## Polymers in Nuclear Applications Conference Stockholm

### Presented 19/20 March 2024

https://energiforsk.se/konferenser/kommande/polymers-in-nuclear-applications-2024

# Cable Ageing in NPP's over Decades – from Qualification to Condition Monitoring: A Perspective on Current Status

**Mathew Celina, Independent Consultant, Albuquerque, NM, USA**
**Visiting Scientist to Los Alamos National Laboratory**
**Editor in chief: Journal of Polymer Degradation and Stability**

**Note: All content discussed herein can be found in the public domain and was previously approved for unlimited public release as conference contributions in SAND2019-0737C and SAND2016-8617C. This work does not contain 'new' R&D results but rather focuses on a historical perspective based on available information. It is not related to any current professional activities.**

# “Cables” are Integral Part of NPP History

- Significant literature and reports available
- Polymeric insulation materials extensively studied
- High quality materials were originally chosen
- Qualification for LOCA and NPP operation

- Condition monitoring and lifetime extension
- Extended use – thermal/low dose rate conditions

- Next generation of materials, modified flame retardant and different down-select criteria

- Challenges: Availability, established manufacturing, new qualification, overall situation of ‘nuclear’ industry

# "Cables" as Everything in NPP Applications are Within Complex Framework

LOCA performance, Extended use, Condition monitoring, Improved cables

Cable selection

Regulators
Standards

Cable qualification

Utilities
Support Orgs.

R&D materials
science

Political
decision making

Manufacturing
Industry

Design needs

**Different approaches depending on country, also different emphasis on R&D**

# Previous Overarching R&D Goals - Cables

**Predictive aging studies:**
**Age cable materials, how to achieve predictive value?**

**Material characterization needs:**
**Develop additional diagnostic tools and characterization methods**

**Radiation-thermal oxidative degradation of cable insulation materials:**
**Recognition of 'combined' environment complexity**

**Relationship of ambient and accelerated aging with qualification testing and condition monitoring:**
**Correlation between cable aging and guidance for field performance**

**Keywords: Cable insulation aging, predictive aging and extrapolations, qualification testing, condition monitoring**

# Key US Literature – LOCA to CM Methods

**IEEE Std. 323-1974**, IEEE Standard for qualifying class IE equipment for nuclear power generating stations.

**SAND91-1776**, Aging, Condition Monitoring, and Loss of Coolant Accident (LOCA) test class 1E cables, prepared by Sandia National Laboratories for the US Department of Energy August **1992**. (NUREG/CR-5772 Vol.1-3).

**NUREG/CR-6202**, Long-Term Aging and Loss-of-Coolant Accident (LOCA) Testing of Electrical Cables, U.S./French Cooperative Research Program, Nelson, C. F.; Gauthier, G.; Carlin, F.; Attal, M.; Gaussens, G.; Le Tutour, P.; Morin, C.,", IPSN 94-03, SAND 94-0485, **1996**.

**NUREG/CR-6384**, Literature Review of Environmental Qualification of Safety-Related Electric Cables, Prepared by Brookhaven National Laboratory, April **1996**.

**SAND05-7331**, Nuclear Energy Plant Optimization (NEPO): Final Report on Aging and Condition Monitoring of Low-Voltage Cable Materials, prepared by Sandia National Laboratories for the U.S. Department of Energy, November **2005**.

**JNES-report 2009**, Japanese Nuclear Energy Safety Organization. Assessment of Cable Aging for Nuclear Power Plants, prepared by JNES July **2009**.

**SAND 2013-2388**, Nuclear Power Plant Cable Materials: Review of Qualification and Currently Available Aging Data for Margin Assessments in Cable Performance, Celina MC, Gillen KT, Lindgren ER., **2013**.

**SAND 2014-17779**, Summary Report of Cable Aging and Performance Data for Fiscal Year 2014, Celina M, Redline E, Bernstein R, Giron N, Quintana A, White II G., **2014**.

**Material reliability studies and prediction towards low dose rate and low temperature aging behavior**

# Qualification Testing and Long-term Aging

- **Does qualification testing offer margins for extended use?**
- **How does ambient aging contribute to material changes?**

IEEE Std. 323-1974
Rapid qualification
LOCA performance

Test conditions:
High temperature
High dose rate
Dose: 150 Mrad
Air, steam

**Predicts ?**
**Standard does not clearly specify how extrapolation was justified**

40 year expected performance
Plus lifetime extension?

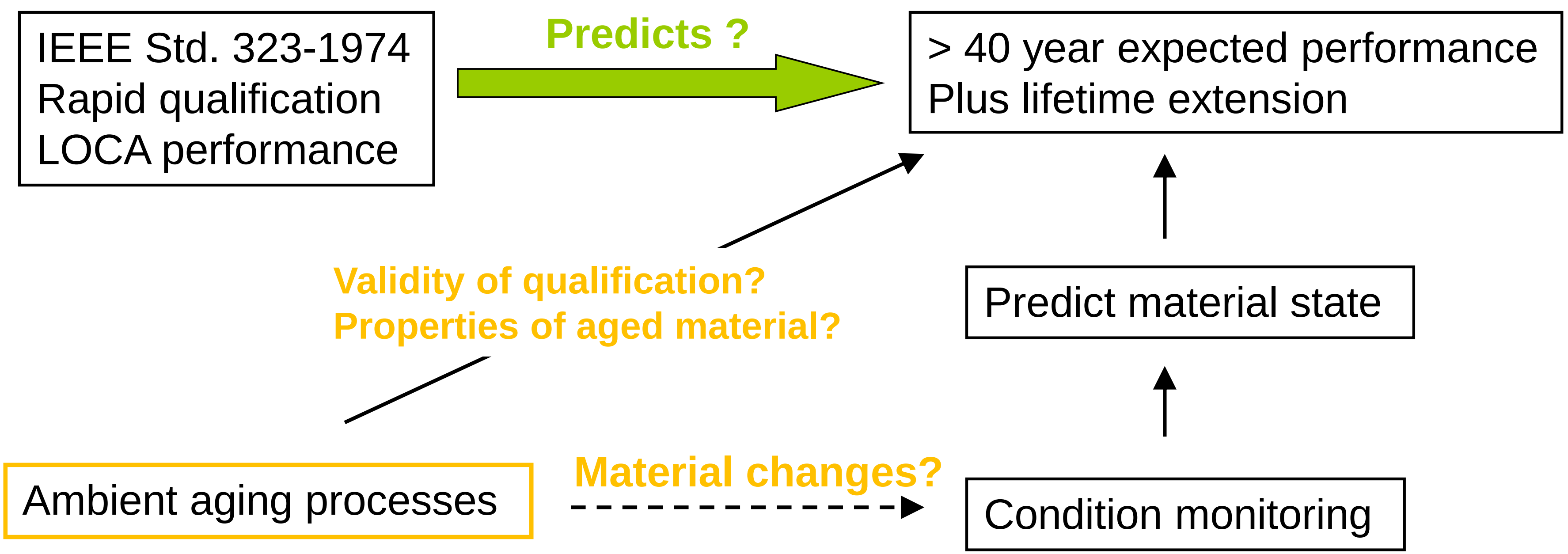
Ambient plant aging:
Expected dose rates: 0.2-1 Gy/h
Expected dose: 0.1-0.4 MGy
Temperature: 40-50°C

- **Dose rate of 0.6 Gy/h = 5.3 kGy/y or 0.26 MGy (26 Mrad) for 50 years**
- **If this dose were to be deposited within 2 weeks as part of an accelerated test, an extrapolation factor of 1300 times is implied**

**Could qualification testing easily cover ambient aging processes?**

# Qualification Testing and Long-term Aging

- **Does qualification testing offer margins for extended use?**
- **How does ambient aging contribute to material changes?**




**How valid is IEEE Std 323-1974 qualification testing?**
**Can condition monitoring overcome some uncertainty?**

# *Cable Insulation Materials*

XLPE, XLPO, CPE
crosslinked
semi-crystalline
often flame-retardant

EPR based
elastomers

Others
often for jacketing
materials

Brandrex
Rockbestos
GE Vulkene
Dekoron Polyset
Anaconda Flameguard

**Semi-crystalline**
**Morphology**
**Tie molecules**

Dekoron Elastoset
Anaconda Flameguard
Anaconda Durasheet
Okonite EPR

**Some materials may have crystallinity**

Hypalon jackets
Neoprene (RB Firewall III
Silicone (RB Firewall II)
ETFE

**Amorphous 'rubbery' type materials**

- **Polymer, filler, stabilizer, flame retardant, phys/chem properties**
- **There are significant differences in the aging behavior of these materials**
- **Standard qualification does not distinguish between materials (cables)**

# *A Few Material Science Aspects have Increased our Understanding of Cable Aging Phenomena*

- *DLO*
- *Morphology in semi-crystalline materials*
- *Mechanistic aspects*
- *Extrapolation to extended low T/low dose rate conditions*
- *Oxidation rate and synergistic behavior*

# *Discussion of a XLPO Material*

- **Is there an ideal aging behavior that matches 'standard testing'?**
- **Is actual aging behavior more complex and how?**

**Assumptions for accelerated aging with predictive value (theory):**

- **Accelerated conditions provide guidance 'slow aging'**
- **Aging processes do not change with temperature, dose rate**
- **Identical mechanical property changes for similar 'chemistry'**

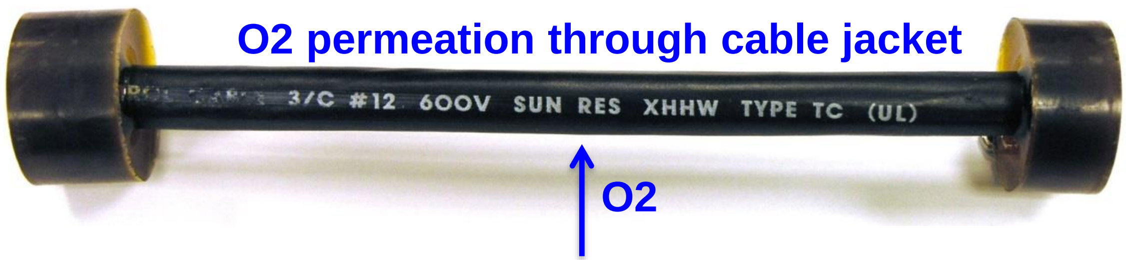
**Issues and complications for real world aging (in NPP application):**

- **Arrhenius curvature?**
- **DLO? Dose rate effects?**
- **Inverse temperature phenomena?**
- **Complex correlation of chemistry with mechanical properties?**
- **Complications due to morphology?**

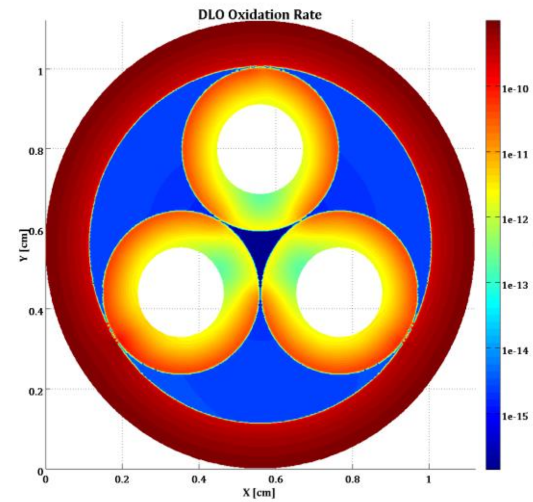
**Degradation of Brandrex XLPO has been studied in great detail**

# DLO Phenomenon in Rapid Cable Aging

- Requalification and accelerated testing of cable assemblies
- Is accelerated testing representative of ambient aging?
- Basis for condition monitoring approaches?




Brand-Rex Cable
300 kGy, 340 Gy/hr (2/20/15)
Accelerated testing




Modeled aging in XLPO cable.
Weak gradient in jacket, DLO through jacket and in cable interior

**DLO phenomena are not considered in rapid qualification testing**



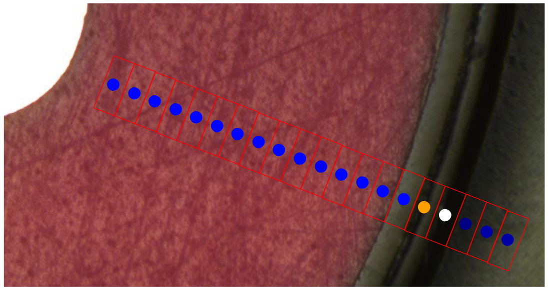
**Celina MC, Gillen KT, Lindgren ER. Nuclear Power Plant Cable Materials: Review of Qualification and Currently Available Aging Data for Margin Assessments in Cable Performance, Sandia National Laboratories, 2013, SAND 2013-2388, pp 136.**

# DLO Affects Accelerated Aging Behavior

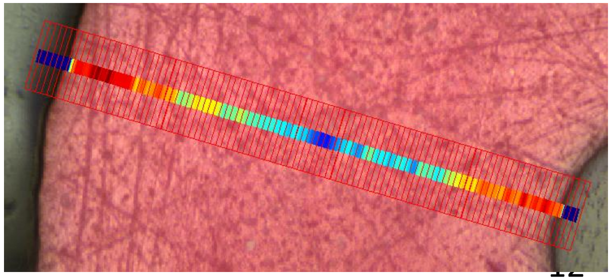
- Insulation within cable assembly does not experience oxidative aging
- Individual polymer removed from cable/conductor oxidizes
- **Fast accelerated aging DOES NOT represent ambient aging processes**


Brand-Rex Cable
300 kGy, 340 Gy/hr
Accelerated testing

Carbonyl imaging
1790-1675
**with ATR IR microscopy**

**DLO implies major mechanistic differences**



Celina MC, Gillen KT, Lindgren ER. Nuclear Power Plant Cable Materials: Review of Qualification and Currently Available Aging Data for Margin Assessments in Cable Performance, Sandia National Laboratories, 2013, SAND 2013-2388, pp 136.

# Why does DLO Behavior Matter? LOCA Test Exposure Conditions

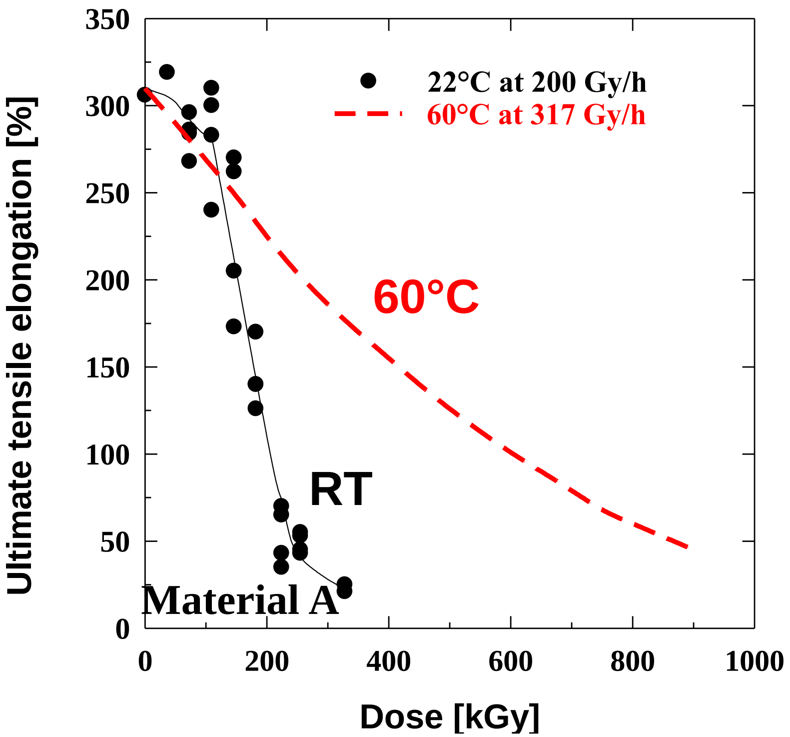
- **LOCA irradiation at a constant rate over a relatively short period of time:**
- **In SAND 91-1766 the LOCA irradiation was conducted at ambient temperature and a dose rate of 6 kGy/hr to a total dose of 1.1 MGy over an ~8d period.**
- **In JNES-SS-093 the LOCA irradiation was conducted at ambient temperature and a dose rate of <10 kGy/hr to a total dose of 1.5 MGy over ~ 7d period.**
- **In SAND 94-0485 the LOCA irradiation was delivered at 70°C over a 30 day period at a dose rate of 0.8 to 0.9 kGy/hr to a total dose of 0.60 MGy.**

- **Appendix A of IEEE Std. 323-1974 provides guidance on the time dose signature of a PWR LOCA. The dose rate during the first hour is 40 kGy/hr and for the next eleven hours 15 kGy/hr. After 30 days the total dose delivered is 0.55 MGy and the rate has dropped to 0.31 kGy/hr. The total dose after 6 months is 1.1 MGy and the total dose required after one year is 1.5 MGy and the final dose rate is 0.09 kGy/hr. Two thirds of the total LOCA dose is delivered at 0.12 kGy/hr over an eleven month period.**

**Some variability in LOCA test simulations, but generally high dose rate, high dose and often sequential thermal exposure**

# Inverse Temperature Behavior
# Mechanistic Variations with T

- Anomalous aging effect in temperature-radiation environments
- Observed for various crosslinked polyolefin materials (cable insulation)
- Reflects mechanistic variations in degradation mechanism




- Radiation + thermal environments at similar dose rates
- 30 Mrad is sufficient for significant embrittlement at RT (compare with LOCA test of 150 Mrad at high T)

**Inverse temperature behavior**

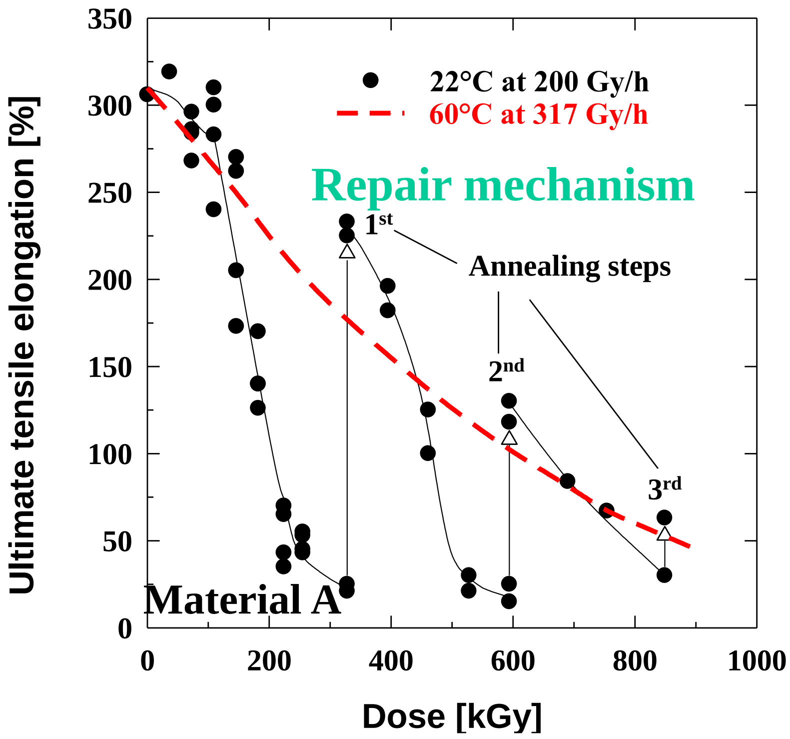
**Accelerated aging does not predict low temp + dose rate behavior**

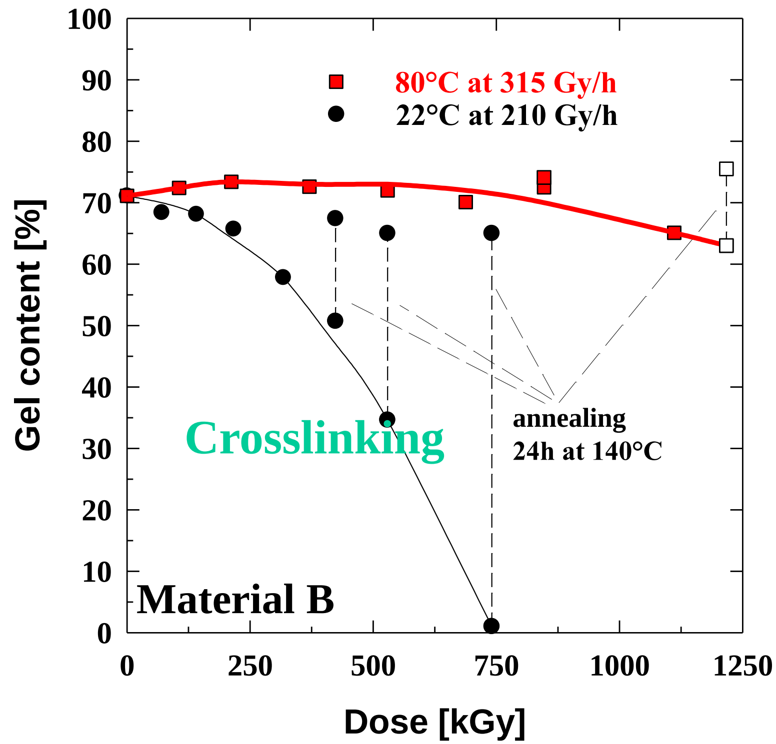
**What is the reason that lower temperatures show faster aging?**

M. Celina, K. Gillen, J. Wise, R. Clough, *Radiat. Phys. Chem.*, *48* (1996) 613
M. Celina, K. Gillen, R. Clough, *Poly. Deg. Stab.*, *61* (1998) 231

# Scission versus Crosslinking

- Elevated temp aging could not predict low temp degradation
- Competition between scission and crosslinking
- Crosslinking is only active for high T aging
- Faster aging at lower temperature (scission dominated)




**Low temperature aging is strongly scission dominated**

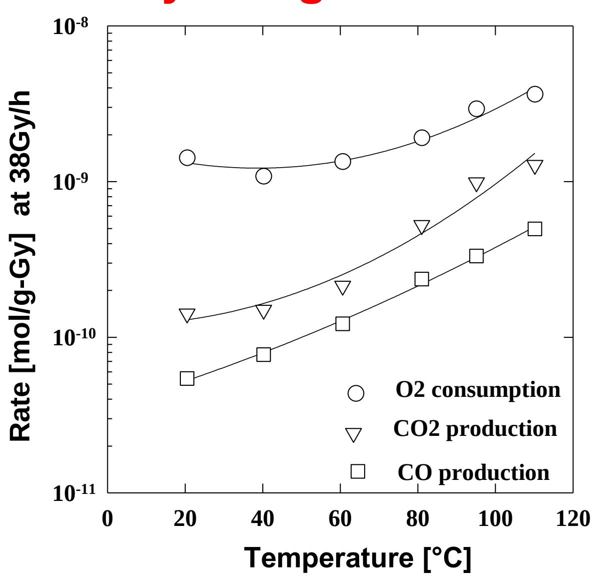
M. Celina, K. Gillen, J. Wise, R. Clough, *Radiat. Phys. Chem.*, *48* (1996) 613
M. Celina, K. Gillen, R. Clough, *Poly. Deg. Stab.*, *61* (1998) 231

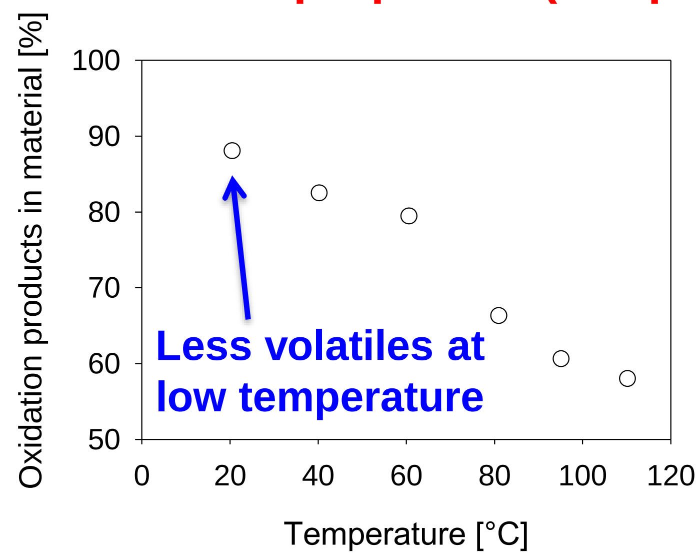
# Mechanistic Aspects

- **Correlation of oxidation level with mechanical failure depends on T**
- **More oxidation chemistry develops in material at lower T**

| | 25°C | 40°C | 60°C | 80°C | 95°C | 110°C |
|---|---|---|---|---|---|---|
| Ox. rate at 38 Gy/h [mols/g/Gy] | 1.40E-09 | 1.10E-09 | 1.30E-09 | 1.90E-09 | 2.90E-09 | 3.60E-09 |
| Est. ox. rate at 100 Gy/h [mols/g/s] | 3.90E-11 | 3.10E-11 | 3.60E-11 | 5.30E-11 | 8.10E-11 | 1.00E-10 |
| DED (100% elo.) at 100 Gy/h [Gy] | 1.70E+05 | 2.10E+05 | 4.70E+05 | 4.00E+05 | 2.30E+05 | 2.00E+05 |
| Time to 100% elongation [h] | 1.70E+03 | 2.10E+03 | 4.70E+03 | 4.00E+03 | 2.30E+03 | 2.00E+03 |
| **Oxidation at surface [weight %]** | **0.76** | **0.74** | **2.00** | **2.40** | **2.10** | **2.30** |

**Low T chemistry ≠ high T chemistry, impact on mech. properties (morphology!)**

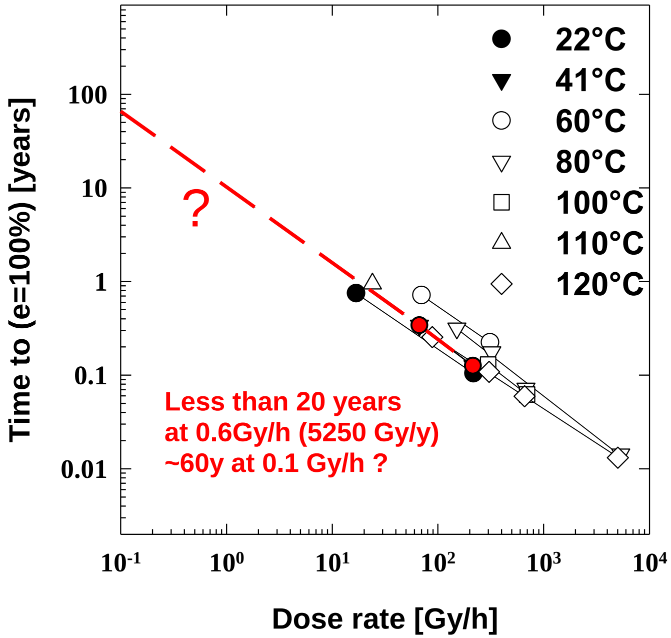



**The critical chemistry level for equiv. damage drops with T, also less volatiles are being generated**

# Extrapolation to Low Dose Rates?

**Question: Where is the transition to thermal dominated degradation at very low dose rates? How to predict lifetimes?**




**Apparent dose rate effects in accelerated rad-thermal aging due to: Thermal degradation aspects, inverse temperature behavior, DLO, and changes in chemistry pathways (hydroperoxide contributions)**

**Dose rate dependence needs to be deconvoluted and its origin better understood**

# Basic DED and TED Models (Theory)

- **Ideal model disregards DLO, dose rate effects, inv. temperature behavior**

$T_f$: thermal damage component to failure [mol/g]
$k_T$: thermal oxidation rate [mol/g-s]
$R_f$: radiative damage component to failure [mol/g]
$k_R$: radiative oxidation rate [mol/g-Gy]
$t_f$: time to failure under combined environments [s]
$\gamma'$: dose rate [Gy/s]
$\gamma_f$: total dose to failure [Gy]
$C_f$: critical oxidation to failure [mol/g or % oxidation]

$$\gamma_f = \gamma' t_f \qquad T_f = k_T t_f$$

$$\delta = \frac{T_f}{R_f} = \frac{k_T}{k_R \gamma'}$$

$$\frac{R_f}{C_f} = (\delta + 1)^{-1} = \frac{k_R \gamma'}{k_T + k_R \gamma'}$$

$$\frac{T_f}{C_f} = \left(1 + \tfrac{1}{\delta}\right)^{-1} = \frac{k_T}{k_T + k_R \gamma'}$$

$$R_f = k_R t_f \gamma' = k_R \gamma_f$$

$$C_f = T_f + R_f = t_f (k_T + k_R \gamma')$$

$$\gamma_f = \frac{C_f \gamma'}{k_T + k_R \gamma'}$$

(DED - dose to equivalent failure)

$$t_f = \frac{C_f}{k_T + k_R \gamma'}$$

(TED - time to equivalent failure)

**Model for primary degradation chemistry**

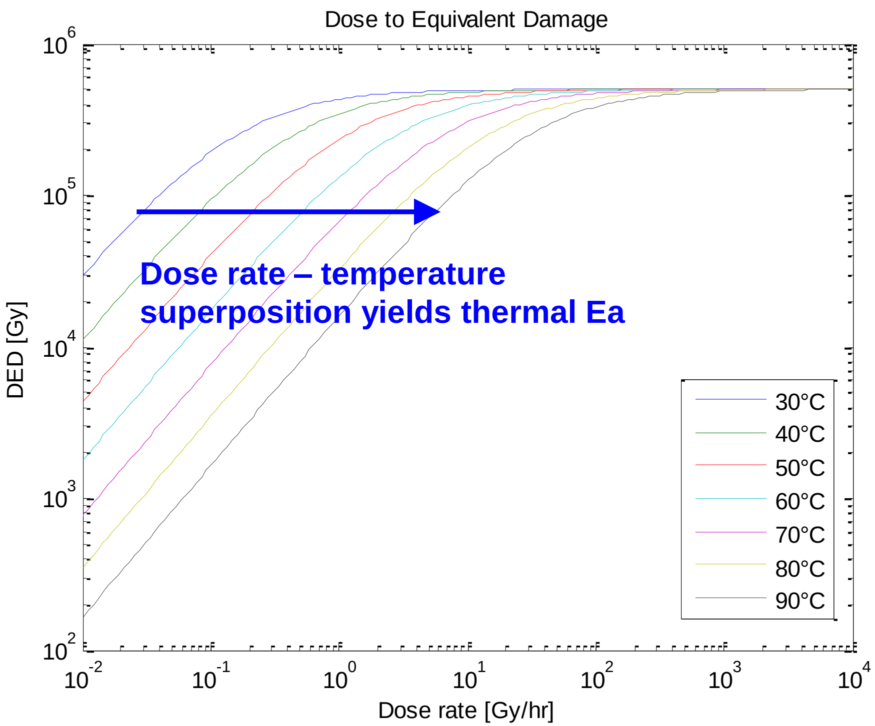
**Parallel processes for thermal and radiation induced degradation**
**This approach allows for theoretical aging trends to be established**

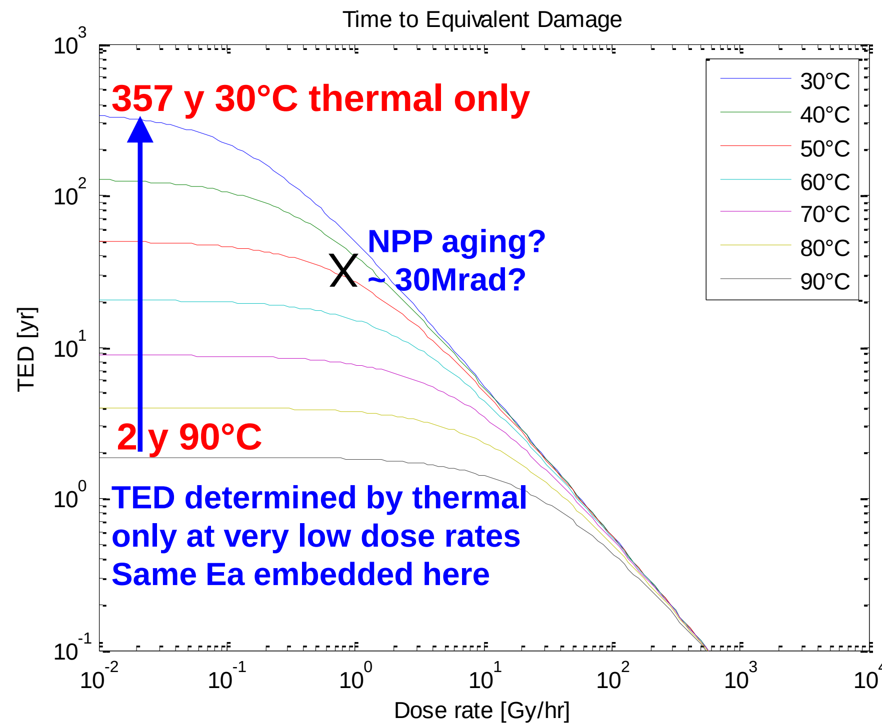


**Gillen KT, Clough RL. Time-temperature-dose rate superposition: a methodology for extrapolating accelerated radiation aging data to low dose rate conditions. *Polym Degrad Stab* 1989;24:137**

# Basic DED and TED Models

- Model for Ea=80 kJ/mol for thermal degradation
- Model assumes regular aging behavior with a single thermal Ea
- Model can be modified with additional parallel processes for dose rate effect and changes in critical oxidation level with temperature




**Visualization of transitions between thermal and radiation process**
**Without thermal process, DED would be independent of dose rate**

# Polymer Degradation Principles also Feed into Condition Monitoring

- **Aging process is expected to be similar at all conditions**
- **Fast aging trends (accelerated aging) could be used as calibration**
- **Condition should be established based on partial aging state**

Relationship between aging parameter (tensile or elasticity) and CM degradation variable from accelerated aging

↓

CM method:
OIT, indenter, torsion, surface C=O, gel/uptake, dielectric, etc.

Predict ambient aging processes and remaining margin

**CM approaches require consistent relationship between aging state and multiple material parameters, independent of aging environment**

# R&D Summary

- **Cable insulation (polymer) aging is complex**
- **Oxidative aging much worse than inert irradiation,**
- **O2 penetration dynamics into the jacket/insulation during aging is critically important (accelerated versus ambient)**
- **Material physics as important as degradation chemistry**
- **Identified issues with many parallel efforts in the community**

- **Important areas:**
- **DLO, inert temperature behavior, and deconvolution of combined thermal-radiation aging**
- **Intrinsic limits in the value of predictive aging experiments all the way to misguided interpretation of data**
- **CM approaches should rely on appropriately aged cable specimens**

**Meaningful aging studies should be carefully planned and incorporate existing knowledge based on polymer degradation principles**

# Recommendations

- ***Consider cable insulation not only as materials but also as polymers (much has been learned over the last 50 years)***
- ***Dependent on design needs, qualify new materials also for low T/low dose rate conditions (extended exposure)***
- ***Consider temperature and radiation, also moisture as convoluted parallel aging environments***
- ***Embrace feedback from polymer degradation science, fast versus slow aging, mechanism etc.***
- ***New materials have been designed, their extended aging is less well understood***
- ***50 year cable use in NPP also offers a tremendous resource to refine our understanding***

## *Backup Slides*

## *Some references used in USA R&D efforts on cable ageing*

# Publications 1980's

Clough RL, Gillen KT. **Combined environment aging effects: Radiation-thermal degradation of poly(vinyl chloride) and polyethylene**. J Polym Sci Polym Chem Ed 1981;19:2041.

Clough RL, Gillen KT. **Investigation of cable deterioration inside reactor containment**. *Nucl Technol* 1982;59:344.

Clough RL. **Radiation resistant polymers**. In:Kroschwitz J, ed. Encyclopedia of Polymer Science and Engineering, 2nd ed. New York, John Wiley & Sons, 1988, p 667.

Clough RL, Gillen KT. **Detailed studies of thermal oxidation**. Polym Mater Sci Eng 1988;58:209.

Clough RL, Gillen KT. **Polymer degradation under ionizing radiation: The role of ozone.** J Polym Sci, Part A: Polym Chem 1989;27:2313.

Gillen KT, Clough RL**. Occurrence and implications of radiation dose-rate effects for material aging studies.** Radiat Phys Chem 1981;18:679.

Gillen KT, Clough RL, Ganouna-Cohen G, Chenion J, Delmas G. **The importance of oxygen in LOCA simulation tests**. Nucl Eng Des 1983;74:271.

Gillen KT, Clough RL. **A kinetic model for predicting oxidative degradation rates in combined radiation-thermal environments. J Polym Sci Polym Chem** Ed 1985;23:2683.

Gillen KT, Clough RL, Quintana CA. **Modulus profiling of polymers**. Polym Degrad Stab 1987;17:31.

Gillen KT, Clough RL. **Time-temperature-dose rate superposition: a methodology for extrapolating accelerated radiation aging data to low dose rate conditions**. Polym Degrad Stab 1989;24:137.

Gillen KT, Clough RL. **Techniques for monitoring heterogeneous oxidation of polymers**. In:Cheremisinoff NP, ed. Handbook of Polymer Science and Technology. New York, Marcel Decker, Inc., 1989, p 167.

# Publications 1980's

- **What was recognized?**
  - **Definition and importance of environment variables: Oxygen, Ozone, Radiation, Thermal**
  - **Importance of $O_2$ in LOCA**
  - **Apparent dose rate effects**
  - **Beginning of kinetic models and evidence for aging heterogeneity**
  - **Modulus profiling**

**Accomplishments: Recognition of mechanistic pathways and aging complexity**

# Publications 1990's


Gillen KT, Clough RL. **Accelerated aging methods for predicting long-term mechanical performance of polymers**. In:Clegg DW, Collyer AA, eds. Irradiation Effects on Polymers. London, New York, Elsevier Applied Science, 1991, p 157.

Gillen KT, Clough RL. **Rigorous experimental confirmation of a theoretical model for diffusion-limited oxidation.** Polymer 1992;33:4358.

Gillen KT, Clough RL. **Predictive aging results in radiation environments**. Radiat Phys Chem 1993;41:803.

Clough RL, Gillen KT, Dole M. **Radiation resistance of polymers and composites**. In:Clegg DW, Collyer AA, eds. Irradiation Effects on Polymers. London, New York, Elsevier Applied Science, 1991, p 79.

Clough RL, Shalaby SW, eds. **Radiation Effects on Polymers**. Washington, D. C. ACS Publications #475, 1991.

Clough RL, Shalaby SW, eds. **Irradiation of Polymers: Fundamentals and Technological Applications**. Washington, D.C. ACS Publications #620, 1996.

Celina M, Gillen KT, Wise J, Clough RL. **Anomalous aging phenomena in a crosslinked polyolefin cable insulation**. Radiat Phys Chem 1996;48:613.

Celina M, Gillen KT, Clough RL**. Inverse temperature and annealing phenomena during degradation of crosslinked polyolefins**. Polym Degrad Stab 1998;61:231.

Wise J, Gillen KT, Clough RL. **Time development of diffusion-limited oxidation profiles in a radiation environment**. Radiat Phys Chem 1997;49:565.

# Publications 1990's

- **What was recognized?**
  - **Model development for Diffusion Limited Oxidation (DLO)**
  - **Distinguish inert versus oxidatively driven degradation**
  - **Description of polymer degradation based on 'chemistry' within a theoretical mathematical framework**
  - **Aging complexity due to polymer morphology**
  - **High dose rate irradiation is not predictive**

**Accomplishments: Foundation to describe DLO and inverse temperature phenomena for rad-thermal situations**

# Publications 2000's

Gillen KT, Celina M, Bernstein R. **Review of the ultrasensitive oxygen consumption method for making more reliable extrapolated predictions of polymer lifetimes**. Ann Tech Conf Soc Plast Eng 2004;62:2289.

Gillen KT, Bernstein R, Clough RL, Celina M. **Lifetime predictions for semi-crystalline cable insulation materials: I. Mechanical properties and oxygen consumption measurements on EPR materials**. Polym Degrad Stab 2006;91:2146.

Gillen KT, Assink R, Bernstein R, Celina M. **Condition monitoring methods applied to degradation of chlorosulfonated polyethylene cable jacketing materials**. Polym Degrad Stab 2006;91:1273.

Gillen KT, Celina M, Bernstein R, Shedd M. **Lifetime predictions of EPR materials using the Wear-out approach.** Polym Degrad Stab 2006;91:3197.

Gillen KT, Assink RA, Bernstein R. **Nuclear energy plant optimization (NEPO): Final report on aging and condition monitoring of low-voltage cable materials**, Sandia National Laboratories, Albuquerque and Livermore, 2005, SAND2005-7331, pp 286.

- **Better characterization of polymer oxidation reactions**
- **Better understanding of semi-crystalline material behavior**
- **Development of principles for successive aging exposure**

**Accomplishments: Mechanistic pathways feeding into wear-out aging and condition monitoring (NEPO report)**

# Publications 2010's

Gillen KT, Bernstein R. **Review of nuclear power plant safety cable aging studies with recommendations for improved approaches and for future work**, Sandia National Laboratories, Albuquerque and Livermore, 2010, SAND 2010-7266, pp 79.

Gillen KT, Bernstein R, Celina M. **Challenges of accelerated aging techniques for elastomer lifetime predictions**. Rubber Chem Technol 2015;88:1.

Gillen KT, Celina M. **Predicting polymer degradation and mechanical property changes for combined radiation-thermal aging environments**. Rubber Chem Technol 2018;91:27.

Celina MC, Gillen KT, Lindgren ER. **Nuclear Power Plant Cable Materials: Review of Qualification and Currently Available Aging Data for Margin Assessments in Cable Performance**, Sandia National Laboratories, 2013, SAND 2013-2388, pp 136.

Celina M, Redline E, Bernstein R, Giron N, Quintana A, White II G. **Summary Report of Cable Aging and Performance Data for Fiscal Year 2014**, Sandia National Laboratories, 2014, SAND 2014-17779, pp 194.

Celina MC. **Review of polymer oxidation and its relationship with materials performance and lifetime prediction.** Polym Degrad Stab 2013;98:2419.

Celina MC, Quintana A. **Oxygen diffusivity and permeation through polymers at elevated temperature.** Polymer 2018;150:326.

Celina M, Linde E, Brunson D, Quintana A, Giron N. **Overview of accelerated aging and polymer degradation kinetics for combined radiation-thermal environments.** Polym Degrad Stab 2019;166:353.

Gillen KT, Celina MC. **Issues with approaches for simulating aging of nuclear power plant cable materials**. Rubber Chem Technol 2022;95:322

**Carbonyl Identification and Quantification Uncertainties for Oxidative Polymer Degradation**. Polym Degrad Stab 2021;188:109550



**Reviews and guidance from polymer aging direction**