Contract No:

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-08SR22470 with the U.S. Department of Energy (DOE) Office of Environmental Management (EM).

Disclaimer:

This work was prepared under an agreement with and funded by the U.S. Government. Neither the U. S. Government or its employees, nor any of its contractors, subcontractors or their employees, makes any express or implied:

1) warranty or assumes any legal liability for the accuracy, completeness, or for the use or results of such use of any information, product, or process disclosed; or
2) representation that such use or results of such use would not infringe privately owned rights; or
3) endorsement or recommendation of any specifically identified commercial product, process, or service.

Any views and opinions of authors expressed in this work do not necessarily state or reflect those of the United States Government, or its contractors, or subcontractors.

For submission to 56th INMM Annual Meeting, paper #150

Aging Behavior of the EPDM O-Rings in the H1616 Shipping Package

T. M. Stefek, W. L. Daugherty, and T. E. Skidmore

Abstract

The H1616 shipping package is used within the DOE complex for shipping tritium reservoirs. The annual recertification frequency can create logistical difficulties with other constraints on the timing of shipments, thus a longer re-certification period is desirable. The ethylene propylene diene monomer (EPDM) O-rings used in the H1616 shipping package are being aged and tested at the Savannah River National Laboratory (SRNL) to provide a technical basis for extending the annual maintenance of the H1616 shipping package.

H1616 EPDM O-rings are being aged at elevated temperature, and tested for degradation in mechanical properties, compression stress relaxation (CSR) behavior, and leak performance. Mechanical properties of aged O-rings show significant degradation can occur, but an inert atmosphere (argon backfill) greatly reduces the rate of degradation. The CSR behavior of O-rings was evaluated in air at 79 to 177 °C. These collective data were used to develop a predictive model for extrapolation of CSR behavior to relevant service temperatures (≤67 °C). O-rings were also aged in H1616 Containment Vessels (CV) in an inert atmosphere at 71 to 149 °C. The vessels are helium leak tested periodically to determine if they continue to remain leak-tight.

The vessel tests provide a solid demonstration that the H1616 O-rings will remain leak-tight at temperatures up to 113 °C for up to approximately 2.3 years. Significantly longer periods of leak-tight service are expected at the lower temperatures actually experienced in service. The predictive model developed from the CSR data conservatively indicates a service life of ~5 years at 67 °C. Although the relationship between CSR behavior and leak-tight performance has not been established for this design, the CSR predictions for this O-ring are conservative relative to leak-tight performance. Based on the collective data developed to date, SRNL has recommended that the maintenance interval for the H1616 package be extended from 1 year to 2 years. Future recommendations in support of even longer maintenance intervals are expected, as additional aging data become available.

Background

The H1616 is a certified "Type B" package for the transport of radioactive tritium reservoirs by the Department of Defense (DoD), United Kingdom (UK) Atomic Weapons Establishment (AWE), and Authorized Users (Savannah River Site (SRS), Pantex). This package utilizes a stainless steel containment vessel, which is sealed with two EPDM O-rings. The seals are compressed 25% in concentric face seal grooves, with no significant stretch. All containers undergo annual re-verification testing, including containment vessel leak testing to verify leak-tightness to <1E-07 ref cc/sec air as per ANSI N14.5 [1]. This frequency derives primarily from

a conservative estimation of the O-ring service life. A nitrogen or argon backfill gas is specified for the H1616 containment vessels. No lubricant is used on the O-rings.

The service temperature range for the H1616 vessel is -40 to 76 °C. At this maximum temperature condition, the maximum temperature at the flange closest to the O-rings is 67 °C. This is recognized to be a non-chronic condition, and typical seal temperatures are expected to be lower. Bounding radiation dose rates for the H1616 O-rings are not significant relative to seal performance.

A literature/data review was performed on EPDM seals as part of this task. Focus was given to data believed to be the most relevant to sealing applications similar to the H1616 application. These data generally involve testing of mechanical and CSR properties, with some data on leak-tightness and oxygen consumption rates. Additional details are given in Reference 2.

Comparison of aging data for different EPDM compounds from multiple sources using varying approaches and failure parameters is complex. Being hydrocarbon-based, EPDM is known to be sensitive to oxidation, therefore typically requiring antioxidants in the formulation. However, once the antioxidant is depleted or consumed, the polymer oxidation rate will likely increase, possibly resulting in accelerated degradation as indicated by loss of mechanical properties and sealing force.

A summary of the EPDM seal lifetimes observed or predicted at various temperatures from different references is given in Figure 1. Direct comparison is difficult as the basis for performance or failure in each reference varies. The trend line shown in Figure 1 is a lower bound of the reviewed failure data. This is intended to show potential lifetimes that might be suggested by the available data, though actual lifetimes could vary. At 67 °C, the peak temperature expected for the H1616 O-rings, the conservative trend line suggests a lifetime of approximately 6 years.

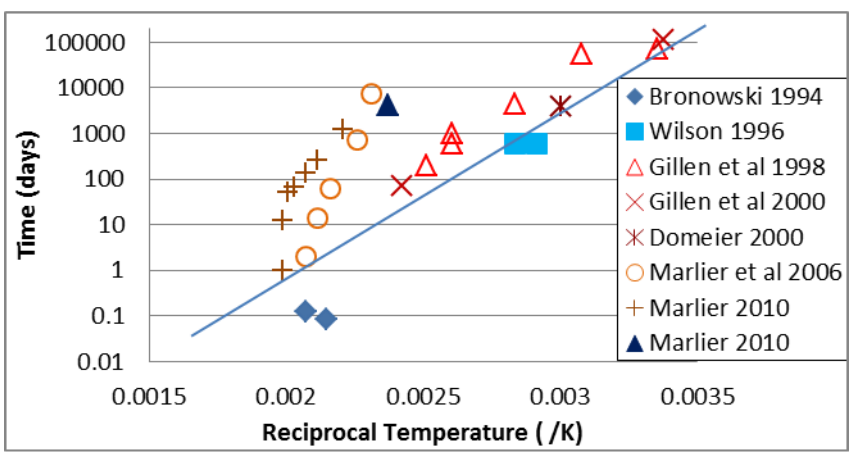

Figure 1. EPDM O-ring lifetime data from References 3 - 9 with a trendline providing a lower bound to the failure points. Samples represented by solid symbols were removed from test prior to failure.

Experimental Approach

Despite the favorable O-ring performance identified in the literature review, there is no substitute for real-time aging at realistic or bounding conditions. Therefore, the periodic examination and

testing of actual seals from a select group of H1616 shipping packages aged at bounding conditions were used to validate assumptions and make predictions based on accelerated-aging methodology. Such examinations cannot predict time to failure until failure is actually observed, but advance notice of degradation may be provided.

Baseline O-Ring Characterization

Confirmatory measurements were performed on a limited number of O-ring samples to verify the thickness, hardness and tensile properties are consistent with the O-ring specification. Thickness measurements were verified at four equally-spaced points along the circumference in both top-to-bottom and side-to-side orientations. Hardness measurements were verified with a calibrated Durometer Shore Hardness tester measured on the top of the O-ring at 5 points using two scales, Durometer Shore A (per specification) and Durometer Shore M for comparison. Durometer Shore M scale (microhardness) is required per ASTM D2240 for O-rings less than 0.25 inch thick. M-scale and A-scale values tend to be very close but there is no direct conversion.

H1616 Vessel Aging and Leak Testing

Vessel aging and leak tests were performed using three full-size containment vessels. Since room temperature aging is not expected to produce leak failure in a timely manner, these test CVs were aged at conditions that bound operating temperatures with the intent to drive the O-rings to failure within a reasonable period. This approach used actual vessels and the leak-tight acceptance criterion for service. The vessels were heated externally such that O-ring temperatures were maintained at 71, 113, or 149 °C. After failure of the O-rings in the 149 °C vessel, new O-rings were installed and the vessel was re-tested at 149 °C with no inert atmosphere. The same vessel (again with new O-rings) was then re-tested at 132 °C.

Each CV was placed in a round metal pan within a test stand. A strip heater wrapped around the upper half of the vessel provided up to 300 watts for heating the vessel. Silica insulation was placed around the vessel. An aluminum block was placed inside each vessel to reduce the amount of gas space and facilitate leak testing.

A thin stainless steel shim was placed on the vessel flange between the O-rings to prevent a possible metal-to-metal seal from masking the leak behavior of the O-rings. Initial leak tests were extended to show permeation (gradual increase in detector response over time) to prove helium access to/through the O-rings. This step eliminates the possibility of false positive results (no leakage path).

Argon was used as a backfill gas. Leak tests were performed periodically, after the vessel cooled to room temperature. The vessel was bagged, and the vessel interior and exterior were evacuated and backfilled with helium (Figure 2). A helium mass spectrometer leak detector was connected to the test volume between the two O-rings to detect leakage from either O-ring. When necessary, vessel connections were re-configured to test each O-ring individually.

The test CV's were opened periodically in conjunction with leak testing. These openings were intended to prevent artificial "sticking" of the O-rings, which could provide a false positive result, and provide a more realistic representation of actual in-service practice. This sticking

behavior has been observed in other studies, particularly at higher aging temperatures [8]. The O-ring hardness was measured when the vessels were opened.

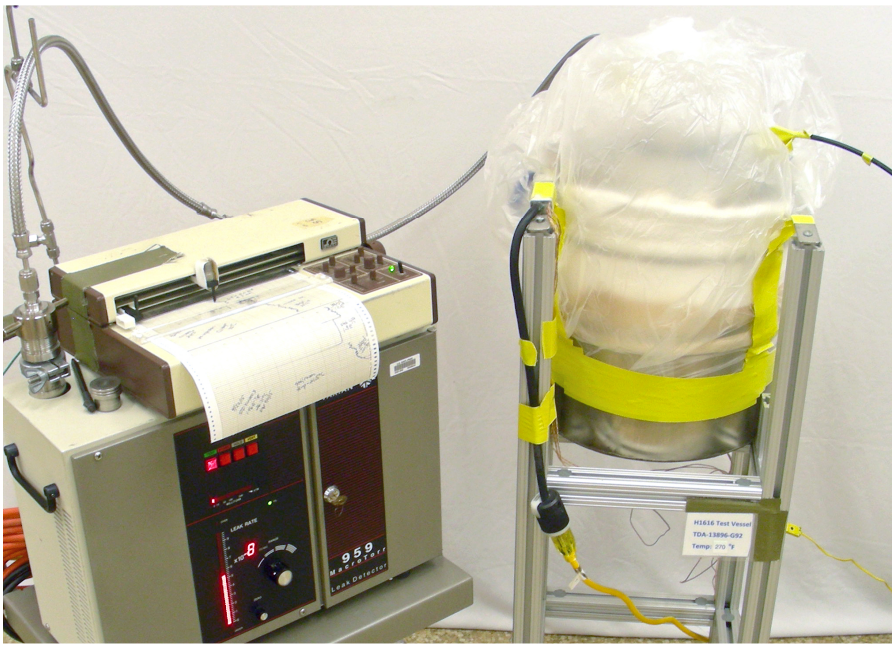

Figure 2. Hooded leak test of containment vessel

Compression Stress Relaxation Testing

Compression stress relaxation (CSR) tests were performed on the H1616 O-rings at several aging temperatures to develop an aging model based on sealing force decay. In the absence of fluid or significant radiation exposure, thermo-oxidative aging and sealing force decay is expected to be the most relevant degradation mechanism for the H1616 O-rings. CSR tests are a common industry method for evaluating the mechanical performance of seals over time at various aging temperatures. CSR tests were performed per ASTM D6147, using the periodic measurement approach.

A single H1616 O-ring was cut into ~1.9 cm long segments, with three segments placed into each CSR jig (Shawbury-Wallace type). The CSR jigs were initially developed to compress large disc samples, but several studies have shown that diffusion-limited oxidation effects are possible with larger samples, and disc samples do not ideally represent actual O-ring behavior, even if made of the same elastomer compound [10]. Three segments were selected to balance the contact area of the compression platens and the surface area of the exposed material. The segments were then compressed 25% as in the H1616 design.

The jigs with compressed samples were placed into aging ovens. Aging temperatures (79, 113, 232, 149 and 177 °C) were selected to bound expected normal service temperatures and to challenge the seals within a reasonable aging period. The highest temperature (177 °C) is recognized to be beyond the normal service temperature range of EPDM elastomers, but failures must be observed in a timely manner in order to predict failure at more reasonable service temperatures. During aging, the CSR jigs were periodically removed from the aging ovens and placed in the relaxometer for measurement of seal counterforce. As the elastomer relaxes and ages over time, this counterforce value is reduced.

The main goal of the CSR tests is to age the seals to a significant degradation point (loss of sealing force) at multiple temperatures, which allows use of the collective data to develop an aging model based on Arrhenius theory and Time Temperature Superposition (TTS) based on the William-Landel Ferry (WLF) method [11]. For CSR testing, a 90% loss in sealing force (F/F_o=0.10) was selected as the end-of-life parameter. This is consistent with end-of-life criteria in other studies. However, it is emphasized that CSR failure does not inherently mean that the seal is no longer functional or leak-tight. The use of 90% sealing force loss leaves 10% of the initial sealing force remaining for margin. This is expected to be more than sufficient for most static seal designs. With TTS, the behavior model can be translated to any temperature of interest if the same degradation mechanism(s) exists over the full aging temperature range and at the expected service temperatures.

Results / Discussion

H1616 Vessel Aging and Leak Testing

Initial baseline and periodic leak tests were performed on each containment vessel throughout the aging period. Table 1 summarizes the time to failure for the O-ring seals. After each periodic leak test, the vessel lid was removed, the O-rings received visual and hardness tests, and the vessel was again leak tested to verify the O-ring seal was re-established. For comparison with the hardness data, additional O-ring segments were also aged in ovens at the same temperatures, both in air and argon atmospheres. Hardness data for the O-rings in the 149 °C vessel are compared with samples aged outside of the vessel in Figure 3. Several observations are drawn from the hardness data:

- Degradation (increased hardness) rates increase with temperature.
- Degradation is significantly faster in an air environment than in argon.
- After the first O-ring leak failure in the 149 °C vessel, segments from that O-ring were aged further in either an air or argon environment. Their subsequent behavior follows that observed for each respective environment.
- New O-rings were placed in the 149 °C vessel with no inert gas backfill to identify the possible benefit of isolation provided by the O-ring groove design. These O-rings remained leak-tight for as long as the first O-ring aged with an argon backfill, and the hardness showed little change over this period. Thus the O-ring groove design provides significant isolation and protection of the O-rings from oxidation. This suggests that CSR behavior in air is likely conservative relative to O-ring aging in service, though multiple opening/closing cycles will allow some oxygen exposure to occur during the lifetime of a given seal.

As the O-rings age at elevated temperature, they tend to become sticky, with an oily residue. They also tend to flatten and retain the shape of the O-ring groove. These effects appear earlier at the higher temperatures.

Table 1. Vessel leak test time to failure

Aging Condition	Aging Time (days) to observe: O-rings found leak-tight and successfully re-sealed	Aging Time (days) to observe: O-rings found leak-tight but would not re-seal
71 °C Argon	>909	No failure to date
113 °C Argon	788 (inner) >959 (outer)	858 (inner)
132 °C Argon	>192	No failure to date
149 °C Argon	174 (inner) 234 (outer)	196 (inner) 253 (outer)
149 °C Air	>193	(Terminated without failure)

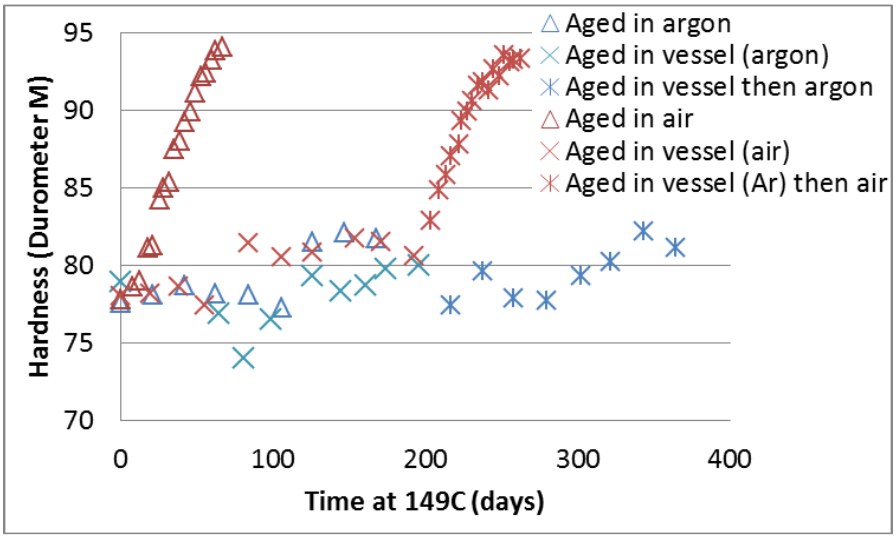

Figure 3. Hardness of O-rings aged at 149 °C

Compression Stress Relaxation Testing

CSR jigs with compressed H1616 O-ring segments were placed in aging ovens at 79, 113, 132, 149 and 177 °C. CSR measurements were recorded periodically. All O-ring segments came from a single O-ring for consistency. Typical sealing force decay curves (CSR curves) at aging temperature are given in Figure 4. In these curves, the sealing force for each jig is normalized to the initial maximum sealing force.

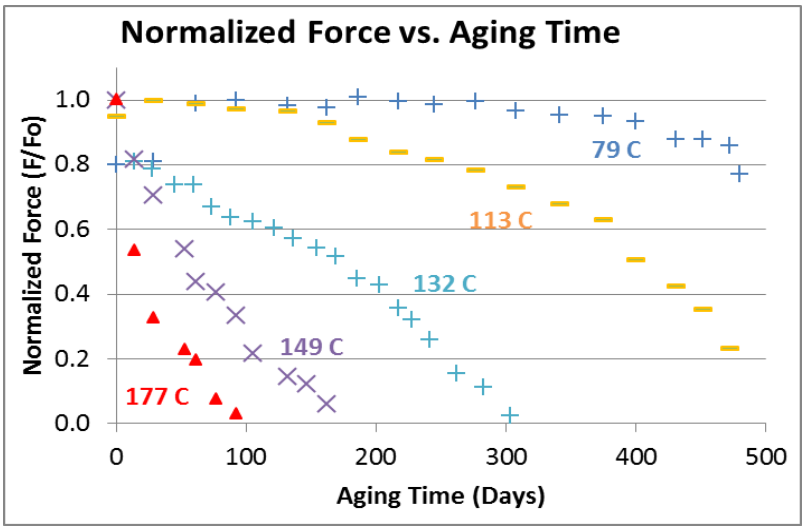

Figure 4. CSR data for the original H1616 O-ring segments at all aging temperatures

After aging at 177 °C for about 9 weeks, some O-ring segments in one jig were observed to be split vertically across the compressed cross-section. However, additional aging was allowed to continue. The 177 °C CSR O-ring segments reached an end-of-life condition (90% loss in initial sealing force) after 11 weeks aging time. O-ring segments that were aging at 149 °C reached an end-of-life condition after 21 - 23 weeks. At the end of life, samples aging at 149 °C did not exhibit signs of cracking as observed at 177 °C. The higher 177 °C aging temperature is quite high for EPDM elastomer, which is normally rated for "continuous" service temperatures of about 120 - 150 °C, particularly in air.

O-ring segments that were aging at 132 °C reached an end-of-life condition after 37 - 43 weeks aging time. The CSR samples aging at 113 °C experienced an unplanned temperature excursion, after reaching ~75% loss in initial sealing force, and were terminated at that time.

Service Life Discussion

Using the TTS principle, the normalized CSR data can be superposed into a "master" curve using shift factors empirically determined to achieve the best curve match. Each shift factor describes the relative difference in degradation rate between two aging temperatures. The shift factors can be used to estimate the time to failure for any other temperature, assuming the same degradation mechanism(s) remain dominant over the extrapolation range. It is noted from Figure 4 that the relative shape of the sealing force decay curve varies. The lower temperature curves are convex, while the higher temperature curves are slightly concave. This suggests that different mechanisms may be active in the two temperature regions, and the data from these regions should be treated separately.

The CSR data are re-plotted in Figure 5, with the time scale for each aging temperature adjusted by the shift factor identified. Since the overall shape of the curves varies somewhat with temperature, it is not practical to use the full data set to define the shift factors. Rather, in this case the shift factors were selected to provide the best agreement at the failure criterion (10% retained sealing force). Also, because of the changing curve shape, the curves are shifted separately for two temperature regions, producing master TTS curves for reference temperatures of 79 and 132 °C. The 132 °C data are plotted with both sets, but they agree slightly better with the higher temperature data than with the lower temperature data.

Each shift factor represents the relative difference in time scale between the average degradation rate at that temperature and the reference temperature. Together, they provide a means for extrapolating CSR behavior to estimate failure times at other temperatures (Figure 6), assuming they follow an Arrhenius relationship, described by the equation:

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

where t = time
A = constant
E_a = activation energy
R = ideal gas constant
T = absolute temperature (K)

The slope provided by the shift factors in Figure 6 can be used to calculate the activation energy: slope * ideal gas constant = activation energy, or 5415 K * 0.0083145 kJ/K-mol = 45 kJ/mol for temperatures above 132 °C, and 30 kJ/mol for lower temperatures. In a case of varying activation energy, extrapolations from one temperature regime to another would not be valid without adjusting for the change in activation energy at the appropriate transition temperature. The time to failure can be calculated for any temperature below 132 °C with the following Arrhenius relationship.

$$\text{Time to failure} = 3.3 \text{ years} * \exp(-3571 * (0.00284 - 1/T_2))$$

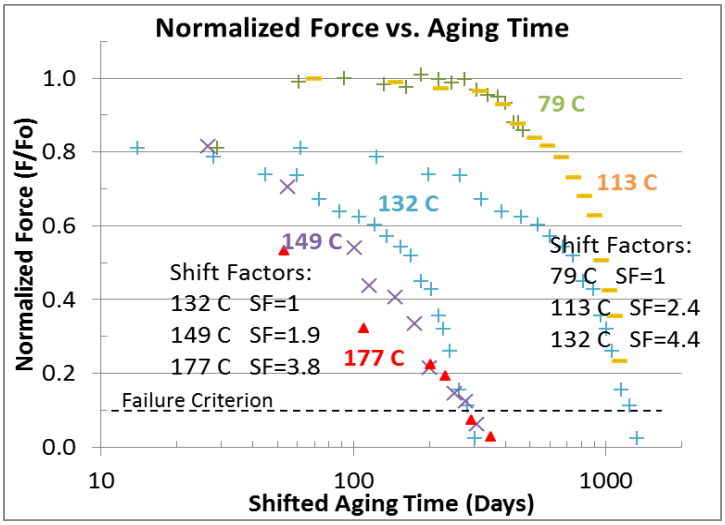

Figure 5. CSR data from Figure 4, adjusted by the stated shift factors to provide the best agreement at the failure criterion. Higher temperature data are shifted to a reference temperature of 132 °C, while lower temperature data are shifted to a reference temperature of 79 °C.

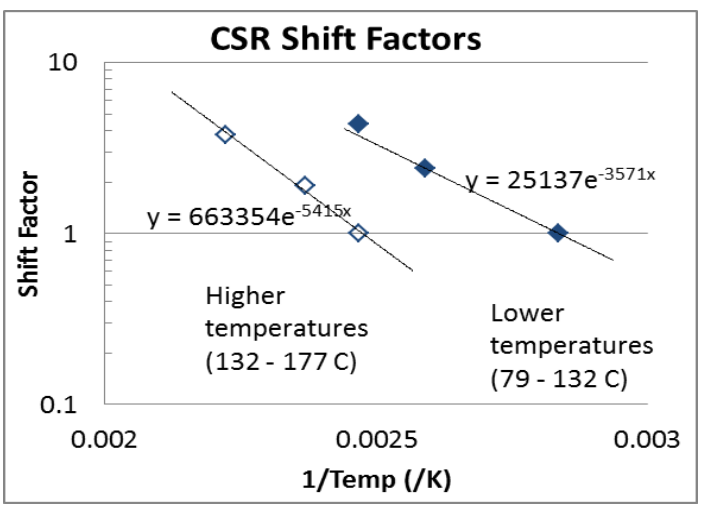

Figure 6. Shift factors vs. reciprocal temperature.

With this relationship, the estimated time to failure at 67 °C is 4.8 years. No direct correlation has been established between CSR behavior and O-ring service life based on leak-tightness. Intuitively, a significantly reduced sealing force should correlate to an increased likelihood of leakage (especially in a dynamic application). However, very few data exist to indicate the actual sealing force needed to maintain leak-tightness, and such data are likely design-specific. The 90% loss of sealing force criterion has been adopted in some studies as a failure parameter, which should be a conservative limit for a relatively static seal such as the H1616 O-rings.

A further consideration in use of the CSR data in a predictive model for leak-tight service life is the test environment. The CSR samples are aged at elevated temperature in an air environment, while the vessels are maintained with an inert gas backfill, limiting the O-ring exposure to oxygen. Comparison of the leak performance of the 149 °C vessel with air and argon backfill indicates that the vessel is effective in limiting the O-ring exposure to oxygen. It is therefore possible that the degradation mechanism(s) leading to leak failure of the vessel are not primarily driven by thermo-oxidative processes. Accordingly, the CSR aging model would not provide an accurate prediction of leak behavior. However, the CSR data are conservative to the vessel leak data at 149 °C, and are more conservative at 113 °C, so the CSR model should provide conservative service life predictions under actual service conditions.

The CSR data suggest that the Arrhenius relationship does not work between the two temperature regimes (above and below ~132 °C) due to changing degradation mechanisms. This has been observed in a similar EPDM compound [5]. In that case, a reduction in activation energy was observed based on oxygen consumption testing. The Reference 5 authors also noted that non-Arrhenius aging behavior was indicated for the similar EPDM compound below 111 °C. The 34% decrease in activation energy suggested by the current testing is very close to the 30% decrease in activation energy reported in Reference 5. While these two EPDM compounds cannot be compared directly, this similarity in behavior is considered significant.

Conclusions

Aging data for EPDM elastomers reviewed and developed within this task demonstrate that the H1616 O-rings should remain functional for at least 2 years at bounding service conditions. A conservative interpretation of the data cited in the literature review suggests that the H1616 O-rings can have lifetimes of 6 years at 67 °C, the maximum O-ring temperature with solar heating at 38 °C ambient. This temperature is conservative relative to typical O-ring temperatures in service.

Leak testing has demonstrated acceptable leak-tight performance up to the two year mark for the 71 and 113 °C vessels, and the continued ability to reseal at that time. The vessel aging at 149 °C maintained leak-tightness and the capability to reseal after 174 days, however it would not reseal after 196 days at temperature. Following leak failure of the O-rings aging in the 149 °C vessel, new O-rings were installed and began aging without an argon backfill. This demonstrates that the vessel design provides significant isolation of the O-rings from the external atmosphere, and suggests that degradation of the O-rings in actual service may not be the same thermo-oxidative processes that are active in other tests where the O-rings are exposed to an air atmosphere.

An aging model based on CSR data predicts a service life of approximately 5 years at the bounding O-ring service temperature of 67 °C. Based on possible differences in the active degradation mechanisms, this estimate is expected to be conservative to actual leak-tight behavior. Based on the demonstrated leak-tight performance at 79 and 113 °C for 2 years, and potential margins as demonstrated by the CSR aging model, recommendations were made to extend the maintenance interval for the H1616 package to 2 years. It is expected that the

continued leak-tight performance at 79 °C will provide the basis for future recommendations for further maintenance interval extensions.

References

[1] ANSI Standard N14.5-97, "American National Standard for Radioactive Materials – Leakage Tests on Packages for Shipment", American National Standards Institute, New York, NY, February 1998.

[2] SRNL-STI-2012-00149, "Review of Aging Data on EPDM O-rings in the H1616 Shipping Package (U)", T.E. Skidmore, Savannah River National Laboratory, March 2012.

[3] SAND94-2207, "Performance Testing of Elastomeric Seal Materials under Low and High-Temperature Conditions: Final Report", D. R. Bronowski, Sandia National Laboratory, 1994

[4] KCP-613-5806, "Accelerated Aging of EPDM and Butyl Elastomers" Federal Manufacturing & Technologies, M. H. Wilson, 1996

[5] SAND98-1942, "New Methods for Predicting Lifetimes in Weapons Part 1: Ultrasensitive Oxygen Consumption Measurements to Predict the Lifetime of EPDM O-Rings", K.T. Gillen, M. Celina, R.L. Clough, G.M. Malone, M.R. Kennan, J. Wise, Sandia National Laboratory, September 1998

[6] SAND2000-0715, "New Methods for Predicting Lifetimes – Part 2: The Wear-Out Approach for Predicting the Remaining Lifetime of Materials", K. T. Gillen and M. Celina, Sandia National Laboratory, March 2000

[7] SAND00-8259, "Experimental Evaluations of O-Ring Thickness Variability and Long-Term Compression Set and Compression Set Recovery", L. A. Domeier, Sandia National Laboratory, 2000

[8] "Seal life of EPDM O-rings at high temperature determined by unique method", R. Marlier, R. Andre, P. Malesys, H. Issard, *Journal of Packaging, Transport, Storage & Security of Radioactive Materials*, Vol.17, No.1, 2006

[9] "First tests results for determination of seal life of EPDM O-rings at high temperature (determined by unique method)", R. Marlier, *Packaging, Transport, Storage & Security of Radioactive Materials*, Vol.21, No.1, pp37-40, 2010

[10] "Validation of improved methods for predicting long-term elastomeric seal lifetimes from compression stress-relaxation and oxygen consumption techniques", K.T. Gillen, M Celina, R. Bernstein, *Polymer Degradation and Stability* Vol. 82 pp25-35, March 2003

[11] P. Hiemenz, *Polymer Chemistry, The Basic Concepts,* Marcel Dekker, New York, 1984.