6. Structural Integrity

6.1 Condition monitoring, thermal and radiation degradation of polymers inside NPP containments (COMRADE)

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Abstract

In COMRADE project several ageing related issues in NPP environment were studied, including setting acceptance criterion for O-rings, use of real components in ageing studies, combined effects of radiation and heat and dose rate effect. As a result, several end-of-life criteria was suggested for EPDM O-rings based on the functional property of the O-ring. FE-simulations were conducted to estimate how O-rings endured in a realistic environment. Feasable ways to acquire polymeric materials from running plants and plants underdecomissioning were evaluated. MD-simulations were applied in explaining the mechanisms governing the reverse temperature effect. As part of studying the synergistic effects of radiation and heat, two different kind of behaviour were observed with EPDM and Lipalon cable jacket material in combined high temperature-radiation environments. Also, it was shown that the used sequence in ageing treatments do matter in case of EPDM. Finally the use of semi-empirical models were estimated in the use of predicting dose rate effect and it seems that they require lot of experimental data to provide reliable predictions.

Introduction

Different polymer based materials are widely used in various applications in nuclear power plants and inside containments, e.g. cable jacketing/insulators, sealants, paint coatings, lubricants and greases. As any other material or component, polymers are susceptible to ageing. Elevated temperature, ionizing radiation and moisture are considered to be the most important ageing stressors and they tend to interact with the polymer structure in different ways. In addition to these ageing stressors, the properties of polymer blend, e.g. crystallinity degree, amount of fillers and antioxidants, has an effect to the ageing behaviour. Thus the degradation mechanism can be quite complex.

COMRADE was developed based on input from a feasibility studies from Energiforsk AB and STUK and through discussions between VTT, SP and the Nordic NPPs through Energiforsk. When developing COMRADE it was understood that there are three topics that research efforts could be concentrated. Firstly, there are gaps in knowledge for setting functional based acceptance criteria at the nuclear power plants. Secondly, a study for acquiring polymeric components from the NPPs was in COMRADE. Thirdly, research on ageing of polymers in thermal-irradiative environments were considered to be important, e.g. dose rate effect and synergistic effects of radiation and heat. Three work packages were constructed around these topics and their content is presented below.

Development of condition monitoring methods for polymeric components including low dose rate radiation exposure

The goal was to find functional based acceptance criteria for polymer materials at the nuclear power plants and to find robust test methods for condition monitoring. Acceptance criteria was also calculated through FEM modelling. Furthermore there is a also need to better understand how a polymeric component reacts to different levels of low dose ionizing radiation and synergistic effects between thermo-oxidative and radiation degradation.

All samples in the study were exposed to both gamma irradiation and thermo-oxidative ageing at elevated temperatures in heating cabinets according to the scheme in Figure 1 below. The ageing was completed in two parallel sequences, one using irradiation – heat – irradiation – heat and one with only heat. The ageing temperatures used were chosen based on the heat resistance of the rubber materials (Table 1) and the total dose was 14-18 kGy at a dose rate of approximately 29 Gy/h.

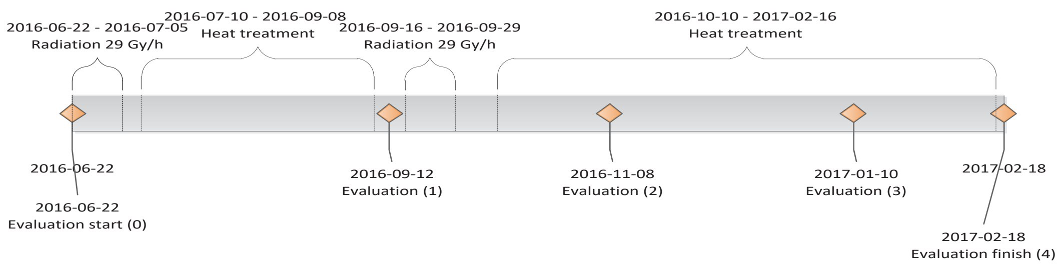

Figure 1. Exposure schedule for the first EPDM ageing treatment; radiation-ageing-radiation-ageing

Three different O-ring rubber materials, supplied by James Walker Ltd, were exposed to three different ageing temperatures each (Table 1). The degradation was followed by measuring deterioration of different material properties as a function of ageing time, for example elongation at break, compression set and hardness. The end of life criteria was set by measuring leakage in a specially designed test rig, see Figure 2. The end of life (leakage) was correlated to the value of the measured material properties. The test data from the two EPDM O-rings was also used in FEM modelling.

Table 1. Materials studied in WP1.

Material	Grade name	Ageing temperatures (°C)	O-ring dimension (mm)
EPDM	LR 9444	90-120-140	2,99
EPDM	LR 9444	90-120-140	6
FKM	FR 10/70	160-180-195	2,99
Nitrile	NM27/70	60-80-100	6

Figure 2. The test rig for leakage measurements, to the left before mounting the O-ring and to the right mounted for leakage test. Leakage was detected at the hole in the cylinder. O-rings were exposed to radiation and heat mounted inside the test rigs.

Table 2 shows end of life criteria for EPDM correlated to material properties. The test values designated “End of life” were measured after 6 months of ageing at 140°C. At this point leakage was also indicated. No leakage was detected at the two lower ageing temperatures.

In Figure 3 compression set is plotted versus the ageing time. The results with and without radiation is very similar indicating that the radiation did not affect the EPDM material significantly. Samples exposed to 140°C for around 150 and 200 days leaked and hence end of life is reached. Compression set is close to or even above 100% when leakage is observed and therefor difficult to use as end of life property.

Table 2. End of life material proerties in comparison to initial values.

Property	End of life	Initial value
Compression set	105%	4,9%
Hardness	80 IRHD-m	72,3 IRHD-m
Elongation at break	50%	182%
Tensile strength	7,5 MPa	12,8 MPa

Stress relaxation is similar to compression set but the force from a compressed O-ring is measured instead of deformation of the O-ring. The force is logged continuously and the method is also more sensitive compared to compression set. The samples are exposed to elevated temperature and measured simultaneously. Because of the sensitivity and amount of test data achieved from stress relaxation theser results were used for FEM calclulations on EPDM rubber.

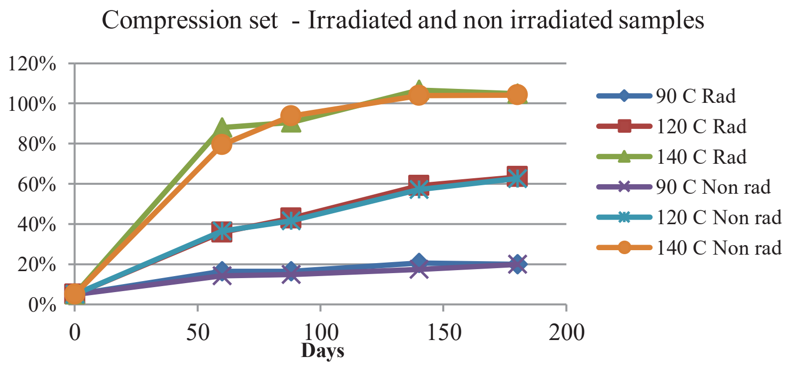

Figure 3. Compression Set Measurements for EPDM O-rings with 2,99 mm diameter.

FKM (Fluorine rubber often known under the trade name Viton) did not show any leakage after terminated exposure and compression set values ended at 90%. FKM materials are known to be very stable at high usage temperatures. FKM was not significantly affected by the radiation.

Finally Nitrile rubber was exposed and analysed. This material became significantly harder upon ageing, and compression set increased. Thermogravimetric analysis showed weight loss starting at approximately 180°C which may explain the increased compression set and hardening of the material when additives evaporate. The effect of higher temperature was significant, but radiation did not seem to affect the material. After initial decreased compression set and hardness the material remained at a rather constant level during ageing.

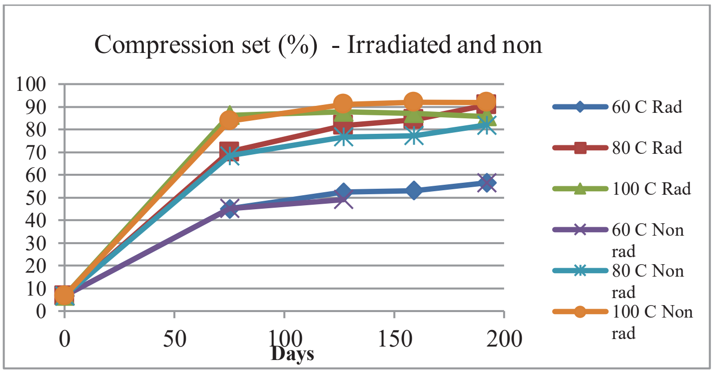

Figure 4. Compression Set for Nitrile Rubber.

Based on the results from three different ageing temperatures activation energies were calculated based on time-temperature superpostion, where curves are shifted along the x-axis, was used to calculate the activation energies and extrapolate service life at 50°C. Degradation rate is dependent on type of polymer, polymer formulation and ageing temperature. Different material properties such as elongation, hardness and compression set are affected differently upon accelerated ageing and as a consequence activation energies varies for different material properties. For EPDM the calculated activation energy is 1,07 eV for compression set whereas the activation energy is only 0,97 eV. In life time prediction it is important to choose a material property relevant for the use of the material, for example compression set for O-rings. By using a low value of activation the service life is not over-estimated. By using activation 0,97 eV activation energy and a end of life value of 50% relaxation the service life for the studied EPDM material at 50°C would be 40 years.

Finite element (FE) simulations of how rubber materials for seals behave over time is performed. A major challenge for the simulations is to find an appropriate material model for the rubber materials and how to calibrate it to experiments. Here is a material model proposed that can include effects like creep, permanent set, and temperature dependence. It is shown how the relaxation tests can be used together with simulations to calibrate rubber material behaviour in seal applications. The visco-elastic (creep) behaviour is the most important in this respect. Compression set data is used in a validation process. A validation process here means that the calibration is done without the validation data. The validation data is instead used to test if the calibrated model can match results from the different validation test. The result is thus a more credible material model.

The effect of temperature is included with calibration of relaxation tests at different temperatures. With this observation the activation energy in Arrhenius equation can be determined. This modelling of the temperature effect is also validated with the compression test data. In the validation, the match between the test and simulated results is reasonable good when considering the rather crude and simple way the temperature effects calibration is performed. Furthermore, the Arrhenius equation is derived for one well defined chemical reaction while creep in rubbers is a complex process. Considering also this, the thermo-effects modelling seems good. This successful use of the Arrhenius equation for more complex effects is an experience that is often seen in various applications. Although not attempted here, it could also be possible to use the Arrhenius equation for ionizing radiation together with temperature.

The material models are used in an leak and tightness simulation attempt. This work is not fully completed. Although such simulations were successfully used in work such as (6), it does not work to full extent here. Numerical difficulties occur that prevent the simulations to be used to simulate leakage with confidence. From the leak and tightness simulations performed here it is shown that the increased creep for higher ageing temperatures seems to have a detrimental effect on the tightness, although one cannot assure or quantify the effect.

Learn from materials used in plants

Possibilities to analyse materials undergone aging in operating and shut down power plants were studied. This includes Barsebäck but also materials from outages in still operating power plants in the Nordic countries. In a pre-study staff at Barsebäck were interviewed and the result was that no suitable materials could be used for durability studies. Barsebäck plant does not have the ability to give radiological clearance in situ so an external authorized regulator must be engaged, and it is not certain that the equipment that has been in the enclosure can be given radiological clearance at all. If the polymeric material cannot be given radiological clearance the examination must be done in the controlled area. If the investigation will be done in situ the following things must be arranged: admission, training of personnel in handling radioactive materials (2-3 day-course), dosimeters and our equipment will have to be given radiological clearance afterwards. This would increase the cost significant compared to testing at a standard material testing laboratory. Another aspect against using materials from Barsebäck is that after the outtake of the reactors the materials have been stored for many years in different temperatures and atmosphere than the normal service conditions.

Therefore a questionnaire was introduced to NPP polymer material experts via COMRADE industry group to identify the polymeric components that can be available to study. Based on the feasibility study and input from the project team the following components were of interest to investigate and present in the questionnaire:

- O-ring of EPDM, Nitrile, Silicone or Viton
- EPDM seals/gaskets
- Joint sealants / sealants
- Cable transits (e. g. Brattberg cable transit)

- Sealing foam (polyurethane, etc.)
- Cables (Lipalon HHSO-type is previously studied in COMRADE)
- Lubricants and greases
- Paint coatings

The questions regarding the components were on availability of materials, material information, environment and storage conditions.

Several O-rings were obtained from Ringhals and two examples are shown in Figure 5.

Figure 5. Two damaged O-rings from Ringhals to the left no EPDM and to the right no 11 NBR.

The EPDM ring to the left has been in service for three years at 162°C at 12 bar pressure in water/steam. After removal it has been stored for one year at room temperature. The NBR sealing to the left was hard and brittle, hardness was 70 shore A from start and has now around 90 Shore A. Service time and environment is unknown. Hardness was measured on a number of o-rings, beside the example above, and the results varied a lot between the materials. To be able to evaluate components further the information about the materials and their environment in use must be more extensive.

To summarize the main hinders to find material to study were to get clearance of the materials and to find documented information about original material properties and service environment. Moreover, extraction of components from plants about to close and outtakes at running plants need a lot of planning in advance. Based on experience from this project, we would specify component for studies carefully in future projects:

- Type of component, for example O-ring, what dimension.
- Amount of material/component needed.
- Specify relevant tests in advance.
- Decide if additional accelerated ageing should be performed.
- Specification example: ten O-rings of minimum core diameter is needed for hardness and tensile testing and one ageing cycle. In this project we asked for any type of material and tests were performed depending on type and amount of materials achieved.

Polymer ageing mechanisms and effects inside NPP containments

WP3 content can be divided into three different subtasks where the first one focuses on using computational modelling techniques in polymer ageing. In WP3 modelling work related task literature survey was completed in 2016 on the synergistic effects of temperature and radiation in polymer ageing, and on possible ways of considering them in the lifetime prediction of nuclear power plant components. The following topics were looked into in more detail: the proposed mechanisms behind the synergistic effects, material modelling methods feasible for studying ageing and an overview of previous research related to the topic. The mechanisms underlying combined thermal and radiation ageing can be exceedingly complex, involving various chemical and physical processes across multiple structural and time scales. There remains a formidable gap between the present multi-scale materials modelling capabilities and practical lifetime prediction. Currently the most recognized practical lifetime prediction methods are semi-empirical and based on accelerated ageing experiments. Methods applicable to combined thermal and radiation ageing include the superposition of time-dependent data method, and the superposition of dose-to-equivalent-damage data method. The semi-empirical methods are limited in their predictive capability, as they cannot address possible changes in the dominant ageing mechanisms. For this reason, anomalous ageing phenomena such as the reverse temperature effect can render their predictions useless. In 2017-2018 the modelling work inside COMRADE was thus focused on a particular synergistic mechanism or some other relevant detail of the ageing process is feasible, such as the reverse temperature effect.

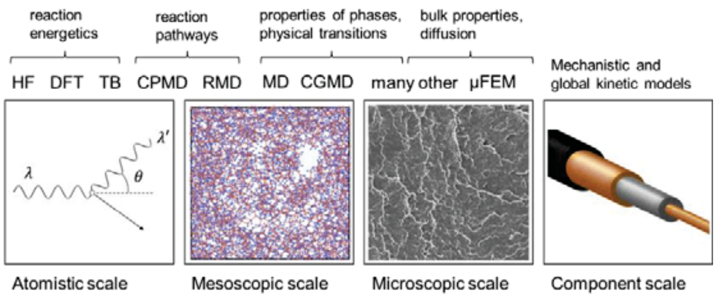

Figure 6. Scales and processes of thermal and radiation ageing coupled with numerical modelling methods.

During 2017 classical molecular dynamics (MD) was used to build united-atom structural models (one particle representing a CH2 or a CH3 unit) for the target material, polyethylene (PE). First, equilibrium structures for fully amorphous polyethylene were created. Then, methods were developed to convert the fully amorphous PE into partially crystalline and/or cross-linked forms. Methods were also tested for measuring the mechanical properties of PE. In addition, detailed all-atom reactive MD simulations were performed to study the mechanisms of radiation induced damage. The threshold recoil energy (energy required to introduce radiation damage) was estimated to be >20 eV in case of PE. Because MD timescales are significantly shorter than timescales for chemical reactions, the reactions of oxygen and radical species with the polymer will not be treated explicitly in the MD simulations, but will be taken into account in the structural details of the model system. This will require adding a chain scission mechanism to the united-atom PE model during 2018 for a proper description of the aging process.

In 2018, the modelling work of WP3 was started by performing an extensive set of simulations on the crystallisation of cross-linked PE. The main finding was that after crystallisation, cross-links were found exclusively in the amorphous regions. A method was developed and tested for simulated aging of XLPE structures, which involves both bond scission and cross-link formation. Simulations of the tensile test were carried out for PE systems with varying chain length and varying cross-link density. A method to include stretch-induced bond breaking was developed for the united-atom description. According to results, the mechanical strength of polyethylene decreased with decreasing chain length until the material became fragile. Conversely, an increasing cross-link density first improved the mechanical strength, but at high cross-link densities the material became increasingly brittle, as evidenced by a decrease in the elongation at break. These results were in qualitative agreement with the experimentally observed reverse temperature effect, as originally reported by Celina et al (Radiat. Phys. Chem. 48 (1996) 613).

The first goal in the experimental task was to study synergistic effects yielding from radiation and heat on EPDM and CSM rubbers. The samples were aged at three different temperatures and irradiated with three different absorbed doses. Based on the elongation at break results obtained with EPDM samples (Figure 2), it can be stated that moderate increase (ca. 75-125°C) in temperature during exposure to ionizing radiation hinders the degradation process. In addition, plane thermal ageing (equivalent to the thermal ageing component during simultaneous ageing) did not result in any changes in elongation at break. CSM (Lipalon) seemed to be more susceptible to both irradiation and thermally induced ageing and only small synergistic effects rising from simultaneous exposure to radiation and heat could be observed when simultaneous radiation and thermal ageing data was compared to plane thermal ageing data. Thermal ageing at 125°C resulted in clear decrease in elongation at break. Only slightly larger decrease was observed at 125°C when irradiation was conducted simultaneously. Simultaneous exposure to increasing temperature with irradiation resulted in increasing degradation. This behaviour was opposite to what was observed on EPDM samples.

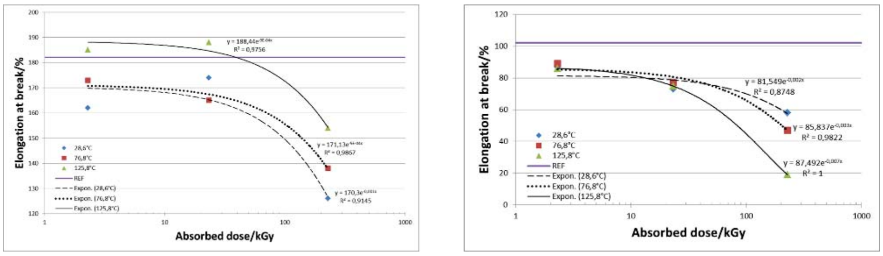

Figure 7. Decrease of elongation at break as function of absorbed dose at different temperatures for EPDM (left) and CSM (right).

In addition the role of aequence in ageing was estimated. In Figure 8 EaB data is presented after three different ageing procedures. The first ageing procedure included thermal ageing at 125°C for three weeks first and then irradiation at room temperature up to 200 kGy dose (blue column in Figure 8). The second ageing procedure (orange column in Figure 8) had the exact same thermal and irradiation ageing's, but their sequence was changed so that at first came the irradiation ageing and then the thermal ageing. In the third ageing procedure, both thermal and irradiation ageing were conducted simultaneously (grey column in Figure 8). The results indicate that the sequence does matter as simultaneous ageing and irradiation-thermal-sequence are compared.

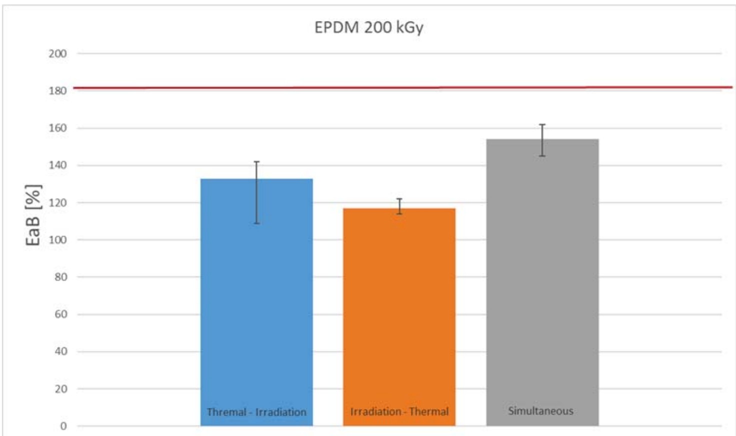

Figure 8. Comparison of sequence of ageing on EPDM samples. Blue column describes the decrease in EaB when sequence is thermal-irradiation, orange column irradiation-thermal and grey column simultaneous thermal and irradiation ageing.

The second goal in the experimental task was evaluating applicability of different techniques on measuring the oxidation profile created on EPDM samples during accelerated ageing and evaluate whether the measured oxidation profile could be correlated to mechanical properties of the sample material. Studied techniques included differential scanning calorimetry (DSC), time of flight secondary ion mass spectroscopy analysis (ToF SIMS) and Fourier transmission electron microscopy (FTIR). The studied material was sulphur and peroxide cured EPDM rubber and it was aged to three different conditions: thermally aged, gamma radiated and simultaneously (peroxide cured EPDM sequentially) thermally and gamma radiated. The overall condition of samples was evaluated by tensile testing (i.e. tensile strength, elongation at break and modulus at 100% strain). Based on the results obtained with ToF-SIMS (see Figure 9), it can clearly detect the oxidation occurring in the vicinity of surfaces of the aged samples. However, careful sample preparation is required since the method is sensitive to surface roughness and other contaminations. The other two methods had limitations on the sample material and resolution when creating an oxidation profile from surface towards the bulk.

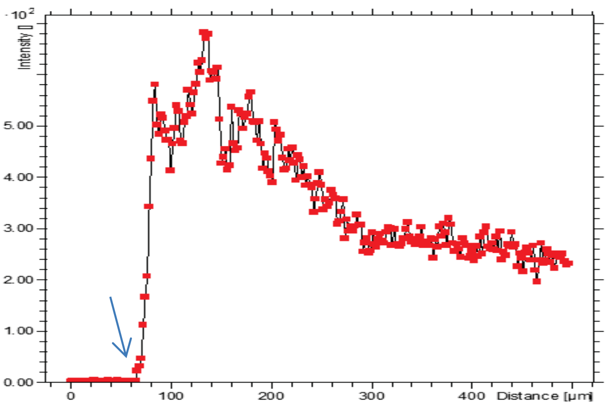

Figure 9. ToF SIMS measurement on EPDM where oxidation (O^- signal intensity) is presented as function of distance from the sample surface-air interface (shown with an arrow) towards bulk material. In this case the ca. 200 µm thick surface layer has oxidized more than the bulk material.

The third goal focused on evaluating different methods that could be used in evaluating dose rate effect, i.e. whether the used irradiation dose rate have an effect to the amount of degradation as the absorbed dose is kept as constant. The applicability semi-empirical power law and superposition models were evaluated whether they could be used in estimating the severity of dose rate effect. In case of the superposition model it was noted that the experimental data obtained was insufficient to make any reliable predictions. With power law model, more reliable results were obtained. However, EPDM showed good radiation resistance which yielded in uncertainty in predictions of dose rate effect when the power law model was applied. In case of Lipalon the dose rate had and an effect to the DED values, as can be seen from Figure 10, but more experimental data from low dose rate irradiations would be required in order to confirm this observation. Overall, it should be stated that the used dose rates during the irradiations were relatively high and homogeneity of oxidation could not be confirmed which would ease the examination of the data quality. For Lipalon material, the activation energy value (69 kJ/mol) could be calculated from the thermal ageing data, which would mean that in 50°C and 25°C the remaining lifetimes would be 680 days and 16 years, respectively.

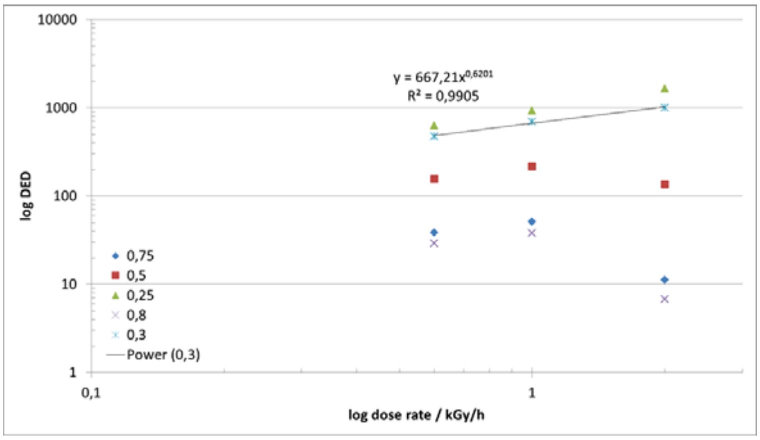

Figure 10. Extrapolation of end-point dose to lower dose rates for Lipalon.

Summary

Several polymer ageing related topics relevant in NPP environments were studied in COMRADE. The most interesting results obtained within the project include:

- An acceptance criterion based on functionality of O-rings can be set for several O-ring material
- Sufficient amount of information is required on material, service and storage environment if they are tended to use in ageing studies
- The simulated changes in crosslink density of the material was shown to be in qualitative agreement with the experimentally observed reverse temperature effect
- EPDM and Lipalon react differently to simultaneous exposure to elevated temperature and irradiation
- The sequence in ageing does matter when EPDM samples are aged
- When semi-empirical methods are used in predicting the severity of dose rate effect, sufficient amount of experimental data is needed

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