USE, LIMITATIONS AND POSSIBILITIES OF ARRHENIUS BASED EXTRAPOLATIONS FOR LONG-TERM OPERATION STUDIES OF POLYMERIC MATERIALS

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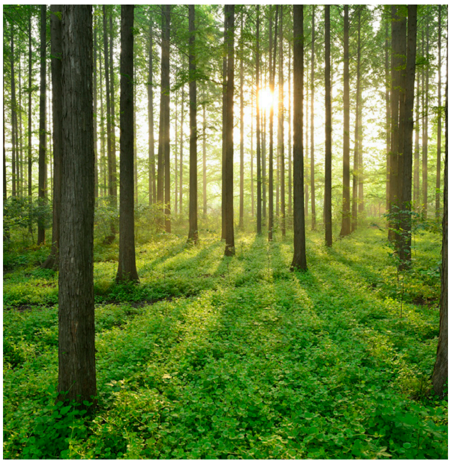
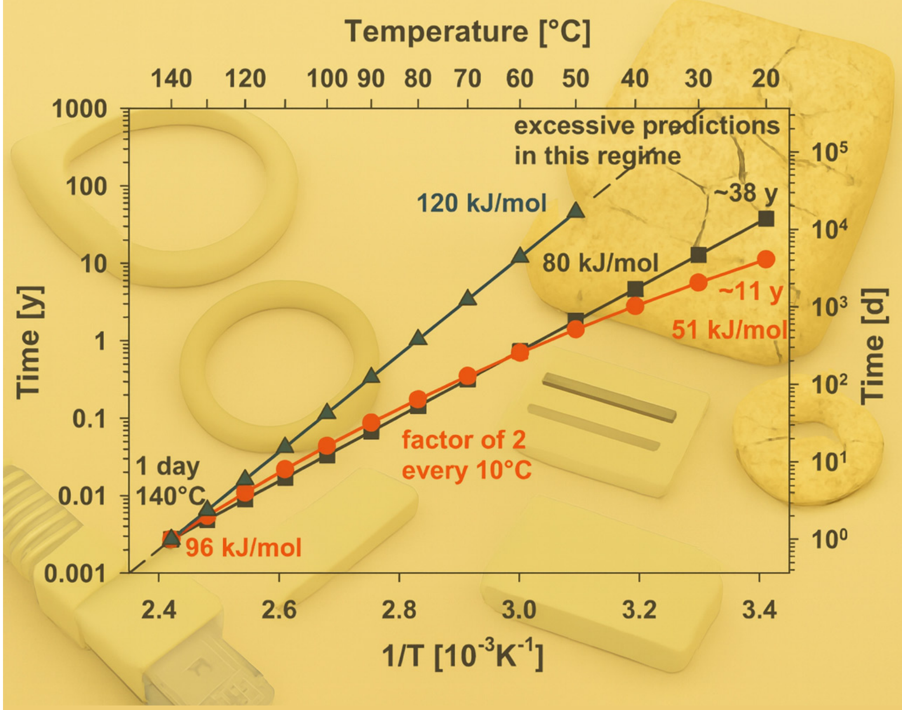


POLYMERIC MATERIALS IN NUCLEAR APPLICATIONS



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Use, limitations and possibilities of Arrhenius based extrapolations for LTO studies of polymeric materials

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Foreword

This report forms the results of a project performed within the Energiforsk Polymers in Nuclear Applications Program. The Polymers Program aims to increase the knowledge of aspects affecting safety, maintenance and development of components containing polymers in the Nordic nuclear power plants. A part of this is to investigate possibilities to facilitate and simplify the work that is performed in the nuclear business.

Long-term operation of nuclear power plants relies on reliable ageing management of polymeric materials used in safety-relevant components such as cables, seals and gaskets. Predicting their long-term performance is essential for safe operation and informed decisions on lifetime extension.

This study examines the use of Arrhenius-based extrapolations in accelerated ageing tests for polymeric materials. Its purpose is to assess the applicability, limitations and risks of current practices and guidelines when predicting material performance for long-term operation.

The results show that no single universally valid testing approach exists. The study concludes that Arrhenius-based extrapolations must be applied cautiously, with consideration of material-specific behaviour, testing boundaries and risk, and that complementary approaches can improve confidence in lifetime predictions.

The study was carried out by Karin Jacobson, PDS Consulting, and Mathias C. Celina . The study was performed within the Energiforsk Polymers Program, which is financed by Vattenfall, Uniper, Fortum, TVO, Skellefteå Kraft and Karlstads Energi.

These are the results and conclusions of a project, which is part of a research Program run by Energiforsk. The author/authors are responsible for the content.

Summary

The Swedish nuclear power plants aim to extend their lifetimes toward 80 years. This requires aging management of the polymeric materials used in e.g. cables and gaskets. However, the long-term property behaviour of polymeric materials is a complex area. Much research has been conducted over the years, but it is still difficult to correctly predict the lifetime of polymeric components. To assess the lifetime within a reasonable time frame, accelerated testing is a necessity. Commonly, acceleration is achieved with increased temperature and then the Arrhenius relationship is used to extrapolate the measured aging time towards the operating temperature with a given activation energy (E_a).

Since the degradation mechanisms can vary depending on temperature, the relationship is not always linear for the extrapolation from higher to lower temperatures. There may also be different activation energies (E_a) for different degradation mechanisms. Because of this, there are existing guidelines on how much a degradation process may be accelerated for e.g. environmental qualification (EQ). However, a number of questions related to both the application of the Arrhenius equation and previous guidelines have arisen in relation to the extended operation of nuclear power plant equipment. The broader framework of short term testing using the Arrhenius methodology is deliberated through a literature study, interviews with international experts, and also a perspective on extrapolations in terms of boundaries and remaining risk. Existing literature data do not easily support rigid thresholds for test conditions, as polymer E_a's show a large distribution, and limits in upper test temperature should also be considered. Highly accelerated single point testing will give some guidance, but choices for acceleration factor, E_a, testing temperature and extrapolative regime should also be coupled with potential failure consequences and hence risk towards a justifiable conservative approach.

The input gathered from the nuclear power plant (NPP) materials experts' community shows that there is NOT a broadly agreed upon single test method or guideline, and global consensus on this topic. However, many opinions and thoughts coalesce around shared challenges and sensible approaches subject to what is well-known, but also the perceived unknowns and risk in these methods.

Keywords

Arrhenius Equation, Activation Energy, Polymer materials Ageing, Oxidation, Service Life Prediction, Long-Term Operation (LTO), Thermal Ageing, Environmental Qualification (EQ), Diffusion Limited Oxidation DLO

Arrhenius ekvationen, aktiveringsenergi, polymeråldring, oxidation, långtidsanvändning, kvalificering, livslängd, diffusionsbegränsad oxidation, termisk åldring.

Sammanfattning

De svenska kärnkraftverkens siktar på att förlänga sin livslängd till upp till 80 år. Detta kräver en åldringshantering av de polymera materialen som används i tex kablar och packningar. Långtidsegenskaper hos polymera material är emellertid ett mycket komplext område. Mycket forskning har gjorts under åren, men det är fortfarande mycket svårt att korrekt förutsäga livslängden för polymera komponenter. För att bestämma livslängden inom en rimlig tidsram används accelererad testning. Oftast görs accelerationen med ökad temperatur och sedan används Arrheniussambandet för att extrapolera den uppmätta åldringstiden till vad de skulle bli vid driftstemperaturen men en given aktiveringsenergi (E_a).

Då nedbrytningsmekanismerna kan variera beroende på temperaturen är inte sambandet helt rätlinjigt för extrapolationen från högre till lägre temperaturer. Det kan också vara olika aktiveringsenergier (E_a) för olika nedbrytningsmekanismer. På grund av detta finns det vissa riktlinjer i hur mycket ett nedbrytningsförlopp får accelereras vid tex miljökvalificering (EQ). Ett antal frågor har emellertid uppstått relaterade till både tillämpningen av Arrhenius-ekvationen och tidigare riktlinjer i samband med förlängd drift av kärnkraftverken. Det bredare ramverket för korttidstestning med Arrhenius-metoden diskuteras genom en litteraturstudie, intervjuer med internationella experter och en diskussion kring extrapoleringar i termer av gränser och kvarvarande risk. Befintliga litteraturdata stöder inte enkelt rigida gränsvärden för testförhållanden, eftersom polymers E_a uppvisar en stor spridning, och att gränser för den övre testtemperaturen också bör beaktas. Högaccelererad enpunktstestning kommer att ge viss vägledning, men val av accelerationsfaktor, E_a, testtemperatur och extrapolationsregim bör också kopplas till potentiella felkonsekvenser och därmed risk mot en motiverad konservativ metod.

De insamlade synpunkterna från experter på material i kärnkraftverk visar att det INTE finns ett brett överenskommet enda test eller riktlinje och global konsensus i detta ämne. Många åsikter och tankar rör sig dock kring gemensamma utmaningar och lämpliga tillvägagångssätt utifrån vad som är välkänt, men också medräknat okända faktorer och riskerna med de använda metoderna.

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List of abbreviations

CSPE	Chlorosulfonated polyethylene
DBA	Design based accident
DLO	Diffusion limited oxidation
DSC	Differential scanning calorimetry
E_a	Activation Energy
EaB	Elongation at break
EQ	Environmental qualification
EPDM	Ethylene propylene diene rubber
EPR	Ethylene propylene rubber
EVA	Ethylene vinyl acetate
FTIR	Fourier transform infrared spectroscopy
KBE	Quality and Inspection Requirements for Electrical Equipment
NEPO	Nuclear Energy Plant Optimization
NPP	Nuclear power plant
OIT	Oxidation induction time
PEEK	Polyether ether ketone
PVC	Polyvinylchloride
RT	Room Temperature
SiR	Silicon rubber
TBE	Technical Requirements for Electrical Equipment
Tg	Glass transition temperature
TGA	Thermal gravimetric analysis
Tm	Melting point
XLPE	Crosslinked polyethylene
XLPO	Crosslinked polyolefin

1 Background

Planned operating times for another 40 years for Swedish and Finnish nuclear reactors means that the need for understanding the aging mechanisms of polymeric materials in nuclear power plants is more relevant than ever. Polymeric materials age when exposed to heat and radiation, but how quickly this happens depends not only on the material type, but also on its additives and physical form. Accelerated testing is commonly used to predict the lifespan of polymeric components. The most common approach for accelerated testing is increasing the temperature, as raising the temperature by 10 degrees approximately doubles the reaction rate. However, this relationship is not exact and often depends on the temperature regime itself, and on which reaction(s) control(s) the degradation. In 1889, Svante Arrhenius proposed a physical interpretation of this relationship in what then became known as the Arrhenius equation.

The Arrhenius equation describes the rate of a chemical reaction at a certain temperature through a specific activation energy and the probability of successful collisions between the molecules:

$$r = Ae^{-Ea/_{RT}}$$

where r is the reaction rate, A is a constant, E_a is the activation energy, R is the universal gas constant, and T is the temperature.

The activation energy is the minimum energy barrier that must be overcome for a chemical reaction or degradation process to proceed. It represents the energy difference between the reactants and the transition state. It quantifies how sensitive the reaction rate is to temperature. A reaction occurs only if enough molecules have kinetic energy equal to or greater than this barrier, which usually requires a sufficiently high temperature. Higher activation energy means that the reaction rate increases more strongly with temperature. It is also important to recognise, that in simplistic terms molecular energy is usually given through a statistical distribution (Boltzmann distribution), meaning some reactants have enough energy and reactions can fractionally progress, whereas other molecules remain below a reactive threshold. Therefore, some reaction will always occur, but the probability increases strongly when more molecules have sufficient activation energy (as provided by heat).

The acceleration factor F is the ratio of the reaction rate at elevated temperature (r_2) to the reaction rate at the temperature during normal operation (r_{ref}) where F becomes a relative r_2 or a_{T2} when the reference rate $a_{Tref} = 1$. There are different names in use: acceleration factor (a_T) or F [1], shift factor, rate multiplier, but the underlying definition is always the same, namely the relative difference in degradation rates between two temperatures. It is calculated from the Arrhenius formula as follows:

$$F = \frac{a_{T2}}{a_{Tref}} = \frac{r_2}{r_{ref}} = e^{\frac{Ea}{R}\left[\frac{1}{T_{ref}} - \frac{1}{T_2}\right]}$$

where T_2 is the elevated temperature and T_{ref} is the temperature during normal operation.

The Arrhenius equation is used extensively, for example, during environmental qualification work (EQ) to extrapolate experimental data to qualified lifetimes. However, it is not entirely certain that it is sensible to extrapolate from a high temperature to a low temperature, as different processes with different temperature dependencies may be behind a change in the material properties. Since the degradation mechanisms can vary depending on the temperature due to, for example, changes in activation energies and DLO phenomena (diffusion-limited oxidation), there are limitations on how much the degradation can be accelerated. In recent years, research has drawn attention to the challenges with different acceleration effects, and more focus has been placed on producing more relevant aging data or to accommodate more caution for extrapolations, which is collectively captured in broader material characterization coupled with 'conservative' predictions.

For radiation safety, the Arrhenius relationship is central since the environmental qualification (EQ) of components included in safety-related equipment requires a simulation or an analysis of the aging expected during the lifetime of the facility, including an accident. For components/equipment that will perform their function during (and sometimes after) an event (accident) and are installed in a space that will have a changed environment in the event (accident), there is a requirement that the component/equipment is environmentally qualified (EQ). This aims to show that the component/equipment will fulfil its function during its qualified service life and have a margin to fulfil its function during (and sometimes after) an event (accident) at the end of its qualified service life. The qualified service life is based on the normal operating environment of the component/equipment. In order to calculate the qualified service life within a reasonable time frame, accelerated testing and the Arrhenius equation are used.

The TBE (Technical Requirements for Electrical Equipment) and KBE (Quality and Inspection Requirements for Electrical Equipment) documents are jointly developed by the Swedish nuclear power plants. In KBE EP 154 [2], which deals with EQ testing, it is stated that the highest acceleration factor that can be used for accelerated thermal aging is 250 and if the activation energy is not known, it should be set to 0.8 eV. In these documents no references are given as to how this guidance originated. However, it is mentioned in the SSM report 2013:10 by Spång and Ståhl [1] that the E_a and acceleration values were derived from studies of insulation materials on cables used in Swedish nuclear power plants. Their report states that the acceleration factor used in artificial thermal ageing should be limited to 250, if it cannot be proven by supporting studies that higher acceleration factors can be used with acceptable accuracy. Such proof should include evidence that the extrapolation method (normally Arrhenius equation) can be applied in the temperature span between the test temperature and the temperature in normal operation, and an analysis of any effects of diffusion limited oxidation.

Polymeric materials are found in many places in a nuclear power plant. The largest fraction in terms of volume is in cable insulation and jacketing, but they are also found in many other applications such as in gaskets, valves and sealants. An ongoing difficulty in nuclear power plants is that so many different materials and in varying qualities are used. Since the aging properties of a material can be very dependent on different additives, it can be difficult to draw general conclusions about the aging of different components, i.e. broad grouping of material types. In addition, there are many different local environments at a nuclear power plant, in terms of temperature, oxygen content, radiation dose, humidity, and chemical environment e.g. oil and this can differ greatly from one plant to another.

All polymers share the common behaviour that their properties depend on temperature (a good introduction to plastics and their properties is for example [3]). Aside from thermal decomposition (pyrolysis), which occurs in the region above 200 to 500°C, for fully amorphous polymers the glass transition temperature (T_g) is the most determining factor for their variation in properties over a temperature range. At the glass transition temperature (short temperature interval) a polymer changes from a rigid, glassy state to a softer, more flexible, rubber-like state. At T_g, the polymer chains gain enough thermal energy to begin moving past one another on a molecular scale, increasing molecular mobility and on a macroscopic scale inducing material ductility and flexibility. Around T_g there is a noticeable change in properties. For example, elastic modulus and hardness drop, while toughness and flexibility increase. Other properties can also be affected by the increased segmental mobility at T_g, such as solubility and permeability and electrical properties such as dielectric constant and electrical conductivity. In addition, because of changes in molecular mobility which are coupled with reactivity, a softer material can more readily experience specific degradation chemistry, which cannot proceed in the 'frozen' glassy state. Rigid amorphous polymers such as epoxies are used below their T_g while elastomers are used above their T_g.

Semi-crystalline polymers also have a T_g but normally it is the melting point range (T_m) which determines their temperature dependence the most. The T_m is the temperature at which the ordered, crystalline regions of the polymer break down and become disordered. At this temperature, the polymer changes from a solid to a highly viscous liquid as the crystalline domains lose their structure and can no longer hold the polymer together via locked-in tie molecules. Unlike the glass transition, melting is a true phase transition that involves a distinct absorption of heat. Above T_m, the material can flow because both the crystalline and amorphous regions are mobile (extrusion of thermoplastics). The T_m (just as the T_g) is normally reported as a single temperature but the phase transitions occur over a small temperature range. Partial melting with some changes in properties can thus start below the reported value of T_m. Even if the melting point is normally the most important transition for semi-crystalline polymers, the T_g can also have an important influence. For example, polypropylene can normally not be used below 0°C since it then becomes brittle and polyphenylenesulfone (PPS), which has a T_g around 90°C, might not be greatly affected by dry thermal ageing above this temperature but its moisture absorption changes drastically. Accelerated ageing for a wet environment should thus not be performed above the T_g in this case. The different polymer transitions can be measured by scanning over a temperature interval using a differential scanning calorimeter (DSC). Degradation chemistry pathways are usually expected to be somewhat different above and below T_g and T_m. Often, it is not a sensible approach to extrapolate specific degradation behavior across material phase transitions, unless a material is very well characterized and any changes in degradation behavior are understood and taken into account.

Within the R&D program on Polymeric Materials in the Nuclear Industry run by Energiforsk, a number of different questions have been raised by the personnel at the nuclear power plants who work with, for example, environmental qualification demands and other LTO issues regarding polymeric materials. One issue that has arisen is the use of the Arrhenius relationship in accelerated testing. Questions that have been asked are the following:

1. Is the maximum acceleration factor of 250 sufficiently general that it can be used for all polymers? If not, which maximum acceleration factor would then be better suited for which polymers?
2. Sometimes products have been qualified by the supplier with a higher acceleration factor than 250. Do they have to be requalified with a lower factor, or can it be proven that the product still meets the relevant requirements without performing a complete requalification? If so, how?
3. How should the activation energy be defined or what sources can be used to determine it? As mentioned above, it is currently stated that with an unknown acceleration factor, a conservative value of 0.8 eV should be used. Is this a reasonable value for all materials/components?
4. What are the general limitations of using the Arrhenius model and what are the uncertainties related to activation energy?
5. In some cases, there are several polymer parts in a piece of equipment that need to be qualified. Is it possible to age at the equipment level or should each polymer part be aged separately?

These questions are not only of interest for extending the service life of existing nuclear power plants, but are also equally relevant for new nuclear power plants that are being built. Here too, the materials need to be qualified for a certain period of operation and some predictive accelerated testing is required.

2 Input gathered from NPP materials experts community

In addition to the thorough review of the "Swedish approach" which is presented in subsequent chapters, input has also been gathered from the broader NPP community. The contacted people originate from both Europe and the Americas and represent scientists, testing institutes, suppliers and end-users. Originally the five questions listed above were posed, and later with the addition of a sixth question. Below is a representative summary of the responses together with some additional references from the literature added by the authors. Some opinions are subjective and may not be broadly shared, but it demonstrates the width of knowledge, suitable references, and the directions that the 'community' embraces or is aware of. It is also clear, that there is NOT a broadly agreed upon single test or guideline, and global consensus on this topic. However, many opinions and thoughts coalesce around shared challenges and sensible approaches subject to what is well known, but also the perceived unknowns and risk in these methods.

1. **Is the maximum acceleration factor 250 general enough that it can be used for all polymers? If not, which maximum acceleration factor would then be better suited for which polymers?**

The general EQ standard IEC/IEEE 60780-323 [4] does not give any numerical value on how much the ageing can be accelerated; it shall just be ensured that the ageing follows homogeneous ageing throughout the sample. It seems as if it is only Sweden (and to some degree Finland) that uses a generic acceleration factor as a way of reducing the risk of too fast acceleration of the degradation mechanisms during thermal ageing for lifetime predictions. Other countries have, however, (just like Sweden) embraced different limitations, but then related to minimum test time and/or maximum temperature. In some cases, the 10 °C rule has been applied, where it is assumed that a 10 °C increase in the temperature raises the degradation rate by a factor of two. I.e. it then reduces the ageing time to half. The temperature used for the thermal component of pre-ageing has in the past been selected to give a test time as short as 100 hours to simulate a 40-year exposure to operational conditions. This was the minimum ageing time permitted under the 1974 version of IEEE 323 [5].

Many of the contacted personnel have considered the 250 factor to be a fairly reasonable and useful number to avoid the most accelerated aging conditions, as to not trigger different degradation mechanisms during accelerated tests. However, especially the scientific community agrees that the best practice is to select an acceleration factor based on the properties and characteristics of the individual materials being tested.

It is particularly important that the selected aging temperature stays below the thresholds where mechanisms may change. Examples are at thermal transitions such as the glass transition temperature (Tg) and/or the melting point (Tm) for semi-crystalline materials. It can also be the onset temperature of oxidative vs. hydrolytic regimes, rapid plasticizer volatilization and antioxidant depletion/degradation kinetics. In short, test temperatures should be selected, so that the in-service degradation mechanism is preserved, and to stay below relevant transitions for specific material formulations. For a more thorough discussion of the 250 factor see subsequent chapters.

In addition, in some countries, materials qualification and continued requalification may be addressed through a broader 'materials behavior package' which incorporates a growing understanding of materials as part of test choices and data interpretation. This brings up a good point, as there are benefits substituting a single test with a more all-inclusive approach which combines screening, targeted testing, material grouping, experience, and feedback from existing similar materials e.g. via condition monitoring. The 'lessons learned' and existing knowledge is a growing contributor towards decision making, but is not easily captured with a locked-in single E_a and acceleration factor for 'all polymers'. Indirectly, this also confirms that methods similar to the existing Swedish test have been recognized as being somewhat limited in their value, perhaps not in all but certainly some situations.

2. **Sometimes products have been qualified by the supplier with a higher acceleration factor than 250. Do they have to be requalified with a lower factor, or can it be proven that the product still meets the relevant requirements without performing a complete requalification? If so, how?**

A case specific engineering evaluation should be able to support acceptance without full re-qualification if it is shown that the dominant degradation mechanism at the elevated temperature is the same as in service. For this the test temperature normally needs to be safely below critical transitions (Tg, softening, melting, oxidation onset etc., see above), and does not induce new mechanisms (e.g., plasticizer loss that would not occur in service). As mentioned in the background, Spång and Ståhl [1], also stated that a higher acceleration factor is acceptable if it can be proven that it can be used with acceptable accuracy. It is also important that the evaluated property is the limiting functional property (e.g., compression set for seals, EAB/IR for cable insulation/jackets, etc). Post aging performance should also meet acceptance criteria with margin (function tests, leakage checks, dielectric tests, etc.).

3. **How should the activation energy be defined or what sources can be used to determine it? It is currently stated that with an unknown acceleration factor, a conservative value of 0.8 eV should be used. Is this a reasonable value for all materials/components?**

Guidance for determinations of cable lifetime are provided in industry standards such as IEEE 98 [6], 99 [7], and 101 [8], IEEE 323 [5] and IEEE 383 [9]. The IEEE 383 states that the activation energy should be derived from a minimum of three data points, at least 10 °C apart. The lowest exposure temperature shall give a life of more than 5000 hours. Beyond these standards, there are multiple documents that provide recommendations for selecting conservative activation energies to establish cable lifetimes. IAEA NP-T-3.6 [10] recommends using 0.65 eV as a conservative activation energy. They also add that the E_a of silicone rubber may be even smaller, 0.43 eV. NUREG/CR-7153 vol 5 [11] recommends using a conservative activation energy ranging between 0.72 eV and 0.78 eV to calculate lifetimes for semicrystalline polymers using the Arrhenius model.

Sweden and Finland use a conservative value of 0.8 eV. One opinion suggests that it seems as if the 0.8 eV historically was a common fall-back option used when the actual E_a was unknown, but it is not universally conservative. In one research group there is support for using 1.0 eV as a conservative value, if coupled with many years of studies on polymeric components extracted from service and hence a solid understanding of material behaviour. This is certainly beyond the starting point of treating polymers as unknown materials. Interestingly, this is somewhat in divergence with the distribution of reported E_a's for polymers, since many ageing processes with lower activation energies have been documented (see discussion and data in section 4).

There are numerous compilations of activation energies, e.g. 'A Review of Equipment Aging Theory and Technology: Revision 1 of NP-1558' [12] provides methods and example E_a values, as well as the Curtiss-Wright Nuclear System 1000 EQDB Environmental Qualification Data Bank [13]. They are not open to the public, but the NRC report (TLR-RESDE 2025-08) [14] also has an appendix listing activation energies compiled from the literature. When known, the property that has been evaluated, e.g. elongation at break, indenter modulus etc., and the temperature interval at which each value was calculated is also listed and a reference is given to the original test data.

Using listed activation energies can, however, be tricky as the E_a can be lower or higher depending on mechanism, material formulation, and environment. When possible, the E_a should be derived from targeted testing which explores the limiting property for the actual material/formulation. Activation energy values will be discussed in more detail in subsequent chapters.

4. What are the general limitations of using the Arrhenius model and what are the uncertainties related to activation energy?

As mentioned above, the conditions of accelerated aging, such as the temperatures selected for determining time to endpoint for E_a calculation, should be confirmed to result in degradation via the same mechanisms as the service temperature aging. For instance, thermal aging at too high temperatures can result in diffusion limited oxidation (DLO). In simplistic terms, DLO means the material ages differently on the surface than its interior, the process becomes more heterogeneous and there are property gradients as a consequence. This means that the degradation of that polymer at the high temperature (e.g., 150 °C) may proceed according to different effective reactions than those that occur at the service temperature (e.g., 30 °C). This is because the measured E_a is for a different reaction (the one that occurs at DLO temperature) than the targeted reaction (the one that occurs at service temperature). Material ageing at low use temperatures is usually rather uniform.

The NUREG/CR-7153 vol 5 [11] shows a couple of examples of decrease in activation energy (E_a) at lower aging temperatures. The NRC report (TLR-RESDE 2025-08) [14] has a chapter dedicated to non-Arrhenius behaviour and non-constant activation energy with some graphical examples of curved Arrhenius behaviour and its impact on qualified life. In addition to variation in E_a values between material formulations, calculated activation energies have deviation and uncertainty based on scatter from the measured values used in the calculation and accuracy of the measurement technique. That is, a calculated E_a value of 1.1eV is more accurately 1.1 ± 0.1, for instance.

As mentioned above, the listed activation energies in the NRC report (TLR-RESDE 2025-08) [14] are given (when known) with the property that has been evaluated. It is important to note that the activation energy depends on the polymer property that is evaluated and also the choice of endpoint e.g., in EaB 50% of initial value or 50% of remaining absolute value. There are some variations whether the E_a should be defined by the limiting property of the ultimate failure mode, or by using more sensitive early warning signals for degradation. Example of the former is for cable systems to use elongation at break (EaB) since this normally correlates best with the integrity of the insulation/jackets. For O-rings/seals, the E_a should instead be derived from compression set/force retention rather than elongation at break, because seals fail under compression and leakage, not tensile rupture.

Others have argued that experiments conducted to estimate E_a should be made at temperatures close to service temperatures using techniques such as oxygen consumption, that have the ability to cover wider temperature ranges with shorter experiments. This ability allows one to use the oxygen consumption results to confirm a correlation (same E_a) with the mechanical properties (e.g., elongation) at the higher temperatures and to use low temperature oxygen consumption results to probe any changes in E_a in the low temperature extrapolation region [11].

A problem with the latter approach is that E_a values vary between different testing methods. One reason for this is that different methods probe different stages of aging, where the predominant aging mechanism could be associated with different E_a values. For example, OIT is correlated with loss of antioxidants, which occurs at an early stage of degradation. The oxidation will usually not start until after this stage. Note also that oxidation is a chemical change and not a mechanical change. Chemical changes typically happen earlier than mechanical embrittlement as measured by e.g. a decrease in EaB, but there is no universal conversion between degree of chemical degradation such as oxidation and loss of mechanical properties. Colour change (including yellowing due to the conjugated species produced during aging), oxygen uptake and the FTIR absorption peaks in the carbonyl region are also measurements related to the formation of new chemical structures and not directly to loss of mechanical integrity.

Non-homogeneity between material batches has been reported to have been common in the past. If the tested samples are of good or poor quality, the extrapolated service life can vary significantly. One example for an older cable resulted in a predicted lifetime of approx. 40 ± 26 years. For modern materials this is normally less of a problem, but there are still examples where variations in filler materials, pigments and fire retardants have influenced the failure time to a very large degree.

There are uncertainties with using the Arrhenius model that are recognized and discussed in industry guidance documents such as Reg Guide 1.89 Revision 1 [15] and Revision 2 [16]. During the EQ process, these uncertainties are typically accounted for by the margin and conservatism incorporated into the cable lifetime determination (e.g., 40 years at a specific temperature). Margin is incorporated in during DBE testing by subjecting cables to simulated accident conditions that exceed what they would experience in the plant (e.g., the peak temperature for the LOCA test is 15°F (8°C) higher than the expected accident peak temperature for the plant environment). Conservatism can be factored in when establishing the qualified lifetime and qualified service temperature.

5. **In some cases, there are several polymer parts in a piece of equipment that need to be qualified. Is it possible to age at the equipment level or should each polymer part be aged separately?**

In IEEE 383-2015 [17] it is stated that cable components, like the jacket and the insulator can be aged separately. However, the overall qualification documentation package shall include a documented rationale for the approach used for the accelerated ageing of the composite assembly. Sample form, size and shape shall be considered. The sample thickness should be representative of what will be used in service. In general, it can be possible to age components separately when the assembly/disassembly does not change stresses or it is possible to impose representative stress states (e.g., seals should be aged under compression).

When conducting aging at the equipment level, it is good to identify the life-limiting component of the equipment first, so that it becomes clear what to expect (i.e., the polymer most susceptible to age-related degradation). In addition, defining and testing for changes in the expected key use properties is advantageous. For example, for seals their compressive state (compression set) may matter less, as long as sealing force and seal tightness are maintained. For material assemblies, the end user is encouraged to define the most important performance expectations and test accordingly. Qualification testing should focus on the needed use properties and the material purposes, and less on the academic nature of general polymer behaviour. Another concern is whether the aging occurs differently for the polymers in the combination product than when they are aged individually. There can be interactions between materials that contribute to aging, such as a chlorinated jacket releasing hydrochloric acid that reacts with neighbouring materials, and attenuation of aging from materials protected in an assembly, such as inhibited oxidative aging of insulation polymer inside a shielded cable assembly. These can be considered as different aging mechanisms based on the polymer exposure to the aging stress. It is also important to look for accelerated aging phenomena that can occur when polymers are aged in contact with other materials (e.g., the copper catalytic effect that has been observed in many polymer types). Equipment level aging is preferable when interaction/stress states (compression, clamping, wiring harness bend radii, enclosure thermal gradients) matter for performance. Combined material ageing may demonstrate unexpected behaviour that individual polymer testing may not capture. Hence, combined material testing for qualifications purposes is in fact encouraged. But any such testing should also ensure O_2 access to avoid inadvertent DLO conditions.

In a piece of equipment, the lowest activation energy of all materials within is often used to recalculate the qualified life, ensuring the most conservative results, i.e. the shortest reassessed qualified life. The IAEA IGALL TLAA201 guidance [18] has a chapter on "Selection of Appropriate Material for the Assessment of Equipment

Ageing" which describes "the Thermal Leading Material (TLM) approach" which can be used instead, but it assumes robust datasets for each critical material.

6. **Would it be more reasonable to put maximum testing temperatures as a limitation (depending on polymer type) rather than a general maximum acceleration factor?**

As discussed under question 1, it is particularly important that the selected aging temperature stays below the thresholds where mechanisms change. Some polymers have these transitions not very far from the usage temperature, which means that lower acceleration temperatures must be used which will certainly extend the time of the test. Other polymers are much more temperature stable and could be accelerated using much higher temperatures. From this perspective a maximum test temperature by polymer type would be more rational than a generic acceleration factor. The main challenge is that modifications such as curing system, fillers, plasticizers, antioxidants, and the processing can all shift transitions and hence prevailing mechanisms. A guideline based on just polymer type would thus not be generically valid.

2.1 SUMMARY OF CHAPTER 2

These questions and discussions with feedback received from multiple experts across the field summarize the following:

- A 'gold standard' high fidelity short-term test does not exist
- Everyone recognizes the challenge towards the most meaningful predictions
- Aging test temperature, transitions, temperature that induce different mechanisms, acceleration factor, E_a, non-linear and perhaps Arrhenius curvature due to mechanistic changes need to be considered
- Variations in E_a and ageing behaviour within a class of material are well-known
- There is also no firm cut-off for a lower most conservative threshold E_a for unknown materials. A low E_a boundary is a compromise
- Materials with lower E_a's than 0.8 eV (77.2 kJ/mol) in their ageing behaviour exist
- Material characterization packages add value beyond single point extrapolations

3 Alternatives to the Arrhenius Equation

3.1 RATE CHANGE PER 10-DEGREE METHOD

Both, van't Hoff and Arrhenius worked on chemical kinetics in the late 1880s and recognized the underlying dependence of reaction rate on temperature [19]. It is possible that Arrhenius received more credit than deserved while building on original work by van't Hoff. As a consequence of their parallel efforts developing the concept of an activation energy and rate behaviour, it was quickly recognized that with moderate E_a's the rate changes by two to three times when the temperature is raised by 10°C. This knowledge is very helpful for quick estimations, and some practitioners or engineers may regard this as a '10-degree rule', also called the Q10 rule, which postulates that the polymer thermal aging rate k is doubled for every temperature delta of 10°C. However, this concept factually does not match the mathematics of the Arrhenius equation, and it is unlikely that such a rule has a rigorous science-based definition, although it does offer empirical guidance. The effort required to determine whether the assumption of the rate doubling per 10-degree is a sufficiently good approximation for polymer ageing is about the same as the effort required to use the Arrhenius model. Importantly, any temperature changes of 10°C resulting in a doubling or halving of rate and reaction time, respectively, is by default nonlinear or curved Arrhenius behaviour. Arrhenius defines the relative change in rate/time per 10°C to depend on temperature (as a consequence of its 1/T relationship). However, in some small temperature regime a doubling of rate per 10°C is mathematically correct subject to the common E_a's encountered. In some cases, Arrhenius with its linear relationship in 1/T will be a boundary, in other cases curved Arrhenius with a near doubling of rate per 10°C may in fact more closely resemble actual polymer behaviour. This will be briefly discussed after we examine the basic Arrhenius behaviour in section 7.2.

3.2 TIME–TEMPERATURE SUPERPOSITION

A time–temperature superposition principle is often used to determine temperature-dependent mechanical properties of linear viscoelastic materials from known properties at a reference temperature. The WLF-equation (Williams–Landel–Ferry) is a procedure for shifting data for amorphous polymers obtained at elevated temperatures to a reference temperature. In order to relate strains at different temperatures a time shift factor, a_T is introduced. The shift factor, a_T, is defined as the ratio between the time for a process to reach an arbitrary temperature and the time for the same process to reach a reference temperature. It must be noted that the WLF equation is defined for viscoelastic properties only, and is only valid when there is no degradation of the material, meaning the WLF approach deals with pure underlying physical phenomena of a polymer. It can be used for creep and compression set data governed by viscoelastic behaviour, when there is no chemical degradation or physical loss of additives.

3.3 THE EYRING MODEL

The Eyring model has a theoretical basis in chemistry and quantum mechanics and extends Arrhenius by including multiple stress factors, not just temperature. This makes it useful for predicting polymer degradation when ageing is driven by combinations of e.g. temperature, mechanical stress, and humidity. Polymer degradation mechanisms (e.g., oxidation, chain scission, hydrolysis) often depend on more than temperature alone.

In practice, the Eyring Model is usually too complicated to be used in its most general form and must be "customized" or simplified for any particular failure mechanism.

4 Perspective on the range of E_a's in large data compilation

Analyzing the data from the appendix in TLR-RES/DE 2025-08 [14] it can be concluded, that after removing data from e.g. water absorption and oxygen permeation as well as OIT and TGA measurements, the number of data points falling below 77.2 kJ/mol (0.8 eV) is ~ 13% of the total. OIT and TGA based E_a-data should be discounted as they are usually associated with excessively high temperature and fast degradation behavior, meaning rapid stabilizer consumption or the beginning of pyrolytic decomposition that does not reflect long term use conditions (clearly mechanistic changes). The data can be plotted through basic statistical analysis showing the number of reported values with increasing activation energy. Figure 1 shows the available cumulative data in kJ/mol and eV. Figure 2 shows the same data as the derivative of the fitted sigmoidal distribution yielding a normal distribution. Importantly, we note that approximately 13% of the data fall below the 0.8 eV threshold. This means that not all 'ageing data' which have been captured in this broad compilation yield E_a's greater than 0.8 eV.

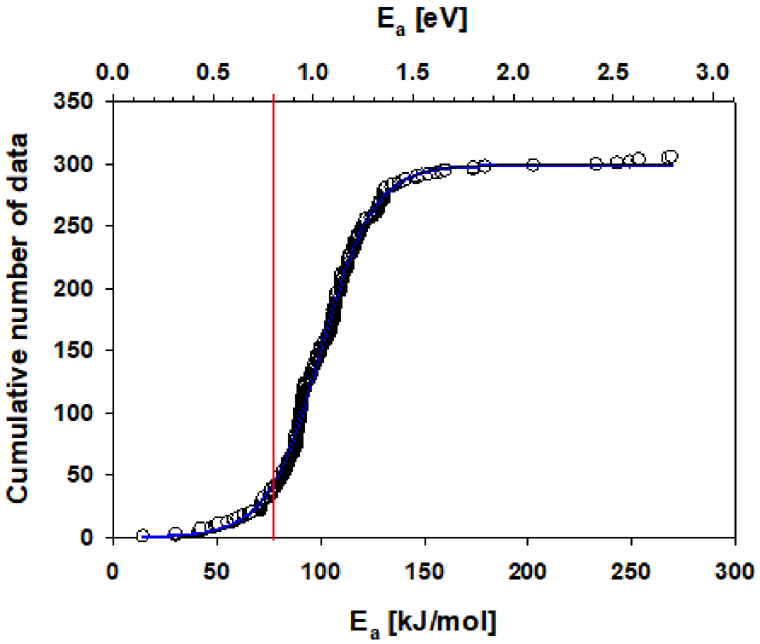

Figure 1. Cumulative number of tabulated E_a data from reference [14] with activation energy as both kJ/mol (bottom x-axis) and eV (top x-axis). The red line shows 0.8 eV (77.2 kJ/mol). Some E_a's are below this threshold. There are a few low and high E_a data points that are not perfectly captured by a simple sigmoidal fit, but this data set closely follows a 'normal distribution'.

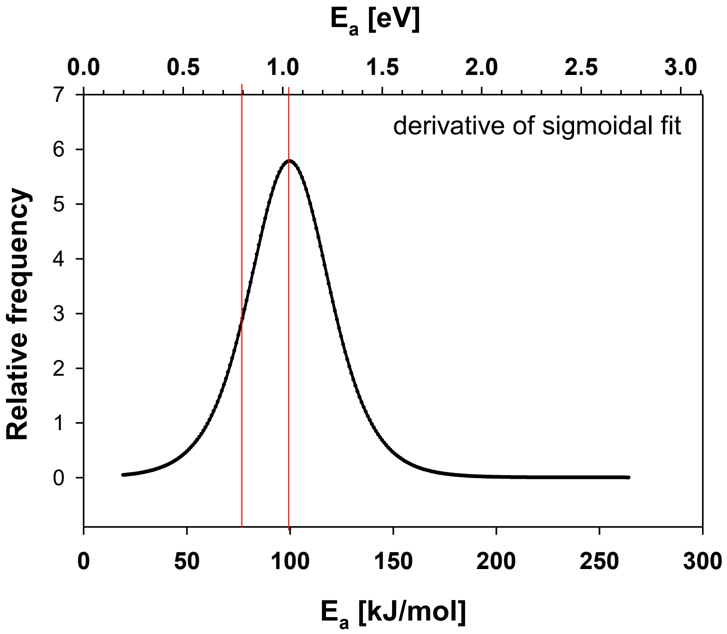

Figure 2. Derivative of the sigmoidal fit shown in Figure 1 yielding a 'normal distribution' with a center at 100 kJ/mol (1.04 eV).

The average activation for this data set is 100 kJ/mol (1.04 eV) as the center of this contribution. When filtering the data to select only E_a values that have been derived using temperatures below 100°C, the average value drops to ~ 82 kJ/mol. This is in line with numerous reports showing lower activation energies for lower temperature intervals. In addition, the number of reported values below 77.2 kJ/mol (0.8 eV) increases to 37%. It can be noted that most of these low temperature data points are from oxygen consumption studies, hence not directly linked to loss of mechanical integrity, but nevertheless indicative of oxidative polymer degradation processes.

Considering the range of E_a data it is not possible to easily recognize any trend and grouping of unique polymer types that are more or less represented in the group of low E_a values. The temperature ranges for the measurements and the evaluation method is a more dominant variable rather than the material type. Any such generalization based on polymer type can be misguiding, as was mentioned above, since modifications such as curing system, fillers, plasticizers, antioxidants, and the processing can all influence the prevailing degradation mechanisms and its E_a. In addition, many of the lower E_a data originate from extended experiments of material ageing, and oxidation rates at low temperature, and are not necessarily indicative of material type.

The variation in reported E_a within one group of polymeric material shows significant spread, even when selecting only the same type of data set, in this case elongation at break (EaB); see examples below for EPR (Table 1) and XLPE (Table 2). This means grouping of materials does not easily yield a single representative E_a, although 80 kJ/mol could be seen as a conservative value for EPR and XLPO, but then many materials have not been examined at low temperatures where lower E_a's have often been observed. The problem is that many existing E_a's originate from readily available higher temperature data and a limited temperature range. The available data are best discussed as a distribution which then also includes guidance for how to accommodate 'unknown materials', which means some materials could easily fall below the 0.8 eV threshold, and this is what matters.

Table 1. Spread of E_a's in a group of EPR (ethylene-propylene-rubber) elastomers. From reference [14].

Ea (kJ/mol)	Temperature range (°C)	Polymer	Dataset
63	100 to 120	EPR	EAB
83.8	100 to 120	EPR	EAB
84	100 to 120	EPR	EAB
85.1	100 to 120	EPR	EAB
85.4	100 to 120	EPR	EAB
87.2	100 to 120	EPR	EAB
87.3	100 to 120	EPR	EAB
88	99 to 138	EPR	EAB
88	99 to 139	EPR	EAB
93.52	100 to 120	EPR	EAB
94.5	100 to 120	EPR	EAB
95.9	100 to 120	EPR	EAB
102	100 to 120	EPR	EAB
106	100.9 to 170	EPR	EAB
106	109 to 160	EPR	EAB
106	100 to 170	EPR	EAB
106	104 to 170	EPR	EAB
106.13	140 to 170	EPR	EAB
106.13	120 to 160	EPR	EAB
110	100 to 120	EPR	EAB
112.2	121 to 165	EPR	EAB
130	120 to 175	EPR	EAB

Table 2. Spread of E_a's in a group of XLPE (crosslinked polyethylene). From reference [14].

Ea (kJ/mol)	Temperature range (°C)	Polymer	Dataset
66.1	100 to 120	XLPE	EAB
83.8	100 to 120	XLPE	EAB
94.5	100 to 120	XLPE	EAB
94.57	100 to 120	XLPE	EAB
100	100 to 120	XLPE	EAB
101.4	121 to 165	XLPE	EAB
105	70 to 160	XLPE	EAB
109.6	121 to 165	XLPE	EAB
110	100 to 120	XLPE	EAB
128.32	120 to 160	XLPE	EAB
232.76	115 to 165	XLPE	EAB
242.95	115 to 165	XLPE	EAB
249.12	115 to 165	XLPE	EAB
253.04	115 to 165	XLPE	EAB
253.49	115 to 165	XLPE	EAB
267.52	115 to 165	XLPE	EAB
269.11	115 to 165	XLPE	EAB

5 Screening of thermal polymer stability for performance assessment

A current 'Swedish' approach for the evaluation of polymers, materials and components for their thermal performance in NPP applications (nuclear power plant environment) is based on assumptions of a boundary (lowest) activation energy (E_a) and maximum rate multiplier (acceleration factor), both being applied for material testing purposes. This approach is summarized in an existing report [1] and has been used previously for screening tests of material behavior and extrapolation guidance. It is clear that such a basic 'accelerated ageing' screening test is not meant to replace in-depth lifetime prediction studies, and importantly, that by the nature of this limited approach there is remaining risk for performance predictions. First of all, we shall agree and emphasize:

- Overly simplified screening tests cannot replace comprehensive ageing studies
- Short screening tests incorporate risk subject to limited data and assumptions
- Screening tests rely on boundary assumptions for material behavior to justify some predictions
- Meaningful screening tests, however, can offer good initial guidance and perhaps identify material vulnerabilities, thereby justifying further material examination, or contribute to material data packages for qualification
- Depending on risk assessments, reliability expectations, failure consequences and the application environment, rapid screening tests versus more in-depth ageing studies will always need to be carefully balanced

The current discussion offers a pragmatic evaluation of this screening test by examining its boundary and assumption, predictive nature, likely limitations and the pro/cons of modifications/alternatives. It is obvious that any accelerated ageing test for the purpose of basic predictions must involve an E_a and acceleration factors. Further, in many cases linear Arrhenius behavior is assumed and applied, subject to the absence of other guidance, or better informed understanding of material behavior. We shall focus on the following aspects which defines such a screening test:

- The existing recommendation for testing involves a maximum accelerating factor of 250 and an E_a of 0.8 eV which equals 77.2 kJ/mol.
- In principle, a single-point ageing exposure is sufficient to fulfil the expectations of this test. As long as we accept the applicability of linear Arrhenius behavior, any predictions will be mathematically correct (meaning they fit the linear Arrhenius model). However, it is also well known that extrapolations over a large temperature regime (i.e. 140 to 20°C) have increased uncertainty and cannot reliably predict excessively long times at RT (the same issue as using a very high acceleration factor).

- A lower acceleration factor demands longer ageing at a lower temperature thereby reducing the extrapolative regime. In contrast, a higher acceleration factor means shorter aging at an even higher temperature, thereby further removing the test from the application condition.
- The E_a stated (0.8 eV) represents a lower boundary. A lower E_a means the degradation rate drops less as the temperature is lowered. Or less ageing per time (enhanced stability or performance period) occurs at the testing temperature. This means that for low E_a's, even long accelerated testing will predict limited application lifetimes. A high E_a gives the opposite, i.e. that relatively short term thermal ageing can be used to predict long application lifetimes. In essence a more limited test, but substantial performance expectations are implied in comparison.
- Any approach that defines only E_a and acceleration factor leaves open the target and test temperature, as well as relative timeframes (test and application demands).
- With defined application target for time/temperature, a minimum performance at the elevated T testing condition can be calculated and checked. This likely matches the original intent of this test.
- If actual E_a's are lower or unexpected non-linear Arrhenius behavior with curvature towards lower E_a at lower temperature occurs, then this test implies flawed over-confidence for performance.
- Any actual E_a's lower than the boundary (0.8 eV = 77.2 kJ/mol) means risk for predictions.
- The above considerations show that a quick single-point screening test for equipment qualification (EQ) purposes is intrinsically challenging, despite the best intentions with this test.
- No single test usually matches a broad framework of expectations and scenarios.

Importantly, this screening method involves a lower boundary for E_a (0.8 eV), and if the actual E_a is lower, will result in performance overestimations. Hence, the suitability of this test to a first degree relies on capturing the collective behavior of polymers in terms of applicable activation energy boundary. The spread in E_a's in polymer ageing is reviewed in chapter 4. It is fair to state that historically 0.8 eV is a reasonable and justifiable definition at the lower end of the many E_a's observed for thermal polymer ageing. E_a's are often higher than 0.8 eV (77.2 kJ/mol); for the purpose of further discussions we can round this value to 80 kJ/mol. Thermal decomposition E_a's (pyrolytic, TGA, etc.) are usually much higher than this, into the range of 150 – 250 kJ/mol. Thermal ageing of polymer is often seen with E_a's between 80 – 120 kJ/mol. However, as discussed in chapter 4, lower E_a's have been measured and non-linear Arrhenius behavior with curvature toward lower E_a's has also been reported [20]. Many observations for curved Arrhenius behavior in polymer oxidation were summarized to highlight the resulting challenges in predictive polymer aging studies [21]. If the Swedish report and its testing guidance originates from the 1980s to 2000s, it represents a reasonable approach subject to the existing knowledge at the time. However, our awareness and understanding of polymer ageing behavior has grown over the years. In particular, more has been learned about non-linear Arrhenius behavior and the need to conduct testing either with multiple points or with a reduced spread between testing and application temperature. Hence, we need to discuss the following:

- Is the lowest E_a of 0.8 eV still a good choice considering improved knowledge in polymer ageing?
- Can an acceleration factor of 250 still be justified? What will be more appropriate?
- What are the pro/cons and implications of this suggested testing approach?

6 Thermal E_a data for materials examined for nuclear power plant environments

A good reference report which includes thermal degradation aspects is the 'NEPO work' (Nuclear Energy Plant Optimization) and its associated papers from the early 2000's [22]. Some earlier studies discussed a large temperature range for thermal behavior [23]. A nitrile elastomer showed E_a in the range of **90 to 80 kJ/mol**, and an EPDM elastomer in the range of **118 to 82 kJ/mol** [23]. In follow-up work an EPR elastomer yielded an E_a of ~ **106 kJ/mol**, although with indications of a drop at lower temperatures. The observation of slight curvature in Arrhenius plots has been commented on before, and such a behavior is now commonly accepted, although its magnitude requires careful studies [20,24-33].

The NEPO report discusses a crosslinked polyolefin (XLPO-04) with very linear Arrhenius behavior of ~ **110 kJ/mol** [22]. For XLPO-02B this discussion is offered. "If we use the shift factor of 1.9 found in Fig. III-50 between 99°C and 109°C, this leads to an activation energy of **76 kJ/mol** (18.1 kcal/mol) between these two temperatures. Using this E_a to extrapolate the lower x-axis time scale at 99°C to 50°C leads to the upper x-axis time scale shown in the figure. For a 50% residual elongation this extrapolation predicts a 470-year lifetime at 50°C, not really surprising given that practical end of life has not been reached after **11 years at 99°C**. To have the predicted lifetime drop below 60 years at 50°C would require the Ea to drop to an average value of ~**33 kJ/mol**, an exceedingly low Ea". For XLPO-5 the authors conclude that "The empirically derived shift factors from these three figures are then plotted on an Arrhenius plot and the results (Fig. III-58) indicate an Arrhenius activation energy of ~**130 kJ/mol**".

A neoprene cable jacketing material displays linear behavior with an Arrhenius E_a of **98 kJ/mol**. As discussed in this report, "It is interesting to note that the reduction in E_a values found for Neo-02 from a combination of elongation and oxygen consumption results (**96 kJ/mol** above 80°C dropping to ~**76 kJ/mol** at 25°C) is similar to the results found for elongation on the Neo-01 material (Fig. III-7)." For chlorosulfonated materials (Hypalon cable jacketing materials) "at temperatures above ~90°C, the results are reasonably linear yielding an average Arrhenius activation energy of ~**107 kJ/mol**. Below 90°C, there is evidence of a downward curvature in the Arrhenius plot, similar to that found from elongation results for the Neo-01 material (Fig. III-7)".

Chlorinated polyethylene "(CPE-02) indicates an Arrhenius activation energy of ~**112 kJ/mol**. If this activation energy remains unchanged at lower temperatures, an extrapolation to 50°C leads to a predicted elongation lifetime (50% absolute) of ~ 1300 years. Even though there is no data available to probe the extrapolation region, this "Arrhenius" extrapolated lifetime is so large that no realistic drop in activation energy below 109°C would yield 50°C lifetimes less than 100 years. In particular, the **112 kJ/mol** activation energy found above 109°C would have to drop to an average Ea of ~**66 kJ/mol** (15.8 kcal/mol) from 109°C to 50°C in order to reduce the 50°C lifetime to 100 years. Thus we conclude that the CPE-02 material should have a very long lifetime at typical aging temperatures encountered during aging of nuclear power plants”. This discussion resembles the Swedish approach emphasizing a lowest Ea and minimum higher temperature accelerated ageing behavior that can be extrapolated.

Further, in the NEPO report [22] for an EPR (EPR-01) elastomer an “Arrhenius plot of the empirically derived shift factors is shown in Fig. III-34 and the results give very linear behavior with an Arrhenius activation energy of ~**106 kJ/mol**. In particular, the **106 kJ/mol** activation energy found above 101°C would have to drop to an average E_a of ~**35 kJ/mol** (8.4 kcal/mol) from 101°C to 50°C (a 65% drop) in order to reduce the 50°C lifetime to 60 years. Since such a large drop in E_a has never been reported over such a small temperature range, we conclude that the EPR-01A material should have a very long lifetime at typical aging temperatures encountered during aging of nuclear power plants”. Another EPR (EPR-04) is discussed as “Given the uncertainties inherent in extrapolating nicely behaved Arrhenius results, attempting to extrapolate results for EPR-04 would be even more problematic and dangerous. However, it should be noted that our accelerated studies involved aging times up to ~ **7 years at 99°C**. With “practical end of life” requiring ~ 7 years at this temperature, the activation energy from 99°C to 50°C would have to drop to an average value of ~ **44 kJ/mol** (10.5 kcal/mol) in order for the extrapolated 50°C lifetime to be less than 60 years.” For EPR-03 “The Arrhenius plot gives reasonable linearity with an activation energy of ~ **88 kJ/mol**. An extrapolation of this activation energy to 50°C predicts a lifetime of ~300 years. In order for the lifetime to fall below 60 years at this temperature, the average E_a from 99°C to 50°C would have to drop below ~ **56 kJ/mol** (13.4 kcal/mol).”

These discussions emphasize that a) E_a’s below the 70 to 80 kJ/mol regime are not anticipated and b) often extensive thermal ageing studies were conducted with data available that are not too far removed from assessed application temperatures. A stability of 11 years at 99°C or 7 years at 99°C equates to acceleration factors of less than 10 for 50-year lifetime predictions at 50°C. It is clear that experimentally confirmed extended higher temperature lifetimes (beyond years) coupled with boundary activation energies offers meaningful and low risk extrapolations. However, we do need to capture the following:

- There is documented value in longer-term thermal ageing evaluations
- E_a’s between 76 and 130 kJ/mol were observed
- Curvature and hence non-linear Arrhenius behavior was recognized as a concern
- Margins in test results were used to overcome possible Arrhenius curvature

7 Basic principle of materials testing using Arrhenius

The underlying principle for any accelerated ageing, material testing or polymer performance screening - whatever we may wish to call this methodology - is to accelerate the degradation chemistry or physics through increased temperature. Of course many materials ageing processes can also be accelerated via increased humidity exposure, other reagents, oxidants, catalysis, presence of acids/bases, applied stress, radiation, increased oxygen pressure and similar means. However, increasing the temperature is a simple acceleration approach in any ageing test, which can occur in parallel with any other added degradation accelerants. Increased temperature under atmospheric conditions captures oxidative degradation chemistry, a key issue for polymer ageing. Diffusion processes will also be accelerated, as is molecular mobility.

Arrhenius based ageing embraces the concept that chemical rates increase with temperature, and that when ln(rates) vs inverse temperature are plotted, the slope of this plot contains a factor called the Activation Energy (E_a). In mathematical terms Arrhenius establishes shift or acceleration factors for rate and time with temperature. The main implications are:

- Aging rates increase with T
- Relative lifetimes shorten with T
- A longer ageing test (withstanding the applied condition) at equal T means better relative performance
- An identical aging time but at higher T also means better relative performance

We also recognize that accelerated materials testing has some intrinsic shortcomings.

- Not all degradation mechanisms are accelerated equally
- Short term testing implies significantly accelerated processes
- The underlying E_a or behavior with T may not be known particularly well
- Extended extrapolations have increased error margins

Since there are no viable alternatives than having to use some accelerated testing (higher T exposure) for screening purposes of material behavior, and in particular polymer reliability, we are however required to conduct accelerated ageing as best as we can. This means we relate to the concepts of Arrhenius behavior and its mathematical background and wish to design ageing tests that have meaningful boundaries, are conservative in their design and reduce risk as best as possible. We all agree that a poorly conducted accelerated ageing test will have high uncertainty and essentially no predictive value. If we know little about specific material behavior, have no understanding of how it degrades and with what E_a, we shall all agree that a simple 1 d performance test at 120°C is probably not a good indicator to justify performance of 50 years at 50°C. However, a 10-year test at 100°C would very likely give excellent confidence to successfully predict a minimum of 50 years at 50°C. This means intuitively we can all recognize what will not be a meaningful test and instead what could be a justifiable approach, perhaps even including over-testing.

Designing a reasonable screening test of some duration/temperature that offers predictive value becomes the challenge: The questions then are manifold. What might be a meaningful test? What might be best testing when building on current knowledge of polymer degradation? What gives better confidence through improved testing design? Which test best captures Arrhenius behavior? Which testing approach reduces risk in its prediction? Of course there will always be remaining risk through the underlying nature of accelerated testing, but what can be done to minimize risk and increase predictive value or margins?

7.1 RATE AND EQUAL CONVERSION TIME WITH T ARE DESCRIBED BY THE ARRHENIUS EQUATION

While ‘materials degradation science’ is usually focused on the rate of some deterioration process (chemical or physical property changes described as ageing or degradation), the emphasis for our engineers and materials users is usually the opposite, meaning performance over time. Degradation rate and performance time are indirectly proportional and dependent on temperature with E_a. The Arrhenius approach captures the following:

- Degradation rates (k_T) usually increase when the temperature is raised
- Materials performance time (t_T) decreases as a consequence
- The relationship that couples (k_T) and (t_T) with temperature is the Arrhenius approach
- Arrhenius behavior often applies to chemical rates and also materials aging, and often is found to display linearity in Arrhenius plots ($\ln k \propto {}^{1}/_{T}$)
- Absent any experimental evidence for deviations from linear Arrhenius behavior meaning curvature, Arrhenius based extrapolations are an accepted and widely used method
- However, some risks are associated with this approach and will be discussed later

It is important to recognize that both (log) or (ln) Y-axes scales serve to show a linear Arrhenius relationship. There are however different factors for their slopes to yield E_a, meaning 8.314 J/mol-K (gas constant) for the ln-scale, and ln10*8.314 = 2.3026 * 8.314 = 19.144 J/mol-K when a slope is obtained from the plotted (log) scale. Point is, as long as log or ln scales, or log or ln of rate or time (= 1/rate) on linear Y-axes are plotted, the Arrhenius relationship implies straight lines in its 1/T dependency. This is shown in Figure 3 with multiple axes visualizing logarithmic/natural-log scales or linear scales of log/ln data. Logarithmic scales (inner left and right axes) have one key advantage, as they show the primary data and help the reader by being able to directly compare data.

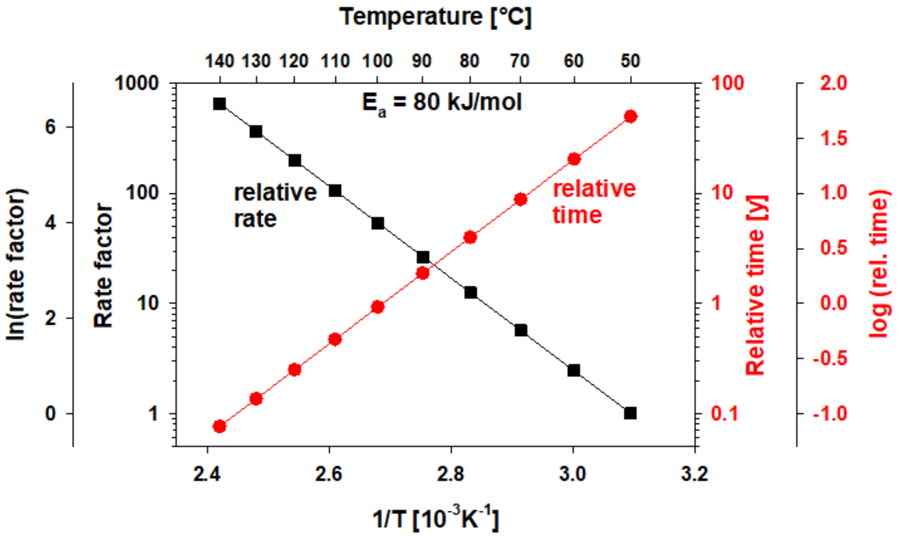

Figure 3. Common Arrhenius plot for 80 kJ/mol showing relative degradation rate and time with 1/T.

For example, for an E_a of 80 kJ/mol, in relative terms a rate will increase by ~ 660 times between 50 and 140°C, with the corresponding time decreasing from 50 years to ~ 4 weeks, respectively. We note that Arrhenius behavior is used to calculate the increase in rate – acceleration factor (a_T) - with increasing temperature. This is expressed by a rate multiplier, meaning the rates are becoming X times (a_T) faster. The opposite holds as well, meaning the time (t_T) to reach equivalent damage, expressed in simple terms as a 'lifetime' decreases with increasing temperature in reciprocal $1/a_T$ fashion. Arrhenius is based on chemistry and chemical rates. And as long as degradation chemistry is involved, materials failure and hence performance times are given by a degree of 'chemical conversion'. For polymers those are for example expressed as oxidation level, oxidation state, oxidative damage etc., and simply as a damage level that defines and limits the expected performance time. While Arrhenius is focused on rates and is then also related to time, the situation with degradation state or 'conversion' is more complex. Material degradation as the 'translation' from primary material chemistry to physical properties often involves polymer physics and secondary processes that a-priori are not covered by Arrhenius. Point is, material damage as the expression of some change of properties is often more sensitive at lower temperatures, and Arrhenius cannot accommodate such effects as it relies only on the kinetics themselves.

- The use of the Arrhenius methodology originates from chemical kinetics under ideal conditions (gas phase, solution, or liquid with rapid mixing of reagents)
- The Arrhenius equation serves to calculate the changes in degradation rate (k_T) with T
- It yields a rate multiplier factor, here defined as a_T when ratioed to a reference value (a_{Tref})

- For equal conversion levels, the required times t_T are inversely proportional to k_T or a_T
- For polymer degradation (i.e. oxidation), damage levels (conversion) are often a combination of reactions (kinetics) and physics (how chemistry results in physical property changes). Hence, degradation is more complex than only considering rate dependence on temperature.

$$k_T = A \times e^{(\frac{-E_a}{RT})} \quad \text{or} \quad \ln k_T = \ln A + \frac{-E_a}{RT}$$

$$k_T = \frac{1}{t_T} \propto a_T \; (shift\, factor)$$

$$\frac{a_{T_2}}{a_{T_{ref}}} = e^{\frac{E_a}{R} \times (\frac{1}{T_{ref}} - \frac{1}{T_2})} \propto k_T$$

Note: For discussions here, the ‘Swedish approach’ uses an acceleration factor of $a_{T2} = 250$.

7.2 THE MATHEMATICAL EFFECT OF THE MAGNITUDE OF ARRHENIUS E_a FOR TESTING AND TIME PREDICTIONS

When considering accelerated material testing and its predictive value, we first need to highlight the implications of high or low activation energies. In principle terms, a high E_a means ‘high’ acceleration factors, a ‘high’ shift with temperature and consequently long times at low temperature. A low E_a relates to the opposite, meaning limited shifting with T, longer times at high temperature or when predictions are made relatively shorter times at lower temperature. The two illustrations below in Fig. 4 highlight these scenarios when implying strict linear Arrhenius behavior, by arbitrarily comparing an E_a of 80 or 120 kJ/mol with a) an assumed ‘lifetime’ of 50 years at 50°C; and b) a 28-day testing regime at 140°C used for minimum ‘lifetime predictions’.

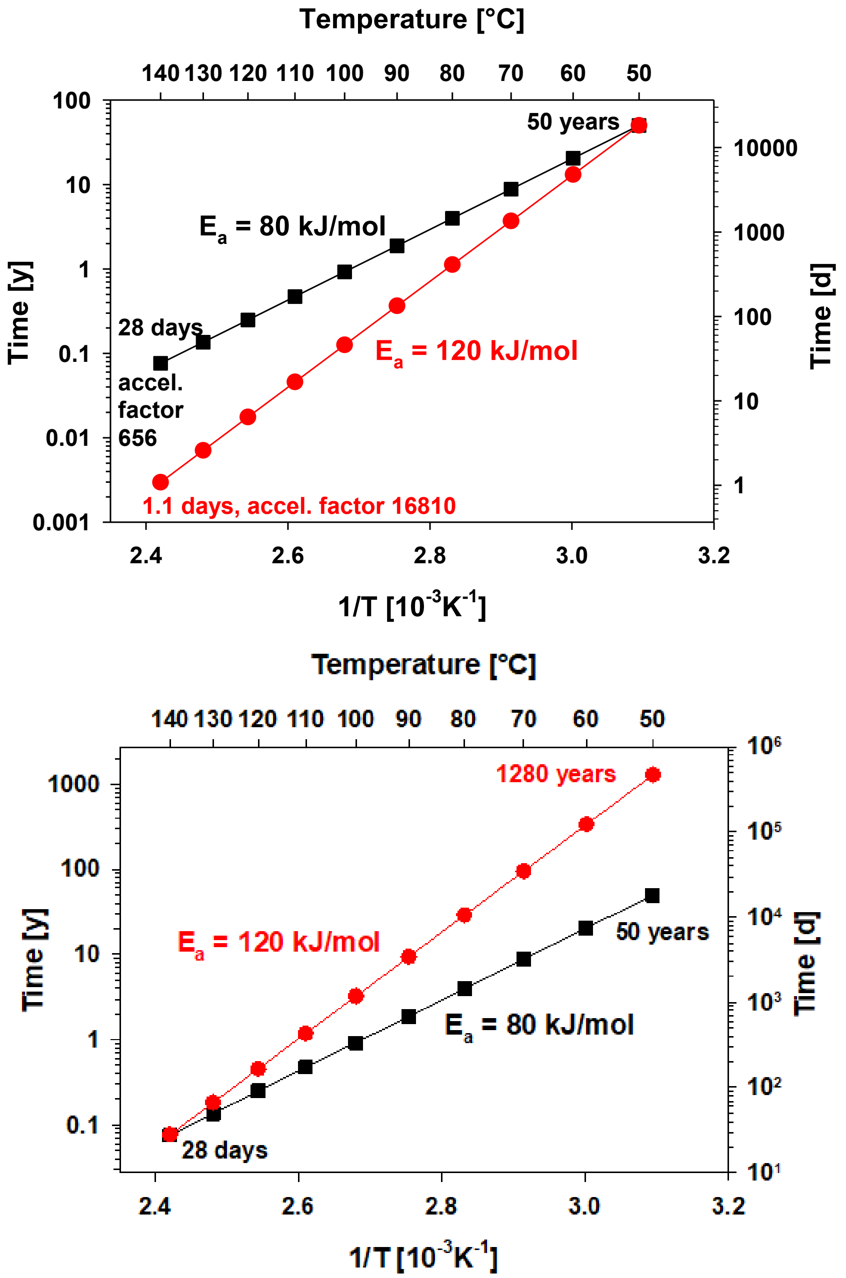

Figure 4. Required minimum testing times at 140°C to predict 50 years at 50°C for 80 and 120 kJ/mol (top), and the predictions from specific test time at 140°C towards 'mathematical lifetimes' at 50°C (bottom).

Let's assume an arbitrary lifetime expected of 50 years at 50°C is probed with accelerated aging (Figure 4). When performance tested at 140°C, a material with 80 kJ/mol will require 28 days, but with 120 kJ/mol only ~1 d. In comparison, if a material is confirmed to perform for at least 28 d at 140°C, an E_a of 80 kJ/mol will predict 50 years at 50°C, but the 120 kJ/mol will 'numerically' predict 1280 years at 50°C. It is also important to recognize that any data points at lower accelerated aging temperatures which fall on the Arrhenius line will predict identical lifetime at 50°C (subject only to E_a). For example, with 80 kJ/mol, 28 d at 140°C, 3 m at 120°C, ~ 11 m at 100°, and 4 y at 80°C will all predict 50 y at 50°C. But the acceleration factors will decrease from ~ 660 to 12.5. It becomes clear that a required maximum acceleration factor also defines the maximum ageing temperature (any higher ageing temperature and the factor would then be above its limit). For 80 kJ/mol and in reference to 50 y at 50°C, an acceleration factor of 250 will equate to ~ 10.5 w at 124°C meaning ageing will need to be conducted at no more than ~ 75°C above the intended application temperature.

Higher acceleration factors will allow higher ageing temperatures that will then permit shorter test times, but the spread between test and application temperature becomes larger and this approach therefore has less predictive value due to increasing risk and unknowns in a large scale extrapolation regime. This goes back to the key issue discussed before. Can a single short term highly accelerated ageing test confidently predict extended performance? Even if we were to insist on perfect linear Arrhenius behavior, the answer would be a firm NO, as the likelihood for mechanistic changes and ageing anomalies increases as well. On the contrary, we have to question whether an acceleration factor of 250 is justifiable or already implies too much spread between test and application target temperatures.

In polymer degradation there has been an ongoing research focus and discussion whether degradation rate kinetics are best described by linear or nonlinear curved Arrhenius behavior. Examples exist for both processes and so far we lack the ability to predict actual material behavior [20]. The evidence here is experimentally driven. In light of approaches to reasonable 'material testing' it makes sense to compare linear Arrhenius behavior with the behavior when degradation times double with each step of lowering the temperature by 10°C (see early discussion in section 3.1). Figure 5 below shows that 80 kJ/mol in its upper temperature regime is closely related to the doubling of time per 10°C steps. With 80 kJ/mol, 1 d at 140°C projects to ~ 38 years at 20°C. Using a doubling in time for lowering the temperature in ten degree steps, projects 1d-140°C (2d-130°C, 4d-120°C, and so on) to ~ 11 y (4096 d) at 20°C. The E_a between 1d-140°C and 2d-130°C is ~ 96 kJ/mol (i.e. higher than 80 kJ/mol, and a lower E_a of 51 kJ/mol is obtained between 2048d-30°C and 4096d-20°C. The deviation from linear behavior is most noticeable at the lower temperatures. Using the 'doubling approach' shows that the E_a changes between each ten-degree step (the red curved plot in Fig.5 has a changing E_a with temperature). The average E_a for this 'doubling process' is 69.8 kJ/mol (calculated between 1d-140°C and 4096d-20°C). A constant but higher E_a of 80 kJ/mol will therefore predict a longer lifetime at 20°C than the curved plot (38 years instead of only ~ 11 years). In addition, shorter temperature intervals make a distinction between curved or linear Arrhenius more difficult. For example, 1d-130°C extrapolated to 256d-50°C (acceleration factor of 256) equates to an average E_a of 75 kJ/mol (quite close to 80 kJ/mol). The main points are that a doubling of time per 10°C lower temperature generates curved (nonlinear) Arrhenius behavior, yet that the average E_a's are reasonably similar with 69.8 kJ/mol for the 'doubling approach' versus 80 kJ/mol for the constant E_a approach. Further, a lower E_a of ~ 70 kJ/mol (0.73 instead of 0.8 eV) matches the average E_a of 69.8 kJ/mol for curved Arrhenius from 'doubling approach' between 140 and 20°C. It is certainly understandable that in some discussions both approaches have been considered or even used, and particularly in shorter temperature regimes their distinction based on available data and accuracy becomes challenging. The doubling of time per ten-degree method also represents a more conservative testing approach, since its average E_a of ~70 kJ/mol is lower than the 80 kJ/mol for the current approach.

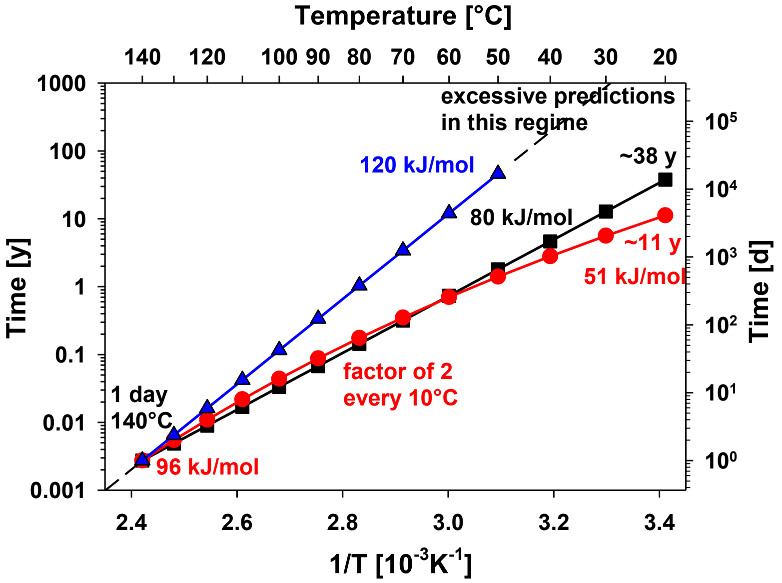

Figure 5. Comparison of linear (two E_a's) and curved Arrhenius behavior originating when the 'ageing time' doubles with each step of lowering the temperature by 10°C. In this example, for the regime between 140 and 20°C, this nonlinear behavior results in an average E_a of ~ 70 kJ/mol.

7.3 KEY POINTS FROM THIS OVERVIEW:

- A high E_a means substantial rate multipliers between high and low temperature performance
- Because high E_a and only limited short-term testing implies long 'lifetimes' at lower temperatures, there is intrinsic risk in this approach.
- High E_a's over a large temperature range may be assumed, but are difficult to confirm. This increases risk with this testing, assumptions and predictability.
- A conservative testing approach must therefore involve a low E_a.
- For low E_a, extended testing at elevated T correlates with shorter low temperature lifetimes. Low E_a means extended testing at higher T is required to predict a needed performance at lower T.

The visualization below (Figure 6) shows how acceleration factors depend on E_a and ageing temperatures. For such a plot to be obtained, a reference temperature is needed, which for simplicity and as used before is 50°C. We note how an acceleration factor of 250 times falls between 120 and 130°C for 80 kJ/mol. It is also clear that as discussed previously higher E_a's push up acceleration factors, but also that identical acceleration factors are obtained at lower relative ageing temperatures subject to increasing E_a.

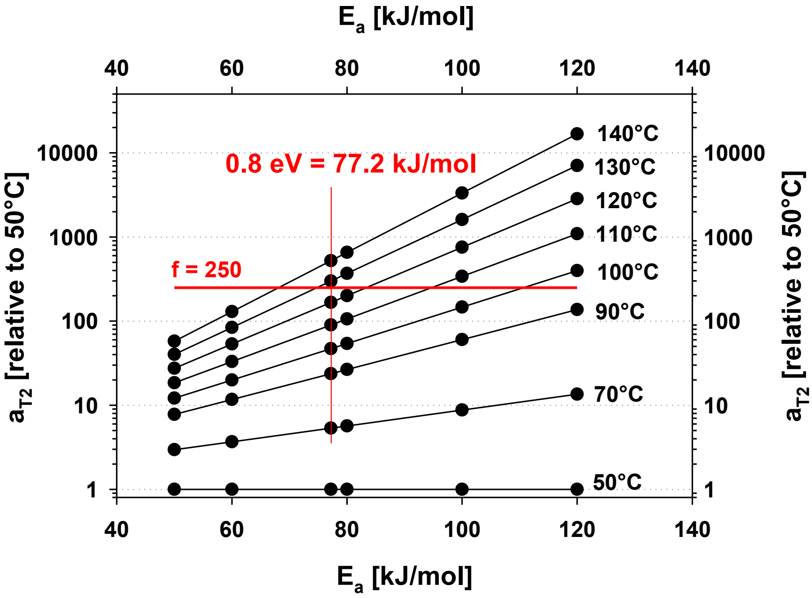

Figure 6. Arrhenius based acceleration factors for different aging temperatures and activation energies in relation to 50°C (aTref = 1) as upper boundary.

Because of their 1/T dependence, higher ageing temperatures are required for identical acceleration factors if the application target temperature is raised (see Fig. 7). For example, with an E_a of 77.2 kJ/mol an acceleration factor of 100 times exists between 20 and 70°C (a temperature difference of 50°), but for the same factor and a target application temperature of 60°C the ageing temperature will have to be raised to 126°C (a difference of 66°C). This is demonstrated in the plot shown below (see Figure 7). It shows how the absolute difference between ageing and application temperature depends on E_a, the required acceleration factor and the application target temperature itself. This emphasizes an important aspect in all of these considerations. With a larger separation between ageing test and application target temperature, the uncertainty and risk in predictions increases due to possible mechanistic changes or beginning curvature in Arrhenius behavior. Predicting performance at 20°C with 77.2 kJ/mol using an ageing test conducted at 82°C which equates to an acceleration factor of 250 does not immediately appear to be unreasonable; subject to firm knowledge of the actual E_a being larger than the minimum boundary of 77.2 kJ/mol (0.8 eV) in this case. This also goes back to the initial discussion that the recommended 'Swedish test' as originally intended was reasonably well justified. We will explore possible improvements later. It is important to clearly understand the interdependency between multiple factors that are involved in this estimation, namely E_a, maximum acceleration factor (aT2), minimum testing temperature (T2) and application target temperatures (Tref). The test temperature (all temperatures are in Kelvin) can be calculated with the equation below:

$$T_2 = \frac{1}{\left(ln\frac{1}{a_{T2}} \times \frac{R}{E_a}\right) + \frac{1}{T_{ref}}}$$

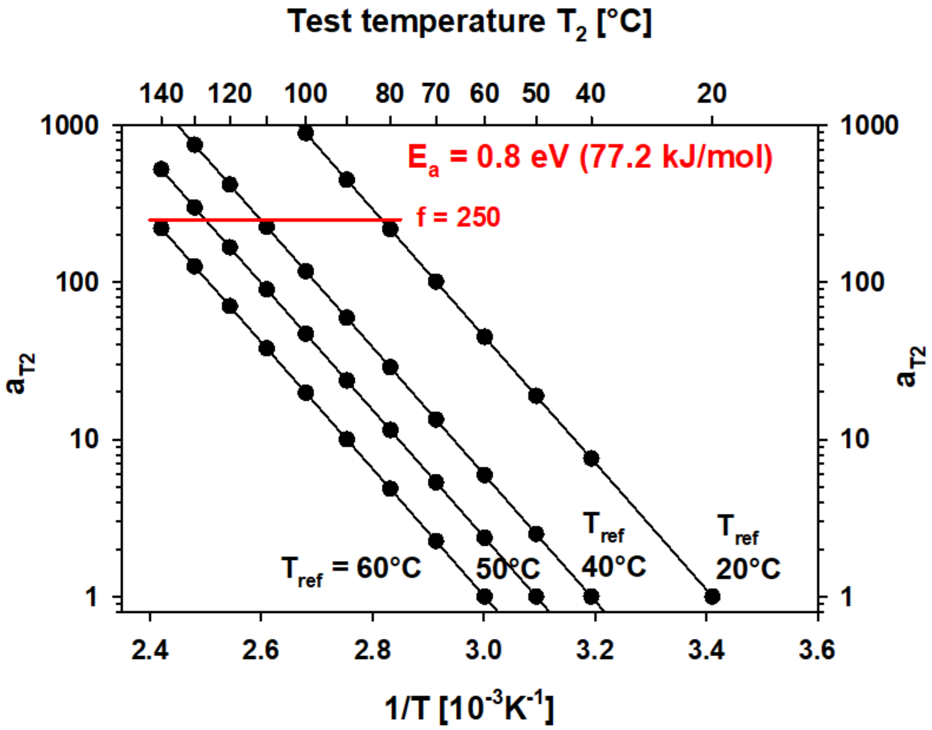

Figure 7. Visualization of acceleration factors between a range of application and ageing temperatures for the 77.2 kJ/mol (0.8 eV) under discussion (aTref = 1 at application target).

The dependence of testing temperature on Ea, acceleration and application temperature is further visualized in Figure 8. A more conservative test, which reduces risk that predictions fall outside out of actual behavior (as Ea's are not always known) is given by the use of a lower Ea. However, a lower Ea also means that the degradation rate will increase more slowly with increased temperature. This means the required testing temperature must move up for equal acceleration demand. For example, for a qualification target temperature of 50°C with the 250 times acceleration, the 0.8 eV test requires 127°C, but 137°C when the Ea is lowered to 0.73 eV. However, from a test credibility point of view, lowering the Ea, but then indirectly raising the test temperature, is not necessarily favorable. Higher testing temperatures mean increased chances for mechanistic changes, which is commonly captured by a larger gap between test and application temperature, meaning the extrapolation regime involves more uncertainty. This behavior means that a more conservative test given by lowering the assumed Ea, should also embrace a reduced acceleration factor. And this is consistent with the general knowledge in polymer degradation, that a test which reduces risk requires a low boundary Ea, lower acceleration, and reduced extrapolation regime. The consequence here is that the acceleration factor should be lowered to avoid a higher test temperature, which can only be accomplished if longer testing at a lower temperature is conducted. An alternative approach could be derived by setting explicit limits for upper test temperature; however, the result will be the same, namely longer testing (lower acceleration factor) to reduce uncertainty and hence predictive risk.

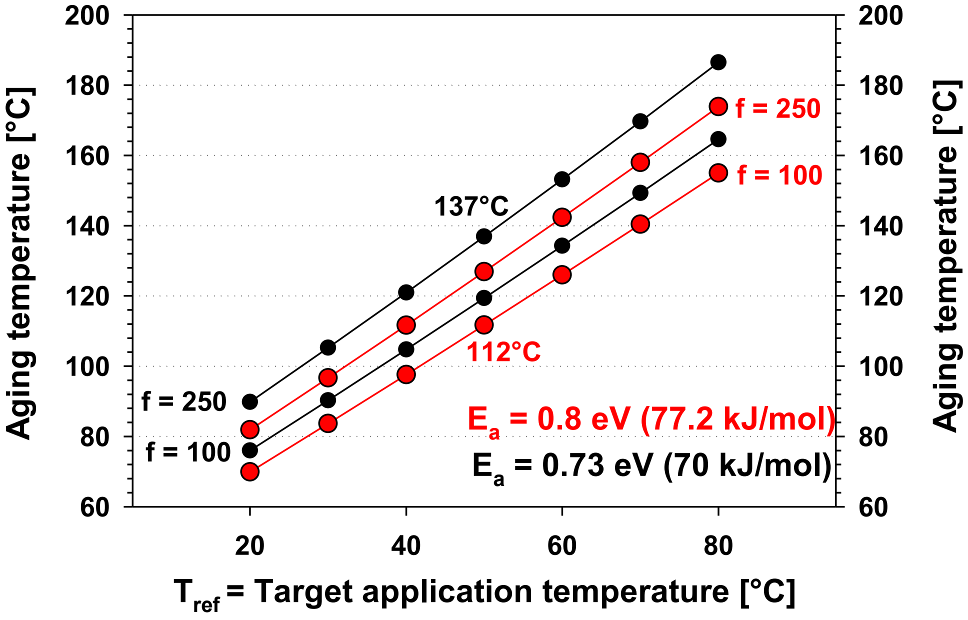

Figure 8. Visualization of 'ageing temperatures' as they depend on the application target, acceleration factor and Ea. A reduction in Ea pushes up the required testing temperature for equal acceleration.

An overview of boundary conditions as they relate to test temperatures is given in Table 3. Test temperature depends on Ea and qualification target temperature. Test time depends only on the acceleration factor. Highlighted are: Test temperature increases with lower Ea, while a low Ea and highest application T requires the highest test temperature ('m' stands for ageing time in months).. Predictions are shown for either RT or 50°C as application target, and required times ranging from 30 to 100 years, for two different acceleration factors (250 and 100), and E_a ranging from 70 to 100 kJ/mol. When accommodating a lower E_a (70 kJ/mol) and a target of RT, plus a lower acceleration (factor 100), the maximum test temperature is limited to 80°C. For identical conditions but higher acceleration (factor 250), the maximum test temperature goes up to 94°C. However, for a target temperature of 50°C, the test temperature then goes up to 137°C. For crosslinked polyolefin materials - commonly used for cable insulation – such test temperatures are above their key material transition as they often have melting ranges for their crystalline phase between ~ 80 to 120°C, although even lower phase changes have also been observed for some materials (see EPR in [21]). High temperature testing then probes the polymer without its semi-crystalline morphology being present. The framework in Table 1 clearly shows the underlying issue. Accelerated ageing through phase changes or transitions in physical properties (this may also include T_g for amorphous high T materials) is a known concern. A lower acceleration will keep the required testing temperature down, but this becomes more difficult when high application temperatures are at stake and the E_a is lowered. We stress again, that acceleration factor, E_a and target/test temperature should be considered jointly, although accelerated testing for high application temperatures becomes an intractable issue when the test temperature is required to stay below known material transitions. The polymer degradation science issues behind this challenge is the observation that polymers in their melt phase are less sensitive to ageing induced damage. A semi-crystalline morphology is subject to functional tie molecules between the crystallites, and as these are cleaved or oxidized the material may experience a more pronounced loss in mechanical properties. Materials with semi-crystalline morphology when aged in their solid state are usually more sensitive to ageing. This issue has been recognized, with the most drastic example being inverse temperature aging phenomena [34,35], although these examples included some radiation damage which may induce more local molecular scission, whereas thermal oxidation often results in more crosslinking. Prediction of thermal ageing for cross-linked polyolefins below their melting regime remains an ongoing challenge.

This situation is further visualized in Figure 9. A ceiling for test temperature limits the acceleration factors, particularly when elevated use temperatures have to be accommodated. The only way to handle low maximum test temperatures for equal acceleration, would be to raise the E_a. However, this defeats the purpose of using a conservative E_a for less well-known materials. Special experimental planning may be required in such cases, perhaps with over-testing below the ceiling, or lower acceleration has to be dealt with. One avenue may also be found in materials characterization/testing packages, rather than the preferred single-point test here, with perhaps comparison of established performance for near identical materials. An existing database coupled with wear-out ageing for materials recovered from use will be greatly beneficial.

Table 3. Test temperature depends on E_a and qualification target temperature. Test time depends only on the acceleration factor. Highlighted are: Test temperature increases with lower E_a, while a low E_a and highest application T requires the highest test temperature ('m' stands for ageing time in months).

Target T	**time [y]**	**Required test time/temperature**					
		Factor 250 – Ea [kJ/mol] / [eV]			**Factor 100 – Ea [kJ/mol] / [eV]**		
		70/0.73	**77.3/0.8**	**100/1.04**	**70/0.73**	**77.3/0.8**	**100/1.04**
23°C (RT)	30	1.44 m 94°C	**1.44 m** **86°C**	1.44 m 70°C	3.6 m 80°C	**3.6 m** **74°C**	3.6 m 61°C
23°C (RT)	50	2.4 m 94°C	**2.4 m** **86°C**	2.4 m 70°C	6 m 80°C	**6 m** **74°C**	6 m 61°C
23°C (RT)	80	3.84 m 94°C	**3.84 m** **86°C**	3.84 m 70°C	9.6 m 80°C	**9.6 m** **74°C**	9.6 m 61°C
23°C (RT)	100	4.8 m 94°C	**4.8 m** **86°C**	4.8 m 70°C	12 m 80°C	**12 m** **74°C**	12 m 61°C
50°C	30	1.44 m 137°C	**1.44 m** **127°C**	1.44 m 107°C	3.6 m 119°C	**3.6 m** **112°C**	3.6 m 96°C
50°C	50	2.4 m 137°C	**2.4 m** **127°C**	2.4 m 107°C	6 m 119°C	**6 m** **112°C**	6 m 96°C
50°C	80	3.84 m 137°C	**3.84 m** **127°C**	3.84 m 107°C	9.6 m 119°C	**9.6 m** **112°C**	9.6 m 96°C
50°C	100	4.8 m 137°C	**4.8 m** **127°C**	4.8 m 107°C	12 m 119°C	**12 m** **112°C**	12 m 96°C

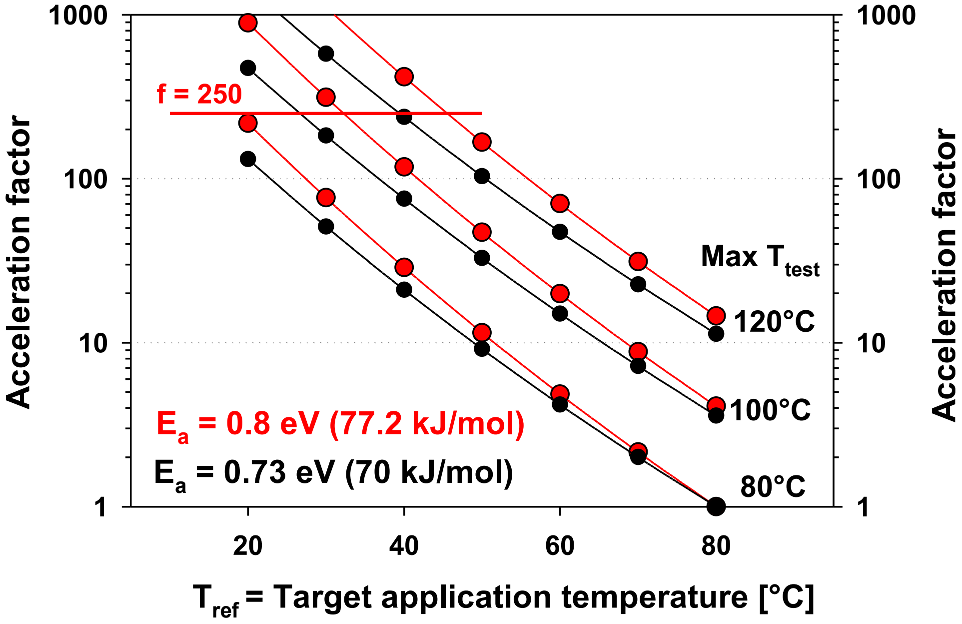

Figure 9. Maximum acceleration factors for two activation energies subject to maximum test temperatures (80 to 120°C). With a ceiling of 80°C, testing can barely be conducted for a 20°C application. Testing for elevated use temperatures requires lower acceleration unless ceiling temperatures are raised. Low maximum test temperatures imply reduced acceleration and therefore longer testing times.

8 Discussion of highly accelerated test approach

The current material screening test applies an acceleration factor of 250 and E_a of 0.8 eV (77.2 kJ/mol). In practice, it is acceptable if a lower acceleration factor or E_a is used, because such divergence results in a more conservative test. The more important question is whether the E_a or acceleration factor could easily be raised. Could this be a justifiable approach in consideration of current knowledge in polymer materials degradation and best practices?

The recommended aging condition only defines a single test point dependent on the target application temperature (which may range from RT to 50°C or beyond), unless additional high T ageing tests (multi-point) are conducted as part of a more comprehensive material characterization package (but this test does not ask for it). Hence, some questions can be considered. What is more and less severe testing? What type of testing will reduce uncertainty and risk? What are the pro/cons of this test from an engineering/science point of view, absent the fact that any test incurs expenses, takes time and effort? As was shown above, a lower E_a on its own will increase test time, but also the test temperature for equal acceleration factor. This is not necessarily advantageous. However, a lower E_a and acceleration factor in combination can reduce the testing temperature, increase test time and therefore will give more confidence in the test's predictive value. The current 'Swedish' test is limited in its scope and contains uncertainty given by a number of factors:

- Any single point test is a limited test for predictions. A two-point test could add credibility.
- Using a low boundary for E_a introduces some margin for materials that have higher E_a, but cannot offer margin for materials that are not well-characterized (meaning have unknown or low E_a).
- High acceleration implies a large extrapolation regime meaning short testing despite extended use demands (for example a 2.4-month test for 50 years). This is not the worst test that can be conducted, but it is pushing known limits in accelerated aging studies.
- When the application target temperature is > 50°C, the test temperature increases significantly and approaches non-favorable conditions subject to more convoluted higher T polymer behavior.
- No explicit over-testing or margins are added to this test. For example, one could test for 100 years even if only 50 years are required. Similarly, one could test for higher application temperature (for example use material at RT but test for assumed 50°C performance).

Higher acceleration as given by TGA methods at approx. > 180°C are generally not accepted for extrapolation toward extended low temperature performance [36]. In addition, there is a transitionary regime (generally testing polymers above ~ 130-140°C) that is usually not regarded favorably for meaningful accelerated aging studies as mechanistic changes may become important. These could be contributions from DLO, stabilizer volatility, beginning of pyrolytic decomposition of some constituents, and additional chemical processes that are usually very slow (high temperature organic chemistry), but perhaps become important subject to high E_a’s. Hence, meaningful accelerated aging studies should take the aging temperature and its separation to the application condition into account. For the testing of PP materials (just one brief example), it is known that fast testing at 150°C became discredited over time. Particularly for hindered amine thermal stabilizers aging temperatures towards 130°C became more meaningful as 150°C seemed to affect the stabilizer as well. There are many examples for very good linear Arrhenius behavior in polymer degradation [37,38], but curvature at lower T has been documented, mostly with oxidation rate measurements [21,24-27,39,40]. There is currently no known correlation between material type and linear or curved Arrhenius behavior. Only extensive testing can establish the nature of material behavior. It is, however, not possible to predict the occurrence of curvature based on the base polymer. For example, just changing one additive can change the behavior from one to the other. It is currently accepted that the underlying Arrhenius behavior of polymer materials must be experimentally determined rather than predicted or assumed based on existing analogies. There are good examples for linear behavior and many examples for curvature in the literature often involving similar materials [20].

‘Known activation energies’ is another aspect that deserves discussion. Many ageing studies or documents that describe testing approaches and recommendations – as often found from the various groups dealing with materials qualification for NPP applications – use terminology for established or known E_a’s, yet this language can be misleading. Instead, E_a’s are often not fully known for a large temperature range, although guidance may exist. E_a ‘s can only be known from actual ageing data, and such are often only available for high temperature testing over limited timeframes. For an E_a to be known, multiple properties and perhaps oxidation sensitivity (a key driver for thermal ageing) should have been probed all the way to RT. As long as only limited high temperature thermal aging data are available, any ‘known’ E_a to be used for the Arrhenius approach towards other temperatures involves assumption, analogies, grouping or similar justifications for extrapolation. This means there are in fact unknowns (the true behavior of E_a over a large temperature range is often not well-understood) and therefore underlying risk associated with this approach. Any test should re-examine the origin of ‘semi-known’ E_a in the context of temperatures and times that were previously evaluated. For what temperature range are original data available? How far removed was any testing from the target application temperature? Of course, for completely unknown materials, it requires us to set a low boundary as the required safety margin. The best ‘known’ E_a’s originate from large temperature range screening of oxidation rates, measurements that have sometimes demonstrated straight or near-linear Arrhenius behavior down to RT (nitrile and neoprene [41,42], epoxies [37,38], butyl O-ring elastomers [43], EPR elastomers [44], but often also in observations of curved Arrhenius behavior (EPDM [24], neoprene [40], HTPB polyurethane [39], CSPE [27] and other polymers [20].

Additional consideration is required for two other perspectives. Firstly, of key importance is whether the ‘Swedish accelerated test’ is a standalone test for immediate decision making towards qualification, or whether limited accelerated testing is conducted in parallel with other material characterization efforts. Engineers often consider a materials behavior ‘package’, which may include accelerated testing perhaps involving multiple temperatures, comparison with similar materials based on experience and observed past behavior, or coupled with condition monitoring efforts. Point is, if a large data base exists, predictive accelerated ageing can be reduced to a prudent cross-check for unexpected anomalies, rather than single point extrapolation and decision making. Secondly, due to expectations for extended use situations meaning more extended operational demands, the expectations on any predictive test should also increase. The existing test has no defined limitations in its test time and temperature, and hence no defined framework that considers its predictive fidelity for extended use conditions. It is an open test in terms of its limited variables (acceleration factor and E_a) and as we showed earlier, for shorter operation at RT, this testing approach appears reasonably consistent with its historical derivation and use. However, it will encounter unfavorable boundaries in test temperature when qualification is required for higher use temperatures and much longer operational demands. This can be summarized by our concern that this single-point test should not be used to justify an overly broad application window without questioning its original focus. Historically, much longer operation, particular when coupled with increased temperature, may not have been the intent. However, because other boundaries and limits were not specified, we lack clarity on this point.

9 Conclusions

Any high value use of polymers in safety-relevant or must-perform demanding applications requires some type of qualification testing and informed material selection approach. This is particularly mandatory if severe consequences can occur, should materials fail or display unexpected performance limits. Demanding applications are found in defense, communication, mobility and power plant environments. Of particular concern are also materials used in nuclear related applications involving power generation. While 'high consequence' signifies the potential for severe impact if material failure occurs, only few materials and use demands may fall into this category; and such material demand situations are generally well known, often with special selection and appropriate monitoring in place. In parallel, the performance of many materials may fall into general use, where nevertheless repairs may be difficult or costly, and bare minimum performance checks are either mandated or are part of best design practices.

It is obvious that screening and/or ageing studies are required to confirm materials reliability and informed decision making. Usually there are distinctions between performance screening, enhanced testing, or comprehensive in-depth ageing and material characterization studies. The magnitude of such evaluations is usually proportional to the primary demands on the materials, ease of replacement and associated costs, consequences of failure and its effects on overall systems reliability, should failure issues propagate through a more complex system. There is often a need to balance basic screening (which can eliminate obvious poor materials) versus extended in-depth ageing studies. The latter approach is costlier and requires time, but of course reduces overall risk. Hence, material testing efforts will usually correlate with demands, risks and consequences of failure. In some cases, a legitimate approach could be based on simple comparisons with reference materials that are already well-known and where a family of materials is understood.

This leads to a discussion that material qualification testing for NPP applications is often country specific, although experience and knowledge on materials ageing phenomena and best testing approaches is readily shared (technical reports, regulatory guiding documents, conferences, personal networking). However, the emphasis and choice on what tests to pursue varies with country and local regulators. A contributing issue that nearly all counties with active nuclear power programs have to deal with, is aging infrastructure, extended operation more than originally planned for, perhaps requalification of materials or on on-site condition monitoring. This in turn means that demands on qualification testing methods have also increased. A review of the Swedish test under discussion here is timely. Simple tests are more meaningful and represent less risk when qualification is required for 30 years, rather than perhaps obtaining predictions for 80 years where unknown slow ageing processes are more likely to occur. Original tests from 30 or more years ago were not necessarily designed to handle the challenges we face today. Hence we need to consider original scope/intent versus current needs. Commensurate with expanded expectations for material qualification (i.e. much longer operational lifetimes), it is imperative to scrutinize existing test approaches and better understand their intrinsic limits and emphasize perhaps shortcomings and vulnerabilities. A single-point screening test for equipment qualification (EQ) and material validation purposes is intrinsically challenging, despite best intentions, and no single test can usually handle a broad framework of expectations and scenarios. This is the reason that in some countries, materials qualification and continued requalification may be addressed with a 'materials behavior package', meaning an all-inclusive approach combining screening, targeted testing, material grouping, experience, and feedback from existing similar materials perhaps via condition monitoring. No approach is perfect, but everyone cares and wishes to pursue meaningful qualification; much can be learned from a comparison of different approaches.

9.1 CURRENT 'SWEDISH APPROACH' FOR PREDICTIVE POLYMER MATERIAL AGEING

Thermal performance predictions will invariably involve higher temperature testing and some type of extrapolation or comparative evaluation. Therefore, the Arrhenius approach is widely used for lifetime extrapolation assessments, absent any better approaches, of which there are few. Using an approach with a doubling of rate per each ten-degree increase is an alternative strategy, but implies by default non-linear Arrhenius behavior. It is a more conservative test method, as its average E_a (on the order of 70 kJ/mol) is somewhat lower than the 80 kJ/mol. It is similar to embracing the contribution of nonlinearity as part of the general Arrhenius approach anyhow, also yielding a lower average E_a. Other approaches towards increased confidence in available data are discussed below in section 9.2 and 9.3. Some improvements are usually derived from the availability of rate data across a wider temperature range, and accommodating non-linear Arrhenius behavior. All of these methods evaluate degradation rates or performance times on a logarithmic scale versus inverse temperature. The suitability of the existing 'Swedish approach' for polymer reliability screening matches a basic Arrhenius methodology. This is given by its limited scope - meaning single-point testing in this context - in light of our growing understanding of polymer materials ageing and reliability. The current 'Swedish approach' is summarized as:

- Multiple factors define this test. E_a, acceleration factor, time and temperature to be qualified, as well as test time and temperature
- Boundary E_a at lower end (0.8 eV) for polymer degradation; a reasonable value but not inclusive of all known scenarios
- Test temperature is not a limiting variable, only E_a and acceleration factor
- High acceleration factor (250) meaning fast testing and significant extrapolation regime
- Significant separation between 'testing' temperature and application condition when the qualification temperature is high. Test temperature also increases should the E_a be lowered

Such a test approach is certainly suitable for inconsequential material choices, meaning situations where quick guidance from bare minimum reliability screening with remaining risk is acceptable. Using such screening for decision making will also be subject to the understanding and concurrence of system engineers and other stake holders. However, risk in material qualification with this test remains, particularly if used for qualifying very long material application times (80 to 100-year timeframe). When risk is taken into account, the suitability of the current 'Swedish test' as a standalone method for polymer reliability screening falls between category A and B below.

9.2 THE 'SWEDISH APPROACH' IN THE CONTEXT OF RISK FOR PREDICTIONS

For simplicity, we shall distinguish between three scenarios based on test approach, effort, material demands and risk.

A) low demand on material – high risk is acceptable: Screening/testing for obvious weakness, single point testing or basic quality checks (type, manufacturer etc.). Somewhat limited confidence in extrapolated performance, high remaining risk, suited for inconsequential, low cost and easily replaceable materials.

B) medium demand on material – some risk is accepted: Additional materials comparisons with qualified materials for which specific performance is known. Or limited testing with some assumptions for extrapolations. Some confidence in this type of testing but risks remain. They need to be recognized in terms of potential consequences of material reliability concerns and taken into account for decision making.

C) high demand on material - 'near zero' remaining risk: Extensive accelerated ageing studies for carefully defined application demands. High cost, but high value of the data generated. Such testing is required for situations where failure modes are highly consequential, cannot be accepted or at least must be fully understood. In-depth knowledge may also result in limited use materials, mandatory replacement schedules and/or ongoing materials performance monitoring.

9.3 POSSIBLE IMPROVEMENTS

When demands on materials reliability are higher and risk must be reduced, we need to embrace an improved test method. This is certainly doable, although involves more time, effort and cost. Improvements could be made by the following adjustments:

- Introduce maximum test temperature perhaps material specific, which results in more extended testing below an upper temperature boundary
- Avoid phase transitions and test below any known material transitions (T_g and partial melting). This could substantially limit the test temperature, but will in-turn certainly increase test time. Upper boundaries for XLPO's could be in the range of 80°C, but will be difficult to implement as very long ageing times need to be studied.
- Use a lower more conservative boundary for E_a. Suggested are at least 70 kJ/mol (0.73 eV).

- Use an acceleration factor of no more than 100. This means a 50 year extrapolated lifetime will at minimum require 0.5 y testing. Still a large separation in temperatures (ageing vs use), but it is more reasonable. And it lowers the test temperature which is preferred.
- Expand test to involve at minimum two points. The second point could be conducted at 10 to 20°C higher and hence could involve the predicted temperature for the original factor of 250.

There are two advantages with a two-point test approach. Firstly, a quick estimation of minimum E_a becomes possible and secondly, if the tests are conducted for equal time, the higher temperature may offer some validation of better than expected performance. For example:

- Assume test to screen for 50-year lifetime at 50°C
- 70 kJ/mol with acceleration of 100 demands successful test of 6 m at 120°C
- Add second test for equal time (6 m) at 137°C (acceleration factor of 250)
- With E_a of 70 kJ/mol and factor of 250, the material would need to be tested for 2.4 m at 137°C. If, however, it also performs for 6 m at 137°C, it will represent a successful 2.5 times over-test (6 months achieved, yet only 2.4 months required; 6/2.4=2.5). If both tests are successful, one could assume that over a narrow temperature range similar absolute performance shall apply, meaning the material tested up to 6 m at 120°C (minimum time required with factor of 100) will likely perform at least 6 m x 2.5 = 15 months (also 2.5 times better).
- If material also lasts for 6 months at 137°C, it will suggest at least 2.5 times better performance and indirectly a minimum E_a of ~ 56kJ/mol (estimated 15 months at 120 and 50 years at 50°C). This gives more confidence in this testing since the material is not likely to have an E_a below 56 kJ/mol. However, such testing should still consider upper boundaries for test temperature, which as mentioned is problematic for XLPO materials subject to melting transitions.

In addition to possible improvements for the test itself, there is always the option of combining any test with a more comprehensive materials characterization and testing package. Such an approach will reduce overall predictive risk from the single-point testing as is currently used.

9.4 ADDITIONAL SCRUTINY OF TESTED MATERIALS

In addition, the fundamental challenge with any short-term testing of polymers under highly accelerated conditions, is the issue that diffusion (permeation) processes cannot be equally accelerated, as their activation energies are usually much lower (below 50 kJ/mol) [45-47]. Therefore, any high temperature screening as described above should involve examination of the aged material samples for surface versus bulk anomalies and divergence in apparent ageing behavior. This means any specimens from single or two-point screening in the temperature regime of 90 to 140°C should be checked for evidence of surface changes that do not appear in bulk. These could be checks of color in cross-section, loss of stabilizer from surface, a hard surface, cracking etc., while the bulk may appear more unaffected. If homogenous ageing during the test can be confirmed, there is more confidence in the validity for the test to be extrapolated.

Considering that published ageing studies on materials used in NPP environments have sometimes involved multiple years of thermal ageing [22] (and associated refs), it is documented that extended ageing can be conducted and that there is value in datasets that a) offer multipoint ageing behavior with better guidance and b) involve extended testing with much lower acceleration factors. Such in-depth studies offer comprehensive insight into material behavior, meaningful extrapolation, a clear understanding of boundaries and hence imply significantly reduced risk for continued operation, condition monitoring or new material design/selection and qualification purposes.

10 Recommendations

The current polymer degradation test with 0.8 eV and 250 as acceleration factor is at the boundary of what we would currently consider justifiable, subject to our evolving knowledge in polymer degradation behavior (growing examples for lower E_a's and curved Arrhenius behavior). It deserves reconsideration and an honest assessment of scope and reduced risk in qualified materials reliability, i.e. the primary intent of this test. Any material testing will balance time, cost and effort with risks in predictions and expectations on the test. Any discussion should consider this topic comprehensively including polymer degradation behavior and best practices. This is also in light of increased demand on this qualification test, meaning extended timeframe for predictions, which is very likely beyond its original scope.

The existing test does not offer margin aside from unknown E_a and its lower boundary. It is recommended to carefully consider lowering the E_a to 70 kJ/mol (0.73 eV) and not to accelerate testing beyond a factor of 100. Going all the way to 0.7 eV would certainly be a bonus. In addition, two-point testing that involves over-testing, and/or additional margins through selection of higher application target temperatures could offer more fidelity for this testing approach. Similarly, maximum test temperatures and thereby avoiding material phase transitions or partial melting will increase confidence in the applied test.

Any testing for a material qualification decision should also consider the broader framework beyond the simple application of this test. Material qualification goes in parallel with a risk assessment, which this test does not capture well, yet what qualification is ultimately all about. The other variables that contribute to material qualification are equally important:

- Time, cost and efforts will invariably be involved in any material testing considerations. We shall agree that this will always be a primary concern. Yet it needs to be coupled with risk and costs, or impact on operations should the qualification have erroneous predictions.
- Is the extrapolation of single-point thermal ageing mostly a stand-alone test, or part of a more comprehensive material characterization effort (data package from multiple directions)? If available, then the risk from the accelerated ageing test is reduced by complementary information. A testing package can offer improved credibility towards decision making and thereby reduce the expectation on the current test.
- Consider qualification needs, is it a critical material or less important? What is the underlying demand on the material? What if the test guidance turns out to be erroneous? Somewhat acceptable or not?
- Risk evaluation should be conducted in parallel. If a 'must perform' material demand for critical locations is involved, then a single-point highly accelerated test has substantial weakness. This needs to be recognized and dealt with.

- In summary, as in other material qualification challenges, any test selection and testing package for polymeric materials should be commensurate with perceived operational demand and risk for the performance of the material.

In practical terms, it might be helpful to consider the following. Based on current and evolving knowledge in polymer degradation, there is growing evidence for some materials showing lower E_a's than 0.8 eV and also Arrhenius curvature over a broad range of ageing temperature. To accommodate this trend, some adjustments to the existing 'Swedish test' appear meaningful. For unknown materials it makes sense to pursue somewhat more conservative testing:

- Lower the threshold E_a to ~ 70 kJ/mol (0.73 instead of 0.8 eV).
- Limit the ageing temperature to no more than 120°C
- Conduct two-point testing, or use existing ageing data and obtain improved guidance on applicable E_a at higher temperature (but again, do not use data originating above a reasonable upper temperature limit). Pursue a justifiable comparison of at least two test times at such reasonable temperatures where a material has performed satisfactorily. If a higher E_a can be confirmed, it could then be used to qualify the material without the lower threshold limit being mandatory under such circumstances. Such approaches could be discussed when updating the existing test method.

If materials under consideration are well understood, have incurred only minor modification in comparison with existing materials, and the E_a has been clearly shown to fall within a narrow range (not much scatter in the data) and are above the 70 to 80 kJ/mol regime, then a well-documented evidence based approach could be used to overrule the unknown E_a threshold guidance and conduct testing under higher E_a considerations. Point is, the rationale for raising the E_a should be justifiable.

Under unfavorable combinations the current approach appears in conflict with materials science, as it does not define any upper temperature boundaries. Unfavorable situations are the combination of high application temperatures that need to be qualified, a firm intent of keeping the factor of 250 and the existing 0.8 eV, with neither limits in testing temperature nor consideration for transition in polymer behavior. There are better practices which can accommodate limits given by current materials science knowledge, meaning establishing upper boundaries for test conditions. The issue here is the balance between materials testing based on calculations with quite open variables, as anything can be tested and predicted, versus applicable materials science that suggests justifiable limits in acceleration factor, E_a, test temperature and extrapolative regime.

When moving forward, it is recommended to carefully consider the 'big picture' for decision making, by balancing the demands for which materials and components must be qualified versus the risk associated with the chosen approach if predictions have vulnerabilities. We already start from the point that predictions are predictions, they have in-built uncertainty and that absolute qualification remains a goal. While reasonable and documenting an acceptable method at that time, the existing test has uncertainty through assumptions and cannot yield 100% absolute performance expectations. Any such testing is about risk minimization and best practices.

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USE, LIMITATIONS AND POSSIBILITIES OF ARRHENIUS BASED EXTRAPOLATIONS FOR LONG-TERM OPERATION STUDIES OF POLYMERIC MATERIALS

The Swedish nuclear power plants aim to extend their lifetimes toward 80 years. This requires enhanced aging management of the polymeric materials used in components e.g. cables and gaskets. However, the long-term property behavior of polymeric materials is complex and multifactorial in nature. Much research has been conducted over the years, but it is still difficult to confidently predict the lifetime of polymeric components.

In Sweden there are existing guidelines on how much a degradation process may be accelerated for environmental qualification (EQ) purposes. This report focuses on the broader framework of short-term testing based on the Arrhenius methodology and the practicality and suitability of the existing guidelines. It is deliberated through a literature study, interviews with international experts, and also a perspective on extrapolations in terms of boundaries, underlying material science, and remaining risk.

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