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Overview of Current Practices and Guidance Applicable to Seals for use in Radioactive Materials Transport Packages and other Nuclear Safety Applications

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Executive Summary

The Convention on Nuclear Safety, initiated by the International Atomic Energy Agency (IAEA) commits Contracting Parties operating land-based civil nuclear power plants to maintain a high level of safety by establishing fundamental safety principles to which States would subscribe. These safety principles are embodied in the IAEA Fundamental Safety Principles and other guidance which require that the design and construction of nuclear installations should provide reliable safety levels and protection against the release of radioactive materials. One effective method of achieving safety and protection from release lies in the design of reliable sealing arrangements for nuclear plant and transport flasks.

A comprehensive review has been carried out in this report to gather together a wide range of information on the different ways that seals and sealing arrangements are incorporated into the UK nuclear industry and the regulations that govern them. The regulatory aspects are enforced by the Office of Nuclear Regulation, ONR, and are driven from international regulations and codes of practice assembled by the IAEA.

The use of seals in the UK nuclear industry covers an immense range of applications and in the main, their most important function is to prevent the leakage and loss of radioactive materials into the environment. There is an equally large choice of seal types and materials for the nuclear design engineer. An overall description of the different types of sealing arrangements that are available has been provided with recommendations for seal types and materials for different nuclear applications. However, an overriding consideration in seal material selection and use is the choice of suitable tests to indicate that the sealing arrangement can perform reliably and safely for its intended service lifetime.

The properties of different types of polymeric seal materials have been compared and contrasted in terms of their use across the wide range of conditions that may be expected across the UK nuclear industry. The response of seals to specific ageing conditions such as ionising radiation, elevated temperatures, pressure harsh chemical environments and low temperatures is discussed in terms of long-term ageing effects and functionality.

One of the most important factors associated with the reliability of polymeric seals in the nuclear industry is the assessment of service lifetime or qualified life. The qualification process for nuclear applications is explained in some detail in terms of the interpretation of international standards and best practice. The qualification process is discussed in terms of the implementation of test programmes that are representative of nuclear environmental conditions. Driven by IAEA regulations, test programmes are discussed that simulate postulated accident conditions for seals in nuclear power generation plant and transport flasks.

Glossary

ABAQUS	A software suite for finite element analysis and computer-aided engineering,
ACoP	Approved Code of Practise
Activation Energy	The energy level that reactant molecules must overcome before a chemical reaction can occur.
ADR	European Agreement concerning the International Carriage of Dangerous Goods by Road
ALARP	As Low As Reasonably Practicable
ANSYS	Multi-physics engineering simulation software for product design, testing and operation
Arrhenius Equation	A mathematical expression that describes the effect of temperature on the rate of a chemical reaction
Arruda-Boyce	A hyper-elastic constitutive model used to describe the mechanical behaviour of rubber and other polymeric substances
ASTM	American Society for Testing and Materials, now known as ASTM International
Brinell	Hardness testing method of a metal or alloy measured by hydraulically pressing a hard ball under a standard load into the specimen
Brittle	When subjected to stress, a ***brittle*** material will fracture with little elastic deformation and without significant plastic deformation
BS	British Standards
BWR	Boiling Water Reactor
CA	Competent Authority
CANDU	CANada Deuterium Uranium pressurised water reactor (Atomic Energy of Canada Limited)
CDG	Carriage of Dangerous Goods
Chain scission	Degradation of a polymer by scission of main chain bonds, often caused by thermal stress or ionizing radiation
Class 1E Equipment	The classification of the electric equipment and systems essential to safety that are to be used in nuclear power generating stations
CNAF	Compressed Non-Asbestos Fibre
Compression set	The apparent permanent deformation of an elastomeric material that has been subjected to compressive stress, usually for a prolonged time period
CONN3D2	Connector element between two nodes or ground and a node used in ABAQUS
Cross link	A covalent bond (or series of bonds) between adjacent chains of a polymer
DBA	Design Base Accident
DBE	Design Base Event
DLO	Diffusion Limited Oxidation
DMA	Dynamic Mechanical Analysis
DNSR	Defence Nuclear Safety Regulator
DSC	Differential Scanning Calorimetry
E-CTFE	Ethylene-chlorotrifluoroethylene polymer
EDF	Electricité de France
Elastomer	A polymer that displays rubber-like elasticity
EPDM	Ethylene propylene diene monomer
EPR	Ethylene propylene rubber

EQ	Equipment Qualification
ESC	Environmental stress corrosion/cracking. May occur in some polymers when stressed in certain liquids – not to be confused with stress corrosion cracking in steels
ETFE	Ethylene-trifluoroethylene
EU	European Union
FEA	Finite Element Analysis
FEM	Finite Element Method
FKM	FKM is the ASTM designation for a class of fluorinated, carbon-based synthetic rubber, commonly known as fluoroelastomer
Fluoroelastomer	Fluorocarbon-based synthetic rubber
Fluropolymer	Fluorocarbon-based polymer defined by its carbon-fluorine bonds
Free radical	A molecule with an unpaired electron
FTIR	Fourier Transform Infra-Red
Glass transition, T_g	The temperature at which the transition occurs in an amorphous polymer between the glassy and rubbery states
Gough-Joule Effect	The tendency of an elastomer to contract if heated whilst under tension
Gray (Gy)	The derived SI unit of ionising radiation dose. One Gray is equal to the absorption of one joule of radiation energy per kilogram of material
HLW	High-level radioactive waste
Hooke's law	Hooke's law states that the strain induced in a material is proportional to the applied stress - within the elastic limit of that material.
HVAC	Heating, ventilation, and air conditioning
Hysteresis	Hysteresis occurs when the work done by a material in returning to its original shape is less than the work done by the applied force when it is deformed. The resulting difference in energy is absorbed by the material, usually in the form of heat
IAEA	International Atomic Energy Agency
IEC	International Electrotechnical Commission
IEEE	Institute of Electrical and Electronics Engineers
IRHD	International Rubber Hardness Degrees
ISO	International Organization for Standardization
Knoop	A measure of the hardness of a material, calculated by measuring the indentation produced by a diamond tip that is pressed onto the surface of a sample.
LET	Linear Energy Transfer
LOCA	Loss of Coolant Accident
MARC/NASTRAN	Powerful, general-purpose, nonlinear finite element analysis software
Mole (mol)	The mole is the SI unit of measurement for the amount of substance
Mooney- Rivlin	A method for modelling the large strain, nonlinear behaviour of incompressible materials
NAFEMS	National Agency for Finite Element Methods and Standards
NDT	Non-Destructive Testing
Newton	SI unit of force representing the force needed to accelerate one kilogram of mass at the rate of one metre per second squared in the direction of the applied force
Nitrile	An organic compound, usually elastomeric, in which a cyano- group (—C ≡ N) is attached to a carbon atom (C)
ONR	Office for Nuclear Regulation

Ozone	A highly reactive gas composed of three oxygen atoms
PA	Polyamide
PAI	Polyamide-imide
Pascal	A pressure or stress of one newton per square metre
PCTFE	Polychlorotrifluoroethylene
PEEK	Polyetheretherketone
PES	Polyphenylenesulphide
PFA	Perfluoroalkoxy
PFAS	Per- and polyfluoroalkyl substances
Photodegradation	Light-induced polymer degradation associated with the physical and chemical changes in an organic material when exposed to ultraviolet or visible light
PIEs	Postulated Initiating Events
Plasticiser	A substance added to a synthetic resin to produce or promote plasticity and flexibility and to reduce brittleness
Poisson's Ratio	The ratio of the relative contraction strain which is normal to an applied load - to the relative extension strain in the direction of the load
PPS	Polyphenylenesulphide
PTFE	Polytetrafluoroethylene
PVC	Polyvinyl chloride
PWR	Pressurised Water Reactor
R- Gas constant	The gas constant R, with a value of 8.314 J K^{-1}, is the product of the pressure and the volume of one mole of an ideal gas divided by the absolute temperature
Radiation dose	The amount of energy from ionising radiation deposited per unit mass of a medium
Radiolysis	The dissociation of molecules by ionising radiation
RAM	Radioactive material
RCC-E	Standards/codes that detail the rules of design and construction of electrical equipment of nuclear islands (Regles de Conception et de Construction et de Surveillance en Exploitation des Materiels des Chaudieres Electro-Nucleaires)
REACH	Registration, Evaluation, Authorisation and Restriction of Chemicals
Resin	A solid or liquid synthetic organic polymer used as the basis of plastics, adhesives, varnishes, or other products
RID	Regulations concerning the International Carriage of Dangerous Goods by Rail
Rockwell	A hardness scale based on indentation hardness of a material
RTI	Relative Temperature Index - the temperature above which a polymer will degrade prematurely
SAPs	Safety Assessment Principles
SEALS	An Excel spreadsheet with Visual Basic code, available to the UK nuclear industry, to provide the capability to predict the compression set of elastomeric seals as a function of time under specified radiation /thermal ageing conditions.
SFAIRP	So far as is reasonably practicable
Silicone	A class of synthetic polymers with a chemical structure based on chains of alternating silicon and oxygen atoms.
SI	International System of Units
SLC	Site Licence Company
SSG	Specific Safety Guide (IAEA)

SSR	Specific Safety Requirements – IAEA Regulations for the Safe Transport of Radioactive Material
SLR	Standardised Leak Rates
Stiction (Slip-stick)	Where the seal, usually an elastomer, can bond to sealing faces of a gland when in contact over an extended period
Stressor	External stimulus or an event seen as causing stress to a material, such as radiation and high temperatures in the case of organic polymers
Synergy	Interaction or cooperation giving rise to a whole that is greater than the simple sum of its parts, e.g., radiation/thermal synergy
TAG	Technical Assessment Guide
TCSC	Transport Container Standardisation Committee
Tensile strength	The tensile strength of a material is the maximum mechanical tensile stress that a material can withstand until failure occurs
Thermoplastic	A thermoplastic as a polymeric material which softens and hardens reversibly on heating and cooling. In the softened/melt state, thermoplastics may be moulded into shape and then, on cooling, become rigid
Thermoset	Polymers that form well-defined, irreversible, chemical networks when cured through heating or the addition of a curing agent
TI	Temperature Index. This is a value of temperature which allows the comparison of the time/temperature characteristics of polymers
TPE	Thermoplastic Elastomer - defined as a polymer, polymer blend or compound which exhibits thermoplastic characteristics when heated enabling it to be formed into fabricated articles. At lower temperatures it takes on elastomeric characteristics
TR-10	The temperature in degrees Celsius at which an elastomer, which was stretched to a certain amount and then frozen, recovers elongation by 10% as it begins to warm up
Type A package	Packages used for the transport of relatively small, but significant, quantities of radioactive material
Type B package	Robust and very secure packages used for high level waste, used fuel, and mixed oxide fuel containment. There are two types: Type B(U) and Type B(M): Type B(U) packages, which meet certain design criteria, must be approved by the competent authority of the country of origin only; Type B(M) packages, which do not meet all design criteria, must be approved by the competent authorities of the country of origin and of all the countries through or into which the package is to be transported.
Type B(U)F package	Is a Type B(U) with fissile material packaging together with its fissile material content
Type C package	Packages containing smaller amounts of high-activity materials transported by aircraft
UHMWPE	Ultra-high molecular weight polyethylene
Ultimate tensile strength (UTS)	Ultimate tensile strength is the maximum stress that a material can withstand while being stretched or pulled
UV	Ultraviolet
Vickers	A measure of the hardness of a material, calculated from the size of an impression produced under load by a pyramid-shaped diamond indenter
Viton	A brand of FKM fluorocarbon elastomer manufactured by DuPont, commonly used in seals
WWER	Water-Water Energetic Reactor

Youngs modulus	A property that gives the dimensional changes that occur in a material when a force is applied. It is defined as the ratio of applied stress (σ) to corresponding strain (ε)

1. Introduction

The Convention on Nuclear Safety aims to commit Contracting Parties operating land-based civil nuclear power plants to maintain a high level of safety by establishing fundamental safety principles to which States would subscribe. These safety principles are embodied in the IAEA Fundamental Safety Principles and other guidance which require that the design and construction of nuclear installations should provide reliable safety levels and protection against the release of radioactive materials. One effective method of achieving safety and protection from release lies in the design of reliable sealing arrangements for nuclear plant and transport flasks.

One of these technologies is based on sealing techniques which use discrete components such as O-rings or gaskets to provide seals that contain or protect from radioactive materials or other aggressive substances. In many cases these components are manufactured from organic polymers, especially elastomers which usually offer improved ease of use and cost effectiveness over other seal types such as metallic O-rings. However, organic materials have a drawback when used in the nuclear industry in that they are sensitive to ionising radiation, heat and harsh chemicals. Consequently, elastomers may be limited in their use in nuclear plant applications and if they have to be used, an assessment of their reliability and long-term performance will be necessary especially in safety related applications. It is the responsibility of duty-holders such as the Site Licence Companies (SLCs) and Radioactive Materials transport organisations, to ensure that any use of seals in nuclear safety applications has been properly assessed and that the seals are demonstrated to be suitable for purpose.

The effects of nuclear environments (ionising radiation, heat and chemical environments) on organic materials are complex and may be difficult to assess. However, in seal assessments, the duty-holders may decide to carry out some form of testing that will attempt to simulate the effects of long-term service and/or accident conditions and demonstrate that the seal is fit for purpose. In many cases the testing will involve some form of accelerated ageing for long term ageing assessments and thermal/pressure transients to simulate accident conditions. Clearly the tests will be driven by the specifics of the application, for instance a transport flask seal may also require impact assessments.

In drawing up testing schemes, duty-holders will often look to support organisations to design and carry out tests to demonstrate seal suitability and functionality. In some cases, support organisations will look towards their own experience in the field; in other cases, they may consult nuclear industry test standards or other 'Relevant Good Practice'. The test standards that provide guidance for testing of components in the nuclear industry are available through organisations such as the IEC (International Electrotechnical Commission) and IEEE (Institute of Electrical and Electronics Engineers). These standards recommend test procedures to achieve environmental qualification (EQ) of components i.e., to demonstrate that the components will continue to function throughout their design lifetime and also through accident conditions.

The radiation and thermal ageing processes in organic polymers can be very complex, however the understanding of these processes has improved substantially in recent years. The newer understanding of these processes has led to questions surrounding the efficacy of some the methodologies provided in the standards and whether test conditions that are recommended are representative of service conditions.

One of the main aims of this document is to provide guidance to ONR inspectors on the current understanding of the ageing mechanisms in polymeric seal materials and how they can be better represented during accelerated ageing tests. It is intended that the provision of relatively high-level guidance, with some appropriate detail, on polymer degradation in nuclear environments will help inspectors to further evaluate related license submissions in the light of the advances in current knowledge.

This document is also aimed at the provision of information on the following topics:

- Seal material considerations and an overview of typical use in nuclear applications;
- Property changes in seals arising from irradiation, heat exposure, pressure and the effects of aggressive chemicals;
- Assessment of applicable Finite Element Analysis (FEA) methodologies to seals performance;
- Guidance and potential improvements to seals testing and characterisation;
- Review current practises for seals usage and material selection by duty-holders;
- Applicable legislation and relevant good practice;
- Identification of knowledge gaps and potential areas for future research.

The report also incorporates input from the wider industry including seals manufacturers, SLCs, designers, service providers and transport organisations.

This report has been prepared with the aim of providing a generic source of information on the uses and properties of the types of seals used in the UK nuclear industry. It is intended to be of use to designers, manufacturers, regulators and any other interested parties. Guidelines to seal degradation assessments and methods of test are described and relevant sources of documentation (e.g., regulations, standards and guides) are discussed.

2. Use of Seals in the nuclear industry

2.1 Overview

Mechanical seals are used in industrial and commercial applications to close a gap/joint by providing a physical barrier that prevents or limits any leakage of liquids, solids or gases (under pressure). They are also used to form a barrier to the ingress of contamination particles such as dust or dirt. There is a wealth of different seal design configurations and materials available, where some are commercially available, and others are bespoke formulations or geometries for specialist applications [1].

Mechanicals seals can be thought of as predominantly falling into two categories: static and dynamic. Static seals, as the name suggests, are used to seal between surfaces that do not move relative to each other and tend to be classed as O-rings, gaskets or direct contact seals. Dynamic seals are used where the surfaces are moving, i.e. rotary movement of a shaft relative to the housing or reciprocating movement of a piston into a cylinder. However, there are a few exceptions, for example, where static seals may be subject to limited movement of the sealing surfaces but not sufficient to be classed as a dynamic seal.

Seals are used in many different applications throughout the nuclear industry from plant operation to waste management and decommissioning, many of which include safety critical equipment. The variety of potential service conditions and broad demands on material performance means that the use of a wide range of seal geometries and material types can be expected. The following list summarises the key applications of seals across the nuclear industry as a whole.

The following list provides examples of some of the key applications of seals across the UK nuclear industry:

- Radioactive waste containment packages;
- Transport flasks;
- Glove box window seals and gaskets;
- Shielding window seals;
- Transfer port seals;
- Access doors and hatch seals;
- Repair systems;
- Ventilation systems;
- Robotics and manipulators;
- Electric penetration assembles;
- HVAC systems;
- Vibration dampening;
- Secondary seals in primary circuits;
- Valves and switches;
- Hydraulic rams;
- Motors;
- Pumps;
- Pipe seals.

2.2 Design considerations in seal selection

When designing a component for use in a nuclear environment there are a number of considerations, but in many cases the component will have to remain functional in a harsh environment(s) with limited access, if any, for maintenance or in the event of a failure. Accordingly, there needs to be a high level of confidence during the design stage that the component will operate reliably in the local environment for the required timescales. This is of particular concern where seals are used in a safety critical role, whether to help manage a safe plant shutdown or contain harmful radionuclides. Any interventions arising from seal failures could result in unforeseen costs in terms of equipment replacement and associated man-time. Furthermore, health and safety issues are likely to arise due to conventional and radiological risks to personnel carrying out the work. Metallic components are usually better able to withstand the harshest environments, whilst polymeric materials tend to be more susceptible to damage. However, polymers offer a number of advantages and with appropriate assessment and qualification, are used successfully across many important and diverse applications in the nuclear industry. In some cases, polymers may be the only currently available option open to designers and their selection and deployment will need to be made on an assessment of their strengths and weaknesses.

Given the wide range of options, the selection of an appropriate seal or gasket material can be challenging. It is also critical that the designer fully understands the operating environment not only in terms of functionality and internal stresses within a component, but also external influences such as radiation. Any component testing should include not only rigorous testing of a working prototype under operating conditions, but also assess the more susceptible components such as seals separately. As a seal ages its ability to maintain a sealing force will be reduced so it is key to understand what changes, if any, are likely to occur during operation in specific environments over a given duration. There are various standards and guidance documents that advise on appropriate qualification programmes used to justify a particular service lifetime. These usually involve some form of accelerated testing. As will be discussed later in this document, carrying out accelerated ageing that remains representative of the long-term service conditions can bring significant challenges.

One of the outputs of a qualification test might be a qualified service life. For example, the working lifetime could be limited to 10 years and would therefore require periodic replacement over a 40 or even 60-year plant lifetime. The periodic replacement of aged seals is common practice, so it is important that the design of a component allows for accessibility and ease of removal for periodic maintenance or replacement. There are also a number of sensors that can be incorporated into designs to monitor operational parameters and detect changes in operation before a failure occurs. This type of approach offers additional confidence in a component's operational health.

This document aims to discuss, in broad terms, the different aspects of seal use and explores the different types of seal materials, the key tests used to assess changes in a seal's properties and how they change over time, guidance on carrying out accelerated testing, seal ageing under accident scenarios and the role of FEA modelling in predicting performance.

2.3 Types of Seal Material

2.3.1 Metallic Seals

Metallic seals are manufactured from a variety of materials to form standardised or custom-made seal shapes (e.g. O-, C-, E-, W-rings and square sections) and sizes (diameter/length) as required by an application. Typical metallic materials are made to the highest levels of purity and include aluminium, copper, brass, gold, silver, nickel, platinum, steel, or stainless steel. Additional resilience can be introduced by plating a generic metal seal with silver, gold, cadmium, copper, nickel or indium for example. Plated materials tend to be soft deformable metals that can deform to infill minor surface roughness features, e.g., silver on 316 stainless steel O-rings. However, they have very limited resilience to thermal movement where surface sliding is induced across the seal interface. The thickness of the deposited layer can be altered to cope with rougher surfaces and there are specific coating materials that can sustain sealing where wear is being considered. Other non-plated metallic O-rings can be heat-treated, age-hardened, or annealed to impart required properties.

Metallic seals are used in conditions where there are very demanding or wide-ranging conditions [2]. For example, metallic seals are used in extremes of radiation, temperatures and pressure ranging from very high to cryogenic or vacuum conditions that are beyond the safe working limits of other seal types. Metals are also used in service conditions where very low permeation rates, negligible outgassing, chemical inertness or resistance to corrosive atmospheres are required.

However, the very high sealing performance of metallic seals can only be achieved under certain operational requirements. A large proportion of metal gaskets are hard and do not have any resilience or flow. As a result, very high contact pressures are required on precision engineered flanges to create a leak-tight seal. In order to achieve such high contact forces, a large number of bolts and much higher bolt-torques may be required making for lengthy and more complicated installations.

During assembly the contact forces on a metal seal leads to plastic deformation thus preventing it from being re-used or re-installed during any maintenance activities. As such, this family of sealing materials can be costly to employ and may be better reserved for specialist environmental conditions or applications.

2.3.2 Metal jacketed seals

There is a further subset of the metallic seals called metal jacketed or clad seals which comprise a metal outer layer partially or fully encasing either a different, softer metallic material or a non-metallic filler. The metallic outer layer protects the filler material and provides some of the properties of pure metal seals; ability to withstand high temperatures (not applicable to elastomeric cored seals), high pressure and corrosion resistance but also compressive strength and blow out resistance. The softer filler material can vary from flexible graphite, fibres, PTFE or high temperature millboard depending on the environmental conditions expected in service. The jacketed gaskets can be manufactured in a number of configurations and sizes to meet service requirements, and due to the resilient nature of the filler, are better able to accommodate any minor flange imperfections than the pure metal seals. Whilst less contact force may be required for these hybrid seals, joint relaxation can occur over time and so they are not suitable for some applications.

2.3.3 Polymeric Seals

Polymeric seal material can be divided into three generic categories:

- **Thermoplastics** are a class of polymers that can be softened and melted by the application of heat. When in the softened form they can be processed into shape by thermoforming. In the melt, they can be formed by extrusion and injection moulding. When they have cooled down after processing, they possess the same properties that the original un-heated polymer possessed. Although care is required that processing temperatures and times are not so long that degradation can ensue.

- **Thermoplastic elastomers (TPEs)** are defined as polymers, polymer blends or compounds which exhibit thermoplastic characteristics when heated that enable them to be formed into fabricated articles. At operating temperatures, they take on elastomeric characteristics although no chemical cross-linking occurs during the fabrication stage. The process is reversible and the product can be reprocessed/remoulded as desired.
- **Elastomers** or rubbers are long chain polymers which are lightly cross linked. They are essentially thermosetting polymers which means that when they are cured (vulcanised) to create three-dimensional, lightly cross-linked structures, the process is irreversible and they cannot be re-formed. It is this process that confers the unique viscoelastic properties that make these elastomers ideally suitable for use as flexible seals. The properties of elastomers and their suitability as seals is discussed in detail in Section 3 of this document.

Although thermoplastic O-rings are available, there are few instances where they offer advantages over elastomers and their use in generic face to face sealing applications is limited. However, the ease with which thermoplastics can be fabricated and their relative toughness and resilience mean that they can provide ideal solutions to situations where complex seal geometries are required such as valve seats and other complex seal geometries in pumps and other plant components.

Thermoplastics such as the fluoroplastic family of materials can provide excellent heat stability and corrosion resistance. However, their radiation resistance can be poor, for example PTFE has one of the best overall chemical and thermal stabilities available because of the highly stable C-F bonds in its structure. Unfortunately, it is the stability of the C-F bond that makes PTFE probably the least radiation tolerant of all organic polymers. This is because the C-C backbone bonds are much weaker than C-F bonds which renders the PTFE backbone more susceptible to radiation damage. Fluoropolymers such as PVDF and some fluoro-ethylene copolymers can, however, show significantly better radiation resistance than PTFE and have found applications in the nuclear industry where chemical and thermal stability may be required alongside some tolerance to radiation.

There are a number of different thermoplastic materials used in the manufacture of valve seats and similar seals. A guide to some of the currently available materials is shown in Table 1 along with brief descriptions of their advantages and disadvantages when considering them for use in the nuclear industry. Some of the materials listed, such as PEEK, show excellent radiation resistances for organic materials. It is, however, important to bear in mind that the information shown in sources such as Table 1 should only be used as a high-level guide. The radiation tolerance of polymeric components should always be characterised by appropriate radiation testing before use is considered for safety-critical nuclear applications where exposure to radiation is expected.

Many of the thermoplastics listed in Table 1 are halogenated. In many applications in nuclear plant, the use of halogenated materials is prohibited because of the potential for leaching of aggressive species such as chloride ions into aqueous environments. The presence of halides in aqueous streams may result in damage to important components, for instance chloride induced stress corrosion cracking in stainless steels. Consequently, appropriate engineering judgement should also be applied when considering the use of certain thermoplastic components in nuclear applications.

In respect to TPE materials, there are numerous types of these flexible seal materials available to the end user. One of the more commonly available TPEs are styrene/butadiene TPE-S materials based on two-phase block copolymers with hard and soft segments. The styrene end-block component provides the thermoplastic properties and the butadiene mid-blocks provide the elastomeric properties. Other types of TPE may be produced from polymer blends/alloys where control of the ratio of the different materials that are mixed, can provide seals that offer a wide range of hardness, high strength, thermal stability and low permeability.

A significant advantage in the use of TPEs over typical elastomers lies in the ease with which they can be processed and manufactured resulting in faster, more efficient production cycles coupled with reduced energy costs. Finally, at end of life, TPEs may be suitable for recycling thus reducing environmental impact whereas thermoset elastomers can only be disposed of through conventional landfill or other waste routes.

However, thermosetting elastomers have a number of advantages over TPEs. The ease of processability in TPEs is driven by the low temperatures required by the materials to be heated and reformed. Clearly this ability will be detrimental if service conditions involve the use of high temperatures. The more strongly cross-linked thermosetting elastomers are able to withstand not only higher operational temperatures but they also have better chemical stability and creep resistance.

Both classes of polymeric elastomers offer a component designer access to a wide range of material properties, where the advantages or disadvantages for use in a particular application will be driven by the accompanying service conditions and must be carefully considered.

Unlike metallic seals, polymeric seals are resilient enough that they can accommodate small flange surface imperfections to produce a good seal, thereby reducing high machining and detailed finishing costs. This also means that they will only require a relatively modest amount of compression to form a seal. This makes implementation and installation an easier process. In summary, the relatively low cost of manufacture, ease of use/replacement and ability to provide efficient and reliable sealing of many components means that polymeric seals are often the preferred choice of sealing material. In the harsher radiation environments experienced in a nuclear plant, these organic materials can have reduced service lifespans and so confidence in their reliable operation is required. Accordingly, much of the emphasis of the remainder of this document focusses on this family of materials.

Table 1: A list of thermoplastics currently available for use in pumps and valve seats. This is a generic guide for comparison and should not be used as an absolute source of information.

Thermoplastic type	Advantages	Disadvantages
PTFE (Polytetrafluoroethylene)	Excellent chemical resistance High operating temperature	Low strength and hardness Very poor radiation resistance
ETFE (Ethylene-trifluoroethylene)	Good chemical resistance Good mechanical properties	Expensive Attacked by esters and aromatics Radiation dose rate effects
PCTFE (Polychlorotrifluoroethylene)	Good chemical resistance Higher modulus than PTFE	Very expensive Attacked by esters, ethers and halogenated hydrocarbons
ECTFE (Ethylene-chlorotrifluoroethylene)	Good chemical resistance Good mechanical properties	Expensive Attacked by esters and aromatics
PFA (Perfluoroalkoxy)	Highest nominal maximum operating temperature of fluoroplastics Melt processible	Very expensive Low strength and hardness Only fair radiation resistance
PA (Nylon 6, 6/6,6/12)	Tough abrasion resistant Cost effective	High water absorption Only fair radiation resistance
PA (Nylon 11 and 12)	Tough abrasion resistant Cost effective Lower water absorption than Nylon 6	Lower thermal stability than Nylon 6 Only fair radiation resistance
PAI (Polyamide-imide)	High strength Good wear resistance	Very expensive Attacked by alkalis Moderate radiation resistance
PEEK (Polyetheretherketone)	High operating temperature Good chemical resistance Melt processible Probably the thermoplastic with best radiation resistance	Very expensive Attacked by acids
PPS (Polyphenylenesulphide)	High operating temperature Good chemical resistance Good radiation resistance	Expensive Difficult to process Poor impact resistance
PES (Polyethersulphone)	High operating temperature Good radiation resistance	Very expensive Attacked by polar solvents ketones, chlorinated solvents
UHMWPE (Ultra high molecular weight polyethylene)	Good abrasion resistance Heat processable	Low operating temperature Fair radiation resistance

2.3.4 Other Non-metallic Seal Materials

There are a wide range of other non-metallic seal materials available for use in certain service conditions. A high-level overview of these materials is provided below:

2.3.4.1 Foam Seals

Foam or sponge materials can be divided into two classes: open or closed cell. Within an open cell structure, the porosity is connected and provides an easy leak path for gases or liquids. Accordingly, foam seals and gaskets are formed from a closed cell structure where thin walls of the foam material isolate individual cells and restrict gas flow between them. Closed cell foams are typically manufactured from materials such as silicone, EPDM, polyethylene and polyurethane. Different closed-cell densities and morphologies can be produced according to the requirements of the application. Key properties of this class of materials are centred on their soft, flexible structure that ensures good cushioning with the ability to prevent dust, moisture, oils and chemical ingress. Foam structures are also excellent thermal insulators. However, when subjected to radiation environments typical of those expected in a nuclear plant, the thin walls of the cell structure may be quickly broken down and result in high compression sets and loss of sealing characteristics.

2.3.4.2 Compressed Fibres

Compressed fibre gasket materials are widely used in many industries and may be produced from a range of different fibre types bonded together by different resin combinations [3]. The popularity of this group of sealing materials may be attributed to its low cost and versatility given to ease of handling and ability to be simply shaped on site if required. Historically, asbestos fibres were commonplace, however synthetic fibres such as carbon, glass or aramid (e.g., Kevlar) are used today under the initialism CNAF (compressed non-asbestos fibre). If compressed asbestos fibre gaskets require changing out on older equipment, the appropriate safety considerations would apply.

The fibre and inorganic filler matrix in this type of seal provide structural integrity which is often combined with an inert filler such as silica for bulking. A polymeric resin binder is then typically used to bond the fibres together; these resins often include nitrile rubber (NBR), ethylene-propylene rubber (EPDM), natural rubber, styrene-butadiene, chloro-sulfonated polyethylene or PTFE. In the case of certain specialised applications, the choice of binder may have an influence on the selection of a suitable CNAF product. Other additives may be included during production that initiate resin cure, add colour or even generate a low friction surface if required.

2.3.4.3 Cork

Cork gaskets and seals can also be found in various different grades and compositions; and are considered an economical, general purpose material. Perhaps the simplest form is natural cork where cork granules are bonded together with resin. The size of the granules drives the material properties, whilst cork seals are usually fragile, they are popular where flexibility is required to accommodate uneven flange mating surfaces or light bolt torques are required. They demonstrate good anti-vibration properties, good oil and solvent resistance, but cannot withstand elevated temperatures or pressures.

In most applications the cork granules are bonded together using a neoprene or nitrile elastomer matrix. The addition of the elastomer provides greater resilience and flexibility whilst enhancing the working temperature range, increasing mechanical strength and compressibility. Chemical compatibility is determined by the properties of the binder which can be selected to show good resistance to oils and hydrocarbons as required. However, these materials are not recommended for acidic or alkaline conditions.

2.3.4.4 Flexible Graphite Seals

Flexible graphite is a soft, rolled sheet manufactured from compressed pure graphite flake without the need for any binders or fillers. With such high levels of purity, the flexible material retains many of the advantageous properties of graphite such as self-lubrication, excellent thermal, radiation, chemical and corrosion resistance with negligible gas permeability. Over long-term use, pure graphite seals tend not to harden or embrittle, mainly because of the absence of other materials such as binders which may be less stable than the graphite. The flexible and compliant nature of graphite enables the accommodation of irregular flange sealing surfaces, but it also demonstrates very low stress relaxation and maintains its shape when under compression. Some manufacturers have developed very high purity, certified grades of graphite for use as seals in some nuclear plant applications.

However, flexible graphite sheet is fragile and has low tensile strength and elasticity. This can make handling and installation difficult. Tensile strength can be improved through lamination with metal foils, typically stainless steel. Although these reinforced products tend to retain an excess of 97% graphite, their maximum operating temperatures can be reduced compared to the pure materials. Graphite is also susceptible to oxidation when at elevated temperatures and will be attacked by highly oxidising acids such as concentrated nitric, sulphuric or chloric acids together with permanganates, chromium solutions and some reactive molten metals. Initially oxidation would occur at any exposed faces of the seal, but laminated grades can show an increased susceptibility to attack through their profile.

The use of graphite-based sealing arrangements for some applications, e.g., seawater, may result in effects such as crevice corrosion on stainless steel flange faces [4]. Therefore, careful consideration of the compatibility between graphite seals and metallic components will be important. However, graphite seals demonstrate many advantages over some of the polymer/elastomer resin bound fibre sheets in terms of their overall environmental resistance.

2.3.4.5 Lubrication

The use of lubricants is important during the assembly of both static and dynamic seals. The application of a small amount of lubricant to a static O-ring seal will aid insertion into its groove and minimise abrasion, pinching and cutting. This becomes even more important where seals are pressed into groove geometries such as dovetails where pinching and cutting may be likely if the process was attempted without lubrication.

In dynamic seals applications, lubrication is necessary because both the shaft and the seal require lubrication before assembly, otherwise damage is likely to the seal mating surfaces. In addition to the application of a suitable lubricant, cleanliness is also a pre-requisite and the introduction of contaminants such as particulates and moisture needs to be avoided. It is also important that the correct lubrication levels are maintained through the life of a dynamic seal. If lubrication is lost, direct contact between seal and shaft will cause wear. Furthermore, over lubrication can cause an increase in working temperature because the system incurs additional work during any movement cycle if it needs to push excess lubricant aside.

As lubricants are often organic oils or greases, problems have the potential to arise if the lubricant and the seal are incompatible. The solubility parameter of an organic material is a property related to how it interacts with other organics. If one material has a similar solubility parameter to another, both materials are likely to be miscible. Should a lubricant have a similar solubility parameter to an elastomer, it is likely that the lubricant will be absorbed by the elastomer. In a seal, this is likely to result in swelling which will, in turn, result in a reduction in properties such as hardness, tensile strength and tear strength. Excessive swelling could cause the seal to extrude between metal components resulting in further, more extreme damage.

Consequently, different seal materials require different lubricants. Seals and lubricants of similar chemical structures, for example silicone O-rings and silicone greases should not be used together. In a similar manner ethylene-propylene based seals (e.g., EPDM) should not be used with mineral oils because these lubricants generally contain high levels of hydrocarbons. However, documents such as the Parker O-ring handbook provide good guidance for the correct selection of lubricants over a wide range of elastomers [1].

One of the additional benefits of the use of lubricants with seals is that the lubricants can protect the seal material by acting as a surface film to protect from external atmospheric ageing stressors. It has been shown that presence of lubricants can reduce the amount of compression set that can accumulate in radiation aged O-rings [5].

2.4 Importance of Material Composition

An elastomeric seal is a lightly cross-linked material that comprises a base polymer mixed with selected additives which are used to modify the seal's physical and chemical properties. Selection of the base polymer will typically be built on generic properties required to withstand the demands of operating conditions. For example, silicones show excellent heat resistance but poor resistance to oils, whereas nitrile-based elastomers offer excellent resistance to oils but relatively poor resistance to heat. However, generic properties can be improved by the incorporation of additives; for example, some improvement to nitrile heat stability may be achieved by the use of alternative heat stabilisers.

Consequently, during manufacture, a number of additives and fillers may be selected to compliment the base polymer and enhance properties as well as providing protection during mixing and processing activities [6]. These additives might include different types of fillers. For example, carbon black is a multifunctional additive that can enhance mechanical properties when used as a filler but also provide UV protection. On the other hand, calcium carbonate may be used as a filler to enhance properties but also as a diluent type filler because of its abundance and low price. The quantities of reinforcing fillers that are used to enhance mechanical properties are carefully managed to optimise for the required application. For example, increasing levels of carbon black are often accompanied by decreases in elongation at break and too much carbon black could result in an un-acceptably hard material. A diluent filler is, as the description implies, a cost-effective additive that usually increases the non-rubber content and “fill-out” the material. However, the quantity of these types of filler should also be carefully controlled as some mechanical properties can be reduced with over-fill.

Other additives are added to polymers to provide a level of protection in aggressive environments such as high temperatures and radiation that would otherwise lead to degradation and a deterioration in properties. These include stabilisers, anti-rads, antioxidants and antiozonants that preferentially react with heat, light or radiation induced free radicals before they can attack the base polymer. Although these additives are usually added in low quantities (1-3% by weight), they are evenly distributed throughout the material and can greatly influence service life. There is a wide variety of other chemical compounds that can be added to impart specific properties. These may include flame retardants, extenders, desiccants or coloured pigments to list just a few.

The use of plasticisers can be another important consideration in the production of seal materials. The function of plasticisers is to increase the flexibility/softness of a polymer by allowing increased chain movement. Plasticisers can be either internal or external; internal plasticisers are chemically bonded sub-structures in the material that enhance chain movement. External plasticisers are usually organic liquids that are partially dissolved in the base polymer and decrease chain attraction forces. These types of plasticiser are not chemically bonded within the base polymer and can be lost as a result of permeation at high temperatures, reverting the base polymer back to a less flexible material. The loss of external plasticisers from elastomers is usually described as bleeding and is characterised by a shiny and sometimes sticky surface.

Another key process that underpins the properties of an elastomeric seal is the vulcanisation or heat induced cure process. This leads to the formation of an elastic polymer with a stable three-dimensional cross-linked network. To aid this process, polymers will also contain chemically active species that act as activators and initiate the cross-linking reactions. Other products such as accelerators are used to help increase or control the rate of cure [6].

Once the compound ingredients have been selected, they are carefully mixed using one of the following common processes; an internal mixer, an open or two-roll mill or a continuous mixer. The mixing will occur over a number of stages, starting with softening of the base polymer before the addition of other additives [6]. The high viscosity of the mixture can make mixing difficult and is often accompanied by a rapid increase in temperature. These elevated temperatures could initiate curing reactions, so the mixture is allowed to cool before the final step where the vulcanising agents are added. After passing appropriate quality checks the newly mixed material is then prepared for moulding, or shaping and vulcanisation, into the desired form. A number of methods can be used depending on required product but include compression, injection and transfer moulding techniques.

Clearly, the careful selection and ratio of each and every chemical component that is added to a seal material compound is undertaken to impart desired properties, ensure chemical compatibility and resistance to degradation. The chemistry of these materials is complex and not all fillers or additives are compatible with each other or suitable for certain applications. Given that the specific combination of chemical ingredients heavily influences the properties and stability of a seal material, it is critical that the same formulation is used if replacement is required. It is important to recognise that any changes to composition, even within a generic grade of polymer, is likely to result in changes to the long-term properties, performance and stability. Such a change in properties has the potential to invalidate previous qualification claims and would therefore require a new qualification assessment, particularly for a safety related application.

Furthermore, when specifying seals for an application, care should be taken in the use of generic seal names such as nitriles and EPDM. If a designer were to specify just “EPDM” for a seal on a drawing, a very large number of seal materials would satisfy that instruction and it is entirely possible that an inappropriate seal could be chosen. Therefore, it is suggested to be good practise during design to specify seal formulations with appropriate manufacturer’s codes, material descriptions and formulation certification as appropriate.

2.5 Supply chain Robustness

2.5.1 General Overview

There are various challenges associated with maintaining quality and resilience in the supply chain over the timeframes required during the commissioning and operation of nuclear plant [7]. Supply chains have become more complex, sometimes reaching across global markets, which increases the risk of potential disruption. In the case of polymeric and elastomeric seal production this not only includes the ability to source particular chemicals of the appropriate grade but also sustaining manufacturing capability over many decades when sealing technologies/materials are continually developing.

Given the significance of maintaining the exact formulation and ratio of compounds with respect to continuity in expected performance and changes in properties over the longer term, it is vital that this is safeguarded, sometimes over many decades. The availability and cost of additives can be variable, and so the exchange of one type of additive with another can occur. The manufacturer may attempt to ensure that any change in additive(s) will have no impact on the unaged material properties, especially if a material is manufactured to a defined specification. However, the response of the re-engineered formulation to elevated temperatures or radiation can vary significantly. Any changes to the long-term performance could then invalidate qualification assessments used to underpin the safe use of equipment on plant. However, manufactures and designers may not be aware of these implications when exchanging additives. To help safeguard consistency in material composition and build confidence when re-purchasing at a later time, samples of the new and old material could be subject to independent testing to confirm key compounds, alongside auditing of the manufacturers quality control system. Whilst securing the long-term availability of a particular formulation from a supplier is both challenging and expensive, an alternative approach would be to purchase spare samples and place them in storage under a controlled environment until needed (Section 2.5.2).

Consistency in a materials properties and long-term performance is also dependent on the manufacturing approach taken during compounding or processing. As technology advances, so do manufacturing processes.

Any changes in production can be accompanied by variations in material morphology such as molecular alignment and crystallinity which influence key properties such as elastic modulus, tensile strength and response to stressors such as radiation and high temperatures. Therefore, when designing and sourcing a material which is expected to function safely over many decades of operation in a nuclear environment, an open and transparent relationship with manufacturers is required to address any potential for changes in chemical ingredients or manufacturing processes.

2.5.2 Long-term Storage Conditions

One potential method of mitigating issues with the supply chain is to obtain significant quantities of the required elastomeric seals (or other polymeric seal types) and store them ready for replacement, or otherwise, as required. However, as elastomers are polymers, they will slowly age even under what might be considered to be benign conditions.

Historically, single, pre-defined storage times for elastomeric seals have been classified in terms of their resistance to ageing. A recently cancelled US military standard, MIL-HDBK-695C [8], defined three groups of generic elastomer materials deemed suitable for separate storage periods in terms of their stabilities. For example, MIL-HDBK- 695C stipulated that storage periods of 5, 10 or 20 years should apply to NBR, EPDM and fluoroelastomer O-rings respectively. Although this standard also defines appropriate storage methods, history has demonstrated that storage conditions are significantly more important in determining the useful life of O-rings than storage time.

ISO 2230 also applies storage times for three groups of generic elastomer types as shown in Table 2 [9]. In this case, however, the storage times are divided into two periods. Firstly, an initial maximum storage period is stipulated for which an elastomeric product may be stored before a sample of the product needs inspection or a re-test. This initial period starts from the time of manufacture and the products must also be stored in appropriate packaging and under specified conditions. If the sample is deemed to be in a satisfactory condition after inspection/testing, a further, extended period may be applied before an additional inspection and retest is required [9], see summary in Table 2.

Table 2: Summary of seal storage periods as defined by ISO 2230 [9].

Seal Material Group (with examples)	Initial Maximum Storage Period	Extended Storage Period
Group A (including natural rubber, polybutadiene, SBR, polyurethane)	5 years	2 years
Group B (including nitriles, acrylics, butyls)	7 years	3 years
Group C (including EPR, EPDM, silicones, fluroelastomers)	10 years	5 years

Coupled with stipulated storage times, ISO 2230 also defines the approved methods of storage [9]. The materials used to package polymeric seals must not contain substances such as additives that could degrade the properties of the elastomer. Suitable packaging materials include heat sealable, polyethylene coated kraft paper, opaque polyethylene film or polymer-based laminates (e.g., polyethylene / paper / aluminium foil). Bags or materials manufactured from plasticised PVC or any other plasticised polymer should not be used because plasticisers from PVC bags in close contact can readily diffuse into an elastomer and affect its properties. In practise, opaque polyethylene bags of at least 75 µm thickness are suitable for single wrapping [9]. However, if there is an increased risk of moisture ingress, for example, the use of composite or laminate packaging should be used.

A summary of the key points put forward by ISO 2230 [9] for the storage of appropriately packaged seals is provided in the list below:

- **Environment:** Seal should be stored indoors;
- **Temperature:** Seals require storage at temperatures below 25°C, away from direct sources of heat. However, if stored for long periods at temperatures below 15°C they should be warmed to 30°C before being put into service. Warming will reduce the risk of distortion during handling if the seal has become stiff at low temperatures;
- **Ozone:** Ozone can be particularly damaging to elastomeric seals, see Section 3.1.9. Storage environments should not contain any equipment that is capable of generating ozone. Typical equipment to avoid include mercury vapour lamps, high voltage electrical equipment giving rise to electrical sparks or silent electrical discharges. Furthermore, substances such as combustion gases and organic vapours need to be excluded from storage environments because they can produce ozone via photochemical processes;
- **Humidity:** The relative humidity in storage should be less than 70%. For moisture sensitive formulations such as polyurethanes, the relative humidity should be less than 65%;
- **Light:** Elastomeric seals require protection from light sources, in particular sunlight or intense artificial light having an ultraviolet content and should therefore be stored in dark enclosures. The choice of appropriate storage bags also will provide the best overall protection as long as the bag materials are UV stabilised;
- **Radiation:** Clearly, in nuclear environments, contact with all forms of ionising radiation must be avoided;
- **Material mixing:** Seals produced from different materials or formulations of the same generic material type should not be packaged together;
- **Good housekeeping:** Contact with debris, other foreign matter or metals (especially metals such as copper and iron) must be avoided. These types of metal can have a deleterious effect on elastomers;
- **Stock rotation:** Stored elastomeric seal stock should be rotated on the first in, first out (FIFO) principle;
- **Storage under stress:** Elastomeric seals require storage free from superimposed tensile and compressive stresses or other causes of deformation e.g. hanging. O-rings with a large inside diameter will require to be formed into at least three superimposed loops to avoid creasing or twisting. It is not possible to achieve this condition by forming just two loops, three are required.

2.5.3 Changes to legislation

At the time of writing this report, a group of member EU states recently announced their intention to introduce a restriction under the Registration, Evaluation, Authorisation and restriction of Chemicals, (REACH) for the manufacture, marketing and use of all poly- and perfluoroalkyl substances (PFAS) in the EU. The PFAS are a widely used group of man-made organic chemical substances that include fluorelastomers and fluoropolymers, such as Viton and PTFE respectively. These materials offer advantageous properties such as high chemical and temperature resistance. However, when discarded, the low molecular weight fractions have been found to have very high persistence in the environment, high mobility in water and soil giving rise to a high potential for long-range transport and contamination of drinking water. Research has shown evidence of their bioaccumulation in humans, animals and plants and links to serious effects for human health and the environment.

PFAS materials are commonly used within the nuclear industry, including safety critical applications, and a ban would require each relevant safety case to be revisited, replacement materials sought and qualified or even substitution of components and equipment where PFAS are integral to their operation.

Whilst it is unclear what the results and breadth of any future changes to EU legislation will be, it is clear that an EU ban on this family of materials would have significant implications for all industries relying on their manufacture and supply. Now that the UK has left the EU, there is also further uncertainty over the response of the UK Government and direction of future UK policy in this regard. Accordingly, it is important that designers should remain up to date with any proposals or changes in EU and UK regulation relating to the use of chemicals, not only in the introduction of new components but also in the use and ongoing maintenance of materials and equipment currently qualified for use on plant.

2.6 Regulatory Expectations

2.6.1 General

Where seals and sealing systems need to be employed to assure nuclear safety, a documented safety case is required. The term 'safety case' is used to encompass the totality of the documentation developed by a designer, licensee or duty-holder to demonstrate high standards of nuclear safety, best practise and radioactive waste management. This also applies to any subset of this documentation.

When assessing the adequacy of safety cases to support regulatory decisions, ONR apply the Safety Assessment Principles (SAPs) [10]. The SAPs provide ONR's inspectors with a framework for making consistent regulatory judgements on nuclear safety cases. The SAPs also provide duty-holders with information on the regulatory principles against which their safety provisions will be judged. However, they are not intended or sufficient to be used as design or operational standards, reflecting the non-prescriptive nature of the UK's nuclear regulatory system. In most cases the SAPs are guidance to inspectors, but where guidance refers to legal requirements, they can be mandatory depending on the circumstances.

It is noted that Sections 2 and 3 of the HSW Act 1974 require the employer to reduce the risks to employees and other persons, so far as is reasonably practicable (SFAIRP). Therefore, it is a fundamental requirement that the safety case should demonstrate how nuclear risks have been reduced to as low a level as is reasonably practicable. This concept may also be referred as demonstrating that risks have been reduced to levels that are “As Low As Reasonably Practicable” (ALARP). The starting point for demonstrating that risks are ALARP and safety is adequate is that the normal requirements of good practice in seal engineering, environmental qualification, operation and safety management are met. This is a fundamental expectation for all safety cases.

2.6.2 Transport of Radioactive Materials

The civil transport of radioactive material (Class 7 dangerous goods) is regulated in the UK under the Carriage of Dangerous Goods (CDG). and Use of Transportable Pressure Equipment Regulations 2009 (CDG). CDG implements within GB the international requirements for transport of hazardous goods by road and rail, ADR[1] and RID[2]. These are set harmonised standards for the safe transport of dangerous goods within and between

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[1] European Agreement concerning the International Carriage of Dangerous Goods by Road, issued by the United Nations Economic Commission for Europe, Committee on Inland Transport.

[2] Regulations concerning the International Carriage of Dangerous Goods by Rail, Appendix C of the Convention concerning International Carriage by Rail, issued by the Intergovernmental Organisation for International Carriage by Rail.

IAEA member states and incorporate the requirements of the IAEA Safety Standards 'Regulations for the Safe Transport of Radioactive Material' – SSR-6 [11]. Furthermore, the CDG authorises the ONR as the Competent Authority (CA) for the transport of radioactive materials in the civil sector. With respect to RAM transport in the defence sector, DNSR acts as the Competent Authority.

The regulations provide a regulatory framework to ensure that the control of risk from the transport of radioactive material is reduced to 'as low as is reasonably achievable, economic and social factors being taken into account' (ALARA), which is equivalent to SFAIRP and also ALARP in UK legal terms. The regulations achieve this by establishing a set of prescriptive requirements that must be satisfied to ensure safety and to protect persons, property and the environment from the effects of radiation in the transport of radioactive material. ONR use the SAPs together with supporting TAGs to guide their regulatory judgements and recommendations when undertaking technical assessments of nuclear site licensees' safety submissions. Appendix A provides examples of SAPs applicable to the use of seals in the UK nuclear industry.

SSR-6 [11] applies a graded approach to contents limits, and performance standards for package designs, and for conditions on operation and maintenance etc depending upon the hazard of the radioactive contents. CA approval is required for higher hazard transport package designs and shipments as defined within the regulations. These are typically Type B(U), Type B(M) and Type C, fissile packages, certain shipments and other design types.

Where seals form part of a containment boundary, SSR-6 [11] specifies a number of requirements dependent on the package design, including but not limited to:

- [213] Explicit definition of where seals form part of the containment boundary;
- [659] For each radionuclide within the contents, maximum leakage rate limits under both normal and accident conditions of transport;
- [666] Low and high temperature withstand requirements under normal conditions of transport;
- [726] Tests for demonstrating ability to withstand accident conditions of transport.

Additional guidance on the requirements specified in SSR-6 [11] is given in SSG-26 [12].

3. Introduction to the generic properties of sealing elastomers and polymers, ageing and testing

3.1 What are the properties of elastomers?

3.1.1 Viscoelasticity

Under normal room temperature conditions, an elastomer has an amorphous structure that consists of lightly cross-linked, long chain molecules that continuously change their position due to Brownian motion – a term often used to describe the motion of elastomer chains is “wriggling”. The attractive forces between the chains are weak and if a force is applied the molecules align and a large elastic deformation occurs. The amount of alignment is controlled by the number and type of cross-links which pin the chains together. Therefore, although significant alignment or flow is allowed, the molecules cannot flow completely over each other. The cross-links that prevent complete alignment can be thought of as providing memory locations for the chains to return to when the force is removed.

As the elastomer is stretched under the external force and the chains partially align, there is an associated loss of entropy in the material. However, the second law of thermodynamics stipulates that a system will always tend towards high entropy. Therefore, with increasing alignment, an internal force exerted by the entropy in the system will tend to drive the chains back to their original positions. The constant drive to push chains back to their original position when under load provides elastomers with unique properties such as the tendency for a compressed elastomeric O-ring to spring back to maintain a seal.

As the elastomer continues to be stretched, as shown in Figure 1, there is no distinct yield point (i.e., no permanent deformation occurs) and it will still try to return to its original condition. However, the properties of elastomers are complex and the stretched elastomer will not immediately return to its original position after the load is removed. Under normal conditions it will quickly retract to a certain position after a fixed time, but not fully, and then after a longer period of time it will slowly approach its original dimensions.

In comparison, when a material such as a metal or ceramic is subjected to a stress, it will develop a strain which is in phase with the stress (i.e., the strain develops at the same time at the force is applied). Elastomers however, show a property called *viscoelasticity* where the elastomer can respond elastically but it also responds in the manner of a viscous liquid (like a spring and dash-pot). As a consequence, when a force is applied, the resulting strain is not immediate but it is out of phase with and lags the force. The strain is therefore time dependent.

Viscoelasticity in elastomers is responsible for the following characteristics:

- **Strain rate dependence –** The response of an elastomer will be different if it is stretched or compressed at different rates. At low strain rates, the elastomer will appear to be relatively soft and compliant. In comparison, at high strain rates, the elastomer appears to be harder and requires more force to produce equivalent elongations. In some cases, care may be required because brittle-type failure can ensue if strain rates are very high.

- **Stress relaxation** - If a fixed displacement is applied to an elastomer, the force required to maintain the displacement will decrease over time. The reduction in force is as a result of both chemical and physical changes in the material and is dependent on environmental conditions, particularly temperature [13]. This property is important in assessing the long-term performance of a seal as a reduction in the contact pressure or force exerted by the seal on the surrounding housing could result in a leak path and failure.

- **Creep –** In an elastomer under constant load, the extension will slowly increase with time. When the load is removed, significant periods of time may be required for the elastomer to approach its original condition. This behaviour can be important in applications where operation requires certain clearances to be maintained between the seal and housing. Over time creep reduces the clearance and eventually the seal is in contact and failure occurs. Creep rupture can also occur where the continuous stress leads to the formation of cracks. Again, higher temperatures can accelerate creep behaviours.

- **Damping/hysteresis –** During cyclic loading of an elastomer, the relationship between the applied load and extension is non-linear and will differ depending on whether the elastomer is being loaded or unloaded, as illustrated in Figure 1. The area of the resulting loop or hysteresis between the loading and unloading cycles represents the amount of energy dissipated, or damping. The higher the level of hysteresis in an elastomer, the greater the damping. Therefore, a rubbery material with a high degree of hysteresis might find use as a shock absorber or for sound insulation.

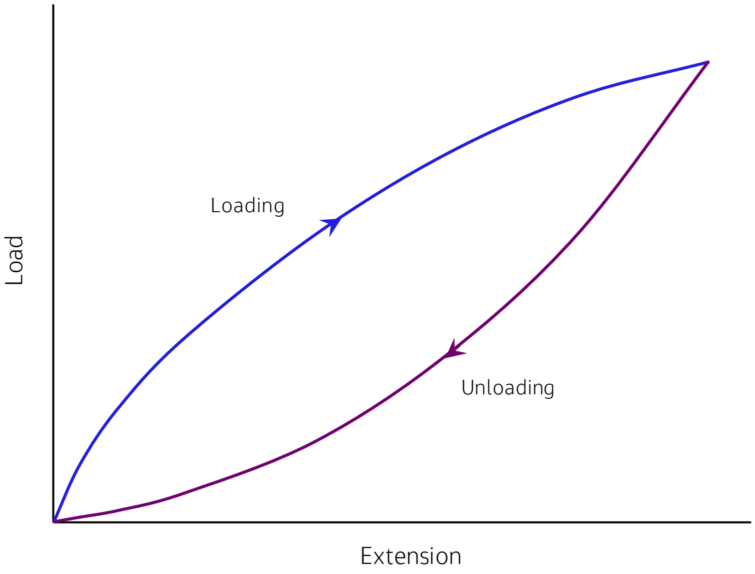

Figure 1 A schematic chart showing a hysteresis loop for an arbitrary elastomer.

3.1.2 Glass Transition

The high mobility of the molecular segments in an elastomer at ambient temperature is the condition for the rubbery state, i.e., high elastic elongation described above in Section 3.1.1. If the temperature is reduced, the chain mobility and wriggling capability reduces accordingly. As the temperature decreases further towards a particular temperature molecular mobility is frozen. The properties of the elastomer change from soft and rubbery to hard, rigid and brittle. The particular temperature is defined as the glass transition temperature, T_g, where the transformation from viscoelastic to glassy behaviour occurs. This process is entirely reversible and if the material is heated back above T_g it assumes elastomeric properties again [14].

There is no change in molecular structure at T_g, as sometimes mis-conceived, but the molecular structure will define the temperature at which it occurs. For example, a highly cross-linked elastomer will have a higher T_g than an elastomer with lower cross-linking. Additional factors such as elastomer chain length and composition will also affect T_g which is why a wide range of elastomers is available with an equally wide range of transition temperatures. Typical glass transition temperatures for a range of elastomers are shown in Table 3. When consulting Table 3, care is needed because the T_g values listed are singular, typical and can vary significantly with changes in elastomer formulation. Furthermore, significant variation in T_g can also occur depending on the method of measurement.

Table 3: Glass transition temperatures for a number of common elastomers. These temperatures are typical values and may vary significantly for different formulations of the generic material.

Elastomer type	Glass transition Temperature T_g °C
Silicone rubber, SiR	-123
Natural rubber, NR	-62
Ethylene propylene diene monomer, EPDM	-53
Styrene butadiene rubber (emulsion), ESBN-R	-50
Polychloroprene, PC (Neoprene)	-37
Low acrylonitrile NBR (nitrile butadiene rubber)	-45
Medium acrylonitrile NBR	-32
High acrylonitrile NBR	-18
Styrene butadiene rubber (liquid), L-SBR	-20
A-type fluoroelastomer (dipolymer)	-18
B-type fluoroelastomer (terpolymer)	-9
Tetrafluoroethylene/propylene (TFE/P)	2

From an engineering point of view, T_g is a very useful property because it can act as a reference to help define the low temperature properties of a polymer. For example, the use of a fluoroelastomer like those listed in Table 3 as shock absorbers for modes of transport would be completely inappropriate. As soon as winter arrived, especially in central Europe, the transport's ability to absorb the energy of an impact would be severely compromised because the rubber shock absorbers would essentially not be a rubbery material anymore at sub-zero temperatures.

A similar scenario would apply to elastomeric seal materials because transformation to a glass and loss of viscoelasticity below T_g will render the seal inoperable. The impact of low temperatures on serviceability of seals is discussed in detail in Sections 3.2.14-3.2.16.

3.1.3 Compression set

3.1.3.1 Importance and how it develops over time

As an elastomeric seal ages, any changes to the physical and chemical properties are often accompanied by a reduction in elasticity as chain mobility is reduced. Such changes could lead to a reduction in sealing force and give rise to leak pathways. This change in property is a useful measure of the materials ageing characteristics, however measurement of changes in leakage rates or sealing force can be difficult to assess and the results may not show any significant changes until the seal is heavily degraded. Figure 2 is a simple schematic illustrating how changes in the sealing force and leak rate typically might relate to changes in compression set. Compression set is often used as a benchmark test for rubbers of nominal hardness values between 10-95 International Rubber Hardness Degrees (IRHD) as it can be carried out using simple apparatus and provides a measure of changes in the material's elastic resilience as a function of ageing.

As discussed in Section 3.1.1, the viscoelastic properties of elastomers mean that they are subject to time dependent effects when a force is applied. In elastomeric seals under compressive loads, the compression set will increase with increasing time even under ambient conditions. There are two dominant mechanisms that influence the development of compression set, creep and structural changes in the elastomer, usually chemical. Over long periods of time under benign conditions, creep is the dominant factor whereas in the hostile conditions of a nuclear plant, changes in the molecular structure of an elastomer caused by radiation or otherwise, are expected to have a greater effect on compression set. However, in many applications, compression set will arise as a combination of both creep and structural change.

The sealing force that a compressed elastomeric O-ring exerts on the mating components will also slowly decay with time due to stress relaxation. Therefore, as compression set develops and increases in the O-ring over time, the sealing force will decrease. Over long timescales as a seal degrades, its compression set coupled with a decrease in sealing force may result in the formation of a leakage path. This is shown schematically in Figure 2 where the sealing properties of an elastomer are shown to change with an increase in the degree of degradation. The compression set in green and the sealing force in blue reach critical points at which the leak rate in red rapidly increases.

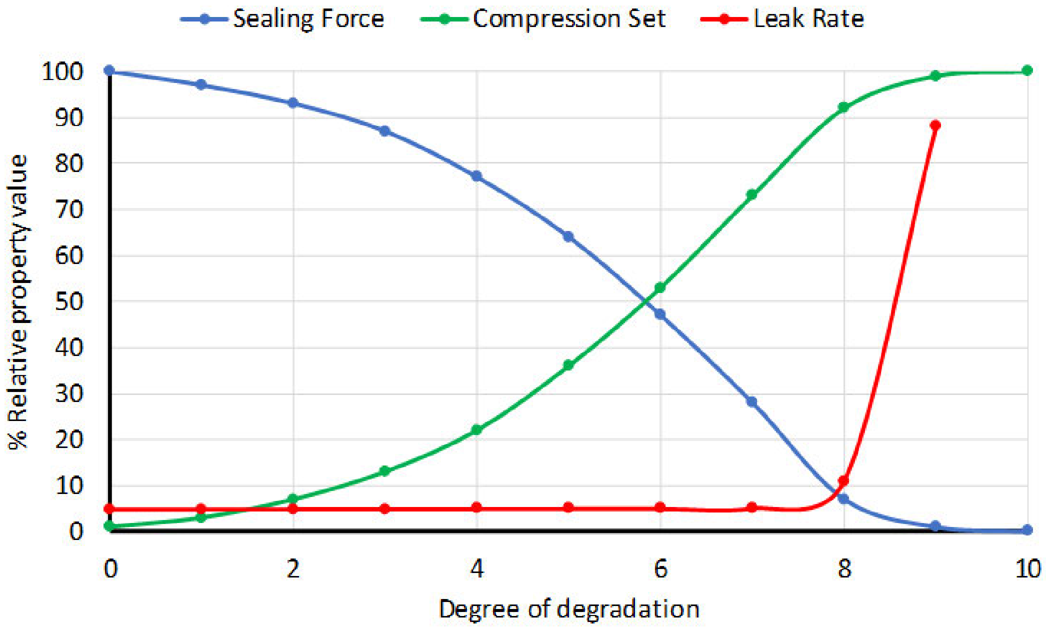

Figure 2 Relative changes in sealing properties of an elastomer.

3.1.3.2 Measurement of compression set

To carry out a compression set measurement, the seal material of interest is usually formed into a cylindrical disc and the thickness is measured. The disc is then clamped between compression platens to a level of compression commensurate with the material hardness. For example, spacers are added to enable 25% compression for materials with hardness values up to 80 IRHD. Standard test methods for determining compression set provide guidance for consistency in test approach and sample preparation [15].

Once the test pieces have been compressed between the platens and subjected to a constant level of strain, they may be exposed to one or more of the relevant ageing stressors (e.g., heat, radiation) as required by the application and aged for a prolonged period. At a suitable ageing interval, the compressive load is removed, and the seal is left to recover for a defined period of time (usually 30 minutes) before the sample thickness is then measured. As the seal material undergoes increasingly high levels of ageing over time, the ability of the seal to recover and return to the initial thickness is reduced. The difference between the initial and aged thickness values is then used to determine the compression set. Multiple measurements can be made on the same test pieces over the ageing period by simply compressing in the platens again and resuming ageing under the same experimental conditions.

The compression set (C), expressed as a percentage of the initial compression is calculated using the following formula:

$$C = \frac{D_0 - D_f}{D_0 - D_s} \times 100 \qquad \text{(Equation 1)}$$

Where:

C is the compression set in %

D_o is the original sample thickness

D_f is the final sample thickness after ageing

D_s is the thickness of the spacers (to enable appropriate level of compression)

It should be noted that in some cases, the compression set is calculated as a percentage of the initial thickness of the test piece and no account of the spacer height/deflection is included. Although the approach described by Equation 1 is one of the most commonly applied in seals assessments, it highlights the requirement for a clear definition of test methods used when reporting data.

A compression set value of 0% indicates that the material has fully recovered to its original thickness/shape and has retained all of its viscoelastic properties. Conversely, a seal material with a compression set of 100% is very heavily aged, has undergone permanent deformation and it no longer has the ability to supply any spring back force. The failure threshold of a seal in terms of compression set will be dependent on the application and conditions of use (for example a relatively low value of compression set may be agreed as end of life for a high-pressure application compared with the likely higher value set for a low-pressure ventilator seal). However, IAEA suggest 80-85% can be considered as end of life [16, 17, 18, 19]. In a very limited number of applications seals can remain operational at compression sets of 100%. However, since any small disturbance of the seal could lead to leakage, it would be prudent to ensure that such high levels of set are not reached and the seal is replaced before these levels are approached.

Whilst compression set testing is often carried out under standard conditions, alternative approaches may be required to simulate more representative environments, particularly for different seal geometries such as lip seals for example. It has been shown in this case, that a longer recovery period after removal of the compression may yield more reliable data. For comparable data, consistency in experimental approach across a specific test or series of tests is key. For example, comparisons between compression set values measured after 30 minutes relaxation time should not be directly compared to those determined after longer relaxation periods.

When in the compressed state, elevated temperatures or radiation will enhance the onset of higher compression set values. However, care should be taken if elevated temperatures are used as means of accelerating the ageing seen over long-term service conditions, for example using the Arrhenius equation. This is discussed in greater detail in Section 4, but there is usually no simple approach to correlate levels of compression set observed at elevated temperature with those expected in service at room temperature. Furthermore, some seal materials have been found to show surface oxidation effects, also discussed within Section 4, which can alter degradation mechanisms and provide a non-conservative representation of material performance.

3.1.3.3 Typical compression set data

Figure 3 shows how compression set typically develops in an elastomer as it ages over time. The compression set usually increases relatively quickly in the early stages of ageing. As time progresses, the rate of set slowly decreases with time but it eventually reaches a point at which the set is high enough to significantly affect sealing characteristics. The different coloured traces in Figure 3 represent different severity of ageing conditions with the blue trace representing high temperatures or dose rates and the red trace lower temperatures or dose rates.

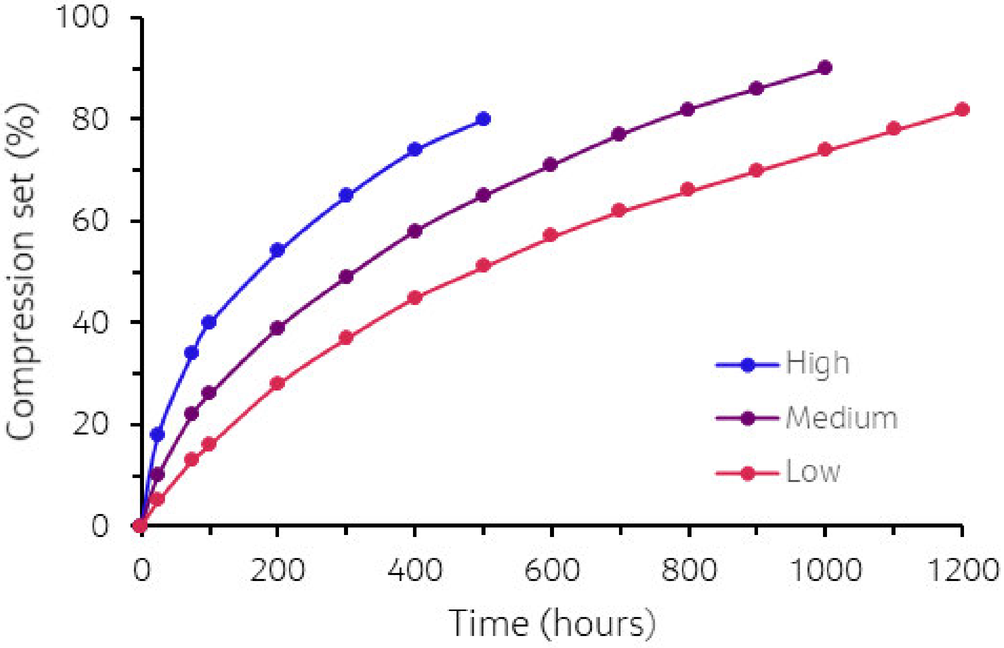

Figure 3 Development of compression set in a seal over time.

Figure 3 is a generic example of ageing and each seal material will have its own response to environmental conditions. An important consideration for seal design will be the time taken to reach the point at which the seal is no longer fit for purpose. For example, under IAEA guidelines of 80-85% compression set, the time taken to reach this value will define service life (or qualified life) [16,17,18,19].

3.1.3.4 O-ring squeeze

Another important parameter to consider in the evolution of the compression set in a seal is the amount of squeeze (or amount of relative compression) that is applied. In typical experiments to measure compression set, a nominal squeeze of 25% is applied, and the time taken to reach 80-85% under relevant conditions will be used to help assess seal selection. If a larger squeeze is applied, it is usual for a seal to take longer to reach an equivalent compression set. This may sound counter-intuitive but with a larger amount of squeeze, more force is applied and the time for the residual “spring-back” force to decay, as a result of stress relaxation, is usually longer. However, the application of a larger squeeze to generate an improved lifetime has its drawbacks such as over stressing of components, increased friction and wear. Some elastomers with low elongation at break or tensile strength could even rupture if high compression forces are applied in an attempt to improve a seal’s ageing characteristics.

3.1.4 Elastomer hardness

The hardness of a material may be interpreted as a measure of its ability to resist plastic deformation. This is usually determined from a standard test where the resistance to indentation of its surface is measured [20]. Although it is not usually recognised as a fundamental property of a material, it is one of the most widely used measurements to assess strength, ductility and wear resistance. There are a number of methods to measure hardness, using either portable or bench mounted instruments. However, selection of the appropriate method is determined by a number of factors that include the type of material e.g., metal or elastomer; the homogeneity in the material microstructure, sample geometry, the nature of the application and whether testing to a standard is required. Some hardness measurements are better suited to larger samples requiring large test loads above 1 kg, whilst other methods such as micro-indentation hardness testing are suited to small samples.

During a typical hardness measurement, a probe or indenter, which has a shape defined by the test method, is pressed into the surface of the material under a defined load and duration. The hardness value is then taken from the depth of the indenter penetration into the surface (e.g., Shore durometer, Rockwell, IRHD) or from the area of the indentation (i.e., Vickers, Knoop or Brinell). Furthermore, the different hardness tests also apply different scales, although some scales can be cross-correlated to others. In limited cases, hardness can be cross-correlated to changes in properties such as tensile strength in some metals and polymers. When comparing the results of hardness measurements, it is important to take account of the type of measurement and indenter load, load duration and the indenter geometry.

Hardness in elastomeric seals and polymers is usually measured using a Shore type durometer scale or IRHD instrument. These two hardness scales are measured using different test procedures with different indenter geometries, loads and test durations. However, standardised approaches to sample dimensions, preparation, set-up and test procedure are specified for both methods. This use of a standardised approach is important when cross-correlating results, for example, in the IRHD method, if an elastomeric sample is very thin, contributions from the steel instrument base plate can give incorrect values of hardness.

Shore hardness is measured using a calibrated spring-loaded indenter and the indentation depth is recorded after a specified dwell time defined by the material under test [21]. For a vulcanised rubber, the duration is three seconds whilst for a harder thermoplastic the duration is fifteen seconds. To take a measurement, the sample is placed on a flat hard surface and the durometer pressure foot is placed on the sample and a reading recorded.

There are 12 shore durometer scales in use where selection of the most appropriate scale will be dependent on the material properties. Each scale is linear and has a value between 0 and 100, where a higher value indicates a higher level of hardness or greater resistance to indentation. If Shore hardness values below 10 or above 90 on a particular scale are recorded for an unaged sample, they should not be considered reliable and a different scale selected [22]. Elastomers and polymers are typically measured using three scales, Shore A, D or 00. The Shore A scale is most often used to measure the hardness of elastomers, Shore D is used for harder rubbers and plastics and Shore 00 is used on the softest materials such as gels and foams in ASTM D2240-5 [23]. Furthermore, the ISO standard ISO48-4 uses Shore A0 for elastomers in the low hardness range and also cellular rubbers [24]. The nature of the indenter and spring loading varies in each of these tests ranging from truncated cones at high loads for the harder plastics to a spherical indenter configuration with low loads for softer materials.

The IRHD scale is measured using a dead load system where the sample is firstly placed under an initial contact force before the larger ‘indenting’ load is applied for a defined period. The instrument may give a direct hardness reading or the differential indentation depth is measured and converted into IRHD using tables such as those found in [25]. Similarly, to the Shore hardness scale, a lower value of IRHD hardness signifies a softer material that more readily deforms.

There are four IRHD methods used on samples with flat surfaces; a normal test or Method N for materials with a range of 30 to 95 IRHD, a high-hardness test or Method H for materials with a range of 85 to 100 IRHD, a low-hardness test or Method L for materials with a range of 10 to 35 IRHD and finally a microhardness test or Method M. The latter method is similar to Method N but used on thinner samples. Each of the four test methods can be modified for the measurement of the 'apparent' hardness of curved or non-flat test samples such as O-rings. In this case, the method is given a C-prefix e.g., CN, CH, CL and CM. All methods use a spherical shaped indenter, although the indenter diameter and foot geometry vary between each of the four IRHD methods. The IRHD test usually requires six measurements to be taken at different sample locations and the mean calculated to give the definitive IRHD value.

Structural changes in an elastomer are brought about by degradation mechanisms such as cross-linking or chain scission. When an elastomer or polymer ages and degrades the hardness often increases as the structure becomes more rigid from increased cross-linking. However, materials that undergo chain scission will be expected to soften with increased degradation clearly yielding lower IHRD values.

Hardness can be a useful tool to explore any heterogeneous ageing characteristics in a sample. It is not uncommon that the ageing of elastomers can introduce variations in molecular structure across the cross sectional of an O-ring, for example. Hardness profiling is a technique where multiple measurements are taken across a sample cross section to map changes in hardness associated with heterogeneous ageing. For example, hardness profiling may show increased hardness levels at the sample surface when compared to the bulk in the form of a U-shaped profile. If heterogeneous ageing has occurred in an elastomer sample, characterised by a U-shaped hardness profile, it is a good indication that the ageing has been carried out at too high a dose rate or temperature. The importance of understanding the potential impact of accelerated testing on material behaviour is discussed in further detail in Section 4.

3.1.5 The tensile properties of elastomers

An elastomer's tensile properties are most commonly used for quality control and monitoring of batch consistency during manufacturing. Whilst the tensile strength of a seal is not usually directly related to its sealing performance, it can be used to indicate the onset of degradation in the material as a result of ageing such as exposure to fluids, elevated temperatures or radiation. Another important tensile property for monitoring ageing in elastomers is the elongation at break, which usually decreases as ageing progresses.

There are a number of measures of tensile properties in seals that are determined by applying a tensile stress to a sample that leads to a level of deformation or strain in the material. Depending on the nature of the polymer, the material behaviour when placed under a stress, such as extension, will be different. Typical differences in material behaviour from polymers are shown in the stress-strain curves in Figure 4.

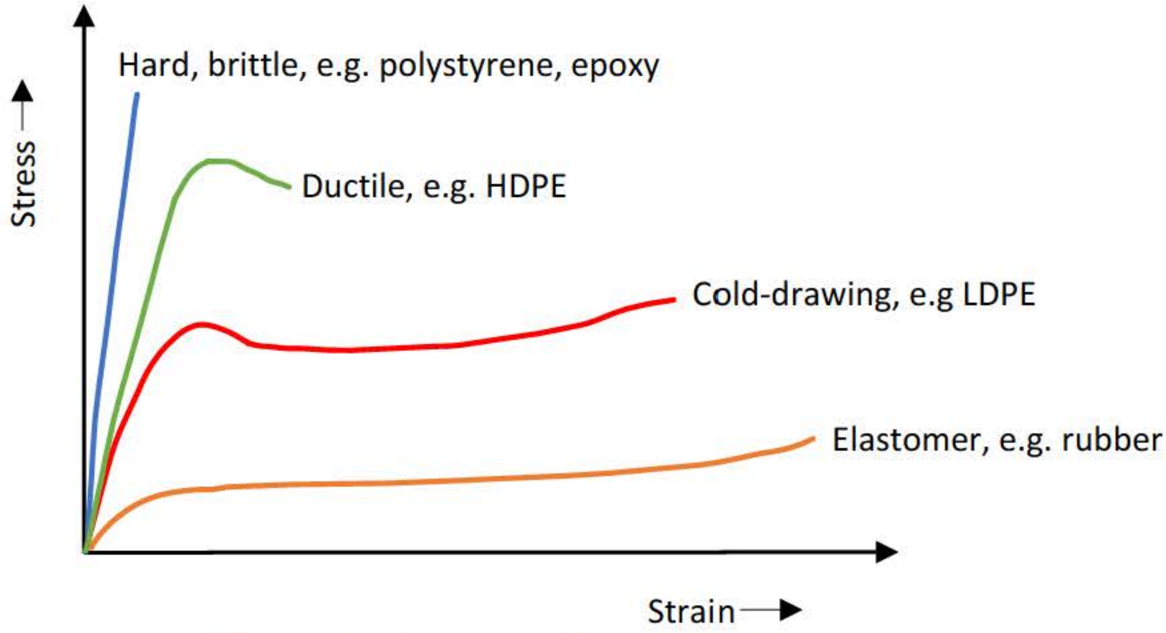

Figure 4 Typical stress-strain behaviours for different polymers.

The tensile strength of a polymeric material, measured in MPa, also termed as the ultimate tensile strength (UTS), is the maximum tensile stress that the material can withstand before it fractures or ruptures when tested under uniaxial tension, see Equation 2. Some assessments may also refer to the Tensile strength at break, where a value is recorded at the point of rupture, however, this may not be the maximum value observed during the test. In polymers, the relative increases of strain with load are large and a property known as elongation at break is preferred when assessing polymer performance. The elongation at break, or the maximum elongation before the sample ruptures is expressed at a percentage of the original sample gauge length and is defined by the expression shown in Equation 3.

$$TS_{MAX} = \frac{F_{MAX}}{A_{OCS}} \qquad \text{(Equation 2)}$$

$$E_b = \frac{L_{b-}\ L_0}{L_0} * 100 \qquad \text{(Equation 3)}$$

Where:

TS_{MAX}	Tensile Strength, MPa
F_{MAX}	Maximum force, N
A_{OCS}	Original cross-sectional area m^2
E_b	Elongation at break, %
L_0	Initial test length, mm
L_b	Test length at break, mm

Testing should be carried out in accordance with standard guidance where stress-strain properties can be assessed preferably by using either a dumbbell or ring test sample [26]. The standards allow for a choice of test sample size or 'Type', dependant on the available material. However, it should be noted that direct comparison of the results from dumbbells and rings of the same material are not always comparable and care should be taken accordingly. Similarly, when comparing the results of tensile testing from different materials or formulations, the same test sample size and geometry should be used. Experimental and material variability should be minimised by testing of multiple samples (preferably a minimum of five per condition) and calculating the means and standard deviations from the tensile test data.

Dumbbell samples are cut from sheet using appropriately sized dies and rings can be moulded. Before testing begins, the dumbbell thickness or the internal diameter and axial thickness for the ring samples should be noted. The samples can then be placed within the grips of a tensile test machine, or round pulleys for rings, and stretched at the nominal rate indicated in the standards for the specific test piece. The extension rate is also an important parameter when testing and should be consistent when comparing different samples.

It is also important to control the environmental conditions during the testing and ensure that these are closely aligned to those expected in service. The tensile properties of elastomers can vary considerably across different temperatures such that data recorded at room temperature cannot be applied to the use of the same material at higher temperatures. It has been reported that some elastomers exhibit a 90% reduction in their tensile strength at elevated temperature when compared to room temperature [6].

Typical values of tensile strength in elastomers range from 5 – 30 MPa and will vary according to the type of polymer, morphology, molecular weight distribution, cross-link density, and polymer composition (especially additives such as fillers or plasticisers). The viscoelastic properties of elastomers give rise to considerable deformation under stress and elongation at break values of several hundred percent are expected. Elongation is also an important property when designing a component to ensure that the seal can stretch as required during installation to prevent any damage that could lead to premature failure.

3.1.6 Elastomer modulus

An elastomer is essentially an incompressible material that usually deforms under a force by changing shape rather than by changing volume. At very low stresses, the ratio of the resulting strain to the stress, Young's modulus, is constant and applies whether the elastomer is in tension or compression. Within these very low stress/strain limits, the material follows Hooke's law as shown by the arrow on Figure 5. However, with increasing stress the linearity stops, and strain values become so high they become effectively redundant and measurements of elongation are preferred. As the linearity between stress and strain stops, the elastomer no longer follows Hooke's law. At this point, the relationships between stress and strain when in tension become different to those for compression.

It is this deviation from Hooke's law that results in a different way of measuring modulus for elastomers from metals, ceramics or rigid polymers. In the latter material types, Young's modulus is defined as the ratio of the stress to the strain in the elastic region. In elastomers, the modulus is often defined as the stress at a pre-determined value of elongation. For example, in Figure 5, there are two values shown, M-100 and M-300. These correspond to two different modulus values for the elastomer, stresses of ~4.5 and ~6.6 MPa for 100 and 300% percent elongations respectively. M-100 and M-300 are typically used to define and measure the values of modulus for an elastomer. These stress values are very important for the characterisation and comparison of vulcanised rubber compounds. It should be borne in mind, however, that the use of the word modulus in this case is strictly incorrect because these values are taken where Hooke's law no longer applies. However, the use of the term modulus in this case is still commonly encountered in the industry or even the norm.

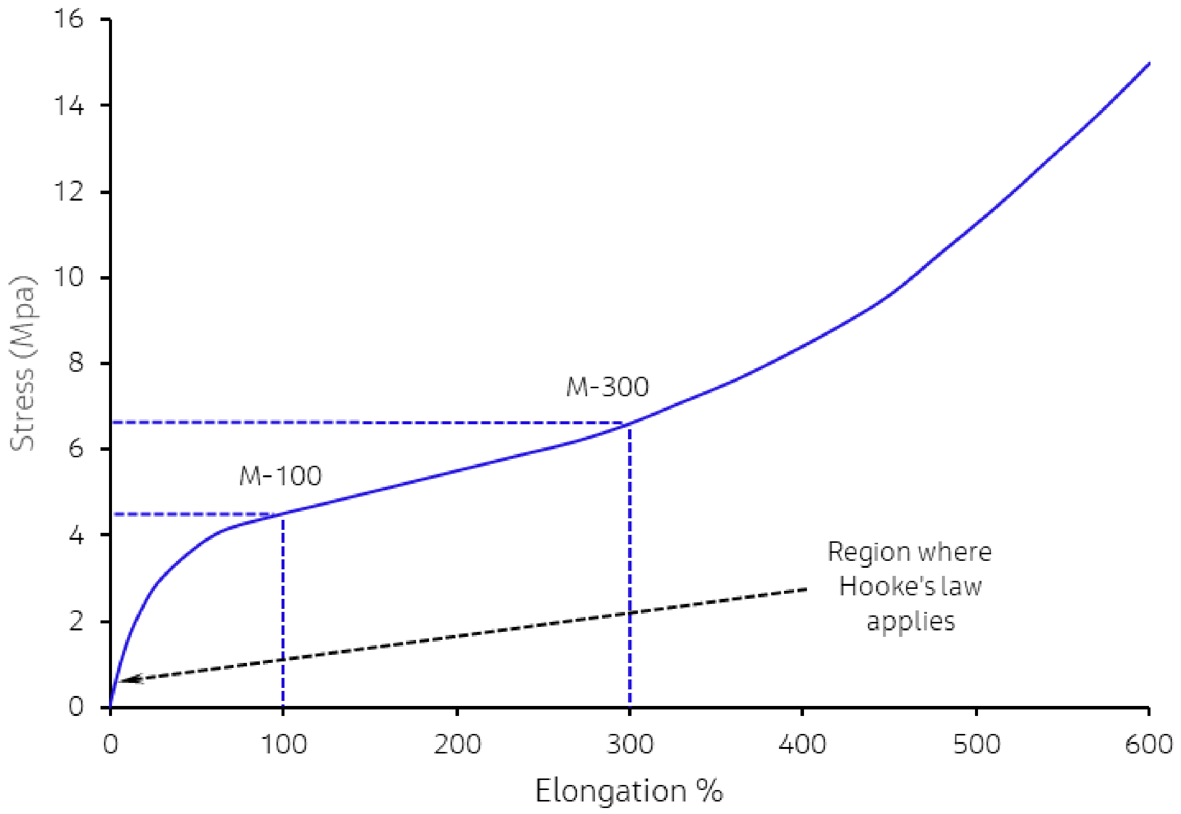

Figure 5 Stress against elongation for a typical elastomer showing how modulus values are estimated.

It is common to confuse modulus with stiffness. The modulus of a material is an intrinsic property of that material and is independent of geometry. However, stiffness is a property related to geometry and modulus and is not equivalent to the modulus alone. For example, compare a rod and an I-beam section: both are manufactured from the same material, the modulus is the same in each case but the stiffness is different for each.

3.1.7 Tear strength

The tear strength of an elastomer is simply defined as the resistance force of an elastomer to the propagation of a tear or cut and is a useful measure of an elastomer's performance as a seal material [22]. An elastomer with poor tear resistance could fail quickly and catastrophically if a defect occurred during installation or service and it was then placed under further stress. This property can be assessed using a variety of test specimen geometries, defined by Standards such as BS ISO 34-1 [27], which include trouser, angle or crescent test pieces. Multiple test pieces are cut from uniform sheet using dies before a sharp blade is used to introduce a cut or nick in the sample. The samples are then placed between the grips in a tensile test machine which separate at a defined, constant rate until the sample tears/breaks. The tear strength is expressed as kN m^{-1} and is calculated from the maximum force required to break the sample divided by the median sample thickness. In ISO 6133: 2015, however, the tear strength is defined in newtons, N [28].

Typical values of good tear strength in elastomeric materials are in the range 50-100 kN m^{-1}, and values greater than 100 kN m^{-1} are considered to be excellent. Natural rubber and polyurethane are both considered to have high tear resistance whereas values for silicones have been shown to be low. Low tear strength can also be indicative of poor abrasion resistance which may lead to early failure of an O-ring used as a dynamic seal.

3.1.8 Radiation

An inevitable consequence of using elastomeric seals and polymers in a nuclear environment is the potential for exposure to radiation. Seal materials are used in a wide range of applications that include current operational fleet, transport, waste management and decommissioning activities and as such could be exposed to different types of ionising radiation. Each of the different types of radiation will result in damage to the polymeric materials, but differences will arise according to their respective linear energy transfer (LET) or the rate at which a particular type of radiation deposits energy as a function of distance as it travels through the material.

Alpha radiation, consisting of strongly charged helium nuclei, has a high LET when compared to other forms of radiation and will therefore deposit high levels of energy over a relatively short distance. For this reason, alpha damage is limited to a depth of ~ 40 µm and is surface specific. Whilst the bulk of a specimen may not be affected by the radiation and retain much of the original strength, damage to the surface may facilitate crack propagation and lead to premature failure. That said, high LET radiation can be easily attenuated making shielding of more sensitive components and materials relatively straightforward during component design and service.

A lower LET, or more penetrating form of radiation, is emitted from beta decay. A beta particle is a high energy electron, or positron, that has been ejected from a nucleus through the conversion of either a neutron to a proton for the emission of an electron (or vice-versa for a positron) during radioactive decay. Different radioactive isotopes will emit beta particles of different energy that have varying penetration distances into the absorbing material. Each beta particle will lose energy through ionization and excitation of atomic electrons in its path. Beta decay is readily stopped by aluminium sheet, however very high energy electrons can undergo abrupt deceleration leading to the emission of secondary energetic photons such as gamma rays.

Gamma rays are very high-energy electromagnetic waves (short wavelengths) that travel at the speed of light and are the most penetrating of the three types of radiation. Absorption of the gamma radiation leads to the formation of primary species such as electrons which then further impart energy leading to the formation of secondary products such as excited molecules, positive and negative ions and energetic free radicals. The high energy of gamma rays enables them to pass through many kinds of materials and are only stopped by very dense materials such as lead. It is the more penetrating nature of gamma that proves more difficult to contain and therefore the most likely to be the cause of radiation damage in components such as seals. It should also be borne in mind, however, that alpha/beta damage may be a significant factor in seals that are in contact with fluids that contain radionuclides, for example highly concentrated process solutions in some nuclear plant.

When gamma radiation passes through a material it results in the formation of a series of excited species, however it is the subsequent production and reactions of energetic free radicals that are thought responsible for the radiochemical processes in polymers. There are two key degradation mechanisms that occur in a material during irradiation: cross-linking and chain scission. Due to the random nature of the radiation interactions both processes will occur at the same time, however depending on the nature of the polymer and the ageing environment, one mechanism would be expected to dominate and result in characteristic changes in key properties. Cross-linking is the term used to describe the formation of new bonds between adjacent polymer chains that leads to the production of a 3D network. The increase in bonds between chains leads to an increase in molecular weight and with increasing radiation dose and number of cross-links, an increasing reduction in chain mobility is observed. Conversely, chain scission is where bonds along the polymer backbone are broken to form multiple shorter polymer chain lengths of lower molecular weight. These shorter chain lengths result in an increase in overall chain mobility.

In the case of some polymeric materials, free radicals may remain trapped within the structure for some time after exposure and lead to further deterioration of properties beyond those expected for the received dose. The changes in properties that sometimes arise at extended times after irradiation are known as post-irradiation effects. Accordingly, assessment of any radiation degradation in specimens should be carried out promptly after exposure and the length of time between irradiation and property assessment should be minimised and recorded.

Polymeric materials show a diverse resistance to radiation and as such the selection of a suitable seal material will have to balance all the mechanical, physical and chemical demands of the service requirements. For example, PTFE has many desirable properties such as chemical inertness, low friction and thermal tolerance, yet it demonstrates one of the poorest levels of radiation tolerance. As noted in Section 2.4, the material composition and selection of additives and stabilizer can have a profound impact on radiation tolerance, even within the same family of materials. There are many formulations of EPDM seals available, however only a few have been developed and compounded to provide excellent radiation tolerance. Whilst details of the material compositions often remain propriety, it is important that exactly the same material is procured for replacement to maintain confidence in the original equipment qualification and justification for use in harsh environments. However, with increasingly longer plant/operation lifetimes there are occasions where a particular formulation may become obsolescent and a suitable replacement sought. Ideally the ageing of a potential candidate material should be compared directly with the older composition, but where that is not possible, a full materials qualification assessment that is representative of service conditions should be undertaken.

There are a number of compilations of radiation damage test data available in the open literature that aim to provide guidance on the radiation tolerance of a wide range of polymeric materials [29]. The data is based on radiation tests of commercially available materials and provides a very useful overview of the different groups of materials and their relative radiation tolerance. However, the total dose ranges quoted in these compilations, and other available literature, should be treated with caution such that selection of a material for use in a radiation environment should be accompanied by robust justification for its use in the particular application. Care should be taken for a number of reasons; the influence of polymer formulation has already been discussed but other factors such as radiation environment, radiation dose rate and acceleration factors play a critical role in the nature of the degradation mechanisms and subsequent assessment of radiation tolerance (see Section 4 for further details).

The radiolysis of organic polymers also leads to the generation of gaseous species. The quantity and nature of the gases evolved is dependent on the chemical composition of the polymer and the ageing environment but typically includes low molecular weight species such as hydrogen and small hydrocarbons together with oxygen bearing species such as CO_2 and CO when irradiated in air. Some polymers contain halogens such as chlorine (e.g., Neoprene) or fluorine (e.g., fluoroelastomers) which can release aggressive corrosive gases HCl and HF that readily combine with moisture to form acidic species. Production of these acidic gases may present difficulty in their safe handling. ability to attack nearby metallic or electronic components and their effects on aqueous chemistry in some nuclear applications. Furthermore, the production of these gases can also affect the condition and properties of some inorganic fillers in certain halogenated polymer compounds.

3.1.9 Ozone and UV Photodegradation

Ozone is a highly oxidizing and reactive species that readily attacks unsaturation in polymeric structures, an unsaturated organic molecule is one which contains carbon-carbon double or triple bonds [13]. Ozone-rich environments can be generated by discharge close to high-voltage electrical equipment or by the radiolysis of air, however only trace amounts are required to initiate damage in seals and polymers. Ozonolysis, or the oxidative scission of the polymer backbone caused by ozone, can lead to cracks that grow in the areas of a seal with a high stress concentration (stress-cracking). Ozone cracking may also form on the surfaces of seals during long-term storage. Initially, the cracks form on the outer surface, but over time the cracks will propagate through the seal thickness and lead to failure. Accordingly, ozone damage would be of more concern in thinner seals or elastomeric components.

Elastomers such as natural rubber and nitriles that contain unsaturation, are most susceptible to ozone induced stress-cracking. Elastomers with limited unsaturation or those containing polar atoms such as chloride are less susceptible, whilst silicones and fluoroelastomers are intrinsically ozone-resistant. Further protection can be provided by the addition of anti-ozonants that preferentially react with the ozone and reduce the rate of attack on the elastomer. However, over time, these ozone scavengers will become completely consumed and will then no longer offer any resistance. Alternatively, susceptible seals can be replaced during regular maintenance outages throughout the operational life of the plant/component.

Photodegradation by ultraviolet (UV) radiation occurs when UV photons of sufficient energy are absorbed at the surface layers of the polymer and free radicals are formed, consequently UV damage is a generally limited to polymer surfaces. Photodegradation in the presence of oxygen, or photo-oxidation, results in oxidative chain scission along the polymer backbone and subsequent reductions in molecular weight and elastic behaviour. Free radical generation by UV can also lead to the onset of other types of structural change at surfaces such as cross-linking especially if the atmosphere is depleted of oxygen. However, this will be dependent on the nature of the material. Although UV degradation occurs via free radical mechanisms akin to those that occur during gamma irradiation, it is suggested to be unwise to infer that surface damage caused by UV in a polymer will be a good indicator of the damage it will sustain under equivalent levels of highly penetrating gamma radiation.

In common with ozone attack, some polymer/elastomer formulations are more susceptible to UV degradation than others, although there is a plethora of stabilizers and scavengers available that can provide a good level of UV protection. However, photodegradation can still occur in materials with nominally good UV resistance because impurities or unreacted processing compounds may act as initiators for free radical formation.

Photodegradation is often visible at the material surface by the formation of cracks, crazing and discolouration. A process called chalking or the appearance of a fine powdery residue can also occur after degradation of the surface organic layers exposes fillers and pigments. The degradation effects of UV in polymers and elastomers can be of significant concern during long-term storage where exposure to both direct or indirect sunlight can occur.

3.1.10 Elevated Temperatures

Elastomeric seals may be expected to experience a wide range of temperatures during service in nuclear environments. Materials will need to be selected according to the anticipated range of operating temperatures and specialist grades may be required in particular applications. At elevated temperatures, elastomers will experience changes which are dependent on the length of time and the temperature to which they have been exposed. Short term exposures to elevated temperatures are likely to introduce immediate changes in physical properties, such as softening, which are reversible if the elastomer is returned to ambient conditions. Softening of the material will have an impact on many properties, whether that is to indirectly accelerate rates of ageing through increased oxygen diffusion rates or cause the seal to extrude through sealing gaps or other orifices under high pressure.

Over longer-term exposures, further chemical changes brought about by thermal degradation mechanisms will result in permanent deformation (assuming that the seal is under stress during operation). It is important at this point to distinguish between thermal degradation and thermal decomposition. Thermal degradation is caused by thermally activated free radicals which lead to changes in molecular structure such as cross-linking and chain scission, which in turn affect elastomer properties. Thermal decomposition is a process that occurs at very high temperatures and involves the dissociation and destruction of the molecules of the elastomer. These two processes are often confused with each other.

An additional factor for consideration in elastomers that are used at elevated temperatures for extended periods of time is additive migration. This applies in particular to softening agents (plasticisers). As temperatures increase, plasticisers in an elastomer may diffuse to surface and evaporate. This effect is characterised by the development of a shiny film on surfaces, a process called bleeding. Plasticiser loss can have a significant effect on elastomers such as volume shrinkage and hardening.

3.1.11 Thermal Expansion

When elastomers undergo thermal expansion, changes in length, area, and volume are all likely to be encountered. The magnitude of these changes is captured by a material specific parameter called the thermal expansion coefficient. Elastomers have significantly higher coefficients of thermal expansion than metals – a rule of thumb is that elastomers have a thermal expansion coefficient which is about ten times than that of a metal. Some fluorelastomers have expansion coefficients which are even higher than this rule suggests. Some expansion in an elastomeric seal may improve sealing performance in low pressure applications.

However, component design is important; consider a simple rotating shaft on a pump which is sealed by an elastomeric O-ring in a metallic gland assembly. If the O-ring fits tightly into the gland any increases in temperature will increase the size of the O-ring relative to the gland enclosure and potentially develop large forces in the gland. Essentially the system has no capacity to accept the increased O-ring size. In extreme cases, expansion mismatch has resulted in rupture of the gland itself. Clearly design considerations should allow for this eventuality and gland fill should not exceed 95%. Any elastomeric sealing configuration that is designed to withstand high temperatures should demonstrate the ability to allow for thermal expansion mismatch between the seal and its housing as appropriate.

3.1.12 The Gough-Joule Effect

The Gough-Joule effect is a unique property of elastomeric materials which can sometimes be overlooked by component designers - but could lead to premature failure of a seal. When most materials are heated, they expand according to their coefficient of thermal expansion, and this is also applicable to an elastomer. However, when an elastomer is stretched and held at a fixed extension and then heated, it will try to revert back to its original high entropy state by contracting, thus increasing the tension already existing in the material. This unusual behaviour is called the Gough-Joule effect [30].

From a practical perspective this is of significance where an O-ring is used to seal a rotary shaft. Whilst it might initially be considered advantageous to create a good seal by using a tight-fitting O-ring around the shaft, these seals can often fail prematurely. The rotation of the shaft in operation can cause frictional heating and the tight-fitting seal will tighten further around the shaft. Typically, the seal will abrade, crack and then fail as a consequence or even lead to shaft seizure. The Gough-Joule effect can be overcome by using an O-ring that has an internal diameter ~1-5% larger than the shaft diameter and a seal housing designed to use peripheral compression, rather than tension, to hold the seal in place. Finally, the Gough-Joule effect can sometimes be observed in high temperature, static seal applications where the seal is stretched during installation and operation. Again, failure can be minimized by careful consideration of the service conditions together with appropriate component design to ensure elastomeric seals used at elevated temperatures are not under strain.

3.1.13 **Chemical Resistance**

The ability of an elastomer to withstand chemical attack and degradation is an important consideration when designing a component where contact with aqueous environments (acid, alkali), oils, greases, lubricants and other process chemicals is expected to occur [1]. Elastomers can be susceptible to chemical attack, however the severity of any changes in properties and the ability to maintain the seal will be dependent on the chemistry of both the elastomer and the attacking species, temperature, seal geometry and the nature of any inherent stress or strain. There are three key changes to the physical properties of an elastomer as a result of chemical attack: swelling, shrinkage and degradation of the polymer structure [22].

In most cases an elastomer will absorb a contacting fluid, sometimes increasing its volume by several times. This 'swelling' will occur over time by diffusion along a concentration gradient into the free volume that exists in an elastomer. The fluid's occupation of the free volume reduces the already weak inter molecular forces leading to softening of the elastomer. In many cases the chemical interactions between the elastomer and fluid are limited and changes in properties are simply due to the fluid's physical presence and swelling. Where more aggressive species are present, irreversible chemical interaction may occur between the absorbed fluid and the polymer backbone. In some cases, the fluid can interact with elastomer compounding ingredients such as fillers and affect mechanical properties.

Depending on the application, a limited amount of swelling could be advantageous and improve sealing properties, however the degree of acceptable volume change will vary according to the specific application and operational conditions. In the case of static seals, a greater amount of swell can usually be accommodated than in dynamic applications, however properties such as resistance to extrusion will be expected to change. Premature failure due to swelling in dynamic operations are usually caused by an increased friction and wear rate. Typical changes expected during visual inspection of a seal subjected to chemical attack would include surface effects such as cracking, blistering or discolouration.

Conversely, the contacting fluid could result in leaching or extraction of additives which are soluble in the fluid, often plasticisers. Whilst loss of additives such as plasticisers may be compensated for by the absorption of the attacking medium, a seal may still undergo a degree of shrinkage which could then lead to failure through a reduction in compression and the generation of a leak pathway.

In general, the degree of interaction between an elastomer and contacting fluid can be assessed by reviewing their respective solubility parameters, as discussed for lubricants Section 2.3.4.5. If the fluid has a similar solubility parameter to that of the elastomer, it will be easily absorbed leading to a high degree of swelling. However, the greater the difference in solubility parameters, the lower the level of swelling. For example, most polar polymers will readily dissolve in polar solvents but have limited solubility in non-polar solvents (and vice versa). The rate of fluid uptake will also be dependent on the rate of diffusion; however, the diffusion coefficient will increase with increasing temperature and by extension an increase in the chemical rates of reaction would be expected at higher temperatures if the fluid is chemically aggressive. Accordingly, an assessment of a seal's chemical compatibility at room temperature may not be appropriate if it is to be used at higher operating temperatures.

Elastomer compositions can be tailored to minimise swelling, such as increasing cross-link density so that the corresponding constraints on chain mobility reduce swelling. Elastomers with high glass transition temperatures tend to have low free volumes and therefore low fluid uptakes compared to those with low transition temperatures. Another approach may include the use of high filler loadings to present a more tortuous diffusion path to the penetrating fluid. Adjustment of elastomer compositions will have an impact on physical properties such as hardness and tensile strength and may not be an appropriate measure for certain applications.

When selecting a seal to be used in an application where there is a likelihood of contact with any fluids where compatibility is uncertain, or where more severe operating conditions have been identified for an existing seal, it is important to ensure that the seal material can demonstrate chemical resistance. The literature has an abundance of chemical compatibility tables for the most common elastomeric material groups. However, in a similar approach to radiation tolerance charts, care should be taken as there are many different grades and compositions within each material group. Whilst the compatibility tables help to identify suitable material groups, further guidance should be sought for specific formulations from seal manufacturers or qualification assessments under service conditions undertaken.

3.1.14 **Water and moisture**

Most elastomeric seals would be expected to perform very well whilst in contact with water due to the perception that they are a neutral, benign substance. However, contrary to initial perceptions, many elastomers that are held in contact with water over long periods of time will swell, some significantly. Water will permeate into polymers at rates determined by the relative solubility characteristics (discussed above in Section 3.1.13) and diffusion rates. As a result, the polymer structure will swell to accommodate the water that is present.

In static seal applications swelling associated with water absorption is not likely to be a significant concern because a certain degree of swelling will prevent leaks. If the seal assembly is dismantled, the swollen seal can be changed out, noting that difficulty will be experienced if attempting to re-fit, so an equivalent replacement would be required. If the seal is used in a dynamic application however, the swelling of the seal will slowly increase friction between surfaces and eventually cause premature wear and even failure, Section 3.2.8.

Some elastomers can be attacked chemically by water (hydrolysis) and materials such as polyester based polyurethane elastomers can be rapidly attacked by water over relatively short periods of time. Hydrolysis in elastomers can be accelerated by changes in pH and increases in temperature. In the nuclear industry it has been shown that if radiation is present, hydrolysis reactions can be strongly accelerated. Polyurethane seals can rapidly decompose if they are irradiated in the presence of water.

As operating temperatures increase, the stability of some elastomers to moisture tends to decrease. If very hot water or even steam may be encountered during operations, the choice of suitable elastomers begins to narrow appreciably. The Parker O-ring handbook provides a comprehensive assessment of the compatibility and suitability of a wide range of elastomeric seal material for use in water/high moisture environments [1].

Clearly, although water is generally considered to be a benign substance, it can significantly undermine the performance of elastomeric seal materials and in the nuclear industry, synergistic effects between moisture and radiation can lead to premature failure of some elastomers.

3.1.15 Permeation

The gas permeability of an elastomer is defined as the rate at which a gas permeates through the elastomer from a high pressure to a low pressure when equilibrium has been reached. It is represented by the symbol P and is also defined as the product of the solubility of the gas, S, and the diffusion rate, D, i.e., P=DS. This is an important physical property when considering gas containment because a seal with a high gas permeability might not effect a seal that is considered adequate in some applications [14].

The amount of gas permeation that can occur through a seal varies considerably and is dependent on factors such as the elastomer formulation, the size of the gas molecules, the solubility of the gas in the particular elastomer formulation and the geometry of the elastomer seal (especially its thickness). Permeation can be minimised when using lubricants and by the use of harder elastomers formed into smaller cross-sections, accompanied by higher levels of compression or squeeze during operation. Gas permeability is a thermally activated process and will rise with increasing temperature as changes to the structure of the elastomer occur, for instance an increase in free volume coupled with increased vibrational frequency of the gas penetrant.

3.1.16 Pressure

When an O-ring is placed in a groove and clamped into position by a sealing surface it is compressed to provide the required sealing force [1,22]. In most sealing systems, a reasonable level of pressure in the contained fluid is expected to enhance the sealing efficacy as the seal is pressed more firmly against the mating surfaces. However, at higher pressures, or over longer ageing/service times, a small area of the seal may begin to extrude or flow into the narrow clearance gap between the mating surfaces. A low level of deformation or extrusion may not affect sealing properties initially, however with continued seal deformation a leak path will develop as seen in Figure 6.

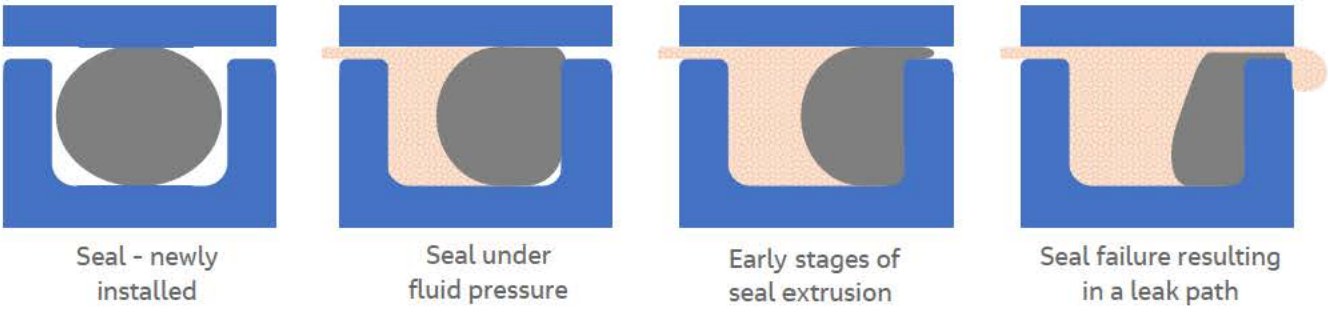

Figure 6 Schematic showing extrusion of a seal through a clearance gap.

In some dynamic sealing applications where there are cyclic fluctuations in pressure, gland parts may expand under higher pressure and then contract and as a direct result, the size of the clearance gap will also vary. In cases where an O-ring has begun to extrude into the clearance gap, the repeated trapping of the seal between sharp mating surfaces can lead to physical damage to the surface of the seal sometimes referred to as 'nibbling' which can hasten seal failure.

In higher pressure applications a seal material with a higher degree of hardness will be better able to resist extrusion under dynamic loads or where there are larger clearance gaps. Any additional environmental effects that lead to softening of the seal during operation, for example chemical swelling or elevated temperatures, must be taken in account during system design.

Additional attention may be given to the groove design and size of the clearance gaps in an effort to reduce the likelihood of extrusion occurring, although anti-extrusion or back-up rings can also be used alongside the elastomer. These back-up rings are commonly used in high pressure systems and are made from hard, rigid plastics such as PTFE, Nylon or metal [22]. The rings are positioned between the elastomeric seal and clearance gap providing a physical barrier that prevents extrusion. If the use of back-up rings is considered any thermal, chemical or radiation tolerances together with compatibility of the material, and any potential degradation products, with the seal material should also be investigated.

However, in low pressure systems a softer seal material is preferred. As there is insufficient pressure to create additional sealing force as described above, a softer seal material will more readily flow into the microfine grooves and imperfections as it is squeezed and pressed against the mating surfaces.

3.1.17 Rapid Gas or Explosive decompression

During some applications seals are subjected to high working pressures. Given the permeability of elastomers, some gas from the surrounding high-pressure environment will permeate into the seal over time and reach equilibrium. It therefore follows that the amount of gas dissolved in the seal will be greater in the higher-pressure environments. When the external pressure is reduced, the high-pressure gas will then attempt to permeate back out of the seal.

If the pressure release is rapid, the gas trapped in the outer surfaces of the seal will escape rapidly. However, the gas trapped in the interior can only escape at the rate defined by the seal’s permeability. The gas thus trapped inside the seal structure expands rapidly to equal the low pressures in the surfaces and local environment. This, in turn, leads to high internal stresses which may exceed the strength of the elastomer. After multiple decompression cycles, cracks and tears may develop. Depending on the amount of gas trapped, damage in the elastomer leads to surface blistering, internal fissions such as cracking or splitting. In the most severe cases the seal can fully rupture or undergo explosive decomposition.

The severity of the damage from rapid decompression will be dependent on a number of factors including the initial pressure (>35 bar for 90 IRHD), the rate of pressure decrease, the nature of the trapped gas, the particular elastomer material and its permeability as well as O-ring and seal housing geometry. It has been shown that high strength elastomers are the most resistant to rapid decompression, however strength can be affected by other operational parameters such as elevated or low temperature and swell from chemical attack. Therefore, if a seal is to be exposed to significant pressure differentials during service, material selection should be made in light of careful consideration of component design, working environment, physical and chemical parameters. Alternatively, some duty holders may choose to change out high pressure seals at defined service intervals as part of a maintenance plan.

3.1.18 Environmental Synergies

Whilst this section has focused on how potentially hostile environments may affect elastomer properties, equipment designers should recognise that a seal will most probably be exposed to a number of these environments at the same time. There may appear to be many similarities in the generic seal degradation mechanisms in different environments which may lead to similar changes in properties. However, the extraordinary complexity of the chemical and structural changes that occur in elastomers and polymeric materials, particularly where combined environments are encountered, cannot be overstated. Some degradation mechanisms are still not yet fully understood, but synergistic effects have been observed where the combined effects of two stressors are greater than the sum of each individually. Section 4 further explores the synergies between radiation and temperature; however, any materials assessment or justification should carefully consider the potential impact of environmental synergies on the degree of changes in properties and operational lifetime.

3.2 Changes in the properties of elastomers brought about by long term ageing/use

As described in Section 3.1, prolonged exposure of polymers to hostile environments will cause changes to their molecular structures and therefore their properties. In an elastomer for example, the viscoelastic properties are controlled by its special molecular structure. This consists of long polymer chains which are free to move relative to each other. The degree to which they can move however, is controlled to an extent by cross-links that pin the chains. The greater the number of cross-links, the more rigid the structure will become.

Most elastomers are relatively soft and elastic and the number of cross-links is usually low. Other organic polymers also rely on the interaction and movement of their molecular chains for their desirable properties and these can depend on chain length and chain structure. For example, a polymer such as polyethylene has a simple structure of chains of carbon atoms bonded to each other with two hydrogen atoms on each carbon. This means that there is little in the way of strong interactions to stop the chains moving relative to each other and the chains will align readily to form ordered region known as crystallites. Therefore, polyethylene normally exists as a mixture of ordered and amorphous regions and is described as a semi-crystalline thermoplastic.

In polymers with more complicated structures such as polystyrene which has benzene rings forming part of its structure, chain alignment is far more difficult and crystallinity formation is minimised. Polystyrene is thus a rigid, amorphous thermoplastic. Where polymers have large atoms in their structure such as the highly electronegative chlorine atoms in PVC, molecular movement is restricted by electronic attraction and in its un-modified form PVC is also an amorphous thermoplastic.

Clearly, the nature and properties of all organic polymers are initially dependent on their molecular structures. Any permanent changes in structure that arise from exposure to hostile environments will result in a corresponding change in properties. Furthermore, commercial polymer formulations contain a selection of additives which help improve functionality and stability, as described in Section 2.3. Any loss of additives from the polymer or changes to their chemical properties will also result in a change of the overall properties of the material.

With increased exposure time to heat and radiation, free radicals will be produced in polymers which cause chemical changes to their structure. The dominant effects are cross-linking and chain scission as described in Sections 3.1.4. and 3.1.8. These changes in molecular structure will affect the generic properties of each type of polymer with ensuing changes in their sealing characteristics.

3.2.1 Compression Set

The development of compression set is one of the most important properties to understand in terms of seal ageing and the expected progression of compression set with time is illustrated in Figure 3, Section 3.1.3.3. When an elastomer is compressed, it will creep and tend to conform to its compressed shape over time. Environmental factors will also play an important role. The long-term ageing of a compressed elastomer by the action of heat, radiation or otherwise, will result in the structural changes described above and will affect its viscoelastic properties. If the dominant mechanism is cross-linking, the elastomer molecules will be pinned by the additional cross-links in the compressed position and when released from the compressive force will show an enhanced set. On the other hand, if chain scission were to dominate, the compression set will also be expected to increase but in this case the elastomer chains will be broken in between cross-links and their ability to spring back is impaired. As ageing progresses, the structural changes increase and eventually the elastomer will not be able to recover and show 100% compression set.

The loss of additives such as plasticisers from elastomeric seals can also affect compression set because when they migrate from the seals, usually under the action of heat, they will leave behind a more rigid structure which will also cause the elastomer to shrink, both of which will cause an increase in compression set. Coupled with the structural changes expected during ageing, it is likely that plasticiser loss will enhance any compression set that arises from thermal or other forms of ageing.

3.2.2 Modulus and Hardness

Although these two properties are different, they are affected by changes in polymer structure in a similar manner. Increased cross-linking will increase hardness and modulus, whilst chain scission will reduce hardness and modulus. Plasticiser loss will also result in an increase in modulus and hardness. These changes are expected to happen steadily with long-term ageing.

3.2.3 Elongation at break

Except in rare cases where some polymers can show an enhanced value of elongation at break as a result of chain scission, all long-term ageing will be expected to result in a steady decline in elongation at break. However, some materials, for example polyethylene-based polymers can show a “cliff-edge” effect where the decline in elongation at break is slow in the initial stages of ageing, but after a particular time period, it can decrease very rapidly. Cliff-edge effects are of concern because there is usually little warning that a rapid decline of properties could be imminent.

3.2.4 Tensile Strength

Chain scission will cause a reduction in tensile strength which is expected to decrease steadily with ageing. Cross-linking and plasticiser loss will usually produce an initial increase in tensile strength although elongation at break may be reduced. However, with increasing cross-link density, the tendency towards brittle failure increases. Brittle failure or fracture is defined as the sudden fracture of a material due to rapid crack propagation with little or no evidence of ductility or plastic deformation ahead of the crack, as would be seen in a glass material.

3.2.5 Environmental Stress Cracking (ESC)

The tendency towards a brittle type failure can be enhanced by synergy between stress and the environment in which the polymer is in service. Environmental stress cracking (ESC) is an important cause of embrittlement and unexpected failure in polymers. In the presence of active fluids such as solvents, vapours and even detergent solutions, a stressed polymer can fail prematurely even though it would not fail in the absence of these fluids. Furthermore, the polymer may not be affected if it was held in the fluid in an unstressed state, however frozen in stresses from moulding or other production techniques may be sufficient to initiate ESC.

The active medium in the ESC process usually interacts with the stressed material at stress concentrations present as defects. Over time, the polymer weakens at the defect, a crack initiates and can quickly propagate and cause failure. The most common observations of ESC are with mainly amorphous polymers in contact with organic solvents, although the classically reported instance of ESC is that of low-density polyethylene in detergent solution.

In establishing a suitably long service lifetime, an assessment should be carried out to analyse whether the seal material can come into contact with potential ESC activating fluids during service. If so, appropriate seal material choices will be required. For example, one such ESC active fluid is tri-n-butyl phosphate, commonly encountered in nuclear reprocessing plant.

3.2.6 Tear strength

The tear resistance of a polymer is expected to decrease with increased ageing and essentially track the tensile strength with exposure time. However, under certain circumstances tear resistance can be dependent on sample geometry and correlation between test data and component geometry is recommended.

3.2.7 Gas permeability

As described in Section 3.1.14, the molecular structure and amount of free volume in a polymer are two of the factors that control gas transport through polymers. Increases in cross-link density will lead to more tortuous paths for gases to follow and reduce permeability rates whilst reductions in molecular weight associated with chain scission are expected to increase free volume and increase permeability. Such an increase could be of importance for seals that immobilise radioactive gases. It is suggested that in such a case, any potential changes in the gas permeabilities of aged seals should be considered as part of long-term storage plans, especially where seal replacement is not a viable option.

3.2.8 Dynamic applications

When used in dynamic applications, seals can be subject to rotary motion, oscillation (vibration) and reciprocating motion. In each of these cases, the nature of the motion is likely to result in wear at contact surfaces. If steps are not taken to reduce wear, damage to the seal is likely to be inevitable. The damage can manifest itself as flattening of the seal contact surface, scratches or deeper wear lines on the seal in the direction of motion and uneven wear. If the wear process carries on un-checked, loose seal particles may be produced, wear lines may enlarge, lacerations and tears can develop on the seal surface. Clearly the production of particulates can also accelerate wear and also result in contamination of equipment.

Some of the causes of excessive wear have already been explored in this document, for example the Joule Gough effect, Section 3.1.2. However, poor surface finish on seal and mating surfaces, overheating, poor cleanliness and poor lubrication are all factors that can contribute to excessive wear.

Some steps to prevent and/or mitigate excessive seal wear include:

- Good seal materials choice, for example hard seal formulations tend to have better wear resistance;
- Good practise with parameters such as gland design, dimensional accuracy and surface finish;
- Good housekeeping – eliminate the potential for particulate contamination;
- The use of appropriate and compatible lubricants, Section 2.3.4.5;
- If possible and appropriate, consider the use of internally lubricated seals.

3.2.9 Stiction or Slip-stick

In some sealing applications, problems associated with stiction and slip-stick can arise. It is not unusual to find that some information sources will describe stiction as slip-stick and vice versa. However, they are two quite distinct terms which describe different ways in which surfaces can interact. In a tribological review, stiction is defined as any tendency for static friction to increase with the period of dwell between movements [31]. With reference to elastomeric seals, stiction is suggested to occur as a result of viscous creep of the elastomer onto the sealing surface. The elastomer takes on the contours of the sealing surface and forms, what is in some cases, a strong adhesive bond. Stiction can result in sealing faces bonding together making it very difficult to remove them if required during maintenance or decommissioning. Practises such as over pressurisation to help separate flanges for example, can lead to sudden movement of the flanges as the frictional forces are overcome. This movement can be uncontrolled in what could be a very heavy flange and the practise should be avoided in favour of other methods of separation.

Stick-slip, however, is a movement mode dependent on the difference between static and dynamic friction coefficients where relative movement between two surfaces 'stutters' repeatedly producing short movements followed by static dwells. A good example of stick-slip is getting a wine glass to 'sing' by slowly moving a finger on the glass rim. Another example of stick-slip is the production of a note when a violin bow is drawn across a string. If stick-slip occurs in dynamic seals applications, accelerated wear can ensue reducing seal lifetime.

Instances of stiction followed by slip-stick can be observed in applications such as piston seals where a long period of inactivity might result in lubricant loss between the elastomeric seal and the gland resulting in adhesion – stiction, followed by an irregular stop-start movement – slip stick. This can result in severe damage to the seal and, in extreme cases, to the metal components. The tendency for systems to develop stiction or slip stick will depend very much on the design and materials selection. Some considerations that can be implemented into designs to help reduce the problem are:

- Ensure compatibility between the hardness, elasticity, friction and chemical properties of the sealing surfaces;
- The surfaces of shafts and cylinders should be neither too smooth nor too rough;
- Where appropriate, make the correct choice of lubricants;
- In a similar manner to compensation for the Gough-Joule effect, keep the contact pressure between seal and the shaft/gland to a minimum;
- Design to allow dissipation of any heat generated by friction.

3.2.10 **Long-term thermal effects**

The development of compression set is certainly one of the most important properties to understand in terms of seal ageing and the expected progression of compression set with time is illustrated in Figure 3, Section 3.1.3.3. When an elastomer is compressed, it will creep and tend to conform to its compressed shape over time. But environmental factors will also play an important role. Ageing of the elastomer whilst compressed by the action of heat, radiation or otherwise, will affect its molecular structure and thus its viscoelastic properties. If the molecular arrangement in a seal such as an O-ring is altered by chain scission or cross-linking, the ability of the O-ring to spring back and seal will be affected. With increased ageing time the changes in molecular structure become more profound and compression set will increase. However, compression set is not the only property to be affected in this respect, ageing will affect most elastomer properties such as tensile strength, tear strength wear resistance, hardness and modulus for example. Each of these properties can have an effect on the structural integrity of a seal and they will slowly degrade with ageing time. It is therefore important for the design engineer to be able to understand and predict, where possible, how seal properties will evolve during service.

Although the nuclear industry is likely to involve a wide range of environmental conditions, the long-term effects of prolonged exposure to heat and radiation are likely to be the most important. Therein lies the potential for confusion from the supply chain in terms of the long-term thermal performance of elastomers and thermoplastics. A number of terms are used to describe thermal performance, these include: Relative Temperature Index (RTI), Thermal Classification, Thermal Index (TI) and Continuous Operating Temperature amongst others. It is important that when a design engineer receives material property data from a supplier, an acceptable level of assurance of reliability is provided. Whilst it is incumbent on the supplier or manufacturer to provide the necessary data, the designer should be aware of the meaning of the data and their relevance to the application.

In some cases, this may present difficulties because some of the generic information that is available may have no real technical meaning i.e., a property that has been established by a standard or other industry definition. For example, a continuous operating temperature provided by a supplier, whilst potentially useful for material comparisons has little value unless the information as to how the temperature has been arrived at is available. Furthermore, data sheets may apply to a generic class of material rather than a specific formulation and can be easily mis-interpreted if the appropriate attention is not paid to the source and meaning of the data provided.

3.2.11 Thermal Endurance

This is an index that allows comparisons to be made of the temperature capability of polymers based on specific, controlled test conditions. The time taken for a specific property of a polymer to fall below 50% of its original condition is described as the thermal life. The value of 50% is open to some interpretation when applied to the compression set of elastomers, for example, because a failure condition set at 50% compression set may be considered as over-conservative, Section 3.1.3.2.

3.2.12 Relative Temperature Index, (RTI)

The RTI (previously known as the continuous use temperature rating CUTR) is the temperature above which a polymer will degrade prematurely. One way of using this property for the assessment of a replacement part for example, is to compare the thermal ageing performance of the new material against that of the already established proven, material under identical conditions. RTI may also be assessed against the known performance of the generic class of the material from which it is manufactured. This approach should not be favoured because of the critical dependence of polymer composition on its stability at elevated temperatures. The influence of polymer composition is discussed in some detail in Section 2.4.

3.2.13 Temperature Index (TI)

This is a value of temperature which allows the comparison of the time/temperature characteristics of polymers. The temperature is usually arrived at by using the Arrhenius relationship to extrapolate a plot of component life against temperature to a particular time, usually 20,000 hours. An IEC standard, IEC 600835 allows for the grouping of certain insulation materials in terms of their thermal indices [32]. Although this standard is aimed at electrical insulating materials, the logic can be used for other polymeric components. The Arrhenius relationship for the estimation of component lifetime can be very useful but great care is needed in terms of the understanding of the chemical principles, activation energy use and acceleration factors during ageing. The use of Arrhenius relationship for component qualification purposes is discussed in detail in Section 4 of this document.

3.2.14 Temperature rating

This is the temperature below which a critical property of a polymer will not be unacceptably compromised through thermal ageing over its lifetime.

The material stability information supplied to end users by elastomeric seal manufacturers is usually based on a series of charts or tables with an indication of thermal or chemical stability by series of letters. For example, the chemical compatibility of an elastomer to a certain substance might be listed as E = excellent, G = good, F = fair, U = unsuitable and P = poor. Other descriptors may be used depending on the origin of the data. For long term thermal suitability, many suppliers will provide a horizontal bar chart, such as the chart shown in Figure 7. This shows the maximum and minimum operating temperatures of a range of different elastomers. These types of chart are also available to provide similar data for different thermoplastic polymers. The first thing that the reader should be aware of in Figure 7 is that the chart presents the thermal properties of generic elastomer classes, not individual compositions. The use of generic classes means that there will be a range of thermal properties within each class depending on elastomer composition. Furthermore, the data in such a chart should only be used as a high-level guide in the initial stages of material selection. The chart cannot be used to define the service lifetime of a component.

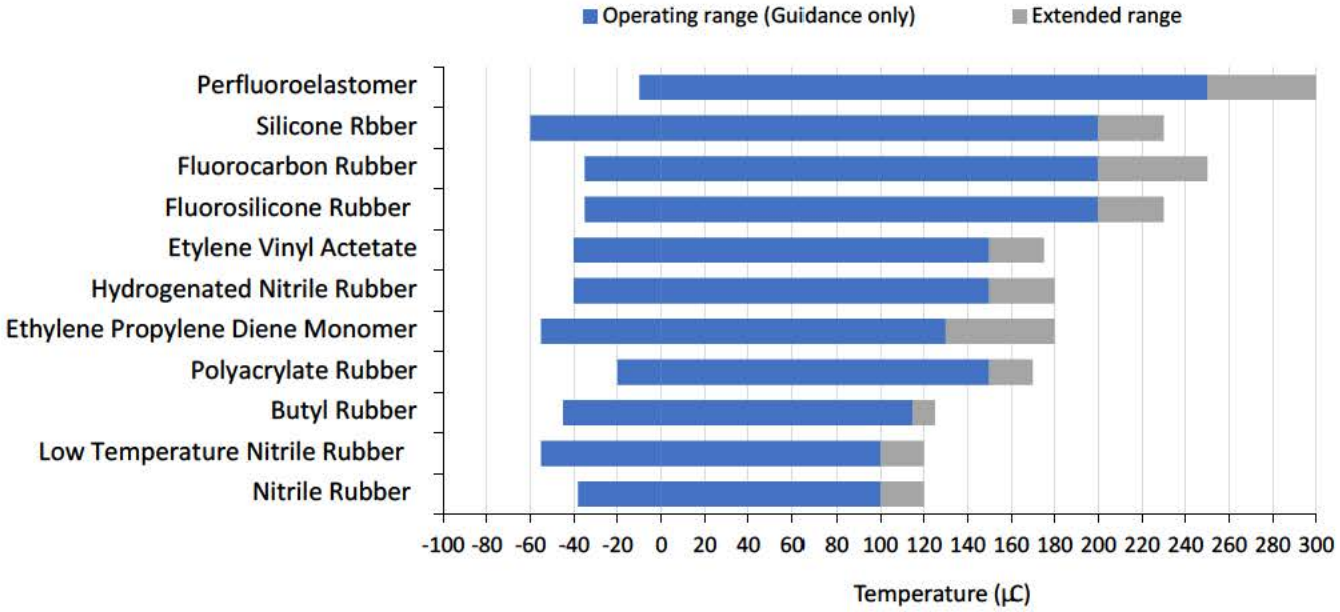

Figure 7 Bar-chart indicating the operating temperature ranges of a number of elastomers.

Figure 7 also shows where extended operating temperature ranges may be considered in each material class. This may be achieved by alteration of elastomer composition such as the inclusion of more efficient stabilisers or a blend of other additives.

In the nuclear industry, very high confidence levels in the safe operation of components over a defined lifetime is, more often than not, a pre-requisite. There is no effective substitute for an ageing assessment for a polymeric component based on an adequate simulation of operating conditions. This assessment would be expected to be carefully constructed and based on some form of accelerated ageing programme, as described further in Section 4.

In addition to the designer being able to understand the long- term performance of a polymeric seal material at elevated temperature, the predominantly amorphous morphology of a polymeric seal mean that reversible property changes will also occur over a range of temperatures. One of these property changes in the transition from a rubbery to a glassy state, known as the glass transition T_g, which has already been described in Section 3.1.2. However, the change in a seal material's properties from a rubbery polymer to a glassy material will have a profound effect on its sealing characteristics.

Figure 8 shows an amorphous polymer will undergo a series of thermal transitions as the temperature is increased. These transitions will cause changes in the characteristics of the polymer.

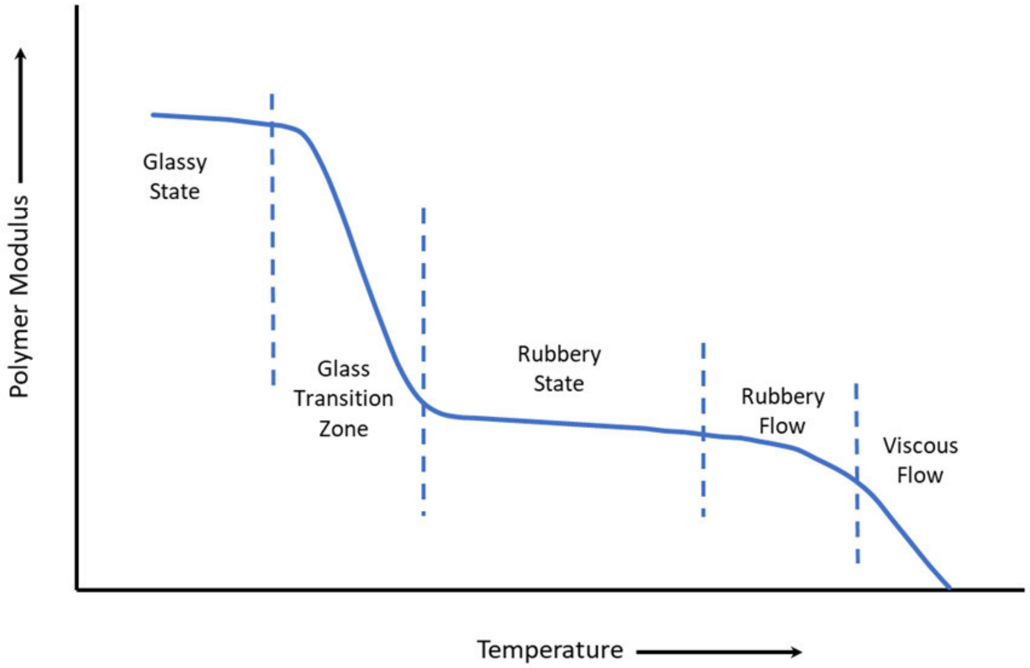

Figure 8 A plot of the modulus of an arbitrary amorphous polymeric seal material against temperature showing how property changes develop with increasing temperature.

The T_g of a polymer is a thermal transition which may be measured by a number of different techniques (differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA) and dilatometry to name three) and usually involves cooling a sample at a pre-determined rate and measuring a relevant property. When the property of interest changes by a certain amount, for example the modulus in a DMA test, the temperature is recorded and is usually expressed as an appropriate thermal transition temperature. However, the different techniques may generate different values of T_g for an identical material [33]. Three different values of T_g from the tests above may lead to confusion in terms of what value to assume during design considerations.

The schematic diagram in Figure 9 shows a cross correlation of how the modulus of an elastomer/polymer and the sealing force it exerts, change with temperature. The sealing force generated by a polymeric seal, especially elastomers in this respect, is, to a first approximation inversely proportional to the seal material's modulus. The curves in Figure 9 show that when the temperature is low enough and the transition is complete, the sealing force is effectively negligible. The elastomer at this point is effectively a rigid uncompliant glass and leak paths are likely to be inevitable.

The glass transition of a seal material could present operational issues where working temperatures are low. Immediate consideration is drawn to the sealing arrangements in radioactive material transport flasks. Even in the UK, external temperatures have fallen below -27°C (the lowest temperature ever recorded in the UK is -27.2°C in Aberdeenshire, 1982). Clearly any transport flask sealing arrangement should provide adequate sealing capabilities at this temperature. For example, the seal should have low temperature properties which allow functionality at temperatures significantly lower than -27°C or provisions should be made in flask design, if possible, to prevent the seal's temperature from falling to this level.

However, if a number of different values of T_g are available for a seal material, it is suggested that if justifications are made using T_g, a conservative approach would be to take the highest value available and apply a justified margin to that value. This will help define a temperature below which the seal material should not be used. It is also suggested that one of the most effective methods of determining T_g for seal materials is DMA. This is because it interrogates the modulus of the seal material as the temperature decreases and allows an assessment of the temperature at which the modulus begins to rise. This occurs at significantly higher temperatures than that for which the T_g is defined and allows an informed margin to be applied. If sealing force data are also known for the seal, the DMA and sealing force data can be used together to help provide justifications for the minimum temperature at which the seal can be used.

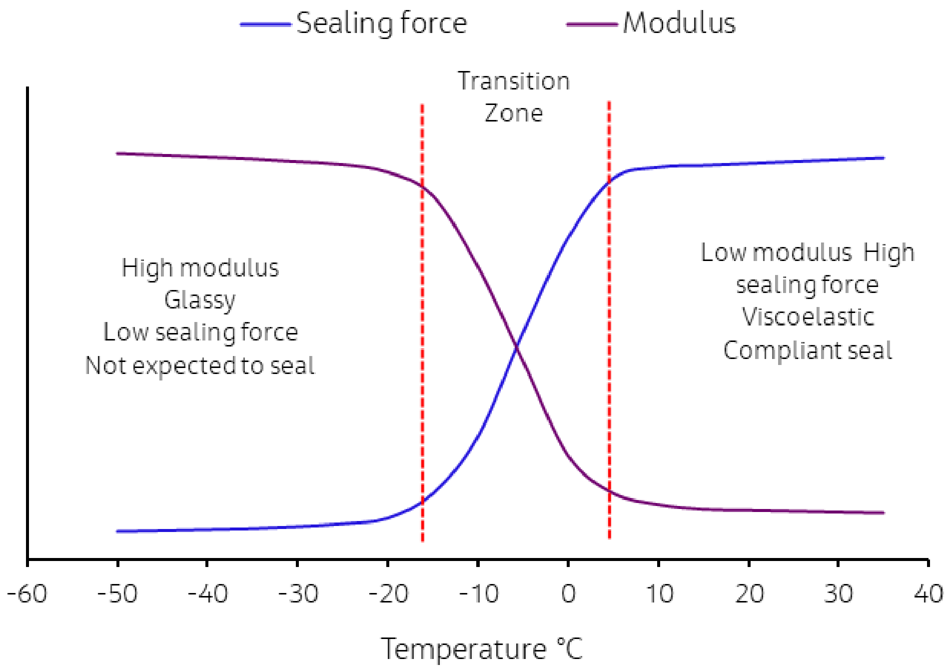

Figure 9 A schematic diagram of how the modulus and sealing force of a seal material may change as a function of temperature.

In addition to glass transition measurement, there are other low temperature seal data which are available to the designer which are discussed in the following sub sections.

3.2.15 Brittleness Temperature

It has already been described how the properties of an elastomer change as the temperature is decreased. The brittleness temperature is the temperature at which 50% of test samples undergo brittle failure under specific impact conditions, as defined in ASTM D746, ASTM D2137 and BS ISO 812. Essentially the seal temperature will be much lower than T_g at this point because it will have assumed glassy behaviour. If the seal is demonstrated to be brittle, it is unlikely to survive an impact and should not be in service under such conditions. However, if a justified upper margin is applied to a suitable T_g value, for instance that measured by DMA (which generates an output similar to the violet curve corresponding to elastomer modulus in Figure 9), brittleness should not be a concern.

3.2.16 TR-10 values

Another method of characterising the low temperature properties of a seal is the measurement of its TR-10 value. This value, according to ASTM D1329 or ISO 2921, is the temperature in degrees Celsius at which an elastomer, which was stretched to a certain amount (usually 25% or 50%) and then frozen, recovers elongation by 10% as it begins to warm up. Essentially, this method provides a measurement of the temperature at which the viscoelastic properties of a seal recover when slowly heated from below the T_g. The TR-10 value is suggested to be one of the most informative cold temperature characteristics for the assessment of the seal performance of O-rings or similar seals. It is understood to constitute a conservative low temperature limit and often has an additional 8°C margin [1]. Therefore, if an elastomer has a TR-10 temperature of -20°C, it should still be expected to seal at -28°C.

Fluoroelastomers cover a wide range of elastomers with a wide range of properties. There are TR-10 values of -17°C for some of the A-type fluoroelastomer grades used in the UK nuclear industry. This would suggest that, using the 8°C margin suggested for TR-10 values, that an A-type grade should still be operational as a seal at - 25°C. However, leak tests carried out by Burnay and co-workers reveal that an as-received, unaged A-type fluoroelastomer compound acts as a leak tight seal only down to -22°C [34]. Furthermore, mild radiation ageing to the equivalent of 20% compression set increased its minimum temperature to -16°C. This shows that low-temperature sealing with elastomers is a complex subject and advice should be sought from a seal manufacturer or third-party test house where appropriate.

3.2.17 Gehman Torsional Modulus

An additional method of examining the low temperature properties of an elastomer is the determination of the Gehman torsional modulus as described in ISO 1432 and ASTM D1053 [35{,36]. In this test, strip samples of elastomer are cut from sheet, placed in a sample holder and attached to a torsion wire arrangement. The whole arrangement can be twisted and the torsional modulus calculated at room temperature. The sample/wire assembly is then placed in a chiller to cool down to as low as -150°C. After stabilisation, the temperature of the sample is raised in a controlled manner and the torsional modulus of the elastomer calculated and plotted as a function of temperature. The temperature at which a torsional modulus of 70 MPa (T70) is achieved may be used to set the minimum operating temperature of the elastomer. The minimum operating temperature may also be estimated by using the modulus v temperature plot to determine the point at which the ratio of the room temperature and the low temperature moduli reaches a certain value. This may, in some circumstances, be a more reliable option for the characterisation of low temperature properties than other methods.

3.2.18 Compression set at low temperatures

The development of compression set in a seal at low temperatures around or below T_g is currently not well characterised. The transition from rubber to glass does not involve a change in chemical structure so the long-term compression set properties would not instinctively be expected to change a great deal from ambient conditions. However, the reduced mobility of the polymer chains at low temperatures due to glass hardening or even crystallisation effects in some compounds, can affect time dependent recovery after deformation. As these property changes will reverse at high temperatures, a standardised test method to characterise the compression set of seals at low temperature is available - BS ISO 815-2:2019 [15].

3.3 Monitoring of Seal Condition During Service

Premature seal failure is one of the primary causes for equipment or plant downtime and the consequences could lead to additional maintenance equipment costs far exceeding the cost of a replacement seal. Once a seal has been qualified for use on plant, a qualified life is assigned which defines the working life before replacement is required and maintenance schedules put in place to assess the component or periodically replace the seal. Condition monitoring is the term used to describe regular inspections of identified parameters that can signal a change in the operation or material properties that might be indicative of a developing fault.

The difficulty with condition monitoring of seal materials is that often the seal is not accessible, being clamped between flanges or housed within a piston for example. Consequently, on-going condition monitoring is usually carried out by the assessment of key operational parameters of the component. This can be carried out using in-situ sensing equipment for vibration, temperature and oil or fluid pressure as required. The development and application of new technology/sensors to interrogate operational conditions is ongoing and may include acoustic emission and ultrasonic waves.

During plant and equipment inspections it is important to remain vigilant to any unforeseen changes in the local environment. For example, an overhead pipe/component could develop a small leak and introduce an incompatible fluid to the seal or the ambient conditions in that area are higher than expected during design, even for a limited period. The effect of such instances on any seals may not be the first consideration, but review of the qualification should be undertaken.

If a seal has been assigned a particular qualified life, remains functional and is replaced as part of scheduled maintenance it could be beneficial to assess the condition of the aged seal to better understand the level of ageing and how that compares to the original qualification data. Conversely, if a seal were to fail unexpectedly before the qualified life, then an investigation to determine the cause would also necessitate a review of the original qualification and any underpinning data.

Whilst the retrieval and characterisation of used seals from plant may be desirable for failure analysis for example, in many nuclear applications the retrieval and post-ageing analysis of seals from active plant may not always be possible. This is likely to be due to contamination control unless specialised transport of components to active tests facilities is available, even then retrieval may not always be possible.

4. Suggested best practise for testing and the assessment of ageing in elastomers for use in nuclear environments

4.1 Concept of environmental qualification

The convention on Nuclear Safety requires that the design and construction of nuclear installations should provide a number of reliable safety levels and protection against the release of radioactive materials [37]. To this end, the technologies incorporated in the design of such installations should be proven by experience or qualified by testing or analysis.

These protection methods include design provisions that aim to prevent the loss of safety functions caused by equipment failure and the potential common cause failures that might arise from the failure of a single component or otherwise. A common cause failure is a failure in a system where multiple parts of a system fail as a result of the failure of a single component. For example, a seal on high pressure pipeline might fail causing equipment in its vicinity to sustain damage and malfunction.

Therefore, a system of qualification, performance assessment and ageing management is required in nuclear installations to ensure that equipment and components important to safety maintain their ability to function for the required service lifetime under service conditions and also accident conditions.

In nuclear plant, components and equipment may be exposed to conditions that include ionising radiation, elevated temperatures and harsh chemical environments such as acids or alkalis. However, polymeric materials such as elastomers are sensitive to these conditions and components such as elastomeric seals may suffer degradation after continued exposure to these environments. In order to comply with safety requirements i.e., to ensure reliable and safe operation, safety cases and design considerations will normally require some assurance that, for example, a nuclear containment seal, will maintain its sealing capability over its design lifetime and any accident conditions.

Polymeric seals are expected to degrade in terms of their sealing capability if exposed in-service to ionising radiation, elevated temperatures, aggressive substances and possible combinations of the three. This is why the use of these materials is usually limited in nuclear plant to areas of low dose radiation dose rate and moderate temperatures. However, even at low dose rates and temperatures in service, typically up to 1 Gy h^{-1} and 50°C respectively, elastomers will still eventually degrade. Consequently, nuclear equipment is usually assigned a service lifetime which is usually limited to the stability of the most radiation/thermal sensitive materials within the said equipment.

As with many industries, engineers and equipment designers in the nuclear industry usually have limited timescales before a piece of equipment is manufacture and accepted for use in plant. Where components may be susceptible to accumulated damage over time, some form of accelerated ageing is usually required to simulate long term environmental exposure. This ageing will be aimed at bringing the components to the condition that they would be expected to be in at the end of their service life. However, the methods used to carry out these simulations are very important because they must ensure that the condition of the components after accelerated ageing is as close to that from real time ageing as possible. This can sometimes be very difficult to achieve especially for new or upgraded materials that must be assessed within short timescales under design and delivery pressures.

The methods adopted for accelerated ageing of equipment in the nuclear industry are very often based on environmental qualification (EQ) standards. In this case, EQ defines an initiative to demonstrate that components will retain safety functionality throughout their defined service lifetime in nuclear applications and also under potentially harsh accident conditions. In the UK there are a number of specific nuclear EQ standards that are usually consulted and followed for the qualification of components in safety related applications:

- International Electrotechnical Commission, IEC 60780, *Nuclear Power Plants - Electrical Equipment of the Safety System – Qualification* [38]. This International Standard describes the basic requirements for qualifying electrical equipment important to safety and interfaces (electrical and mechanical) that are to be used in nuclear facilities.
- Institute of Electrical and Electronics Engineers (IEEE) standards, IEEE 383 *Standard for Qualifying Electric Cables and Splices for Nuclear Facilities* [39] and IEEE 323-2003 - *IEEE Standard for Qualifying Class 1E Equipment for Nuclear Power Generating Stations* [40]. IEEE 323 is the standard used to qualify electrical equipment for safety-related use in nuclear power plants. This includes all components that would be used in equipment such as the seals and gaskets in valves and pumps.
- IEC/IEEE 60780-323:2016, *Nuclear facilities - Electrical equipment important to safety – Qualification* [41]. This is a newly compiled, joint-badged standard between the two organisations which combines the above standards with the view of unifying the international approach to EQ.
- AFCEN RCC-E 2019 Edition, 2019 [42]. *Design and construction rules for electrical and I&C systems and equipment*. This EDF led consortium (AFCEN) driven standard/code for nuclear plant design, construction and qualification. The 2012 edition of this standard constitutes a significant contribution to the basis of the construction of Hinkley Point C (HPC) nuclear power station.

Although the standards above refer in the main to electrical equipment, they cover polymeric materials used in typical components such as electrical cables, penetrations, housing seals, safety seals on doors and fire dampers, valve seats, pump seals and gaskets and many others. Each of these standards provides guidance on how to carry out the appropriate qualification tests on candidate components and materials for deployment in nuclear power generation plant, typically BWR and PWR.

The standards recommend the environmental test conditions that should be used to accelerate the ageing in components to simulate long term ageing in plant and also prove their ability to function through accident conditions. Their importance to continued nuclear safety means that they are frequently consulted to help assess material and equipment suitability across the nuclear industry. Consequently, the testing concepts and methodologies described are commonly transferred to other generic materials testing throughout the nuclear industry.

Clearly, where components such as seals are used in radioactive material transport activities, other specific regulations and requirements will also apply, Section 2.6, but any accelerated ageing type activities are likely to involve EQ standards or their concepts.

4.2 Qualification and accelerated ageing conditions

In this section of the document, a comprehensive description of the suggested best practise is provided for EQ activities and how to accelerate the ageing of seal materials to gain a representative assessment of real time ageing in nuclear plant. Some of the guidelines and references will refer to principles adopted for the testing of electrical equipment, e.g., polymeric cable materials. However, as electrical equipment will also cover pumps, valves, penetrations and other components that require seals, the documentation is equally applicable to seals. Furthermore, as elastomers are polymeric materials, the generic ageing mechanisms and principles that are described in these documents apply to most organic polymers.

The selection of test conditions and exposure times in not always a straightforward task. Inevitably, a careful balance has to be struck between selecting ageing conditions to achieve representative ageing in the polymeric material/component of interest and the commercial considerations involved (e.g., the price of test facilities, the man-time required to carry out tests, the time to analyse data and the overall price to carry out the whole EQ task within acceptable timescales to plant design and construction). As described in Section 2.6.1, the over-arching requirement during qualification processes is that risks posed by equipment ageing are ALARP and that safety is adequate. Consequently, a robust rationale for the selection of the accelerated ageing conditions to simulate sealing ageing during EQ activities should be made available to demonstrate that ALARP principles have been applied and that the appropriate balance has been struck between safety and commercial considerations.

4.2.1 Qualification of polymers/elastomers for use in radiation environments

An elastomeric O-ring, for example, may be required to function over a service lifetime of 20 years in a nuclear plant at a location within the plant that has an environmental dose rate of 1 Gy h^{-1} at ambient temperature. This means that and the end of its service life, the O-ring will have been exposed to a total radiation dose of about 175 kGy. A typical approach to qualification of this O-ring will be to irradiate at a high dose rate to about 192.5 kGy (175 kGy plus a 10% margin, see Section 4.5.4) and measure the O-ring properties, compression set and other relevant properties, to ensure that radiolytic changes do not affect the O-ring’s sealing performance. The accelerated radiation dose rates are usually chosen to minimise expensive irradiation time and can be as high as 10 kGy h^{-1}. Such a dose rate might seem attractive to designers because the irradiation time in such a case will only be 19 hours or just under a day. This kind of radiation testing approach is based on an initial assumption that the radiation damage sustained by the material is proportional to the total radiation dose it receives or:

$$\text{Equal dose} = \text{Equal damage} \qquad \text{(Equation 4)}$$

This phrase or relationship has been used extensively throughout the nuclear industry and has defined the approach to radiation testing of materials for as long as nuclear facilities have been in existence.

If, after irradiation to 192.5 kGy, the O-ring is assessed to perform suitably e.g., its compression set has not increased sufficiently to cause concern, it may then be assessed as qualified and therefore suitable for purpose. That is, of course, dependent on the veracity of Equation 4.

4.2.2 Factors that might affect the conclusions reached during radiation tests - Radiation dose rate effects.

As described in Section 3.1.8, when an organic polymer is exposed to ionising radiation, the dominant mechanism is the production of free radicals. These can react within the polymer’s molecular structure to initiate chain scission or cross-linking and change the polymer’s structure and properties. The free radicals may also react with free oxygen within the polymer to form aggressive peroxy radicals which can attack the polymer structure. If this occurs oxidative chain scission usually occurs. In many cases, the formation of and action of oxidising peroxy radicals are essentially the controlling steps of the radiation ageing processes that usually occur in polymers within nuclear environments.

An important aspect to appreciate at this juncture is that all polymers are permeable to gases to a greater or lesser extent. Oxygen will permeate through all polymers at rates which are usually dependent on their molecular structures. For example, unfilled silicone has a high gas permeability whilst Viton is an example of an elastomer with low permeability. During irradiation, the free radicals initially generated in a polymer by excitation and ionisation processes will readily react with and consume any equilibrium dissolved oxygen to produce peroxy radicals. As oxygen supplies become exhausted during continued irradiation, they will be replaced at a rate determined by diffusion from the local environment. As long as oxygen is available, the peroxy radical formation processes will continue and cause radiolytic oxidation throughout the polymer.

At the low dose rates expected for polymers in typical nuclear plant environments (i.e., in the presence of air), ageing is usually dominated by radiolytic oxidation. This process will clearly cease if, for some reason, access to oxygen becomes restricted. Furthermore, some components in plant may be irradiated in the absence of oxygen in which case oxidative processes will be suppressed and other processes such as cross-linking will tend to dominate, depending on the nature of the polymer.

During radiation testing to assess the radiation tolerance of polymers, the use of dose rates that are significantly higher than service dose rates are required to arrive at damage assessments within reasonable experimental timescales. Traditionally, a balance has usually been struck between irradiation test time and dose rates.

Intuitively, it would seem appropriate to irradiate materials for as long as possible if environmental conditions during service are to be simulated. However, it is not uncommon to learn that radiation testing has been carried out very quickly. This is probably for a number of reasons which might include the rationale that shorter test times in radiation facilities are more cost effective and delivery schedules might demand an "answer" to be reached as soon as possible. As a consequence, radiation qualification test data on polymers may have been generated using dose rates as high as 10 kGy h^{-1}, which is a radiation acceleration factor of over 10,000 compared to some in-service dose rates.

In polymers at dose rates much above a few hundred Gy h^{-1}, the efficiency of free radical generation is expected to be very high and the equilibrium dissolved oxygen within the polymer will be rapidly consumed. Although polymers are permeable to oxygen, at high dose rates the lag between oxygen consumption and supply is such that in most cases only the outer extremities of the polymer become oxidised. The interior regions of the material continue to be irradiated but will not be oxidised and any structural changes will occur anaerobically. As dose rates decrease and the time taken to reach the service dose increases, oxygen will have time to diffuse into the polymer and oxidation will extend further. Finally, if service conditions involved a dose rate of 1 Gy h^{-1}, the polymer maybe oxidised completely at a dose of 192.5 kGy and heavily degraded. The overall process is shown schematically in Figure10.

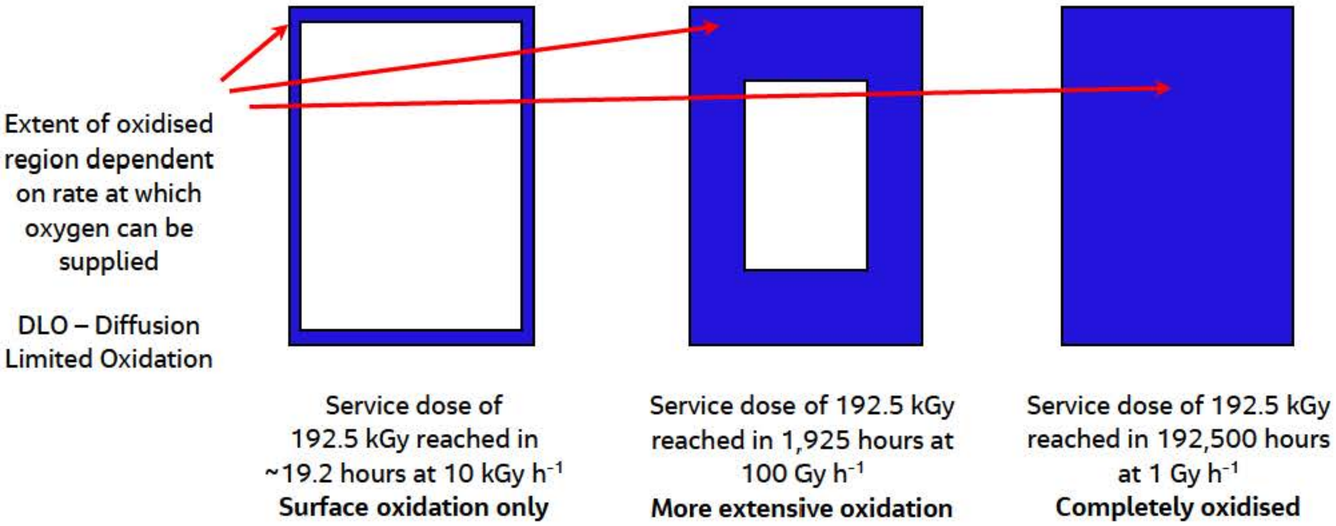

Figure 10 Schematic diagram showing dose rate effects in a polymer irradiated in air at different dose rates - diffusion limited oxidation, (DLO).

If Figure 10 is taken to represent a sample cross section of an elastomer, it is very likely that the rates and amount of compression set that accumulates in the sample whilst irradiated at 10 kGy h^{-1} will be quite different to those observed in the sample aged under service conditions. Furthermore, if the sample in Figure 10, irradiated at 10 kGy h^{-1}, represented a polymer under a tensile test, it is entirely possible that, because oxidation is limited to the surface, little change in strength may be observed. On the other hand, the long-term aged sample, oxidised throughout, might be heavily aged and friable. Whether compression set or strength is important, an irradiation test at 10 kGy h^{-1} would be non-representative of the ageing processes occurring in service.

The dose rate effect shown schematically in Figure 10 is known as diffusion limited oxidation, DLO. Two of the original pioneers of the initial research into the process were R. Clough and K. Gillen of Sandia Labs in the USA [43]. These effects have been extensively studied since ~1980 and are now reasonably well understood but, nevertheless, are still complex in nature.

However, even though scientific and technological advancements have led to a much-improved understanding of radiation effects in polymers, the concepts put forward by standards for EQ radiation testing do not seem to have kept up with this understanding.

In addition to dose rate effects arising from DLO, rate effects can occur for other reasons and a detailed analysis of other mechanisms is beyond the scope of this document. However, for more information, further reading is suggested for example Clegg and Collyer which is a text that pulls together a number of aspects of polymer radiation chemistry [44]. When it comes to radiation effects in polymeric materials, it is not uncommon to observe that Equation 4 does not hold. Therefore, care is needed when accessing radiation test data to ensure that the data are as representative as possible of the intended service conditions.

4.3 Qualification of polymers/elastomers for above ambient temperature use at negligible dose rates

The properties of a polymeric component will also degrade over time in the absence of ionising radiation due to thermally initiated free radicals. However, the efficiency of free radical production by thermal processes is significantly lower than the efficiency of radical production arising from the direct ionisation processes from radiation. Nevertheless, thermal ageing will occur in polymers, even at ambient temperatures. The structural changes brought about by long-term exposure to ambient temperatures will occur at extremely low rates and, over the operational timescales of nuclear plant, would be expected to be negligible. However, as the environmental temperatures are increased, the thermally initiated degradation rates in polymers will also increase.

The compression set of an elastomeric seal will be expected to increase slowly with ageing time at modest temperatures. As the ageing temperature increases, however, the degradation rates will increase, compression set will therefore increase (Section 3.21) and service life will decrease accordingly. Historically and in accordance with EQ standards, the method of evaluating the thermal stability of a polymeric material at nuclear plant operating temperatures has been to use the Arrhenius law. The Swedish scientist Svante Arrhenius discovered that the rate of a chemical reaction was controlled by temperature and:

$$k^* = Aexp\frac{-E}{RT} \qquad \text{(Equation 5)}$$

Where:

k^* is the rate constant for a given chemical process;

A is a coefficient of proportionality which is a constant for a given process and system;

E is an activation energy;

R is the ideal gas constant, 8.31 J mol^{-1} K^{-1}

T is the absolute temperature of the system in K.

Equation 5, the Arrhenius law, defines the relationship between the rate of a chemical reaction (in this case the mechanism for the thermal ageing of an elastomeric seal), the absolute temperature and the activation energy of the process. As the temperature increases, the seal ageing rate will increase.

An often-applied rule of thumb is that the rate of a chemical process will increase by a factor of two for every 10 degrees increase in temperature as used in the RCC-E 12 standard used at HPC, Section 4.1. This rule of thumb corresponds to an activation energy of about 80 kJ mol^{-1} (~0.8 eV). However, the activation energy of a thermal ageing mechanism can be significantly higher or lower than this value, hence it is only a rule of thumb and should be used with a good deal of caution. To simulate the exposure of an elastomeric seal or other polymeric component for a period of service at a constant temperature, the Arrhenius equation (Equation 5) can be rearranged and used in the following form:

$$\frac{t_{service}}{t_{test}} = exp\left(\frac{E}{R}\left(\frac{1}{T_{service}} - \frac{1}{T_{test}}\right)\right) \qquad \text{(Equation 6)}$$

Where:

$t_{service}$ is the required service lifetime (or qualified life), usually in hours;

t_{test} is the duration of the accelerated ageing test, usually in hours;

$T_{service}$ is the temperature during service;

T_{test} is the accelerated test temperature.

To the letter, Equation 6 allows the designer or qualification engineer to determine the accelerated ageing test duration at a specified temperature if all other ageing parameters are known (including an accurate value of the activation energy of the material under test). The aim being to generate an equivalent level of thermal ageing in a material intended for use at a lower in-service temperature. The Arrhenius approach is essentially the back-bone of many qualification activities for component selection in the UK nuclear industry. This approach is for the simulation of the ageing of components expected to receive negligible radiation doses in service. In many cases, the equation has provided the ability for workers to choose an elevated test temperature that fits in with contract design timescales. However not everybody fully understands the fundamental assumptions that underpin the proper use of this relationship in accelerated ageing activities. These assumptions are:

- Only one degradation mechanism is in operation;
- No thermal transitions, changeovers in mechanism or reaction rates occur below the accelerated test temperature;
- The activation energy remains constant and an accurate value is known for the material in question.

The dominant mechanism in the thermal ageing of polymeric components is also oxidative degradation which occurs as a result of free radical processes. Consequently, thermal ageing is usually dependent on a supply of oxygen. Oxidative degradation processes in polymer are very complex and are often combinations of several different reactions each of which may have their own reaction rate at specific temperatures and their own activation energies.

As the selected test temperature for a qualification test increases away from service conditions, the probability that alternative reaction mechanisms will be present and will begin to dominate increases. This change in process could cause significant changes in the material compared to those occurring slowly during service. Although it is a significant digression from the subject in hand, the following comparison serves to illustrate a purpose: a fertilised chicken egg will produce a chick after about three weeks at 37°C. If held at 25°C for a longer time period it will go bad. On the other hand, if it is placed in boiling water for 4 minutes a hard-boiled egg will result. Significant changes in dominant ageing processes may also apply when many polymers are thermally aged at different temperatures.

Figure 11 shows an Arrhenius plot from an accelerated ageing programme for an EPR elastomer. The time taken to reach a specific ageing condition in hours is on a logarithmic y-axis and the reciprocal absolute temperature on the X-axis. This is the usual way of showing Arrhenius type data where a rate dependent relationship is related to reciprocal temperature by a straight line. The slope of the line normally enables the activation energy to be calculated. However, in Figure 11, the data suggest two lines of different slopes which define two different activation energies of 63 and 130 kJ mol^{-1}. Clearly in this case, a change in ageing mechanism occurs at about 135°C.

A method of estimating service lifetime using Arrhenius is to extrapolate the data on a plot back to the service temperature (section 4.1.4). In the case of Figure 11, this is assumed to be 40°C. If the line corresponding to the 63 kJ mol^{-1} activation energy is extrapolated back to 40°C (reciprocal 313 K), the projected time to equivalent ageing at 40°C would be about 200,000 hours or about 23 years. If, however, the line corresponding to the higher activation energy of 130 kJ mol^{-1} is extrapolated back in the same way, as shown by the blue dashed line in Figure 11, the service lifetime will not fit on the plot. If it was plotted on a different scale, it would predict a lifetime of about 10^8 hours or about 11,400 years, which appears to be very optimistic if not unlikely.

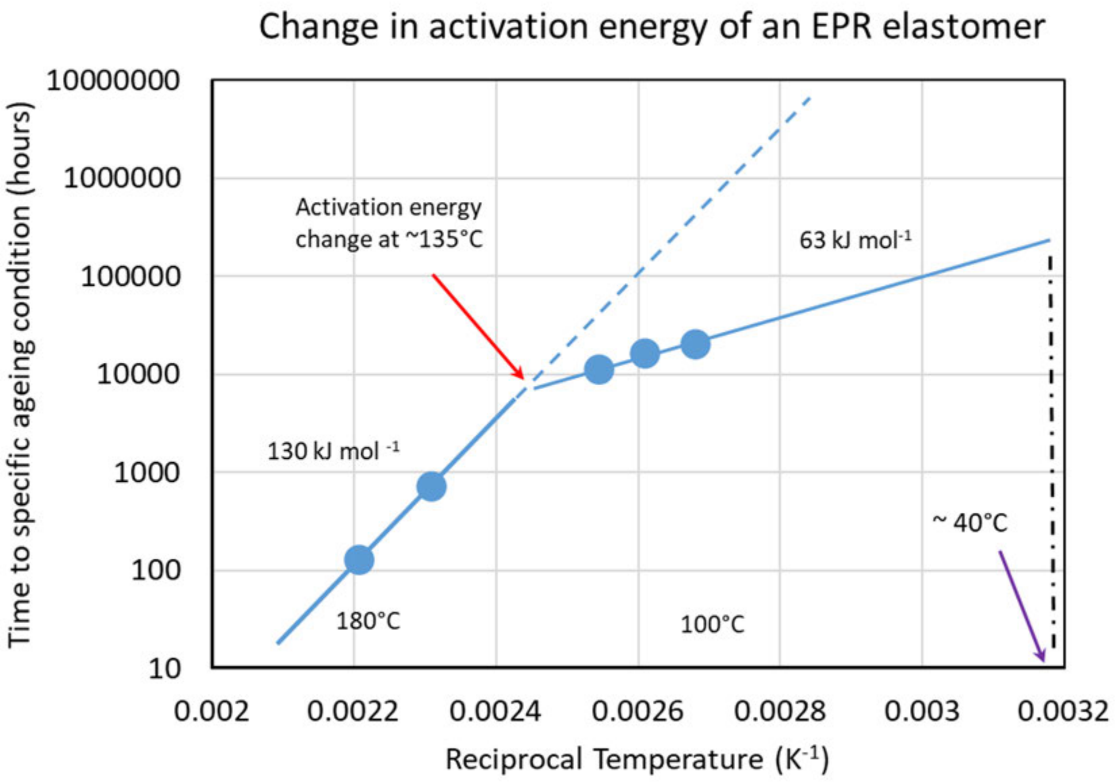

Figure 11 A plot showing the time to a specific ageing level against reciprocal temperature for an EPR elastomer.

Figure 11 is important because it demonstrates that, over a wide temperature range, thermal ageing in polymers can show a distinct change in mechanism. If Equation 6 was to be used to estimate the accelerated ageing temperature for qualification in an application that requires a short ageing timescale due to design pressures, the calculation will deliver a high ageing temperature. However, Figure 11 demonstrates that as the ageing temperature increases for this EPR formulation, a change in mechanism occurs which means that any testing above 135°C is more than likely to be non-representative of real ageing conditions. A lot of care is therefore required when using Arrhenius to estimate accelerated ageing temperatures. Pressure to get results in a short space of time can lead to the generation of test data that are not representative of the conditions that need to be simulated. This becomes very important for safety related applications.

A case study that is very relevant to this report section concerns the accelerated thermal ageing of a commonly used O-ring seal material used widely in the UK nuclear industry, EPDM 30H. This is a bespoke ethylene propylene diene monomer formulation with good radiation resistance. It is used for the main seals in a number of transport flask applications. During the initial characterisation of this material for a specific flask configuration, a question was raised of the potential for thermal ageing of the seals that could occur due to insolation when the flasks are in transport activities but exposed to the elements during storage. Consequently, a series of accelerated ageing tests were carried out on O-rings clamped in solid stainless-steel flanges at different temperatures as high as 160°C. It was observed during this series of tests that the compression set in the EPDM 30H was lower at 160°C than for equivalent times at 100°C. This was clearly not the expected outcome if the ageing had occurred in accordance with Arrhenius.

On examination of the O-rings, it was discovered that at temperatures above 120°C, oxidation of the EPDM had accelerated and formed a skin on the outer exposed surface of the O-rings. This skin served as a barrier that restricted oxygen diffusion into the internal parts of the O-rings and effectively protected them from oxidative degradation. Below 120°C, however, the skin was not observed and oxygen could diffuse in to the O-ring more easily and allow uniform oxidation. It should be borne in mind that during these tests the O-rings were compressed in dove-tail grooves and only a small proportion of the O-ring was in contact with air. Thus, the skin formed above 120°C plus the stainless-steel flanges provided an effective barrier protecting the seal material from oxygen diffusion. These observations meant that a modified series of tests had to be put in place to age the EPDM 30H at lower temperatures and over longer timescales.

The observations for EPDM 30H indicate that when accelerated ageing tests are conceived during qualification activities, it is very important to keep the test temperatures as low as possible and accept that good representative ageing tests will require appropriate time periods to complete.

Another important assumption for the use of the Arrhenius equation is that the value of activation energy used in any calculation for a particular material is accurate. Figure 12 has a bar-chart that shows how changes in activation energy can affect the estimated qualified lifetime of a component. In this case the accurate activation energy for the component Ea is ~87 kJ mol^{-1}. The chart shows how the estimated lifetime of the component can vary with deviations from the true value. For example, if an activation energy of 10% higher than the accurate value was used for Arrhenius calculations, instead of a lifetime of around 17 years, a lifetime estimate of 30 years would be made. This could mean that the use of the wrong activation energy during qualification leads to heavy ageing in the component 13 years before it was predicted to happen.

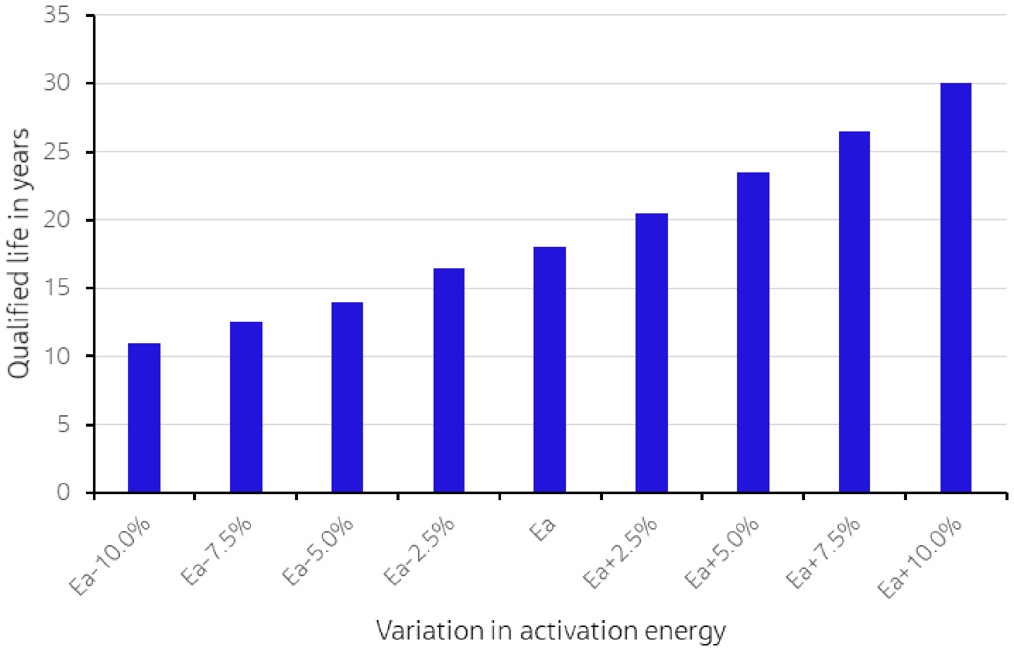

Figure 12 Example of the influence of changes in the assumed value of activation energy Ea on qualified life determined from artificial thermal ageing at 110°C extrapolated to a normal service temperature of 50°C.

It is therefore clear that where a step-change or transition occurs in the thermal ageing characteristics of a polymer or inaccurate values of activation energy are used, extrapolations using the Arrhenius approach can provide over optimistic estimates of component lifetime. Consequently, is it recommended that acceleration factors are kept as low as possible and initial characterisations should be carried out to determine whether the polymer shows any significant transitions at temperatures of interest.

4.4 Qualification of polymers/elastomers for above ambient temperature use in the presence of radiation

In many applications in the nuclear industry, it is likely that polymeric components, including seals, will be required to function in a location that has a radiation field and also elevated temperatures. Therefore, there is the strong possibility that there will be multiple stressors on the component during service. This situation is acknowledged by the EQ standards and methodologies are provided that are intended to simulate ageing in these types of conditions. The IEE and IEC standards favour a sequential ageing approach where components are aged thermally using the Arrhenius approach, followed by an irradiation to the service dose [38, 39, 40, 41]. These qualification tests often follow the approaches described previously: high temperature ageing and high dose rate irradiations both over as short a series of timescales that will fit within design requirements.

However along with factors such as radiation dose rate effects, it is been reported that when polymers are irradiated at elevated temperatures, the effects of the thermal and radiation components are not additive but synergistic. This means that a polymeric seal, for example, can undergo greater levels of compression set when irradiated at elevated temperatures than if it had been exposed to the ageing conditions sequentially. This means that sequential thermal and radiation testing may provide data which are even less representative than previously described. The RCC-E code (and associated standards) attempts to overcome the synergy issue by stipulating that the default ageing conditions should be irradiations carried out at 70°C but at dose rates of 1 kGy h^{-1} [42].

Radiation/thermal synergy in polymers can be represented by the series of curves in Figure 13. This shows the ageing behaviour of an arbitrary silicone elastomer when exposed to gamma radiation at different temperatures. The time in years to reach a pre-determined ageing point is plotted against dose rate. The different coloured curves correspond to the ageing sustained by the elastomer at different temperatures whilst irradiated.

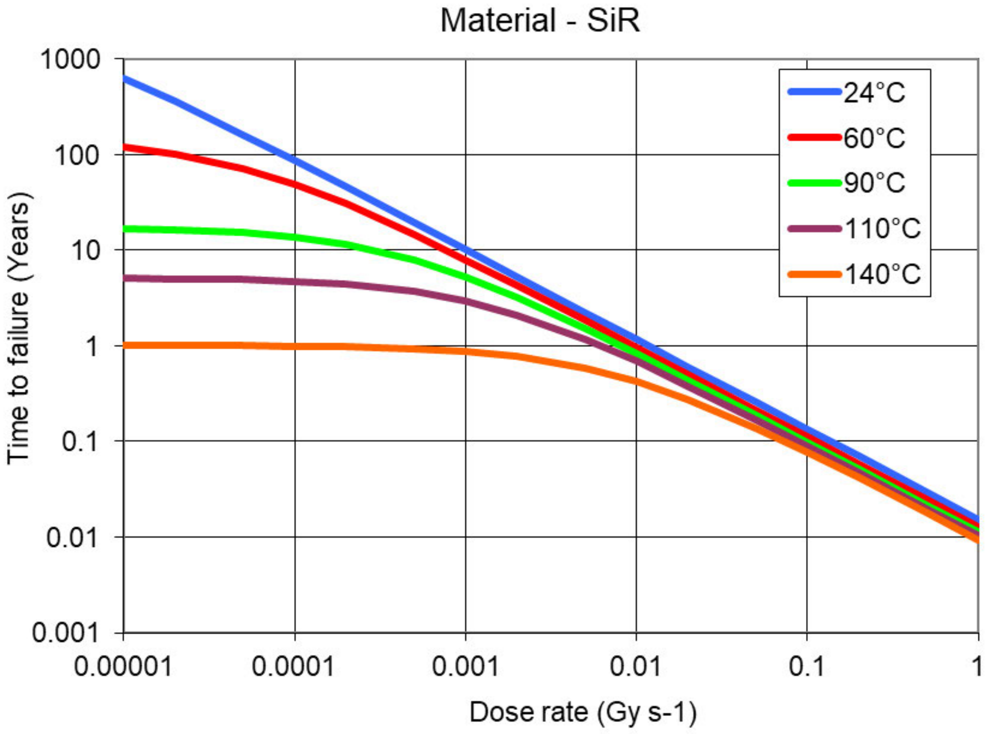

Figure 13 A series of curves relating the times to failure to radiation dose rate for a silicone rubber compound irradiated at different temperatures.

The curves are closely spaced at the right-hand side of the figure, corresponding to high radiation dose rates and show that increases in temperature have little effect on elastomer property changes under these conditions. On the left-hand side of the figure, where the dose rates become very low, the curves are widely spaced and here thermal ageing dominates. If the intercepts at the y-axis are taken for each temperature and plotted against inverse absolute temperature, it is probable that Arrhenius behaviour will be shown. Clearly where seals are used in applications where dose rates are negligible or absent, Transport flasks for example, radiation ageing considerations do not apply.

If radiation is present, at intermediate dose rates, both radiation and temperature contribute to the ageing of the elastomer. The curves vary in gradient and spacing in this region of the plot, between dose rates of 0.0001 and 0.01 Gy s^{-1} (or between ~0.4 and 40 Gy h^{-1}). The lower end of this range corresponds to the dose rates that some polymers may be expected to experience in nuclear environments. Consequently, under typical service conditions, the ageing of polymers in nuclear environments will be dependent on the synergy between radiation and thermal effects.

Although Figure 13 shows a complex series of curves, the changes in elastomer properties for any radiation dose rate or temperature can be interpreted by the use of an empirical ageing model shown in Equation 7 and described in details in the literature [45]:

$$a(D,T) = \exp - \frac{E}{R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\left(1 + kD^{x} exp\,\frac{Ex}{R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right) \qquad \text{(Equation 7)}$$

Where :

$a(D,T)$ is the shift factor at the specified temperature and dose rate

D is the radiation dose rate in Gy s^{-1}

T_{ref} is a reference temperature in K

T is the ageing temperature in K

E is an activation energy for the thermal ageing process in kJ mol^{-1}

R is the gas constant ~8.3 J mol^{-1} K^{-1}

k and x are material constants

Whilst this expression may at first appear to be rather foreboding, it is a combination of contributions from both the radiation and thermal components and Equation 7 can be simplified to a form of the Arrhenius equation, if for example, there is no radiation present and $D = 0$. Equation B.1 in Appendix B and Reference [45] provide more detail and background to these concepts.

The traces in Figure 13 correspond to the ageing characteristics of an arbitrary silicone elastomer. For different elastomer materials or silicone formulations, parameters k, x and E will be different, and each material will be expected to show a similar distribution of curves on the same type of plot. However, the intercepts on the y-axis will be at different values and the dose rate at which the curves converge will be different.

In order to use Equation 7 for the assessment of a polymer's sealing characteristics, a matrix of test data is required to evaluate the ageing model parameters k, x and E. This matrix is produced by measuring the time dependent changes in compression set for the seals aged at different radiation dose rates, different temperatures and combinations of the two. The compression set test methodology is described in detail in

Section 3.1.3. The compression set data are then analysed using superposition techniques, please see Equation B.1 in Appendix B, to calculate the parameters. This is nowadays a relatively simple task using modern computer applications such as Microsoft Excel. Other material properties such as tensile strength and elongation at break may also be required for different applications; the analysis principle is identical but the test data will be delivered from tensile tests in these two cases rather than compression set measurements.

The UK nuclear industry is somewhat unique in that it has at its disposal, a validated empirical model for the prediction of the compression set of a number of the commonly used elastomeric seals in the industry: EPDM, Viton, nitrile and silicone elastomers. The model has been incorporated into Microsoft Excel, is known as SEALS and is available to some duty-holders. The SEALS model has been developed from extensive arrays of accelerated ageing data generated in the 1980’s to 1990’s and using the techniques described in Appendix B. The model was verified by a long-term seals test programme that ran for twenty years under funding from UK nuclear industry.

If the environmental conditions within a nuclear application are known (radiation dose rates and/or temperatures), the compression set of these seals materials can be quickly estimated for a defined time exposure, thus providing an estimate of service lifetime. The accuracy of the model has been validated by comparing model predictions with long term test data from a verification programme which lasted almost twenty years from 1990 to 2010. The long-term test programme measured compression set in seals as a function of time at the low radiation dose rates and elevated temperatures expected in typical UK nuclear installations. Whilst the SEALS utility is powerful, it should only be used by qualified personnel and is only reliable for the specific seal materials in the utility within the stated boundary conditions. It should not be used as a method of assessing the response of generic seal materials in nuclear environments.

As well as being able to predict the compression set development for the stated seal materials under specific nuclear environmental conditions, the SEALS approach can also be used to provide much more representative accelerated ageing conditions for EQ activities. If too high an acceleration factor is suggested, SEALS can identify this issue before a test programme starts and a more representative set of ageing conditions can be substituted.

The convergence of the lines at high dose rates on the plot shown in Figure 13 demonstrates that the radiation test conditions recommended by the RCC-E standard [42], which are 1 kGy h^{-1} at 70°C, do not account for radiation/thermal synergy. The figure clearly demonstrates that increasing the temperature has little or no effect on material properties at such high dose rates. It is suggested that readers should be aware of potential uncertainties arising from any claims that synergy is adequately represented in this manner. Furthermore, the curves in Figure 13 also bring into question the emulation of synergistic effects by sequential ageing operations proposed by the IEC and IEEE standards [4138, 39, 40, 41]. A good example of the differences in property changes between different ageing simulations is shown in Figure 14 [46]. As part of a major national project in Japan, silicone cable insulations of different colour were aged under sequential ageing conditions and also under combined ageing conditions for equivalent timescales i.e.:

- Thermal followed by irradiation;
- Irradiation followed by thermal;
- Combined – irradiated and heated at the same time to representative plant conditions.

Clearly, from Figure 14, a significantly larger level of ageing occurred under combined conditions, showing that the sequential ageing approach had, in this case, demonstrated a lack of conservatism. It is suggested therefore that for qualification purposes, combined irradiation/thermal ageing methodologies would be preferred. Furthermore, readers should be ready to question any claims by licence applicants that radiation/thermal synergy in components during service has been adequately represented by sequential ageing tests. Although the data in Figure 14 are for a silicone cable insulation, the same principle would apply to seals made from the same material. The degradation mechanisms would have essentially been the same, the way their effects were measured for Figure 14 would have been different to the way sealing performance would have been assessed.

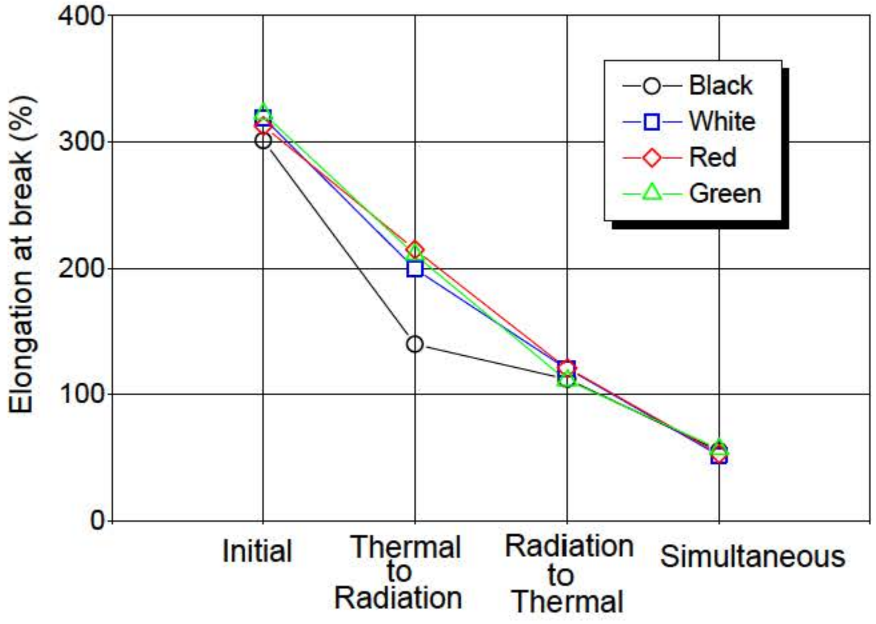

Figure 14 Comparison of ageing in silicone elastomers brought about by different accelerated ageing conditions during qualification tests [46].

A technical document has been issued by the IAEA which deals with the issues and complications that can arise during the qualification of polymeric cable materials for nuclear plant [47]. Although Reference 36 deals with cable materials, the underlying principles which apply to polymeric materials in general are identical. The document describes the concepts, flaws and mis-conceptions associated with the accelerated ageing of polymeric materials for qualification in safety related applications in nuclear power plant. The document also offers advice on the choice of test parameters with a view to generating ageing conditions that are as representative of service conditions as is possible to achieve.

4.5 Summary

In summary, Section 4 has attempted to explain how the current EQ standards for nuclear plant have been interpreted to set up qualification test procedures. The way in which the standards can be interpreted may lead to a series of accelerated ageing tests on a seal material which are not representative of service conditions. If a designer/qualification engineer submits test data to regulators to support the selection of polymeric seals for use in safety critical nuclear applications, the following points are suggested for consideration:

4.5.1 Radiation levels

As a first consideration, is the seal's generic radiation resistance capable of maintaining functionality at the radiation doses expected in service. For example, the choice of PTFE as a seal material in radiation environment would be a poor one because it is very sensitive to radiation. If a material is deemed to be radiation resistant, what are the sources of data that support any claims in this respect?

If the seal is to be used in a safety related application in a radiation field, its functionality over its service life needs to be assessed by appropriate radiation tests. Any data submissions should include the radiation test dose rates used, the test environment (e.g., irradiated in air), the total dose reached during the test and the properties used to assess seal functionality as a function of dose (e.g., compression set, elongation at break etc). Radiation dose rates should be kept as low as reasonably possible within acceptable timescales. If a high radiation dose rate is necessary (dose rates in excess of 100 Gy h^{-1} can sometimes cause significant dose rate effects), a suitable justification should be provided. It is also suggested that, if high dose rates are employed, some form of high-level test should be carried on the seal to demonstrate that any radiation ageing that has occurred in the seal is homogenous throughout its thickness.

4.5.2 Thermal ageing: use of Arrhenius relationship

Before using Arrhenius type tests, the following steps are suggested:

Assurance that the seal's thermal activation energy is correct for that particular formulation, the IAEA NP-T-3.6 document stipulates that an accurate activation energy is essential for Arrhenius type tests [47]. If a value is obtained from the literature or manufacturer, the data source should be provided. If the activation energy is unknown or un-reliable, a suitable series of tests to establish an accurate activation energy is recommended. If timescales do not permit such a series of tests, an activation energy which is as low as is reasonable should be used. The IAEA NP-T-3.6 document advocates an activation energy value of ~63 kJ mol^{-1} where experimental determination is not feasible.

The use of excessive thermal acceleration factors is not recommended. Therefore, the choice of ageing times and temperatures for Arrhenius testing should be made in an appropriate manner. An acceleration factor of 250 is suggested to be the maximum allowable for safety related equipment in Swedish plant, the documentation supporting this guidance is available through the IAEA INIS NCL collection store [48].

4.5.3 Combined radiation and thermal environments

Synergy effects and data such as those shown in Figure 14 suggest that where polymeric seal materials are exposed to both heat and radiation in service, sequential testing (for example by carrying out an Arrhenius thermal test followed by a room temperature radiation test) may not be representative [46, 49]. Such an approach can underestimate the damage that can develop in a polymer under combined ageing conditions. If combined ageing conditions are expected for polymeric seal materials in safety related nuclear applications, a combined radiation/thermal ageing approach is suggested.

Such an approach could involve spot check type tests (for example use of a single low radiation dose rate at a number of different temperatures) to establish whether synergistic effects are strong for certain seal materials compared to sequential test data. Spot check data may also be used for comparison against pre-existing model data for specific seal formulations, for example the SEALS model available in the UK.

If sequential test data are the only data available for the seals in question, a robust justification would be suggested to support these data in terms of their use for a safety related application in a multi-stressor environment.

4.5.4 The use of margins

During the life of a nuclear facility, there could be instances where the local environmental conditions become more demanding than the original design conditions used to qualify seals and components. The concept of postulated initiating events (PIEs) is used to describe occurrences that can affect the operating conditions of a nuclear plant (especially nuclear power generation plant) [50]. PIEs include events that might be expected to occur occasionally such as loss of off-site electric power and others which should not occur but are theoretically possible such as a Loss of Coolant Accident (LOCA) which could result in activity release (see Section 5 for more detail about LOCA). A detailed discussion of PIEs is beyond the scope of this document; however, the occurrence of a PIE is likely to increase the severity of the environmental conditions on a component and thus the level of ageing it may sustain.

As PIEs may result in environmental conditions outside the normal operating conditions of the plant, an EQ assessment needs to account for such occurrences, and this is usually achieved by the use of margins or conservatism. An example of a margin, as defined in the IEEE 323-2003standard for example, considers the total radiation dose that a component might receive over its design lifetime and adds a 10% margin to cover for PIEs [40], please see Section 4.2.1. In a similar manner the peak design operating temperature during an EQ test may be increased by 8°C during the thermal ageing component of the test.

Whilst the use of EQ margins is recommended and offers additional confidence that a component will maintain functionality over its service lifetime, attention should be drawn to potential claims that the margins applied during accelerated EQ tests could be used to offset factors such as dose rate effects or inappropriate choice of activation energy.

5. Seal performance under postulated accident conditions

When assessing the potential for accident conditions within a nuclear facility, the terms DBE (Design Basis Event) or DBA (Design Basis Accident) are most usually referred to. The Nuclear Regulatory Commission in the USA defines a DBA as *"A postulated accident that a nuclear facility must be designed and built to withstand without loss to the systems, structures, and components necessary to ensure public health and safety*". In most cases the DBE/DBA takes that form of a postulated LOCA. However, the nature of any postulated accident in a nuclear power plant will be defined by the operating conditions of the facility. For example, LOCA will be applicable to nuclear power generation plant such as BWR, PWR and other designs such as CANDU.

In other applications such as radioactive material transport flasks, accident simulations associated with fire or impact are appropriate. In nuclear reprocessing plant, accident conditions, if applicable, will be defined by a specific rather than a generic simulation process.

In the EQ processes described in Section 4, safety related equipment must be shown to be able to withstand operating conditions for its service lifetime plus a DBE. Possibly the worst-case scenario therefore is likely to be a DBE towards the end of the plant's lifetime when many susceptible components have a degree of ageing associated with them. This is why the EQ process involves accident testing on aged rather than newly acquired components. Consequently, it is suggested to be appropriate that where possible, any accident testing for safety related applications should be carried out on seals that have received accelerated ageing which is representative of long-term service conditions.

5.1 Nuclear power plant

The conditions that could be experienced by in-containment safety related components during a LOCA are expected to be severe. They will probably involve exposure to accident radiation doses at high dose rates plus high temperature and pressure transients. An example of a typical qualification and accident simulation for a seal material is described for an expansion joint seal in a CANDU plant [51]. The seal was subject to an initial pre-ageing sequence as defined by EQ standards and then postulated accident conditions involving an additional radiation dose plus a plant-defined thermal and pressure transient.

During the thermal /pressure transient part of the process (i.e., the LOCA simulation), the joint seal was mounted in a specially designed frame which was placed in test chamber. The special frame allowed the seal to be compressed during the simulation to ensure representative test conditions. The LOCA simulation was started at 35°C and super-heated steam injected into the test chamber such that the seal was subject to the temperature/pressure profile shown in Figure 15. The seal was sprayed with soap solution to visually identify leaks and although instrumentation suggested low leakage at the low-pressure stage of the profile, no leaks were observed visually. The seal was found to be leak tight at the end of the LOCA test and the torque associated with the original compression of the seal was confirmed, thus indicating a successful test.

The profile shown in Figure 15 reflects the postulate conditions for CANDU plant design. Different reactor designs will feature different temperature and pressure transients. For PWR/BWR designs, there is an IEEE standardised LOCA profile which has been historically applied for electrical equipment [52] and components such as pumps and valve actuators [53] which will incorporate seals. The same IEEE EQ protocol has been applied to Sizewell 'B' in the UK [54]. The environmental conditions associated with the postulated pressure and temperature transients laid down for the PWR/BWR profile are shown in Figure 16. These conditions are significantly more onerous than for the CANDU designs where the maximum temperature and pressure during the transient for the PWR/BWR design is 174°C and 800 kPa compared to 130°C and140 kPa for CANDU [47, 5247]. Furthermore, in defence applications, where PWR reactors may be utilised in limited spaces, initial postulated pressure surges are expected to be even higher than 800 kPa.

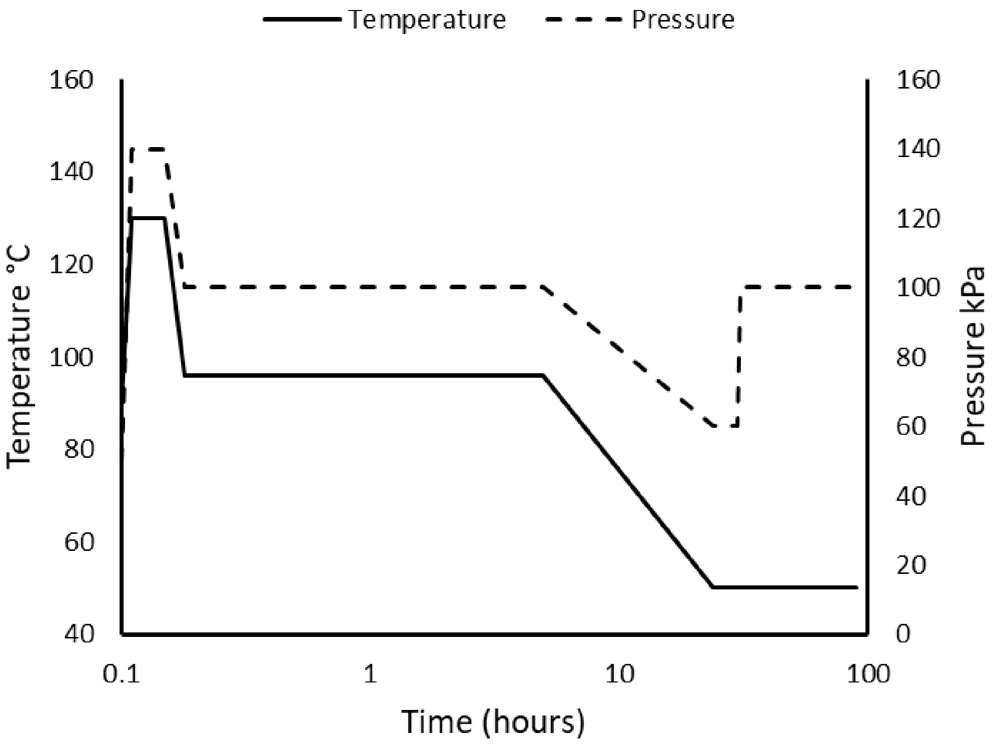

Figure 15 LOCA time/temperature/pressure profile for a component in a CANDU facility.

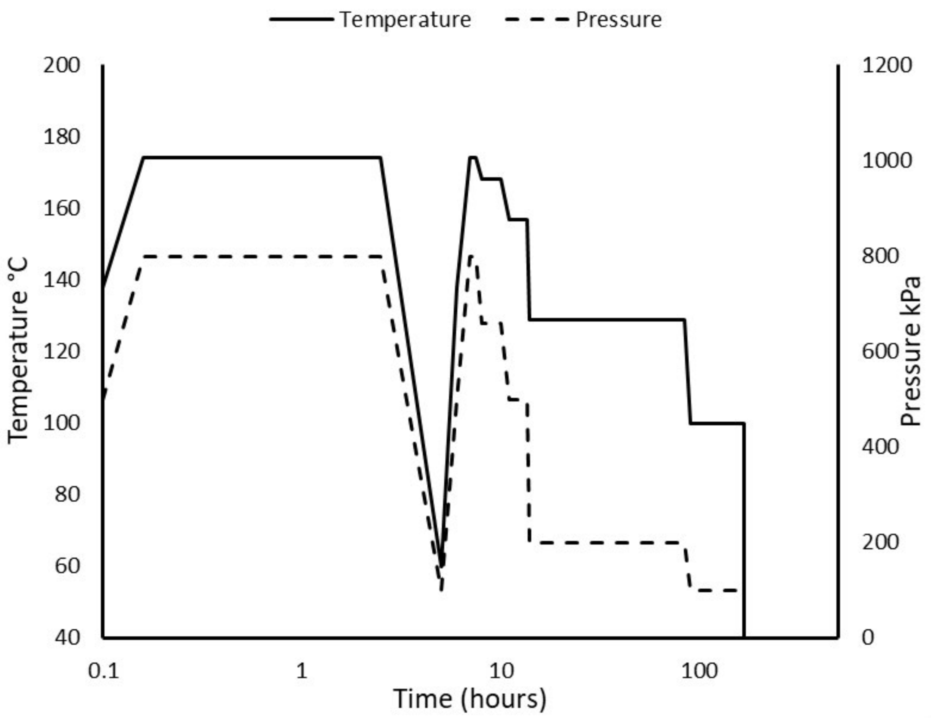

Figure 16 LOCA time/temperature/pressure profile for a component in a PWR/BWR facility.

Clearly, to demonstrate the suitability of seals for safe utilisation in nuclear power generation plant, pre-ageing of the seals before LOCA tests is necessary to capture any ageing that occurs in the seal over its service lifetime which might affect its LOCA survivability. Furthermore, each reactor system design will have its own characteristic LOCA profile which must be incorporated into the test conditions used to assess of seal functionality during accident conditions.

Ideally, the large radiation dose that is received be a seal during a LOCA scenario would be applied during the transient phase. This is normally impossible with most irradiation facilities. However, there are some facilities which are capable of carrying out LOCA simulations on significantly scaled down test components. It is suggested that where an appropriate justification can be made for scaled-down experiments, combined irradiation/transients may be favoured to arrive at as comprehensive and representative a LOCA simulation as possible.

5.2 Transport flasks

The seals in radioactive material transport flasks are unlikely to receive a radiation dose that will affect long-term sealing performance. The ageing that is likely to occur in these flasks is expected to be primarily associated with thermal ageing due to insolation, for example, during periods of inactivity. In the unlikely event of an accident occurring during the operational life of such a flask, there are IAEA regulations which must be followed to account for accident conditions.

The regulations that govern the transport of radioactive material in the UK are based on standards developed by the IAEA in SSR-6 [11]. The IAEA regulations are prescriptive and apply internationally to enable the safe transport of packages across international borders.

In order to obtain design approval for a transport package, RAM transport organisations are required to demonstrate that the package design is compliant with the regulatory requirements specified in SSR-6 [11]. The requirements include allowable leakage rates for each radionuclide which are applicable under routine (incident free), normal (minor mishaps) and accident conditions of transport. Thus, where seals form part of the containment boundary, justification that the leakage across the seals is within the allowable limits is required.

For packages containing higher activity material (Type A, B, and C packages) testing requirements to represent accident conditions of transport include a drop test of at least 9 m. For Type B and C packages, there is an additional requirement to demonstrate withstand against a thermal environment equivalent to that of a hydrocarbon fuel–air fire at an average temperature of at least 800°C for thirty minutes. For Type B(U) packages, IAEA (666) in SSR-6 specifies a design ambient temperature range of −40°C to +38°C. For Type B(M) packages, where transport is restricted to surface transport within, and in waters immediately surrounding, the UK, then in accordance with IAEA (667), an ambient temperature range less stringent that the IAEA generic requirements may be used by agreement with the competent authority [11]. However, where this is the case, the relaxed temperature range will become an operational limit applicable at all times during storage and transport of the container.

The drop test is used to simulate an impact during transport accident conditions. A special test rig is available in the UK that can carry out 10 m drop tests on candidate flask prototype designs utilising a 4 metre-deep impact block [55]. The flasks are carefully instrumented using an array of transducers to measure deceleration at critical locations in the flask to generate data that can be used to model seal functionality.

Specialised, instrumented test rigs have been developed to simulate seal behaviour when compressed in a flask exposed to fire conditions. The test rigs will be specific to the flask design and a test rig design incorporating a double O-ring seal arrangement has been utilised in the UK to characterise some flask designs, in line with IAEA recommendations [56]. This arrangement involves a stainless-steel lower flange with double dove-tail O-ring grooves machined into the sealing face. The upper flange has pipe fittings at the centre of the flange and also at a position directly above the interspace between the two O-rings. This allows transducers to be fitted enabling the pressure to be measured in the test rig main cavity and the double seal interspace during a test [56].

The stainless-steel flanges are mounted in high heating capacity blocks so that the flange temperatures can be raised rapidly. This enables a fast temperature ramp and transient at the O-ring positions that would be typical of the temperatures seen by the seals during a fire. A postulated thermal transient for a UK flask design is shown in Figure 17. This transient was derived from a detailed thermal analysis carried out to determine the temperature profile at the seal positions in a type B(U)F flask for the duration of a postulated accident as defined by IAEA SSR-6 with an appropriate post-accident cooling period [11]. The step-change temperature profile in Figure 16 was used to programme the temperature control equipment to follow the expected seal temperatures over the timescales of a fire accident and ensure that a conservative assessment of seal performance was carried out. The time and temperature envelope in Figure 17 captures the conditions predicted at the seal positions during accident conditions for a B(U)F flask with a nominal initial flask load of 28 kW. It should not be confused with the external 800°C temperature fire accident profile defined in IAEA SSR-6 [11]. In a fire that could ensue during accident conditions the maximum temperature and duration of the associated transient will also depend on the nature of the package materials (e.g. wooden shock absorbers in some package arrangements that could add to the thermal load at the seal location).

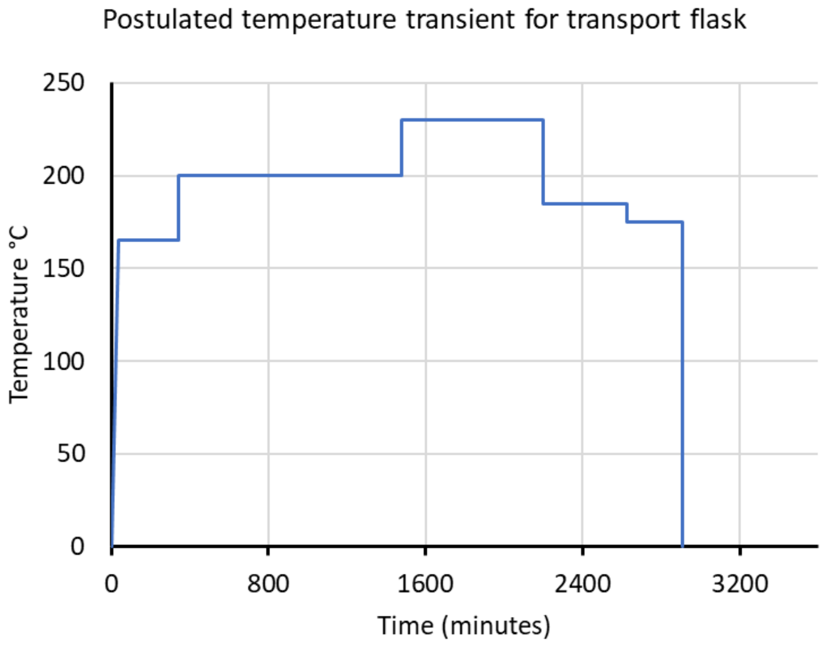

Figure 17 Postulated thermal transient representing accident conditions for a Type B(U)F radioactive materials transport flask.

Leak testing is an important method of assessing seal functionality during simulated accident tests. The inclusion of a pressure measurement capability allows cavity and interspace pressures to be monitored throughout the thermal transient. Standardised leak rates (SLR) for the container seals can be calculated from any reductions in pressure that occur as a function of transient time to ensure that they fall within regulated boundary conditions. Clearly, the methodologies adopted during leak testing should include the highest standards of cleanliness. The inclusion of dirt or other foreign matter on seals and surfaces during assembly of test equipment is likely to result in the detection of a leak which is not the result of problems with the seal itself. More detail on specific methods of leak testing in packages may be found in ISO 12807:2018 [57] and [58].

The stainless-steel flanges can be designed to allow pre-ageing of the O-ring seal to be carried out and, furthermore, shims can be introduced to simulate flange distortion associated with impact/thermal distortion. This flexibility allows a full assessment of the seals' functionality during a fire scenario, whether the seals are new or aged. In practice, seals will be expected to be replaced routinely but, where extended timescales might occur between replacements, testing of pre-aged seals provides a comprehensive assessment of seal functionality [59].

Figure 18 shows two pre-aged EPDM O-ring seals after exposure to a thermal transient of maximum temperature of 195°C and cavity pressure of 52 bar, representing the conditions inside a flask with an initial flask heat load of 20 kW [60]. A shim of 1.25 mm thickness was introduced to produce a gap between sealing faces representing distortion during accident conditions. Little or no extrusion of the seal was observed for this material but the magnified image shows hardening of the outer seal at its external edges associated with skin formation. Slight extrusion of the inner cavity seal can also be seen in Figure 18, but no significant leakage was observed.

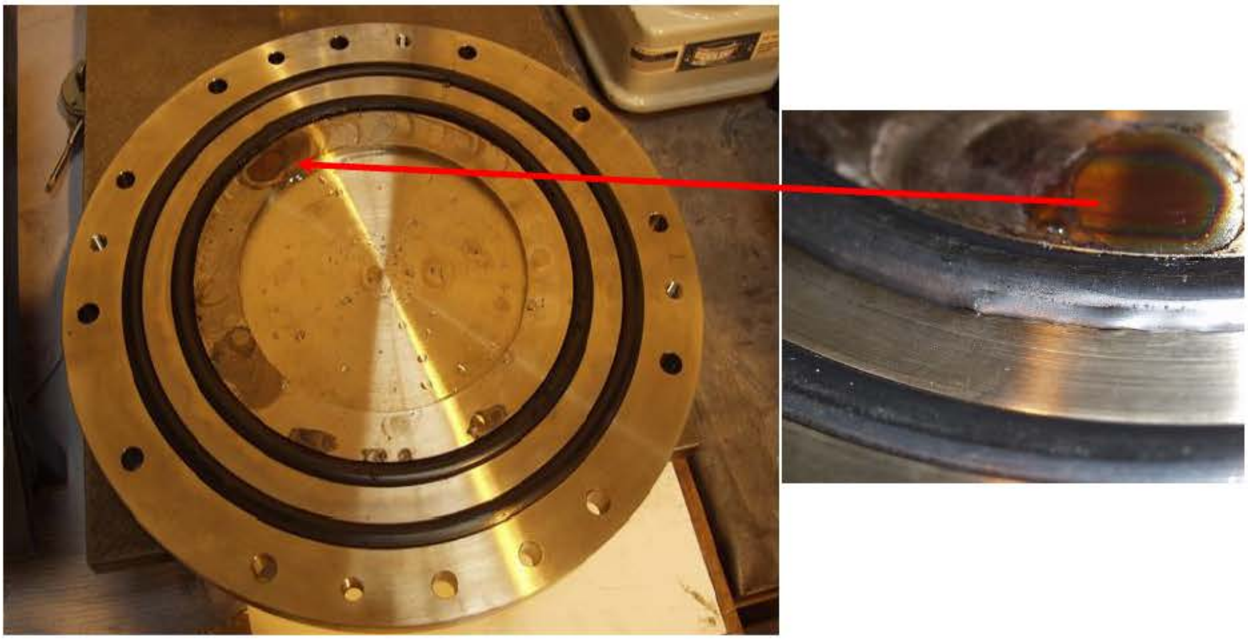

Figure 18 Pre-aged EPDM 30H flask seals after a thermal transient to 195°C representee of a 20 kW initial heat load.

Similar experiments were carried out on FKM fluorocarbon seals in the same test rig and the condition of the seals is shown in Figure 19 [61]. In this case the maximum temperature was 204°C with a cavity pressure of ~42 bar, this corresponds to a higher temperature but lower pressure than used for the EPDM seal in Figure 18. There was a higher level of extrusion of the inner FKM O-ring compared to the corresponding EPDM seal, but in this case the spacing shim was thinner, 0.3 mm, which would have caused more squeeze on the FKM O-ring hence higher extrusion. It was also observed that significant corrosion had occurred on the stainless-steel flange faces, Figure 19, this was attributed to FKM degradation products.

The allowable leak rates for different flask designs are specified in SSR-6 [11] in terms of allowable activity release. For each flask design, there will be a requirement to determine the allowable leak rates of radioactive gaseous, liquid and particulate species from the amount of radioactive payload and its nature (e.g., solid, liquid or gas).

Generally, in practice, the leak rates below (as SLR) are the standards that would need to be demonstrated to signify that type B(U), B(M) and C packages are leak tight, SSG-26 [12]:

- For flasks carrying liquids or gases, the acceptable SLR is 10^{-8} Pa m^3 s^{-1} (10^{-7} bar cm^3 s^{-1}) at a pressure differential of 10^5 Pa (1 bar);
- For flasks that carry only solids, the acceptable SLR is 10^{-6} Pa m^3 s^{-1} (10^{-5} bar cm^3 s^{-1}) at a pressure differential of 10^5 Pa (1 bar).

If these SLRs cannot be obtained, a greater SLR may be justified by agreement with the appropriate competent authority after consideration of the parameters relevant to the containment in question.

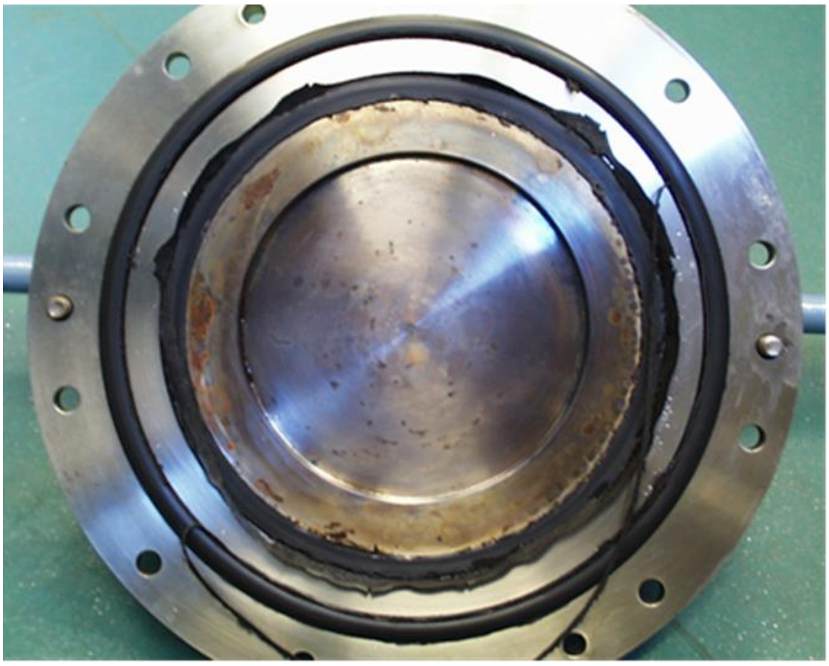

Figure 19 Aged FKM flask seal after a maximum of 204°C and a cavity pressure of 42 bar.

6. Finite Element Analysis

6.1 Introduction

At its simplest the approach toward modelling of seals, irrespective of material type or product form, is no different for any other type of finite element analysis (FEA). That is, there is a physical problem that needs to be understood and finite element modelling (FEM) is being used to aid that understanding. In such cases the basic modelling approach is the same as that expected for any stress analysis and is summarised as comprising the following aspects:

- A mathematical model is developed:
    - A geometric representation of the seal and surrounding structure(s) is made using finite elements (the 'mesh');
    - Appropriate material models and properties are applied to the various components;
    - Component interactions (e.g., contact) are defined;
    - Boundary conditions and loadings are defined.
- The mathematical model is solved for the given loadings;
- The solution is post-processed and the results used to understand the physical problem.
- Appropriate validation and verification is carried out.

So, in considering seal modelling, the majority of common FEA approaches and expectations are unchanged and guidance can be found in publications from NAFEMS or TCSC [62, 63, 64, 65]. The aspects that differ from, for example, modelling a pressure vessel or a piece of pipe work, will largely come down to the approach toward modelling the seal itself and the material model applied which will be driven by the analysis objectives. These and other aspects are considered below.

In the discussion below 'seal' is used generically to encompass rubber or elastomeric seals, metallic and composite seals as well as gaskets. Where discussion of specific aspects is presented this will be qualified. Furthermore, an assumption has been made that the analyst is familiar with the basics of FEA to ensure the discussion is focused on the modelling of seals with specific detail of commands etc. not presented as this varies significantly from FEA code to FEA code.

6.2 FEA Codes

There are a wide range of FEA codes available commercially and in-house that are capable of modelling a range of linear and non-linear behaviours. Some examples of commercial FEA codes include ABAQUS [66], ANSYS [67] and MARC/NASTRAN [68].

A review of FEA codes is not presented here as the capabilities for modelling seals whether elastomeric, metallic, composite or other forms will vary dependent on the material models, element types and mathematical solvers available within each code.

At a high level most analysis codes in relation to modelling seals will typically offer the following:

- 2D and 3D general element types for representing seals (predominantly solid continuum elements, but could include shells or beams);
- 2D and 3D special purpose elements e.g. gasket and gap elements;
- Contact methods to allow for seal interaction with surrounding structures;
- Material models including;

  - Elastic;
  - Non-linear material models including, for example, the hyper-elastic Mooney-Rivlin, Ogden and Gent models, which often allow for the direct use of seal test data;
  - Viscoelastic (time dependent) models.
- Non-linear solvers for:
  - Static analysis;
  - Dynamic analysis.
- Sub-Modelling.

In the discussion below, the FE code ABAQUS has been used to provide some specific examples illustrating discussion points.

6.3 Defining the Modelling Approach – the Analysis Objectives

When modelling a seal, the analysis objectives need to be understood as these will define the modelling approaches. It should be recognised, as with all FEMs, that the greater the complexity (detail, material models, non-linearity etc.) the more likely for error and the harder it is to verify and validate the model. Therefore, if the seal can be ignored because the interest is not in the seal behaviour but rather, for example, separation of mating faces then modelling becomes much simpler.

This leads to a simple question, what is the objective of the analysis? That is, is the interest in the bulk structure behaviour or in the seal itself? In the former, simpler FEA approaches can be taken whereas for the latter the seal is modelled with all the associated complexity.

Considering the case where the main structure is the focus, the seal does not have to be modelled though the analysis objective may mean there is a need to extract data relating to seal operation. There are two approaches; in the simplest approach if the seal is of no interest i.e., the concern is the main structure, then typically, given the differences in stiffness due to the relative size, strength and elastic modulus of the seal compared to the main structure, the seal is not modelled. For example, for a ductile cast iron intermediate level nuclear waste container drop analysis, the seal can be ignored as the container is not likely to be affected by the seal. However, there may be cases where the difference in stiffness between the seal and the structure is limited such that the seal itself may act to resist any imparted loads, for example, where a metal or elastomeric O-ring is used to seal between thin-walled components. In such a case the seal cross-section dimensions may be of a similar size to or a significant percentage of the container wall thicknesses. Hence the relative stiffness difference may be reduced; in this situation the seal needs to be modelled.

The other approach is where the main structure is of concern but some behaviour e.g., separation of a lid from a container is of interest e.g., a sealed waste storage container under impact loading. In the static condition the lid is bolted down to the container body and the seal compressed by a set amount. However, under an impact load due to, for example, being dropped, the load could cause the lid to move or try to separate either instantaneously or permanently whereby permanent deformation after the event may lead to the lid not sitting correctly. In this type of investigation, the focus would be on how much separation has occurred and could the seal accommodate it, i.e. will the seal spring back to maintain its sealing function. Therefore, it is only necessary to understand the level of separation between the lid and body and comparing this with the level of seal deformation. Similarly, under thermal loading, for example a fire, thermally induced stresses could lead to distortion and leakage. It should be recognised that in these cases the issue over seal vs main structure stiffness also applies.

Where understanding the seal behaviour under single or repeat loadings or where significant time dependency is a concern the seal will have to be modelled explicitly utilising 2D or 3D element techniques with appropriate element, materials models and solution types selected. An example of such a situation may be where a container retains the same seal for a significant period during which the seal may see cyclic loads and also experience degradation which needs to be understood.

The examples above have considered containers but the approach can also be applied to other components e.g. pressure vessels, pumps, valves etc. where seals are utilised. From a FEA perspective the type of component application is arguably less important than how the seal is to be considered.

In considering the above discussion, then Figure 20 shows a simple flow chart representing the different approaches outlined where the modelling approach depends on the FEA objective.

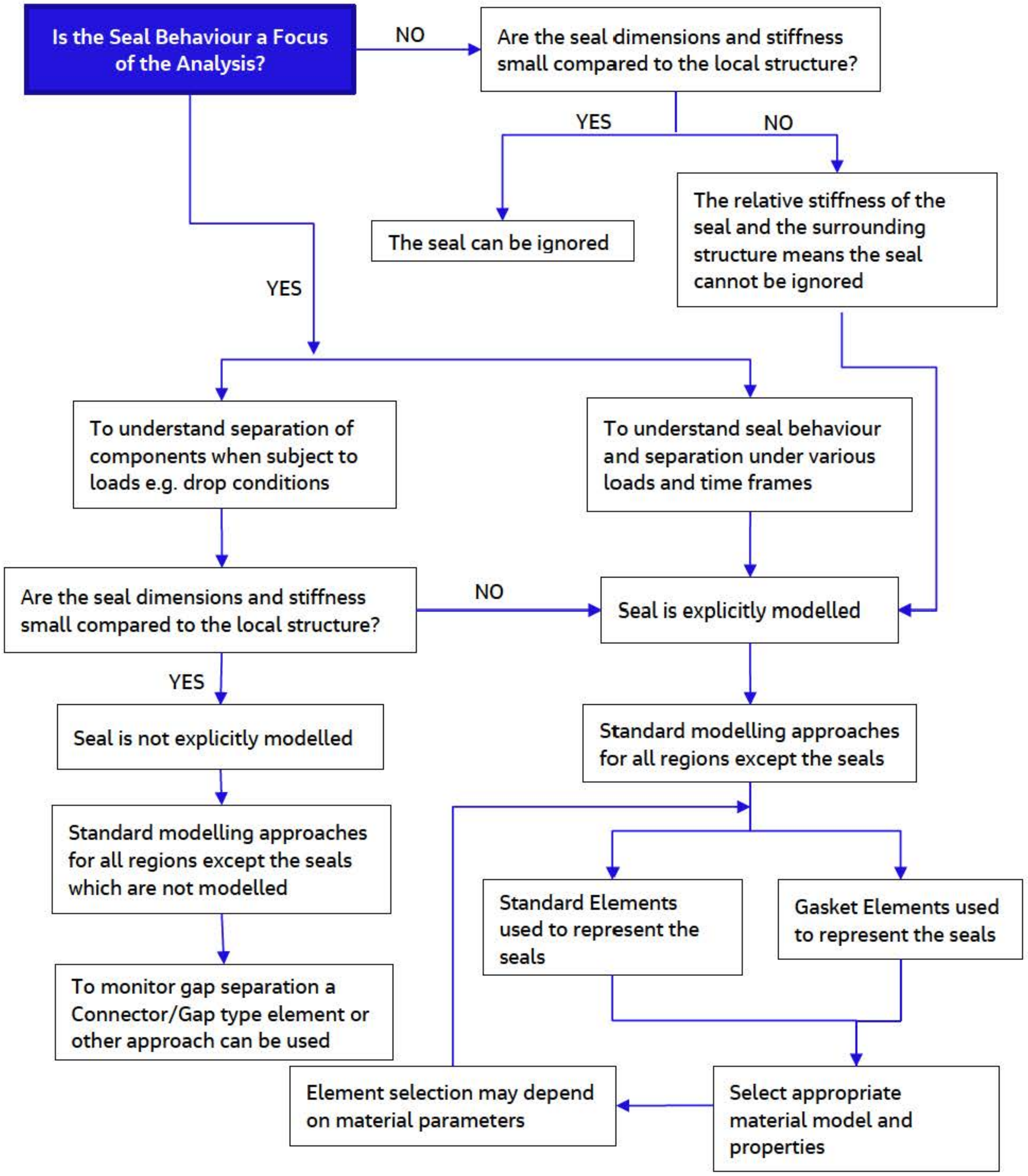

Figure 20 Selection of Modelling Approach.

6.4 Modelling Approaches

This section looks at modelling approaches when considering seals with the focus being on mechanical behaviour i.e. stress analysis as the major concern is deformation and whether the sealing function is maintained. Discussion is presented regarding general structures i.e. a container and lid and specific seal modelling representations. Some discussion regarding other analyses is also included.

6.4.1 General Structures

6.4.1.1 Element Types and Modelling

In practical terms the structure surrounding the seal would be expected to follow standard FE modelling approaches where the mesh would use standard element types e.g., ABAQUS C3D8R linear brick or C3D20R quadratic brick elements with sufficient mesh density to predict the behaviour adequately given the loads applied and any contact conditions, whilst also ensuring that the results data is appropriate. As such, if the seal is not of interest, then no additional requirements have to be considered. Such guidance on model development is available in the various documentation supplied with the FEA codes as a starting point. FEA code guidance can be very generic and is typically supplemented by the user’s experience and also corporate guidance to ensure adequacy in practical application.

If the seal is of interest in some way, then there are two areas which may lead to additional requirements. Firstly, where the seal is not modelled but component separation is of interest then, adequate mesh density will be required on the parts of the model that will be used to allow separation to be evaluated and the meshes will need to match to make evaluation easier. This is discussed further below; see ‘’Separation Models’.

If the seal is modelled, then it is likely that around the seal a ‘contact’ approach will be used in the FEM to define the interaction. This approach will allow the seal to move, compress and interact under assembly and other loading conditions. In such cases the local mesh density of the structure and the seal will need to reflect the expectations outlined in the relevant analysis code for contacting bodies. The ideal situation is that both have the same mesh density in the surfaces of contact, but if there are different mesh density, the finer mesh should be in the side of the softer part. However, it should be realised that because the seal behaviour due to the material models can be complex, mesh sensitivity studies may be required to ensure the interaction is adequately represented and that the seal response is appropriate. Element selection aspects are discussed further below; see ‘Gasket Models; and ‘Seal Models’.

The above discussion is applicable to any analysis type whether thermal, impact or creep for example. Similar standard approaches will be needed for the general structures for all analysis types i.e. select the right element type, density, material model etc.

6.4.1.2 Assembly Loads

On a general point, any bolt or other assembly loads that clamp a seal in place, whether the seal is modelled or not, are of interest. As such they should be monitored during the analysis for any relaxation of the assembly load as this can indicate;

1) The potential for a short-term leak to occur during a dynamic loading event due to relaxation of the load;

2) A permanent relaxation of load at the completion of the loading event may indicate a potential leak path or at least a reduction in sealing capability.

The method for monitoring assembly loads will vary depending on the exact analysis type and the FEA code being used. Criteria that could be used to monitor behaviour include bolt loads and/or contact pressures. For example, ABAQUS and MARC both offer a specific methodology for applying bolt loads which ensure that a specific bolt force is applied. ABAQUS requires the definition of a pretension section and a force representing the target bolt load. In this case, after applying the bolt load the section is ‘fixed’ so that as operational loads are applied the FEA code does not try to reapply the bolt load. Although ‘fixed’, as other loads are applied the bolt force may increase or decrease in response and this can be monitored offering an indicator of whether seal behaviour may be impacted.

6.4.1.3 Material Models

The basic materials models applied to the general structures, which are typically metallic, will be those reflecting the analysis being considered. Therefore, properties such as coefficient of thermal expansion, conductivity, elastic modulus, Poisson’s ratio and in some cases plastic or dynamic material properties are needed depending on the analysis aims. These properties are likely derived from either specific test of materials or handbook data. Von Mises yield criteria and isotropic or kinematic hardening material models are commonly used.

6.4.2 Separation Models

6.4.2.1 Element Types and Modelling

In this approach the objective is to model the relative separation of, for example, a lid and a flask under load. There are two parts to this approach;

1) A route for monitoring the relative displacement of the lid and flask is required at specific points around the seal without imparting any stiffness into the structure that limits behaviour of the components being modelled.

2) As discussed above, monitoring of the bolt loads used to originally clamp the lid to the flask.

In terms of monitoring displacement there are a variety of means with different levels of complexity in modelling and/or in post-processing. The lid and flask will utilise the standard modelling approaches discussed above. Options to understand separation include monitoring the displacement at specific nodes throughout the analysis, using very weak springs or special elements such as multi-point constraints or connectors to monitor relative separation. The ABAQUS connector element CONN3D2, for example, allows the relative separation of two nodes (one on the lid and the other on the flask) to be directly calculated and plotted allowing ready evaluation against seal compression criteria.

In all cases the mesh density needs to be adequate to allow the separation around the seal to be monitored. For example, a three-dimensional model may require monitoring positions every 5° which would require control of the mesh density of the model. In some cases, greater mesh density may be required. Depending on the approach chosen the mesh on the lid and body have to match, after assembly and prior to applying other loads, to ensure correct alignment of a spring or a connector, for example.

In terms of a thermal analysis, in this approach the seal is so small that it considered to have no thermal impact. Similarly, in terms of expansion under temperature loading, it will be so constrained by the surrounding structure that it will have negligible impact. In terms of other analysis types, the approach is unchanged as the focus for an impact or creep analysis would still be the relative separation of the lid and flask.

6.4.2.2 Material Models

As the seal itself is not of explicit interest and not modelled, no specific material model is applicable outside of those needed for the general structures.

6.4.3 Gasket Models

6.4.3.1 Element Types and Modelling

Gaskets are typically used to seal joints between metal mating faces to prevent fluids, steam or gases from escaping; those used for car engines are the most readily identified. Gaskets are typically very thin and made using multiple layers and manufactured for specific behaviour in the thru-thickness direction. Typically, there is a sealing ring and a body that supports the ring. The thru-thickness behaviour is often very complex and non-linear as it reflects a relationship between the load on the gasket and the closure distance of the gasket.

The combination of complex material model and thickness means that modelling can be very difficult. Therefore, many FEA codes include a gasket element and material model (discussed below). Gasket elements are available for most modelling approaches e.g. axisymmetric as well as three dimensional models and analysis types. These elements are often used with thru-thickness behaviour only as the focus is on the sealing situation but they can also be modelled with transverse and membrane behaviour. The element types replicate the gasket as a single element representing the thickness of the gasket with different material behaviours and thicknesses assigned to different elements representing the different parts of the gasket i.e. the ring and the body.

These elements can be tied i.e. share nodes with the general structure or can use contact to allow the gasket to be tied to one flange surface and thus allow the other to move across the gasket and to allow separation to occur under loading. Arguably to fully replicate behaviour one of the gasket surfaces has to be a contact type to allow for movement and separation if it occurs. It needs to be recognised that the mesh density is important.

Gasket elements are available for most analysis types except for thermal analysis. For thermal analyses standard thermal elements would be used instead; the focus being to ensure a conduction path between components.

6.4.3.2 Material Model

Outside of defining the elastic modulus, the typical mechanical thru-thickness behaviour model for a gasket requires a series of loading and unloading curves representing pressure vs closure data from gasket tests with a curve being required for the ring and the body; though the body is of lesser import as it mainly functions to hold the ring in place. Typically, the data is presented and used with closure as positive that is with no load closure is zero and as the gasket is compressed then closure increases. Similarly, transverse or membrane behaviour can be specified.

ABAQUS for example expects a single loading curve and one or more unloading curves to be defined. The curves may be non-linear elastic or non-linear plastic; in the elastic form the pressure closure behaviour is non-linear but after load removal the gasket returns to the uncompressed state. In the plastic case there may be some permanent deformation present which is represented in the unloading curves.

In general, due to the non-linear through-thickness behaviour of gaskets, data is only applicable to a single gasket type. Furthermore, from one batch of gaskets to another the curves may change hence data acceptability can be questioned. Hence, the representative nature of the gasket manufacturers’ data needs to be revisited to ensure it remains valid.

Thermal expansion and creep data can also be applied to gasket elements as desired. The element formulations used mean that density is typically not modelled.

6.4.4 Seal Models

6.4.4.1 Element Types and Modelling

Seals can be modelled using standard element types, such as the ABAQUS three dimensional C_3D_8 and C_3D_{20} brick elements. However, these standard element types may not always be suitable as they may only be applicable to metallic O-rings or similar seals due to the incompressible behaviour of elastomeric type materials. As Poisson's ratio approaches 0.5 (incompressible) the standard element behaviour (displacement based) breaks down. Such breakdown is often seen as 'mesh locking' where the element distorts into shape similar to an hourglass mode, where strains are zero but large displacements occurs and very high stresses are predicted rapidly varying between elements.

So, for incompressible or near incompressible materials more complex element types are typically required for seals that are capable of accommodating behaviour where small displacements cause significant pressure changes within the element. In some cases, standard linear elements are capable of replicating near-incompressible behaviour but this would need to be demonstrated. Most FEA codes that offer a capability for modelling incompressible or near incompressible materials will offer a range of hybrid elements that incorporate additional formulations to account for the pressure aspect. ABAQUS includes a three-dimensional C_3D_8H brick element that includes a constant pressure term with more complex elements such as the $C_3D_{20}H$ allowing for linear variation of pressure across the element.

As noted in the general structure discussion above, sensitivity studies may be required to ensure that the mesh density is appropriate for the seal response. Such studies would also likely cover element choice to ensure that the element selected is the most appropriate. In this matter it should be recognised that the seal geometry is a factor so generic models may not be adequate to show the element choice is appropriate. Sensitivity studies would not need to rely on the whole structure being present or on modelling the whole of the seal to understand element choice and mesh density. Sub-modelling is an option for the modelling of seals to keep overall mesh densities manageable whilst modelling the seal region in finer detail. Adaptive meshing is also a possible technique that can be used in analyses where significant localised high deformation occurs.

There may also be limitations on element usage that have to be considered. For example, most hybrid elements in ABAQUS cannot be used in dynamic analyses potentially limiting modelling approaches.

By modelling the seal explicitly most analysis types and behaviours can be accommodated.

6.4.4.2 Material Models

There are a wide range of material behaviours that may need to be considered when modelling seals directly including;

1) Elastic;
2) Plastic;
3) Hyper-elastic:
    a. Rubbers e.g. Mooney-Rivlin and Arruda-Boyce models;
    b. Elastomeric Foams;
    c. Stress softening.
4) Viscoelastic;
5) Hysteresis.

Of the material behaviours listed above, only 1), 2), 3) b. and 4) apply to both metallic and elastomeric seals. The remainder are mainly applicable to elastomeric seals. The focus below is on hyper-elastic material properties.

In practical terms hyper-elastic behaviour can be expressed as either a series of constants or as test data with the specific model being identified as part of the material definition. Looking at the Mooney-Rivlin model, as an example, then two constants (C_{01} and C_{10}) are required to define shear behaviour and a third (D_1) to define the bulk modulus; these constants can be temperature dependent. Ultimately these constants are derived from test data so they could be supplied directly by the seal manufacturers or in the form of test data. In terms of using the test data the specific material model, such as Arruda-Boyce, has to be identified so that the coefficients can be correctly determined.

However, in terms of test data there are a wide range of options that can be used, for example, ABAQUS allows for the use of the following either singly or a combination of up to four tests to determine the appropriate constants for the selected hyper-elastic model:

- Uni-axial;
- Bi-axial;
- Planar;
- Volumetric.

It should be recognised that tests need to be set up so that the testing procedure itself doesn't influence the parameters [69]. Furthermore, these tests can be either tensile or compressive and lead to the provision of generic materials properties rather than a seal specific data set due to the need to provide adequate test specimens. As such the test may not represent the processed seal, though depending of the seal size it may be possible to generate specific seal data that account for the seal manufacturing process. Furthermore, material batch to batch variation will affect the parameters and any generic data sets or coefficients need to be shown to be valid. A key aspect with directly using test data will be the smoothness of the data set; if the various curves are not smooth it is unlikely that a valid set of coefficients can be generated.

Separately, whilst specific seal testing may not be possible due to size limits, the use of FEA to represent and compare against tests of actual seals in simple situations will provide confidence in the validity of the material model.

6.4.4.3 Calculation Issue

One aspect to consider with the seal models is the system of units; seals are normally very weak compared to the surrounding structures. This can lead to significant difference in stiffness and using an incorrect system of units can exaggerate this leading to calculation issues. Whilst less likely with current computer systems and FEA software, utilising systems of units such as the mm-MPa-tonne-sec system rather than pure SI units will reduce the likelihood of stiffness effects causing significant calculation issues.

6.5 Modelling Degradation and Other Complex Effects

In the preceding discussions whilst behaviours such as creep or temperature effects can be considered, complex interaction and changes over time are not fully reproduced. In a creep analysis, there are creep properties that are linked to time dependent behaviour but the loading and unloading curve used to derive, for example, the Mooney-Rivlin coefficients is unlikely to be linked to long-term behaviour i.e., it will reflect a specific point in time. In practice such curves are likely to be for new materials only.

Degradation of seals, particularly elastomeric ones, can occur due to excessive temperature variations, ageing over time or irradiation. This may cause seals to lose elasticity and develop permanent 'set' or otherwise physically degrade. To correct for degradation effects that impact seal performance more complex models may be required. This likely leads to the use of a user material model, typically in the form of a purpose written subroutines, which can encompass a wide range of material properties and degradation models as needed.

User materials are only as good as the underlying data set; therefore, a significant amount of testing may be required of seals at different points in time for the application of interest. This means that it may not be possible to decouple some effects e.g. thermal and irradiation. This also reflects the likelihood that long-term seal behaviour will be from testing operational seals producing a time dependent all-encompassing 'effects' model rather than a series of models exhibiting a full mechanistic understanding of each time varying property.

6.6 Summary

In summary:

1) Generically the approach toward modelling seals and associated general structures in FEA is no different to those for any component.

2) Seals do not always have to be modelled explicitly. This is dependent on the overall analysis objectives and the relative stiffness of the seal to the general structure.

3) Where seals are modelled either as a gasket or explicitly then:

- Meshing and contact considerations may greatly increase the FEA run times
- Material property test data maybe required, particularly where manufacturers data is unavailable
- A variety of material models are available for elastomeric seals in FE codes that can directly use the test data
- Consideration of degradation effects may lead to the use of more complex user material routines or conservative treatment of the seal behaviour

4) Care over the system of units is needed to ensure the calculation accuracy.

5) Validation and verification need to be considered.

7. Overall summary and suggested knowledge gaps and uncertainties in the use of seals in the UK nuclear industry

One of the aims of this document was to highlight any gaps in the current knowledge and understanding of the ageing and functionality of seals across the nuclear industry. Whilst there are clearly considerations to be made in terms of the use of metallic seals in the UK nuclear industry, the correct choice of metallic material will normally ensure reliable operation and stability in the potentially aggressive environments in service.

Seals produced from organic polymers, however, are significantly less stable in nuclear environments and require detailed assessments of their tolerance to environmental stressors such as heat and radiation. The numerous factors that can affect the stability of these materials form the rationale behind the weighting of the guidance and information provided in this document towards seal ageing tests and modelling.

The ageing characteristics and mechanisms of organic polymers can be very complex and are not always well understood; although significant advances have been made in this respect over the past few decades. One of the clear outcomes of this document is that there is a disparity between the current state of knowledge and the methods used to qualify seals for nuclear applications. This is particularly applicable to new nuclear facility constructions which might have life expectancies of 60 years. The reliability and accuracy of the accelerated testing used to assess and justify seal selection becomes more and more important as longer operational plant lifetimes become the norm.

Even with a continuously improving understanding of polymer degradation processes and also continuously improving in-plant operational experience, there will be knowledge gaps and uncertainties. This especially applies to the selection of polymeric seals and their long-term reliability.

A number of areas of interest are described in the following text that highlight perceived knowledge gaps and potential uncertainties associated with the use of seals in the UK nuclear sector. These subject areas have been recognised by the authors and internal reviewers of the document and been presented generically and at high level. They are intended to raise awareness and contribute to an even stronger reliability and safety culture for the use of seals in the industry.

7.1 Seal obsolescence

One of the major uncertainties associated with the use of polymer seals in the nuclear industry is obsolescence. This may manifest itself in a number of ways, two of which are:

- Where manufacturers cease production of a polymer;
- Reduced availability of additives or base materials in the supply chain, Section 2.5.

Although the UK nuclear industry has, in the SEALS utility, a good source of data for elastomeric seal materials which are in current use; going forward, there could be instances where manufacturers withdraw certain elastomer types. A relevant recent example was the withdrawal of a nitrile base polymer, Zeon Nipol N36C50. This base polymer was used in the Foxglove elastomer, a declared formulation nitrile rubber compounded by James Walker and used by EDF UK and Sellafield Ltd. This was also one of the materials fully characterised in the SEALS utility. Foxglove has now been superseded by a qualified replacement elastomer – Wolfglove. Furthermore, manufacturers will sometimes change additives in elastomer compounds through lack of availability or for commercial reasons. Even slight changes in elastomer formulation can have significant effects on polymer stability, particularly in radiation environments, Sections 3.1.8 and 4.2.

There appears to be little definitive guidance available on how to mitigate such events across the nuclear industry apart from completely re-qualifying a seal. However, one method of mitigation is to hold a series of qualified variants of a generic seal type for specific applications. Even in this case, care may be required because qualification test methodologies are not always representative and could lead to the selection of variants that are not suitable for some applications.

7.2 The potential for non-destructive testing (NDT) of seals in-situ

In-situ, non-destructive testing of seals in nuclear environments to assess their current condition against EQ data could be very desirable for some applications. This capability could be particularly useful where disassembly of equipment for seal replacement could present operational problems. Furthermore, if scheduled seal replacements could be scaled back because they are still in good condition, there could be significant commercial benefits to be gained.

In-situ testing is a topic that has received a good deal of attention and evaluation for the condition monitoring of polymeric cable materials in nuclear power generation plant through the IAEA. There have been co-ordinated research programmes in the cables area initiated by the IAEA and the issue of corresponding technical documentation detailing EQ and methods of test.

Polymeric seals have seen little attention in this respect. However, it could be of significant benefit in the long term to own a system that could deliver reliable data on the condition of seals as they are being used in plant. Feedback from the UK nuclear industry suggests that research and development into a method of in-situ seal analysis is a prime requirement. Added value could also be obtained if any condition assessments could be incorporated into verified predictive models such as SEALS.

Clearly some seals will be inaccessible in many applications but some may be renewed under routine maintenance whether by direct replacement or replacement of the complete system e.g., a valve or pump. Two areas in which knowledge of elastomer ageing in service could possibly be considered and developed are:

- Initiating an ongoing test programme to characterise seals that have been removed from service. Any data generated from real time aged seal that have been removed, or still present in components that have been removed, could be compared and contrasted with the data generated from EQ activities or SEALS model predictions where applicable;
- Undertaking of initiatives to examine whether it is possible to introduce methods of interrogating seal ageing, in-situ. This will require an understanding of the scope for potential design changes in some components that can allow access to the seal material for monitoring. Clearly this would involve collaboration with component designers and manufacturers as appropriate.

7.3 Plant life extension (PLEX)

A proportion of nuclear facilities in the UK have or are in the process of applying for an extension of their originally proposed service lifetime (PLEX). For elastomeric seals used in these facilities, many of the PLEX justifications have been made using extrapolations of Arrhenius data used in previous EQ activities. However, in Section 4.3 of this document, a significant amount of attention has been paid to how the Arrhenius equation should be applied to polymeric seal materials and also how important the test conditions are for generating representative data.

Figure 12 shows how incorrect values of activation energy used in Arrhenius type testing can affect qualified life. Should there be inaccuracies in the activation energies used in previous qualification tests, the errors in qualified life made by extrapolation of data generated using these activation energies could be compounded further.

Therefore, there is scope for significant uncertainty associated with the possibility of inappropriate use or lack of understanding of the Arrhenius relationship when used in PLEX activities.

Furthermore, there could also be uncertainties in the extrapolation of EQ irradiation test data for PLEX where the dose rates that were used were high, Section 4.2.2.

7.4 Seal integrity under defuelling conditions

The EDF lifetime strategy for its UK nuclear power stations is to seek life extensions, where it is safe and commercially viable. Over recent years, the operating lives of individual stations in EDF's AGR fleet have been extended. As the older stations reach the point where further extensions are not viable, focus turns to the next phase which is defuelling in preparation for decommissioning. Part of supporting the defueling safety case may involve assessing the integrity of critical seals during defuelling activities (for example, seals at the pressure boundary or on the fuelling machines). Such an assessment would need to review each seal type, material, location and function under environmental operating conditions for defuelling activities allowing a judgment to be made on the integrity of the seals. Specific considerations should be made to seal performance under temperatures and pressures not bound by normal operation and also the condition of the seals in an aged state. For example, under low pressure defuelling conditions, pressure activated seals may not adequately seal and leakage could occur.

7.5 Retro engineering

A task often requested, typically by a duty-holder, is retrospective identification of the constituents of the polymeric compounds used to produce seals and other components which have been removed from service, normally as a result of routine maintenance or otherwise. This information is often missing in the form of material data sheets or manufacturer's product information due to age and obsolescence. However, it is often required as part of lifetime extension programmes where more information on the chemical composition of a component is required in order to correlate with physical properties and determine a residual life.

Where it may be possible to identify material type using standard laboratory techniques such as FTIR, it is almost always impossible to determine the exact chemistry of a formulation including base polymer, additives and relative ratios. It could be advantageous in this respect to explore the more recently available, higher resolution techniques that could be used to help identify the composition of these components.

Due to the critical dependence of the long-term stability of polymers on composition, a suitable methodology to identify the composition of seal and other polymers could also be used for quality control to ensure materials consistency.

7.6 The use of seals in New Build

One of the most significant areas of discussion in this guidance document has been the qualification of seals materials for the nuclear industry and how representative current EQ activities are in terms of polymeric seal ageing. Of significant importance is the reliability of and how much confidence can be attributed to current EQ policies and methodologies when it comes to polymeric components. It is understood that the EQ for HPC new build will be carried out under the 2012 RCC-E code. However, a number of the practises that are currently advocated by this code were devised in the 1970's. Since then, the understanding of polymer ageing has advanced at a rapid rate, however the methods used for EQ testing have not, especially where polymer accelerated ageing is involved. Although some of the known issues associated with current approaches to polymer testing for EQ have gained mention in some of the standards described in Section 4.1, there still appears to be a reluctance to define changes in approach that align with the current understanding.

It is uncertain whether the resistance to change is sustained by commercial considerations, for example those associated with the anticipated higher cost of more representative testing. Another consideration is that license applicants may be concerned that more representative approaches to ageing could affect regulators' views on EQ in currently operational plant. In either case, it is suggested none of these perceived issues should affect any strides towards improving EQ to enhance reliability and safety.

The current state of the art on polymer ageing is available for implementation and, although there will always be advances in knowledge, there are no clear knowledge gaps in terms of how the current understanding of polymer ageing can be implemented into EQ. The knowledge gaps, per se, are associated with how the balance between current knowledge and commercial considerations can be maintained to ensure that EQ follows the ALARP culture. Furthermore, the approach to EQ (in polymer ageing) for new build for the UK could also be identified as an area of uncertainty in terms of how testing ensures component reliability. It may also be suggested that the current EQ approach seems to lack continuous improvement when it comes to materials ageing.

7.7 Low temperature ageing of seals

Some seals may be expected to show sustained sealing performance over long periods of time at low temperatures. It has been shown in Figure 9 in Section 3.2.13, that the properties of seals can change abruptly over a relatively short temperature range around the glass transition. The restriction of polymer chain mobility below this temperature may cause changes in material effects such as creep and the development of compression set.

Some FKM Viton seals have relatively high glass transition temperatures and are used to seal storage flasks containing nuclear materials. However, these flasks could see use over extended periods of time at temperatures below freezing. There is some uncertainty over how the performance of the seals would be affected at temperatures where the glass transition may occur.

Although there is instrumentation available to measure the compression set of elastomers at sub-zero temperatures and there are data from Burnay and co-workers [34] on how the sealing characteristics of these types of seal change at low temperatures. In reality, there appears to be a paucity of information and knowledge of how seals used in the UK nuclear industry behave in the long term at low temperatures. One uncertainty, for example, is whether long term compression of elastomeric seals at low temperatures near or below T_g, affects sealing characteristics should containers be raised back to ambient or higher temperatures. Furthermore, the long-term effects of radiation on the sealing characteristics of elastomers at low temperatures is a topic that seems to have received little or no attention.

There is also a significant level of uncertainty concerned with the determination of a safety margin associated with low temperature data that can be applied to seal functionality at low temperatures. For example, the temperature taken from the TR-10 test for an elastomer, lowered further by the 8°C margin may be claimed as the lower working temperature of a seal. However, that temperature may be significantly lower than a measured Tg value or a low temperature torsion value generated by the Gehman test. Furthermore, leak rate data at low temperatures may reveal that a seal starts to lose its sealing characteristics at a higher temperature than would be suggested by the other low temperature techniques, Reference 34. These uncertainties suggest that research activities to assess the methods used to define the low temperature characteristics of seals in the nuclear industry would be appropriate - with a view to the establishment of reliable low temperature safety margins.

8. Guidance for assessment of seals for use in nuclear safety-related applications

This guidance report has been prepared with the aim of providing a generic source of information on the uses, properties and characterisation of the types of seals used in the UK nuclear industry. It is intended to be of use to assessors, regulators, designers, manufacturers and any other interested parties. However, the report contains a significant amount of information and, on occasion, the reader may be interested in addressing a specific area of seals usage, materials selection or how a seal may perform in an intended application.

This annex has therefore been constructed to help direct the reader should specific items of interest arise in respect to the qualification and use of seals. A table format has been used so that assessors, for example, can quickly associate the questions that could arise from safety submissions to the appropriate SAP (Table A1) and the corresponding report section. On the other hand, this annex can also provide duty-holders with a list of points for consideration should they wish to use seals in nuclear applications.

It should be borne in mind, however, that this section of the guidance document is aimed at providing a non-prescriptive, high-level summary of the approach to the use of seals in the nuclear industry. It is intended to assist with inspections and the judgements that relate to the adequacy and suitability of any proposed sealing arrangements in a safety related nuclear application. The information in the table is intended to be neither exclusive or exhaustive and is subject to change. However, it provides an overview of aspects of seal compliance requirements that might be examined during routine inspections carried out on the basis of sampling.

Table 4 Summary guidance for assessment of seals for use in nuclear safety-related applications

Description	Related SAPs [10]	Report Section
High level overview of operational demands and environments		
Component Safety: Categorisation and Classification Does the safety submission include appropriate identification and classification of the system/component in which the seal will be used - Where seals are claimed to deliver a formal safety function, is the seal appropriately classified on the basis of its importance to nuclear safety? Has the assessment taken this into consideration when justifying appropriate levels of material assessment/performance testing?	ECS.2	N/A
Performance Requirements in-service Has the assessment outlined the expected operational and environmental conditions that a seal/component will be required to withstand during normal operating, fault and accident conditions? For example, this may include leakage, pressure withstand or temperature withstand. Has the assessment taken this into consideration when justifying appropriate levels of material assessment/performance testing?	EKP and EDR Series	N/A

Description	Related SAPs [10]	Report Section
Consequences of Failure In the event of premature failure of the seal, does the applicant fully analyse the consequences from radiological/chemical, environmental and operational perspectives? For example, can the seal/component be readily accessed for repair/replacement? Has the designer considered what, if any, remedial action could be taken? Are appropriate safety measures in place?	EKP Series, ERL.2	N/A
Materials Selection		
Properties of seal Choice of seal material should be based on performance requirements. The properties of the seal should be assessed against the long-term performance and safety requirements for operation in the environmental conditions.	EMT.1, ENC.1	2 and 3
Seal Composition Has the composition (or formulation) of the seal been considered in terms of defining the suitability for the application	EAD.5	2.3
Material Compatibility Does the safety submission identify requirements for material compatibility? Justification should include all materials that may come into contact with the seal during commissioning, normal operation and maintenance including cleaning agents, lubricants, and test mediums. For seals used in radioactive transport packages, compatibility with the radioactive contents and package materials should be justified. Has the assessment included the production and fate of seal degradation products in the plant environment? Or, what is the impact of degradation that arise from the environment on the seal? In the case of metallic seals, compatibility assessments may also require a review of any potential corrosion effects over long-term use. (Note: Corrosion effects between dissimilar metals is not covered in the scope of this document and appropriate advice sought).	ECH.3	2, 3, 4 depending on attributes of seals
Supply Chain and Manufacturing Have the designers identified a seal manufacturer with robust quality measures to ensure consistency in formulation and manufacturing processes? How has any potential requirement for replacement over the longer-term been addressed? For example, can the material formulation be safeguarded over the longer-term?	EAD.5, EDR.2, EMC.18, MS.1	2.5.1

Description	Related SAPs [10]	Report Section
Obsolescence Does the submission/qualification plan for periodic seal replacement over the defined operational life? Does the submission consider the possibility of seal obsolescence over the longer-term?	EAD.5, EDR.2	2.2, 2.5, 3.1.4,3.3, 4, 5.2
Storage Where applicable, have the appropriate considerations been made about long term storage. Will seals storage be required to ensure supply and overcome obsolescence? Is there a defined strategy to safeguard material properties during storage?	EAD.2, EAD.5	2.5.3
Environmental Qualification		
Qualification Standards and Guidance Has the applicant clearly justified the selection and application of an appropriate standard and/or guidance documentation for use in required application? The choice of documentation is expected to be driven by the application e.g. nuclear power plant, reprocessing plant, transport etc.	EQU.1 ECS.3, ECS.4	4
Representative Testing Are the ageing conditions used for qualification tests representative? What are the justifications behind the selection of: - Ageing conditions (e.g. radiation dose rates) - Physical and chemical testing? - Use of specific appropriate ageing parameters i.e., activation energy, E_A. - The appropriate seal property assessments to ensure functionality and safe operation. Does the submission justify the use of pre-qualified or manufacture qualified seals/component? How appropriate is the approach to qualification with respect to relevant standard(s) and representative conditions in the desired application?	EQU.1, ECS.5	4.2, 4.3, 4.4
Accident Conditions Are the seals qualified so that they will survive postulated accident conditions whether as part of a component in nuclear plant or as a transport flask seal?	EQU.1, EKP.4	5
Pass/failure criteria-failure modes Is there a set of key seal property criteria that defines pass/fail status? These criteria will depend on the specific properties of the seal and how these change with ageing and whether functionality/safety is compromised.	EDR.3, EDR.4	2, 3, 4 depending on attributes of seals

Description	Related SAPs [10]	Report Section
Lifetime Margins Does the safety submission define margins to accommodate PIEs? If so, what is the justification for the use of the margins and their magnitude?	EAD.2	4.2.1, 4.54
Ageing and Degradation Does the safety submission provide justification that any ageing and degradation of the seals that occurs over their intended service lifetime will not undermine their structural integrity? Where applicable, justification should include consideration of factors such as the effects of radiation and thermal ageing on properties such as compression set and appropriate mechanical properties that apply to both polymeric and metallic seals. If seals are used outside, the adverse effects of UV, insolation, precipitation and marine environments should be considered where applicable. Where testing has been undertaken, any observed degradation of the seals would be expected to be addressed in qualification submissions and assessment of safe working life.	EAD Series	3.2
Safe Working Life Is the proposed safe working life justified by the EQ methodology and data? Have the appropriate margins been incorporated into lifetime predictions? Have modelling activities been carried out, where possible, to help justify safe working life?	EAD.1	4.4, 6.3, 6.4
Reliability		
Maintenance and Testing Where applicable, does the safety submission identify requirements for in-service testing, inspection and other maintenance procedures? Does the submission specify the appropriate test/ageing parameters for seal assessment e.g. compression set, leak rates, or other component performance parameters? The safety submission should provide justification that all specified testing methods and frequencies are appropriate to the given application with reference to allowable leakage rates or any formal claims on seal reliability over the lifespan of the seal. Justification of maintenance and testing methods should include reference to applicable codes and standards.	EMT Series	3.3

Description	Related SAPs [10]	Report Section
Key Uncertainties		
Seal Obsolescence (see previous table entry)	EAD. 5	7.1
In situ non-destructive testing of seals – can it be carried out successfully and help reduce need for un-necessary replacements?	EAD.3, EMT.2, ENC.2	7.2
Plant life extension (PLEX) – How is justification made for extending life of seals beyond original qualification? Ensure appropriate use of Arrhenius and/or model parameters to justify additional service life.	EAD.1, EAD.2, EQU. 1	7.3 (4.3, 4.22)
Seal integrity under de-fuelling conditions	EMT.5	7.4
Retro engineering -linked to obsolescence-understanding the complexity when attempting to establish the composition of seals in service – exploration of diagnostic techniques	EAD.5	7.5
The use of seals in new build – Can the current EQ codes and interpretation of qualification requirements be improved to ensure appropriate assessment of a material for the required service conditions.	ECS.3, ECS.5, EQU.1, EAD.1, EDR.2	7.6
Low temperature ageing in seals - There is a need for a better understanding of the long term ageing and performance of seals and the application of low temperature margins	EMT.1, EMT.6, EMT.7, EAD.1, EAD.2	7.7
Theoretical Modelling – Finite Element Analysis		
Modelling Approach Overall analysis objectives and modelling approach should be considered, as summarised in the Flow Diagram (Figure 20). Consider the finite element mesh, element types, loading and boundary conditions, modelling of contact, materials models and data. Validation and verification of the analysis needs to be considered.	AV Series	6.3 6.4
Material Degradation Are the effects of temperature, environment and ageing on materials properties significant?	EAD Series	6.5

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Appendix A. Tables Summarising SAPs applicability to Seals in Nuclear Safety applications

SAPs applicability to elastomeric seals (and other forms of seals) for use in Radioactive Materials Transport Packages and other Nuclear Safety applications

The Table below is a high-level review of the ONR Safety Assessment Principles, 2014 Edition, Revision 1 - January 2020 [10]. The review considers whether the identified guidance within the SAP's is applicable to situations where seals and sealing methodologies have been, or are to be introduced into a facility, system or site.

The table is not a detailed review of each piece of guidance, and only indicates whether the guidance appears to be applicable to instances where seals are considered to perform significant safety related functions. The text within the table is intended to direct further attention, or where to apply effort to understand the implications of the use of seals in nuclear applications.

SAP. Ref.	SAP. Description	Page/Para	Applicability	Comment
	Introduction/Regulatory Background	P8, para 7 and 8	Yes	One of the main roles of seals and sealing systems in the nuclear industry is the prevention of exposure to radioactive materials, harsh chemicals and fluids which may be hot/under pressure. Consequently, the use and design of nuclear sealing systems must not only comply with current UK safety legislation, standards and ACoP's but also appropriate international guidance (IAEA) as described in the main document. Seals will be required to comply with current legislation, standards and ACoPs and appropriate international guidance as listed in the main report.
	Introduction/SFAIRP, ALARP and ALARA	P9, para 14	Yes	Seals and sealing systems are required to meet the fundamental requirement to reduce risks ALARP through the application of good engineering practice. In the nuclear industry, where choices of seal materials have been or need to be made, comprehensive characterisation of the effects of environmental conditions and their long-term effects on the seals are required. These activities will be in conjunction with appropriate risk assessments carried out to identify potential limitations or weaknesses in the materials for specific sealing applications.
Fundamental principles guidance, below, has been assessed as applicable to seals in the following case:				

SAP. Ref.	SAP. Description	Page/Para	Applicability	Comment
FP.6	Prevention of accidents	Page 17	Yes	All reasonably practicable steps must be taken to prevent and mitigate nuclear or radiation accidents. Seals are expected to play a fundamental role in systems designed to prevent and/or reduce the impact of nuclear/radiation accidents. Correct choice of materials and configuration is crucial in this respect.
Key engineering principles guidance, below, has been assessed as applicable to seals in the following cases:				
EKP.1	Inherent safety	Page 37	Yes	Seals and sealing systems are used throughout different types of nuclear plant and contribute to the inherent safety of nuclear facilities
EKP.2	Fault tolerance	Page 38	Yes	Any sealing system design or seal material should not increase the sensitivity of the facility to potential faults. Appropriate materials selection is important for some applications
EKP.3	Defence in depth	Page 38	Yes	Seals must not reduce or degrade independent barriers to fault progression.
EKP.4	Safety function	Page 39	Yes	Seals which contribute to a facility safety function should be appropriately qualified and demonstrated as suitable for safe operation during service and under postulated accident conditions.
EKP.5	Safety measures	Page 39	Yes	The function and long-term stability of seals which contribute to or constitute safety measures should be understood and characterised. (Above comment to EKP 4 also applies here).
Safety classification guidance, below, has been assessed as applicable to seals in the following cases:				
ECS.3	Codes and Standards	Page 42	Yes	Codes and standards which apply to seals EQ and deployment should be applied. Appropriate consultation and conformity with correct standards and codes should be demonstrated. In some cases, justifications or additional

SAP. Ref.	SAP. Description	Page/Para	Applicability	Comment
				assessments of material suitability may be required where standards do not fully address specific applications.
ECS.4	Absence of established codes and standards	Page 43	Yes	Following on from the comment on ECS3, where there are no appropriate established codes or standards for seals, an approach derived from existing codes or standards for similar equipment in applications with similar safety significance, should be adopted
ECS.5	Use of experience, test or analysis	Page 43	Yes	In the absence of established codes and standards, the use of suitable experience, tests or analysis should be applied e.g., to devise a specific justification for analysis and/or testing based on, and representative of, the service conditions.
Equipment qualification guidance, below, has been assessed as applicable to seals in the following case:				
EQU.1	Qualification procedures	Page 43	Yes	Using an appropriate EQ process, seals and sealing systems should be qualified to demonstrate that they will perform their safety function(s) in all normal, fault and accident conditions identified in the safety case and for the duration of their operational lives.
Design for reliability guidance, below, has been assessed as applicable to seals in the following cases:				
EDR.1	Failure to safety	Page 44	Yes	Seals often form a part of safety systems (which act in response to a plant fault, to protect against or mitigate a radiological consequence). Where possible, they should be designed to be inherently safe, or to fail in a safe manner. Consideration should be given to spurious operation, unsafe failure modes and how modes of failure can be predicted or revealed and then repaired.

SAP. Ref.	SAP. Description	Page/Para	Applicability	Comment
EDR.2	Redundancy, diversity and segregation	Page 44	Yes	Redundancy, diversity and segregation should be considered in the design of seals. The relevant qualification process should demonstrate that the required level of reliability for their intended safety function has been achieved. .
EDR.3	Common cause failure	Page 45	Yes	Common cause failure (CCF) should be addressed explicitly where a structure, system or component employs redundant or diverse components, such as seals, to provide high reliability.
EDR.4	Single failure criterion	Page 45	Yes	Any seal that is the principal means of fulfilling a Category A safety function should, other than in exceptional circumstances, always be designed to meet the single failure criterion. However, seals which make a contribution to fulfilling the same safety function, but are independent of the principal system, do not necessarily need to meet the single failure criterion.
Maintenance, inspection and testing guidance, below, has been assessed as applicable to seals in the following cases:				
EMT.1	Identification of requirements	Page 48	Yes	Where applicable, the requirements for the in-service testing, inspection, frequency of testing and other maintenance procedures for seals and equipment that rely on seal functionality should be defined in the safety case.
EMT.2	Frequency	Page 48	Yes	Where appropriate and possible, seals should receive regular and systematic examination, inspection, maintenance and testing as defined in the safety case.
EMT.3	Type-testing	Page 48	Yes	Seals should be tested under representative environmental conditions before installation. The test conditions should reflect the most onerous for which they are designed including accident conditions.
EMT.4	Validity of equipment qualification	Page 49	Yes	The continuing validity of suitably qualified seals and systems should not be affected or the seals unacceptably degraded by any modification. Furthermore, validity should not be affected by maintenance, inspection or testing activities.

SAP. Ref.	SAP. Description	Page/Para	Applicability	Comment
EMT.5	Procedures	Page 49	Yes	Commissioning and in-service inspection procedures for seals and associated components should be adopted to ensure initial and continuing quality and reliability.
EMT.6	Reliability claims	Page 49	Yes	Provision should be made where possible for testing, maintenance, monitoring and inspection of seals and associated structures in service or at intervals throughout their life, commensurate with the reliability required of each item. Any in-situ tests that may be used should be non-invasive with the bare minimum of equipment disturbance. In some cases, equipment disturbance may not be allowed and this should be considered and mitigated during the design/qualification stage.
EMT.7	Functional testing	Page 50	Yes	In-service functional testing of structures, systems and components, including seals, should verify the operation of complete systems and the safety function of each functional group.
EMT.8	Continuing reliability following events	Page 50	Yes	Seals should be inspected and/or re-validated after any event that might challenge their continuing reliability.
Ageing and degradation guidance, below, has been assessed as applicable to seals in the following cases:				
EAD.1	Safe working life	Page 50	Yes	The safe working lifetime of seals and systems important to safety should be evaluated at the design stage using appropriate EQ methodologies and representative ageing simulations.
EAD.2	Lifetime margins	Page 50	Yes	Adequate margin should exist throughout the life of a facility to allow for the effects of additional seal material ageing and degradation processes (understanding the potential implications of "hot-spots" and the realistic application of margins to radiation dose, elevated temperatures, for example).

SAP. Ref.	SAP. Description	Page/Para	Applicability	Comment
EAD.3	Periodic measurement of material properties	Page 51	Yes	Provision should be made for periodic measurement of seal material properties which could change with time during service and thus affect the safe operation of equipment.
EAD.4	Periodic measurement of parameters	Page 51	Yes	Where parameters relevant to the design of plant could change with time and affect the ageing of seal materials (e.g. hot-spots) and/or safety functions, provision should be made for their periodic measurement.
EAD.5	Obsolescence	Page 51	Yes	A process for reviewing the obsolescence of seals important to safety should be in place. This is particularly relevant where seal materials/formulations may be become obsolescent and superseded.
External and internal hazards guidance, below, has been assessed as applicable to seals in the following case:				
EH.9	Earthquakes	Page 58	Yes	The design of sealing systems should, where appropriate, allow for un-scheduled movement of plant/equipment associated with earthquakes.
Pressure systems guidance, below, has been assessed as applicable to seals in the following cases:				
EPS.2	Flow limitation	Page 62	Yes	Flow limiting devices should be provided to fluid transport systems that incorporate seals to minimise over-pressure.
EPS.3	Pressure relief	Page 63	Yes	Adequate pressure relief systems should be provided for pressurised systems that incorporate seals and provision should be made for periodic testing.
EPS.4	Overpressure protection	Page 63	Yes	Overpressure protection should be consistent with any pressure-temperature limits of operation in systems that include seals.
The integrity of non-metallic components guidance, below, has been assessed as applicable to seals in the following cases:				

SAP. Ref.	SAP. Description	Page/Para	Applicability	Comment
ENC.1	Limits of application	Page 76	Yes	Where a non-metallic component or structure is chosen in preference to a metallic equivalent, the safety case should identify and then justify any limitations arising from this choice compared to using a metallic item.
ENC.2	Examination through life	Page 76	Yes	The design of non-metallic components or structures should, where possible, include the ability to examine the item through life for signs of degradation.
Human factors guidance, below, has been assessed applicable to seals in the following cases:				
EHF.1	Integration with design, assessment and management	Page 102	Yes	A systematic approach to integrating human factors within the design, assessment and management of systems and processes should be applied throughout the facility's lifecycle. Applicable where seals are integrated into systems and processes.
EHF.3	Identification of actions impacting safety	Page 103	Yes	A systematic approach should be taken to identify human actions that can impact safety for all permitted operating modes and all fault and accident conditions identified in the safety case, including severe accidents. Applicable where seals are integrated into systems and processes.
EHF.8	Personnel competence	Page 105	Yes	A systematic approach to the identification and delivery of personnel competence should be applied. Applicable where seals are integrated into systems and processes.
EHF.11	Staffing levels	Page 106	Yes	There should be sufficient competent personnel available to operate the facility in all operational states. Applicable where seals are integrated into systems and processes.
Control of nuclear matter guidance, below, has been assessed applicable to seals in the following cases:				

SAP. Ref.	SAP. Description	Page/Para	Applicability	Comment
ENM.4	Control and accountancy of nuclear matter	Page 108	Yes	Nuclear matter should be appropriately controlled and accounted for at all times. Seals are likely to be an essential component e.g., including details of location, containers and packaging and facilitating control of nuclear matter.
ENM.6	Storage in a condition of passive safety	Page 109	Yes	Seals are likely to be an essential component during the storage of nuclear matter e.g., containment seals. The impact of seal performance on passive storage over extended periods should be understood.
ENM.7	Retrieval and inspection of stored nuclear matter	Page 110	Yes	Storage of nuclear matter should be in a form and manner that allows it to be retrieved and, where appropriate, inspected. The design and selection of suitable materials and sealing systems should enable this.
Chemical (Process) Engineering guidance, below, has been assessed applicable to seals in the following cases:				
EPE.1	Design and operation	Page 111	Yes	The design and operation of nuclear chemical processes and facilities that incorporate seals should be fault tolerant and ensure safety functions are delivered with suitable capability and sufficient reliability and robustness.
EPE.3	Experimental processes	Page 113	Yes	Where an experimental chemical process is proposed which incorporates seals, the safety case should establish an appropriate degree of confidence in the safety of the process and that it will deliver sealing functions and protection as intended.
EPE.4	Severe accident data	Page 113	Yes	Process behaviour under severe accident conditions should be analysed where processes employ seals.
EPE.5	Process design and commissioning	Page 114	Yes	The process design and commissioning should provide inputs to operational safety parameters defining limits and conditions necessary in the interests of safety (operating rules). This should apply where a process incorporates seals.
Chemistry guidance, below, has been assessed applicable to seals in the following cases:				

SAP. Ref.	SAP. Description	Page/Para	Applicability	Comment
ECH.3	Control of chemistry	Page 116	Yes	Suitable and sufficient systems, processes and procedures should be provided to maintain chemistry parameters within the limits and conditions identified in the safety case. Applicable to seals where environmental chemistry could cause ageing of the seals or the degradation of seals could affect environmental chemistry e.g., leaching of degradation products.
ECH.4	Monitoring, sampling and analysis	Page 116	Yes	Suitable and sufficient systems, processes and procedures should be provided for monitoring, sampling and analysis so that all chemistry parameters important to safety are properly controlled. Applicable where seals have been incorporated.
Containment and ventilation guidance, below, below, has been assessed applicable to seals in the following cases:				
ECV.1	Prevention of leakage	Page 117	Yes	Radioactive material should be contained and the generation of radioactive waste through the spread of contamination by leakage should be prevented. Seals are likely to play an important role in the containment of radioactive materials and the prevention of leakage from waste containers and ventilation systems.
ECV.2	Minimisation of releases	Page 117	Yes	Containment and associated systems containing seals should be designed to minimise radioactive releases to the environment in normal operation, fault and accident conditions.
ECV.3	Means of confinement	Page 118	Yes	The primary means of confining radioactive materials should be through the provision of passive sealed containment systems and intrinsic safety features, in preference to the use of active dynamic systems and components. This is applicable to containment systems utilising seals.
ECV.4	Provision of further containment barriers	Page 119	Yes	Where the radiological challenge dictates, waste storage vessels, process vessels, piping, ducting and drains (including those that may serve as routes for escape or leakage from containment) and other plant items that act as containment for radioactive material, should be provided with further

SAP. Ref.	SAP. Description	Page/Para	Applicability	Comment
				containment barrier(s) that have sufficient capacity to deal safely with the leakage resulting from any design basis fault. Containment barriers utilising seals should be designed to meet the radiological challenge.
ECV.9	Containment and ventilation system design	Page 120	Yes	The design should ensure that controls on fissile content, radiation levels, and overall containment and ventilation standards are suitable and sufficient. Applicable where seals have been utilised.
ECV.10	Ventilation system safety functions	Page 121	Yes	The safety functions of the ventilation system should be clearly identified and the safety philosophy for the system in normal, fault and accident conditions should be defined. Applicable where seals have been utilised.
Radioactive waste guidance, below, has been assessed applicable to seals in the following case:				
RW.5	Storage of radioactive waste and passive safety	Page 173	Yes	This is likely to be an important consideration in the design of long-term storage containers for radioactive waste. Suitable design and qualification of seals for waste storage should follow the guidelines outlined in this document.

Appendix B. Appropriate method of accelerated ageing and modelling of elastomeric seals for nuclear applications

Polymeric seals are used in nuclear plant throughout the UK and are expected to be exposed to low levels of ionising radiation, elevated temperatures and combinations of the two. In assessing the long-term behaviour and functionality of seals, some form of accelerated tests is required to enable estimates of component lifetimes under service conditions. This activity is very important where seals are used in safety related applications.

Compression set has been found to be one of the most useful ageing parameters relevant to routine assessments of seal functionality (i.e., leakage) under the harsh conditions expected in nuclear applications. As compression set is a property that can be readily measured, a comprehensive analysis of the effects of radiation and elevated temperatures on the sealing characteristics of elastomers can be carried out.

To achieve this, a matrix of data is assembled across a range of radiation dose rates and temperatures and combinations of the two. It is important to use ageing conditions that are not too highly accelerated away from normal ageing conditions. The data matrix will consist of compression set measurements recorded against time for each ageing condition.

Figure B.1 shows a series of simulated compression set plots that might be obtained for a typical seal material against the logarithm of time, not actual time. The plots will have been generated at different dose rates D and temperatures T. The curves are displaced along the log time axis by time increments a (D,T). The shapes of the plots are similar and if they are shifted along the log time axis, they will superpose. This is known as time/temperature superposition and if the individual curves have the same shape on log time axes, there is confidence that the degradation processes are consistent within the ageing conditions that have been used.

If very high dose rates or temperatures are used, it is likely that the shape of the compression set curves against log time will be different to those that superpose in the main test matrix. This will indicate that different ageing mechanisms are in force under highly accelerated conditions. This is the reason why the accelerated ageing conditions should not deviate too greatly away from service conditions. However, some pragmatism is usually needed to use ageing conditions that will deliver test data within acceptable timescales.

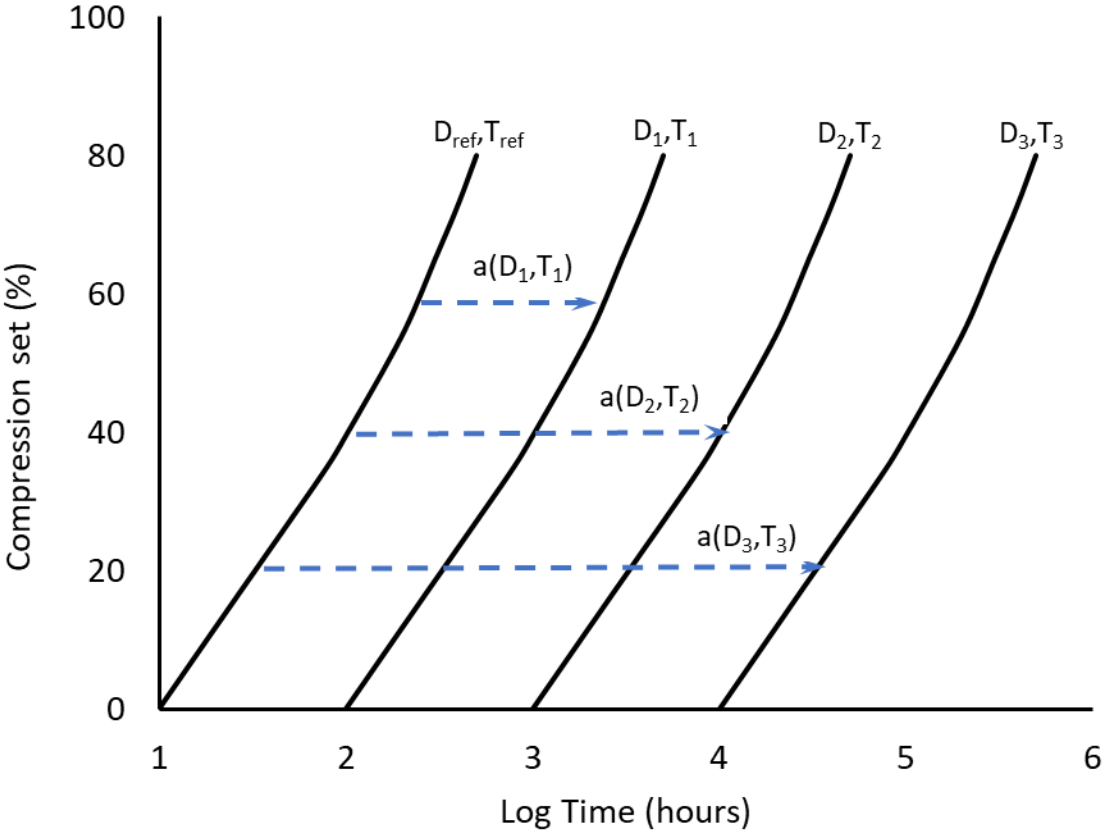

Figure B.1 A series of compression set curves plotted against the logarithm of time for an elastomeric seal material aged under different dose rates and temperatures, D and T respectively.

The parameters a(D_1,T_1), a(D_2,T_2) and a(D_3,T_3) are log time displacements or the shift factors required to make each curve superpose onto the reference curve. If the ageing was carried out whilst seals were irradiated at room temperature, the shift factors would be: a(D_1), a(D_2) and a(D_3) for different dose rates only. In this case, the shift factors $a(D)$ will be related to the dose rate by a power law:

$$a(D) = 1 + kD^x \qquad \text{(Equation B.1)}$$

Where:

$a(D)$ is the shift factor at the ageing dose rate

D is the radiation dose rate in Gy s^{-1}

k and x are material constants

On the other hand, if the environment has negligible radiation present but elevated temperatures, the radiation dose rate is zero and the shift factors are temperature controlled. In this case the shift factors become a(T_1), a(T_2) and a(T_3) from the curve plotted for the reference temperature. The temperature shift factors will then be related to the reference temperature, by a re-arranged form of the Arrhenius equation, Equation B.2:

$$a(T) = exp - \frac{E}{R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right) \qquad \text{(Equation B.2)}$$

Where:

$a(T)$ is the shift factor at the ageing temperature

T is the ageing temperature in K

T_{ref} is a reference temperature in K

E is an activation energy for the thermal ageing process in kJ mol^{-1}

R is the gas constant ~8.3 J mol^{-1} K^{-1}

In many applications in the nuclear industry, polymeric seals will be required to function at low dose rates, usually less than 1 Gy h^{-1} but also at elevated temperatures. As the dominant effects in both radiation and thermal ageing in polymers are usually free radical processes it is logical to assume that the application of both radiation and thermal stressors to a polymer will result in shorter lifetime expectancy than if the polymer was irradiated at the same dose rate but at a lower temperature. Where this occurs, Equations B.1 and B.2 may be combined to form Equation B.3. In this case the shift factors $a(D)$ and $a(T)$ become $a(D,T)$ and:

$$a(D,T) = \exp - \frac{E}{R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\left(1 + kD^{x} exp \frac{Ex}{R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right) \qquad \text{(Equation B.3)}$$

Where:

$a(D,T)$ is the shift factor at the specified temperature and dose rate

Inspection of Equation B.3 reveals that if the ageing is carried out at constant temperature, Equation B.3 reverts back to Equation B.1. If the ageing is carried out without radiation, D=0, and for elevated temperature ageing, Equation B.3 reverts back to Equation B.2.

Each different polymeric material will have its intrinsic values of E, k and x which are known as model parameters. The importance of k is that its value is related to the degree of synergy between the thermal and radiation stressors, whilst x is a parameter that can reveal dose rate effects. It is normally close to unity but lower values of x than 1 are indicative that the material shows dose rate effects.

Although Equation B.3 appears to be a rather complicated expression, it is relatively straightforward to solve for values of E, k and x if a range of values of $a(D,T)$ are available for different ageing temperatures, dose rates and combinations of the two. For example, if radiation is absent, the parameter E can be calculated from thermal data. At room temperature, k and x can be determined from radiation test data. The advent of computer applications such as Microsoft Excel has now made the analysis of time-temperature superposition data and solutions of Equation B.3 for different materials a routine task. Furthermore, the larger the matrix of data generated at different temperatures and dose rates, the better the accuracy of the model parameter calculations.

When the model parameters have been determined, it is then a simple process to use the model in reverse to predict the shapes of the compression set curves for any temperature or dose rate and thus enable predictions of compression set under any combinations of ageing conditions.

An important point to consider is that the model is only usually valid within certain boundary conditions. The model assumes a single ageing mechanism applies over the dose rate and temperature range for which the compression set data superpose. At very high temperatures or dose rates, different ageing rate mechanisms are likely to apply and the model loses validity. Therefore, each seal material will not only have its intrinsic values of E, k and x, it will also have a range of dose rates and temperatures within which the model will be valid. It should also be noted that different formulations within generic classes of elastomers will also have different values of E, k and x. It will be incorrect to assume that the parameters for one EPDM formulation will transfer to another EPDM. However, the concept of spot checks can be employed to examine how closely the properties of one formulation follow another.

Nevertheless, the UK nuclear industry is in an effectively unique and powerful position because model parameters are available for a large proportion of the elastomeric seal materials that are currently in use in the industry. These parameters have been entered for each material into an Excel spreadsheet with Visual Basic code to provide a predictive model utility called SEALS. Therefore, the compression set of any of the seals in the SEALS utility can be accurately predicted if the environmental dose rates and temperatures are known, providing that the dose rates and temperatures are not so large that they fall outside the model's boundary conditions. The model can be used with some confidence. It has been validated against long-term seals test data generated under simulated service conditions (low dose rates at elevated temperatures) over a twenty-year period between 1990 and 2010.

The model is not only applicable to elastomers, it has been used to assess predict the changes in mechanical properties of a range of polymeric materials used for nuclear applications for instance polymeric cable materials. It is therefore not restricted to compression set data, properties such as tear resistance and elongation at break if the appropriate matrix of data has been generated