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HYDROGEN PIPELINES – DESIGN AND MATERIAL CHALLENGES AND MITIGATIONS

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EXECUTIVE SUMMARY

Hydrogen has been produced, transported and stored in steel for hundreds of years and there are currently thousands of kilometres of hydrogen pipelines in service around the world. These pipelines have, almost without exception (1), (2) been designed and built in accordance with hydrogen-specific codes. These codes tend to be more prescriptive in terms of allowable loading (both static and dynamic) than their natural gas equivalents and the pipelines tend to be manufactured from lower strength steel, but their existence proves that it is possible to transport gaseous hydrogen through pipelines.

The exact mechanism(s) of hydrogen damage are still the subject of much debate. It is generally agreed that most damage mechanisms involve concentration of hydrogen at regions of high stress in the metallic lattice (e.g. crack tips), and that this concentration is highest where direct dissociation from gaseous external hydrogen can occur. This dissociation of gaseous hydrogen leads directly to a various affects as discussed below.

Surface coatings and the addition of some impurities (e.g. oxygen) to gaseous hydrogen have both been shown to be effective in reducing the damage arising from hydrogen. Unfortunately it is difficult to visualise how either of these methods could be proven to be effective 100% of the time.

The principal effects of gaseous hydrogen are an increase in fatigue crack growth rate, a decrease in fracture toughness and a decrease in ductility. The magnitudes of these effects appear to vary according to different reports, this variation may be due to differences in materials, hydrogen purity or testing methods. Strength may be reduced slightly, but this is unproven.

Fatigue crack growth rates increase even in very low concentrations of hydrogen, with large increases being reported even in low partial pressures of hydrogen. Higher concentrations of hydrogen lead to higher fatigue crack growth rates, although the magnitude of these increases is dependent on multiple other factors.

Most sources appear to agree on a significant reduction in fracture toughness when measured as a stress intensity factor or CTOD, although there are large variations in the results reported. The origin of these variations appears to be related to various factors, including the hydrogen partial pressure, strain rate and steel microstructure. Importantly a number of sources report fracture toughness values in hydrogen of less than 55 $MPa.m^{1/2}$. This value is referenced in ASME B31.12 as a default minimum threshold for preventing hydrogen assisted cracking (time dependent crack growth) for Option B[1] designs, but the derivation of it is unclear. The toughness of material in hydrogen is dependent on the pipeline material as well as the hydrogen concentration. This has implications for the conversion of existing pipelines, however there is also reason to believe that laboratory small scale tests are not entirely representative of full scale pipes, and therefore may be unnecessarily conservative.

Ductility appears to decrease by 20-80% in hydrogen, with the magnitude of this decrease varying due to the material and test method used.

There does not appear to be any risk of direct hydrogen cracking under normal gaseous transportation conditions, although there is a theoretical risk associated with hard spots or welds.

[1] Option B refers to “Performance Based Designs” using fracture mechanics and material specific properties as compared to the rule based “Prescriptive Design” of Option A. Option A designs are limited to a design factor of 0.50 or 0.40 depending on location class.

Hydrogen appears generally compatible with most polymeric materials in natural gas service, however permeation and hence leakage rates may increase. Hydrogen has differing effects on non-carbon steel metals, with austenitic materials generally being less affected and higher hardness or martensitic materials being more prone to damage.

There is no clear industry consensus regarding the maximum allowable hydrogen content in existing natural gas transmission pipelines. Most guidelines refer to maximum levels of ~10-20% volume, however some documents refer to up to 100% hydrogen. The existing codes already allow up to 100% hydrogen, but are both high level and fairly restrictive in how conversions can be managed. The principal limits appear to be fatigue loading and the possibility of low toughness material or large pre-existing flaws in natural gas pipelines.

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1 INTRODUCTION

This report has been prepared by ROSEN on behalf of the European Pipeline Research Group (EPRG) as part of EPRG project 221/2020.

The climate emergency has provided a catalyst for change in the global energy system. Demand for decarbonised sustainable energy has introduced new challenges and new opportunities in both the electricity and gas networks, with particular focus on utilising hydrogen as a clean energy vector. On the European level, there are already currently several projects of varying degrees of maturity looking at options for hydrogen.

This ongoing move to a European hydrogen infrastructure has been given new impetus by recent initiatives by the European Investment Bank (3) and the ongoing revisions to EN 1594 (4) and EN 16348 (5).

The report is a literature study aimed at clarifying and summarising available information with respect to the effect of hydrogen on the structural integrity of steel pipelines and non-metallic pipeline materials.

As part of this literature study the current standards for hydrogen pipelines ASME B31.12 (6) and the AIGA / EIGA guidelines (7) are assessed, together with the draft ISO roadmap for hydrogen conversion (8), and focus areas for follow up research identified.

2 HISTORY OF HYDROGEN AND STEEL

The presence of hydrogen in steel is a not a new phenomenon. Hydrogen can be introduced into the steel lattice either during construction (steel making or welding), as a result of corrosion (particularly in the presence of hydrogen sulphide) or directly through dissociation of gaseous hydrogen at the steel surface through Sieverts' law (9). Historically the effects of construction and corrosion related hydrogen have been mitigated either through enhanced process controls (e.g. the use of low hydrogen welding techniques or "hydrogen bake-out" heat treatments) or through the use of tailored "sour service" steels with microstructures specifically designed to be resistant to hydrogen cracking.

The primary focus of this literature study is the transport of gaseous hydrogen through pipelines, therefore the main mechanism of interest is the dissociation of molecular hydrogen at a steel surface and its consequent absorption into, and diffusion through, the steel lattice following Fick's law (10). Once again, it is important to emphasise that this phenomenon is not new. Gaseous hydrogen has been produced, transported and stored at relatively high pressures in carbon steel for over a hundred years. Hydrogen pipelines have been in existence since the 1930s (11), and currently it is estimated that there are over 4500 km of hydrogen pipelines in operation worldwide (12). Data is summarised in Table 1 and Table 2.

Company	km	Miles
Air Liquide	1936	1203
Air Products	1140	708
Linde	244	152

Company	km	Miles
Praxair	739	459
Others	483	300
World Total	**4542**	**2823**

Table 1 - Existing Hydrogen Pipelines by Company

Region	km	Miles
U.S.	2608	1621
Europe	1598	993
Rest of World	337	209
World total	**4542**	**2823**

Table 2 - Existing Hydrogen Pipelines by Region

It should be noted, however, that the vast majority of these pipelines were purpose built in accordance with specific hydrogen codes. These codes differ from their (natural) gas equivalents in various ways which are detailed later in this study, although in general terms the allowable stress levels are lower for hydrogen service and there are more restrictions on material grades.

As a final note on the history of hydrogen and steel, it should be noted that a proportion of the existing European (natural) gas distribution network has already successfully transported hydrogen. For example in the UK "town gas" contained ~50% hydrogen and was widely used and transported until the early 1970s. The replacement of town gas by natural gas led to the pipeline infrastructure being re-purposed. These old pipelines have therefore already transported significant concentrations of hydrogen, although there is a significant caveat involved in that town gas also contained a large amount of carbon monoxide, which is thought to mitigate against the effects of hydrogen (see Section 9).

3 THEORY OF HYDROGEN DAMAGE

3.1 Terminology of Hydrogen Damage

Hydrogen damage is most often characterised as "hydrogen embrittlement", or HE. Barthelemy et al. (13) defined HE as " *a degradation of the steel ductility properties, the initiation of internal cracks (with or without applied stress), delayed failure ruptures, reduced fatigue lives or reduced stress intensity factors for cracks initiation, etc....*". The current draft ISO report (8) reiterates this definition of hydrogen embrittlement, and states that cracking resulting from hydrogen is a specific example of a hydrogen embrittlement mechanism. This interpretation is broadly supported by Robertson et al. (14) who state that hydrogen embrittlement is a mechanism "*in which hydrogen-enhanced plasticity processes accelerate the evolution of the microstructure, which establishes not only local high concentrations of hydrogen but also a local stress state. Together, these factors establish the fracture mechanism and pathway*".

Interestingly, in a separate paper Barthelemy (15) defines "gaseous hydrogen embrittlement" as occurring when hydrogen is found in metallic solution, with "hydrogen attack" defined as occurring when the hydrogen is present in a combined state. By this definition, "hydrogen attack" can lead to internal cracking but "hydrogen embrittlement" is related to deterioration in mechanical properties. Hydrogen attack in this case appears to relate to high temperature hydrogen attack, however the definition also appears to cover hydrogen induced cracking (HIC).

The ASM handbook **(16)** contradicts both the above, and classifies hydrogen damage as one of the following mechanisms:

- Hydrogen embrittlement
- Hydrogen-induced blistering
- Cracking from precipitation of internal hydrogen
- Hydrogen attack
- Cracking from hydride formation

This apparent confusion over terminology is symptomatic of the complexity of hydrogen damage.

3.2 Hydrogen Concentration

The susceptibility to hydrogen damage is a priori dependent on the amount of hydrogen present. At this stage it is important to recognise that, per Sieverts' law, the hydrogen concentration present within a metal is dependent on the pressure of the hydrogen gas. Although conversations about hydrogen in gas pipelines often revolve around the allowable percentage of hydrogen, the driving factor is actually the partial pressure of hydrogen which will depend on both the percentage of hydrogen and the pressure[2] (for the purposes of this review assumed to be design pressure) of the pipeline. This partial pressure can be calculated as $P_{H2} = X_{H2}.(P_{design} + 1)$ (if working in bar) where P_{H2} is the partial pressure of hydrogen, X_{H2} is the proportion of hydrogen in the blend, and P_{design} is the design pressure of the pipeline. Some examples of this are shown in Table 3.

[2] Strictly speaking the driving factor is the fugacity of the hydrogen. Calculations performed by Sandia demonstrate that for pressures below ~150 bar the difference between pressure and fugacity is < 10% therefore for ease of use the pressure may be used (101).

	Pipeline Design Pressure / barg				
	1	16	40	80	100
H_2 [%]	Hydrogen Partial Pressure at Design Pressure / bara				
1	0.02	0.17	0.41	0.81	1.01
5	0.1	0.85	2.05	4.05	5.05
10	0.2	1.7	4.1	8.1	10.1
20	0.4	3.4	8.2	16.2	20.2
50	1	8.5	20.5	40.5	50.5
100	2	17	41	81	101

Table 3 - Hydrogen Partial Pressures for Different Percentages / Design Pressures

The amount of hydrogen introduced into the steel for putative different partial pressures of hydrogen can be theoretically calculated using Sieverts' and Fick's laws. The draft ISO report (8) references these calculations and presents the following as shown in Table 4.

Hydrogen Source	Equilibrium Hydrogen Concentration (atomic ppm)*	Equivalent Hydrogen Pressure (bara)
81 bara gaseous hydrogen	0.25	81
0.01 bar H2S	14	7100
Active cathodic protection	56	11000
3 ml H2 / 100 g welding electrode	150	15000
1 bar H2S	185	16000
Cathodic Charging	650	21000

Table 4 - Hydrogen Concentrations in Steel from Different Sources

*0.25 atomic ppm hydrogen means 1 hydrogen atom per million iron atoms

Note that available literature assumes that the natural gas component of any hydrogen / natural gas blend is essentially inert and has no effect on the interaction of hydrogen and steel. Although theoretically plausible, this hypothesis does not appear to have been directly validated through testing.

From the above it appears clear that, assuming the calculations are correct, the equilibrium concentration of hydrogen in steel resulting from gaseous hydrogen transport at "standard" temperatures and pressures is orders of magnitude lower than the concentrations seen from other mechanisms.

3.3 Hydrogen Mechanisms

As part of some early research into hydrogen as an energy source, the then European Economic Community (EEC) funded work by Barthelemy et al. looking at the hydrogen embrittlement of steels (13). This work was published in 1985, and concluded that the major effect of gaseous hydrogen is to reduce the cohesive energy at the tip of a pre-existing defect. Although not explicitly called such, this appears to be a reference to the HEDE (Hydrogen Enhanced DEcohesion) mechanism although no further details were hypothesised as to exactly how this occurred. As a corollary to this, Barthelemy et al. reported that "ideal" materials with no defects (e.g. pure iron whiskers) were relatively immune to gaseous hydrogen embrittlement. The possibility of cracking generated by internal gaseous hydrogen pressure (the classic mechanism of Hydrogen Induced Cracking / HIC in sour service) was found to be less important for gaseous hydrogen transport and storage.

These broad conclusions (that gaseous hydrogen transport can degrade the mechanical properties of steel but is unlikely to directly cause cracking in the absence of pre-existing defects) appear to have gained consensus acceptance today, although the exact mechanism of embrittlement is still under discussion. As part of a PHMSA report Chen et al. summarised the competing mechanistic models as HEDE, Hydrogen Enhanced Localised Plasticity (HELP) and Adsorption Induced Dislocation Emission (AIDE) (17). This report also discussed the concepts of Internal Hydrogen Assisted Cracking (IHAC) and Hydrogen Environment Assisted Cracking (HEAC). IHAC was characterised as occurring where the hydrogen was present in the bulk material, with subsequent loading causing redistribution of the hydrogen and concentration at defects and crack tips, while HEAC was characterised by direct hydrogen dissociation at the crack tip and hence direct gaseous embrittlement.

Much academic work has been performed looking at HEDE, HELP, AIDE and other potential mechanistic models (17), although there appears still to be uncertainty regarding which models to use. Definitive conclusions appear to be lacking due to a lack of reliable experimental data. The relative importance of IHAC and HEAC is likewise still a subject of research, however there appears to be a general implicit consensus that HEAC is the dominant mechanism for gaseous hydrogen transport. The primary mechanism by which hydrogen enters the steel lattice at the crack tip appears to be by direct dissociation of gaseous hydrogen rather than by means of diffusion of pre-adsorbed hydrogen from the bulk lattice. For example Woodtli and Kieselbach (18) claim that the diffusion coefficient of hydrogen in (unstressed) steel at room temperature is very low, Chen's mechanistic model assumed direct dissociation at the crack tip as did Suresh and Ritchie (19). In contrast, Hejazi et al. when looking at the effect of gaseous hydrogen on tensile properties implied that the bulk hydrogen level was more important (20).

3.4 Importance of Steel Microstructure

There appears to be some uncertainty with respect to the importance of microstructure and steel grade with respect to hydrogen damage. Mechanistically the behaviour of hydrogen in a higher strength "modern" steel (relatively clean and a bainitic or bainitic / ferritic microstructure) would be expected to be somewhat different from a "vintage" steel with ferrite / pearlite microstructure. In the related field of hydrogen damage in sour service there is an understanding that steels of lower hardness are less prone to cracking (21). Current design codes reflect this uncertainty and do not give much detail regarding the mechanisms of damage. In general the use of lower grade materials is encouraged although there are less restrictions on the actual rather than specified minimum properties.

ASME B31.12 (6) does explicitly allow the use of grades up to X80 / L555 for hydrogen service, but tempers this by stating that the allowable stresses and operating pressures should be restricted to an extent that there is very limited value in using the material. Nonmandatory appendix A of ASME B31.12 (6) also explicitly states that only grades up to X52 / L360 are proven for service in hydrogen gas, and references the AIGA / EIGA guidelines (7) for material selection purposes.

The AIGA / EIGA guidelines (7) themselves appear somewhat confused and contradictory. Within the AIGA / EIGA guidelines (7) there is a differential between "carbon steels" and "microalloyed steels". In either case, only lower strength grades (X52 / L360 or lower) are recommended although there are significantly more restrictions in terms of chemistry and mechanical properties for microalloyed steels. Curiously, the additional restrictions for microalloyed steels only apply to electric resistance welded (ERW)[3] pipes and there appears to be no recognition that microalloying is applied to other product forms (e.g. SAW pipes).

From a fundamental understanding point of view, Koyama et al. (22) gives a good overview of recent (pre-2017) progress in microstructure-specific hydrogen mapping techniques. An example of the kinds of hydrogen segregation that could be anticipated is shown in Figure 1. Practical application of these techniques and their implications for pipeline steels appears to require further research.

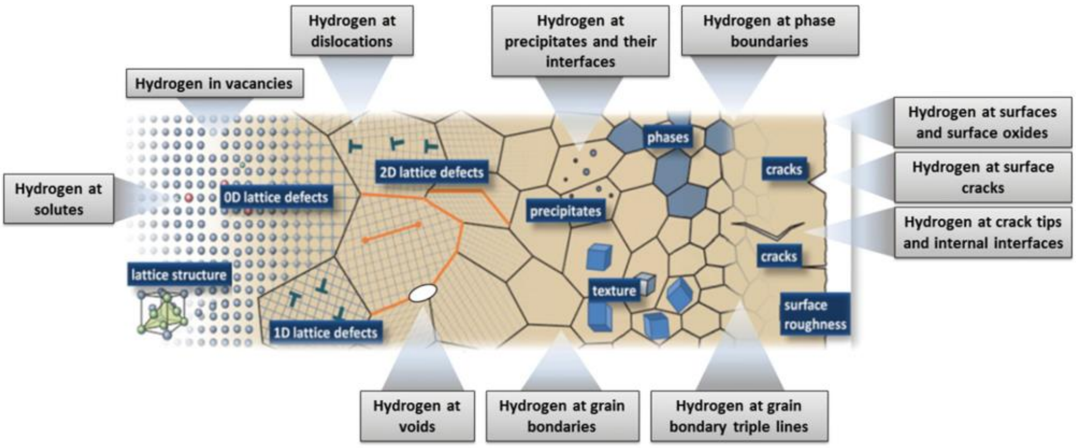

Figure 1 - Schematic Showing Possible Hydrogen Traps from Koyama et al.

The Sandia technical reference report (23) states that hydrogen permeability and solubility is only mildly affected by carbon content and microstructure, the Sandia report also reports various data looking at the effect of hydrogen on mechanical properties, in most of these cases microstructure appears to be a secondary factor with the somewhat surprising exception of fatigue crack growth rate. In this case, Sandia reported various fatigue crack growth rate tests on differing microstructures, and postulated that hydrogen facilitated fatigue crack growth principally in ferrite rather than pearlite. Fatigue is discussed in more detail in Section 7 of this report.

Hayden and Stalheim (24) report that, during development of the ASME B31.12 standard, some testing was performed on steels with various microstructures. This testing implied that the amount and morphology of any pearlite present could have an effect on the steel's resistance to hydrogen, with bainitic or bainitic / ferritic microstructures appearing to be more resistant. Hayden's paper does however caution that additional testing is required to quantify these effects.

[3] The EIGA guidelines explicitly refer to ERW; it is not clear if the intent is any form of EW pipe using the API description.

Depover et al. (25) report that for bainitic microstructures the amount of hydrogen embrittlement, as quantified by ductility loss, is dependent on the amount of diffusible hydrogen, which in turn was dependent on the carbon content and hence microstructure. Depover also reports a dependence on crosshead deformation speed (strain rate), with an increase in embrittlement reported for a decrease in strain rate.

Unsurprisingly, as-quenched martensitic microstructures appear to be most prone to hydrogen embrittlement however measured, as reported for example by Chan (26).

At a crude level it is often assumed that increasing material strength leads to an increased susceptibility to hydrogen embrittlement, this is embodied in the restrictions to maximum yield strength permitted within the AIGA / EIGA guidelines (7) and implied in ASME B31.12 (6). Tau et al. (27) tested this theory by taking three different bainitic and three different martensitic microstructures in AISI 4130 steel, then measuring the "hydrogen assisted" fatigue crack propagation for each microstructure. Tau reports that the bainitic microstructures all showed similar fatigue crack propagation rates despite having entirely different tensile strengths, whereas the martensitic microstructures exhibited higher fatigue crack propagation rates for higher tensile strengths. The simplistic correlation between increased strength and increased susceptibility to hydrogen embrittlement therefore appears to be also microstructure dependent.

Although important in terms of theoretical understanding and mechanistic modelling of hydrogen damage, of more interest for practical applications is the empirical effect. In accordance with this approach, this literature study will primarily address the empirical effects of hydrogen while paying cognisance to the ongoing mechanistic debate.

4 ROLE OF SURFACE TREATMENT AND COATING

It is axiomatic that, for any form of hydrogen damage to occur in steel, the hydrogen must first be introduced into the steel. As noted above, for gaseous hydrogen transport this can occur via Sieverts' law at the internal pipe surface. This dissociation will be dependent on the local conditions at the steel surface, ipso facto any surface treatment or coatings present will have an effect. In broad terms, the internal pipe surface can be treated, an organic coating can be applied or a metallic layer can be present (clad or lined pipe).

4.1 Current Available Design Criteria

ASME B31.12 (6) references the fact that "*Organic or inorganic coatings, alloy cladding or linings are often used as a barrier to mitigate wet H_2S corrosion and subsequent cracking*" and states that internal corrosion may be mitigated against by means of application of an internal coating. However there is no specific or explicit guidance as to what kinds of coating, and no allowance with respect to expected reduced hydrogen damage if a coating is present. There is no reference to any internal surface metallurgical treatment. The ASME code does state that the use of cladding or lining should be considered, and states that clad material in accordance with ASTM A263 (28), ASTM A264 (29) or ASTM A265 (30) can be utilised. For these materials it is permissible to design based upon the total thickness of base material and clad. The allowable stresses for these materials are calculated individually for base and clad materials and there is no increase in allowable stress for the base material to account for the presence of the cladding. For all other clad and metallic lined materials, allowable stress is based purely upon the base material thickness, and fluid service requirements are determined by the base material.

The AIGA / EIGA guidelines (7) do not make any reference to internal coatings, cladding or surface treatment.

In the analogous field of clad materials in sour service, ISO 15156 (31) states that "*Unless the user can demonstrate and document the likely long-term in-service integrity of the cladding or overlay as a protective layer, the base material, after application of the cladding or overlay, shall comply with ISO 15156-2*......." (i.e. it should be sour resistant). For coatings (not clad), the standards do not appear to allow any account to be taken of their potential protective effect.

4.2 Other Available Literature

There does not appear to be any literature available quantifying the effect of coatings, either flow coats or cladding, and as noted above, existing design codes make no allowance. Although the solubilities and diffusivities of, for example, hydrogen in stainless steels are documented (for example in (23)) and therefore the equivalent equilibrium concentration of hydrogen in the base metal could be calculated this would take no account of the possibility of damage, defects or deliberate gaps (e.g. at girth welds) in the internal coating or cladding.

The existing draft ISO technical report (8) does state that hydrogen embrittlement can only occur in the absence of a protective oxide layer, although there is no further explanation of this and no discussion about the kind of oxides required.

Holbrook et al. offer a good summary of the potential effects of oxides or other barrier coatings (and of potential inhibition methods) (32), although again the difficulties of ensuring complete effectiveness are recognised.

5 STRENGTH AND DUCTILITY IN HYDROGEN

5.1 Mechanistic Description

The exact mechanism whereby hydrogen affects the strength and ductility of steel is still somewhat under discussion (see Section 3) however there is no doubt that there is an effect on ductility, although the effect on strength is less defined. Hejazi et al. (20) reported that the fracture faces of tensile test pieces following exposure to 10 MPa gaseous internal hydrogen pressure showed partial or complete brittle fracture by quasi-cleavage, compared to the ductile fracture observed in the control argon-charged specimens. As part of her PhD thesis Moro (33) reports that API X80 tensile specimens exposed to hydrogen showed multiple cracks in the necked area and that the fracture was a combination of ductile and brittle, compared to purely ductile in the control nitrogen atmosphere.

5.2 Current Available Design Criteria

ASME B31.12 (28) includes a "materials performance factor" for derating of strength to account for the effect of hydrogen. Unless specific testing is performed, these derating factors are grade dependent, and constant for partial pressures up to 2200 psig / ~152 barg as shown in Table 5. The derivation of these numbers is unclear.

Specified Min. Strength / ksi (MPa)		System Design Pressure / psig (MPa)		
Tensile	Yield	=<1000 (6.9)	2000 (13.8)	2200 (15.2)
=<66 (455)	=<52 (359)	1.0	1.0	0.954
>66 – 75 (455 – 517)	=<60 (415)	0.874	0.874	0.83
>75 – 82 (517 – 565)	=<70 (483)	0.776	0.776	0.742
>82 – 90 (565 – 620)	=<80 (552)	0.694	0.694	0.662

Table 5 - Carbon Steel Pipeline Materials Performance Factors from ASME B31.12 Table IX-5A

These materials performance factors are separate from, and need to be multiplied together with, the design factor, which varies between 0.40 and 0.72 depending on location and design method.

The AIGA / EIGA (7) guidelines states that "hydrogen gas will reduce the tensile strength / ductility and notched tensile strength of susceptible materials in high pressure environments" but gives no quantification.

The draft ISO technical report (8) states explicitly that the "yield and tensile strength, elasticity and strain hardening are not affected" although it does state that "the fracture strain is affected and the effect becomes greater as the displacement rate in the test becomes smaller".

As noted above, despite the codes generally being based on nominal strength values there are additional restrictions on maximum permissible stresses which tend to become more onerous as the nominal strength increases. The AIGA / EIGA guidelines recommend restricting hoop stress to < 30% of the SMYS or < 20% SMTS, as well as having restrictive maxima for yield and tensile stresses while ASME B31.12 restricts the hoop stress to < ~28 or 40% (dependent on design method) of SMYS for X80 material in location class 4 (high consequence). In addition to the above, ASME B31.12 states explicitly that "*All pipelines whose material of construction has a SMYS >358 MPa (52 ksi) shall be considered Location Class 4 pipelines*". Note that X52 material supplied in accordance with recent editions of API 5L (34) has a SMYS of 360 MPa (52.2 ksi), and therefore arguably pipelines constructed of X52 should be treated as Location Class 4. It is unclear whether this interpretation is intended.

An example of the increasing restrictions applied to higher strength steels is found in Table IX-1A of ASME B31.12. This quantifies the basic allowable stresses in tension for metal piping materials, and states that the basic allowable stress at room temperature for X52 material is 22 ksi, while for X80 material it is 30 ksi (i.e. a 54% increase in SMYS only equates to a 36% increase in allowable stress).

5.3 Effect on Strength

Despite code guidance that strength is unaffected there is some evidence that this is not necessarily the case. Some published data suggests there may be slight decreases in both yield strength and ultimate tensile strength in hydrogen compared to a reference environment (either air or nitrogen).

For example according to San Marchi et al. (23) the average yield strength and UTS of a variety of steels in hydrogen are 6.4 MPa and 9.1 MPa less respectively than in the reference environment, although the difference in results is not statistically significant as proven by an Anderson-Darling Test.

Steel Grade	Reference YS / MPa	H2 YS / MPa	Reference UTS / MPa	H2 UTS / MPa
A516	375	364	535	551
A516	364	359	566	571
A106 Gr B	462	503	559	576
1080	414	421	814	794
1080(T)*	414	407	814	787
X42	366	331	511	483
X42 (T)*	311	338	490	476
X52	414	429	609	597
X60	427	422	594	590
X65	504	506	605	611
X70	584	548	669	659
X70 (T)*	613	593	702	686
X70	626	566	693	653
X70 (Arctic Grade)	697	695	733	733

Table 6 – Smooth Specimen Tensile Properties of Carbon Steels in 6.9 MPa Hydrogen Gas at Room Temperature from San Marchi et al.

*T signifies a transverse specimen

In (20) the tensile testing of a sample of X70 grade materials was carried out at a number of temperatures in 10 MPa hydrogen compared to a benchmark of 10 MPa argon at room temperature. Although the same strength grade, the study used specimens of markedly different composition and microstructures. Only one of the specimens was from the "standard" supply condition, hence the reported reference yield strengths for the other specimens being below SMYS for X70. The 3 samples were identified as S-X70 ("standard" alloy design X70 strip steel), M-X70 (lower Mn content X70) and NTB (S-X70 sample taken prior to the finish hot rolling stage). Despite the different microstructures and compositions the relative effect of hydrogen on strength was consistent. In contrast to San Marchi the effect on YS was minimal, but there was a noticeable drop in UTS.

Steel Grade	Reference YS / MPa	H2 YS / MPa	Reference UTS / MPa	H2 UTS / MPa
NTB	386	384	536	516
S-X70	518	517	606	579
M-X70	475	475	588	567

Table 7 - Effect of hydrogen on strength of X70 steels - from Hejazi et al.

Boukott et al. (35) recognise various literature sources identifying a small decrease in the yield strength (quantified by them as 2.5%) but state that "there is practically no effect of the hydrogen embrittlement on the yield strength and ultimate strength, whatever the yield strength". It should be noted that this statement is not entirely supported by the evidence presented, see Figure 2.

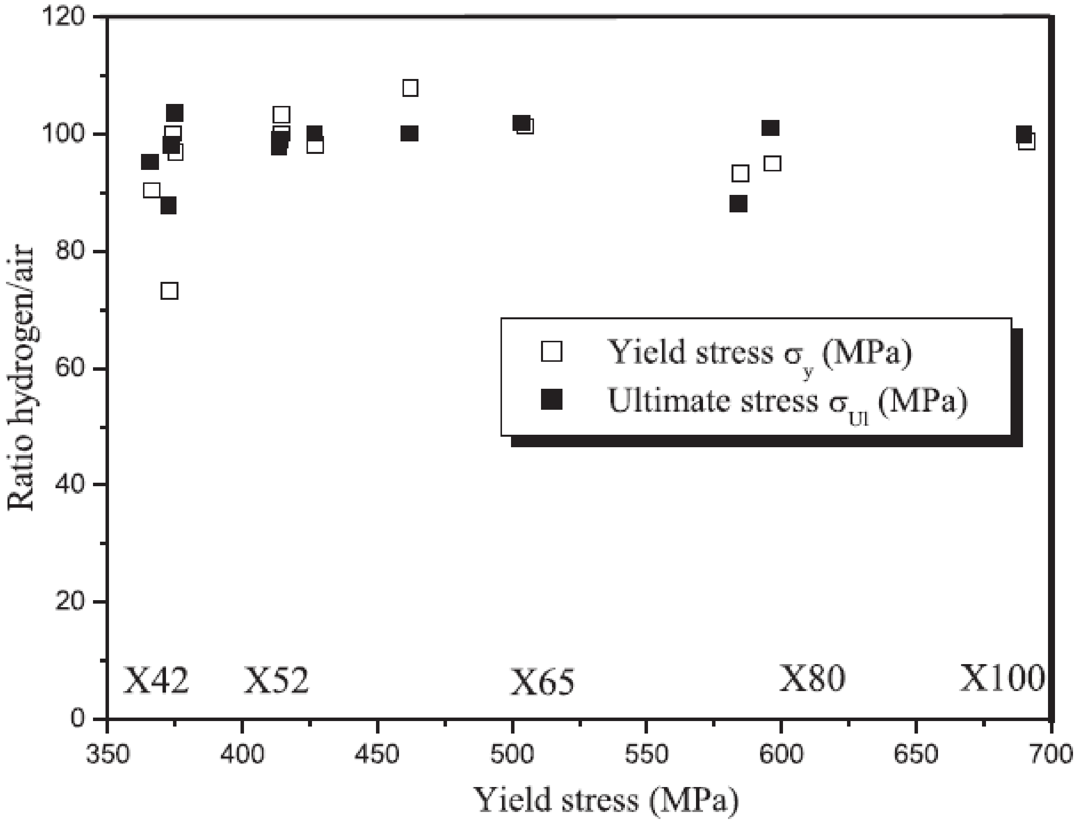

Figure 2 - Influence of Hydrogen on Strength from Boukott et al.

The effect on welds is less well defined. San Marchi also presents various data on welds indicating that exposure to 6.9 MPa gaseous hydrogen results in a slight increase in yield strength, although again not statistically significant.

Steel Grade / Welding Process*	Reference YS / MPa	H2 YS / MPa	Reference UTS / MPa	H2 UTS / MPa	Location of Fracture**	Orientation***
A106 Gr. B / MMA	393	385	615	553	NR	X
X52 / ERW	513	499	633	621	NR	X
X65 / SAW	516	505	633	624	NR	X

Steel Grade / Welding Process*	Reference YS / MPa	H2 YS / MPa	Reference UTS / MPa	H2 UTS / MPa	Location of Fracture**	Orientation***
X70 / SAW (Arctic Grade)	649	643	686	678	NR	X
A516 / MMA	338	366	531	524	BM	X
A516 / MMA	386	373	545	545	FZ	X
A516 / MMA		462		531	FZ	X
A516 / MMA		435		552	FZ	X
A516 / TIG	435	435	593	593	BM	X
A516 / TIG		462		580	FZ	X
A516 / GMA	373	386	573	517	FZ / TZ	X
A516 / MMA	424	444	505	528	FZ	P
A516 / MMA	483	386	593	559	HAZ	P
A516 / TIG	600	517	690	600	FZ	P
A516 / TIG	421	497	566	600	HAZ	P
A516 / GMA	600	580	690	676	FZ	P
A516 / GMA	331	407	559	566	HAZ	P

Table 8 - Effect of Hydrogen on Strength for Welds - from San Marchi

* MMA = Manual Metal Arc, ERW = Electric Resistance Welding, SAW = Submerged Arc Welding, TIG = Tungsten Inert Gas Welding, GMA = Gas Metal Arc Welding

** NR = Not Recorded, BM = Base Material, FZ = Fusion Zone, HAZ = Heat Affected Zone, TZ = Transition Zone

*** X = Perpendicular to the weld, P = parallel to the weld

5.4 Effect on Ductility

The effect of gaseous hydrogen on ductility is less well defined in the literature. San Marchi et al. (23) report data showing a significant decrease in reduction in area (RA) (measured on a smooth tensile specimen) in 6.9 MPa gaseous hydrogen compared to a reference environment, see Table 9.

Steel Grade	RA (%) in hydrogen	RA (%) in air or nitrogen	Ratio of hydrogen to reference RA
A516	43	69	0.62
A516	37	62	0.60
A106 Gr B	50	58	0.86
1080	7.2	16	0.45
1080(T)*	6.5	14	0.46
X42	44	56	0.79
X42 (T)*	41	52	0.79
X52	37	60	0.62
X60	27	49	0.55
X65	36	57	0.63
X70	47	57	0.82
X70 (T)*	38	53	0.72
X70	37	77	0.48

Steel Grade	RA (%) in hydrogen	RA (%) in air or nitrogen	Ratio of hydrogen to reference RA
X70 (Arctic Grade)	37	77	0.48

Table 9 - Effect of 6.9 MPa Gaseous Hydrogen on Reduction in Area on Smooth Tensile Specimens from San Marchi et al.

San Marchi also reports the effect on RA for notched tensile specimens (V notch with a 90 degree included angle, diameter 2.44 – 2.87 mm, notch root radius 0.025 – 0.051 mm) in 6.9 MPa hydrogen compared to a reference environment. As can be seen in Table 10, the reduction in ductility was even more pronounced for notched tensile specimens than for smooth. The mean reductions in RA reported were 37% for smooth tensile specimens, and 71% for notched tensile specimens.

Steel Grade	RA (%) in hydrogen	RA (%) in air or nitrogen	Ratio of hydrogen to reference RA
A516	5.4	30	0.18
A106 Gr. B	8.0	26	0.31
X52	7.0	15	0.47
X60	8.4	23	0.37
X65	6.1	21	0.29
X70	8.7	45	0.19
X70 (Arctic Grade)	8.6	42	0.20

Table 10 – Notched Tensile Ductility in Hydrogen Compared to a Reference Environment - from San Marchi et al.

Li (36) reports a decrease in ductility of 15-30% for X80 pipeline steels when electrolytically charged to simulate the (relatively low) concentration of 0.72 MPa gaseous hydrogen. Hejazi et al. (20) also report a decrease in ductility (as measured by elongation) of 22-35% for X70 steels, although their measurements were performed using a gaseous hydrogen concentration of 10 MPa. Boukott et al. (35) concur that there is a significant impact on ductility, they report that the magnitude of the effect is strongly influenced by the yield strength of the pipe (higher strength pipes showing a greater decrease), see Figure 3. Note that this appears to be based on a lot of the same data already referenced in San Marchi.

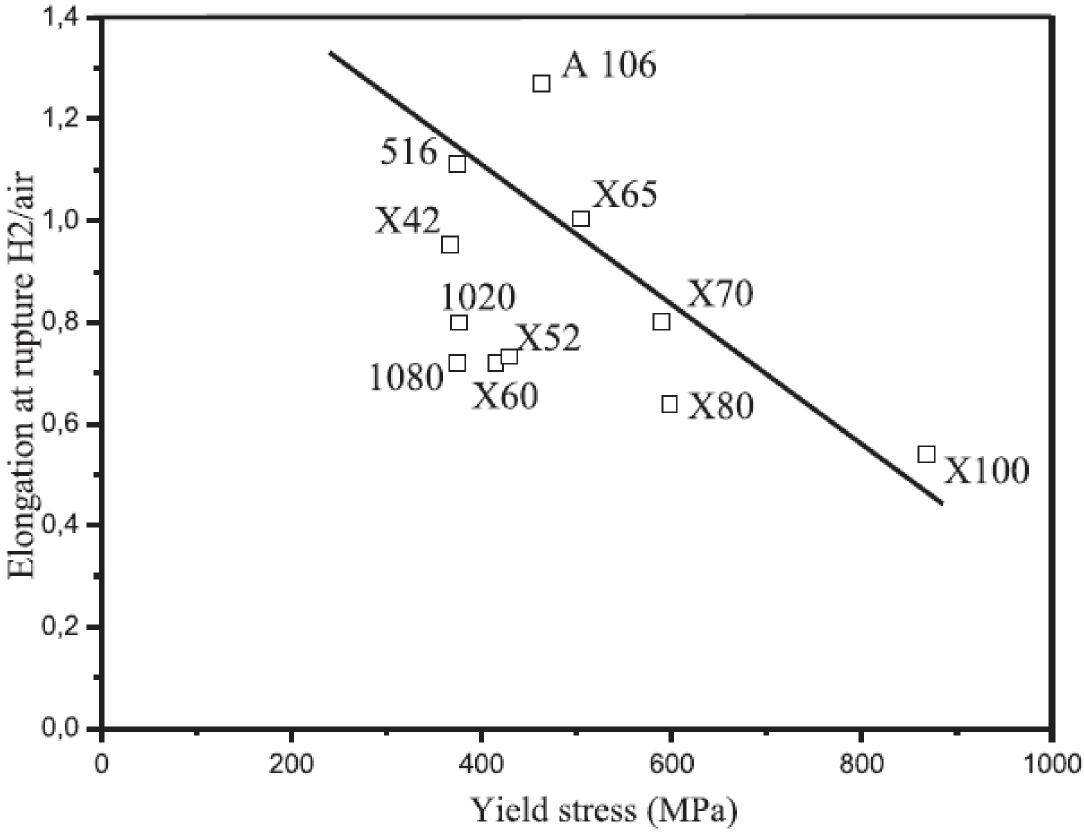

Figure 3 - Effect of Hydrogen on Elongation - from Bourkott et al.

The current draft ISO technical report (8) states that the "fracture strain" is affected by gaseous hydrogen, with this effect becoming greater as the displacement rate in the test becomes smaller, however this is not quantified.

Once again, the effect on welds is less defined, San Marchi presents some data for smooth tensile specimens tested in 6.9 MPa gaseous hydrogen compared to an inert reference environment as shown in Table 11.

Steel Grade / Welding Process*	RA (%) in hydrogen	RA (%) in air or nitrogen	Orientation**	Ratio of hydrogen to reference RA
A106 Gr. B / MMA	40	77	X	0.52
X52 / ERW	20	40	X	0.50
X65 / SAW	30	56	X	0.54

Steel Grade / Welding Process*	RA (%) in hydrogen	RA (%) in air or nitrogen	Orientation**	Ratio of hydrogen to reference RA
X70 / SAW (Arctic Grade)	37	69	X	0.54
A516 / MMA	31	72	X	0.43
A516 / MMA	48	69	X	0.70
A516 / MMA	77		X	1.12
A516 / MMA	66		X	0.96
A516 / TIG	38	71	X	0.54
A516 / TIG	20		X	0.28
A516 / MAG	12	73	X	0.16
A516 / MMA	46	82	P (FZ)	0.56
A516 / MMA	38	66	P (HAZ)	0.58
A516 / TIG	44	67	P (FZ)	0.66
A516 / TIG	58	64	P (HAZ)	0.91
A516 / MAG	42	67	P (FZ)	0.63
A516 / MAG	47	70	P (HAZ)	0.67

Table 11 - Effect of Hydrogen on Smooth Tensile Ductility for Welds - from San Marchi

*MMA = Manual Metal Arc, ERW = Electric Resistance Welding, TIG = Tungsten Inert Gas, MAG = Metal Active Gas, SAW = Submerged Arc Welding

** X = Cross weld, P(FZ) = Parallel to the weld, specimen in the fusion zone, P(HAZ) = Parallel to the weld, specimen in the HAZ.

San Marchi also presents equivalent data for notched tensile specimens, as shown in Table 12.

Steel Grade	RA (%) in hydrogen	RA (%) in air or nitrogen	Orientation	Ratio of hydrogen to reference RA
A106 Gr. B / MMA	14	49	X	0.29
X70 / SAW (Arctic Grade)	10	35	X	0.29
X70 / MMA (Arctic Grade)	9	20	X	0.45
A516 / MMA	10	62	P (FZ)	0.16
A516 / MMA	17	32	P (HAZ)	0.53
A516 / TIG	17	36	P (FZ)	0.47
A516 / TIG	9	32	P (HAZ)	0.28
A516 / MAG	12	25	P (FZ)	0.48
A516 / MAG	10	34	P (HAZ)	0.29

Table 12 - Notched Tensile Ductility of Carbon Steel Welds - From San Marchi

6 FRACTURE TOUGHNESS IN HYDROGEN

6.1 Mechanistic Description

As discussed in Section 3, the mechanism by which hydrogen affects the fracture toughness of steels is complex, with various different mechanistic models available. It is important to note that all of the competing models assume that the driving factor is the concentration of hydrogen at the tip of pre-existing defect or crack. Again as noted above, the diffusion coefficient of hydrogen in a steel lattice at ambient temperatures is relatively low. In turn this can lead to potential situations where the speed of crack propagation is such that the tip rapidly outruns the initial hydrogen concentration and propagates into the (comparatively low hydrogen and hence tougher) matrix. The potential paradox implied by this (crack initiation / propagation in a high hydrogen localised environment followed by crack arrest in the low hydrogen matrix) is discussed in more detail below. Koers et al. (37) reported various testing and modelling activities, demonstrating the importance of loading rate and proposing a numerical model to explain their experimental results.

A consequence of this loading rate dependence is that gaseous hydrogen does not significantly affect Charpy impact energy (see Li (36)). This unfortunately means that correlations between Charpy impact energy and fracture toughness which are valid in air or natural gas may not be applicable for hydrogen service. The Sandia report (23) explicitly states that "*Consequently, correlations between impact properties and fracture toughness are not appropriate for hydrogen-assisted fracture*".

6.2 Current Available Design Criteria

ASME B31.12 (6) offers two methods for design for fracture control and arrest, although these are only required when a pipeline is designed to operate at a hoop stress over 40% of the SMYS. Option A is a prescriptive design method, while Option B is performance-based.

ASME B31.12 Option A is based on testing in accordance with Annex G of API 5L (34), and hence in air. No specific fracture toughness nor environmental testing is required, and the relevant "design factor" varies between 0.40 and 0.50 depending on location. Allowable stress levels are restricted by "materials performance factors" as outlined in Table 5. It should be noted that the requirements within Annex G are completely based on tests for crack arrest in natural gas, although they do assume higher design factors. The mechanistic derivation of the approach within Option A is unclear, as is the rationale for only requiring 40% shear area in the Drop Weight Tear Test.

ASME B31.12 Option B allows that "the pipe and weld material shall be qualified for adequate resistance to fracture in hydrogen gas at or above the design pressure and at ambient temperature", and references Article KD-10 of ASME BPVC, Section VIII, Division 3 (38) with various additional restrictions. Option B allows a "material performance factor" of 1.0 to be used, but is restrictive in that only material of the same grade and heat treatment condition with tensile and yield strengths not more than 5% higher than the material qualified can be used. Option B is also restrictive, in stating that K_{IH} shall not be less than 50 ksi.in$^{1/2}$ (55 MPa m$^{1/2}$). The derivation of this value is unclear.

The AIGA / EIGA (7) guidelines for toughness reference Charpy testing in air, with acceptance criteria being more demanding than base API 5L requirements. Example requirements for micro-alloyed steels tested at 0 deg. C are shown in Table 13.

	Absorbed Energy Transverse / ft-lb (J)		Absorbed Energy Longitudinal / ft-lb (J)	
Specimen Size	Average	Minimum Individual	Average	Minimum Individual
Full size	69 (94)	52 (71)	87 (118)	65 (88)

	Absorbed Energy Transverse / ft-lb (J)		Absorbed Energy Longitudinal / ft-lb (J)	
3/4	52 (71)	39 (53)	65 (88)	49 (67)
2/3	35 (48)	35 (48)	58 (78)	43 (58)
1/2	26 (35)	26 (35)	43 (58)	32 (43)
1/3	17 (23)	17 (23)	29 (39)	22 (30)
1/4	13 (18)	13 (18)	22 (30)	16 (22)

Table 13 - Charpy Energy Requirements for Micro-alloyed steels - from AIGA / EIGA Guidelines

In an appendix the AIGA / EIGA guidelines reference various tests as being "typical tests for hydrogen embrittlement" as detailed in Table 14, however no additional guidance is given on acceptance criteria.

Type of Test	Description	Applicable Test Standards
Tensile and notched tensile	"The susceptibility of metals to hydrogen embrittlement can by evaluated by conducting tensile tests on smooth or notched specimens in a hydrogen environment"	ASTM G142-98 (39)
K_{IH} test	"K_{IH} test is a fracture mechanics test to evaluate the threshold stress intensity factor for hydrogen stress cracking"	Modified versions of various ISO and ASTM specifications
Slow strain rate (SSR) test	"Since the hydrogen attack is a time dependent process, a slow strain rate test can be employed to evaluate the strain rate sensitivity of the materials in hydrogen environment"	ASTM G129-00 (40)
Disk pressure test	"Disk pressure test measures susceptibility to hydrogen embrittlement of metallic	ASM F1459 (41)

Type of Test	Description	Applicable Test Standards
	materials under high pressure hydrogen”	

Table 14 - Hydrogen embrittlement tests - from AIGA / EIGA guidelines section B4

API 579-1/ASME FFS-1 (42), although not a design code, does address hydrogen embrittlement in service. Section 9F.4.6.2 states that “*Hydrogen dissolved in ferritic steel can significantly reduce the apparent fracture toughness of a material. Fracture initiation is enhanced when hydrogen diffuses to the tip of a crack. If rapid unstable crack propagation begins, however, diffusing hydrogen cannot keep pace with the growing crack, thus the resistance to rapid crack propagation increases with increasing rate and the rate slows to establish equilibrium between the growth rate and the hydrogen delivery rate. Subcritical growth may then continue at the equilibrium rate*”. According to API 579, fracture toughness or Charpy data tested in air may be used to assess hydrogen charged steels for dynamic crack initiation and arrest since the Master Curve is a lower bound and sufficiently conservative. It is however noted that sub-critical crack growth is not addressed by this approach, so a flaw that is acceptable may grow over time to become unacceptable. Attention is also drawn to the fact that long term exposure to hydrogen may produce irreversible damage to material (micro-cracks) which will reduce the apparent fracture toughness (see Section 8), however no guidance is given as to how to address this. It is noted that API 579 is primarily a fitness for service code for downstream process vessels which typically have a richer alloy chemistry than typical carbon steel pipelines.

It should be emphasised that, given the uncertainties outlined below, the correlations between laboratory measurements in hydrogen, in-air crack arrest toughness and the true behaviour of pipeline carbon steel should be treated with caution pending further experimental validation.

6.3 Available Fracture Toughness Data

The most comprehensive recent summary of available data is presented by Somerday (43). This is reproduced in Table 15.

Steel	Yield Stress (MPa)*	Reduction in Area (%)*	Environment	Displ. rate (mm/s)	K_{Ic} (MPa / $m^{1/2}$)	K_{IH} (MPa / $m^{1/2}$) **	dJ/da (MPa)	K_{IH} / K_{Ic}
A516	375	69	Air	8.5×10^{-3}	166***	-	516	-
			3.5 MPa H_2		-	131	47	0.79
			6.9 MPa H_2		-	113	55	0.68
			20.7 MPa H_2		-	98	54	0.59

Steel	Yield Stress (MPa)*	Reduction in Area (%)*	Environment	Displ. rate (mm/s)	K_{Ic} (MPa / $m^{1/2}$)	K_{IH} (MPa / $m^{1/2}$) **	dJ/da (MPa)	K_{IH} / K_{Ic}
			34.5 MPa H_2		-	90	57	0.54
1080	414	16	6.9 MPa N_2	$2.5 \times 10^{-4} - 2.5 \times 10^{-3}$	111	-	42	-
			6.9 MPa H_2		-	81	13	0.73
X42	366	56	6.9 MPa N_2	$2.5 \times 10^{-4} - 2.5 \times 10^{-3}$	178***	-	70	-
			6.9 MPa H_2		-	107	63	0.60
X42	280	58	Air	$=<3.3 \times 10^{-4}$	147***	-	111	-
			2.0 MPa H_2		-	101 - 128	-	0.69 - 0.87
			4.0 MPa H_2		-	85	36	0.58
			6.5 MPa H_2		-	69	31	0.47
			7.0 MPa H_2		-	73****	-	0.50
			8.0 MPa H_2		-	59****	-	0.40
			10.0 MPa H_2		-	53****	-	0.36
			12.2 MPa H_2		-	57****	-	0.39
			16.0 MPa H_2		-	46****	-	0.31
X60	473	62	6.9 MPa He	8.5×10^{-3}	142	-	123	-

Steel	Yield Stress (MPa)*	Reduction in Area (%)*	Environment	Displ. rate (mm/s)	K_{Ic} (MPa / $m^{1/2}$)	K_{IH} (MPa / $m^{1/2}$) **	dJ/da (MPa)	K_{IH} / K_{Ic}
			6.9 MPa H_2		-	104	43	0.73
X70	584	57	6.9 MPa N2	$2.5 \times 10^{-4} – 2.5 \times 10^{-3}$	197	-	251	-
			6.9 MPa H_2		-	95	23	0.48
X60	434	88	5.5 MPa H_2	$8.3 \times 10^{-5} – 8.3 \times 10^{-4}$	-	85	-	-
			21 MPa H_2		-	82	-	-
X80	565	81	5.5 MPa H_2	$8.3 \times 10^{-5} – 8.3 \times 10^{-4}$	-	105	-	-
			21 MPa H_2		-	102	-	-

Table 15 - Fracture Toughness for Carbon Steels in Hydrogen Gas at Room Temperature - from Somerday

* YS and RA based on smooth tensile specimen in air

** Calculated from $K = (JE/1-v^2)^{1/2}$

***reported fracture toughness may not be valid plane strain measurement

****measured from burst tests on pipes with machined flaws.

As seen above, Somerday reports the fracture toughness in gaseous hydrogen to be ~31-87 % of that reported in a reference environment (as defined by K_{IH} / K_{IC}). This order of magnitude is also reported as part of the draft ISO report (8), see Figure 4. Notably, the reported K_{IH} is mainly above the ASME restriction of 55 MPa $m^{1/2}$ but does drop below this in a couple of instances.

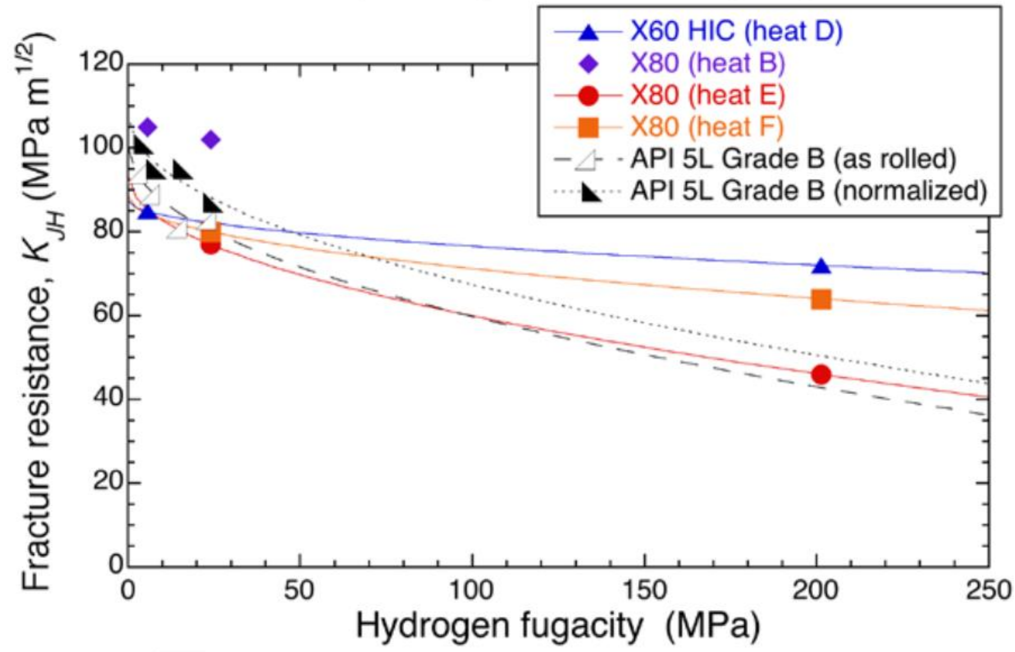

Figure 4 - Example effect of hydrogen gas pressure on fracture toughness of pipeline steels – from CEN/TC 234 WI 00234080

Mueller-Syring (44) also reports reductions in fracture toughness of ~30-70% as shown in Table 16.

Environment	100%N2	20 bar H2	40 bar H2	60 bar H2
Toughness (MPa.m$^{1/2}$) for X52	150	108	90	76
Toughness (MPa.m$^{1/2}$) for X70	120	76	58	44

Table 16 - Effect of Hydrogen on Toughness - from Mueller-Syring

Capelle et al. (45) reported slightly different results as part of the NATURALHY project. Results for fracture toughness were reported for various pipe steels in terms of $K_{p,i}$ (notch stress intensity factor at fracture initiation), $K_{I,i}$ (stress intensity factor at fracture initiation) and δ_i (crack tip opening displacement. Results were reported for steels tested in air, and the same steels following electrolytic charging, and are summarised in Table 17 (all values are mean of 2 results unless stated otherwise).

Steel Grade	Fracture Toughness Parameter	Value in Air	Value with Electrolytic Hydrogen Charging	% Change
X52	$K_{p,i}$	69.25 $MPa.m^{1/2}$ (mean of 8 results)	65.73 $MPa.m^{1/2}$ (mean of 6 results)	-5.1
X52	$K_{I,i}$	95.54 $MPa.m^{1/2}$	85.55 $MPa.m^{1/2}$	-10.5
X52	δ_i	0.178 mm	0.098 mm	-44.7
X70	$K_{I,i}$	118.59 $MPa.m^{1/2}$	112.97 $MPa.m^{1/2}$	-4.7
X70	δ_i	0.112 mm	0.090 mm	-19.9
X100	$K_{I,i}$	151.82 $MPa.m^{1/2}$	150.61 $MPa.m^{1/2}$	-0.8
X100	δ_i	0.108 mm	0.121 mm	+11.6

Table 17 - Effect of Hydrogen on Fracture Toughness of Pipe Steels - from Capelle et al.

According to Capelle, the stress intensity factor at fracture initiation is largely unaffected by hydrogen. The crack tip opening displacement (CTOD) at fracture initiation is reported to be affected, but this appears to be strongly strength dependent. For X100, hydrogen charging even appears to increase δ_i.

In a separate report also based on NATURALHY data, Capelle et al. (46) emphasise the time dependence of “fracture toughness” in hydrogen by calculating the absorbed hydrogen concentration under electrochemical charging and comparing this to both time and the “work of local fracture” emanating from a notch. In the example shown below, the effective fracture toughness of the material (in this case X52) decreases significantly after ~100 hours exposure.

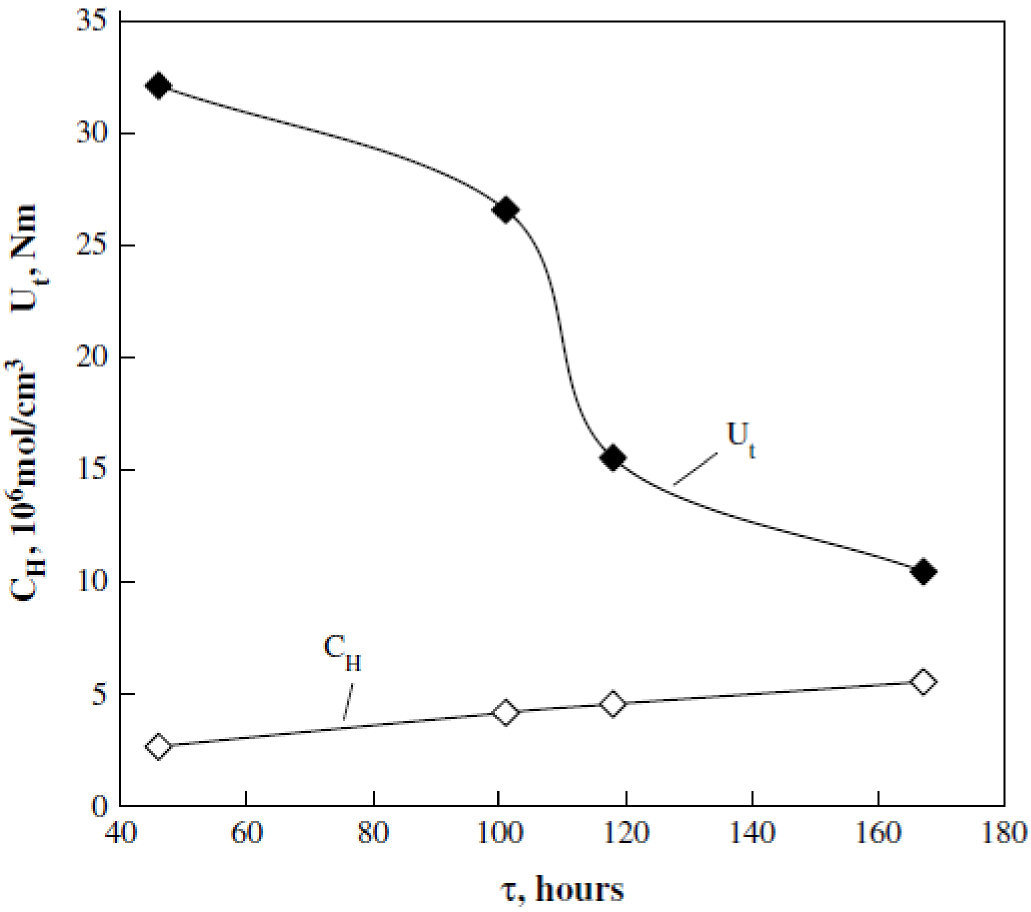

Figure 5 - Effect of Time on "Total Work of Local Fracture (U_t)" and Hydrogen Concentration (C_H) - From Capell et al.

Conversely, Briottet et al. (47) report a significant decrease in fracture toughness (as represented by CTOD) for X70 steels with even small partial pressures of hydrogen as shown in Figure 6. Note that total pressure in all these tests was 85 barg, with the environment being nitrogen unless otherwise stated.

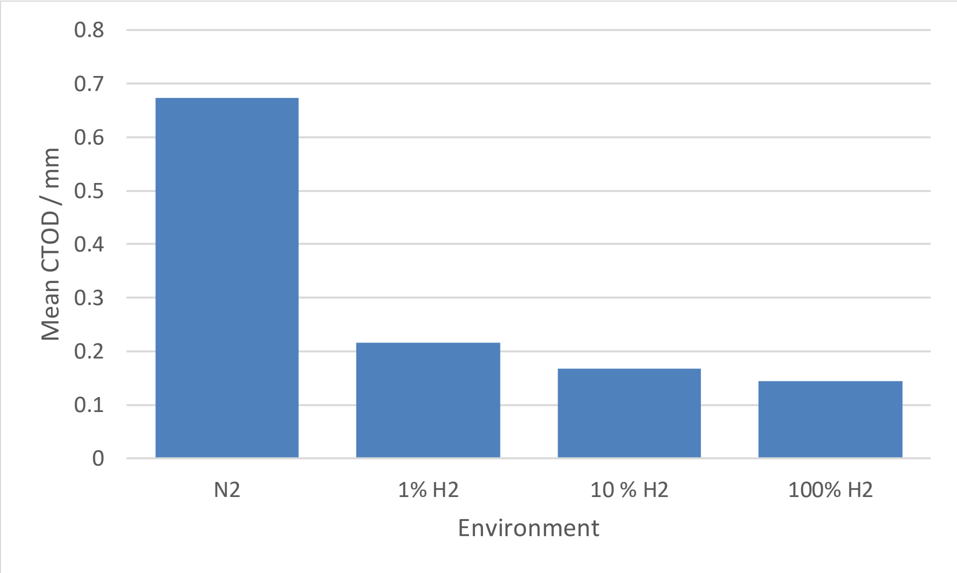

Figure 6 - Effect of Hydrogen on Fracture Toughness - from Briottet

Barthelemy (48) reports a reduction in toughness for low alloy steels of up to 50%, and also reported a significant grade dependence.

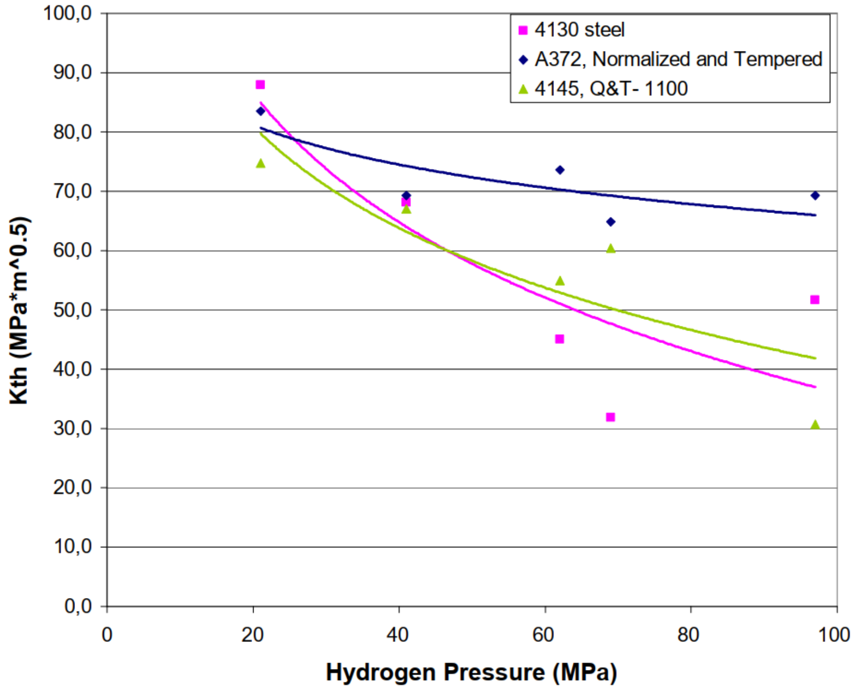

Figure 7 - Effect of Hydrogen on Fracture Toughness - from Barthelemy

The NATURALHY project report itself (49) shows very small decreases in toughness. According to the NATURALHY results, the effect of H2 can vary from zero down to a maximum 40% (X52) or 20% (X70) loss in toughness at crack initiation or 50% (X52) or 30% (X70) loss in toughness at maximum load. Within the framework of the NATURALHY project, these results and other literature sources were combined to derive the results shown in Table 18.

Parameters		Toughness (MPa.m$^{1/2}$) (pre-1975)	Toughness (MPa.m$^{1/2}$) (post-1975)
0-20 bar	100% NG	70	200
	25% H_2	68	194
	50% H_2	66	190
	75% H_2	63	180
	100% H_2	61	174
20-60 bar	100% NG	70	200
	25% H_2	73	180
	50% H_2	56	160
	75% H_2	49	140
	100% H_2	42	120
60-80 bar	100% NG	70	200
	25% H_2	61	175
	50% H_2	53	150
	75% H_2	44	125
	100% H_2	35	100
80-120 bar	100% NG	70	200

Parameters		Toughness ($MPa.m^{1/2}$) (pre-1975)	Toughness ($MPa.m^{1/2}$) (post-1975)
	25% H_2	60	170
	50% H_2	49	140
	75% H_2	39	110
	100% H_2	28	80

Table 18 - Effect of Hydrogen on Fracture Toughness - from NATURALHY

As may be seen above, there does not appear to be consensus regarding the relative effects of hydrogen on fracture toughness for different grades and strengths of material, with some sources reporting greater effects on stronger material while some report greater effects on weaker material.

From the above, it can be seen that, while there is broad agreement that hydrogen decreases the fracture toughness of steels, the magnitude of this decrease is unclear. Most sources appear to agree on a reduction of 35-70%, although the reported range varies between a reduction of ~85% and an increase of 11%. Importantly a number of sources report fracture toughness values in hydrogen of less than the default threshold for time dependent growth K_{IH} of 55 $MPa.m^{1/2}$ as referenced in ASME B31.12 Option B.

Although the literature seems to be converging on a reduction of 35-70% in fracture toughness, there is some reason to believe that these laboratory measured fracture values are not necessarily representative of pipeline service. As noted above, API 579 explicitly states that, if rapid unstable crack propagation begins in a hydrogen environment, the diffusing hydrogen cannot keep pace with the growing crack, meaning that the crack growth rate slows to establish equilibrium between the growth rate and the hydrogen delivery rate. Fracture toughness in hydrogen is therefore time dependent, and by inference not a true material property. In addition it should be noted that, by their nature, most laboratory tests involve small scale samples with machined surfaces completely immersed in hydrogen. In a pipeline the surface will (probably) be covered in scale or lining, and only the internal surface of the pipe will be exposed to hydrogen. An analogy to this is the widespread, although not code compliant, practise of coating most surfaces of HIC specimens in beeswax to ensure that the H_2S corrosion only occurs on one face.

Further, there is very little available fracture toughness data available for pipeline welds in gaseous hydrogen. Presumably in an attempt to compensate for this, both ASME B31.12 and the AIGA / EIGA guidelines restrict the permissible hardness of welds as shown in Table 19

Code	Material	Maximum Permissible Hardness
AIGA / EIGA Hydrogen Pipeline Systems	Steels (Parent and Welds)	22 HRC / 250 HB / 248 HV
	Microalloyed Steels (Parent and Welds)	95 HRB
ASME B31.12:2014 (50)	PWHT Carbon Steel	200 HV
	PWHT Alloy Steels Cr =< 2%	225 HV
	PWHT Alloy Steels 2 ¼ % =< Cr =<10%	241 HV
	Production Testing	237 HB
ASME B31.12:2019	Carbon Steel	235 HV10
	Alloy Steels Cr =< 2%	235 HV10
	Alloy Steels 2 ¼ % < Cr =< 10%	248 HV10

Table 19 - Allowable Hardness in Hydrogen Service

As may be seen, the maximum allowable hardness in ASME B31.12 increased between 2014 and 2019. This change was made following a review of the requirements of B31.12 against other industry standards (API RP 582 (51), API RP 934-A (52), API RP 934-C (53), NACE SP 0472 (54) and NACE MR 0175 / ISO 15156 (21)) and does not appear to have been driven by new research[4].

This in turn points to the fact that the mechanistic effect of hydrogen on material embrittlement and crack growth is still a subject of industry debate and research as detailed in Section 3. While the implication that laboratory test results, particularly for higher grade steels, are unnecessarily conservative appears to be plausible, the amount of conservatism is unclear. It is unclear how this uncertainty can be resolved without a concerted industry effort to perform a suite of larger scale (ring or full pipe) tests in hydrogen across a range of different materials and conditions

The other unknown with respect to fracture toughness is the applicability of existing ductile fracture arrest models to hydrogen service. Limited shock tube tests (55) have shown that up to about 10%

[4] E-mail from O.J.C. Huising to members of ASME B31.12 committee

hydrogen in natural gas did not affect the decompression behaviour and so the driving force for crack propagation would not change. Higher levels of hydrogen would probably have similar effects, or even increase the decompression wave propagation velocity and so reduce the driving force. This hypothesis is supported by Aihara et al. (56) who report that a full scale burst test on a SAWL X65 559 mm diameter x 13.5 mm linepipe pressurised with 16 MPa hydrogen gas showed a shorter crack arrest distance than in equivalent methane tests. Aihara does caution however that the test was performed using modern high-toughness steel (>450 J Charpy energy and 100% BDWTT shear at 0^{o} C). The results are therefore potentially not representative of older, lower toughness, material. The behaviour, and energy release rate, of hydrogen charged steel would be expected to differ from that in (natural) gas service adding an extra layer of complexity to the toughness uncertainties outlined above. Earlier the same group had carried out tests on smaller diameter (267 mm) EW pipe (57) pressurised using pure methane or pure hydrogen; the tests using hydrogen arrested more quickly than the corresponding tests pressurized with methane, which is consistent with more rapid decompression. As with the SAWL test the material's Charpy energy was about five times that required for crack arrest using the Battelle Two Curve Model, so that rapid arrest would have been expected in any case. Liu et al. (58) report some CFD modelling aiming to address these complexities. Crack arrest tests are required in lower toughness materials which are closer to the limit for crack arrest to confirm that there are no issues for hydrogen service.

Given the complexity and number of different papers referenced in this section, and the importance of understanding the effect of hydrogen on fracture toughness, papers have been summarised below.

Title	Reference	Summary	Major Findings
Technical Reference on Hydrogen Compatibility of Materials – Plain Carbon Ferritic Steels: C-Mn Alloys (Sandia Report)	(43)	Comprehensive 2012 summary of available fracture toughness data. Compilation of various historic test results with different test protocols, materials, hydrogen concentrations etc.	Text concludes that "At a constant pressure of 6.9 MPa, the fracture toughness is degraded by as much as 50% in hydrogen gas", various data presented in tables reflects degradation of between 13 and 69%, reflecting the difficulties in quantifying different effects.
Integrity Management for Pipelines Transporting Hydrogen – Natural Gas Mixtures (Muller-Syring on behalf of NATURALHY)	(44)	2009 summary of NATURALHY findings. No details given about test protocols or materials (nominal grade only).	Cracks are identified as the most critical defects in the presence of hydrogen. Drop of 49% in fracture toughness for X52 (150 to 76 MPa.m$^{1/2}$) and 63% for X70 (120 to MPa.m$^{1/2}$) when comparing 60 bar hydrogen to nitrogen. The impact of pure hydrogen on critical initial crack depth is significant (up to 62% smaller for the examples presented) but

Title	Reference	Summary	Major Findings
			reduced for smaller hydrogen partial pressures.
Hydrogen Effect on Fatigue and Fracture of Pipe Steels (Capelle et al., NATURALHY work)	(45)	Summary of work performed during NATURALHY looking at electrolytically charged X52, X70 and X100 material. Compact Tension (CT) tests performed, actual hydrogen concentration was not reported. Some fatigue tests also reported as part of this paper.	Relatively small effect (<10%) of hydrogen on $K_{I,i}$ but larger (up to ~44%) effect on δ_i. Effect is reported to be higher for X52 than for stronger steels. This is attributed to the fact that the X52 was 1960's construction with presumably lower quality standards than modern steels, but no details are given.
Sensitivity of pipelines with steel API X52 to hydrogen embrittlement (Capelle et al., NATURALHY work)	(46)	NATURALHY paper demonstrating the importance of hydrogen concentration (and hence time) on "fracture toughness". "Roman tile" electrolytically charged tests used. Full scale burst tests also reported.	Time dependence of local hydrogen concentration and "fracture toughness" is measured and quantified. Up to ~65% reduction in total work of local fracture emanating from a notch.
Influence of hydrogen and oxygen impurity content in a natural gas / hydrogen blend on the toughness of an API X70 Steel – Briottet et al.	(47)	Toughness measured as CTOD per ISO 12135:2002 (59) on CT specimens of X70 steels. Testing performed in-situ with various different concentrations of hydrogen and oxygen.	Large decreases in δ for small additions of hydrogen (0.85 bar). Significant mitigating effects for small (100ppm) additions of oxygen. Different fracture morphologies noted under nitrogen, hydrogen and with small oxygen additions.
Effects of purity and pressure on the hydrogen embrittlement of steels and other metallic materials – Barthelemy	(48)	Literature survey reporting various publicly available test data. Test data reported for wedge opening load and compact tension specimens.	Decreases in both threshold stress intensity factor and fracture toughness with increasing hydrogen pressure. Magnitude of the decrease depends on various factors including steel microstructure.

Title	Reference	Summary	Major Findings
Full-scale burst test of hydrogen gas X65 pipeline – Aihara et al.	(56)	Report into full scale burst test and small scale hydrogen embrittlement / fracture mechanics tests (3PB pre-charged specimens, J-integral resistance curves constructed). Test was performed on modern high-toughness line pipe.	Crack arrest occurred after a short propagation in the burst test. Simulations predicted the arrest distance to be shorter than for methane gas, and no clear influence on the slope of the dynamic J resistance curve of hydrogen.
Durability of Steels for Transmission Pipes with Hydrogen (NATURALHY report R0096-WP3-C-0)	(49)	Extensive testing performed on varying materials of different grades and vintages using both gaseous hydrogen and electrolytically charged samples, and investigating the role of oxygen.	Fracture toughness decreases with increasing hydrogen partial pressure, but amount of decrease is relatively small and low levels of oxygen additions counteract this effect. Up to 25% v/v hydrogen the effect is not considered significant.

Table 20 - Summary of Hydrogen Fracture Toughness Sources

6.4 Test Protocols

Most available data do not reference international test standards for fracture toughness testing in hydrogen. ASME B31.12 references article KD10 in ASME BPVC VIII Division 3 (38). This in turn references ASTM E1681 (60). It is noticeable that ASTM E1681 is written around environment-assisted cracking rather than specifically hydrogen, and is not restrictive with respect to control of the hydrogen content in steel.

BS EN ISO 11114-4 (61) includes guidance, although written from the point of view of gas cylinders rather than pipelines. The recommended test protocol is based on the use of machined compact tension test pieces in general accordance with ISO 7539 (62).

It is also important to note that all of the fracture toughness data referenced within this report is based on small scale laboratory testing. The applicability of this data, particularly for crack arrest, to full scale pipes is open to question, with there being a lack of published full scale tests in hydrogen. The mechanism by which fracture toughness is decreased is also important, and may mean that small scale testing is unnecessarily conservative.

This lack of consistency in testing may explain some of the variability noted.

7 FATIGUE IN HYDROGEN

7.1 Mechanistic Description

As described in Section 6.1, hydrogen can have a large time-dependent effect on the apparent fracture toughness of steels. Similar mechanisms have an effect on sub-critical (fatigue) crack growth with the nature of this effect, and the interaction between fatigue and fracture, being the subject of much current research.

7.2 Current Available Design Criteria

ASME B31.12 (6) design option A has no specific fatigue requirements, but as mentioned above is prescriptive with respect to allowable stress levels. ASME B31.12 design option B references Slifka et al (63) and Amaro et al. (64), and states that in the absence of measured data the fatigue crack growth rate (FCGR) for carbon steel can be represented by:

Equation 1 - FCGR for Carbon Steels in hydrogen - from ASME B31.12

$$\frac{da}{dN} = a1\Delta K^{b1} + \left[\left(a2\Delta K^{b2}\right)^{-1} + \left(a3\Delta K^{b3}\right)^{-1}\right]^{-1}$$

In this equation, a1, a2, a3, b1, b2 and b3 are all materials constants with da/dN being the crack growth rate and ΔK being the stress intensity factor range. The fracture assessment to determine the final (end of life) crack size is based on either the calculated growth by fatigue from the initial defect size or an assumed critical elliptical surface crack with depth t/4 and length 1.5t, where t is the pipe wall thickness. Alternatively the fatigue design rules specified in Article KD-10 of ASME BPVC, Section VIII, Division 3 can be used, so that a fracture mechanics fatigue life assessment is required rather than using a S-N approach.

The AIGA / EIGA guidelines (7) cover fatigue in Appendix B. The guidance is somewhat contradictory, since it is stated both that “Since pipelines normally operate at near constant pressure, fatigue cracking is usually not a concern” and “Despite the supposed absence of fatigue conditions in pipelines, fatigue may be a problem in some cases”. The guidelines are also explicit in that FCGR and fatigue endurance limits degradation have been observed in dry hydrogen gas environments, even on smooth specimens and relatively low hydrogen pressures.

7.3 Testing Standards

There are no testing standards specific to fatigue in gaseous hydrogen. The recent work by Slifka and Amaro referenced in ASME B31.12 appears to have been conducted in accordance with ASTM E647 (65) using CT specimens machined from the C-L orientation in accordance with ASTM E399 (66). It should be noted however that there is a large number of testing parameters, as described below, which are not prescribed as part of ASTM E647, and the level of environmental control required is not specified.

7.4 Effect of Hydrogen Pressure

Unsurprisingly, fatigue crack growth rates increase, and fatigue endurance decreases, with increasing hydrogen pressure. This has been documented in many papers, including in early research by Barthelemy et al. (13).

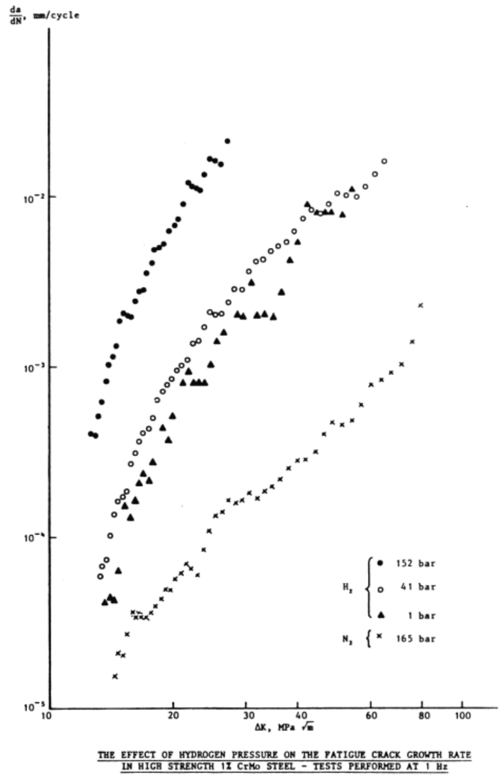

Figure 8 - Effect of Hydrogen Pressure on FCGR - from Barthelemy et al.

The effect on fatigue endurance was reported by Capelle et al. (45) as part of the NATURALHY project, although this work was performed using hydrogen charged samples rather than samples exposed to hydrogen gas.

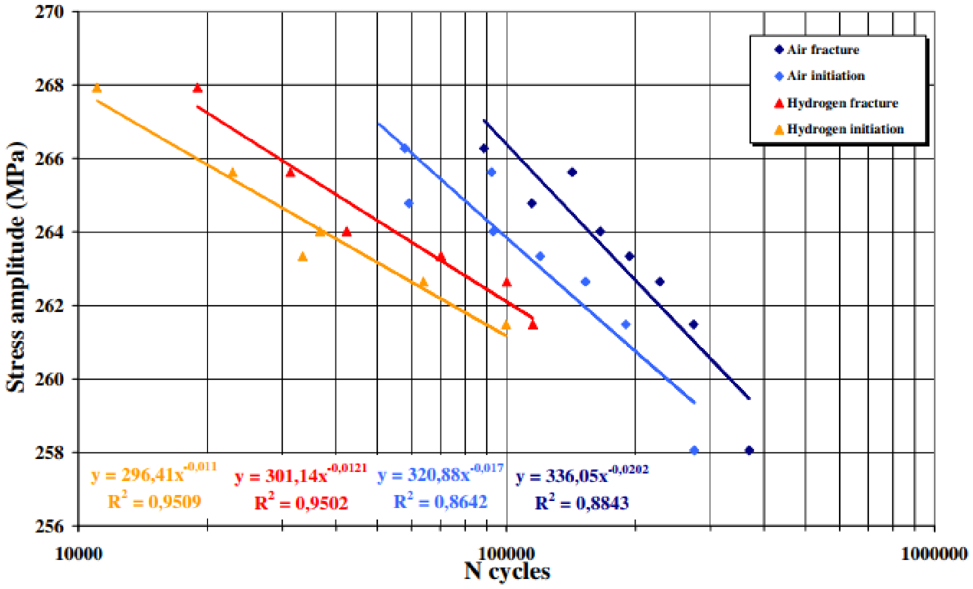

Figure 9 - Effect of Hydrogen Charging on Fatigue Endurance - from Capelle et al.

Fairly comprehensive recent reviews of the effect of hydrogen on fatigue performance are available from Somerday et al. (43) and Zhang et al. (67).

Zhang concluded that as the hydrogen pressure increased so did the FCGR, with noticeable acceleration occurring at hydrogen pressures as low as 0.2 MPa / 2 bar. In terms of the fatigue endurance of steels, Zhang concluded that there was less effect of hydrogen, with the effect only being evident in the low cycle regime and when specimens contained a severe notch or defects. Somerday concurs that FCGR is significantly adversely affected even under very low partial pressures (0.088 MPa / 0.88 bar) of hydrogen (see Figure 10).

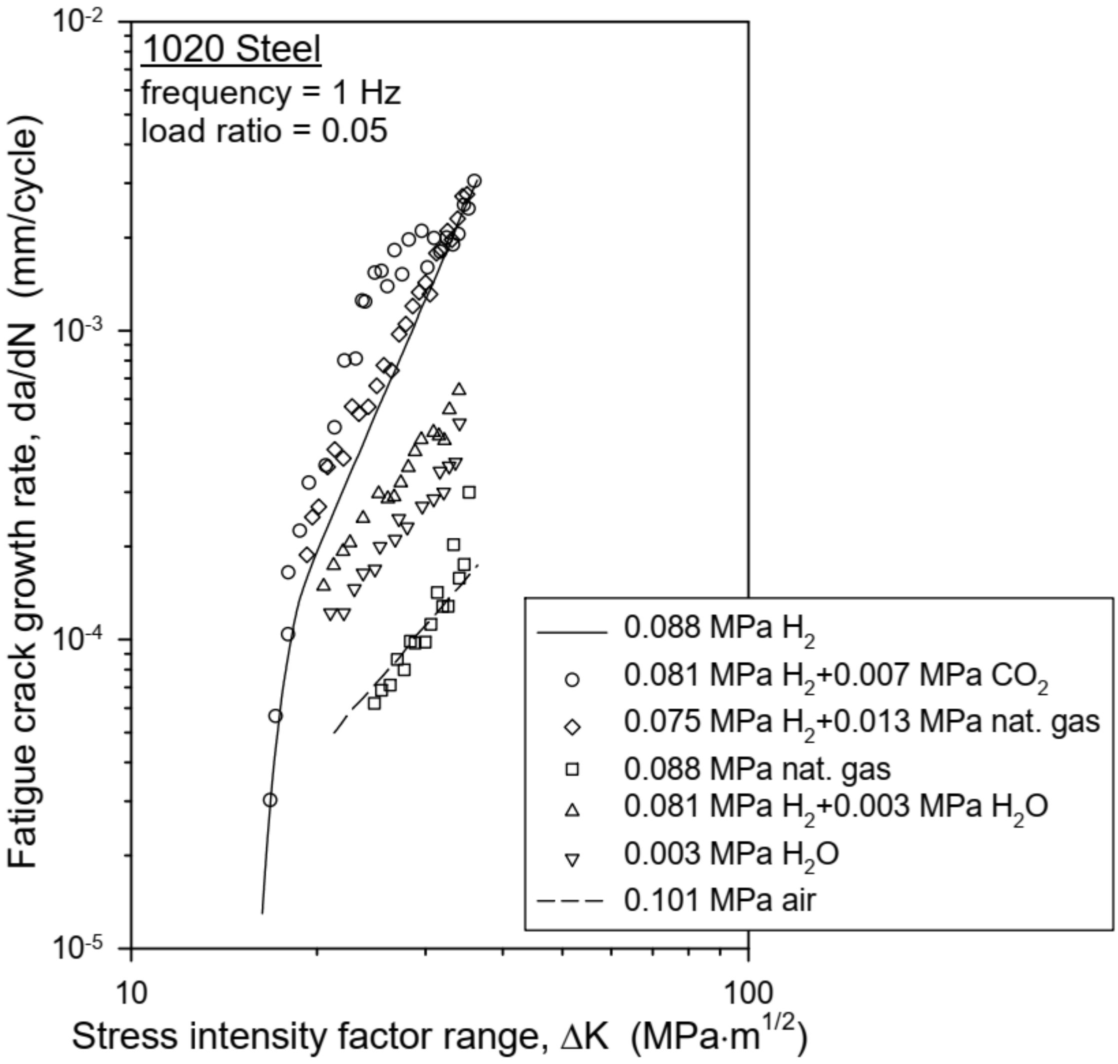

Figure 10 - FCGR in various environments including hydrogen and air - from Somerday et al.

As hinted at above, incremental increases in hydrogen pressure once hydrogen is present do not have as significant an effect as the presence of hydrogen in the first place. Chen et al. (17) summarise data for X52 and X70 steels in gaseous hydrogen in Figure 11.

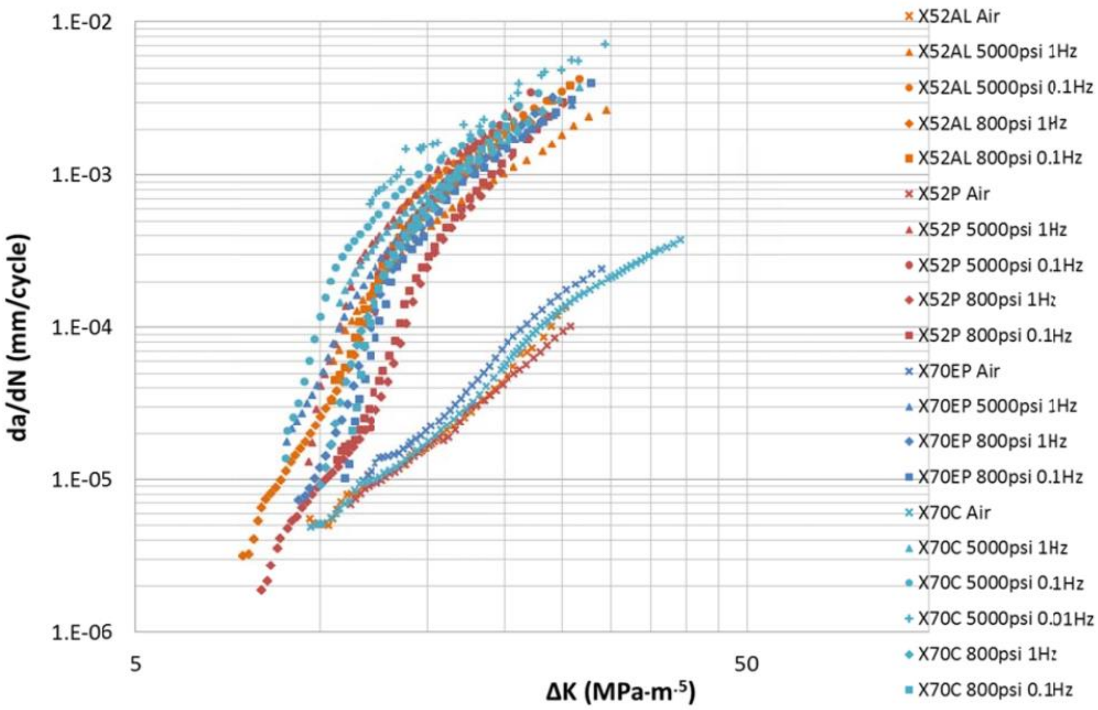

Figure 11 - FCGR for Steels in Air, 800 psi (5.5 MPa) and 5000 psi (34.5 MPa) Hydrogen - From Chen et al.

Similar results are reported by Briottet et al. (68), although in their case a low alloy steel (EN 10083-3 (69) 25CrMo4) was used for testing, while work by Holbrook et al. (70) indicated the FCGR for X42 steel in 5 psia / 0.4 bar hydrogen was a factor of 10 more than in air (see Figure 13). It therefore appears that there is no “safe” lower bound of admissible hydrogen below which the effect on FCGR can be discounted.

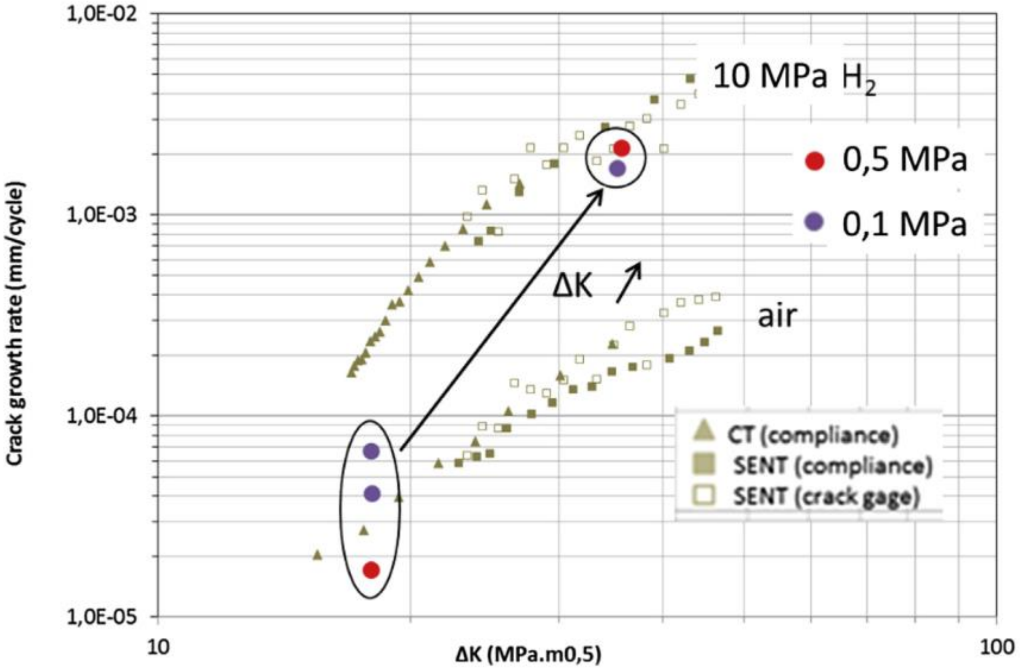

Figure 12 - Effect on FCGR of Low Hydrogen Pressures - from Briottet et al.

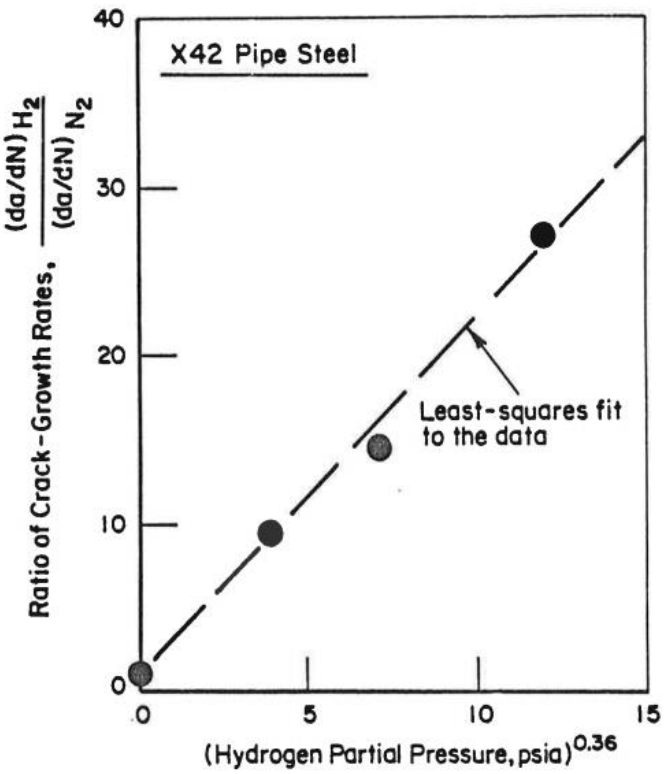

Figure 13 - Effect of Hydrogen Partial Pressure on FCGR - from Holbrook

Amaro et al. (71) report that an increase in hydrogen pressure from 6.89 MPa to 20.68 MPa increases the FCGR for ΔK values below ~20 MPa.$m^{1/2}$, but as can be seen in Figure 14 this increase is small compared to the difference with air for higher values of ΔK.

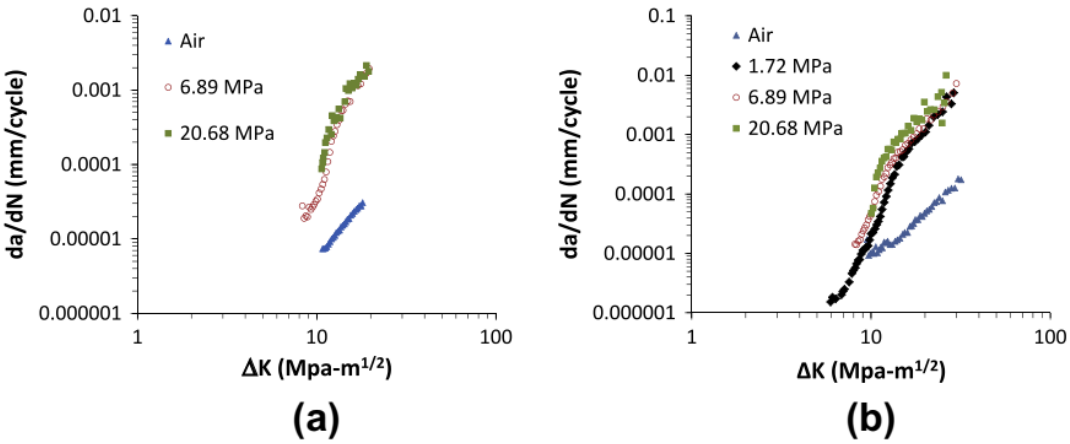

Figure 14 - Effect of Hydrogen Pressure on FCGR for X52 (a) and X100 (b) Steels - from Amaro et al.

Amaro proposes that at low hydrogen pressures and sufficiently low ΔK the hydrogen assisted FCGR (HA FCGR) approaches that of the air response. Amaro further proposes that there is a transition point of stress intensity factor above which the HA FCGR converges regardless of hydrogen pressure. This assumes that hydrogen increases the FCGR due to the effect of localised hydrogen concentration at the crack tip. Once the crack extension (per cycle) extends beyond this localised concentration the FCGR decreases due to the lower (bulk) hydrogen concentration. This hypothesis appears plausible, but does not take into account the different bulk concentrations expected for different hydrogen levels.

The NATURALHY project (49) performed various fatigue tests using both gaseous and electrolytically charged hydrogen at different concentrations. From these tests and from published literature a "Threshold value" (defined as the stress intensity factor range below which the crack growth rate was <0.01 μm / cycle) for various different materials (X42-X70, different vintages and containing both parent and weld metal samples) was derived. In addition Paris law coefficients were calculated.

Parameters		ΔK_{th} (MPa.$m^{1/2}$)	m	$Log_{10}C$ (μm/(cycle.MPa.$m^{1/2}$))
0-20 bar	100% NG	10.7	3.57	5.69
	25% H_2	9.9	3.72	5.69
	50% H_2	8.2	3.51	5.22
	75% H_2	8.5	5.05	6.69

Parameters		ΔK_{th} (MPa.m$^{1/2}$)	m	$Log_{10}C$ (µm/(cycle.MPa.m$^{1/2}$))
	100% H_2	7.1	4.80	6.09
20-60 bar	100% NG	10.7	3.57	5.69
	25% H_2	9.9	3.72	5.69
	50% H_2	8.2	3.51	5.22
	75% H_2	8.5	5.05	6.69
	100% H_2	7.1	4.80	6.09
60-80 bar	100% NG	10.7	3.57	5.69
	25% H_2	9.9	3.72	5.69
	50% H_2	8.2	3.51	5.22
	75% H_2	8.5	5.05	6.69
	100% H_2	7.1	4.80	6.09
80-120 bar	100% NG	10.7	3.57	5.69
	25% H_2	9.9	3.72	5.69
	50% H_2	8.2	3.51	5.22
	75% H_2	8.5	5.05	6.69
	100% H_2	7.1	4.80	6.09

Table 21 - Fatigue Performance of X42 up to X70 Material - from NATURALHY

Note that the data in the table above is taken directly from Table A of the NATURALHY report. The values reported are the same for all the different pressure ranges (and independent of absolute pressure). This leads to apparent inconsistencies such as the relevant coefficients for 25% H_2 in an 80 bar total pressure system (20 bar partial pressure H_2) being different from 100% H_2 in a 20 bar total pressure system (also 20 bar partial pressure H_2).

It is important to note that no available reference sources directly reported dissolved hydrogen concentration. While mechanistically critical, the difficulties inherent in measuring the "true" hydrogen content mean that proxy values (e.g. the partial pressure of hydrogen) are widely used.

7.5 Influence of ΔK Magnitude

As a general trend, the acceleration of crack growth rates in a hydrogen environment increases with the stress intensity factor range. This can be seen in Figure 15 based on the review by Somerday et al. (43)

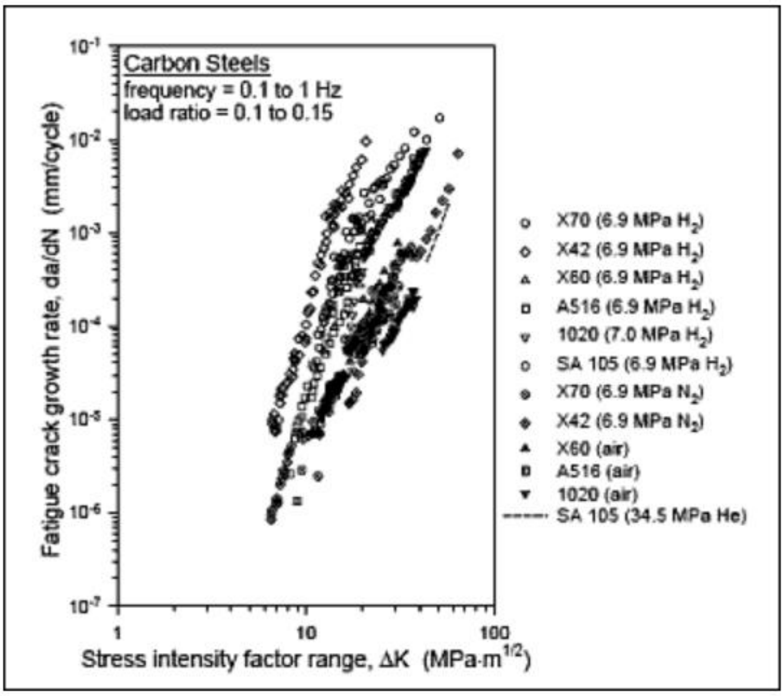

Figure 15 - FCGR v Stress Intensity Factor Range - from Somerday et al,

The cumulative effects of hydrogen pressure and ΔK have already been discussed above. In addition Suresh and Ritchie (19) examined the effects of gaseous hydrogen on ambient temperature fatigue crack propagation over a wide range of growth rates (10^{-8} to 10^{-2} mm/cycle) in lower strength steels (σ_y = 290-770 MPa). The following conclusions were made:

1. Two distinct growth rate regimes exist where moist air environment leads to significantly slower crack growth rates than in dry hydrogen gas.
2. In the mid-range of growth rates, typically exceeding 10^{-5} mm/cycle, growth rates in hydrogen are enhanced by up to 20 times compared to air, coincident with a fracture mode change from pre-dominantly transgranular to predominantly intergranular cracking. Behaviour in this regime is sensitive to load ratio (r=0.05-0.75), cyclic frequency (0.5-50 Hz), and hydrogen pressure (0.14-6.9 Mpa) and is analogous to stress corrosion fatigue in high strength steels.

3. At ultralow, near threshold growth rates (10^{-6} to 10^{-8} mm/cycle), crack propagation rates in moist air are progressively slower than in dry hydrogen (by up to 2 orders of magnitude) as the fatigue threshold is approached. The effect is only evident at low load ratios; little difference is seen at R=0.75.
4. Primary mechanisms for environmentally-influenced crack growth in the two regimes are reasoned to be entirely different, whereas the mid-growth regime is attributed to hydrogen embrittlement. The role of hydrogen at near threshold levels is principally one of dry, oxygen - free environment which minimises the decelerating effect of oxide-induced crack closure.

It follows from this, that, according to Suresh and Ritchie, the principal difference between hydrogen and air FCGRs at low stress intensity ratio ranges is due to the presence of moisture in air. Unfortunately no data is presented comparing dry air to dry hydrogen to validate this.

7.6 Effect of Loading Ratio

Somerday et al. (43) report that for loading ratios of < ~0.5 there is little effect on the FCGR, however above this ratio the FCGR increases as the loading ratio increases.

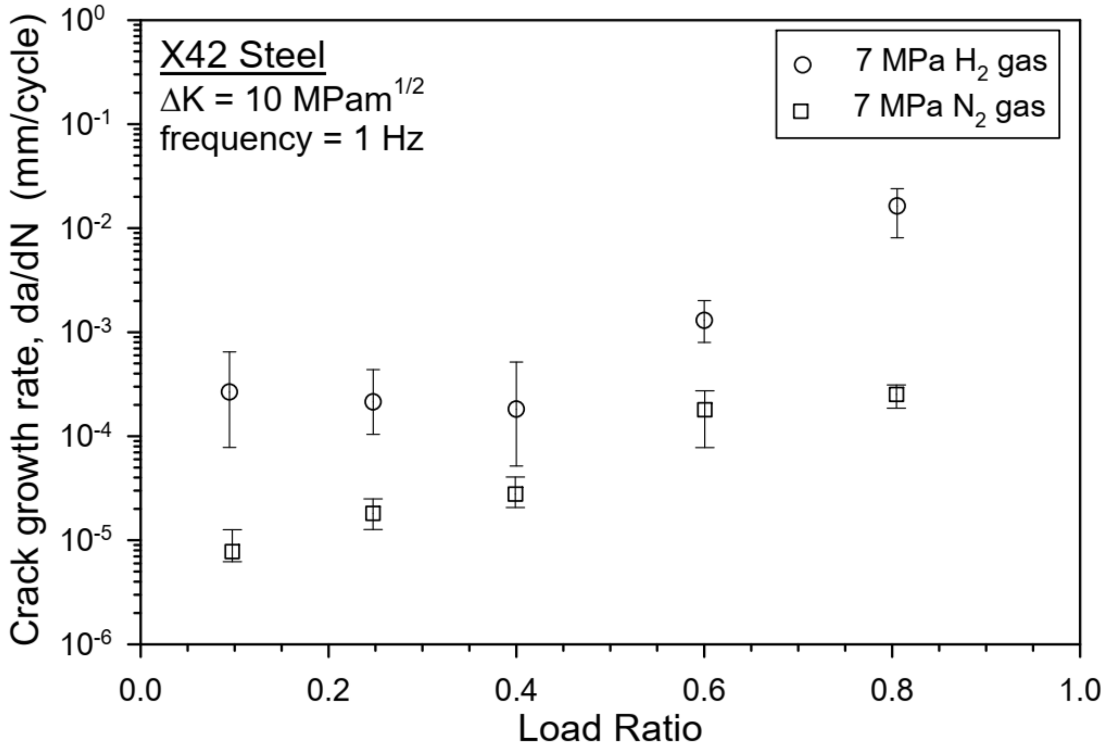

Figure 16 - Effect of Loading Ratio on FCGR - from Somerday

Suresh and Ritchie (19) report a slightly more nuanced effect, albeit on low alloy rather than carbon steel, as shown in Figure 17.

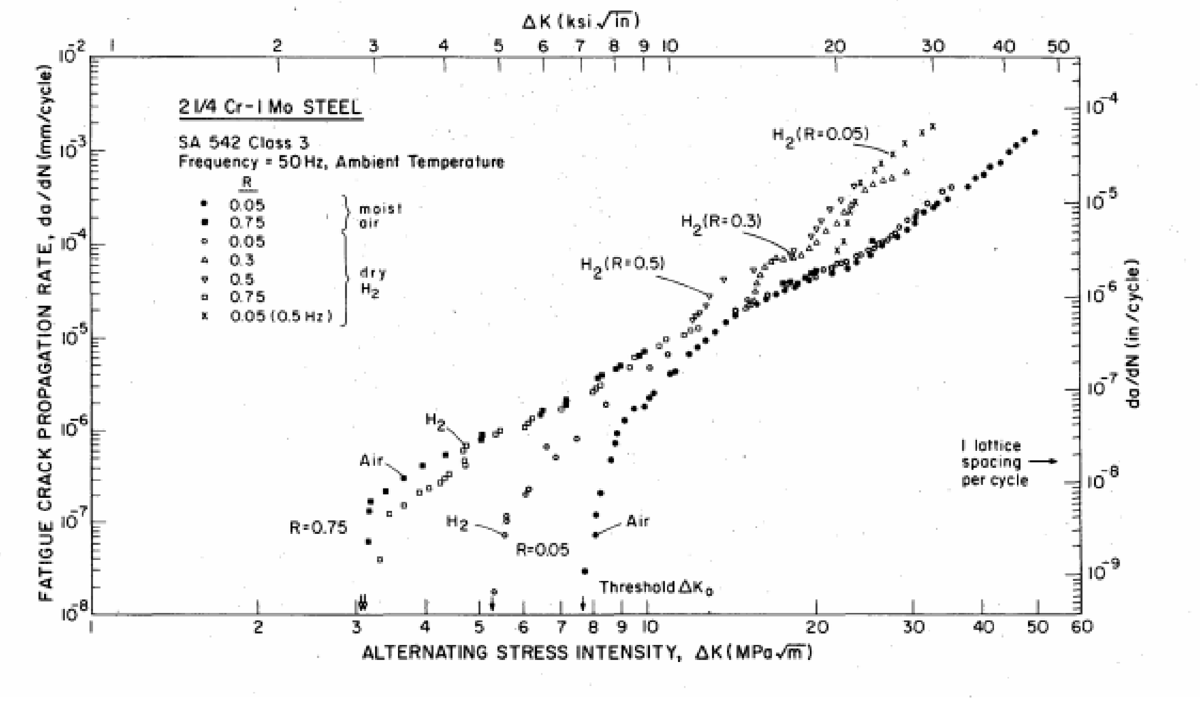

Figure 17 - Influence of Loading Ratio on FCGR - from Suresh and Ritchie

Holbrook et al. (70) report the direct opposite to Somerday, with a decrease in FCGR with stress ratio for R values <0.5, see Figure 18 (constant ΔK of 18 ksi.in$^{1/2}$, loading frequency of 1 Hz). Holbrook also references some other results which appeared to show that increasing R ratio actually reduced the FCGR, this was believed to be due to contamination of the hydrogen during test, although this hypothesis was not proven. It follows from the above that the effect of loading ratio is still not fully understood.

The influence of R is of importance as pipelines tend to operate at high mean stresses and hence R values are usually greater than 0.5 unless the pressure swings are very large.

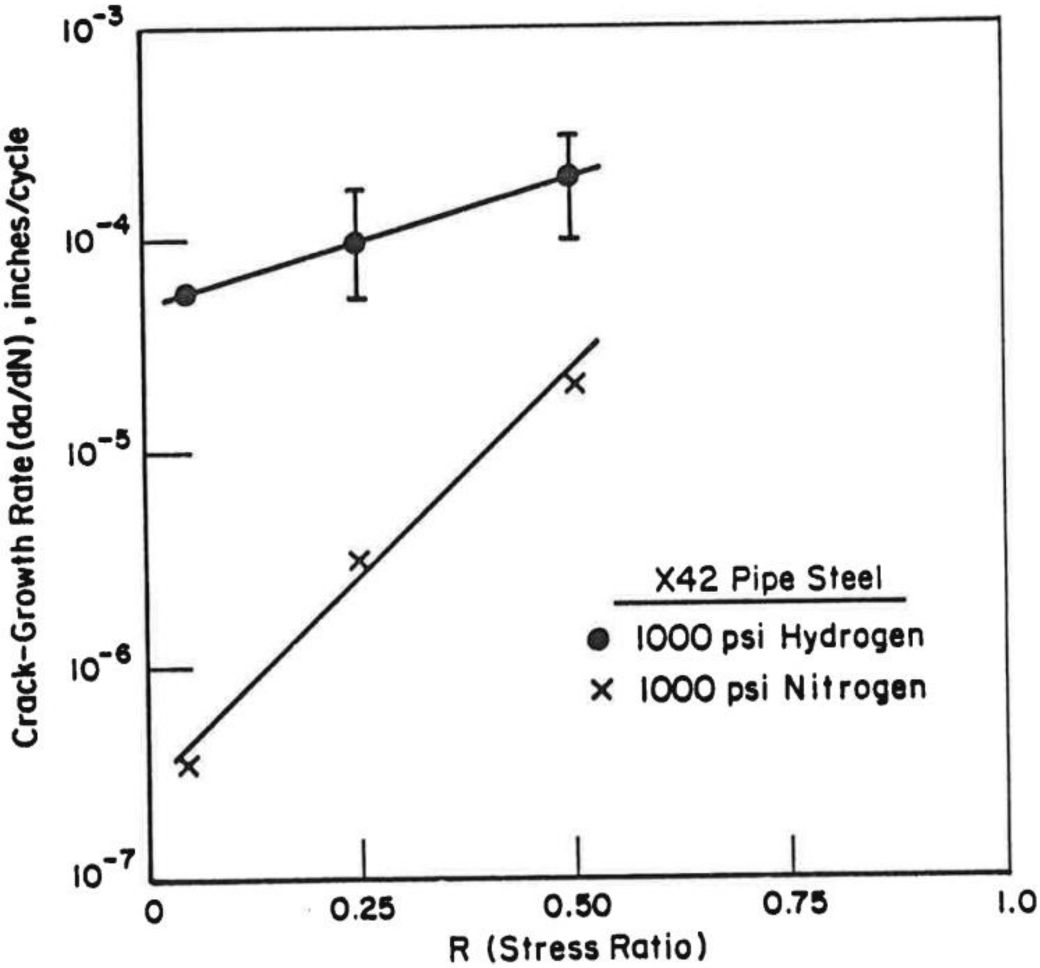

Figure 18 - Influence of R Ratio on FCGR in 1000 psi (6.9 MPa) Hydrogen - from Holbrook

7.7 Effect of Loading Frequency

It is generally accepted that FCGR (measured per cycle) increases with decreasing loading frequency. Somerday et al. (43) summarise this in Figure 19. Slifka et al. (63) report broadly similar results, although confusingly one instance is also reported of the FCGR at a loading frequency of 0.01 Hz being lower than that at either 0.1 or 1 Hz, see Figure 20. Note that Slifka's data is based on a constant ΔK of 14 $MPa.m^{1/2}$

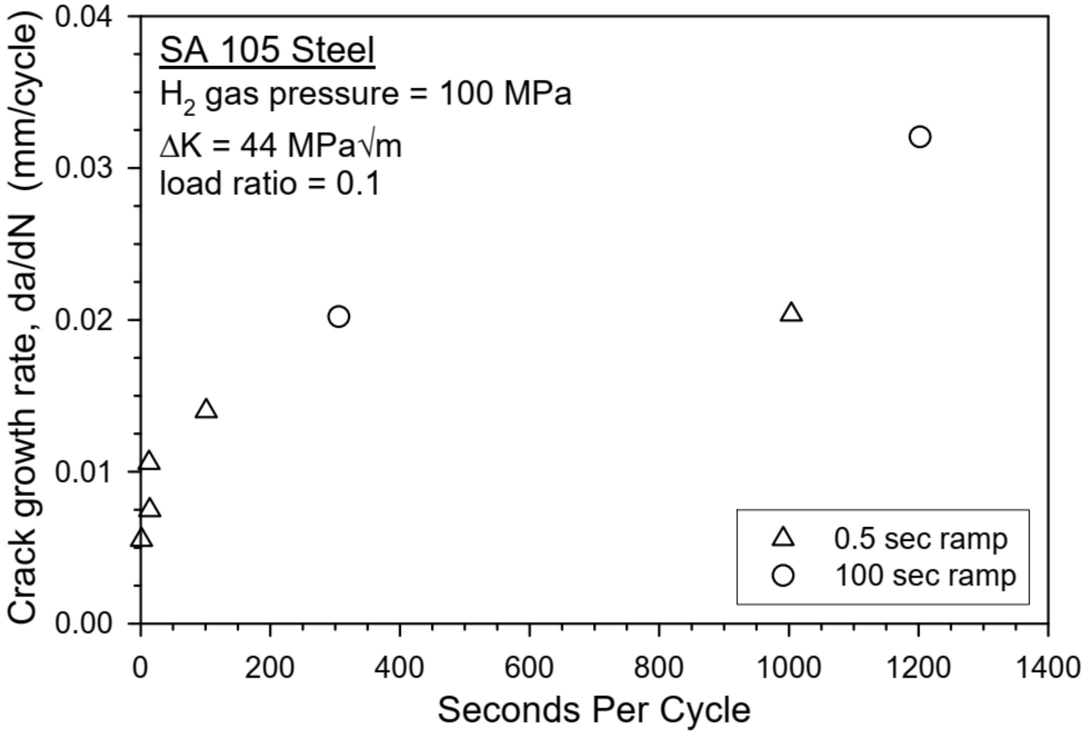

Figure 19 - Effect of Loading Frequency on FCGR - from Somerday et al.

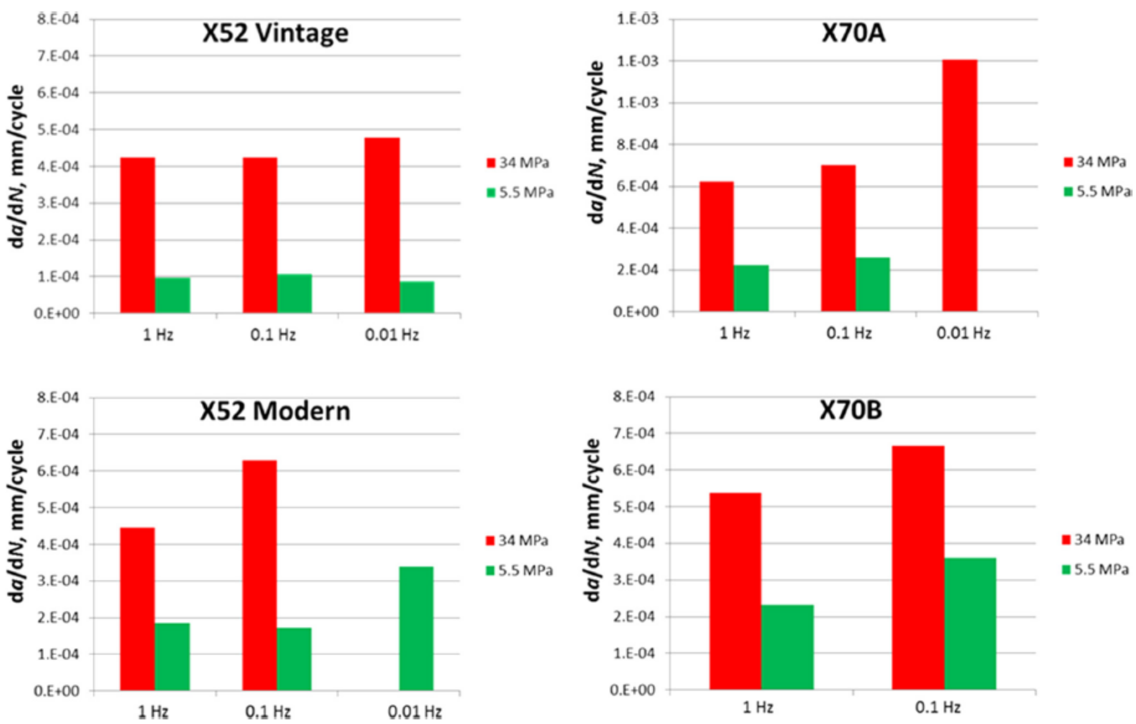

Figure 20 - Fatigue Crack Growth Data for Different Loading Frequencies - from Slifka et a;.

7.8 Effect of gas composition

Adding small concentrations of particular gases such as Oxygen or Carbon Monoxide to Hydrogen gas has the potential to inhibit the adsorption of hydrogen onto the steel, thus reducing or inhibiting the effect of hydrogen embrittlement. This effect is discussed below, although it should be noted that there are potentially other consequences, particularly with respect to safety, of adding either oxygen or carbon monoxide to a fuel.

Likewise, the effect of additives to hydrogen gas on fatigue crack growth rate has been comprehensively investigated by Fukuyama and discussed by Zhang (67). The fatigue crack growth rates of 2.25Cr-1Mo steel in hydrogen with small amounts of different additives were determined at a constant ΔK of 758N/mm$^{3/2}$ and a hydrogen gas pressure of 1.1 MPa. The results are shown in Figure 21.

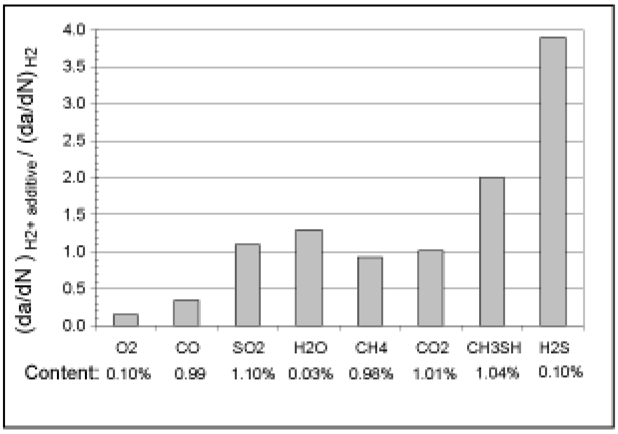

Figure 21 - Effect of Additives on FCGR - from Zhang

The effects of adding O_2 and CO to prevent hydrogen embrittlement thus appear to be beneficial in reducing the FCGR, while the additions of H_2S and CH_3SH cause an acceleration in the FCGR. Similar effects, even for very small amounts of O_2, are reported by Adams et al. (72) (ΔK fixed at 15 ksi.in1/2, R=0.1).

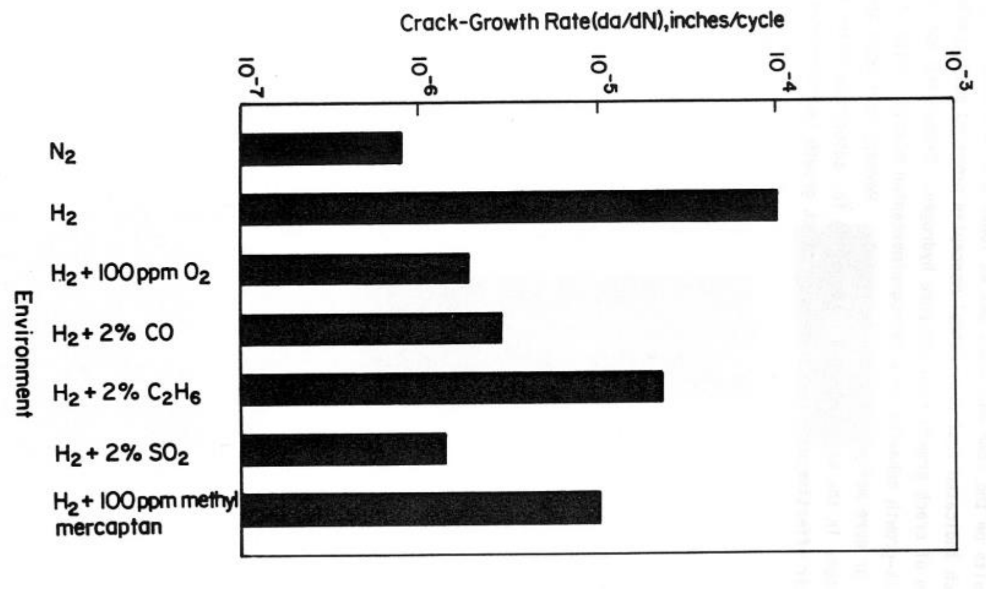

Figure 22 - Effect of Additives on FCGR - from Adams, adapted from J.H. Holbrook et al., Battelle Labs, 1988

The effect of water vapour is complicated. As discussed in Section 7.5, Suresh and Ritchie showed the effect of low concentrations of moisture at different loading ratios and frequencies, and Section 9.3 illustrates the uncertainties present. It appears that small amounts of moisture can be beneficial, however there does not appear to be agreement regarding how to quantify this.

7.9 Effect of materials and microstructures

Fatigue crack growth rates in air in carbon steels are generally considered to be controlled by the crack tip stress intensity factor and independent of microstructure, however there is some evidence that this is not the case in hydrogen. Nanninga et al. (73) summarise data for different microstructures as seen in Figure 23.

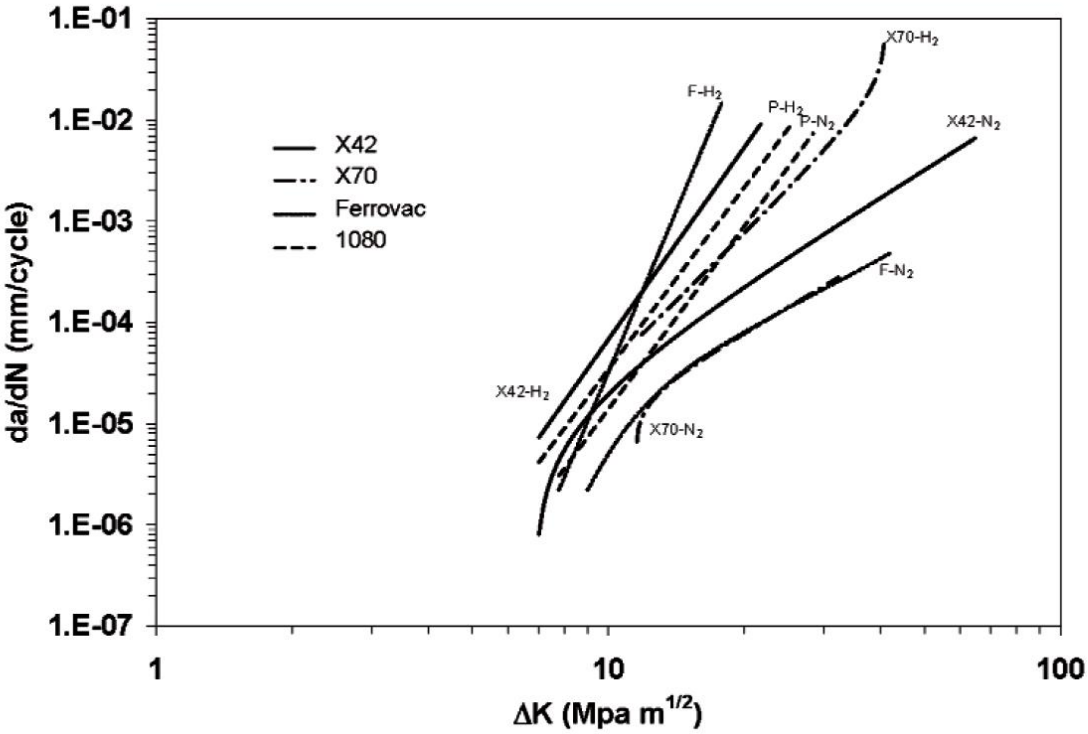

Figure 23 - HA-FCGR for Different Microstructures (P = 1080 fully pearlitic steel, F = fully ferritic) – from Nanninga

Nanninga also states that fatigue crack growth in the fully ferritic alloy in hydrogen was almost entirely along grain boundaries (intergranular), while for the pearlitic 1080 steel fatigue crack growth was mainly transgranular.

Ronevich et al. (74) performed a test using laboratory controlled microstructures to examine the role of microstructural constituents, grain size, and grain orientation on susceptibility to HA-FCG. Ronevich found that of all the variables tested, microstructural orientation (e.g., induced from the rolling process) was observed to have the largest effect on reducing HA-FCG. When the crack was oriented perpendicular to the rolling direction, HA-FCG was reduced up to 5 times compared to when the crack was oriented parallel to the rolling direction. This suggests that interfaces (e.g., grain boundaries) have a significant effect on suppressing HA-FCG.

In some studies as suggested by Zhang (67) lower strength steels were found to be more susceptible to accelerated FCGR in hydrogen than their higher strength equivalents. Zhang references work on high strength steel, showing that the crack growth rate in HY80 at high ΔK levels exceeded that in HY130 by a factor of 10. It is possible that these differences in FCGR may be due to microstructural differences, such as the work completed by Ronevich.

Somerday et al. (43) collated data on FCGR for heat treated ASTM A516 steels with various different microstructures (ferritic, pearlitic and bainitic) and yield strengths varying between 305 and 415 MPa. The reported FCGR for all these different microstructures in 6.9 MPa hydrogen gas was virtually identical (see Figure 24).

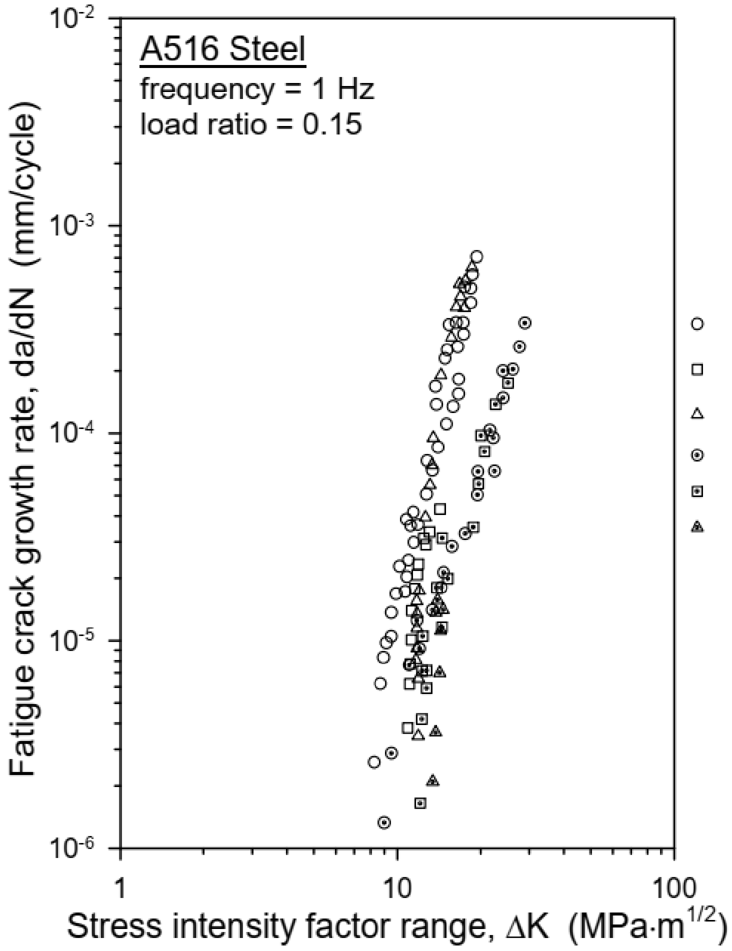

Figure 24 - FCGR in Hydrogen for Different Microstructures - from Somerday

Drexler et al. (75) agree that FCGR can differ in a hydrogen environment for different steel grades, however on the basis of tests on X52 and X70 steels in 5.5 MPa gaseous hydrogen and air they have posited an upper bound limit. Figure 25 is taken from Drexler, with the black line being the upper bound limit, the grey circles being data in air and grey diamonds in hydrogen.

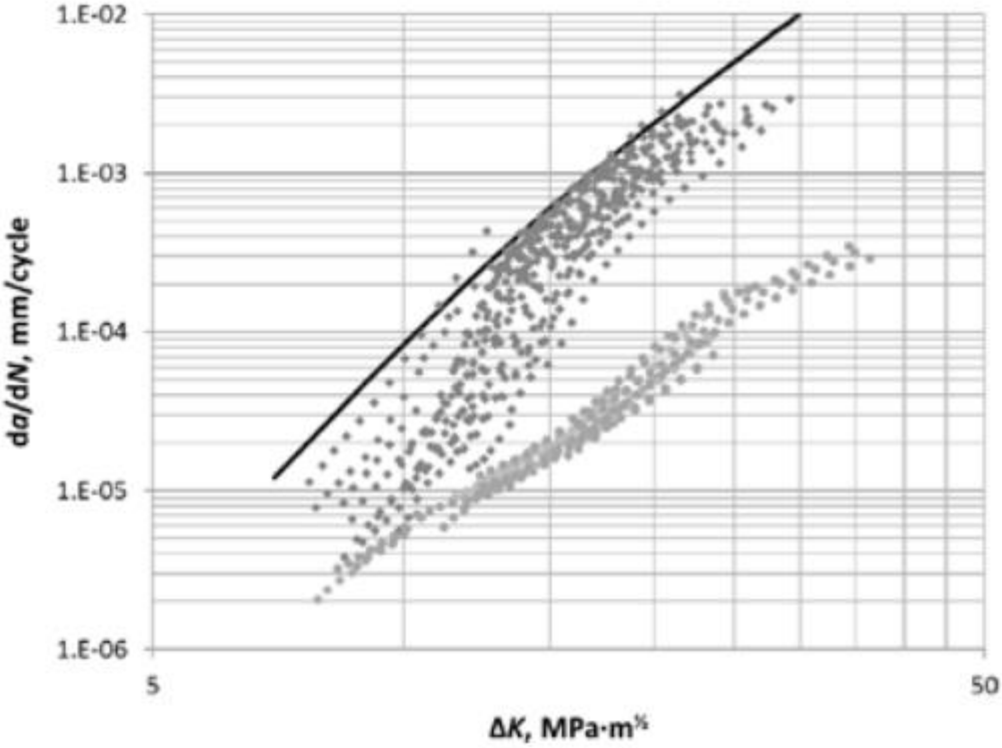

Figure 25 - FCGR of X52 and X70 Steels in Air and Hydrogen Gas – from Drexler et al.

This upper bound has been accepted by ASME and is incorporated into the 2019 version of B31.12.

7.10 Welded joints

For non-corrosive environments it is normally assumed that fatigue propagation is not microstructure dependent, therefore the crack growth rate for welds can be assumed to be equivalent to that for parent material. Since the mechanism of fatigue crack growth is affected by hydrogen, this assumption may be invalid for gaseous hydrogen service and it has been challenged by various authors.

Drexler et al. (76) studied the effect on FCGR of hydrogen gas pressurised to 5.5 MPa for X52 and X70 seam and girth welds, however the results were inconclusive as shown in Figure 26. Examples were found where the FCGRs in the HAZ and weld metal were each of higher, lower and equivalent to the base material.

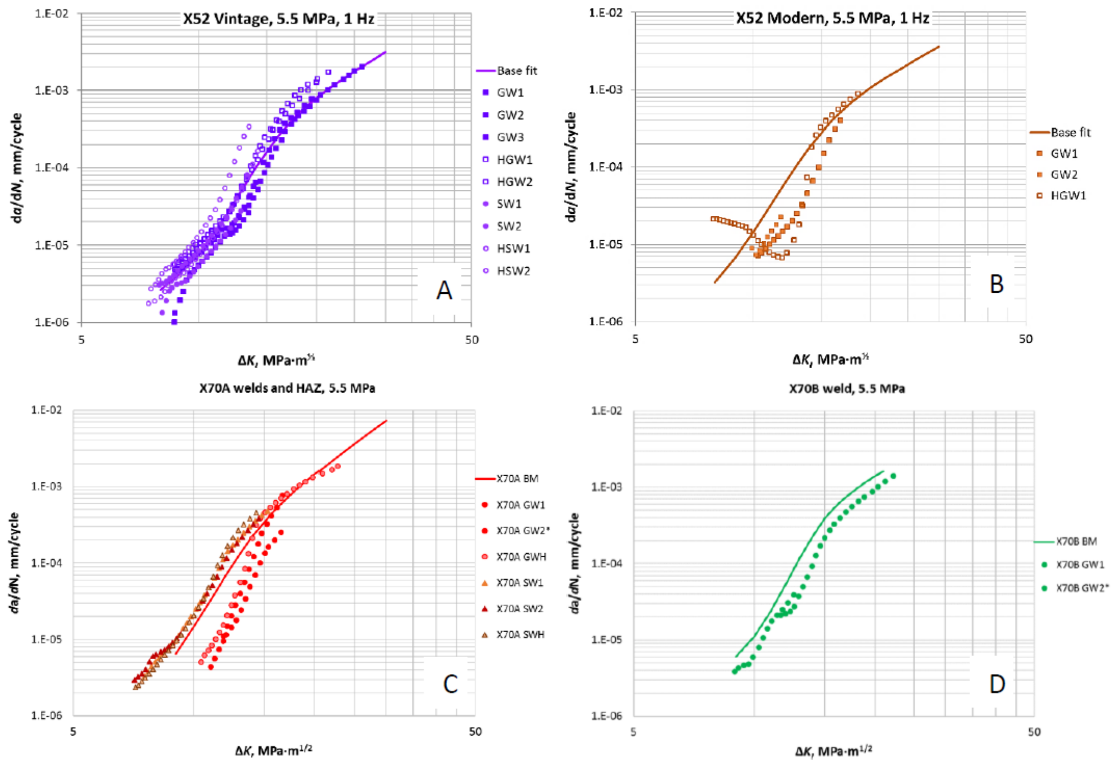

Figure 26 - FCGR of Parent, Seam and Girth Welds in X52 and X70 Steels - from Drexler

A 2018 study performed by Ronevich et al. (74) explored the fatigue performance of five high-strength X100 steel pipeline welds in high pressure (21 MPa) hydrogen gas.

Results are summarised in Figure 27 and show a large amount of variability. Ronevich notes that the HAZ FCGR was in general lower than the weld metal equivalent, but cautions that this, and the variability seen, may have been due to the differing residual stress levels. The FCGR for X100 welds was noted to be slightly higher than for lower strength (X52, X65 and X70) welds but still in general accordance with the B31.12 curve.

Ronevich has separately also published some data regarding the susceptibility of X65 welds (77), this time implying that welds were more susceptible to hydrogen accelerated FCGR than base metal, although again emphasising the uncertainties present.

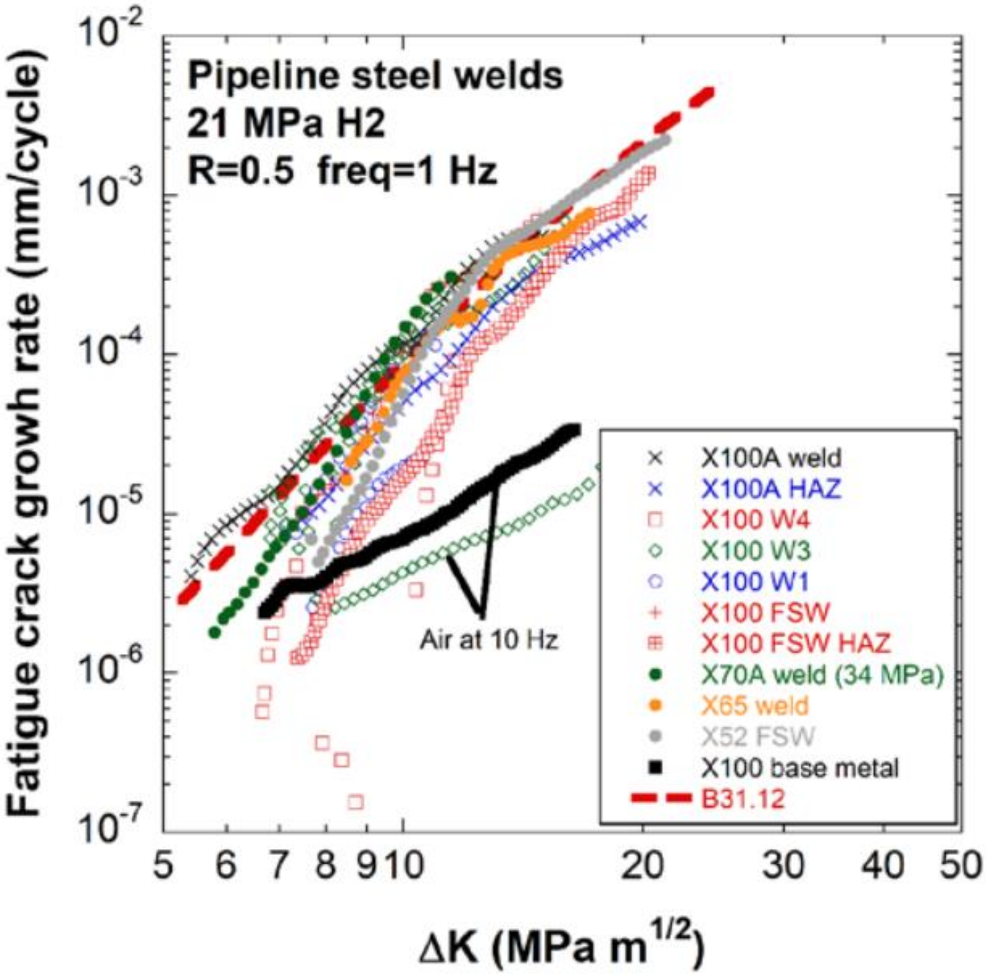

Figure 27 - FCGR of X100 Pipeline Steel Welds in Hydrogen - from Ronevich

As part of the Sandia Technical Reference (23), San Marchi et al. state that the FCGR for X60 steels are nearly identical for base metal, HAZ and fusion zone of a submerged arc weld (6.9 MPa H2, 1 Hz test frequency, load ratio 0.15).

7.11 Effect of Temperature

Barthelemy and Pressouyre (13) showed that, when measured through disc tests, hydrogen embrittlement is maximum at room temperature (~20 °C) and at 100 °C embrittlement is generally low. Although the relationship between embrittlement and temperature is understood, the same cannot be said for FCGR and temperature influences. Zhang (67) reports some work by Fuquent-Molano and Ritchie investigated the effect of temperature on fatigue crack growth rates in both air and hydrogen. Specimens prepared from 2.5Cr-1Mo steel were tested at temperatures of 28, 54, 65 and 110 °C at a hydrogen pressure of 0.138 MPa. The stress ratio and loading frequency were 0.05 and 50 Hz, respectively. The test results showed that the crack growth rates in both air and gaseous hydrogen increased, and the intensity factor threshold value ΔK_{th} decreased, with increasing temperature, although the effect of temperature diminished at higher growth rates. The crack growth results at 110 °C in hydrogen, however, opposed this trend and showed significantly higher threshold values.

Conversely, as also discussed by Zhang, Stewart investigated the influence of temperature on FCGR and found that over the range 23 °C to 85 °C the FCGR was progressively reduced as the temperature increased. At 85 °C, there was no significant change in crack growth rate in hydrogen when compared to that in air at 23 °C.

7.12 Summary of fatigue performance

Currently ASME B31.12 controls the effects of hydrogen in steel by recommending lower strength steels in the non-mandatory Annex A. It should however be noted that higher grade steels are permissible, and a formula for calculating FCGR is presented within ASME B31.12 (see Section 7.2). Although hydrogen embrittlement is prominent in high-strength steels, fatigue performance is less linear and is degraded in both ferritic and austenitic steels, and in both low and high strength steels. The findings from the review for the effects on the FCGR are summarised:

- Compared to the crack growth rates in air, the acceleration in hydrogen depends on the ΔK magnitude. The largest hydrogen effect is often found to occur in the high ΔK regime.
- The degradation of crack growth resistance increases with increasing hydrogen partial pressure. Crack growth acceleration can occur in hydrogen pressure as low as 0.2 MPa.
- The acceleration in crack growth rates in hydrogen increases with decreasing loading frequency.
- Although crack growth rates in hydrogen increase with increasing stress ratio R, as in air, the acceleration is more evident at lower stress ratio.
- The effect of material strength on fatigue crack growth rates in hydrogen is not conclusive.
- Inhibitor additives such as O_2 and CO are seen to drastically reduce the effects of both HE and FCGR.

ASME B31.12 uses 'Design factors' to make system design more conservative until actual material test data is available. When the code was written, the 'Design factors' were based on limited data and obtained under the most severe conditions for the hydrogen effect, such as determination of crack growth rates at high ΔK range, high hydrogen pressure, low loading frequency etc. Thus, the method using 'Design factors' is considered over-conservative for some applications. Therefore, it is desirable to obtain the necessary data under testing conditions appropriate to the proposed service to avoid over-conservatism.

8 HYDROGEN CRACKING

8.1 Mechanistic Description

The phenomenon of “hydrogen cracking” is well known within the industry. Common types of “hydrogen cracking” include sour service cracking (Sulphide Stress Corrosion Cracking (SSCC), Hydrogen Induced Cracking (HIC) and Stress Oriented Hydrogen Induced Cracking (SOHIC)) and “cold cracking” in weldments. In both these cases, cracking susceptibility is heavily dependent on material hardness (as a proxy for microstructure), with harder martensitic type materials being more susceptible. Importantly, the level of hydrogen introduced into steel either through H_2S corrosion or high hydrogen welding processes is significantly higher than that seen from gaseous hydrogen at typical pipeline operating conditions.

8.2 Current Available Design Criteria

Existing codes (ASME B31.12 (6) and the AIGA / EIGA guidelines (7)) make reference to the potential for hydrogen cracking, but do not consider that the level of hydrogen introduced through gaseous hydrogen alone make the threat credible.

8.3 Susceptibility Factors

According to ASME B31.12, hydrogen embrittlement (and by extension hydrogen cracking) has been reported to be a form of stress corrosion cracking. As with any form of stress corrosion cracking, three basic elements are required. A susceptible material, a corrosive environment and stress (applied or residual). As noted above, for normal pipeline steels and operating conditions the material is not susceptible therefore this threat can be discounted. This approach is supported by the fact that no instances of hydrogen cracking induced purely by gaseous hydrogen at "normal" pipeline pressures and temperatures have been reported. There is however some anecdotal evidence that extremely hard materials have cracked in gaseous hydrogen (78). It is unclear whether conventional pipeline steels would ever have this level of hardness, even with a martensitic microstructure (e.g. a "hard spot" or poorly controlled welding), however this potential threat does not appear to have been explicitly addressed.

8.4 Test Protocols

There are well established test protocols available for susceptibility to HIC and SSCC (e.g. NACE TM0177 (79) and NACE TM0284 (80)) but nothing specifically for cracking in the absence of applied stress for gaseous hydrogen. ISO 11114-4 (61) offers some guidance, as does CHMC-1 (81) but all test methods appear to be predicated on the existence of applied stress and (mostly) a pre-existing crack-like defect.

9 INFLUENCE OF IMPURITIES AND ADDITIVES

9.1 Mechanistic Description

As hydrogen embrittlement requires the absorption of hydrogen into the steel followed by diffusion to microstructural locations, factors that change the ease of this absorption and its interaction with the steel, such as impurities in the hydrogen, affect the susceptibility of the component to cracking or embrittlement. These impurities can include natural gas (as part of a blended fuel), impurities deliberately added for their potential beneficial effects (e.g. oxygen as discussed below), or unavoidable contaminants (e.g. water). Staykov et al. (82) report that potentially beneficial additives such as O_2 and CO effectively compete with H_2 for surface adsorption sites due to the greater attractive force acting on the impurity molecule compared to hydrogen, therefore small additions of oxygen can lead to large reductions in the amount of adsorbed hydrogen. In contrast Staykov reports that CH_4 has no effect on H_2 dissociation. Water is a special case, since if liquid water forms inside a gas pipeline then electrochemical corrosive reactions can occur. These are likely to have a larger effect on the hydrogen content in the pipe wall than the dissociation of gaseous hydrogen. Finally there are unavoidable contaminants which actively increase susceptibility to hydrogen embrittlement such as H_2S and components such as CO_2 which are often present in transmission pipelines at low levels. It appears likely that these contaminants increase susceptibility by increasing the absorption rate of hydrogen into the steel lattice, however the exact mechanism by which this happens still appears to be unclear.

9.2 Current Available Design Criteria

ASME B31.12 (6) covers pipelines with a hydrogen content above 10% by volume. The remaining fluid content is not specified, but is implied to be natural gas. The moisture content within the transported fluid is specified to be less than 20 ppm, however there are no other specific restrictions. There is no reference to the potential beneficial effect of oxygen additives.

The AIGA / EIGA (7) guidelines cover pipelines carrying “pure hydrogen and hydrogen mixtures”. Appendix G within the guidelines specifically states that the water content should be less than 20 ppm with the CO_2 content being less than 100 ppm. The balance should be “inerts and / or methane”. The hydrogen content is 10% or more and CO is specified to be less than 200 ppm. There is no reference to the potential beneficial effect of oxygen additives.

9.3 Relevant Research

Despite the lack of recognition within design codes, there is a large body of research which demonstrates that some additives can have a beneficial effect when added to hydrogen. It therefore appears likely that the omissions from the design codes are related more to concerns about relying on accurate control and monitoring of these additions or safety concerns rather than fundamental questions about their effectiveness.

Barthelemy et al. (13) described the following molecules and their effect on hydrogen embrittlement:

- HE Inhibitors – O_2 and SO_2
- No Effect – CH_4 and N_2
- HE Accelerators – H_2S and CO_2
- Inhibitor or accelerator – H_2O

Barthelemy quantified the effect of oxygen additives by means of comparing the rupture pressure in a disk rupture test performed in helium, pure hydrogen and different amounts of oxygen additive as shown in Table 22. In this case P He / P x refers to the ratio of disk rupture stress in helium compared to the test environment (either pure hydrogen or hydrogen with either 120 or 10000 ppm oxygen addition).

<table>
<tr><th>Steel Grade</th><th>UTS (MPa)</th><th>PHe / P H2</th><th>PHe / P (H2 + 120 ppm O2)</th><th>PHe / P (H2 + 10000 ppm O2)</th></tr>
<tr><td rowspan="2">10N14</td><td rowspan="2">605</td><td>2.6</td><td rowspan="2">1.35</td><td rowspan="2">1.2</td></tr>
<tr><td>2.1</td></tr>
<tr><td rowspan="2">API 5L X70</td><td rowspan="2">500 – 600*</td><td>2.7</td><td rowspan="2">1.5</td><td rowspan="2">1.2</td></tr>
<tr><td>2.15</td></tr>
<tr><td>20CND10</td><td>690</td><td>2.1</td><td>1.3</td><td>1.1</td></tr>
</table>

Steel Grade	UTS (MPa)	PHe / P H2	PHe / P (H2 + 120 ppm O2)	PHe / P (H2 + 10000 ppm O2)
		1.9		
		1.8	1.5	
		1.9	1.7	
"Steels from gas cylinder"	900 - 1000	1.8	1.5	
		2.0	1.85	

Table 22 - Effect of Oxygen Additions on Disk Rupture Pressure - From Barthelemy

*UTS values for X70 taken from the original paper, noting that they appear low.

Briottet et al. (47) investigated the effect of oxygen on fracture toughness in hydrogen, and concluded that oxygen can mitigate the detrimental effect of hydrogen on X70 steel for values higher than 50 vol. ppm. Results are shown in Figure 28 and Figure 29, based on a total pressure of 8.5 MPa.

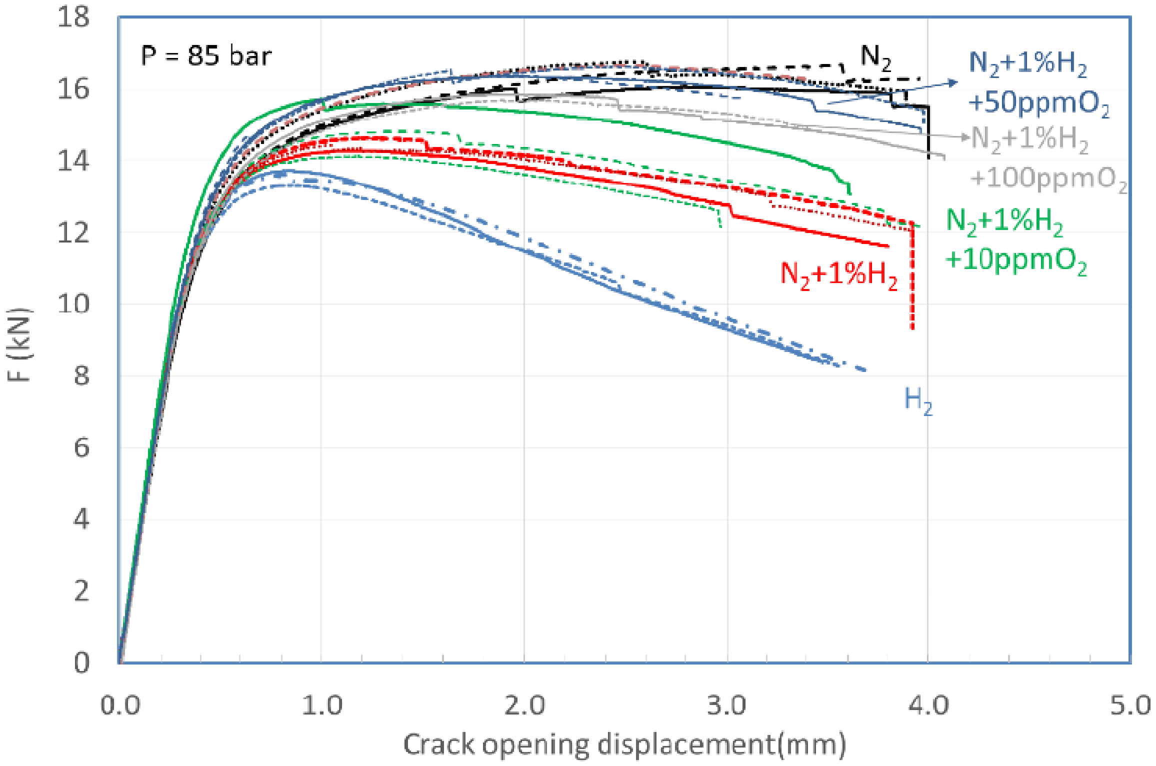

Figure 28 - Effect of Oxygen on Hydrogen Fracture Toughness - from Briottet

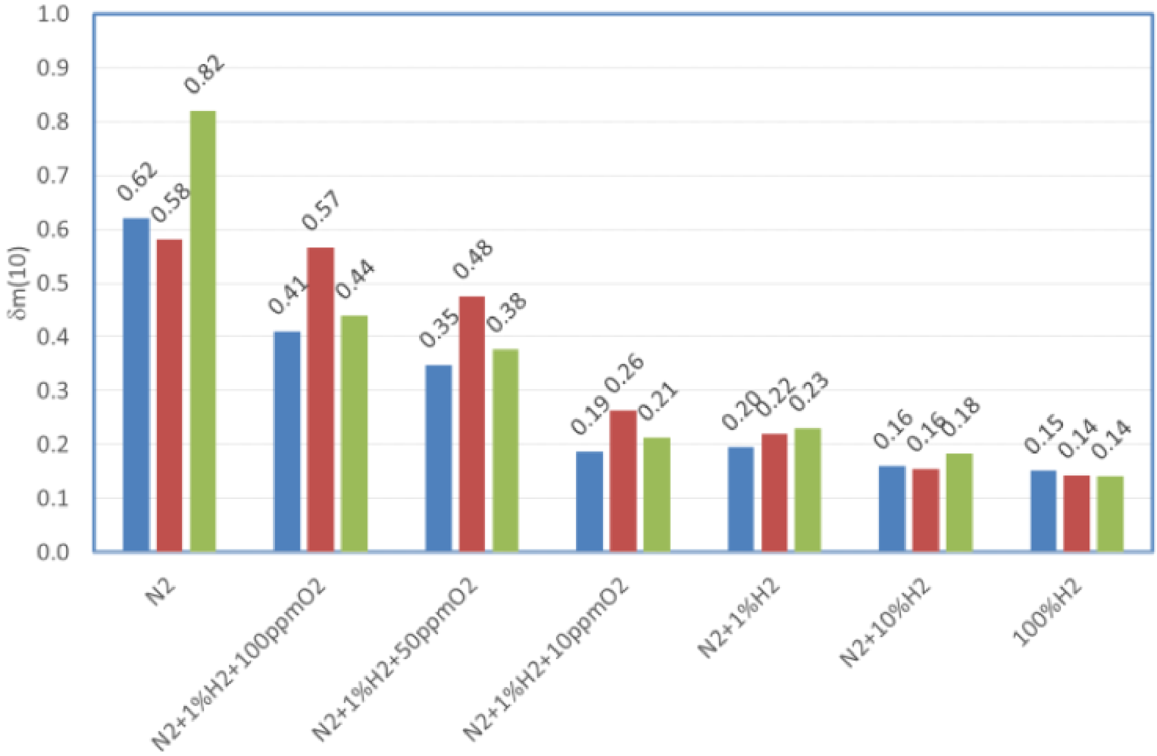

Figure 29 - Effect of Hydrogen and Oxygen on CTOD of X70 Steel - from Briottet

Somerday et al. (43) demonstrate similar beneficial effects on FCGR, showing improvements with additions of SO_2 and CO as well as O_2. The detrimental effects of CO_2, and the ambivalent effects of water, are also shown.

Note that the purpose of the above graphs is to illustrate the effects of additives. It is recognised that the absolute fracture toughness values reported in Figure 29, even in pure hydrogen, would be considered acceptable for many applications. It is also noteworthy that even in pure hydrogen the failure mode was maximum load rather than unstable crack growth.

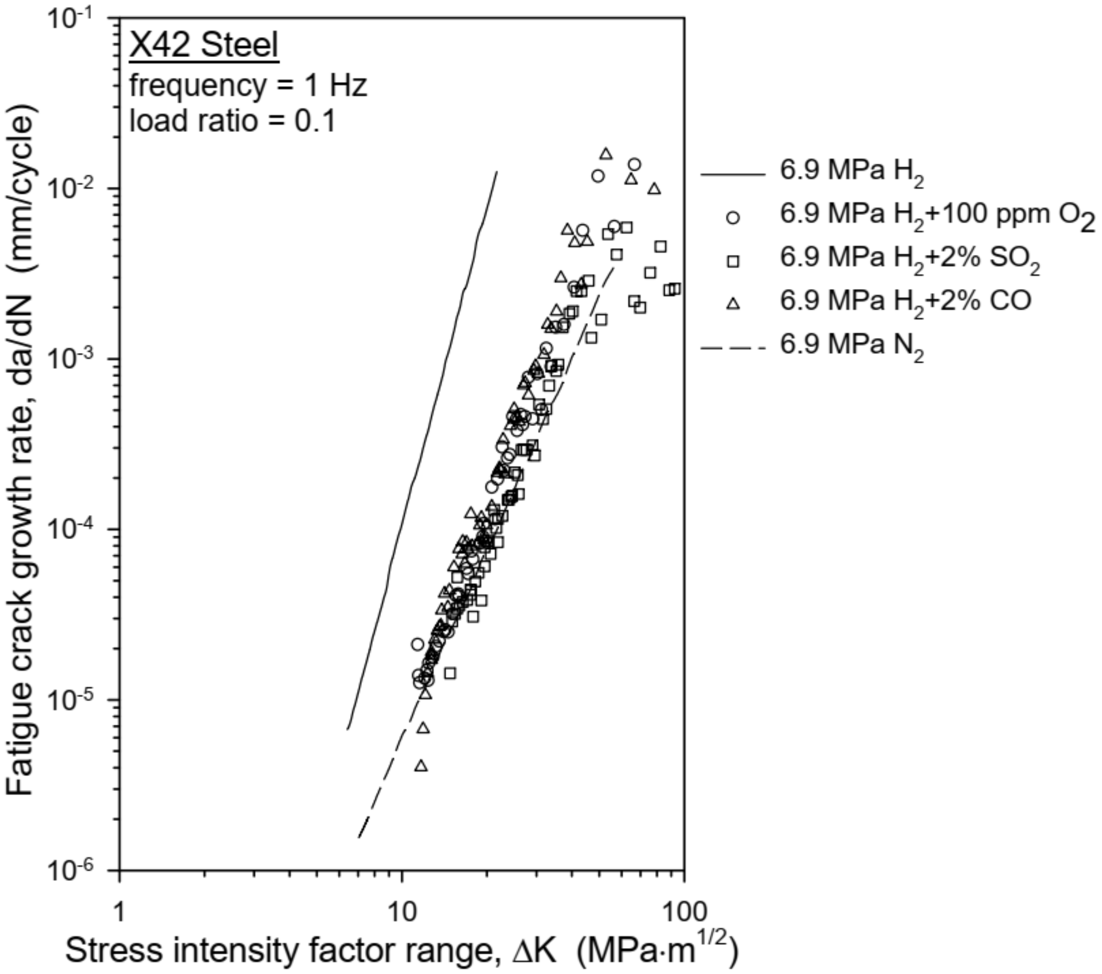

Figure 30 - Effect of Impurities on FCGR in Hydrogen - from Somerday et al.

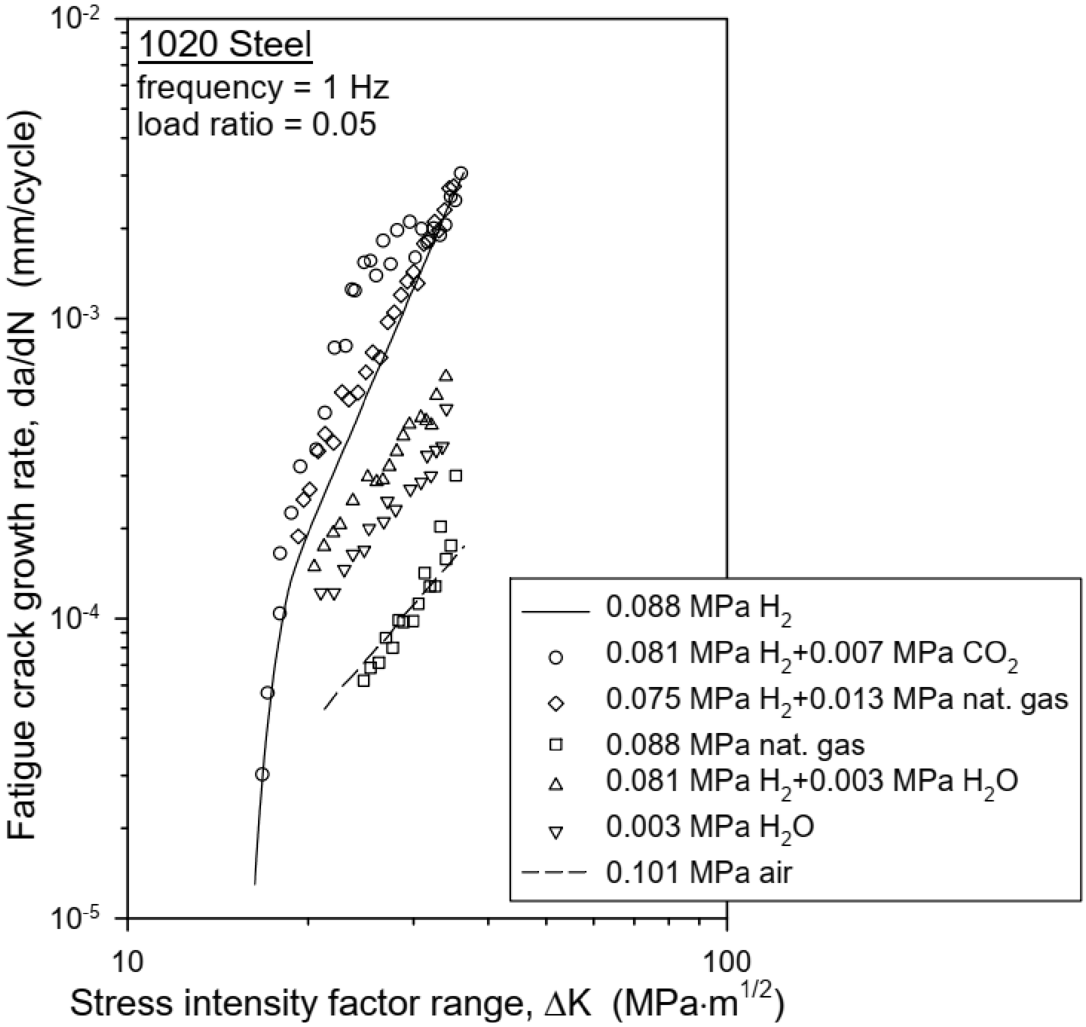

Figure 31 - Effect of Water and CO_2 Impurities on FCGR - from Somerday

The effects of various impurities on FCGR are summarised in Barthelemy (48) as shown in Figure 32

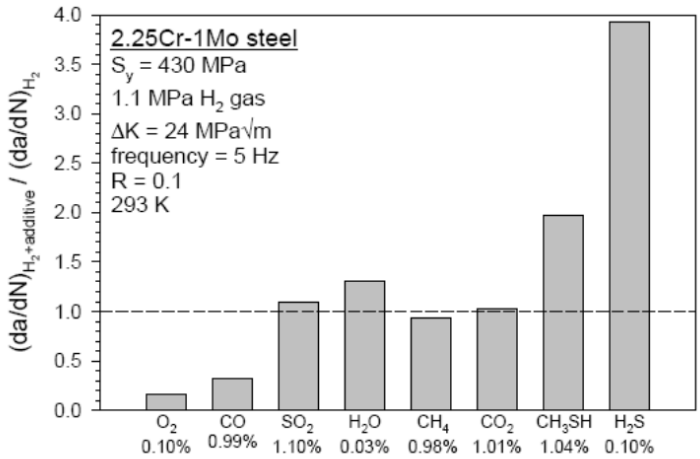

Figure 32 - Effect of Various Impurities on FCGR - from Barthelemy

Holbrook (70) reports that, according to Batelle, "*Hydrogen acceleration of fatigue-crack growth in pipeline steels is essentially eliminated by the presence of as little as 90 ppm oxygen*". This finding is expanded upon later in Holbrook's report, where it is stated that "*the information in the literature is not sufficient to draw conclusions on how much oxygen is needed to inhibit hydrogen effects in all cases. In fact, the amount of oxygen required appears to depend on the yield strength of the steel (and possibly the microstructure and chemical composition), the absolute hydrogen pressure, and the particular mechanical property that hydrogen is degrading*". For the purposes of their own research, Holbrook chose an upper limit of 100 ppm oxygen as being "*uncontaminated*", but admits that this was essentially arbitrary.

Somerday et al. (83) performed more work looking at the effect of oxygen on FCGR, and found that the oxygen effect decreased with increasing ΔK as shown in Figure 33.

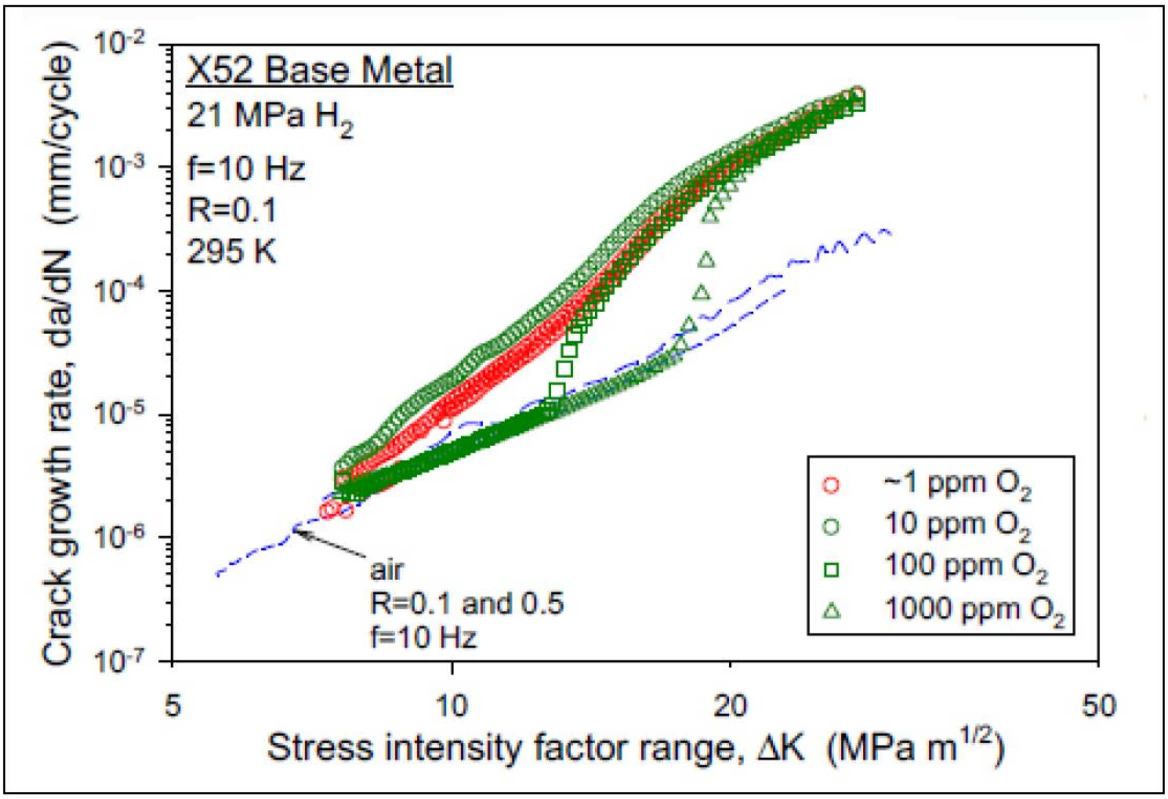

Figure 33 - Effect of Oxygen on FCGR at Various ΔK Ranges

It should be noted that all the above research appears to have focussed on defined, and controlled, levels of impurities / additives. It appears inevitable that, particularly in the case of oxygen or other impurities that "out-compete" hydrogen at absorption sites, there will be some consumption of the impurity and therefore variable concentrations along a pipeline.

10 HYDROGEN AND NON-METALLIC MATERIALS

10.1 Mechanistic Description

A Sandia study (84) indicates that polymers are not subject to hydrogen embrittlement in the same way as metals. In metals, hydrogen dissociates at the metal surface, whereas polymers are able to absorb diatomic hydrogen. However, even though the hydrogen remains chemically intact, it can still influence the properties of polymers. The study indicated that some gases, using carbon dioxide as an example, become strong solvents for many polymers at high pressure and have a plasticising effect. Hydrogen is expected to be inert in the presence of most polymers but its effects have rarely been specifically studied at high pressures. Table 1.1 in the reference document is reproduced below.

Table 1.1 Examples of polymer materials used in high-pressure hydrogen infrastructure

Component	Description	Example materials[a]
Compressed hydrogen pressure vessels	Type III	Metallic liner; composite vessel: glass fiber or carbon fiber, epoxy resin
	Type IV	Polymer liner: HDPE, nylon; composite vessel: glass fiber or carbon fiber, epoxy resin
Pipelines	Multi-layer construction for high-pressure distribution (>10 MPa)	Polymer liner: HDPE, nylon; composite vessel: glass fiber or carbon fiber, epoxy resin
Piping, tubing	Monolithic construction for low-pressure distribution (<10 MPa)	HDPE, PP, PVC, CPVC
Mechanical compressors	Seals and coatings	Teflon composite, PEEK
Dispensing hoses		Proprietary/unknown material
Flange connections (low pressure)	O-rings, gaskets	Nitrile rubber, Viton, Teflon
Threaded connectors (high pressure)	O-rings	Nitrile rubber, Viton
Valves (manual, actuated, check, velocity, relief devices)	Pistons	PEEK
	O-rings, fittings, etc.	Nitrile rubber, Viton, Teflon
	Seals and gaskets	Teflon, Viton, nitrile rubber, EPM, fluorosilicone, silicone, Neoprene, Nylon, PEEK
	Valve seats	Nylatron, Vespel, PCTFE, Teflon

Table 23 - Examples of Polymer Materials Used in High-Pressure Hydrogen Infrastructure – from Barth

As the generic term of polymer covers a wide range of material types, it is important to acknowledge there are marked differences within the groups that exist, based on their specific microstructures. These are semi-crystalline thermoplastics, amorphous thermoplastics, elastomers and epoxies. Within each group, polymers are not only based upon their chemical structure which defines their group allocation but also on a number of other elements. These include molecular weight and processing history. The latter impacts such factors as the degree of crystallinity within the polymer that is related to the cooling rate from molten. Processing techniques such as extrusion can influence properties. Fillers, plasticisers and crosslinking agents may be added to modify and or enhance specific properties. Unlike metals, polymer properties are affected by hydrostatic pressure and again, unlike most metals, polymers are highly sensitive to test conditions such as temperature and rate of testing.

Studies (for example by Menon et al. (85)) have shown that in high pressure hydrogen applications, polymers can be susceptible to a number of failure and / or degradation mechanisms. These include blistering due to rapid decompression, ageing and microstructural damage. Ageing in the study is used to describe the evolution of the microstructure due to exposure to gaseous hydrogen in the range of intended service temperature and pressure. Blistering is irreversible damage caused to the polymer where the saturated gas absorbed at high pressure becomes supersaturated upon decompression. The gas comes out of solution and gathers in microscopic voids (defects) in the material or at interfaces between polymer and filler particles. Multiple cycles of this can lead to eventual failure.

Typically polymeric materials are used in relatively low pressure distribution pipes in gas networks. The conditions which can lead to the failure and degradation mechanisms outlined above are therefore unlikely to be seen. It should however be noted that recently some polymeric composite (HDPE and aramid fibre) pipes are reported to have been used at an operating pressure of 32 barg, with no issues being reported (86).

10.2 Current Available Design Criteria

ASME B31.12 (6) does not reference requirements for non-metallic materials. There is however some guidance available within the AIGA / EIGA guidelines (7). The guidelines state maximum temperatures for various materials below which resistance to hydrogen seems assured, see Table 24, a summary of the chemical resistance of elastomers to hydrogen, see Table 25, and a quantification of permeation coefficients, see Table 26.

Material	Maximum Temperature / deg. C
Plasticised cellulose	20
Cellulose diacetate	20
Formo-aniline	20
Formo-urea	20
Phenol-formaldehyde	20
Furaphenol	20
Polyamides	20
Polyfuran	110
Polychloroprene	100
Polyepoxydiphenylopropane	90
Polyethylene glycol terephthalate	20
Polyurethane	20
Polyurethylmethylacrylate	20
Polyvinyl acetate	20

Material	Maximum Temperature / deg. C
Polyvinyl chloride	60
Polytrifluorochloroethylene	180
Polytetrafluoroethylene	250
Polyethylene	60
Polyisobutylene	100
Polystyrene	20
Polyacrylonitrile	20
Polyvinyl-vinylidene chloride (20-80%)	60

Table 24 - Maximum Temperatures for Polymeric Materials in Hydrogen - from AIGA / EIGA Guidelines

Material	Compatibility
Natural Rubber	Fair
Butyl Rubber	Good
Silicone Rubber	Fair
Neoprene ®	Good
Buna S ®	Good
Hypalon ®	Good
Viton ®	Good

Material	Compatibility
Buna N ®	Good

Table 25 - Elastomers Compatibility With Hydrogen - from AIGA / EIGA Guidelines

Material	Permeation*
Natural Rubber	492
Butyl Rubber	74
Buna S ®	399
Perbunan ® G	158
Neoprene ® G	133
Hycar or 15 ®	74
Polybutadiene	424
Polymethylpentadiene	428
Perbunan 18 ®	251
Isoprene-methacryl-nitrile copolymer	138
Hycar or 25 ®	118
Polymethylbutadiene	172
Vulcoprene A ®	64

Material	Permeation*
Isoprene-acrylonitrile copolymer	74
Thiokol S	16

Table 26 - Permeation of Hydrogen Through Elastomers at 25 deg. C - from AIGA / EIGA Guidelines

*Values to be multiplied by 10^{-10} to obtain cm^{-3} S.T.P.mm.sec.$^{-1}$.cm^{-2}($cmHg^{-1}$)

There are no specific design guidelines available for composite pipes (those made from a combination of polymeric and metallic materials). It appears reasonable to assume that the inner layer (i.e. that layer in direct contact with the transported hydrogen) will be subject to the same effects as the equivalent material in a solid pipe, with outer layers being less affected due to the difficulties associated with permeation through the inner layer. There is however the possibility of relatively high pressure gaseous hydrogen becoming concentrated in pockets in the annuli between layers. This will give rise to mechanical threats to integrity e.g. resulting from rapid gas decompression. This does not appear to have been explicitly investigated in the literature.

10.3 Relevant Research

According to the Sandia study, there is no indication that gaseous hydrogen has a measurable effect on the mechanical properties of polymers, however the following key points require further understanding:

- Fracture and fatigue
- Failure modes
- Rapid gas decompression
- Friction and wear
- Test methods
- Plasticisation
- Transport properties
- Contaminants

(87) gives a similar high level review of compatibility, as shown in Table 27.

Polymers	Compatibility
Polyethylene	Good
Polyvinyl Chloride	Good
Natural Rubber	Fair

Polymers	Compatibility
Butyl Rubber	Good
Silicone Rubber	Fair
Neoprene (CR)	Good
Viton	Good
Buna N (NBR)	Good

Table 27 - Compatibility of Various Polymeric Materials with Gaseous Hydrogen - from Melaina

To date the limited available literature appears to conclude that the principal concern for polymeric materials in gaseous hydrogen service is increased permeability, and hence leakage, rather than specific threats to integrity. For example Melaina et al. state that the leakage rate for hydrogen is roughly a factor of 3 greater than that for natural gas. Even the normally comprehensive Sandia technical reference (23) gives no further guidance on hydrogen compatibility for common polymer materials, instead restricting itself to a “non-exhaustive summary of hydrogen transport data in common polymer materials”.

11 HYDROGEN AND NON-CARBON STEEL METALLIC MATERIALS

11.1 Mechanistic Description

The mechanisms of hydrogen degradation for non-carbon steel metallic materials are unsurprisingly the same as those for carbon steels, however the magnitude and severity of these effects differ according to the microstructural characteristics of the materials in questions.

For the purposes of this report, non-carbon steel metallic materials are split into low alloy steels, stainless steels and non-ferrous based alloys. For obvious reasons, data on these materials in gas transmission line pipe applications is scarce however what data is available is presented below.

11.2 Current Available Design Criteria

ASME B31.12 (6) only explicitly refers to carbon steels as being “listed materials” for pipelines. Reference is made to ASTM A381 (88) which does allow the use of low alloy steels by agreement however this does not appear to be the intent of B31.12. Notably B31.12 is significantly more open for piping and piping components, with various low alloy and austenitic steels being listed. In addition various specifications for copper, brass, bronze and aluminium alloys are listed.

The AIGA / EIGA guidelines (7) reference some low alloy steels as conceivably being welded to a gas transmission pipeline, and cautions that additional care should be taken when welding but is not specific.

Austenitic stainless steels are stated by the AIGA / EIGA guidelines to be suitable for hydrogen service, particularly for high pressures. The guidelines state that "Type 316L is preferred to 304L for hydrogen gas service because 316L has higher austenite stability and is less subject to hydrogen embrittlement". This statement appears erroneous, since the major difference between 316L and 304L is the presence of molybdenum in 316L, and molybdenum is widely recognised as being a ferrite (not austenite) stabiliser. Other stainless steels (ferritic, martensitic, duplex or precipitation hardened) are stated to be suitable for use provided that they are used at low stress and at the low end of their strength ranges. "Low stress" and "low strength" are not quantified.

The AIGA / EIGA guidelines also reference nickel, copper and cobalt alloys. Nickel and copper alloys are considered susceptible to hydrogen damage and it is stated that care should be taken, although beyond general guidance on limiting applied stresses and hardness there are no specific requirements. Cobalt alloys (e.g. Stellite hard facing coatings on valves) are considered acceptable.

The draft CEN/ISO report (8) has some high level information regarding compatibility as shown in Table 28.

Pressure / bar g	Materials	=< 2 Vol. %	=< 5 Vol. %	=< 10 Vol. %	=< 100 Vol. %
< 5.0	Steel	✓	✓	✓	✓ *
	Stainless Steel	✓	✓	✓	✓
	Copper (alloys)	✓	✓	✓	-
	Multilayer / PEX	✓	?	?	?
	PE	✓	✓	✓	✓
<8.0	Steel	✓	✓	✓	-
	Stainless Steel	✓	✓	✓	-

Pressure / bar g	Materials	=< 2 Vol. %	=< 5 Vol. %	=< 10 Vol. %	=< 100 Vol. %
	Copper (alloys)	✓	-	-	-
	PE	✓	✓	✓	✓
< 10.0	Steel	✓	✓	✓	?
	Stainless Steel	✓	✓	✓	?
	Copper (alloys)	✓	?	?	?
	PE	✓	?	?	?
< 60.0	Steel	?	?	?	?
	Stainless Steel	?	?	?	?
	Copper (alloys)	?	?	?	?
	PE	?	?	?	?

Table 28 - Piping Materials versus H_2 Concentrations - From Draft RC 234 WI 00234080:2020

✓ : No effect expected

-: No short term effect expected

?: Unknown

*: Up to 20 vol. %

11.3 Relevant Research

11.3.1 Low Alloy Steels

San Marchi et al. (23) emphasise that "*Hydrogen gas degrades the strength and ductility of Ni-Cr-Mo steels, particularly in the presence of stress concentrations. Additionally, hydrogen gas lowers fracture toughness and renders the steels susceptible to crack extension under static loading. Hydrogen gas also accelerates fatigue crack growth. The severity of these manifestations of hydrogen embrittlement depends on mechanical, material, and environmental variables*". A similar statement is also made with respect to Cr-Mo steels. It will be noted that a degradation of strength is explicitly noted, the data to support this assertion, while compelling, is based on a test environment of 69 MPa hydrogen gas. No strength data is presented for lower pressures more representative of pipelines.

For fracture toughness, Somerday presents various data showing that the threshold stress intensity factor for crack extension in low pressure hydrogen gas increases with loading rate and temperature, decreases with yield strength and hydrogen gas pressure, and is dependent on microstructure and chemical composition. The effects of gas pressure are comparable to those already noted for carbon steel, with the specific reported effects of loading rate, temperature, yield strength, microstructure and chemical composition being shown below.

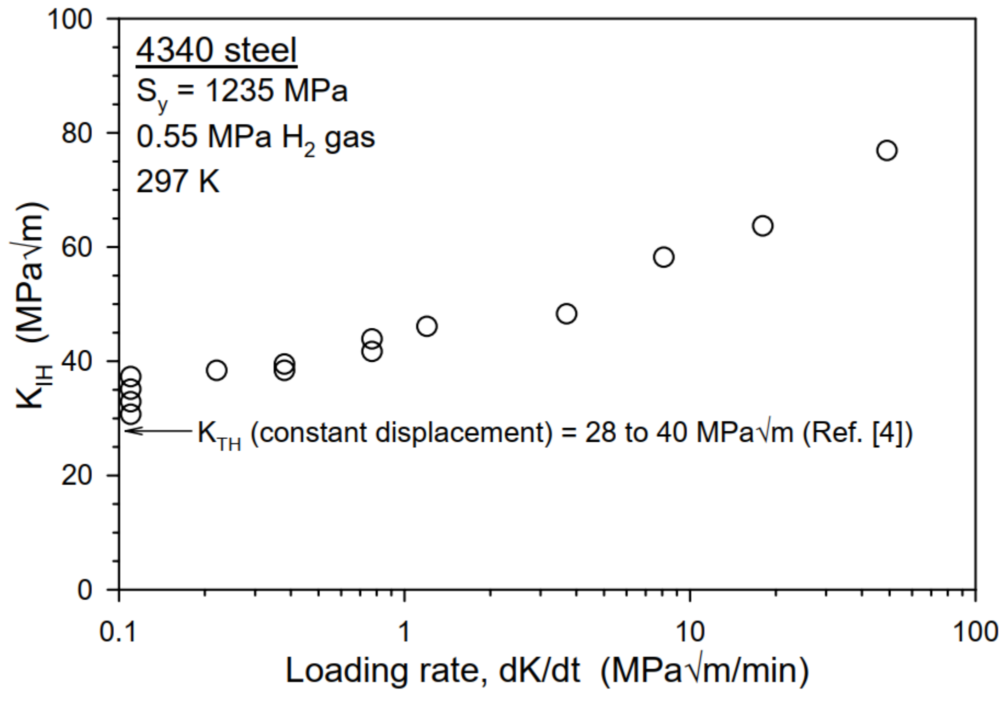

Figure 34 - Effect of Loading Rate on Fracture Toughness for 4340 Low Alloy Steel - from Somerday

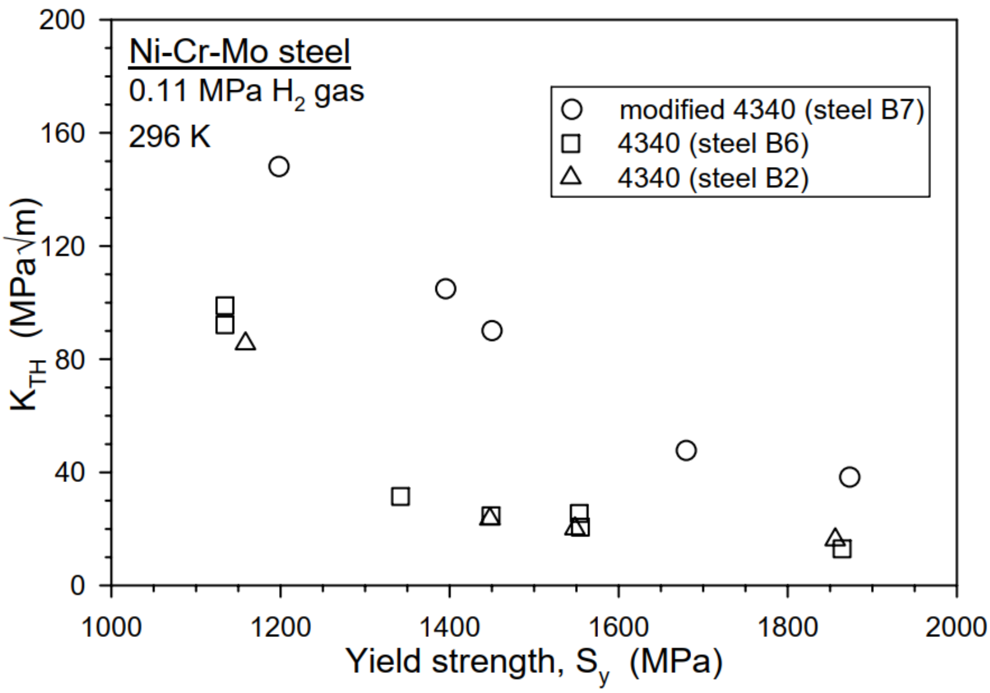

Figure 35 - Effect of Yield Strength on Threshold Stress-Intensity Factor for Crack Extension for Low Alloy Steel - from Somerday

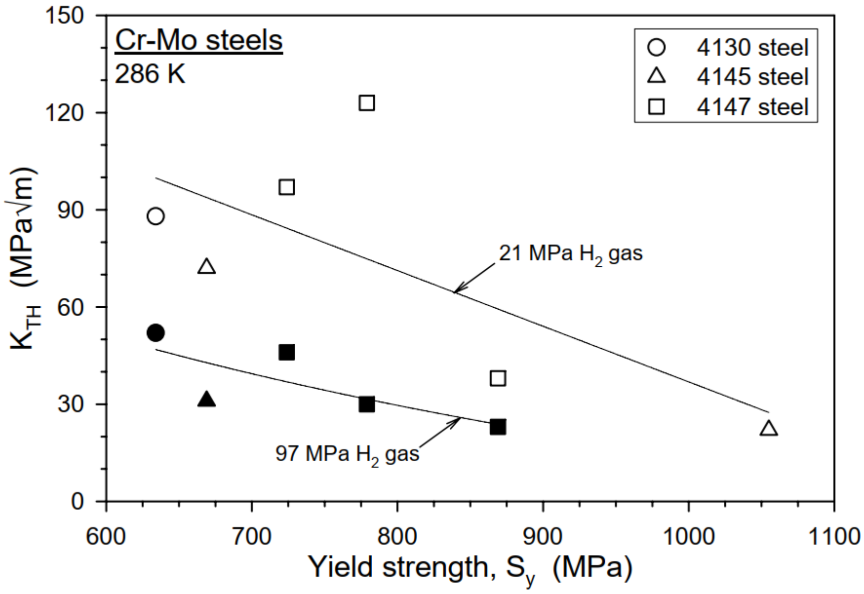

Figure 36 - Effect of Yield Stress on Threshold Stress-Intensity Factor for Crack Extension in Low Alloy Steel - from Somerday

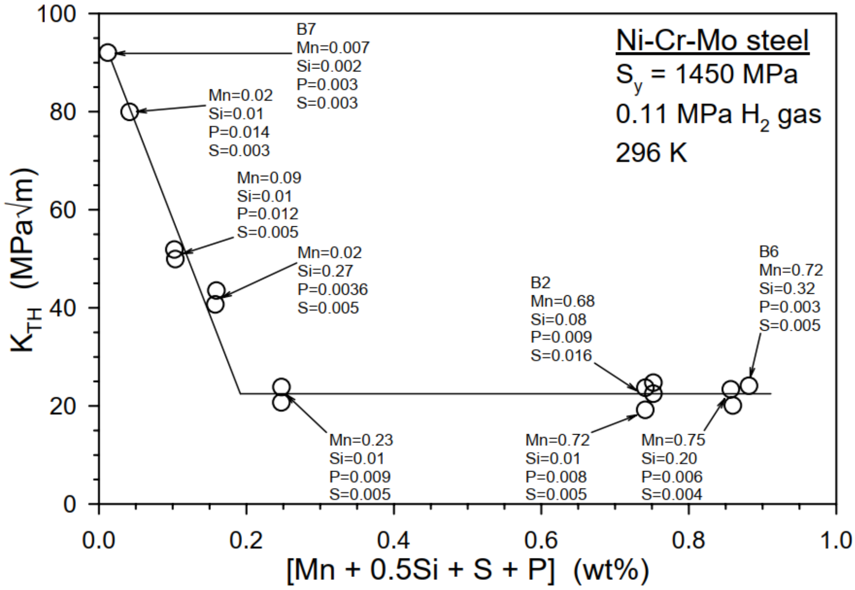

Figure 37 - Effect of Chemical Composition on Threshold Stress-Intensity Factor for Crack Extension in Low Alloy Steel - from Somerday

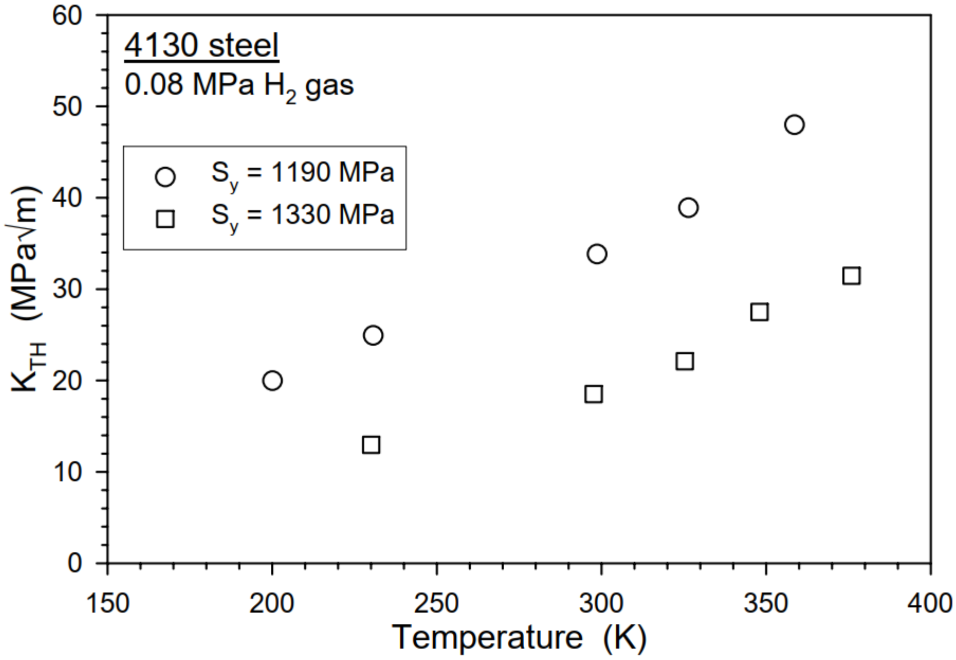

Figure 38 - Effect of Temperature on Threshold Stress-Intensity Factor for Crack Extension in Low-Pressure Hydrogen Gas for Low Alloy Steel - from Somerday

11.3.2 Stainless Steels

Stainless steels in this context include a huge number of different alloys. It is not feasible to address each individual grade individually as part of this review, however it is possible to derive some broad conclusions. The Sandia technical reference (23) includes more comprehensive data for non-carbon steels, and has been drawn upon extensively for this and following sections.

It is known that austenitic microstructures are more resistant to hydrogen attack than their ferritic or martensitic equivalents, as shown for example in the field of sour service (21). According to Somerday et al. both 304L and 316L type steels show good resistance to gaseous hydrogen, various data are presented which show minor effects on strength, ductility and fracture resistance however almost without exception these are based on experiments performed at hydrogen pressures significantly above those to be expected in pipeline service (typically 34 – 69 MPa). The only data specific to the relatively low pressures of interest in pipelines is reproduced in Table 29.

Environment	UTS (MPa)	% Reduction in UTS Compared to Air
Air	896	0
0.1 MPa H2	786	12.3
1.0 MPa H2	703	21.5
6.9 MPa H2	662	26.1

Table 29 – Effect of Gaseous Hydrogen on UTS of 304L Steel, V-notched specimen, 30 degree included angle, diameter 3.35 – 4.80 mm, notch root radius 0.127 mm, from San Marchi

As can be seen, there is a decrease in the UTS as measured on a notched specimen in hydrogen compared to air however San Marchi also notes that, for smooth tensile specimens even after pre-charging of the specimen at 470 K for 35000 hours in 69 MPa hydrogen gas the UTS only decreased by 25%.

Zhang (67) concurs that austenitic stainless steels are generally resistant to hydrogen attack, and references various papers which demonstrate negligible effects of hydrogen on the fatigue endurance of austenitic stainless steels. Tsay et al. (89) reported an increase in fatigue crack growth rate of a factor of ~10 for 304L parent and weld materials tested in 0.2 MPa hydrogen with an R ratio of 0.1 and a loading frequency of 20 Hz.

There is limited data available for other stainless steels at hydrogen concentrations and temperatures of interest for gas transportation. San Marchi reports a significant reduction in both strength and ductility for smooth tensile specimens of solution annealed AM-350 (UNS S35000, a Cr-Ni-Mo precipitation hardenable steel) when exposed to deuterium gas.

Test Environment	Yield Strength / MPa	UTS / MPa	Elongation
Air	420	1160	70
69 MPa Helium	420	1240	55
0.69 MPa D2	410	455	3
6.9 MPa D2	345	430	4
69 MPa D2	430	520	2.6

Table 30 - Smooth Tensile Properties of AM-350 in Hydrogen Gas - from San Marchi

11.3.3 Aluminium and Aluminium Alloys

San Marchi et al. (23) report that the tensile properties of commercially pure aluminium or aluminium alloys are unaffected by testing in gaseous hydrogen at pressures of up to 345 bar, as measured on either smooth or notched tensile specimens. San Marchi also reports that the fracture toughness of aluminium or aluminium alloys appears to be unaffected by exposure to gaseous hydrogen, although there is a limited amount of data available to confirm this.

11.3.4 Copper and Copper Alloys

There is limited data available for the behaviour of copper and copper alloys in gaseous hydrogen in the conditions expected for pipeline transportation. What data there is appears slightly ambiguous, San Marchi reports that "*nominally pure oxide-free coppers appear to be relatively unaffected by high-pressure hydrogen gas*" but caveats this by reporting some instances where a decrease of up to 16% in UTS was reported. San Marchi postulates that the variation in results is due to varying oxide contents, however this is unproven.

11.3.5 Nickel Based Alloys

Given the variety of nickel based alloys available an exhaustive review of the effects of gaseous hydrogen has not been performed as part of this scope. Despite this, some high level conclusions can be drawn. According to the Sandia technical reference, tensile ductility tends to be reduced in gaseous hydrogen although the magnitude of this reduction varies, and one example (Hastelloy X) is reported which was apparently unaffected by gaseous hydrogen. Fracture toughness was either significantly reduced or unaffected, with the effect again heavily dependent on the specific alloy and temperature tested. Fatigue performance (as defined by the number of cycles to failure for a given value of total strain range) decreased in hydrogen compared to helium, however this was based on a very limited dataset.

12 WELDABILITY

12.1 Mechanistic Description

Hydrogen cracking, or "cold cracking" associated with welding has been the subject of extensive research most of which is outside the scope of this review. In summary, for hydrogen cracking to occur three factors are necessary. There must be a susceptible microstructure, tensile stress (either applied or residual) and a source of hydrogen. Historically hydrogen cracking has been controlled by addressing all three of these factors, and specifically by controlling the presence of hydrogen in the weld pool through the use of low hydrogen welding processes, ensuring clean and dry conditions etc. For the case of pipelines which have already been used for hydrogen transport, the steel matrix likely already contains hydrogen, therefore intuitively controlling the hydrogen content will be more challenging. Where existing pipelines are to be converted, the microstructure and stress levels will, to an extent be fixed, therefore it is necessary to understand the effect of the increased hydrogen content.

12.2 Current Available Design Criteria

ASME B31.12 (6) has various requirements regarding welding. For construction of new-build facilities these requirements are based on ASME BPVC Section IX (90) or API 1104 (91) although there are some additional restrictions in terms of pre-heat and post weld heat treatment requirements, together with extra testing and limitations on mechanical properties (hardness and Charpy impact tests). ASME B31.12 also explicitly prohibits "*metallurgical notches*", defined as "*Stress concentrations that may or may not involve a geometrical notch [that] may also be created by a process involving thermal energy in which the pipe surface is heated sufficiently to changes its mechanical or metallurgical properties*". Specifically ASME B31.12 prohibits arc strikes and states that they must be removed or ground out, however this definition would also appear to cover metallurgical hard spots. The rationale behind this requirement is unclear, and it may be based on a perceived risk of cracking analogous to sour service, however this risk in gaseous hydrogen has not been quantified (see Section 8.3). These requirements appear difficult or impossible to apply retrospectively to existing pipelines being repurposed for hydrogen service.

There is limited guidance within ASME B31.12 for in-service welding, however there is some guidance for hot tapping. The use of a thermal analysis programme is mandated and restrictions are placed as to where the hot tap may be carried out in terms of location, allowable thickness and hardness. No additional restrictions are required for to account for the effect of dissolved hydrogen when welding of materials which have been in hydrogen service but have been taken out of service for modification or repair.

The AIGA / EIGA guidelines (7) have similar restrictions for the construction of new build facilities. For example there are limits on the maximum allowable hardness, although they specify that microhardness traverses should be used. The AIGA / EIGA guidelines also require that seam welded pipes shall be normalised locally in the seam weld, strangely this requirement appears to apply to SAW pipe as well as ERW, the rationale or uptake of this requirement is unclear. The necessity of avoiding hard spots is emphasised within the AIGA / EIGA guidelines.

There are similar restrictions on hot tap welding within the AIGA / EIGA guidelines to those referenced in ASME, again there are no additional requirements (e.g. bake-out) to account for the effect of dissolved hydrogen when welding of materials which have been in hydrogen service but have been taken out of service for modification or repair.

It is reported that EN 12732:2013 (92) is currently under revision, and it is believed that this revision will take hydrogen aspects into account however no further information on this is publicly available.

12.3 Available Research

Pargeter and Wright (93) have previously published work identifying the impact of arc welding on materials that are deemed to have absorbed hydrogen during service. The samples used during the tests simulated material that had been hydrogen charged in-service but the tests did not consider pipeline specific issues such as the velocity of flow of the contents. Although no prescriptive boundaries are identified, the outcomes demonstrate there is a relationship between absorbed hydrogen and the propensity to hydrogen induced cracking. These can be considered in conjunction with the requirements of an in service weld and the impact the flow conditions have on variables such as preheat and heat input, which were considered as part of the study.

In summary, Pargeter and Wright give recommendations for welding of both carbon manganese and low alloy steels containing hydrogen, these recommendations mainly involve good welding practise (e.g. cleanliness of the joint, appropriate levels of pre-heat, heat input and PWHT etc.) although a hydrogen bake-out prior to welding of low alloy steels is also recommended.

For hot tap welding specifically, a good summary is given by Amend and Bruce (94). Although not specific to hydrogen, the importance of controlling the inside surface temperature of the pipe is shown. Since the thermal characteristics inside a hydrogen pipeline will differ from those of a (natural) gas pipeline, hot tap procedures for natural gas will not necessarily be suitable for hydrogen.

13 INFLUENCE OF HYDROGEN ON IN-SERVICE CHANGES TO MATERIAL

13.1 Mechanistic Description

In any pipeline there is the possibility of mechanical damage, primarily arising due to external factors (e.g. ground movement or third party damage). This damage will normally result in plastic deformation and consequent work hardening of the pipeline steel, this can be manifested as dents or gouges. The decrease in steel ductility noted in hydrogen service (see Section 5) can affect the severity of this damage.

In addition to the “standard” dents and gouges mentioned above, existing pipelines will also be vulnerable to areas of high strain, volumetric corrosion, dents and gouges associated with welds etc., in addition to historic repairs performed at various times in accordance with various codes. Assessment of the acceptability of these features has historically relied on various criteria which have been developed for natural gas service. It is not known whether these criteria are appropriate for hydrogen charged materials.

13.2 Current Available Design Criteria

ASME B31.12 (6) states that dents that affect the curvature of the pipe at the longitudinal or any circumferential weld shall be removed. ASME also states that all dents of a depth greater than 6.35 mm (for pipes of DN 300 or smaller) or 2% of the nominal pipe diameter (for pipes greater than DN 300) are not permitted for pipelines intended to operate at hoop stress levels of 40% or more of the SMYS. No guidance is given for dents where the hoop stress is below 40% of SMYS.

The AIGA / EIGA guidelines (7) mention dents and gouges as being potential threats, however no detailed guidance is given. Reference is made to ASME B31.8S (95) for determining and assessing defects.

13.3 Available Research

Unfortunately there appears to be very little research available in the public domain regarding the susceptibility of hydrogen pipelines to damage, and potential repair strategies. As part of the NATURALHY project Alliat and Heerings (96) referenced the challenges involved and it is believed that a significant amount of work was performed addressing these challenges. Unfortunately the majority of this work does not appear to have been published in an open forum.

Some of the NATURALHY work was published by Capelle et al. (46). This work concluded that "*The burst tests of externally notched pipes under pressure of hydrogen and natural gas (methane) showed that there is no gaseous hydrogen effect on the strength of notched pipes for considered testing conditions*", however Capelle also found that hydrogen led to a change in the mechanism of local fracture and recommended further work. Separately the same authors report that hydrogen makes no difference to the burst pressure of an X52 pipe, but does reduce the "safety factor" in the presence of a severe surface gouge defect by 14% (97). Note that this wording (safety factor) is taken from the conclusion, the body of the paper states that the "safety factor" decreases by 18% while the "security factor" decreases by 14%.

Alvarez et al. have investigated potential fitness for service approaches for hydrogen pipelines (98) looking at the different degradation mechanisms and the effect of pre-existing defects. This work only applied the standard FAD fracture assessment method to axial cracks with a reduced material fracture toughness to allow for the effects of hydrogen. Pipeline industry specific methods such as the NG-18 method for axial cracks and other assessment methods for defects such as volumetric corrosion (such as B31G, RSTRENG and LPC) or dent-gouges were not considered, and indeed there appears to be no published research on the effect of hydrogen on these methods. All of these methods are semi-empirical and have been calibrated against test data pressurized with "inert" media. The potential effects of hydrogen, through reduced ductility and fracture toughness, are not known.

14 IMPACT OF USE OF PIPELINE SYSTEMS FOR STORAGE AS WELL AS TRANSPORT

14.1 Mechanistic Description

Pipelines offer the most efficient way to transport bulk quantities of gaseous fuel from production to end users. Typically, natural gas pipelines are sized to deliver gas at times of peak demand; equally they are capable of storing gas through line packing methods at times of low demand. Numerous studies have raised concerns regarding the reduced line pack capacity of hydrogen in the existing gas grid. For instance, in the UK network, pipes in different parts of the system are constructed of different materials, with the variations mainly reflecting the operating pressure and ages of the pipelines. A breakdown of the UK pipe network is provided in Table 31. Note that this table has been reproduced largely verbatim from (99) and does not fully agree with the usual description of the UK gas network and the timing of the change to PE at lower pressures. However, the overall breakdown is approximately correct.

Network	Network Component	Pressure (bar)	Material		Length (km)
			Pre-1970	Post-1970	
Transmission	Transmission	70-94	High-strength steel		7,600
Distribution	High Pressure	7-30	High-strength steel		12,000
	Intermediate Pressure	2-7	Steel	HD PE	5,000
	Medium Pressure	0.075-2	Iron	MD PE	30,000
	Low Pressure	<0.075	Iron	MD PE	233,000
Service	Building Connections	<0.075	Copper, steel	MD PE	255,000

Table 31 - UK Gas Network, Lengths Estimated in (99) from Transco data

The energy carrying capacity of hydrogen is about 20-30% less for a pipeline of the same pipe diameter and pressure drop for natural gas according to Dodds and Demoullin (99), despite the much lower volumetric energy density of hydrogen being offset by a much higher flow rate.

As discussed by Dodds and Demoullin, the linepack capacity of the UK network for hydrogen is more than four times smaller than for natural gas based on the relative volumetric density of the fuel. Due to the line pack regime, the pressure cycle and low loading rate can promote the formation of fatigue cracks in steels and the presence of hydrogen has been found to exacerbate the fatigue crack growth rate of pipeline steels as discussed in Section 7.

Pressure changes in hydrogen pipelines could potentially lead to significantly larger crack growths per cycle. This could make line packing less attractive.

15 EVALUATION OF THE CRITICAL HYDROGEN CONTENT FOR EXISTING NATURAL GAS TRANSPORTATION LINES

As noted extensively above, even small additions of hydrogen can have a substantial effect on the integrity of existing natural gas transportation lines. The difficulty lies in defining an acceptable level of hydrogen. Importantly, existing codes (e.g. ASME B31.12 and the AIGA / EIGA guidelines) have no maximum limit on hydrogen concentration. It therefore follows that any restrictions on maximum allowable hydrogen concentration in converted pipelines are due to the differing materials, construction and operational parameters rather than being inherently part of hydrogen service.

A summary of some important publications is presented in Table 32

Publication	Maximum Hydrogen Percentage	Comments
European Commission JRC Final Report (100)	Up to 10% v/v	10% limit based on current consensus, some areas need further investigation
HSE Report (101)	Up to 20% v/v	Vulnerable appliances to be identified and modified for hydrogen levels >10%
NREL Report (87)	Up to 15% v/v	Appears to be feasible with very few modifications to existing pipeline systems or end-use appliances
CEN / ISO Draft Roadmap (8)	Up to 100% v/v	Allowable hydrogen content is dependent on the partial H2 pressure and the fatigue load. If fatigue cycling can be controlled, "*100% hydrogen gas up to the design pressure can be transported in existing natural gas pipelines without affecting the integrity of the pipeline during its lifetime*"
ASME B31.12 (6)	Up to 100% v/v	Guidelines for conversion of pipelines to hydrogen service are included in section PL-3.21 although these are relatively high level and restrictive, and not particularly useable for existing gas pipelines.
AIGA / EIGA Guidelines (7)	Up to 100% v/v	Guidelines for conversion of pipelines to hydrogen service are included in Appendix H. These have similar restrictions to ASME B31.12.

Table 32 - Allowable Hydrogen Concentrations According to Various Sources

Given the complexity and uncertainties involved in the interactions of hydrogen and steel it appears difficult to draw definitive conclusions about allowable maximum hydrogen content for all pipelines.

As stated in the CEN draft roadmap, the principal time dependent threat in hydrogen service for the temperatures and pressures to be expected in transmission pipelines is fatigue cracking. As shown in Section 7 even small additions of hydrogen can lead to significant increases in FCGR. The other principal threat is the reduction in fracture toughness expected in hydrogen service as shown in Section 6. This is more dependent on the partial pressure of hydrogen present, but is also dependent on the original material. Both ASME B31.12 and the AIGA / EIGA guidelines mandate digs to obtain material samples every mile along the length of a pipeline due to be converted if original material test certificates are not available. It is possible to imagine cases where existing pipelines are made of low toughness (but acceptable to code) materials and contain pre-existing flaws. A detailed assessment of the acceptability (or otherwise) of these flaws is therefore required.

16 SUMMARY OF HYDROGEN STATE OF THE ART

16.1 Current Status of Hydrogen Pipelines

Hydrogen has been produced, transported and stored in steel for hundreds of years and there are currently thousands of kilometres of hydrogen pipelines in service around the world. These pipelines have, almost without exception, been designed and built in accordance with hydrogen-specific codes. These codes tend to be more prescriptive in terms of allowable loading (both static and dynamic) than their natural gas equivalents and the pipelines tend to be manufactured from lower strength steel, but their existence proves that it is possible to transport gaseous hydrogen through pipelines.

16.2 Hydrogen Damage Theories and Mitigation

The exact mechanism(s) of hydrogen damage are still the subject of much debate. It is generally agreed that most damage mechanisms involve concentration of hydrogen at regions of high stress in the metallic lattice (e.g. crack tips), and that this concentration is highest where direct dissociation from gaseous external hydrogen can occur. This dissociation of gaseous hydrogen leads directly to a decrease in fracture toughness, an increased fatigue crack growth rate and a decrease in ductility.

Surface coatings and the addition of some impurities (e.g. oxygen) to gaseous hydrogen have both been shown to be effective in reducing the damage arising from hydrogen. Unfortunately it is difficult to visualise how either of these methods could be proven to be effective 100% of the time.

16.3 Hydrogen Damage Effects

The principal effects of gaseous hydrogen are an increase in fatigue crack growth rate, a decrease in fracture toughness and a decrease in ductility. The magnitudes of these effects appear to vary according to different reports, this variation may be due to differences in materials, hydrogen purity or testing methods. Strength may be reduced slightly, but this is unproven.

Fatigue crack growth rate increases even in very low concentrations of hydrogen, with increases of ~10x being reported even in 0.4 bar hydrogen. Higher concentrations of hydrogen lead to higher fatigue crack growth rates, although the magnitude of these increases is dependent on multiple other factors.

Most sources appear to agree on a reduction of 35-70% of fracture toughness, although the reported range varies between a reduction of ~85% and an increase of 11%. Importantly a number of sources report fracture toughness values in hydrogen of less than 55 $MPa.m^{1/2}$. This value is referenced in ASME B31.12 for Option B designs, but the derivation of it is unclear. The toughness of material in hydrogen is dependent on the pipeline material as well as the hydrogen concentration. This has implications for the conversion of existing pipelines, however there is also reason to believe that laboratory small scale tests are not entirely representative of full scale pipes, and therefore may be unnecessarily conservative.

Ductility appears to decrease by 20-80% in hydrogen, with the magnitude of this decrease varying due to the material and test method used.

There does not appear to be any risk of direct hydrogen cracking under normal gaseous transportation conditions, although there is a theoretical risk associated with hard spots or welds.

16.4 Hydrogen and Non-Carbon Steel Materials

Hydrogen appears generally compatible with most polymeric materials in natural gas service, however permeation and hence leakage rates may increase. Hydrogen has differing effects on non-carbon steel metals, with austenitic materials generally being less affected and higher hardness or martensitic materials being more prone to damage.

16.5 Maximum Allowable Hydrogen Content in Natural Gas Steel Pipelines

There is no clear industry consensus regarding the maximum allowable hydrogen content in existing natural gas transmission pipelines. Most guidelines refer to maximum levels of ~10-20% volume, however some documents refer to up to 100% hydrogen. The existing codes already allow up to 100% hydrogen, but are both high level and fairly restrictive in how conversions can be managed. The principal limits appear to be fatigue loading and the possibility of low toughness material or large pre-existing flaws in natural gas pipelines.

16.6 Future Work

This literature survey has demonstrated the amount of existing research which has already been carried out and reported, as well as identifying some of the uncertainties still outstanding. In particular, areas such as how to assess pre-existing defects, and the translation of the codal high level prescriptive guidance for re-purposing of pipelines into a safe practical approach need to be further considered. It is recommended that these areas be addressed both as part of the proposed fitness for service methodology and as inputs into a roadmap for EPRG.

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