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Pacific Northwest
NATIONAL LABORATORY

Light Water Reactor Sustainability Program

Progress on Analysis of Inverse Temperature Effects, Submerged Cables, Diffusion Limited Oxidation and Dose Rate Effects

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Director, Nuclear Science Project Management Office

ABSTRACT

Use of electrical cables in nuclear power plants much beyond their initial 40 year license period will require confidence that cable systems will continue to perform according to their design basis. Though much research has been performed to understand the aging and degradation of polymer materials used in nuclear cables, there remain gaps in the predictive knowledge of long-term performance of the most commonly used polymers in environments encountered in nuclear plants. This report provides an update on the status of research at the Pacific Northwest National Laboratory to address knowledge gaps in cable aging including activation energies, inverse temperature effects, dose rate effects, diffusion limited oxidation, and submerged cables.

SUMMARY

In fiscal year 2015, Pacific Northwest National Laboratory (PNNL) has extended existing thermal accelerated aging capabilities for nuclear power plant (NPP) cables to include gamma-irradiation accelerated aging capabilities and capabilities for combined exposure aging, including both temperature and dose rate control. During this time, capabilities and resources for cable characterization and testing have also been extended and newly developed including a new dedicated lab space, new instruments, and new test protocols. These resources are being developed to address knowledge gaps in NPP cable aging and degradation such as those identified in the Environmental Materials Degradation Assessment Volume 5. Targets for increased understanding being addressed by the PNNL program include activation energies for thermal and radiation degradation, inverse temperature effects in which damage from radiation is greater at lower temperatures, dose rate effects that might challenge the total dose equivalency assumption, and diffusion limited oxidation related phenomena that might obscure the relation of accelerated aging to natural, long-term aging. Increased understanding of the degradation of cables in wet environments is also considered. While the research at PNNL is at an early stage, the status of ongoing work and the vision of the program next steps are described.

CONTENTS

FIGURES

ACRONYMS

CSPE	Chlorosulfonated polyethylene
CPE	Chlorinated polyethylene
DOE	U.S. Department of Energy
DLO	Diffusion limited oxidation
DMA	Dynamic mechanical analysis
DRE	Dose rate effects
DSC	Differential scanning calorimetry
E_a	Activation energy
EAB	Elongation at break
EDX	Energy dispersive x-ray spectroscopy
EMDS	Environmental materials degradation assessment
EPDM	Ethylene-propylene-diene rubber
EPR	Ethylene-propylene rubber
EPRI	Electric Power Research Institute
FTIR	Fourier transform infrared spectroscopy
HEF	High Exposure Facility
ITE	Inverse temperature effect
MPa	Megapascal
NPP	Nuclear power plant
NRC	Nuclear Regulatory Commission
PNNL	Pacific Northwest National Laboratory
PVC	Polyvinyl chloride
SEM	Scanning electron microscopy
TGA	Thermogravimetric analysis
THz	Terahertz
XLPE	Cross-linked polyethylene
XLPO	Cross-linked polyolefin
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

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1. INTRODUCTION

Nuclear cables, including Class IE safety cables were originally qualified for 40 years using extrapolation of cable resilience from short term exposure to thermal and/or radiation stress much higher than is actually present in the nuclear power plant (NPP) environment [1]. The assumptions of the extrapolation and the ability of the approach to accurately predict long-term cable performance in the relatively mild conditions actually experienced by most cables in operating U.S. NPPs has been challenged, particularly in the context of extending the use of historically qualified cables for periods much longer than forty years—up to 60 years, 80 years, or longer [2]. Recognizing that uncertainties exist in the understanding of long-term aging of cables in operating plants, expert opinions in the field were drawn upon to summarize the most important cable materials, the most relevant NPP conditions, and the state of knowledge of the aging behavior of these materials [3]. This exercise identified ethylene-propylene based rubbers, including ethylene-propylene rubber (EPR) and ethylene-propylene-diene rubber (EPDM), and cross-linked polyolefins (XLPO), including cross-linked polyethylene (XLPE), as the most prevalent materials of interest. A much less frequently used material also indicated of importance is silicone rubber (SiR). Knowledge gaps identified with regard to the aging of these materials include activation energies (E_a) for degradation, diffusion limited oxidation (DLO) and radiation dose rate effects, inverse temperature effects (ITE), and moisture effects on cable aging. The knowledge gaps identified in the EMDA report, operating experience of NPP cable program managers as communicated in EPRI Cable User Group meetings, input from the NRC, EPRI and DOE in the Cable Collaboration and Communication group, and information available in the literature help to inform PNNL priorities for DOE-funded cable research.

2. MATERIALS CONSIDERED

PNNL is currently focusing on XLPE and EPR cable insulation materials. Chlorosulphonated polyethylene (CSPE), chlorinated polyethylene (CPE), and polyvinyl chloride (PVC) are jacket materials currently under investigation. Cables materials fall in the categories of either ‘new’ or ‘vintage’. New cable is of modern formulation, is currently being manufactured, and is available for study in virtually unlimited amounts. Vintage cable is of the same formulation of cables currently installed in NPPs that is under consideration for continued operation beyond original license period. It may have been stored for decades since its manufacture, or actually installed in NPPs. This cable is the most relevant for study, but is only available in small diminishing quantities. Stored vintage cable is potentially valuable as a baseline control for consideration of degradation due to environmental stresses experienced in the plant.

Selection of new cable on which to focus has been based on discussions with subject matter experts at cable suppliers. The Okonite Company suggested that Okonite®-FMR® (flame and moisture resistant) EPR-insulated cable, sold for marine application with an Okoseal® PVC jacket (Figure 1), has insulation that is most similar in composition to historically installed EPR insulation. Small quantities of fielded and vintage EPR have been received from EPRI. RSCC Wire & Cable has indicated Firewall® III XLPE (Figure 1) to be similar in composition to historically installed XLPE in NPPs. Cables with the suggested formulations of EPR and XLPE insulation have been procured from Okonite and RSCC, respectively. Additional fielded EPR and XLPE samples are anticipated to become available from the recently decommissioned Zion and Crystal River 3 nuclear reactors.

Figure 1. Phot of EPR Insulated Cable (Left) and XLPE Insulated Cable (Right).

3. EXPERIMENTAL APPROACH

Increased understanding of dose rate effects, inverse temperature effects and inhomogeneous aging are being addressed through exposure of the target materials to aging at controlled temperatures, dose rates, and exposure times followed by a battery of characterization and test methods. The equipment and capabilities for controlled thermal and combined thermal and radiation aging have been established at PNNL in FY15 and are being applied to produce a library of samples. Some exposure experiments, particularly those at lower temperatures and lower dose rates, may take months or year to complete. Intermediate samples are being obtained for analysis of the evolution of material degradation. New equipment and capabilities for test and characterization of aged material are being added in FY15 to those that previously existed at PNNL.

4. COMBINED EXPOSURE

This year PNNL demonstrated the capability to simultaneously expose polymer insulation specimens to temperatures between 25°C and 200°C and gamma dose rates from 5 to 500 Gy/hr in the High Exposure Facility (HEF) (Figure 2). It is anticipated that this resource will be used on a continuing basis to produce a library of target material specimens that will enable analysis of degradation as a function of temperature, dose rate, and total dose.

Figure 2. Video Feeds of Exposure Chamber From the HEF Control Room.

The first experimental campaign exploring combined exposure is being performed on XLPE insulation in collaboration with Iowa State University. New two-conductor, shielded cable with XLPE insulation and CSPE jacket was obtained from RSCC. Insulation specimens are isolated from the cable in two forms: with conductor intact and with conductor removed. Specimens are supported in an air-circulating oven with an external temperature control and placed in the gamma beam of a Co-60 source. Each row of specimens represents a distinct dose rate as a function of distance from the source. Sets of specimens are removed from exposure at engineered intervals to produce comparable total doses for comparison. The specimen sizes, numbers, and forms included in each set provide sufficient material for all of the targeted post-irradiation characterization methods with at least five measurements per method to account for statistical variation (Figure 3).

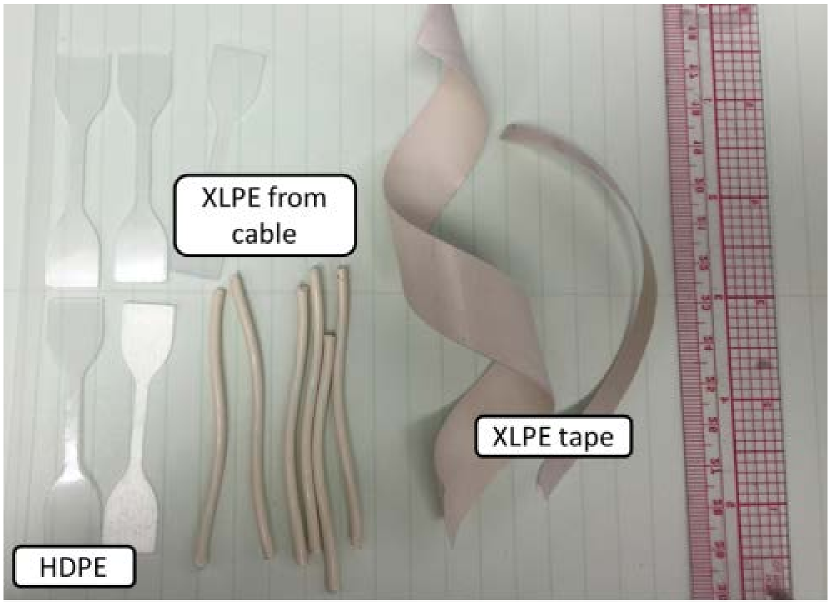
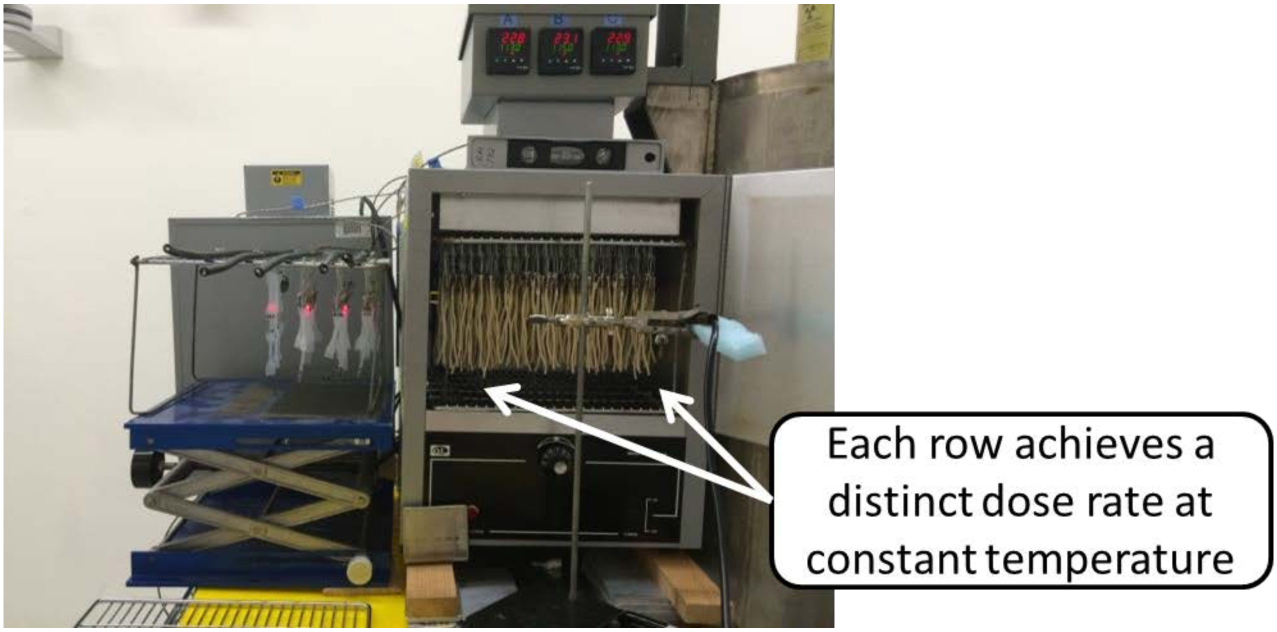


Figure 3. Example Specimen Set of Specimens for Exposure Time Point.

The planned exposure temperatures for the current XLPE series are 60°C, 90°C, 115°C and 135°C. This range of temperatures includes selections above and below the ~120°C phase change temperature of XLPE. Dose rates for these specimens range from ~500 to ~50 Gy/h in 24 distinct increments (Figure 4). Exposure occurs in 5-day sessions. The current series plans to include 5 rounds of exposure at each temperature. A multiple thermocouple data logger is used to record actual temperatures. An ion gauge is used to quantify gamma attenuation through oven walls and other samples for precise calculation of dose rates.



Each row achieves a distinct dose rate at constant temperature

Figure 4. Specimen Rack in Oven and Outside of Oven for Gamma Irradiation Exposure.

Test and characterization methods planned for the current XLPE campaign include elongation at break (EAB), weight change, density, differential scanning calorimetry (DSC), dynamic mechanic analysis (DMA), thermogravimetric analysis (TGA), Fourier transform infrared (FTIR) spectroscopy, Raman spectroscopy, x-ray diffraction (XRD), x-ray photoelectron spectroscopy (XPS), indenter modulus, gel-fraction, swell ratio, electrical permittivity, breakdown voltage, terahertz (THz) spectroscopy, and scanning electron microscopy (SEM) with energy dispersive x-ray (EDX) spectroscopy.

Future rounds of combined exposure of materials to thermal and radiation stress will be performed on additional materials such as EPR (Figure 5).


Figure 5. Rack of EPR Specimens for Thermal Exposure.

5. DYNAMIC MECHANICAL ANALYSIS

A common method for assessment of cable insulation degradation state is tensile elongation at break in which a specimen is pulled to failure. The displacement to failure divided by the original sample length gives a measure of the elasticity of the material. Elasticity diminishes as polymer aging progresses. DMA is a more sophisticated technique that investigates the response of a material to a mechanical force applied in an oscillating manner. It can be performed in tensile as well as compressive and other modes. A small sinusoidal displacement is applied, the resulting force and the phase shift of the force with the displacement application is determined. This technique is being explored at PNNL as a sensitive method to detect changes in polymer state.

DMA is being used to investigate changes in mechanical properties of EPR with thermal aging. The majority of work with DMA at PNNL to this point has been performed on specimens of molded "pink" EPR sheet provided by The Okonite Company. This material is of modern formulation containing iron oxide pigment giving it the characteristic Okonite EPR pink color. The DMA tensile mode has also been demonstrated on insulation straws, with conductor removed. The standard analysis protocol that has been adopted ramps the temperature of the specimen from -150°C to 140°C at 2°C per minute while applying a displacement of 10 micrometer amplitude at a frequency of once per second. Outputs of the technique include the storage modulus and the loss modulus, in megapascal (MPa), of the material at each temperature during the scan (Figure 6). The storage modulus is a measure of the elastic character, or the solid-like nature of the polymer insulation. Its value reflects the stiffness of the material. The loss modulus is a measure of the viscous character, or the liquid-like nature of the polymer insulation. Its value reflects the damping of the material. The ratio of loss modulus to storage modulus is known as the 'material loss factor' or the 'loss tangent', commonly referred to as tan δ or "tan delta". Tan δ values range from zero for an ideal elastic solid to infinity for an ideal viscous liquid. It is the ratio of energy dissipated to energy stored per deformation cycle [4]. Peaks in the tan δ trace indicate abrupt changes in the solid/liquid nature of the material such as phase changes from liquid to solid or from below to above the glass transition. Storage modulus in pink EPR has been observed to increase precipitously with aging at 150°C after an initial induction period (Figure 7), perhaps corresponding to antioxidant consumption. Glass transition temperature of the EPR, as revealed by tan δ peak position, has been observed with aging to increase (Figure 8), perhaps corresponding to changes in the semi-crystalline or cross-linked structure of the polymer.

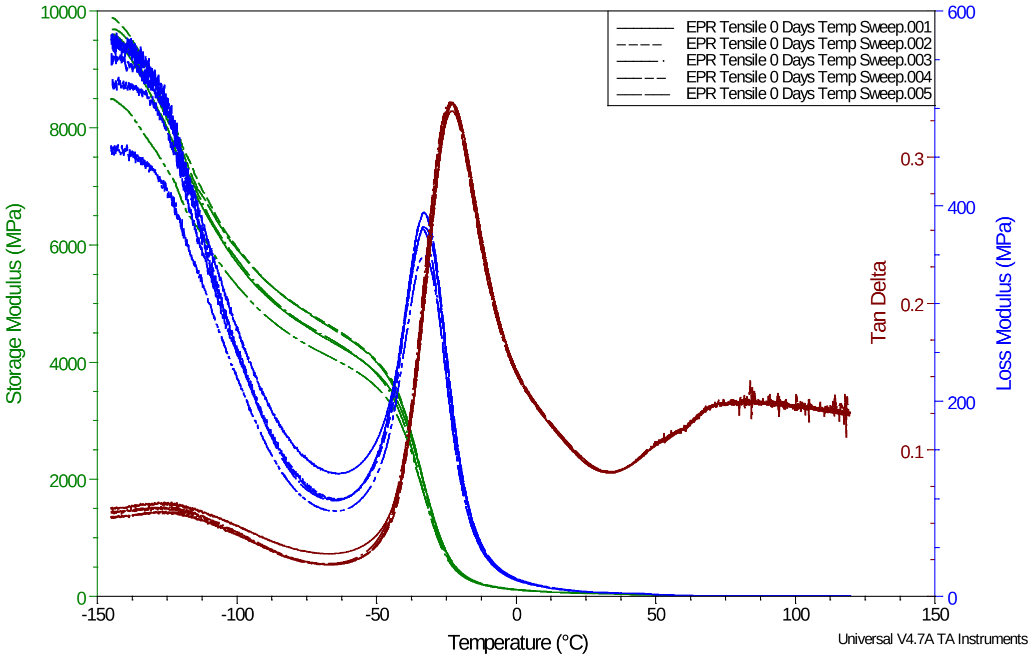


Figure 6. DMA Plot Showing Storage Modulus, Loss Modulus and Tan δ Versus Temperature.

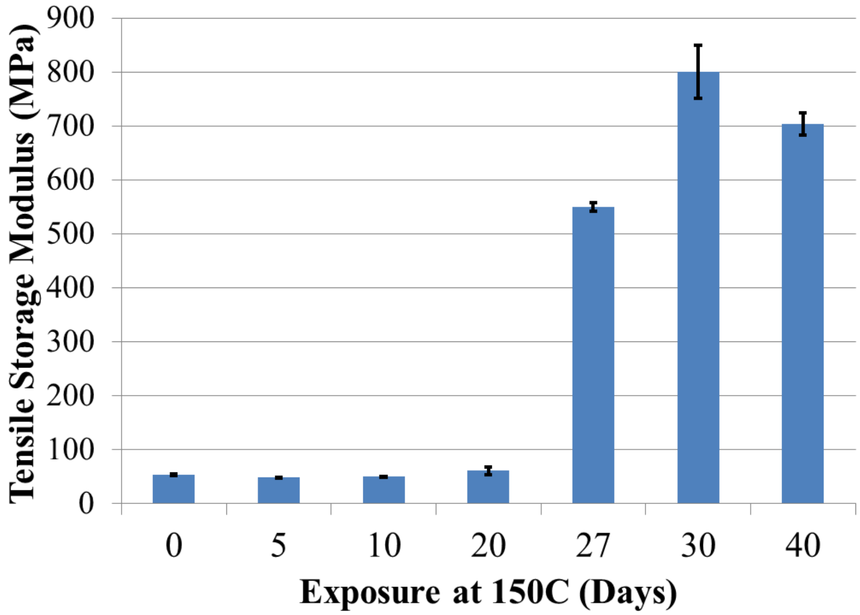


Figure 7. Plot of Storage Modulus of Pink EPR with Aging in Air At 150°C.

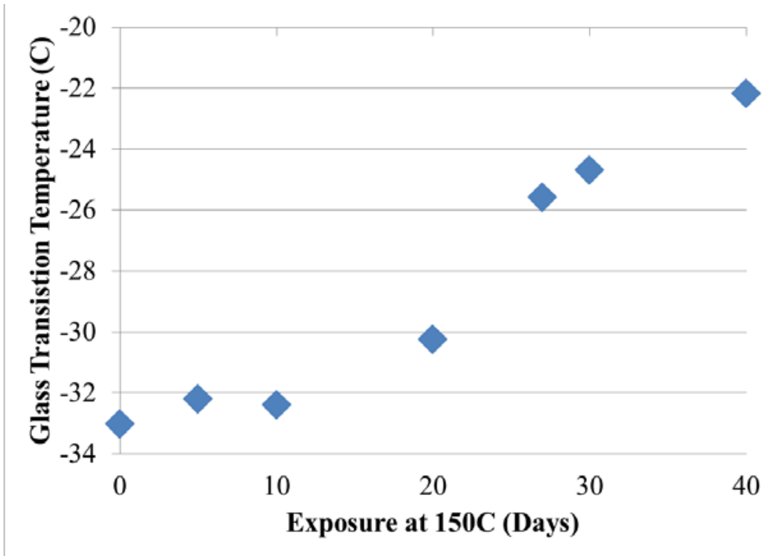


Figure 8. Plot of Glass Transition Temperature of EPR with Aging at 150°C

6. TIE OF PNNL ACTIVITIES TO KNOWLEDGE GAP TARGETS

The activation energy (E_a) of a material degradation process relates the changes in chemical, mechanical, physical and electrical properties of the material with exposure time and conditions. Characterization of these properties in XLPE and EPR with exposure will assist in reducing E_A uncertainties for these materials. The largest knowledge gap is for E_A of materials at lower temperatures and lower dose rates.

Inverse temperature effects (ITE) describe the increased degradation that is sometimes observed for materials irradiated at lower temperatures compared to the same materials irradiated at higher temperatures. Characterization of changes in material characteristics of XLPE and EPR exposed to temperatures above, below, and near material phase transitions during gamma irradiation are assisting in understanding these effects. The question of dose rate versus total dose effect on material degradation is also being addressed through analysis of XLPE and EPR exposed at different temperatures, different dose rates, and different total doses.

Inhomogeneous aging of samples, a phenomenon that complicates accelerated aging approximations of long-term natural aging, includes diffusion limited oxidation (DLO) and is being better understood at PNNL through microstructural characterization of aged XLPE and EPR. The understanding that the aging of cable in NPPs occurs under equilibrium conditions whereas accelerated laboratory aging is kinetically limited can be evaluated to determine under which conditions it is significant. This is being done through relation of microstructural spatial evidence of aging to bulk aging indicators such as EAB an indenter modulus.

Increased understanding of cable degradation in moist environments is currently being by collaboration partner EPRI in a long-term study of immersed cables under load [5]. The most appropriate laboratory conditions to approximate long term wet environment degradation may require additional research. Wet and potentially wet environments for cables continue to be a common issue of concern for NPP operators [6].

7. CONCLUSION

PNNL is pursuing the narrowing of knowledge gaps in cable aging and degradation through identification of priority cable materials for study, establishment of capabilities for controlled exposure, and establishment of capabilities for testing and characterization of samples representing different exposure histories. Archiving of exposed samples and sample data for data analysis is key to the program. Cable aging activities are closely tied with assessment and development of methods to monitor cable condition and predict cable performance.

The anticipated outcomes of this program are:

- Improved understanding of appropriate +accelerated aging conditions
- Improved knowledge of correlation between observable aging indicators and cable condition in support of advanced NDE methods
- Practical knowledge of condition-based cable lifetime prediction.

8. REFERENCES

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