

Long-term safe sealing of hydrogen with SIGRAFLEX®

Hydrogen sealing is on everyone's lips. Hydrogen is an energy source of the future, and more and more operators are being confronted with this operating medium. Hydrogen is used in many industrial processes, and it is likely to be used more and more in the future as a source to generate clean electrical energy.

Everyone knows that hydrogen is the lightest element, it sits at position one of the periodic table of elements. Hydrogen is abundant in our environment and no matter the production process hydrogen is always the same colorless, odorless and tasteless gas consisting of two hydrogen atoms paired together forming the hydrogen molecule H_2 .

This raises many questions for operators and users: What special features need to apply to seal selection? How critical is hydrogen? How does this affect the leakage of a gasket? Buzzwords such as hydrogen embrittlement also make people sit up and take notice.

Sealing of hydrogen

In the production process, transfer, storage and use of hydrogen gas it is essential for the reliable and safe operation of the mechanical handling equipment including pipe flanges, vessels, valves etc. and it is of paramount importance that all equipment is sealed safely and effectively.

Tightness testing

Apart from the chemical resistance and the long-term mechanical stability of the gasket or sealing material, the leakage behavior is crucial. Leakage measurements with pure hydrogen according to EN13555 undertaken by the company AMTEC for SIGRAFLEX UNIVERSAL PRO, SIGRAFLEX HOCHDRUCK, SIGRAFLEX HOCHDRUCK PRO and SIGRAFLEX MF® at a thickness of 2 mm each have exhibited low leakage rates, see graphs 1, 2, 3 and 4.

Using standard flanges according to EN 1092-1 and hydrogen at 40 bar (580 psi) media pressure and with a typical gasket surface stress of 30 to 70 MPa (4350...10,150 psi), the measured leakage rates were below the TA Luft 2021 limit value of L0.01 [TA Luft = German clean air act].

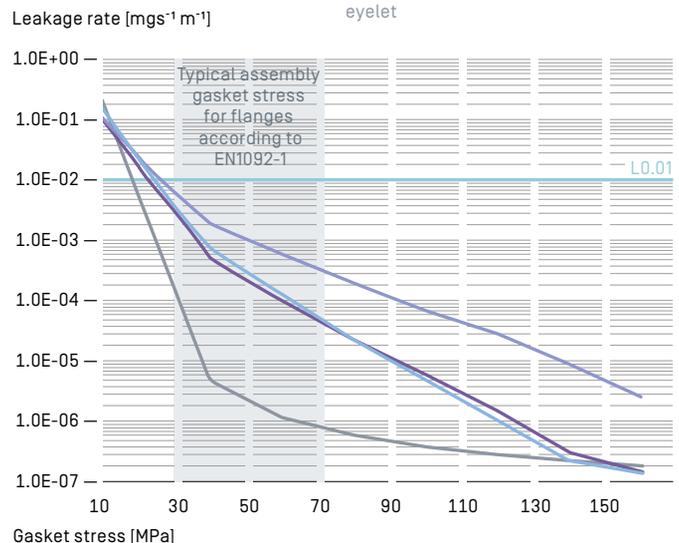
In addition to the mean values of the double tests, the leakage rates in graphs 1 to 4 also include the TA Luft limit of L0.01 as well as the typical range of the gasket assembly stress for raised face flanges according to EN 1092-1. As the lowest leakage rate that could be measured due to the test rig limitations was $1.5 \cdot 10^{-7} \text{ mg}/[\text{s}\cdot\text{m}]$, some of the curves are somewhat bent at the highest gasket stress of 160 MPa (23,200 psi).

Graph 1 shows the comparison of the loading curves of the leakage rates according to EN 13555 of all the tested materials.

Hydrogen leakage rates of all materials tested

Graph 1: Hydrogen leakage rate, measured according to EN 13555 at 40 bar (580 psi) pressure

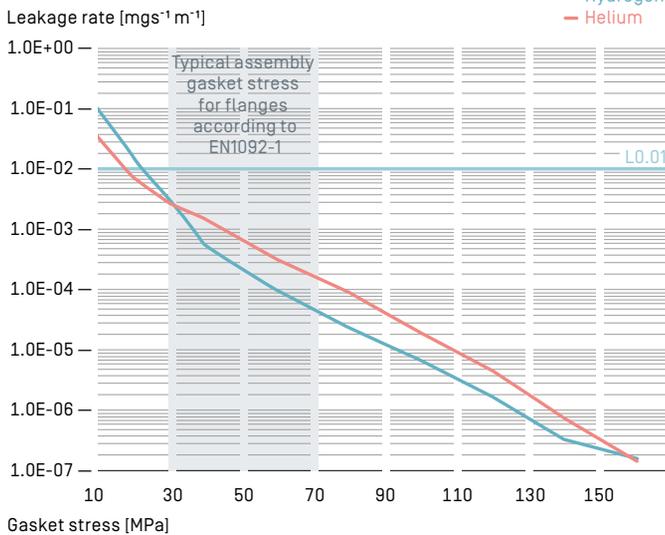
- SIGRAFLEX HOCHDRUCK V20011Z3I
- SIGRAFLEX UNIVERSAL PRO V20010C2IP
- SIGRAFLEX HOCHDRUCK PRO V20011Z3IP
- SIGRAFLEX MF V20011Z2MF with inner eyelet



Depending on the material, the leakage rate of hydrogen at a gasket stress of 10 MPa (1450 psi) to 20...40 MPa (2900...5800 psi) is somewhat higher than that of helium, but above this gasket stress the leakage rate of hydrogen is lower than that of helium. For example, graph 2 shows the comparative leakage rate of helium and hydrogen for SIGRAFLEX HOCHDRUCK PRO.

Hydrogen and helium leakage rate of SIGRAFLEX HOCHDRUCK PRO V20011Z3IP

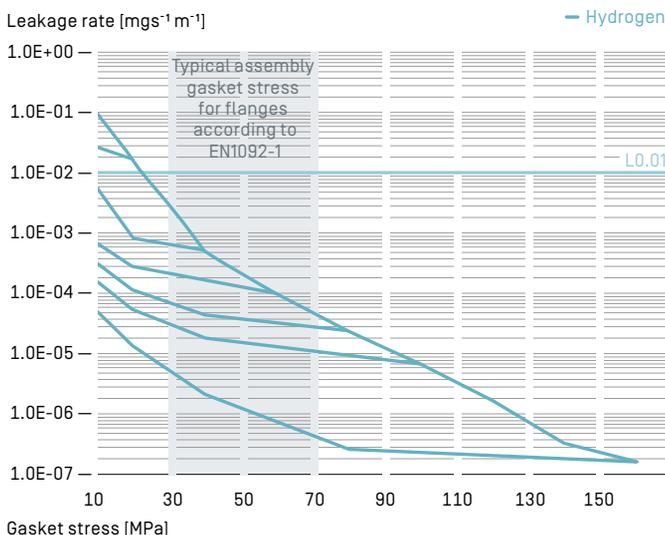
Graph 2: Hydrogen and helium leakage rate, measured according to EN 13555 at 40 bar (580 psi) pressure



Using the same material SIGRAFLEX HOCHDRUCK PRO in graph 3 we show the leakage rate according EN 13555 including the unloading curves. As the gasket stress is reduced the leakage rate behavior of hydrogen is the same as that of helium where the leakage initially increases only slightly when the gasket stress is reduced.

Leakage rate (loading and unloading curves) of SIGRAFLEX HOCHDRUCK PRO V20011Z3IP

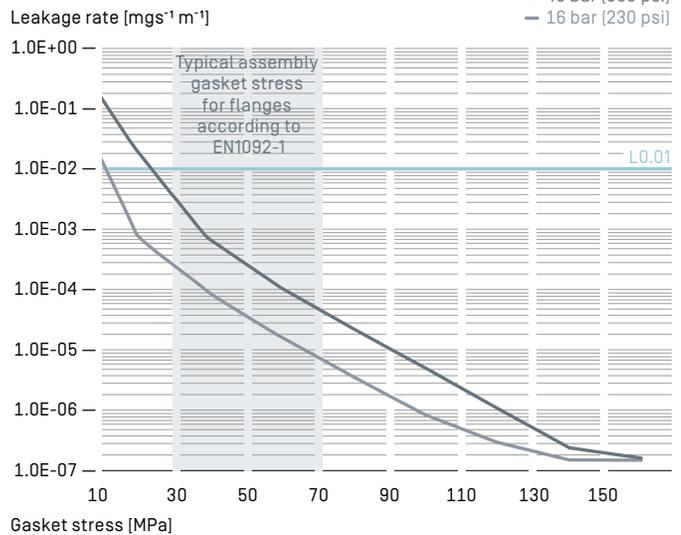
Graph 3: Hydrogen leakage rate, measured according to EN 13555 at 40 bar (580 psi) pressure



For SIGRAFLEX UNIVERSAL PRO the leakage rate at 16 bar (230 psi) medium pressure was measured in addition. Graph 4 shows a comparison of the leakage rate at 16 bar (230 psi) and 40 bar (580 psi) hydrogen. As expected, the leakage rate at 16 bar (230 psi) is lower than at 40 bar (580 psi). The bend in the leakage curves at 140 and 160 MPa (20,300 and 23,200 psi) is due to the measurement limit of $1.5 \cdot 10^{-7}$ mg/(s·m), as mentioned previously.

Hydrogen leakage rate of SIGRAFLEX UNIVERSAL PRO V20010C2IP at 16 and 40 bar

Graph 4: Hydrogen leakage rate, measured according to EN 13555 at 16 and 40 bar (230 and 580 psi) pressure



Flange tightness calculation

One question that is being asked is “is it necessary to perform additional flange calculations?”. The answer is “no”, the standard calculation for flange connections according to EN 1591-1 using EN 13555 gasket factors determined using helium can be used for hydrogen applications as well. To help explain why hydrogen leakage is not higher than that of helium: Leakage largely depends on the size of the atom, or the molecular size of the media being sealed. Helium does not form molecules, but it is a single atom He. The hydrogen atom is smaller than the helium atom but exists as a dumbbell-shaped molecule H₂ and is therefore larger in the axis direction.

This means that for hydrogen applications the flange calculation according EN 1591-1, EN 13555 gasket factors determined with helium can be used for SIGRAFLEX gasket materials. For the majority of materials these gasket factors are publicly available, e.g. at www.esadata.org

Chemical resistance

For SIGRAFLEX stainless steel reinforced graphite gaskets to be used for hydrogen sealing, the flexible graphite and the stainless steel must be chemically resistant. As must the PTFE for our SIGRAFLEX MF sheets.

SIGRAFLEX flexible graphite has been and is being used successfully to seal hydrogen and it has done so for decades. It is chemically resistant against hydrogen in a temperature range from -269 °C [-452 °F] to approx. 900 °C [1652 °F]. Starting from approx. 900 °C [1652 °F] it is possible that the carbon atoms of the graphite lattice react, and methane [CH₄] is formed.

Hydrogen embrittlement of steel is well known. To assess the chemical resistance of the stainless steel used in SIGRAFLEX sealing materials we therefore would like to dig deeper:

Hydrogen can strongly impair the properties of metals through interactions with the material. Dissolved hydrogen leads to the embrittlement "phenomena", especially in iron or low-alloy steel. Mechanical properties such as ductility, deformability or fatigue strength can be adversely affected.

The absorption of hydrogen in steel can only take place in atomic form, simply due to the size of the hydrogen molecule. There are a variety of processes in which atomic hydrogen is generated. Hydrogen atoms are generated during electrochemical corrosion processes, electroplating and during cathodic protection. Also, during thermal processes by dissociation of hydrogen-containing molecules (ammonia, hydrocarbons), pure hydrogen or media containing hydrogen (e.g., 10% hydrogen in natural gas), petroleum refining or heat treatment processes, and casting and welding processes. In addition, atomic hydrogen is produced in the presence of catalytically active metals such as palladium or platinum.

After penetrating the metal lattice, the hydrogen atoms can occupy interstitial sites, attach to lattice impurities, or form hydridic bonds under certain conditions.

Therefore, the lattice structure of the alloys influences the amount and manner of intercalation of atomic hydrogen and thus the deformation mechanisms. In general, ferritic steel is considered more susceptible to hydrogen embrittlement, compared to austenitic steels, e. g. CrNi steel 1.4404 [316L]. Austenitic steel is therefore one of the standard materials in hydrogen technologies.

The various damage processes caused by hydrogen are generally referred to as hydrogen embrittlement (HE). One reason for embrittlement is that iron and steels can by themselves generate crack-opening internal stresses due to hydrogen, without the need for additionally applied stresses. This type of cracking is called hydrogen-induced cracking (HIC) and is characterized by internal cracking and/or surface blistering.

Also, if loads are applied in the form of mechanical tensile stress, hydrogen-induced stress corrosion cracking (HSCC) can occur.

These facts are crucial to the pervasive problem of hydrogen embrittlement in the petroleum industry.

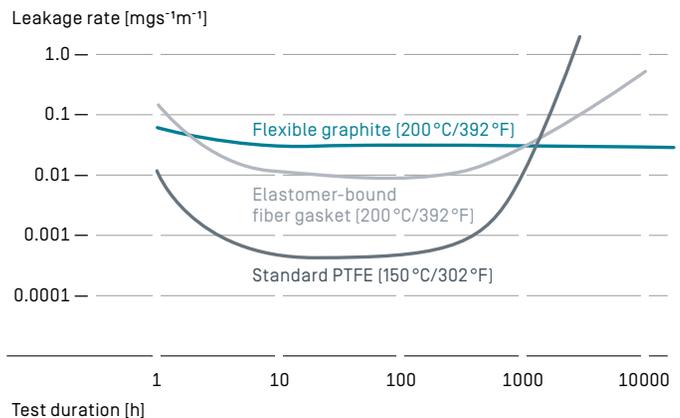
For SIGRAFLEX flat gaskets, thin smooth or tanged foils made of austenitic stainless steel 1.4404 [316L] are used for reinforcement. As the installation situation is a flat gasket in between the flange faces, these stainless steel foils are in compression and tensile stresses are negligible. SIGRAFLEX flat gaskets are not susceptible to hydrogen corrosion. They are chemically resistant.

Long-term stability

Some sealing materials used to seal hydrogen are susceptible to aging or embrittlement, which is a problem for a long-term stable leak tightness. It is well known that gaskets containing elastomers embrittle over time, especially at higher temperature, and that the creep of PTFE is resulting in a loss of gasket stress. Both problems cause a significant increase of leakage over time, please see graph 5.

Over 10000 hours and beyond stable leakage rate

Change in leakage rates of various sealing materials in long-term trials, measured on a DN 40 PN 40 flange in accordance with DIN 28090-1 and -2



Due to the warm flow characteristics of PTFE, the test temperature for this material was set at only 150 °C [302 °F]

Operational safety should be of paramount importance, not just short-term. Flexible graphite stands for safe, reliable, and long-term sealing, it does not age or embrittle when in contact with hydrogen. SIGRAFLEX flexible graphite gaskets are the optimum choice.

Range of applications

For high pressure hydrogen, e. g. 325 bar (4700 psi), metallic sealing is used. For lower pressures of typically up to 100 bar (1450 psi) high quality low leakage SIGRAFLEX graphite gaskets and sealing materials are a perfect match for a temperature range from -269 °C [-452 °F] to typically around 450 °C or 800 °C [842 °F or 1472 °F], depending if air (oxygen) is present or not. Our SIGRAFLEX technical information on temperature resistance is available at www.sigraflex.com/downloads for more details, we especially recommend to consider that there might be limitations in life time at high temperatures.



Additional information on our SIGRAFLEX sealing materials can be found under "Download Center" on our homepage. www.sigraflex.com/downloads



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Conclusion

SIGRAFLEX gasket materials help to reduce the emissions of hydrogen in numerous industrial applications, not just for the short term but for many years ahead. The same can be said for die formed packing rings made from SIGRAFLEX flexible graphite foil, used to seal valves for example. SIGRAFLEX gaskets and seals are and have been successfully used to seal hydrogen for many, many years.

One should bear in mind that similar to other energy sources such as oil or natural gas, hydrogen is highly flammable. So safe and reliable hydrogen sealing are important safety factors and demand gaskets with long-term and stable sealing characteristics with the optimum leak tightness.

Therefore, we recommend using SIGRAFLEX HOCHDRUCK PRO, SIGRAFLEX UNIVERSAL PRO or SIGRAFLEX MF.

Literature sources for assessing the durability of stainless steel:

- G. Heinke und G.H. Wagner, Mat.-wiss., u. Werkstofftech. 27, 259 – 266 (1996) VCH Verlagsgesellschaft mbH
- E. WENDLER-KALSCH. Grundlagen und Mechanismen der Wasserstoff-induzierten Korrosion metallischer Werkstoffe. In: D. KURON (Hrsg.): Wasserstoff und Korrosion. Bonn: Irene Kuron 2000, S. 7 – 52
- C.A. ZAPFFE, C.E. SIMS. Hydrogen Embrittlement, Internal Stress and Defects in Steel. In: Trans. AIME 145 (1941), S. 225 – 271
- E. Kunze, Korrosion und Korrosionsschutz, Band 1, Wiley-VCH, Berlin, 2001

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