Sealing Solutions for Hydrogen Applications

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The effect of climate change on humans and nature is leading to an increased importance of alternative sustainable energy sources that create lower emissions. Hydrogen is an essential element of the transition to renewable energy, due to the possibility of “green” production and the many diverse application possibilities. However, Hydrogen is an extremely challenging medium, which requires efficient sealing solutions. Currently, there are hardly any official norms, approvals or confirmations for gaskets in hydrogen applications available. As the number of hydrogen applications is increasing rapidly, gasket specialist Frenzelit has developed a test procedure, to prove the suitability of Frenzelit gasket materials for hydrogen applications.

1 Introduction

Calculations which were published in the world climate report in 2021 by the IPCC (intergovernmental panel on climate change), [1] describe the increase of the global surface temperature depending on various scenarios which are all based on human-caused climate change. Five simulations, based on different amounts of greenhouse gas (GHG) emissions were presented.

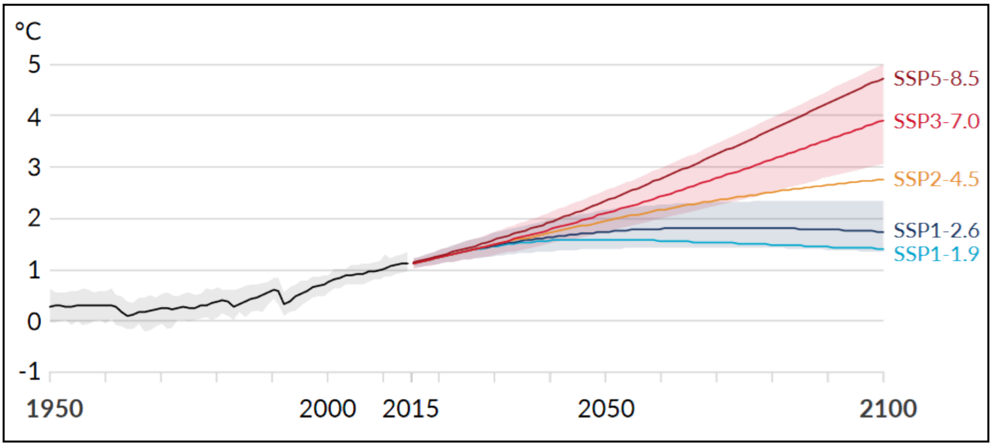

Figure 1: Development of the global surface temperature based on different calculation methods.

The less optimistic models SSP3-7.0 and SSP5-8.5 predict an average annual temperature increase of 3 °C to 5 °C until 2100. The more positive calculations assume smaller GHG- and CO_2-emissions which can be reduced to net-zero starting from 2050. In these scenarios, a minimum temperature increase of 1.5 °C is expected. Those results clearly show that the extremely high efforts have to be taken by states, industries and private households to reduce climate change and the resulting global temperature increase to the smallest possible amount. This will only be possible by a rapid switch to new, sustainable, low-emission energy sources.

Hydrogen as a sustainable energy source

The possibility to generate “green hydrogen” by using renewable energy sources, and the many different application possibilities for hydrogen have turned it into an important and promising elemtent of the energy transition. Hydrogen can be produced by various procedures, which are characterized by different color codes. Grey hydrogen is produced using fossil energy sources, usually by steam reforming, a thermal process where natural gas is transformed into H_2 and CO_2. The byproduct carbon dioxide is released into the atmosphere unused. Blue Hydrogen is produced in the same process, but here the CO_2 which is formed during the steam reforming process is captured and stored with CCS (carbon capture and storage). In contrast, green hydrogen is produced by electrolysis without any CO_2-formation. During this process, water is transferred into H_2 and O_2 using electricity from renewable energy sources (e.g. solar- or wind power) [2].

The possible applications of H_2 are extremely diverse:

- Direct use as a fuel for engines – the heating value of H_2 (33.3 kWh/kg) is approx. three times higher compared to crude oil (11.6 kWh/kg) [3].
- Use for the generation of electricity in a fuel cell.
- Further processing or transformation to alternative storage forms, fuels or chemicals (Power-to-X).

Hydrogen which is produced from renewable energy sources can be transferred to other gases, such as methane, or fuels by a chemical reaction with CO_2. This process is referred to as Power-to-X, whereas the X is a variable for various substances, such as methane, ammonia, gasoline, diesel, jet fuel or solid synthetic products. The high diversity of possible substances which can be produced ecologically with Power-to-X lead to an increasing interest in green hydrogen by the chemical industry or in mobility (shipping, aviation, or automotive industry) [4].

Reliable sealing solutions for hydrogen-infrastructure

To transport hydrogen from its production facilities to the manufacturing sites, a fully functioning and safe infrastructure is mandatory. During production as well as for transport and further processing, connections between pipe systems, tanks and valves are necessary, which require suitable gasket solutions. Sealing hydrogen gas is a very challenging task, as the H_2 is the lightest and smallest of all molecules. In comparison, with a covalent radius of 71 ppm, nitrogen is more than double the size of hydrogen (31 ppm). An even higher difference can be observed when looking at the density (H_2: 0.09 kg/m^3, N_2: 1.25 kg/m^3). In combination, these properties lead to a high mobility and diffusibility and therefore to very challenging requirements for the sealing system. Furthermore, hydrogen is also extremely challenging concerning the safety aspect, as it is highly reactive, inflammable and potentially explosive. The possibility of using metallic sealing solutions is limited, as hydrogen-induced corrosion can occur with certain types of metals.

Test procedures for hydrogen-suitability of gasket materials

Currently, official norms, approvals, and certifications about the requirements for gaskets in hydrogen applications are being created. However, with a steadily increasing number of hydrogen applications, Frenzelit has decided to conduct in-house laboratory tests on gasket materials to prove their suitability for hydrogen applications. These tests comprise of two separate parts, the first being the verification of the chemical resistance of the gasket material to hydrogen based on a procedure established by Carrier for the examination of cooling agents. The second part is a leakage test which is performed in a self-developed test rig using hydrogen as a test gas.

2 Media resistance to hydrogen

The Carrier test-procedure requires the loose storage of the test objects in an autoclave. The evaluation is done according to optical analysis and the measurement of the mass and geometry of the sample.

Figure 2: Autoclave for the loose storage of test objects in hydrogen

In total, three fiber-based gasket materials have been tested for chemical resistance:

- novapress® 850
- novapress® 880
- novapress® UNIVERSAL

The storage conditions were 3 bar and room temperature for six weeks. Three samples of each material were tested, each with a geometry of 100 mm x 64 mm.

a) novapress® 850 b) novapress® 880 c) novapress® UNIVERSAL

Figure 3: novapress® gasket material - on the left before and on the right after the media resistance test.

Optical analysis did not show damages, cracks, embrittlements or any other changes of the material. Table 1 sums up the weight- and size-changes of the material after the storage in hydrogen.

Table 1: Summary of hydrogen resistance test results, based on the Carrier test-procedure.

Material	Change of thickness [%]	Change of weigh [%]	Change of length [%]	Change of broadness [%]
novapress® 850	-0.02	-0.08	0.15	0.21
novapress® 880	0.03	0.01	0.07	0.18
novapress® UNIVERSAL	0.03	-0.01	0.00	0.03

The results of the optical examination were confirmed by the determination of geometry- and weight-change. The change of test values is generally extremely small, with magnitudes significantly lower than one percent. Therefore, the tested Frenzelit gasket materials are resistant to hydrogen and fulfill the requirements easily.

Additional, leakage tests according to DIN EN 13555 were performed using the tested novapress®-materials. Figure 4 shows two leakage curves of the gasket material novapress® 850, the blue one having been recorded prior to the storage in hydrogen, the green one afterwards.

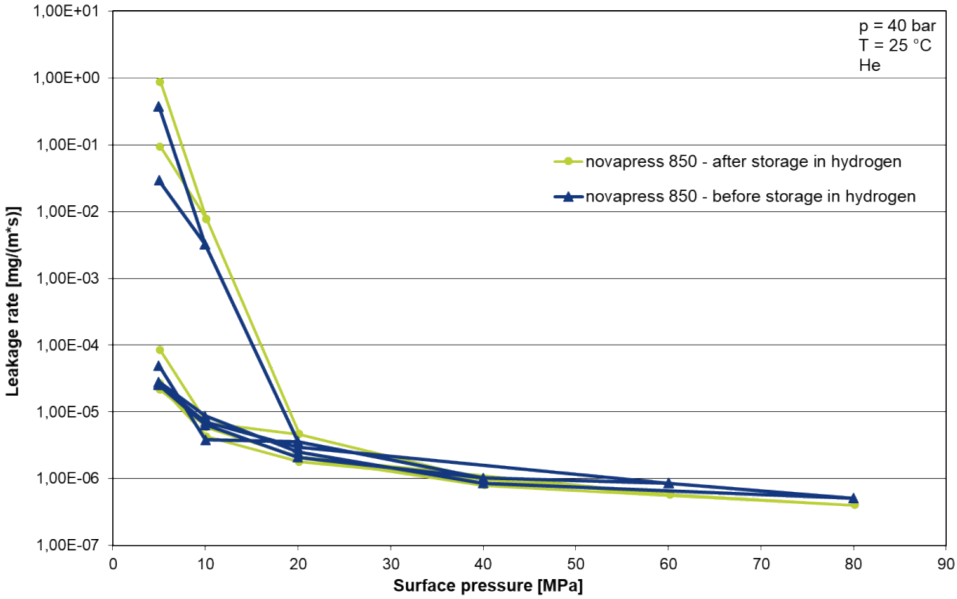

Figure 4: Leakage test of novapress® 850 according to DIN EN 13555, before (blue) and after (green) storage in hydrogen

The results obtained in the optical evaluation and the mass- and geometry-changes are confirmed by the leakage test. The curves of the original material, and the material which has been stored in hydrogen are almost identical. Although the material has been subjected to hydrogen gas for six weeks, no difference in the leakage performance can be observed.

3 Leckage Tests

Confirming the media resistance in hydrogen was the first step for confirming the suitability of our gasket materials for hydrogen applications. The leakage performance of gaskets is usually measured with nitrogen or helium as a test gas. However, hydrogen is significantly more challenging to seal due to its extremely low density and small molecule size. Therefore, the leakage performance or our gasket materials was supposed to be tested with hydrogen. To enable these tests, a test rig for initial leakage tests was designed in our in-house laboratory, where leakage rates could be determined in the flange with hydrogen as a test gas, based on DIN 28090-2/1995. According to the norm, the leakage tests are performed in a DN40/PN40 flange, where the gaskets are installed with a surface pressure of 32 MPa. An inside pressure of 40 bar hydrogen is applied, which leads to an effective surface pressure of 30 MPa on the gasket during operation. Once the hydrogen inside pressure is applied, the system is closed and remains under pressure for one hour. Afterwards, the pressure loss in the system during this time can be determined. Based on this pressure difference, the leakage rate can be determined and can be converted in different leakage units, such as ml/min or mg/(s*m).

Initially, the hydrogen leakage tests were performed for some fiber-reinforced elastomer gaskets from the novapress® product line. These results were compared to the analogous measurements with nitrogen as a test gas. In the first diagram (figure 5), the leakage rates are shown as differential pressure in [bar/h] – measurements with nitrogen in blue and hydrogen in green. For all tested materials, a higher-pressure loss in one hour is observed with hydrogen as a test gas compared to nitrogen. This confirms the assumption that compared to other gases, it is more challenging to seal hydrogen, due to its unique properties such as small size, low density and high diffusibility. Nevertheless, the pressure-loss of Frenzelit high performance gasket materials is still extremely low, especially when compared to a standard fiber-based material under the same test conditions.

As differential pressure in bar/h is not a well-established leakage unit, the results obtained in the measurements were converted into the volume-based unit ml/min (figure 6). Here, the results are very similar to the results depicted as differential pressure: The volume-based hydrogen leakage was higher than the corresponding nitrogen leakage for all tested materials. These results show that with the same application conditions and gasket materials, a higher volume of hydrogen gas will be lost due to leakage than in an identical flange system which is operated with other gases, like for example nitrogen.

Loss of gas-volume can be limited significantly by high-performance gasket materials

The measurements also show, that by using modern high-performance gasket materials, the loss of hydrogen volume can be limited to an extremely low amount. It can be observed, that extremely low leakage rates can be obtained also for hydrogen, with materials like the novapress® 850 or the novapress® 880 with the new Frenzelit inner eyelet technology, which have both been designed specifically for reducing leakage rates to the lowest possible amount. The improved inner eyelet technology developed by Frenzelit uses an innovative approach by coating the metallic eyelet material with a special elastomer layer. The elasticity of the soft layer enables an ideal adaption of the eyelet to the flange surface. Combined with the high-performance gasket material novapress® 880, this technology can increase the leakage performance significantly.

In the gasket industry, leakage rates are usually published in the weight-based unit mg/(m*s) (figure 7), for example in technical datasheets or in the gasket data according to DIN EN 13555. On the first glance, the leakage rates look extremely different when depicted in this unit. This is due to the extremely low density of hydrogen compared to nitrogen, which is a factor in the conversion from volume- to weight-based leakage (density - nitrogen: 1.25 kg/m^3, hydrogen: 0.09 kg/m^3). This means that, even though during the same time a significantly higher volume of hydrogen is leaking from the system compared to nitrogen, the leaking hydrogen gas is so light due to the low density, that the weight-loss of the leaking gas is still higher for nitrogen. This should be kept in mind, when the established leakage values in mg/(m*s) from measurements with nitrogen or helium are compared to the corresponding hydrogen leakage rates. The novapress® 850 and novapress® 880 with the new Frenzelit inner eyelet technology are at the lower detection limit of this detection method (0.001 mg/(s*m)). Therefore, no lower leakages are depicted in these diagrams, although in reality even lower leakage rates could be obtained with these high-performance gasket materials.

These results confirm once more that the gasket materials and technologies which have been designed specifically for obtaining extremely low leakage rates also give the best results in the hydrogen tests and the superior performance of novapress® 850 and the new inner eyelet technology is confirmed again.

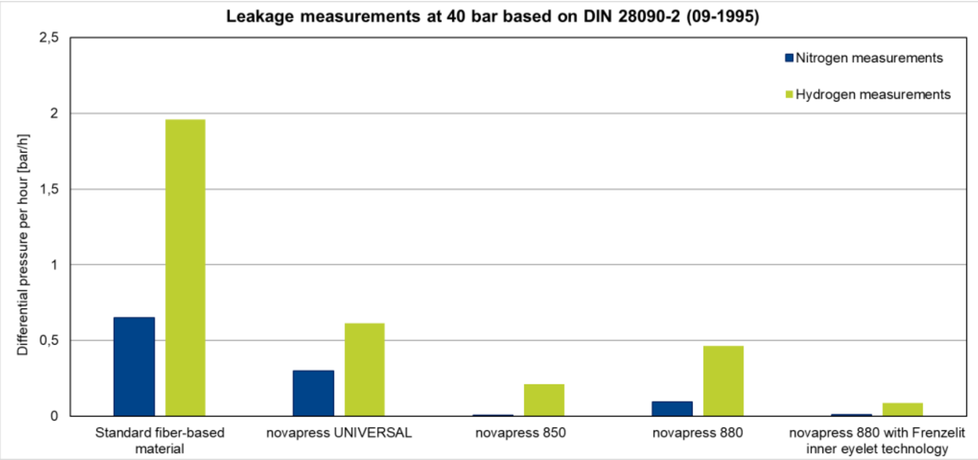

Figure 5: Leakage tests of novapress® materials with 40 bar of nitrogen and hydrogen according to DIN 28090-2 (09-1995) – leakage rate is depicted as differential pressure [bar/h].

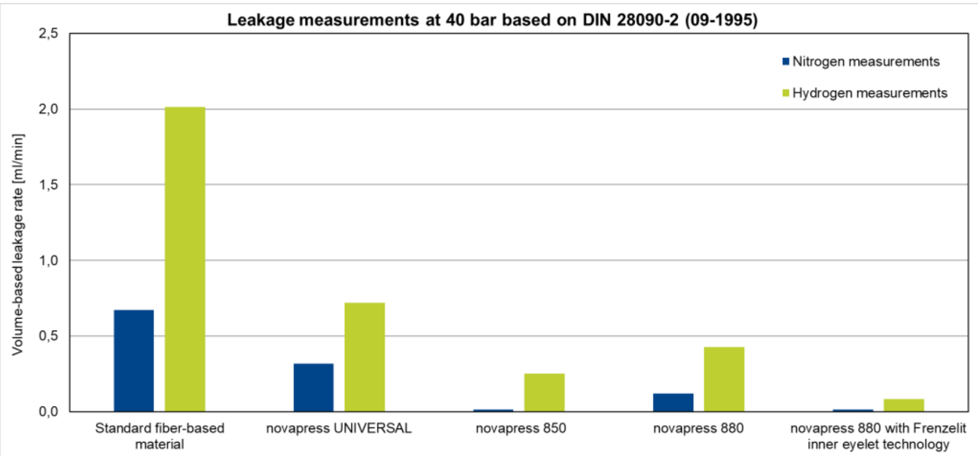

Figure 6: Leakage tests of novapress® materials with 40 bar of nitrogen and hydrogen according to DIN 28090-2 (09-1995) – leakage rate is depicted as volume-based leakage [ml/min].

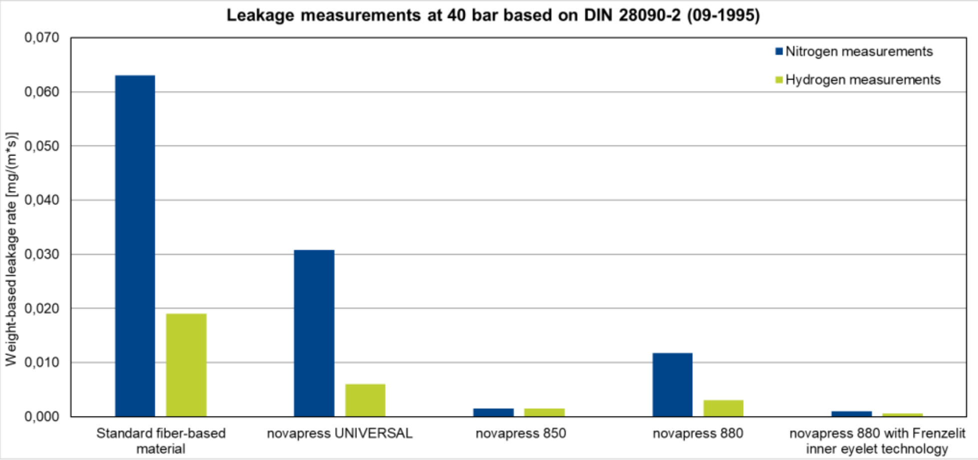

*Figure 7: Leakage tests of novapress® materials with 40 bar of nitrogen and hydrogen according to DIN 28090-2 (09-1995) – leakage rate is depicted as weight-based leakage [mg/(m*s)].*

The same measurements were also performed with some graphite-based gasket materials from the novaphit® series. Analogously, the results were also analyzed in differential pressure [bar/h], volume-based leakage [ml/min] and weight-based leakage [mg/(m*s)] (figure 8). The results of the different methods of depiction show a behavior which is analogous to the novapress® products. For the novaphit® products, it can also be seen that the products which have been designed for minimizing leakage rates are particularly well-suited for sealing hydrogen. In the case of novaphit®, this is mainly the case for the TA-Luft technology, which is included in the products novaphit® SSTC^{TA-L} and novaphit® MST. The measurements show significantly lower leakage rates for these products, compared to the novaphit® SSTC without TA-L treatment. Additionally, the new Frenzelit inner eyelet technology performs also very well in combination with novaphit® products and shows again an excellent leakage performance in hydrogen applications.

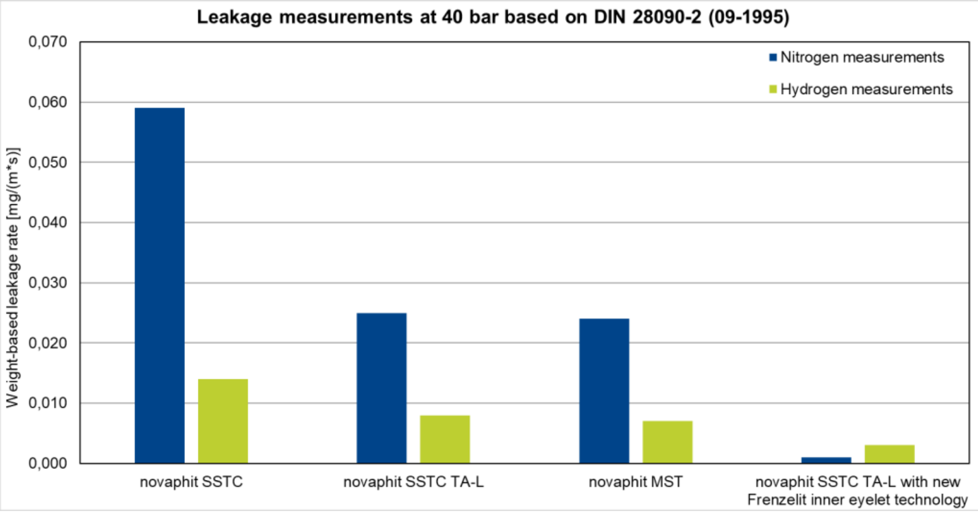

*Figure 8: Leakage tests of novaphit® materials with 40 bar of nitrogen and hydrogen according to DIN 28090-2 (09-1995) – leakage rate is depicted as weight-based leakage [mg/(m*s)].*

A universal conversion factor does not exist

It was noticeable in all the measurements that there seems to be no universally valid conversion factor for transferring nitrogen into hydrogen leakage-rates and vice-versa. For example, the pressure loss per hour is significantly higher for the novapress® UNIVERSAL than for the novapress® 850 when the measurement is performed with nitrogen. When the same test is done with hydrogen as a test gas, the novapress® 850 still clearly shows a better leakage performance than the novapress® UNIVERSAL, but the difference in pressure loss is smaller than in the measurements with nitrogen. This observation was confirmed in all other leakage tests and therefore it can be assumed, that it will not easily be possible to find a universal conversion factor for transferring nitrogen or helium leakage rates to hydrogen leakage rates.

4 Summary and Conclusion

Combination of tests approves suitability for hydrogen applications

In conclusion, the combination of the two test procedures media resistance and leakage performance is able to provide a reliable approval for the suitability of gasket materials in hydrogen applications. The media resistance test did not pose any problems for the Frenzelit gasket materials which have been tested so far. In contrast to that, the leakage performance can be quite critical for hydrogen applications. Which gasket materials is suited best for a specific hydrogen application is strongly dependent on the exact application conditions (pressure, temperature, or installation conditions). For challenging applications with higher pressures, the products novapress® 850, novaphit® MST and all products which are equipped with the new Frenzelit inner eyelet technology are especially well-suited. High-temperature applications with temperatures exceeding 550 °C can be solved by using products from the novamica® range.

5 References

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