Aging of elastomer seals for nuclear waste containers – Methods and lifetime prediction

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Background/Motivation

Role of BAM

- BAM is involved in the current licensing procedures for storage (and transport) casks for nuclear waste
- Extending interim storage of radioactive waste containers will be necessary due to delays in the final repository projects in Germany
- Safety of casks will have to be evaluated with regard to extended storage periods – can the components retain their functionality for several more decades?
- BAM has started several test programs for
  - evaluating long-term safety of components
  - developing suitable methods for accelerated aging, lifetime prediction and modelling
- With focus on
  - metal and elastomer seals
  - polyethylene neutron shielding materials
  - brittle failure of spent fuel claddings

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Elastomer seals are used as main seals or auxiliary seals depending on the cask type.
Complex lid system of the casks.
Risk of exposure when opened.
Seals cannot be exchanged easily.
They need to maintain leak tightness for extended storage periods (will be more than 40 years in Germany).

Aging investigations and lifetime predictions are needed.
Aging program
Materials – Elastomers for sealing applications

**HNBR**
- Hydrogenated Acrylonitrile Butadiene rubber
- Oil resistant

**EPDM**
- Ethylene Propylene Diene rubber
- Low Tg, water resistant

**FKM**
- Fluorocarbon rubber
- High chemical and heat resistance
Aging program – O-rings
uncompressed – compressed – in flanges

Uncompressed on punched sheets on a rack

Compressed by 25% between plates

Compressed in flanges for leakage rate measurements

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Aging program
Sheets (2 mm) and standard specimen
Aging program
Times & Temperatures

Start: May 2014

Ageing times:
1 d  3 d  10 d  30 d  100 d  0.5 a  1 a  1.5 a  2 a  2.5 a  3 a  3.7 a  4.3 a  5 a

Ageing temperatures:
150°C, 125°C, 100°C, 75°C (additionally for compression set: 60°C, 23°C)

EPDM O-Ring after ageing for 1 year at 150°C
Aging program
Analysis

Material properties
• Tensile Tests
• Hardness
• Density
• DMA
• Mass loss
• TGA
• Relaxation and Recovery behaviour
• IR spectroscopy
• Kinetic analysis
• ...

Seal properties
• Compression Set
• Compression Stress Relaxation
• Leakage rate

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Aging program

Relevant questions/aims

- Analysis of material property changes during aging and investigation of the respective degradation processes
- Determination of a suitable end-of-lifetime criterion for seals
- Reliable lifetime prediction

HNBR O-ring after 1 year at 150°C
Results
EPDM (sheets)

- Hardness and density increase → crosslinking and/or oxygen insertion through chain scission (increase of polarity and intermolecular attraction, heavy O-atoms)
- Decrease of both elongation at break and tensile strength
  - Both crosslinking and chain scissions are relevant degradation processes
Method
Compression Set (CS)

- Samples are aged compressed by 25%
- After release, some time is allowed for recovery
- CS is calculated from remaining deformation

\[
CS = 100\% \frac{(h_0 - h_2)}{(h_0 - h_1)}
\]

- \( CS = 100\% \) \(\Rightarrow\) no recovery
- \( CS = 0\% \) \(\Rightarrow\) full recovery
**Method**

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**Compression set after 101 days of ageing**

- **HNBR**
  - 75 °C: 33%
  - 100 °C: 59%
  - 125 °C: 82%
  - 150 °C: 80%

- **EPDM**
  - 75 °C: 13%
  - 100 °C: 23%
  - 125 °C: 56%
  - 150 °C: 94%

- **FKM**
  - 75 °C: 10%
  - 100 °C: 10%
  - 125 °C: 19%
  - 150 °C: 29%
Method

Compression Set (CS)

- Samples are aged compressed by 25%
- After release, some time is allowed for recovery
- CS is calculated from remaining deformation

However, CS values depend on recovery time after release:
- 30 min according to standards ASTM D395 and DIN ISO 815-1
- ~ 5 days in previous experiments
- after tempering (1 d at 100°C) to be close to the equilibrium value

For the application, short times after release are often more relevant, but for comparing material degradation, equilibrium values are more meaningful
Results
EPDM – CS

Bad data quality due to uncertainty of release time

Regular data

Lower values, especially for less-aged samples
Results
EPDM – CS

after 30 min

after 5 days

after tempering

Bad data quality due to uncertainty of release time

Regular data

- Equilibrium values
- No time-dependence
- More reliable data
Results

EPDM

- CS increases much faster than e.g. hardness and density
- Explanation: Hardness/density shows only the net effect of the influence of crosslinking and chain scission, while CS increases additively through both reaction types

➢ Property changes are measurable much faster
• As compression set is more sensitive to degradation and related to the sealing function, it is chosen as the property for lifetime prediction using TTS
• TTS allows shifting data measured at higher temperatures to lower temperatures
• Lifetime at 75°C is 450 times longer than at 150°C
• For lifetime predictions, we need an end-of-lifetime criterion
Results

Determination of end-of-lifetime criterion

- End of the lifetime should be correlated to leakage as the point of seal failure.
- Under static conditions, the leakage rate hardly changes and O-rings can remain leak tight down to almost zero sealing force.
- A modified, more demanding leakage test involving a fast small partial decompression of the seal was developed.
Results

Determination of end-of-lifetime criterion

- End of the lifetime should be correlated to leakage as the point of seal failure
- Under static conditions, the leakage rate hardly changes and O-rings can remain leak tight down to almost zero sealing force
  - A modified, more demanding leakage test involving a fast small partial decompression of the seal was developed

23% compression ($\Delta = 0.2 \text{ mm}$)
Results

Determination of lifetime criterion for EPDM O-Ring

- Under static conditions, the seal remained leak tight for up to 101 d at 150°C
- During the fast partial decompression, the seal remained leak tight for up to 70 d, but became untight after 101 d ageing time at 150°C during the partial decompression
  - Seal lifetime lies somewhere between 70 und 101 d
- During a second experiment, this range could be narrowed to 70-80 d
- The lifetime is conservatively assumed as 70 d
Results

Lifetime of EPDM O-Ring and general criterion

- Using the shift factors from TTS, the lifetime can be calculated for the other temperatures

- 70 d at 150°C corresponds to 84% CS (in equilibrium)

- An EPDM O-ring aged at 125°C remained leaktight in the leakage test with the partial decompression for up to 278 d

- This corresponds to 86% CS

- 80-85% CS could be a general end-of-lifetime criterion (for non-lubricated seals), however, this has to be verified for other materials

<table>
<thead>
<tr>
<th>Temp.</th>
<th>a_T</th>
<th>Lifetime</th>
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<tr>
<td>150°C</td>
<td>1</td>
<td>70 d</td>
</tr>
<tr>
<td>125°C</td>
<td>5</td>
<td>350 d</td>
</tr>
<tr>
<td>100°C</td>
<td>45</td>
<td>8.6 a</td>
</tr>
<tr>
<td>75°C</td>
<td>450</td>
<td>86 a</td>
</tr>
</tbody>
</table>
Results

HNBR (sheets)

- Hardness and density increase
- Decrease of elongation at break, increase of tensile strength
  - Embrittlement due to dominant crosslinking reactions
Results

HNBR (O-rings) – CS

- Clearly distorted results for 150°C due to pronounced DLO effects
Results

HNBR (O-rings) – DLO effects

- Clearly distorted results for 150°C due to pronounced DLO effects
- Slight DLO effects at 125°C
- No DLO effects at 100°C (and below)
Results
HNBR (O-rings) – CS - TTS

- No superposition for 150°C values with pronounced DLO effects
- Exclusion of 150°C and 125°C from fit for Arrhenius line
- 85% CS is reached after 585 d/1.6 a at 100°C
- Using the shift factors, this corresponds to 10.7 a and 42.7 a at 75°C and 60°C
Results
FKM (sheets)

- Hardly any changes visible with these methods due to the high stability of FKM
Results
FKM (O-rings) – CS - TTS

- Stronger degradation visible for CS, perhaps due to cage effect
- Highest reached CS after 5 years is 72%
- Using TTS/shift factors, 72% would be reached after 600 years at 75°C
- Note: $E_A$ of FKM is the lowest, but lifetime is the highest
  - $E_A$ is a measure for the spread between the temperatures, but not for stability
Conclusions

• Crosslinking and chain scission are relevant degradation mechanisms for EPDM, for HNBR it is mainly crosslinking
• DLO effects distort aging data of HNBR at 150°C and (less) at 125°C
• Compression set shows more pronounced degradation than other methods
• Additionally, CS is related to the sealing force/function
  ➢ Lifetime predictions should be performed using (equilibrium) CS data
• Time-temperature superposition is a suitable method for extrapolation
  ➢ End-of-lifetime criterion was determined using a modified leakage test involving a small fast partial decompression of the seal
• Using this test, EPDM seals remained fully functional for up to 70 d at 150°C and 278 d at 125°C (corresponds to 84% and 86% CS)
• Lifetime at 75°C was about 86 years (EPDM), 11 years (HNBR) and 600 years (FKM, for 72% CS)
• Activation energy is not a direct indicator of the oxidative stability
Publications


Thank you for your attention!