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AGING PERFORMANCE OF VITON® GLT O-RINGS IN RADIOACTIVE MATERIAL PACKAGES

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ABSTRACT

Radioactive material packages used for transportation of plutonium-bearing materials often contain multiple O-ring seals for containment. Packages such as the Model 9975 are also being used for interim storage of Pu-bearing materials at the Savannah River Site (SRS). One of the seal materials used in such packages is Viton® GLT fluoroelastomer. The aging behavior of containment vessel O-rings based on Viton® GLT at long-term containment term storage conditions is being characterized to assess its performance in such applications. This paper summarizes the program and test results to date.

INTRODUCTION

Radioactive material packages (DOT Type B) are used to transport Pu-bearing materials sealed in containers [1]. Such packages often provide double containment of payload via nested stainless steel primary (PCV) and secondary (SCV) containment vessels [2]. The Model 9975 vessel is closed by a conical plug sealed with dual O-rings (Figure 1). The outer O-ring is credited as part of the containment boundary. The inner O-ring facilitates assembly verification leak testing and provides an additional material release barrier. This design provides a leak rate of <1E-07 ref cc/sec (air) as required by ANSI N-14.5 for leak-tight containment.

The 9975 package was designed and qualified for transport but is also being used for interim payload storage. Therefore, the aging performance of the containment vessel O-rings is being studied at bounding storage conditions to provide the storage facility a technical basis for service life prediction and documented safety analysis.

SEAL MATERIAL & CONDITIONS

The O-rings used in the radioactive materials package being studied are generically based on Viton® GLT fluoroelastomer. Viton® GLT, a polymer consisting of vinylidene fluoride (VF2), perfluoromethylvinylether (PMVE), tetrafluoroethylene (TFE), and a proprietary cure site monomer (CSM), was the first commercial fluoroelastomer to use the PMVE monomer for improving low-temperature flexibility [3]. The O-ring compound being evaluated in this study (Parker V0835-75) has a general service temperature range of -40°F to 400°F.

For the 9975, the maximum PCV O-ring temperature at Normal Conditions of Transport (NCT) is 264°F with solar heating, 100°F ambient, and maximum payload heat (19W). The O-rings are also required to seal down to -40°F for transport applications, but this is not a storage requirement. In reality, these conditions are not expected on a continuous basis, but are used for design purposes.

In storage, solar heating is absent and the peak PCV O-ring temperature at 19W is lower than during NCT. At a maximum ambient temperature of 130°F, the peak PCV O-ring temperature anticipated in storage is 202°F. In the event of loss of building ventilation, a maximum O-ring temperature of 300°F could be reached. However, at the highest recorded ambient temperature in the storage facility (104°F), the peak O-ring temperature is reduced to 176°F. For lower heat load packages, the O-ring temperatures are further reduced.

The bounding radiation dose rate for the PCV O-rings in this application is ~2 rad/hr. This dose rate requires approximately 30 years to reach a total dose of 5E+05 rad, a dose often considered a threshold for initial damage in elastomers [5]. Higher doses are needed for significant degradation. Thermal aging/oxidation is therefore expected to dominate O-ring behavior, though synergistic effects are possible.

To understand O-ring behavior, a dimensional analysis was performed. The V0835-75 O-rings are molded on dimensionally-compensated tooling to produce final parts with Class AN nominal dimensions and Class III tolerances. Dimensional analysis determined a nominal ID stretch of ~16% and 19% for outer SCV and PCV seals respectively. Worst-case ID stretch values based on smallest O-ring and widest plug dimensions are 18% (SCV) and 21% (PCV).

The ID stretch values are higher than the 1-5% recommended by most seal manufacturers. The impact of this variation on O-ring aging performance is not known, but it has two general effects: 1) reduced thickness and percent compression and 2) tensile stress. The nominal ID stretch values in this case reduce effective O-ring thickness by roughly 8-10%, leading to a nominal 20 and 22% compression for PCV and SCV seals, assuming zero gap between mating surfaces. Maximum ID stretch reduces the percent compression to 16% (PCV) and 18% (SCV). All values are within the 15-30% compression range typically recommended for static seals, though on the lower end. All values are less than 25% used in most ASTM test methods. Any gap further decreases the % compression.

TEST PROGRAM

Current literature and limited testing of the Viton® GLT-based O-ring compound indicate that the O-rings would maintain leak-tight containment during a 10 year storage period at anticipated conditions. A Surveillance Program was implemented to monitor and validate O-ring seal performance during storage.

The Surveillance Program consists of three main elements: field surveillance, laboratory monitoring and accelerated aging/life extension. The program is intended to provide the storage facility advance notice of degradation at bounding conditions and to develop a technical basis for life prediction.

Field surveillance involves annual examination of packages wherein packages are opened and the containment vessels are subject to an assembly verification leak test with a <1E-03 cc/sec sensitivity. O-ring thickness after compression is determined for compression set calculations. O-rings are also visually examined for degradation and presence of lubricant.

Laboratory monitoring involves leak testing of 62 empty mock-PCV fixtures (Figures 2-3) exposed at bounding storage conditions, with the primary variables of temperature (200/300°F), radiation (high/low dose rate), cover gas (air/CO_2) and lubricant (vacuum grease). The mock-PCV fixtures emulate the PCV closure and were fabricated to the same requirements, but are shorter (6 in.) with an additional leak test port to allow testing of either O-ring or both simultaneously. For shipping, annual certification leak tests are performed at room temperature with a new outer O-ring. In surveillance, laboratory fixtures with dual O-rings are leak tested at both room temperature and elevated temperature to evaluate leak-tightness at storage conditions.

Accelerated-aging tests are needed to develop a model for service life prediction. Baseline compression stress relaxation (CSR) behavior of the O-ring compound was determined per ASTM D6147 at elevated temperatures (200-400°F) using an Elastocon® continuous stress-relaxation measurement system. CSR tests were performed on O-rings compressed axially (non-constrained) and O-rings constrained in a simulated PCV groove. Longer-term CSR tests are planned to validate predictions from short-term data.

RESULTS & DISCUSSION

To date, field surveillance has been performed on approximately 49 radioactive material packages (196 O-rings) since FY05. O-rings removed from storage service exhibit no obvious signs of degradation. O-rings remain pliable and retain circular cross-section upon removal. For these O-rings, estimated average compression set of 13% is based on nominal part dimensions. No O-rings examined to date are from maximum payload packages subjected to bounding storage conditions.

Sixty-two mock-PCV fixtures have been in test for at least one year. The O-rings in all fixtures continue to maintain a leak rate of $<1x10^{-7}$ cc/sec at room temperature and meet the assembly verification criterion (<1E-03 cc/sec) at both room temperature and test temperature. Elevated temperature leak test results are being evaluated. O-rings aged at 300°F show more permanent deformation than O-rings aged at 200°F or examined from surveillance (Figure 4). In one case, the compression set of inner and outer O-rings based on radial thickness measurements was ~80%. This is a relatively high value but alone may not compromise seal integrity.

The true measure of seal performance is leak rate, which can vary with design parameters. Historically, compression set has been used to evaluate seal performance but it has several limitations. Compression stress-relaxation (CSR) is a direct measure of sealing force over time at temperature. As part of this study, baseline CSR data for nonconstrained V0835-75 O-rings at 200, 300, 350, and 400°F (Figure 5) indicate approximately 12, 30, 70 and near-100% loss in sealing force after 1000 hours. Constrained CSR results indicate slight improvement at 400°F but similar behavior at lower temperatures. This is believed to be due to greater expansion and constraint at the higher temperature.

In some studies, a 90% loss in sealing force (F/Fo = 0.10) is used as the mechanical "lifetime" criterion of elastomeric seals [6, 7]. This value does not represent failure defined by leak rate. For the V0835-75 O-rings, this value was reached after ~500 hours at 400°F, with nearly all sealing force lost at ~1000 hrs. This is consistent with the vendor "continuous" service temperature rating for the compound, which is generally based on 1000 hours. A recent paper [8] addresses the limitations of using vendor thermal ratings for design purposes.

Baseline CSR data were used to develop a preliminary aging curve. Since the 90% loss value was not reached at all temperatures during this test period, these values were linearly extrapolated. The log of time to reach 90% loss in sealing force (F/F_o=0.10) was plotted at each test temperature versus the inverse of temperature (Figure 6). Assuming the time to reach near-zero sealing force is double that to lose 90% at all temperatures, the near-zero force curve was also plotted.

From these basic data, the time to lose 90% of sealing force is estimated at ~100,000 hours or ~11.4 years at 176°F (maximum O-ring temperature at 104°F ambient with maximum payload heat). At 200°F, 90% loss is reached at 5.1 years. At 300°F, 90% sealing force is lost at ~208 days. However, if near-zero sealing force is used as the "lifetime" criterion, these estimates are doubled to 22.8 years, 10.2, and 1.2 years respectively. For packages with less than maximum payload heat, O-ring temperatures are reduced and service life (based on CSR) is further increased.

Baseline CSR data was initially performed on O-rings compressed a nominal 25% (per ASTM standards). The effect of reduced percent compression due to higher ID stretch was not initially evaluated to understand material behavior independent of the design. CSR tests with ID stretch and lower degree of compression are planned to refine the model.

In a separate test, an empty actual PCV was sealed with an outer O-ring and helium leak tested just as for annual certification. The sealed PCV was aged at 400°F for 1500 hours to duplicate the near-zero sealing force condition from CSR data (Figures 7-8). The PCV was removed from the furnace every 250 hours, cooled to room temperature and helium leak tested. The PCV passed all room-temperature leak tests with no obvious trend. This test indicates that even a highly aged and relaxed O-ring can maintain seal integrity at room temperature after thermal cycling. Leak rates at elevated temperature were not determined.

The preliminary aging model has several limiting assumptions, including: 1) linear extrapolation of short-term data, 2) Arrhenius behavior, 3) 25% compression and no ID stretch, 4) no radiation exposure, and 5) failure defined by sealing force. Additional experiments are either in process or planned to refine the model, including:

- long-term CSR behavior to validate baseline data
- oxygen consumption measurements to evaluate possible non-Arrhenius behavior
- correlation of sealing force to leak rate

Longer-term CSR tests will use Shawbury-Wallace CSR jigs and a Wallace Mark IV relaxometer (Figure 9). To account for ID stretch effects, a custom insert was designed (Figure 10). Ultrasensitive oxygen consumption techniques may be used to evaluate the potential for non-Arrhenius aging behavior [6]. Experiments to correlate sealing force and leak rate are also planned [7].
Some or all of these techniques may be used to evaluate new O-rings based on Viton® GLT-S, a polymer recently developed by DuPont to replace Viton® GLT with improved processing characteristics.

CONCLUSIONS

The aging behavior of Viton® GLT-based O-rings used in radioactive materials packages for interim storage of plutonium-bearing materials is being characterized. O-ring performance is being evaluated through a combination of field surveillance, laboratory testing of mock-PCV fixtures at bounding conditions and accelerated aging tests. Approximately 200 O-rings have been examined from packages after three years storage, with no degradation observed. Mock-PCV fixtures have been aged at bounding storage temperatures for one year, with seal performance evaluated based on leak rate. A preliminary aging model based on short-term compression stress relaxation (CSR) data will be refined with additional experiments.

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REFERENCES

[1] DOE-STD-3013-2004, Stabilization, Packaging, And Storage Of Plutonium-Bearing Materials.
[2] WSRC-SA-2002-00008, Revision 0, *Safety Analysis Report for Packaging – Model 9975*.
[3] Viton® GLT Technical Bulletin 300682A, DuPont-Dow Elastomers, 1997
[4] SAND-94-2207, "*Performance Testing of Elastomeric Seal Materials Under Low- and High-Temperature Conditions: Final Report*", D.R. Bronowski, June 2000.
[5] "*Radiation Effects on Organic Materials in Nuclear Plants*", EPRI NP-2129, November 1981.
[6] Gillen KT, Celina M, Bernstein R. "*Validation of Improved Methods for Predicting Long-term Elastomeric Seal Lifetimes from Compression Stress-Relaxation and Oxygen Consumption Techniques*", *Polymer Degradation and Stability*, 2003; 82:25.
[7] K.T. Gillen, R. Bernstein, M.H. Wilson, "Predicting and Confirming the Lifetime of O-Rings", *Polymer Degradation and Stability* 87 (2005), 257-270.
[8] "*Seal Life of EPDM O-rings at High Temperature Determined by Unique Method*", R. Marlier*, R. Andre, P. Malesys and H. Issard, *Packaging, Transport, Storage & Security of radioactive Materials*, Vol.17, No.1, 2006.

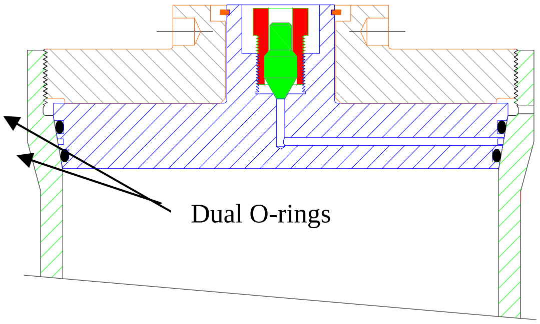

Figure 1. Containment Vessel Seal Configuration

Figure 3. Mock-PCV Storage Rack

Figure 2. Empty Mock-PCV Fixture Sealed With O-Rings

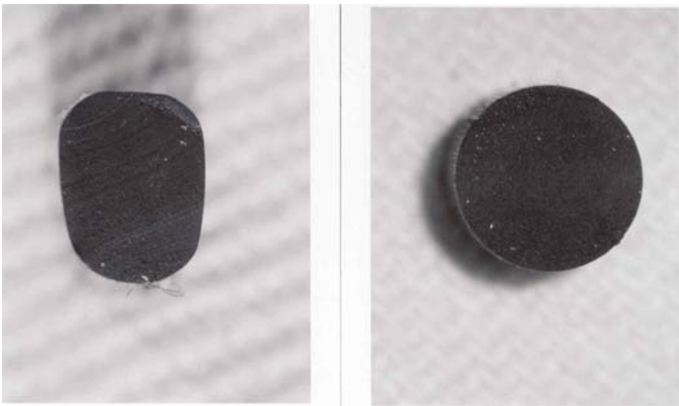

Figure 4. O-ring cross-section after aging at 300°F for 395 days (left); new O-ring on right. Photo taken five days after removal.

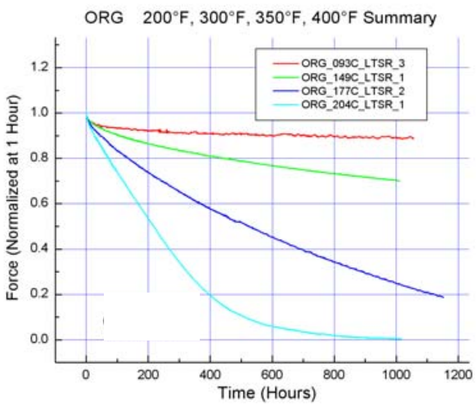

Figure 5. Baseline CSR Data for V0835-75 O-rings

Figure 8. O-ring profile after 1500 hours at 400°F

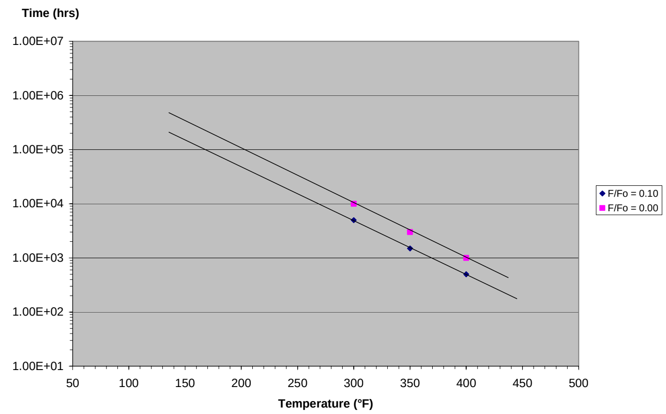

Figure 6. Basic service life plot based on Arrhenius CSR

Figure 9. Mark IV Compression Stress Relaxometer

Figure 7. Full-size, empty sealed PCV aged at 400°F

Figure 10. CSR Jig with custom insert for ID stretch