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.



9975 Shipping Package Component Long-Term Degradation Rates

W. L. Daugherty June 2017 SRNL-STI-2017-00369, Revision 0

SRNL.DOE.GOV

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.

Printed in the United States of America

Prepared for U.S. Department of Energy

SRNL-STI-2017-00369 Revision 0

Keywords: K-Area Fiberboard O-Ring Service Life

Retention: Permanent

9975 Shipping Package Component Long-Term Degradation Rates

W. L. Daugherty

June 2017

Prepared in conjunction with work accomplished under contract number DE-AC09-08SR22470 with the U.S. Department of Energy (DOE) Office of Environmental Management (EM).



OPERATED BY SAVANNAH RIVER NUCLEAR SOLUTIONS

SRNL-STI-2017-00369 Revision 0

APPROVALS:

W. L. Daugherty	Date
Author, Materials Science and Technology	
T. E. Skidmore	Date
Technical Review, Materials Science and Technology	
B. L. Garcia-Diaz	Date
Pu Surveillance Program Lead, Materials Science and Tech	nnology
K. E. Zeigler	Date
Manager, Materials Science and Technology	
R. J. Grimm	Date
NMM Engineering	
REVIEWS:	
D. R. Leduc	Date
Savannah River Packaging Technology	
B. B. Kiflu	Date
NMM Engineering	

Summary

Special nuclear materials are being stored in the K-Area Complex using 3013 containers that are held within Model 9975 shipping packages. The service life for these packages in storage was recently increased from 15 to 20 years, since some of these packages have been stored for nearly 15 years. A strategy is also being developed whereby such storage might be extended beyond 20 years. This strategy is based on recent calculations that support acceptable 9975 package performance for 20 years with internal heat loads up to 19 watts, and identifies a lower heat load limit for which the package components should degrade at half the bounding rate or less, thus doubling the effective storage life for these lower wattage packages. The components of the 9975 package that are sensitive to aging under storage conditions are the fiberboard overpack and the O-ring seals, although some degradation of the lead shield and outer drum are also possible.

This report summarizes degradation rates applicable to lower heat load storage conditions. In particular, the O-ring seals should provide leak-tight performance for more than 40 years in packages for which their maximum temperature is ≤ 135 °F. Similarly, the fiberboard should remain acceptable in performance of its required safety functions for up to 40 years in packages with a maximum fiberboard temperature ≤ 125 °F.

In order to maintain confidence in these conclusions, it is recommended that 9975 surveillance efforts continue in support of packages that might be stored for periods beyond 20 years. This includes both KAC field surveillance and SRNL testing directed toward long-term fiberboard aging behavior. It is also recognized that an extreme of package variation may exist for which moisture concentration and related effects (mold growth, fiberboard compaction and fiberboard assembly shrinkage) may be greater than observed to date. For such packages, current assumptions may not bound their behavior beyond 20 years in storage. Prior to any packages with softwood fiberboard exceeding 20 years storage, the validity of representing these packages beyond 20 years with cane fiberboard data should be re-confirmed or separate softwood fiberboard analyses performed.

In addition to O-ring and fiberboard degradation, it is recognized that corrosion of the lead shield can impact performance of the 9975 package. Although the effective lead corrosion rate assumed in Reference 8 is conservative to lead corrosion data, the applicability of this assumption to lower wattage packages beyond 20 years in storage should be evaluated.

Background

The 9975 surveillance program [1] includes elements to predict the service life of 9975 shipping packages used to store special nuclear materials in the K-Area Complex (KAC). Recent efforts provided a technical basis to increase the approved storage life for 9975 packages in KAC from 15 to 20 years for all packages. Additional efforts are underway to anticipate the likelihood of further increases in this storage life, potentially up to 40 years. This additional life extension strategy seeks a lower heat load threshold below the 19 W package rating for which existing data might justify a 40 year service life, while recognizing that some higher wattage packages (depending on their content) will likely be re-packaged after 20 years.

The primary components of the 9975 package that might limit its storage life are the fiberboard overpack and the O-ring seals. Both of these components are subject to degradation mechanisms that are driven by thermal processes (i.e. the degradation rates increase with increased component temperature). While component temperatures will vary with seasonal changes in the facility ambient temperature, the primary source of elevated temperature for the 9975 package components is the internal heat load. The strategy to extend package storage life to 40 years seeks an internal heat load threshold that will produce degradation rates less than half the degradation rate for packages with 19 W. Based on 9975 surveillance program data generated to date, it was judged that such a 40 year storage life might be justified for packages for which the peak fiberboard overpack temperature (averaged over 40 years) is ≤ 135 °F. A bounding average ambient temperature of 95 °F is assumed, consistent with other recent facility calculations. This report will review the available data relevant to these temperatures and identify associated bounding degradation rates for the material properties of interest to the safety functions of the 9975 package.

It is noted that additional concerns regarding corrosion of the lead shield and outer drum will also need to be addressed before the storage life can be increased past 20 years.

Data and Analysis – O-Rings

It was judged that a 40 year storage life might be justified for packages for which the peak Oring temperature (averaged over 40 years) is ≤ 135 °F. Data are available from two test sources to provide degradation rate estimates for this temperature. These data address specific Parker Oring compounds fabricated from Viton[®] GLT and GLT-S fluoroelastomers.

Compression stress relaxation (CSR) testing of elastomers provides a measure of how long the material retains a counterforce to maintain a seal. The end of life is taken as the time when the counterforce drops below 10% of its initial value. This value does not inherently correlate to leak failure and was adopted from other studies performed on seals in nuclear weapon components [e.g. 2]. CSR data are available for O-ring samples aged at temperatures of 175 to 450 °F. The samples aged at \geq 300 °F have reached the end-of-life criterion, while data from the lower temperature samples have been extrapolated to the end-of-life criterion through time-temperature superposition (TTS) (see Figure 1). Reference [3] summarizes this data and develops a basis to predict service life at lower temperatures using the time-temperature superposition principle. This approach can be applied to estimate the service life for O-rings at 135 °F, as follows.

- The overall shape of the counterforce decay curve is the same for each aging temperature. The actual curves vary only in the time scale, with the time to reach the end-of life criterion increasing for lower aging temperatures.
- The difference in time scale between any two aging temperatures is called a shift factor. If these factors fall in a straight line when displayed on a semi-log plot as a function of reciprocal time, then they follow Arrhenius behavior and can be described more generally by the equation

Shift Factor = A $exp(-E_a/R^*T)$ where A is a constant, E_a is the activation energy, R is the ideal gas constant, and T is the absolute temperature

- With this relationship, the shift factor for any temperature of interest can be calculated, provided the same degradation mechanisms are active over the entire temperature range of interest.

Using this approach for GLT O-rings (calculated activation energy of 60 kJ/mol, and ~19 years to reach the end-of-life criterion at 175 °F [3]), the estimated time to reach the end-of-life criterion at 135 °F is about 77 years. The bounding GLT O-ring model also estimates a storage life of 40 years if the maximum O-ring temperature is 153 °F. Similarly for GLT-S O-rings (calculated activation energy of 81 kJ/mol and 344 years to reach the end-of-life criterion at 175 °F [3]), the estimated time to reach the end-of-life criterion at 135 °F is about 2200 years.

Additional data relevant to the service life of these O-rings are available from PCV fixture testing [4]. In this task, O-rings are aged at elevated temperature inside PCV fixtures and periodically leak tested to determine the time they are able to remain leak-tight. Fixtures with GLT and GLT-S O-rings have reached a failure point (no longer leak-tight) at aging temperatures of 300 to 450 °F, while no failures have yet occurred after aging for 5.7 to 10.5 years at 200 to 270 °F (Figure 2).

The fixture leak test data do not show a clear difference in failure time for the two O-ring compounds. The GLT O-rings had the shortest failure times at 300 and 400 °F, while the GLT-S O-rings had the shortest failure time at 350 °F (no GLT-S O-rings were aged at 450 °F). With both materials, there is some scatter in the time to failure at a given aging temperature. The earliest failures for GLT at each aging temperature define a lower bound curve which can be extrapolated to estimate a storage life at lower temperatures. (All GLT-S failure points lie above this lower bound curve.) This leads to an estimated lifetime of 1980 years at 135 °F. It is emphasized, however, that with relatively few failure points and scatter in the failure time at each aging temperature, there is significant uncertainty in extrapolating these data this far below 300 °F.

A key assumption in extrapolating the CSR and PCV fixture results to the lower temperatures of interest for storage is that the same degradation mechanisms remain active over the entire range of extrapolation. This is a well-known limitation of accelerated-aging theories and models such as Arrhenius, Eyring, etc. Therefore, this assumption is being tested with measurements of the oxygen consumption rates of samples aging at temperatures ranging from 104 to 250 °F [5]. Polymer aging in an elevated temperature environment (with minimal ionizing radiation and no aggressive chemical exposure) is typically driven by oxidation processes (thermo-oxidation). The Viton fluoroelastomer O-ring compounds are highly resistant to aging and oxidation. However, comparison of oxygen consumption rates at different temperatures over the range of interest should either confirm that activation energy estimates remain valid at the lower storage temperatures of interest, or identify an alternate extrapolation process (Figure 3). This approach has been used for aging of weapon component seals based on hydrocarbon elastomers such as butyl and EPDM. This testing is in progress, with some initial oxidation rates at the higher

temperatures, though none of the samples has yet reached the steady-state oxidation rate needed for valid comparison of the different aging temperatures.

Recommendation – O-Rings

It is recommended that the minimum extrapolated storage life of 77 years at 135 °F be assumed for both GLT and GLT-S O-rings until additional data are available to update the CSR and PCV fixture aging models and until the assumption that the existing data can be extrapolated to storage temperatures of interest is confirmed. This recommendation is valid so long as the other package components (particularly the fiberboard) continue to display sufficient integrity to provide adequate protection for the O-rings.

Data and Analysis - Fiberboard

It was judged that a 40 year storage life might be justified for packages for which the peak fiberboard overpack temperature (averaged over 40 years) is ≤ 125 °F.

Fiberboard properties are obtained from several types of samples. Thermal conductivity samples are at least 6 x 6 inches with a thickness between 1 and 2 inches, and are oriented to provide heat flow either parallel or perpendicular to the fiberboard layers (i.e. representing heat flow radially or axially within the package, respectively). Physical property samples are approximately 2 x 2 x 2 inches, and provide periodic measurement of dimensions, weight and density. Since the physical property samples are handled regularly for measurement and are subject to some material loss during handling, sample degradation rates are adjusted by the average degradation rate of control samples (samples held at ambient conditions, with no expected environmental degradation, and measured at about the same frequency). Compression test samples are also approximately 2 x 2 x 2 inches. Since the compression test is destructive, each of these samples provides a single stress-strain curve when loaded either parallel or perpendicular to the fiberboard layers.

The main parameter of interest from compression testing is energy absorption capacity, which has been approximated as the area under the stress-strain curve up to 40% strain (this is not a specified parameter for performance, but provides a metric for direct comparison). Since the compression test is destructive, each sample provides a measure of energy absorption for only one point in time. Sample-to-sample variation can lead to significant scatter in energy absorption data for a given aging environment, making it difficult to extrapolate this behavior with confidence. A further complication is introduced by performing the compression test without constraint – the sample is free to spread out laterally during the test. Samples tested in the parallel orientation tend to spread significantly, depending on their moisture content, which decreases the observed energy absorption. In contrast, samples tested in the perpendicular orientation tend to be self-constrained by the glue layers and general fiber orientation. This more closely mimics the fiberboard within the 9975 package which is mostly constrained by the drum and shield, with small gaps that might allow limited movement during an impact. For this reason, it has been previously identified that parallel orientation samples can be very conservative to actual energy absorption behavior within the 9975 package, while perpendicular orientation samples provide a more realistic estimate of package behavior. References 6 and 7

recommended that the averaged behavior of samples from both orientations might provide a reasonable conservative approximation of energy absorption behavior.

Physical Properties and Thermal Conductivity for Fiberboard at 125 °F

Average degradation rates based on samples aged in a 125 °F oven and in a 125 °F 70 %RH environmental chamber through ~August 2015 were reported for cane fiberboard in Reference 5, and for softwood fiberboard in Reference 7. Degradation rates for thermal conductivity and physical properties in these two environments are summarized in Table 1. As thermal and physical properties degrade over time in a specific environment, their decrease is generally linear or slightly concave. In other words, they degrade at a constant rate or at a slightly decreasing rate. Extrapolating this behavior can be accomplished by assuming a constant degradation rate over time. In cases where the actual degradation is slightly concave, this assumption will be conservative.

Reference 8 reviewed these fiberboard degradation data and concluded that a degradation rate of 0.3 %/year was bounding to the thermal conductivity and physical property degradation described in Reference 6 for cane fiberboard at temperatures ≤ 145 °F. Since this rate did not account for fiberboard compaction, shrinkage from moisture re-distribution or mold, it was increased to a bounding degradation of 10% over 20 years for these properties. While some degradation rates for softwood fiberboard are higher than this level, they also contain greater uncertainty and may be overly conservative. Therefore, Reference 8 concluded that the bounding degradation rate for cane fiberboard properties was also appropriate for softwood fiberboard. With this level of bounding degradation and additional allowance for fiberboard compromised by mold, calculations have shown the package performs its required safety functions in facility fire, forklift impact and 30 foot drop accident scenarios [8 - 11].

Therefore, it is expected that a similar favorable result would be produced for packages following 40 years in storage provided none of these properties has degraded more than 10% during that period. This corresponds to an average degradation rate of 0.25 %/year with little or no compaction or shrinkage. For each of the fiberboard properties summarized in Table 1, the average degradation rate is below this value. Therefore, these properties would support a 40 year storage life for 9975 packages which maintain a peak fiberboard temperature ≤ 125 °F.

Energy Absorption for Fiberboard at 125 °F

In Reference 11, the energy absorption data for samples aged in like conditions were normalized, averaged and plotted. These data were then extrapolated to estimate the energy absorption capacity at 20 years. The extrapolated estimates were used as inputs to calculate the effect of hypothetical forklift impact and 30-foot drop scenarios. Separate estimates were made for parallel and perpendicular orientation data. As recommended in Reference 6, the estimates for the two orientations were averaged to get a reasonably conservative value of the degraded fiberboard condition. This process was performed separately for cane fiberboard and softwood fiberboard. Due to changes that reduced the calculated temperature profile after this work began, the degraded condition that was originally assumed and ultimately used in References 10 and 11 is conservative to the final calculated 20 year degraded condition. References 6 and 7 identified

a threshold of ~120 °F below which there appears to be no fiberboard degradation, and this threshold was applied to fiberboard regions below this temperature.

Figure 4 shows the fiberboard degradation zones used in the Reference 10 and 11 calculations, along with the relative energy absorption values associated with each zone. The degradation zones provide a conservative bound to the average behavior of fiberboard within each zone. Small regions (located primarily just under the lower bearing plate) of each zone might experience temperatures slightly above the zone designation. However, this part of the fiberboard assembly contributes relatively little to absorbing energy in the postulated forklift impact scenario. The average temperature within each zone is below the zone designation, and basing zone properties on the zone designated temperature is conservative.

Figure 5 shows the same fiberboard degradation zones along with two sets of temperature contours. The first set shows select temperature contours for a 19 W package after 20 years. These contours were produced by the same program used in Reference 8. The second set shows the corresponding temperatures of the same contour lines for a package with 125 °F maximum fiberboard temperature.

Estimating the energy absorption degraded condition after 40 years at 125 °F will be described for cane fiberboard in the parallel orientation. The same process is repeated for the perpendicular orientation and for softwood fiberboard to provide the results shown in Table 2. Figure A-6 in Reference 11 was developed to estimate the 20 year degraded condition, and is extrapolated to estimate the 40 year degraded condition, as illustrated in Figure 6. With a specific interest in packages with a maximum fiberboard temperature of 125 °F, only the degraded values for the 125 °F oven and 125 °F 70%RH aging environments are now considered, with extrapolated 40 year values of 92% and 60%, respectively (see Table 2). Reference 11 identifies that for a constant absolute humidity of 16.04 g/m^3 within the package, the relative humidity in fiberboard regions at 125 °F will be 18%. Estimating the degraded energy absorption for this condition (125 °F 18 %RH) is illustrated in Figure 7. In this case, the 20 %RH contour line provides an estimate that 88% of the baseline energy absorption capacity remains after 20 years. As seen in Table 2, the energy absorption capacity decreases by ≤ 2 percentage points between 20 years and 40 years for either humidity condition (oven or 70 %RH). Therefore the energy absorption capacity after 40 years at 18 %RH will be at least 86% of the baseline value.

The process just described is repeated for cane fiberboard in the perpendicular orientation and for softwood fiberboard in both orientations. These values are applied to all regions with fiberboard temperatures between 120 and 125 °F. As noted in References 6, 7 and 11, fiberboard regions below 120 °F are assumed to experience no degradation. (Note: While estimates of degraded energy absorption values were developed for all cases in the preparation of Reference 11, the extrapolated results for softwood fiberboard samples tested in the parallel orientation were not presented in that reference. The energy absorption data and curve fits for softwood fiberboard, parallel orientation at 125 °F (oven and 70%RH), that were used in Reference 11 are shown in Figure 8. Linear interpolation was used to get the expected behavior for 125 °F 18 %RH as shown in Figure 8. These extrapolated values presented in Table 2 were developed by the author of Reference 11 and should be documented in a future revision of that calculation.)

The energy absorption values extrapolated to 40 years are summarized in Table 3, and compared to the values used in the Reference 10 and 11 calculations. The estimated fiberboard degradation after 40 years storage at temperatures ≤ 125 °F is less than assumed in the Reference 10 and 10 calculations for 19 W packages after 20 years. Therefore, the Reference 10 and 11 calculations are conservative relative to performance of a package with maximum fiberboard temperature of 125 °F after 40 years.

Assumptions and Conservatisms in Fiberboard Analysis

References 5 and 6 identify that most properties appear to exhibit a threshold around ~120 °F below which there is little or no degradation. With any appreciable internal heat load, there will be a temperature gradient across the fiberboard, and the maximum fiberboard temperature will occur along the inner surface adjacent to the shield. A corresponding counter-gradient in relative humidity will develop, with regions of higher relative humidity along the cooler outer fiberboard surfaces. The absolute humidity tends to remain ~constant throughout the fiberboard assembly [12, 13]. In a package with a maximum fiberboard temperature of 125 °F and a minimum temperature close to the bounding average ambient temperature of 95 °F, the relative humidity along the cooler outer surfaces will be approximately 2.5 times higher than that along the inner surface, based on published psychrometric charts.

The specific values of relative humidity within a given package will depend on the fiberboard temperature profile and the total amount of moisture present in the fiberboard. In extreme cases, enough moisture might be present that moisture levels in the bottom fiberboard layers approach saturation (~28 wt%) and mold will become active. For example:

- Saturated cane fiberboard and mold has been observed in a test package with nominal initial fiberboard moisture content (~10-12 %WME) and 19 W internal heat load with slightly elevated ambient temperature [14]. The elevated moisture levels in this package eventually decreased over several years.
- Two test packages with cane fiberboard were held at ambient temperature with varying internal heat loads [12]. One had an initial fiberboard moisture content of ~8 9 %WME while the other was ~13 15 %WME. The average local moisture content in the first package remained below saturation for all heat loads up to 19 W. Local areas at the bottom of the second package reached saturation with 10 W heat load, and mold was observed following several weeks at 15 W, and was much heavier after several weeks at 19 W. These packages did not remain in test long enough to identify a trend of overall moisture loss from the package.

This first example shows that the elevated local fiberboard moisture levels eventually decreased. This is due in part to the small degree of air infiltration driven by minor variations in ambient room pressure. However, one should expect variation in the degree of leakiness from one package to another. If the bottom fiberboard layers approach saturation in a drum that is sealed better than average, it is possible that the elevated moisture and mold growth will persist long enough to consume more fiberboard than has been observed to date. This scenario has not been quantified, and cannot be addressed through available data.

As the moisture content of the bottom fiberboard layers increases, those layers tend to weaken and compact under the weight of the shield and containment vessels. This effect, as well as general shrinkage of the remainder of the fiberboard assembly, will contribute to an increase in the axial gap at the top of the package. Reference 8 addressed these effects (mold, compaction and shrinkage) with a bounding assumption that the bottom 2 inches of fiberboard were gone after 20 years in storage. With the consideration of packages for which the maximum fiberboard temperature is no greater than 125F, the rate at which these effects progress is expected to be less than in a 19 W package. For example, with a reduced moisture gradient, the peak moisture content of the bottom fiberboard layers will be reduced. Accordingly, these layers will not weaken as much, the compaction rate will be reduced, and the total compaction will be less [15]. This effect is seen in Reference 16, which shows a statistical difference in the rate of axial gap increase based on internal heat load. The axial gap in packages with a heat load of \geq 14 W increases faster than the axial gap in packages with lower heat load. However, existing data do not fully address how the combined effects of mold, compaction and shrinkage will change with temperature. The impact of this should be examined prior to exceeding 20 years storage.

Reference 8 concluded degradation rates based on cane fiberboard were appropriate for softwood fiberboard as well. While existing softwood fiberboard data show some trends outside of the range of cane fiberboard, there are fewer softwood fiberboard data covering shorter durations and fewer environments than cane fiberboard. Additional longer-term softwood data continue to accumulate, and should be used to re-evaluate this conclusion prior to any softwood fiberboard assemblies exceeding 20 years storage.

There are several aspects to the extrapolated energy absorption values that are potentially nonconservative. These include:

- The Reference 10 calculation assumed a maximum absolute humidity of 16.04 g/m³, which was the largest value from 26 packages in storage which were documented in Reference 17. But SRNL test packages have shown higher values, up to 20 25 g/m³ [12, 13]. With higher humidity levels, degradation rates are expected to increase.
- Energy absorption values used were averaged across multiple source packages, and the degradation rate was taken as a nominal fit to these averaged data. While it is appropriate to average the behavior of small regions (individual samples) within a larger package to represent the macroscopic package behavior, this approach does not provide for package-to-package variation.
- The curve fits and interpolations used to develop estimated lines of strength ratio vs temperature for constant RH values are approximations and are not rigorously derived from the data.

These examples are identified as a cautionary note, while recognizing that there are also conservative elements. It is recommended that the overall conservatism of this assessment be verified prior to exceeding 20 years storage.

Recommendation - Fiberboard

Each of the fiberboard properties reviewed is relevant to one or more calculations [8 - 11] used to demonstrate that the 9975 package will perform its required safety functions after 20 years in storage. Using the methodology of these calculations and the fiberboard degradation data supporting them, it has been shown that lower wattage packages (for which the maximum fiberboard temperature during storage is ≤ 125 °F) have sufficiently low degradation rates that even after 40 years in storage they should still perform their required safety functions.

This conclusion does not address three specific phenomena which can act in concert to increase the axial gap; as moisture concentrates in the bottom fiberboard layers, these layers can experience mold growth and compaction, and the remainder of the fiberboard assembly can shrink. The incidence and persistence of mold in fiberboard regions with elevated moisture has not been well characterized in terms of understanding the range of possible behavior. In particular, most packages in which mold has been observed have presented evidence that elevated moisture levels may drop over time and the mold activity will decrease. However, minor variation in the degree to which a 9975 package can "breathe" under ambient pressure variations could significantly extend the period of elevated moisture and active mold growth. The assumption in References 8 - 11 of moisture-related degradation in the bottom 2 inches of fiberboard may not bound the potential behavior of all packages in storage for periods beyond 20 years.

Several potential non-conservative elements to the Reference 10 and 11 calculations were identified, although it is recognized that there are a number of conservative elements present as well. It is recommended that the overall conservatism of this assessment be verified prior to exceeding 20 years storage. This assessment could include consideration of additional test data which will become available in the future as test samples continue aging.

It is recommended that 9975 surveillance efforts continue in support of packages that might be stored for periods beyond 20 years. This includes both KAC field surveillance and SRNL testing directed toward long-term fiberboard aging behavior. Prior to any packages with softwood fiberboard exceeding 20 years storage, the validity of representing these packages beyond 20 years with cane fiberboard data should be re-confirmed or separate softwood fiberboard analyses performed.

Conclusions

This report summarizes degradation rates for 9975 package components applicable to lower heat load storage conditions. In particular, the fluoroelastomer O-ring seals should provide leak-tight performance for more than 40 years (up to 77 years) in packages for which their maximum temperature is \leq 135 °F. The fiberboard should perform its required safety functions for up to 40 years in packages with a maximum fiberboard temperature of 125 °F or less.

In order to maintain confidence in these conclusions, it is recommended that 9975 surveillance efforts continue in support of packages that might be stored for periods beyond 20 years. This includes both KAC field surveillance and SRNL testing directed toward long-term O-ring and

fiberboard aging behavior. It is also recognized that an extreme of package variation may exist for which moisture concentration and related effects (mold growth, fiberboard compaction and fiberboard assembly shrinkage) may be greater than observed to date. For such packages, current assumptions may not bound their behavior beyond 20 years in storage. Prior to any packages with softwood fiberboard exceeding 20 years storage, the validity of representing these packages beyond 20 years with cane fiberboard data should be re-confirmed or separate softwood fiberboard analyses performed.

In addition to O-ring and fiberboard degradation, it is recognized that corrosion of the lead shield can impact performance of the 9975 package. Although the effective lead corrosion rate assumed in Reference 8 is conservative to lead corrosion data, the applicability of this assumption to lower wattage packages beyond 20 years in storage should be evaluated.

References

- 1. WSRC-TR-2001-0286, Rev. 7, "The Savannah River Site Surveillance Program for the Storage of 9975/3013 Plutonium Packages in KAC", Jan 2015
- "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 (2003) pp25–35.
- SRNL-STI-2015-00683, "CSR Behavior and Aging Model for the Viton® Fluorelastomer O-Rings in the 9975 Shipping Package", A. J. McWilliams, W. L. Daugherty and T. E. Skidmore, December 2015
- 4. SRNL-TR-2016-00191, "Eleventh Interim Status Report: Model 9975 O-Ring Fixture Long-Term Leak Performance", W. L. Daugherty, August 2016
- SRNL-TR-2014-00057, "Task Technical and Quality Assurance Plan for Characterization and Surveillance of Model 9975 Shipping Package O-Rings and Fiberboard Materials", K. A. Dunn, April 2014
- 6. SRNL-STI-2015-00610, "Status Report Cane Fiberboard Properties and Degradation Rates for Storage of the 9975 Shipping Package in KAC", W. L. Daugherty, December 2015
- 7. SRNL-STI-2015-00611, "Status Report Softwood Fiberboard Properties and Degradation Rates for Storage of the 9975 Shipping Package in KAC", W. L. Daugherty, December 2015
- 8. M-CLC-K-00788, "The Initial and 20-year Thermal Performances of the 9975 Shipping Packages due to Fire-Drop-Smoldering Accidents in KAC", B. B. Kiflu, January 17, 2017
- 9. M-CLC-K-00789, "The initial and 20-year storage thermal performances of the 9975 shipping packages due to fire accident in KAC facility", B. B. Kiflu, February 8, 2017

- 10. M-CLC-K-00786, "Dynamic Analysis of 30-ft Drop for 9975 Package in Storage Conditions", J. Johnson, January 18, 2017
- 11. M-CLC-K-00787, "Structural Analysis of the 9975 Package for a Facility Condition Forklift Accident With 20 year Aged Package Conditions", C. McKeel, January 23, 2017
- 12. SRNL-STI-2016-00254, "Humidity Data for 9975 Shipping Packages with Cane Fiberboard", W. L. Daugherty, May 2016
- 13. SRNL-STI-2017-00009, "Humidity Data for 9975 Shipping Packages with Softwood Fiberboard", W. L. Daugherty, January 2017
- 14. SRNL-STI-2017-00045, "Model 9975 Life Extension Test Package 3 Interim Report", W. L. Daugherty, January 2017
- 15. SRNL-STI-2012-00429, "Analysis of the Axial Gap vs Fiberboard moisture Content in a 9975 Shipping Package", W. L. Daugherty, September 2013
- LA-UR-16-23255, "Analysis to Evaluate Predictors of Fiberboard Aging to Guide Surveillance Sampling for the 9975 Life Extension Program", E. J. Kelly, W. L. Daugherty and E.R. Hackney, May 9, 2016
- 17. SRNL-STI-2015-00324, "Fiberboard Humidity Data for 9975 Shipping Packages", W. L. Daugherty, July 2015

Table 1.	Degradation rate d	lata for cane	fiberboard at 1	25 °F from	Reference 6.	In this table, a
negative	degradation rate re	presents a po	ositive increase	e in the proj	perty.	

<u> </u>				<u>1 1 7</u>		
Cane fiberboard	Samples aged in 125 °F			Samples aged in 125 °F 70		
Property	oven (~10 %RH)			%RH chamber		
	Average Duration of			Average	Duration of	
	degradation available			degradation	available	
	rate (%/yr)	aging data (yr)		rate (%/yr)	aging data (yr)	
Thermal cond., axial	-0.372*	1.1		-0.026	3.2 - 4.2	
Thermal cond., radial	-0.041	8.4 - 9.3		-1.160	4.2	
Height	0.032	9.2		0.054	4.3	
Length, width	0.039	9.2		0.034	4.3	
Density	0.120	9.2		0.197	4.3	

* A portion of the 56 wks aging time for the 125 °F oven axial thermal conductivity samples was spent at 125 °F 70% RH, but the degradation rate was calculated from data taken after aging in a 125 °F oven only.

estimate the relative numbers of interest (18 % RH) as described in the text.								
	Degraded energy absorption extrapolated values							
	Cane fiberbo	ard	Softwood fiberboard					
	20 yrs [11]	40 yrs	20 yrs [11]	40 yrs				
125 °F oven, parallel	93%	92%	100*%	100%				
125 °F 70 %RH, parallel	62%	60%	6*%	0%				
125 °F 18 %RH (estimated),	88%	86%	87*%	85%				
parallel								
125 °F oven, perpendicular	100%	100%	87%	85%				
125 °F 70 %RH, perpendicular	72%	71%	78%	77%				
125 °F 18 %RH (estimated),	97%	96%	82%	80%				
perpendicular								

Table 2. Curve fits for 125 °F aging environments from Reference 11, extrapolated further for energy absorption (% remaining) after 40 years. Results from the two environments are used to estimate the relative humidity of interest (18 %RH) as described in the text.

* Extrapolations for softwood fiberboard in the parallel orientation were not shown in Reference 11. These extrapolations are shown in Figure 8, and should be included in a future revision of Reference 11.

Table 3.	Relative	energy	absorption	values	used	to define	the	40 year	degraded	condition	for
packages	with 125	°F max	imum fiberł	board te	empera	ature.					

Analysis	Maximum	Relative En	nergy	Relative E	Value Used in	
Zone	Zone	Absorption, Cane		Absorption	References 10	
	Temperature.	-			and 11	
		Parallel Perpendicular J		Parallel	Perpendicular	
120F	120 °F	100%	100%	100%	100%	100%
140F	123 °F					74%
145F	125 °F	86%	96%	85%	80%	67%
145F (B)	125 °F					60%
Saturated	<120 °F	NA NA		NA	NA	5%



Figure 1. Summary of CSR data for Viton GLT and Viton GLT-S O-rings. The solid symbols are actual times to reach the end-of-life criterion. The other symbols and trendlines are extrapolated estimates of the end-of-life criterion based on time-temperature superposition (TTS).



Figure 2. Summary of PCV fixture data for Viton GLT and Viton GLT-S –rings. The red symbols are failure points, the green symbols have not yet reached failure. The trendline is a lower bound to the failure points (GLT and GLT-S combined).



Figure 3. O-ring models showing temperature range of end-of-life data (solid lines) and extrapolated region (dashed lines). The temperature range for the oxygen consumption data is also identified and should provide confidence in the validity of the model extrapolations.



Figure 4. Fiberboard degradation zones and associated relative energy absorption values used in References 10, 11 calculations to define the 20 year degraded condition.





Figure 6. Reproduction of Figure A6 from Reference 11, showing extrapolation to estimate the 40 year degraded condition. Given the straight line fit with a logarithmic time scale, the decrease in relative energy absorption from 20 to 40 years is the same as the decrease from 10 to 20 years. Similar extrapolations were made for 125 °F oven and 125 °F 70 %RH environments, for both orientations and fiberboard materials.



Figure 7. Reproduction of Figure A13 from Reference 11 highlighting the degraded energy absorption value at 20 years for an environment of 125 °F 18 %RH. In this case, the contour line for 20 %RH is used to approximate an actual value of 18 %RH.



Figure 8. Relative energy absorption data and curve fits for softwood fiberboard, parallel orientation at 125 °F (oven and 70%RH), used in Reference 11. The middle line represents the expected behavior at 18%RH based on linear interpolation between the two curve fits.

Distribution

G. A. Abramczyk, 730-A R. J. Bayer, 705-K J. S. Bellamy, 730-A W. L. Daugherty, 773-A B. L. Garcia-Diaz, 999-2W T. W. Griffin, 705-K R. J. Grimm, 705-K E. R. Hackney, 703-H S. J. Hensel, 705-K J. M. Jordan, 705-K B. B. Kiflu, 705-K D. R. Leduc, 730-A P. L. Livengood, 705-K J. W. McEvoy, 707-C T. E. Skidmore, 730-A D. E. Welliver, 705-K K. E. Zeigler, 773-41A Document Control