
**Petroleum, petrochemical and natural gas
industries — Non-metallic materials in
contact with media related to oil and gas
production —**

**Part 2:
Elastomers**

*Industries du pétrole, de la pétrochimie et du gaz naturel — Matériaux
non métalliques en contact avec les fluides relatifs à la production de
pétrole et de gaz —*

Partie 2: Élastomères





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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 23936-2 was prepared by Technical Committee ISO/TC 67, *Materials, equipment and offshore structures for petroleum, petrochemical and natural gas industries*.

ISO 23936 consists of the following parts, under the general title *Petroleum, petrochemical and natural gas industries — Non-metallic materials in contact with media related to oil and gas production*:

— *Part 1: Thermoplastics*

— *Part 2: Elastomers*

The following parts are planned:

— *Part 3: Thermosets*

— *Part 4: Fibre-reinforced composite*

— *Part 5: Other non-metallic materials*

Introduction

ISO 23936 is intended to be of benefit to a broad industry group, ranging from operators and suppliers to engineering companies and authorities. ISO 23936 covers relevant generic types of non-metallic material (thermoplastics, elastomers, thermosetting plastics, fibre-reinforced plastics, etc.) and draws upon a wide range of existing technical experience, which has never before been summarized in a technical standard.

ISO 23936 does not cover polymeric coatings such as thermal insulation and paint that are applied to the outside of components but that are not in contact with oilfield fluids.

The evaluation and qualification process described in this part of ISO 23936 is intended to ensure that the user of non-metallic materials has sufficient understanding and knowledge of the applicable materials to obtain acceptable performance in the specified environment, and that the user can rely on stable quality to meet given specifications. A quality system is useful to ensure compliance with the requirements of this part of ISO 23936.

Successful qualification of a manufacturer and a specific material is intended to be valid for other projects and different operators. The consideration of qualification of a manufacturer is at the discretion and determination of the purchaser, normally on the basis of documentation provided by the manufacturer, as required in this part of ISO 23936 or any specific additional documentation.

The purchaser is responsible for ensuring (if necessary, with external competence) that the manufacturers selected are qualified.

This part of ISO 23936 is based on Norsok standard M-710.

Petroleum, petrochemical and natural gas industries — Non-metallic materials in contact with media related to oil and gas production —

Part 2: Elastomers

1 Scope

ISO 23936 describes general principles and gives requirements and recommendations for the selection and qualification of non-metallic materials for service in equipment used in oil and gas production environments, where the failure of such equipment could pose a risk to the health and safety of the public and personnel, or to the environment. It can be applied to help avoid failures of the equipment itself. It supplements, but does not replace, the material requirements given in the appropriate design codes, standards or regulations.

This part of ISO 23936 describes the requirements and procedures for qualification of elastomeric material used in equipment for oil and gas production.

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 34-1:2010, *Rubber, vulcanized or thermoplastic — Determination of tear strength — Part 1: Trouser, angle and crescent test pieces*

ISO 37, *Rubber, vulcanized or thermoplastic — Determination of tensile stress-strain properties*

ISO 48, *Rubber, vulcanized or thermoplastic — Determination of hardness (hardness between 10 IRHD and 100 IRHD)*

ISO 815-1, *Rubber, vulcanized or thermoplastic — Determination of compression set — Part 1: At ambient or elevated temperatures*

ISO 2781, *Rubber, vulcanized or thermoplastic — Determination of density*

ISO 2921, *Rubber, vulcanized — Determination of low-temperature retraction (TR test)*

ISO 3601-3:2005, *Fluid power systems — O-rings — Part 3: Quality acceptance criteria*

ISO 7619-1, *Rubber, vulcanized or thermoplastic — Determination of indentation hardness — Part 1: Durometer method (Shore hardness)*

ISO 13628-10:2005, *Petroleum and natural gas industries — Design and operation of subsea production systems — Part 10: Specification for bonded flexible pipe*

ASTM D297, *Standard Test Methods for Rubber Products — Chemical Analysis*

ASTM D395, *Standard Test Methods for Rubber Property — Compression Set*

ASTM D412, *Standard Test Methods for Vulcanized Rubber and Thermoplastic Elastomers — Tension*

ASTM D624, *Standard Test Method for Tear Strength of Conventional Vulcanized Rubber and Thermoplastic Elastomers*

ASTM D1414, *Standard Test Methods for Rubber O-Rings*

ASTM D1415, *Standard Test Method for Rubber Property — International Hardness*

ASTM D2240, *Standard Test Method for Rubber Property — Durometer Hardness*

API 17K, *Specification for Bonded Flexible Pipe*

3 Terms, definitions and abbreviated terms

For the purposes of this document, the following terms, definitions and abbreviated terms apply.

3.1 Terms and definitions

3.1.1

accelerated test

test undertaken under conditions designed to speed material deterioration

NOTE This is usually accomplished by increasing temperature, in order to raise chemical reaction rates, but fluid concentration and stress are variables which can also be manipulated.

3.1.2

asset operator

person who operates an asset, who has knowledge of well parameters and who transmits this information to the **user** (3.1.15)

NOTE 1 An asset can be a well, a production train, a plant, etc.

NOTE 2 Well parameters can be fluid exposure, temperatures, pressures, duration, etc.

3.1.3

compression set

difference between the original sample height and the post-test height, divided by the interference, expressed as a percentage

3.1.4

elastomer

rubber

amorphous material mechanically mixed with other constituents to form a rubber compound, which is then shaped by flow into articles by means of the manufacturing processes of moulding or extrusion, and then (invariably) chemically cured at elevated temperature to form an elastic insoluble material

3.1.5

fluid

medium such as a gas, liquid, supercritical gas, or a mixture of these

3.1.6**interference**

difference between the original sample height and the height of spacer bar, each measured in the same direction as the direction of compression

3.1.7**compound manufacturer
manufacturer**

producer of the elastomer material or of semi-finished products made from elastomer materials

3.1.8**modulus**

tensile stress at a given elongation

NOTE In the rubber industry, the modulus at 50 % elongation is often chosen.

3.1.9**polymer**

high molecular weight molecule, natural or synthetic, whose chemical structure can be represented by repeated small units which collectively form molecular chains

NOTE This material class has three main sub-groups: elastomers, thermoplastics and thermosets.

3.1.10**rapid gas decompression****RGD**

depressurization

explosive decompression

rapid pressure-drop in a high pressure gas-containing system which disrupts the equilibrium between external gas pressure and the concentration of gas dissolved inside any polymer, with the result that excess gas tries to escape from the solution at points throughout the material, causing expansion

NOTE If large enough, and if the pressure-drop rate is faster than the natural gas diffusion rate, blistering or rupturing can occur.

3.1.11**room temperature**

temperature of (23 ± 2) °C

3.1.12**seal cross-section****cross-section diameter****CSD**

free height of a seal at room temperature, measured normal to seal diameter in the direction of compression in the test

NOTE The measurement is taken at three circumferentially equidistributed positions.

3.1.13**seal type**

seal design of specified geometry, size and orientation

EXAMPLE An O-ring.

3.1.14**thermoplastic**

material capable of being repeatedly softened by heating and hardened by cooling through a temperature range characteristic of the plastic and, in the softened state, of being repeatedly shaped by flow into articles by moulding, extrusion or forming

3.1.15

user

person responsible for the selection of suitable materials for a service operation based on information received from the **asset operator** (3.1.2)

3.1.16

purchaser

party responsible for procuring the elastomer material or component

3.2 Abbreviated terms

BOP	blow-out preventer
BRE	base resistant elastomers
COC	certificate of conformance
CSD	cross-section diameter
DMA	dynamic mechanical analysis
DMTA	dynamic mechanical thermal analysis
DSC	differential scanning calorimetry
GMPHOM	Guide to Manufacturing and Purchasing Hoses for Offshore Moorings
HNBR	hydrogenated nitrile butadiene rubber
HP	high pressure
LNG	liquefied natural gas
NBR	nitrile butadiene rubber
OCIMF	Oil Companies International Marine Forum
PBR	polished bore receptacle
RGD	rapid gas decompression (rapid gas depressurization)
SPS	solubility parameter spectroscopy
TMA	thermo mechanical analysis

4 Technical requirements

Technical requirements depend on material property characteristics and specific functional tests for an application.

Elastomer selection shall be based on evaluation of compatibility with service environment, functionality under service and the design lifetime. This part of ISO 23936 covers materials tests and not functional tests. The following should be considered as appropriate to the component requirements and evaluated when selecting the material:

- a) adequate physical and mechanical properties (density, hardness, tensile strength, elongation at break, modulus of elasticity, compression set, tear strength, etc.); standard properties from which design specifications are selected and for quality assurance and control aspects;
- b) resistance against RGD events; a property of importance in high pressure gas sealing applications, covered in depth in this part of ISO 23936;
- c) long-term behaviour; resistance to chemical/physical change of the material; an important characteristic regarding sealing generally in the oil and gas sector, covered in this part of ISO 23936;
- d) low temperature flexibility; a property highly relevant to low temperature sealing applications;
- e) for large components exposed to gaseous production fluid, high pressure gas permeation; a property highly relevant to possible gas pressure build-up within the component structure, e.g. for hoses;
- f) resistance to high pressure extrusion or creep (functional tests not covered by this part of ISO 23936);
- g) resistance to thermal cycling and dynamic movement (functional tests not covered by this part of ISO 23936).

Clause 2 gives references to relevant standards for elastomeric materials. The standards describe the test methodology for performing particular materials tests. The test conditions and durations shall be as described in this part of ISO 23936 and shall take precedence in those cases where this part of ISO 23936 deviates from the referenced standards.

Long term (ageing) test objectives are described in Clause 7; procedural details are given in Annex A. RGD test objectives and procedures for elastomer O-ring seals are described in Clause 7 and Annex B.

It is the responsibility of the asset operator to provide all necessary information about service conditions and environment.

Information on elastomer characteristics is provided in Annex C.

5 Documentation requirements

NOTE The required documentation of material properties of thermoplastic materials is described in ISO 23936-1.

Required documentation of material properties is given in Table 1. Requirements pertaining both to documentation of properties and quality control are given. Each elastomer material used shall be traceable to the compound manufacturer and their quality control documentation as required in Table 1. Each batch of material shall be supplied with, as a minimum, a certificate of conformance (COC) and traceability information.

Table 1 also defines the minimum amount of production and quality control testing required during manufacturing of the elastomer materials. The final procedures, with respect to key parameters and tolerances, shall be defined based on results from testing performed according to this part of ISO 23936.

The user shall define the necessary requirements with tolerances in the purchase specification.

Guidelines on selection of standards are given in parentheses. Characteristics, which are not relevant for expected service conditions and/or material type, may be omitted.

Table 1 — Required documentation for elastomer material properties

Properties	Documentation	Quality control tests
Density (ISO 2781 or ASTM D297)	D ^a	B ^c
Hardness (IRHD/Shore A) (ISO 48/ISO 7619-1, ASTM D2240/ASTM D1415)	D	B
Tensile and elongation properties (ISO 37, ASTM D1414, ASTM D412)	D	B
Compression set (ISO 815-1, ASTM D395/ASTM D1414)	D	
Low temperature characteristics by DSC, DMA or TMA	D	
Tear strength (ISO 34-1:2010, Method A, ASTM D624)	D	
Temperature of retraction (ISO 2921)	D	
Ageing/RGD characteristics (Annexes A/B)	D	
High pressure gas permeation	DH ^b	
<p>^a D: Properties to be documented for each supplier for each type of material. Nominal values with tolerances shall be given (Data Sheet).</p> <p>^b DH: As for D, but specifically when using all large components exposed to high pressure gas.</p> <p>^c B: Properties to be documented on a batch-wise basis, minimum 5 samples per test per batch with all results presented. The acceptance criteria shall be established prior to the test and based on qualification test results.</p>		

Material property tests may also be omitted if users have documented performance-based functional tests that they use to approve rubber materials.

6 Requirements for manufacturers

6.1 General requirements

It is the requirement of the manufacturer to provide documents attesting that the material has been manufactured and tested appropriately and that the material has met the relevant quality control requirements in this part of ISO 23936.

The testing shall be performed on specimens produced from specific rubber formulations and, where possible, production procedures. The COC should include as a minimum density, batch hardness, tensile properties (moduli, strength, elongation at break), date of manufacture and (where referenced) the sample curing process. The COC should be signed by a quality representative. For large rubber components, tests on small components shall be suitable for the properties of the large component unless otherwise agreed between the interested parties.

This part of ISO 23936 specifies the required types of tests that shall be performed in order to document the material suitability and compatibility with test fluids specified in this part of ISO 23936 which are applicable to the intended application.

The testing shall apply for the elastomer materials and the results shall be valid as long as the requirements stated in 6.2 are satisfied. For later supplies of identical material from the same manufacturer, a quality control of each batch of material shall be sufficient. Table 2 lists typical quality assurance and quality control document templates showing imaginary data.

Table 2 — Typical quality assurance and quality control information

Material			
Manufacturer	Acme Seals, Inc.		
Compound grade	FabFluoro		
Elastomer type	ASTM D1418-05	FKM Type 3	
Lot/batch no.	FF2344rw4r/07		
Cure date	Q4 2010		
Typical Properties	Applicable standard	Unit	Value
Density	ISO 2781	g/cm ³	1,8
Hardness	ISO 48	IRHD	85
Tensile strength	ISO 37	MPa	21
Modulus at 50% elongation	ISO 37	MPa	10,1
Modulus at 100% elongation	ISO 37	MPa	18,5
Elongation at break	ISO 37	%	125

It may not be necessary to perform qualification testing for a particular material, if relevant successful well-documented in-service experience with traceable production records and quality control documentation is available to all relevant parties. This shall be agreed between interested parties.

Such documentation shall contain detailed information about service conditions such as time, temperature, pressure, fluid composition and chemicals added. An asset operator can, for example, provide the documentation of flawless service. The existing service temperature recorded therein shall be in the same range as for the new application (it shall be a maximum of 10 °C below), the existing service pressure shall not be more than 10 % below that for the new application, and the existing service life shall be a minimum of 50 % of design life.

The manufacturer who has tested and qualified his compound(s) can make a statement making this known. Such a statement shall define which parts of ISO 23936 are complied with. Further, the statement shall include whether the testing was done according to Annex A and/or Annex B, and define the fluid composition, conditions and overall duration for the testing.

6.2 Validation of compliance

The elastomer properties shall apply to each specific elastomer compound produced by each specific manufacturer. The existing elastomer data used by one purchaser may also be accepted by subsequent purchasers, provided the requirements in this part of ISO 23936 are still complied with.

A compound shall be re-tested if changes are made to the compound or the process. If compound mixing and/or moulding is carried out at different plants/locations, a separate qualification shall be performed for each plant.

NOTE All materials previously approved in accordance with NORSOK M-710 are approved in accordance with this part of ISO 23936.

7 Qualification of elastomer materials (ageing and RGD)

7.1 General

The technical necessities for the testing of elastomeric materials are divided into two parts:

- 7.2 defines the chemical ageing test requirements (see Annex A);
- 7.3 defines the requirements for RGD testing (see Annex B).

The test regimes shall be selected based on an analysis of the service conditions applying to the material in question, if these are known. Such an assessment shall include the nature and type of all fluids which contact the elastomer. The service life of the seal material in the relevant service environment shall be evaluated using appropriate techniques.

7.2 Requirements for ageing tests

7.2.1 General

This part of ISO 23936 defines test procedures for the prediction of the progressive degradation of elastomeric materials exposed to fluids at elevated temperatures over extended periods of time. It is applicable where it is necessary to forecast material life in a specific application and for directly comparing the performance of candidate elastomer materials. Other standards, such as API TR6J1, also provide methods to assess life of elastomer materials.

The objective is to assess the physical effects of the fluid on the elastomer and to thermally accelerate chemical reaction (if this occurs) between the fluid and the elastomer, causing tensile and related property levels to shift systematically towards a pre-defined limit of acceptability. The material is considered to have “failed” (i.e. reached the end of its useful life) when this limit is attained. These data are then used to quantify service life and suitability for service.

By running exposure tests with test fluids at three different elevated temperatures above the operating temperature, three different times to reach the acceptance boundary will result, with the highest test temperature producing the shortest “time to failure”. Plotting the log of failure times against the reciprocal of the test temperature should result in a linear trend, enabling an estimate of service life at the operating temperature.

For accelerated testing, the upper test temperature should be limited to give some confidence that only service-relevant chemical and/or physical processes will occur.

The preferred test piece geometry is the tensile dumbbell; various standards apply (see Table 1). The ageing of moulded sheet, for subsequent stamping-out of tensile test pieces, is not allowed. The elastomer shall be tested in unconstrained mode; that is, free-standing, with fluid able to freely access all surfaces.

When extrapolating data from the present procedures, appropriate statistical techniques shall be applied. For example, if progressive degradation is apparently dependent on a single chemical ageing process, a method based on the Arrhenius relationship shall be used as described in Annex D. It is recommended that results always first be assessed on an Arrhenius basis. If an Arrhenius relationship does not exist or ageing does not occur, see Annex E for further guidance.

Test media, conditions, equipment, procedures and test report requirements are described in detail in Annex A.

7.2.2 Acceptance criteria for elastomers

The acceptance criteria shall be established prior to commencing the ageing test. The following criteria have been established as the maximum acceptable ranges for three particular properties; any relaxation of these

requirements shall be agreed upon by the user. A narrower acceptance range can be applied to any of these if required by circumstances.

- Hardness: +10/–20 units (+5/–20 units when initial nominal hardness is 90); applies to Shore A and IRHD scales
- Volume: +25 % /–5 %
- Tensile: ± 50 % [modulus (at 50 % or 100 % elongation), tensile strength, elongation at break]

Tensile test results shall be used to extrapolate the service life according to Arrhenius equation (see Annexes A and E). Other properties may be used by agreement between all parties.

7.3 Requirements for rapid gas decompression testing

7.3.1 General

This part of ISO 23936 gives test procedures for measuring the effect on elastomeric O-ring seals of rapid depressurization after periods at elevated temperature and high pressure in gaseous environments. In addition, guidance notes for interpretation of the results are provided. The supplier shall discuss with the user those applications for which this failure mode is relevant.

The test fluids, conditions, procedure, equipment, inspection procedure and test reporting requirements are described in Annex B.

7.3.2 Acceptance criterion

No seal cross-section shall have a rating of more than 3 (see Clause B.4).

8 Qualification of elastomeric materials in bonded flexible hose

8.1 General

Bonded flexible hose is the general class of flexible hose constructed from layers of elastomer and wire, wire fabric or textile fabric reinforcement that are bonded together by vulcanization during manufacture. The hose section from the internal to external diameter generally consists of the following:

- liner: inner layer of elastomer providing resistance to the fluids being transported;
- body layers: layers of reinforcement typically including textile fabric or parallel cords impregnated with elastomer, parallel steel wire cords impregnated with elastomer, and embedded helical wire. Infill elastomer layers may also be present;
- cover: outer layer of elastomer providing resistance to the external environment;
- insulation or buoyancy: an additional outer layer for hoses where either insulation or buoyancy is required.

The hose structure is integrated into suitable end fittings according to the specific design, usually by bonding of the elastomer to the metal end fitting with a suitable curable adhesive system during the vulcanization of the hose.

Bonded flexible hose usage can be generally classified into:

- a) lower pressure applications that are typically used for loading and discharge of liquids and LNG in offshore mooring situations;

- b) higher pressure applications used in oil and gas production.

For a), guidance is provided in GMPHOM/OCIMF [*Guide to Manufacturing and Purchasing Hoses for Offshore Moorings (Oil Companies International Marine Forum)*], including materials tests for the liner and cover materials for materials acceptance and prototype hose approval.

For b), ISO 13628-10 specifies material property requirements and test procedures for the qualification of liner, breaker and reinforcing layers in terms of mechanical/physical properties, thermal properties, permeation characteristics and compatibility/ageing properties covering all pressures.

In the context of this part of ISO 23936, the main consideration is the qualification of the liner material that is in contact with the fluids being transported. For the longer term, the effects of the permeation of fluids through the liner to other elastomer layers should also be considered as well as ageing effects on mechanical/physical properties. Because of the multi-layer construction of bonded hoses, not only should the properties of the individual elastomer layers be considered, but also the adhesion between layers including the bonding with the end fittings.

8.2 Qualification of bonded flexible hose liner material

8.2.1 General

Qualification should be according to the subclauses below, which are based on the existing guidelines mentioned in 8.1.

8.2.2 Guide to manufacturing and purchasing hoses for offshore moorings

The procedure of GMPHOM/OCIMF should be applied or adapted as appropriate with regard to materials test procedures. It possesses two clauses entitled Materials Tests, one under “Acceptance Tests” and one for “Prototype Hose Approval”; the most relevant should be agreed between supplier and purchaser and employed. Particular points are:

- a) Within both clauses termed Material Tests, for resistance to liquids, GMPHOM/OCIMF specifies the use of ISO 1817 using the conditions 48 h at 40 °C in the test liquid as a volume swell test, with a requirement of swell being no greater than 60 %.

NOTE GMPHOM/OCIMF specifies use of (ASTM) liquid C, which can still conform to this part of ISO 23936 if liquid C is stated to be the bespoke liquid agreed between participants (see Annex A).

This part of ISO 23936 allows the same procedure for use with a standard liquid selected to be reasonably representative of the composition of the service fluid to be transported or contained, in accordance with Annex A. Bespoke acceptance properties will be required if alternative low temperature requirements and/or products and/or service fluids are relevant.

- b) GMPHOM/OCIMF specifies for temperature resistance “no significant deterioration” at –20 °C using the Gehman test to ISO 1432.
- c) Under “Acceptance Tests”, GMPHOM/OCIMF also specifies adhesion testing between bonded layers of body and end-fitting elastomer using a standard peel test as described in ISO 36:2005, which specifies a test method for measuring the force required to separate two plies of fabric bonded with rubber, or a rubber layer and a fabric ply bonded together. The ply surfaces should be plane or nearly so, with no gross irregularities. Supplier and user should agree a threshold force for acceptance, based on experience.
- d) If the service temperature is higher than ambient, the material test temperature should be increased accordingly. The test conditions, test duration and acceptance criteria should be agreed between supplier and purchaser. Consideration to the temperatures and fluids chosen should be made with consultation to ISO 1817.

8.2.3 ISO 13628-10 and API 17K

ISO 13628-10 and API 17K specify property tests for liner and reinforcing layers (see Tables 9 and 11 in API 17K:2005) and describe test procedures and acceptance criterion for fluid permeability (liquid and gas), blistering, fluid compatibility, ageing and void formation (the last being a component test), concerning interlayer failures. Much of ISO 13628-10 and API 17K is useful for incorporation in this part of ISO 23936, but some variations are required.

8.2.4 Requirements for gas permeation

Gas permeation testing should be made at appropriate high pressure on a specimen from liner or other layer material, and procedures shall vary depending on conditions and fluid type. Test gases shall be in accordance with Tables A.2 and A.3, using the bespoke category for testing single gases.

For high pressure (HP) gas permeation testing of an elastomer material, a test assembly pressure cell with the following features is required.

- a) A chamber which can be pressurized to high pressure by a gas supply. This will be separated from a low pressure chamber by a suitably sealed elastomer test piece. Facilities for continuous monitoring of the pressures in the high and low pressure chambers are required.
- b) Heating (insulated band heater) facilities and temperature monitoring and control of the permeation cell to within ± 2 °C.

Test times are governed by diffusion characteristics of candidate elastomers (see Annex E). In one test arrangement, test pieces of test elastomer of diameter 10 mm are bonded during vulcanization into a suitable holder. Moulding pressure shall be high to minimize porosity and microporosity. The test specimen holder is installed and sealed in the HP permeation cell. A porous steel sinter necessary for supporting the specimen is inserted appropriately. The cell is then heated to test temperature and allowed to equilibrate before applying test gas to the specimen and pressurizing. As a minimum, the following test conditions shall apply:

- high pressure (P_1): hose design pressure, may be used if pipe design pressure is not known;
- temperature (T): service, or three higher temperatures for three accelerated tests followed by Arrhenius-extrapolation of the three resulting data points to service (see Annex D).

The pressure increase due to permeation in the low pressure chamber with time may be converted to the rate of gas permeation (cm^3/s at standard temperature and pressure), assuming the gas to be ideal, by Equation (1):

$$\frac{dq}{dt} = \left(\frac{\partial P_2}{\partial t} \right) \left(\frac{273 \times V_{lp}}{T_{lp}} \right) \quad (1)$$

where

V_{lp} is the volume of the low pressure chamber;

T_{lp} is the temperature (ambient) of the low pressure chamber.

P_2 is expressed in atmospheres.

The permeation coefficient Q can be obtained from the gradient, at steady state conditions, of the permeated gas pressure versus time plot using Equation (2) (see also Annex E):

$$\left(\frac{q}{t} \right) = QA \left(\frac{P_1 - P_2}{h} \right) \quad (2)$$

where

- h is the specimen thickness;
- P_1 is the pressure in the high pressure chamber;
- P_2 is normally zero unless stipulated otherwise.

The initial transient stage of the test can be used to provide an estimate of the diffusion coefficient D , as shown in Equation (3):

$$D = \frac{h^2}{6\tau} \quad (3)$$

where time-lag τ is the value of time where the back-extrapolated steady state line intersects the time axis.

The solubility coefficient s is then determined from Equation (4):

$$Q = D \times s \quad (4)$$

The concentration c of a single gas absorbed into the polymer surface may be calculated from Equation (5):

$$c = s \times P_1 \quad (5)$$

The measured criteria are the permeation coefficient Q in $\text{cm}^2/\text{s}/\text{atm}$, the diffusion coefficient D in cm^2/s , the solubility coefficient (s) in atm^{-1} , and the dimensionless (i.e. $\text{cm}^3 \text{ gas}/\text{cm}^3 \text{ elastomer}$) concentration c applying at the high pressure face. For a lining material contacting an essentially impermeable layer (e.g. external steel piping), c will eventually be achieved (or nearly so) throughout. For a series of accelerated tests, these coefficients can be used for Arrhenius extrapolations (see Annex E). Q values can be used to predict permeation rates through hose liners (see Annex E). D can be used for rough estimates (root mean squares) of migration distance within the material after time t , using $(2Dt)^{1/2}$. Experience suggests that breakthrough time can reasonably be taken as $1/2(\tau)$.

For mixed gases – yielding apparent coefficients only by the above procedures – any following estimates should be for guidance only.

The presence of the steel sinter support may reduce measured permeation rates. For tests carried out as above, this observation should be included on the test report.

8.2.5 Requirements for RGD

RGD performance for hose linings according to this part of ISO 23936 should follow the procedures of 6.2.3.2 in ISO 13628-10:2005 or API 17K, but using gas compositions taken from Tables A.2 to A.4 of this part of ISO 23936.

Because diffusion rate is proportionate to the square of distance migrated, soak times for hose linings should be increased from those used for testing small seals by a factor, K , which relates distances to be migrated in seals and hoses raised to the power of 2. This factor to calculate the soaking time is as shown in Equation (6):

$$K = (h/r)^2 \quad (6)$$

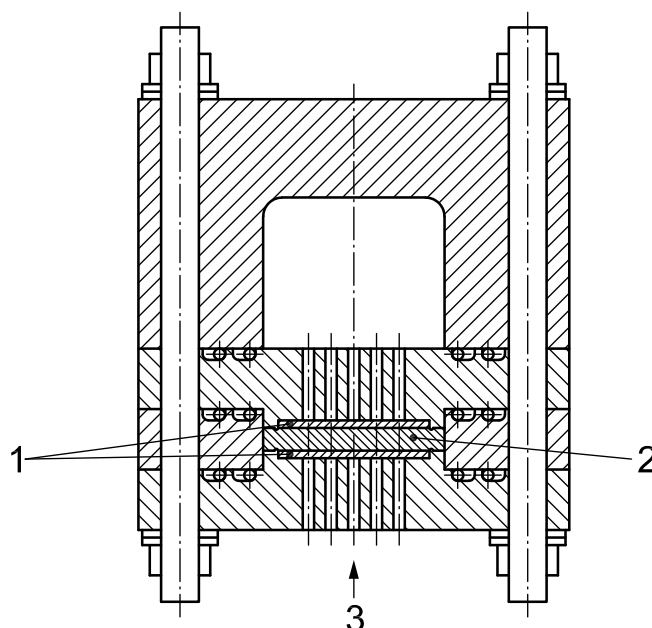
where

- h is the hose lining thickness with fluid entering the lining from one exposed surface only;
- r is the radius of the seal cross-section for the test arrangement described in Annex B.

The starting point is a seal cross-section radius of 2,66 mm with a minimum soaking time of 68 h.

The specimen for RGD testing of hose lining should include some fabrication to allow assessment of the elastomer's RGD resistance when supported as in service. Single textile fabric layers should sandwich the elastomer lining layer. The specimen should be moulded to the required thickness and cured in a plunger mould. Moulding pressure should be $0,7 \text{ MPa}^1$) to be similar to that met in hose manufacture or as agreed between interested parties. Lining thickness including fabrics should be 3 mm to 4 mm and specimen diameter 30 mm, or as similarly agreed. Fabrics should be rubberized and of the type used in the manufacture of hoses for this service.

Figure 1 shows the specimen and portholes for high pressure gas to enter it through one face only. More portholes above the specimen allow permeated gas to arrive in a vented chamber (a vertical line showing the vent). Figure 2 shows the test arrangement with a stack of seal jigs located in a suitable pressure chamber (to accommodate test pressure plus a safety factor), and the vented gas led outside it.

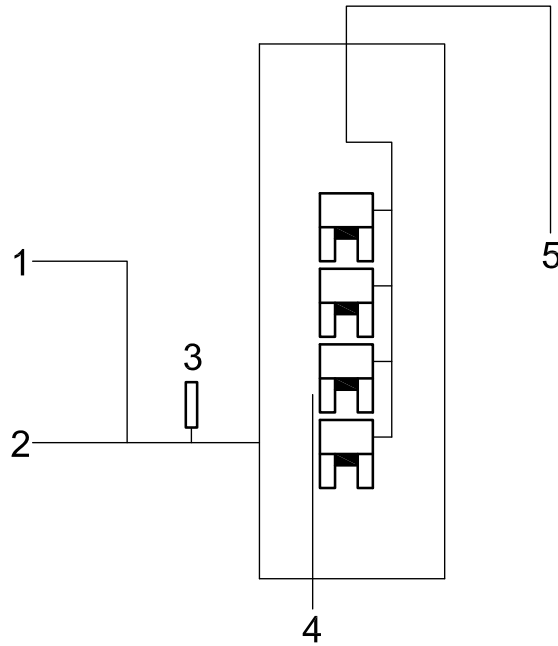


Key

- 1 fabric layers
- 2 elastomer
- 3 high pressure gas

Figure 1 — RGD test jig holding fabricated specimen; HP gas applied unidirectionally

1) 1 bar = 0,1 MPa.



Key

- 1 gas in
- 2 PC controlled blowdown
- 3 pressure transducer
- 4 thermocouple
- 5 permeated gas vent

Figure 2 — Hose lining jigs stacked in a pressure chamber during testing

The temperature, pressure, number of test cycles, decompression rate and acceptance criteria of ISO 13628-10 and API 17K shall apply.

Test fluids should be selected from Tables A.2 to A.5 in this part of ISO 23936; those from Table A.3 and Table A.5 (sour conditions) should only be used if gas emitted during decompression can be handled safely.

8.2.6 Requirements for ageing tests

In ISO 13628-10 and API 17K, the test liquid used for exposure tests is chosen by the component purchaser; to comply with this part of ISO 23936, liquids given in Tables A.1, A.4 and A.5 should be used. Ageing as a materials test procedure should use the same approach as that taken in this part of ISO 23936 for seal elastomers (Clause 7), with the acceptance criteria also being the same.

8.3 Qualification of bonded flexible hose – Layers outside the liner

The cover material should possess good mechanical properties, including tear strength/impact resistance, to resist mishandling issues, etc.; low sea-water uptake should be demonstrated if the cover is subject to seawater immersion. Layers between liner and cover should be manufactured from elastomer types intermediate in characteristics between the two, each having evidence provided of good bondability to adjacent layers and to any fabric, textile, wire reinforcement, etc. embedded in them.

9 Qualification of elastomeric materials in other large components

9.1 General

For large components, although it is likely that component testing under particular conditions required by the user will take on increased relevance, materials testing will often still be required to aid material selection for the component and for qualification purposes. This clause describes qualification for elastomers in different components.

9.2 Qualification of elastomeric materials in flexible joints

9.2.1 General

Flexible joints are part of the subsea system used in the production and export transportation systems for offshore production platforms. The joints provide rotational flexibility at the connection points that reduces bending stresses and increases the fatigue life of the metallic components in critical regions. The flexibility is provided by a spherical joint that consists of a laminated construction of spherical layers of steel and elastomer bonded together during the vulcanization process. Rotational flexibility is achieved by shearing of the elastomer layers referred to as structural layers, whilst internal pressure and tension loads in the line are reacted by compression of these layers. The edges of the steel plates and structural elastomer layers may be protected from direct fluid/gas exposure by an elastomeric cover layer which is usually a similar material to the main structural layers. Typical constructions employ either nitrile butadiene rubber (NBR) or hydrogenated nitrile butadiene rubber (HNBR) materials. The fluids being carried are in contact with one side of the joint, whilst the other side is in contact with either seawater or air. Fluids transported include production fluids imported to the platform, and gas and oil exported from the platform after processing. Risers may also transport well injection fluids such as gas or water and any other additives to control wax build-up and to provide corrosion protection.

The flexible joint vendor will carry out a fatigue analysis using the specified conditions to demonstrate an acceptable life of the design to the user's satisfaction. Contributions from time dependent creep rupture failure under the mean components of the loading should be considered as well as cyclic fatigue damage arising from the dynamic components (see Reference [20]). Compression of the rubber layers due to pressure and tension loads results in concentrations of shear at the edges of the layers; in typical designs, these are highest on the seawater/air side of the layers.

9.2.2 Specific sections relating to the qualification of flexible joints

Fluid compatibility with the cover and structural layers is covered by ISO 1817.

The effects of fluid permeation through the cover layer and into the structural layers and bonds should be addressed, as should the effects of ageing in terms of their impact on the design life of the flexible joints. The effects of any chemicals used in the lines and which may come into contact with the elastomer may also need to be assessed in terms of chemical compatibility and swelling. The effects of gas decompression on the integrity of the cover layers and structural layers may also need to be addressed.

Due to the complexities involved regarding different design solutions that can limit fluid/gas exposure and how the rubber layers perform in protecting the structural layers, testing for fluid/gas exposure will need to be performed using test specimens and techniques agreed upon between the asset operator and the component manufacturer, including any third-party verification as required.

9.3 Qualification of elastomeric materials in blow-out preventers

9.3.1 General

Elastomeric seals employed in blow-out preventers (BOPs) should be qualified as appropriate in accordance with Clause 7. Test conditions based on operational conditions should be agreed upon by the user and/or asset operator. Other components are much larger, which will lead to some differences in approach.

9.3.2 Specific sections relating to the qualification of BOPs

The performance testing given in ISO 13533 or API 16A for elastomer materials should be followed using relevant standards. ISO 16070 covers flow control equipment which does not relate to packers. Additionally API 14A applies to surface and subsurface safety valves and again does not relate to packers. Ram shear seal elastomeric components should be specified and qualified with regard to an acceptable magnitude of appropriate properties and fluid resistance. Exposures to fluids should be based on the most appropriate of those tabulated in Annex A. RGD assessments should be based on the approach used for hoses rather than used for seals in 8.2, because they are also larger components.

9.4 Qualification of elastomeric materials for packers

This subclause refers to all types of packers including permanent and retrievable casing packers and bridge plugs, inflatable thru tubing, casing and open hole packers, and open hole mechanical packers. Use of this equipment may reflect both short- and long-term performance requirements.

Elastomeric seals employed in packers generally shall be qualified as appropriate according to Clause 7. Validation procedures for packer assemblies are covered in ISO 14310. Generally, for retrievable casing packers and bridge plugs, packing element sealing compounds should offer a combination of high extrusion resistance and adequate strain capability to pack off without suffering fracture. Maximum extrusion resistance of a permanent packer, due to typically near 100 % mechanical back up, is slightly less important than adequate strain capability. Inflatable packers should demonstrate high tear strength magnitudes and high extensibility at high temperatures, which should be specified from the options in Table A.6.

The requirements for qualification of materials for permanent packers, traditional and polished bore receptacle (PBR) shall be the same as for other large components. High pressure gas permeation testing may be required.

Drilling fluids and later production fluids may be contacted in sequence; testing may need also to be conducted in sequences to mirror this.



Annex A (normative)

Test media, conditions, equipment and procedures for ageing of elastomeric materials

A.1 Test requirements

SAFETY PRECAUTIONS — The test procedures involve the use of pressurized fluids, which may be flammable and may have toxic effects. These media may be extremely hazardous if not handled correctly. Multiphase mixtures give particular problems. Hydrogen sulphide is extremely toxic. The testing organization shall ascertain and implement the appropriate safety precautions before commencing any test work.

A.1.1 Ageing test media

A.1.1.1 General

Tests fluids shall be representative of the application environment and be stable at the test temperature. This might be in the form of sweet service, sour (H₂S-containing) service, or might involve testing in completion brines or other added fluids such as corrosion inhibitors, drilling muds, injection fluids, hydraulic fluids, etc. The fluid contacting each side of the seal needs to be considered.

A.1.1.2 Simulated production fluid

The production fluids are defined as either sweet or sour and can be single phase (e.g. gaseous or liquid) or multiphase (e.g. oil and water and gas). Fluid composition options for testing are given in Tables A.1 to A.5. The reasoning behind these choices is given in informative Annex E. The fluid compositions are given in scales of severity except the bespoke variant which may be more or less severe. For example, qualifying a material to A.1.ii also qualifies a material to A.1.i, but not vice versa. Similarly, testing in sour service conditions will also qualify the seal material for sweet service conditions.

Table A.1 — Hydrocarbon liquid phase options for sweet and sour ageing tests

Variation classification	Type	Composition volume
A.1.i	Non-aromatic	70 % heptane, 30 % cyclohexane
A.1.ii	Aromatic	70 % heptane, 20 % cyclohexane, 10 % toluene
A.1.iii	Bespoke	As agreed between interested parties

Table A.2 — Gas phase options for sweet ageing tests

Variation classification	Type	Composition mol%
A.2.i	Normal	5 % CO ₂ , 95 % CH ₄
A.2.ii	Bespoke	As agreed between interested parties

Table A.3 — Gas phase options for sour ageing tests

Variation classification	Type	Composition mol%
A.3.i	Normal	3 % CO ₂ , 2 % H ₂ S, 95 % CH ₄
A.3.ii	High H ₂ S	5 % CO ₂ , 10 % H ₂ S, 85 % CH ₄ ^a
A.3.iii	Bespoke	As agreed between interested parties

^a Accords with a fluid choice in ISO 10423.

Table A.4 — Fluid phase distribution for classification A.4 — Sweet multi-phase fluid ageing

Liquid phase volume%	Gas phase volume%	Composition
—	30	Any variation in Table A.2
10	—	Deionized water
60	—	One of liquids in Table A.1

Table A.5 — Fluid phase distribution for classification A.5 — Sour multi-phase fluid ageing

Liquid phase volume%	Gas phase volume%	Composition
—	30	Any variation in Table A.3
10	—	Deionized water
60	—	One of the liquids in Table A.1

The composition of all fluids to which the test specimen is exposed shall be detailed in the test report.

A.1.1.3 Other test fluids

In addition to production fluids, it will be necessary in many instances to perform application-specific testing of materials in contact with other types, e.g. drilling fluids, scale inhibitors, hydrate inhibitors, well stimulation fluids and corrosion inhibitors. Specific test procedures shall be written detailing the exposure environment. The test methodology shall be according to this part of ISO 23936.

A.1.2 Ageing test conditions

A.1.2.1 Test temperatures

Since data from accelerated tests are required to enable extrapolation, tests shall be run at a minimum of three temperatures, all of which are above operating temperature. If the service level is not known, the temperatures selected should be as high as possible for the material type. Exposure test temperatures should be selected from Table A.6. Particular care is required to ensure that reactions occurring are representative of those which will occur at the operating temperature. The limitations to extrapolation regarding temperature inherent in the Arrhenius method shall apply.

Table A.6 allows test temperatures according to ISO 10423:2009, if required (see Annex E). However, a temperature service range rather than value is specified for the classified ratings. Three higher test temperatures are shown for each service temperature range; using these, an Arrhenius extrapolation may be possible to provide a result for the highest temperature in the range – thus qualifying the whole range from a worst-case viewpoint.

Alternatively, the extrapolation can be continued to a lower specific temperature if required. If a more precise test temperature is agreed between interested parties, the bespoke option should be used.

Table A.6 — Test temperature

Temperature classification	Operating minimum °C	Operating maximum °C	Elevated test temperatures °C
K	–60	82	97, 112, 127
L	–46	82	97, 112, 127
P	–29	82	97, 112, 127
R	Room temperature	Room temperature	36, 51, 66
S	–18	66	81, 96, 111
T	–18	82	97, 112, 127
U	–18	121	136, 151, 166
V	2	121	136, 151, 166
X	–18	180	195, 210, 225
Y	–18	345	Not possible
Non-ISO/API	0	150	165, 180, 195
Bespoke	As shall be agreed between interested parties		

NOTE This is consistent with ISO 10423 and API 6A temperatures or relevant to down-hole applications.

The tolerance on test temperature is ± 2 °C. Test temperature versus time details plus classification, if appropriate, shall be fully described in the test report.

A.1.2.2 Test pressure

For chemical ageing, it is important to start each ageing period with the same quantity of the sour gas mixture present in the vessel. The length of each interval at test temperature will vary but is not likely to exceed 14 days.

A typical procedure is to pressurize the test vessel to $(6 \pm 0,5)$ MPa at room temperature with the test gases and then heat to the required temperature. The changing pressure should be continuously recorded. An alternative method is to add a fixed amount of the test gas at a given low temperature before heating the vessel to the test level. Cell pressure, once temperature stabilizes, will then vary with target temperatures but the starting quantity of (reactive) H_2S in the vessel will always be the same. Hence, the test vessel should be heated to $50\text{ }^\circ\text{C}$ and $(6 \pm 0,5)$ MPa of the test gas mixture admitted, before raising temperature to the required level. The pressure should be continuously recorded.

A.1.2.3 Exposure periods

The time required for relevant tensile properties of an elastomer compound to reach the pre-defined "failure" limit will vary with temperature and material type: some elastomers will not exhibit any chemical ageing characteristics at all. Elastomers will saturate quickly at elevated temperatures but can take much longer to react chemically with H_2S (if present) to a meaningful extent. It is recommended that the highest temperature exposure test be started first, in order to gauge the extent of material chemical change with time. Several weeks may be required to determine material behaviour trends (see Annex E).

A.1.3 Ageing test specimens

Tensile specimens shall be obtained from moulded sheet of elastomer, having a nominal thickness of 2 mm. Any tensile test piece defined in a published standard will be acceptable; the same geometry shall be used throughout the test programme. The level of tensile test piece replication shall be a minimum of five. It is not permitted (or desirable) to age moulded sheet and subsequently cut tensile specimens from it.

A.2 Equipment

A.2.1 Test vessel

The test vessel shall be rated for use at the test temperature and pressure and the metallic materials shall be resistant to the test fluid. The fluid capacity shall be such that the ratio of fluid to test specimen volume is at least 25:1. The vessel shall be capable of being purged to remove air before testing. The test pieces shall be immersed in a free state such that test fluid can contact all surfaces.

A.2.2 Exposure in fluid mixtures

The polymer samples shall be exposed in the liquid phase for a multiphase fluid ageing.

A.3 Test procedure

A.3.1 General

The following clauses describe the procedures to be employed to determine the chemical ageing characteristics of elastomeric materials.

This procedure aims to quantify the rate of change of material properties as a function of time and temperature. All property measurements shall be made at room temperature. The measurements in A.3.2 shall be made before and after immersion testing. All measurements shall be recorded and reported in the test report.

The level of tensile test piece replication per fluid exposure condition (time/temperature) shall be five. A minimum of three elevated temperature fluid exposure tests shall be run, with an initial test plus a minimum of four time periods per temperature.

A.3.2 Material property measurements

The hardness and tensile property levels (modulus at 50 % and 100 % elongation, tensile strength, elongation at break) of as-received material shall be measured at room temperature according to the referenced procedures; individual and mean values shall be reported.

The tensile property levels of liquid saturated material (i.e. not chemically aged – no H₂S) for reference purposes can be determined in two ways. First, an extra set of replicate specimens can be included in the exposure test vessel and the cell is heated to test temperature and vapour pressure for 48 h; the sour gas mixture is not added. The vessel is then cooled and opened and one set of tensile test pieces is removed for tensile testing. The sour gas mixture is added and the vessel is re-heated in accordance with A.1.2.2, to commence the ageing portion of the test. Alternatively, a single set of replicates can be heated to test temperature in a suitable vessel (containing the relevant test liquids) in an oven for 48 h before retrieval.

The mass and volume change of the elastomer versus exposure time at each temperature shall be determined by including a small piece of the rubber in each test cell; a 25 mm × 25 mm sample is sufficient. The volume change shall be determined according to the displacement method. A balance with an accuracy of 1 mg shall be used. The percentage change in mass and volume as a function of time at each temperature shall be included in the test report, preferably in graphical form.

A.3.3 Sequence for fluid immersion test

A.3.3.1 A recommended sequence of actions is given below. The procedure used shall be documented in the test report.

- a) Add test liquid(s) to vessel.
- b) Install test specimens in the liquid phase of the test liquid; close vessel.
- c) Purge vessel with nitrogen gas (< 5 ppm O₂); bubbling the nitrogen through the liquid phase with a flow rate of 100 ml/min for at least 15 min is preferred to remove most of the oxygen.
- d) Pressurize the vessel with at least 4 MPa nitrogen and perform leak check.
- e) Release the nitrogen at 0,1 MPa/min, heat the closed vessel to test temperature and hold for a period of 48 h minimum; this ensures that the elastomer test pieces will be saturated.
- f) Cool to room temperature, open the vessel and remove the 5 reference test pieces, close vessel, repurge with nitrogen and leak check vessel.
- g) Add test gas at room temperature to a pressure of (6 ± 0,5) MPa.
- h) Raise temperature to test level.
- i) Record the changing test pressure and maintain and record temperature for the specified period.

A.3.3.2 When a vessel is cooled for sample removal and at the end of the exposure period, the following procedure is recommended to reduce the risk of decompression damage.

- a) Cool the vessel naturally to ambient temperature; overnight is usually sufficient.
- b) Reduce remaining pressure safely at a maximum rate of 0,1 MPa/min, neutralizing the sour gas with a scrubber.
- c) Flush vessel with nitrogen to remove remaining H₂S, if used.
- d) Open vessel and retrieve test specimens; these should be kept wet by following the procedure in A.3.5.
- e) Carry out post-test procedures of inspection (see A.3.4) and measurement (see A.3.2).

A.3.4 Visual inspection

The test specimens shall be visually inspected for damage directly after removal from the vessels. The nature of any damage, e.g. embrittlement, swelling, blistering, shall be recorded. A photographic record of representative damage features shall be included in the test report.

A.3.5 Sample handling and storage procedures

Test specimens retrieved from ageing fluid shall be stored in fresh fluid (of the same composition used in the immersion test) until required for measurement. When weighing, remove sample from the liquid, pat dry and weigh in air and then in water within 3 min to minimize evaporative losses; return to liquid immediately until put back into the test vessel. When removing samples for tensile testing, remove each sample individually from the storage liquid, measure neck dimensions and tensile test, all within 10 min.

Tensile tested material shall be stored in re-sealable polyethylene bags, appropriately labelled.

A.4 Test report (ageing)

A.4.1 Test material details

The compound manufacturer, manufacturer's compound name/number or other reference, recipe revision level, batch/lot number and cure date shall be reported. The base elastomer type according to the definitions in the current issue of ASTM D1418 should be specified. However, it is recognized that developments in material technology exceed the pace of standard development and it may not be possible to assign an elastomer type in all cases – this is particularly true of fluoroelastomers.

A.4.2 Exposure test conditions

Exposure test conditions are as follows:

- a) test medium identification with classification, sub-classification where appropriate, and detailed composition;
- b) test temperature (°C) and temperature history;
- c) test pressure (MPa) and pressure history;
- d) test duration (hours);
- e) date and time for start and end of test.

The ageing time is the time the material was subjected to test pressure and test temperature; time spent heating and cooling the test-cell shall not be included in the calculation. Significant deviations of test temperature and/or pressure shall be justified technically.

A.4.3 Material measurements

The following material properties shall be measured:

- hardness (Shore A or IRHD scale is acceptable);
- mass and volume change versus exposure time;
- modulus at 50 % and 100 % elongation, tensile strength, elongation at break; individual and mean values using the original measured dimensions of the sample;
- visual condition.

A.4.4 Life estimation

Tensile properties and mass/volume change at each test temperature shall be presented graphically as plots versus immersion time. If applicable, an Arrhenius graphical presentation [logarithmic time against $1/T$ (absolute temperature (K))] based on trends for tensile properties shall be made. A best-fit line should be drawn to permit interpolation or extrapolation to service temperatures and the equation stated. Annex C and Annex E provide more detail.

A.4.5 Test report

The test report shall include the following information, as a minimum:

- a) a reference to this part of ISO 23936;
- b) all details necessary for complete identification of the material or product tested;
- c) the type of specimen used, its method of preparation, its dimensions, surface condition, etc.;
- d) the conditioning procedure used, ageing test conditions;
- e) pre-test measurement details in accordance with A.3.2;
- f) post-test measurements details in accordance with A.4.3;
- g) estimated service life.

See Table A.7 for an example of a test report.

Table A.7 — Example test report

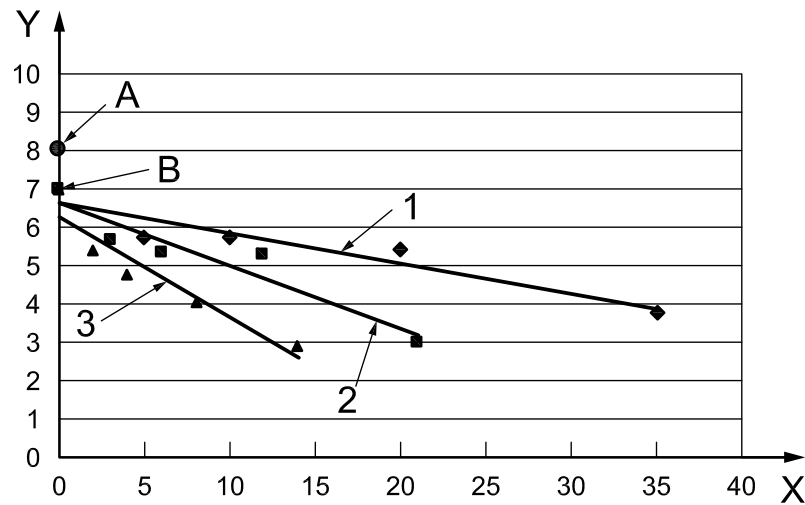
Material		
Manufacturer		Acme Seals, Inc.
Compound name/number/reference		FabFluoro
Elastomer type	ASTM D1418	FKM Type 3
Recipe revision level		
Lot/batch no.		FF2344rw4r/07
Cure date		Q4 2010
Type of specimen		O-Ring
Size		AS568-325
Ageing test conditions		
Fluid	Classification	A.5 subclass A.3.i/A.1.ii
		Composition
	Gas	2 % H ₂ S, 3 % CO ₂ , 95 % CH ₄
	Liquid	10 % toluene, 70 % heptane, 20 % cyclohexane /seawater
Test temperatures	°C	210, 220, 230
Pressure	MPa	10
Ageing periods	days	7, 14, 21, 35

Table A.7 — Example test report (continued)

General			
Test lab		Ace Test Company	
Test date		10 June - 25 October 2010	
Test gas certified	YES/NO	YES	
Pressure calibration available	YES/NO	YES	
P/T logs available	YES/NO	YES	
Pre-test measurements			Standard
Hardness	Shore A/IRHD	85	ISO 48
Modulus at 50 % elongation	MPa	8,0	ASTM D1414
Modulus at 100 % elongation	MPa	12,4	ASTM D1414
Tensile strength	MPa	16,1	ASTM D1414
Elongation at break	%	98	ASTM D1414
Modulus at 50 % elongation (saturated)	MPa	7,0	ASTM D1414
Tensile strength (saturated)	MPa	12,5	ASTM D1414
Elongation (saturated)	%	140	ASTM D1414
Post-test measurements			Standard
Hardness	Shore A/IRHD (minimum/maximum)	76 to 84	ISO 48
Mass change	% (maximum/minimum)	+3,5 -0,8	ASTM D1414
Volume change	% maximum/minimum)	+5,6 -1,6	ASTM D1414
Modulus at 50 % elongation	MPa (minimum/maximum)	2,9 to 5,7	ASTM D1414
Tensile strength	MPa (minimum/maximum)	5,8 to 11,4	ASTM D1414
Elongation at break	% (minimum/maximum)	137 to 205	ASTM D1414
Visual condition		Unchanged	
Test time at temperature			
Modulus at 50 % elongation			
time to 50 % change at 210 °C	days	39,4	
time to 50 % change at 220 °C	days	19,0	
time to 50 % change at 230 °C	days	10,6	
Service life calculated via Arrhenius extrapolation			
time to 50 % change at 150 °C	years	11,5	
time to 50 % change at 100 °C	years	180	

Table A.7 — Example test report (continued)

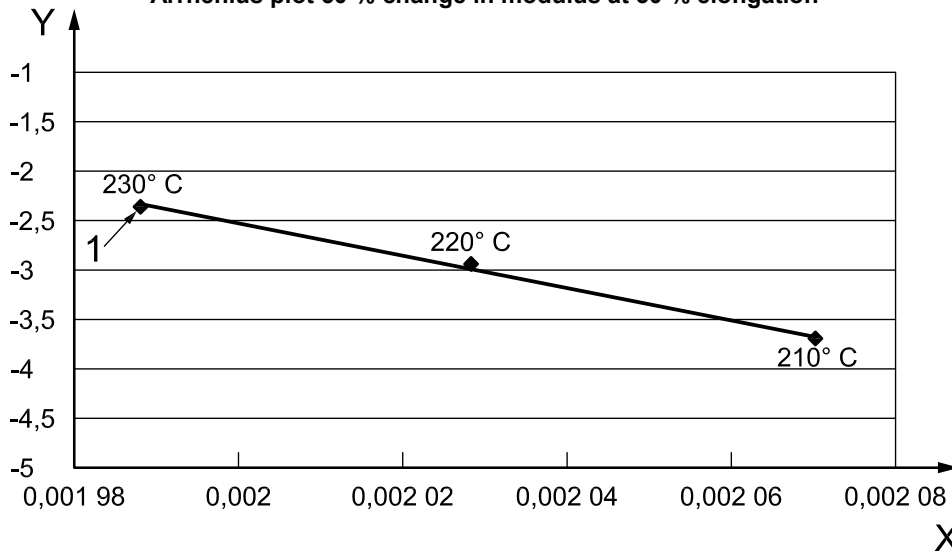
Change in modulus at 50 % elongation with exposure temperature and time



Key

- X exposure time, days
- Y modulus at 50 % elongation, MPa
- 1 210 °C; $y = -0,079 2x + 6,618 2$
- 2 220 °C; $y = -0,163 5x + 6,613 6$
- 3 230 °C; $y = -0,260 6x + 6,259 1$
- A modulus at 50 % elongation of a dry unaged sample
- B modulus at 50 % elongation of a wet unaged sample; zero reference

Arrhenius plot 50 % change in modulus at 50 % elongation



Key

- X inverse temperature, $1/T_K$
- Y $\ln(1/t_{50})$
- 1 $y = -15 958x + 29,386$; $R^2 = 0,997 3$
 time to 50 % change at 150 °C: 11,5 years
 time to 50 % change at 100 °C: 180 years

STAMP/SIGNATURE

Annex B (normative)

Test media, conditions, equipment and procedures for rapid gas decompression testing of elastomeric materials

B.1 Test requirements

SAFETY PRECAUTIONS — The test procedures involve the use of pressurized fluids, which may be flammable and may have toxic effects. These media may be extremely hazardous if not handled correctly. The testing organization shall ascertain and implement the appropriate safety precautions before commencing any test work.

B.1.1 RGD test conditions

B.1.1.1 General

In this annex, options are given for fluid composition, temperature and pressure, as well as the variables having less of an effect on RGD performance. The applicability of each of the alternatives will depend on the intended application for the seal, if known.

Successful testing at particular values of temperature and pressure will automatically qualify the material for use in applications where the service temperature and pressure lie below these values. Extrapolation of RGD resistance to temperatures and pressures above the test levels is not permitted.

B.1.1.2 Test fluid

The use of dry gas is sufficient to provide an adequate indication of elastomer resistance to RGD events. However, where liquid (e.g. hydrocarbon oil, methanol) is known to be present in service, it should be included in the test; the procedure should ensure replenishment of added liquid between pressure cycles. The RGD test fluid options are defined in Table B.1.

Table B.1 — Test fluid options for RGD testing

Standard gas mixture	Composition
B.1.i	10 mol% CO ₂ , 90 mol% CH ₄
B.1.ii	10 mol% CO ₂ , 90 mol% N ₂
Bespoke	As agreed between interested parties; can include liquids

Testing in B.1.i also qualifies for B.1.ii, and testing in B.1.ii also qualifies for B.1.i.

CO₂ is currently considered to be a suitable substitute for H₂S; however, see Annex F. Hence, when RGD testing for sour gas applications, the H₂S can be replaced by CO₂ in the test gas mixture. Seal material sour ageing characteristics shall be qualified according to relevant environment and requirements of Annex A.

B.1.1.3 Test temperature

The RGD test shall be conducted at one of the following temperatures:

- a) $(100 \pm 2) \text{ }^\circ\text{C}$;
- b) bespoke, with agreement between interested parties.

For a sealing compound to be certified, it shall meet the acceptance criterion after being tested at a temperature of $100 \text{ }^\circ\text{C}$ and a pressure of 15 MPa (see B.1.1.4); these are considered to be reasonable minimum conditions for RGD resistance. RGD testing at any temperature below $100 \text{ }^\circ\text{C}$, with pressure below 15 MPa, is not sufficient to be certified. The bespoke option allows any other temperature to be selected, perhaps associated with a particular application.

Temperature shall be recorded during the test with calibrated temperature measurement equipment, preferably linked to a PC running data acquisition software. The thermocouple should be located in the centre of the test vessel. The temperature-time log shall be included in the test report.

When performing the RGD test, the temperature shall be increased to the test level and be steady for at least 15 min before the gas pressure is applied. The temperature shall be maintained during the depressurization stages of the test as far as possible, although slight (and transient) reductions are unavoidable during depressurization events. After the final depressurization, the test vessel shall be allowed to stand at test temperature with port(s) open for at least 12 h to allow the test seals to degas, before cooling.

B.1.1.4 Test pressure

The RGD test shall be conducted at one of the following pressures:

- a) $15 \begin{smallmatrix} +1 \\ -0,5 \end{smallmatrix} \text{ MPa}$;
- b) bespoke, with agreement between interested parties.

For a sealing compound to be certified, it shall meet the acceptance criterion after being tested at standard conditions of pressure (15 MPa) and temperature ($100 \text{ }^\circ\text{C}$; see B.1.1.3); these are considered to be reasonable minimum conditions for RGD resistance. RGD testing at any pressure below 15 MPa, with temperature below $100 \text{ }^\circ\text{C}$, is not sufficient to be certified. The bespoke option allows any other pressure to be selected, perhaps associated with a particular application.

Pressure shall be measured with calibrated pressure measurement equipment, and recorded during the test. The measuring rate should be reduced for the depressurization stages of the test; an interval of 30 seconds is recommended. The pressure-time log shall be included in the test report, as well as sensor calibration details.

When performing the RGD test, the vessel should be pressurized only after it has been stable at test temperature for at least 15 min. After the final depressurization, the vessel shall be allowed to stand at test temperature with port(s) open for at least 12 h, to allow the test seals to degas, before cooling.

B.1.1.5 Exposure periods and number of cycles

The initial exposure period (first cycle) shall be a minimum of 68 h continuously at test pressure and test temperature. The total number of pressure cycles shall be eight; see Annex F for additional information.

Each cycle of the RGD test shall consist of the following operations conducted at test temperature:

- a) increase pressure to the test level;
- b) maintain pressure for the required time period;
- c) reduce pressure at the rate specified in B.1.1.6;
- d) hold at ambient pressure for 1 h (+10/–0 min).

After the eighth depressurization and the degas period, the vessel should be cooled (according to B.1.1.3).

The eight cycle RGD test is designed to be completed within a one week period, commencing on a Friday; an example schedule is given in Table B.2. There is no provision in the standard test procedure for intermediate sampling; see Annex F.

Table B.2 — Example RGD test schedule

Day	Time	Cycle	Action
Friday	morning	0	load vessel, heat and pressurize; hold for at least 68 h
Monday	morning	1	depressurize, hold, re-pressurize; hold for at least 6 h
	afternoon	2	depressurize, hold, re-pressurize; hold for at least 12 h
Tuesday	morning	3	depressurize, hold, re-pressurize; hold for at least 6 h
	afternoon	4	depressurize, hold, re-pressurize; hold for at least 12 h
Wednesday	morning	5	depressurize, hold, re-pressurize; hold for at least 6 h
	afternoon	6	depressurize, hold, re-pressurize; hold for at least 12 h
Thursday	morning	7	depressurize, hold, re-pressurize; hold for at least 6 h
	afternoon	8	depressurize; leave at test temperature to degas
Friday	morning		cool cell
	afternoon		retrieve and inspect test seals

The test seals shall be inspected according to the guidance given in Clause B.4.

B.1.1.6 Rate of depressurization

The rate of test cell depressurization shall be one of the following:

- a) $(2 \pm 0,2)$ MPa/min;
- b) bespoke, with agreement between interested parties; this includes multiple rates.

As far as possible the gas pressure shall be released continuously via the valve attached to the test cell. The depressurization rates shall be calculated from the pressure log and the mean value included in the test report.

B.1.2 RGD test specimen

The standard test specimen shall be an O-ring seal with a (nominal) CSD of 5,33 mm. A minimum of four replicate O-ring seals shall be tested. There is no limit to the number of replicate seals that can be included in an RGD test; however, all of the tested seals shall meet the acceptance criterion (see 7.3.2) for the compound to be certified in accordance with this part of ISO 23936.

The smallest allowable O-ring size is 312. There is no upper size limit but practical considerations mean that O-rings larger than size 329 are unlikely to be employed as test pieces. All seals shall conform to ISO 3601-3:2005, class N.

It has been found that if a 5,33 mm section O-ring passes the RGD test under a given set of conditions, then smaller section O-rings (e.g. 3,53 mm, 2,62 mm) of the same compound shall be considered to pass providing all else is equal (i.e. method of seal manufacture, housing geometry). Extrapolation of RGD performance from a small section seal to a larger section diameter seal is not permitted. If the standard RGD test is applied successfully to O-ring seals having, for example, a CSD of 3,53 mm, then 5,33 mm O-rings of the same compound would also have to be successfully tested in order for O-rings having this CSD to be certified.

B.1.3 Test seal housing details

RGD testing shall be performed using replicate whole O-ring seals, constrained radially in appropriate metallic grooves which allow gas to access both sides of every seal. Performance information obtained from the testing of free-standing seals or housed seal sections is not acceptable.

Groove dimensions shall be measured and reported, along with the radial CSD of each test O-ring. The level of groove fill, calculated on a sectional area basis using the measured CSD, shall be reported. The percentage deflection (or squeeze) imposed by the assembled housing on the O-ring shall be reported, using the measured CSD and groove dimensions.

The arrangement that shall be tested is one in which the O-ring seal

- a) is deflected radially by $(14,5 \pm 3) \%$ of its nominal CSD, and
- b) occupies 80 % to 85 % of groove volume.

The choice of alternative groove geometry for the O-ring test seals is open and the source shall be given in the test report, e.g. International Standard, corporate specification, etc.

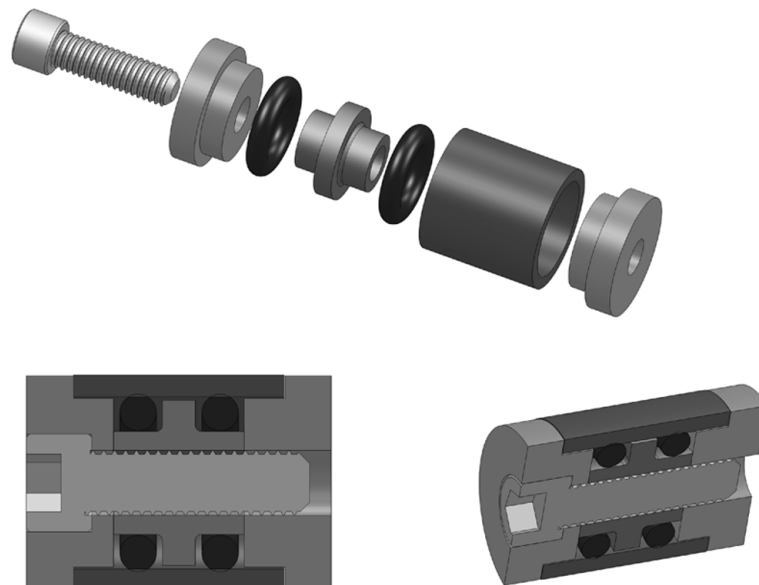
Alternative deflections and groove fill parameters can be used if agreed between the parties.

It is convenient to test O-rings in metallic fixtures designed to house two or four seals. Figure B.1 a) shows a photograph of the component parts of a steel fixture which can hold two size 312 O-rings; Figure B.1 b) shows dimensions.

B.2 RGD test equipment

The test vessel shall be rated for use at the required test pressure and temperature. The vessel lid sealing arrangement shall be appropriate to the test conditions. If O-ring seals are employed then the compound shall

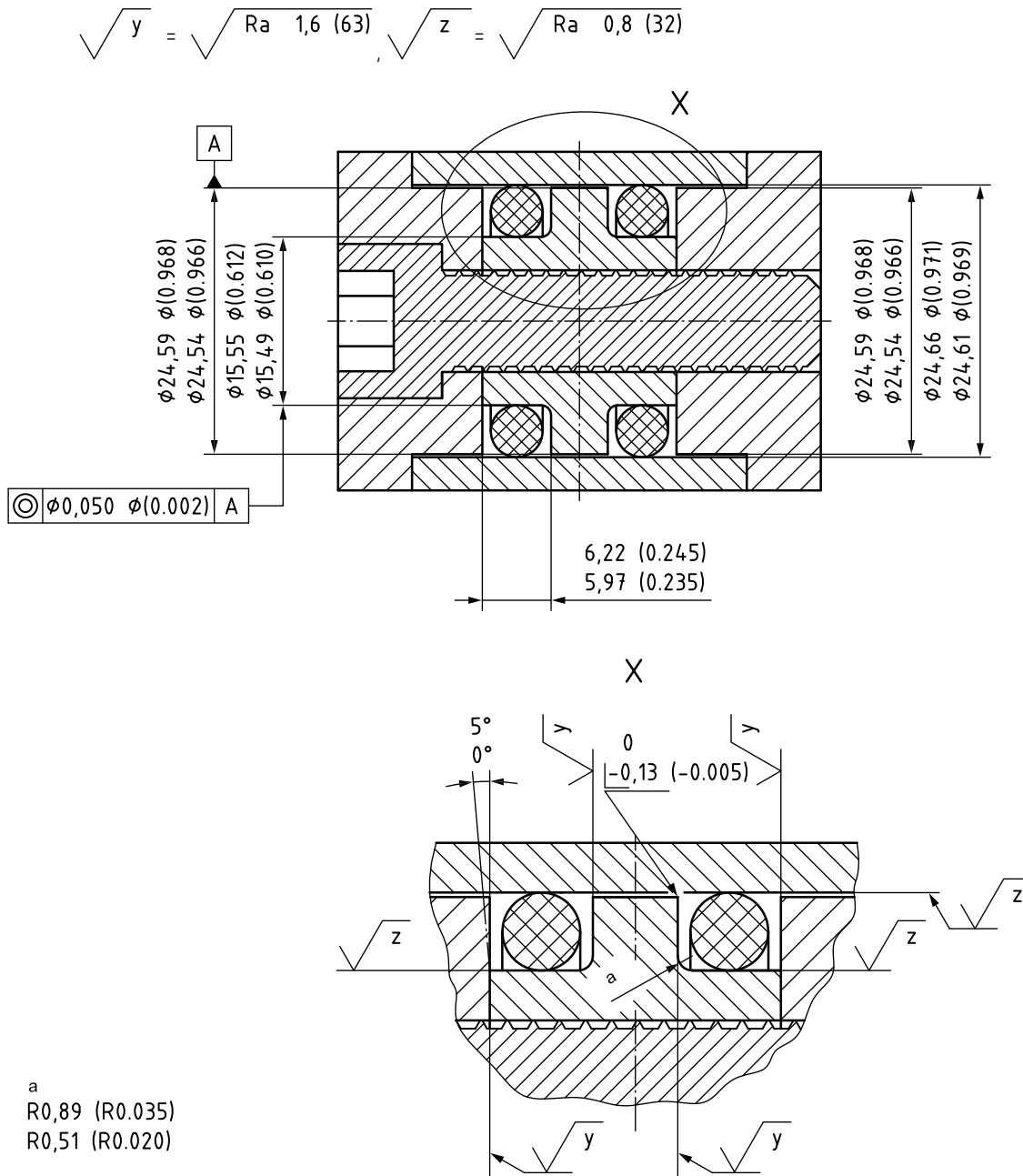
- a) have the necessary RGD resistance, and
- b) be supported by anti-extrusion rings of an appropriate material.



a) Example of a stainless steel fixture designed to hold two O-rings for RGD testing

Figure B.1 (continued)

Dimensions in millimetres (inches)
Surface roughness in micrometres (micro-inches)



b) Dimensions of a stainless steel fixture designed to hold two O-rings for RGD testing

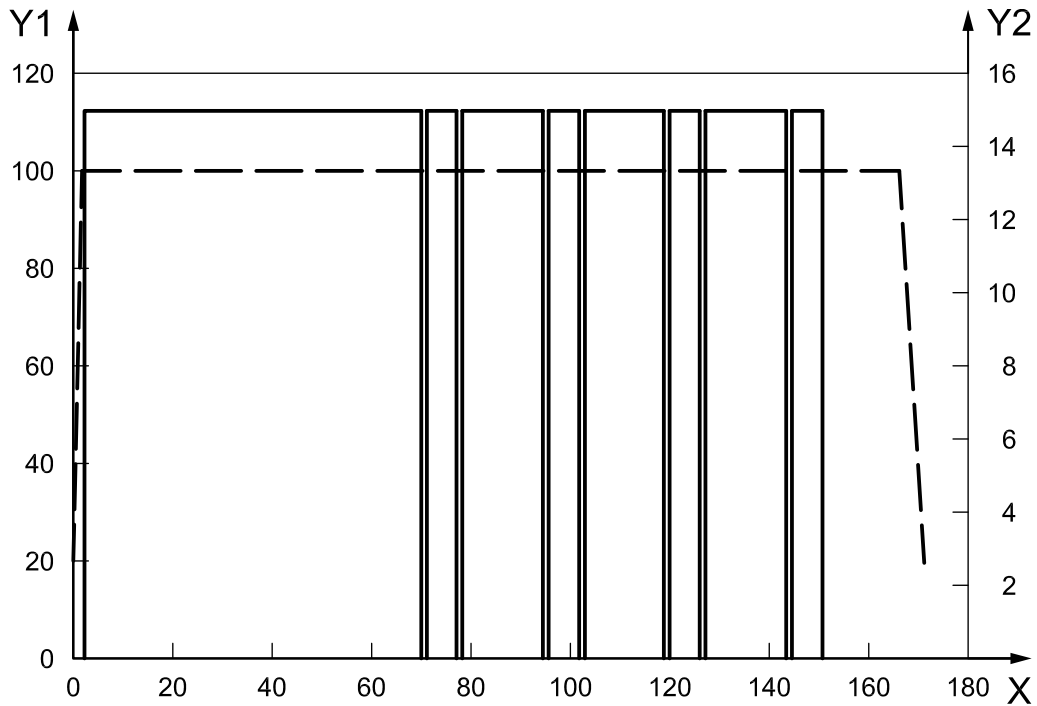
Figure B.1 — Stainless steel fixture designed to hold two O-rings for RGD testing

B.3 Test procedure

The procedure for the standard dry gas RGD test is as follows:

- measure the CSD of each replicate test seal in the radial direction at three circumferentially equidistributed positions. Measure each test fixture groove ID, OD and width;

- b) install the test seals in the test fixtures; light lubrication to aid installation is permitted;
- c) place the fixtures in the test vessel and close it;
- d) charge the vessel with nitrogen to 1 MPa minimum and check for leaks. Release the nitrogen;
- e) heat the vessel to test temperature;
- f) once temperature has been stabilized at the test level for at least 15 min, charge the vessel with the test gas mixture to the test pressure: temperature and pressure should be recorded continuously; a sampling interval of 10 min is recommended; this should be reduced to 30 seconds for depressurization and pressurization operations;
- g) maintain test pressure and temperature for a minimum period of 68 h (cycle 0);
- h) depressurize the vessel at the required rate and hold at ambient pressure and test temperature for 60 min +10/–0 min (cycle 1);
- i) re-pressurize the vessel to test pressure and hold for a minimum of 6 h;
- j) repeat step (h) (cycle 2);
- k) re-pressurize the vessel to test pressure and hold for a minimum of 12 h;
- l) repeat step (h) (cycle 3);
- m) repeat step (i);
- n) repeat step (h) (cycle 4);
- o) repeat step (k);
- p) repeat step (h) (cycle 5);
- q) repeat step (i);
- r) repeat step (h) (cycle 6);
- s) repeat step (k);
- t) repeat step (h) (cycle 7);
- u) repeat step (i);
- v) depressurize the vessel at the required rate and hold at ambient pressure and test temperature for a minimum period of 12 h, with port/valve open (cycle 8);
- w) cool the vessel to room temperature: a schematic pressure/temperature profile for the standard RGD test is shown in Figure B.2;
- x) open the vessel and retrieve the test fixtures;
- y) remove the test seals from the fixtures: describe the appearance of each test seal within 30 min; photograph relevant features;
- z) section and rate each test seal according to the procedures given in Clause B.4.



Key

- X time, hours
- Y1 temperature, °C
- Y2 pressure, MPa

Figure B.2 — Schematic of pressure (solid line) and temperature (dashed line) versus time requirements for the standard 8 cycle RGD test

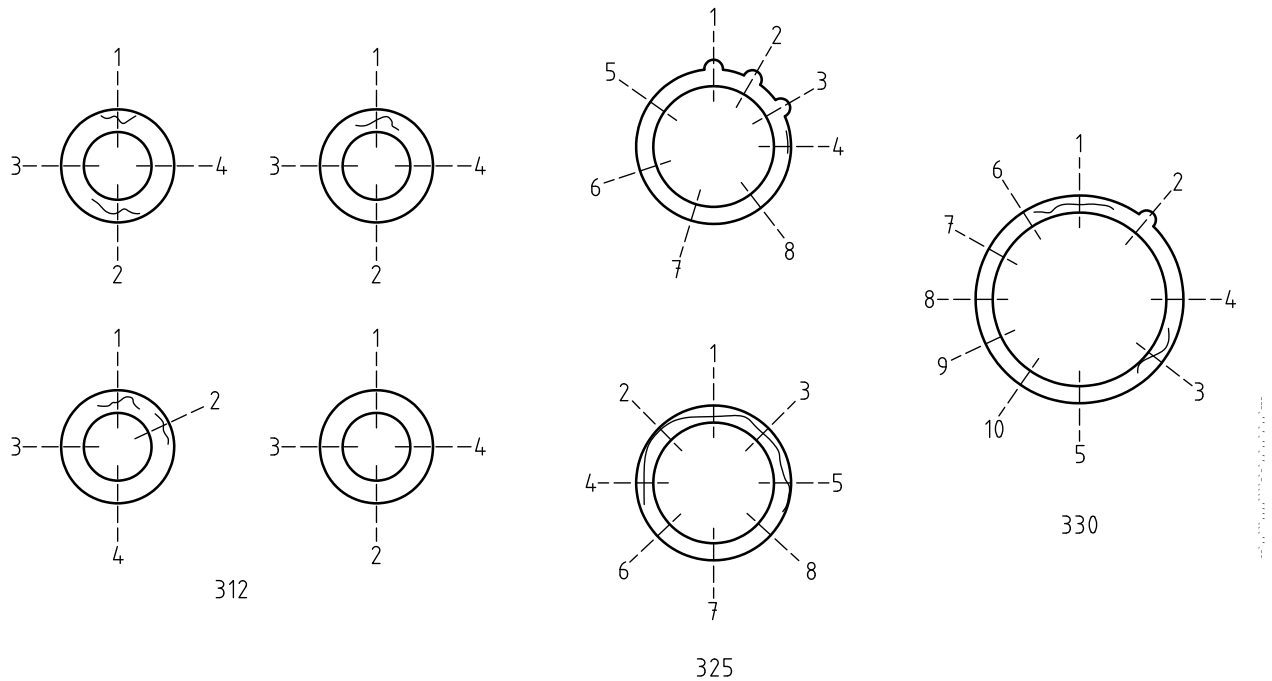
B.4 RGD damage rating system

In order to evaluate the extent of RGD-induced damage in the O-ring test seals, each shall be sectioned and rated according to the number and length of cracks present. The number of sections is linked to seal size; the larger the seal, the greater the number of cuts required for characterization, see Table B.3 for O-rings having a CSD of 5,33 mm.

Table B.3 — Relationship between O-ring size and number of cuts for rating purposes

O-ring size	Number of cuts
312-316	4
317-324	6
325-329	8
330-3XX	10

Sections should be made with a sharp blade, e.g. a new scalpel, razorblade; the latter is recommended for high hardness seals. The blade can be wetted with soapy water to facilitate cutting and improve exposed surface quality. The first cut should be made through the centre of the largest visible damage feature (e.g. a blister or crack). The second cut should be made through the next most obvious unrelated feature. The remaining cuts should then be made at approximately equal intervals in the intervening regions. If there is no damage visible on the seal, the initial cut can be made anywhere, with the remaining cuts distributed in a symmetric pattern around the seal. Examples of O-ring sectioning are displayed in Figure B.3.



The line on certain O-rings represents a visible fracture; the protruding bump a blister.

Figure B.3 — Examples of how to section test O-rings of different sizes

B.4.1 Crack type and measurement

Examine each cut section surface using a loupe (or other optical device) which gives a magnification of at least 10 \times . For the purposes of rating, three crack types have been defined – internal, external and split; these are illustrated schematically in Figure B.4.

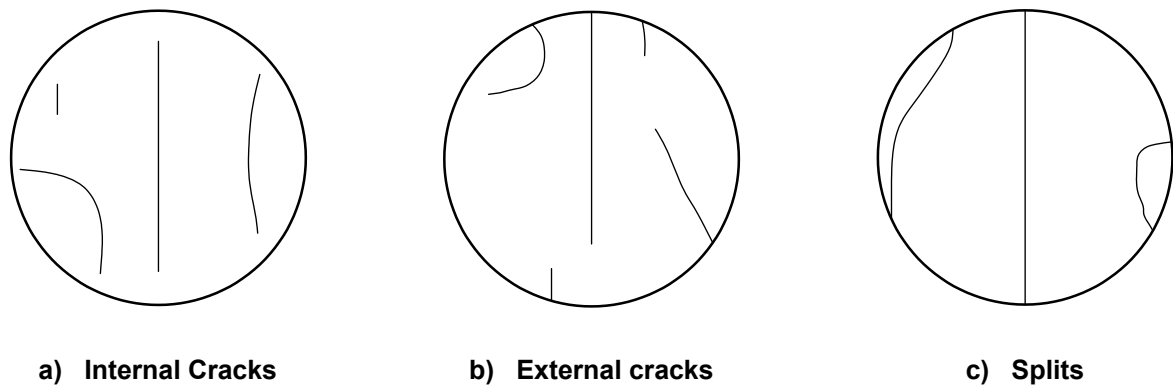


Figure B.4 — Crack types in an O-ring seal section

Crack length is defined as a percentage of the nominal seal CSD. For example, the CSD of series 3XX O-rings is 5,33 mm. This value shall be used in the calculation of the crack length; the use of the actual sectional dimensions is forbidden. Experience has shown that most exposed seal sections can be rated easily by inspection, with crack measurements only required in those cases where the rating could be a 3 (pass) or a 4 (fail).

The majority of RGD cracks are expected to be linear, or near linear. Accordingly, the preferred measurement method is direct end-to-end; for fractures with some curvature, length can be measured along the crack path. Crack orientation and location are not relevant factors. Projection of a crack onto a plane for measurement purposes is not permitted.

B.4.2 Damage rating system

Each seal section shall be rated according to the system given in Table B.4. The single digit represents the number, length and type of cracks present in the exposed section.

NOTE The rating system in Table B.4 is only applicable to O-ring seals. A satisfactory system for less symmetric seal profiles (e.g. spring-, T-, chevron) has yet to be developed.

Table B.4 — Rating number system for exposed O-ring seal section surfaces

RGD damage features	Rating	Pass/fail
<ul style="list-style-type: none"> • No cracks, holes or blisters permitted. - the exposed surface shall be intact. 	0	PASS
<ul style="list-style-type: none"> • Any number of cracks, each < 25 % CSD: total crack length shall not exceed CSD. - external cracks shall be < 10 % CSD; no splits permitted. 	1	
<ul style="list-style-type: none"> • Any number of cracks, each < 50 % CSD: total crack length shall not exceed 2X CSD. - external cracks shall be < 25 % CSD; no splits permitted. 	2	
<ul style="list-style-type: none"> • Any number of cracks of which 2 internal cracks can each have length 50 % to 80 % CSD: total crack length shall not exceed 3X CSD. - external cracks shall be < 50 % CSD; no splits permitted. 	3	
<ul style="list-style-type: none"> • Any number of cracks having total length greater than 3X CSD, or • at least 1 internal crack > 80 % CSD, or • 3 or more internal cracks each > 50 % CSD, or • any external crack > 50 % CSD. - no splits permitted. 	4	FAIL
<ul style="list-style-type: none"> • Any split, regardless of location and length. - no exceptions permitted. 	5	

Schematic representations of the range of fracture damage associated with ratings 1 through 5 are shown in Figures B.5 to B.9, along with photographic examples.

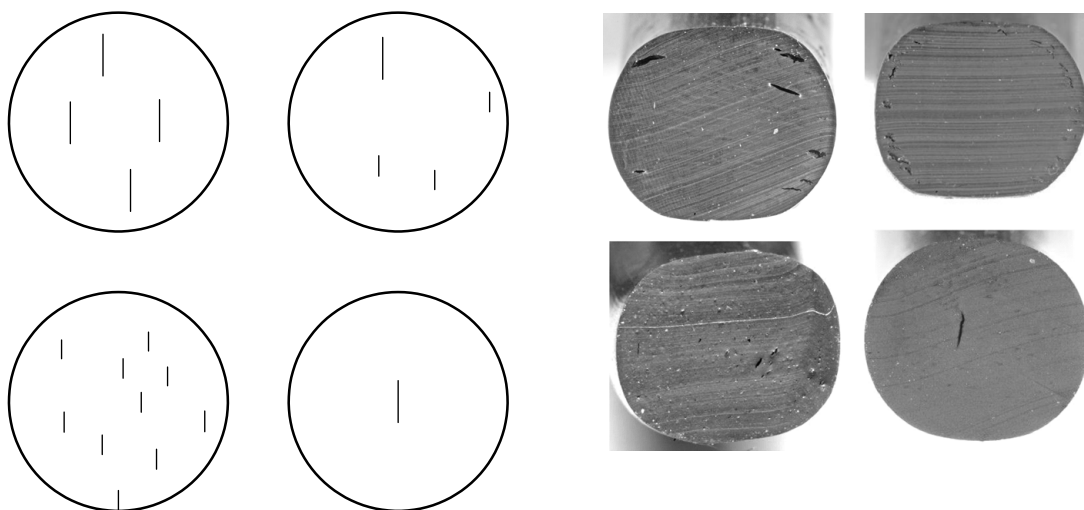


Figure B.5 — Schematic representations of the “1” rating, and photographic examples

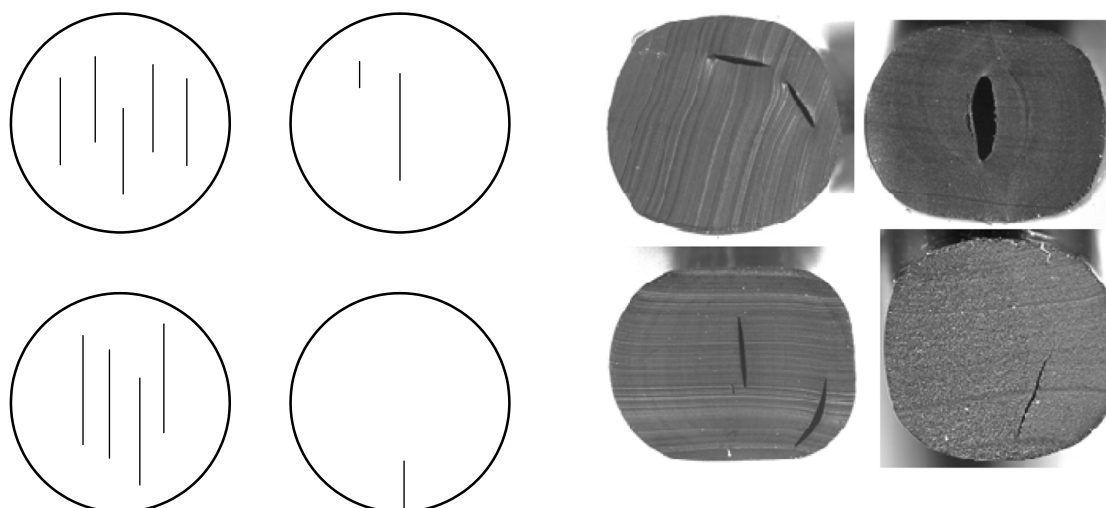


Figure B.6 — Schematic representations of the “2” rating, and photographic examples

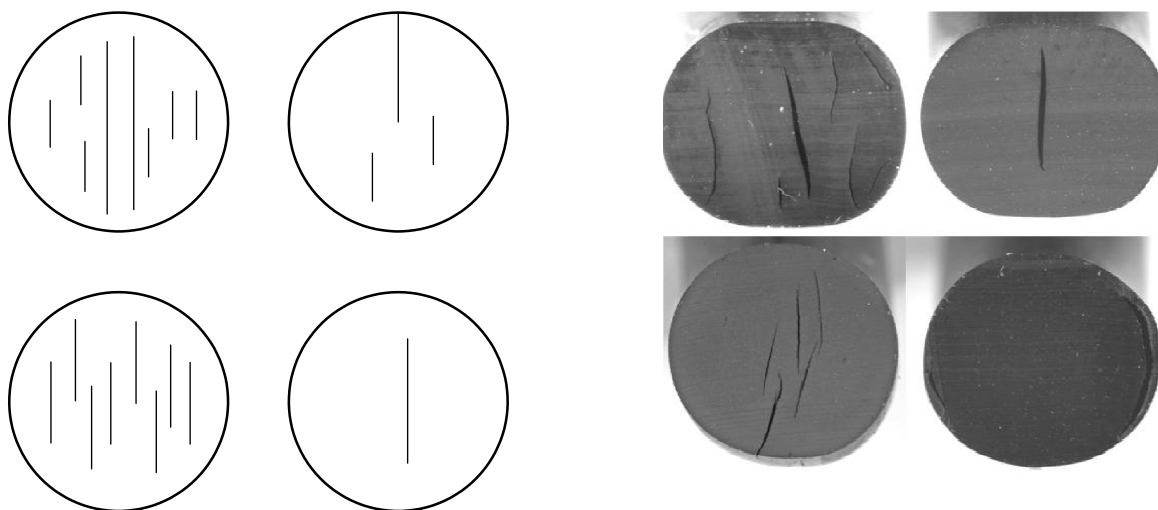


Figure B.7 — Schematic representations of the “3” rating, and photographic examples

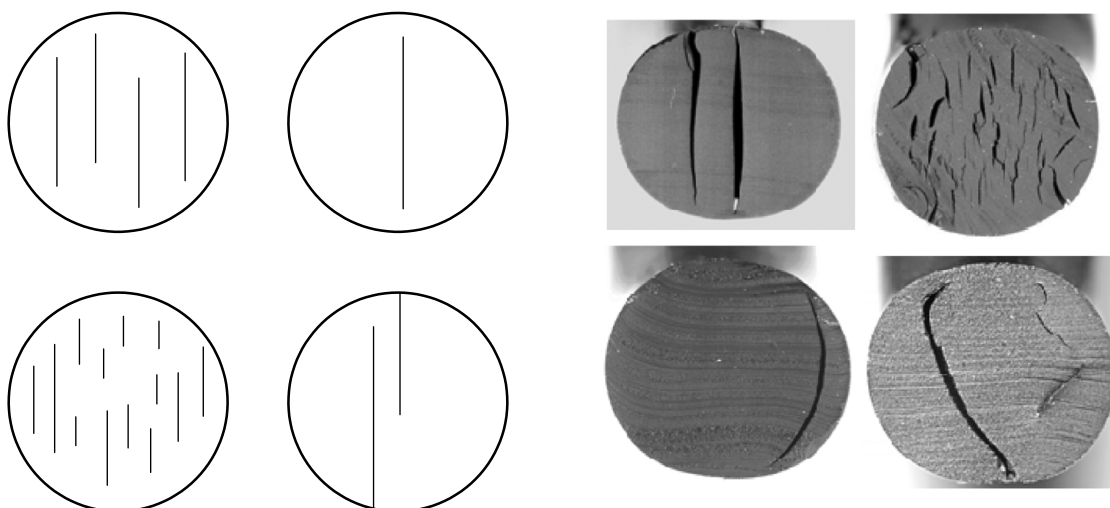


Figure B.8 — Schematic representations of the “4” rating, and photographic examples

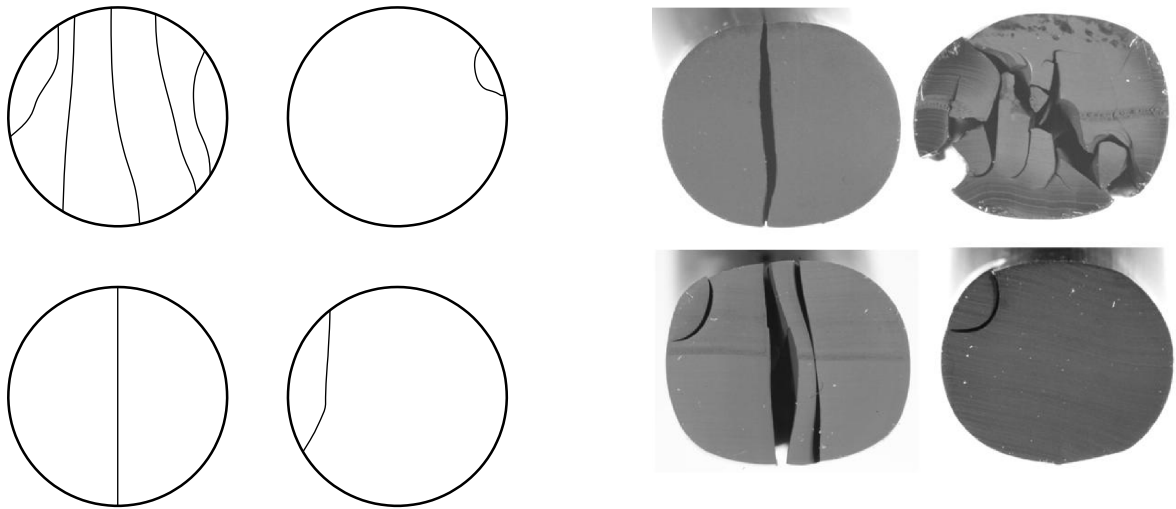


Figure B.9 — Schematic representations of the “5” rating, and photographic examples

For each tested O-ring the ratings should be listed in descending order, with the four highest values defining the RGD performance of the seal. Examples are given in Table B.5.

Table B.5 — Seal rating examples

O-ring size	Ratings in circumferential order	Final seal rating
312	1341	4311
319	003210	3210
325	34543210	5443
329	1121002210	2221

Additional information is provided in Annex F. Photographic documentation of representative seal section surfaces shall be included in the test report.

B.5 Test report (RGD)

The test report shall include the following information:

- reference to this part of ISO 23936;
- date of test;
- test seal CSD (radial); fixture groove ID and OD; % deflection (squeeze) and % groove fill;
- seal reference information: compound manufacturer, compound name/number, batch/lot number, elastomer type, manufacturer, seal manufacturing method, date of cure;
- test fluid composition, temperature, pressure;
- the temperature/pressure versus time logs in graphical form;
- average depressurization rate;

- h) seal ratings according to Table B.4;
- i) representative seal section surface photographs;
- j) other pertinent information, e.g. any deviation from the test procedure.

A basic report template example is shown below, for a standard dry gas RGD test.

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Table B.6 — Example test report

RGD TEST COMMISSIONED BY		
Acme Seals, Inc.		
SEAL COMPOUND DETAILS		
Seal manufacturer	Acme Seals, Inc.	
Supplied by	Acme Seals, Inc.	
Compound name/number/reference	SuperDuper Nitrile	
Elastomer type to ASTM D1418	NBR	
Lot/batch no.	SDN 2344rw4r/07	
Seal type	O-ring	
Manufacturing method	Not disclosed	
Seal size (ISO 3601-1/AS 568)	325	
CSD (nominal)	mm	5,33
Mean CSD (actual, radial)	mm	5,21
RGD TEST CONDITIONS		
Temperature	°C	100 ± 2
Pressure	MPa	15 +1/-0,5
No. of cycles		8
Dwell between cycles	hour	1
Decompression rate (average)	MPa/min	2
Gas type	Mol%	90/10 CH ₄ /CO ₂
SEAL HOUSING DETAILS		
Seal compression direction	Radial	
Groove ID	mm	15,9
Groove OD	mm	25,0
Groove width	mm	7,2
Squeeze (average)	%	13,5
Groove fill (area basis)	%	80
Number of seals tested		4
ISO TEST SEAL RATINGS		
SEAL REPLICATE	RATING	PASS/FAIL
1	3000	PASS
2	1110	PASS
3	4300	FAIL
4	4420	FAIL
OVERALL RATING	FAIL	
GENERAL		
Test laboratory		Ace Test Company
Test date		10-18 August 2010
Test gas certified and available	YES/NO	YES
Transducer calibration available	YES/NO	YES
P/T log available	YES/NO	YES
TEST LABORATORY STAMP/SIGNATURE		

Annex C (informative)

Most commonly used elastomeric materials

Table C.1 gives the general designation of the most commonly used elastomeric materials from ASTM D1418. For the range of different grades, an upper temperature value or range is given along with common characteristics. In addition, the general fluid resistance to a number of common fluids is given to identify fitness for purpose. This is a guide only and it is strongly recommended that each compound be characterized for the specific environment in which it is to be used. The cure system is highly influential for the performance of elastomers.

Table C.1 — Characteristics of most commonly used elastomeric materials

Elastomer type	Upper temp ^a °C	Characteristics	Selected general fluid resistance				
			Crude oil	Alkaline	MeOH	Water	H ₂ S
EPDM	150	Good in water and steam; poor in hydrocarbons	NO ^b	OK ^c	OK	OK	OK
CR	100	Good in water; can be used as a hose cover, good weathering properties	C ^d	NO	OK	OK	C
NBR	120	Nitrile; highly unsaturated; a good general purpose sealing material, susceptible to ageing; vary acrylonitrile content to affect low temperature performance and oil swell	OK	OK	OK	OK	NO
HNBR	160	Hydrogenated nitrile; largely saturated, improved heat ageing, chemical and weather resistance; vary acrylonitrile content to affect low temperature performance and oil swell	OK	OK	OK	OK	C
FKM 1	200	Copolymer; most widely specified type; poor in methanol and alkaline fluids	OK	NO	NO	OK	C
FKM 2	200	Terpolymer; high fluorine grades good in methanol	OK	NO	OK	OK	C
FKM 3	200	Terpolymer; low <i>T_g</i> ; low fluorine grades not good in methanol	OK	NO	NO	OK	C
FKM 5	200	Pentapolymer; developed for alkaline fluid resistance; very little performance info available	OK	OK	OK	OK	C
FEPM	230	TFE/P copolymer; poor in aromatic solvents; good H ₂ S, steam and alkaline resistance; high <i>T_g</i>	C	OK	OK	OK	OK
	200	ETP – Ethylene containing terpolymer; developed for alkaline resistance	OK	OK	OK	OK	C
FFKM	220 to 315	Thermal performance depends on crosslink chemistry; very good fluid/chemical resistance;	OK	OK	OK	OK	OK

^a Maximum rated temperature in air.

^b **NO**: considered unsuitable for service; excessive volume swell at equilibrium: also, chemical ageing may occur.

^c **OK**: considered suitable for service, in terms of volume swelling (< 20 %) and ageing.

^d **C**: could be suitable for service, in terms of volume swelling and ageing, but refer to qualifying notes: also, fluid contact may not be relevant.

NOTE 1 OK covers a range of performance, e.g. FKM crude oil resistance is better than that of NBR/HNBR, although nitrile are usually considered as acceptable.

NOTE 2 Service situations involving CR contact with H₂S are unlikely to exist.

NOTE 3 Nitriles will chemically age, NBR more readily than HNBR, in contact with H₂S; temperature and concentration factors apply.

NOTE 4 Methanol is 100 % (neat); dilution with water will make methanol less aggressive.

NOTE 5 FKM 5 has better resistance than FKM 1-3. As some fluids may degrade this elastomer type testing is recommended.

NOTE 6 FKM cure important; generally, peroxide cure gives better chemical resistance than bisphenol cure chemistry.

Annex D (normative)

Procedure for estimation of material service life using the Arrhenius relationship

D.1 Service life prediction

One of the aims of this part of ISO 23936 is to provide a procedure with which to estimate the useful life of a material in a particular test fluid. The latter may be identical to the service situation (e.g. inhibited brine), or a representation of it (e.g. synthetic hydrocarbon oil). This annex describes how data obtained from a laboratory ageing test can be used to predict how long a material will retain 50 % of its tensile property levels. The procedure is only applicable if the polymer chemically ages in the test fluid. Background information can be found in ISO 11346 and ASTM D3032.

Ageing data has been obtained for an FKM elastomer exposed to the fluid shown in Table D.1 and to the conditions listed in Table D.2.

NOTE 1 The fluid and test details were based on conditions relevant to NORSOK M-710 and might not apply directly to this part of ISO 23936, but the procedure for service life derivation remains the same. For this part of ISO 23936, suitable test fluid compositions are given in Annex A and the applicable test procedure is given by ISO 37.

Table D.1 — Fluid composition

Volume %	Composition
30	2 % H ₂ S, 3 % CO ₂ , 95 % CH ₄
10	Distilled water (conductivity < 5 µS)
60	70 % heptane, 20 % cyclohexane, 10 % toluene

The polymer samples were placed in the hydrocarbon liquid phase while being exposed to a sour test gas. Test temperatures and exposure periods used in the programme are shown in Table D.2; test pressure was nominally 10 MPa.

Table D.2 — Test conditions

Temperature °C	Sampling intervals days
210	5, 10, 20, 35
220	3, 6, 12, 21
230	2, 4, 8, 14

Table D.3 lists the average results for the modulus at 50 % elongation recorded as a result of the exposure testing. The samples were tested at room temperature while still soaked with fluid. Also included in Table D.3 are values of the modulus at 50 % elongation obtained by soaking the material in the hydrocarbon phase of the fluid only (that is, without the sour test gas present) as well as the original dry unaged modulus at 50 % elongation for comparison. This exposure was performed separately to the ageing tests and for 3 days at

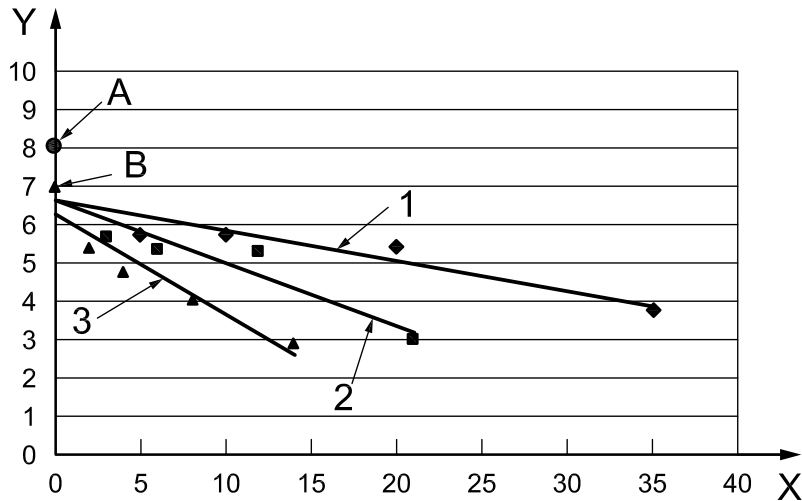
230 °C in order to obtain a modulus at 50 % elongation for the saturated material without ageing (wet unaged), referred to as the zero reference. This value can have a significant effect on the subsequent service life determination.

Modulus at 50 % elongation is most often used for predictive purposes because it can directly reflect the degree of ageing occurring in elastomers and thermoplastics either through its relation to crosslink density (for elastomers) or polymer chain degradation (for thermoplastics). Chemical bonds are frequently formed or broken during the ageing process, thereby increasing or decreasing (respectively) the stiffness or flexibility of the material. Elongation at break will often mirror the changes in modulus at 50 % elongation but because it is a destructive property, it has less relevance to service; that is, if a seal physically breaks during service (in other words exceeds its tensile strength or elongation limits), there are likely to be other more important factors occurring than chemical ageing. Therefore, elongation at break and tensile strength are less often used for predictive purposes but can be used if modulus at 50 % elongation is insensitive to the changes measured.

Table D.3 — Test results for elastomer modulus at 50 % elongation

Exposure conditions		Modulus at 50 % elongation
		MPa
Dry unaged		8,0
Wet unaged ^a		7,0
210 °C	5 days	5,7
	10 days	5,7
	20 days	5,4
	35 days	3,8
220 °C	3 days	5,7
	6 days	5,3
	12 days	5,3
	21 days	3,0
230 °C	2 days	5,4
	4 days	4,8
	8 days	4,0
	14 days	2,9
^a Zero reference obtained at 230 °C; this value applies for testing at all temperatures.		

The data in Table D.3 are plotted together as exposure time versus modulus at 50 % elongation in Figure D.1.



Key

- X exposure time, days
- Y modulus at 50 % elongation, MPa
- 1 210 °C; $y = -0,079 2x + 6,618 2$
- 2 220 °C; $y = -0,163 5x + 6,613 6$
- 3 230 °C; $y = -0,260 6x + 6,259 1$
- A modulus at 50 % elongation of a dry unaged sample
- B modulus at 50 % elongation of a wet unaged sample; zero reference

Figure D.1 — Change in property level with exposure duration and temperature

Figure D.1 shows how increasing temperature accelerates the decrease in modulus at 50 % elongation.

NOTE 2 An increase in modulus at 50 % elongation can also occur for materials which form crosslinks during ageing, such as HNBR elastomers.

Also apparent is the change in initial modulus at 50 % elongation brought about by measuring the material after saturation in hot test liquid; compare point A (8,0 MPa; dry unaged sample) to point B at time 0 (7,0 MPa; zero reference).

Best fit straight lines have been added at each temperature using the zero reference value, and the equations describing each line are given in the key to Figure D.1.

NOTE 3 Other fitting solutions might need to be assessed depending on the data. For example, some materials might show an initial decrease in property level (often attributable to swelling) followed by increases; the region associated with continuous change affects long-term performance, thus forming the basis for life estimation. Additional information is given in Annex E.

D.2 Arrhenius approach, trends, calculation and interpretation

The equations in Figure D.1 are used to calculate the time to 50 % change from the initial property value (taken here as the zero reference point B, 7,0 MPa). For example, at 210 °C:

$$y = -0,079 2 x + 6,618 2$$

so that for a modulus at 50 % elongation, y , equal to half the zero reference point, i.e. 7/2:

$$7/2 = -0,079 2(\text{days}) + 6,618 2$$

Therefore, the time to reach 50 % change of the initial modulus at 50 % elongation at 210 °C is 39,4 days.

Similar reasoning gives the values shown in Table D.4.

Table D.4 — Time to 50 % change in property level

Temperature °C	Time to 50 % change
	t_{50} days
210	39,4
220	19,0
230	10,6

These times are then re-calculated as the natural logarithm of the rate [$\ln(1/t_{50})$] and plotted against the inverse of the test temperature ($1/T_K$), expressed in K^{-1} , which is the fundamental relationship described as the Arrhenius relationship. Table D.5 shows the values. The associated plot is shown in Figure D.2.

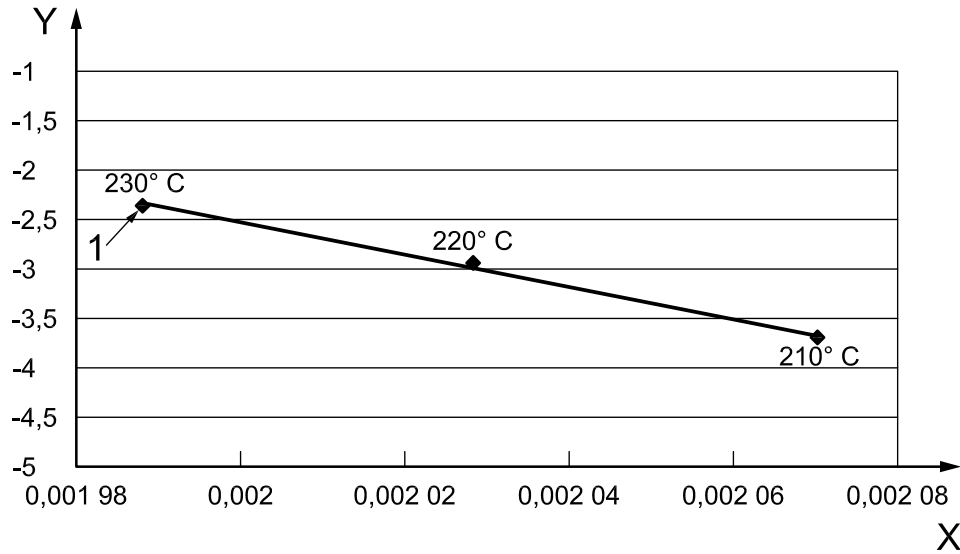
NOTE The Arrhenius relationship describes the rates of chemical reactions in terms of the energy required to force the reaction to progress, hence the dependence on temperature.

Table D.5 — Rates of change in property level and test temperatures expressed as Arrhenius variables

Temperature °C	Inverse temperature	Time to 50 % change	$\ln(1/t_{50})$
	$1/T_K$ K^{-1}	t_{50} days	
210	0,002 070	39,4	-3,674
220	0,002 028	19,0	-2,944
230	0,001 988	10,6	-2,361

The straight line shown in Figure D.2 is then used to back-extrapolate data to lower temperatures. For thermoplastics, back-extrapolation across a thermal transition (e.g. T_g) should not be performed.

This is accomplished by reference to the equation given in the key to Figure D.2, which can be used to calculate the time to 50 % change in modulus at 50 % elongation at temperatures other than test temperatures, e.g. the seal service temperature. This becomes the estimated service life of the material. The R^2 term indicates the “closeness” of the data points to the straight line fit; the nearer to 1,0 the better and the more appropriate an Arrhenius approach becomes to life estimation.



Key

X inverse temperature, 1/T_K

Y ln(1/t₅₀)

1 $y = -15\,958x + 29,386$ $R^2 = 0,997\,3$

Figure D.2 — Arrhenius relationship for 50 % decrease in modulus at 50 % elongation

In the Arrhenius equation, the temperature is given as an absolute temperature expressed in kelvins, which gives the value for *y*. The time to 50 % change, expressed in years, is (1/e^{*y*})/365. Thus:

$\ln y = x + \text{constant}$

$\ln(1/t_{50}) = 1/T_K + \text{constant}$

$y = e^x + \text{constant}$

Table D.6 gives examples.

Table D.6 — Estimated service life for 50 % decrease in modulus at 50 % elongation

Temperature °C	Service life years
100	1 802
150	11,5
180	0,9

As the prediction at 180 °C in Table D.6 shows, values are often conservative but give a good indication of expected material performance in high levels of hydrogen sulphide (in this instance) and a general assessment of operation in sour fluids; in this case, good long-term performance is indicated at moderate temperatures.

If no ageing occurs and the property levels stay within the specified limits at the test temperatures, then the material can be described as having indefinite life at the lowest test temperature and temperatures below this.

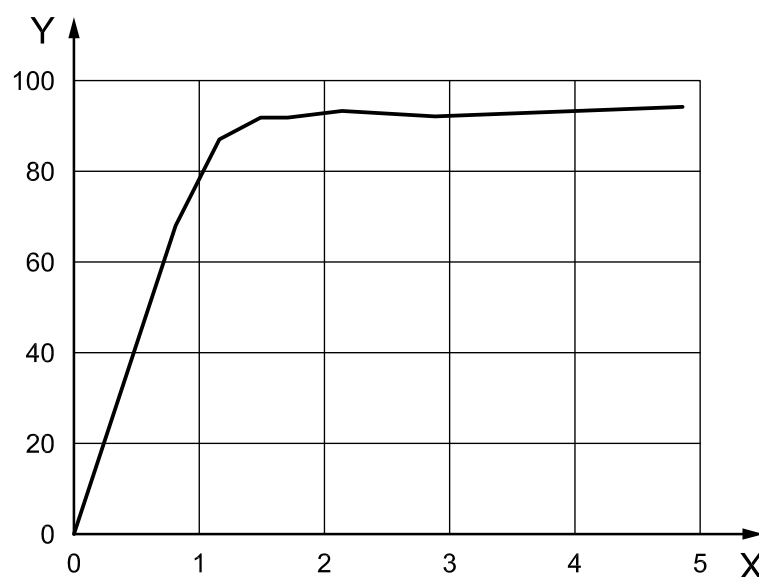
Annex E (informative)

Physical and chemical ageing

E.1 Physical ageing

For a polymer exposed to a fluid (liquid, gas or vapour) which is not chemically hostile, fluid will enter the polymer, the polymer may swell if sufficient fluid is involved, and a change in property level may occur – for modulus at 50 % elongation, a decrease will occur. The property-level change merely reflects a physical material change where absorbing the fluid has plasticized the polymer, softening it. The effect can be most marked in elastomers, as these are amorphous polymers and capable of absorbing a large quantity of a chemically compatible liquid.

The kinetics of absorption are ruled by diffusion, so that, for example, during absorption of a single liquid the mass uptake versus root time plot is ideally essentially linear until conditions are reached where the polymer has reached its equilibrium mass uptake and will absorb no more liquid (see Figure E.1). If required, diffusion and solubility magnitudes can be obtained from such a plot (and even associated permeation rates can be estimated by using the appropriate coefficients).



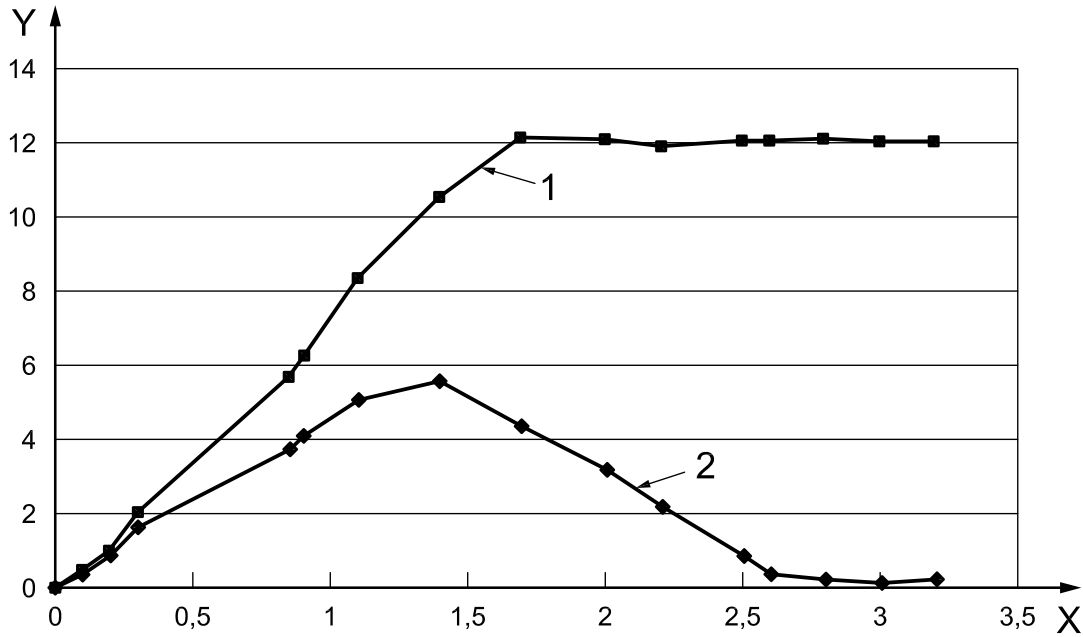
Key

- X time in solvent, in hours^{1/2}
Y mass change, in %

Figure E.1 — Mass change curve for an unaged elastomer sheet sample immersed in a solvent

This swelling behaviour and associated effects are consequences of physical ageing. Another physical effect could arise if the contacting liquid leaches out of a polymer some liquid plasticizer which the manufacturer had added during processing (see Figure E.2).

The polymer would theoretically harden (and shrink) as a result, although in reality a balance will eventually be achieved between leaching (to give hardening) and absorption of the liquid itself (to give softening), likewise for swelling and shrinkage.



Key

- X time in solvent, in hours^{1/2}
- Y mass change, in %
- 1 deplastitized
- 2 plasticized

Figure E.2 — Mass change versus time for plasticized and deplastitized material immersed in a solvent

Regarding the swelling aspect, individual liquids and polymers each possess their own “solubility parameter” (δ) (see Reference [21]). This is a thermodynamic property which is related to the energy of attraction between molecules. In its simplest form, a polymer will possess a drive to absorb a liquid of similar δ , and be swollen by it.

NOTE Additional contributions to δ from, for instance, hydrogen bonding forces (studied in detail in Reference [22]), have not been relevant to the present general usage of this parameter.

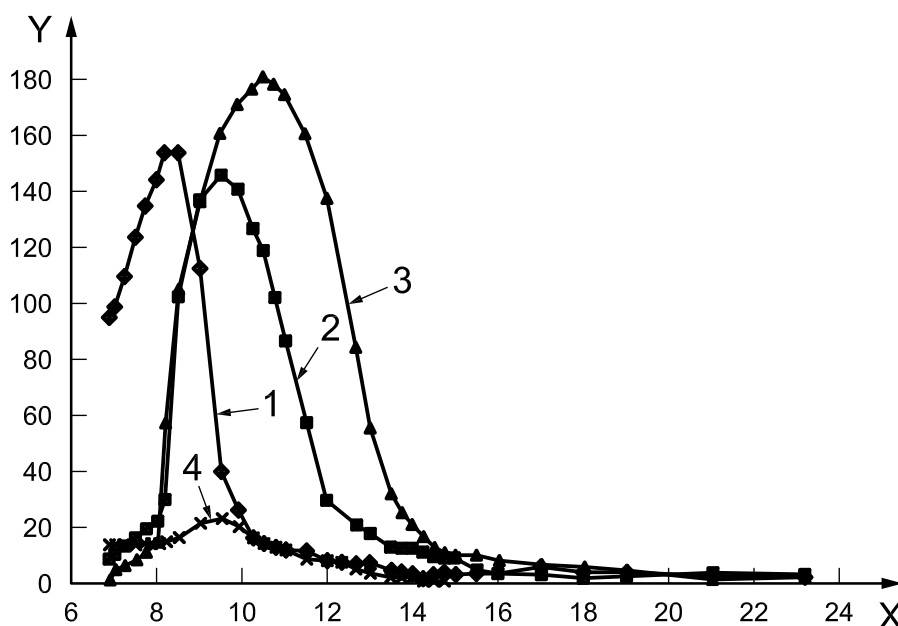
As the difference between the solubility parameter values of species increases, so their affinity for each other decreases. The commonest units for δ in the literature are (cal/cm³)^{1/2}; to convert these values to MPa^{1/2}, multiply by 2,05.

Thermodynamically, intermixing as above arises from achieving a negative free energy from the process; in turn, this arises by balancing a contribution from enthalpy (heat content) with another from entropy (involving material structural aspects). The solubility parameter reflects the enthalpic term.

Solubility parameter spectroscopy (SPS) is a means of determining the δ value of a polymer, and furthermore gives a better indication of the δ range across which swelling might occur for a polymer/liquid system – frequently more useful when selecting materials for an application involving a known liquid. For SPS, replicate polymer samples are immersed in a series of carefully selected liquids or miscible liquid mixtures, each of known solubility parameter, and a plot (spectrum) of equilibrium mass uptake versus liquid solubility parameter is thus developed. The δ value coinciding with the maximum of the plot is taken as the δ value for the polymer.

SPS spectra obtained for four common oilfield elastomers of benchmark recipes are shown in Figure E.3 and four other fluorine-containing benchmark elastomers in Figure E.4; these should be considered as guides only for elastomers based on the same generic species as these, but based on different recipes. An added benefit

from such plots is that the width of its solubility parameter peak indicates the δ range across which substantial swelling of an elastomer can occur in low viscosity solvents. As viscosity increases when using other solvents or real crude oils, peak width and height are reduced.



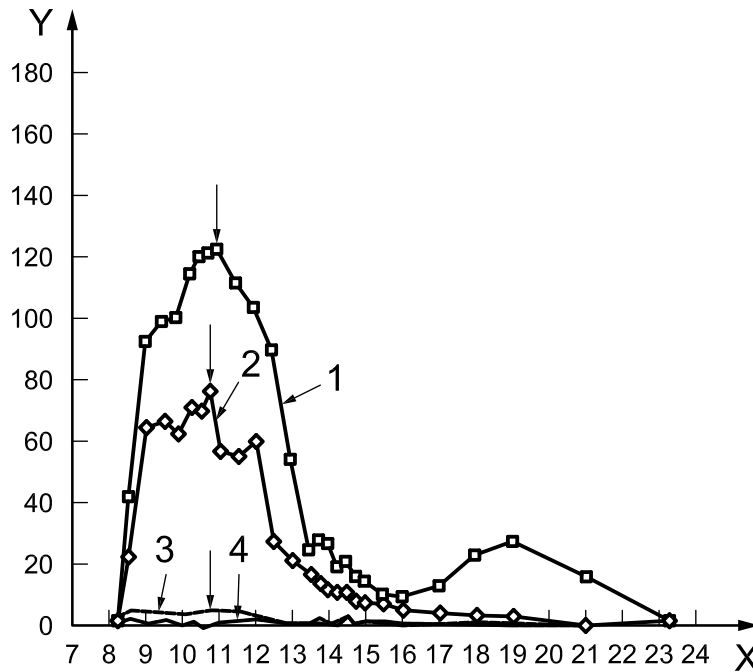
Key

- X solubility parameter, in $(\text{cal}/\text{cm}^3)^{1/2}$
 Y equilibrium mass uptake, in %
 1 EPDM
 2 22% ACN NBR
 3 38% ACN NBR
 4 TFE/P

Figure E.3 — Solubility Parameter Spectra for elastomers ethylene propylene, nitrile (at 22 % and 38 % acrylonitrile content) and tetrafluoroethylene propylene copolymer

Five pure liquids of different δ values have been used for SPS; intermediate liquid δ values were obtained by mixing these. The δ value of the mixture is equal to the volume-weighted sum of the individual component liquid δ values. Thus the mass uptake of a miscible liquid mixture by a polymer may be very much greater than the swelling which would occur when immersed in either one of the constituent liquids alone. The mixture could of course comprise more than two liquid components, and an analogous situation reasonably applies; this approach has been extended and applied to the offshore oil production sector to give test liquid mixtures (see Clause E.2).

The technique of reverse solubility parameter spectroscopy has been developed to determine the δ value for a liquid (e.g. an oil), from a series of swelling measurements using a range of elastomers of known δ . In this way, δ for crude Brent oil from the North Sea has been found to be $8,2 (\text{cal}/\text{cm}^3)^{1/2}$.



Key

- X solubility parameter, in $(\text{cal}/\text{cm}^3)^{1/2}$
- Y equilibrium mass uptake, in %
- 1 FKM copolymer (FKM 1)
- 2 FKM terpolymer (FKM 2)
- 3 FFKM
- 4 another FFKM

Figure E.4 — Solubility parameter spectroscopy plots for selected fluoroelastomers (FKMs) and perfluoroelastomers (FFKMs)

E.2 Simulated production media for testing purposes

Both sweet and sour cases could involve media comprising oil alone, gas alone, oil mixed with other liquids, or a multiphase mixture, probably with the test pieces being exposed to the liquid phase. Within each case, other variations are theoretically possible.

Regarding liquids, different combinations of hydrocarbon and other liquids possess different values of δ – as indicated above, a factor strongly affecting the degree of liquid absorption by the polymer. In order to minimize testing the vast range of liquid mixtures possible in service, a selection of model oils has been devised. In addition, to minimize secondary factors associated with intermolecular forces that act within liquids, these model oils comprise a mixture of aliphatic (or paraffinic), naphthenic, and aromatic hydrocarbons. The most convenient hydrocarbons to use in this way as test liquids are respectively heptane, cyclohexane and toluene, present in proportions which follow two conditions:

- a) ideally, they should replicate the aliphatic-naphthenic-aromatic proportions for the oilfield crude oil being simulated;
- b) they should give a δ value similar to that possessed by the oilfield crude oil.

For testing according to this part of ISO 23936, it is clearly impracticable to cite the many variations that would be needed to simulate all crude oils that might be met by users. However, if a number of different general compositions are developed, these can be selected to give a reasonable choice for most applications.

Similarly, more variation of gas mixture is necessary, for instance, to give a model gas akin to natural gas (but simplified), or to allow a high CO₂ mixture for use with RGD resistance tests. A further aspect is the desire to align a number of these gas phase conditions with some of those employed in ISO 10423:2009, F.1.13.5.2 and Table F.2, which applies to wellhead testing. ISO 10423 allows use of any oil for its liquid phase so that the liquids in this part of ISO 23936 are suitable. This approach allows concurrent testing of equipment and material. Tables A.1 to A.5 show the compositions for testing developed in this way.

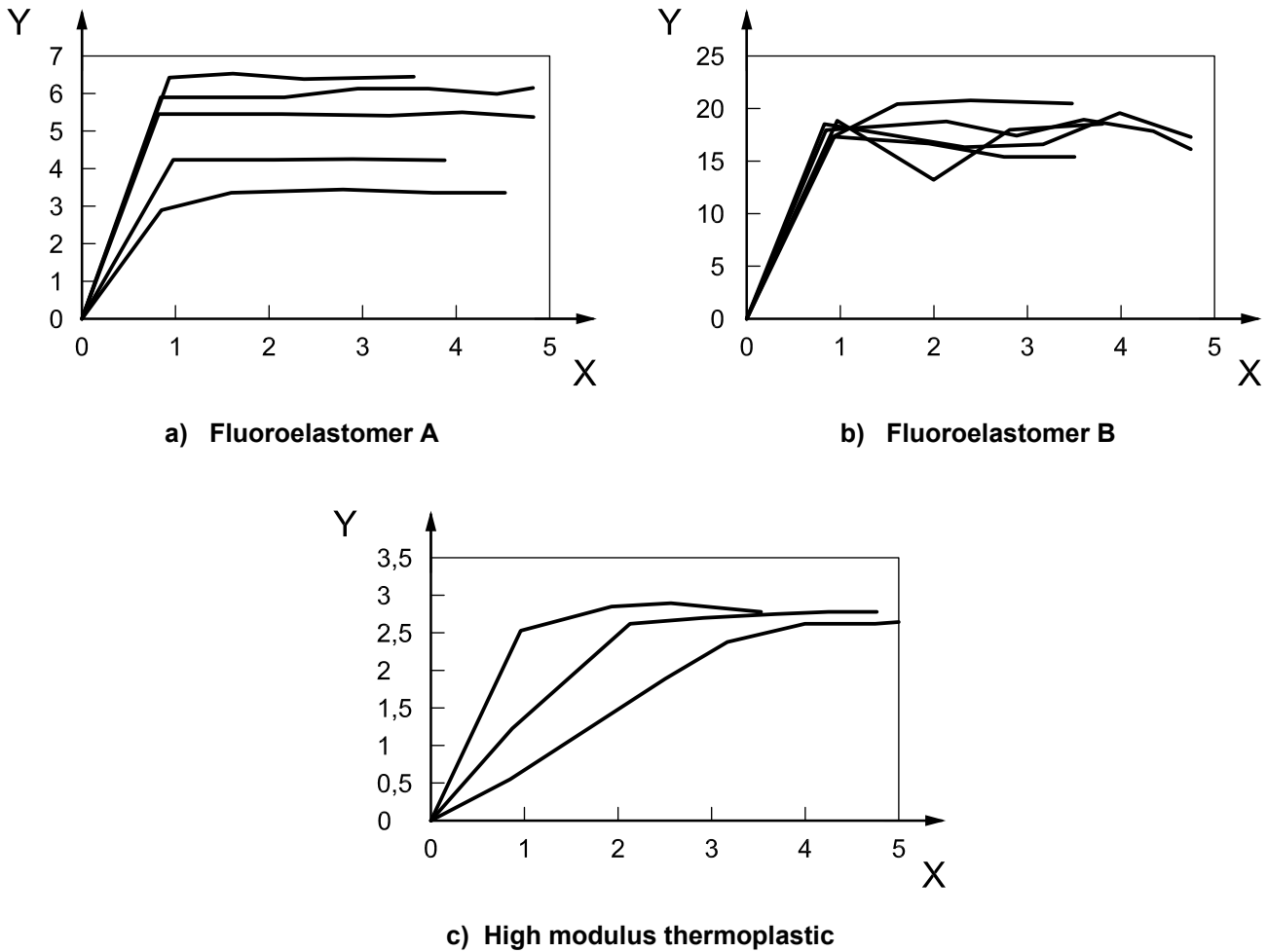
E.3 Test temperatures

To allow material and equipment testing to be performed concurrently if desired, test temperatures should also be in accordance with wellhead equipment standard ISO 10423, with an option for some other agreed temperature if preferred. Table A.6 is developed using this approach.

E.4 Swelling characteristics

The rate of liquid absorption by a polymer tends to increase with temperature; this is linked to the diffusion coefficient, which has a well known temperature dependency. Sample thickness has an influence, with thinner samples absorbing the liquid more quickly. However, for a given material, the level of equilibrium swelling achieved by both thin and thick specimens will be identical. Geometric factors can mean that very thick samples cannot reach the level of swelling of a thin sample of the same material.

The level of equilibrium swelling can be highly temperature dependent for a given polymer. This is illustrated in the plots shown in Figure E.5. These show mass change curves for polymers immersed in a hydrocarbon liquid at several different high temperatures (but measured at room temperature). Fluoroelastomer A swells more as temperature is raised, whereas the equilibrium swelling of fluoroelastomer B is relatively insensitive to exposure temperature. The tensile property levels of fluoroelastomer A are therefore temperature dependent. The third chart shows curves for a high modulus thermoplastic immersed in the same liquid at three different temperatures, all well above its glass transition temperature. Here the rate of swelling increases noticeably with temperature. The time scales should be noted: the elastomers swell rapidly compared to the thermoplastic. Hence when saturating reference samples, sufficient time should be allowed.



Key
 X time, in days^{1/2}
 Y mass change, in %

Figure E.5 — Mass change plots versus time immersed in hydrocarbon liquid at different elevated temperatures

E.5 Fluid kinetics

When a liquid comes into contact with a polymer surface, it dissolves rapidly up to a concentration c_0 . The movement of the liquid into the material bulk is then controlled by diffusion, which is governed by Fick’s law. Diffusion-related phenomena such as swelling increase with the square of polymer layer thickness. This is usually only discernible for liquids, although high pressure gases can swell polymers after an initial hydrostatically-induced compaction. At one temperature, both the liquid dissolution process and diffusion rates are dependent on vapour pressure and hence essentially independent of actual pressure.

To determine the diffusion coefficient D (discussed below) for a liquid, absorption tests involving weighings are used. Then

$$\frac{m_t}{m_\infty} = \left(\frac{2}{h'}\right) \left(\frac{Dt}{\pi}\right)^{1/2} \tag{E.1}$$

where

m_t is the mass uptake at time t ;

m_{∞} is the mass uptake at equilibrium swelling;

$2/h'$ is the sample thickness.

Eventually D becomes concentration-dependent as, after a while, liquid that has already entered the polymer can contribute to the rate at which fresh liquid diffuses. One simple and convenient method of obtaining a representative value of diffusion coefficient is to measure D_{av} , an “average” D at the point of 50 % mass uptake, so that:

$$0,5 = \left(\frac{2}{h'} \right) \left(\frac{D_{av} t_{av}}{\pi} \right)^{1/2} \quad (E.2)$$

Note that thickness is expressed as $2/h'$ in this equation, but will be denoted as h in later discussions. D_{av} can be conveniently derived from plots of m versus t , reading off t_{av} at 50 % uptake. A miscible liquid mixture is treated herein as if it were a single species – a representative D is obtained as above.

Gas also enters a polymer by a process of solution (in the polymer surface) followed by diffusion. However, in contrast, the amount of gas dissolved depends on its actual pressure. Gas permeation involves two steps, as described below.

- a) The gas is dissolved in the surface of the polymer according to Henry's Law:

$$c = s \times P \quad (E.3)$$

where

c is the concentration;

P is the applied pressure;

s is the solubility coefficient.

In the event of a gas mixture, the concentration of any constituent gas in the surface of the polymer may be determined by using its partial pressure in the above expression.

- b) Diffusion of gas through polymeric materials is governed by Fick's law, an integrated version of which is given for a sheet membrane sample as:

$$\left(\frac{1}{A} \right) \left(\frac{q}{t} \right) = D(c_1 - c_2) \left(\frac{1}{h} \right) \quad (E.4)$$

where

q is the gas volume diffused in time t ;

D is the diffusion coefficient;

A is the surface area available for permeation;

h is the thickness.

The initial and final concentrations are denoted c_1 and c_2 respectively.

The permeation coefficient is simply the product of the coefficients of diffusion and solubility:

$$Q = D \times s \quad (E.5)$$

The equation for gas permeation through a sheet membrane – often the situation when testing – is therefore as follows:

$$\left(\frac{q}{t}\right) = QA(P_1 - P_2)\left(\frac{1}{h}\right) \quad (\text{E.6})$$

For a hollow cylinder containing gas, i.e. an elastomeric hose, the analogous equation is:

$$\left(\frac{q}{t}\right) = \frac{2\pi LQ(P_1 - P_2)}{\ln(r_2 / r_1)} \quad (\text{E.7})$$

where

L is the length of the hose;

r_1 is the inner radius;

r_2 is the outer radius.

With outer surface unrestricted, P_2 would be zero.

Annulus environment predictions in terms of the presence of CH₄, H₂S, CO₂ and H₂O should take gas permeation (likely to be reduced by the contacting armour layer) into consideration, as well as venting flow rate, reduction of annulus volume due to water condensation and consumption of CO₂ in corrosion reactions.

For liquids and gases, all of the coefficients Q , D and s (collectively termed C) are described by Arrhenius-type relationships with temperature as follows:

$$C = C_0 \exp(-E_a/RT) \quad (\text{E.8})$$

where C_0 , E_a and R are all constants. Hence plots of $\log C$ versus reciprocal temperature are linear and suitable for extrapolations to service temperatures from accelerated tests made at higher temperatures.

E.6 Chemical ageing

E.6.1 Where chemical ageing occurs at moderate temperatures, it will start at the surface it is contacting and will occur simultaneously to physical absorption. As the chemically-aggressive fluid is absorbed into the polymer, the same chemistry will occur after an appropriate delay. Levels of properties such as modulus at 50 % elongation will slowly change accordingly – either increasing or decreasing, depending on the chemical mechanism applying for the specific ageing situation. An increasing modulus level is due to an increase in the number of crosslinks between the molecular chains brought about by chemical reaction between fluid and polymer; a decrease will reflect chain scission or the like.

Where elevated temperatures exist, the aggressive species can be assumed to have diffused into the polymer bulk quickly, so that chemical ageing can be considered to have started at the same time throughout the polymer.

Relative rates of physical and chemical ageing might become obvious. For a chemically-resistant elastomer, the physical absorption of fluid will probably occur more quickly, so that initial modulus changes will be negative. Subsequently, chemical ageing induced by the hostile fluid might in time reverse this trend by causing stiffening; conversely, the chemistry might continue the downward trend. In addition, it has been observed on occasions for those elastomers that stiffen that a second reaction can occur after even longer times to cause softening again; this is again thought to be associated with molecular chain or crosslink scission, but here this reaction only occurs slowly.

Slower absorption can delay onset of both physical and chemical aspects of ageing. Also, slow absorption and fast chemical ageing could probably involve an increase in modulus at 50 % elongation from the start. This is one reason for allowing materials to saturate with oil before introducing the chemically hostile H₂S.

Points to note are:

- a) with gases, concentration increases with pressure;
- b) sequential exposures are common.

Examples of chemically-aggressive oil and gas sector fluids are:

- H₂S;
- amines (chemical treatments – inhibitors);
- formate brine (completion fluid);
- thiazoles, etc. (treatment chemicals);
- water (for certain elastomers);
- methanol (hydrate inhibition);
- oxygen.

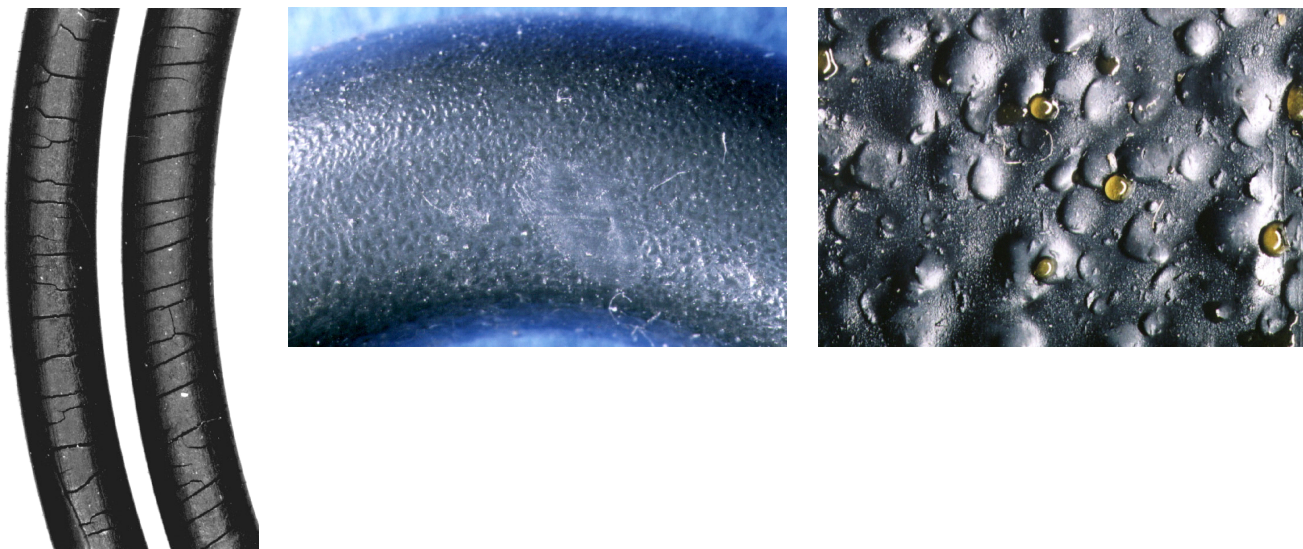
E.6.2 Regarding sour gas, H₂S can interact chemically with certain oilfield polymers. FEPM and FFKM generally perform well in the presence of H₂S even at elevated temperatures. FKM resistance is more variable at high temperatures. Differences in performance can be observed between different grades of one elastomer, and compounding can also make a difference.

Thermoplastics PTFE, PEEK and PPS can resist H₂S well; the high stiffness of PEEK and PPS, especially when fibre reinforced, makes them especially useful materials as back-up (anti-extrusion) rings for elastomeric seals.

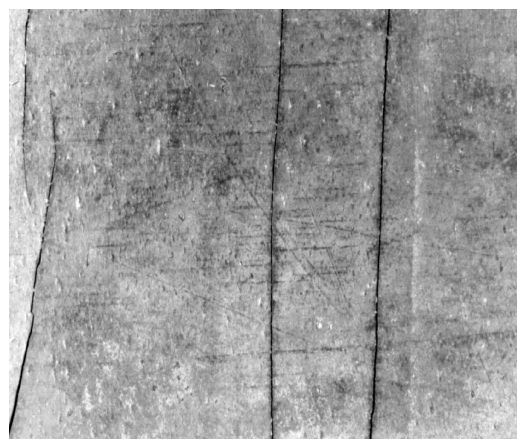
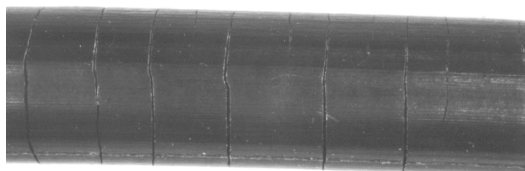
Some details about amines, which affect some FKM elastomers:

- These are added to produced, completion, etc., fluids to perform specific functions, e.g. corrosion inhibition, H₂S scavenger, etc., duties.
- Their concentration is invariably low, but they are active chemicals that form basic solutions.
- Alkalineresistant FKMs are now available. These are called base resistant elastomers (BRE).

Figure E.6 shows some examples of chemical attack of polymers where visible evidence of change is apparent.



a) Examples of polymer deterioration due to chemical attack



b) Examples of polymer deterioration due to ageing

Figure E.6 — Examples of polymer deterioration

Other points to note are as follows:

- a) methanol physically swells some FKMs (previous clause) to an unacceptable extent; slight dilution with water solves the problem;
- b) water can be chemically aggressive, e.g. nylons and some elastomers depending on compounding ingredients, but also can have physico-chemical effects;
- c) FKM compounded with MgO and Ca(OH)₂ degrades after long times in water at 150 °C and above; PbO as substitute solves the problem.

E.7 Service life predictions

Materials which age over time after exposure to a chemically aggressive fluid will display a change in magnitude for a (performance) property such as modulus at 50 % elongation. If a failure situation can be specified by whatever means possible, then exposure testing can be conducted at three or four temperatures which are well above that of service (to increase reaction rate) so that testing can occupy a reasonable timescale, e.g. as outlined below.

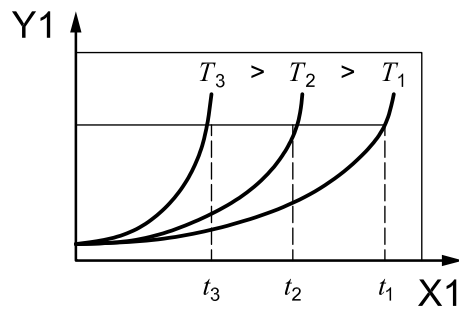
- a) Experience in a previous similar application might show that a 50 % increase in modulus at 50 % elongation is associated with a loss of sealing ability during thermal changes. Therefore, for the current work, the testing times needed to achieve this 50 % increase in modulus at 50 % elongation should be measured in each case. A suitable plot of temperature against testing time to the 50 % increase might yield a straight line which can be back-extrapolated to the service temperature, to give the service period that can be accommodated before this failure condition is reached.
- b) Such definitive data, particularly from actual service, is unlikely to be available, so recourse shall be made to choosing the best material available (as identified by testing) by deciding upon a failure criterion which gives confidence in the ability of a material to perform long term, before again testing at several elevated temperatures to give a back-extrapolation.

The back-extrapolation made above is purely empirical. Ideally, the best type of plot to track ageing in this way is an Arrhenius one, based on firm physical chemistry principles. A chemical reaction results in a decrease in reactant concentration and an increase in that of the product. With all-fluid reactants, the rate of the reaction can be calculated from the change in concentration of reactants or products with time. Various factors can influence the rate of a chemical reaction, including temperature, pressure, light, catalytic activity, etc. In classical physical chemistry, their influence can be explained by collision theory, that is, for a reaction between two chemical species to take place, their molecules shall initially make contact (collide) and stay contacted for a short instance. But this in itself is not enough; only those temporarily joined pairs which attain a level of energy above the so-called activation energy E_a will proceed to complete the chemical reaction – the pair will thus change to become a new molecule of the product. This approach can be applied to elastomer ageing by linking concentration – here, of crosslinks between molecular chains – with property magnitude.

This view helps understand why increasing temperature also increases reaction rates. Increasing temperature puts more kinetic energy into the system, causing increased molecular motion, hence increasing the number of reactive pairs formed and their energetics, so that more of these attain the required activation energy and the reaction will proceed more quickly. Mathematically, Arrhenius developed an equation in 1889 which shows that the Boltzmann factor ' $\exp(-E_a/RT)$ ' is the fraction of molecules that manage to obtain the necessary energy. More practically, when handling test data, applying this equation in its logarithmic form allows so-called Arrhenius extrapolations to be carried out.

In Arrhenius plots, as indicated in Figure E.7, the logarithm of reciprocal of the time to reach a certain change in property (a rate) is plotted against reciprocal absolute temperature, with the slope of the resulting linear plot divided by the gas constant (R) quantifying E_a . The link for its usage with elastomers is that material modulus increase is associated with an increase in the number of crosslinks within the polymer brought about by the ageing – hence there is a change in the concentration of crosslinks. There is also no reason why the approach should not also be applied to the other situation sometimes seen in oilfield usage as a second, long-term, ageing effect occurs after long times where the fluid interaction with an elastomer brings about a decrease in modulus at 50 % elongation.

An example of how this approach can be used is given in Annex D.

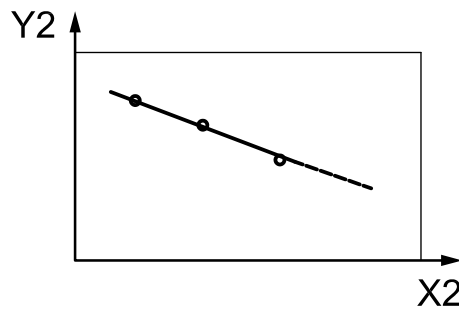


Key

X1 time

Y1 property, e.g. stiffness

a) Step 1: Measure property change with time at constant temperatures, T



Key

X2 $1/T$

Y2 $\ln(1/t)$

b) Step 2: Plot $\ln(1/t)$ versus $1/T$ and obtain activation energy from gradient

Figure E.7 — Schematic of procedure for Arrhenius extrapolation

For seals, in some cases, the effect of ageing on actual O-ring seals with regard to compression set may be needed. If such testing is agreed, the seal cross-section height after test in the direction of compression should be measured 24 h after removal from the test fixture. The measurement should be reported as a “% Compression Set”:

$$\% \text{ Compression Set} = 100 \times [(\text{Original seal height} - \text{Post-test seal height}) / \text{Interference}]$$

NOTE Interference is defined in 3.1.6.

From a practical viewpoint, when sour-testing, if purchasing gas cylinders containing already mixed gas compositions, pressures higher than cylinder pressure may require topping up resulting in reduced H_2S concentrations within the test vessel. This situation should be agreed between interested parties.

E.8 Ageing profiles

The change in tensile property levels versus exposure time in wet sour oil are characteristic for materials which

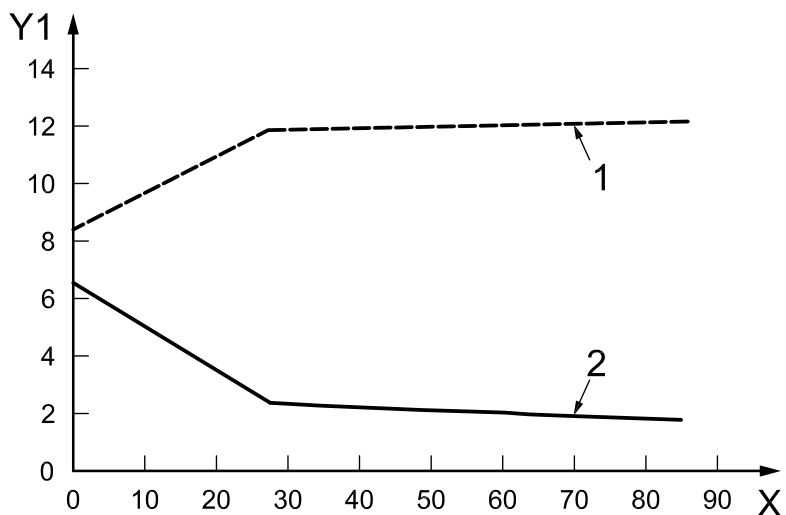
- a) are resistant to chemical ageing, and
- b) age by the formation of new chemical crosslinks.

In Figure E.8, the mean values of modulus at 50 % elongation [see Figure E.8 a)], tensile strength [see Figure E.8 b)] and elongation at break [see Figure E.8 c)] are plotted against immersion time for two fluoroelastomer types, FKM and FEPM. This particular FKM ages in the fluid, shown by the increase in modulus at 50 % elongation, and decreases in elongation (which both occur despite some initial swelling). The FEPM is resistant to chemical change under these conditions; modulus at 50 % elongation decreases initially due to swelling and then remains constant over the longer term. Elongation increases in response to swelling but changes little thereafter. For both materials, tensile strength reduces significantly at the first sampling point but alters little with additional exposure time: tensile strength is not particularly sensitive to ageing.

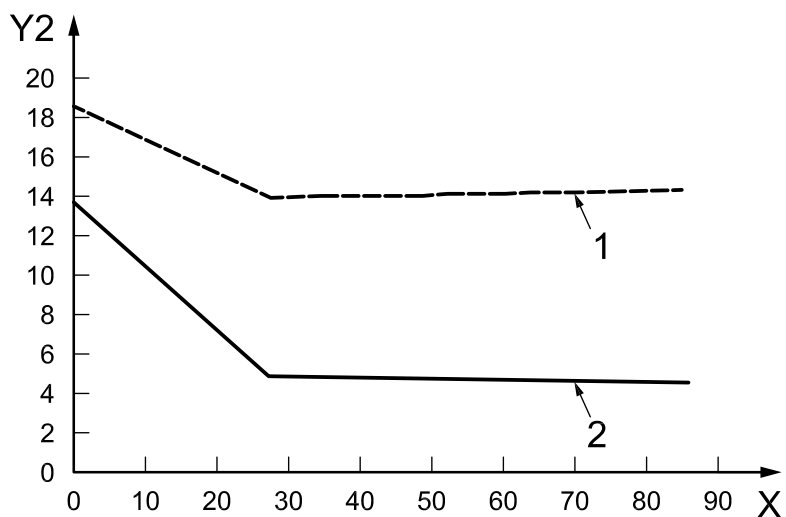
The large fall in FEPM modulus at 50 % elongation is a consequence of the aromatic content of the test hydrocarbon oil (A.1.ii, Table A.1); the level of swelling is enough (here) to fail the material on the volume swell criterion. Hence, a non-aromatic oil option has been specified (A.1.i, Table A.1); it is probable that this formulation will be specified for FEPM-TFE/P compounds submitted for sour ageing evaluation.

Polymers which are very resistant to sour ageing cannot be appraised using methods which rely on progressive property level changes with time and temperature. Instead, such materials are best described as being chemically stable under all the accelerated test conditions employed, and therefore very likely to have a long useful life at lower temperatures.

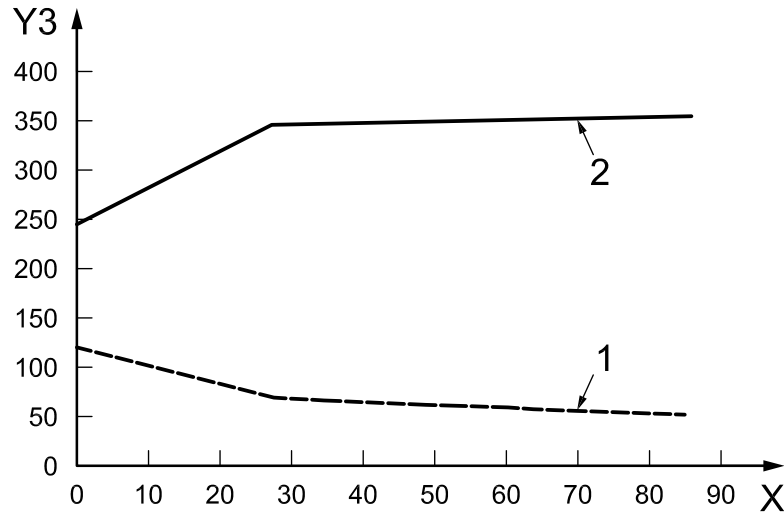
Another ageing trend is illustrated in Figure E.9: modulus at 50 % elongation exhibits an initial fall, before establishing a rising linear trend over the longer term. The initial reduction can be the result of swelling. The region associated with continuous change affects long-term performance and so should form the basis for life prediction.



a)



b)

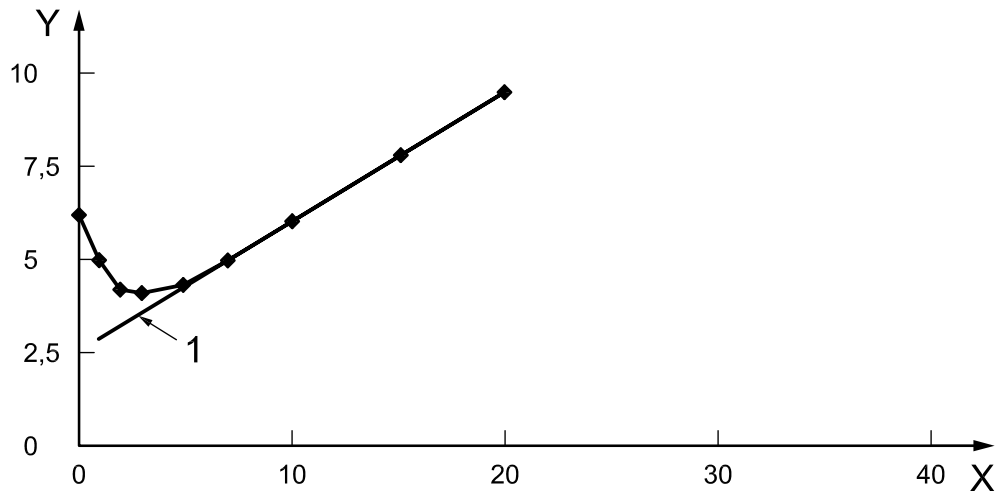


c)

Key

- X time, in days
- Y1 modulus at 50 % elongation, in MPa
- Y2 tensile strength, in MPa
- Y3 elongation at break
- 1 FKM
- 2 FEPM

Figure E.8 — Tensile property levels as a function of immersion time in wet sour oil at elevated temperature for FKM (dashed) and FEPM (solid)



Key

- X time
- Y modulus at 50 % elongation
- 1 trend for life prediction

Figure E.9 — Tensile property change as function of immersion time in ageing fluid, illustrating portion to be employed for life estimation calculations

Annex F (informative)

Rapid gas decompression (RGD)

F.1 Definition

Rapid pressure-drop in a high pressure gas-containing system disrupts the equilibrium between external gas pressure and the concentration of gas dissolved inside any sealing elastomer. Excess gas seeks to come out of solution at points throughout the material, causing expansion. If large enough, and if the rate of pressure release exceeds the diffusion rate of gas in the polymer, blistering or rupturing of the elastomer can occur, which can compromise sealing function.

F.2 Discussion

When an elastomer part contacts pressurized gas, many times its own volume of gas can become dissolved at equilibrium; this arises from Henry's law which directly relates equilibrium concentration of dissolved gas to applied gas pressure. An ensuing rapid drop of external pressure will disrupt this equilibrium. Just as carbon dioxide dissolved in lemonade appears as bubbles when the pressure is released by opening the bottle-cap, so gas dissolved under pressure in elastomers will come out of solution when the external pressure is reduced, e.g. by shutting down a pumping system. Carbon dioxide bubbles in lemonade can be seen to grow with time as they rise to the surface. This is because, with time, more gas is coming out of solution. However, bubbles similarly growing inside an elastomer are trapped – and as they expand they may eventually possess enough energy to tear the rubber, perhaps between bubbles with coalescence occurring, or through the elastomer bulk. In extreme cases the elastomer seems to explode – hence the term “explosive decompression”. This description is rather emotive and the term “rapid gas depressurization”, or RGD, is preferred to describe the phenomenon. Many examples are shown photographically in Annex B, which illustrates a grading system for the severity of the damage in O-ring seals.

Where do the bubbles initiate? Although there is ample evidence to show that the presence of flaws is not necessary to bring about RGD damage, it has been shown in filled sealing elastomers that micro-discontinuities present due to processing considerations do contribute in promoting failure, as do contaminant particles present in the elastomer. By moulding samples in non-standard ways, it has been possible to induce moulding flow to traverse sheet samples – rather than follow the plane of the sheet as is more usual – and in subsequent RGD testing, failures unusually followed this crossways direction, rather than occurring in the more normal planar direction for this geometry. However, even in the most homogeneous of elastomers, at the molecular level, local momentarily existing low density regions arising from chain fluctuations according to the kinetic theory could reasonably still be starting points for RGD failure. It should be evident from above that the method of O-ring manufacture can influence its RGD resistance.

At the start of an RGD event, as external pressure diminishes, gas concentration at the elastomer outer surface drops at an equally rapid rate, so that gas further into the bulk is now at a relatively higher concentration. Gas will try to escape by diffusion to satisfy the drive of equilibrating its concentration magnitudes throughout. At some time, any of this excess gas which has not yet escaped by diffusion to the outer surface seeks to come out of solution at points throughout the material, causing expansion – but before this happens the elastomer will probably withstand some excess of gas concentration; this gas is then supersaturated, a meta-stable, if stressed, state. If the pressure-drop becomes large enough and acts at a rate significantly faster than the diffusion rate of escaping gas from inside the elastomer, a critical stress will be achieved, gas molecules will come out of solution, bubble growth will follow, and material blistering or rupturing can occur. This process could continue with more rupturing if the elastomer is re-pressurized and then decompressed again, and so on.

The simplest strategy for avoiding RGD damage in an elastomer, if it is practicable, is slow decompression. If the pressure can be reduced sufficiently slowly, then gas which is dissolved in the elastomer can diffuse out of the rubber naturally without building up sufficient internal stresses to cause damage. The rate of decompression required may be roughly calculated if the diffusion coefficient of the gas and its solubility in the elastomer are known – but in practice it will probably require a laboratory simulation.

Table F.1 shows a summary of the variables involved in gas decompression damage, their effects and preferred magnitude to reduce RGD damage.

Table F.1 — Ways to lessen risk of RGD damage for sealing elastomers in service

Variable	“Ideal” level	Comment on ideal level
Material modulus at 50 % elongation	HIGH	Restricts initial bubble inflation
Tear strength	HIGH	To prevent subsequent rupture; however, a high level is not usually achievable in high modulus elastomers
Gas pressure	LOW	Above 7 MPa to 14 MPa (1 000 psi to 2 000 psi), risk of RGD damage greatly increases
Gas concentration	LOW	Depends on gas, elastomer and temperature
Gas type	LOW CO ₂	CO ₂ tends to be more soluble in some oilfield elastomers than methane; hence high CO ₂ levels increase the chance of RGD damage occurring
Diffusion coefficient	HIGH	Depends on gas, elastomer and temperature (high best)
Temperature	LOW	Although gases are more soluble and escape by diffusion more slowly at lower temperatures, material mechanical properties are beneficially high
Decompression rate	LOW	If very low, RGD damage will not occur; however, often an impracticable procedure in service
Seal cross-section	SMALL	RGD damage is more likely in thicker sections for gas diffusion reasons (the gas has further to travel and therefore more opportunity to cause damage in the process)
Seal constraint (groove fill)	HIGH	Inhibits seal expansion, and hence could limit (i) amount of gas taken up initially, (ii) any expansion and hence bubble formation plus rupturing during/after decompression
Squeeze level	APPROPRIATE	High levels of elastomer O-ring deflection when housed can exacerbate RGD damage
Decompression cycles	FEW	Likelihood of damage increases with cycle number

Many subtleties associated with RGD, for instance, accompanying thermodynamic cooling issues, failure processes and effects of localized stresses, are discussed in detail in an extensive review on this topic (see Reference [23]). Other workers have observed similar fracture effects arising from rapid temperature increases whilst maintaining pressure (see Reference [24]): the connection here with RGD is via Henry’s law linking dissolved gas concentration and solubility coefficient, and the fact that solubility coefficient decreases (in an Arrhenius fashion, as it happens) for readily-condensable (i.e. less volatile) gases when temperature increases.

The number of permutations involving the above variables is huge. Fortunately, some have more influence than others in determining elastomer RGD resistance. The key material properties are stiffness and tear strength: here, a balance should be struck when compounding. Very stiff (often high hardness) compounds can resist bubble inflation but are less able to prevent crack propagation, should initiation occur – they have low tear strength, particularly at elevated temperatures.

There are many sealing elastomer compounds on the market, and many organizations are active in development of new compounds for high pressure gas service. The great majority (if not all) are high hardness materials (85-95 Shore A), designed to resist bubble formation. There are various ways to increase material stiffness, e.g. increased filler loading (thereby diluting elastomer content), or tighter crosslinking.

Groove fill is an important part of seal design for pressurized gas applications. By restricting the volume available for the seal to expand during/after an RGD event, blistering and crack growth can be suppressed. Levels of groove fill in the 80 % to 85 % range are appropriate. Exceeding 90 % is not advisable: an O-ring shall have some free space around it in the groove, to accommodate thermal expansion and fluid absorption. Similarly, the deflection applied to the O-ring when housed should not be excessive; high levels of squeeze (say above 20 %) can exacerbate decompression damage. Experience has shown that a deflection range of 11 % to 17 % in the radial direction is adequate for O-rings seals in pressurized gas service.

Temperature is an important operational variable. Not only does it determine the behaviour of a gas – diffusion and concentration characteristics – but it has a large influence on the ability of the elastomer to withstand the forces associated with decompression damage. As temperature is increased, elastomer stiffness and tear strength decrease, reducing RGD resistance. Conversely, at elevated temperatures gas solubility is reduced (lowering gas concentration) and gas diffusion coefficient rises (enabling faster gas exit from the rubber). At very high temperatures (e.g. above 150 °C) in pressurized gas, although there may be little gas dissolved in the elastomer and the diffusion rate is high, the mechanical condition of the material is so poor that little energy is required to cause irreversible fracture damage.

At low temperatures (undefined, but say below 60 °C) the stiffness and tear strength magnitudes of many sealing compounds are sufficiently high to resist blister and fracture formation. The quantity of gas dissolved can be significant, however, and when the seal is released from its housing, it instantaneously expands; over time, as the gas diffuses out, it gradually contracts but is unlikely to regain its original (as-manufactured) dimensions.

The test conditions given in this part of ISO 23936 (see B.1.1) are intended to act as a baseline for materials development, screening, selection, etc. Accordingly, temperature (100 °C) and pressure (15 MPa) are set at levels which provide a reasonable (but not a severe) challenge for materials under test. Only compounds which pass under these conditions should be considered worthy of being taken to the next level, e.g. a functional test.

Many service fluids include hydrogen sulphide (H₂S) in the gas phase. For obvious reasons, RGD testing with H₂S (or gas mixtures containing H₂S) is rarely (if ever) undertaken. Currently, CO₂ is considered as a suitable substitute gas but there is evidence, for nitrile elastomers at least, that H₂S is absorbed more readily and in greater quantities at equilibrium than is carbon dioxide. Hence the strong possibility exists that H₂S is the more hostile gas, all else being equal, in terms of elastomer RGD resistance. Research activity continues in this area.

The inclusion of a liquid in an RGD test can strongly influence performance, although the quantity of public domain information available on this topic is very limited. The elastomer will absorb liquid (or vapour) resulting in swelling. While such expansion weakens the elastomer mechanically, reducing RGD resistance, it can also increase groove fill, helping to prevent blister formation. When performing RGD tests with gas and liquid, it may be prudent to include fixtures in each phase (if two phases exist at test conditions).

The rate of pressure release from a gas system in real life will invariably be non-linear. It is more likely to start rapidly and then slow as the pressure falls towards ambient. It is not necessary to replicate this profile in a test intended to evaluate basic RGD resistance; a linear drop is adequate. The release of pressure at 2 MPa/min is best achieved manually via the valve attached to the test vessel. Continuous gas release is preferable to stepped depressurization. This is easily accomplished if there is a reasonable quantity of gas in the vessel; a pressure gauge attached to the cell and a stopwatch are the only items required. Automated depressurization is specified by some end users and this can be accomplished using appropriate control equipment and software. Releasing the pressure linearly in two or more stages, at different rates, is also possible.

The number of pressure cycles can clearly affect material performance. The standard 8 cycle test described in Annex B is designed to be run without interruption for O-ring compounds which have been developed to a degree which gives the supplier a high level of confidence in their surviving intact. It can be completed in 7 days, a convenient interval for many laboratories. For development work, or where the RGD resistance of a

compound is not known, intermediate sampling is beneficial in allowing the onset of fracture damage to be established. As a minimum, at least two replicate seals should be examined after the first and third (or fifth) cycles in such test programmes.

It is also possible to run RGD tests with more than 8 cycles, perhaps to find the point at which fracture damage eventually appears in a resistant material. A high number of cycles may also be a requirement specified by an end user for a particular service situation. In such cases, it is recommended that the compound first be certified under the standard conditions, with subsequent RGD testing to end user conditions, with intermediate sampling points included.

The damage rating system specified in Table B.4 can be used to rate O-ring seals subjected to RGD tests that do not comply with this part of ISO 23936. For instance, seals removed from a functional test could be rated, for interest. The acceptance criterion should not be relaxed (i.e. increased to 4). However, it can be tightened should the user require a more searching acceptance criterion for their materials; some organizations consider ratings greater than 1 to be unacceptable.

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