Aging Behavior of Viton® O-Ring Seals in the 9975 Shipping Package - 12594

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ABSTRACT

The Savannah River Site (SRS) is storing plutonium (Pu) materials in the K-Area Materials Storage (KAMS) facility. The Pu materials were packaged according to the DOE-STD-3013 standard and shipped to the SRS in Type B 9975 packages. The robust 9975 shipping package was not designed for long-term product storage, but it is a specified part of the storage configuration and the KAMS facility safety basis credits the 9975 design with containment. Within the 9975 package, nested stainless steel containment vessels are closed with dual O-ring seals based on Viton® GLT or GLT-S fluoroelastomer. The aging behavior of the O-ring compounds is being studied to provide the facility with advanced notice of nonconformance and to develop life prediction models. A combination of field surveillance, leak testing of surrogate fixtures aged at bounding service temperatures, and accelerated-aging methodologies based on compression stress-relaxation and oxygen consumption analysis is being used to evaluate seal performance. A summary of the surveillance program relative to seal aging behavior is presented.

INTRODUCTION

The Savannah River Site (SRS) is storing plutonium (Pu) materials in the K-Area Materials Storage (KAMS) facility. The Pu materials are packaged according to the standard DOE-STD-3013 which requires nested, welded, stainless steel containers [1]. The welded 3013 containers are then shipped in Department of Transportation (DOT) Type B 9975 packages, which are also used for storing the 3013 containers. The robust 9975 package consists of two nested stainless steel containment vessels closed with threaded cone-seal plugs, surrounded by a lead shielding body and fiberboard overpack, all contained within a 35 gallon stainless steel drum, Figure 1. Receipt of packages in the storage facility began in 2002.

Both the inner or primary containment vessel (PCV) and the outer or secondary containment vessel (SCV) are sealed with dual O-rings based on Viton® GLT or GLT-S fluoroelastomer (Dupont Performance Elastomers, Wilmington, DE). Two seal compounds (Parker Hannifin Corporation, Lexington, KY) are approved for use, V0835-75 (GLT) and VM835-75 (GLT-S), respectively. The VM835-75 compound was more recently approved (2008) due to ceased production of Viton® GLT. The O-ring sizes are AS568 2-244 (PCV) and 2-252 (SCV), respectively. The O-ring thickness is 3.53 +/-0.127 mm. The installed ID stretch of the O-rings is nominally 19% (PCV) and 16% (SCV). The percent compression on the PCV O-rings (zero gap) is nominally 20%. The surface finish for mating surfaces is 0.81 μm (32 μinch).

In transportation service, the O-rings are replaced during annual maintenance and leak tested to a 1 x 10^{-7} ref cm^3/s (leaktight) criterion per ANSI N14.5 [2]. However, while in storage, the O-rings are not replaced and cannot be helium leak tested. The outer O-ring in each vessel is credited for containment. The inner O-ring provides a volume for leak testing and a secondary barrier to product release.

The packages are being continuously exposed to the storage environment for a period of time greater than the approved transportation service period. Therefore, the aging behavior of the fluoroelastomer O-rings and the fiberboard materials is being studied to verify the integrity of the package during storage. The initial storage period of 10 years has recently been extended to 15 years. In addition, aging models are being developed to provide the storage facility with service life predictions for component replacement if necessary.

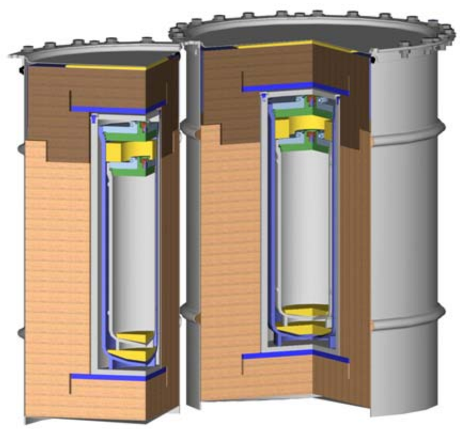

Figure 1. Cutaway illustration of the 9975 shipping package including fiberboard overpack, lead shielding, and double containment vessels.

METHODS

Experiments to monitor the aging performance of O-rings based on Viton® GLT and GLT-S based O-rings used in the Model 9975 package have been ongoing since 2003 at the Savannah River National Laboratory. The methods employed include: 1) field surveillance of O-rings, 2) leak testing of fixtures aging at bounding conditions, 3) accelerated-aging studies using compression stress-relaxation and oxygen consumption to develop life prediction models.

Field Surveillance

Field surveillance involves the opening of selected packages in the storage facility, post-assembly leak tests on containment vessels and inspection of components, including O-rings within 30 minutes of removal, followed by additional inspection in the laboratory.

O-rings are carefully examined for evidence of degradation. Thickness, both axial and radial, is measured for compression set determination, as well as hardness.

Accelerated Leak Tests

Sixty-two mock-ups of 9975 PCVs were initially assembled with V0835-75 (GLT) O-rings, baseline leak tested and heated to 93 or 149 ºC. These values represent initial maximum seal temperatures anticipated in the facility at either normal or loss of ventilation conditions. The vessels replicate the full-sized PCV closure, but were shortened to facilitate handling and leak testing. The vessels are heated with a flexible, wound-wire heater wrapped around the vessel circumference. Ceramic fiber batting is used to insulate the exposed ends of the fixture. Stainless steel tubing is attached to the leak test port on the top of the fixture lid via a high pressure fitting and to a threaded hole machined into the bottom of the fixture body.

This arrangement allows for helium leak testing of both O-rings together or individually. This differs from annual certification which only involves helium leak testing of a single O-ring. A thermal fuse was added to each heater to prevent excess temperature excursions. The heaters are controlled by a desktop computer running LabView™ software, with feedback via a type-K thermocouple attached to the mock-PCV body, Figure 2. A one-time leak test was performed for each fixture until permeation was detected, proving positive helium access to the O-rings.

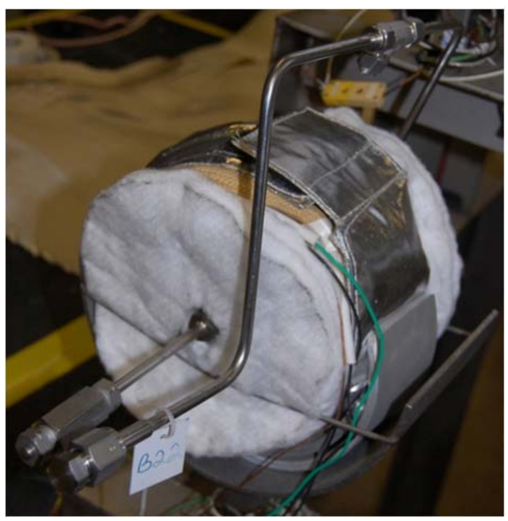

Figure 2. Assembled, insulated mock-up PCV in aging storage rack

The original 62 fixtures are leak-tested at nominal six month intervals using a Varian helium leak detector (Varian, Inc. Vacuum Technologies, Lexington, MA) to determine if it meets the criterion of leaktightness defined in ANSI standard N14.5 [2]. The original test matrix was developed to determine the effect of temperature, backfill gas composition, and irradiation dose and dose rate on the condition of the PCV O-rings over time. A total of 62 tests, with 22 separate sets of conditions were developed. Replicates of tests were performed based on a modified full-factorial statistical design.

The test variables are listed in Table I. Five additional mock-up fixtures were included in 2008 and exposed to higher temperatures (177, 204, and 232 ºC) in an attempt to accelerate aging of the GLT based O-rings, and to improve the predictive capability of the first set of leak tests. Leak testing was performed in shorter intervals of 3 weeks or less on the elevated temperature fixtures with the expectation that these would fail in a much shorter time. All of these fixtures were assembled with the normal O-ring lubricant and contained no backfill CO_2. Three fixtures, one at each aging temperature, were irradiated to 2000 Gy in 72 minutes.

Table I. O-Ring Fixture Aging Test Variables

Variable	Values	Basis
Temperature	93 ºC	Bounding normal seal temperature anticipated in storage.
	149 ºC	Bounding seal temperature due to loss of ventilation. Also the maximum design temperature for the containment vessels.
	177, 204, 232 ºC	Elevated temperatures added to increase predictive value of leak tests
Radiation Dose	2000 Gy in 72 min	The bounding dose rate for the PCV seals is 0.02 Gy/hr. A 2000 Gy dose represents 10 years of storage.
	2000 Gy in > 200 hr	A slower exposure rate may reveal the added effect of diffusion-limited oxidation (DLO) that may occur with longer-term exposure.
	None	Many packages will have little radiation exposure. This also serves as an experimental control.
Internal Atmosphere	≥75% CO_2, balance air	The free volume of the PCV is diluted with CO_2 as a cover gas. A small portion of the air originally in the vessels may remain.
	Air	Supplies comparative data and acts as a control (oxidation is conservative)
O-ring Lubricant	Silicone grease	Specified for O-ring installation in the 9975 package.
	Krytox® 240AC	Specified on lid components of the 9975 PCV and SCV. Possibly used on the 9975 O-rings in limited cases.
	None	Supplies comparative control data. Represents cases where O-rings may have been installed without grease.

A third set of 14 mock-up fixtures were assembled with GLT-S O-rings and heated (93 °C to 204 °C). Testing variables included temperature and radiation dose (2000 Gy in 72 minutes or no dose). Backfill of 75% CO_2 was not used for these fixtures as it was no longer considered relevant for aging purposes. Leak testing was performed nominally every 3 weeks. Two additional GLT fixtures were added in April 2011 at 132 °C to provide an intermediate indicator of leak performance as a result of long-term failures at 149 °C.

Once a fixture leak rate surpassed the criterion, diagnostic leak testing was performed to determine whether one or both O-rings had failed. If only one failed, the fixture was typically returned to test until the second O-ring failed. If both O-rings failed, the fixtures were disassembled and O-rings were visually examined. O-rings were measured for axial and radial dimensions. O-ring thicknesses were typically measured again 1-2 weeks after disassembly, and 30 days after disassembly. Hardness values were also measured.

Compression Stress-Relaxation

The compression stress-relaxation (CSR) behavior is being monitored over time at various aging temperatures as a measure of seal performance. CSR is an industry standard method to directly measure the sealing force or counterforce in an elastomer as it pushes on mating surfaces. This approach provides a direct measure of material behavior independent of leak performance. CSR tests involve the compression of O-rings or segments of O-rings in special fixtures per ASTM D6147 [3], with periodic removal of the fixtures from aging ovens and counterforce measurement in a Wallace Mark III - C11 relaxometer. The break force of each fixture is initially determined prior to testing and then subtracted from later values.

Smaller O-rings of the same compounds and thickness are being aged at 79 °C, 113 °C, 121°C, 149 °C and 177 °C until a failure criterion is reached. These temperatures were chosen to bound normal service without exposing the compounds to excessive temperatures that are not realistic. A challenge in accelerated-aging testing is to achieve meaningful results within a reasonable test period without being overly aggressive and possibly obtaining non-conservative data.

As every design is different, the actual failure criterion is often unknown. For the 9975 design, a 90% CSR value (10% retained sealing force) was selected as the failure criterion, consistent with similar work done on critical weapon components and other systems at relatively stable conditions [4, 5]. A custom insert was designed to duplicate the ID stretch and degree of compression in the 9975 design (Figure 3). A hole and groove were machined into the insert to allow oxygen access to both sides of the O-rings, which is conservative for aging.

Figure 3. Compression Stress-Relaxation (CSR) Fixture – Shawbury/Wallace C16

Oxygen Consumption Analysis

A more recent aspect of the program is the use of ultrasensitive oxygen consumption analysis to determine oxidation rates of the O-ring compounds and to identify any degradation mechanisms that may lead to non-Arrhenius aging behavior. This methodology has been shown to be effective in refining service life predictions for polymers and elastomers, particularly those that may contain antioxidants or other protective ingredients that may be consumed during the aging process [4-7]. Once consumed, a “cliff” response may occur, with a more significant drop in mechanical properties and seal performance.

The methodology for oxygen consumption analysis using a fuel cell respirometer is described by Assink et al. [6], and is used in the present work. Slabs of the GLT O-ring compound (0.3 cm thick) were cut into 0.6 x 5.0 cm pieces which were individually weighed. Groups of four were placed in mini Conflat® flanged vessels (Varian, Inc.) sealed with gold-coated copper gaskets and connected to a valve on each end. The assemblies were helium leak tested to ensure leaktight seals. A free volume measurement was also performed. The vessel was connected to a Sable Systems Oxzilla II dual fuel cell respirometer and cylinder air was passed at 20 cc/min through the vessel to flush out any remaining helium and establish a known oxygen content consistent with pure air. The valves were then closed. Vessels with enclosed samples were thermally aged at 40, 60, 80, 100, or 120 ºC for periods up to 1000 hrs.

Upon completion of thermal aging, the vessel with enclosed samples was reconnected to the respirometer and an oxygen depletion measurement was determined relative to an empty reference vessel. In this process, the same cylinder air used to fill the sample vessel flows through the reference vessel and a bypass line. Upon reaching equilibrium in reading the correct oxygen concentration in both the reference vessel and the bypass line, the sample vessel is valved into the bypass line and the measurement begins. The oxygen concentrations of the gas flushed from the reference vessel and from the sample vessel are tracked separately. The difference in measured oxygen concentration between the sample vessel curve and the reference vessel curve was calculated and converted to percent oxygen depletion.

RESULTS

Field Surveillance

Field 9975 packages containing plutonium materials are selected and opened for surveillance activities. Containment vessels are leak tested to a sensitivity of 10^{-3} ref cc air/s, consistent with post-assembly verification or pre-shipment testing performed at room temperature by measuring pressure drop over time. To date, 195 packages have been examined. Only three vessels (2 SCV, 1 PCV) have failed the post-assembly leak test. The failures were investigated and attributed to debris on the O-ring, not degradation of the elastomer. The package with the longest time in service (6.8 years) passed the post-load leak test.

Since 2005, approximately 780 O-rings have been examined. No O-ring material degradation has yet been observed. The O-rings retain mechanical properties and exhibit near-complete dimensional recovery. The original dimensions of each O-ring are unknown, but compression set values based on nominal initial O-ring dimensions and those taken within 30 minutes of removal range from 10 to 40% (avg 24%). Accounting for ID stretch, which reduces the effective thickness by ~10%, the actual compression set values are lower. Over time, these values further decrease as the O-rings elastically recover.

Aging Leak Tests

The time to leak failure data are summarized in Table II. Within the original set of fixtures containing GLT O-rings aged at 93 ºC, all remain leaktight at room temperature after 5.5 years at temperature. All fixtures being aged at 132 °C remain leaktight after 6 months. At 149 °C, seven fixtures with GLT O-rings have shown leak failures, with 12 total O-ring failures. The earliest O-ring leak failure at 149 °C was at 2.8 years. Eighteen O-rings still remain leaktight at 149 °C after up to 5.5 years.

Table II. Time to leak failure data for GLT and GLT-S O-rings

Aging Temperature	GLT	GLT-S
93 °C	All fixtures leaktight at 5.5 years	All leaktight at 2.5 years
132 °C	All fixtures leaktight at 6 months	None in test
149 °C	12 O-ring leakage failures (7 fixtures, earliest at 2.8 yrs) 18 O-rings leaktight at 5 yrs	No failures at 2.5 years
177 °C	Leak test failures in 0.9 - 1.6 yrs	Leak test failures in 0.3 - 1.6 yrs
204 °C	Leak test failures at 28 - 45 days	Leak test failures at 50 – 75 days

Five fixtures with GLT O-rings exposed to 177, 204 and 232 ºC have also failed. At 177 °C, the outer O-ring in one fixture failed after 324 days (0.9 years). The longest failure time was 1.6 years. At 204 °C, failure of both O-rings in both fixtures was noted at 28 and 45 days. These values are relatively consistent with seal manufacturer "continuous" thermal ratings (204 °C) for the fluoroelastomer compounds, typically based on 1000 hours (42 days) of exposure. In the 232 ºC fixture, the outer O-ring failed the leak test after 8 days at temperature, and the inner O-ring failed after 12 days at temperature. It is important to note that these temperatures are for accelerated-aging purposes and are much higher than anticipated in either transport service or storage.

For fixtures containing GLT-S O-rings, all fixtures remain leaktight after aging at 93 °C and 149 °C for 2.5 years. Leak failures were observed in fixtures aging at 177 °C after 0.3 to 1.6 years. At 204 °C, leak failures were observed after 50-75 days in all fixtures. With the exception of one fixture, GLT-S O-rings have shown similar if not superior leak performance. The one early failure at 177 °C (0.3 years) is shorter than observed for GLT fixtures (earliest at 0.9 years). That fixture was carefully disassembled and the O-rings were examined. There was no notable cause for leak failure and the compression set on the O-rings was within the range observed for other O-rings aged at the same or more severe conditions. Therefore, the cause of that single early failure is unknown.

Compression Stress-Relaxation

Using WLF (Williams-Landel-Ferry) time-temperature superposition principles, all of the compression stress relaxation data can be time-shifted to a single master curve [8]. The advantage of this approach is that all of the experimental data can be used, rather than simply using a few time to failure data points. The shift factors (a_t) are determined and plotted on a log scale versus the inverse temperature (1/T). Assuming Arrhenius behavior, the shift factor can then be determined for any service temperature desired and used to translate the master curve to that temperature. Using this approach for various temperatures, a seal life prediction model was developed. This model, along with time to leak failures for GLT O-rings, is given in Figure 4. Both CSR data and time to failure data suggest a decrease in seal performance with increasing temperature. The early CSR model predicts conservative lifetimes relative to lifetimes based on time to leakage, at least for temperatures below ~190 °C (375 °F). A similar model is currently being developed for the GLT-S compound.

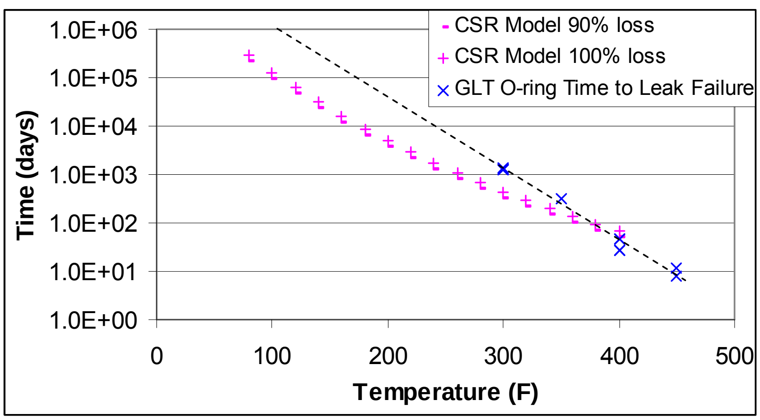

Figure 4. Seal life prediction based on CSR and leak test data for GLT O-rings

Oxygen Consumption Analysis

Preliminary results from oxygen consumption analysis have been presented elsewhere [9-10]. Early data suggests oxygen consumption rates may level off within the first 100,000 hours (10-12 years) at 40 ºC and that sharp changes in the degradation mechanism are not expected over the temperature range examined. This is consistent with the known resistance of fluoroelastomers to thermo-oxidation relative to hydrocarbon-based elastomers. In absence of antioxidants that may be consumed over time, non-Arrhenius aging behavior is therefore not anticipated. However, longer aging periods are likely needed to validate this assumption. Additional experimental effort is underway in the short term range within the first 100 hours of thermal aging to further refine the oxygen consumption rate.

DISCUSSION

From available data, aging temperature is the most critical parameter for the performance of both GLT and GLT-S based O-rings in the storage environment when compared with gamma radiation dose, lubricant composition, and atmosphere. Cumulative radiation dose may influence degradation more extensively at some point, but not likely within any reasonable storage period.

A more extensive study has thus far been performed on the GLT-based compound then the GLT-S based material. This is a matter of practicality as the GLT-S material was urgently introduced later in the program due to discontinued production of the GLT polymer. However, the available data thus far indicates that the lifetime of GLT-S based O-rings is similar and possibly superior to that of GLT material. Additional characterization of both GLT and GLT-S seal compounds was performed and reported elsewhere [11]. With minor formulation exceptions, the compounds are chemically very similar. Stress-relaxation data for the GLT-S compound generally indicate higher initial sealing stress and higher retained values at the same time/temperature conditions. This is consistent with the more efficient curing and cross-linking network claimed by the polymer manufacturer (DuPont Performance Elastomers) for the GLT-S polymer.

For a given service temperature, current data suggests that O-ring lifetime based on leak testing will be higher than the lifetime based on CSR testing. This result suggests that a decrease in CSR force is not singularly critical to the leak performance of the O-rings when tested at room temperature. Note, the GLT O-ring lifetime curve based on time to leakage is assumed to be linear on a log scale over the entire temperature range. This assumption has not been proven at temperatures below 149 ºC, as leaks have not yet been observed.

At a maximum anticipated seal temperature of 93 °C in storage, the early CSR model predicts a seal lifetime of approximately 12 years. However, ambient conditions in storage are moderated by the facility structure and ventilation, such that peak temperatures would not likely be reached for any extended period of time. At the highest ambient temperature recorded in the facility to date (41 °C), peak seal temperatures are limited to around 80 °C with maximum payload. At 80 °C, the early CSR model predicts a seal lifetime of approximately 25 years. Such temperatures, if reached, are also transient and buffered by the presence of fiberboard insulation. A sustained period of time (several days) is needed for seal temperatures to reach equilibrium. Therefore, actual seal temperatures are expected to be significantly lower.

Additional Benefits

The aging behavior of the O-rings used in the 9975 shipping package is principally being studied to support the 9975 Pu surveillance program at the Savannah River Site. However, the data obtained thus far has potentially broader benefit than for storage alone. For example, the aging data obtained has been used to help support the extension of annual maintenance on the 9975 shipping package for transport service. A safe upper temperature limit of 93 °C is currently established for the seal temperature during transportation. Degradation of the O-rings in real-time storage for periods longer than the extended maintenance period has not been observed. In addition, the same O-ring compounds are used in other shipping package designs. Each shipping package has its own set of unique conditions that must be carefully evaluated. However, the aging data obtained for the Pu storage program at the Savannah River Site may be useful for many applications where the same O-ring compounds are specified and where the service conditions are bounded by the available data. In any case, the condition and performance of components should be closely monitored to identify aging or other degradation mechanisms not fully accounted for in field surveillance or laboratory studies. There is no true substitute for real-time aging under realistic conditions.

CONCLUSIONS

The aging behavior of fluoroelastomer seals based on Viton® GLT and GLT-S is being studied to develop life prediction models in support of long-term storage of plutonium materials in the 9975 shipping packages at the Savannah River Site. Field surveillance data in combination with accelerated-aging data suggest a significant lifetime for the seals. Typical storage conditions are not anticipated to challenge the leaktightness of the seals for many years. Early life prediction models based on compression stress relaxation indicate a seal lifetime of ~12 years at the maximum service temperature predicted (93 ºC). Seal lifetimes at lower, more realistic conditions are likely significantly longer. Service life predictions based on CSR data are thus far conservative relative to predictions based on time to leakage failure. Surveillance data on packages examined after 6 years in storage show only minor compression set of the O-rings and no significant degradation. Surveillance and testing will continue as needed to validate and refine life prediction models.

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