USED FUEL DISPOSITION CAMPAIGN

Irradiation and Test Plan for Polymeric Materials for Cask Transportation and Storage

Fuel Cycle Research & Development

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1. Introduction

The bolted joint closure in the design of used nuclear fuel dry storage casks and dual-purpose storage and transportation casks includes lids, bolting, metallic seals, and polymeric seals. A lid, bolting, and metallic seal are used for the primary confinement for the cask, with a secondary lid and metallic seal configuration typically used for a secondary confinement seal. The polymeric seals cannot be used for primary confinement, but they can be used for secondary confinement and/or to aid in leak testing of the joint [1].

Polymeric material systems are also used in cask designs to provide neutron shielding [1].

Both radiation and thermal stressors can degrade the polymeric materials, leading to a loss of their intended function. Extended storage and transportation of the cask must consider materials aging and the impact to the safety functions provided by the materials systems. The bolted closure joint has been identified as a high priority component in the gap analysis of dry cask storage systems under extended storage and transportation [2].

This report describes the plan for irradiation and testing of polymeric material systems at conditions relevant to extended storage and transportation of casks for used nuclear fuel. The results of this irradiation and testing are expected to feed in to a generic Aging Management Program to be developed for the bolted closure joint.

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2. Purpose/Scope of Work:

The test plan outlined herein is intended to describe the irradiation and test parameters for evaluating and characterizing the aging behavior of polymeric components used in spent nuclear fuel (SNF) casks, particularly for extended storage periods beyond an initial license period of 40-60 years. Principally, the use of polymeric components in such designs is limited to elastomeric seals and neutron shielding materials.

Elastomeric seals are not used for primary confinement of SNF material but they do serve important functions during cask shipping and storage periods. Specifically, in at least some designs, elastomeric seals are used as auxiliary or secondary seals to provide leak test volumes for confinement verification tests in designs using metallic seals and bolted closures. Aging of the elastomeric seals due to oxidation, radiation exposure, and thermal degradation with service time is expected, leading to a reduction in their sealing function with the unmitigated consequence being a compromise of the seal. Replacement of the gasket would be the only remediation action at that point. The goal of this testing is to develop a technical basis for life prediction and characterization of such components.

Neutron shielding materials maintain neutron dose rates from spontaneous fission and (α, n) reactions below acceptable levels at the surface of the cask, and thus perform an important function in radiological hazard analysis and associated safety requirements. Similar to the polymeric materials in the gaskets, aging of the polymeric shield materials in the dry cask storage system is expected. The neutron shield materials should not creep or slump to an extent that impacts the shielding function [1].

Data on irradiation and thermal performance of polymeric gasket and shield material systems will be developed to strengthen the evaluation of their performance in casks under conditions of extended storage and transportation, and support development of an Aging Management Program for the bolted closure joint. The first task in this work is to provide refined radiation and thermal exposure profiles with storage time at the locations of the polymeric seals and neutron shielding materials. Test matrices with the materials, sample configuration, target irradiation/thermal/cover gas exposure conditions for sample exposure will be developed in the second task. Detailed testing and characterization activities would follow.

3. Cask Design and Service

The main features of a bolted closure cask design typically includes a monolithic body made of either a ductile cast iron or forged steel into which rods or sheets of a neutron-shielding polyethylene material is inserted. Two lids or a "double-lid" system are used with the metallic gaskets providing the double seal. Polymeric gaskets are adjacent to an external to each of the metallic seals.

The design configuration, seal geometry, distance and shielding parameters and other aspects will dictate actual radiation dose and thermal profiles at the material locations. The specific cask designs considered for initial test planning purposes are the NUHOMS 61BT and the CASTOR/V21 casks. These casks are selected to provide widely used designs at nominal service conditions (i.e. radiation dose rates and thermal profiles applicable to the elastomeric seals and neutron shielding materials).

3.1 Polymeric Components

3.1.1 Elastomeric Seals - Overview

In general, elastomers include many different types such as ethylene-propylene diene monomer (EPDM), FKM fluoroelastomer (Viton® or similar), FFKM/perfluoroelastomer (Kalrez® or similar), silicone, butyl, neoprene (polychloroprene), nitrile butadiene rubber (NBR, nitrile), styrene-butadiene rubber (SBR), fluorosilicone, polyurethane, acrylate and other types. Within each generic family of elastomer, a range of grades and properties are achieved and available depending on the specific chemistry and processing involved. For example, Viton® is not a single elastomer type but rather a family of grades with many similar as well as different properties. As with many polymeric materials, the final end-use elastomeric seal is a combination of base polymer, curatives, antioxidants, processing aids, fillers, reinforcement aids and other ingredients necessary to provide the final properties desired. Therefore, when dealing with such materials, it is important to identify which specific type, grade, manufacturer and compound is being used. The properties, including the aging response, of specific grades and compounds may vary.

As with most applications, the specific elastomer type and compound used should be dictated by the anticipated service conditions as well as the desired service life. Some elastomer types are inherently more resistant than others to aging, thermal degradation, oxidation, ionizing radiation, ozone, UV light and other environmental factors. Elastomer types such as EPDM, FKM (Viton or similar), FFKM (Kalrez or FKM) and silicone/fluorosilicone types are the most resistant to general aging. Butyl rubber, polyurethane and neoprene types are relatively resistant to aging but each has various sensitivities that tend to rule out their selection and use in critical applications such as SNF casks. Neoprene (polychloroprene) is also highly chlorinated, which is not desirable from corrosion potential viewpoint, particularly if in contact with stainless steel. Nitrile/NBR elastomer, SBR and other types are among the least resistant to aging, oxidation, ozone and other environmental factors. Polyurethane elastomers tend to age relatively well and are highly resistant to outdoor weathering, but are sensitive to humidity/hydrolysis effects and have limited heat resistance. Silicones are highly resistant to thermal aging, ozone and UV degradation but tend to have relatively high permeability and only moderate mechanical properties.

In spent fuel casks, EPDM, FKM and possibly butyl rubber seals tend to be the most commonly specified elastomer types, with EPDM and FKM compounds being more commonly specified due to their relative temperature ranges as well as resistance to ionizing radiation, ozone and thermo-oxidation. Silicones may be used for secondary purposes, being highly resistant to aging effects, but permeability behavior can be limiting. Butyl rubber generally exhibits the lowest resistance to ionizing radiation, but may be acceptable if dose rates are sufficiently low. EPDM compounds are generally useful in the temperature range of -60°F to 250-300°F, whereas FKM elastomers are generally useful in the range of -20°F to 400°F, depending on the specific grade and time at temperature. Some FKM grades (GLT types) may be useful to lower temperatures (-40°F) depending on the specific compound and joint design.

It is important to note that general temperature ranges are for design purposes only and should not be used for life prediction purposes. The service life of a given seal at the upper end of the allowable temperature range will be much shorter than at lower temperatures.

3.1.2 Neutron Shielding Materials - Overview

Typical polymeric materials used for neutron shielding include polyethylene, polypropylene, and borated polymer (e.g. BISCO®). These polymeric material systems are subject to the same intrinsic irradiation degradation phenomena as the gasket materials such as through chain scission and cross-linking, and thermal degradation phenomena such as oxidation. A primary concern for shielding materials is reconfiguration by slumping or granulation.

3.2 Service Conditions

Of the anticipated service conditions within SNF cask designs, the parameters considered the most important for the aging of elastomeric seals and neutron shielding materials are:

- Temperature (peak temperature and thermal profile with time)
- Radiation (total dose, dose rate,, dose rate with time)
- Ozone/oxidation (with air contact to cause diffusion-limited oxidation effects)
- Mechanical stress (creep/relaxation)

For aging/life prediction purposes, it is important to determine and model these exposure parameters and their effects as accurately as possible. In experimental design, aging factors should be duplicated as closely as possible, otherwise false or overly optimistic results may be obtained. This can occur in both thermal and radiation aging schemes, principally due to diffusion-limited oxidation (DLO) effects as well as dose rate effects. There is no substitute for real-time aging at realistic (or at least bounding) service conditions, so accelerated-aging tests must account for as many factors as possible that can contribute to degradation.

For SNF casks, references often quote radiation field/neutron flux rates for a typical DCSS for extended storage such as:

gamma field of ~10^5 R/hr and a neutron flux ($E_n > 1$ MeV) of 10^4-10^6 n/cm^2-s [3-4]

However, such dose rates are not necessarily applicable to specific components within a given design. That is, dose rates should be determined for the specific materials and cask geometries involved, especially in consideration of the sensitivity to dose rate as it is important co-parameter in the degradation phenomenon of DLO. The total absorbed radiation dose (rad (R) or Gray, 1 Gy = 100 rad) is thus only one exposure parameter to consider.

As an example, initial SRNL estimates for the dose rates to the O-rings in the lid design of a a fully loaded NUHOMS 61BT cask containing 40GWD burnup @ 4 years cooling are between 50-80 mrem/hr. Assuming 1 rem = 1 rad for general discussion and that the dose rate is constant over time, the O-rings in this particular cask would see a maximum dose rate of 0.08 rad/hr x 24 hr/day x 365 days/yr = 701 rad/yr or 7 Gy/yr.

At ~700 rad/yr, the O-rings would see a total absorbed dose of 3.5E+04 rad at 50 years (for reference Teflon PTFE is likely only slightly affected at this dose), 7E+04 rad at 100 years and a dose of 2.1E+05 rad at 300 years. These time periods (50, 100, 300 years) were arbitrarily selected for extended storage discussion purposes, and are not absolute or limiting periods. Using a 1E+06 rad (1 Mrad) damage threshold (not a failure point), typically quoted in references for elastomer degradation, it would take well over 300 years to reach this value (approximately 1430 years), ignoring dose rate and oxidation effects.

However, it is well-known that most polymers are sensitive to the dose rate and that the significance of the dose rate effect typically depends on the presence of oxygen and the rate of oxidation (a diffusion-limited process). Assuming an arbitrary dose rate factor of 100, the O-rings could theoretically see an “equivalent” dose of 3.5E+06 rad at 50 yrs, 7E+06 rad at 100 yrs, and 2.1E+07 rad at 300 yrs. Alternatively, the level of damage at any given time period could be 100X more severe than anticipated at very high dose rates. In this case, the elastomeric seals might see threshold changes at an effective dose of 1 Mrad or within 14.3 years, assuming adose rate factor of 100. Therefore, while elastomeric seals are expected to degrade and are not credited for confinement in SNF cask designs, the ability to predict seal life is complicated by both radiation and thermal aspects, with dose rate effects and diffusion-limited oxidation likely playing a significant role.

As a comparison point, the dose rate above (0.08 rad/hr) is far less than the bounding rate of 2 rad/hr estimated for the Viton® GLT/GLT-S O-rings in the 9975 shipping packages used for shipment of Pu-bearing materials. A number of these packages are now being used for interim storage at the SRS. At 2 rad/hr, the 9975 containment seals would see 1.75E+04 rad/year or 8.76E+05 rad in 50 years. Assuming no significant dose rate effects at this dose rate, the 9975 seals will not likely see threshold radiation damage until at approximately 60 years (1 Mrad). The seals in most packages also see dose rates far less than 2 rad/hr. If dose rate effects are significant, damage could occur in shorter time. However, thermal degradation has been considered more significant for these seals than radiation damage.

Therefore, for SNF cask elastomeric seals, it is likely that degradation will be dominated by thermo-oxidative degradation rather than radiation damage alone, unless specific designs impose radiation dose rates higher than discussed above

4. Seal Component Testing Considerations

For service life prediction, the critical properties of a given component and the failure criteria for that component must be defined. Often the failure criterion is a performance parameter (i.e. leakage rate for a seal) rather than a material property. Further complicating the matter is the fact that the correlation between performance (i.e. leakage) and a relevant property (compression set, compression stress-relaxation) may not be known, as performance can often be influenced by many aspects specific to a particular design.

As an example, the leakage behavior of an elastomeric seal depends on several design-related factors, including dimensional parameters, surface finish, differential pressure, ID stretch and other aspects. In one design, a given material may readily fail at a certain damage point, but in another design, the same material with the same level of damage or degradation may still be quite functional. The ideal case is when the material behavior can be predicted and strongly correlated to functional performance.

For elastomeric seals, the functional failure point is often unknown. For highly static environments, the seal can likely tolerate a much greater amount of degradation (i.e. relaxation) compared to a dynamic application. It may be possible that the seal can essentially lose all measureable sealing force and still maintain confinement under certain conditions. Therefore it is often necessary to establish an arbitrary failure criterion to allow development of an aging or life prediction model, in combination with an effort to determine the level of degradation that can be imposed before failure or unacceptable performance occurs.

For elastomeric seals in a highly static environment, an arbitrary failure criterion of 90% loss in sealing force (0.10 F/F_o) has been used in a number of studies at Sandia and SRNL for critical components (nuclear weapon seals, radioactive material packaging seals). This is considered a reasonable measure of mechanical lifetime in a reasonable or typical seal design, leaving 10% of initial sealing force as a level of margin against moderate changes in the environment (thermal swings, vibration, etc.).

Therefore, 90% loss in sealing force is proposed as the failure criteria for elastomeric seals in SNF casks and other sealing applications of interest, unless alternative values are known to well-correlate with unacceptable performance. Alternative failure criteria or end-of-life criteria may be proposed if already established or if functional testing shows it is more appropriate.

Based on the previous discussion that radiation dose rates for the elastomeric seals in SNF casks may not be that significant, radiation exposure to seal samples is not currently recommended. However, if such effects are of mutual interest, the following testing/characterization are suggested:

- Accelerated aging of irradiated and non-irradiated seal materials at 4 elevated temperatures. Irradiated samples would be exposed at 3 different dose rates using a low, medium and high dose rate approach to evaluate the potential for dose rate effects. Irradiation dose rates proposed would be approximately 1 krad/hr, 10 krad/hr and 100 krad/hr. Target doses of 0.1 Mrad, 1 Mrad and 10 Mrad are proposed. Irradiation times would be determined accordingly. The 10 Mrad dose would require the longest irradiation time of approximately 417 days or 1.14 years. These dose rates may not represent actual dose rates in service, but are intended for purposes of evaluating dose rate effects. As a minimum, they are more realistic than very high dose rates often used for nuclear component qualification (1 Mrad/hr). These dose rates can be adjusted to fit specific dose rates in service if later determined to be more appropriate.
- CSR jigs cannot likely be irradiated over long periods of time and heated within the irradiation chamber. The feasibility of this approach has not been demonstrated. Shawbury-Wallace type jigs are relatively bulky and would limit the number of jigs that could be irradiated in a given exposure period. Alternative CSR jig types are currently being evaluated to improve this aspect. A proposed alternative method is to place samples into a smaller compression device to simulate the same degree of compression during irradiation. Periodically, the samples would be removed from the irradiation chamber and from the compression device and placed into a CSR jig (or similar device) at the same degree of compression temporarily and the sealing force would be determined. A noted difficulty with this approach is that the sealing force can significantly vary with the degree of compression, so it would be critical to obtain the same degree of compression imposed during irradiation.
- The dimensions of the sample would also be measured at the time of removal from the compression jig to determine compression set. This value would be determined at a fixed period of time (ex. 30 minutes) to allow direct comparison. Recovery dimensions will likely change with time after removal, so measurements should be taken at the exact same time period for best comparison. The sample would be returned to the compression jig and placed back into the irradiation chamber. The cumulative dose at the time of removal and measurement would be recorded.
- Compression set is a measure of dimensional recovery only, not a direct measurement of sealing force, but it is often used to evaluate the comparative performance of elastomeric seals.As an alternative to performing CSR measurements on irradiated samples, CSR jigs would only be used for non-irradiated samples that were thermally aged. For each temperature (4), 2 samples at each condition would be tested for replication. Aging temperatures to be selected upon obtaining relevant thermal profile data. Typical aging temperatures might range from 175-350F, depending on the elastomer involved. Samples would be compressed 25% and periodically removed from the aging ovens for sealing force measurement.
- Additional non-compressed samples would also be thermally aged and irradiated at the defined dose rates to target doses and subjected to other characterization techniques (hardness, density, tensile/elongation, FT-IR spectroscopy, DSC analysis). Changes in these parameters would be tracked and correlated with CSR and compression set behavior.

- Changes in properties as a function of dose rate and thermal aging (non-irradiated only) would be monitored and used to develop a thermal/dose rate-aging model using time-temperature dose rate superposition principles.
- Alternatively, if radiation dose rates for elastomeric seals in SNF casks are determined to be insignificant relative to thermo-oxidative aging (suspected), only the non-irradiated samples would be subjected to thermal aging and described characterizations. Irradiations would not be performed.

5. Tasks

1. Evaluation of the service conditions of dose (and dose rate) and temperature for the NUHOMS 61BT and CASTOR/V21 loaded casks for extended service

This task will be performed through utilization of currently available literature data and industry standard neutronics and thermal analysis codes. The task will involve a review of the available literature regarding the expected radiation and thermal service environments experienced by polymeric seals during used nuclear fuel storage scenarios. Literature data will be supplemented as necessary with simplified neutronics (depletion and radiation transport) and thermal analysis models to establish a reference extended service history relative to radiation and thermal exposure to the polymers over the projected extended service life of the two cask designs.

2. Exposure testing (gamma/thermal/gas) of polymeric materials

The seal material testing under this task will be performed using the Shepard 484 irradiator facility using seal material samples in a small version CSR jig.

For neutron shielding materials (i.e. polyethylene of specific variety), the following properties would be evaluated as a function of radiation/thermal aging. Sample geometry and quantity to be determined for each characterization/analytical technique.

- Dimensional stability
- Tensile strength/elongation
- Polymer density
- Degree of crystallinity
- Cross-link density
    - gel content per ASTM D2765
    - swell ratio, crosslink density per ASTM F2214
    - transvinylene yield per ASTM F2381
    - oxidation index and induction time (OIT) per ASTM F2102
    - ASTM melt temperature (related to above parameters)

The effects of radiation exposure and/or thermal aging would be further characterized by the following techniques:

- X-ray diffraction (degree of crystallinity),
- FT-IR spectroscopy (polymer/chemical changes, carbonyl peaks)

Specifically, the peaks at 720-730 cm^{-1} indicate C-H rocking, characteristic of polyethylene.

Peaks at 1460 cm^{-1} indicate C-H scissioning with peaks at 1715 cm^{-1} typical of carbonyl stretching. Peaks at 2850 and 2920 cm^{-1} indicate C-H stretching, with peaks at 3400 cm^{-1} typical of O-H stretching.

- FT-Raman spectroscopy (complementary to FTIR),
- Differential Scanning Calorimetry (thermal transitions)

The irradiation/thermal exposure test matrices and test/post-test parameters to be measured under Task 2 will be prepared following the completion of Task 1. Records of the full test description and controls (e.g. M&TE), and test results will be recorded in a laboratory notebook.

6. References

1 ASTM C1562-03, Standard Guide for Evaluation of Materials Used in Extended Service of Interim Spent Nuclear Fuel Dry Storage Systems," American Society for Testing and Materials, 2003.

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