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AGING AND SURVEILLANCE OF VITON® GLT O-RINGS IN MODEL 9975 SHIPPING PACKAGES

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Introduction

Radioactive material packages (DOT Type B) such as the Model 9975 are used to transport Pu-bearing materials [1]. The 9975 package provides double payload containment via nested stainless steel primary (PCV) and secondary (SCV) containment vessels. The containment vessels are closed by a conical plug sealed with dual O-rings (Figure 1) made of Parker Seals compound V0835-75, based on Viton® GLT fluoroelastomer. The outer O-ring is credited as being leaktight per ANSI N14.5 [2] with a leak rate of <1E-07 ref cc/sec. The 9975 package is being used for interim storage in the K-Area Material Storage (KAMS) facility at the Savannah River Site. The aging performance of the O-rings is being studied to provide the storage facility a technical basis for service life prediction and safety analysis.

Experimental

An aging and surveillance program was implemented to monitor and validate O-ring performance during storage. The program consists of three elements: field surveillance, laboratory monitoring at bounding conditions and accelerated aging studies. Field surveillance involves examination of O-rings after removal, with thickness measured within 30 minutes of removal and later in the laboratory for comparison and estimation of compression set based on nominal dimensions.

Laboratory monitoring involves periodic helium leak testing of empty PCV fixtures (Figure 2) aged at bounding storage temperatures (200/300 °F), with other variables such as radiation (high/low dose rate), cover gas (air/CO_2) and lubricant (vacuum grease) included. The PCV fixtures emulate the PCV closure, but are shorter (~4 in.) with an additional leak test port to allow testing of each O-ring if needed. O-rings are leak tested for 3 minutes, consistent with annual certification procedures. Leak tests are repeated nominally every 6 months.

Compression stress relaxation (CSR) tests have been performed to develop a life prediction model. Short-term (1000-hour) tests were performed on an Elastocon® system to assess behavior. Long-term CSR tests are being performed on size 2-213 O-rings using Shawbury-Wallace C11 jigs and a Mark IV relaxometer. A custom insert was designed to mimic the 9975 O-ring design, imposing a nominal ID stretch of 20% and a nominal 18% compression during aging (Figure 3). The ID stretch is notably higher than typically recommended by O-ring manufacturers (<5%). Some O-rings are being tested in the non-stretched condition for comparison.

CSR aging temperatures range from 175 to 350 °F. The 175 °F value represents the peak O-ring temperature for a maximum payload package (19 W) at 104 °F ambient, the maximum recorded in the facility. 250 °F is considered the maximum seal temperature during loss of facility ventilation. 300 ºF is the containment vessel design limit. Baseline tests showed that essentially all sealing force is lost at 400 °F within 1000 hours, consistent with vendor ratings.

To address possible radiation effects, some O-rings were irradiated to a 50-year dose (0.88 Mrad) at 0.44 Mrad/hr prior to thermal aging. This exposure is limited for material degradation but does not fully duplicate 50 years of aging, as dose rate effects are possible. However, such effects are not expected to be significant at the low dose rates anticipated ($\leq$2 rad/hr).

CSR measurements are taken as close to isothermally as possible to minimize thermal expansion effects. CSR measurements are performed five consecutive times for each jig. CSR forces are plotted as a relative force ($F/(F_0)$) over time, after the breakforce for each jig is subtracted. The relative force rather than actual force is used for comparison purposes due to the unique individual response of each CSR jig.

Results and Discussion

Field surveillance has been performed on approximately 86 packages (344 O-rings) since FY05. O-rings removed from storage after up to eight years exhibit no signs of degradation. O-rings remain pliable and generally retain a circular cross-section upon removal or very soon thereafter. The average compression set is estimated at 13% based on ASTM D395 Method B, expressed as percentage of deflection [3]. The packages selected for field surveillance include some of the highest wattage packages in storage, but none thus far have experienced bounding conditions.

Initial PCV fixture tests involved sixty-seven fixtures. Sixty-two were heated to 200 or 300 ºF, and five were heated to 350 – 450 ºF. A number of fixtures have been removed from testing for various reasons, including accidental overheating. Currently, 36 fixtures are still in test after 3+ years. All initial fixtures still in test continue to maintain a leak rate $<1x10^{-7}$ cc/sec at room temperature, meeting ANSI N14.5. Though a positive observation, fixture tests alone are limited for life prediction purposes without knowing time to failure. Additional PCV fixtures recently aged at 400 and 450 °F have shown leak failures within 8-12 days at 450 °F and within 27-45 days at 400 °F. These fixtures were dimensionally verified prior to assembly and leak testing. Post-failure disassembly indicated no anomalous findings. Two fixtures aging at 350 °F for four months are currently still leaktight at room temperature.

Time-temperature superposition principles were used to relate all long-term CSR data to a single plot. This approach is based on the Boltzmann time-temperature superposition principle and the well-known WLF (Williams-Landel-Ferry) equation developed for polymeric materials [4]. The primary advantages of this method are: 1) all experimental data are used, and 2) the "master" curve at a single reference temperature can be translated to any other temperature. All CSR data were empirically shifted to find the best curve fit and shift factors (a_T). This approach is similar to that used by other researchers to predict the lifetime of critical nuclear weapon seals [5-7].

Shift factors are plotted on a log scale versus inverse absolute temperature in Figure 4. A linear plot strongly indicates that the O-rings are aging with Arrhenius-type behavior, based on available data. Non-Arrhenius behavior would be indicated by a change in slope of the plot which can complicate life prediction. Such behavior may be related to antioxidant consumption, oxygen consumption of the base polymer and other mechanisms. The data currently suggest such an effect might be present, but cannot be confirmed without further data at the lower temperatures.

Assuming Arrhenius behavior, the shift factors are used to translate all of the experimental data to a "master" TTS curve at a reference temperature of 175 ºF (Figure 5). This temperature represents the maximum seal temperature at maximum heat load and a bounding ambient temperature of 104 ºF. This plot indicates that the O-rings could lose all measurable sealing force after ~500,000 hours (57 years) at 175 °F. The sealing force required for leaktightness is unknown. Using 90% loss as a more conservative failure criterion, slightly reduced lifetimes are estimated (300,000 hrs or 34 years). The statistical basis for the model is limited due to the number of O-rings currently in test.

The "master" TTS curve in Figure 4 can be time-shifted to other temperatures. From Figure 5, the shift factors for several temperatures ranging from 70 ºF to 250 ºF were estimated and used to translate the time to CSR failure values at 175 °F to the selected temperatures. These values are plotted in Figure 6 to provide a seal lifetime model with two curves representing "low" and "high" lifetime estimates based on the range of time to zero sealing force values at 175 °F. For realistic seal temperatures (<175 °F), the model predicts seal lifetimes of several decades.

The model predicts a seal lifetime of approximately 3200 years at 25 °C for the Viton® GLT O-rings, based on near-zero sealing force. At 90% loss, the model predicts a lifetime of approximately 2200 years. In comparison, Reference 4 estimates a 2000 year service life (90% loss) for EPDM O-rings at 25 °C, accounting for oxygen consumption rates [5]. Assuming the activation energy does not go below a certain level, Reference 4 estimates a respectable seal lifetime of at least 150-200 years for EPDM at room temperature. Since Viton® fluoroelastomer is generally more resistant to aging and thermooxidation than EPDM and is rated for higher temperatures, longer service life at comparable temperatures is expected. Using similar logic above for the Viton® GLT O-rings, a lifetime of 200-300 years at 25 °C may be possible. Oxygen consumption analysis experiments are planned to evaluate this aspect.

At the other extreme, recent leak tests of PCV fixtures aged at 400 and 450 °F have shown leak failures within 8-12 days at 450 °F and within 27-45 days at 400 °F. For seal lifetime defined as time to near-zero sealing force, the current CSR model predicts a seal lifetime of ~47 days at 400 °F and ~18 days at 450 °F. For seal lifetime defined as 90% loss, the model predicts ~ 15 days at 450 °F and ~39 days at 400 °F. Note that 400 °F is the upper "continuous" service temperature rating of the O-rings. Package designers and other end-users must recognize the limitations of such ratings for long-term service.

O-ring life prediction is complex, as seal performance depends on many factors. The TTS curve and life prediction model are heavily dependent on the shift factors (a_T). The current model assumes constant exposure at a given temperature. In reality, seal temperatures vary with ambient condition and payload, though such changes do not occur rapidly in the packages due to presence of thermal insulation and thermal mass of the facility.

The relationship between sealing force and leakage must be better understood. Sealing force is certainly important. However, even in a highly relaxed state, the O-ring could remain leaktight if undisturbed. Alternatively, leak rates could increase at higher sealing force values with variation in O-ring dimensions, component fabrication or assembly methods. Investigators in Reference 7 indicate that a threshold sealing force (1 N/cm) may be needed to maintain leaktightness, though this is not presented as an absolute value. For the 9975 PCV seals, this represents <5% of initial sealing force.

Bonding to mating surfaces has been observed at temperatures $\geq$ 300 °F. Elastomer-to-metal bonding may aid or maintain sealing at very low sealing force values. Bonding is more likely at higher aging temperatures due to thermal expansion and faster degradation, but bond integrity may be broken during the drop to room temperature for leak testing. At lower aging temperatures, the drop to room temperature is less severe but the tendency for bonding to occur is also likely reduced. Uniformity of the bond is also questionable, at least in terms of providing a seal. Experiments to evaluate bonding behavior are in process.

CONCLUSIONS/FUTURE WORK

Model 9975 shipping packages with containment vessels sealed with Viton® GLT O-rings are being used for Pu storage at the Savannah River Site. Approximately 344 O-rings have been examined from packages after up to eight years storage, with minimal compression set observed. Mock vessels are leaktight after 2-3 years at bounding storage temperatures. A preliminary model based on compression stress-relaxation measurements and time-temperature superposition methods predicts a seal lifetime of approximately 35-60 years at a bounding seal temperature of 175 ºF, with lifetime defined as 90-100% loss in sealing force. Longer lifetimes are possible at lower seal temperatures. Leak tests of fixtures aged at 400-450 °F indicate leakage within 8-45 days, with 400 °F being the "continuous" service temperature rating of the compound. Fixtures aging at 350 °F for four months remain leaktight. Experiments are planned to evaluate the relationship between leakage and sealing force. CSR tests will continue at lower temperatures to validate the model. Oxygen consumption analysis will also be employed. The current model only applies to the V0835-75 compound based on Viton® GLT. A new compound (VM835-75) based on Viton GLT-S was recently approved for transportation and storage. CSR tests on this compound have initiated and results will be presented at a later date.

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[2] ANSI N14.5-1997, American National Standard for Radioactive Materials – Leakage Tests on Packages for Shipment.
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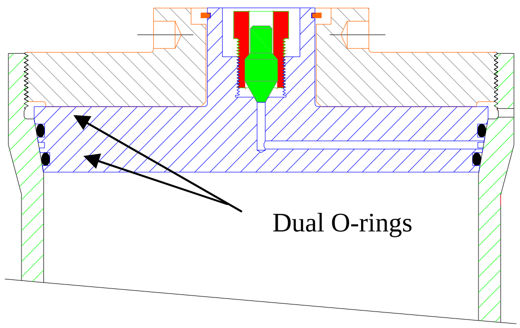

Figure 1. Containment Vessel Seal Configuration

Figure 2. Mock-PCV Storage Rack

Figure 3. C11 CSR jig with custom 9975 insert

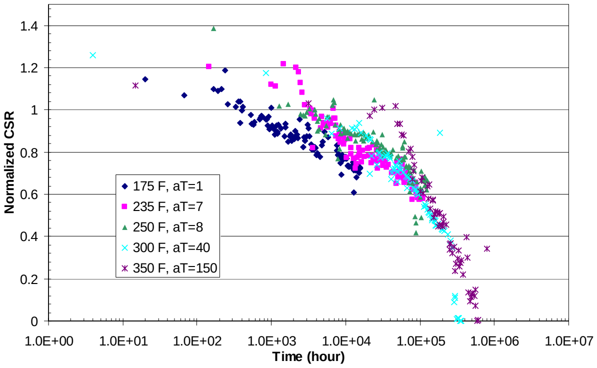

Figure 4. TTS Curve for CSR Data (T_{ref} = 175 °F)

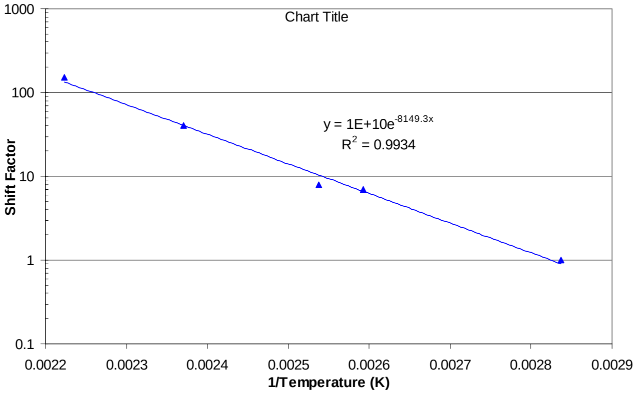

Figure 5. Shift factors vs. Inverse Temperature

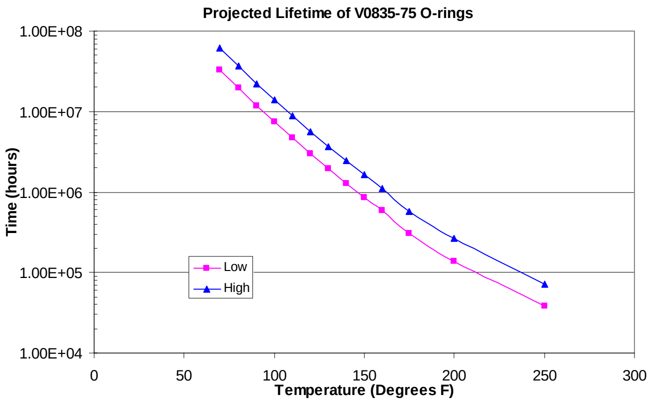

Figure 6. O-Ring Service Life vs. Temperature