Testing of Oilfield Elastomers

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Contents

(To be developed prior to publication)

1 Scope

This recommended practice communicates recognized industry practices for the evaluation of elastomer test samples or actual elastomeric seal members intended for use in the oil and gas industry. It can also serve as a general guideline for elastomer materials or elastomer seal members used for other applications, which have similar materials and application issues.

It is the intent of this document to review testing criteria, environments, evaluation procedures, guidelines for comparisons, and effects of other considerations on the evaluation of elastomeric seal materials and members.

It is not within the scope of this document to either offer any correlation between the data obtained from a screening test and the actual service performance of the seal member or to present any pass/fail criteria.

In the oil and gas industry the relationship between elastomer screening test conditions and actual service conditions is only approximate, at best. Consequently, the correlation between the results of any screening tests and actual service life or performance is also approximate. It has been shown that the gross effects, observed in the screening tests may identify possible problems in field applications. The extent of the correlation has not been recognized or quantified. The result should be used with caution combining with the field operation experience.

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.

API Specification 6A, 21st Edition - Specification for Wellhead and Tree Equipment.

API 17D, Specification for Subsea Wellhead and Tree Equipment

API 20L, Qualification of Polymeric Seal Manufacturers for Use in the Petroleum and Natural Gas Industries

ASTM D395-STM for Rubber Property, Compression Set.

ASTM D412-STM for Rubber Properties in Tension.

ASTM D471-STM for Rubber Property - Effect of Liquids.

ASTM D1414-STM for Rubber O-rings.

ASTM D1415-STM for Rubber Property - International Hardness.

ASTM D1418-Standard Practice for Rubber and Rubber Latices - Nomenclature.

ASTM D2240 - Rubber Property, Durometer Hardness.

ASTM D4483 - Standard Practice for Rubber - Determining Precision for Test Method Standards.

ISO 23936-2, Non-metallic materials in contract with media related to oil and gas production.

NACE - TM0187 - Evaluating Elastomeric Materials in Sour Gas Environments.

NACE – TM0296 - Evaluating Elastomer Materials in Sour Liquid Environments.

NACE TM0297 Effects of High – Temperature, High-Pressure Carbon Dioxide Decompression on Elastomeric Materials.

NORSOK M710, Qualification of non-metallic sealing materials and manufactures.

ACS Rubber Division, Paper No. 83 - "A User's Approach to Qualification of Dynamic Seals for Sour Gas," October 1988.

ACS Rubber Division, Paper No. 44 - "Swelling of Some Oilfield Elastomers in Carbon Dioxide, Hydrogen Sulfide and Methane at Pressures to 28 MPa, October 1983.

Underwriters Laboratory Inc., "UL 746B Standard for Polymeric Materials - Long Term Property Evaluations," 4th Ed., 1991.

3 Terms, Definitions and Abbreviations

3.1 Terms and Definitions

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

3.1.1 Antiextrusion Device

Plastic, metal, wire, etc., rings and packings used to block the extrusion of the elastomer seal.

3.1.2 Button

A cylindrical shaped, standardized size rubber specimen or pellet used for testing physical and chemical properties.

3.1.3 Compound

The mixture of raw rubber or elastomer with other ingredients and additives.

3.1.4 Compression Set

The residual deformation of a material after removal of the compressive stress.

3.1.5 Cure

The act of vulcanization.

3.1.6 Dumbbell

A dog bone shaped flat specimen of rubber used for testing of physical and chemical properties.

3.1.7 Elastomer

This term is used synonymously with rubber, particularly synthetic rubber; generally a non-metallic material which resists deformation, up to a point, and has the ability to recover its original shape after the deforming force is removed. See Rubber.

3.1.8 EPDM

Terpolymer of ethylene, propylene, and a diene with the residual unsaturated portion of the diene in the side chain

3.1.9 Extrusion (Processing)

One of the methods to form rubber and plastic materials into usable shapes, such as gaskets, seals, etc.

3.1.10 Extrusion

One of the common modes of failure of seals. This usually refers to the flow of rubber seal particles into the gap between a piston and cylinder.

3.1.11 **FLUOROELASTOMER**

Fluorine-containing elastomer. See ASTM D1418 for guidance.

3.1.12 **Gas Diffusion**

Gas penetration through a seal material, usually under high pressures: see Explosive Decompression.

3.1.13 **Modulus**

Stress at a given elongation; in the rubber industry modulus refers to the tensile stress of rubber compounds at 50 percent, 100 percent, 200 percent, etc., stretch. Consequently the rubber strength values are usually given as 50 percent modulus, 100 percent modulus, 200 percent modulus, respectively.

3.1.14 **Packing**

A deformable material which is generally less flexible than homogeneous rubber seals and energized by squeezing **or** compressing it by mechanical means.

3.1.15 **Polymer**

A broad group of high molecular weight materials which includes rubber, elastomers, and plastics.

3.1.16 **Plastic Packing**

Various soft materials used to inject behind or around a certain type of seal and thereby to hydraulically energize it. The plastic itself is usually not intended to be a sealant.

3.1.17 **Plastics**

Synthetic, moldable, castable, pliable material with some elastic properties. In seal technology, plastics are often used for backup rings and anti-extrusion devices.

3.1.18 **Rapid Gas Decompression or Explosive Decompression**

A type of seal failure manifested by gas bubbles, blisters, cracks, etc., on the surface of a seal or internally in a seal which has been exposed to high gas pressure and then subjected to a rapid release of pressure.

3.1.19 **Rubber**

Natural or synthetic, pliable material with elastic, and springy properties, often stretchable to several times its original length, and with the ability to recover the original length. Rubber is always used in a mixture with other ingredients in order to make it moldable and to improve its mechanical properties; see Elastomer, also Compound.

3.1.20 **Seal**

A device that prevents the leakage of fluids (liquid or gas) from a pressure vessel. Seal material may be elastomer, metal, plastic, or a composition of several materials.

Dynamic Seal

A seal where there is any one of several possible modes of relative motion between the sealing surfaces: lateral, rotary, etc.

Face Seal - A static seal between two surfaces.

Rotary Seal - A type of dynamic seal where the relative motion is circular.

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Static Seal - A seal where there is no relative motion between the seal and the sealing surface. The seal may be energized by compression in the vertical or radial direction.

3.1.21 **Sour**

The presence of hydrogen sulfide (H_2S) in natural gas or crude oil.

3.1.22 **Sweet**

The well product contains no H_2S; see Sour.

3.1.23 **Volume Fill**

(Also seal/gland occupancy ratio) is the ratio of seal volume to available seal groove volume, often expressed in terms of percentage.

3.1.24 **Vulcanization**

The crosslinking of molecules of the raw rubber material; an irreversible thermo-chemical process that takes place during and/or after molding, extruding, casting of raw rubber compounds.

3.2 Acronyms, Abbreviations, Symbols, and Units

For the purpose of this document, the following abbreviations apply.

ACS - American Chemical Society.

ASTM - American Society for Testing and Materials.

NACE - National Association of Corrosion Engineers.

NBR - Standard abbreviation of nitrile rubber (acrylonitrile-butadiene).

P_e - Critical pressure.

T_c - Critical temperature.

Tg - Glass transition temperature; below this point rubber becomes rigid, glass-like material.

4 Environment

4.1 General

Oilfield equipment can be exposed to a wide variety of environments. In one instance, it is expected to work within the full range of chemical, thermal and pressure conditions in order to drill, produce, process, and transport the products of gas and oil wells. In the second instance, it is expected to perform reliably in any geographical or seasonal locale of the world - from the Tropics to the Arctic.

When used, elastomer seals and packing are typically the performance-limiting components of oilfield equipment. The materials of construction of nonmetallic seals are generally lower strength and less resistant to the environmental factors than the metallic portion of the wellheads, valves, etc. Consequently, understanding the environmental factors is of utmost importance before the material selection, the design, and the testing procedures of the sealing mechanisms are undertaken.

4.2 Chemical Environment

The following list contains the most common fluids, both liquids and gases, found in the oilfield. It should be noted that the effect of all chemicals is dependent on the concentrations, temperature and other conditions. The effect of multiple chemicals and their reaction products is beyond the scope of this listing.

However, the design engineer and the end user should be wary of the complexities of this possibility and should consult a chemist who is expert in this field.

a) **Primary Chemicals** (Fluids - Drilling, Completion and Produced).
    −   Crude Oil
    −   Natural Gas
    −   Hydrocarbon Condensates
    −   Brine (Produced)
    −   Hydrogen Sulfide
    −   Carbon Dioxide
    −   Steam (Geothermal)
    −   Drilling Fluids - Oil- and Water-Based
    −   Packer Fluids - Brines, Acidic Zinc Brines, Corrosion Inhibitors, Biocides, etc.

b) **Secondary Chemicals** (Fluids - Testing, Cleaning, Conditioning, Treatment).
    −   Diesel and Arctic Diesel Fuel
    −   Motor Oil
    −   Jet Fuel
    −   Water - Fresh, Salt, Steam
    −   Corrosion Inhibitors - Water and hydrocarbon carrier
    −   Solvents - Kerosene, Methanol, Highly Aromatic, Trichloroethene, etc.
    −   Hydraulic Fluids
    −   Acids - Inorganic and Organic
    −   Scale Inhibitors

4.3   Temperature Conditions

Thermal conditions can be steady state, transient, cyclic or a combination of all three. High temperatures can have a significant impact on the life of an elastomeric element. These effects can either be thermal-chemical and/or thermal-mechanical. The higher the temperatures and the longer the time of high temperature exposure, the more likely the seal element can be degraded. However, seals can tolerate short-term excursions at considerably elevated temperatures beyond their published service temperature rating, providing that the mechanical property limitations are not exceeded at that temperature.

Seals at low temperatures become stiff and brittle and their sealing capability may be severely reduced as the temperature approaches the glass transition (T_g,) of the elastomeric material. This latter effect is reversible and raising the temperature of the seal sufficiently above its T_g, should cause the seal to function normally.

The following list shows the temperature classifications generally recognized by the Industry:

— Standard: Majority of wellheads: -18°C to 121°C (0°F to +250°F)

— High Temperature: Greater than 121°C (250°F)

— Arctic: Ambient Temperatures: -60°C to - 29°C (-75°F to -20°F)

— Flowing Temperatures: usually high as +82°C (180°F)

— Geothermal and Steam Injection: as high as 345°C (650°F)

The 21st Edition of API 6A Specifications and Annex G recognizes the temperature classifications shown in Table 1.

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Table 1—Temperature Ratings

Temperature Classification	Temperature Range			
	°C		°F	
	Min.	Max.	Min.	Max.
K	-60	82	-75	180
L	-46	82	-50	180
N	-46	60	-50	140
P	-29	82	-20	180
S	-18	60	0	140
T	-18	82	0	180
U	-18	121	0	250
V	2	121	35	250
X [a]	-18	180	0	350
Y [a]	-18	345	0	650

[a] Annex G of API 6A, 21st Edition

4.4 Pressure Conditions

The following pressure listing is traditionally used in the drilling and production segment of the oil and gas industry (Pressure shall be pressure differential):

— Low to Moderate Pressure: up to 34.5MPa (5000 psi)

— High Pressure: greater than 69.0MPa (10,000 psi)

Pressure can be exerted on the seal gradually, incrementally or suddenly; in a constant or cyclical manner. Higher pressure may mean shorter seal life. A sudden drop of gas pressure can be very destructive to a seal by a phenomenon known as explosive decompression. Pressure-energized seals designed for high pressure applications can sometimes leak at low pressures. One practice to avoid this is to use two sets of seals – one for high pressure and one for low pressure sealing. A small, measurable leak can be related to the permeability of the elastomeric material. Consequently, the leak rate of a well-designed seal is in the molecular scale and is usually not discernible with conventional leak detection devices.

4.5 Seal Function

Seals can be static or dynamic (moving) types. If dynamic, the abrasion resistance and the coefficient of friction between the seal and the mating surfaces are very important properties. Seals can also be classified by the way that they are energized.

— Pressure Energized: The higher the pressure, the tighter the seals hold - within limits. Extrusion failure is the result of exceeding the limit. Piston and rod seals are examples. Higher modulus should improve the extrusion failure resistance of a seal to a large extent. Reduced gap clearances alleviate seal extrusion failures.

— Mechanically Energized: Face seals, lockdown screw packings and some valve stem packings.

— Plastic Injection: Energized by hydraulic means.

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Extrusion resistance for an elastomer or a backup system is a very critical property for all seal systems at high pressures and temperatures. To be successful, back-up materials used in anti-extrusion devices need to survive the pressure and temperature conditions with little or no yielding.

4.6   Time Duration

Elastomeric materials deteriorate with time and this process can be accelerated under certain environmental conditions. The longer a seal is exposed to these conditions, the shorter may be its life expectancy. The higher the temperature and pressure and the more concentrated the attacking chemicals, such as hydrogen sulfide, the shorter the life expectancy. See 5.2.4.

4.7   Storage Conditions

The storage conditions should conform to API 6A and API 20L.

It is primarily concerned with the protection of the seals before they are put into service. Exposure to UV radiation (sunlight), ozone and heat are the source of most storage problems. Proper packaging in a shielded plastic bag or wrap and stored out of the sun in a cool warehouse away from high voltage, ozone-producing equipment assure a long storage life for the seal. In cold climates storage should be in a heated warehouse.

Elastomers such as NBR are much more susceptible to storage degradation than the chemically resistant materials such as the fluoroelastomer seals. The latter frequently have a shelf life greater than 20 years.

5   Testing Options for Evaluation

5.1   Immersion Testing

In immersion test, the detailed test procedures should be in accordance with ASTM D471 for the measurement of changes in volume, tensile strength, modulus, elongation and hardness.

5.1.1   Test Specimens

Standard test specimens shall be O-rings (O-ring 214 or 325) or ASTM D-412 dumbbell, unless otherwise agreed by the manufacturer and purchaser.

5.1.2   Test Media

A standard test media is provided in Table 2. Other test media may be used as appropriate for the intended application.

5.1.3   Test Vessel

a)   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 and gases.
b)   Ratio of liquid and gas volume to test specimen volume shall be at least 25:1 for unconstrained tests, and at least 10:1 for constrained tests.
c)   The vessel shall be capable of being purged to remove the air or other gases.

5.1.4   Unconstrained or Constrained Testing

5.1.4.1 Unconstrained and constrained specimens

a)   Typical immersion testing can determine changes in elastomer stress/strain characteristics, changes in hardness, volume (swelling), and compression set. Results of immersion testing do not answer the question of how suitable an elastomer sealing element is for a particular application.

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b) The use of unconstrained specimens (O-ring or dumbbell) in an immersion test exposes 100 percent of the exterior surface of the specimens to the test media. For screening tests to quickly determine the effect of test media on an elastomer, this technique is satisfactory. Stressed specimens, such as bent loop specimens, may be included.

c) The use of constrained specimens, or seals made from an elastomeric material in a seal gland simulates actual surface exposed to test media in service. This is considered a more realistic test simulation than the use of free sample immersions.

d) In either free or constrained immersion testing, the effects of the test media plus pressure and temperature can be studied. However, immersion testing cannot directly quantify how long the elastomeric sealing component can continue to function in the test media.

5.1.4.2 Standard constrained geometry

− For screening test, the standard open constrained condition should have a squeeze of 14,5 ± 3%; For O-ring test specimens, the squeeze should be in radial direction; The standard confined constrained conditions should have a radial squeeze of 14,5 ± 3% and a volume fill of 80-85%.

− For qualification test, constrained specimens should be tested in a manner that mimics the important design considerations for the application, for example squeeze and volume fill. These values shall be captured in test documentation by manufacturer.

5.1.5   Test Temperature

Test temperature shall be according to the temperature rating described in Table 1, unless otherwise agreed by the manufacturer and purchaser.

The test temperature shall be either the maximum specified temperature rating for the temperature class being tested or the maximum temperature at the seal location (see Table 1) for the equipment at the maximum test temperature class of the test product, as established by product testing and/or design analysis.

During the exposure period, the rate of temperature change shall be less than 0.5 °C (1 °F) per minute and shall not exceed the extreme by more than 11 °C (20 °F).

5.1.6   Test Pressure

− Standard test pressure should be 6.9MPa ±0.7MPa (1000psi ±100psi). The pressure may be hydrostatic pressure or differential pressure in confined constrained geometry if needed.

− For the constrained immersion specimens in a pressure test fixture, the pressure should conform with API 6A pressure rating.

− Bespoke pressure, under agreement between the manufacturer and purchaser.

5.1.7   Test Durations

Unless otherwise agreed between the manufacturer and the purchaser, the test duration should be,

a) One-week standard immersion test or,

b) Immersion test with multiple intervals. The standard multiple intervals may include 0, 1, 2, 4, 8 weeks or 0, 2, 4, 8, 16, 32 days

5.1.8   Measurements

Measurements include non-destructive measurements and destructive measurements. Volume change, hardness change and appearance are non-destructive measurements, while tensile properties such as modulus, tensile strength and elongation changes are destructive measurements. For a one-week standard

immersion test, all measurements should be tested after the immersion test. For immersion test with multiple intervals, there are two options depends on test conditions, materials properties, and design requirements. Option 1 is to test non-destructive measurements after each interval, and only test destructive measurements after the final intervals. In this case, the same test specimen could be used during the whole test. Option 2 is to test all measurements after each interval. In this case, each interval needs separated test specimens.

5.1.9   Acceptance Criteria

i)   hardness change:
        – for < 90 Durometer (Shore A), +10 to -20 points,
        – for ≥ 90 Durometer (Shore A), +5 to -20 points,
ii)   percent volume change: +25 to - 5%
iii)   appearance: no blistering, cracking, disintegration or change in the appearance of the chemical (color, precipitates, etc.) with no magnification.
iv)   percent tensile strength change: ± 50%;
v)   percent change in the % elongation: ± 50%
vi)   percent change in the 50% modulus: ± 50%;

5.1.10   Reference Samples

An as received sample (or dry unaged sample) should normally be used as the reference sample for immersion test. However, sometime, the reference sample could also be a wet unaged sample (or zero reference). A wet unaged sample reveals the initial swelling and therefore provides more information about chemical degradation during aging test. Generally, no significant chemical degradations should be involved when preparing the wet unaged sample. Unless otherwise agreed between the manufacturer and the purchaser, the immersion duration for wet unaged sample should be 3 days.

5.2   Performance Testing

Performance testing is sealing performance testing or sealing validation testing. O-rings should be used in a standard performance test.

Performance tests may also be conducted after the seal is aged under various chemical, thermal and mechanical conditions (e.g. aging under confined or non-confined configuration). The sealing performance test may be static testing or dynamic testing.

In both static and dynamic testing, no attempt is generally made to accelerate the thermochemical degradation of the elastomeric sealing element. Sometimes elevated temperatures, high pressures, and high concentrations of corrosive media are used in an attempt to create an "excessive" environment or a worse case condition. However, unless the testing is conducted for an extremely long period of time, the life of the sealing element in the test media cannot be determined.

5.2.1   Static Testing

Static Testing is defined as a sealing element being exposed to the test media with constant or varying pressures without relative motion between the two fixed elements against which the seal acts. See Figure 1 below. Along with test media, pressure and temperature (high and/or low) are applied to the sealing element to verify or estimate performance. In the static testing, the pressure hold should be at least one hour, and the test procedure and acceptance criteria shall be according to API 6A Annex F.

Factors to be considered for static test: Extrusion gap, back up ring, compression ratio, volume fill, pressure, and temperature.
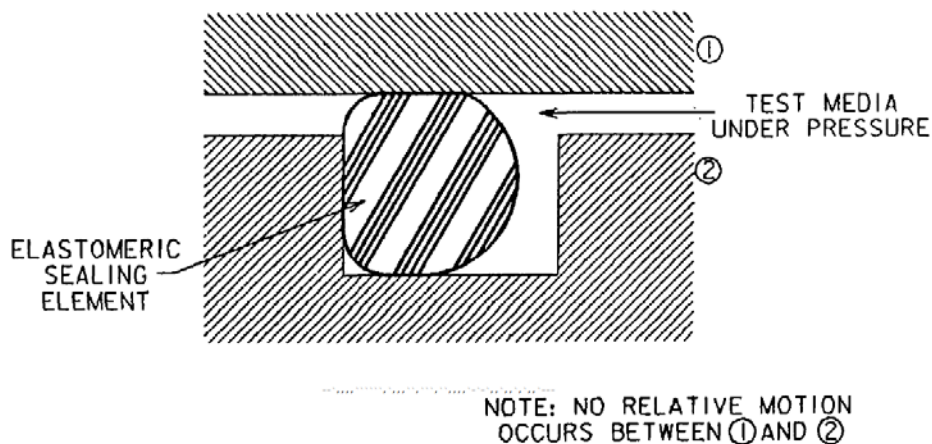
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Figure 1—Static Seal Testing

5.2.2   Dynamic Testing

Dynamic testing is defined as testing a sealing element being exposed to the test media with constant or varying pressures with relative motion between the two fixed elements against which the seal acts (Figure 2). Along with test media, pressure and temperature (high and/or low) are applied to the sealing element to verify or estimate performance.

In dynamic testing, the pressure hold should be at least one hour, and the test procedure and acceptance criteria shall be according to API 6A Annex F.

In addition to the factors that listed in previous section, other factors that should be considered are the motion speed, relative move direction, the number of cycles, surface conditions such as surface frictions, coatings.
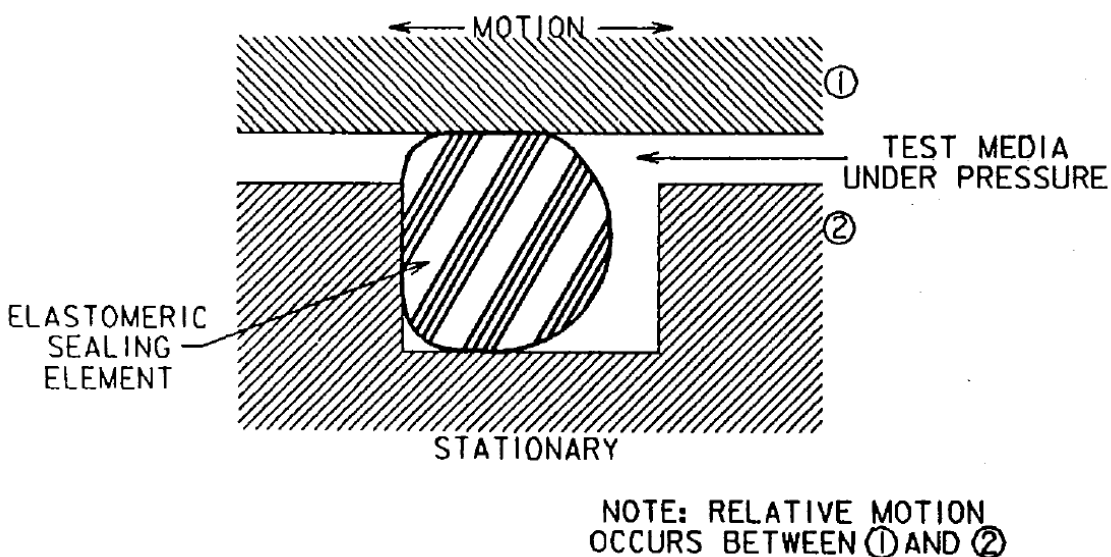

Figure 2—Dynamic Seal Testing

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5.2.3   Aging Test of Elastomer Seals

5.2.3.1   General

This clause specifies the aging tests that may be performed on an elastomer sealing element under simulated operating conditions. In this case, the seal element is installed in a test fixture and holding the operating pressure using the simulated test media. The standard aging test of elastomer seals should be conducted under the same conditions as these defined in life prediction test described in Section 5.2.4, except that the test duration and test temperature could be customized defined based on the applications. Therefore, it is a simple version of life prediction test.

Aging of sealing element under simulated operating conditions could be used for prediction of the progressive degradation of elastomeric materials during sealing the operating or simulated test media at elevated temperatures over extended periods of time. It is especially applicable where it is necessary to forecast potential sealing life in a harsh application conditions, and it could also be used for directly comparing the performance of candidate elastomer seals under certain harsh operation conditions. For instance, when the seals are exposed to extremely volume swelling chemicals, highly reactive chemicals, or under high pressure high temperature (HPHT).

5.2.3.2   Test Conditions

Annex A provides guidance of aging test of a sealing element during pressure holding.

5.2.3.3   Test Durations

The standard sealing aging test durations should be 1, 2, 5 or 10 standard test cycles. A standard test cycle is defined in Annex A.

5.2.3.4   Acceptance Criteria for Leakage (or Time to Fail, Sealing Failure)

Leakage criteria should be defined by applicable API product specification. In the absence of API product specification, leakage criteria should be defined by agreement between manufacturer and purchaser.

5.2.4   Life Prediction Testing (or Life Estimation Testing)

An objective of life prediction testing is to assess the life time of an elastomer seal function by accelerating the thermochemical degradation of the seal element in a known test environment. This technique is based on the Arrhenius aging technique utilized for material evaluation in the nuclear industry and by the Underwriter Laboratories in life prediction testing.

Arrhenius life prediction is accomplished by elevating the temperature of the test environment. Elevated temperature testing is conducted until the sealing element fails to hold rated pressure in a test media simulating the service environment. Tests may be conducted in a static or dynamic environment. However, designing a dynamic life prediction test is much more difficult than a static test, but has been reported for a full-size seal system (Paper No. 83 ACS Rubber Div., October 1988).

Care shall be exercised in designing the experiment so that thermomechanical failures (such as extrusion) are isolated and thermochemical failures (compression set, embrittlement) can be studied. Temperature selections are critical to prevent thermal degradation during a study of accelerated thermochemical degradation. The study of seal failure by thermomechanical means can also be pursued by examining the effects of extrusion gap and/or antiextrusion devices.

Life prediction testing should be performed on a real sealing element made of the candidate elastomer.

While exposed to the test media, the sealing element made of the candidate elastomer is repeatedly cycled between ambient conditions and test pressure/elevated temperatures until a failure occurs. For specific applications, other temperatures below ambient can be used. The time to failure is recorded along with the elevated test temperature. This test procedure is repeated with new specimens at several other elevated temperature, with the test pressure being constant. The data are collected according to the Arrhenius Equation:

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$$\log t = \frac{Ea}{2.303R}\left(\frac{1}{T}\right) + \log C$$

Where

> t time to failure
>
> T elevated temperature, degrees Kelvin
>
> R gas constant
>
> Ea activation energy
>
> C constant

The data points can then be plotted on a semi-log graph with the vertical scale as time to failure and the horizontal scales as the reciprocal of the absolute temperature. A least squares regression analysis (best fit) is conducted and a line drawn to the specified service temperature. The validity of a straight line representing the elevated test data is based on Arrhenius aging technique and the occurrence of a zero order chemical reaction. In the analysis of the data using the least squares regression analysis,
a correlation coefficient of greater than 0.90 should be achieved, which indicates that the data points approximate a straight line.

This life prediction technique gives an approximation to the question: "How long would the candidate elastomer seal last in a specified service environment?" Should extrusion failures occur, they may be controlled through the incorporation of antiextrusion devices. Thermochemical failures due to excessive compression set or embrittlement/cracking are the most frequent cause of failure of sealing elements used for long-term sealing (in the order of years).

Annex A defines the detail test conditions and procedure requirements for life prediction testing.

5.2.5   Explosive Decompression (ED)/Rapid Gas Decompression (RGD)/Gas Rupture Testing.

5.2.5.1   *General*

Exposure to pressurized gases can lead to explosive decompression damage of elastomeric sealing elements used in the oil and gas industry. The damage occurs after the pressure is rapidly released from a sealing element. Damage usually shows up as surface blisters and splits in the exposed surface of the sealing element. However, internal damage may also occur without external evidence. Of all the gases encountered, CO_2, H_2S, CH_4, and N_2 are the major contributors to explosive decompression damage.

The effects of explosive decompression can be minimized by slowly reducing the applied pressure to ambient pressure. The slow release of pressure allows the entrapped and dissolved gases to escape and minimize damage to the seal. The crucial portion of the pressure let-down leading to explosive decompression damage has been reported to be uncontrolled depressurization below 1000 psi. Uncontrolled depressurization down to 1000 psi produced little or no sample swelling or subsequent damage. (Paper No. 44, ACS Rubber Div., October 1983).

A number of factors influence an elastomeric sealing element's resistance to explosive decompression damage:

a)   Elastomeric material mechanical properties
b)   Seal/gland occupancy ratio
c)   Temperature
d)   Material processing variables leading to internal voids or defects
e)   Gas/elastomer solubility

Testing materials for explosive decompression damage resistance can be accomplished in either a free or confined state. In unconstrained state testing, the complete outer surface of the elastomeric sample (O-ring or slab) or sealing element is exposed to the test gas in a pressurized test vessel. This is the most severe form of testing. In a NACE test (NACE TM0297) for CO_2 testing, gas bottle pressure (up to 900 psi) has been shown to be sufficient to cause damage when the pressure is rapidly released. Matching the thickness of the field sample is very important for meaningful results: For example, a thin cross-section specimen may pass the test, but a thicker specimen of the same material may fail.

In constrained testing, the elastomeric sealing specimen is confined to a gland or cavity. In this case, only a limited amount of surface area is exposed to the gas, and volumetric swell is limited by the confines of the gland. ED/RGD tests based on Annex B of ISO 23936-2, NORSOK M710 Annex B and Total GS EP PVV142 are constrained testing.

In either of the above procedures, rapid release of pressure causes the maximum amount of damage if a material is susceptible to explosive decompression damage. It should be reemphasized that explosive decompression damage only occurs when rapid depressurization is allowed to take place. Prior to decompression and while the sealing element is under pressure and confined to its gland or cavity, it may function satisfactorily. Damage is often not discovered until repressurization is attempted.

To avoid the RGD effect, the pressure could be rapid released in a single step or multiple steps of 3.4 MPa (500psi) from high pressure to 6.9MPa (1000psi) at intervals of one to several minutes. After that a slow pressure release (less than MPa/min, 20 psi/min reference on ISO 23936) should be applied. Specimens of 6 mm (0.24 inch) (cross-section) or lower may be depressurized more rapidly. Thicker specimens higher than 10 mm (0.4 inch) should be depressurized slowly.

5.2.5.2   RGD Test Methods

a) Standard RGD test

The specimen, test conditions and procedures should be according to ISO 23936-2, NORSOK M710 or NACE TM0297.

b) RGD test combining with sealing performance test

The specimen should be installed in a real or simulated gland in a pressure test fixture. The test pressure, temperature, test media and test procedures could be according to the Annex A of ISO 23936-2 or real applications. A one-hour pressure holding at specified test temperature after RGD test could be used to evaluate the effect of RGD to the sealing performance. This could establish another accept criteria for the RGD test, which is based on sealing performance, not on the size of cracks on the seals. After the RGD test, the seal could be evaluated, or rated and documented based on ISO 23936-2. To eliminate the impact of pressure holding on RGD test, different (or multiple) test specimens could be utilized in this RGD test.

6   Guidelines For Evaluation Of Test Results

6.1   Immersion Testing Results

Immersion testing results may give an indication of the functionality or suitability of a seal material within the limitations noted in Section 5.1.4. Evaluating the effects of property changes in a seal material after an immersion test requires a knowledge and understanding of the seal design and the potential consequence of the observed property changes taking place in the actual service. For example, a seal material may swell 100 percent in an unconstrained sample exposure, but in a tight gland, it may only be allowed to swell 25-30 percent. ASTM D471 and D1414 methods are used.

Caution should be used in evaluation of data from unstressed (unconstrained) specimens.

6.1.1   Hardness
This measures on a nonlinear scale, a sample's resistance to an indenting deformation. It is an indication of the elastic modulus at low strain. If an accurate measurement is obtained after immersion testing, a gross

change in hardness is indicative of a change in elastic modulus or stiffness. ASTM D2240 and D1415 methods are used.

For most applications, hardness change should be in the following ranges after an immersion test,
− for < 90 Durometer (Shore A), + 10 −20 points,
− for ≥ 90 Durometer (Shore A), +5 −20 points.

6.1.2   Volume Swell

An increase in volume is common after an immersion test. Decreases in volume indicate the loss of material from the sample. In many seals, only the slightest decrease in volume is tolerable.

Volume increases are more tolerable. Sample swell typically is a result of a physical process in which an equilibrium swell value is reached or it may be a result of a chemical process in which case equilibrium values may not easily be attained. A multi-point test is necessary to evaluate this situation.

Immersion tests permit an unconfined specimen to swell without external restraint. In service, seals confined in glands or housings may be restricted from swelling beyond the limits of the gland. If the swelling is strictly a physical process, this limited situation can be tolerated in actual use, depending upon the swollen materials response to stress. It is recommended that if swelling beyond 20 percent is expected, it is advised to adjust the gland volume and/or material selection.

In general, volume swell should be in the range of -5% to +25%. This is also applicable to a seal in a constrained immersion test, regardless of the volume swelling in unconstrained immersion test.

6.1.3   Tensile Strength (Ultimate Tensile Strength)

Changes in tensile strength are a common method of evaluating material changes in the seal material. It is not uncommon to first observe an increase through a maximum followed by a decrease when observed versus exposure time. Tensile strength changes shall be evaluated in conjunction with the tensile modulus and elongation changes. ASTM method D471, D412, or D1414 is used.

In general, tensile strength changes should be in the range of -50% to +50%.

6.1.4   Tensile Modulus (or Tensile Stress at Certain Elongation)

Increases in stiffness and modulus are indicative of additional crosslink formation **or** plasticizer extraction. Reductions indicate softening because of swell or perhaps bond scission in the polymer or its crosslinks. Reduced modulus is associated with extrusion and explosive decompression problems. ASTM D471, D412, and D1414 are used.

Tensile modulus changes should be in the range of -50% to +50%.

6.1.5   Elongation at Break.

Swell and softening may lead to elongation increases, and it is almost always accompanied by a decrease in modulus. Excessive crosslink formation can lead to embrittlement and is normally accompanied by modulus increases and elongation decreases. ASTM D471, D412, and D1414 are used.

In general, elongation changes should be in the range of -50% to +50%.

6.1.6   Compression Set (CS)

This is a measure of a material's ability to recover from a compressive deformation after exposure. High set can lead to leakage by compression energized seals. A material may exhibit higher or lower compression set in a fluid relative to an air aging test depending on the interaction with the fluid. ASTM D395 and D1414 are used. CS in air is useful for materials qualification. However, it is hard to have a universal acceptable guidance line for CS in seal applications.

Use of Immersion Test Results is only one aspect of selecting a candidate for an elastomer seal application. In general, these results can only be expected to be helpful if all the ramifications and the

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consequences of changes in mechanical properties are considered. In many applications, some hardening of the seal is inconsequential. If the property changes due to immersion fail to meet specifications, then a fixture test should be considered.

6.2 Boundary Changes

The oil and gas industry has certain specifications for seal material property retention after immersion in produced or treatment fluids. However, that does not guarantee long term performance in all engineered scenarios. It is, therefore, important that an agreement between the manufacturer and purchase should be reached on the time, temperature, environment, and property measurements based on the capability of the elastomer compound being used and the properties relevant to the engineered solution in its application.

Acceptable boundary changes in properties depend greatly on the original value of the property and the minimum required by the design. Therefore, there can be no general hard and fast rules about acceptable changes. It is common practice for the technologist to compare results of several elastomer materials at once, during initial material selection discussions, and look for the least change of properties as their primary focus while striving for a balance in secondary properties.

6.3 Use of the Test Results

Test Results may be used in three ways:

First, as internal materials selection and or qualification.

Second, as a customer qualification test for the seal materials to be submitted in a bid proposal. For example, the customer may specify that the fluid-aged tensile properties (TB, M100, and EB) of the candidate elastomer shall not be less than 50 percent of the original values, the swell be no more than 40 percent, and the hardness not vary more than 5 points after 14 days at 300°F in using 5 percent H2S/95 percent CH4 1000 psi in diesel.

Third, for quality control purposes, to ensure the reproducibility of the production seals, and to determine what changes are acceptable in the aged properties in some standard ASTM test oils or air oven aging. In addition to the properties cited above, compression set limits may also be established - less than 40 percent when the sample is aged for seven days at 250°F, for example.

7   Environmental Simulation

Environmental simulation is complicated, but with care it is possible for many typical situations. Because of the broad range of conditions to which elastomers are subjected, it is necessary to conduct several tests. Elastomer technologists have struggled for some time trying to agree on a limited number of test environments. It appears that the use of several tests continue to be necessary to conduct evaluations for specific application conditions.

In designing any evaluation of elastomer seal materials, environmental simulation is a critical factor. An improperly simulated environment can lead to an erroneous evaluation of a material as acceptable with the consequence of catastrophic field failure.

In any environmental test procedure, the composition and the phase behavior of the environmental models shall be considered. Of particular importance is the stoichiometric ratio of the elastomer seal material and the chemicals in the model environment. That is, enough of the reacting gases or chemicals shall be used *to* sustain proper concentration throughout the duration of the test.

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7.1 Chemical Environments

7.1.1 Field Samples

It is generally recognized that the use of field samples of fluids (liquids and gases) for evaluating elastomers provides the most valid test results. However, several factors deserve consideration:

Simulating a specific environment by the use of field samples can limit an evaluation's usefulness to that environment, similar environments, or those known by experience to be less severe.

The field sample may not accurately reflect the actual media to which the seal is to be exposed. For example, a sample taken after H_2S and water have been separated would not be the same environment that a given seal would be exposed to in production service prior to the separation. When the exposure test is designed, the field sample shall represent the original service environment. This may require replacing separated constituents and/or increasing the amounts of trace corrosive chemicals (H_2S) in order to be sure they are present in sufficient quantity throughout the test period.

An analysis of the constituents of a field sample may be advisable for a thorough evaluation of the seal/environment system. This analysis is imperative if the test results are to be useful for elastomers in applications of a similar environment.

7.1.2 Model Liquids and Gases

Lacking the ability to obtain actual field samples, the environment shall be simulated by the use of model fluids. In order to prepare model test fluids, the technologist should know the qualitative and quantitative makeup of the actual service media. There is a tendency to eliminate minor constituents to simplify the makeup. This action would be incorrect if the minor constituents interact with the seal materials to be tested. For example, distilled water has been shown in some experiments to affect certain elastomers more than seawater and chemically treated seawater could have a more pronounced effect than straight seawater or distilled water. Again, this illustrates the need for care in reproducing the environmental model simulation.

Examples of fluids proposed for use to simulate the effects of crude oil are standard ASTM Oils 1, 2, and 3; standard ASTM Fuels A, B, and C; diesel fuel and Jet Fuel A. ASTM oils are standard fluids developed to simulate typical lubricating oils. The ASTM fuels simulate blends of hydrocarbon/aromatic gasolines. Diesel fuel varies dramatically from source to source because of its broad specification range. Jet A is a relatively tightly controlled aircraft turbine engine fuel and has been specified in API Spec 6A, Appendix F (Table F.2). None of the above fluids, however, are very close to the varied compositions of crude oil from around the world. Therefore, the selection of any model test fluid may be arbitrary and is selected for its availability, reproducibility, and reasonably low viscosity.

The gases present in service are normally simulated by appropriate additions of H_2S, CO_2, of CH_4 to the test. The technologist should address phase behavior, solubility, and interactions of the gases and liquids with themselves, the test vessel, and the elastomer test specimens. In a recent attempt to evaluate a proposed NACE sour test method (NACE TM0296 and NACE TM0187), it was determined that a mix of 95 percent straight chain hydrocarbons and 5 percent toluene would not dissolve sufficient H_2S to cause the expected embrittlement of a standard NBR elastomer. The conclusion was that the 20 percent H_2S gas mix at 1000 psi was not dissolved enough in the 95/5 solvent mix. On the other hand, a 90/10 mix has been successfully used as the base hydrocarbon solvent mix for other sour liquid test procedures.

CAUTION: Aromatics used in test fluids can produce degradation of some elastomer compounds.

Table 2 lists the important standard simulated test fluids for oil field applications.

Table 2. Standard simulated test fluids

Test fluids	Hydrocarbon Liquid phase materials (vol% mixer)	Liquid hydrocarbon	Water cont., vol%	Gas phase materials (vol fraction mixer)	H_2S content in gas	Gas volume, vol%

		volume, vol%			phase, vol%	
Group I	May include, but is not limited to, jet fuel, diesel, kerosene, etc.	60	5	A. 5%CO_2/95%CH_4; B. 80%CO_2/20%CH_4; C. 10%H_2S/5%CO_2/85%CH_4; D. 10% H_2S/80% CO_2/10% CH_4;	0 or 10	35
Group II	A. 70%heptane/30% cyclohexane; B. 70%heptane/20 % cyclohexane/10 % toluene	60	10	A. 5% CO_2/95% CH_4; B. 2%H_2S/3%CO_2/95%CH_4; C. 10%H_2S/5%CO_2/85%CH_4	0, 2 or 10%	30
Group III	A.25%n-hexane/ 20%n-octane/50%n-decane/5%toluene; B. 100% Kerosene; C.70%n-heptane/ 20%cyclohexane/10% toluene	60	5	A. 10%H_2S/5%CO_2/85%CH_4; B. 20%H_2S/5%CO_2/75%CH_4	10 or 20	35
Group IV	25%n-hexane/20%n-octane/50%n-decane/5%toluene;	5	5	A. 5%H_2S/20%CO_2/75%CH_4; B. 20%H_2S/5%CO_2/75%CH_4	5 or 20	90

7.2   Physical Environments

7.2.1   Temperature and Pressure

Elevated temperatures increase most chemical reactions rates - a principle which is useful in accelerating tests. However, elevated temperatures reduce the mechanical properties of elastomers. Test temperatures shall be selected to avoid exceeding the thermal stability or the heat resistance of the elastomers to be evaluated. Pressure and temperature also affect the concentration of gases, density of the test media, volatility, solubility, permeability, and reactivity of the combined test system.

Add to this the fact that service conditions are seldom steady state and the problem of test design becomes even more difficult.

The test temperature generally should be the maximum temperature rating of the materials or close to the maximum application temperatures, while the test pressure for standard test normally should be around 6.0 to 6.9MPa (around 1000psi).

7.2.2   Dynamic

When seals are used in dynamic applications, it is often necessary to simulate the dynamics in a material evaluation. Static tests may not be valid. Simulating dynamics increases the complexity and cost of material evaluations. If the test environment is toxic, special care is required not to compromise safety.

Some of the elastomer properties that are of particular concern in dynamic service include coefficient of friction, swelling, resilience, fatigue, abrasion, and erosion. These properties are all affected by the temperature, pressure, and chemical changes that occur due to environmental reaction.

7.3   Worst Case Conditions

It is normally assumed when evaluating elastomers that testing under worst case conditions is desirable. If the test is valid, service performance is expected to exceed the test results affording an increased margin of safety. Typically, to ensure a worst case evaluation, it is common to increase reactant concentrations, temperature, pressures, and other parameters that increase reaction rates. Caution is required., however, to avoid designing an evaluation to severe that all materials fail the test. As noted, elastomers are often exposed to conditions more severe than actual service. The assumption is that failure mechanisms do not change, but are only accelerated.

7.4   Arctic or Cold Weather Applications

Elastomers are stiffened by low temperature. A thousand fold increase in modulus can be observed by crossing through the glass transition temperature of an elastomer. At sufficiently low temperatures, many elastomers under stress take a 100 percent set in the stressed condition. Reversible embrittlement frequently occurs in cold seals. The chemical effects, fortunately, of most environments are reduced because of slower reaction rates.

Under arctic conditions, anti-freeze-type products may be used in the service environment to permit continued operation and they shall be documented, if used.

The evaluation of elastomers for low temperature service can be conducted by extending the temperature range of tests to incorporate these effects.

8   Other Considerations

The following items should be considered if test results are expected to be valid, reproducible, and to conform to ASTM D4483 (Standard Practice for Evaluating Precision for Test Method Standards in the Rubber and Carbon Black Manufacturing Industries):

a)   Availability of Standard Elastomer *"Control"* Compounds.

b)   Reversible Changes/Compensating Effects.

c)   Irreversible Changes.

d)   Compatibility (Solubility) of phases (gases in liquids).

e)   Stoichiometry.

f)   Temperature Effects.

8.1   Availability of Standard Elastomer Control Compounds

Standard compounds featuring commonly used oilfield elastomers should be made to specific formulas and available from a common source. These would be used, first, to establish test method validity in terms of reproducibility, and secondly, as control samples in subsequent test programs to ensure that tests have been conducted under controlled conditions. The use of the control materials for comparison purposes cannot be stressed too highly. In addition to establishing the improvement (or lack of improvement) of the test material in the environment, the absolute results on the control elastomer indicate that the test method and conditions were correctly carried out.

8.2   Reversible Changes/Compensating Effects

Confined immersion test or aging test of a real sealing element is strongly recommended to evaluate effect of reversible changes (such as certain fluids swelling and thermal expansion) on the elastomer seals.

The final results should be affected if the changes in the sample properties are reversible. It is well known, for example, that certain physical changes are completely and totally reversible. One illustration is the change in elastomer properties above and below the glass transition. When the samples have been brought back up to a temperature above the Tg, test results indicate that the elastomers have not been damaged as a result of being frozen. Swelling is another example of a change that may be reversible, i.e., when the elastomer seal test coupon is removed from the media, the swelling fluid may diffuse out and the seal coupon recover to its size and properties. This recovery is generally time dependent and related to the following variables:

a)   Volatility of Swelling Media

b)   Test Temperature

c)   Test Pressure

d)   Cross-Sectional Thickness of Specimen

e)   Solubility of Media and Sample

f)   Rate of Depressurization

In the case of gases and low boiling point liquids, these can easily be removed from elastomer specimens of thin cross-section through evaporation once the elastomer is removed from the swelling media. However, it is not unusual to see large specimens of rubber remain swollen for an extended period.

Carbon dioxide may diffuse from elastomers under standard temperature and pressure within approximately 24 hours, depending on cross-section and degree of solubility. Thus, elapsed time after removal from immersion media and the commencement of the physical property testing becomes extremely important as far as test results are concerned. This has long been recognized and some procedures specify that the test pieces shall come to constant weight after removal and before physical property measurements are made.

Extracted plasticizer may actually be replaced by the swelling medium and differing results can be expected until equilibrium has been achieved. Other compensating effects can be observed by the softening effects of solvent swell and embrittlement. Examples of embrittlement are those crosslinking reactions such as those obtained with NBR and H_2S or some fluorocarbons with amines.

When evaluating the test results, reversible changes or compensating effects should be considered for a real application. For significant reversible changes such as reversible volume swelling and thermal expansion effects, the test results should be reevaluated to identify the real changes. If there are compensating effects during immersion test, for example, crosslink and swelling or decomposition effect exist at the same time, the use of the immersion test results should consider this compensating effect. The compensating effect could lead to very different trends on volume changes, tensile strength, modulus and elongation changes.

8.3   Irreversible Changes

Constrained immersion testing is recommended as a basic test to evaluate irreversible changes.

Elastomers can be, and frequently are, permanently affected by some reversible changes if the changes occur too rapidly and causes damage in the form of ruptures and splits in the elastomer matrix. This occurs during rapid pressure changes, which lead to the phenomenon defined as explosive decompression. Similar

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physical damage can result from internal heat buildup due to post curing, internal friction, or microwave heating.

Chemical changes in elastomers tend to be irreversible, whether they are temperature induced and associated with the polymer itself or reactions of the polymer with other chemicals. Examples of reactions with other chemicals are those associated with corrosion inhibitors, H_2S or air in oxidative degradation. These generally follow basic reaction kinetics and comply with the Arrhenius equation illustrated in 5.2.3.

The use of this procedure permits accelerated testing to determine data points for regression analysis and prediction of long-term results with a high degree of confidence if the correlation factor is at or near 1.0.

8.4   Compatibility of Phases

Other concerns in severe environment testing are with the critical temperatures and pressures of gases and the solubility and chemical reaction of these gases with the liquid phase. Pressurized mixed gases may not exist in the specified ratio as gases unless they are all above their respective critical temperatures. This is of concern for bottled gases to be added to autoclaves and for the gases in the autoclave.

Critical properties for methane, CO_2, and H_2S, gases commonly used in severe environment testing, are:

	$\dfrac{T_c}{^{o}C}$	P_c	
		atm	PSI (approximate)
Methane	-82.1	46.8	675
CO_2	+31	72.9	1075
H_2S	+100.4	88.9	1300

Adding low pressure gas mixtures directly to autoclaves should be satisfactory only if the final test pressures are also relatively low and enough of each gas is present to complete whatever chemical reactions take place with added liquids and test pieces. Normal test temperatures will not raise the pressure by more than approximately a factor of two which is still below usual test pressures.

Critical point should be considered when test pressure and temperature involved the critical temperature and/or critical pressure during test, especially for these tests under very high pressures. A well-defined test procedure should be applied before the start of the test in this case. Most of standard tests are done either at a temperature higher than 100ºC (212ºF) and/or pressure within 6.9MPa (1000psi), and thus avoiding critical temperature and critical pressure issues.

8.5   Stoichiometry

Low pressure gas mixtures may contain less than stoichiometric amounts of individual gases. A one-liter autoclave at STP would contain no more than 0.045 moles (1.5 grams) of pure H_2S and only a fraction of that if a gas mixture was used in the autoclave, the volume occupied by the liquid added, and the volume of any test fixtures (compression set). The issue of concern is how much H_2S is required to completely react with the several hundred grams of hydrocarbon present in the autoclave in`1 the form of elastomer test coupons and liquid petroleum products. At 523°F (273°C) and 2,940 psi (200 atm), 4.5 moles (150 grams) of pure H_2S (100 times) would be present. For example, if diesel fuel is the test fluid being used, there would be more olefinic bonds reacting with the H2S than in the elastomers being tested.

Extremely small amounts of H_2S are very detrimental to some rubber test pieces, and significantly different results are obtained if the gas at a low concentration is replenished during the test. Meaningful results may not be obtained if the supply of H_2S is not representative of the essentially inexhaustible quantities (zero order kinetics) found in service.

The effects from exposure to a gas phase-only environment versus a liquid phase immersion with gas over-pressurization shall be considered. If the primary effect of the H_2S gas phase is embrittlement and that of the liquid phase is swelling, then the net compensating result could be only minor changes in the physical properties. On the other hand, combined effects sometimes appear to be synergistic.

8.6   Temperature Effects on The Properties of Elastomers

As a general phenomenon, elastomer mechanical properties change with temperature. Thermal expansion (or contraction), hardness, and flexibility are among the more significant properties that relate to seals and packers used in drilling and production equipment. Generally, rubber expands or shrinks about ten times as much as steel for the same change in temperature. When designing elastomers as sealing elements, the coefficient of thermal expansion shall be considered to prevent seal gland (cavity) overfill and possible seal extrusion. On the other hand, thermal contraction during cool down results in loss of sealing force and can potentially produce a leak of contained gas or fluid. Elevated temperatures/pressures accelerate chemical changes such as reversion, crosslinking, chain scission, etc., according to the Arrhenius principle.

These are generally permanent and irreversible changes. Changes due to low temperatures are, however, physical rather than chemical and are generally completely and totally reversible. Two types of changes may occur at low temperature. Both cause increased stiffness in rubber compounds. Thermal stiffening is independent of time providing thermal equilibrium has in the other hand. crystallization occurs over a broad been- achieved and is common to all elastomers. The second is due to crystallization, which is time dependent and is a characteristic of only those elastomers which undergo crystallization. Although glass transition temperatures, as related to thermal stiffening, are reproducible to within ±2˚C, values for compounds of various elastomers are highly dependent on compounding variables such as filler and plasticizer loading. On the other hand. crystallization occurs over a broad temperature range, but occurs most rapidly at a specific temperature for a given elastomer and may take days, weeks, or even months to complete. The rate of crystallization is also influenced by compounding variables including vulcanization chemicals, state of cure, and degree of stress. Highly crystallized elastomers are very stiff and leathery but not brittle.

Annex A
(informative)

Test Media, Conditions, Equipment and Procedures for Aging and Life Estimation

A.1 General

Estimating the service life of elastomeric sealing elements used in severe environments, such as encountered in the oil and gas industry, has been extremely difficult. Elastomeric sealing elements are frequently exposed to methane, hydrogen sulfide, and carbon dioxide gases, along with crude oil, water and corrosion inhibiting chemicals. The following procedure outlines a technique based on the Arrhenius principle of chemical reaction rates, which permits the life of an elastomeric material to be estimated when exposed to a severe service environment. The test procedure should be agreed upon between the manufacturer (or supplier) of the equipment that incorporates the elastomer sealing elements and the purchaser (or end user). The procedure should be based upon a definition of the service conditions and requirements such as:

a) Temperature-steady state or a high and low range of service.
b) Fluids and gases-stagnant or flowing.
c) Pressure-continuous or a low and high range.
d) Chemicals and additives-inhibitors, descales, acidizing, etc.
e) Mechanical requirements-dynamic or static, torque, setting force.
f) Failure criteria-pressure leakage, loss of mechanical function, inability to set or retrieve.

Aging test of a sealing element under simulated service conditions (or seal aging) is also specifically defined in this annex. This aging test provides aging information much closer to real applications than conventional immersion tests. In Annex A, aging indicates aging of a seal such as an O-ring under simulated operating conditions.

A.2 Problem Statement

Traditional methods of evaluating elastomers used for sealing elements involve the use of ASTM or other standard immersion-type tests. In these techniques, samples of the candidate elastomeric material are immersed in the anticipated environment for a specified time period in the free state. Immersion times can vary from hours, to weeks, to months. The samples may be in a pressurized or unpressurized environment. The physical properties before and after immersion are compared and a judgment is made as to the suitability of the elastomer for use in the service environment. The elastomeric material is generally not tested in its end use geometry (form) and not confined to a seal gland. In a properly designed seal gland, minimal seal surface area is exposed to the severe environment, and the gland physically limits the swell of the sealing element within the gland. The use of an immersion testing technique for retained physical properties does not answer the question of how long the elastomeric sealing element will function as a seal in a severe environment. Many sealing elements used in the energy exploration and oil/gas production industries are expected to remain serviceable (not leak) for up to 20 years in a severe service environment.

Traditional immersion tests for retained physical properties have a role in the initial screening of suitable candidate elastomeric materials. A material would not be selected for service, which was severely attacked and deteriorated by the service environment in an immersion test. However, some degradation of physical properties (stress-strain) and volumetric swell can be tolerated. It should also be noted that certain elastomeric materials may sustain minimal property degradation in an immersion test, but they still may not be suitable for long-term sealing service. This is because they exhibit excessive creep or stress relaxation at high pressures and/or temperature.

A.3 Aging and Life Estimation Technique-Overview

The elastomer life estimation technique described below is based on the Arrhenius principle of chemical reaction rates. This principle is concerned with chemical reaction rates and the effects of temperature on

these rates. In general, for every 10°C (18°F) temperature increase, the chemical reaction rate doubles. Conversely for every 10°C (18°F) decrease in temperature, the chemical reaction rate is reduced by 1/2.

A brief theoretical discussion of the Arrhenius principle and its application to accelerated thermo-chemical aging follows:

The Arrhenius equation has the basic form:

$$k = Ae^{-\frac{E_a}{RT}}$$

where
    k = rate constant of a chemical reaction,
    A = proportionality constant related to collision frequency and orientation of molecules,
    Ea = activation energy,
    R = gas constant,
    T = absolute temperature.

Rewriting the above equation using natural logs gives:

$$lnk = -\frac{E_a}{R} \times \frac{1}{T} + lnA$$

If we let *lnk = y; lnA = b; -Ea/R = m;* 1/T = x.

It can be seen that the equation represents a straight line, y = *mx + b,* where *-Ea/R* is the slope.

If the times to failure for various temperatures are converted to natural logs, the experimental data can be plotted on semi-log graph paper. Regression analysis gives the best straight line fit through the experimentally determined data points. If the correlation coefficient is at or near 1.0, the line can be extended and time to failure for other temperatures extrapolated with confidence.

Examples of accepted industry standards that utilize Arrhenius aging techniques are:

ISO 23936-2 - *Non-metallic materials in contract with media related to oil and gas production*, Revision 3, 2011.

NORSOK M710 - *Qualification of non-metallic sealing materials and manufactures*, Revision 3, 2009.

ASTM *D3045 - Heat Aging of Plastics Without Load.*

ASTM *D2990 - Tensile, Compressive, and Flexural Creep and Creep Rupture of Plastics.*

UL 746B, *Standard for Polymeric Materials Along Term Property Evaluations.* Underwriters Laboratories Inc.

To approximate the life of an elastomeric material for use in a severe service environment, tests should be conducted in the specified environment under accelerated temperature and/or pressure conditions. Without some type of accelerated testing, it may be difficult to quantify the service life of an elastomer component. Elevated temperature and/or pressure testing can provide a useful method for estimating elastomeric material capabilities under realistic conditions.

Life estimation testing may be considered as the best estimate of long term service life to evaluate the long-term performance of an elastomer in a severe service environment.

The basic technique involves collecting time to failure data at elevated temperatures (higher than the maximum anticipated service temperature) and plotting the results on semi-log graph paper. The vertical scale is the log of time to failure and the horizontal scale is the reciprocal of the absolute temperature.

Figure A.1 shows a typical life estimation plot. Alternately, the time to failure at the service temperature also can be calculated from the appropriate mathematical formula.
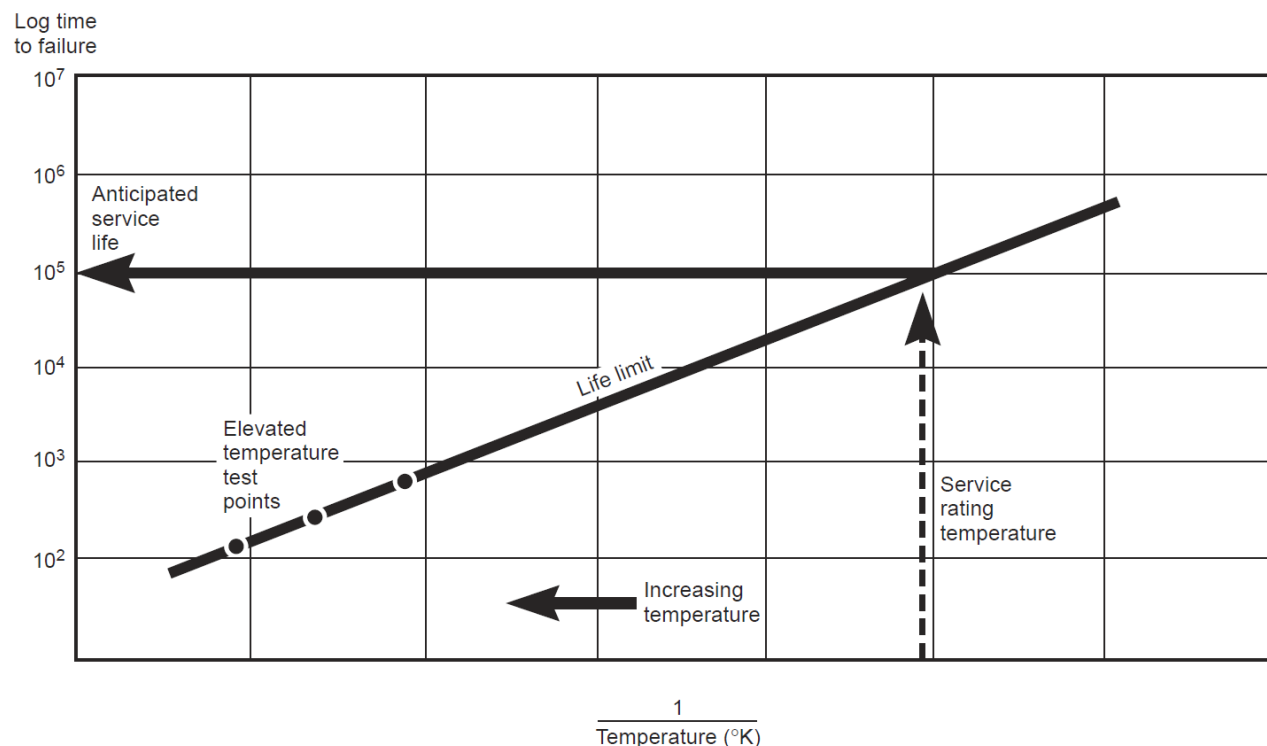
Figure A.1—Typical Life Estimation Plot

Certain precautions should be exercised when performing accelerated temperature and/or pressure tests. It should be verified experimentally that the failure mechanism (and activation energy) does not change with elevated temperatures or pressures. In addition, gas diffusion may occur through an elastomer seal at an accelerated rate and this should be considered if this is used as failure criteria. It also may be helpful to test an elastomer material with known field performance as a reference for comparison. Stagnant fluids and gases may give better or worse life estimation than if the fluids are periodically refreshed.

A.4 Ageing and Life Estimation Test Media

A.4.1 Simulated Test Media

Test media may be as according to Table 2, or as agreed between the manufacturer and purchaser.

The composition of all fluids to which the test specimen is exposed shall be documented.

A.4.2 Other Test Media

Other test media may be used based on the application requirements.

A.5 Ageing and Life Estimation Test Conditions

A.5.1 Test Temperatures

The test temperature shall be either the maximum specified temperature rating for the temperature class being tested or the maximum temperature at the seal location for the equipment at the maximum test temperature class of the test product, as established by product testing and/or design analysis. Elevated test temperatures for aging and life evaluation tests shall be according to Table A.1. During the exposure period, the rate of temperature change shall be less than 0.5 °C (1 °F) per minute and shall not exceed the extreme by more than 11 °C (20 °F).

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Table A.1 Elevated test temperatures for aging and life evaluation tests

Temperature Classification	Temperature Range				Elevated test temperatures, °C	Elevated test temperatures, °F
	°C		°F			
	Min.	Max.	Min.	Max.		
K	-60	82	-75	180	97,112,127	207, 234, 261
L	-46	82	-50	180	97,112,127	207, 234, 261
N	-46	60	-50	140	81,96,111	178, 205, 232
P	-29	82	-20	180	97,112,127	207, 234, 261
S	-18	60	0	140	81,96,111	178, 205, 232
T	-18	82	0	180	97,112,127	207, 234, 261
U	-18	121	0	250	136,151,166	277, 304, 331
V	2	121	35	250	136,151,166	277, 304, 331
X [a]	-18	180	0	350	195,210,225	383, 410, 437
Y [a]	-18	345	0	650	Not possible	Not possible
Non-ISO/API	0	150	32	300	165,180,195	329, 356, 383
Bespoke	As shall be agreed between the manufacturer and purchaser					

The recommended test temperatures in Table A1 is mainly for O-ring 214 with a radius around 2mm. For other O-rings or seals with even larger cross-section, the temperature should be even lower than the corresponding temperatures in this table for life evaluation. This is because the strong diffusion lag effect could skew the test results to an even longer lifetime under higher test temperatures. Combination of aging or life evaluation using standard O-ring 214 and FEA modeling is one of reasonable approaches to achieve the lifetime of a seal with very large cross-section.

A.5.2 Test Specimens
Test specimen such as O-ring 214 may be used. Based on the applications, other geometries of seals are also acceptable.

A.6 Equipment
A.6.1 Test Fixture

A test fixture should be designed that follows best practices for pressure vessel design, and captures the important features of the application. One such seal design may be an O-ring utilizing squeeze and volume fill that represents those used in the application. Design parameters utilized should be documented. Figure A.2 illustrates a typical test fixture.

The aging and lifetime evaluation is mainly based on thermo-chemical aging. To eliminate unnecessary thermo-mechanical impact, the extrusion gap should be as small as possible to reduce the extrusion at high pressure. Plastics and metal back up rings could be used depending on the application requirements.

A.7 Procedure for Aging and Life Estimation Testing of Elastomers

The proposed procedure requires the use of an autoclave (a high temperature pressure vessel) to collect time to failure data. Various autoclave and fixture designs can be used.

Figure A.2 illustrates a life estimation autoclave sealed with standard size O-rings (e.g. O-ring 214) made from the candidate elastomer. The autoclave should be capable of operation, with a proper safety factor, up to the maximum temperature, pressure and test environment needed for the accelerated test. The internal volume should be appropriately sized to avoid depletion of the test environment during the test; the

minimum internal volume should be equal to or exceed 100 ml (the ratio of internal volume to test elastomer seal volume should be more than 25:1 if non-standard elastomer seals were used). The main body and end closures contain O-ring glands that are fabricated from an appropriate alloy. Typically, a corrosion resistant alloy is used to fabricate the test fixture. Since thermo-chemical degradation of the elastomeric sealing element is of interest, thermo- mechanical effects should be minimized. Therefore, clearances between the end closure and the test vessel bore shall be minimized to eliminate extrusion (thermo-mechanical type failure) of the candidate elastomer.

If additional mechanical protection is required for the O-ring seal, an anti-extrusion ring (back-up ring) of suitable material can be used. In life estimation testing, only the thermo-chemical effects of a severe environment on a candidate elastomer are evaluated. Actual geometry and thermo-mechanical effects are best evaluated using full scale testing.
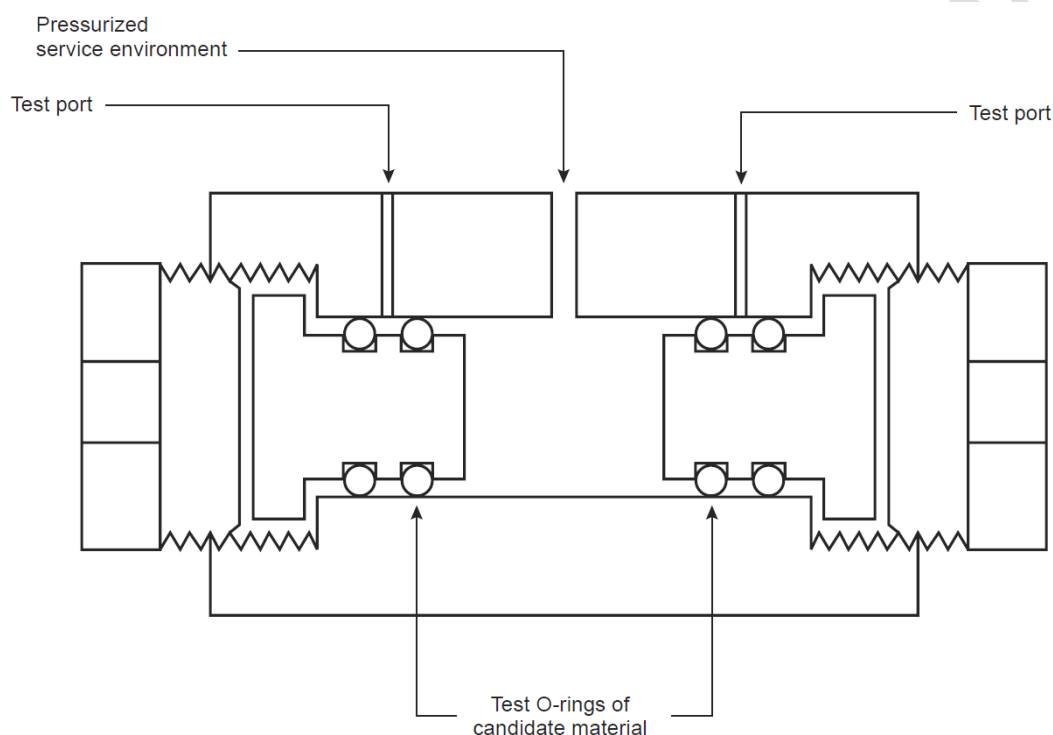

Figure A.2—Standard O-ring Test Fixture

The severe service environment is introduced into the test chamber formed by the two end closures. The test vessel is pressurized and heated to a predetermined temperature during each test cycle.

The length of the test cycle is established by the testing protocol, i.e., steady state temperature for downhole components or alternating low and high temperature cycles for wellhead equipment. In this example for a wellhead application, a 72-hour (3-day) test cycle is used.

Figure A.5 shows how the 3-day test cycle is conducted. The objective of the test sequence is to establish the rate of chemical degradation as a function of temperature.
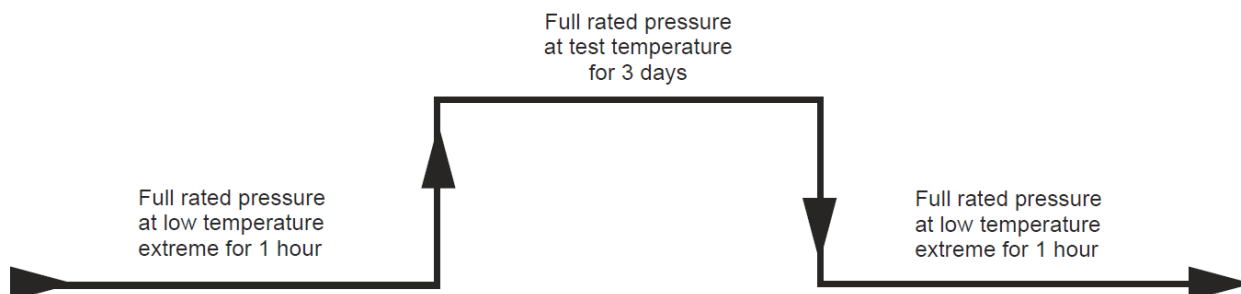
Figure A.5—Typical 3-Day Test Cycle

The selection of a starting temperature for a life estimation experiment is somewhat arbitrary. A good starting point is an elevated temperature that should consistently give a failure in one or two test cycles. Some experimentation may be required to establish this maximum test temperature. Once the maximin test temperature is determined, lower test temperatures can be selected, usually in 10°C (18°F) increments. For example, if 232°C (450°F) is determined to be the maximum test temperature where only one test cycle can be consistently completed, the next lower test temperature would be 222°C (432°F). If the experiment follows the Arrhenius relation, two or more test cycles should be completed at 222°C (432°F). If two or more test cycles are not achieved at 222°C (432°F), the test temperature would be lowered by another 10°C (18°F) until at least two or more test cycles are achieved consistently. At each subsequent test temperature, sufficient test runs should be done to obtain test data that are statistically significant. A minimum of three different test temperatures should be used, but preferably, five temperatures or more should be done with some replicates. To avoid the diffusion-controlled aging, the elevated test temperatures for aging and life evaluation tests are also recommended in Table A.1. These temperatures could also be used as starting temperatures to establish the maximum test temperature.

Use of the Arrhenius principle in estimating the life of an elastomeric component requires that the chemical process that controls degradation remains constant. If test temperatures are excessive, other reactions may occur (such as diffusion-controlled aging) and data obtained may lead to erroneous life estimation. Once sufficient data have been accumulated, a least squares regression analysis is done and the data plotted to look for any non-linearity in the life estimation curve. If a single degradation reaction occurred during testing, the best-fit line should approximate a straight line. For a valid life estimation, the least squares regression analysis on the test data should indicate a coefficient of determination greater than 0.80 for studies that include a single measurement at a given predictor. For studies with repeated measurements at a given predictor, coefficients of determination should not be expected to reach values that high. Once satisfactory test data have been generated, the life estimation line (best fit to data) may be extended to the specified maximum service temperature. An estimate of service life can be read from the vertical scale of the life estimation plot (e.g. Figure A1.2) or it can be calculated from the appropriate mathematical formula.

Proper simulation of the chemical reactions that occur between candidate elastomers and the severe service environment requires a sufficient volume of chemicals to prevent depletion of the reactants. A three (3) day test cycle is used so that the candidate elastomeric material is regularly exposed to fresh chemicals. In service, the elastomer may be constantly exposed to a steady stream of fresh chemicals and/or produced fluids/gases or it may only be exposed to stagnant conditions. At the end of the 3-day test cycle, the test vessel is typically depressurized and purged of the liquid and gas phases. Other decompression cycles can be used with agreement of all concerned parties. Fresh liquid and gas are added and the candidate sealing elements are pressure tested at ambient temperature. For specific applications, other temperatures below ambient can be used. If the seals hold pressure for one hour without leakage, the test vessel is heated up to the test temperature for another 3-day test cycle. This is repeated until failure is observed.

Some examples of typical failure modes observed for elastomers in life estimation testing are excessive compression set, hardening, cracking and chemical softening.

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The life estimation procedure outlined above provides a cost effective technique to evaluate the long term effects of a chemical environment on a elastomer component. Use of the Arrhenius principle of chemical reaction rates allows an accelerated estimation of the thermochemical degradation of the elastomer in a severe service environment. This evaluation technique for studying the long-term effects of an environment on an elastomer compound is an alternative to full scale, long term testing in the field.

A8. Typical Sequence for Aging and Life Estimation Test (3-Day Temperature Cycle Test)

A 3-day temperature cycle test is generally used for wellhead equipment.

The typical sequence is described as follows,

a) Install elastomer test O-ring in the test fixture as illustrated in figure A2.

b) Add liquid(s) to the test fixture through the pressurized port.

c) Commence monitoring the pressure and temperature with a sampling rate of once per minute except for exposure durations where rapid changes of parameters are expected (like heating or cooling periods or pressure increase or decrease).

d) Purge the test fixture to 5 bar 5 times with nitrogen (inert) gas having oxygen content < 5 ppm O_2 to remove most of the oxygen.

e) Raise temperature to the exposure set point and add the test gas mixture to a test pressure; if individual gases are used, fill to correct partial pressures in the order of lowest liquefaction pressure.

f) Hold the temperature and pressure for 3 days. Monitor test ports for leakage. The acceptance criterions of leakage shall be according to section 5.2.3.3. if leakage occur from any of the test ports, record the time and isolated leaking test port, and continue the test.

g) Cool the test fixture to room temperature (or below room temperatures based on requirements) and reduce remaining pressure safely at a maximum rate of 0.1 MPa/min, neutralizing H_2S, if used, with a scrubber.

h) Purge the test fixture with fresh liquid and gas and repressure test fixture to test pressure and monitor test ports for leakage. Maintain pressure for one hour.

i) If no leakage is noted in step h), repeat steps e) to step h) until all test O-rings leak. Record the time to leakage.

j) Repeat above steps for each test temperature until the test O-ring seals fail or test is terminated.

k) Flush test fixture with nitrogen to remove remaining H_2S, if used, via a scrubber.

l) Disassemble the test fixture, retrieve test O-rings.

m) Inspect the O-rings and carry out any necessary post-test if needed.

A9. Typical Sequence for Aging and Life Estimation Test (Steady State Temperature Test)

Steady state temperature test is generally used for downhole components.

Typical sequence is described as follows,

a) install elastomer test O-ring in the test fixture as illustrated in figure A2;

b) Add liquid(s) to the test fixture through the pressurized port.

c) Commence monitoring the pressure and temperature with a sampling rate of once per minute except for exposure durations where rapid changes of parameters are expected (like heating or cooling periods or pressure increase or decrease);

d) Purge the test fixture to 5 bar 5 times with nitrogen (inert) gas having oxygen content < 5 ppm O_2 to remove most of the oxygen.

e) Raise the temperature to exposure set point and add test gas mixture to the test pressure; if individual gases are used, fill to correct partial pressures in the order of lowest liquefaction pressure.

f) Hold the temperature and pressure for 3 days. Monitor test ports for leakage. The acceptance criterions of leakage shall be according to section 5.2.3.3. if leakage occur from any of the test ports, record the time and isolated leaking test port, and continue the test.

g) Cool the test fixture to room temperature and reduce remaining pressure safely at a maximum rate of 0.1 MPa/min, neutralizing H_2S, if used, with a scrubber.

h) Purge the test fixture with fresh liquid and gas, raise the temperature to exposure set point and repressure test fixture to test pressure and monitor test ports for leakage. Maintain pressure for another 3 days.

i) If no leakage is noted in step h), repeat steps g) to step h) until all test O-rings leak. Record the time to leakage.

j) Repeat above steps for each test temperature until the test O-ring seals fail or test is terminated.

k) flush test fixture with nitrogen to remove remaining H_2S, if used, via a scrubber.

l) disassemble the test fixture, retrieve test O-rings.

m) Inspect the O-rings and carry out any necessary post-test if needed.

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