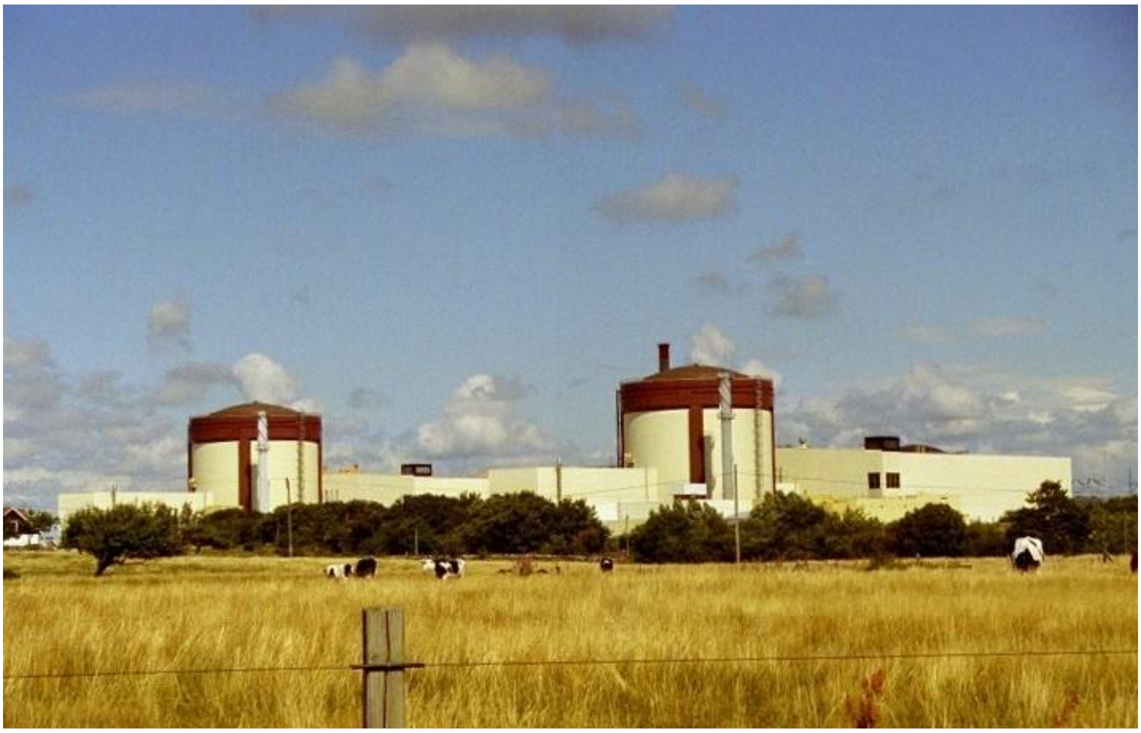
MATERIALS AND PRODUCTION
POLYMERS, FIBERS AND COMPOSITES



Improved estimation of lifetimes for polymer components in NPPs

Anna Bondeson, David Kiefer

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Abstract

Improved estimation of lifetimes for polymer components in NPPs

The SAMPO Task 1.1 project had the aim to investigate the lifetime of chosen polymer components from Swedish and Finnish nuclear power plant (NPP)using traditional mechanical methods. Workshops with each NPP were held in order to identify relevant components for the project. Suitable materials were then chosen based on availability after service in the NPPs and test programs were set up for each component. Where possible reference components were obtained for estimation of the total expected lifetime. The properties of the components received from NPPS were compared with the lifetime estimation. Based on this comparison for two components, i.e., EPDM O-rings and neoprene membranes for pumps, a longer service time may be considered. Instead, for CPE cables the lifetime estimation resulted in results contrary to the service time of the cables. For a fourth component, an EPDM joint seal, a complete lifetime estimation could not be performed due to missing reference material.

Key words: EPDM O-ring, membrane, CPE cable, joint seal, lifetime estimation,

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Content

1 Background and aim

This task makes use of the results and analyses from the completed COMRADE project when suggesting useful and relevant acceptance criteria and safety margins. Results from laboratory aging tests and evaluations have been compared to materials obtained from Nuclear Powerplants (NPPs). Improvements to both test methods and aging environments are required to set acceptance criteria as well as safety margins. Some polymer components are extremely complicated or impossible to change in operating NPPs and thus their endurance during the whole lifetime of a plant is essential. To be able to make reliable lifetime estimations of components, information on material properties on both materials that have been in use at NPPs, and artificially aged materials is extremely valuable. The question of residual lifetime assessment of polymer components in service is often raised. Without sufficient material data and service history of the materials, i.e., temperature, radiation dose, oxygen, and moisture content in the atmosphere, this is almost impossible to predict. By studying materials from NPPs available from outages and decommissioned plants that have been in service for a long time, we have a unique opportunity to develop material lifetime prediction methods with correlation to materials from real service environment and long-term use.

The aim of this task is trying to identify critical components and to investigate the possibilities to obtain such components from plants under decommissioning or during maintenance, including material data. An obstacle with getting interesting components from decommissioning of NPPs, such as Ringhals R2 which were closed December 31, 2019, and Ringhals R1 which were closed December 31, 2020, is that it will not be possible to obtain the materials for several years because the fuel will not be removed from the reactor immediately.

It has proven that it is difficult to get clearance of materials used in the NPPs and it is sometimes also difficult to achieve sufficient amounts of materials to perform relevant tests, therefore a full year project including workshops together with the NPPs was planned for this task to be able to discuss what components to choose. One group of materials mentioned in the running project are cables. Moreover, replaced materials from outages will be considered. In COMRADE many samples were too small and not in sufficient amount to be analysed. Therefore, artificially aged materials will be investigated in parallel. This work package will be run in collaboration with micro-calorimetry (MC) tests in order to calculate activation energies and verify the MC technology.

2 Project plan

The work package task will follow the plan below:

1) Identification of critical components in all plants

2) Possibility to extraction the components from plants

3) Estimating their residual and total lifetime.

4) If possible, order samples made from the same material from the supplier

In year 1-2 workshops with NPPs were arranged. Based on discussions in the workshops; a selection of interesting materials from closed NPPs and/or from outages was be made and suitable reference materials will be found. And there after a preliminary test plan for year 2-4 was made.

3 Methods

The workshops that were held at Ringhals NPP and Forsmark NPP have been the main method to identify critical and interesting materials for further investigating. In a first stage focus was set on Ringhals because of their upcoming decommission of two reactors but during the decommissioning time it will be difficult to get out materials because critical components will still be in use in the reactors for several years to come.

Discussion of materials of special interest for the project were also held at the SAMPO workshop at Fortum, Espoo in November 27-28th 2019.

For investigating residual lifetime of the chosen and obtained materials some testing has been initiated. This initial investigation of the materials has included testing of hardness, tensile strength, and elongation at break.

It has proven that it is difficult to decide what components to be tested in one single workshop and therefore regular digital meeting were planned and held with Ringhals, Forsmark and OKG during the second part of 2021 and will be continued during 2022. The selection will be based on the results from the workshops. By having a continuous dialogue there is time to plan for collection of relevant and suitable components during the annual revisions. It is also important to get enough material to perform accelerated ageing tests.

Testing is performed by using traditional mechanical methods such as tensile testing, compression set and hardness. In addition, microcalorimetry (MC) is used as an attempt to find a sensitive method to analyse status of degradation in a material. The MC method allow use of small material quantities and analyses chemical reactions in samples which either evolve energy, like exothermal oxidative degradation reactions or endothermic reactions which consumes energy.

4 Results and discussion

4.1 Workshops with NPPs

Workshops have been held at Ringhals NPP (29 Oct 2019), at the seminar days at Fortum, Espoo (27-28 Nov 2019) and online with Forsmark NPP (21 Sept 2020).

Summary of comments on interesting materials and other inputs from all workshops:

- Cables
    - New cables from Nexans at Ringhals
        - There is not much information about the material and long-term properties besides the supplier's certification, consisting of polyolefins.
        - Indenter measurements work poorly for these cables: alternative method?
    - PVC cables from the containment used for a long time may be interesting to check, however, most PVC cables are exchanged to other material.
- Valve membranes
    - replaced relatively often and there are the possibilities to increase intervals
    - there are materials of the same type with several different exchange intervals to test on
    - May be more interesting than O-rings as it is more critical in case there is leakage.
    - Previous tests have been done with accelerated aging on natural rubber membranes from Ringhals this can be used for comparing used membranes. Tensile tests are also made on a membrane used for 12 years, which showed that it was a bit more "aged" than expected.
    - The reinforcement is the weakest part of the membranes, this could be investigated more
        - What kind of reinforcement is sensitive?
- Test of LOCA or other accident simulation on replaced materials, as well as on accelerated aged material.
- Cable penetrations
    - There is a variant consisting of some kind of joint sealant (goo) that could be sensitive to a blast, adhesion might be tested on this.
    - Brattbergare is already under investigation.
- Joint mass between concrete elements (e.g., between ceiling and wall)
    - Much of the material has been changed recently, and this has already been investigated.

- Seal between joists
    - Both TVO and Forsmark have some test coupons of joist seal which were installed on at the same time as the actual sea for test purpose. The TVO material is a reinforced EPDM and the Forsmark material is chloroprene.

- Dome seals in highly radiated environment (Forsmark) made in Shieldseal 663 from James Walker
    - These seals are changed every year
    - Probably not possible to get clearance to take out the material from the NPP
    - Shieldseal 663 is similar to the EPDM designated LR9444 provided by James Walker for the COMRADE project

4.2 Selected materials for testing

EPDM O-rings were selected as a special point for interest, as these materials are easy to obtain and may be compared to the tested materials for verifying results in COMRADE WP1 and SAMPO WP1.3. They are common in the NPPs and are regularly replaced. But due to mall sample size many O-rings need to be collected to get a statistically relevant data set. We received several EPDM-O-rings (5.0x246) after their service life at Ringhals and reference O-rings of the same type.

Neoprene membranes from Ringhals NPP: Ringhals has collected membranes from earlier revisions and the collection contains several membranes of similar type and of similar conditions and time in use.
- Outtake was made in September 2018
- They have been in the plant for 8 years (which is maintenance interval)
- There is membranes of three dimensions 40, 19 and 17.5 cm in diameter

Reinforced EPDM seal between structure joists from TVO
- Installed in 2005, planned lifetime until 2025
- Exposure temperature 45 °C, during power operation in nitrogen atmosphere, after outage it has been stored in air
- Installed in L-shape
- Should withstand LOCA, the LOCA profile would be some time at 2,4 bar and 95°C followed by some time at 3,7 bar and 170°C
Only a small amount of material and no reference material was available for analysis.

Cables with CPE (Chlorinated Polyethylene) jacket and EPR (Ethylene propylene rubber) isolation were received from Forsmark NPP. The cables were in service for about 30 years at the NPP. A reference cable of similar type was procured.

4.3 Test program and methods

EPDM O-rings

- Compression set (120, 140 °C)
- Stress-strain characteristic in compression (90, 120, 140 °C)
- Tensile properties (aging at 120 and 140°C)
- Hardness (aging at 120 and 140°C)
- LOCA test were excluded in year 3 of the project due to missing relevance for the component

Neoprene membranes

- Tensile properties (aged at 70, 90, 110 °C)
- Hardness (aged at 70, 90, 110 °C)
- LOCA test were excluded in year 3 of the project due to missing relevance for the component

EPDM joist seal

- Tensile properties: the material from TVO was aged at 120 °C for 45 days
- Due to the small amount of material no further testing could be performed.

CPE cables

- Tensile properties (aged at 90, 100, 110 °C and in oil)
- Hardness (aged at 90, 100, 110 °C and in oil)

Test methods and specimen preparation

Reinforced rubber materials (membranes and joist seal) were split to remove the reinforcing material and specimen were punched from the resulting rubber sheets.

Tensile testing was made according to ISO 37 with type 2 dumbbell on a Zwick Z1 tensile tester at a rate of 500mm/min and with a clip-on extensometer.

The hardness was measured according to ISO 48-2 on a Bareiss Digitest Hardness Tester equipped with an IRHD-m measuring device.

Compression set was measured according to ISO 815 with type B cylindrical test pieces using 25% compression of the original thickness. Specimen thickness was measured using a micrometre gauge.

Stress-strain characteristic in compression (stress relaxation) was performed according to ISO 3384 with O-rings or same specimens as were used for compression set.

4.4 Results and discussion

EPDM O-rings

Several EPDM O-rings after service as well as new reference O-rings were received from Ringhals. The exact conditions during their service life are not known. It is assumed that the O-rings are subject to moderate temperatures.

Figure 1. O-rings delivered from Ringhals NPP.

The overall lifetime was evaluated by measuring the stress relaxation under compression at several temperatures (Figure 2). A common end-of-life criteria for compression set is when F/F_0 reaches 0.5. For aging at 140 and 150 °C this value is reached after ~1000 and ~600 hours, respectively. Instead, for 90 and 120 °C the drop of the initial force progresses significantly slower, and the experiments were terminated after 140 days. Time-temperature superposition fitting of the stress relaxation curves allowed us to extract an activation energy of ~98.1 kJ/mol. Extrapolation of the time required to reach a stress relaxation of 0.5 at 25 °C yields an extremely long theoretical lifetime. This indicates a relatively high quality of the EPDM rubber.

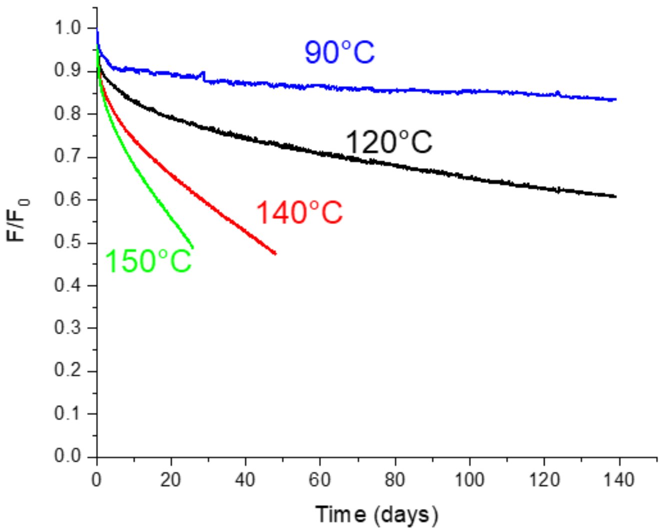

Figure 2. Stress relaxation under compression for O-rings from Ringhals at 90, 120, 140 and 150 °C.

The compression set and hardness of reference O-rings was measured for samples aged at 120 and 140 °C (Figure 3). The compression set of the samples at 120 °C increased from an initial ~20% after 9 days to ~50% after 200 days. Instead, aging at 140 °C increased from ~37% to ~90% after only 100 days. The m-IRHD hardness increased for the same time periods from ~80 to ~85 and ~90 for aging at 120 and 140 °C, respectively. For O-rings a compression set of 80% is often used as end-of-life criterium, which is reached after about 80 days aging at 120 °C.

Moreover, the tensile properties of the O-rings were measured. O-rings had an initial elongation at break of 80%, which decreased to ~20% after aging for just above 100 days at 140 °C. Instead, the elongation at break decreased to ~50 % for after aging for 200 days at 120 °C. For O-rings tensile stress is usually not very high as their compression properties are more relevant for their application.

Both the hardness and elongation at break was measured for four O-rings received from Ringhals after their service life. The results were compared with those O-rings heat aged at 120 and 140°C. All four O-rings from Ringhals have a similar hardness as unaged O-rings which may indicate that they are hardly affected by their service life. This finding correlates very well with the extrapolation of the theoretical lifetime indicating a good quality of the O-ring. Instead, the elongation at break of the O-rings from Ringhals is spread between 60 and 90 % with large error bars. However, elongation at break is usually less relevant in the context of O-rings and no further conclusions may be drawn.

Overall, based on the results it may be possible to increase the service time for the O-rings. However, further characterization and more specific environmental data are necessary to provide a more precise answer to whether longer service times may be suitable.

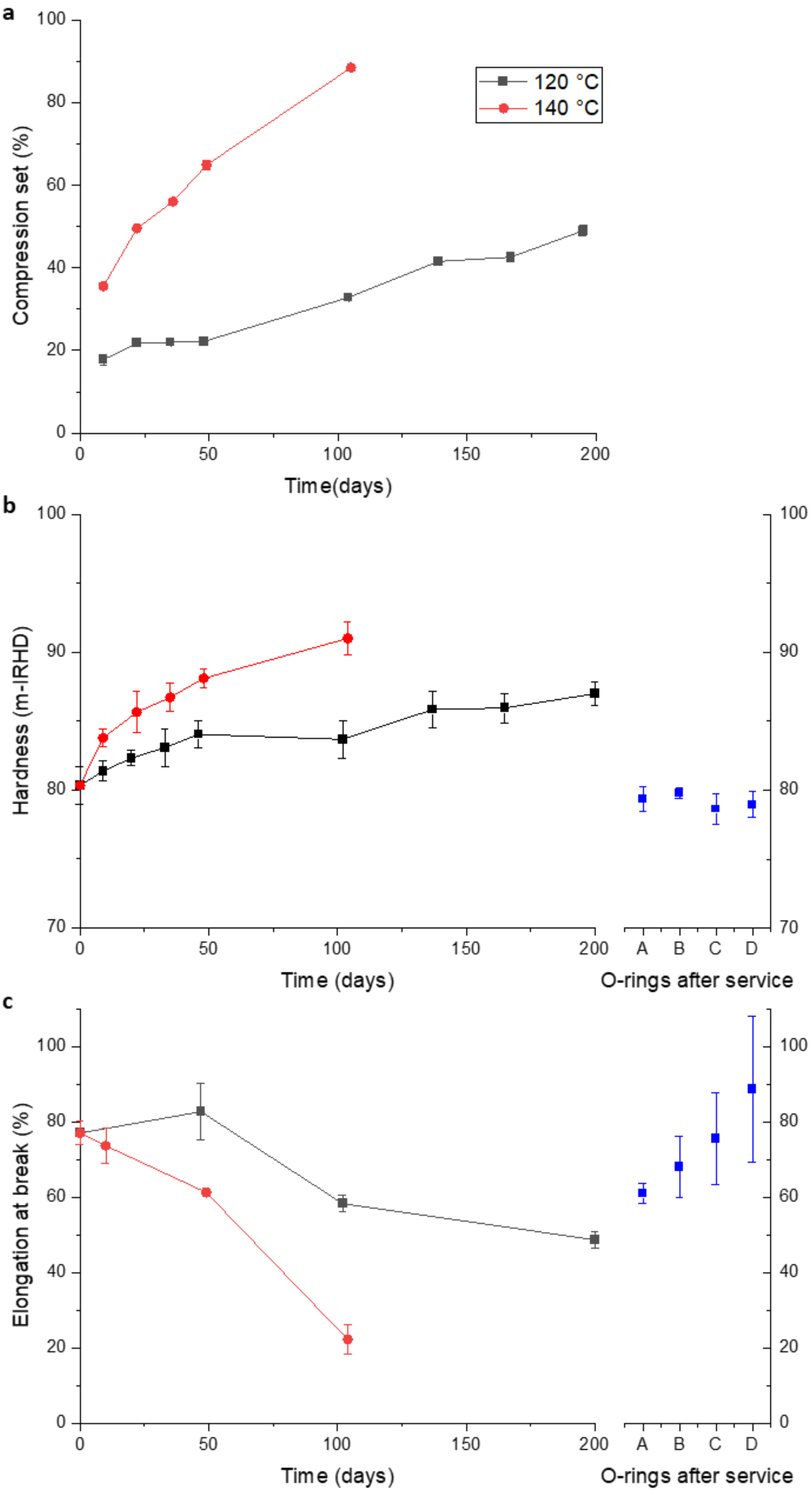

Figure 3. Compression set (a), hardness (b) and elongation at break (c) of O-rings aged at 120 and 140 °C and hardness and elongation at break of O-rings after service at Ringhals NPP. (Lines are guides to the eye.)

Neoprene membranes

Several neoprene membranes were received from outtakes at Ringhals NPP. All membranes were in service for 8 years exposed to air at ambient, but the exact service conditions for each for individual sample is unknown. Two types of membranes with diameters 17.5 and 19.0 cm were investigated. Additionally, five pristine reference membranes (19.0 cm) were received from Ringhals NPP storage (Figure 4). Reference samples for the smaller membranes were not available, but TGA analysis indicates that both membranes are of similar type.

Figure 4. Photograph of new neoprene membranes from Ringhals NPP.

To evaluate the overall lifetime of the neoprene membranes we chose to age reference membranes at 70, 90, and 110 °C and follow the tensile properties and hardness. The tensile strength and elongation at break are plotted in Figure 5a and b. The materials tensile strength is affected by aging to a low degree until long aging time when a sudden drop is noted for high temperatures. This is a common behaviour for rubber samples. Instead, elongation at break is more suitable to follow the aging. For 70 °C a slow decay of the elongation at break with aging time and more drastic changes for 90 and 110°C is noted. In Figure 5c the hardness of the sample with aging is displayed, showing a slow increase in hardness with aging time for 70 °C. Instead, aging at 110 °C degrees lead to a steep increase in hardness.

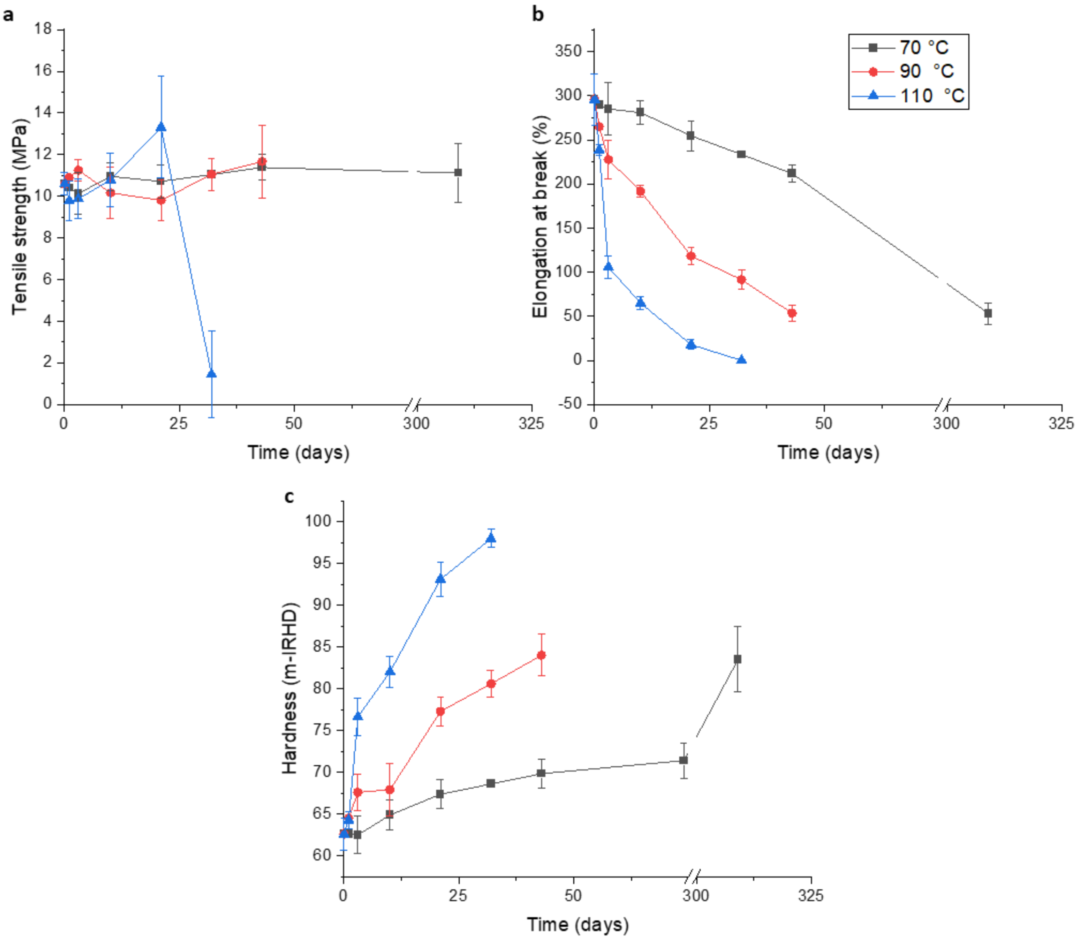

Figure 5. Tensile strength (a), elongation at break (b) and hardness (c) of heat-aged membranes from Ringhals NPP.

The datasets from elongation at break and hardness was used to build time-temperature superposition plots by shifting the x-axis of the curves to fit one master curve. The time-temperature superposition master curve for elongation at break data is shown in Figure 6a. By confirming that the trends from different temperatures are in line with each other it can be assumed that the same mechanism governs aging for all temperatures. Fitted shift factors were used to estimate the activation energy (Ea) of the aging process using Arrhenius equation for both elongation at break (see Figure 6b) and hardness. Results are listed in Table 2. For both elongation at break similar shift factors and hence a similar Ea of around 98 kJ/mol were calculated.

The shift factors and master curve were used to extrapolate the aging behaviour to an ambient temperature of 25°C allowing to estimate the total expected lifetime of the material at this temperature (Figure 6c). A common end-of-life criteria for the elongation at break is a 50% reduction corresponding to an elongation at break of around 150 % in case of the analysed neoprene samples (dashed blue horizontal line). Based on the accelerated thermal aging analysis this end-of-life criteria would be reached after approximately 35 years at 25 °C.

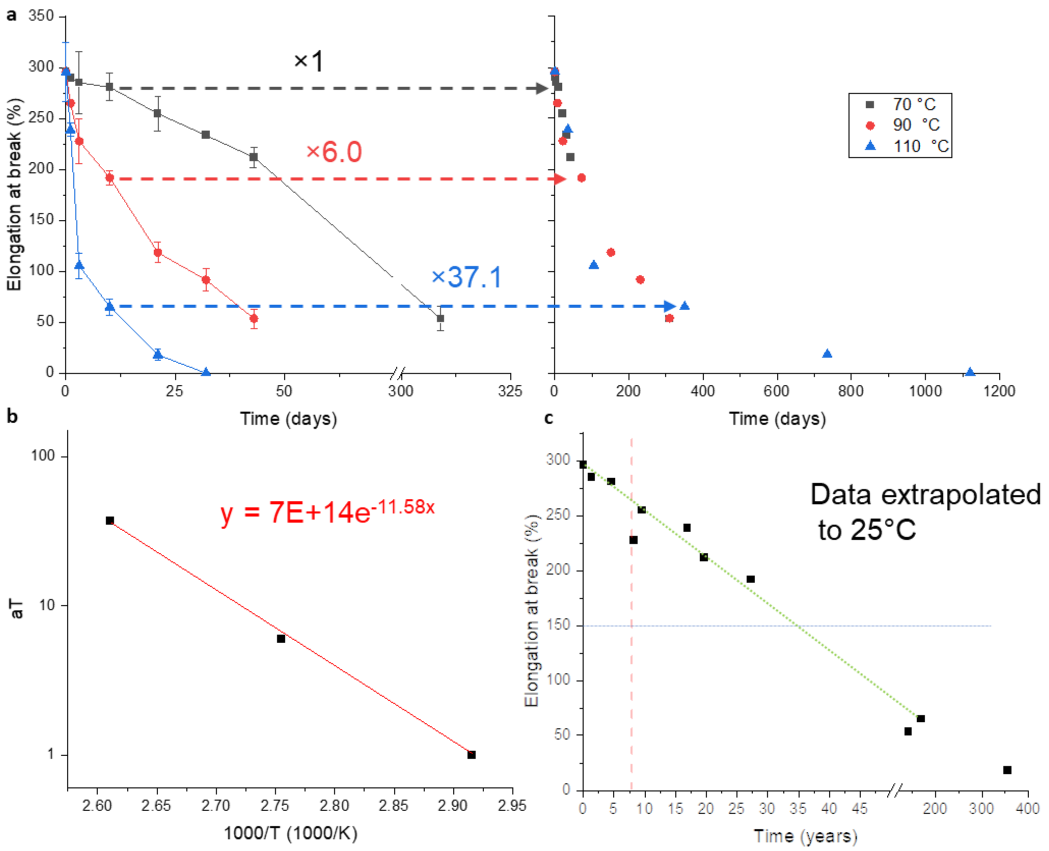

Figure 6. (a) Time-temperature superposition of elongation at break data, (b) Arrhenius fit to shift factors (aT), and (c) elongation at break data extrapolated to 25 °C (Lines are guides to the eye.).

Table 1. Shift factors (aT) and activation energies (Ea) for elongation at break and hardness.

Temperature (°C)	aT – Elongation at break	aT – Hardness
70	1	1
90	6.0	6.5
110	37.1	37.2
E_a (kJ/mol)	98.6	98.7

The tensile properties and hardness of membranes with a diameter of 19.0 cm after 8 years of service are shown in Figure 7. The elongation at break and hardness of all membranes are within the interval 260 – 290 % and 63 – 68 m-IHRD. A good agreement with the extrapolated master curve for elongation at break in Figure 6c (red dashed line) with the samples from Ringhals is noted. Based on this analysis much of the service-life of the membranes remains when membranes are exchanged every 8 years. Depending on what end-of-life criteria may be used the exchange interval may be doubled or even further increased. Note, however, that this analysis does not consider mechanical loads during operation, nor aging of the reinforcement material.

An overall good correlation between the elongation at break and hardness of the material was found. Thus, hardness measurements may potentially be used as non-destructive method to estimate the remaining service life. For example, a 50% reduction of elongation at break correlates with an m-IRHD hardness in the interval of 70 – 75. A disadvantage with hardness measurements is the small scale available, which is why similar microindenter method is often used instead. Note, that further studies would be necessary to confirm the correlation between elongation at break and m-IRHD hardness.

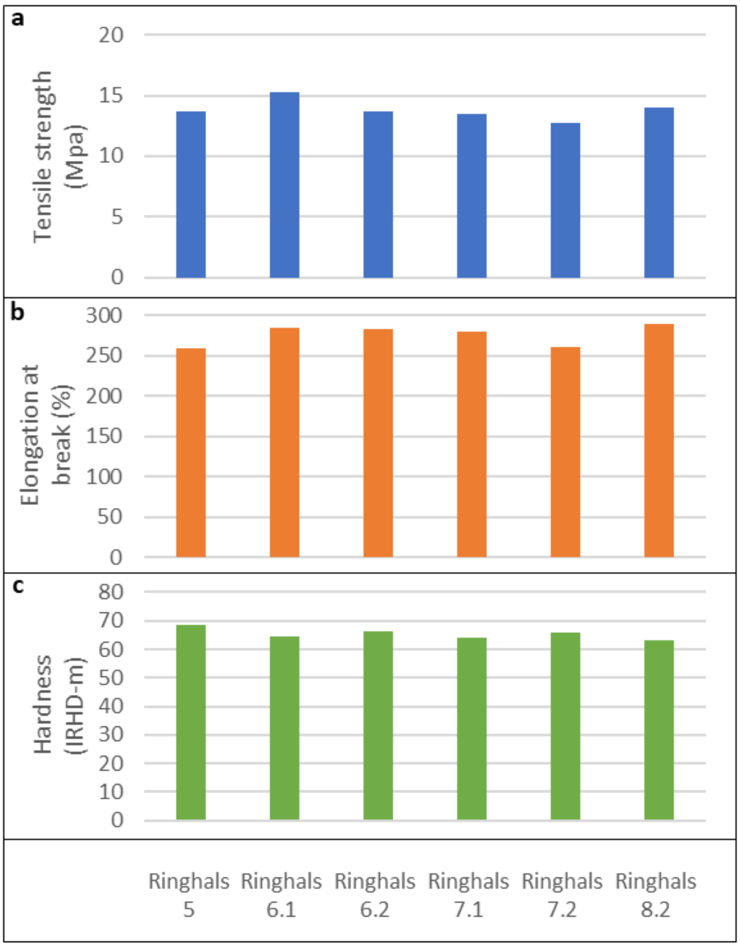

Figure 7. Tensile strength (a), elongation at break (b) and hardness (c) of neoprene membranes with a diameter of 19.0 cm as received from Ringhals NPP.

Analysis of membranes with a diameter of 17.5 cm is limited due to missing reference samples. TGA analysis (not shown) of the different (Ø 19.0 and 17.5 cm) membranes received revealed slightly different material compositions allowing only limited comparison. Tensile properties and hardness of membranes with Ø 17.5 shown in Figure 8 differ strongly between samples. For samples have strongly reduced elongation at break below 100. Instead, three samples have an elongation at break well above 200 %. Unfortunately, the initial values are unknown, but a similar value as for Ø 19.0 membranes may be assumed. It is unknown, if the wide spread of properties reflects different conditions during service life since the exact conditions per sample could not be provided. Also, for Ø 17.5 cm membranes a low elongation at break seam to correlate with a higher hardness.

An estimation of maximum lifetime for these membranes cannot be provided. Nevertheless, the low elongation at break for several samples well below a 50% reduction after similar time in service indicates that the exchange interval for these membranes may need to be adjusted.

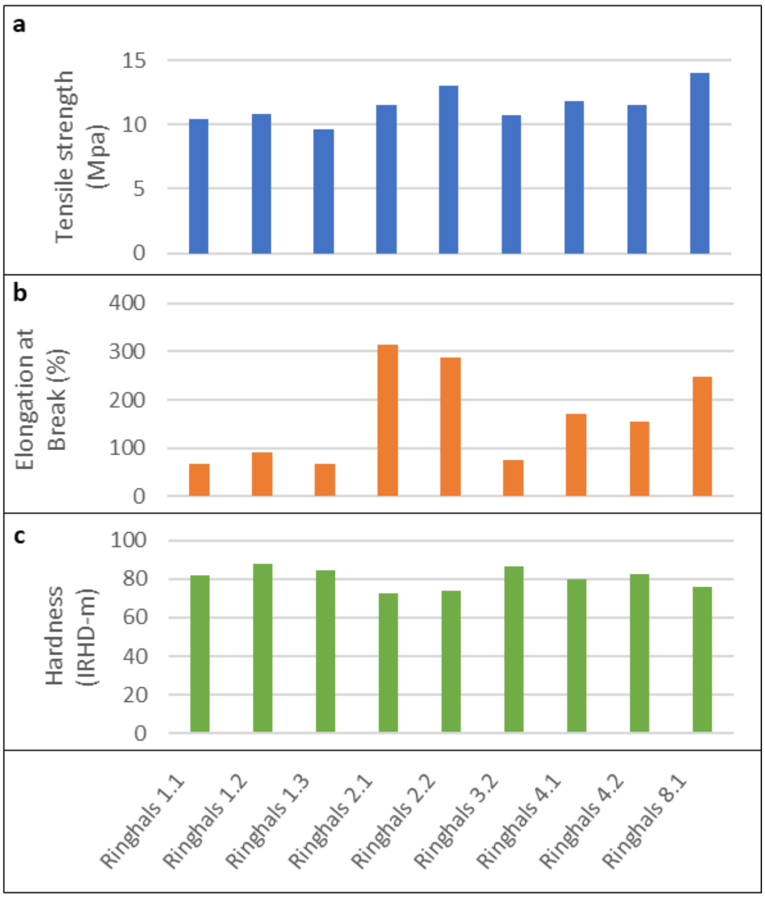

Figure 8. Tensile strength (a), elongation at break (b) and hardness (c) of neoprene membranes with a diameter of 17.5 cm as received from Ringhals NPP.

EPDM joist seal

Figure 9. Photograph of joist seal received from TVO after sample preparation.

The joist seal sample (Figure 9) has approximate dimensions of 33 × 10 cm with a thickness of 9 mm. The sample was exposed to N2- atmosphere at 45 °C during its operation at TVO for approximate 15 years. There is no relevant information regarding the initial properties of the material, such as data sheets or material specifications or pristine reference material available. Without knowing the initial material properties and the small sample amount it is very difficult to provide an analysis of the remaining lifetime of the material. Nevertheless, to gain some information on the status of the material the specimens were additionally heat-aged at 120 °C for 45 days in a ventilated oven and the tensile properties and hardness was measured.

The measurement results for both as-received and additionally heat-aged samples are listed in Table 2. The tensile strength and elongation at break did not significantly change. Instead, an increase in hardness was noted upon heat aging. The results indicate that it is possible to further age the sample, but there is no indication on its remaining lifetime possible.

Table 2. Test results for EPDM joist seals as received and heat aged for at 120°C for 45 days.

	Tensile strength (MPa)	Elongation at break (%)	Hardness (IRHD-m)
naturally aged	6,92	294,5	72,4
naturally+heat aged	7,01	283,1	78,3

CPE cables

A cable with chlorinated polyethylene (CPE) was received from Forsmark NPP (Figure 10). The cable has been removed from the NPP after about 30 years of service at a temperature slightly above room temperature and has been exposed to mineral oil fog. A cable with similar specification was purchased from Draka cables for reference.

Figure 10. Photographs of CPE cables from Forsmark NPP (left) and reference cable (right).

To estimate the total expected lifetime of the reference cables the elongation at break, the modulus at 25% elongation and the hardness of the cable jacket was measured at different intervals after aging at 90, 100, and 110°C (Figure 11). Additionally, the cable was exposed to mineral oil at 100°C to investigate a possible influence of oil exposure at the NPP. The same properties were measured for the cables received from Forsmark. For all aging temperature the elongation at break drops immediately which is more significant with increasing temperature. Instead, the modulus at 25% elongation remains nearly constant after which a sharp rise after only a few days at 110 °C was noted corresponding to a stiffening of the cable jacket. The constant plateau before the sharp increase is inversely related to the aging temperature. For both elongation at break and modulus the exposure to mineral oil at 110°C did not show any significant effect compared with aging at the same temperature without oil present. The hardness of the cable jacket with aging shows a similar trend as for the modulus with a short period of constant hardness followed by a sharp increase. The sudden onset of property changes indicate that the material is well stabilized with antioxidant to a certain point after which the oxidation of the material increases sharply.

By time-temperature superposition fitting an activation energy of 80.0 kJ/mol was estimated for aging of the CPE cable jacket. Using the master curve and an end-of-life criteria of a 50% reduction of the elongation at break yields a total expected lifetime of about 23 years. Interestingly, when comparing the cables from Forsmark which have been in service for about 30 years their properties are similar to those of the unaged reference cables. The result may either be explained by different materials in the cables from Forsmark and the reference cable, which cannot be excluded. Further studies would be necessary to confirm any difference in the materials. Or the method used may not be applicable to the type of sample. The aging mechanisms at low (service) temperatures and those at elevated aging temperatures may not be the same as is also indicated by research done within task 2.2.

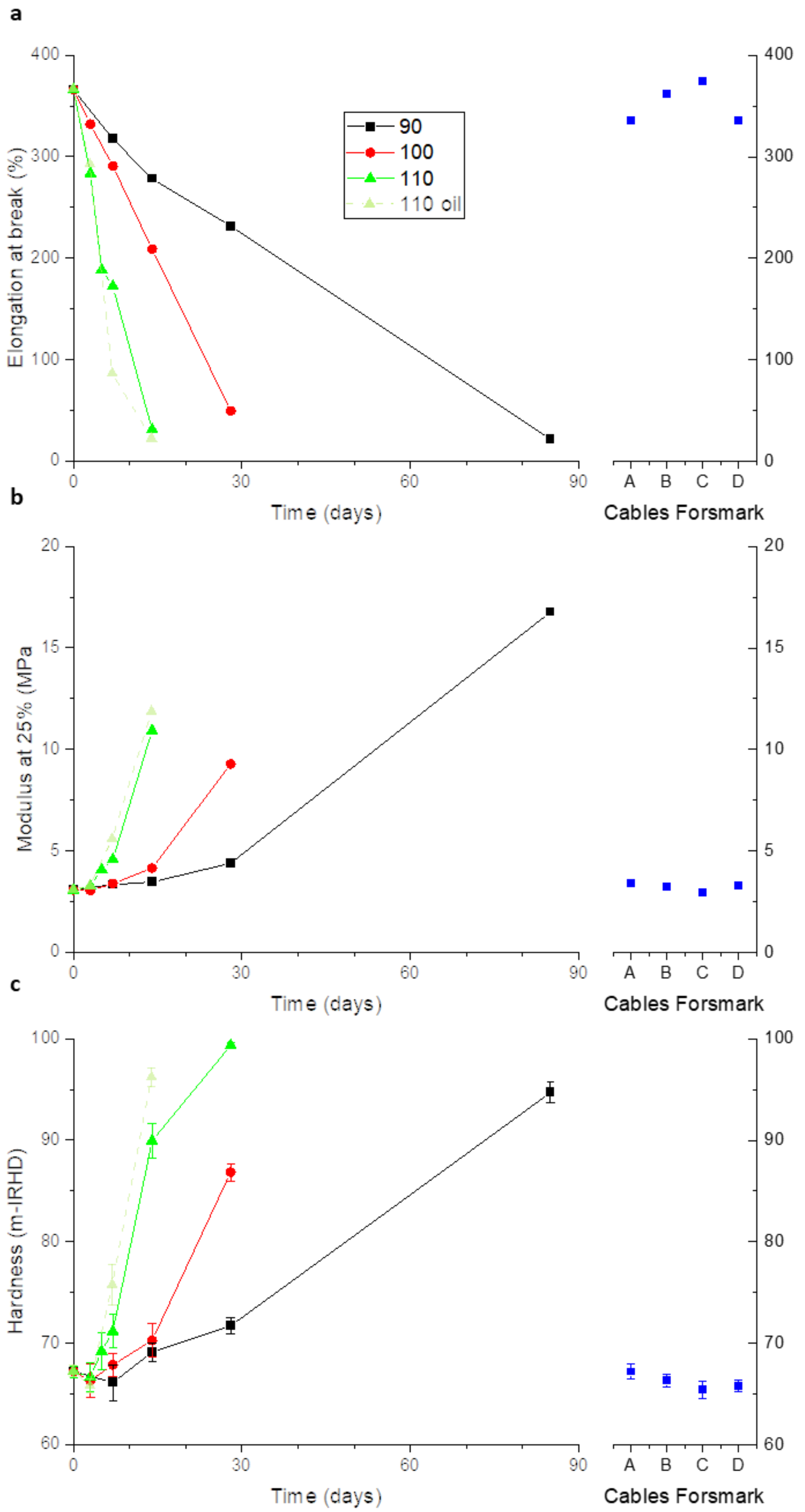

Figure 11. Elongation at break (a), Modulus at 25% elongation (b), and m-IRHD hardness (c) of CPE cable jacket aged at 90, 100, 110 °C as well as in contact with oil at 110 °C and of cables received from Ringhals. (Lines are guides to the eye.)

4.5 Conclusions

Several workshops were held, where potential material candidates from the NPPs were collected and evaluated. Materials were then chosen based on suitability and availability. The workshops were complemented by update meetings and plans to extract more samples during revisions. Unfortunately, no material could be received from Oskarshamn due to staff shortage. Test plans were set up for each material containing traditional mechanical methods to estimate lifetime and compare with materials from outtakes.

EPDM O-rings from Ringhals after their service life were tested against new reference O-rings and their total expected lifetime was determined. The O-rings were found to be of very good quality with a slow aging profile, indicating that prolonged service times may be possible after further testing.

Neoprene membranes from water pumps at Ringhals with different dimensions were investigated. For one size (19.0 cm) reference membranes were available and the total expected lifetime was estimated. Comparison of the membranes after service life with the heat aged membranes indicated that it may be possible to extend the service time of membranes.

A joint seal sample from TVO was analysed without reference by measuring tensile properties and hardness. Due to the missing reference no estimation of total or remaining lifetime was possible

CPE cables from Forsmark were analysed and compared to a similar reference cable. A total expected lifetime of 23 years was estimated for the reference cable which is shorter than the service time of the cables from Forsmark. This may be explained by different cable jacket material or differences in the aging mechanism at low and high temperatures.

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