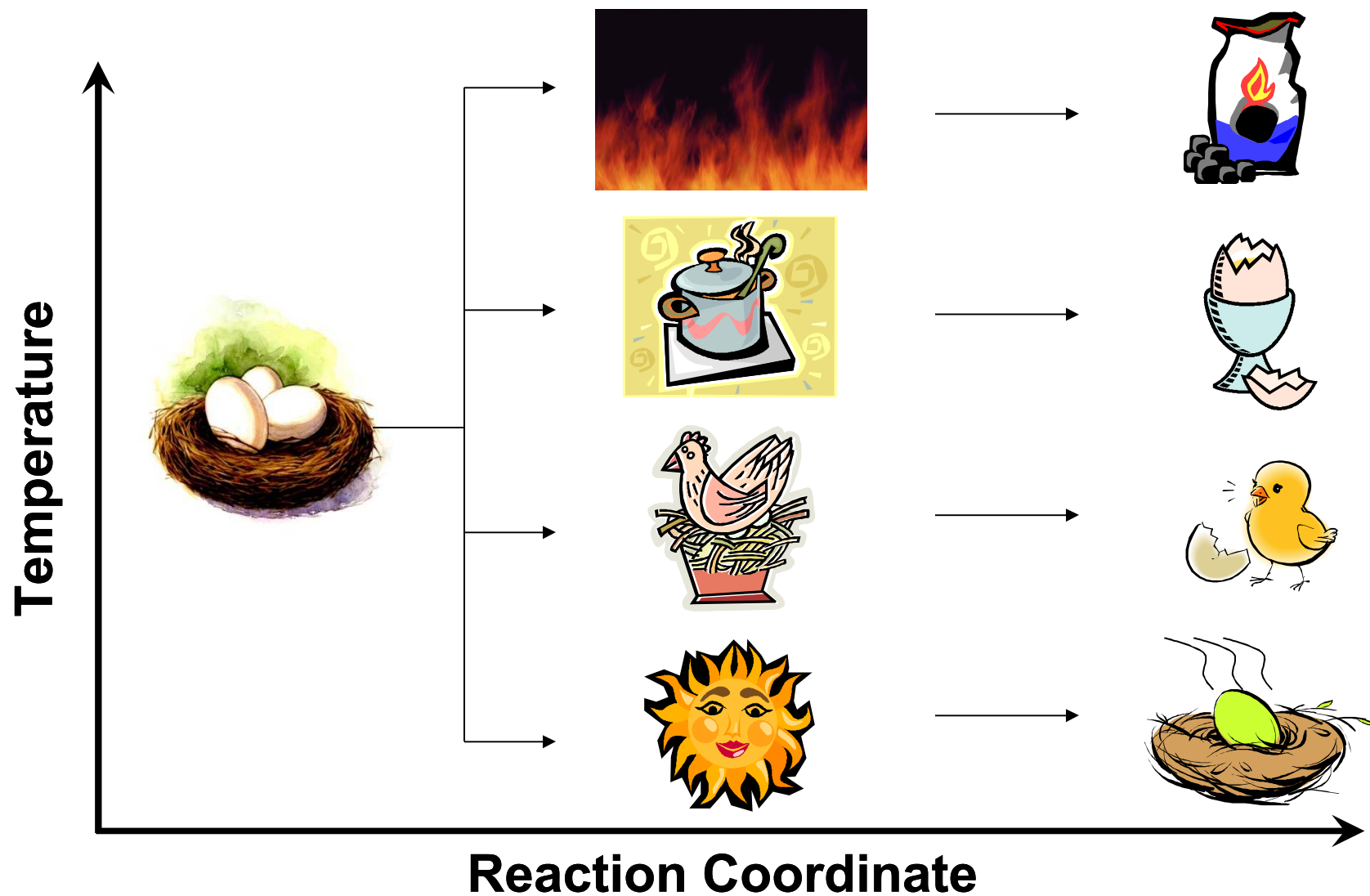
Time-Temperature Superposition



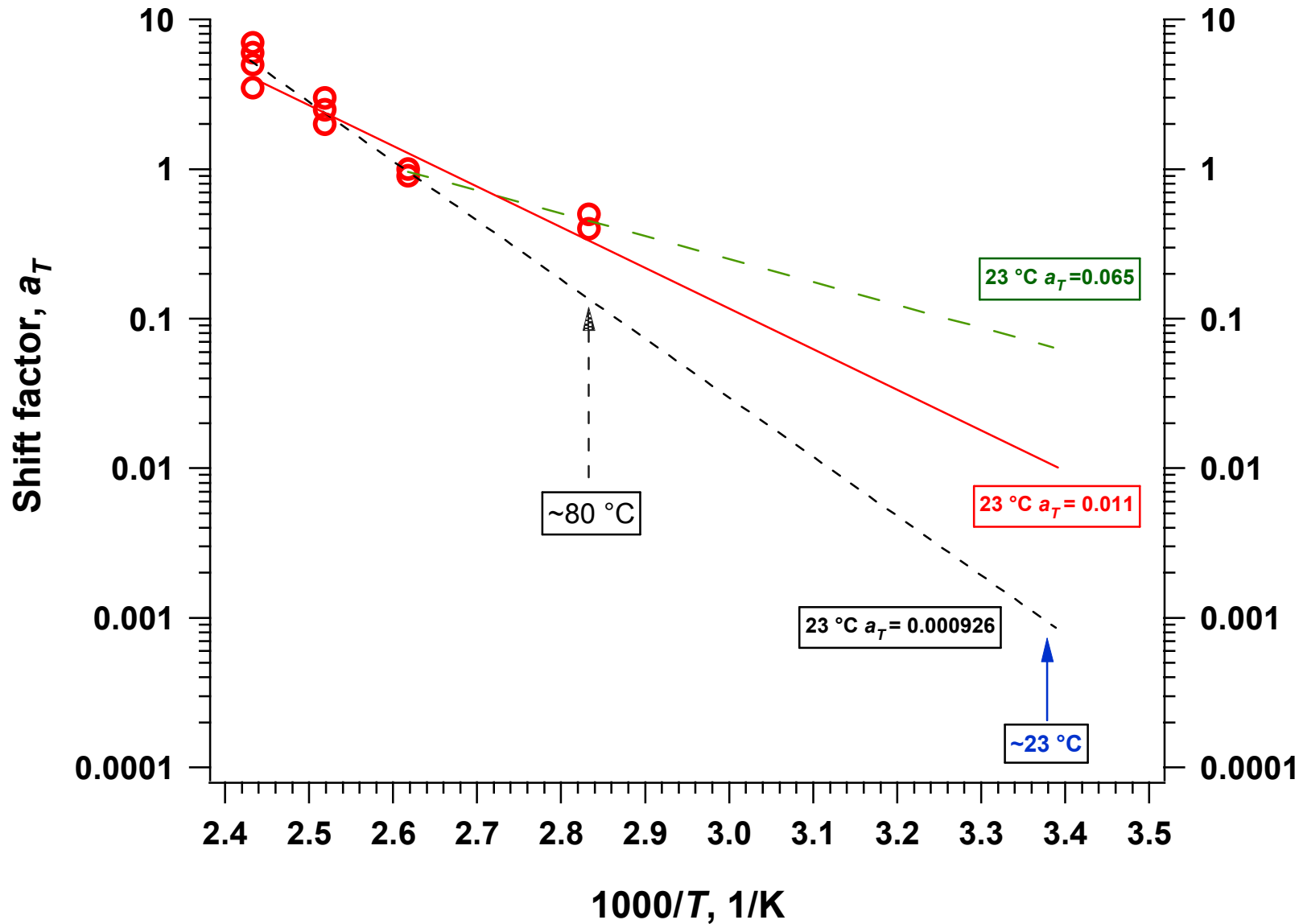
Shift Factor Plot



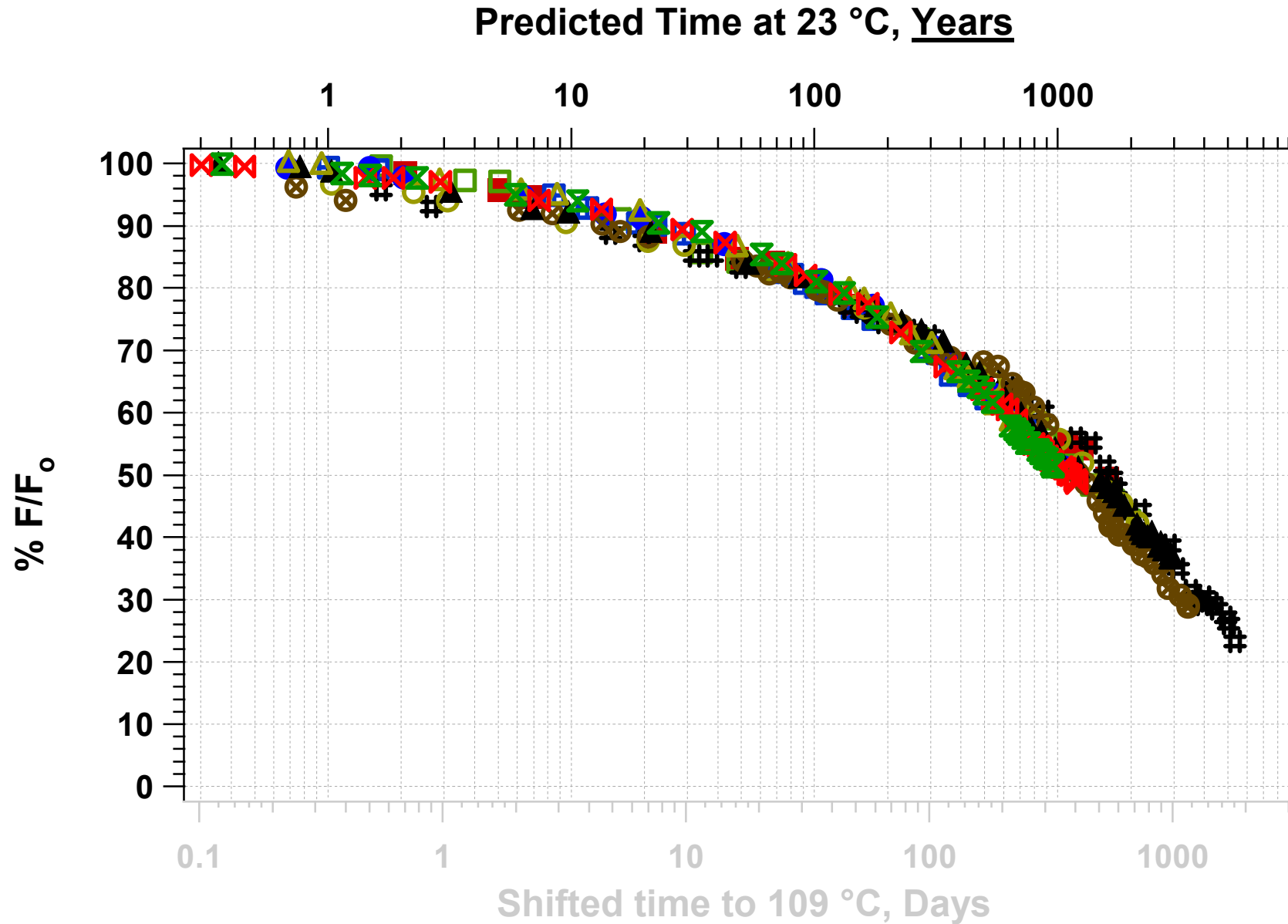
'Accelerated Aging'



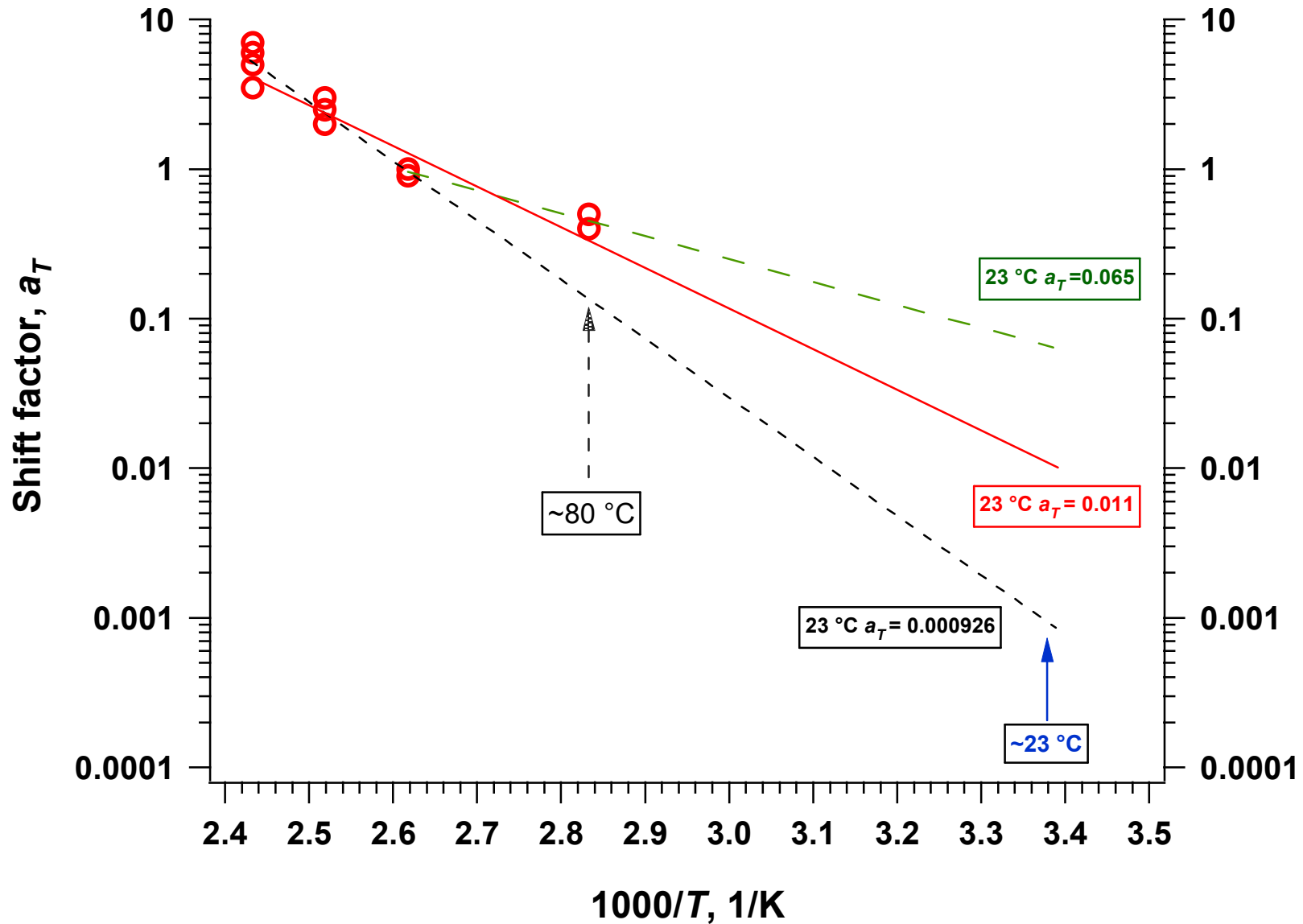
Shift Factor Plot



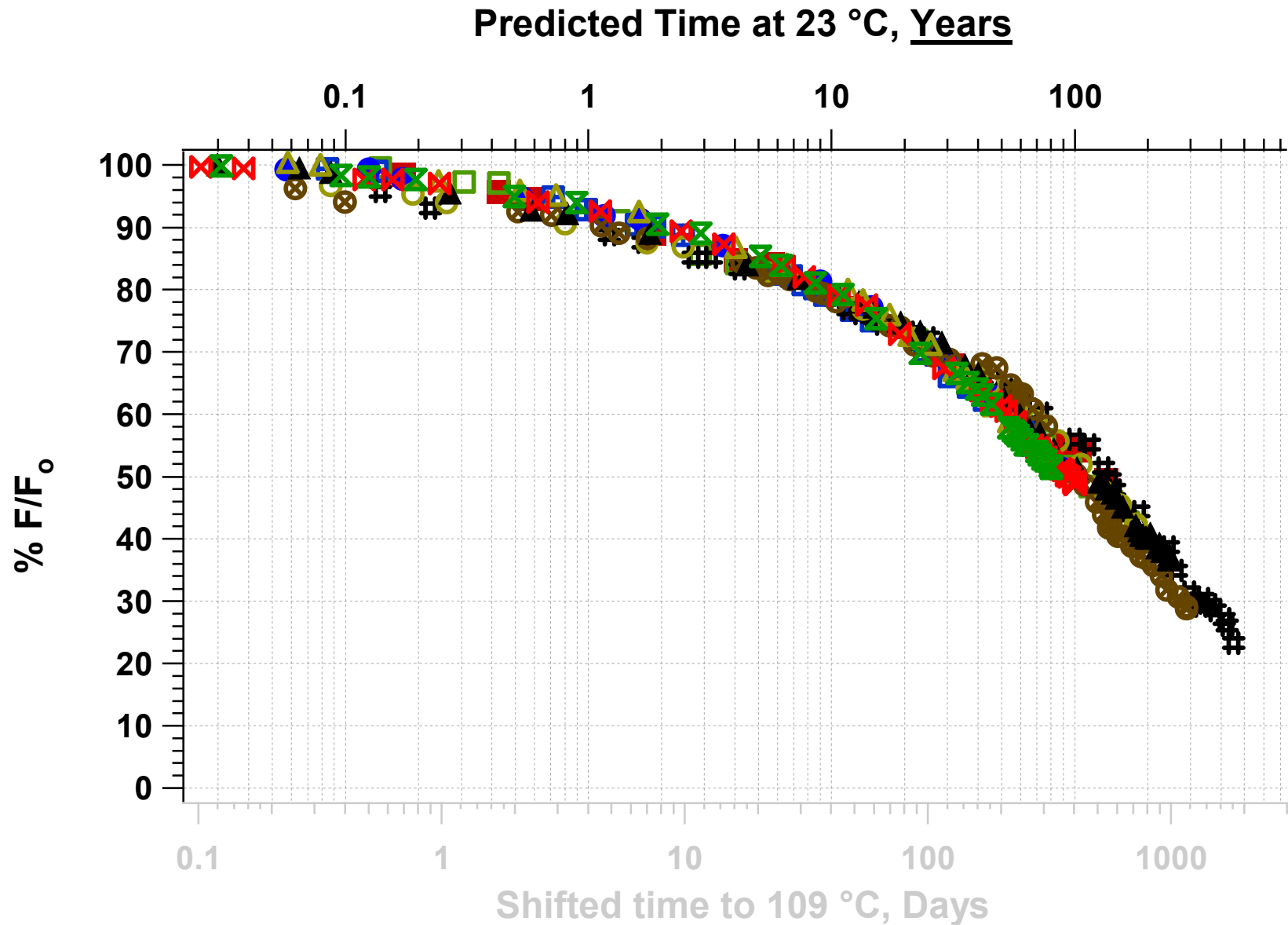
Shifted Data with RT 'Prediction' w/o 80 C data



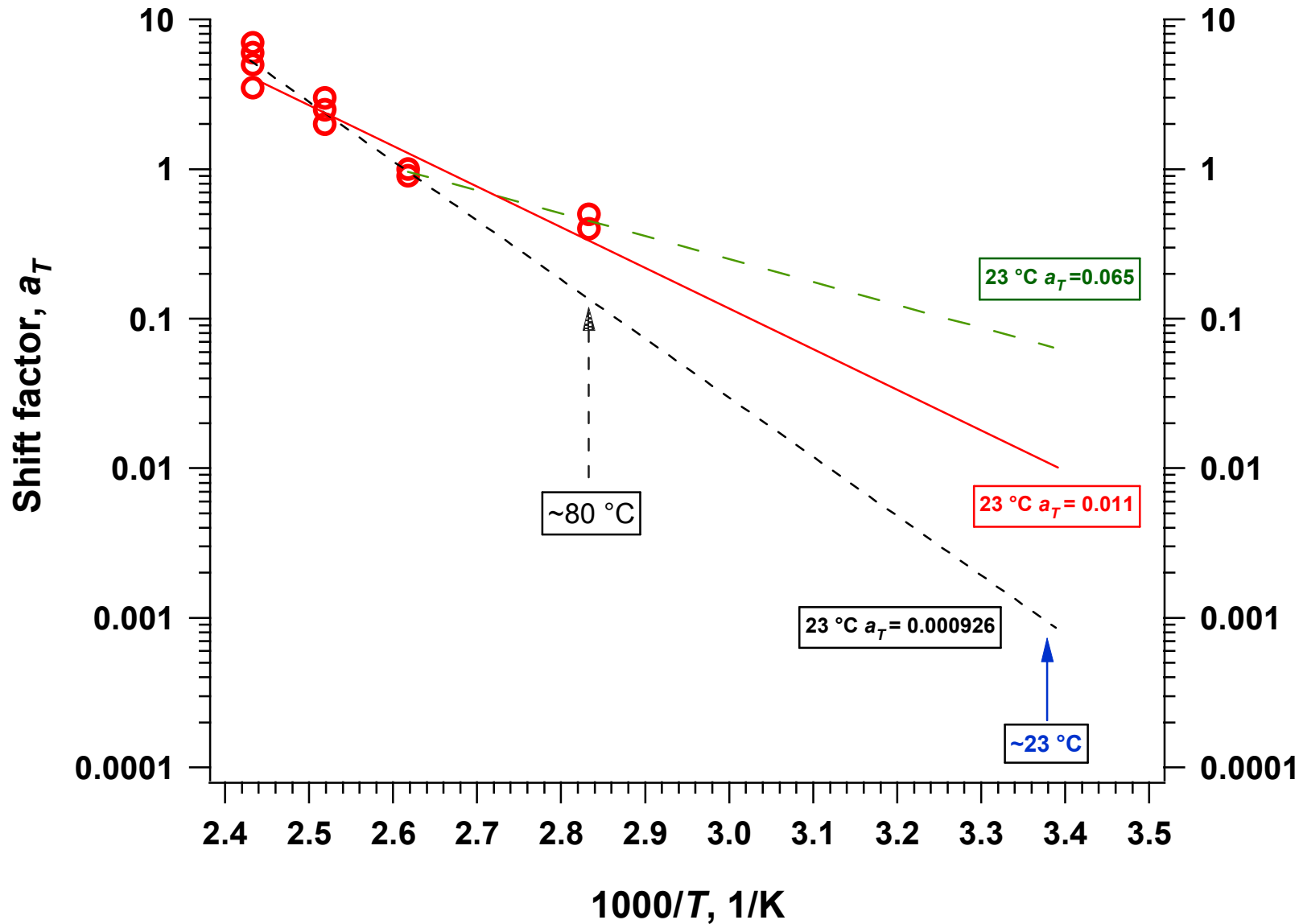
Shift Factor Plot



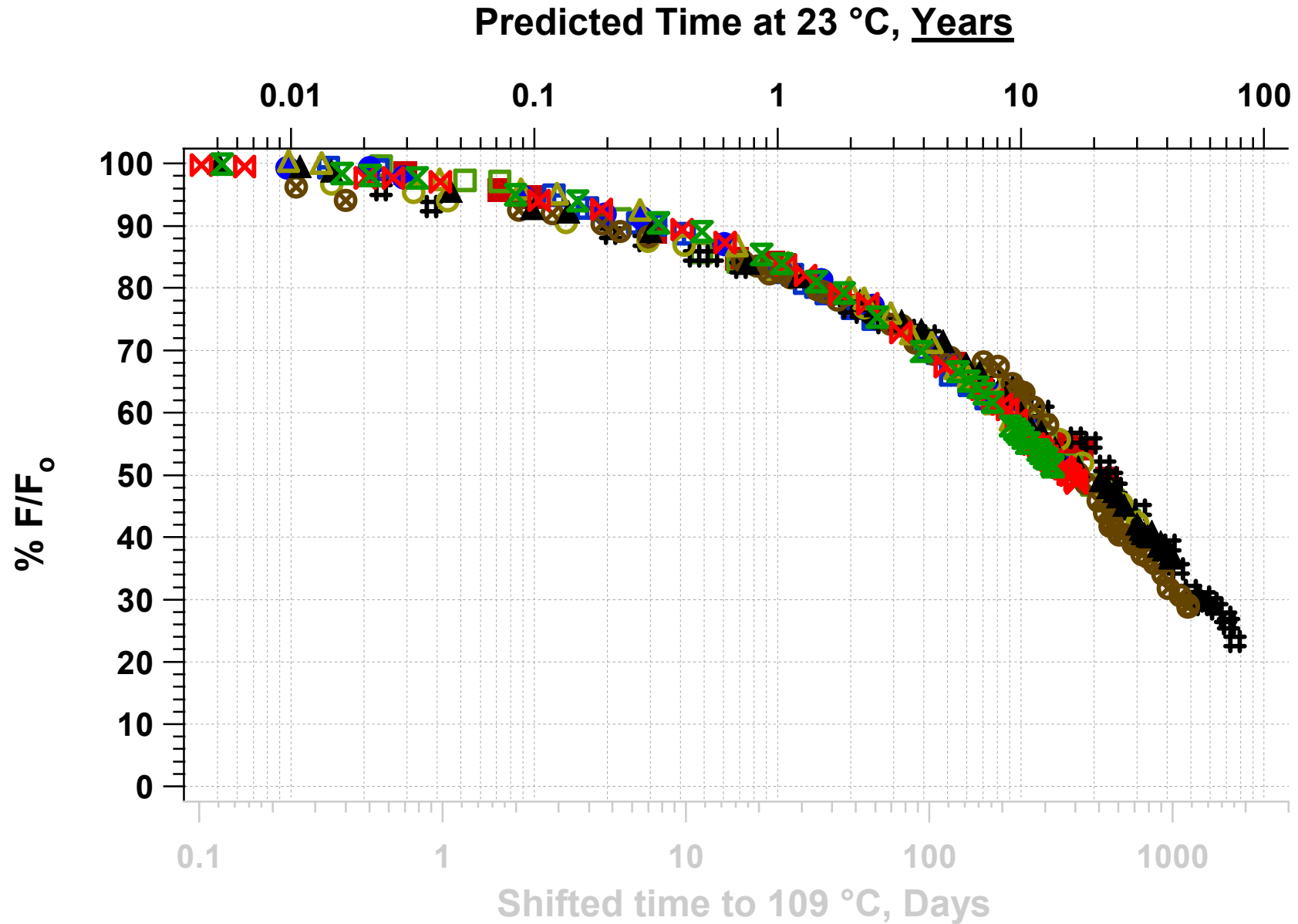
Shifted Data with RT 'Prediction' All data



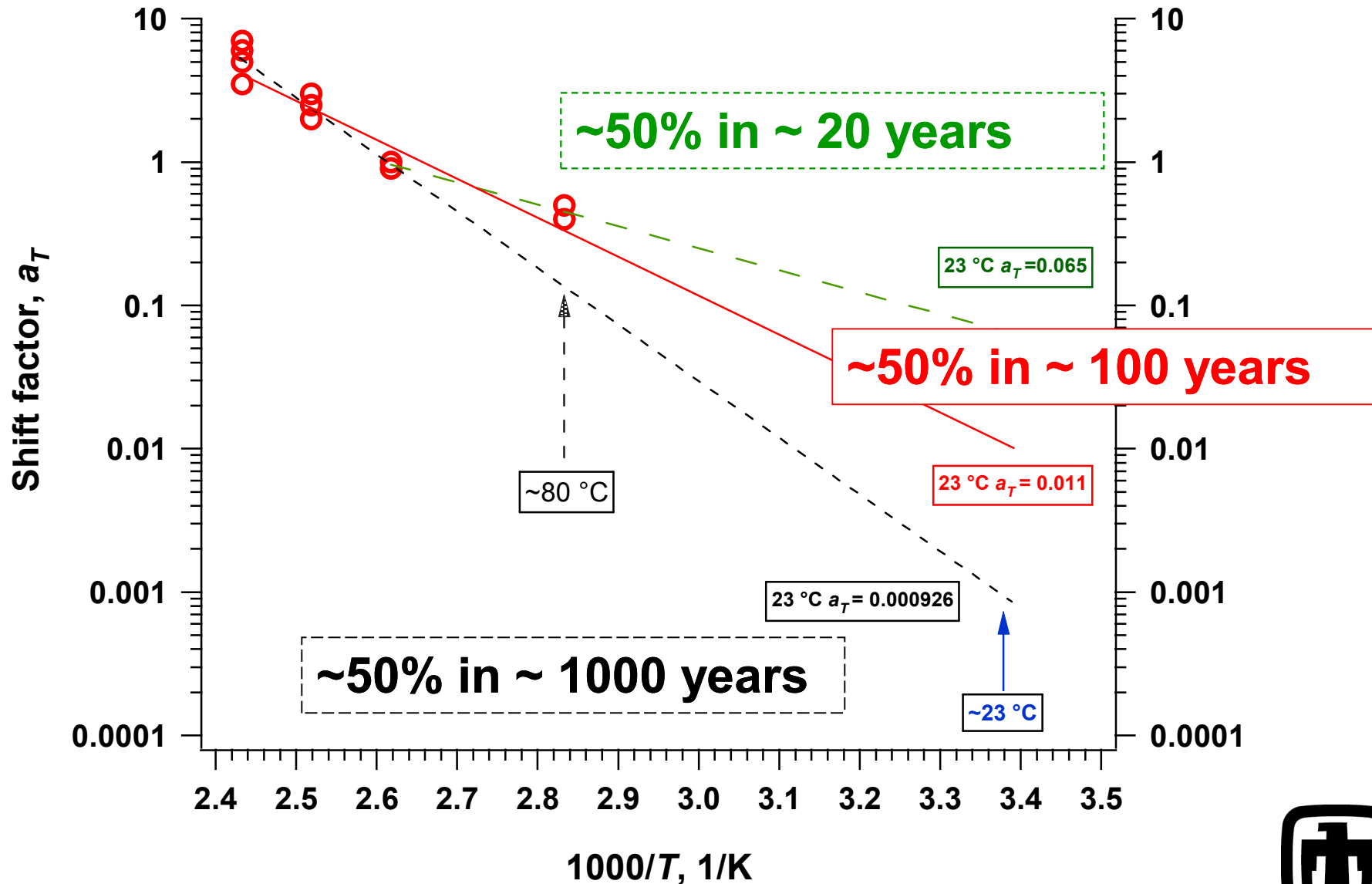
Shift Factor Plot



Shifted Data with RT 'Prediction' 109 and 80 only



Shift Factor Plot



O-rings

Sealing force arguably most important parameter

Correlation between equilibrium values

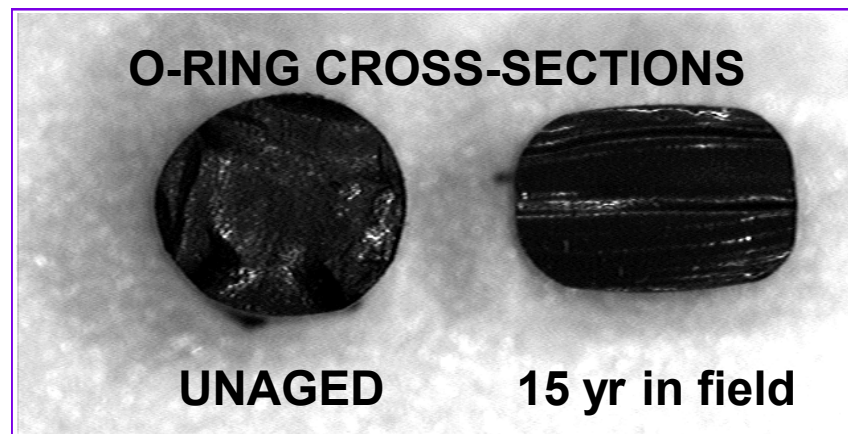
sealing force

Difficult to measure
slow and laborious



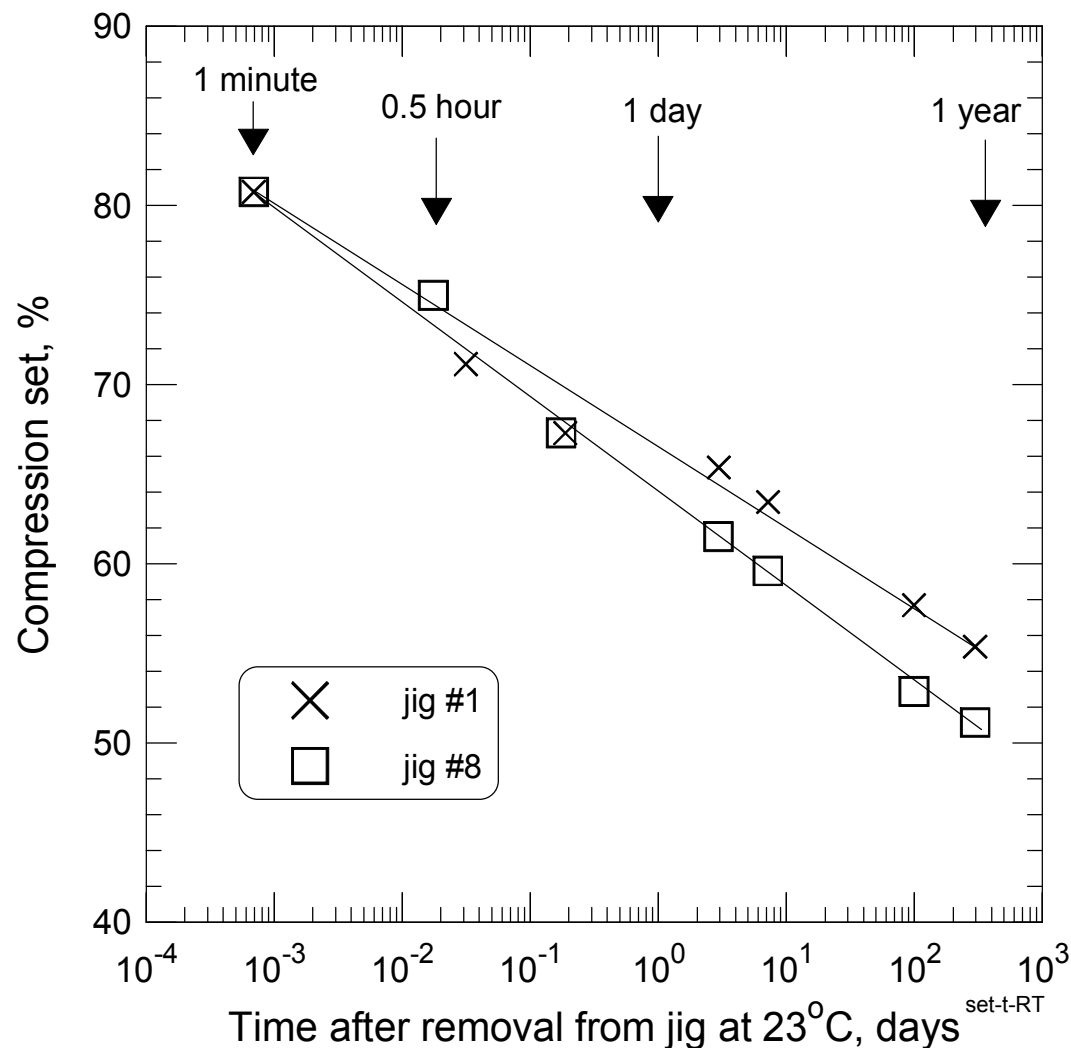
compression set

Easy to measure
quick and simple



O-ring Compression Set

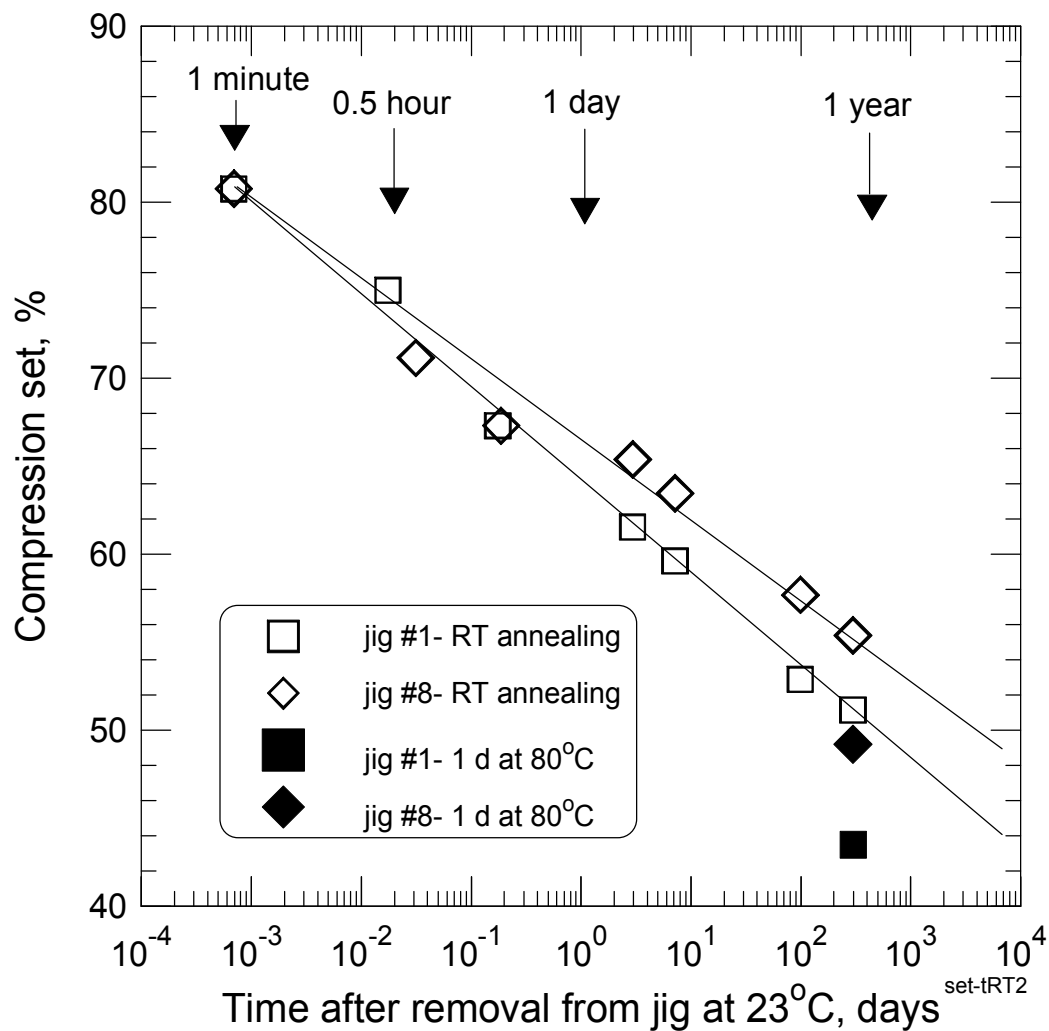
Compression set easy to measure but *changing* with time



Equilibrium set can take a long time



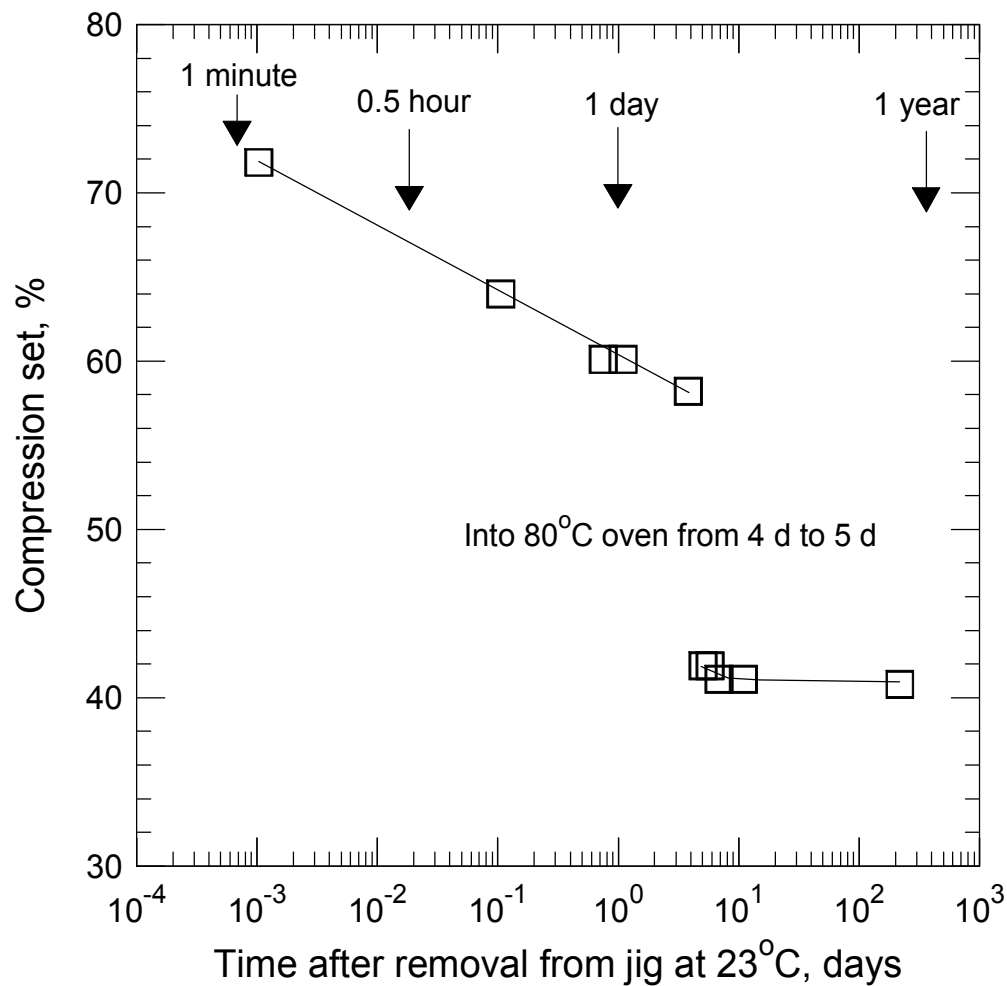
Compression set



**After ~1 year at RT, samples put into 80 C oven for ~ 1 day
(would have taken ~30 years at RT to continue that drop)**



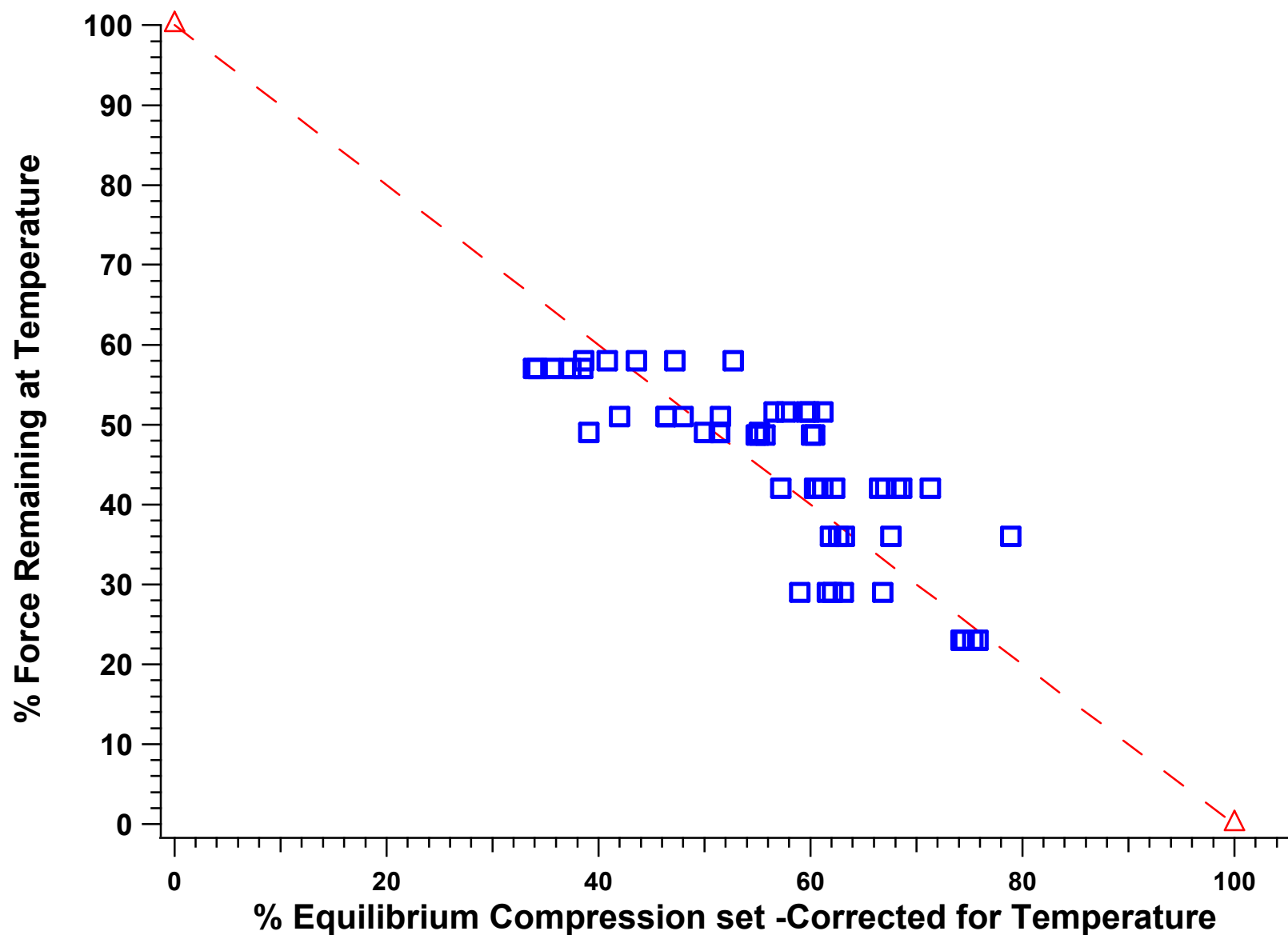
Equilibrium Compression Set



After oven exposure; additional 210 days at room temperature only dropped the set by another 1%



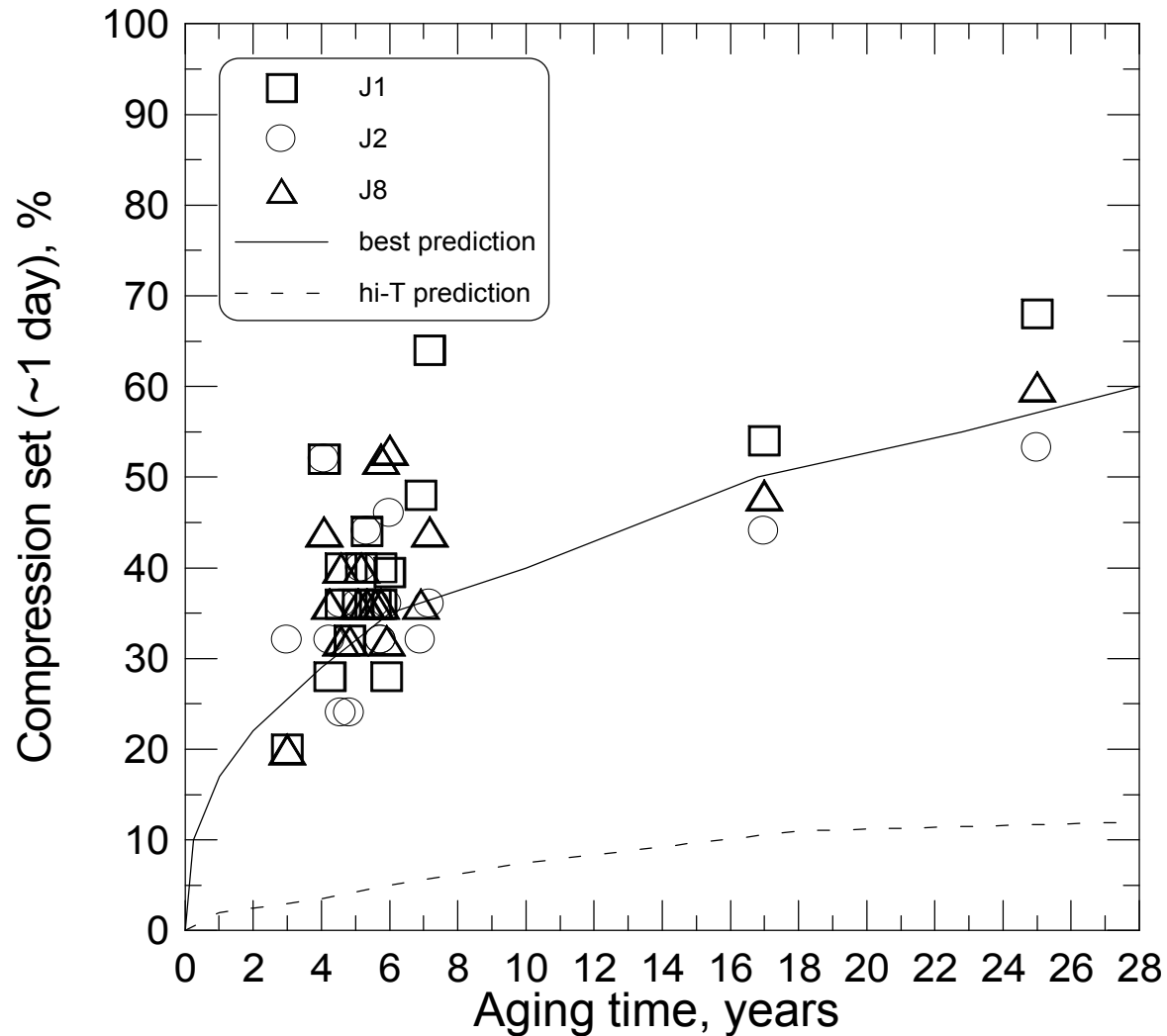
Force versus Compression Set Data -Fluorosilicone



Field Data*

79

* not quite the whole story, but good enough for this conversation!

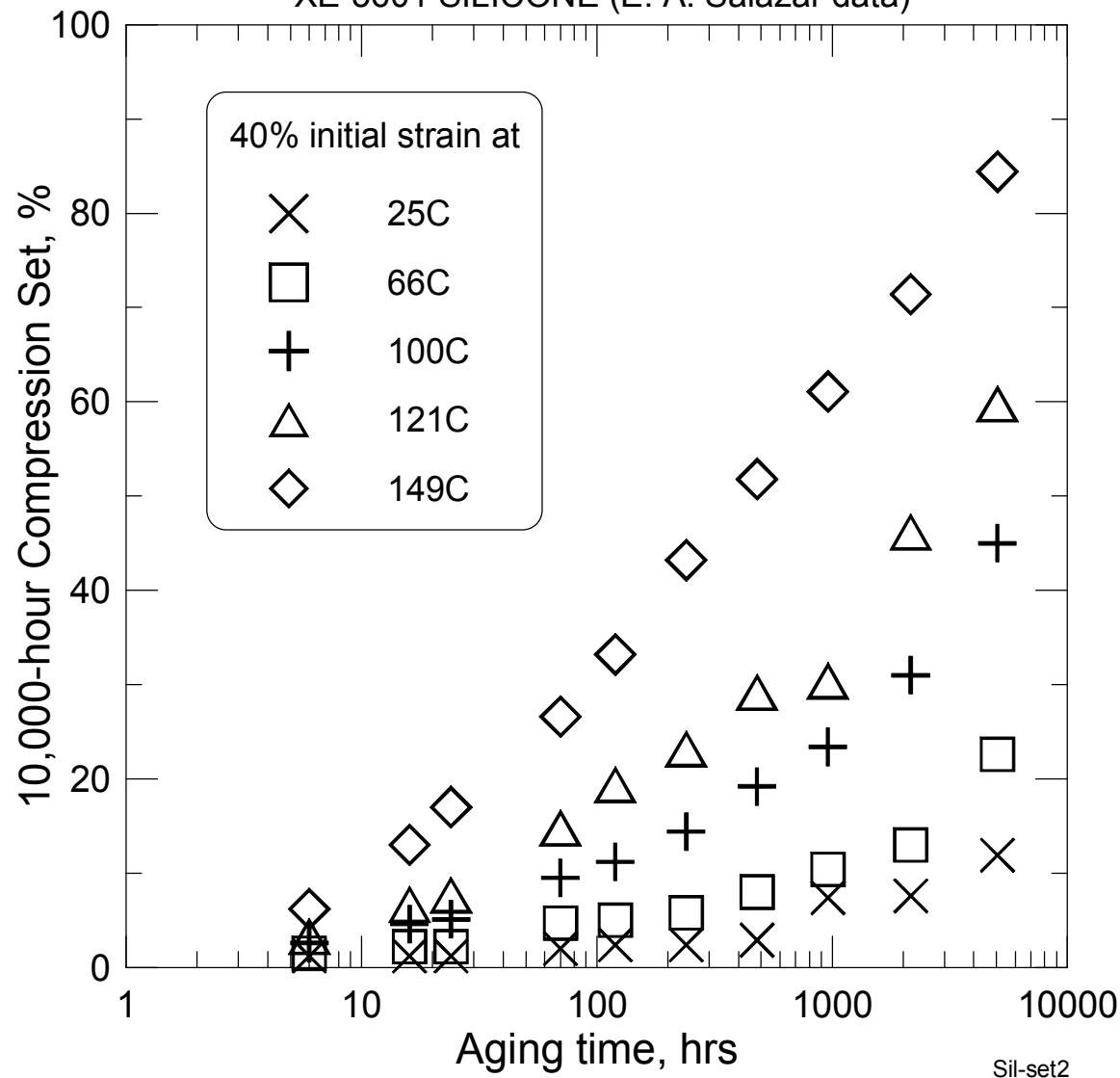


Compression set measurements of three fluorosilicone o-rings taken on surveillance units approximately 1 day after removal from the unit. The solid curve and the dashed curve assume a linear relationship between set and force decay.



Other Compression Set Data

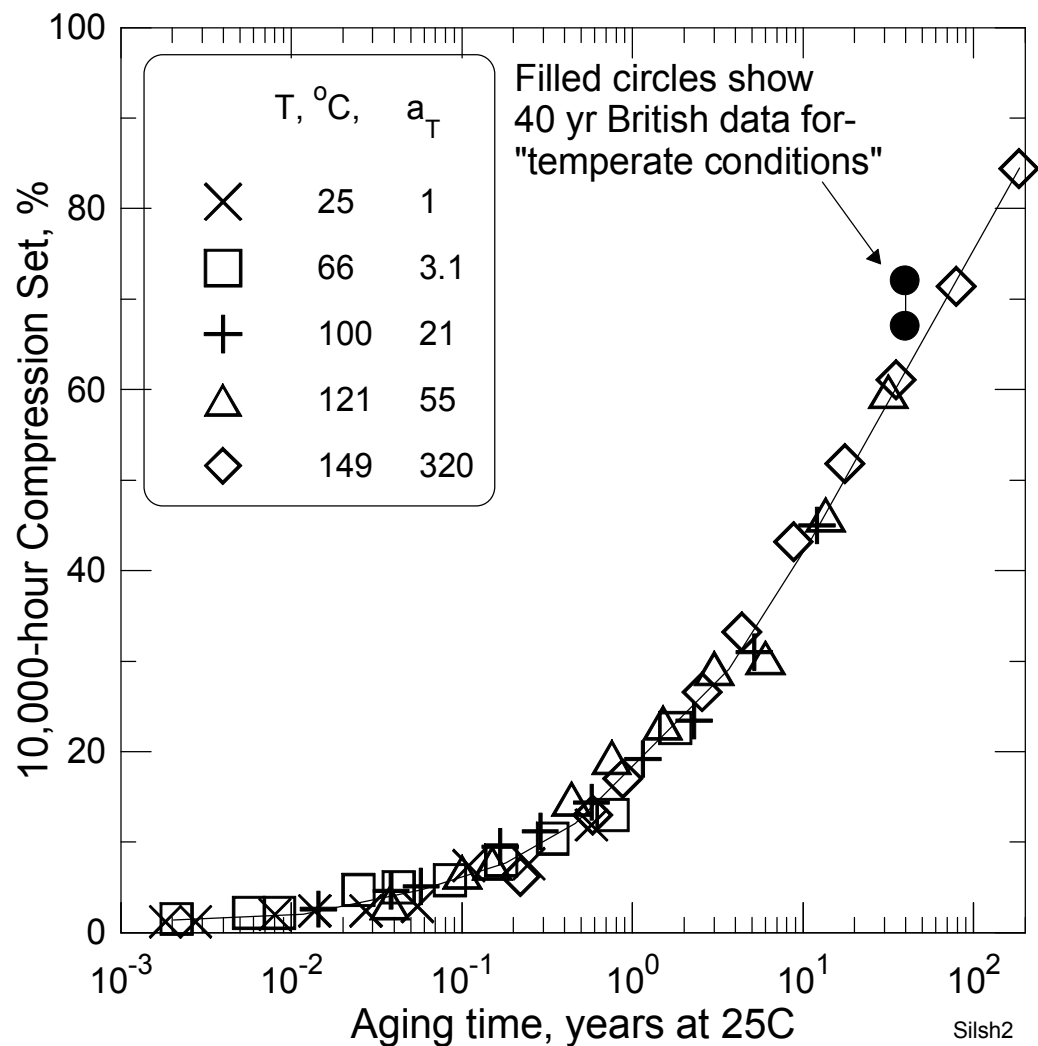
XE-5601 SILICONE (E. A. Salazar data)



Different Silicone
Different Program
Different PI



Compression Set

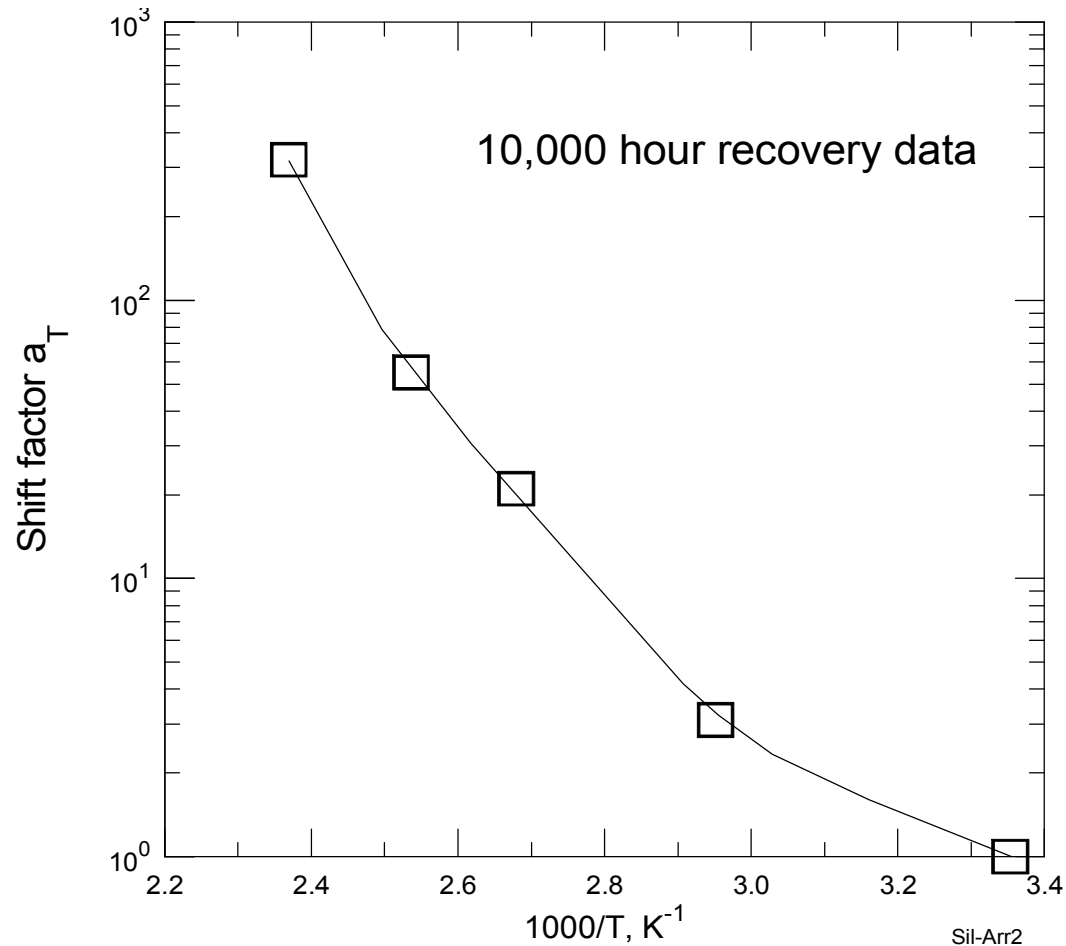


Data Analyzed by Gillen

**Added in 40 year RT
data from another
source**



Arrhenius Plot for Compression Set

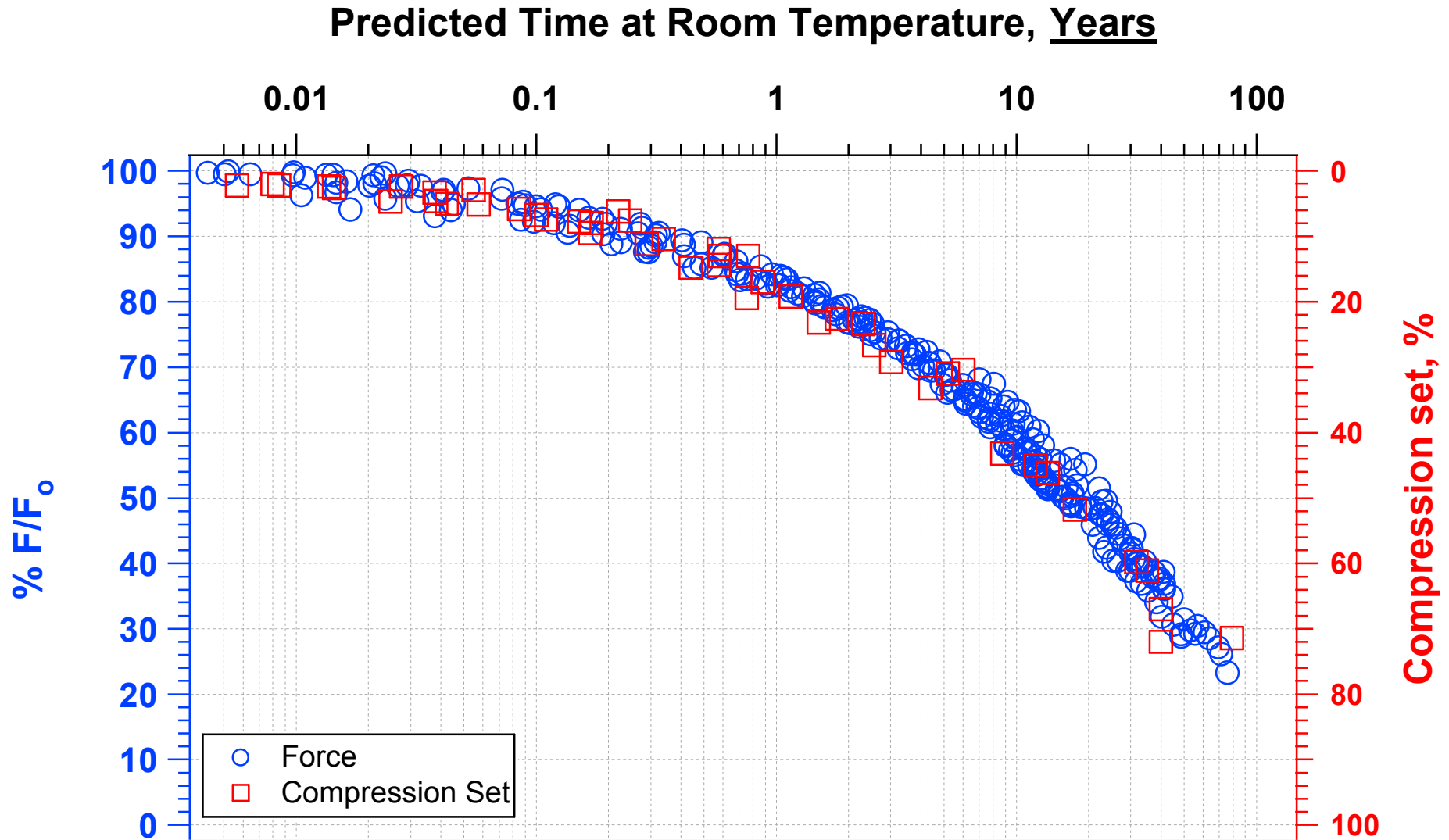


Arrhenius plot of the shift factors for silicone compression set which leads to an aging room temperature prediction for compression set

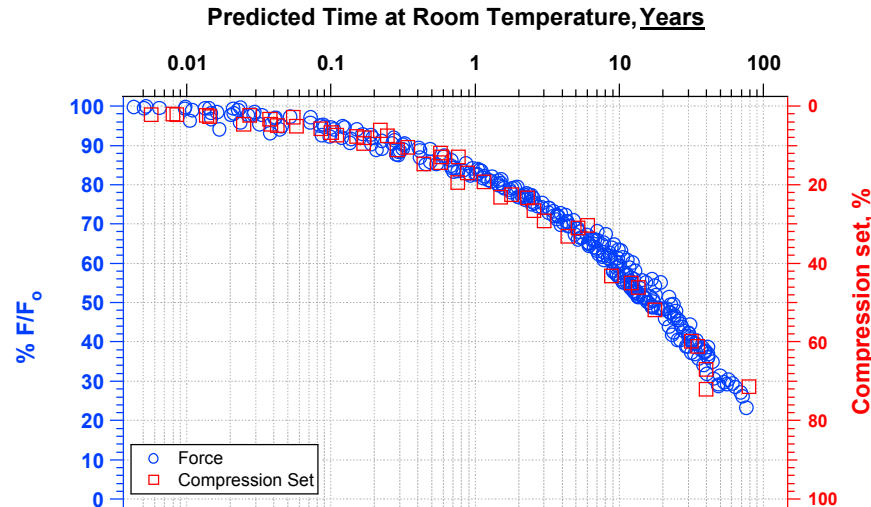
Gillen, K. T. "Silicone seal analysis," Internal Memo, SNL, 2001.



Force versus Compression Set Data



Force versus Compression Set Data



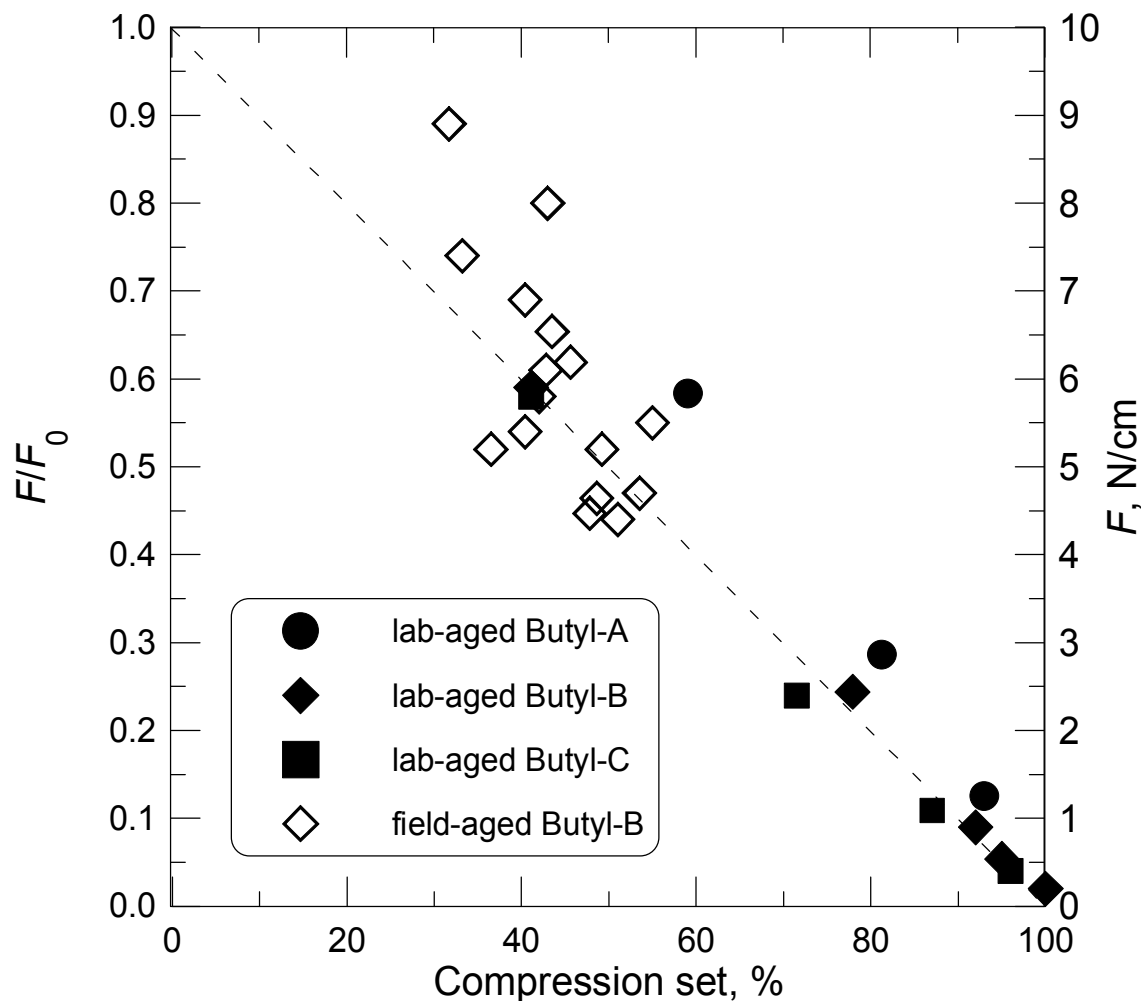
Correlation between current Silicone Force data and Compression set data obtained from *three different sources (and different sizes!)*

Fluorosilicone versus Silicone!!

Displays confidence in generalized predictions about silicone o-rings state of health (CS easy to measure) under oxidative environments*



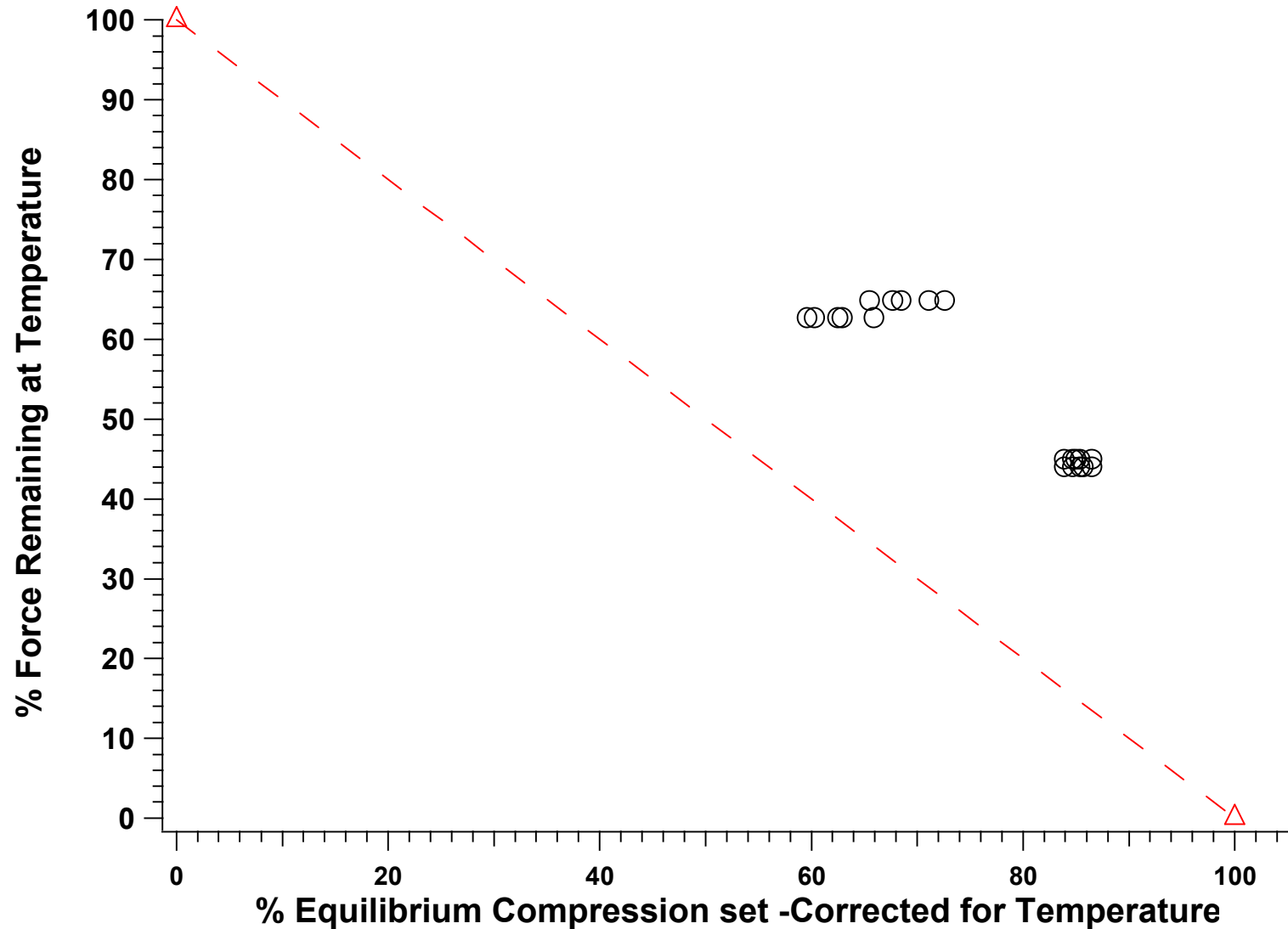
Butyl Force vs. Compression set; lab and field aged



Equilibrium values of compression set plotted versus F/F_0 for laboratory-aged o-rings for three butyl materials plus field results for Butyl-B plotted assuming that $F_0 = 10$ N/cm.



Heavily Filled Silicone



Conducting o-rings compression set versus force remaining



What is 'Lifetime' for an O-ring?

(Our) O-ring Job description: Keep out water and air

Measure leak rate; use that to define 'death'



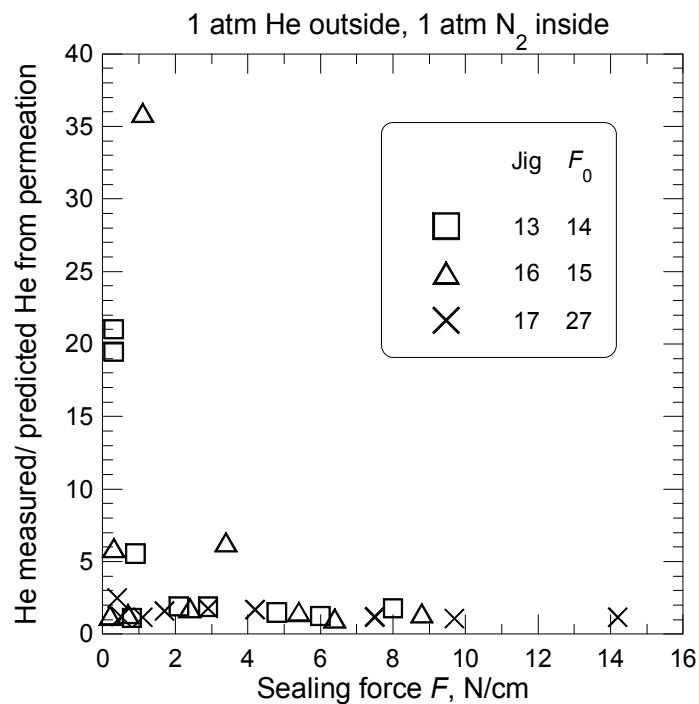
Mark Wilson's Jig



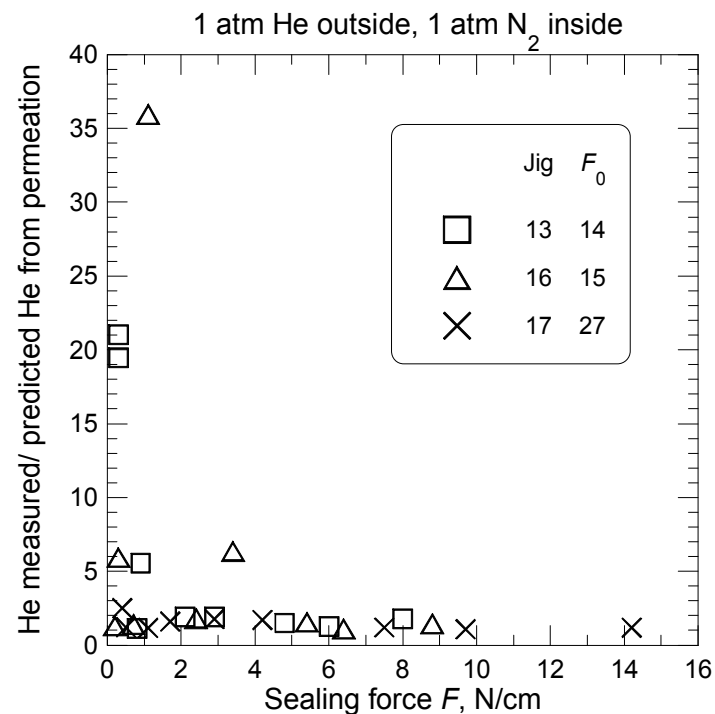
Helium leak detector



Leak Testing of O-rings



1.78 mm cross section

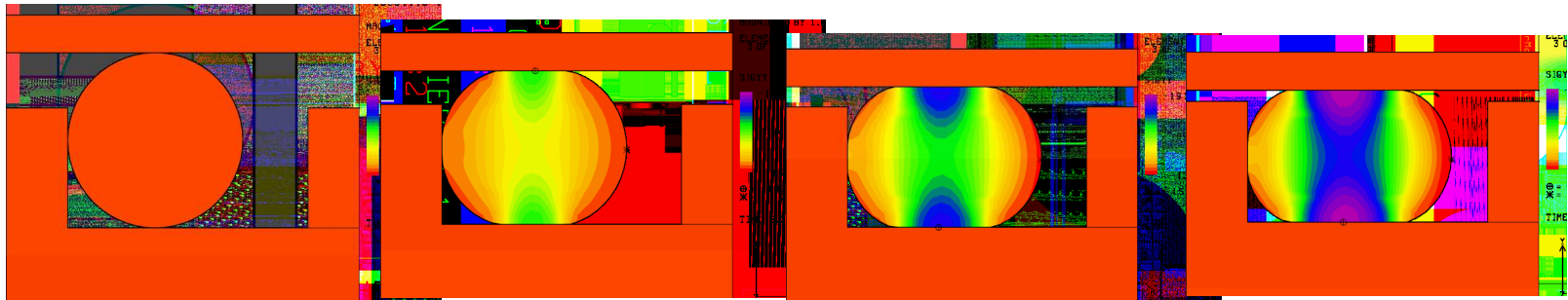
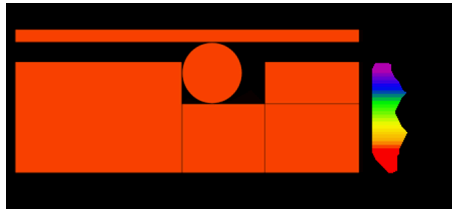


2.62 mm cross section

Death ≈ 1 N/cm sealing force



Progression of Stress Relaxation due to Chemical Aging

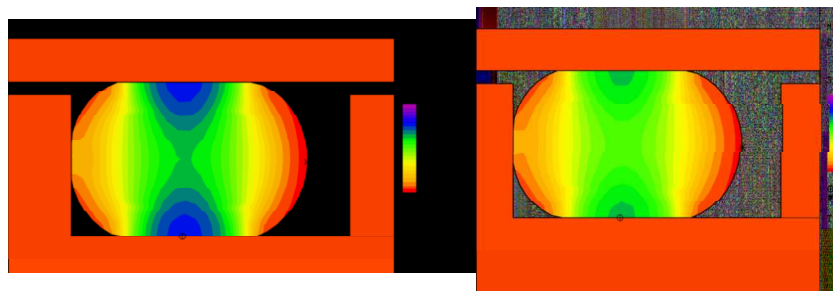


Time = 0

Time = .5sec

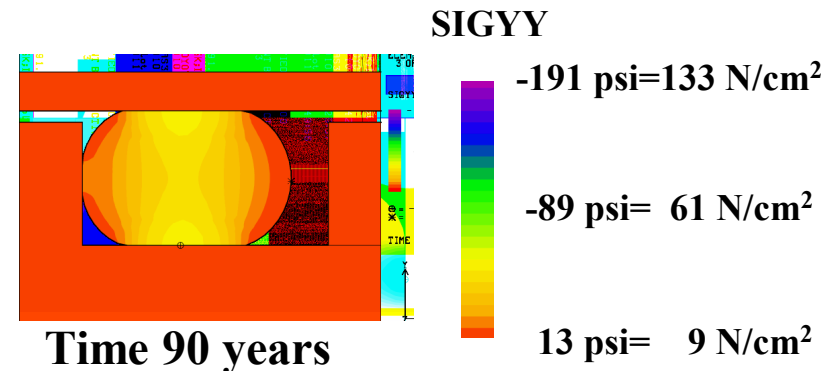
Time = .8sec

Time = 1sec



Time = 30 years

Time = 56 year



Time 90 years

SIGY

-191 psi=133 N/cm²

-89 psi= 61 N/cm²

13 psi= 9 N/cm²

Slide Courtesy of David Lo



Take home messages...

- 1) Be aware of mechanism changes
- 2) Understand chemistry/be careful with the details
 - DLO, O₂ vs. H₂O etc
- 1) Find something to measure
- 2) Do things at many temp (as far apart as possible)
- 3) Do things for very *very* long time
- 4) Validate against real world

- 5) It would be nice to know *your* performance requirements



Lots of help...

Dora Derzon, Brad Hance, Don Bradley, Roger Assink, James Hochrein, Steven Thornberg, David Lo, Kathy Alam, Laura Martin, John Schroeder, Patti Sawyer, Mark Stavig, and Ken Gillen



Questions...

