Article

Reliability prediction of acrylonitrile O-Ring for nuclear power applications based on Shore hardness measurements

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Abstract: The degradation of polymeric components is of considerable interest to the nuclear industry and its regulatory bodies. The objective of this work is the development of a methodology to determine the useful life -based on the storage temperature- of acrylonitrile O-Rings used as mechanical sealing elements to prevent leakages in nuclear equipment. To this aim, a reliability-based approach that allows to predict the use suitability at different supposed storage scenarios (that involve different storage time and temperature) considering the further required in-service performance is presented. Thus, experimental measurements of Shore A hardness have been correlated with storage variables (temperature and storage time). The storage (and its associated hardening) has been proven to have a direct effect on in-service durability, reducing this up to 60.40%. Based on the model, the in-service performance has been predicted; after the three first years of operation the increase of probability of failure (POF) is practically insignificant. Nevertheless, from this point on, and specially, from 5 years of operation, the POF increases from 10% to 20% at approximately 6 years (for new and stored). From the study, it has been verified that for any of the analysis scenarios, the limit stablished criterion is above of the storage time premise considered in the usual nuclear industry practices. The novelty of this work is that from a non-destructive test, like a Shore A hardness measurement, the useful life and reliability of O-Rings can be estimated and being, accordingly, a decision tool that allows to improve the management of maintenance of safety-related equipment. Finally, it has been proven that the storage strategies of our nuclear power plants are successful, perfectly meeting the expectations of suitability and functionality of the components when they are installed after storage.

Keywords: reliability; prognostics; design-for-reliability; aging; elastomers; durability; harsh environments;

1. Introduction

The mechanical characterization of materials provides the basis for the fundamental understanding of the behavior of components that can experience degradation in operation and/or even during storage. A representative example is the thermal aging mechanism that severely affects materials that are ultimately intended to operate in the harsh service environment of a nuclear reactor. Materials based on organic polymers have many applications (sealings, insulations, etc) in nuclear power plants (NPP).

Nowadays, polymer materials hold an important role in the industry, thanks to their unique properties, such as a wide range of operating temperatures, high thermal/electrical insulation, corrosion-and light-resistance and sufficient mechanical properties (high strength-to-weight ratio, stiffness, toughness and ductility) [1-2].

In addition, in some applications, the functionality of a polymeric component can be crucial for the safe operation of the plant [3]. The degradation of such components is therefore of considerable interest to the nuclear industry and its regulatory bodies, generating a large number of studies worldwide [4]. Elastomers are widely used in industry and are particularly often applied in sealing due to their ability to undergo high elastic deformation [5]. Synthetic and natural polymers normally degrade during their service-life, due to the exposure to different environmental conditions [6]. The degradation of polymeric materials is a frequent phenomenon that is accelerated, in many cases, by arduous operating conditions. Being able to predict the lifetime of elastomers is fundamental for many industrial applications [7].

Prognostics and Health Monitoring (PHM) analysis requires several stages, including data collection, data processing, condition monitoring, diagnostics, prognostics, and decision support [8]. The information generated by a PHM system can be divided into diagnostics and prognostics: diagnostics include anomaly detection, fault isolation, fault classification and its uncertainty [9]; while prognostics include the estimation of the remaining useful life (RUL) and the prediction of behavior at design stage. This procedure allows to be sure that the component is in a good condition before installation and operation [10]. One focus of ongoing research is the identification of new indicators of polymer aging, which may be measured nondestructively, and used to predict of further behavior [11]. One of this is the non-destructive procedure to determine the Shore hardness. The mechanical properties are critically important for demanding applications; those include materials hardness since this property is strongly dependent on the operation (or even storage) parameters, the composition of the material and the manufacturing process [12].

One of most usual parts with relevant safety-related function in nuclear equipment is the acrylonitrile (NBR) O-Rings that are used as mechanical sealing elements, since their safety function is being capable of preventing any leakage (whether internal or external) throughout the useful life of the equipment [13]. NBR exhibits a relatively low density, moderate tensile strength, and high oil resistance [14-16]. O-Rings are really the most common type of sealing used in industry due to their robustness, versatility and low cost. The end users typically receive only the end part which needs to be tested [17]. In nuclear plants, Shore A hardness are usually performed when O-Rings are received and/or when they are installed.

Reliability evaluation plays an important role in the design and development of any engineering system [18]; thus, some studies [19,20] have correlated main polymers properties with final performance and durability. Lifetime prediction of elastomer components is a very challenging task due to different factors. Determining a suitable and reliable end-of-lifetime criterion for O-Ring seals is an important issue for long-term seal applications [21]. Ageing is a term used in many branches of polymer science and engineering when the properties of the polymer change over a period of time [22,23].

Polymers, and especially elastomers, play a key role as part of the many mechanical, electrical and electronic components found in nuclear power generation plants [24]. Condition monitoring and an understanding of the degradation processes due to short-term thermal stress have been of interest to the nuclear industry because of qualification requirements [25]. Elastomers, especially rubbers - such as acrylonitrile butadiene, NBR - experience degradation that is favored by contact with oxygen [26]. This type of reaction -which triggers the irreversible damage of the component- is also favored by an increase in the operating temperature. Therefore, it is of interest to analyze how their intrinsic properties influence their thermal aging. When elastomers are exposed to environmental conditions, their functionality in operation might be limited due to degradation [27]. The accurate prediction of the mechanical properties of polymers is important for preventing industrial accidents while operating a machine. In general reactions, the linear Arrhenius equation is used to predict the aging characteristics [28].

The objective of this work is the development of a methodology to determine the useful life -based on the storage temperature- of NBR O-rings using a reliability-based approach that allows to obtain the health condition at different supposed storage scenarios, considering the required in-service performance. For the study, NBR has been selected as a gasket material, since a previous work [20] has shown that acrylonitrile is the best option to withstand moderate levels of radiation thresholds extracted from databases [29,30] as well as its recyclability, providing a sustainable life cycle. The evaluated parameter has been the Shore A hardness in accordance with ISO 868 [31] during a period of five years. Measurements of Shore A hardness consisted in vertical immersion of the indenter into the composite surface [32]. The thermal hardening is quantified based on an adaptation of Arrhenius model-based correlation between hardness and temperature and storage time. The study incorporates a comparison between the results obtained for recent manufactured and existing O-Rings in the warehouse, considering several statistical scenarios.

Using an adaptation of the Arrhenius model, predictions based on hardness results can be made over the 5-year period, including supplies stored for at least 18 years. Once the calculation model has been proposed, different storage limit conditions are obtained after validating the methodology comparing the predicted allowable storage periods and conditions with the real ones.

2. Methodology

The methodology (Fig.1) is based on the analysis (Stage 1) of experimental data of Shore A hardness obtained during qualification processes (between 2014 and 2018) of recently manufactured (when they were measured) and previously stored NBR O-Rings. Thus, by adapting the Arrhenius model for thermal aging -along with the activation energies indicated in the standard EPRI TR 1009748 [33]- predictions (Stage 2) based on three scenarios are considered: very conservative, moderately conservative and minimally conservative. Finally, a validation methodology is performed along with the estimation of in-service durability and the determination of critical storage conditions (Stage 3).

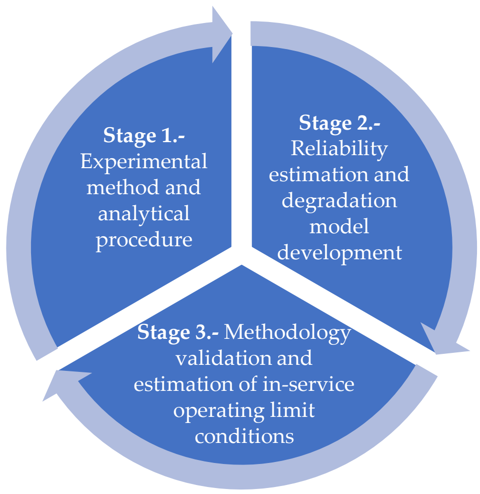


Figure 1. Methodology of analysis.

2.1. Stage 1.- Experimental method and statistical processing of data

2.1.1 Experimental procedure

The experimental procedure consisted of a dimensional checking (a) and polymer composition characterization (b) before performing a Shore A hardness measurement (c), performed all testing at 22±1°C and 55±5% of humidity, using a thermo-hygrometer Testo 608-H1 (Testo SE & Co. KGaA, Lenzkirch, Germany). Table 1 shows the expected Shore A hardness of NBR O-Rings and the hardness acceptance criterion along with the homogenous dimensions of O-Rings.

Table 1. Dimensional characteristics of O-Rings.

Supply description	Composition	Expected Shore A hardness	Typical hardness acceptance criteria	External diameter, *Φext* (mm)	Internal diameter, *Φint* (mm)	Thickness (*t*) (mm)
O- Rings (type V)	NBR	60	60±5	110	100	8

a) Dimensional checking

For reproducibility and comparison purposes, O-Rings with identical nominal dimensions (reported in Table 1) were analyzed in the present study. The dimensional checking was performed using as an acceptance criterion of just ±1% for external and internal diameters, and therefore, for thickness. The thickness seems to be a critical aspect that could influence substantially the measurement as many studies have demonstrated [34]. In addition, the standardized procedure according to ASTM D2240 [35] and some authors [36] recommend that thickness should be at least equal to 6 mm. The measurements were performed on more than 140 O-Rings from 14 different supplies and on an additional batch consisting of previously stored O-Rings. The dimensional measurements were carried out using an equipment ScanMaker 9800XL PLUS TMA1600 III (Microtek, Hsinchu, Taiwan) as it is shown in Figure 2.

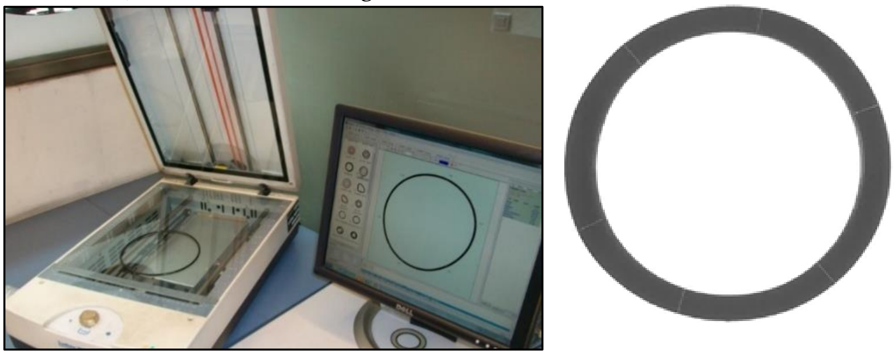


Figure 2. Dimensional checking procedure and example of measurement

b) Polymer composition characterization

Before performing the hardness test, each O-Ring was also analyzed to assess the composition of components. In this case, the expected (and the acceptance criterion) was acrylonitrile butadiene rubber (NBR). The technique used was the Fourier Transform Infrared Spectroscopy (FTIR) that is based on the concept of absorption of infrared radiation by sample. The resulting signal at the detector is a spectrum that characterizes the polymer analyzed and, therefore, it allows obtaining composition data [37]; being this technique a method to determine if the O-Rings composition is the expected one and, therefore, the component is ready to continue the characterization process (hardness test, in this case study). The equipment used has been a Nicolet 5700 (Thermo Electron Corporation, Waltham, MA, USA). Thus, spectra of the NBR components were recorded over a wavenumber range of 4000–500 cm^{-1}, with 32 scanning times at a resolution of 4 cm^{-1}. Figure 3 exhibits the FTIR spectra along with the indicated characteristic peaks of NBR as Table 2 provides.

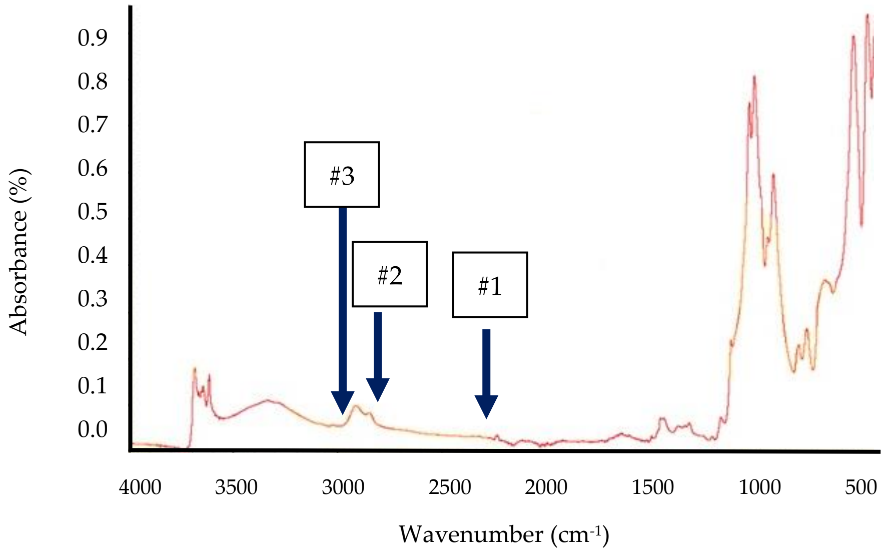


Figure 3. FTIR spectra.

Table 2. Characteristic bonds of NBR as a function of wave number in the Fourier transform infrared spectroscopy test [38].

Polymer	Number of Peak in Figure 3	Wavenumber (cm^{-1})	Indication/Type of Bond identified
	#1	2236	stretching for –C≡N
NBR	#2	2851	–C–H stretch of –CH3
	#3	2922	–C–H stretch of –CH2

Once the composition was checked, the Shore A hardness according to ISO 868 [31] was performed.

c) Hardness Test

The shore hardness is measured by the depth of indentation caused by a rigid ball under a spring load or dead load, the indentation being converted to hardness degrees on a scale ranging from 0 to 100. The reading from a dead load hardness meter is called International Rubber Hardness Degrees (IRHD). The spring-loaded meter gives Shore A values [39]. The energy absorbed by the sample material on impact is then related to the product of a "dynamic yield pressure" and the volume of the indent [40]. As indicated by Brown [41], the test results are affected by the operator, the time of application and deviations from a perfectly elastic despite correct calibration and measurements according to the standard testing procedure. Spetz [42] examined the repeatability of hardness measurements on rubber materials and concluded that the operator was the main source of variability [43]. Thus, during the indentation experiments, hardness changes not only with the hold time but also with loading and unloading rate [44].

Figure 4 provides a detail of the O-Rings (a) along with the position for the indentation (b) and the Testing Measurement Locations (TML). All O-Rings measured exhibit the same geometrical (nominal) characteristics (external and internal diameter and thickness).

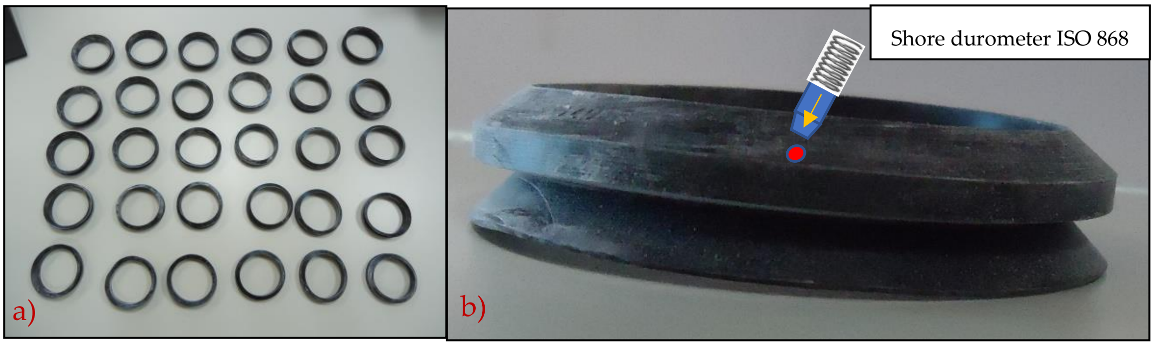


Figure 4. a) Detailed of a batch of tested O-Rings; b) Side view of O-Ring and position of the shore hardness indenter.

Therefore, all measurements were performed by the same operator, using a calibrated equipment and not repeating the hardness measurement at the same place because it provides permanent local changes in the material [45,46]. Thus, Figure 5 shows the Testing Measurement Locations (TML) used in each characterized O-Ring. The hardness testing has been performed by using a durometer Zwick Roel Digi-Test Shore A/B/O (Zwick Roel, Ulm, Germany).

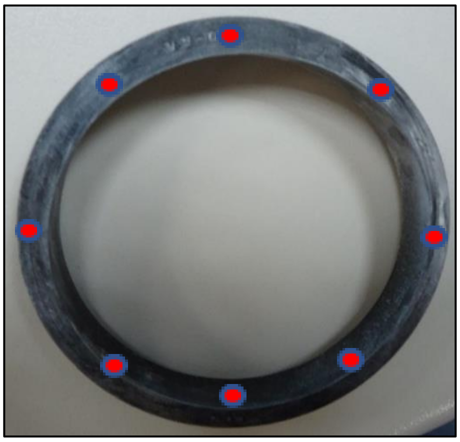


Figure 5. Front view of O-Ring and position of indentations (TML).

Once collected all hardness data, an analytical procedure is carried out.

2.1.2. Analytical procedure

Hardness dispersion of rubber samples can be statistically well described by a normal distribution model [47]. Thus, Shore A hardness is fitted by a random normal distribution. Certainly, the Gaussian or normal distribution is the most established model to characterize quantitative variation of original data. Accordingly, data are summarized using typically the arithmetic mean and the standard deviation, by $\bar{\mu} \pm \sigma$ [48]. Additionally, this type of representation allows to compare easily the mean and deviation among different supplies (from 2014 to 2018). The expression [49] for the one-dimensional normal density is often written according to Equation (1).

$$f(HSA) = \frac{1}{\sqrt{2\pi}\sigma} \cdot e^{-\frac{(HSA-\mu)^2}{2\sigma^2}} \quad (1)$$

where:

HSA: Shore A hardness
μ: mean
σ: standard deviation

Figure 6 provides the normal distribution (density function versus measured hardness) for each supply.

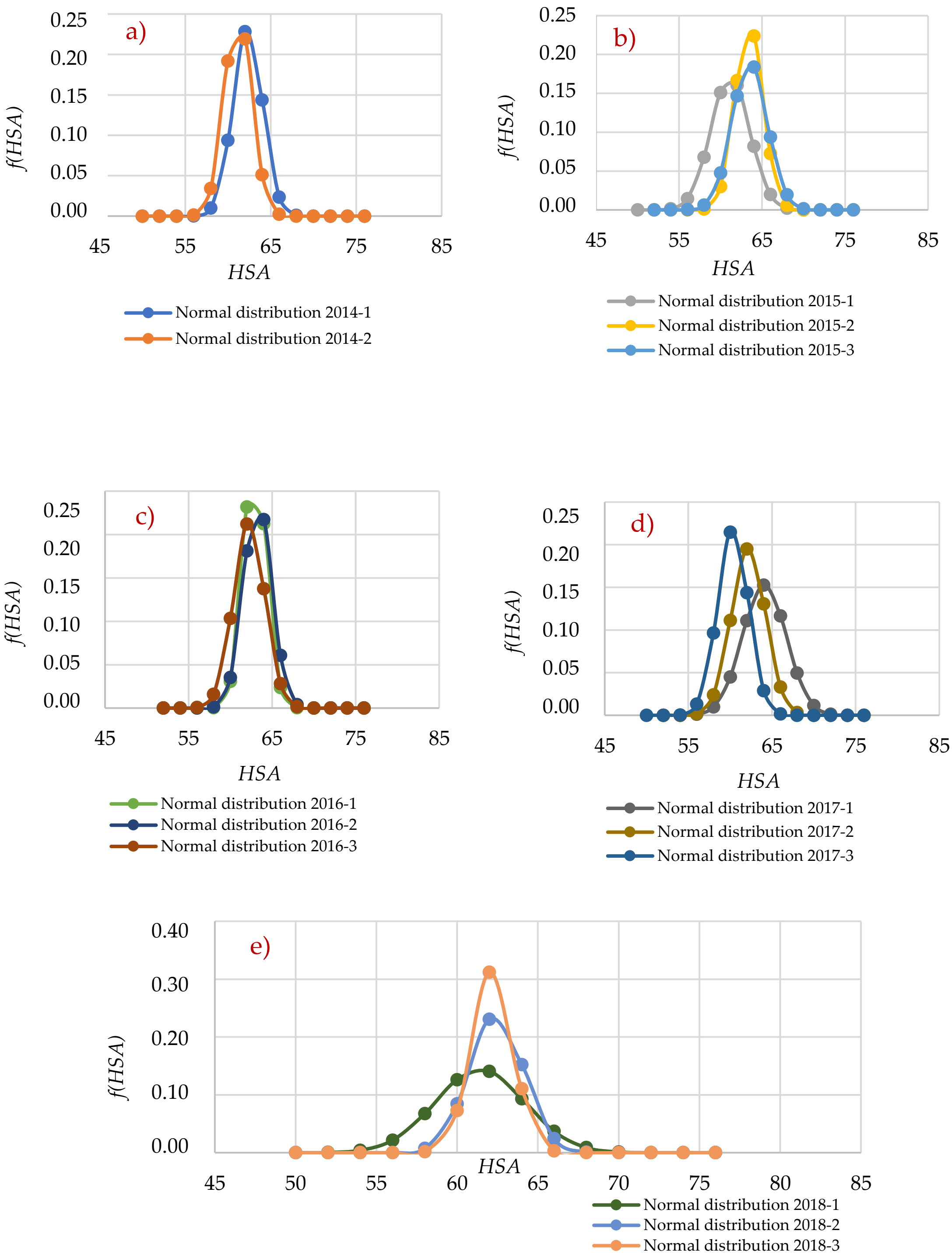


Figure 6. Normal distribution of hardness Shore A for recent manufactured O-Rings. a) 2014 supplies, b) 2015 supplies, c) 2016 supplies, d) 2017 supplies and e) 2018 supplies.

Table 3 shows mean values (μ) along with the standard deviation (σ) between measurements in each group of supplies (batches) and percentage variation in hardness of these measurements of the O-Rings (as supplied) compared to stored O-Rings.

Table 3. Variation of every new supply hardness compared with stored ones and group standard deviation in measurements.

References (year and correlative number)	Shore A - Mean hardness	Percentage variation in hardness compared to stored O-Rings	Standard deviation
2014-1	62.32	-11.98	1.72
2014-2	61.17	-14.09	1.59
2015-1	61.19	-14.08	2.33
2015-2	61.42	-13.62	1.68
2015-3	61.50	-13.47	2.11
2016-1	60.92	-14.56	1.38
2016-2	61.25	-13.93	1.66
2016-3	60.25	-15.82	1.86
2017-1	62.08	-12.40	2.61
2017-2	60-17	-15.98	2.04
2017-3	60.33	-15.66	1.83
2018-1	61.42	-13.62	2.78
2018-2	62.42	-11.80	1.68
2018-3	62.17	-12.25	1.27
Stored batches	69.78	-	2.62

The hardening experienced by the O-Rings has been between 11.80 and 15.98% with a different in means (recent manufactured versus stored ones) of 13.81% (according to Table 4). Consequently, Table 4 shows the mean value of more than 140 Shore A hardness measurements made during the period between 2014 and 2018. Likewise, the study has incorporated 12 hardness tests on stored O-Rings without a defined date [50]. Nevertheless, it is known that they were entered into inventory in 2000 and that they could be dated as much from 1994 (calculated on the test date in 2018).

Table 4. Experimental data analyzed in this work[1]

Supply description	Shore A hardness (mean value)
New supplies (acquired between 2014 and 2018)	61.33
Supplies stored at least 18 years	69.78
Evaluation parameter	**Hardening (difference between means) (%)**
New to storage supplies comparison	13.81

Note*[1]: Storage conditions: temperature= 20±5 °C; relative humidity= 50-60% [42].

A recent study stated that the mean hardening of some NBR samples after 18 years was of 11.66% [51]; therefore, there is coherence in the observed results, moreover, considering that the analyzed storage time is between 18 and 24 years. Consequently, this could be considered as a validated starting point to perform the further methodological analysis. Using, newly, a normal representation, Figure 7 provides the mean hardening for recent manufactured and stored O-Rings.

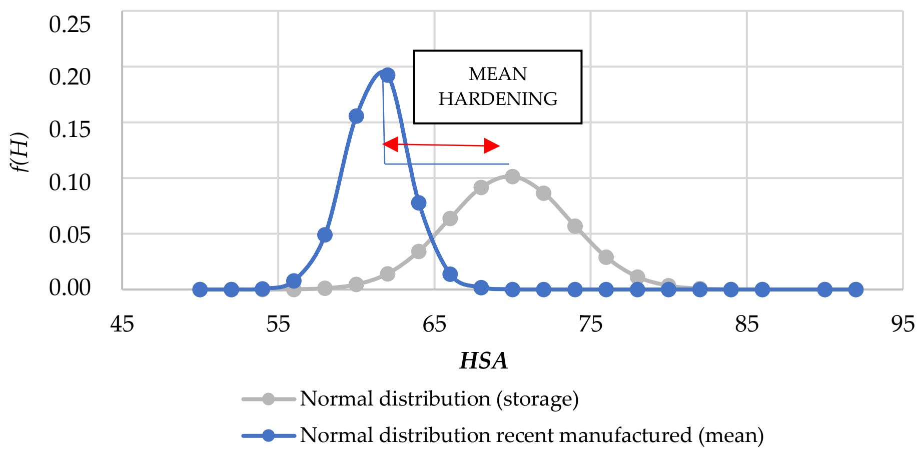
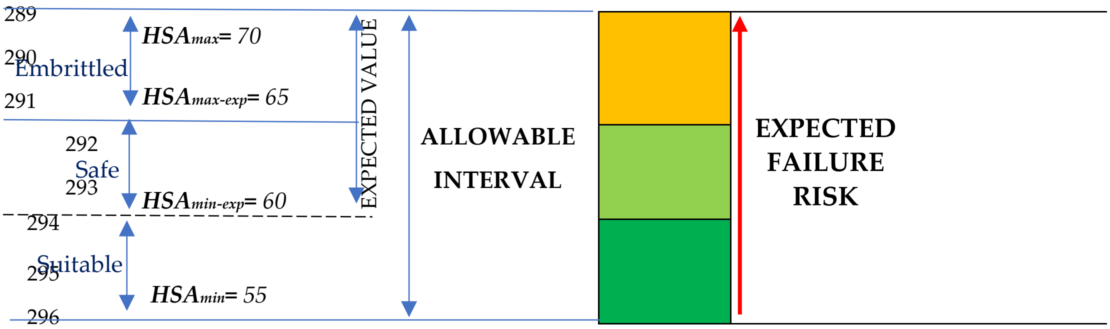


Figure 7. Hardening: difference between recent manufactured and storage normal distributions.

Figure 7 shows as mean value for recent manufactured (HSA_{mean}=61.33) O-Rings is closed to expected value 60 Shore A; whereas mean value for stored (HSA_{mean}=69.78) O-Rings is very close to the maximum allowable hardness (HSA_{max}= 70 Shore A). Experimental findings have demonstrated that O-Rings with a Shore A hardness near to 70 are prone to failure [52]; subsequently, a diagram showing three differentiated ranges are defined (Figure 8): suitable, safe and embrittled zones according to O-Rings hardness. Thus, the risk associated to O-Rings failure increases when Shore A hardness does.



Note: suitable- appropriate vale; safe-already value exhiniting safety condition; embrittled- starting of the embrittlement.

Figure 8. Hardness intervals and their correspondence to the risk of failure (loss of integrity due to aging).

There are a lot of characteristics that have to be necessarily considered when a polymer candidate is evaluated for an application at harsh environment in a nuclear plant. Some of these features are related mainly to thermal and radiation tolerance and its influence on mechanical properties [53]. Thus, defined normal conditions (Figure 9) allow to consider different scenarios depending on the parameters variability inside the constructed range.

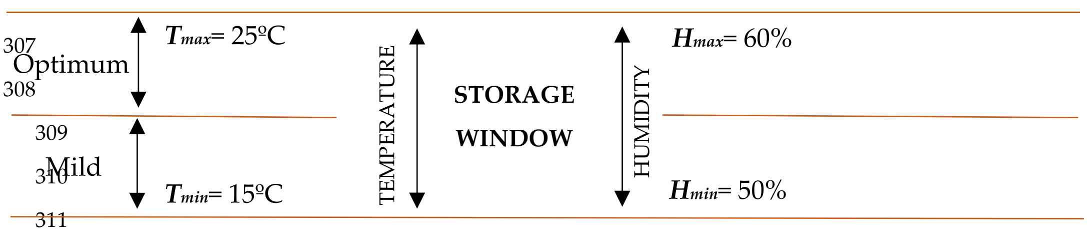


Figure 9. Storage window for temperature and humidity.

After defining the storage parameters window and the ranges of hardness associated to degradation and risk of failure (does not fulfill the safety function; i.e. preventing leakages), an Arrhenius-based model is raised [50], according to Equation (2), to correlate operation (or storage) time with operation (or storage) temperature:

$$t_s = t_a \cdot exp\left[\frac{E_a}{k}\left(\left(\frac{1}{T_a}\right) - \left(\frac{1}{T_s}\right)\right)\right] \quad (2)$$

where:

t_s: Estimated lifetime in service (hours)
t_a: Time considering acceleration in aging / degradation (hours)
T_s: Normal operating temperature (K)
T_a: Hardening temperature (K)
E_a: Activation energy (eV)
K: Boltzmann constant= $0.8617 \cdot 10^4$ eV/K

The activation energy used in the calculation was provided by EPRI TR 1009748 [26], that for NBR is equal to 0.88 eV.

As it was mentioned before, 14 new supplies were compared with a large stored batch. There is, therefore, an uncertainty related to the manufacturing date of stored O-Rings. Considering this uncertainty about the date of manufacture of the previously stored O-rings, three scenarios have been defined for the analysis: very conservative, moderately conservative and minimally conservative. Subsequently, for the conservative interval, it has been considered that the age of O-Rings was 24 years, for the middle one (moderately conservative) was 22.5 years and for the least conservative one, 18 years old (calculated on the test date in 2018).

3. Results and discussion

Once performed the testing and realized the first statistical analysis (Stage 1), a reliability estimation was carried out in order to develop a degradation model with respect to storage conditions such as, temperature or time (Stage 2).

3.1. Stage 2.- Reliability estimation and degradation model development

Considering a well stablished correlation between hardening and temperature, Arrhenius model can be newly arranged [52], according to Equation (3), to obtain in-service durability (t_s):

$$t_s = t_a \cdot exp\left[\frac{E_a}{k}\left(\left(\frac{1}{HSA_{augm}}\right) - \left(\frac{1}{HSA_{exp}}\right)\right)\right] \quad (3)$$

where: HSA_{augm}: it is the Shore A hardness augmented due to thermal aging with respect to HSA_{exp} (expected HSA).

Thus, with the measured hardness for recent manufactured and stored O-Rings, in-service durability was calculated (Figure 10).

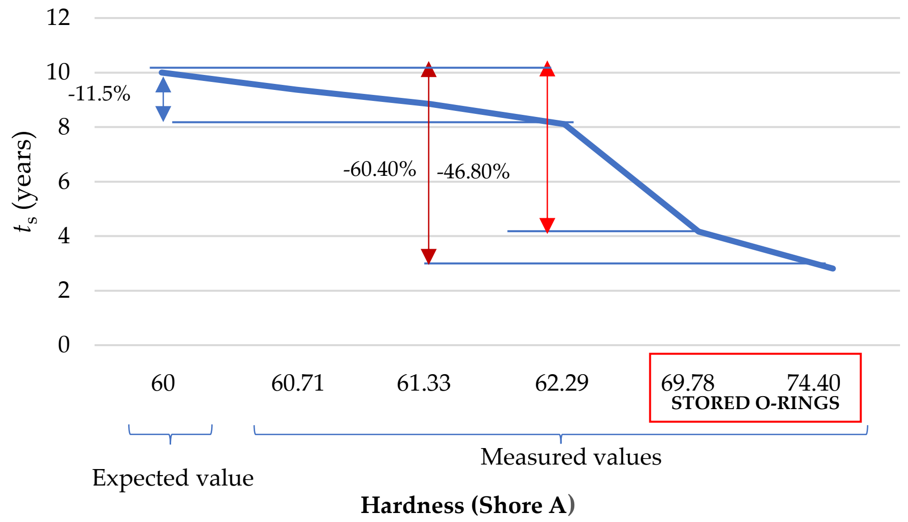


Figure 10. In-service durability as a function of the hardness.

The storage conditions (and their associated hardening) have a direct effect on in-service durability, reducing it up to 60.40%. Thus, Time to Integrity Loss (*TTIL*), considered as the time in operation where a Shore A hardness equals to 65 (beginning of the embrittlement; according to Figure 9), can be calculated by using the Equation (4).

$$TTIL = lim_{HSA_{augm} \to 65} \quad t_a \cdot exp\left[\frac{E_a}{k}\left(\left(\frac{1}{HSA_{augm}}\right) - \left(\frac{1}{HSA_{exp}}\right)\right)\right] \tag{4}$$

It can be concluded that the materials response could be considered similar to a previous operation time of 6 years (52560 hours). If we considered the extreme case in which 70 shore A is reached, TTIL would be equal to 4 years (35040 hours). On the other hand, if a new reformulation of Arrhenius model is performed, Equation (5) provides the hardening as a function of the durability of recently manufactured O-Rings (t_s) and stored ones (t_a) and the measured hardness once stored (HSA).

$$\boldsymbol{Hardening}\ (\%) = \frac{\boldsymbol{100 \cdot k \cdot HSA}}{\boldsymbol{E_a}} \cdot \boldsymbol{ln}\frac{\boldsymbol{t_S}}{\boldsymbol{t_a}} \tag{5}$$

Subsequently, Figure 11 exhibits the maximum recommendable in-service time as a function of hardening (from hardness values). This representation has been performed according to Equation (5).

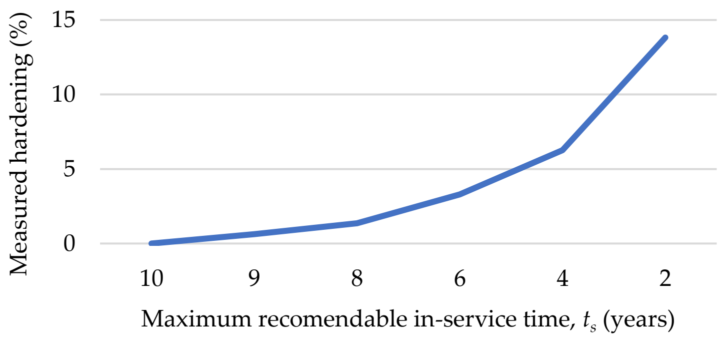


Figure 11. Maximum recommendable in-service time (t_s) as a function of hardening (from hardness values).

As Figure 11 indicates, the measured hardening can be a useful parameter to estimate the maximum recommendable in-service time. Considering that no measurable hardening (i.e. a value of 60 HSA) implies the maximum in-service time (10 years, that it is the usual qualified lifetime for O-Rings in the nuclear industry), a hardening of 5% generates a reduction of the recommended in-service time of 50% (i.e. a recommended time of use of 5 years), while a hardening of 10% implies a usability for only 3 years.

Using an exponential distribution for the degradation (according to the Arrhenius model), the reliability function *R(t)* can be calculated [24] according to Equation (6).

$$R(t) = e^{-\lambda t} \quad (6)$$

where λ is the failure rate, calculated as $\lambda = \frac{1}{TTIL}$ and t, the considered time.

The reliability of new (recent manufactured) and stored O-Rings, represented as a function of the hardness, is shown in Figure 12.

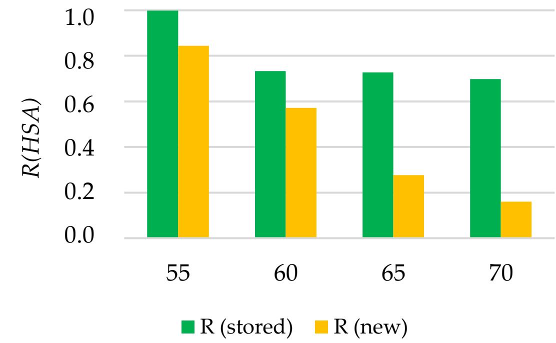


Figure 12. Reliability as a function of measured hardness for new (recent manufactured when measured) and stored O-Rings.

Figure 13 provides the relative hardening of stored O-Rings with respect to each supply of recent manufactured O-Rings (shown in x axis). A loss of reliability for the upper limit of *HSA* established in 69.78 (mean value of hardness for stored O-Rings) is simultaneously represented to be compared with the relative hardening for each recently manufactured supply.

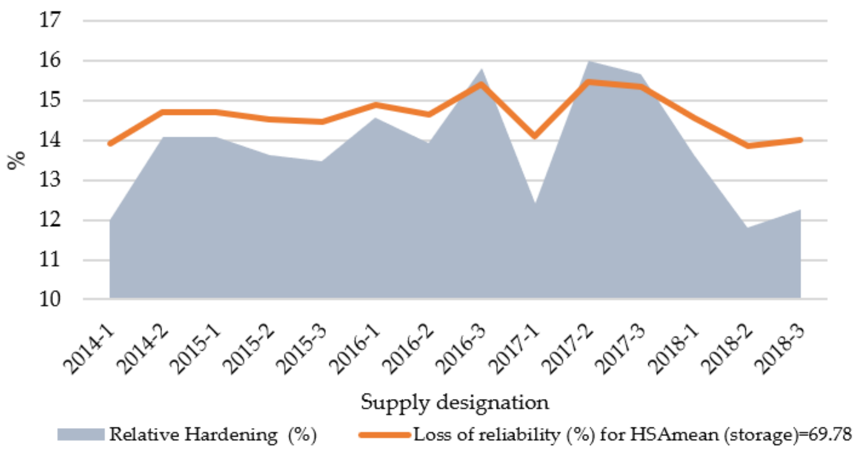


Figure 13. Relative hardening and loss of reliability (stored versus recent manufactured material).

As Figure 13 provides, the $R(t)$ of stored manufactured O-Rings is greater than the $R(t)$ of the recent ones, independently of the hardness range. Nevertheless, the loss of reliability for recent manufactured O-Rings is bigger when the hardening is greater. This is very reasonable because a hardening found in a recent manufactured O-Rings implies probably a defective mechanical integrity or a degraded composition, while the same value for a stored O-Ring just indicates that a hardening process took place. On the other hand, probability of failure distribution $POF\ (t)$ can be calculated [24] according to Equation (7).

$$POF\ (t) = 1 - e^{-\lambda t} = 1 - R(t) \quad (7)$$

Thus, *R(t)* and *POF (t)* related to the performance fulfillment are represented (Figure 14) as a function of the measured hardness.

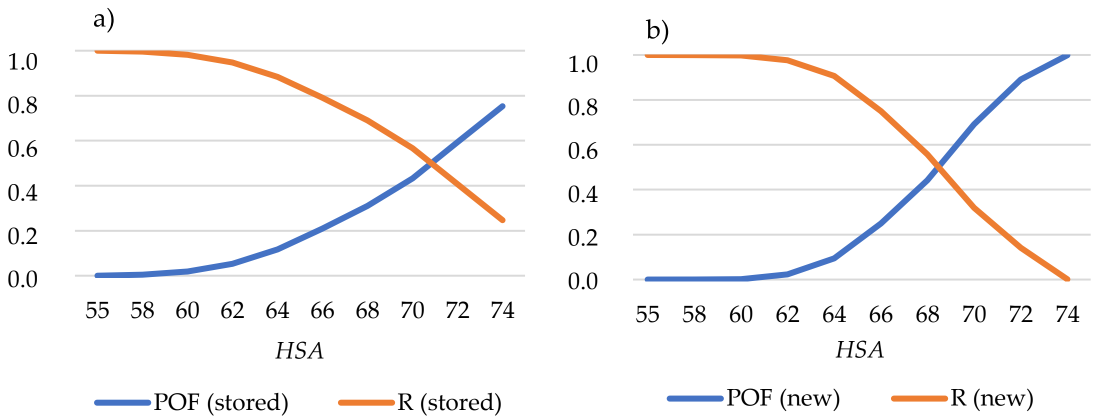


Figure 14. Reliability and Probability of Failure as a function of the measured hardness for the a) stored and b) for the recent manufactured O-Rings.

As a degradation and, therefore, a loss of integrity is expected when hardening takes places, in the case of stored O-Rings (Figure 14a), a loss of more than the 20% of reliability is presented from a value equal to 65 Shore A hardness, being more than 50% from 70 shore A hardness. On the other hand, in the case of recent manufactured O-Rings a hardness equal to 60±5 is expected (as typically required by manufacturer; see Figure 9) showing a good reliability. Thus, a loss of 20% of reliability takes places when hardness is increasing up to 65 shore A hardness, and from 68 HSA the reliability is less than 50% (Figure 14b). In addition, POF as a function of the operation time (years), for both recent manufactured and stored O-Rings (with a hardness close to 65 HSA) is shown in Figure 15.

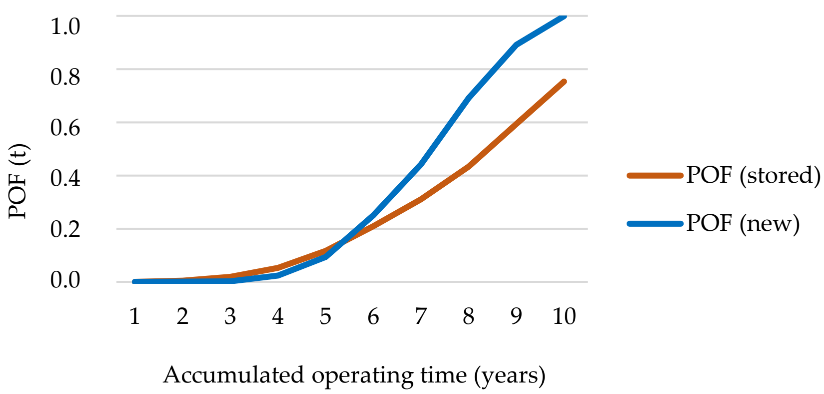


Figure 15. Probability of failure according to the accumulated operating time.

POF (t) represented in Figure 15 indicates how the accumulated in-service time affects the risk of failure (losing their reliability). During the three first years of operation the increase of POF is practically insignificant. Nevertheless, from this point, and specially, from 5 years of operation, the POF increases from 10% to 20% at approximately 6 years (for new and stored). From 6 years, the behavior of curves (for new and stored) are more different: in the case of stored ones, there is a linear progression up to reaching a POF equal to 0.78 at 10 years; while, in the case of the new ones, the POF is practically 100% when they reach an accumulated in-service time equivalent to 10 years. Seen from another point of view, the annualized loss of reliability can be quantified as a function of the hardening (or the measured value of hardness). As the last compared supply was dated in 2018, later three comparative scenarios will be stablished (very conservative: 24 years, medium: 22.5 years and minimally conservative: 18). Thus, Figure 16 provides the annualized loss of reliability considering the three scenarios of analysis; since the loss of reliability is considered –in this case– due to the storage (and, therefore, the comparison needs the three scenarios to be more precise).

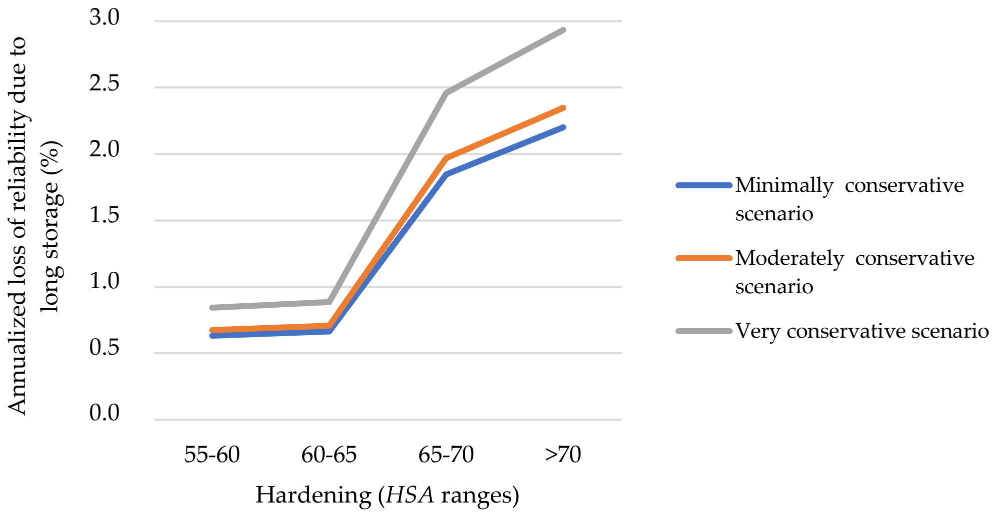


Figure 16. Annualized loss of reliability due to a long storage.

In the range of 55-65 HSA, the loss of reliability due to storage is small, with hardly any difference between 55-60 and 60-65 (zone of acceptable values). The loss of reliability accelerates in the range 65-70 (the slope is greater), being higher from 70 shore A. Equation

(8) provides the Time to Damage (*TTD*) that is calculated from *TTIL* obtained from Equation (4).

$$\boldsymbol{TTD} = -\frac{\boldsymbol{ln(R)}}{\lambda} \quad \forall\ 0<R\leq 0.99 \tag{8}$$

On the other hand, using a defined Safety Factor (*SF*), a recommended replacement interval (RPI) can be calculated using the Equation (9).

$$\boldsymbol{RPI} = \boldsymbol{SF} \cdot \boldsymbol{TTD} \tag{9}$$

According to Equations (8) and (9) and as function of different values of maximum allowable loss of reliability, *TTD* and *RPI* are obtained for recently manufactured O-Rings (as the worst favorable scenario) with HSA>65 and presented in Table 5.

Table 5. Time to Damage (*TTD*) estimation and recommended replacement interval (*RPI*) for O-Rings with HSA>65.

Maximum allowable loss of reliability	*TTD* (years)	*RPI* (years)*2
0.2	1.33	12
0.3	2.14	19
0.4	3.06	27

Note*2: a *SF* equal to 0.75 has been used (but this value can be fit according to the acceptable risk defined by the plant's owner).

Thus, applying this model, if O-Rings are replaced in annual operation of maintenance, the reliability of O-Rings with a hardness of 65 shore A are 0.85, whereas in the case of O-Rings with a hardness of 68 shore A are 0.78. Nevertheless, the recommendation is to use O-Rings with a hardness lower than 60 HSA, to ensure a reliability upper than 0.90.

3.2. Stage 3.- Methodology validation and estimation of in-service operating limit conditions

Table 6 shows the maximum temperature obtained using Equation 1 and the calculation parameters indicated in Note *3 (at the bottom of the Table) and considering the three scenarios (as defined in subsection 3.1).

Table 6. Prediction of the maximum allowable storage temperature according to the Arrhenius model.

Scenario of analysis	Maximum allowable storage temperature (°C)*3	Validation according to the stablished hypotheses
Very conservative	27.50	>upper limit of T=20±5°C
Moderately conservative	26.31	>upper limit of T=20±5°C
Minimally conservative	25.17	>upper limit of T=20±5°C

Note *3: The following parameters have been used for the calculation: normal operating temperature (T_s)= 33°C; operation time= 10 years; activation energy (*Ea*) according to EPRI TR 1009748 for NBR= 0.88 [26].

Note *4: Values > controlled room temperature (T=20±5°C) [42].

In view of the results presented in Table 6, it can be concluded that the limit conditions for prolonged storage considering any of the three contemplated scenarios would be above the real conditions. That is, even in the case of the least conservative scenario, the maximum temperature predicted by the model is 25.17 °C, which is slightly higher than the maximum real temperature (according to Note * 4 in Table 1 = 20 ± 5 °C).

On the other hand, a validation (Table 7) is performed to check if in the analyzed assumptions stated in the analytical procedure (18, 22.5 and 24 years), the maximum allowable hardness value according to the catalog would be reached for these NBR gaskets, that is, a value of 70 Shore A [42].

Table 7. Results of the application of the Arrhenius-based model and validation.

Analysis scenario	Time (years) to reach the maximum allowable hardness (70 Shore A)	Validation criterion (valid if it is "upper than")
Minimally conservative	18.35	18
Moderately conservative	22.93	22.5
Very conservative	24.46	24

Adapting the model to predict in each of the three scenarios in which the maximum allowable hardness value (70 Shore A) -defined as the upper limit- would be reached, it is verified that for any of the scenarios the upper limit value is above of the considered storage time premise (18.35 > 18 years considered for the least conservative scenario, 22.93 > 22.50 years considered for the medium scenario, and 24.46 > 24 years considered for the most conservative scenario). Therefore, it is possible to validate the model, by ensuring that in the predictions (both for temperature ranges and for storage times) the allowable limit value of 70 Shore A is not reached in any case. Finally, an analysis to validate the methodology has been performed (Figure 17) on the basis of the representation of the expected maximum storage time (using the three considered scenarios) versus the time to reach the HSA_{max} (70 HSA). In addition, the starting data (hardness values) has shown coherence with another experimental work; such as the one of Zhong *et al.*, that provides an embrittlement by storage similar for a period of 18 years [51].

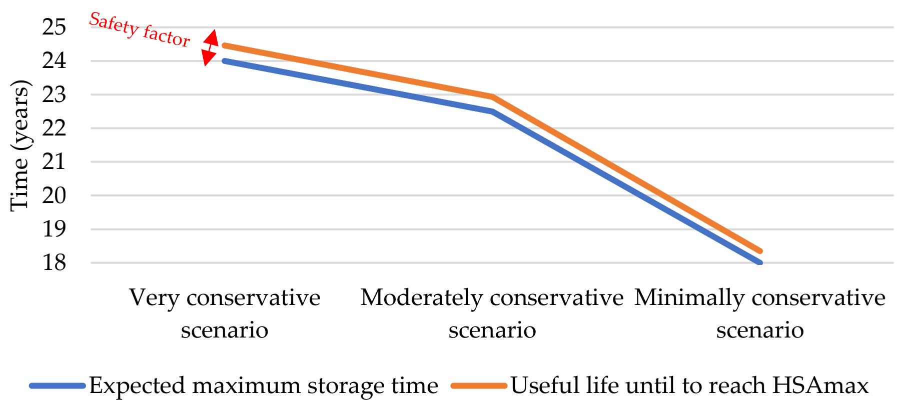


Figure 17. Validation and demonstration that the model provides a safety factor.

4. Conclusions and future works

The major conclusions resulting from this work can summarized as follows:

- The measured hardening can be a useful parameter to estimate the maximum recommendable in-service time. A hardening of 5% generates a reduction of the recommended in-service time of 50% (i.e. a recommended time of use of 5 years), while a hardening of 10% implies a usability for only 3 years.
- The storage (and its associated hardening) of the NBR O-Rings has a direct effect on the in-service durability, reducing this up to 60.40%. Thus, the calculated Time to Integrity Loss (*TTIL*) -considered as the time in operation where a Shore A hardness equal to 65 is reached (beginning of the embrittlement)- is of 6 years (52560 hours).
- During the three first years of operation the increase of *POF* is practically insignificant. Nevertheless, from this point, and specially, from 5 years of operation, the *POF* increases from 10% to 20% at approximately 6 years (for new and stored).
- From 6 years of operation, the behavior of curves (for new and stored) are very different: in the case of stored ones, there is a linear progression up to reaching a POF equal to 0.78 at 10 years; while, in the case of the new ones, the *POF* is practically 100% when they reach an accumulated in-service time equivalent to 10 years.
- In addition, a validation of the methodology has been performed by comparing the predicted allowable storage periods and conditions with the real ones. Thus, applying this model, if O-Rings are replaced in annual operation of maintenance, the reliability of O-Rings with a hardness of 65 shore A are 0.85, whereas in the case of O-Rings with a hardness of 68 shore A are 0.78.
- From the study, the general recommendation is using O-Rings with a HSA less than 60 HSA, to ensure a reliability upper than 0.90. Finally, it has been proven that the storage strategies of our nuclear power plants are successful, perfectly meeting the expectations of suitability and functionality of the components when they are installed after storage.

Finally, this methodology can be used in the future to analyze the suitability of other polymers after a long storage period.

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