COMRADE - COndition Monitoring, thermal and RAdiation DEgradation of polymers inside NPP containments

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T1.2 Progress - Development of condition monitoring methods for polymeric components including low dose rate radiation exposure

- **T1.2 Implementation for the industry:** investigate the implementation of suitable methods (including compression set and hardness measurement) in detecting defective O-rings at plants and thus create a procedure that can be used in detection of faulty O-rings before their installation. The procedure should simple and reliable so it can be adapted in everyday use at NPPs.
- **T1.2 Progress:** Contact person from TVO is Antti Kallio. If these faulty O-rings can be found from the stock, they are analysed with portable XRD (x-ray diffraction) equipment at SP. If not found, the EPDM materials used in task 3.2 and 3.3 are used. XRD should be able to detect sulphur in the material. Use of the equipment for on-site purposes is evaluated.

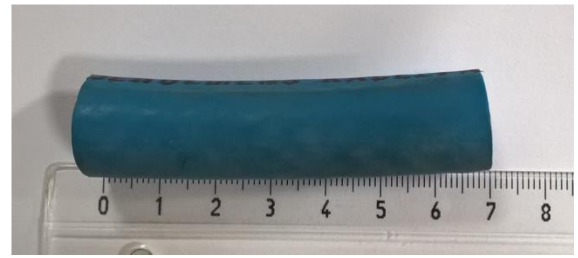
T3.2 Progress - Polymer ageing during service failure

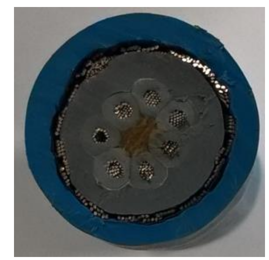
- In this task goal is to experimentally determine which ageing mechanism dominates during a service failure and what kind of synergy effects can be seen during them. EPDM and Lipalon cables are exposed to conditions similar to LOCA in order to perform a series of laboratory tests to clarify the effects of radiation, heat and combination of these two on these two materials.
- Test matrix has been fixed as follows →
  R=radiation ageing (kGy)
  T=thermal ageing
  t=duration for ageing treatment
- Two typical NPP grade materials are tested, EPDM and CSPE. EDPM is used in various sealant applications (e.g. O-rings of pumps) and CSPE is typical cable jacketing material (trademark Lipalon, manufactured in 1970's).
- Three different temperatures and total absorbed doses has been chosen in order to experimentally define severity of radiation and thermally induced ageing as well as combination of these two.
- The dose rate is fixed to be constant to 360 Gy/h

	EPDM (p)	**EPDM (s)**	**Lipalon**
REF	5	5	5
R2 t1	5		5
R20 t2	5		5
R200 t3	5	5	5
R2+T75 t1	5		5
R20+T75 t2	5		5
R200+T75 t3	5		5
R2+T125 t1	5		5
R20+T125 t2	5		5
R200+T125 t3	5		5
T75 t1	5		5
T75 t2	5		5
T75 t3	5		5
T125 t1	5		5
T125 t2	5		5
T125 t3	5	5	5
R+T125 sequential t3	5	5	
TOTAL	85	20	80

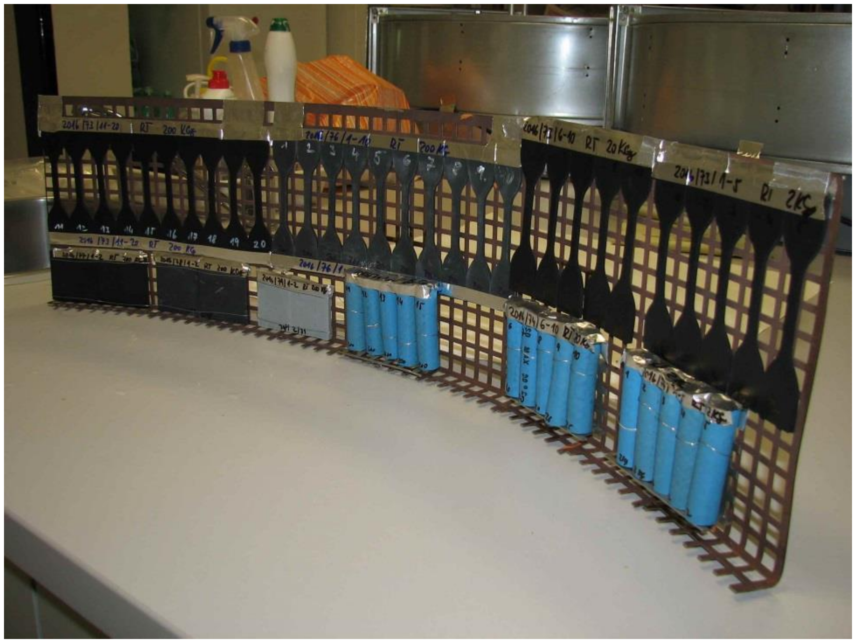
T3.2 Progress - Polymer ageing during service failure

- Since the dose rate is constant, radiation time will increase with increasing dose. Also additional thermal aged samples are required in order to compare sufficiently just thermal ageing to synergistic ageing.
- Samples are currently in irradiation treatment and thermal ageing. Irradiation treatment is going to be completed 22.9. Material testing can be started on the beginning of October.





T3.2/3.3 Sample setup in radiation chamber



T3.3 Progress - Synergy effects between radiation and heat and oxidation depth

- This task focuses on the surface oxidation in comparison to the bulk oxidation and the effect on overall material properties.
- Verify whether the listed techniques can be used in determining an oxidation gradient from sample surface to bulk material after thermal and radiation ageing
- Diffusion limited oxidation (DLO) effects will be compared to mechanical properties, and evaluate how radiation and thermal ageing affect on the phenomenon (will homogenous or heterogenous oxidation dominate)
- Test matrix has been fixed as follows:

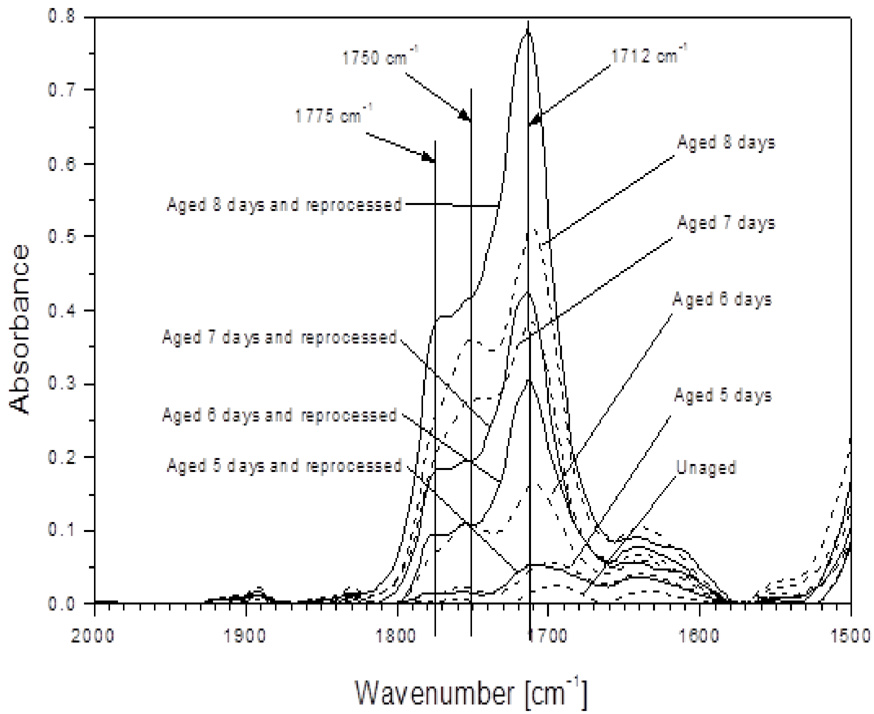
	R	T	R+T	REF	TOTAL
TOF SIMS	2x1	2x1	2x1	2x1	8
DSC	2x1	2x1	2x1	2x1	8
FTIR	2x1*	-	-	2x1*	4
TOTAL	6	4	4	6	20

- Two differently processed EPDM qualities are tested, peroxide and sulphur cured, by using TOF SIMS and DSC. FTIR analysis is conducted to no-carbon black containing samples in order to determine the applicability of the technique in oxidation studies.
- Samples are radiated in room temperature with same parameters as in T3.2 and thermal ageing is done at 125°C

Analyses techniques for WP 3: FTIR

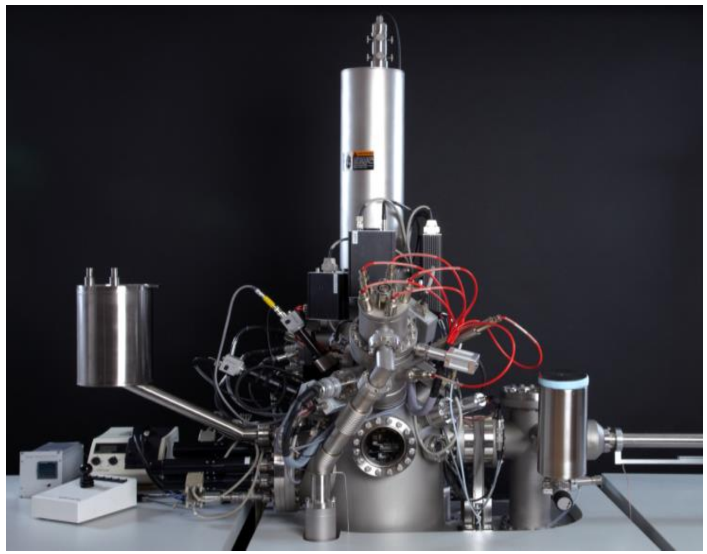
- FTIR Fourier Transform Infrared Spectroscopy
- Measure certain functional groups caused by oxidation.
- ATR Attenuated Total Reflection allows measurement on the surface.

FTIR: Advantages and drawbacks



- Advantages: Non destructive, small sample size.
- Fast method
- Drawbacks: High loadings of carbon black absorbs all infrared light.
- Low sensitivity at low degradation levels

Imaging and Analysis with ToF-SIMS

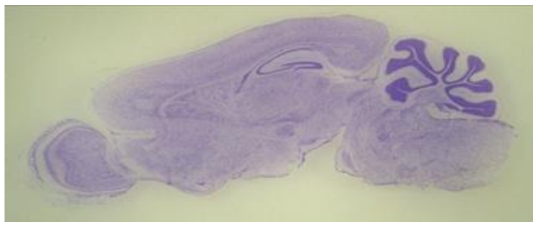


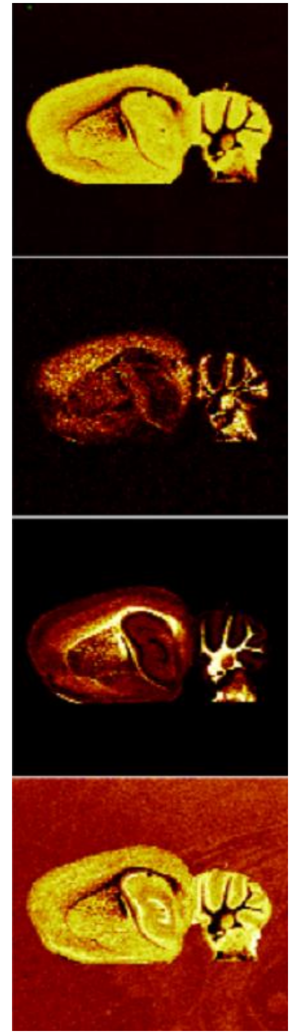
- Louise Carlred

What is ToF-SIMS?

- Time of Flight Secondary Ion Mass Spectrometry

… and why is it an important tool for surface analysis?



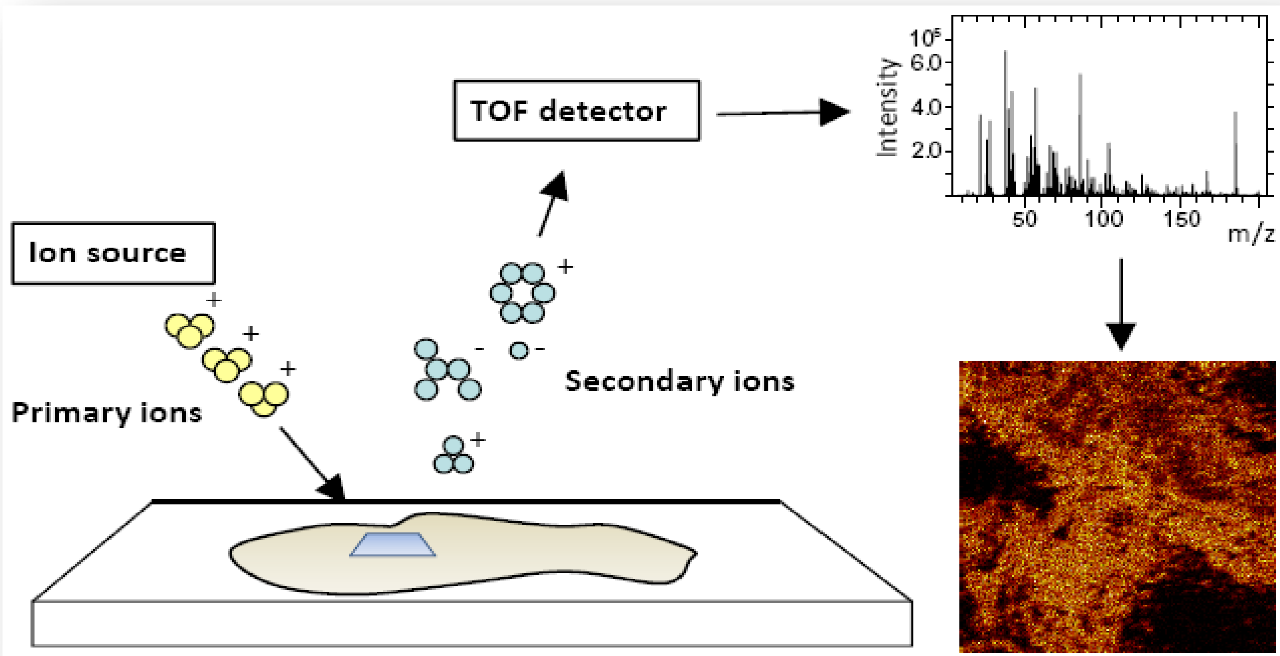


- Determine **what** molecules the sample contain
  (molecular information up to ~2000 Da)

- Determine **where** the molecules are located:
  (spatial resolution down to ~100 nm)

- no labeling; non-invasive analysis method

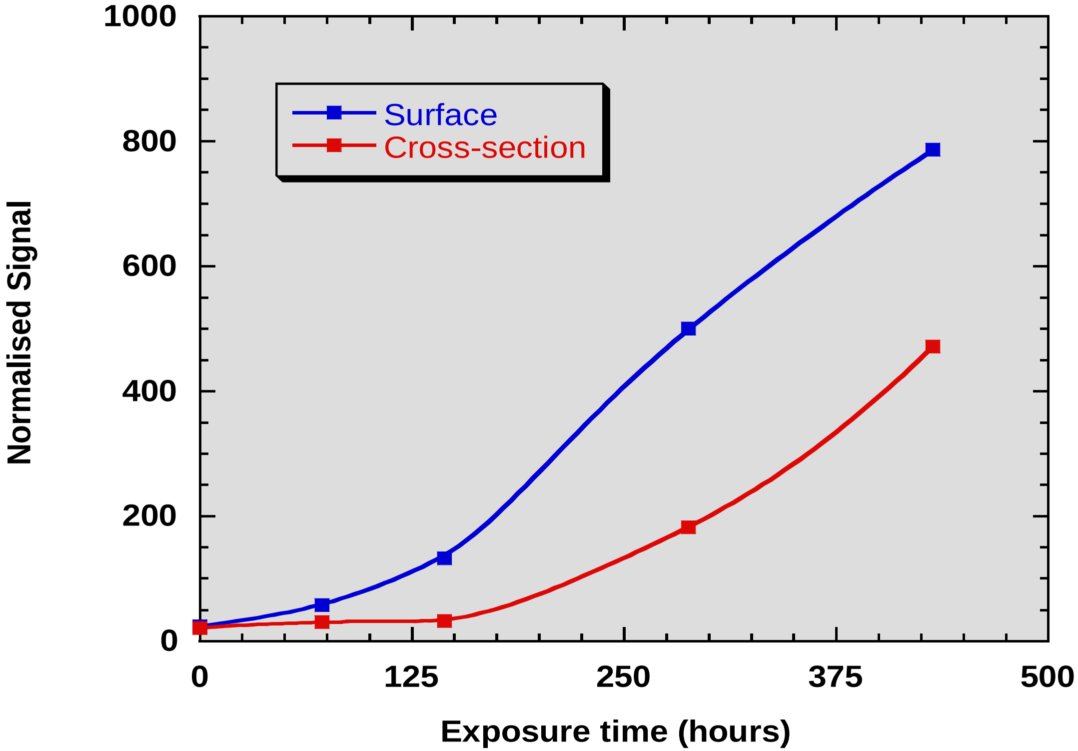
Theory



- Primary ions (Bi_3^+) – Secondary ions – Mass spectrum – Imaging

Surface oxidation measured by ToF-SIMS

$C_2H_3^{18}O^+$ signals from surface and cross section of low stabilised LDPE films after different exposure times at 70°C.



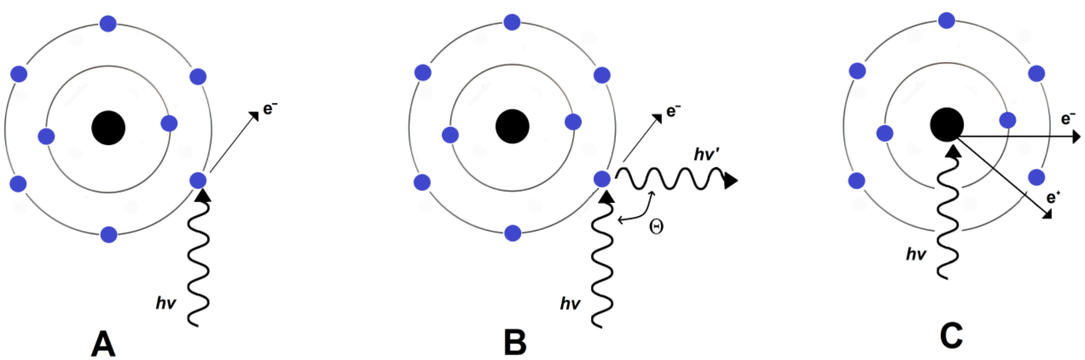
The exposure cell

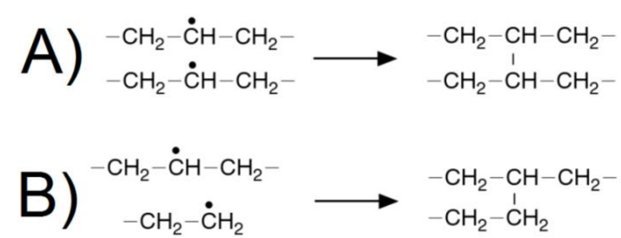
Summary ToF - SIMS

- What is ToF-SIMS?
  - ✓ToF-SIMS is an instrument that can be used for surface analysis to investigate the chemical composition and localization in your sample <u>at the same time</u>
- How does it work?
  - ✓The method uses a beam of primary ions to create specific secondary ions from the surface. The collected secondary ions can be analyzed in a mass spectrum and visualized as images with the spatial distribution in the sample. It is also possible to analyze the sample in 3D: depth profiling
- How can it be applied?
  - ✓ToF-SIMS can be used in many different fields, like biology, geology and in industry to detect and determine contaminations

T3.4 Progress - Evaluation of damage caused by dose rate effect to polymer components used within containments

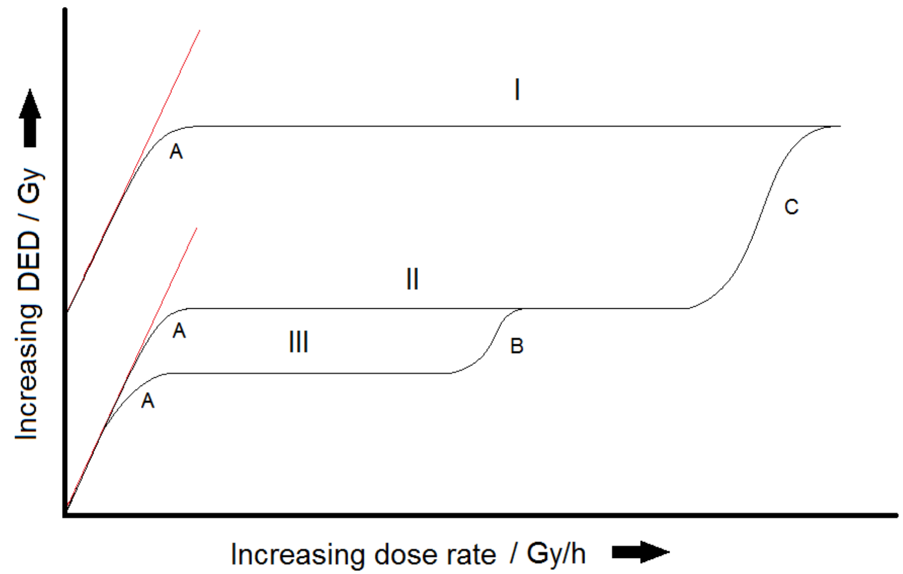
- Since the experimental studying of dose rate effect is costly due to long radiation treatment times, a theoretical approach to estimate magnitude of this phenomenon needs to be found. This task consists of a literature survey that gathers different methods used in extrapolating dose rate effect.
- Gammaradiation induces excited states in atoms → Excited atom is unstable and reacts with surrounding atoms → These reactions can be considered to have chemical nature and will usually end up chain scission, crosslinking or additional radical formation → chain scission and crosslinking have ultimately effect on macroscale behavior of the polymer.
- Oxidation is one of the chemical reactions causing degradation and it is closely related to the diffusion of oxygen. High dose rate radiation will cause radicalization with such intensity that all oxygen is consumed in the very vicinity of the surface where the oxidation will concentrate. Bulk material will be safe from oxidation induced by diffusion of molecular oxygen → Diffusion limited oxidation





T3.4 Progress - Evaluation of damage caused by dose rate effect to polymer components used within containments

- The schematic figure on right can be used in illustrating the dose rate effect. DED parameter represents the dose that is required to cause a certain amount of degradation in a chosen material property (usually 50% of elongation-at-break).
- Curve I represents situation where polymer is aged in inert atmosphere (no oxygen present). The horizontal line indicates that no dose rate effect is observed.
- As the behaviour of curve I is examined at relatively low dose rates curvature follows ending to a straight line. During this curvature small dose rate effect may take place, depending on the governing thermal and radiation degradation pathways [Gillen et al. 1993]. As the dose rate approaches zero value, the effect of radiation induced ageing diminishes and the ageing is only governed by thermal energy. At the linear region the amount of degradation is thus directly linked and solely determined by the time of exposure at the constant temperature. Existence of this linear region is not depending on the nature of the atmosphere.
- When curve II (air) is examined, one can distinct an additional curvature (marked as C) at very high dose rates which resembles the DLO. Contribution of DLO to the degradation will diminish as the dose rate achieves a rate of sufficient magnitude (oxidation thickness small).



- Dose rate effect can be observed also at intermediate dose rates as distinguished by curve III. This is thought to be related to rate-limiting steps of the oxidation chemistry. Radicals having a long lifetime can be trapped inside of crystalline areas or breakdown of intermediate hydroperoxide species take so long that their effect to the degradation is not observed during the relatively short ageing treatment and the following material testing period.

T3.4 Progress - Evaluation of damage caused by dose rate effect to polymer components used within containments

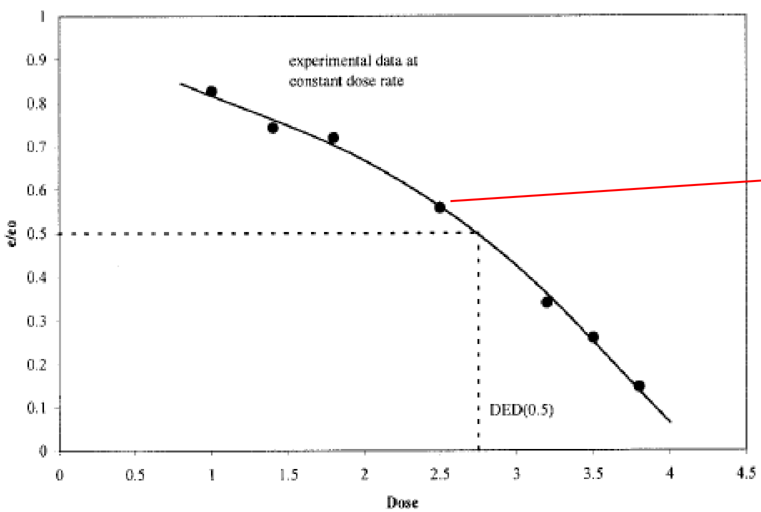
- So far four different methods has been recongized that can be used in lifeteime and/or dose rate effect predictions:

1. Linear model
2. Power law extrapolation method
3. Superposition of time dependent data
4. Superposition of DED data

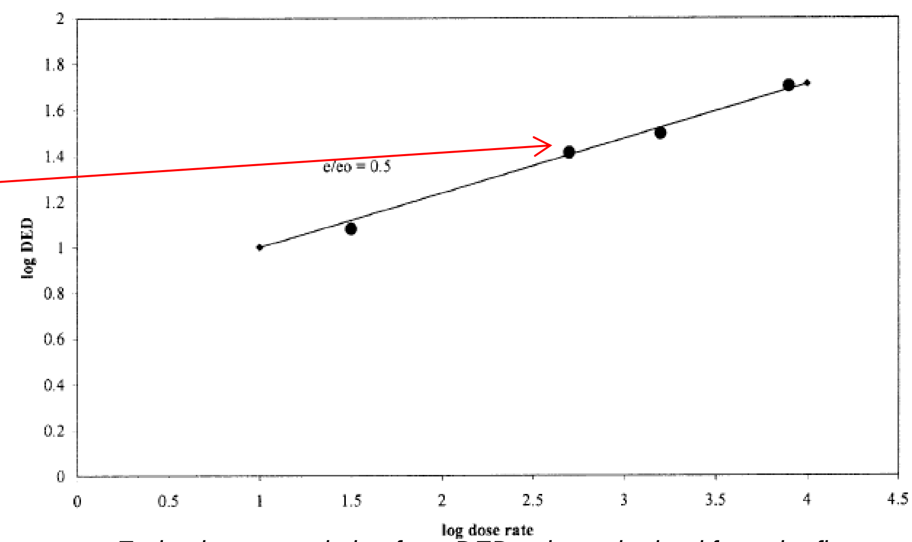
- Linear model is based on linear fitting on experimental data which is obtained by artificial ageing. Linear model is relatively easy and quick to use but since its simplicity it does not take into account e.g. synergistic effects of radiation and heat. Linear model can not be used in extrapolating dose rate effect (since it presumes no such thing exists)

T3.4 Progress - Evaluation of damage caused by dose rate effect to polymer components used within containments

- **Power law extrapolation method:** This method uses experimental data acquired in constant temperature and with different dose rates. It should be noted that only homogenous ageing data is usable → limits the dose rates used during ageing treatments. Experimental data is used to determine an end point criteria (usually relative EAB) which are extrapolated to lower dose rates.
- First, end point criteria is interpolated from several constant dose rate data sets (one is shown below left) and second the interpolated end life criteria is plotted as log DED vs. log dose rate. From this plot (shown below right) effect of dose rate to DED (or dose rate effect) can be observed.
- This method is confirmed to be applicable for certain polymer grades e.g. polyolefins. However predictions to very low dose rates where thermal ageing dominates require additional thermal ageing data. Also it can not be used when heterogeneous oxidation is observed.



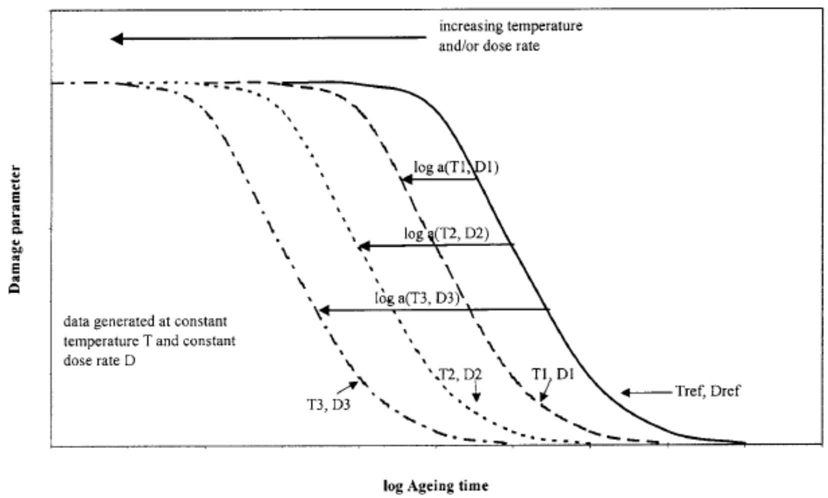
Interpolation of end life criteria. One interpolation provides one point to log DED figure.

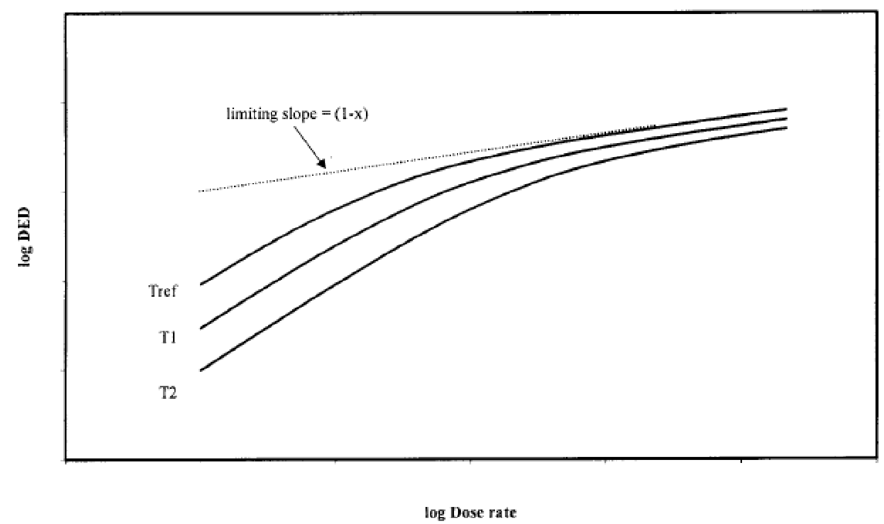


End point extrapolation from DED values obtained from the first stage.

T3.4 Progress - Evaluation of damage caused by dose rate effect to polymer components used within containments

- **Superposition of time dependent data**: This method uses additional thermal ageing data from accelerated thermal ageing tests. In the temperature data, it assumed that ageing mechanism does not change as temperature is raised. A set of curves is formed from the ageing data where damage parameter vs. log ageing time are plotted (see figure on left). As the ageing mechanism is presumed to be constant, the data can be shifted along the time axis by using a shift factors.
- During the first step master curve is formed out of superposed plots (constant temperature data) of damage parameter vs. log time.
- During the second stage combined thermal-radiation ageing data is superposed on the master curve and based on shift factor calculation and parameter fitting, the DED can be estimated at lower dose rates or temperatures (figure on right)
- The method can be used on materials in which a single mechanisms governs the both radiation and thermal degradation. Shape of the curvatures can be analyzed whether there are more than one factor affecting to degradation.



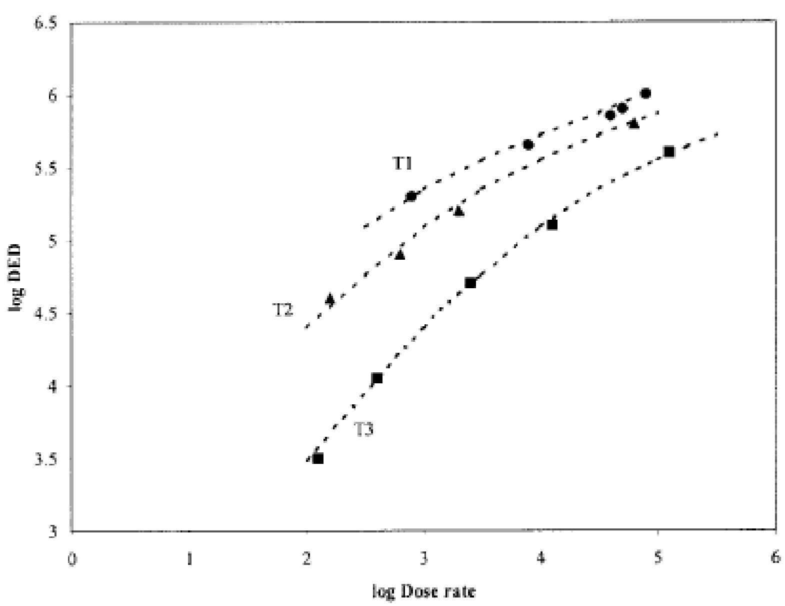


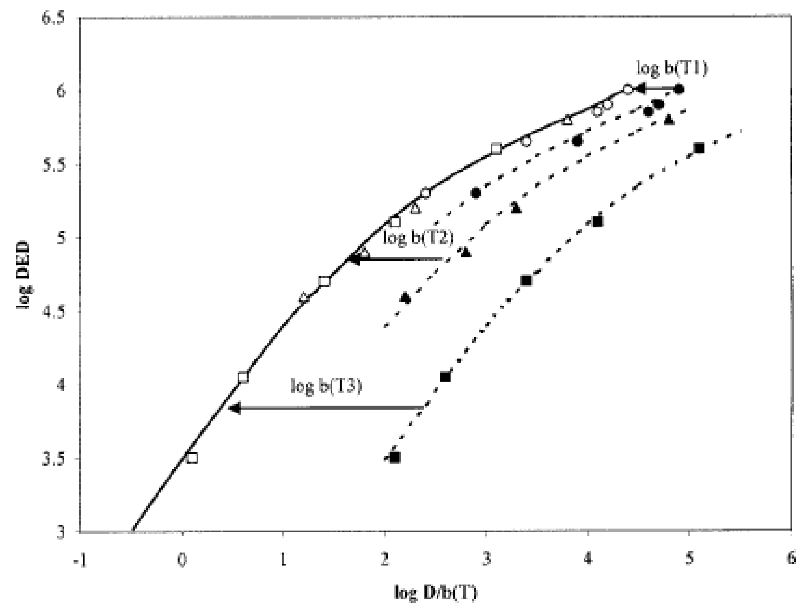
T3.4 Progress - Evaluation of damage caused by dose rate effect to polymer components used within containments

- **Superposition of DED data**: This method uses similar data to previous method but instead of plotting the result in logarithmic form, DED vs. dose rate is used. The procedure can be thought of consisting the following steps:

1. DED values are first determined
2. From these values heterogeneously oxidized data is extracted
3. Superposition is done based on shift factor calculation from the Arrhenius relationship
4. Activation energy is determined by fitting until superposition of all of the data is obtained

- This method can be used in the homogenous and thermally dominated regions. Some limitations to the applicable temperature range since can not be used near a thermal transition of the polymer.





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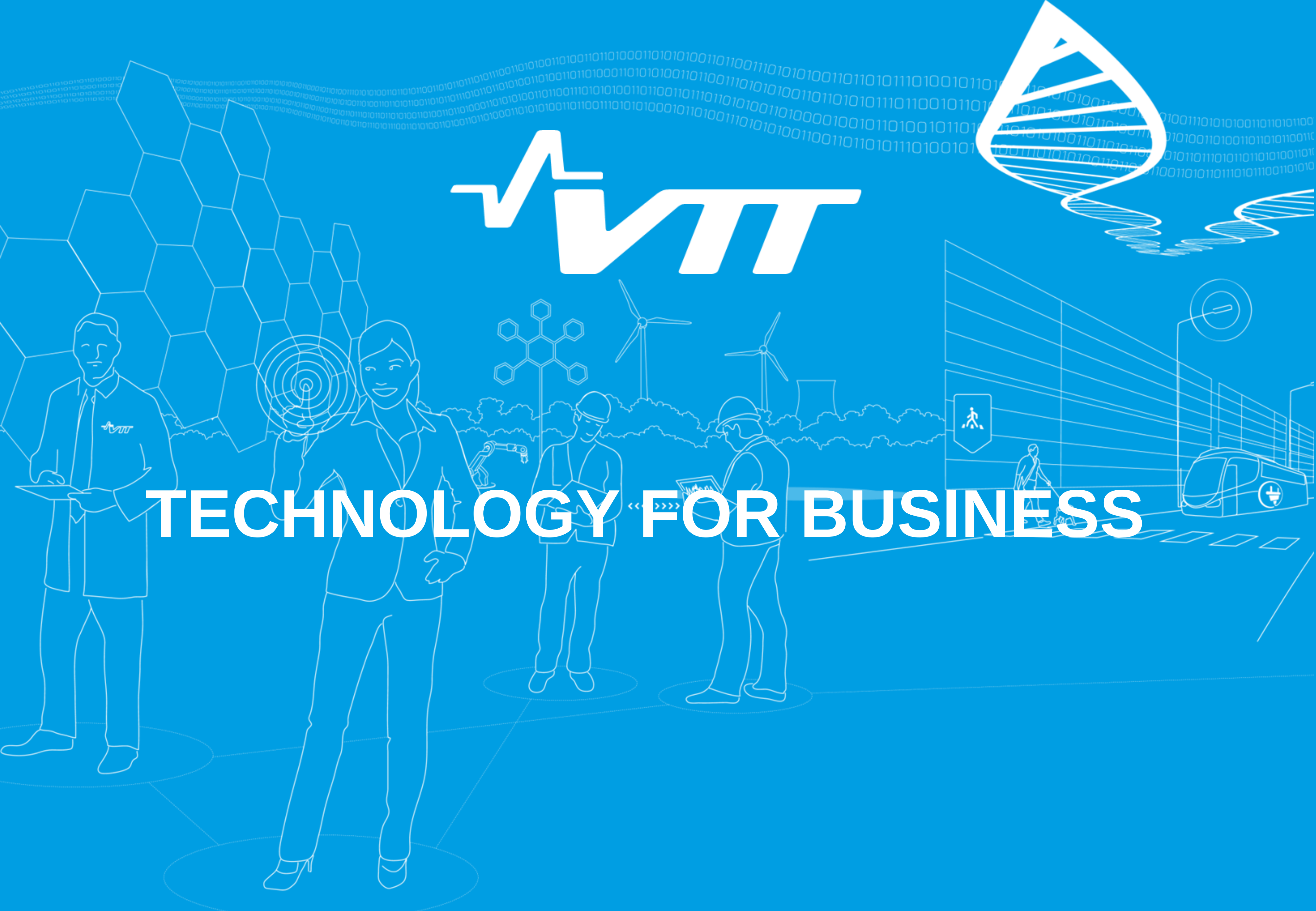
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