Methods for Evaluation of Seal Leakage & Prediction of Thermal Degradation - Enable Product Optimizations & Innovations

Chemraz® Products

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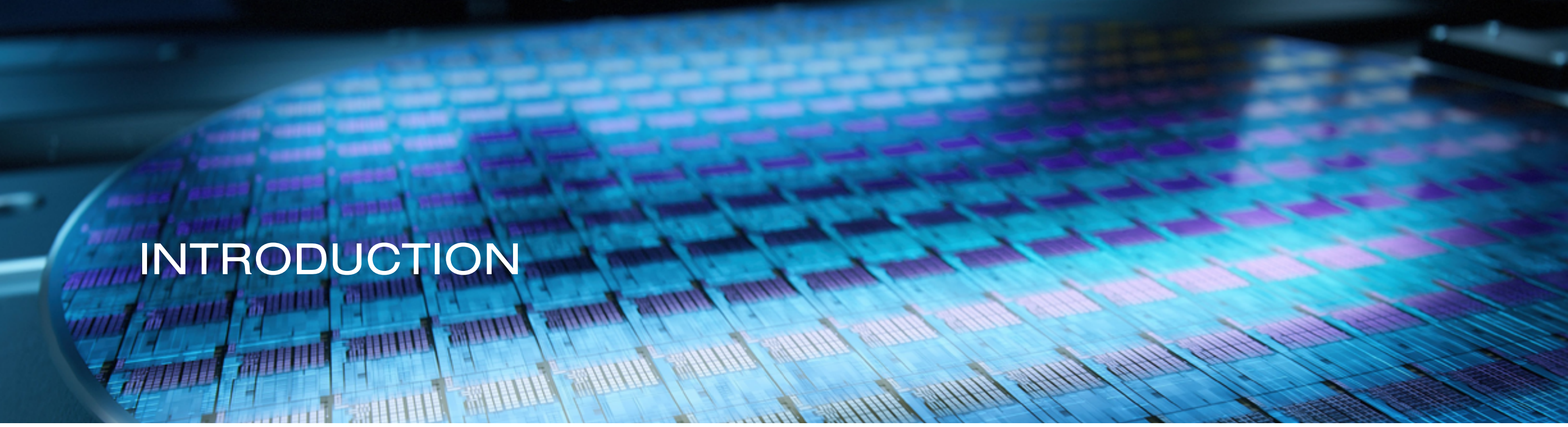


INTRODUCTION

Semiconductor technologies drive elastomer sealing product performances and requirements to the next era. Critical wafer processing applications now require high vacuum (or small number of particles) for high mean free path that demands seal optimization and innovation.

To attain a state of vacuum, a space must be empty, i.e., devoid of all gaseous material. Mean free path is the average distance a particle can travel before colliding with another particle. For the fixed space, mean free path depends on the number of particles in it. If there is an increase in pressure due to admission of particles (leakage) from external environment, the number of particles and collision among particles increase. As a result, with the increase in pressure, the mean free path decreases, which affects semiconductor processing.

It is critical to distinguish leak and permeation in leakage assessment. Gas can diffuse through seal body or flow through channels (leaks) in seal body or at interface between a seal and its counterpart. The process related to diffusion is permeation whereas the flow is leak. Handbook of Vacuum Technology (section 19.2.2.2) defines permeation as NOT representing actual leaks but permeable rate. Good seals for high vacuum systems have both low permeation and low leak. To decide sealing failure mode, in most cases we apply a pre-defined standard or permeability specification for the seal of interest.

Good understanding of chamber rate of rise and differentiation between leak and permeation are important for high vacuum processing. Therefore, it is necessary to develop methods to predict a seal's ability to hold vacuum at elevated temperatures.

Compression set is one of typical measures for sealing ability when using elastomer. It is the percentage of initial compression in ambient temperature that loss in seal height occurs after a seal is compressed for a specified time at a fixed temperature. Compression set is an indicator of the seal's permanent deformation after released from a constant nominal compressive load. In semiconductor processing applications with varying temperature and different geometric designs, seal performance usually requires more than just a standard compression set number, i.e., with a test geometric shape and fixed temperature. Performance evaluation on a specific seal design in a specific condition using calculation and simulation is necessary.

This article will discuss evaluation of elastomeric seal performance due to leak vs. permeation and prediction of seal lifetime due to thermal cycling degradation.

LEAKAGE ASSESSMENT 1

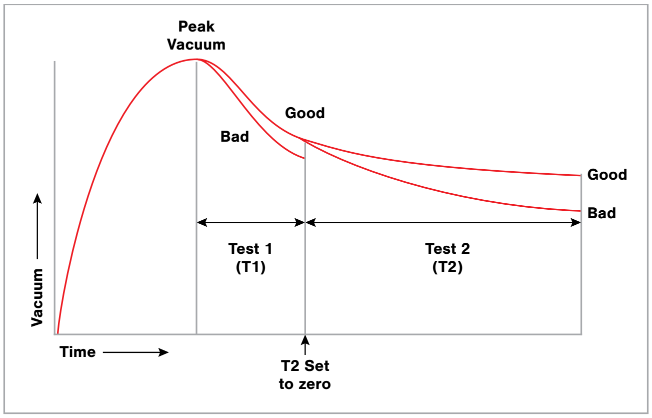
A high vacuum is sensitive to leakage even if it is just from the diffusion of gas molecules through a chamber's walls. Seals are an important part of the system responsible for maintaining the vacuum and are susceptible to leakage. Therefore, it is important to distinguish the sources of leakage (leak or permeation) to the processing chamber and to define acceptable leakage or Rate-of-Rise.

Figure 1 shows a typical chamber Rate-of-Rise. This is a technique used to evaluate leakage integrity of a chamber. The system is isolated, and pressure is monitored over time. Specification can be in Torr/minute or mtorr/sec, or similar.

The formula for rate of rise in a vacuum system is **Q = (P2-P1) V/t.**

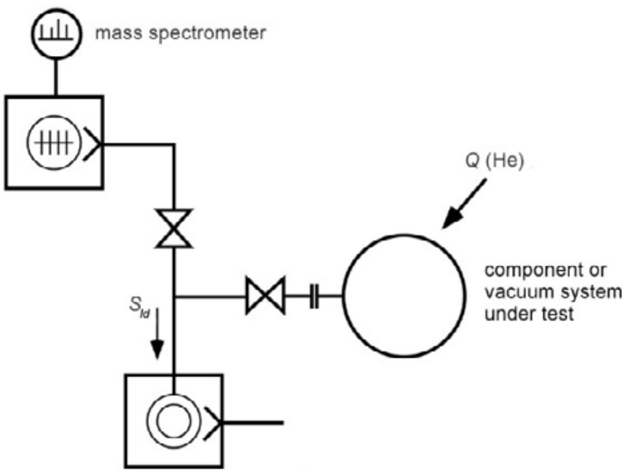
- **P1** is the base pressure of the system in Torr
- **P2** is the pressure in Torr after the high vacuum valve is closed after **t** seconds
- **V** is the volume of the chamber in liters, unit for rate of rise is Torr-liters/sec

FIGURE 1 | Vacuum Decay Leakage Test Curve

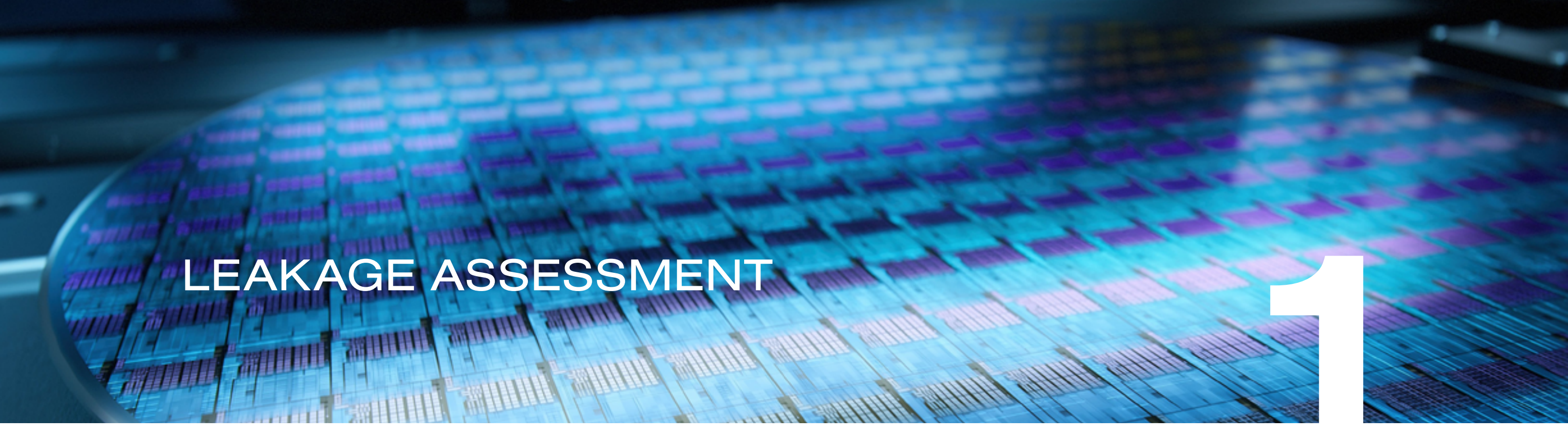


Leak and permeation processes have different time scales. Leak can have much shorter time for failure to appear. In measurement of leak or permeation, we use Helium Mass Spectrometer (MS) and Residual Gas Analyzer (RGA). Helium is a common tracer gas used in leakage testing. It is ideal for applications requiring test sensitivity below 1.0E-3 atm.cc/sec. It is also inert, i.e., not reacting with seal material during diffusion. In measurement, Helium gas is introduced into the test piece and a mass spectrometer analyses a sample from the chamber as the vacuum continues to be drawn. A general diagram of leakage measurement with mass spectrometer is illustrated in figure 2.

FIGURE 2 | He Leakage Test Diagram



In some cases, an alternate test method can be employed using an alternative tracer gas or air. However, Helium is still the best tracer gas given the sensitivity required. This section covers the measurement of permeation and leak.



LEAKAGE ASSESSMENT 1

Leak

In leak (or "true" leak to emphasize the difference from permeation), one measure of leakage rate, typically used for vacuum systems, is defined as the pressure rise over time in each volume:

Q_L	Leakage rate
Δp	Pressure change
V	Volume
Δt	Measurement period

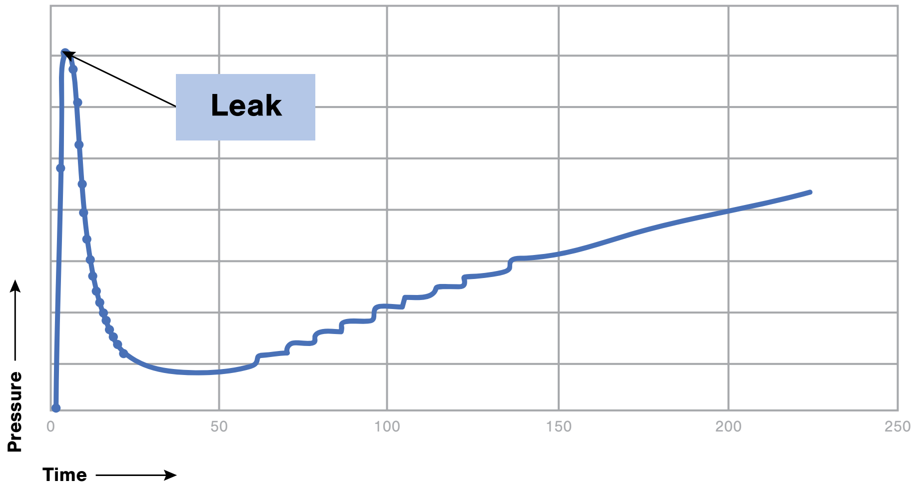
$$Q_L = \frac{\Delta p \cdot V}{\Delta t} \tag{1}$$

Q_L describes the leakage rate, i.e. rate of gas entering the vacuum system.

A leakage measurement with mass spectrometer is given in Figure 3. Leak appears as a peak in brief time when Helium is released. Several factors could cause the system leaks (both seal and groove):

1. Seal type and condition in which seal force is insufficient to hold back the atmospheric pressure
2. Groove types, conditions and defects, e.g., surface finishes.
3. Circular machining follows the gland perimeter (gland cut on a lathe), i.e., machining marks are aligned with the O-ring perimeter.
4. Straight machining crosses the gland, creating possible leaks (gland cut via a dovetail cutting tool, which would also result in swirl marks). Machining marks can cross seal circumference.

FIGURE 3 | System Leak



LEAKAGE ASSESSMENT

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Different surface finishes in straight machining are investigated with Figure 4. Seal leak rate depends on surface finish types and conditions

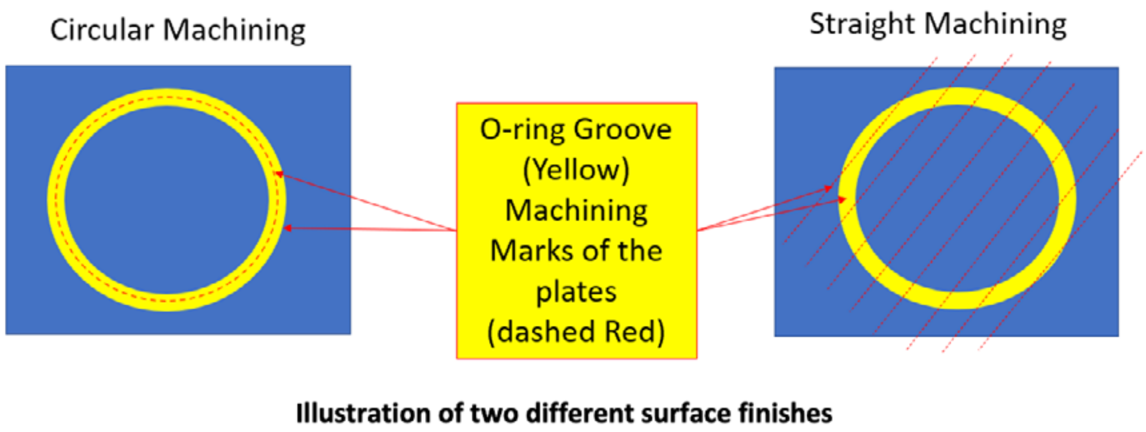


FIGURE 4 | Leakage Tests on Different Straight Finishes

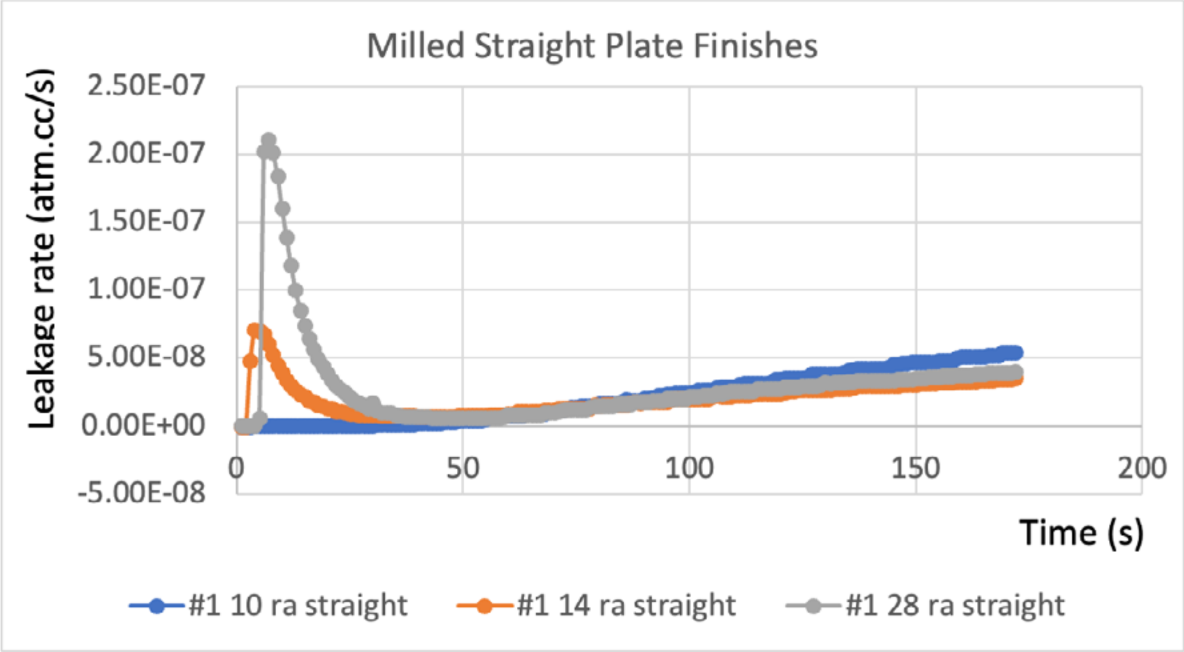
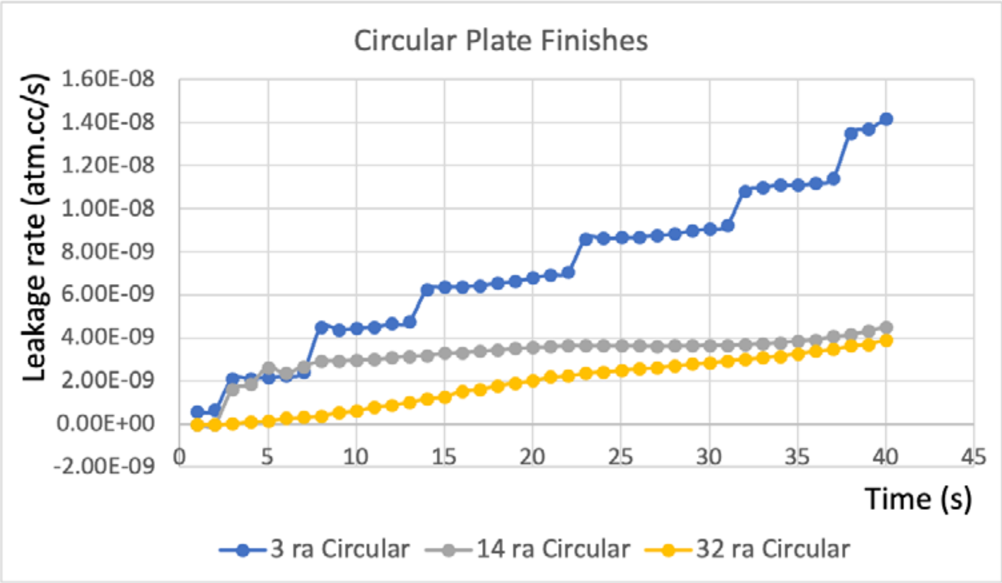


Figure 4 indicates that smoother surface finish (10 Ra) is better than higher roughness surface (14 & 28 Ra) in straight milling.

FIGURE 5 | Leakage Tests on Different Circular Finishes

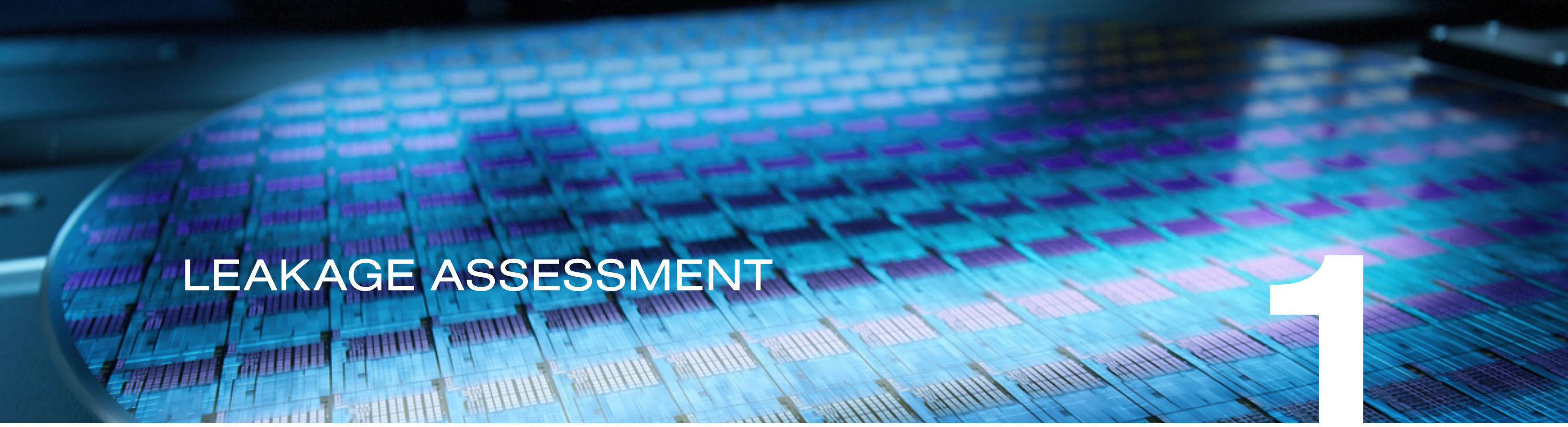


However, leakage testing on circular surface finishes of the grooves in Figure 5 is opposite to that of straight surface finishes. The rough surface finish (32 Ra) is best for circular lay surface. It appears that the type of pattern has larger impact than surface smoothness.

The chart also shows Helium gas permeation (long term part of leakage rate vs. time curves in figure 4 & 5) that slightly increased as a function of time. Therefore, an understanding of the time constant for Helium permeation as well as the steady state total permeation rate will determine the achievable ultimate leakage test sensitivity. With this information, a test can be designed that will distinguish permeation and leak.

Permeation

As introduced, permeation is not actual leak but rather areas permeable for gases. Permeation includes adsorption, diffusion, and desorption. Therefore, permeation varies with materials and tracer gases given the same geometry and the same condition.

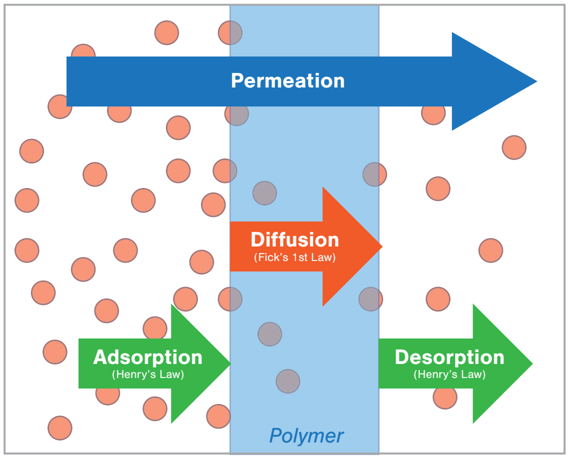


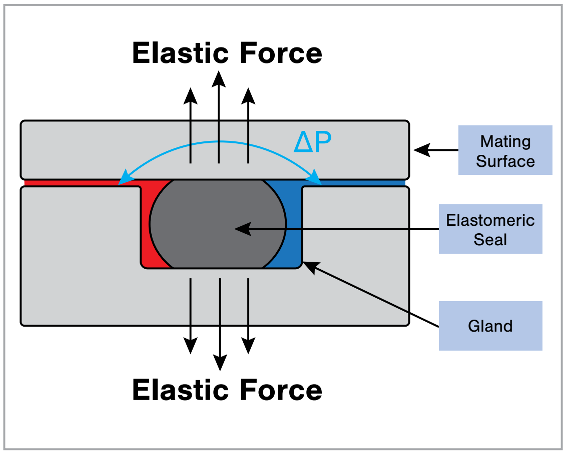
LEAKAGE ASSESSMENT

Leakage rate ***q*** from permeation rises linearly with permeation surface area ***A*** and pressure difference. It drops proportionally to the permeation distance ***L***.

$$q = K_{perm}\frac{A}{L}(p1 - P2) \qquad (2)$$

The proportionality factor K_{perm} is permeability and $K_{perm}\ A/L$ is permeation conductance (like the specific resistance and the resistance of a geometrical body in Ohm's law). ***A*** is the permeable area and ***L*** is effective length.



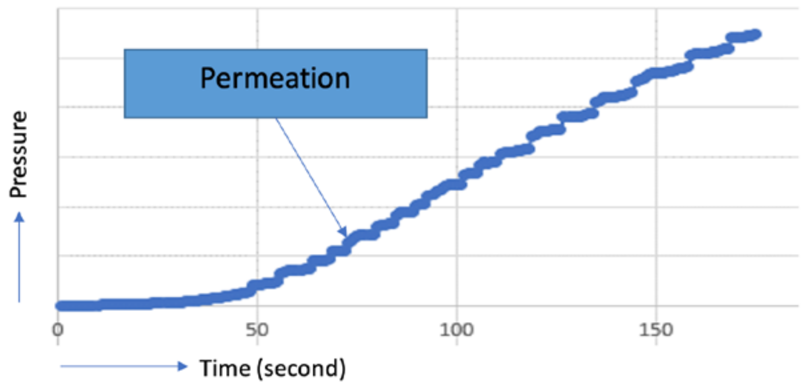


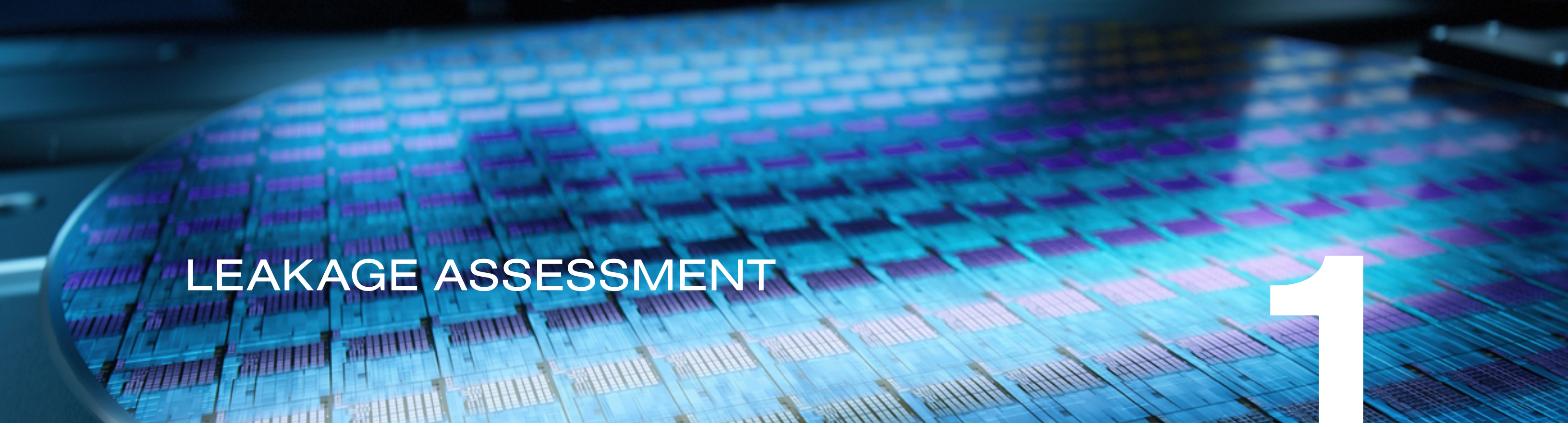
Permeation and leak are both driven by pressure difference. However, their time behaviors differ significantly. For a tracer gas penetrating through an elastomer, starting time is the duration until the permeating gas flux reaches nearly constant. Starting time can spans few tens seconds in practice. This time increases with square of permeation distance L and drop linearly with the diffusion coefficient ***D***. This is so-called inducting time (t_i).

$$t_i = \frac{L^2}{2D} \qquad (3)$$

Figure 6 shows time inducting in permeation and gas permeation occurs after ˜30 seconds. Helium is the tracer gas used in this leakage experiment. Helium has a relatively high permeation rate through the elastomer O-ring (Cross-section.139 inches) in the experiment.

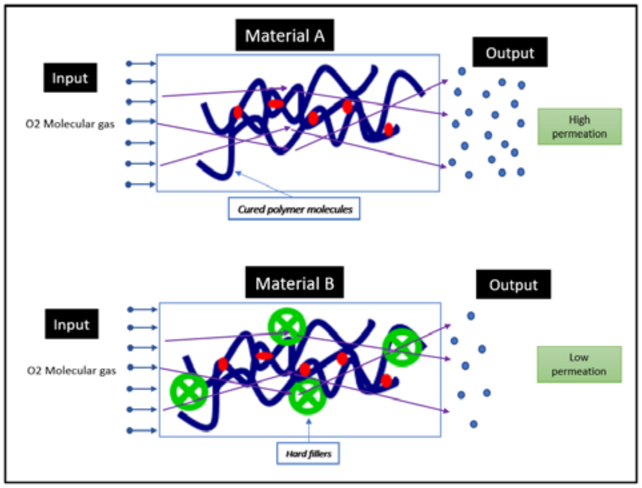
FIGURE 6 | Helium Permeation





LEAKAGE ASSESSMENT 1

Permeation Experiments

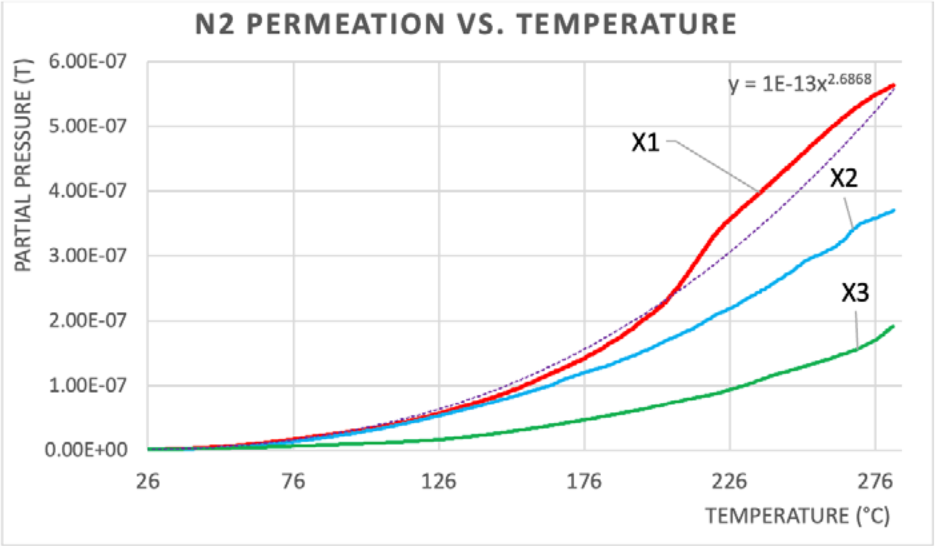


An RGA was used to evaluate permeability of different materials in this study. All seal samples with the same size are subjected to the same testing conditions. Permeation is investigated with different materials, varying temperature, tracer gases, and seal geometries.

In investigation on permeation through different materials, nitrogen gas (N_2) was used as the tracer gas. The data (Fig. 7) shows permeation of three different materials and permeation leakage curves have power of 2 or more with respect to temperature.

On permeation of different tracer gases, figure 8 shows that O_2 permeates less than N_2 through the same material. There are two possible explanations for this: (i) O_2 has lower coefficient of diffusion and lower permeability through Chemraz® X1 than N_2 does; (ii) Oxygen is highly reactive so that it can react, and be captured in the material or exit the material in different chemical species. If the latter dominates, RGA result must be analyzed further as it can be inconsistent in detection of a reactive tracer gas, especially at elevated temperature.

FIGURE 7 | Permeation of Three Materials: X1, X2, X3



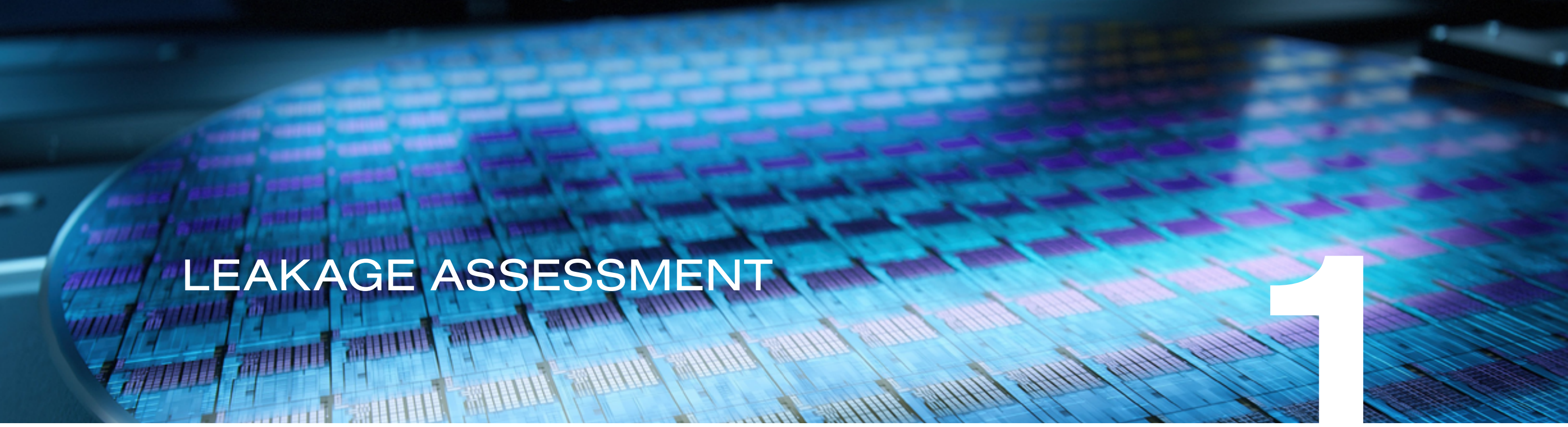
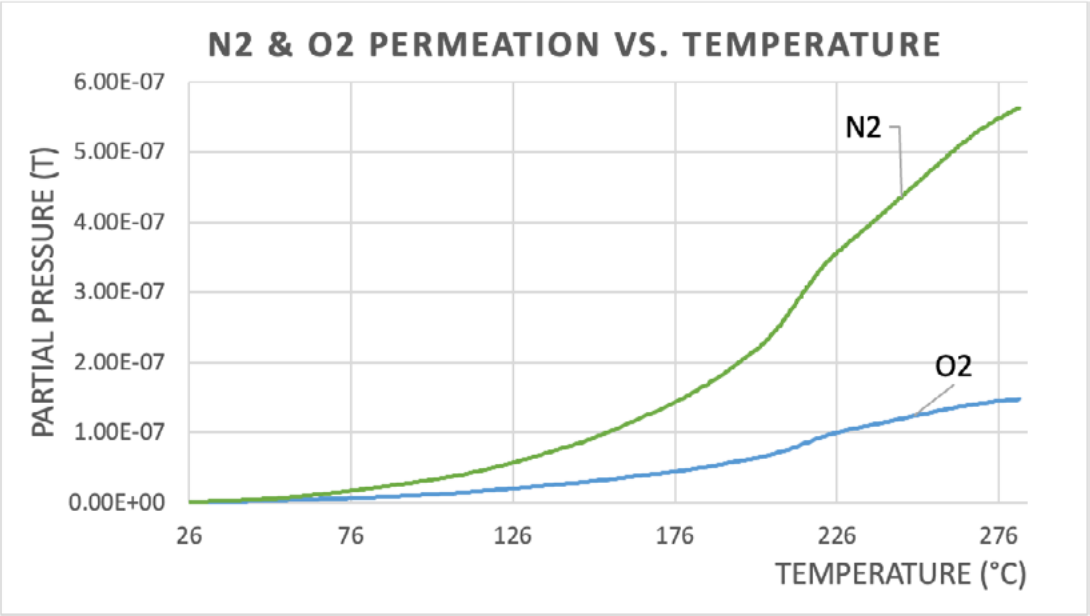


FIGURE 8 | Permeation of Different Tracer Gases



Influence of geometric design is investigated with a gasket and an O-ring (ID 1.00" x CS.139"). The same tracer gas (N2) was used. Equation (2) shows the dependence of permeation on area ***A*** and length ***L***. In this case, ***A*** is the area of a cylindrical surface with height of gland depth and diameter located at cross-section centroid. Effective length ***L*** can be radial average of cross section. The gasket length ***L*** is longer than that of the O-ring while the gasket area ***A*** is smaller than that of the O-ring. As the result, the gasket has lower permeation, which is validated with measurement displayed in figure 9. The measurement data also shows that seal geometry can have significant impact on permeation up to 3 orders of magnitude.

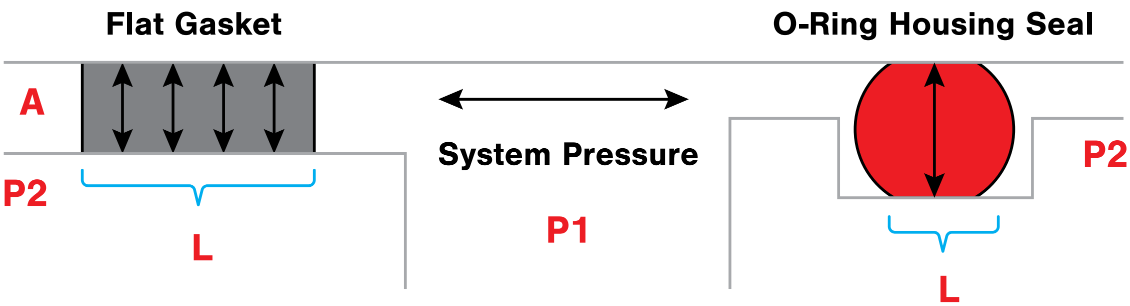
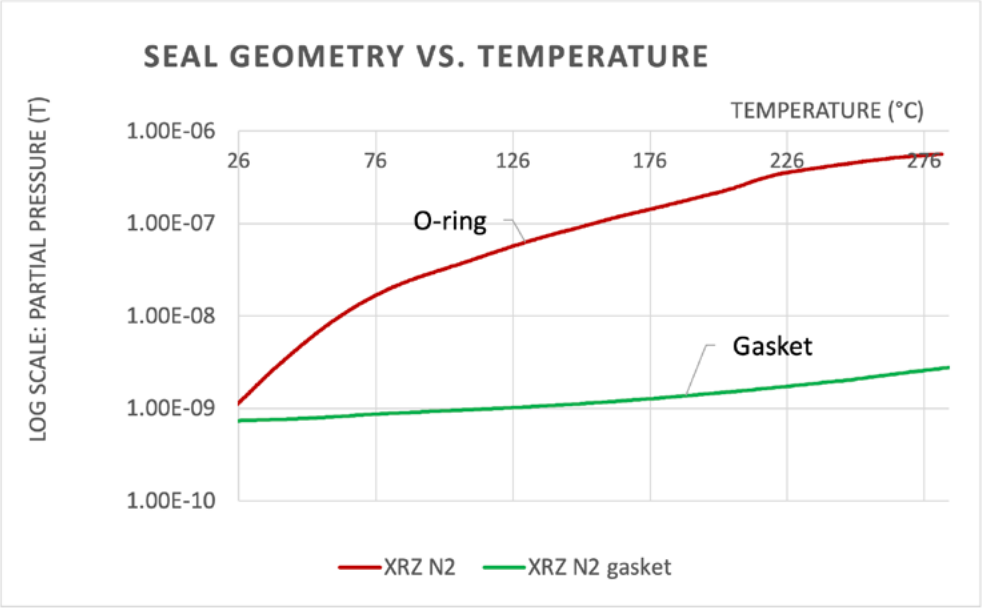
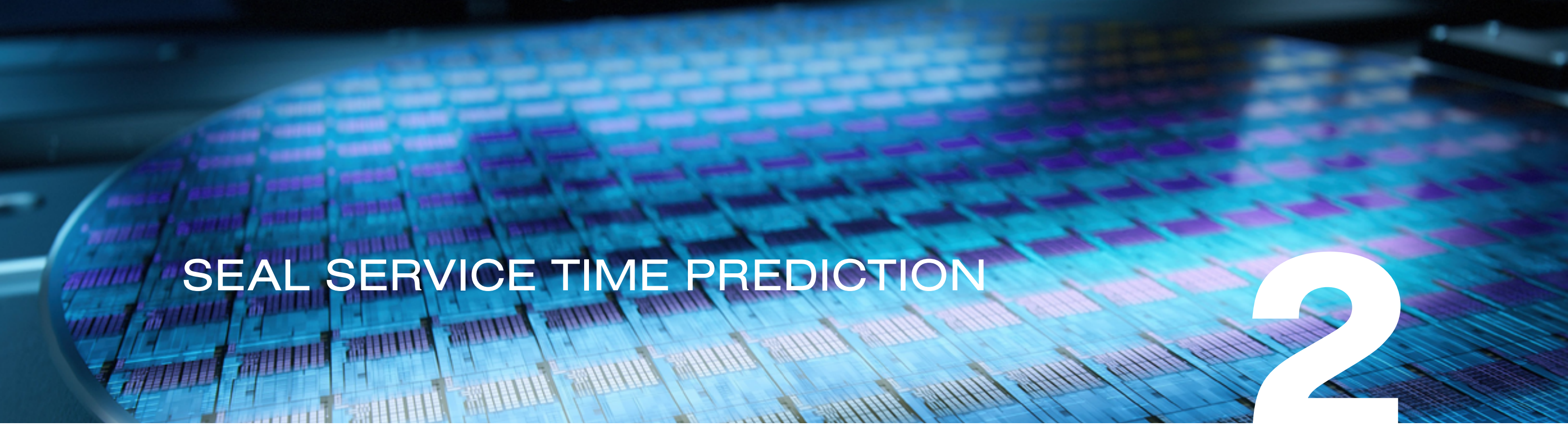


FIGURE 9 | Permeation of Different Seal Geometries



Summary of Leakage Study

In this section, the sealing performance of different permeability coefficients, tracer gases, seal geometries were investigated experimentally and theoretically. True (usually interfacial) leak and permeation could be distinguished with leakage rate in short term and long term. In leak, gas molecules pass through seal or groove defects. Leak can be detected within seconds. Machining pattern can have more impact on leak than surface finish does. On the other hands, permeation relates to diffusion of molecules through seal body and has much longer time scale. It's found that impact of design geometry on gas permeation have larger extent (3 orders of magnitude) than those of permeability and tracer type (within 1 order of magnitude). Permeability must still be considered as one factor in application because it could be easier to switch material than to redesign. Type of tracer gas must be considered for permeation measurements. Helium and Nitrogen gases are inert as opposed to reactive Oxygen. Permeation measurement using media including Oxygen or other reactive gases must be interpreted carefully as they can produce inconsistent results.



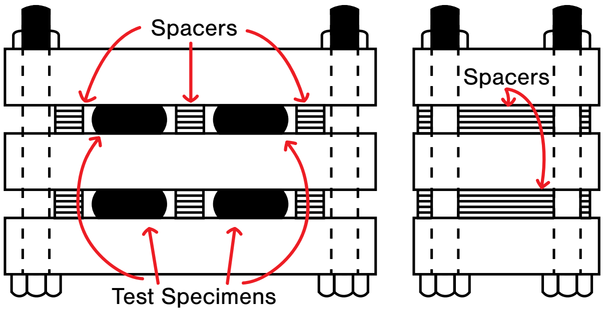
SEAL SERVICE TIME PREDICTION 2

Compression set tests are usually used as a measure to compare O-ring compounds. A standard used for tests of O-rings is ASTM standard D1414 (Fig. 10). Following this protocol, O-rings of standard size (25.4×3.5 mm or 1.0×0.139 in.) are installed between flat plates stacked in a jig, which simulates grooves in actual face seal service. The O-rings are typically compressed 25% of original height using spacers between plates to have uniform circumferent strain distribution. The assembly is then subjected to the prescribed temperature in an air oven for a specified time. After exposure, the jig is removed from the oven and the O-rings are removed and allowed to recover at room temperature for a set time (30 minutes) before measuring final thickness and degree of set (as loss-in-thickness/compression ratio in percent). Measurement results can provide insights into performance of O-ring compounds in static conditions but not in dynamic ones with temperature cycling or with hardware movements.

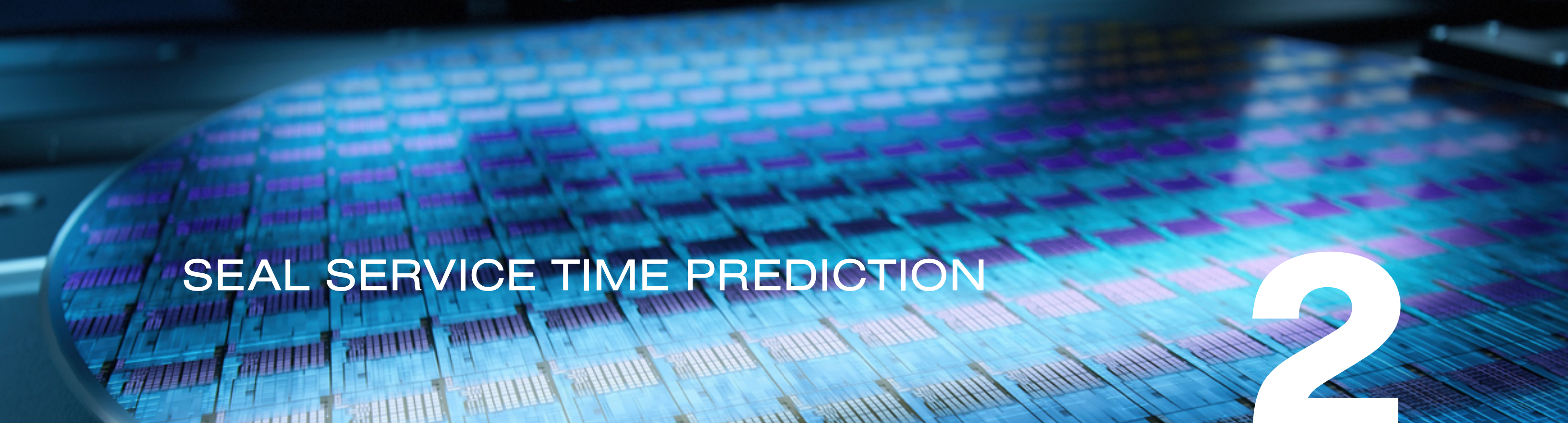
Material Model R&D

Compression set test in general produces reliable comparisons of compounds, but it is very costly and time consuming to be done in actual application conditions. Even if feasible, sophisticated tests usually require theoretical and computational analysis to gain insights. Therefore, physics based numerical simulation can be instrumental in evaluation of a part performance in a specific application. However, most of built-in material models used in solid mechanics simulations of elastomers are monotonic and/or time independent. This study presents a development of a material constitutive model to analyze evolution of inelastic deformation of elastomers over a load history.

FIGURE 10 | Device for Compression Set Test Under Constant Deflection



A set of constitutive equations describing relationships among stress, elastic strain, inelastic strain is considered in finite strain formulation applying parallel approach that has been used in formulation of known Prony series for linear viscoelasticity. The method allows combination of different nonlinear elastic, viscoelastic and viscoplastic components in parallel to capture the time dependent behavior and inelastic deformation. The constitutive model makes use of many characteristic parameters (properties) that need calibrating for a specific material to make a material model. The calibration for a specific material requires some characteristic measurements, such as tension, compression, relaxation at temperatures of interest and is implemented in a process developed in a software platform for parametric optimization. Once a calibration completed, the parameters are inspected for physical relevance and assessed for simulation speed and stability. When accepted, the material model is applied in CAE setups to simulate specific applications. Figure 11 exhibits calibration of a material model whose parameters are simulation-ready for one of Greene, Tweed Co.'s compounds, Chemraz® X1.



SEAL SERVICE TIME PREDICTION

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FIGURE 11a | Tests and Predictions at 23°C

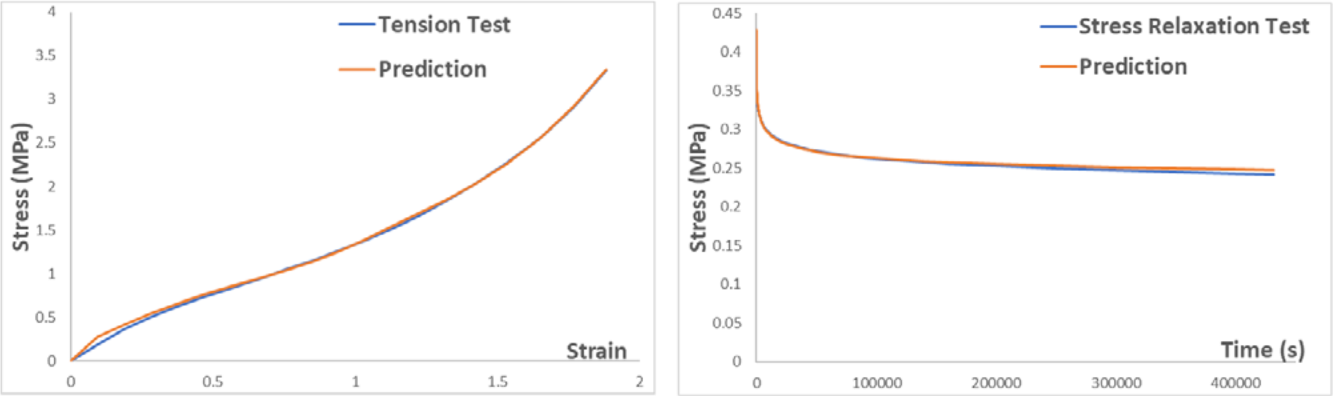
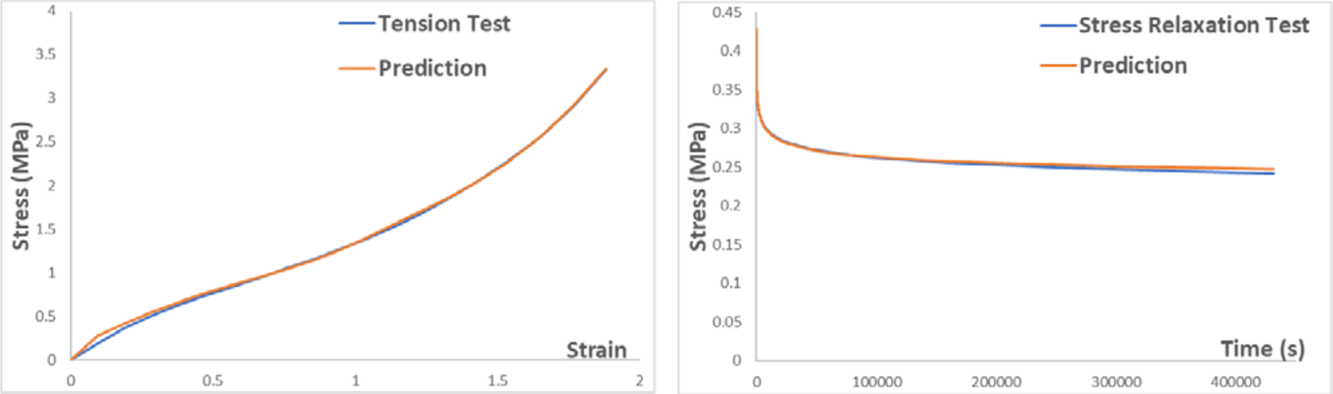


FIGURE 11b | Tests and Predictions at 250°C



SEAL SERVICE TIME PREDICTION

2

Material & Design Studies

For elastomer seals functioning in semiconductor fabrication, one of typical design considerations can be the number of loading cycles at which an elastomer seal will lose 60% of its initial compression because of relaxation and degradation. The number of cycles can help determine the maintenance time for the part. In this study, we consider two seal designs, one O-ring (-109) and one barrel shape seal subjected to the same compression, under 2-minute temperature cycling between 23 C and 250 C and two elastomeric compounds, Chemraz® X1 and Chemraz® X2.

Figure 13, including cross section of the O-ring still compressed in gland (a) and uncompressed (b) after 30 temperature cycles, demonstrates the ability of the constitutive model to capture inelastic deformation with cross section of the O-ring after 30 temperature cycles. Figure 13b indicates that compression set has taken place after 30 cycles with the loss in seal height and the red dashed circle indicating the original shape.

FIGURE 12 | O-Ring (a) and Barrel Shape Seal (b)

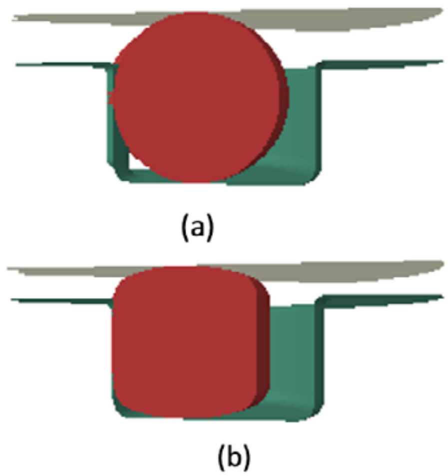
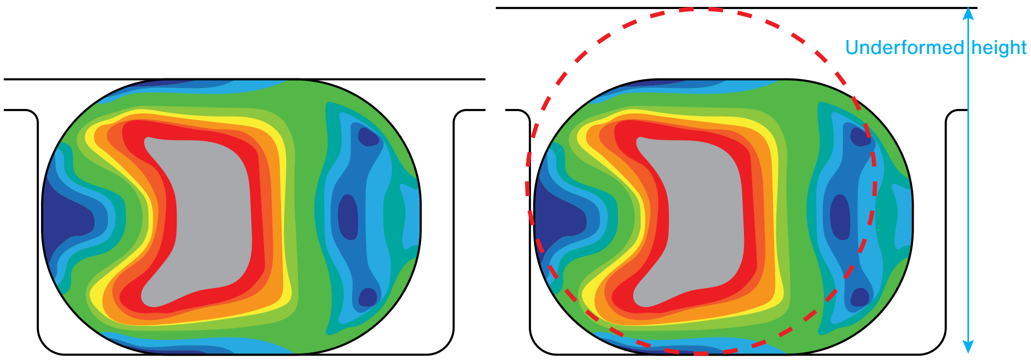
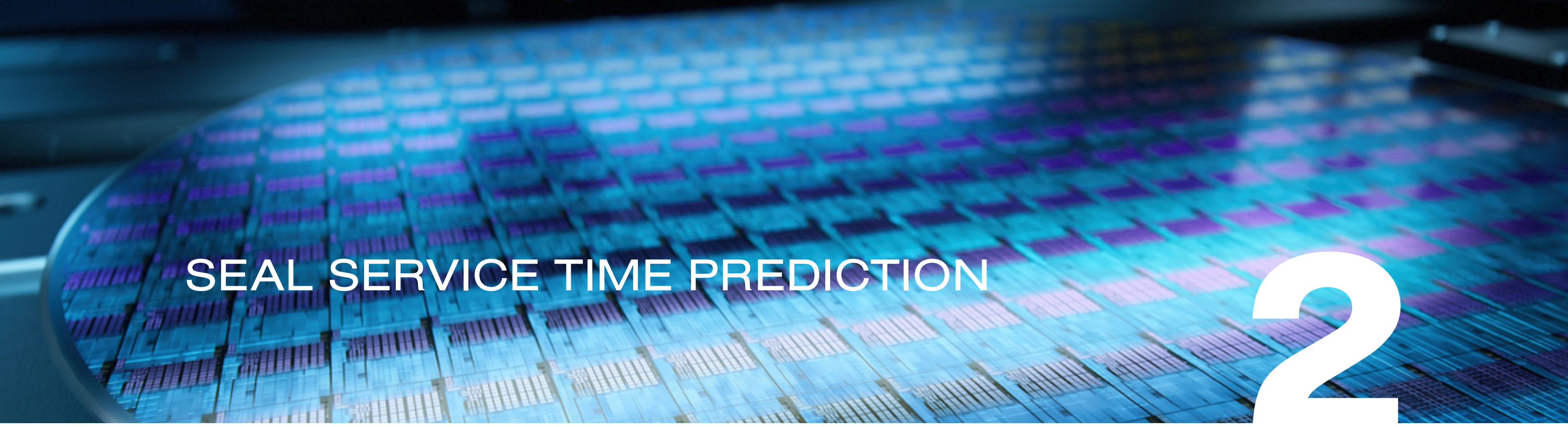


FIGURE 13 | O-Ring Cross Section After 30 Cycles



(a) compressed in gland **(b) removal of top counter surface**



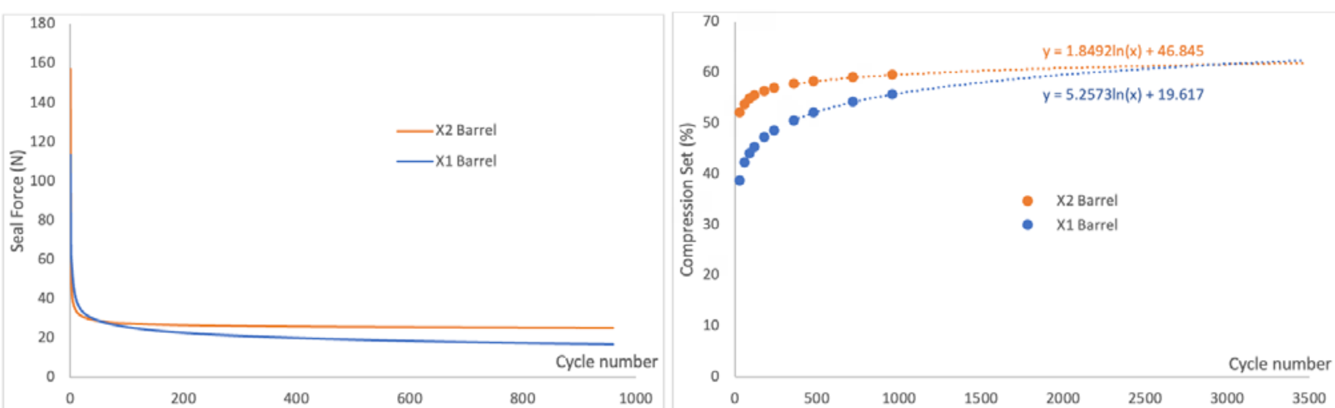
SEAL SERVICE TIME PREDICTION 2

Comparison of Compounds

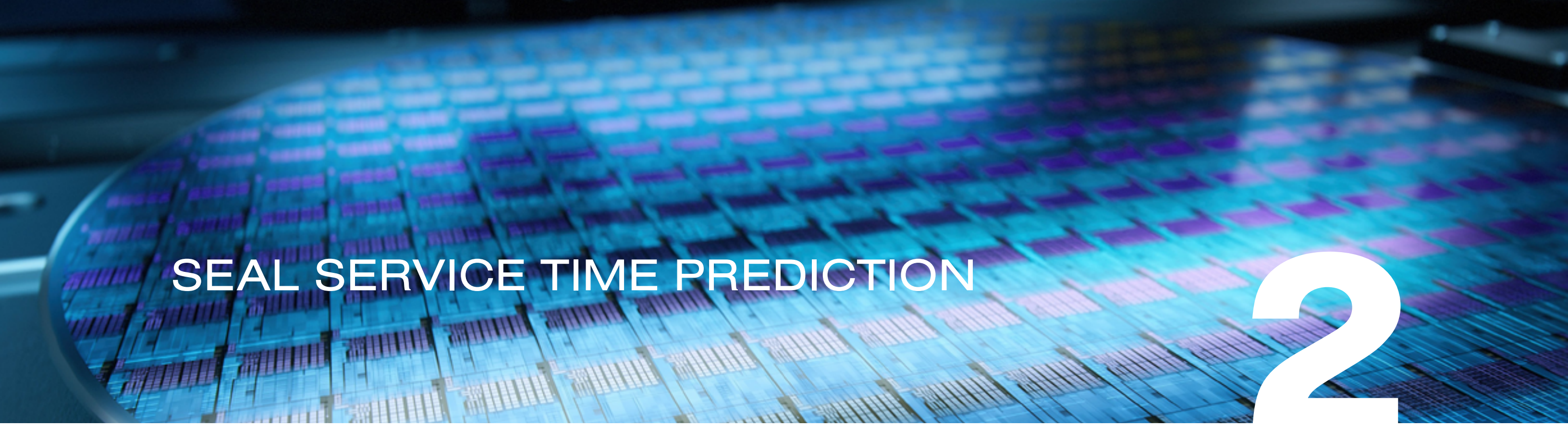
The two materials, Chemraz® X1 and Chemraz® X2, share the same polymer technology but differ in formulation. Figure 14 compares the two materials with the barrel shape seal. The seal force curves (Fig. 14a) at 23 degrees Celsius (beginning and end of each cycle) indicate that the seal force by Chemraz® X2 is higher initially, decreases faster to higher long-term value than that by Chemraz® X1 in both seal designs. Higher seal force and stress in Chemraz® X2 seals, induced by its filler, drive faster inelastic flow that in turn causes drop of stress faster to long-term value.

The curves (Fig. 14b) for compression set vs. temperature cycle show that the seals in Chemraz® X2 have higher initial compression set but lower rate of increasing so that those in Chemraz® X1 meet and surpass at about 2700 cycles. Logarithmic functions, representing relationships between compression set and number of temperature cycles at large number of cycles, can estimate the numbers of cycle at which compression set of Chemraz® X1 seal meets that of Chemraz® X2 seal, i.e., 2949 cycles (98 hours) in continuous cycling for barrel shape seal.

FIGURE 14 | Seal Force at 23°C, Barrel Shape Seal (a) and O-ring -109 (b)



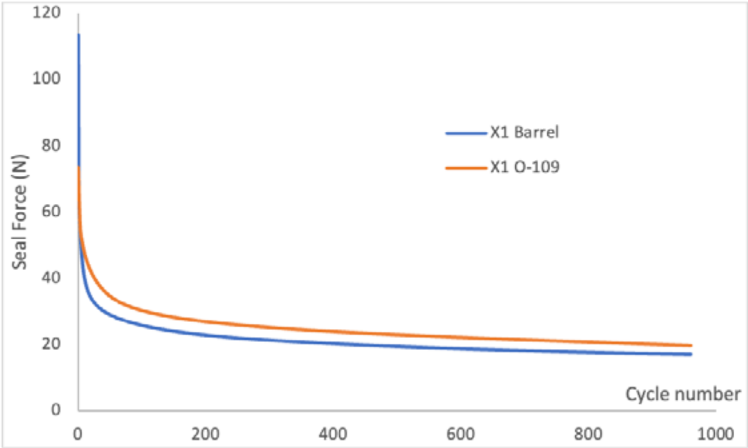
(a) (b)



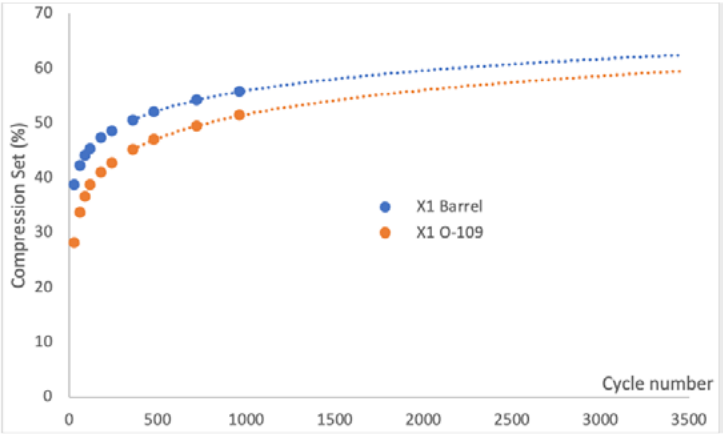
Geometric Impact

For the same material and compression percentage, barrel shape design generates higher initial seal force and lower long-term value but close to that of the O-ring -109 (Fig. 15a). Barrel shape design has consistently higher compression set compared to that of O-ring -109 for the same material and compression (Fig. 15b).

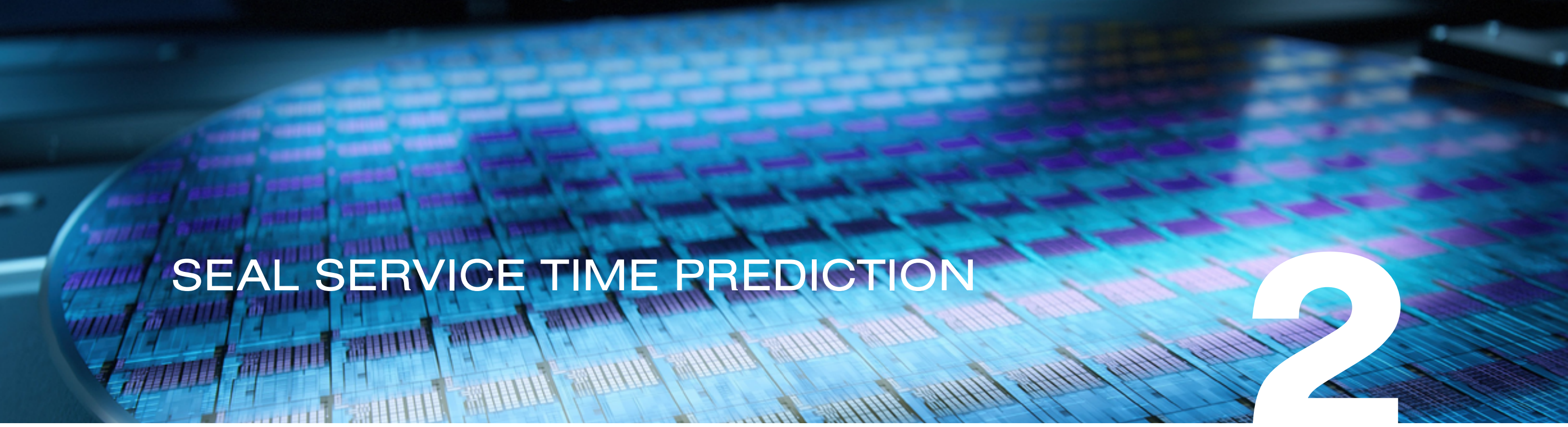
FIGURE 15 | Compression Set - Temperature Cycle Number Curves. X1 vs. X2 in barrel shape seal (a) and O-ring -109 (b)



(a)



(b)



SEAL SERVICE TIME PREDICTION 2

SUMMARY OF MODELING STUDY

A time dependent phenomenological constitutive model has been considered and calibrated for two elastomer materials, Chemraz® X1 and Chemraz® X2. The material models were then applied to investigate the evolutions of compression set of two seal designs, a barrel shape seal and O ring -109, in temperature cycling between ambient temperature and 250 degrees Celsius.

The simulations shown that the seals undergo inelastic deformation when subjected to a certain compression. Due to time dependent nature, the inelastic deformation will attenuate in long time after load removal. Compression set in the study was calculated immediately after load removal to save time for design comparison purpose. The calculated compression set is relevant for seal behavior in fast actions, such as vibration or sudden increase of gland size due to some system disturbances.

The results for materials and designs have shown that compression set of compound Chemraz® X2 is higher in low cycle number but become steady at lower value than that of compound Chemraz® X1. And the O ring design has consistently lower compression set than the barrel shape design given same level of compression.

Accuracy in simulation with the material models depends largely on mechanical tests of the materials. Future development is to investigate and include degradation of polymer backbones and crosslinks to reduce dependency on test inputs.

SUMMARY OF MODELING STUDY

- The permeation and stress relaxation tests supported by Gary Reichel – ATG
- Leak studies reported by Aaron Thrash – Applications Engineer

REFERENCES

Handbook of Vacuum Technology. Edited by Karl Jousten. Copyright © 2008 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. ISBN: 978-3-527-40723-1

Chapman, S. and Cowling, T.G. (1970) The Mathematical Theory of Non-Uniform Gases, 3rd edn, Cambridge University Press, Cambridge, UK.

Redlich, O. and Kwong, J.N.S. (1949) On the thermodynamics of solutions – an equation of state, fugacities of gaseous solutions. Chem. Rev., 44, 233– 245.

Reid, R.C., Prausnitz, J.M., and Poling, B.E. (1987) The Properties of Gases and Liquids, McGraw-Hill, New York.