PNNL-28351

Light Water Reactor Sustainability Program

Report on Initial Evaluations of Effects of Diffusion Limited Oxidation (DLO) Testing

December 2018

U.S. Department of Energy

Office of Nuclear Energy

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Report on Initial Evaluations of Effects of Diffusion Limited Oxidation (DLO) Testing

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Pacific Northwest National Laboratory

December 2018

Prepared for the
U.S. Department of Energy
Office of Nuclear Energy

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Approved by:

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Director, Nuclear Science Project Management Office

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Date

SUMMARY

The Pacific Northwest National Laboratory (PNNL) is investigating diffusion limited oxidation (DLO) in nuclear cables through carefully controlled accelerated aging of cable materials and advanced characterization of aged specimens. The DLO knowledge gap raises the concern that extrapolation of short-term cable material accelerated aging results may overestimate long-term, in-service performance if short-term aging is performed under DLO conditions. Accelerated aging that is too rapid, either using high temperatures or high gamma dose rates, can underpredict damage through a phenomenon in which rapid oxidation forms a protective layer around the exposed material, preventing the interior of the material from aging. This contrasts with the homogeneous aging that is thought to occur in materials during long-term service aging. Accelerated laboratory aging to predict long-term performance thus needs to account for the difference in degradation mechanism that can occur above certain aging intensity thresholds. This work seeks to experimentally determine the thresholds for thermal aging (temperature) and gamma irradiation aging (dose rate) at which DLO is significant for the most common nuclear cable insulation materials from the most common cable manufactures of relevance to plant operation beyond sixty years. Cross-linked polyethylene (XLPE) and ethylene-propylene rubber (EPR) insulation materials from the most significant suppliers have been secured. Accelerated aging at temperatures and dose rates bounding the expected DLO thresholds for each material is underway. Sophisticated surface analysis techniques including Fourier transform infrared spectroscopy (FTIR) microscopy, nanoindentation, and time-of-flight secondary ion mass spectrometry (ToF-SIMS) are being applied to cross-sections of aged insulation to image and quantify the heterogenous aging signature of DLO in each material. The results of this study will provide a basis for understanding the impact of DLO in historic qualification activities for cables currently being considered for operation up to 80 years in subsequent license renewal.

ACKNOWLEDGMENTS

This research was sponsored by the U.S. Department of Energy, Office of Nuclear Energy, for the Light Water Reactor Sustainability (LWRS) Program Materials Research Pathway. The authors extend their appreciation to Drs. Keith Leonard and Thomas Rosseel for LWRS programmatic support.

Pacific Northwest National Laboratory is operated by Battelle Memorial Institute for the U.S. Department of Energy under Contract No. DE-AC05-76RL01830.

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ACRONYMS AND ABREVIATIONS

AFM	atomic force microscopy
DLO	diffusion-limited oxidation
EC-JRC	European Commission Joint Research Centre
EMDA	Expanded Materials Degradation Assessment (NUREG/CR-7153)
EPR	ethylene-propylene rubber
I-NERI	International Nuclear Energy Research Initiative
LWRS	Light Water Reactor Sustainability
NPP	nuclear power plant
NRC	U.S. Nuclear Regulatory Commission
PNNL	Pacific Northwest National Laboratory
SEM	scanning electron microscopy
ToF-SIMS	time-of-flight secondary ion mass spectrometry
XLPE	cross-linked polyethylene

1. INTRODUCTION

Diffusion limited oxidation (DLO) has been identified in the EMDA (NRC 2014) as one of the key knowledge gaps related to confidence in long term operation of cable systems beyond 60 years. The Pacific Northwest National Laboratory (PNNL) is investigating DLO in nuclear cables through carefully controlled accelerated aging of cable materials and advanced characterization of aged specimens. DLO is used here to describe the phenomena in which rapid aging of the surface of a polymer material can effectively protect the interior of material from thermo-oxidation by reducing oxygen permittivity of the aged surface. This effect has the potential to cause underestimation of long-term aging under relatively mild service conditions based on short-term accelerated aging results. Prior research (e.g. Clough 1985) has identified evidence for DLO in several polymer materials and provided a theoretical framework to estimate DLO based on factors including sample thickness, oxygen permeation rate through the material, and oxygen consumption rate in the aging material. This work seeks to address the DLO knowledge gap by assessing the importance of DLO in long term operation cable aging management. Selected examples of the most commonly used low-voltage cable insulation materials from the most common cable manufacturers are being studied to empirically determine the conditions at which DLO may be observed in the cable materials. This report describes the materials currently being investigated, the aging conditions being explored for those materials, and the characterization methods being applied to identify and quantify the presence and extent of DLO in the key materials. The results of this study will provide a basis for understanding the impact of DLO in historic qualification activities for cables currently being considered for operation up to 80 years in subsequent license renewal.

Diffusion limited oxidation (DLO) has been identified as a potential concern in electrical cable qualification methodology that could overestimate predicted service life based on laboratory accelerated aging. This highlighted knowledge gap for nuclear power plant (NPP) operation beyond 60 years is being addressed through investigation of the necessary conditions for and effects of DLO in select cable materials during laboratory aging from both extreme gamma radiation dose rates (>100Gy/h) and extreme aging temperatures (>130°C). This work seeks to address the DLO knowledge gap by assessing the importance of DLO in long term operation cable aging management.

Exposure of a polymer sample to extreme oxidizing conditions such as high temperatures or high gamma dose rates in air can quickly oxidize sample surfaces thus lowering oxygen permeation through the surface into the interior of the sample and inhibiting oxidative degradation of the sample interior as shown in Figure 1. This phenomenon may serve a protective role in application of polymers in extreme conditions, but can obfuscate degradation prediction at milder conditions at which the protective action does not occur from harsh condition accelerated aging performance during which it does occur as illustrated in Figure 2. A specific objective of this effort is to determine the temperature and gamma dose rate thresholds at which DLO become significant for selected materials.

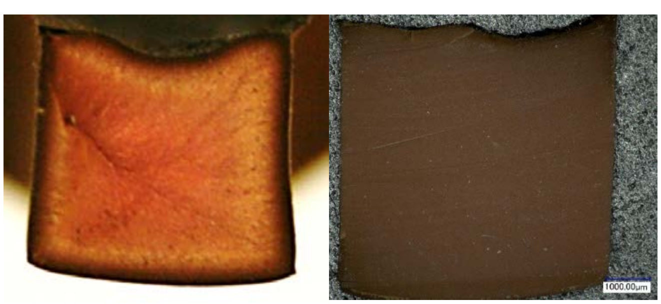

Figure 1. Inhomogeneous aging (Left), possible during rapid laboratory aging (e.g. 180ºC for 3 days), can lead to over-prediction of resistance to heat effects compared to homogeneous aging (e.g. 120ºC for 60 days) (Right), as would occur in long term service.

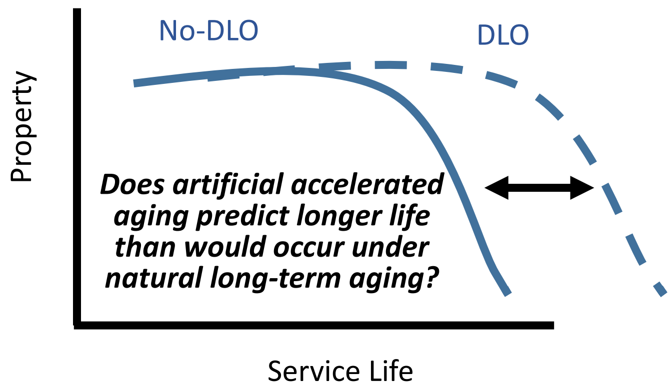

Figure 2. For properties such as elongation-at-break that average over the sample cross-section, DLO can effectively inhibit aging and could lead to overprediction of service life based only on short-term laboratory aging.

2. MATERIALS

The vast majority (95%) of electrical cables in NPPs in the United States are insulated either with cross-linked polyethylene (XLPE) or ethylene-propylene rubber (EPR). Manufacturers of the most common cables, listed in Table 1, include The Rockbestos Company; The Okonite Company; Boston Insulated Wire & Cable Company; Kerite Company; Anaconda Company; Brand Rex, Inc.; Samuel Moore Company; and Raychem Corporation.

Cable Manufacturer	Insulation	Fraction of plants surveyed
Rockbestos Firewall III	XLPE	58%
Anaconda Y Flame-Guard FR	EPR	33%
Brand-Rex	XLPE	28%
Okonite FMR	EPR	25%
Kerite HTK	[EPR-like]	24%
Raychem Flametrol	XLPE	22%
Samuel Moore Dekoron Dekorad	EPDM	18%
BIW Bostrad 7E	EPR	18%

Table 1. Occurrence of cable insulation types in plant constructed before 1978 [4]

The materials used in this study are listed below and pictured in Figures 3 through 12. Each specimen set consists of three 100 mm long straws, insulation with conductor removed, and one of either 50- or 100-mm long insulation with conductor intact. A clamp with unique identification is attached to each specimen and a paper clip is attached to each clamp. During aging the specimens are hung freely from wire racks using the clips.

Anaconda Flame-Guard FR-EP EPR

- PNNL ID: AE21
- Color: white
- Jacket label: ANACONDA-Y 4/C #16 FLAME-GUARD FR-EP 600V, 1-STQ-16 w/#18 Drain copper, Green
- Year of manufacture: 1985

Figure 3. Anaconda EPR (AE21) specimen set

BIW Bostrad 7E EPR-CSPE
(EPR insulation with chlorosulfonated polyethylene individual jacket)

- PNNL ID: BE15
- Color: Black
- Jacket label: BIW CABLE SYSTEMS, INC. BOSTRAD 7E 16 AWG ITSP EPR-CSPE INS/CSPE JKT 600V INST (1983)
- Year of manufacture: 1983

Figure 4. BIW EPR/CSPE (BE15) specimen set

Kerite HTK

- PNNL ID: KH31
- Color: Brown, labeled "WHITE"
- Year of manufacture: 1971

Figure 5. Kerite HTK (KH31) specimen set

Okonite FMR EPR

- PNNL ID: OE34
- Color: Black, labeled “2 - WHITE”
- Jacket label: OKONITE 4 3/C 14 AWG CU OKONITE FMR (EP)CSPE 600V 18C 1998
- Year of manufacture: 1998

Figure 6. Okonite EPR (OE34) specimen set

Rockbestos XLPE

- PNNL ID: RX39
- Color: Black
- Jacket label: 2/C 16 AWG ROCKBESTOS® 600V B/M NO. NK-35A Year of manufacture: 1993

Figure 7. Rockbestos XLPE (RX39) specimen set

RSCC Firewall® III XLPE

- PNNL ID: RX82
- Color: White
- Jacket label: 2/C 16 AWG COPPER RSCC 600V 90 DEG C WET OR DRY FIREWALL® III SUN RES DIR BUR OIL RES II NEC TYPE TC (UL) FRXLPE SHIELDED CSPE I46-0021
- Year of manufacture: 2015

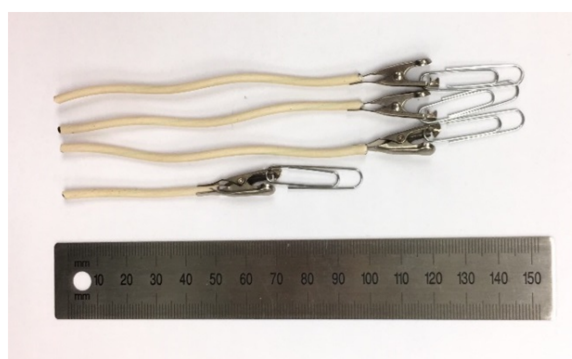

Figure 8. RSCC XLPE (RX82) specimen set

Samuel Moore Dekoron® EPDM

- PNNL ID: SE79
- Color: White
- Jacket label: DEKORON® 2/C 16 AWG 600V SAMUEL MOORE GROUP, AURORA, OHIO

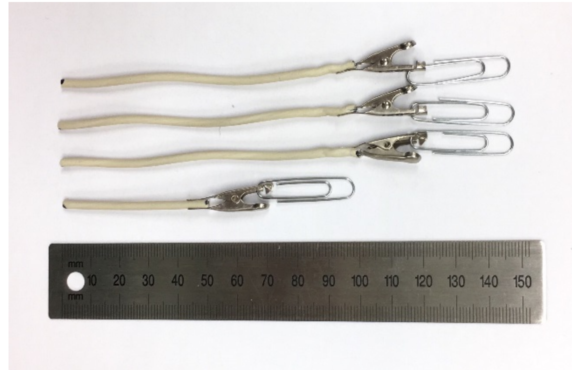

Figure 9. Samuel Moore EPDM (SE79) specimen set

Brand-Rex Ultrol FR XLPE

- PNNL ID: XX28
- Color: White
- Jacket label: BRAND-REX ULTROL INSTRUMENTATION CABLE 600V 1 SHIELDED PR #16 AWG 23XXX
- Year of manufacture: 1986

Figure 10. Brand-Rex XLPE (XX28) specimen set

Brand-Rex XLPE

- PNNL ID: XX50
- Color: White, labeled “2 - TWO”
- Jacket label: BRAND-REX XLP/CU POWER & CONTROL CABLE 3/C #10 600V SUN RES XHHW TYPE TC (UL)

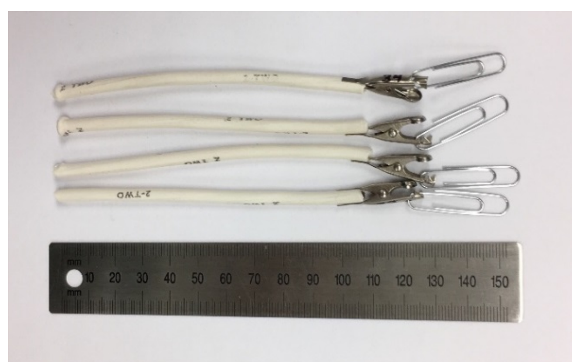

Figure 11. Brand-Rex XLPE (XX50) specimen set

3. ACCLERATED AGING

3.1 THERMAL AGING

Sample sets including insulation straws with conductor removed and insulation with conductor intact are hung from racks in mechanical convection, circulating air ovens at specified temperatures and exposure times. Aging temperatures being evaluated include 165, 150 ,136, and 121ºC.

3.2 RADIATION AGING

To investigate gamma dose rate thresholds for DLO sample sets are hung at room temperature at a series of distances from the Co-60 source in High Exposure Facility at PNNL. Dose rates being evaluated include 1900 Gy/h, 300 Gy/h, 190 Gy/h, and 100Gy/h.

4. CHARACTERIZATION

The key signature of DLO focused on here is heterogeneous aging across the thickness of the sample. The assumption is that oxidative aging that occurs over long periods of time will be consistent through the sample thickness because oxygen will have time to diffuse throughout the sample and be locally replenished as it is consumed in the degradation reaction. Rapid aging creates a kinetic barrier on the sample surface that prevents oxidative aging in the sample interior of over the short time of accelerated aging under harsh conditions. The sign and measure of DLO then is the degree of inhomogeneity and the shape of the aging gradient across the sample cross-section as schematically seen in Figure 12.

Figure 12. Schematic insulated conductor cross-sections illustrating unaged cable (Left), homogeneously aged cable (no DLO) (Center), and heterogeneously aged cable exhibiting DLO (Right).

The central techniques being pursued at PNNL to track and quantify heterogeneous aging in cable insulation cross-sections include:

- Fourier transform infrared spectroscopy (FTIR) microscopy,
- Nanoindention, including dynamic mechanical analysis mode, and
- Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS).

Also available are atomic force microscopy (AFM), x-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), and Raman microscopy.

PNNL has an active collaboration with the University of Bologna, Iowa State University, and the European Commission Joint Research Centre (EC-JRC) under the DOE International Nuclear Energy Research Initiative (I-NERI) entitled “Advanced Electrical Methods for Cable Lifetime Management”. One of the tasks of the I-NERI includes the EC-JRC study DLO using similar techniques.

Sample insulation cross-sections for FTIR microscopy representing a series of exposure times at a given temperature are represented by a schematic in Figure 13 and a photo in Figure 14.

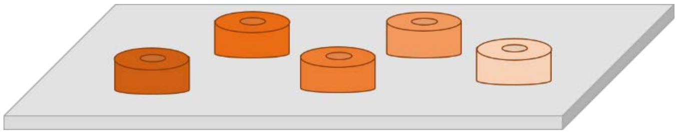

Figure 13. Cable insulation straw cross-sections less than a few millimeters thick for imaging.

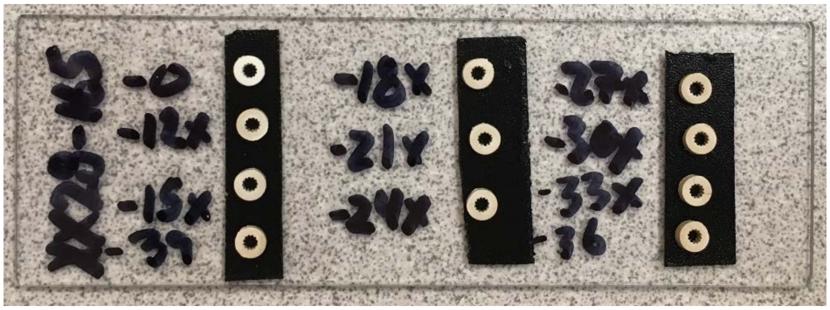

Figure 14. Photo of glass slide containing cross-sections of XX28 XLPE cable aged at 165ºC.

Nanoindentation requires a flat surface to study. Short cable insulation segments with or without metal conductor are potted in an epoxy puck to facilitate polishing to flat and clean surface as illustrated in Figure 15.

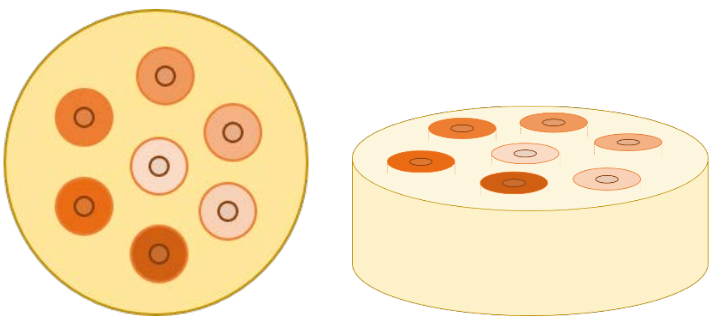

Figure 15. Schematic of epoxy puck containing cable insulation segments for nanoindentation imaging.

Specimens for ToF-SIMS (and XPS) also require a very flat surface, but the presence of carbon from the potting epoxy can interfere with carbon content measurements in the insulation. The epoxy resin can also be problematic for practical use in the high vacuum environment of the ToF-SIMS. Securing of cable insulation straws for cutting flat or insulated conductor for polishing flat as illustrated in Figure 16 is accomplished using metal clamps in preparation for ToF-SIMS imaging of heterogeneous aging.

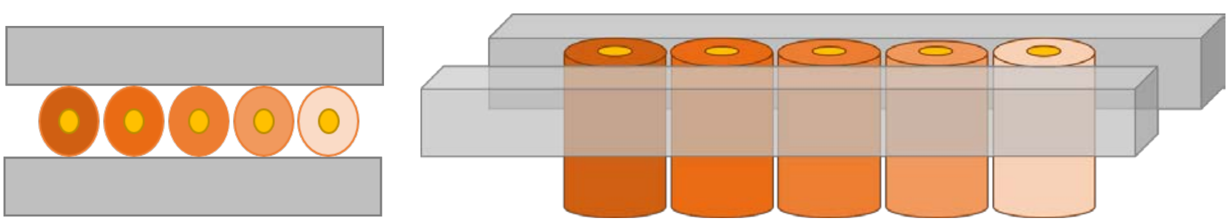

Figure 16. Top view (Left) and side view (Right) of a series of insulated conductors clamped for polishing in preparation for ToF-SIMS (or XPS) imaging.

5. CONCLUSION

DLO is a potential concern for environmentally qualified cables regarding operation beyond sixty years. If qualification tests were performed under conditions in which DLO was significant, the amount of aging present in cables from the short-term acceleration aging prior to design basis event testing may have underestimated what would be present in cables that have aged in service over forty years. PNNL is experimentally determining the extent of DLO as function of aging temperature and dose rate to determine condition thresholds for DLO. Results of this study will be used to inform scrutiny of cable qualification for the selected cable materials in the context of expected cable performance beyond sixty years.

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