Brief Overview of Sandia Capabilities with regard to Nuclear Power Plant Cable Insulation Aging

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Workshop on U.S.-Argentina Binational Energy Working Group (BEWG) in civil nuclear power area
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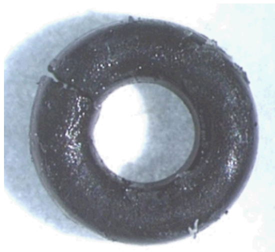
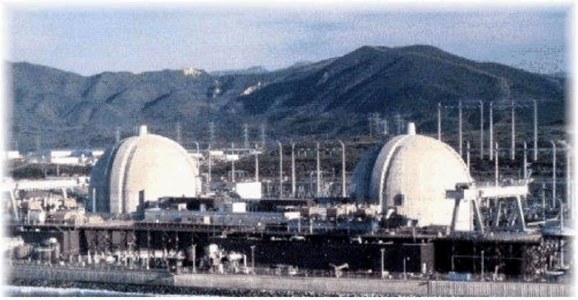
National Nuclear Security Administration

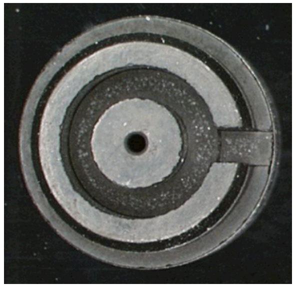
Organic Materials Problems; Organic Materials Aging and Degradation



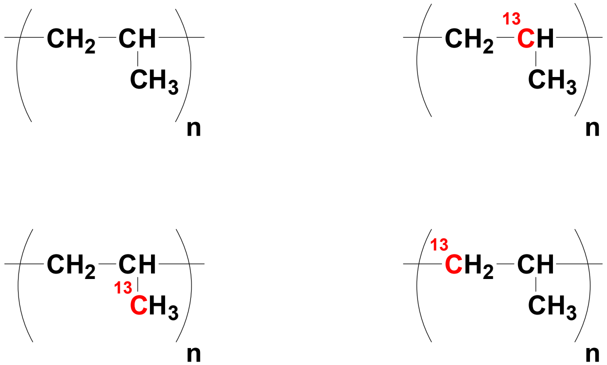
O-rings



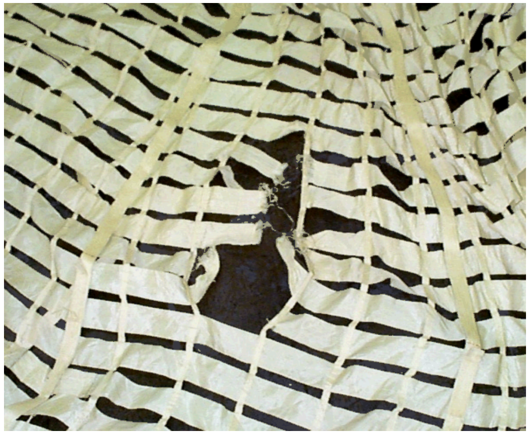
Nuclear Power Plant Cable Insulation



Shorting Plugs



Labeled Polymers



Textiles

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

Infra-red Spectroscopy

X-Ray Analysis

Density

Nuclear Magnetic Resonance

GPC

Goals

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

Overview

Publications on cable insulation aging:

(1) Gillen, K. T.; Bernstein, R. "Review of Nuclear Power Plant Safety Cable Aging Studies with Recommendations for Improved Approaches and for Future Work," SAND 2010-7266, 2010.
(2) Gillen, K. T.; Assink, R. A.; Bernstein, R., "Nuclear Energy Plant Optimization (NEPO) Final Report on Aging and Condition Monitoring of Low-Voltage Cable Materials," 2005, SAND 2005-7331.
(3) Gillen, K. T.; Assink, R. A.; Bernstein, R. *Polymer Degradation and Stability,* Condition monitoring approaches applied to a polychloroprene cable jacketing material 2004, *84*, 419-431.
(4) Gillen, K. T.; Bernstein, R.; Celina, M. *Polymer Degradation and Stability,* Non-Arrhenius behavior for oxidative degradation of chlorosulfonated polyethylene materials 2005, *87*, 335-346.
(5) Gillen, K. T.; Bernstein, R.; Clough, R. L.; Celina, M. *Polymer Degradation and Stability,* Lifetime predictions for semi-crystalline cable insulation materials: I. Mechanical properties and oxygen consumption measurements on EPR materials 2006, *91*, 2146-2156.
(6) Gillen, K. T.; Bernstein, R.; Derzon, D. K. *Polymer Degradation and Stability,* Evidence of Non-Arrhenius Behavior from Laboratory Aging and 24-year Field Aging of Chloroprene Rubber Materials 2005, *87*, 57-67.
(7) Gillen, K. T.; Celina, M.; Bernstein, R.; Shedd, M. *Polymer Degradation and Stability,* Lifetime predictions of EPR materials using the Wear-out approach 2006, *91*, 3197-3207.

Thermal oven banks with ~6 fixed temperature ovens

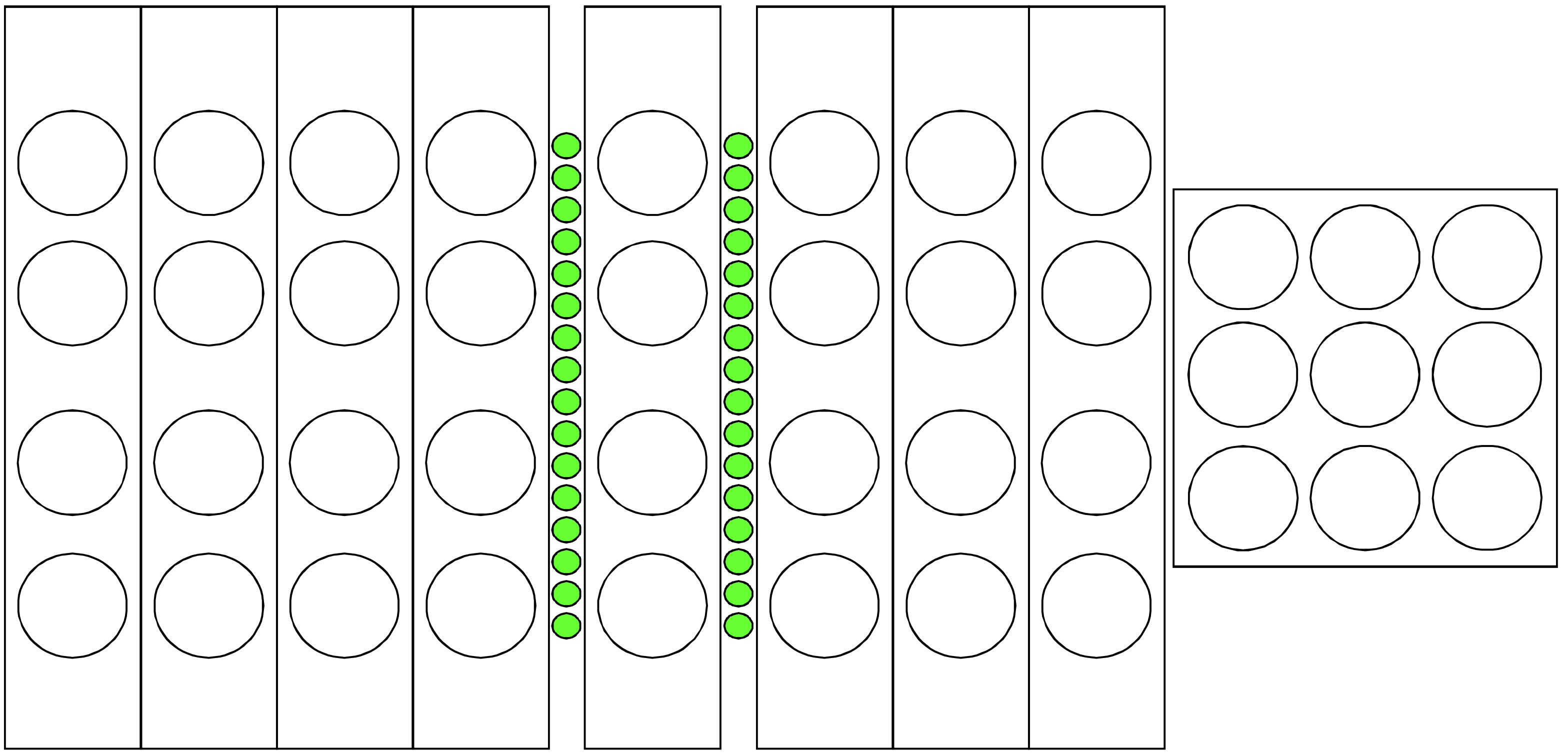
Specialized instrumentation:
Oxygen consumption
Modulus Profiling

Gamma irradiation facilities
–LICA specifically for polymer aging (currently upgrading)

LICA

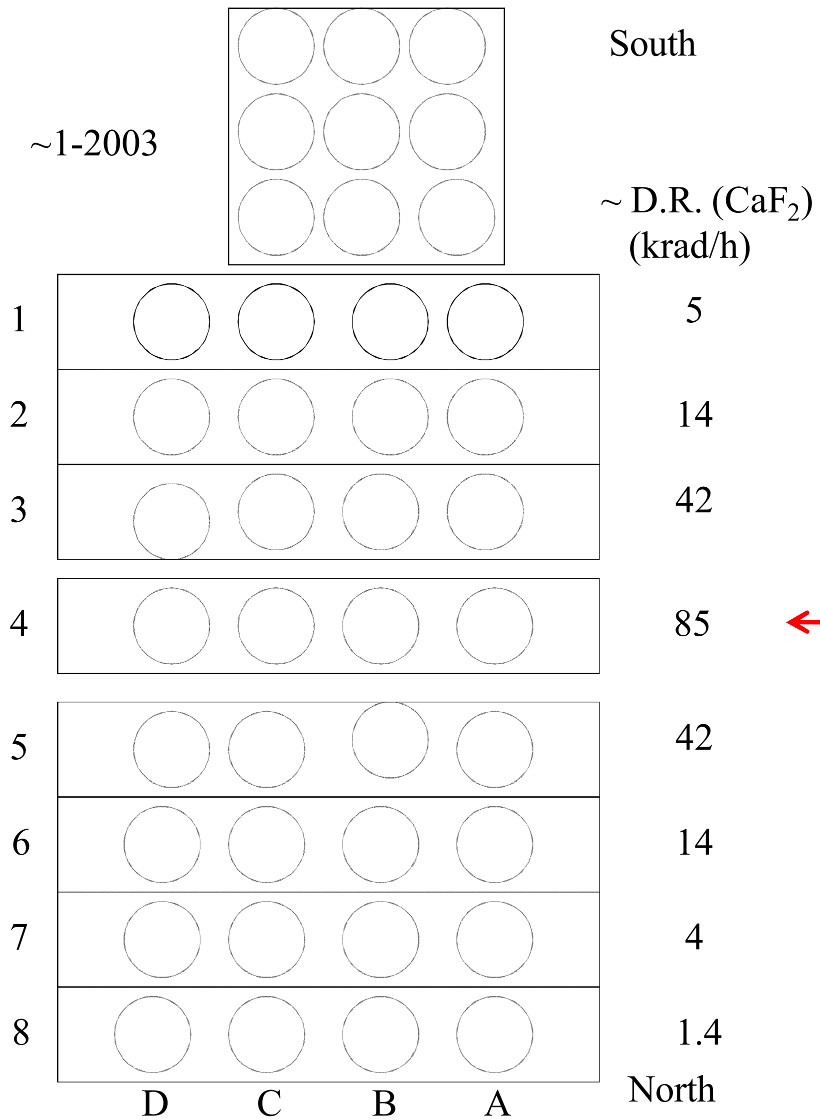
LICA

Low Intensity Cobalt Array



- Headspace gas control (flowing system)
- Thermal control

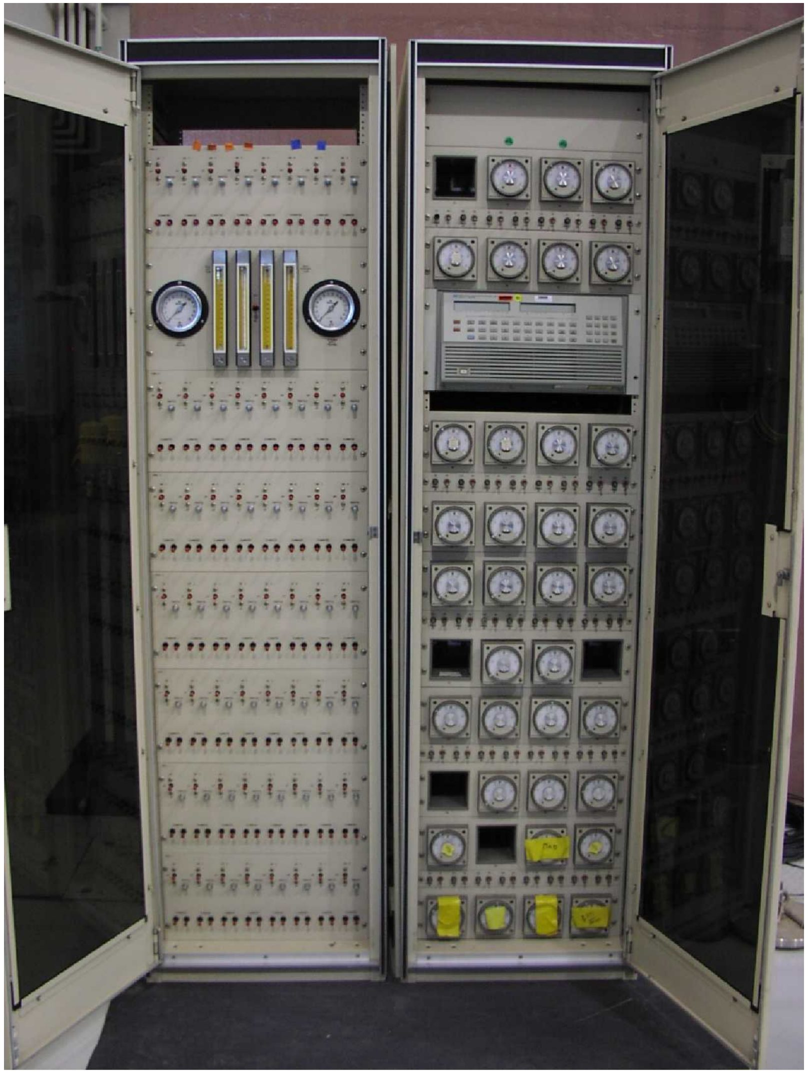
LICA



Configuration changed ~2011;
Pencil removed
Need new calibration

04/2011 -Would have been ~32 krad/hr

Upgrading LICA Facility



Upgrading LICA Facility

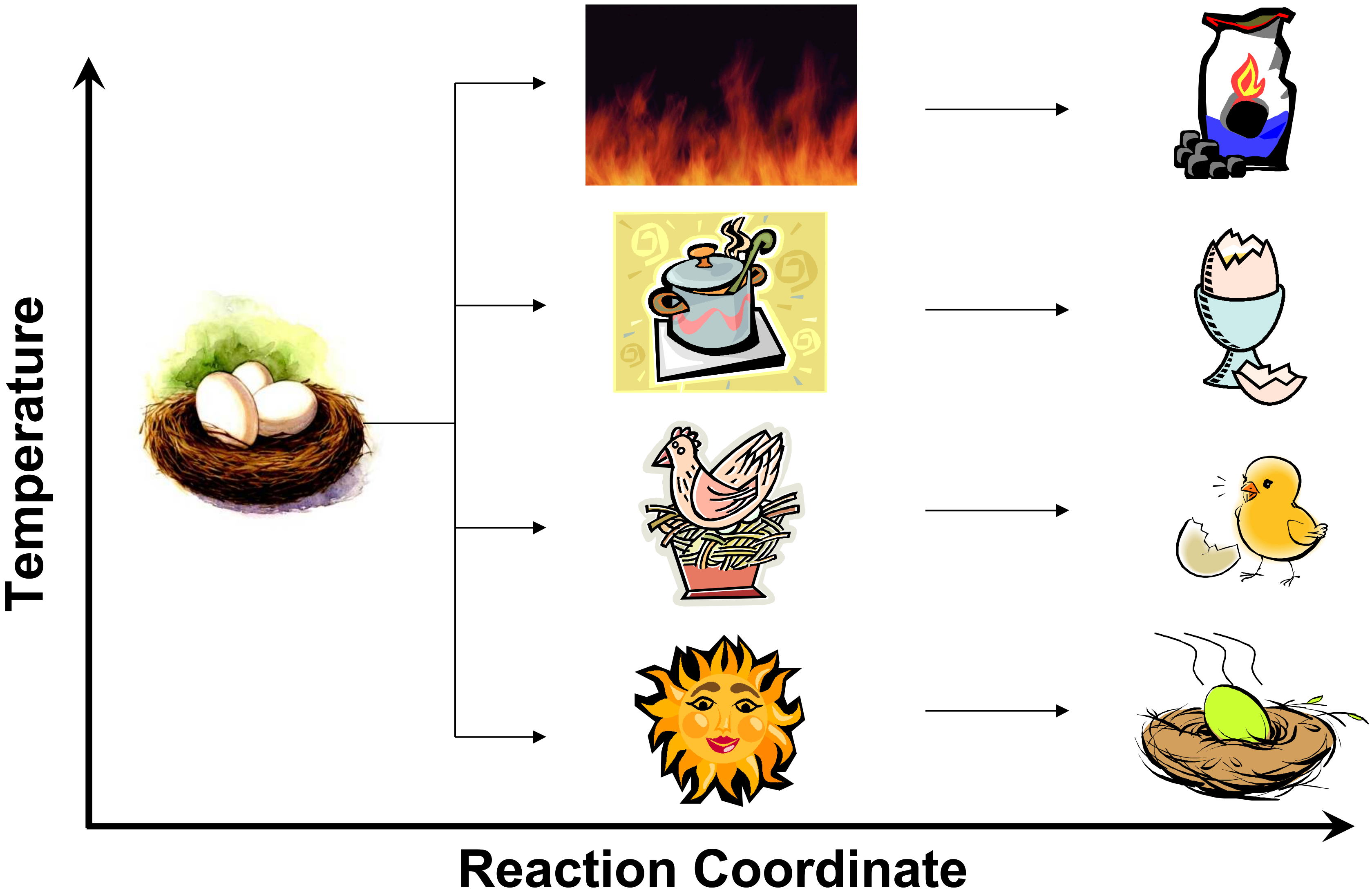
Deception!

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

‘Accelerated Aging’



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

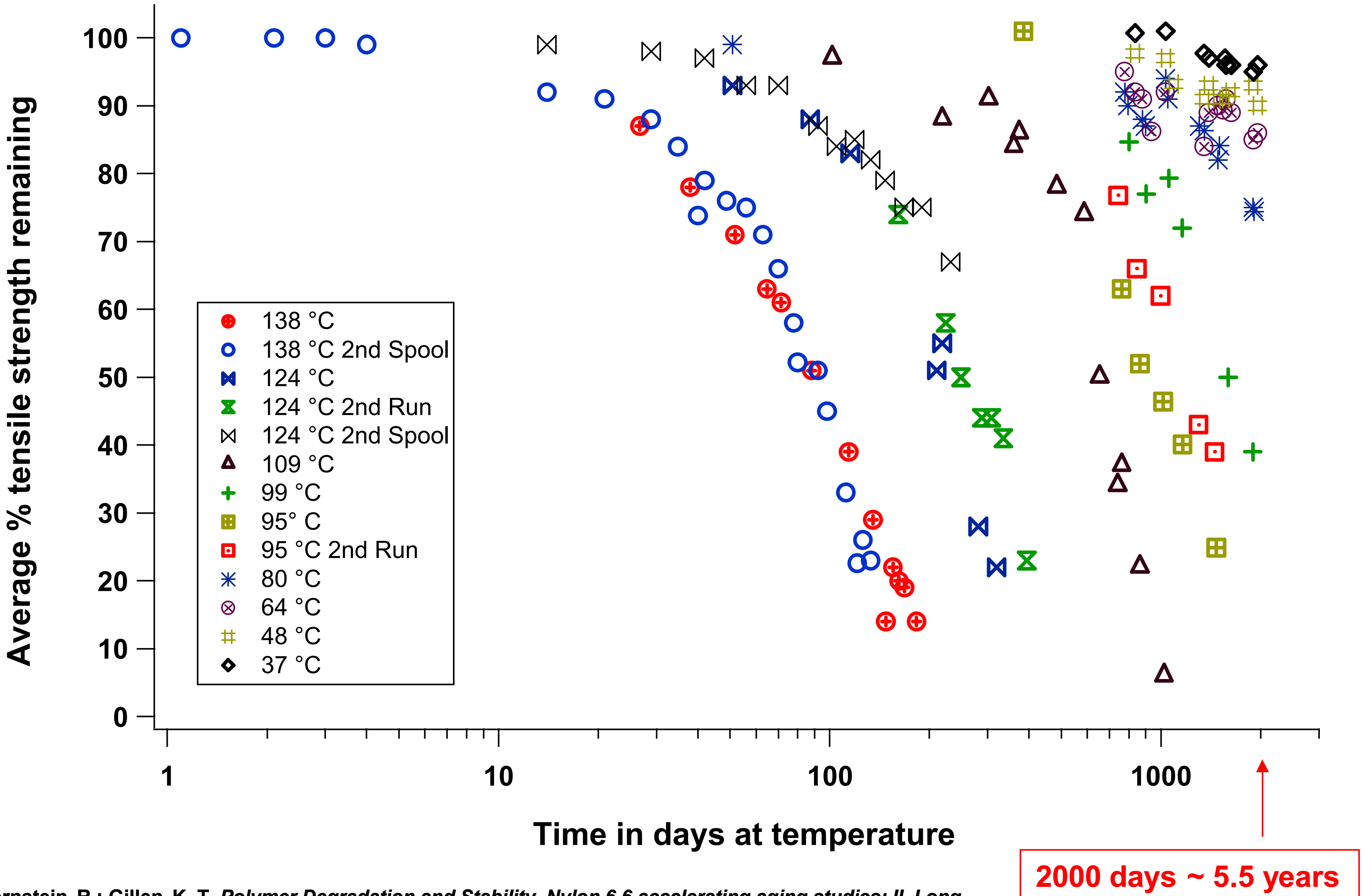
Gillen, K. T.; Celina, M.; Clough, R. L.; Wise, J. *Trends in Polymer Science,* Extrapolation of Accelerated Aging Data -Arrhenius or Erroneous? **1997**, *5*, 250-257.

Arrhenius equation: **Empirical equation**

$$\boxed{k = Ae^{-Ea/RT}}$$

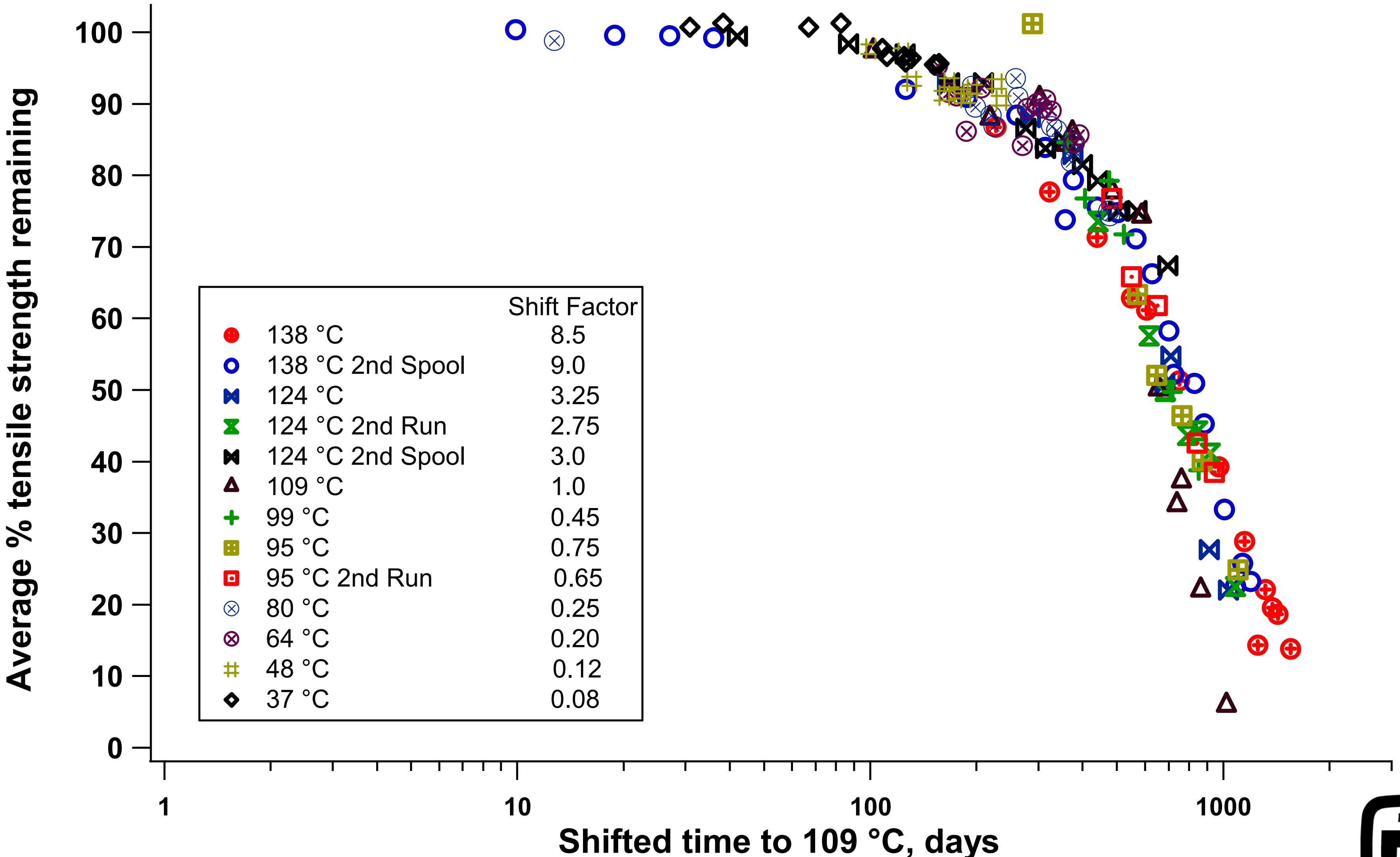
$$\boxed{\ln(k) = \ln(A) - Ea/RT}$$

Thermal-oxidative Aging: Nylon



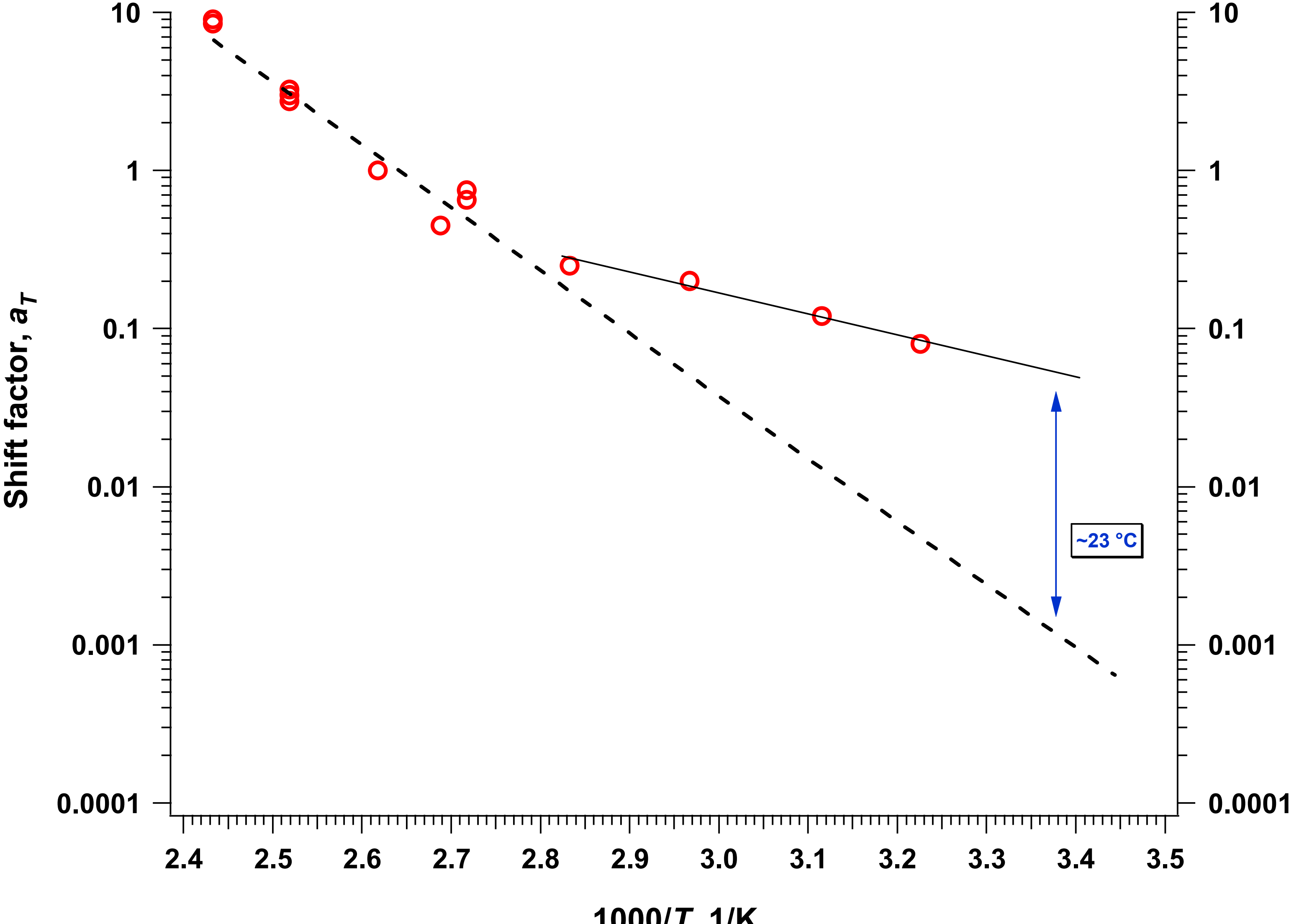
Bernstein, R.; Gillen, K. T. *Polymer Degradation and Stability, Nylon 6.6 accelerating aging studies: II. Long-term thermal-oxidative and hydrolysis results 2010, 95, 1471-1479.*

Thermal-oxidative Aging: Nylon Shifted Data



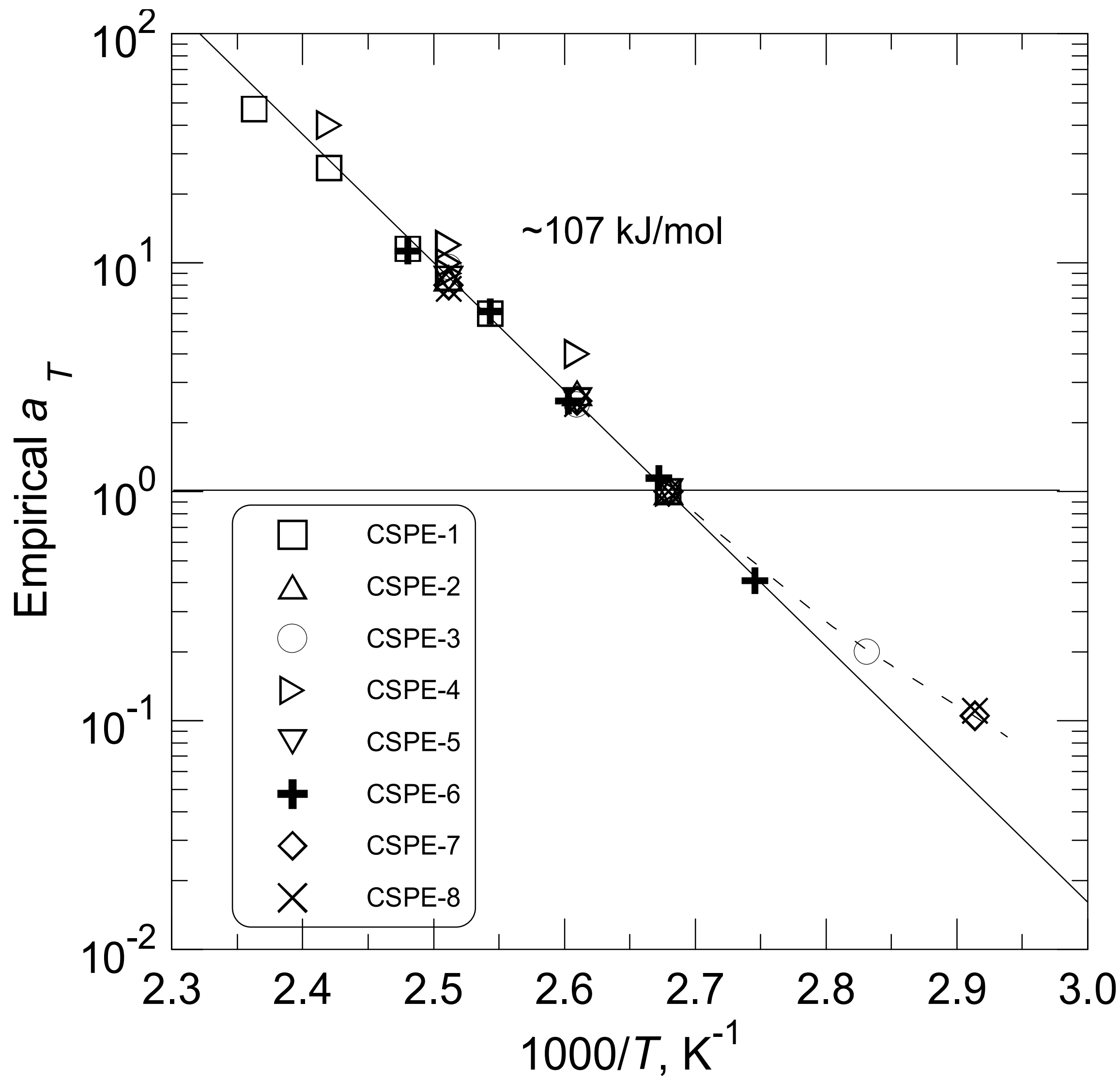
Bernstein, R.; Gillen, K. T. *Polymer Degradation and Stability, Nylon 6.6 accelerating aging studies: II. Long-term thermal-oxidative and hydrolysis results 2010, 95, 1471-1479.*

Thermal-oxidative Aging: Nylon Shift Factor Graph



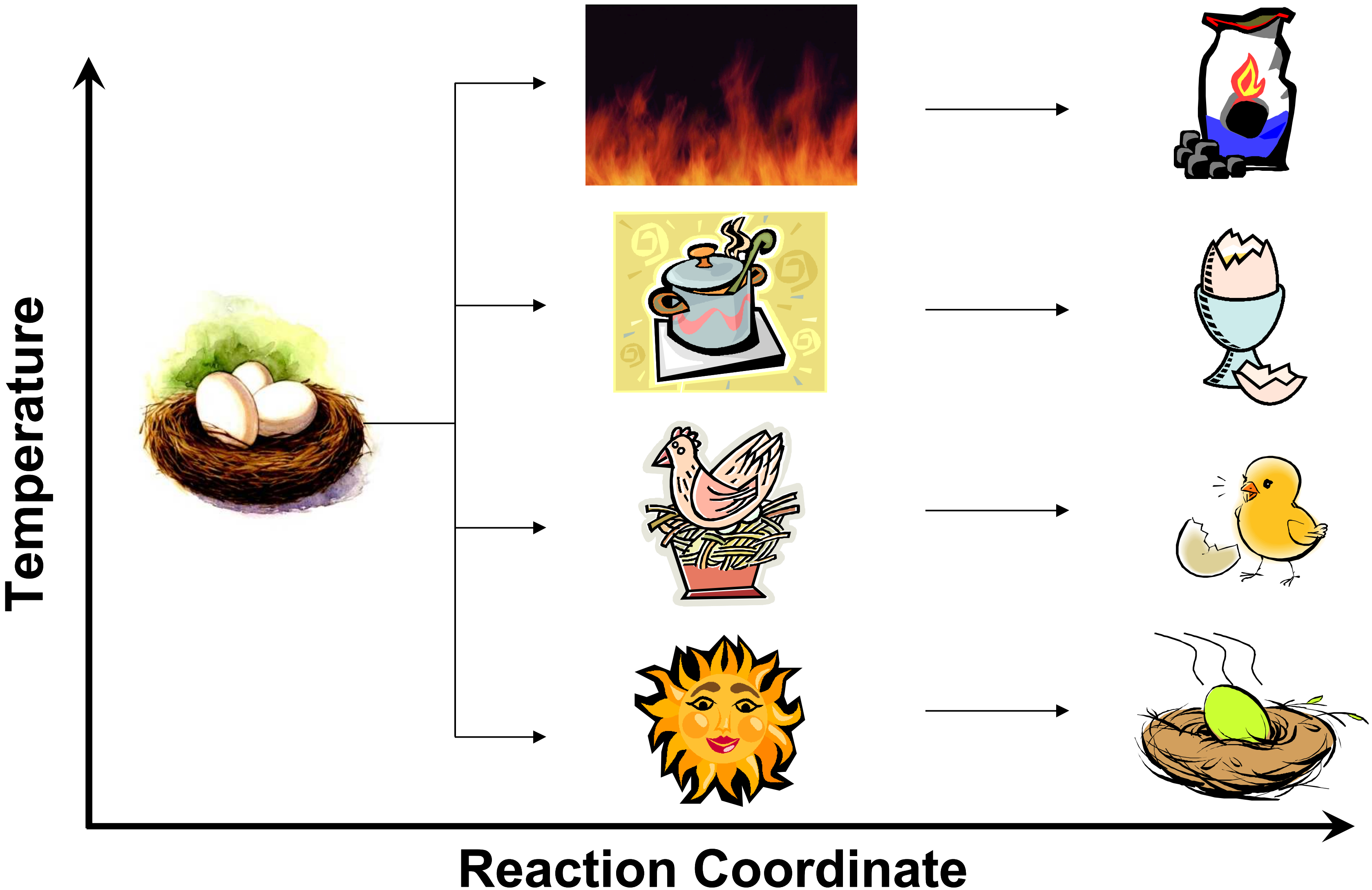
Bernstein, R.; Gillen, K. T. *Polymer Degradation and Stability, Nylon 6.6 accelerating aging studies: II. Long-term thermal-oxidative and hydrolysis results 2010, 95, 1471-1479.*

Hypalon (CSPE) Shift Factor Plot



Gillen, K. T.; Bernstein, R.; Celina, M. *Polymer Degradation and Stability,* Non-Arrhenius behavior for oxidative degradation of chlorosulfonated polyethylene materials 2005, *87*, 335-346.

‘Accelerated Aging’



Thermal Exposure

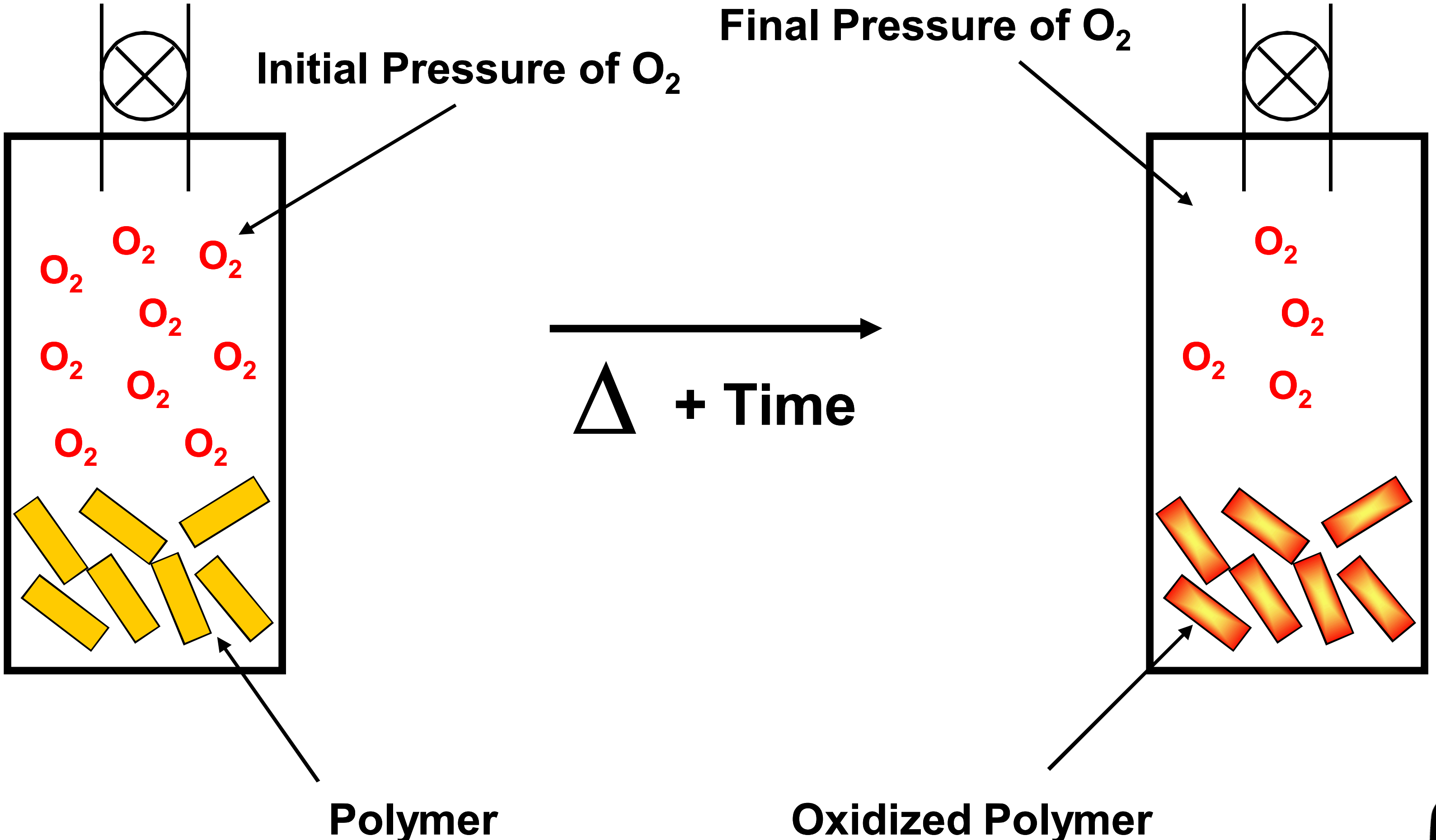
Thermal-Oxidation

$$\text{Polymer} + O_2 \longrightarrow \text{Oxidized Polymer}$$

Quantify amount of oxygen consumed

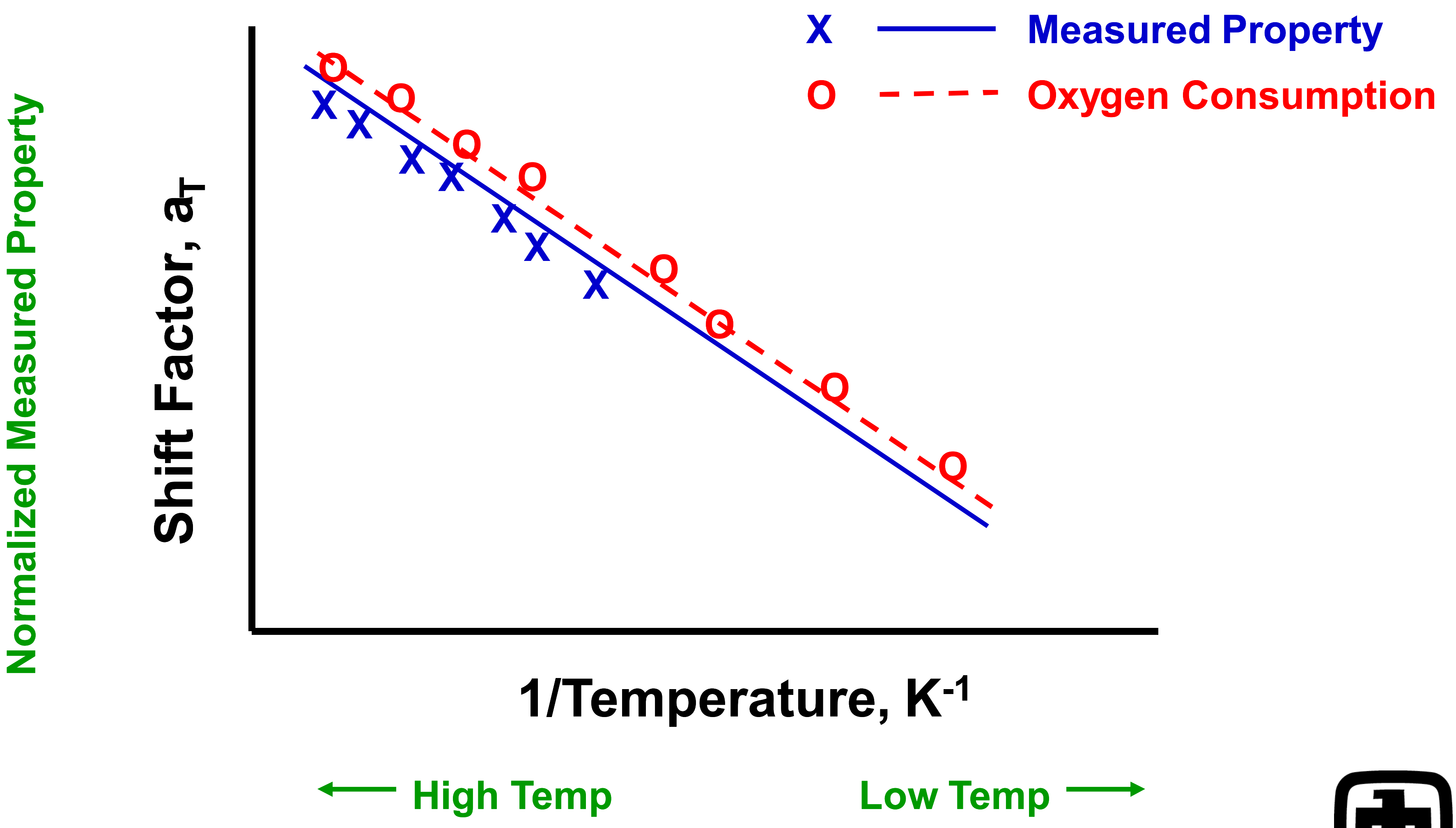
- Simple in theory
- Difficult in practice
- Amazingly sensitive

Schematic of Oxuptake

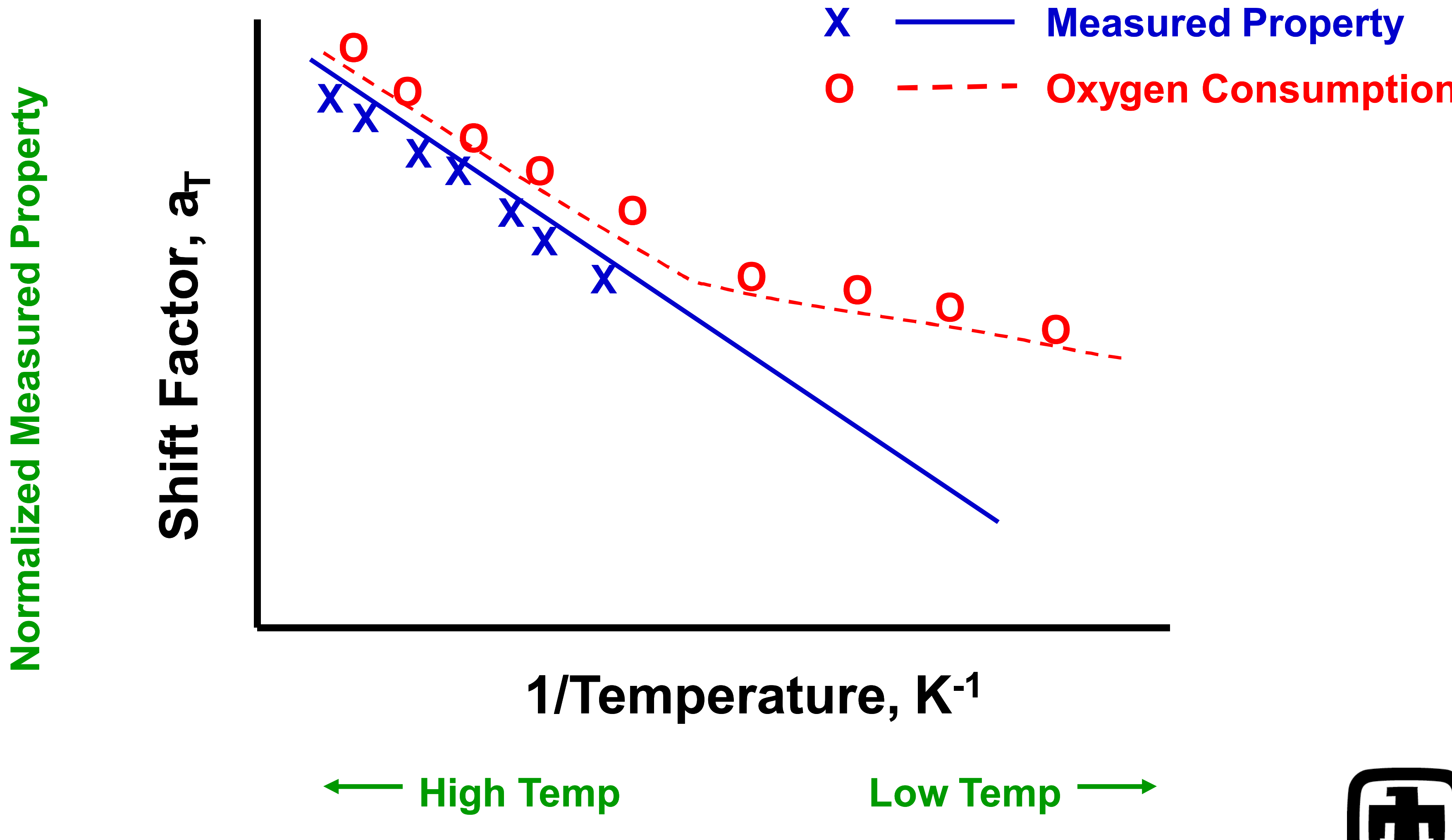


Oxygen Consumption

Enhanced Extrapolation ‘Good’



Enhanced Extrapolation 'Bad'



DLO, Need to Know

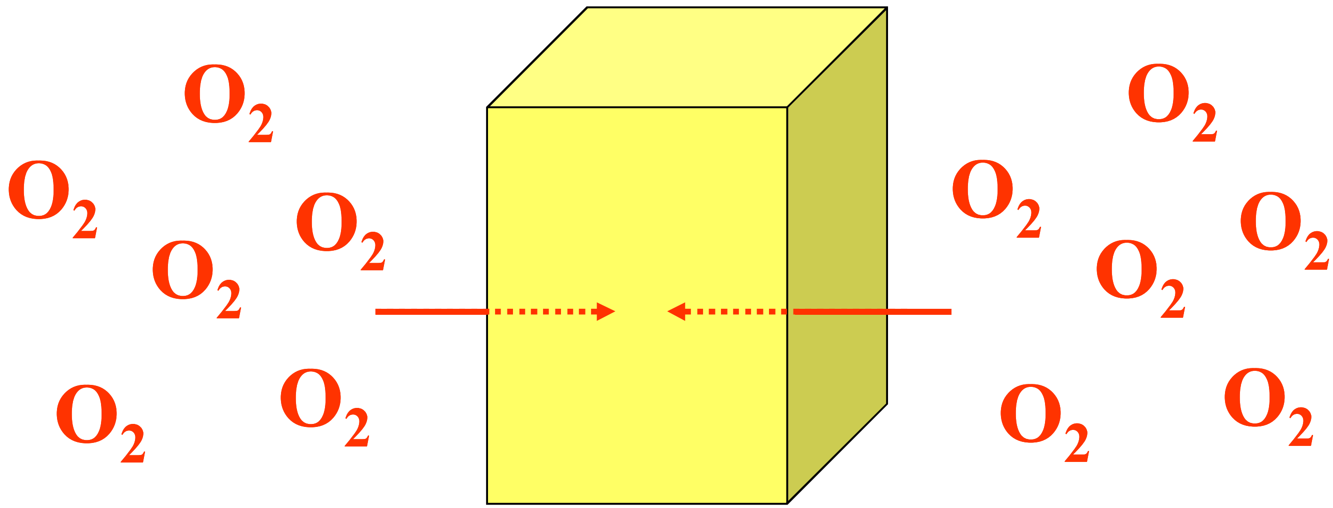
Diffusion Limited Oxidation (DLO) effects if oxygen dissolved in material used up faster by reaction than it can be replenished by diffusion from surrounding air atmosphere

Race between:
the oxygen consumption rate versus the oxygen diffusion rate

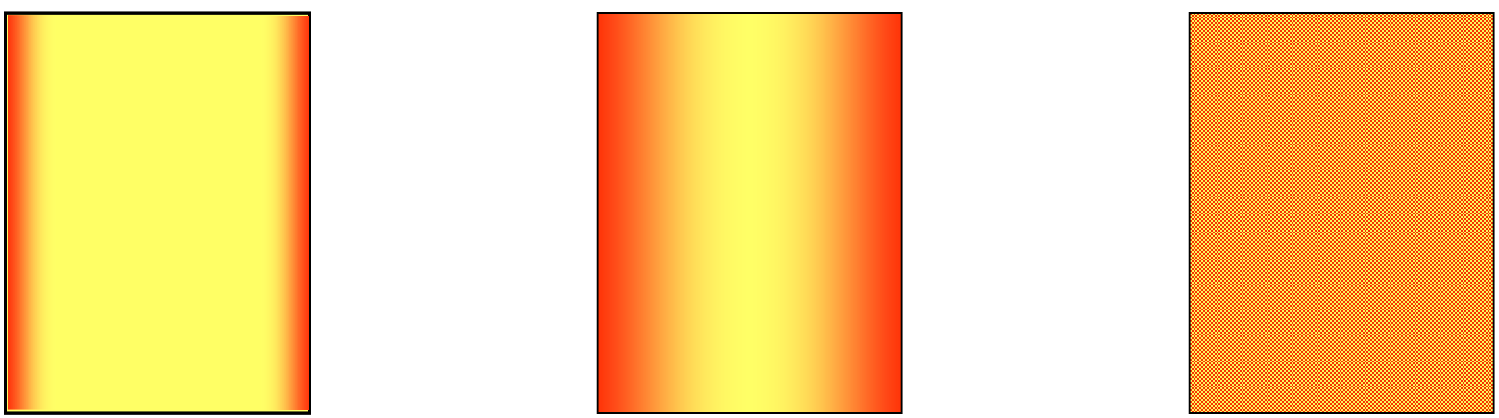
Therefore we need estimates of:

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

Diffusion-Limited Oxidation (DLO)



rxn rate > diffusion rate **rxn rate < diffusion rate**



Heterogeneous **Homogeneous**

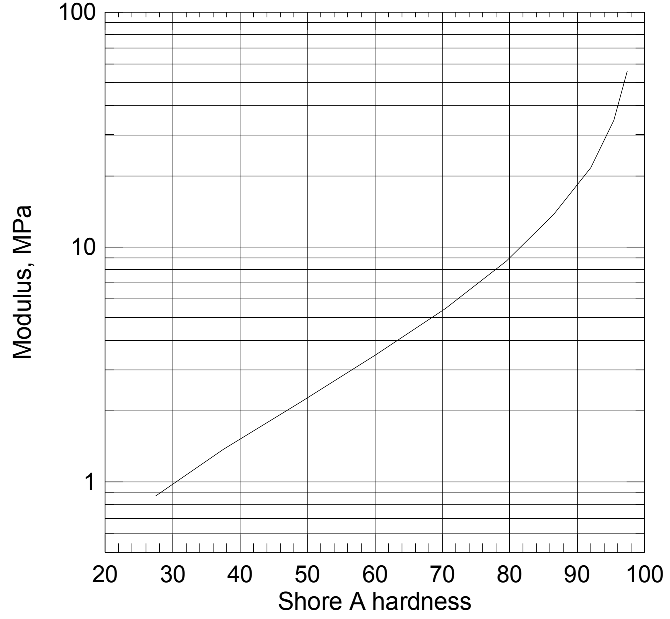
Modulus Profiling

Indentation technique
ca. 50μm resolution

Measure of Inverse tensile compliance

Closely related to tensile modulus

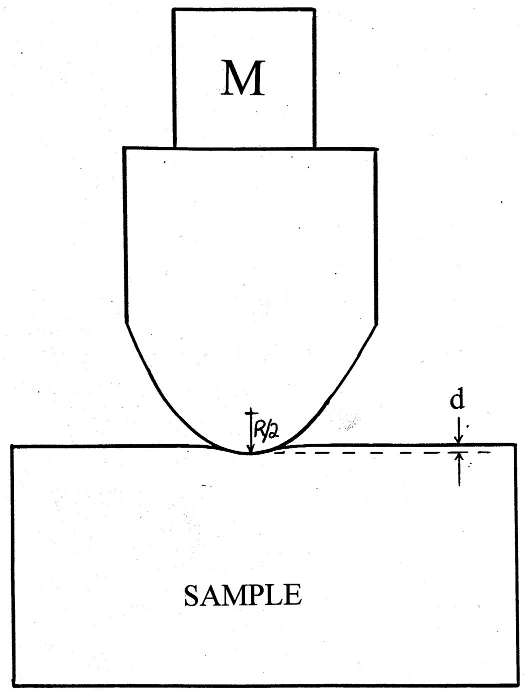
Modulus vs. Shore A



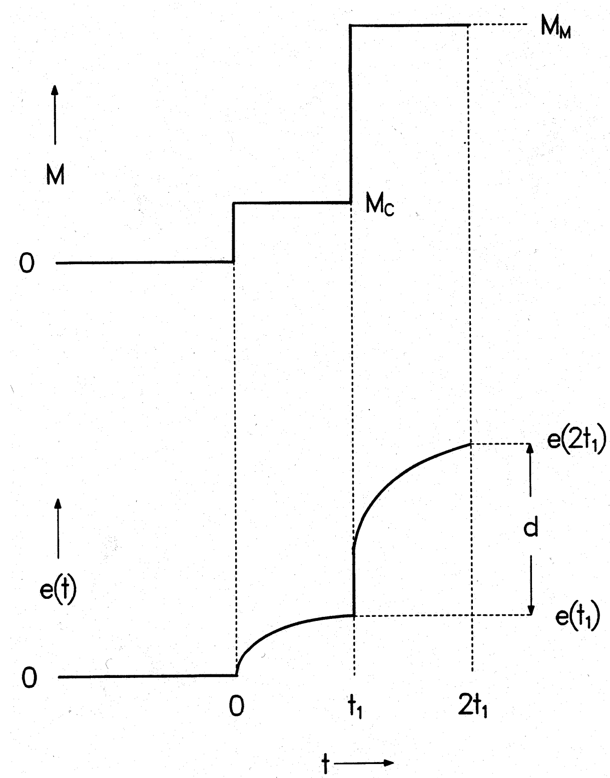
Excellent to examine 'geneity' of aging (heteo- or homo-) (DLO issues)

Schematic of Modulus Profile Experiment

Probe tip, sample and mass



Mass is applied in two steps



Gillen, K. T.; Clough, R. L.; Quintana, C. A. *Polym. Degrad. Stab., Modulus profiling of polymers 1987, 17, 31-47*

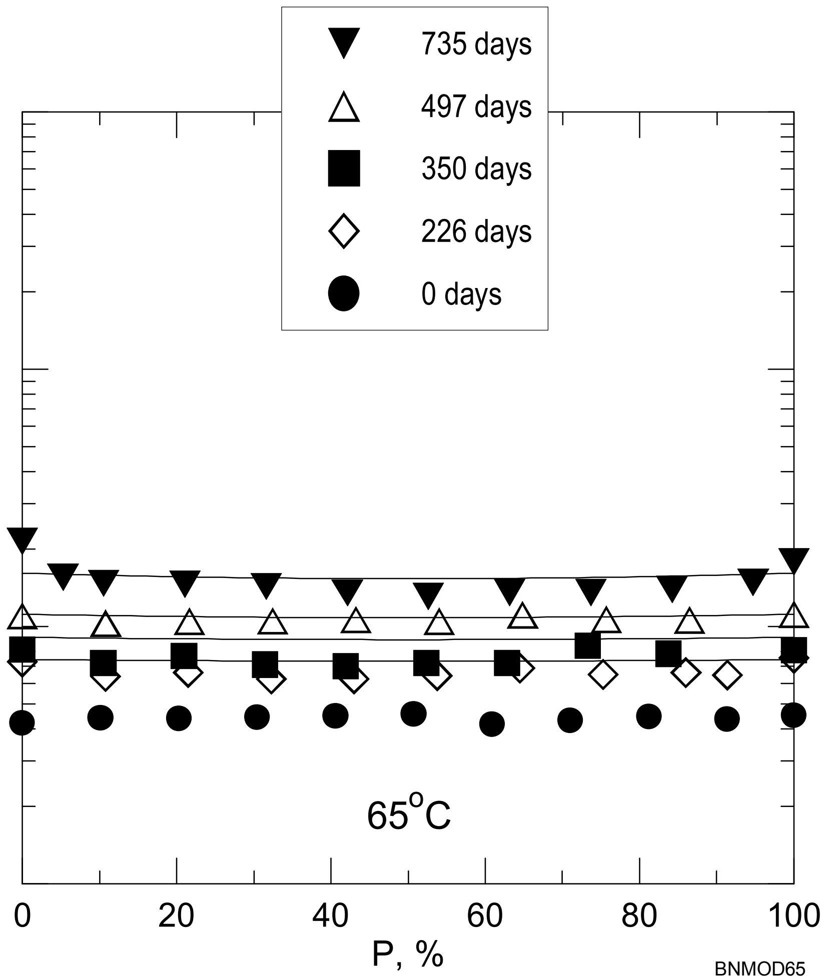
Modulus Profiler

Modulus Profiler Sample

Homogeneous Aging

Aging of a nitrile rubber at temperatures ranging from 65°C to 125°C

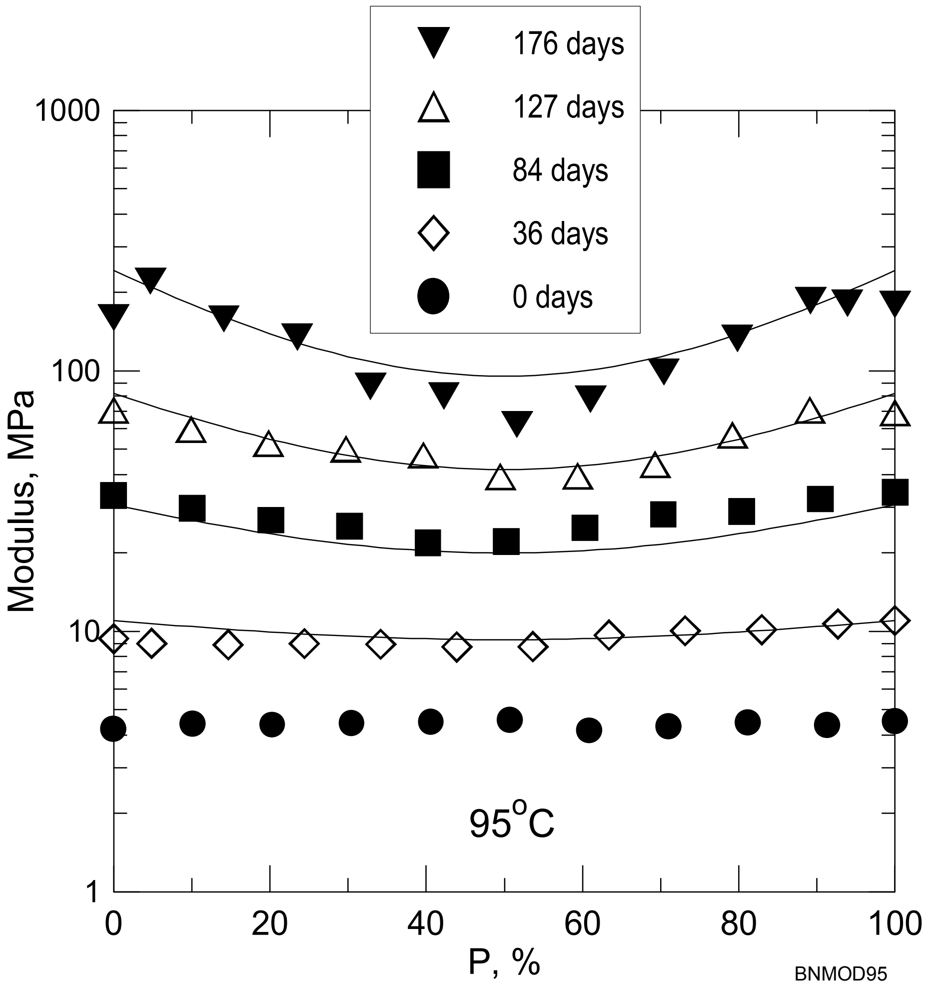
Modulus profiles of samples aged at 65°C indicate the presence of homogeneous aging

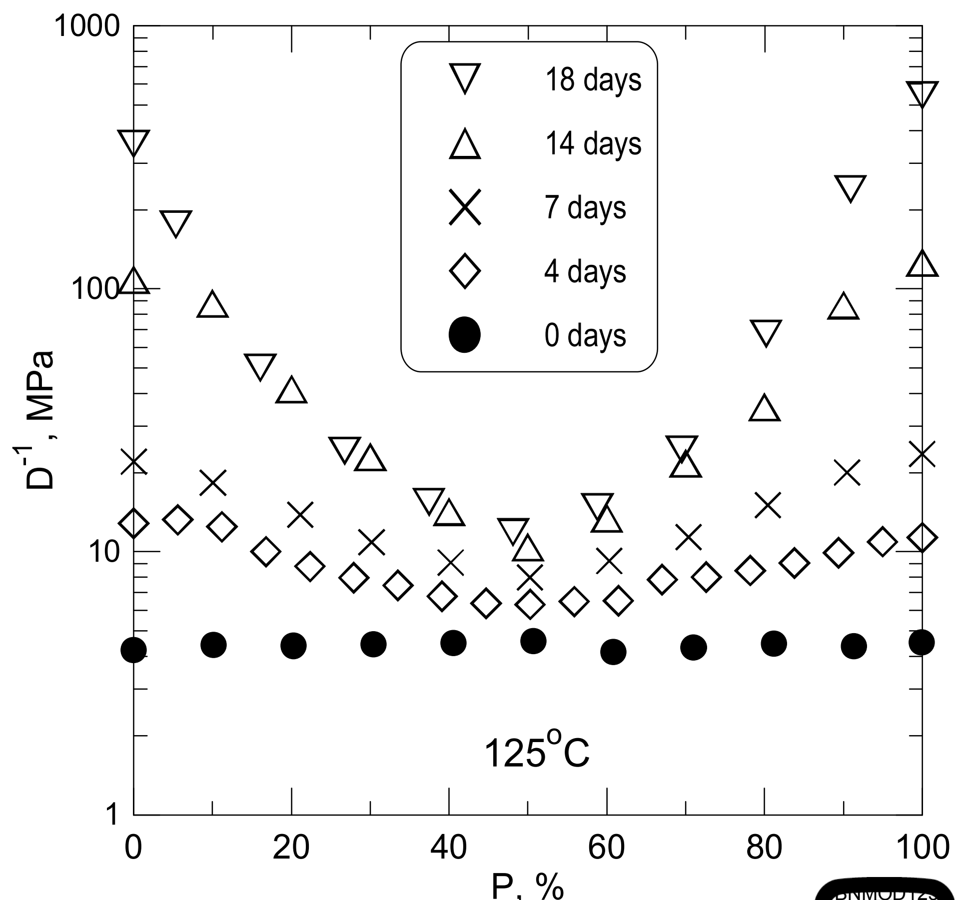


Wise, J.; Gillen, K. T.; Clough, R. L. *Polymer Degradation and Stability, An ultrasensitive technique for testing the Arrhenius extrapolation assumption for thermally aged elastomers 1995, 49, 403-418.*

Heterogeneous Aging

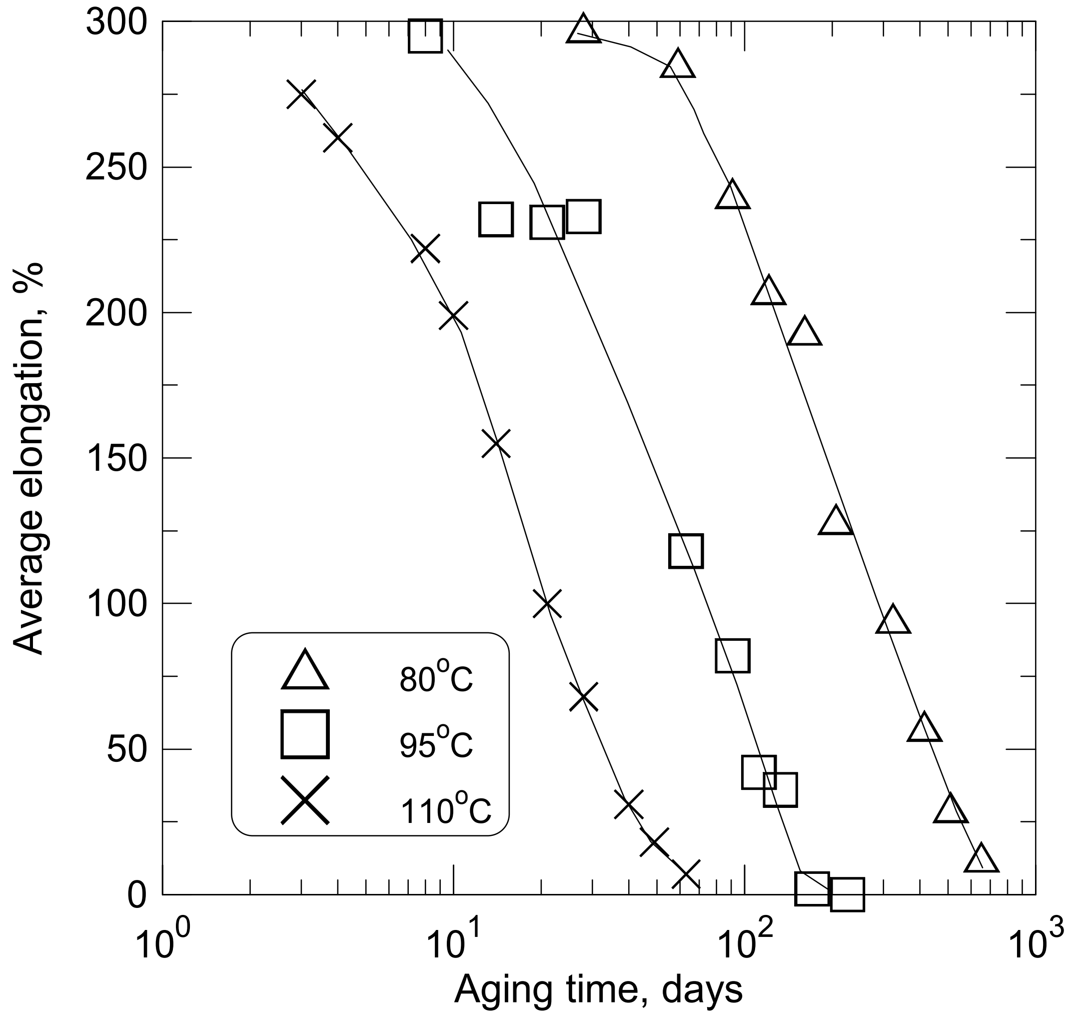
Modulus profiles for samples aged at 95°C show that diffusion-limited oxidation (DLO) is becoming important; at 125°C, DLO effects are very significant





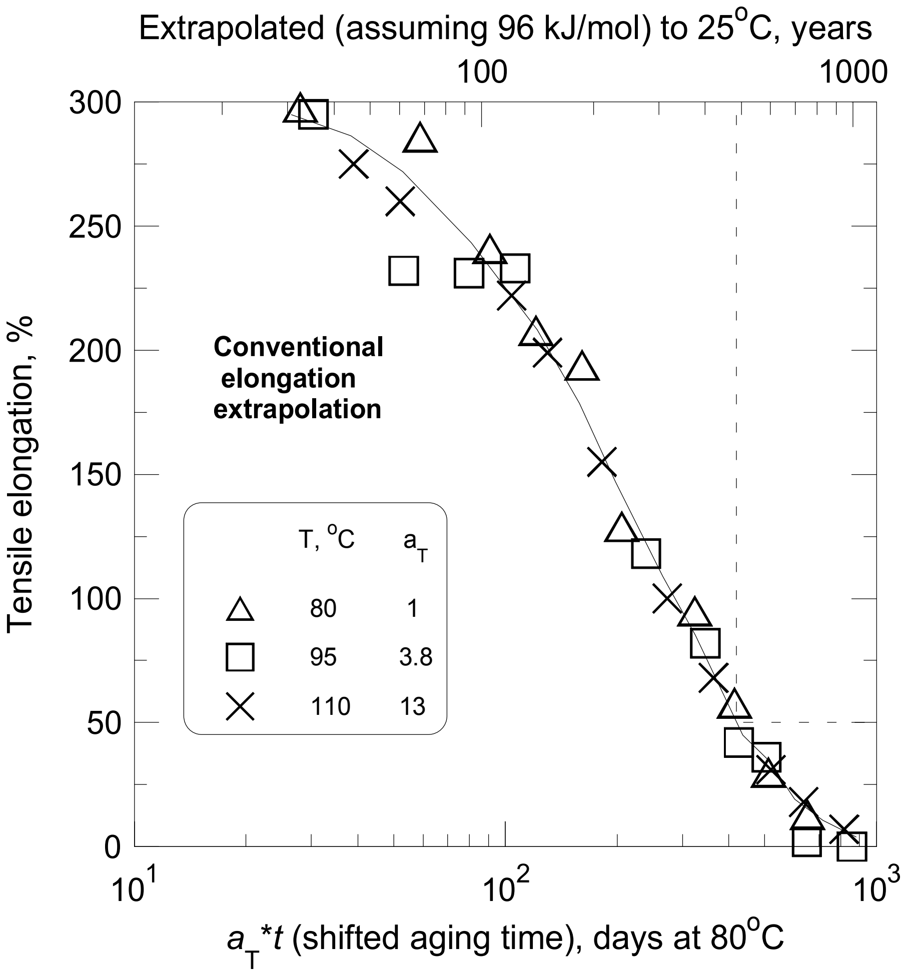
Wise, J.; Gillen, K. T.; Clough, R. L. *Polymer Degradation and Stability, An ultrasensitive technique for testing the Arrhenius extrapolation assumption for thermally aged elastomers 1995, 49, 403-418.*

Neoprene Cable Jacket



Gillen, K. T.; Bernstein, R.; Celina, M. *Polym. Degrad. Stab., Non-Arrhenius behavior for oxidative degradation of chlorosulfonated polyethylene materials 2005, 87, 335-346.*

Neoprene Cable Jacket



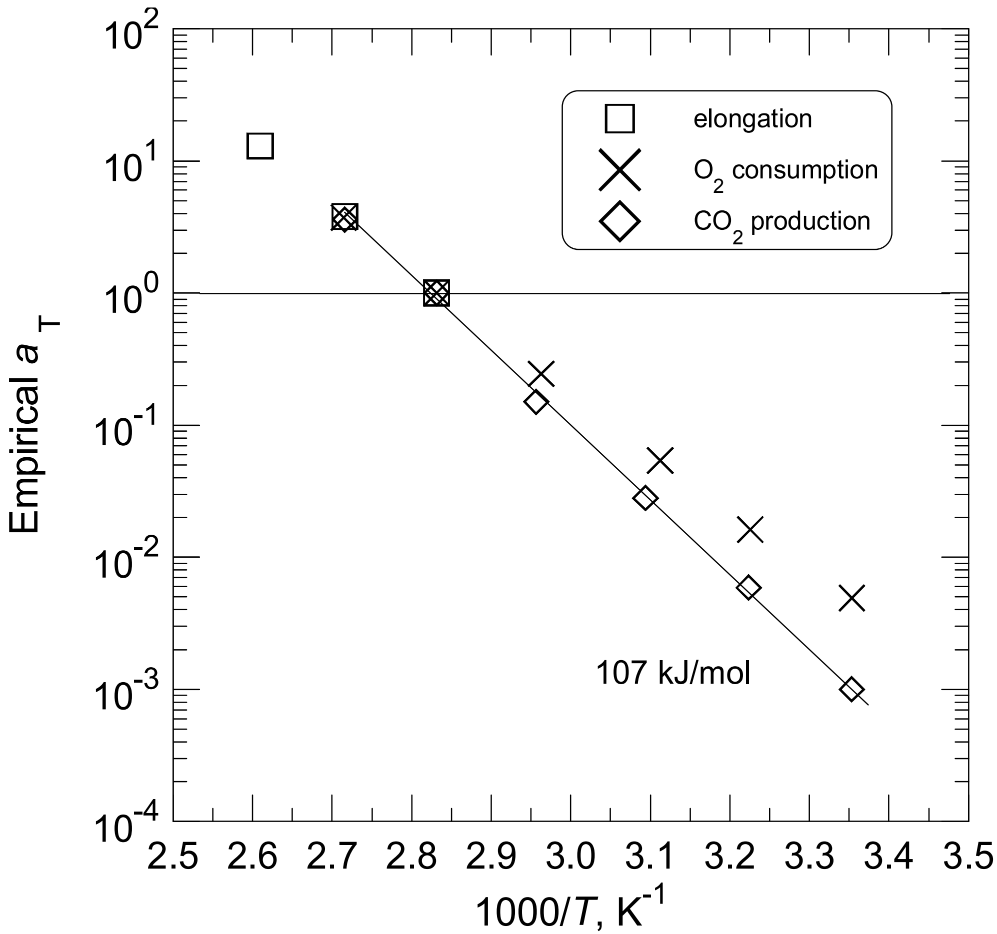
Using just the elongation data:

50% Elongation predicted ~480 years

Gillen, K. T.; Bernstein, R.; Celina, M. *Polym. Degrad. Stab., Non-Arrhenius behavior for oxidative degradation of chlorosulfonated polyethylene materials 2005, 87, 335-346.*

Validation

Using Oxygen Consumption Data



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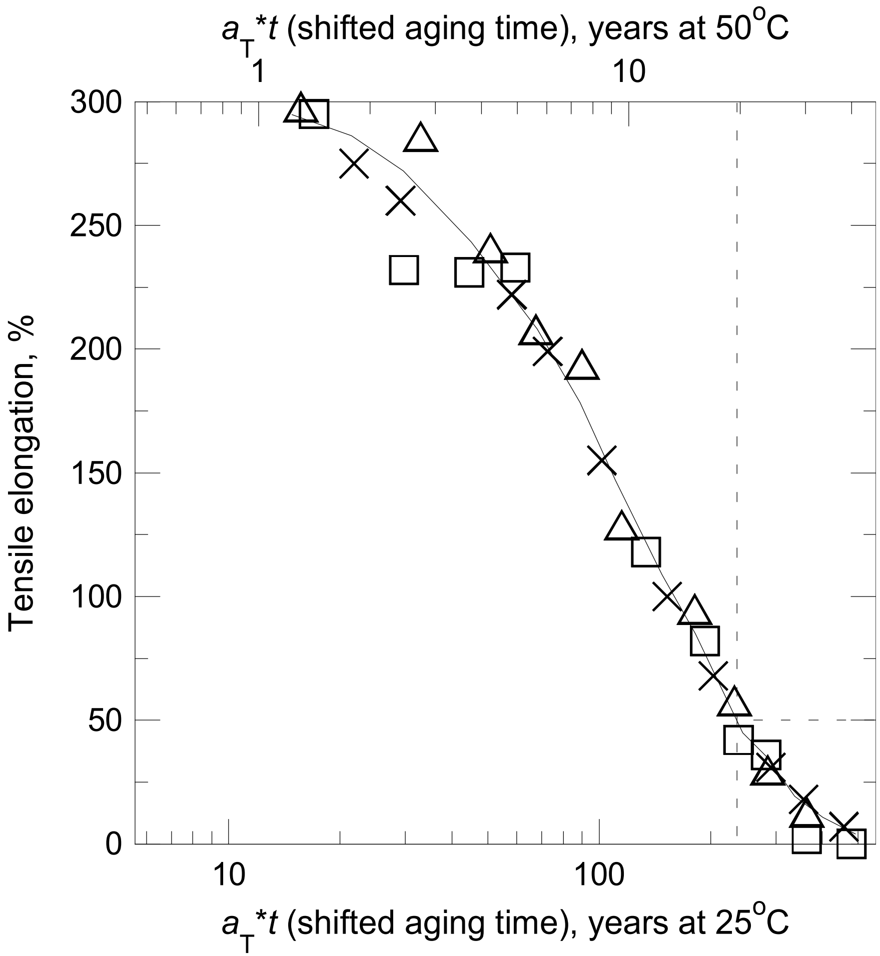
Neoprene Cable Jacket



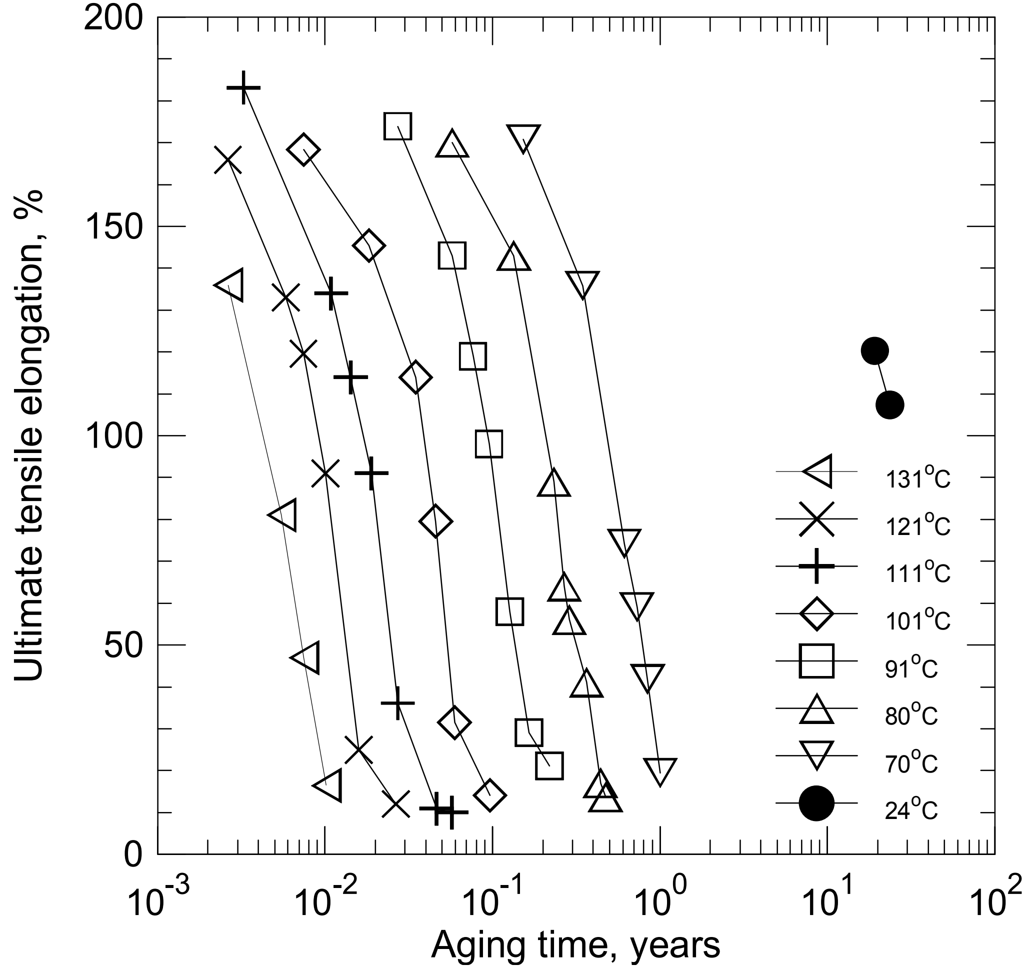
Prediction using the oxygen consumption data:

50% elongation predicted ~230 years

Approximately ½ the prediction from just the elongation

Gillen, K. T.; Bernstein, R.; Celina, M. ***Polym. Degrad. Stab., Non-Arrhenius behavior for oxidative degradation of chlorosulfonated polyethylene materials 2005, 87, 335-346.***

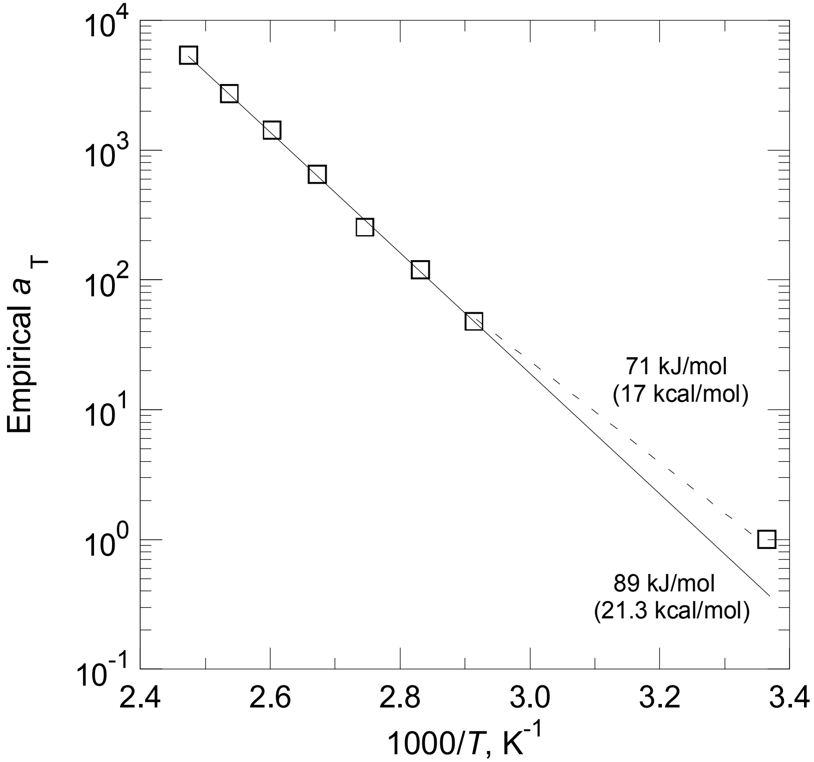
Neoprene (polychloroprene) Aging

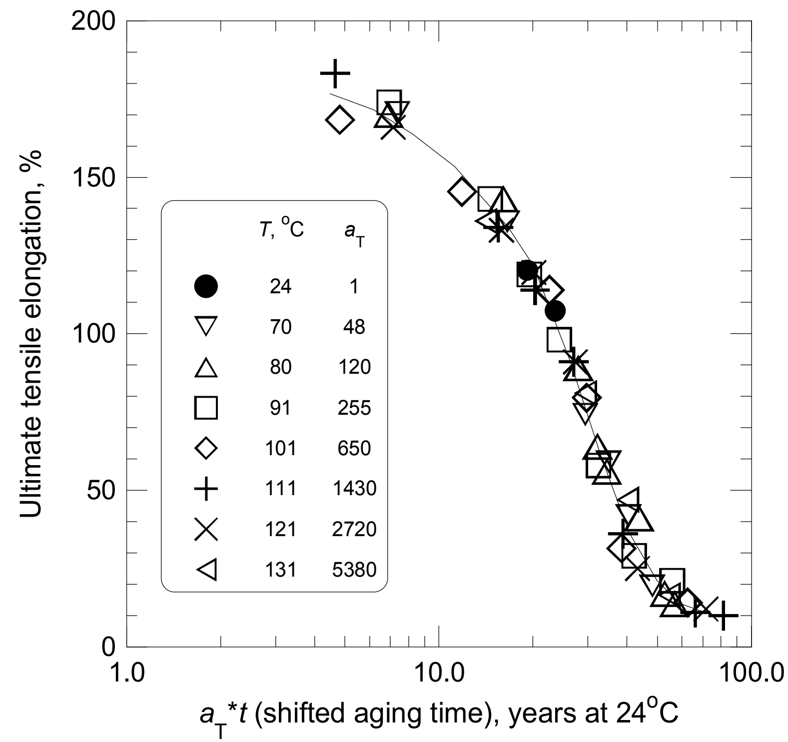


Gillen, K. T.; Bernstein, R.; Celina, M. *Polym. Degrad. Stab., Non-Arrhenius behavior for oxidative degradation of chlorosulfonated polyethylene materials 2005, 87, 335-346.*

Validation

Chloroprene rubber insulation:
Prediction versus 24 year old sample





50% predicted to be ~93 years versus 37 years

Gillen, K. T.; Bernstein, R.; Celina, M. *Polym. Degrad. Stab., Non-Arrhenius behavior for oxidative degradation of chlorosulfonated polyethylene materials 2005, 87, 335-346.*

S.C.R.A.P.S. (Sandia's Cable Repository for Aged Polymer Samples)

- samples collected during >20 year Sandia aging program
- includes many common nuclear cable insulation & jacketing materials
- includes many aging conditions slow enough to eliminate diffusion-limited oxidation (DLO) effects
  - up to seven years under thermal-only conditions
  - up to several years under combined dose-rate + temperature conditions
- elongation measured on all samples; many additional measurements
- conditions without DLO are often known so non-DLO samples can easily be selected to screen CM techniques

- SCRAPS represents a tremendous resource for testing CM techniques- no need to 1) obtain cables, 2) age cables, 3) measure degradation (e.g., elongation), and 4) determine where DLO effects enter prior to CM technique evaluation.
- CM measurements on SCRAPS samples & on new samples currently being aged
- SCRAPS data is entered into an electronic Database and the samples organized for easy access

Summary

Unique Capabilities

LICA
Thermal ovens
Oxuptake
Modulus Profiling
Experience with Nuclear Power Plant Cables
Expertise in area of organic materials degradation

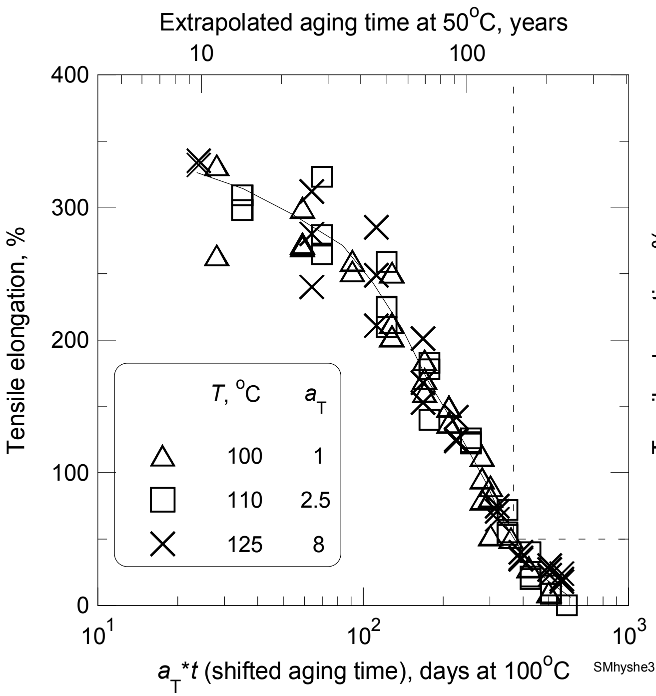
Lots of help…

Dora Derzon, Brad Hance, Don Bradley, Roger Assink, John Schroeder, Patti Sawyer, Mark Stavig

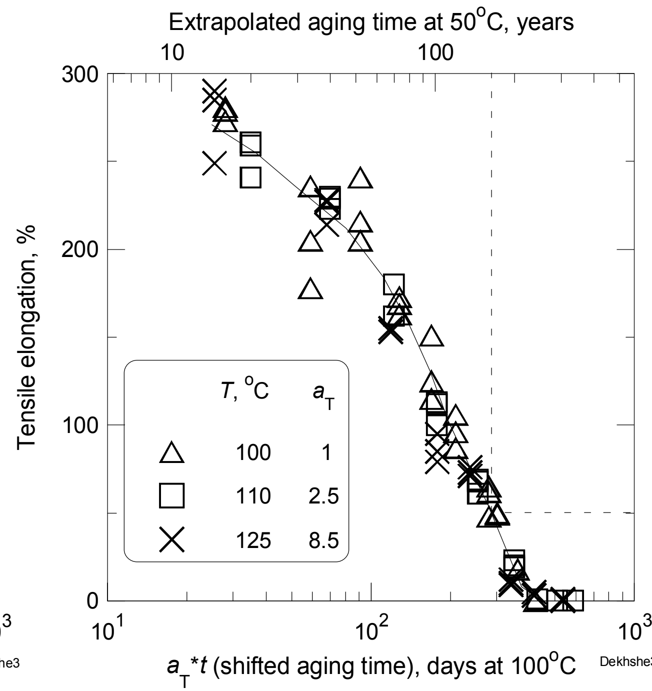
Questions…

Similar results for three additional hypalons

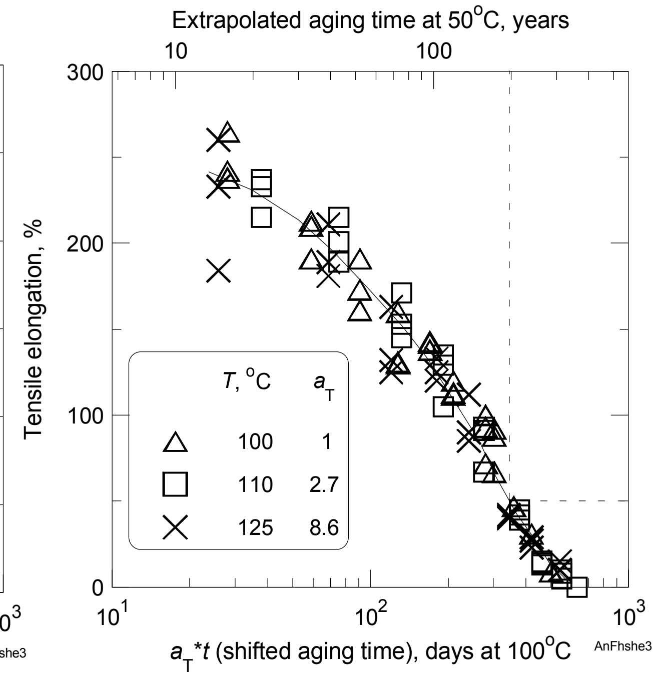
Samuel Moore jacket



Eaton Dekoron jacket



Anaconda Flameguard outer jacket



Predict 160 years at 50°C to reach 50% elongation

Predict 170 years at 50°C to reach 50% elongation

Predict 200 years at 50°C to reach 50% elongation

Results indicate generic behavior may hold for hypalon materials

Gillen, K. T.; Bernstein, R.; Celina, M. *Polymer Degradation and Stability,* Non-Arrhenius behavior for oxidative degradation of chlorosulfonated polyethylene materials 2005, *87*, 335-346.
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