Is waterstofverbrossing een probleem bij hogedruk aardgasleidingen?

WP4 Veiligheidsaspecten en risico's

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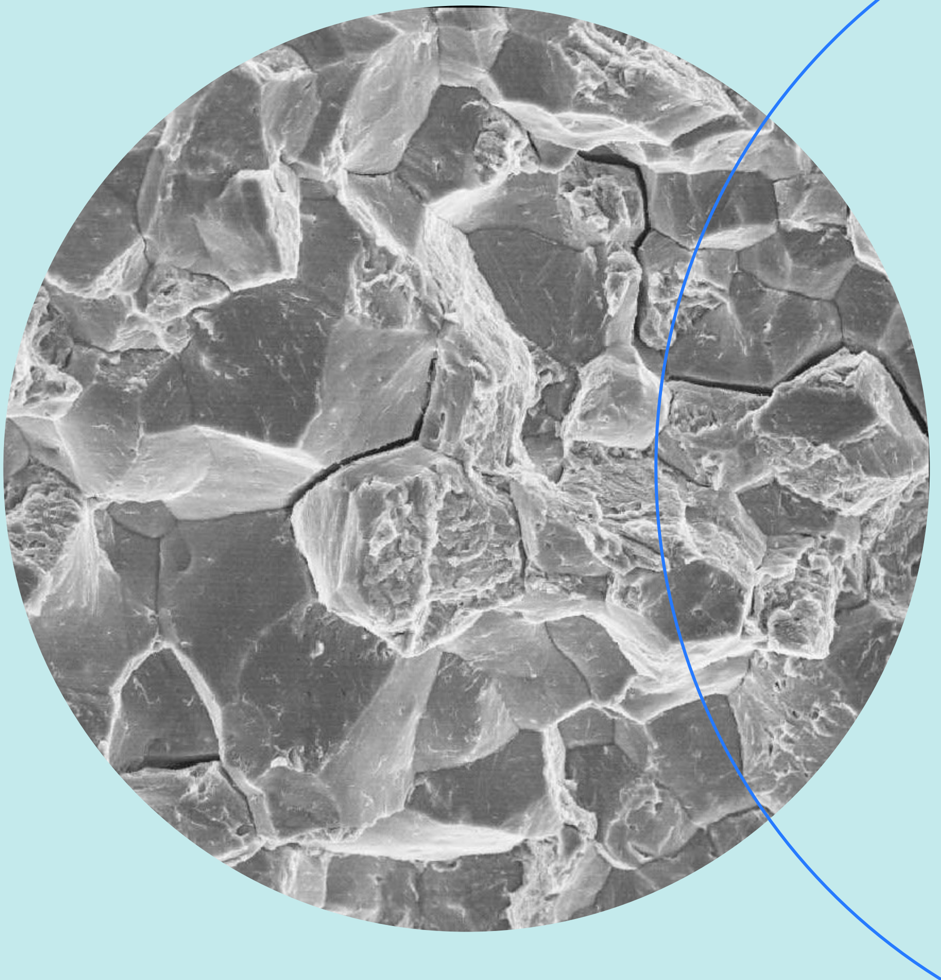
Dit project is medegefinancierd door TKI Nieuw Gas | Topsector Energie uit
de PPS-toeslag onder referentienummer TKI2019 WVIP



NLHydrogen

Augustus 2023, status: final

Kennisvraag: Is waterstofverbrossing een probleem bij hogedruk aardgasleidingen?
- Wat is waterstofverbrossing?
- Onder welke omstandigheden vindt waterstofverbrossing plaats?
- Waar komt waterstof vrij?
- Hoeveel waterstof komt er vrij?

Aanleiding

WVIP WP 4 werkt aan kennisvragen voor het borgen van waterstofveiligheid en heeft als doelstelling:

1. Het inventariseren van alle mogelijke veiligheidsrisico’s die gepaard gaan met de productie, opslag, transport en gebruik van waterstof.
2. Welke maatregelen zijn noodzakelijk om waterstof als veilige en betrouwbare energiedrager grootschalig te kunnen introduceren en daarmee de publieke acceptatie te vergroten.

Dit document is bedoeld voor alle partijen die bezig waren, momenteel bezig zijn, dan wel in de nabije toekomst betrokken zullen zijn bij de ontwikkeling van de waterstofinfrastructuur en specifiek voor vergunningverleners en vergunning aanvragers, leveranciers en beheerders van electrolysers en industrie/eindgebruikers. Dit document geeft handvatten om de vragen en antwoorden die er over dit onderwerp zijn centraal te ontsluiten met het doel de waterstofveiligheid te borgen.

Dit document beantwoordt een van de kennisvragen zoals die zijn geïnventariseerd door de deelnemers van WP4 in 2020. Voor meer informatie over en de totstandkoming van de kennisvragen zie https://nlhydrogen.nl/wp4-inventarisatie-van-kennisvragen van het WVIP project.

Het doel van het behandelen van deze kennisvraag is om de veiligheidsrisico’s van (grootschalige) productie van waterstof te verminderen.

Introduction

The energy transition and climate targets have created a pressing need to scale technologies to decarbonize hard-to-abate sectors, many of which require low-carbon gases as well as greater electrification. It is expected that partially repurposed existing gas infrastructure, combined with new dedicated hydrogen pipelines will enable hydrogen transport over long distances at an affordable cost.

However, when repurposing existing pipelines or building new pipelines, the possible negative effect of hydrogen on pipeline steel has to be considered. The effect was first observed and documented in 19th century and is known now as hydrogen embrittlement. It is defined as the adverse effect on ductility related mechanical properties at room temperature (0 to 30oC).

There is as yet no consensus on the mechanism causing the embrittlement effect in metals with several distinct hypotheses still being debated. There is a general acceptance that the embrittlement is caused by the dissolution of atomic hydrogen (H) into the metal matrix and that molecular hydrogen does not itself cause embrittlement.

In the following chapters, the hydrogen embrittlement and some of the mechanisms will be explained in detail. The relevance of these mechanisms in case of hydrogen in gas transmission pipelines is further discussed. Possible mitigation measures are described in chapter 5. A gap analysis is carried out on whether hydrogen issues in transmission pipelines are sufficiently addressed in international standards and codes.

1. Hydrogen Embrittlement

Hydrogen embrittlement is the result of the absorption of hydrogen by susceptible metals, resulting in the loss of ductility[1] and reduction of load-bearing capacity[2]. The different mechanical properties are not affected with the same intensity. Yield stress, ultimate strength and fatigue endurance limit are little affected. On the other hand, elongation at failure, fracture toughness and resistance to fatigue crack propagation are greatly reduced.

At room temperature, hydrogen atoms can be absorbed into the metal lattice and diffuse through the grains. The absorbed hydrogen may be present either as an atomic or combined molecular form. Regardless of the form, the atoms or molecules combine to form small bubbles at metal grain boundaries. These bubbles act as pressure-concentrators, building the pressure between the metal grains. The pressure can increase to levels where the metal has reduced ductility, causing the formation of minute cracks inside the material. The cracking is intergranular. That is, the crack grows along the metal grain boundaries. There are three required factors for failure due to hydrogen embrittlement (visualized in Figure 1):

High-strength carbon steel and low alloy steels are the alloys most vulnerable to hydrogen embrittlement. Steels with an ultimate tensile strength of less than 1000 MPa or hardness of less than 30 HRC are not generally considered susceptible to hydrogen embrittlement.

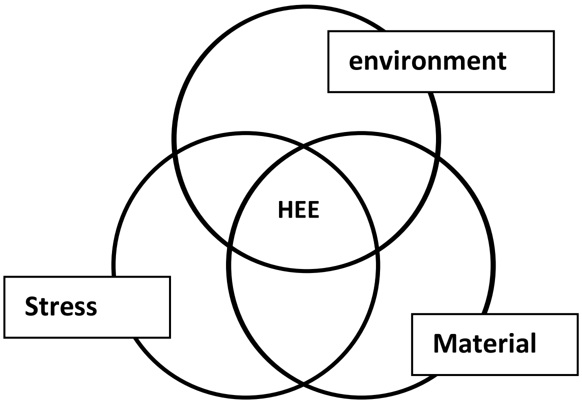


Figure 1: Factors required for failure due to hydrogen embrittlement

Some welding process (arc welding) can lead to hydrogen embrittlement. During these processes, there is a possibility of absorption of hydrogen by the material. During the arc welding hydrogen is released from moisture (for example in the coating of the welding electrodes; to minimize this, special low-hydrogen electrodes are used for welding high-strength steels).

Hydrogen creates so called interstitial solid solutions with a lot of materials due to his small atomic size. The hydrogen atoms occupy interstitial sites which leads to a weakening of the attraction in the metal lattice, resulting in a degradation of the material strength. Additionally, it is assumed that hydrogen atoms disturb the moving of dislocations leading to an embrittlement of the material. Loosing ductility is a precondition for the hydrogen induced stress corrosion cracking.

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[1] ductility is the degree to which a material can sustain plastic deformation under tensile stress before failure

[2] load-bearing capacity is the maximum ability of material to take loading before failure occurs

1.1. Hydrogen Induced Cracking (HIC)

Hydrogen Induced Cracking (HIC) is a common form of wet hydrogen sulfide (H2S) cracking caused by the blistering of a metal due to a high concentration of hydrogen. After the absorption of hydrogen atoms, the atoms of the hydrogen can be trapped at phase borders, pores, shrink holes and inclusions. The trapped atoms can recombine to hydrogen gas molecules. The recombination leads to an increase by which the resulting stress level can exceed the strength of the material. The following material degradations can occur as a result of the process described above:

- Blisters close to the material surface (in ductile materials),
- Cracks close to inclusion’s and shrink holes (mainly in materials with high strength and low ductility but also in combination with surface blisters in ductile materials).

If HIC mechanisms are overlaid by internal or external stresses the HIC cracks can form larger cracks by connecting each other. This type of crack is called stress-oriented hydrogen induced cracking (SOHIC). Hydrogen Induced Cracking is not relevant for transmission pipelines since no H2S present in transmission pipelines.

1.2. Hydrogen Stress Cracking

Hydrogen Stress Cracking is a form of Hydrogen Embrittlement that occurs when corrosion from acids like wet hydrogen sulfide and hydrofluoric acid cause atomic hydrogen to penetrate hardened or higher strength steels and cause stress cracking. The migration of hydrogen into the material and the stress, which leads to the crack growth, have to take place at more or less the same time to initiate the HSSC. The hydrogen induced stress corrosion cracking depends on external stress. If this stress doesn’t occur or stays below a certain level, Hydrogen Stress Cracking will not occur. This mechanism is not relevant for transmission pipelines, since hydrogen sulfide and hydrofluoric acid is present in transmission pipelines.

1.3. High Temperature Hydrogen Attack (HTHA)

HTHA can occur in process equipment exposed to hydrogen at elevated temperatures (at least 400F or 204°C), under dry conditions, when hydrogen dissociates into atomic hydrogen, which is then driven into the steel by the temperature and pressure of the environment. The atomic hydrogen then reacts with unstable carbides in steel to form methane gas, which accumulates in the microstructural grain boundaries, eventually leading to cracking. This is often hazardous as the equipment usually contains hydrocarbons at high pressures and temperatures and is not relevant for transmission since the operating pressure are between 10-50°C.

1.4. Hydrogen Induced Cold Crack

The hydrogen induced cold crack is also known as delayed crack. The hydrogen induced cold crack can occur for example after welding procedures. The cold crack can grow if there is stress, hydrogen or both present. The crack growing in presence of hydrogen is comparable to the HIC. Typical hydrogen concentrations in the steel are significantly higher than the concentrations with hydrogen gas pressures so this mechanism is not relevant for the hydrogen transport.

1.5. Hydrogen Enhanced Fatigue

Hydrogen can also have a significant effect on the fatigue behavior of a pipeline. The extend of this effect depends on several parameters:

- Steel grade
- Pipeline details diameter and wall thickness
- Stress concentrations
- Pressure and pressure fluctuations

This mechanism is relevant for transmission pipelines carrying hydrogen. Weld crack-like defects are always present in pipelines. Such defects can be accepted in natural gas, however when changing to hydrogen they could start to grow under fluctuated pressure and therefore are relevant for transmission pipelines.

2. Gas transmission pipelines

Typically, mid strength steel such as X42 to X60 is used for natural gas transport for pipelines with a diameter of 16-36 inches and pressures of 40-66 bar. Higher steel grades such as X65-X70 are used for large-scale transport at 66-90 bar, and it is these pipelines that are intended for dedicated hydrogen transport. Gas transmission pipelines are typically made of low carbon steels (< 0,3% Carbon) that are alloyed with other elements such as chromium (Cr), Molybdenum (Mo), Nickel (Ni), etc to derive the required strength, toughness and other desired properties. See some pipe specifications as an example (ref API 5L):

	Mass fraction, % based on heat and product analyses								Carbon Equivalent	
	C	Si	Mn	P	S	V	Nb	Ti	CE IIW	CE Pcm
	max	max	max	max	max	max	max	max	max	max
X42M	0.22	0.45	1.3	0.025	0.015	0.05	0.05	0.04	0.43	0.25
X70M	0.12	0.45	1.70	0.025	0.015	Nb + V + Ti ≤ 0.15%			0.43	0.25

2.1. Strength

Strength is the ability of a material to resist deformation caused by external load. The most widely used classification schemes are those of the API 5L and EN-ISO 3183. Both systems refer to the specified minimum yield strength (SMYS) of the steel. In Table 1, API and EN steel grades are referenced to each other for comparison purpose.

Table 1: Overview of API in relation to EN steel grades

API grade	EN Grade	Yield Strength [Mpa]	Tensile Strength [Mpa]
Grade B	L245	245	415
X42	L290	290	415
X46	L320	320	435
X52	L360	360	460
X56	L390	390	490
X60	L415	415	520
X65	L450	450	535
X70	L485	485	570
X80	L555	555	625

2.2. Hardness

Hardness is material's resistance to surface deformation. Usually, the harder the steel, the higher its tensile strength, and the lower its ductility. Hard steels are susceptible for hydrogen embrittlement.

2.3. Toughness

Toughness is the ability of a material to maintain its integrity while being pressed, pulled, or deformed. A metal that plastically deforms is tougher than a metal that will break under the same conditions. At higher temperature steel behaves more ductile then at lower temperature. The energy required at a specific temperature to fracture the steel is the toughness of the steel. Raising the yield strength (higher grade steels) makes the material more brittle.

3. Hydrogen in transmission Pipelines

One key aspect when considering hydrogen embrittlement is that molecular hydrogen, the form present in hydrogen gas at pipeline pressures and temperatures does not enter steel and cause embrittlement. For hydrogen embrittlement or other hydrogen-related degradation mechanisms to occur, atomic hydrogen (H+) must enter the metal matrix. Molecular hydrogen, H2, does not directly cause material issues; it must dissociate to H+ first to cause issues. This dissociation can be promoted by high temperatures, arcs, or other high-energy phenomena, which are rarely encountered in transmission pipelines. However, atomic hydrogen can also be generated at an actively growing fatigue crack, where the fresh metal surfaces catalyze the dissociation mechanism. In addition to H2 interacting with surface-breaking flaws, one often-raised consideration is whether H+ can enter the pipeline steel under typical operating conditions and interact with mid-wall or external defects associated with the pipeline.

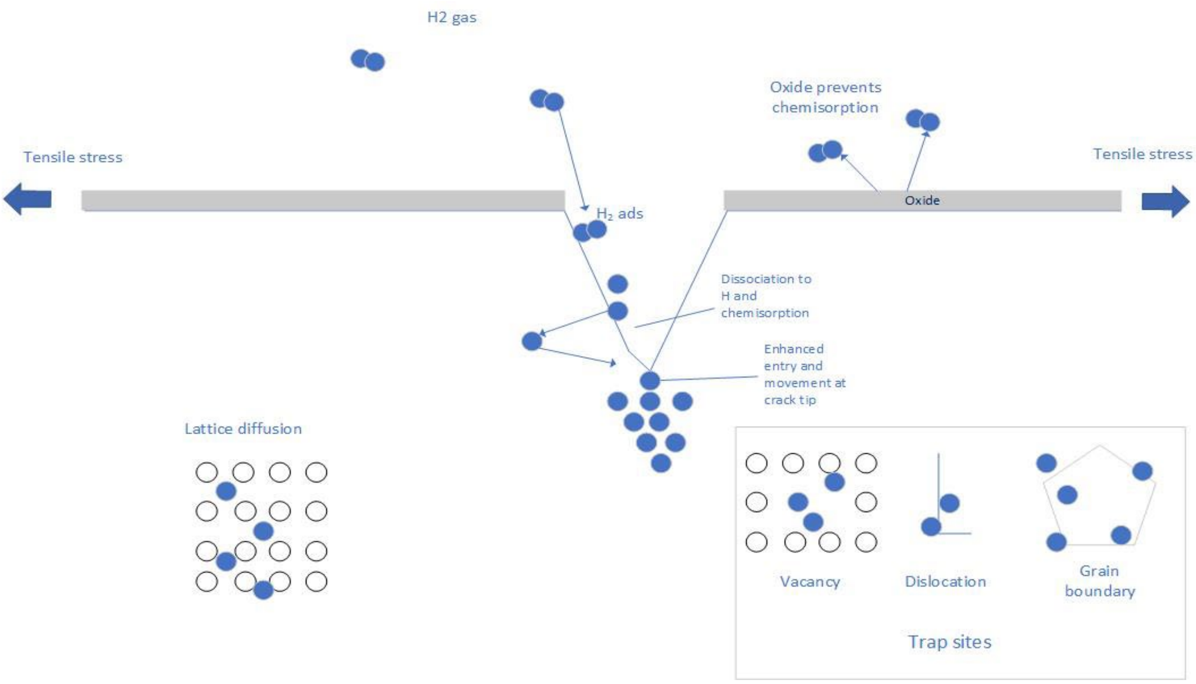

Figure 2: Hydrogen pipeline steel interaction, source: V. Monsma, T. Illson, DNV, Conversion process of the existing natural gas pipelines. Non-compliance with the ASME requirements and possible mitigation measures, PTC 2023, Berlin

The presence of microstructural traps is a key parameter influencing the hydrogen embrittlement susceptibility of pipeline steels. This is reflected in the widespread belief that embrittlement susceptibility increases with increasing yield strength, the observed effect is due to the changes in steel microstructure leading to differing hydrogen solubility and mobility rather than being directly linked to yield strength as a parameter.

Current hydrogen pipeline design codes do not consider the probability of hydrogen entry as a mitigating factor and thus for design purposes it must be considered. The entry of atomic hydrogen, under the typical operating temperatures of a pipeline, through the oxide films of steels is kinetically limited, according to the latest industry understanding. However, limited work has been performed to ascertain whether H2 dissociation and entry can occur over the lifetime of the pipe.

3.1. Crack propagation

Hydrogen, compared with natural gas, reduces the materials resistance to fatigue and enhances the fatigue crack growth rate (da/dN). Existing crack-like defects, e.g. weld defects can start to grow under a fatigue loading due to pressure cycles. The crack growth rate is a function of stress intensity factor ΔK. K is a parameter that is a combination of stress and crack size and an indication for the stress at the crack tip. ΔK indicates the changes in the stress state of the crack tip, due to for example pressure fluctuations and thus is a good parameter for analyzing fatigue crack growth. The Figure below shows crack growth rate (da/dN) vs stress-intensity factor range (ΔK) relationships for a range of carbon steels in approximately 7 MPa hydrogen gas.

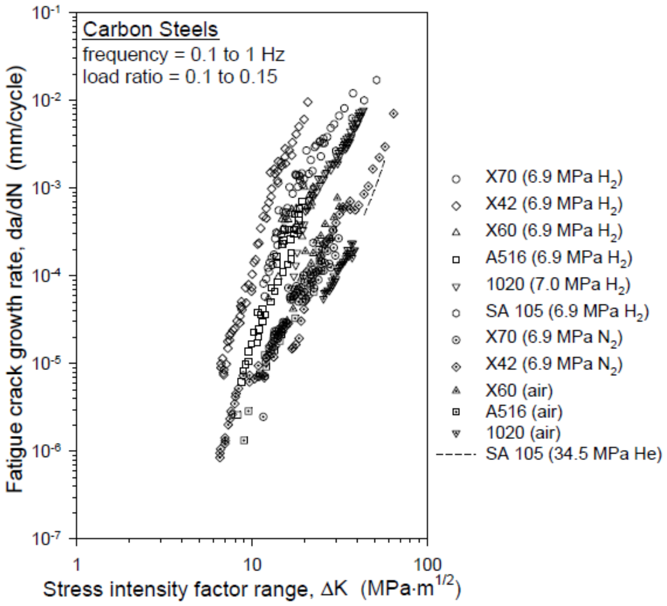

Figure 3: Fatigue crack growth rate vs stress-intensity factor range relationships for carbon steels in hydrogen gas. Fatigue crack growth rate data in air, nitrogen, or helium are included for comparison. [1]

Several general trends are apparent from the data in Figure 3. The fatigue crack growth rates in hydrogen become increasingly greater relative to crack growth rates in air or inert gas as ΔK increases. In the higher range of ΔK, fatigue crack growth rates are at least ten-fold greater than crack growth rates in air or inert gas. While the da/dN vs ΔK relationships in air and inert gas are remarkably similar, the da/dN vs ΔK relationships in hydrogen are noticeably more varied. In the higher range of ΔK, crack growth rates in hydrogen can vary by more than a factor of 10.

The da/dN vs ΔK relationships in hydrogen gas can be affected by numerous variables, including gas pressure, load ratio, load cycle frequency, and gas composition.

3.2. Integrity and safety of repurposing existing pipelines

With regard to the integrity and safety of the of the existing high-pressure natural gas network, it has been concluded that the existing gas network offers good opportunities for the transmission of 100% hydrogen and also for natural gas-hydrogen mixtures [7].

In the Netherlands, Gasunie has already converted an existing gas transmission pipeline from natural gas to a mixture of gaseous hydrogen and methane. This project has been described in "H2 in an Existing Natural Gas Pipeline [8]. To enable this, an assessment was carried out on technical safety, process safety, work safety and external safety. The pipeline, with two valve stations, was constructed in 1996 according to applicable Dutch regulations at that time and actively managed in accordance with Gasunie company standards. The hydrogen content in the pipeline is around 80% and the remaining content is methane.

4. Mitigation measures

One of the mitigation measures is the limiting hoop stress to 40% SMYS[3] of the pipeline at all points on the pipeline. This measure is conservative and has potential large economic implications for repurposing natural gas pipelines.

Another mitigation measure is limiting the pressure fluctuation. By controlling the operating conditions and limiting the pressure fluctuation the crack growth does not have to be a problem. For high pressure transmission pipelines the ΔK limit is 7.1 MPa.m½ for all steels grades with to avoid the negative effect of hydrogen on pipeline steel. A gas transmission system typically has 2 pressure cycles per day, or 75.000 in 100 years. A crack growth below 0.01 µm/cycle results in 0,75 mm in 100 years, this is acceptable for a transmission system. A maximum crack growth rate of 0.01 µm/cycle is considered acceptable for high pressure natural gas pipelines. With 2 main pressure cycles per day, as is common for gas transport pipelines, this would result in less than 1 mm crack growth in a hundred years.

This value 7.1 MPa.m½ is originated from the ASME B31.12 and project NaturalHy. The main outcome of the fatigue tests in mixtures of hydrogen and natural gas, both varying from 0 - 100%, are displayed in the figure below. ΔK indicates the changes in the stress state of the crack tip, due to for example pressure fluctuations and thus is a good parameter for analysing fatigue crack growth.

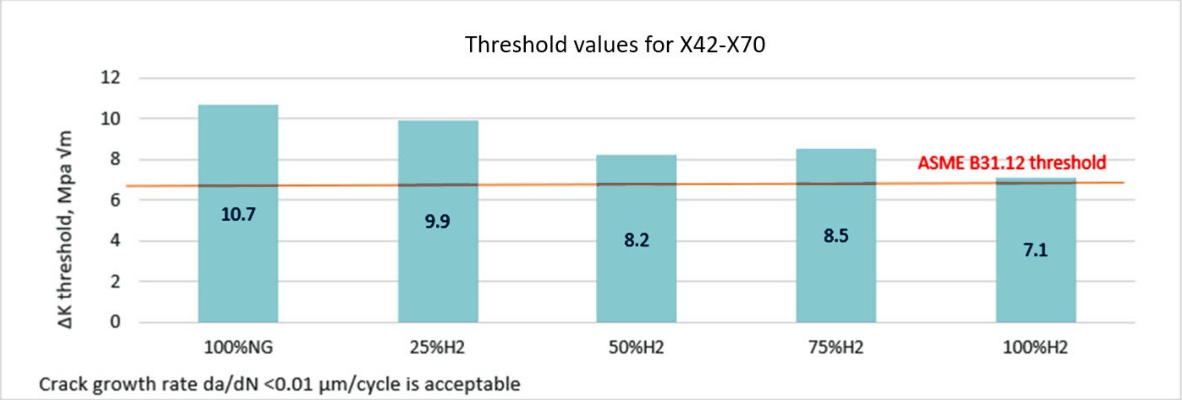

Figure 4: Threshold values for carbon steel NaturalHy vs ASME B31.12

It shall be noted that ASME B31.12 does not make any differences for the hydrogen concentrations, which is more conservative.

Gas composition:

Gas impurities can inhibit, accelerate, or have no effect upon hydrogen embrittlement. For example, O2 and CO work as inhibitors and H2S as accelerator of hydrogen embrittlement. CH4 and N2 have no effect on hydrogen embrittlement. I shall be noted that this phenomenon has not been explored at low load cycle frequencies. Figure below shows da/dN vs K relationships for X42 steel in 6.9 MPa hydrogen gas containing three different additives: oxygen, sulfur dioxide, or carbon monoxide. In each case, the gas additive lowers the fatigue crack growth rate to the crack growth rate measured in nitrogen, at least for the relatively high frequency (1 Hz) used in the study.

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[3] Specified Minimum Yield Strength

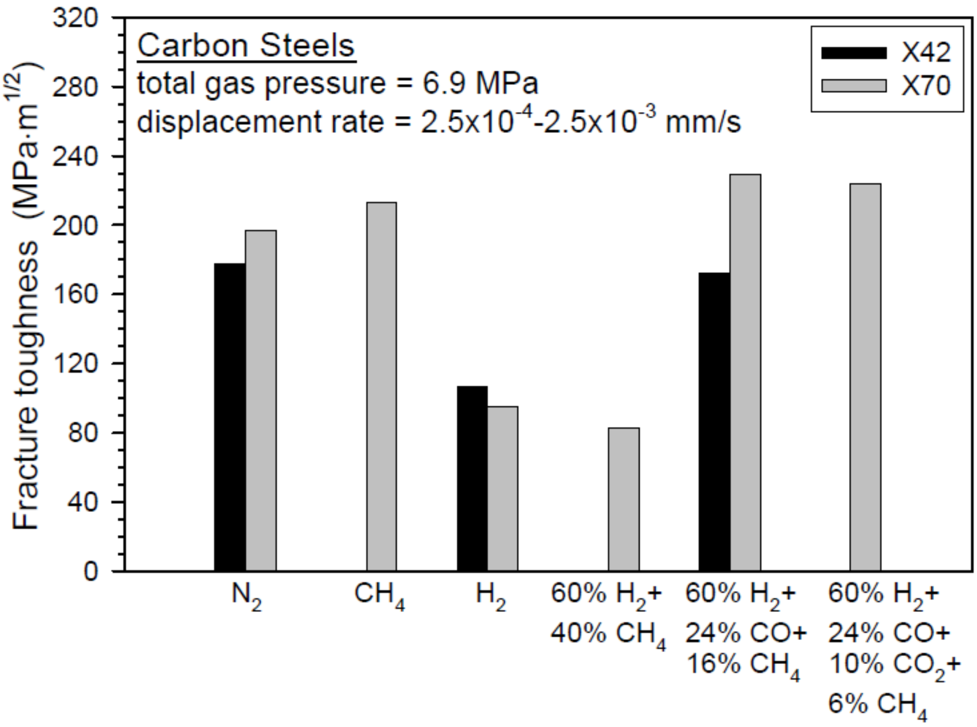

Figure 5: Effect of gas composition on fracture toughness for carbon steels

5. Gaps

Hydrogen issues are not covered (yet) in the European standards and codes. Various industry standards govern the construction and operation of natural gas pipelines, along with local regulations. However, the codes that are currently in place provide limited guidance on the design and use of hydrogen in existing pipelines. The ASME B31.12 is a primary code containing general requirements covering design and conversion of transmission pipeline with hydrogen(blends). Except this code, there is a public document “EIGA guidelines” which is not a mandatory but contains a summary of the current industrial practices for hydrogen.

ASME B31.12 recommends low carbon steel piping grades such as API 5L X52 and ASTM A 106 Grade B are for hydrogen gas, however it is not mandatory. Higher steel grades may be allowed for transporting natural gas/hydrogen blends under certain conditions after evaluation. The existing requirements ASME B31.12 for higher grades steels are quite conservative and sometimes too restrictive for conversion of existing natural transmission pipelines to hydrogen.

Experimental data regarding hydrogen (blends) transport under realistic for transmission systems is not available. A long-term study that evaluates pipeline materials and components (valves, seals, fittings, etc.) integrity under high pressure conditions and with various hydrogen blend levels (5%, 10%, 15%, 20%, 30%+) is needed.
Regarding the material, the following gaps are indicated:

- No information regarding fatigue initiation time before crack growth begins in hydrogen environments. In welded pipelines it is assumed that a defect is present, so initiation is instant, and the fatigue life is controlled by growth. This assumption may not be correct for a hydrogen environment.

- No data available regarding reductions in fracture toughness for realistic defect geometries. Having this data will improve the assessment of defects in hydrogen pipelines and the requalification of existing natural gas pipelines.

More experimental data and further research is needed to solve the identified gaps.

6. Conclusion

This document explains the mechanisms for hydrogen embrittlement in detail. Not all mechanisms are relevant for transmission pipelines. For pipeline steels the probability of hydrogen embrittlement involves a combination of material, environmental and mechanical parameters. This includes aspects such as a steel microstructure thus the probability of hydrogen entry and permeation rate through the metallic matrix, operation conditions such as temperature and pressure, and mechanical aspects such as strain rate or fatigue cycle frequency. The combination of these parameters governs the probability of hydrogen embrittlement.

Possible mitigation measures are discussed, and some could result in potential large economic implications for repurposing natural gas pipelines.

The outcome of the gap analysis showed that hydrogen issues in transmission pipelines are not covered (yet) in the European standards and codes. Several gaps are identified that demonstrate the need for more experimental data and further research.

With regard to the integrity and safety of the of the existing high-pressure natural gas network, it has been concluded that the existing gas network offers good opportunities for the transmission of 100% hydrogen and also for natural gas-hydrogen mixtures [7]. In the Netherlands, Gasunie has already converted an existing gas transmission pipeline from natural gas to a mixture of gaseous hydrogen and methane [8].

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