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Performance of Bolted Closure Joint Elastomers Under Cask Aging Conditions

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ABSTRACT

The bolted closure joint of a bare spent fuel cask is susceptible to age-related degradation and potential loss of confinement function under long-term storage conditions. Elastomeric seals, a component of the joint typically used to facilitate leak testing of the primary seal that includes the metallic seal and bolting, is susceptible to degradation over time by several mechanisms, principally via thermo-oxidation, stress-relaxation, and radiolytic degradation under time and temperature condition. Irradiation and thermal exposure testing and evaluation of an ethylene-propylene diene monomer (EPDM) elastomeric seal material similar to that used in the CASTOR® V/21 cask for a matrix of temperature and radiation exposure conditions relevant to the cask extended storage conditions, and development of semi-empirical predictive models for loss of sealing force is in progress. A special insert was developed to allow Compressive Stress Relaxation (CSR) measurements before and after the irradiation and/or thermal exposure without unloading the elastomer. A condition of the loss of sealing force for the onset of leakage was suggested. The experimentation and modeling being performed could enable acquisition of extensive coupled aging data as well as an estimation of the timeframe when loss of sealing function under aging (temperature/radiation) conditions may occur.

INTRODUCTION

The designs of several storage and transportation packaging solutions for radioactive material have incorporated bolted closure joints. The components of a bolted closure joint which often includes lids, bolting, metallic seals, and polymeric (elastomeric) seals are vulnerable to degradation under stressors of thermal and mechanical loads, as well as radiation and corrosion conditions.

The bare fuel cask design for a Dry Cask Storage System often employs primary (metallic) and secondary (elastomer) O-ring seals to ensure containment of radioactive contents. The elastomer seals provide an ancillary boundary in dry fuel storage casks and in dual-purpose storage and transportation casks that also serves to shield the primary metallic seal from potentially corrosive conditions external to the cask. . And while the mechanical performance of metallic seals have been exceptionally well characterized for use in some DCSS applications [4,5] the factors which influence their degradation can be impacted by the secondary seal. Although both the polymeric and metallic seals in a bolted closure joint are replaceable, it would be cost prohibitive as a routine maintenance item. As such, an estimation of the time at which seals may lose their effectiveness at service conditions is important..

O-ring suppliers typically provide operation limits for their products in terms of continuous or peak temperatures. These specifications do not take into account the degradation effects induced or enhanced by simultaneous exposure to radiation, nor do they define the acceptance criteria (e.g. leakage rate, sealing force decay)..

This paper describes the development and initial application of a testing and analysis approach to evaluate the time/temperature/dose conditions at which an elastomeric seal may lose its ability to provide a seal function. Rather than reporting seal failure as a volumetric leak rate which is dependent on the package/cask configuration being tested, this approach tracks and predicts compression set relaxation (CSR) measurements of the tested materials.

Initial testing with this approach has been performed for a specific elastomer seal compound, Parker Seals EPDM E0740-75, which is intended for nuclear application and has been used in multiple cask designs [1]. CSR measurements obtained for this compound at multiple temperatures and gamma dose rates appear in the report along with a demonstration of the data analysis which would yield projected failure rates of a secondary seal experiencing typical service conditions within a common bolted closure cask, namely the CASTOR V/21.

Test Method and Analysis

Materials used in the construction of storage and transport packages for radioactive material may undergo change in their mechanical properties as a result of their continued exposure to service conditions withfactors such as physical stress, heat, chemical reaction, and radiation damage. Mechanical characteristics of O-rings such as tensile strength, hardness, and elasticity have been extensively studied and are commonly reported as a function of time at temperature. These reported properties, however, do not necessarily give any indication of the seal's effectiveness in service as it is difficult to relate these measurements to the material's leaktightness. Some investigators have used time to leak failure as the only measure of seal performance, but the data are generally limited to leak failures at high temperatures with extensive extrapolations needed to estimate time to leakage at lower, more realistic temperatures. Furthermore, these studies often focus on just one external factor, temperature, and consider only the degradation mechanisms for which it is responsible. In some service applications, elastomeric O-rings may experience significant radiation fluxes and undergo stress-relaxation and radiolytic breakdown of the material which must be considered when evaluating the sealing ability of the O-ring, especially in long-term service.

The mechanisms which affect an O-ring's performance can be complex and interdependent. . An approach to evaluate sealing performance in this case is the development of Semi-empirical models of sealing force developed with experimentally obtained data. The testing method exposes O-ring samples to stress, high temperature, and radiation dose concurrently.s.

The approach proposed and demonstrated in this report to evaluate seal performance involves compression stress-relaxation (CSR) counterforce measurements which can be used to develop sealing force decay curves. While not as direct as time-to-leakage with a leak test, CSR testing allows direct comparison of seal behavior under a specific set of conditions.

Because the time frame over which damage is done to O-rings in service is much longer that can be tested in the laboratory, accelerated aging tests have been employed. Accelerated aging tests involve rapid exposure to extreme conditions such as higher temperatures and dose rates than expected during operation. The degradation effects are frequently recorded over this relatively short period of accelerated aging and then used to extrapolate to normal conditions over long periods of time similar to what would be expected in actual service. In this manner, CSR data can be evaluated against selected failure criteria (e.g. a specific loss of sealing force) and the collective data can be translated to any temperature of interest using time-temperature superposition principles, as long as the degradation mechanism remains constant across the extrapolation range (Arrhenius theory).

Experiment Setup & Data Acquisition

The metric chosen to monitor loss of O-ring sealing force was CSR counterforce. The counterforce measurements were made using a Wallace Mark IV relaxometer with Shawbury-Wallace C11 jigs per ASTM D6147. modified CSR approach was developed to enable irradiation response of the O-ring material in a compressed state while avoiding radiation damage to the CSR jig. For thermal-only exposures, such modifications are not likely necessary, though could still be of benefit by limiting the number of CSR jigs that need to be procured (which can be expensive with procurement lead-times), and reduce the oven space needed to age multiple samples. Back-up or duplicate CSR jigs are still needed, but this approach minimizes the number of jigs that would contribute to inconsistent readings resulting from jig variation, and it removes the need for any jigs to see thermal/radiation exposure conditions which may cause damage to the jig and interfere with its ability to consistently measure counterforce over the life of a sample. The components used for the modified CSR approach are shown in Figures 1-3

O-ring segments are initially appraised for dimensional and hardness values using a snap gauge and Durometer. Segments are then loaded into custom grooved aluminum inserts (Figure 1) designed to hold O-ring segments in place and under a constant compression of 25% during the tests, simulating their configuration in a bolted closure.

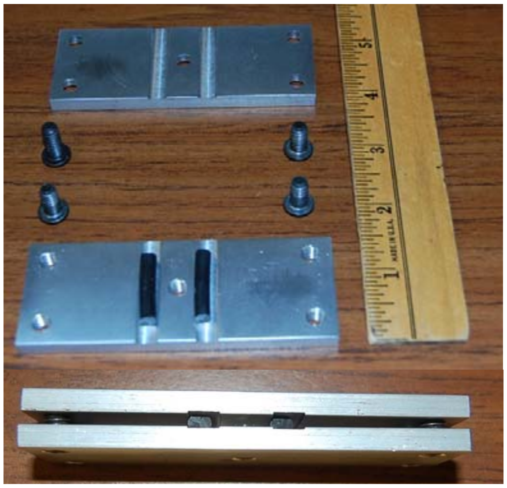

FIGURE 1 CUSTOM CSR INSERTS LOADED WITH EPDM O-RING SEGMENTS

The top insert plate has a smooth counterbored hole in each corner which allows a screw to slide in flush with the top of the plate. The bottom plate has four matching threaded holes. A fifth center hole may be used to obtain desired compression if plate stiffness becomes an issue. With the O-ring segments placed in the centrally located seal groves, the plates are screwed together to achieve the appropriate dimensional compression on the O-rings. This insert allows uninterrupted stress relaxation of the material during the tests and acts as a compact, portable, and dependable testing mount. Due to the insert's small profile, it is very easy to accommodate several samples in an oven or irradiator at one time. Aluminum was chosen as the construction material for its balance between cost, stiffness, creep resistance, and minimal gamma attenuation.

The inserts are loaded into the Shawbury-Wallace C11 CSR jig which is slightly modified to accept an insert (Figure 2).The modified jig features a taller sample holder to accommodate the insert's height as well as an alignment plate which centers the insert between the jig platens.

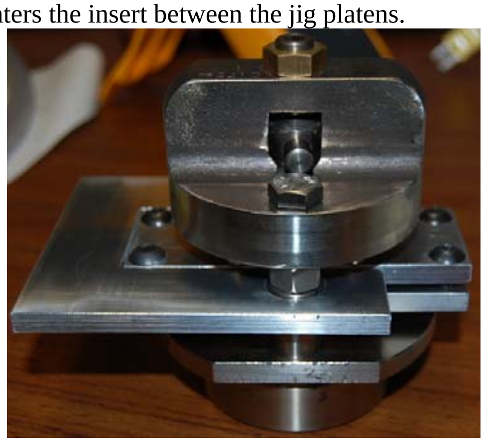

FIGURE 2 MODIFIED SHAWBURY-WALLACE C11 CSR JIG

The CSR measurements are made using a relaxometer (Figure 3) which applies pressure to the top of the jig, compressing the sample until it detects a dimensional change in the sample height. The counterforce value is the force in Newtons supplied by the relaxometer at the point of deformation. This value must be adjusted by subtracting the jig breakforce which is taken from a relaxometer reading of the unloaded jig. Because this method uses removable compression inserts to contain the test samples rather than the CSR jig itself, it is possible to check the unloaded jig breakforce readings before each test to ensure accurate sealing force measurements.

FIGURE 3 COUNTERFORCE MEASUREMENTS ARE TAKEN USING A WALLACE-COGENIX MARK IV STRESS RELAXOMETER

The design of the insert allows the plates to be squeezed together by the jig during the relaxometer test due to the smoothbore screw holes in the top plate. However, friction between the screw and the top plate can still occur if the countersunk holes are not properly centered or if the plates have undergone significant bowing as a result of material creep. In the tests performed and discussed here, the screws were removed after the insert was loaded into the jig so as to avoid the potential of friction affecting the measurements.

Multiple baseline measurements are recorded and averaged together and adjusted to account for jig breakforce. The result is treated as the sample's initial sealing force, the metric to which all future measurements will be compared.

Irradiation is performed using a J.L Shepherd Model 484 Co-60 irradiator, capable of delivering 250,000 Rad/hr to a target within its expansive chamber. The chamber spans 8"W x 8"H x 40"L which allows users to obtain variable dose rates down to 1,000 Rad/hr by adjusting the target's distance from the Co-60 sources. A dose map of the irradiation chamber has been developed using Monte Carlo N-Particle (MCNP5), a general purpose code used to simulate coupled radiation particle transport, to assist with placement of O-ring samples in order to obtain desired dose rates. The results of the model are illustrated in Figure 4. In conjunction with the dose rate model, this particular setup allows several samples to undergo testing simultaneously with accurate predictions of dose rate which accounts for shielding and dose fall off as a function of distance from source.

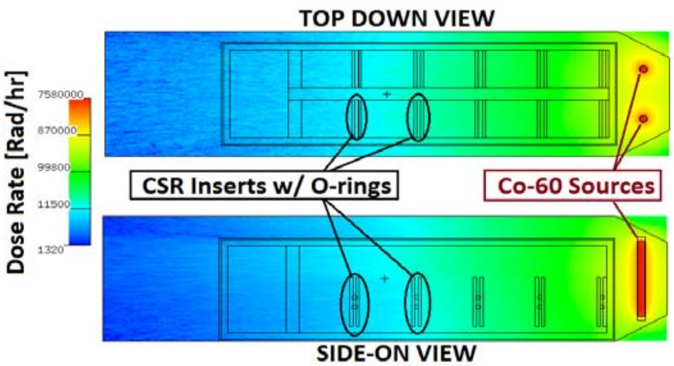

FIGURE 4 DOSE RATE COLOR CONTOUR MAP OF IRRADIATION CHAMBER CROSS SECTIONS

Because several of the sample sets require simultaneous irradiation and heating, an insulated portable chamber was built to house the samples during irradiation. This heated box uses two 200 Watt heat tape strips to bring the samples to the desired temperature while the box itself sits within the irradiation chamber. Several thermocouples are used to monitor the chamber and sample temperatures and control the heat tape output. The setup of the oven box is shown below.

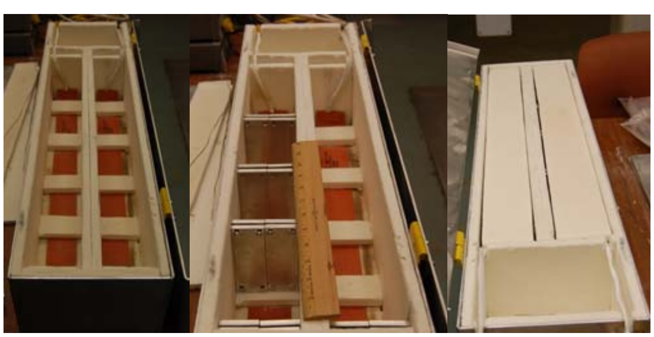

FIGURE 5 CUSTOM INSULATED HEATING CHAMBER DESIGNED TO BE USED WITHIN THE J.L. SHEPHERD MODEL 484 IRRADIATOR

Following initial baseline counterforce measurements, compressed samples are loaded into the preheated oven box at specified locations corresponding to the dose rates desired. The heat tape controllers are set to respective temperatures and the box is closed and loaded into the irradiator. The time and duration of irradiation/heating is recorded for every test. Samples are periodically removed from the irradiator and allowed to briefly cool in order to take CSR measurements at a consistent temperature at regular cumulative dose intervals.

In addition to samples being tested at various combinations of dose and elevated temperatures, separate effects tests are performed which examine the impact of radiation at room temperature and, likewise, elevated temperature in the absence of radiation. Data analysis and semi-empirical modeling are performed to project loss of sealing force rates at conditions not explicitly tested.

Elastomeric Degradation & Compression Set Analysis

In the absence of chemical exposures, the primary cause of elastomer aging/embrittlement is generally due to thermo-oxidation or radiolytic oxidation if radiation exposure is involved. The absorption of high energy ionizing radiation such as gamma rays typically results in the production of free cation radicals and the ejection of electrons within the polymer. The ejected electrons can induce additional ionizations or produce electronic excitation in surrounding molecules. Secondary reactions can include the production of ions (both cations and anions) and free anion radicals. These radicals are unstable and are reactive toward surrounding intact molecules resulting in both crosslinking (bond formation) and chain scission or main chain degradation (breaking of bonds along the polymer backbone). Polymers are viscoelastic materials. Therefore, under compression, elastomers tend to undergo compression stress-relaxation (CSR). CSR is often a combination of physical relaxation (molecules arranging to reach a lower energy state) and chemical relaxation due to potential chemical bond reconfiguration. Early compression stress-relaxation theory dates back to works by Tobolsky, Andrews, Hanson and others [6-10]. Stress-relaxation has long been recognized as primary behavior in elastomeric seals, though test methods and approaches can vary.

Using CSR as a performance parameter, the CSR behavior of compressed seal samples can be monitored over time at various aging conditions. Ideally, the relationship between the measured parameter and seal performance (i.e. leakage) should be known. However, this is not often practical due to the desire for accelerated aging testing, and the testing apparatus involved. Therefore, CSR is often used as an independent parameter to estimate the potential time-to-leakage-failure, at least in terms of retained sealing force of elastomeric seals.

The CSR behavior (or other property) is monitored until a defined failure point is reached at multiple environmental conditions. Then, all of the data can be time-shifted to a single reference temperature following the Williams-Landel-Ferry (WLF) principle of time-temperature superposition [11]. A main advantage of this method is that all of the experimental data can be used, not just a few single data points. Superposition of the aging data provides a "master" curve that can be translated or extrapolated to other conditions of interest. The risk of such methods is while the aging behavior may be assumed Arrhenius (single degradation mechanism and activation energy across the extrapolation range), non-Arrhenius aging behavior can occur, complicating life prediction.

Several studies on the aging behavior of EPDM elastomers (seals, cable insulations, etc.) have been performed [12-14]. Some of these are more relevant to the performance of seals than others, depending on the parameters and properties used to evaluate performance. Some studies focus on thermal-aging only, while others involve radiation exposure. Being hydrocarbon-based, EPDM compounds typically include antioxidants to hinder or reduce degradation by thermo-oxidation. The stability of these additives is critical to the longevity of the elastomer in many cases. The activation energy in many of these studies tends to fall in the range of 50-120 kJ/mol. One notable study [12] investigated the lifetime prediction of EPDM O-rings in nuclear weapon components at ambient temperatures. EPDM O-rings were aged at 110°C to 155°C, with Arrhenius behavior observed over the experimental range. The EPDM compound evaluated in this study (SR793B-80) is based on Nordel® 1440 (DuPont-Dow Elastomers). The authors found that conventional (Arrhenius) extrapolation of this data to 25°C yielded significantly long lifetimes (55,000 years). However, by using an ultrasensitive oxygen consumption analytical technique, activation energy values were found to change in the extrapolation region by 30% (reduction from 116 to 82 kJ/mol). This methodology resulted in a far lower but more defensible lifetime of 150 years at 52°C and ~2000 years at 25°C. .

In Reference 16, SNL researchers evaluated the accident performance of silicone seals used in nuclear power plants [16]. Silicone gasket samples were aged at 200°C and 230°C and irradiated simultaneously at 6 kGy/hr to a total normal aging + accident dose of 450 kGy (45 Mrad), with various properties including CS and CSR properties monitored over time. Samples were only tested over a 75 hour period to simulate the accident period. As the CSR fixtures were not designed to withstand the aging conditions (Shawbury-Wallace type), samples were tested in compression set fixtures, then sealing force measurements were made after transfer to a CSR jig for a room temperature sealing force value. Activation energies for CS and CSR behavior were determined to range from 17 kcal/mol (71 kJ/mol) and 29 kcal/mol (121 kJ/mol) respectively. While these data are for silicone seals, not EPDM, the use of radiation and thermal aging was noted, as well as the limitations of the CSR jigs.

In Reference 17, the authors studied the oxidation induction time (OIT) of EPDM and XLPE cable insulations used in nuclear power plant cables (Class 1E) as a method for lifetime prediction. The OIT values were determined using Differential Scanning Calorimetry (DSC). OIT values for two EPDM cable insulations were measured at multiple temperatures (195-235°C), with values ranging from 13 to 233 minutes. OIT values plotted versus the inverse temperature gave activation energies of 1.52 and 1.55 eV/K respectively.

Much data has been generated on dose rate/temperature effects on nuclear cable insulations, including EPR/EPDM insulations. Many of these studies are well-summarized in Reference 18 (1996).

Castor Demonstration

The test method described above was applied to the elastomeric Parker Compound E0740-75 in an attempt to quantify the degradation rate of this nuclear grade O-ring material in service conditions expected within a CASTOR V/21 cask. The Castor design features a primary and secondary lid, each bolted and sealed with a primary (metallic) and secondary (elastomer) O-ring. These elastomer O-rings, particularly in the primary lid, are exposed to significant temperatures and radiation due to their proximity to the fuel basket. The general configuration of the bolted closure joint is shown in Figure 6 below.

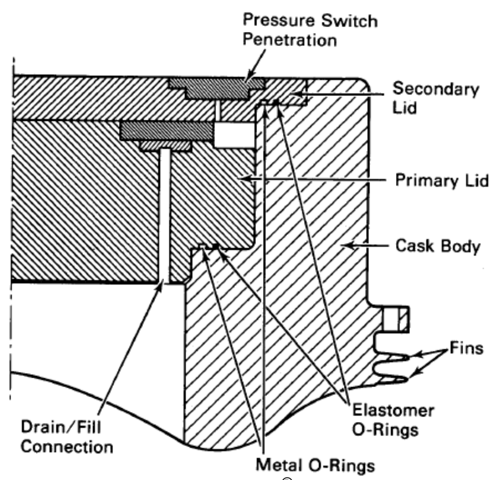

FIGURE 6 CASTOR®–V/21 CASK LID SYSTEM

Dose and Thermal Modeling

The dose accumulation over time of a CASTOR® V/21 storage cask loaded with commercial PWR assemblies at the design conditions was evaluated to determine dosimetric test conditions. A fully loaded CASTOR® V/21 cask was modelled by the Monte Carlo transport code, MCNP5. The model (Figure 3) was simulated to store its maximum allowable fuel loading as per the CASTOR® V/21 license requirements. This consists of 21 W17x17 assemblies burned to 23 GWD/MTU during three 550 day cycles allowing 30 days of cooling in between cycles. Additionally, the spent fuel was allowed to cool 5 years before being loaded into the cask.

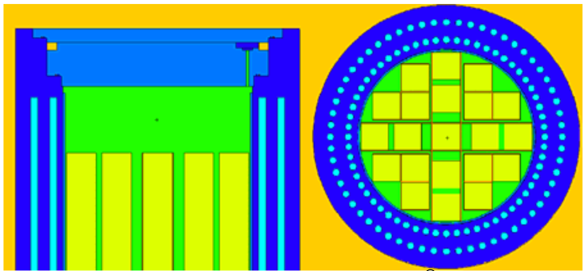

FIGURE 7 MCNP MODEL OF CASTOR®–V/21 LOADED WITH 21 PWR ASSEMBLIES

Dose detector tallies were used in the MCNP model to determine gamma dose rates at the polymeric O-ring location in the primary lid. The dose rate was calculated at 5, 10 15, 30, 50, and 100 years after fuel discharge, and integrated over time to yield the total accumulated dose between 5 and 100 years after discharge. Note that the fuel is stored in spent fuel pools for the first 5 years after leaving the reactor. The absorbed dose rate profile estimated for the seals in a CASTOR® V/21 cask loaded as described is shown in Figure 8.

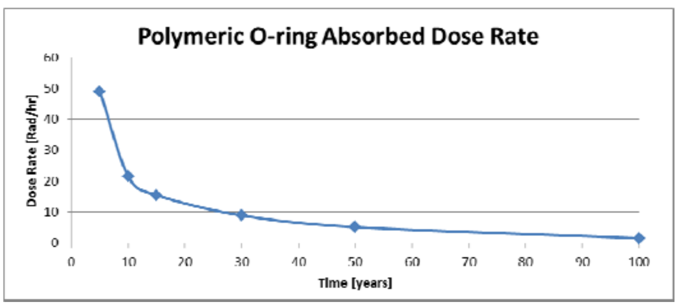

FIGURE 8 DOSE RATE AT ELASTOMERIC SEAL LOCATION FOR CASTOR®–V/21 CASK

The absorbed radiation dose profile for secondary elastomeric seals in the CASTOR® V/21 cask during the first 95 years of storage is a cumulative dose of 5.8E+06 rad (5.87E+04 Gy or 58.7 kGy).

The aging temperatures chosen for polymeric testing conditions were based on reasonable assumptions and conclusions drawn from the CASTOR® V/21 opening & examination performed by Idaho National Laboratory and documented in NUREG/CR-6745. [2]. Thermocouple readings taken from various locations in the cask in 1985 and 1999 suggest that a freshly loaded cask may experience temperatures between 200˚F and 250˚F at the location of the primary lid elastomer seal. These values represent the initial inputs for the proposed test matrix thermal conditions.

A more rigorous evaluation of the O-ring temperature is currently underway to verify the thermal boundaries of this test plan. The thermal power of a fully loaded CASTOR® V/21 basket was estimated using SCALE6 to generate actinide and fission product inventory of 21 PWR assemblies burned to 23 GWD/MTU.

TABLE 1 THERMAL POWER OF 21 PWR ASSEMBLIES WITH 23 GWD/MTU BURN-UP

Decay Heat [Watts]	Fuel Basket Cooling Time			
	5 Years	10 Years	50 Years	100 Years
Fission Products	1.47E+03	9.28E+02	3.24E+02	9.81E+01
Actinides	2.49E+02	2.57E+02	2.54E+02	2.20E+02
Total per MTU	1.72E+03	1.18E+03	5.78E+02	3.18E+02
Total per Cask	1.69E+04	1.16E+04	5.67E+03	3.12E+03
Total per m^3	3.99E+03	2.74E+03	1.34E+03	7.37E+02

Testing Matrix and Results

The experimental test matrix used to demonstrate EPDM degradation rate prediction was designed to evaluate seal responses to a variety of dose and temperature combinations which range from conservative representations of realistic conditions within a cask to well-beyond to identify certain failure conditions.

The conditions for each sample set include irradiation at a prescribed dose rate, exposure to high temperatures or a combination of both. The variations in these combinations should provide insight into the quantitative damaging effect of both radiation and elevated temperatures on the EPDM O-ring compound studied. The test matrix used is outlined in Table 2.

TABLE 2 TEST MATRIX FOR EPDM O-RING AGING EXPOSURE CONDITIONS (RADIATION/TEMPERATURE)

Set	Radiation Dose	Dose Rate	Temperature
A	None	None	149 ˚C
B	100 MRad	240 kRad/hr	116 ˚C
C	100 MRad	100 kRad/hr	116 ˚C
D	6 MRad	10 kRad/hr	116 ˚C
E	None	None	116 ˚C
F	100 MRad	240 kRad/hr	93 ˚C
G	100 MRad	100 kRad/hr	93 ˚C
H	6 MRad	10 kRad/hr	93 ˚C
I	None	None	93 ˚C
J	100 MRad	240 kRad/hr	23 ˚C
K	100 MRad	100 kRad/hr	23 ˚C
L	6 MRad	10 kRad/hr	23 ˚C

The samples underwent testing at their specified conditions for repeated periods of 25 consecutive hours typically. It is desirable to minimize the frequency of heating/cooling cycles experienced by the samples as this more accurately reflects the intransient thermal conditions within a cask seal. A 25 hour cycle also deposits exactly the 95 year cumulative absorbed dose value of 6 MRad to all samples undergoing the 240 kRad/hr dose rate condition.

At the conclusion of a 25 hour testing cycle, samples are removed from their specified environment and allowed to cool to room temperature before being loaded into the CSR jig and evaluated for counterforce measurements. The time allowed for cooling is typically less than 1 hour, although samples generally reach ambient conditions within 15 minutes.

Several consecutive CSR measurements are recorded for each sample, averaged, and adjusted for the inherent break force of the jig used for the measurements. Normalized data for the EPDM Parker Compound E0740-75 are shown in Figures 9-11.

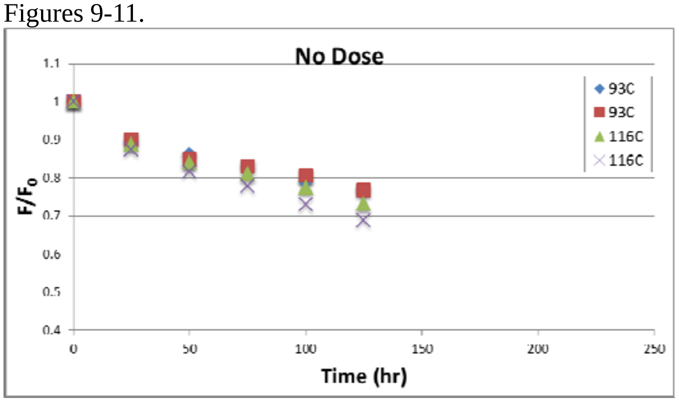

FIGURE 9 NORMALIZED COUNTERFORCE DECAY CURVES FOR NON-IRRADIATED SAMPLES

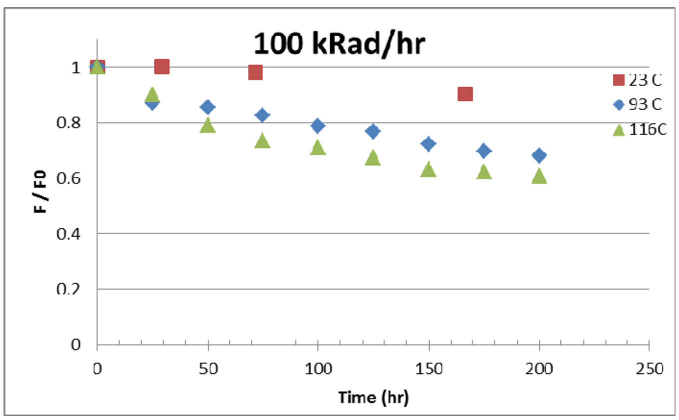

FIGURE 10 NORMALIZED COUNTERFORCE DECAY CURVES FOR SAMPLES IRRADIATED AT DOSE RATE OF 100 kRad/hr

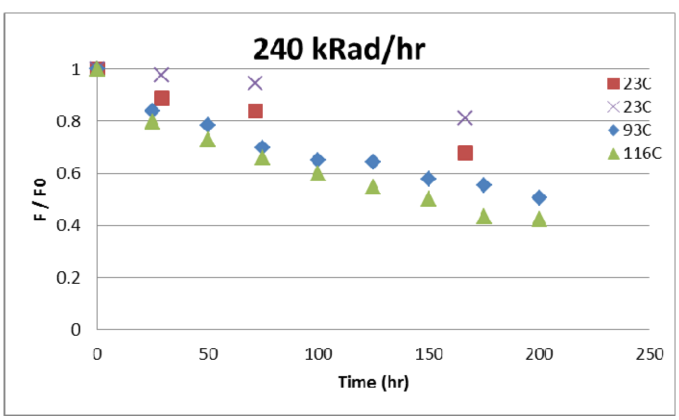

FIGURE 11 NORMALIZED COUNTERFORCE DECAY CURVES FOR SAMPLES IRRADIATED AT DOSE RATE OF 240 kRad/hr

Analysis of CSR Data

The compression stress-relaxation behavior of the EPDM O-rings varies with aging temperature and dose rate, with faster reductions in sealing force for the more extreme environments as expected. None of the O-ring samples have experienced sufficient aging time to have reached a reasonable approximation of a failure point (e.g. 90 – 100% loss of sealing force). Accordingly, these results are preliminary, and the trends based on these data are presented solely to illustrate the process by which the data might be used to develop a predictive capability for exposure to intermediate temperatures. The actual service life can be identified only after at least one of the samples reaches the defined failure point.

Using the time-temperature superposition theory based on the William-Landel Ferry (WLF) method [Hiemenz, P. 1984. Polymer Chemistry, The Basic Concepts. New York: Marcel Dekker.], estimated times for similar behavior at alternate temperatures can be determined for the O-rings based on the 100 kRad/hr data in Figure 10. A master curve using the 23 ºC data set as a reference temperature, T_{ref}, was constructed from the CSR data, Figure 12. Empirically determined shift factors, aT, were utilized to develop the master curve.

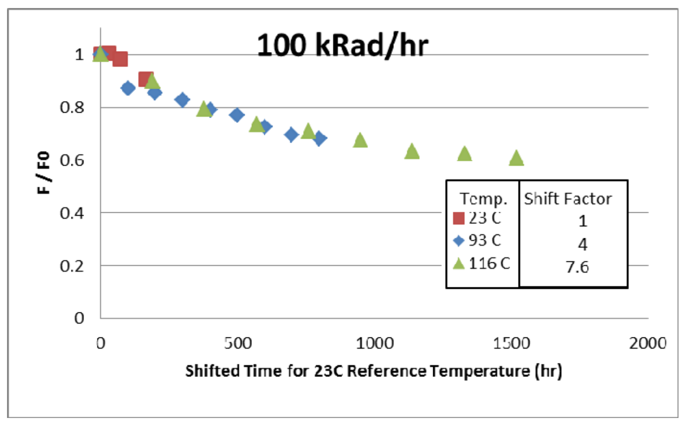

Figure 12 Master curve for the CSR data irradiated at 100 kRad/hr.

The shift factors can be used to estimate the activation energy, Ea through the Arrhenius relationship:

$$t = A \exp(-Ea / RT)$$

where t is the time to failure (or other common reference point on the force decay curve, and R is the universal gas constant (8.3145 J/mol-K). The shift factor describes the ratio between the values of time t for two different temperatures. Writing the Arrhenius equation for these two temperatures (T_{ref} and T_2) and solving for the activation energy gives the following:

$$Ea = R * [(\ln(t_2) - \ln(t_{ref})) / (1/T_{ref} - 1/T_2)]$$

Since the shift factors represent the ratio of the time to failure for two temperatures, one can also write:

$$Ea = R * [(\ln(aT_2) - \ln(aT_{ref})) / (1/T_{ref} - 1/T_2)]$$

With the shift factors plotted on a semi-logarithmic plot as a function of inverse temperature (Figure 13), note that the slope of the line matches the negative of the quantity in the square brackets in this last equation. Accordingly, multiplying the negative of this slope by R gives the activation energy. In this case for a dose rate of 100 kRad/hr, the calculated Ea is ~20 kJ/mol.

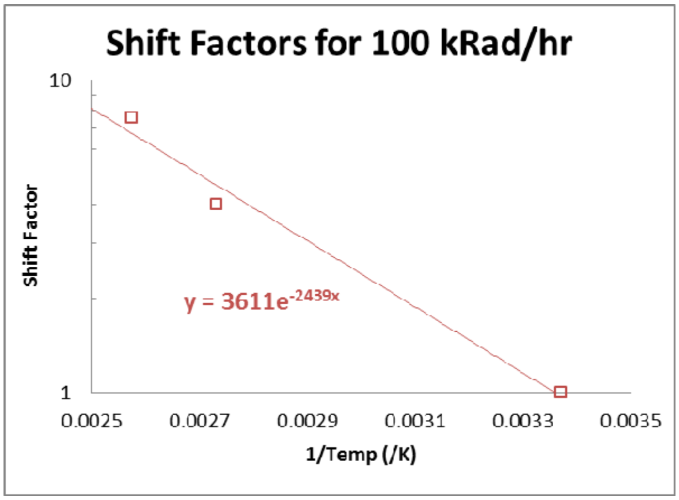

Figure 13 Shift factors for the 100 kRad/hr data plotted on a semi-logarithmic scale as a function of inverse temperature.

It is noted that this activation energy estimate is significantly less than values reported for EPDM compounds based on thermal degradation mechanisms. It is unknown whether the combination of thermal and radiation damage would produce such a reduction in activation energy, although it is certainly expected that the combined effects of multiple degradation mechanisms would speed up the overall degradation rate.

Calculation of these shift factors and activation energy estimates are specific to the 100 kRad/hr dose rate, and may not apply to other dose rates. This process can be repeated for CSR data taken under other dose rates, and the resulting estimates of activation energy can be used to interpolate among a range of intermediate dose rates.

Future Work and Path Forward

Predicting O-ring lifetimes is a difficult and heavily scrutinized practice. A critical understanding of the fundamental mechanisms driving seal damage is necessary for truly accurate predictions. For example, the extent of oxygen reaction and diffusion as a function of temperature and the threshold temperatures at which the mechanical properties and behaviors shift for a testing material are important factors to consider when trying to extrapolate seal effectiveness to operating conditions outside the extreme range of experimental conditions. Further complications arise from the fact that thermal and radiative degradation mechanism appear to either synergize or compete with each other depending on the specific combination being observed.

These complexities hinder the development of a comprehensive lifetime prediction model for all polymers. However, a thorough understanding of the complexities must involve extensive empirical data with which to validate and base theory upon. The testing method demonstrated here has the capacity to generate, for an infinite set of conditions, relevant details regarding sealing force decay and general mechanical property degradation of polymers. The information obtained via this technique can reveal activation energies, time/dose to equivalent damage plots, indications of when a material exhibits diffusion-limited oxidation (DLO) or when thermal dominated effects give way to dose rate dominated mechanism, etc.

To that end, future work will encompass more diverse sets of conditions, longer observation periods, and a variety of polymer materials. A wider range of conditions will provide valuable insight to the fundamental degradation mechanisms behind radiation and high temperature aging such as whether irradiation is simply enhancing temperature dependent processes or if it is inducing significant mechanical damage on its own. Examining sealing force under extreme conditions may reveal the onset of new mechanisms such of self-repair, and landmark events such as depletion of polymer's antioxidants can serve as a benchmark to correlate thermal/radiative conditions, oxygen consumption and mechanical damage.

Extended observation duration also allows for testing of more moderate conditions closer to what would be expected in operational service. These results are crucial in determining the accuracy of accelerated aging tests. Sealing decay curves observed in these conditions will identify to what point predictive models assuming temperature independent activation energy can be extrapolated.

SUMMARY

This paper outlines a technique which enables concurrent testing of high temperature and radiation dose effects on polymeric seal materials found in bolted closures. The compression stress relaxation (CSR) test technique adopted for this work captures the sample in a removable insert to permit aging in an aggressive thermal / radiation environment without risking damage to the CSR jigs. The results are plotted as sealing force decay curves which allow for extrapolation of degradation rate and calculation of activation energy assuming Arrhenius behavior. Upon completion of a broader test matrix which is fully supported by this technique, conclusions will be drawn regarding the fundamental interaction between damage mechanisms caused by both high temperature and radiation. A comprehensive plot of failure rate as a function of exposure conditions can then be integrated to project sealing force out to a time of interest.

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REFERENCES

[1] R.H. Boonstra, "Testing of Ethylene-Propylene Seals for the GA-4/GA-9 Casks", OSTI, Conf-930702-48, E66-M-93100

[2] NUREG/CR-6745, INEEL/EXT-01-00183, Dry Cask Storage Characterization Project-Phase 1: CASTOR® V/21 Cask Opening and Examination, September 2001.

[3] Sindelar, R.L., Duncan, A.J., Dupont, M.E., Lam, P.-S., Louthan, Jr., M.R., and Skidmore, T.E., 2011, "Materials Aging Issues and Aging Management for Extended Storage and Transportation of Spent Nuclear Fuel", NUREG/CR-7116, U.S. Nuclear Regulatory Commission Washington, DC.

[4] Völzke, H. and Wolff, D., "Aspects on Long Term Storage of Used Nuclear Fuel and High Active Waste in Germany," BAM Federal Institute for Materials Research and Testing, presentation at PATRAM 2010, October 07, 2010.

[5] Völzke, H. and Wolff, D., "Spent Fuel Storage in Dual Purpose Casks Beyond the Original Design Basis," in Proceedings of the International High-Level Radioactive Waste Management Conference (INLRWMC), April 28-May2, 2013, American Nuclear Society, 2013.

[6] "A New Approach to the Theory of Relaxing Polymer Media", M.S. Green, A.V. Tobolsky, The Journal of Chemical Physics, Vol. 14, No.2, 1945

[7] "Systems Manifesting Superposed Elastic and Viscous Behavior", A.V. Tobolsky, R. D. Andrews, The Journal of Chemical Physics, Vol. 13, No.1, Jan 1945

[8] "Stress Relaxation of Natural and Synthetic Rubber Stocks", A. V. Tobolsky, I. B. Prettyman, J. H. Dillon, Journal of Applied Physics, Volume 15, Issue 4, April 1944.

[9] Stress Relaxation Studies of the Viscoelastic Properties of Polymers, Tobolsky, Arthur V. , Journal of Applied Physics, Volume 27, Issue 7, 1956 , p.673- 685

[10] The Theory of Permanent Set at Elevated Temperatures in Natural and Synthetic Rubber Vulcanizates, Andrews, R.D, Tobolsky, A.V., Hanson, E.E., Journal of Applied Physics, Vol 17, Issue 5, 1946 , Page(s): 352 - 361

[11] Ferry, John D. (1980), Viscoelastic Properties of Polymers, John Wiley and Sons

[12] SAND98-1942, "New Methods for Predicting Lifetimes in Weapons. Part 1-Ultrasensitive Oxygen Consumption Measurements to Predict the Lifetme of EPDM O-Rings"

[13] SAND98-1726C) , Limitations of The Arrhenius Methodology, October 1998

[14] SAND2000-0715, "New Methods for Predicting Lifetimes – Part 2: The Wear-Out Approach for Predicting the Remaining Lifetime of Materials"

[15] SAND97-2181C, "Evidence that Arrhenius High-Temperature Aging Behavior for an EPDM O-ring Does Not Extrapolate to Lower Temperatures".

[16] SAND97-1666, Nuclear Power Plant Accident Simulations of Gasket Materials Under Simultaneous Radiation Plus Thermal Plus Mechanical Stress Conditions, K.T. Gillen, G.M. Malone, 1997

[17] "Comparison of Oxidation Induction Time Measurements With Values Derived From Oxidation Induction Temperature Measurements for EPDM and XLPE Polymers", L. R. Mason and A. B. Reynolds, POLYMER ENGINEERING AND SCIENCE, JULY 1998, Vol. 38, No. 7 1149.

[18] NUREG/CR-6384, BNL-NUREG-52480, Vol.1, Literature Review of Environmental Qualification of Safety-Related Electric Cables, Summary of Past Work, April 1996