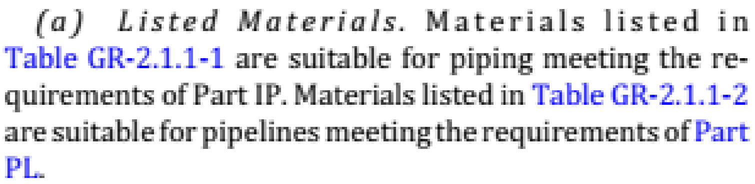
Materials and Welding Selection for Hydrogen Pipelines

Presented by Neil Gallon - September 2024

CODE REQUIREMENTS:
Material Properties

Hydrogen Pipeline Integrity

ASME B31.12 Requirements



(a) *Listed Materials.* Materials listed in Table GR-2.1.1-1 are suitable for piping meeting the requirements of Part IP. Materials listed in Table GR-2.1.1-2 are suitable for pipelines meeting the requirements of Part PL.

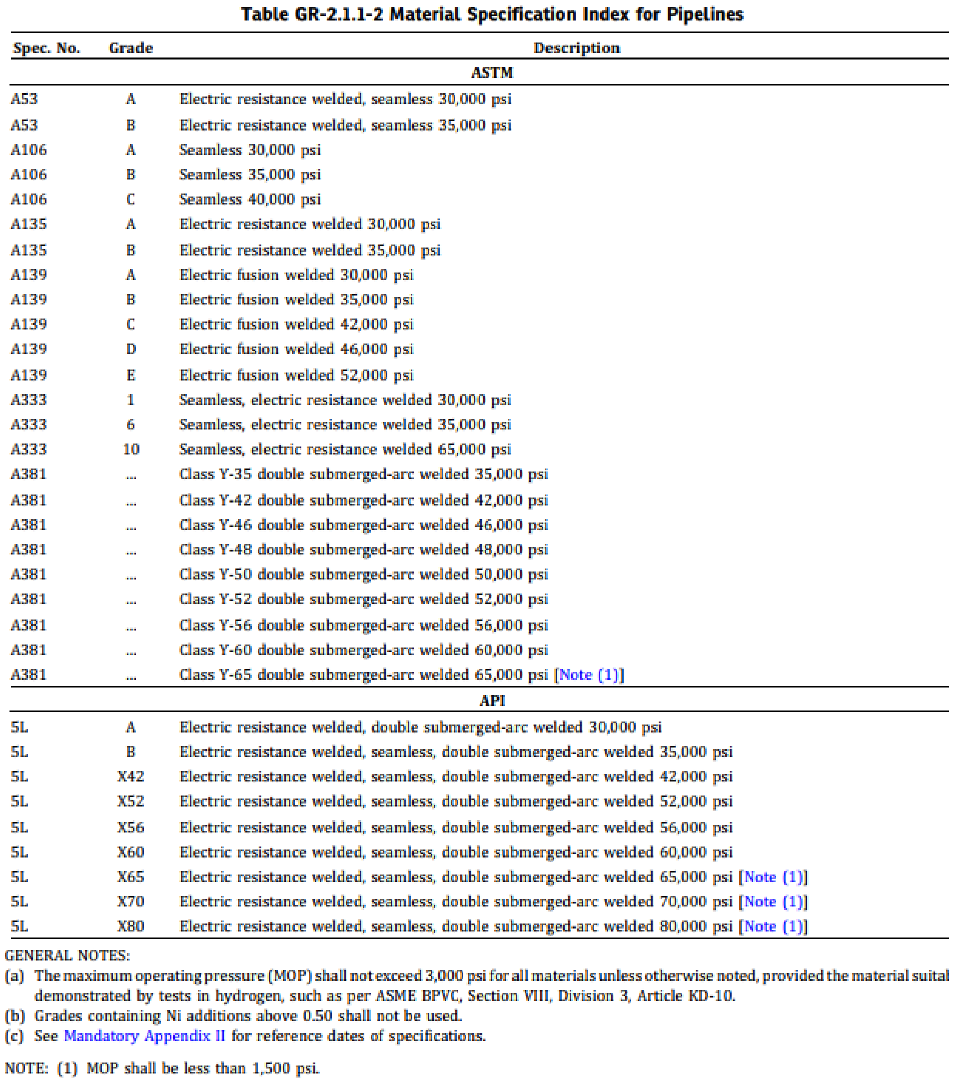


Table GR-2.1.1-2 Material Specification Index for Pipelines

Spec. No.	Grade	Description
ASTM		
A53	A	Electric resistance welded, seamless 30,000 psi
A53	B	Electric resistance welded, seamless 35,000 psi
A106	A	Seamless 30,000 psi
A106	B	Seamless 35,000 psi
A106	C	Seamless 40,000 psi
A135	A	Electric resistance welded 30,000 psi
A135	B	Electric resistance welded 35,000 psi
A139	A	Electric fusion welded 30,000 psi
A139	B	Electric fusion welded 35,000 psi
A139	C	Electric fusion welded 42,000 psi
A139	D	Electric fusion welded 46,000 psi
A139	E	Electric fusion welded 52,000 psi
A333	1	Seamless, electric resistance welded 30,000 psi
A333	6	Seamless, electric resistance welded 35,000 psi
A333	10	Seamless, electric resistance welded 65,000 psi
A381	...	Class Y-35 double submerged-arc welded 35,000 psi
A381	...	Class Y-42 double submerged-arc welded 42,000 psi
A381	...	Class Y-46 double submerged-arc welded 46,000 psi
A381	...	Class Y-48 double submerged-arc welded 48,000 psi
A381	...	Class Y-50 double submerged-arc welded 50,000 psi
A381	...	Class Y-52 double submerged-arc welded 52,000 psi
A381	...	Class Y-56 double submerged-arc welded 56,000 psi
A381	...	Class Y-60 double submerged-arc welded 60,000 psi
A381	...	Class Y-65 double submerged-arc welded 65,000 psi [Note (1)]
API		
5L	A	Electric resistance welded, double submerged-arc welded 30,000 psi
5L	B	Electric resistance welded, seamless, double submerged-arc welded 35,000 psi
5L	X42	Electric resistance welded, seamless, double submerged-arc welded 42,000 psi
5L	X52	Electric resistance welded, seamless, double submerged-arc welded 52,000 psi
5L	X56	Electric resistance welded, seamless, double submerged-arc welded 56,000 psi
5L	X60	Electric resistance welded, seamless, double submerged-arc welded 60,000 psi
5L	X65	Electric resistance welded, seamless, double submerged-arc welded 65,000 psi [Note (1)]
5L	X70	Electric resistance welded, seamless, double submerged-arc welded 70,000 psi [Note (1)]
5L	X80	Electric resistance welded, seamless, double submerged-arc welded 80,000 psi [Note (1)]

GENERAL NOTES:

(a) The maximum operating pressure (MOP) shall not exceed 3,000 psi for all materials unless otherwise noted, provided the material suital demonstrated by tests in hydrogen, such as per ASME BPVC, Section VIII, Division 3, Article KD-10.

(b) Grades containing Ni additions above 0.50 shall not be used.

(c) See Mandatory Appendix II for reference dates of specifications.

NOTE: (1) MOP shall be less than 1,500 psi.

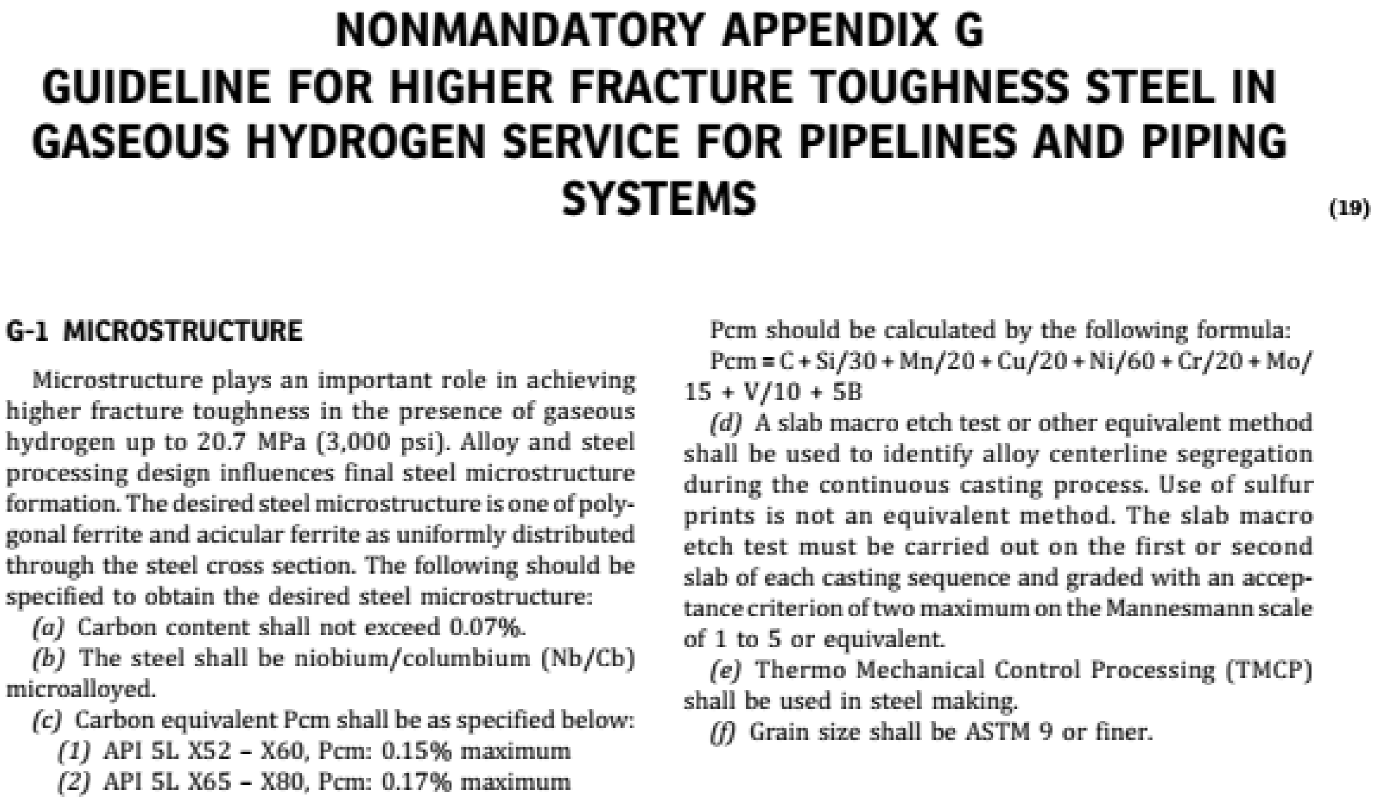
Hydrogen Pipeline Integrity

B31.12 Requirements Summary

Property	Code Requirements	Implication
Material composition and properties	More restrictive than “standard” API 5L requirements Charpy shear area requirement Maximum YS and UTS (including AWT) More restrictive chemical composition (P)	Additional purchasing and manufacturing restrictions are necessary. Existing natural gas pipelines may not meet hydrogen material requirements.
Design Factor	More restrictive in hydrogen service than in natural gas service unless specific hydrogen test data (KIH) is available	Hydrogen pipelines will operate at a lower pressure than their natural gas equivalents
Materials Performance Factor	Additional restrictions on allowable stresses for grades >X52 unless specific hydrogen test data (KIH) is available	Increasing the steel grade does not mean a significant increase in operating pressure
Hardness	Maximum of 235 (qualification) or 248 (production) testing	Even more severe than sour service

Hydrogen Pipeline Integrity

ASME B31.12 Guidelines



NONMANDATORY APPENDIX G
GUIDELINE FOR HIGHER FRACTURE TOUGHNESS STEEL IN GASEOUS HYDROGEN SERVICE FOR PIPELINES AND PIPING SYSTEMS

(19)

G-1 MICROSTRUCTURE

Microstructure plays an important role in achieving higher fracture toughness in the presence of gaseous hydrogen up to 20.7 MPa (3,000 psi). Alloy and steel processing design influences final steel microstructure formation. The desired steel microstructure is one of polygonal ferrite and acicular ferrite as uniformly distributed through the steel cross section. The following should be specified to obtain the desired steel microstructure:

(a) Carbon content shall not exceed 0.07%.

(b) The steel shall be niobium/columbium (Nb/Cb) microalloyed.

(c) Carbon equivalent Pcm shall be as specified below:
- *(1)* API 5L X52 – X60, Pcm: 0.15% maximum
- *(2)* API 5L X65 – X80, Pcm: 0.17% maximum

Pcm should be calculated by the following formula:

$Pcm = C + Si/30 + Mn/20 + Cu/20 + Ni/60 + Cr/20 + Mo/15 + V/10 + 5B$

(d) A slab macro etch test or other equivalent method shall be used to identify alloy centerline segregation during the continuous casting process. Use of sulfur prints is not an equivalent method. The slab macro etch test must be carried out on the first or second slab of each casting sequence and graded with an acceptance criterion of two maximum on the Mannesmann scale of 1 to 5 or equivalent.

(e) Thermo Mechanical Control Processing (TMCP) shall be used in steel making.

(f) Grain size shall be ASTM 9 or finer.

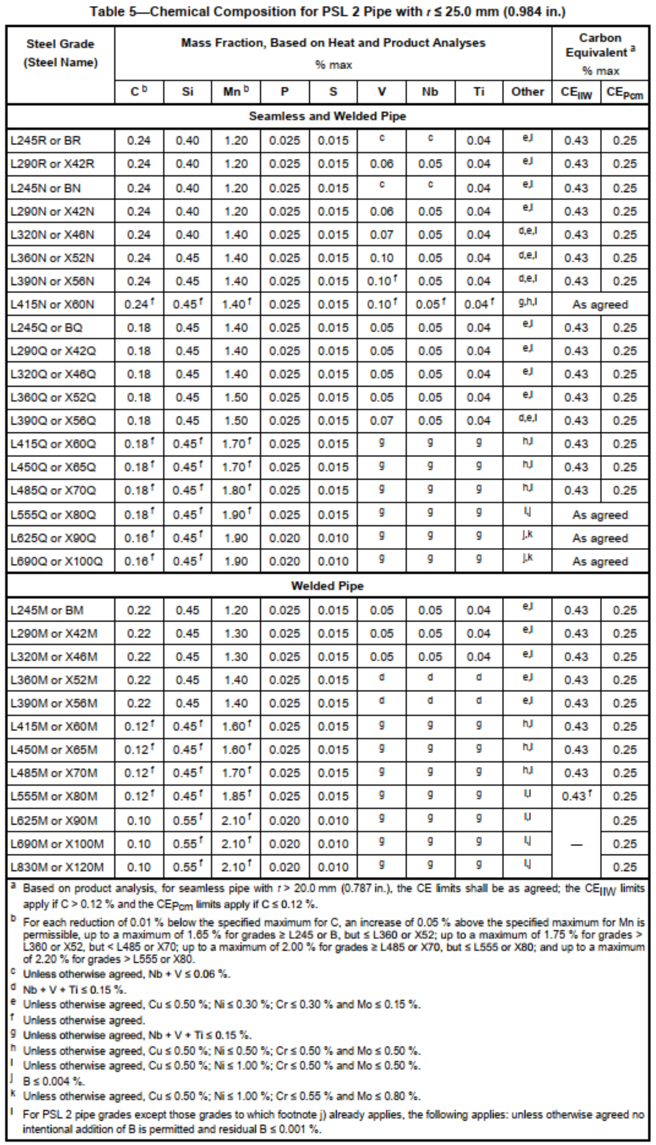


Table 5—Chemical Composition for PSL 2 Pipe with $t \leq 25.0$ mm (0.984 in.)

Steel Grade (Steel Name)	Mass Fraction, Based on Heat and Product Analyses % max									Carbon Equivalent [a] % max	
	C [b]	Si	Mn [b]	P	S	V	Nb	Ti	Other	CE_{IIW}	CE_{Pcm}
Seamless and Welded Pipe											
L245R or BR	0.24	0.40	1.20	0.025	0.015	[c]	[c]	0.04	[e,l]	0.43	0.25
L290R or X42R	0.24	0.40	1.20	0.025	0.015	0.06	0.05	0.04	[e,l]	0.43	0.25
L245N or BN	0.24	0.40	1.20	0.025	0.015	[c]	[c]	0.04	[e,l]	0.43	0.25
L290N or X42N	0.24	0.40	1.20	0.025	0.015	0.06	0.05	0.04	[e,l]	0.43	0.25
L320N or X46N	0.24	0.40	1.40	0.025	0.015	0.07	0.05	0.04	[d,e,l]	0.43	0.25
L360N or X52N	0.24	0.45	1.40	0.025	0.015	0.10	0.05	0.04	[d,e,l]	0.43	0.25
L390N or X56N	0.24	0.45	1.40	0.025	0.015	0.10[f]	0.05	0.04	[d,e,l]	0.43	0.25
L415N or X60N	0.24[f]	0.45[f]	1.40[f]	0.025	0.015	0.10[f]	0.05[f]	0.04[f]	[g,h,l]	As agreed	
L245Q or BQ	0.18	0.45	1.40	0.025	0.015	0.05	0.05	0.04	[e,l]	0.43	0.25
L290Q or X42Q	0.18	0.45	1.40	0.025	0.015	0.05	0.05	0.04	[e,l]	0.43	0.25
L320Q or X46Q	0.18	0.45	1.40	0.025	0.015	0.05	0.05	0.04	[e,l]	0.43	0.25
L360Q or X52Q	0.18	0.45	1.50	0.025	0.015	0.05	0.05	0.04	[e,l]	0.43	0.25
L390Q or X56Q	0.18	0.45	1.50	0.025	0.015	0.07	0.05	0.04	[d,e,l]	0.43	0.25
L415Q or X60Q	0.18[f]	0.45[f]	1.70[f]	0.025	0.015	[g]	[g]	[g]	[h,l]	0.43	0.25
L450Q or X65Q	0.18[f]	0.45[f]	1.70[f]	0.025	0.015	[g]	[g]	[g]	[h,l]	0.43	0.25
L485Q or X70Q	0.18[f]	0.45[f]	1.80[f]	0.025	0.015	[g]	[g]	[g]	[h,l]	0.43	0.25
L555Q or X80Q	0.18[f]	0.45[f]	1.90[f]	0.025	0.015	[g]	[g]	[g]	[i,j]	As agreed	
L625Q or X90Q	0.16[f]	0.45[f]	1.90	0.020	0.010	[g]	[g]	[g]	[j,k]	As agreed	
L690Q or X100Q	0.16[f]	0.45[f]	1.90	0.020	0.010	[g]	[g]	[g]	[j,k]	As agreed	
Welded Pipe											
L245M or BM	0.22	0.45	1.20	0.025	0.015	0.05	0.05	0.04	[e,l]	0.43	0.25
L290M or X42M	0.22	0.45	1.30	0.025	0.015	0.05	0.05	0.04	[e,l]	0.43	0.25
L320M or X46M	0.22	0.45	1.30	0.025	0.015	0.05	0.05	0.04	[e,l]	0.43	0.25
L360M or X52M	0.22	0.45	1.40	0.025	0.015	[d]	[d]	[d]	[e,l]	0.43	0.25
L390M or X56M	0.22	0.45	1.40	0.025	0.015	[d]	[d]	[d]	[e,l]	0.43	0.25
L415M or X60M	0.12[f]	0.45[f]	1.60[f]	0.025	0.015	[g]	[g]	[g]	[h,l]	0.43	0.25
L450M or X65M	0.12[f]	0.45[f]	1.60[f]	0.025	0.015	[g]	[g]	[g]	[h,l]	0.43	0.25
L485M or X70M	0.12[f]	0.45[f]	1.70[f]	0.025	0.015	[g]	[g]	[g]	[h,l]	0.43	0.25
L555M or X80M	0.12[f]	0.45[f]	1.85[f]	0.025	0.015	[g]	[g]	[g]	[i,j]	0.43[f]	0.25
L625M or X90M	0.10	0.55[f]	2.10[f]	0.020	0.010	[g]	[g]	[g]	[i,j]	—	0.25
L690M or X100M	0.10	0.55[f]	2.10[f]	0.020	0.010	[g]	[g]	[g]	[i,j]		0.25
L830M or X120M	0.10	0.55[f]	2.10[f]	0.020	0.010	[g]	[g]	[g]	[i,j]		0.25

[a] Based on product analysis, for seamless pipe with $t > 20.0$ mm (0.787 in.), the CE limits shall be as agreed; the CE_{IIW} limits apply if C > 0.12 % and the CE_{Pcm} limits apply if C ≤ 0.12 %.

[b] For each reduction of 0.01 % below the specified maximum for C, an increase of 0.05 % above the specified maximum for Mn is permissible, up to a maximum of 1.65 % for grades ≥ L245 or B, but ≤ L360 or X52; up to a maximum of 1.75 % for grades > L360 or X52, but < L485 or X70; up to a maximum of 2.00 % for grades ≥ L485 or X70, but ≤ L555 or X80; and up to a maximum of 2.20 % for grades > L555 or X80.

[c] Unless otherwise agreed, Nb + V ≤ 0.06 %.

[d] Nb + V + Ti ≤ 0.15 %.

[e] Unless otherwise agreed, Cu ≤ 0.50 %; Ni ≤ 0.30 %; Cr ≤ 0.30 % and Mo ≤ 0.15 %.

[f] Unless otherwise agreed.

[g] Unless otherwise agreed, Nb + V + Ti ≤ 0.15 %.

[h] Unless otherwise agreed, Cu ≤ 0.50 %; Ni ≤ 0.50 %; Cr ≤ 0.50 % and Mo ≤ 0.50 %.

[i] Unless otherwise agreed, Cu ≤ 0.50 %; Ni ≤ 1.00 %; Cr ≤ 0.50 % and Mo ≤ 0.50 %.

[j] B ≤ 0.004 %.

[k] Unless otherwise agreed, Cu ≤ 0.50 %; Ni ≤ 1.00 %; Cr ≤ 0.55 % and Mo ≤ 0.80 %.

[l] For PSL 2 pipe grades except those grades to which footnote j) already applies, the following applies: unless otherwise agreed no intentional addition of B is permitted and residual B ≤ 0.001 %.

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THEORY OF HYDROGEN EMBRITTLEMENT

QUIZ

What is Hydrogen Embrittlement?

ASME B31.12:

Hydrogen Embrittlement (HE): Loss of ductility of a metal resulting from absorption of hydrogen

Ductility – measure of the capability of a material to be deformed plastically before fracturing

Plastic deformation – permanent deformation caused by stressing beyond the elastic limit

Elasticity – property of a material that allows it to recover its original dimensions following deformation by a stress below its elastic limit

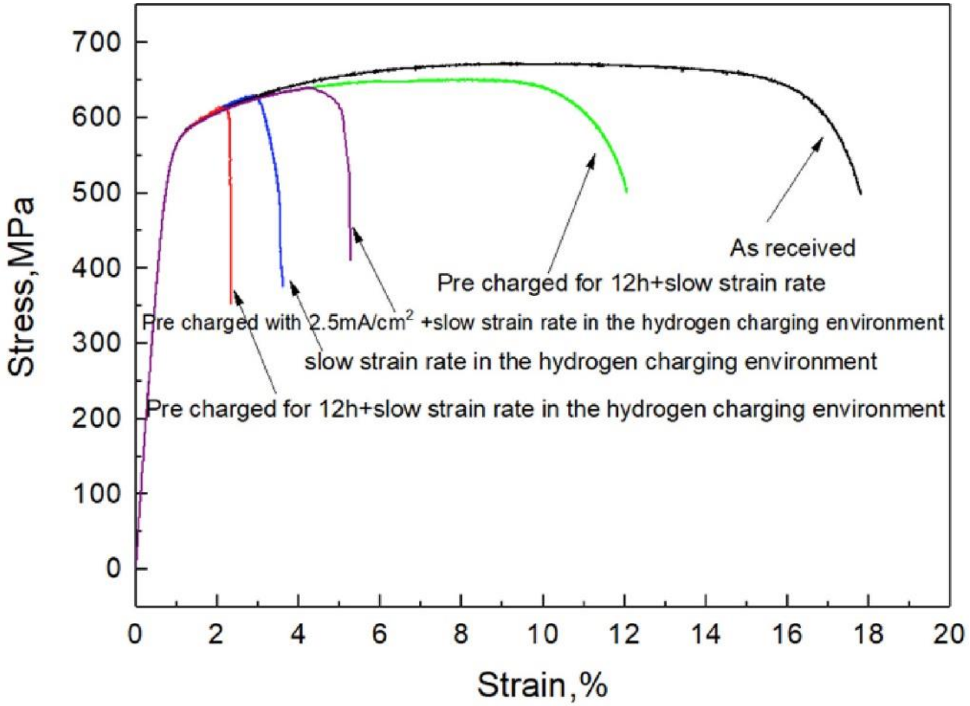
API 579 – 11 references to “Hydrogen Embrittlement” – No definition

BS 7910 – 2 references to “Hydrogen Embrittlement” – No definition

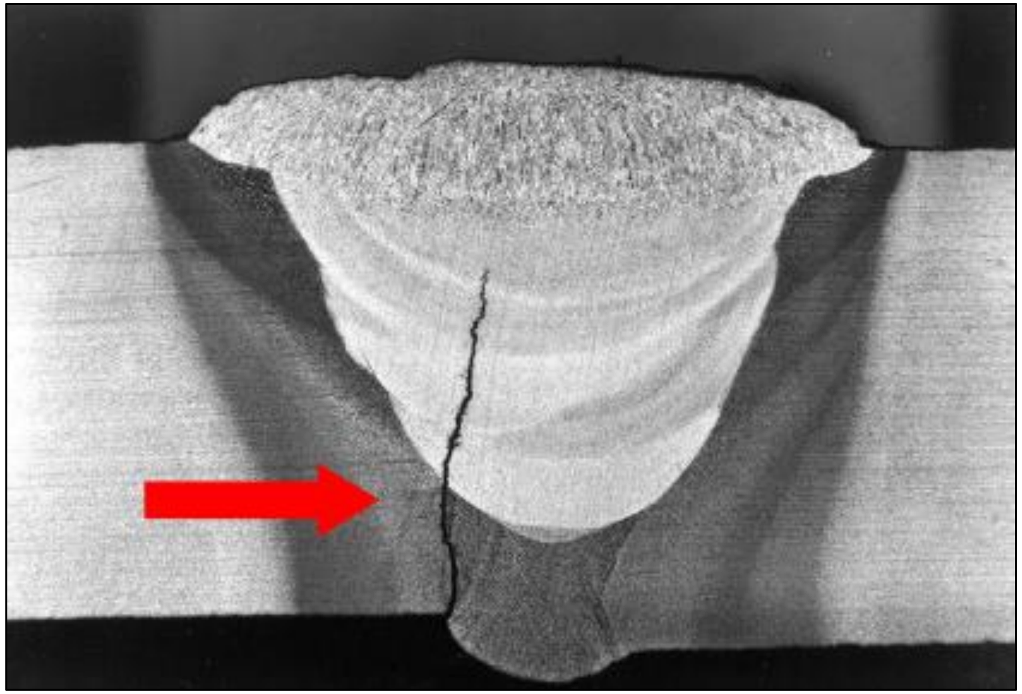
Hydrogen Pipeline Integrity

Theory of hydrogen embrittlement

Hydrogen embrittlement is the detrimental effect of hydrogen on the mechanical properties of metals and alloys.



Zhou, C. *et al.* (2019) “Effects of internal hydrogen and surface-absorbed hydrogen on the hydrogen embrittlement of X80 Pipeline Steel,” *International Journal of Hydrogen Energy*, 44(40), pp. 22547–22558. Available at: https://doi.org/10.1016/j.ijhydene.2019.04.239

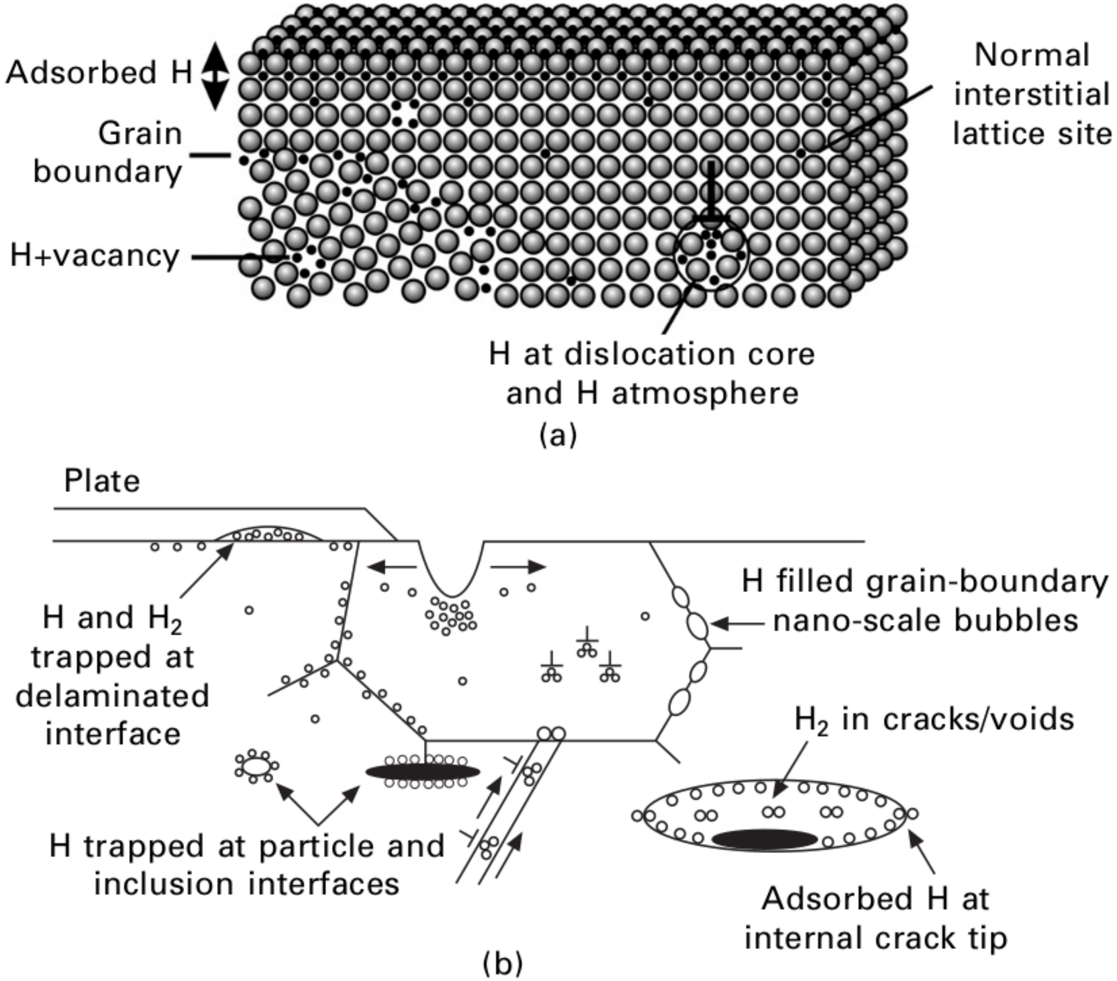


Hydrogen Pipeline Integrity

Challenges

- Steel are complex materials, and their properties can vary significantly from one steel to another.
- This leads to significant data scatter and sometimes contradictory findings.

- Steel have a wide range of microstructural defects.
- Hydrogen interact with all of these defects in different ways, which may or may not result in embrittlement.
- Understanding the interactions of hydrogen with microstructural defects is key.



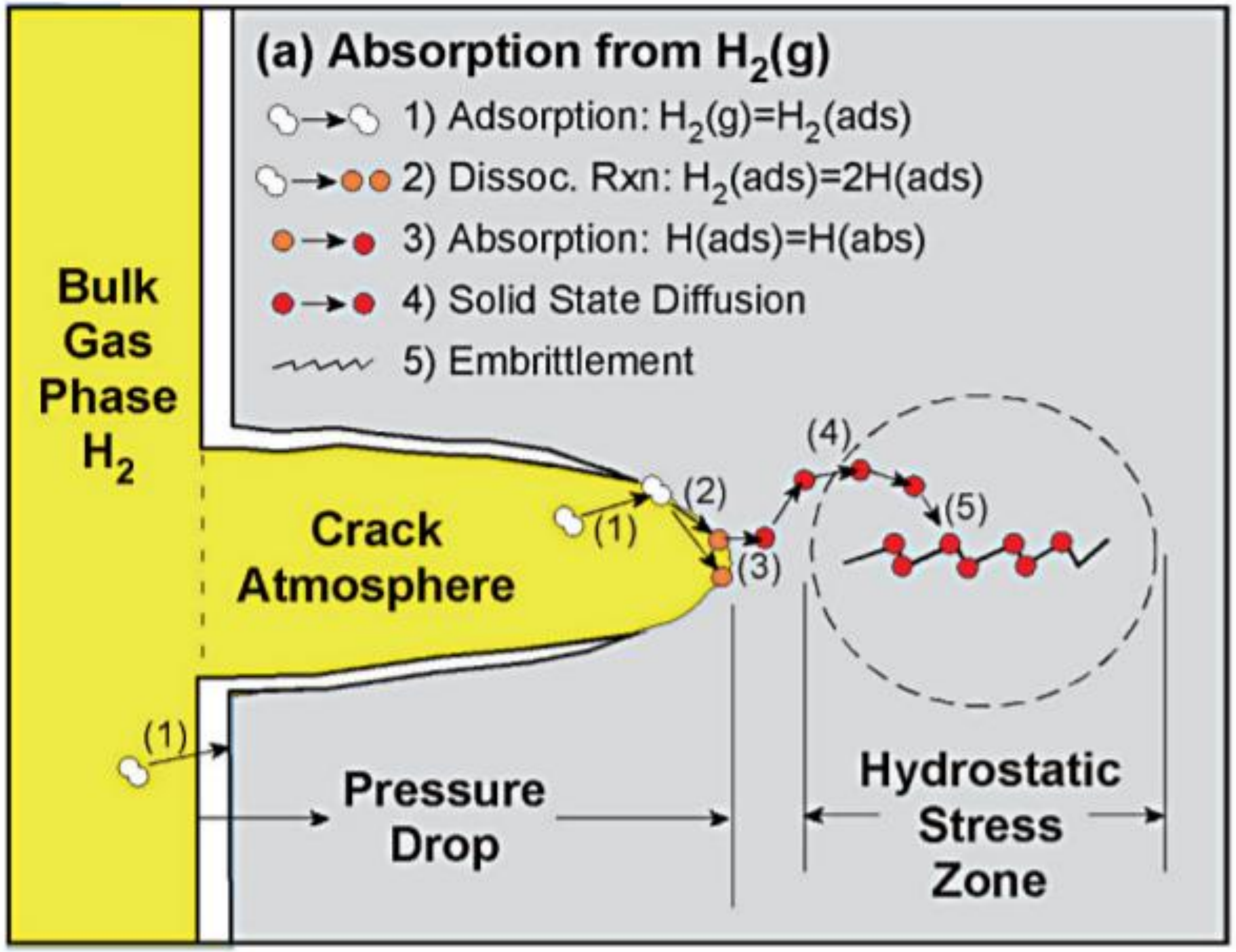
Lynch, S.P. (2011) "Hydrogen embrittlement (he) phenomena and Mechanisms," *Stress Corrosion Cracking*, pp. 90–130. Available at: https://doi.org/10.1533/9780857093769.1.90

Hydrogen Pipeline Integrity

The Process

How does hydrogen embrittle steels?

1. Adsorption of H2 to the steel surface.
2. Dissociation of H2 molecule.
3. Absorption of H atoms into metal matrix.
4. Diffusion to thermodynamically favoured sites e.g. crack tips, dislocation cores, grain boundaries.
5. Actual embrittlement takes place (*mechanism unknown)*



Lee, J.G. (2016) “Computational materials science.” Available at: https://doi.org/10.1201/9781315368429

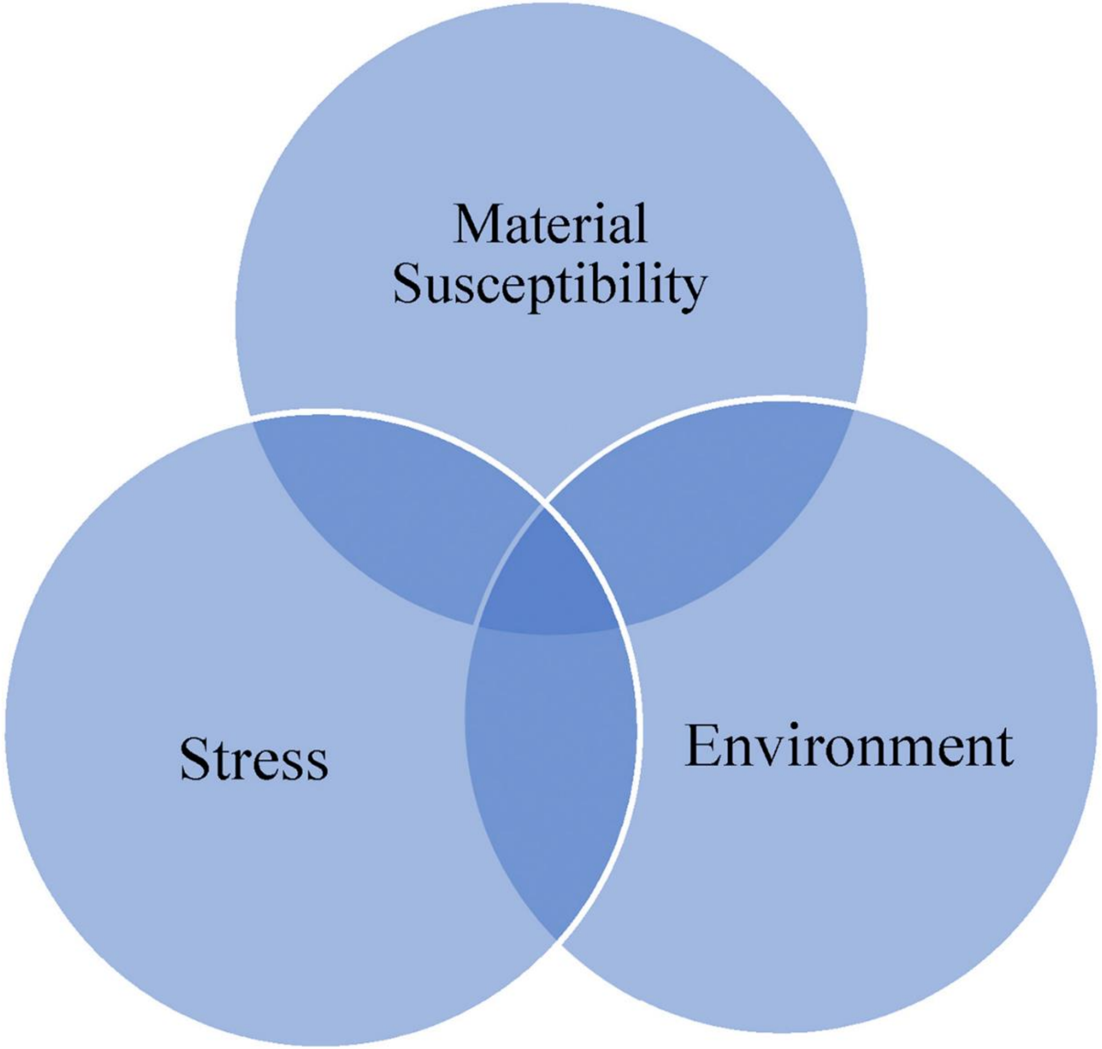
POSSIBILITY OF CRACKING:

Hydrogen Induced Cracking

Hydrogen Pipeline Integrity

Factors

It depends…



Hydrogen Pipeline Integrity
Possibility of Cracking Factors: Environment

Susceptibility to HE is dependent on the amount of hydrogen available.

The equilibrium concentration of hydrogen in the metal depends on the partial pressure of hydrogen (Sieverts' law) and its diffusivity (Fick's law).

At room temperature, H concentration from gaseous hydrogen is very low.

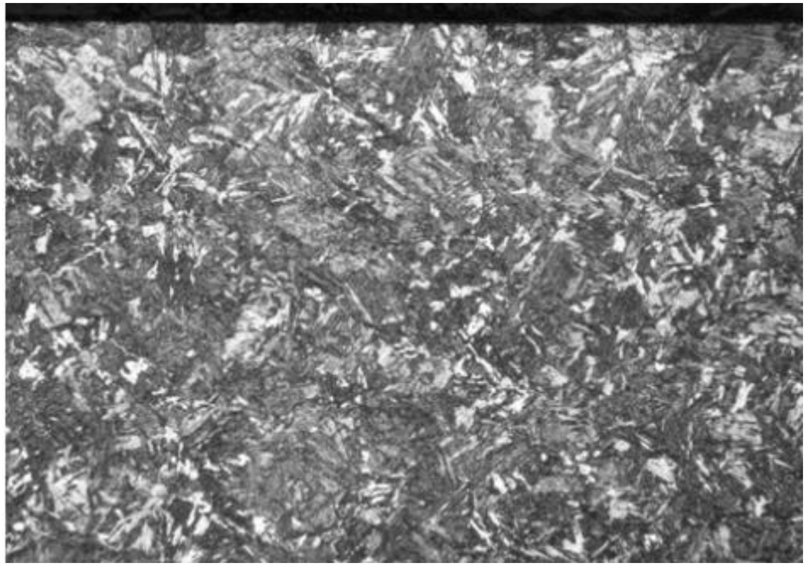
Hydrogen Source	Equilibrium Hydrogen Concentration (atomic ppm)	Equivalent Hydrogen Pressure (bara)
81 bara gaseous hydrogen	0.25	81
0.01 bar H2S	14	7100
Active cathodic protection	56	11000
3 ml H2 / 100 g welding electrode	150	15000
1 bar H2S	185	16000
Cathodic Charging	650	21000

PD CEN/TR 17797:2022 Gas Infrastructure – Consequences of hydrogen in the gas infrastructure and identification of related standardisation need in the scope of CEN/TC 234

IS HYDROGEN CRACKING A PROBLEM?

No

Most of the time……



Hydrogen Pipeline Integrity

Hydrogen Pipeline Codes

ASM
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an
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EIGA

CGA
Compressed Gas Association
The Standard For Safety Since 1913

CGA G-5.6—2005
REAFFIRMED 2013
HYDROGEN PIPELINE
SYSTEMS
FIRST EDITION

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June 2024

PRCI
LEADING PIPELINE RESEARCH

Catalog No. PR337-23115-R01

Consensus Engineering Requirements for Pipelines in Hydrogen and Hydrogen Blend Service

JEFI 04-11

Contract PR337-23115

Prepared for the

Emerging Fuels Institute

Of

Pipeline Research Council International, Inc.

Prepared by:

ROSEN

Authors:

H. Shaw, S. Slater, N. Gallon, D. Sandana, D. Bastidas

Release Date:

August 30, 2024

Version	Date of Last Revision	Comments
1	August 30, 2024	First Issue
2		
3		
4		
5		

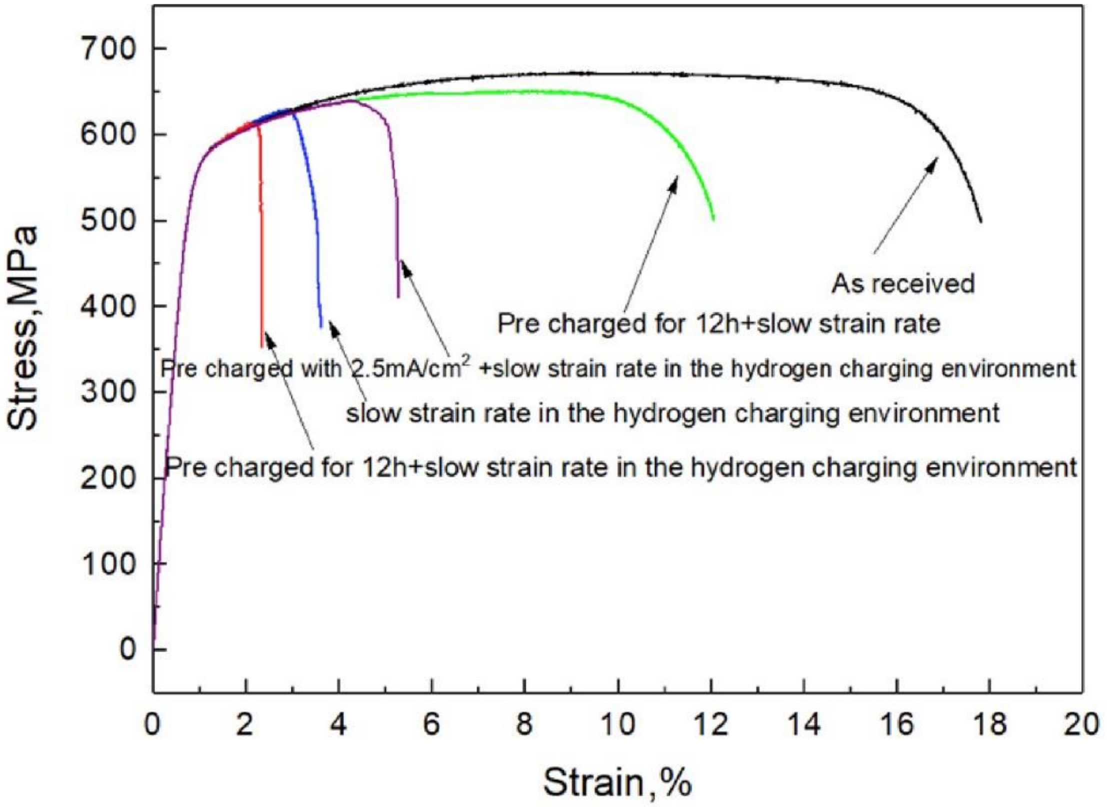
EFFECTS OF HYDROGEN:

On Mechanical Properties

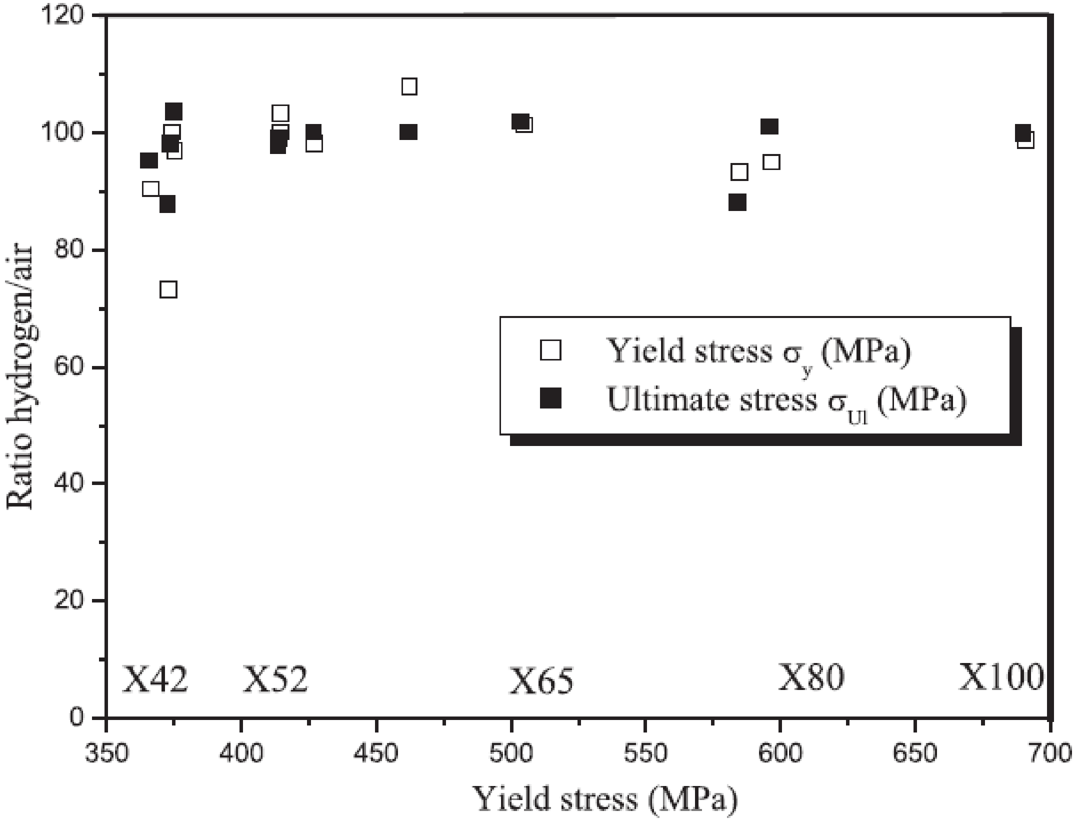
Hydrogen Pipeline Integrity

Strength

The effect of hydrogen is strength is (probably) small at transmission pipeline pressures.



Zhou, C. *et al.* (2019) “Effects of internal hydrogen and surface-absorbed hydrogen on the hydrogen embrittlement of X80 Pipeline Steel,” *International Journal of Hydrogen Energy*, 44(40), pp. 22547–22558. Available at: https://doi.org/10.1016/j.ijhydene.2019.04.239.

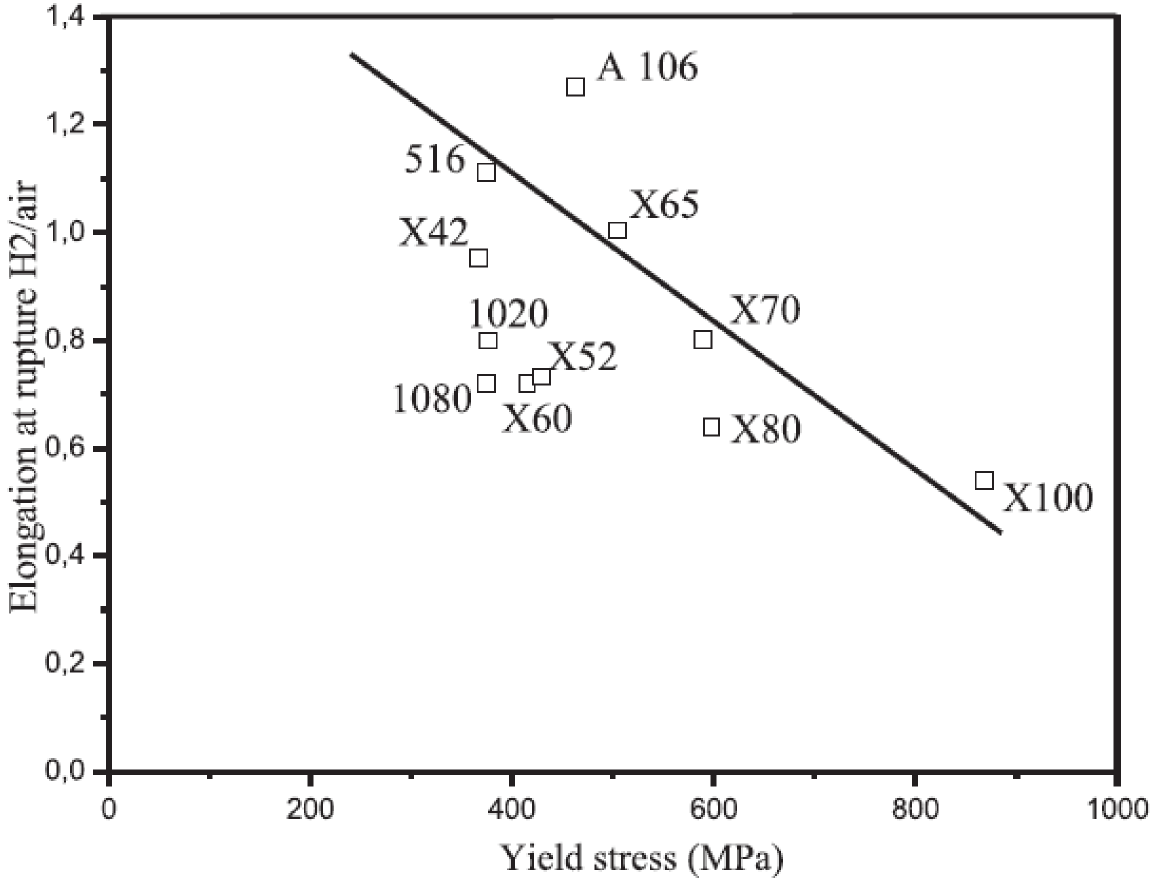


Capelle, J., Gilgert, J., Dmytrakh, I. and Pluvinage, G. Sensitvity of pipelines with steel API X52 to hydrogen embrittlement. *International Journal of Hydrogen Energy.* 33(24), 2008, pp. 7630-7641

Hydrogen Pipeline Integrity

Ductility

Hydrogen effects on ductility are more obvious. However, it is still hard to predict how much it will be affected.

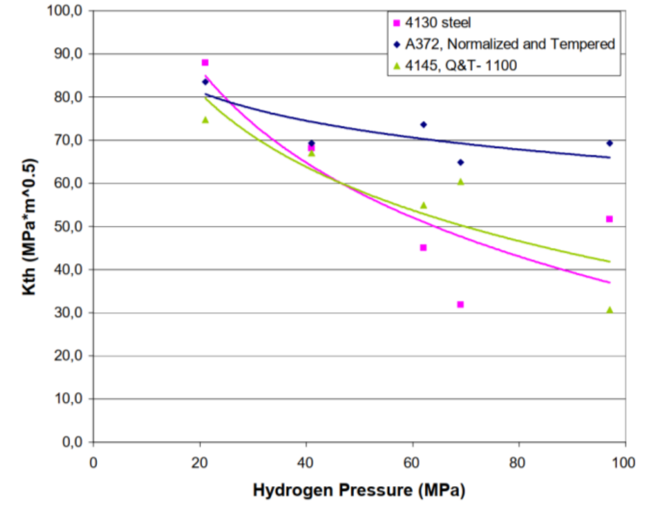


Capelle, J., Gilgert, J., Dmytrakh, I. and Pluvinage, G. Sensitvity of pipelines with steel API X52 to hydrogen embrittlement. *International Journal of Hydrogen Energy.* 33(24), 2008, pp. 7630-7641

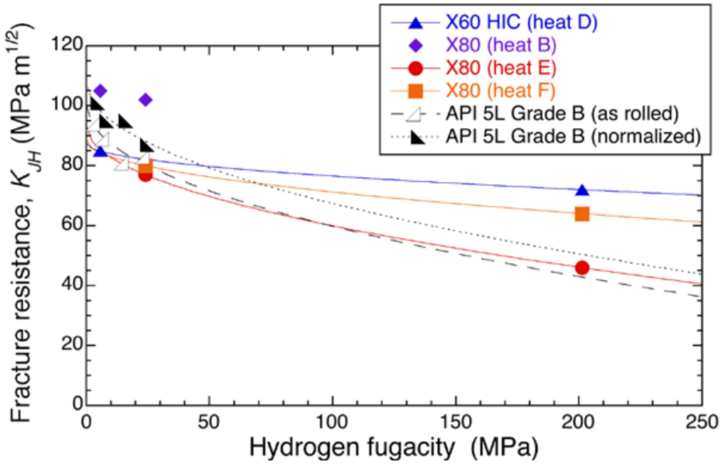
Hydrogen Pipeline Integrity

Fracture Toughness

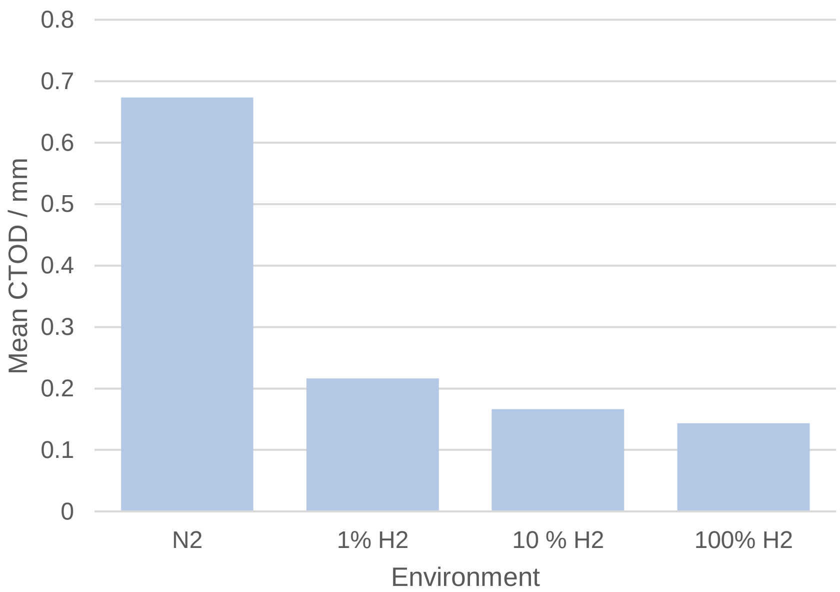
Though it is clear hydrogen reduces toughness, there is large variability on test results



Barthelemy, H. Effects of Purity and Pressure on the Hydrogen Embrittlement of Steels and Other Metallic Materials. [Online] [Cited: 05 October 2020.] http://conference.ing.unipi.it/ichs2009/images/stories/papers/149.pdf



Chen, Y., Liu, M., Wang, Y-Y., Slifka, A.J., Drexler, E., Amaro, R., McColskey, D. and Hayden, L. *Performance Evaluation of High-Strength Steel Pipelines for High-Pressure Gaseous Hydrogen Transportation.* Dublin, OH : Center for Reliable Energy Systems, 2013

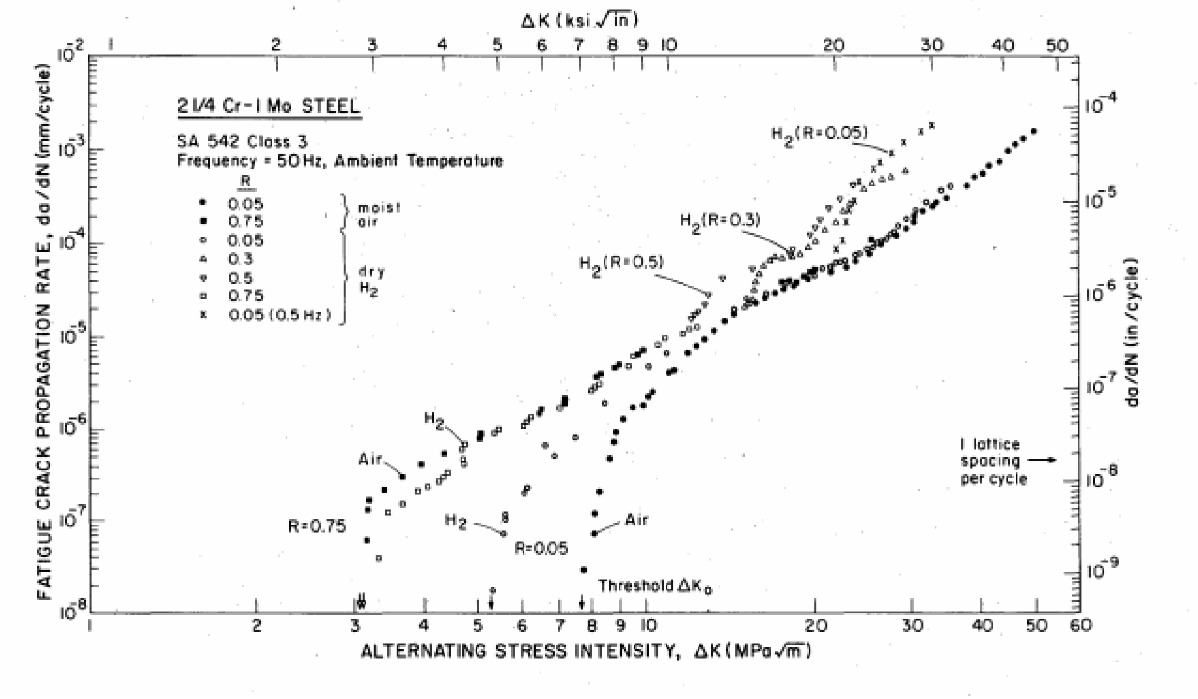


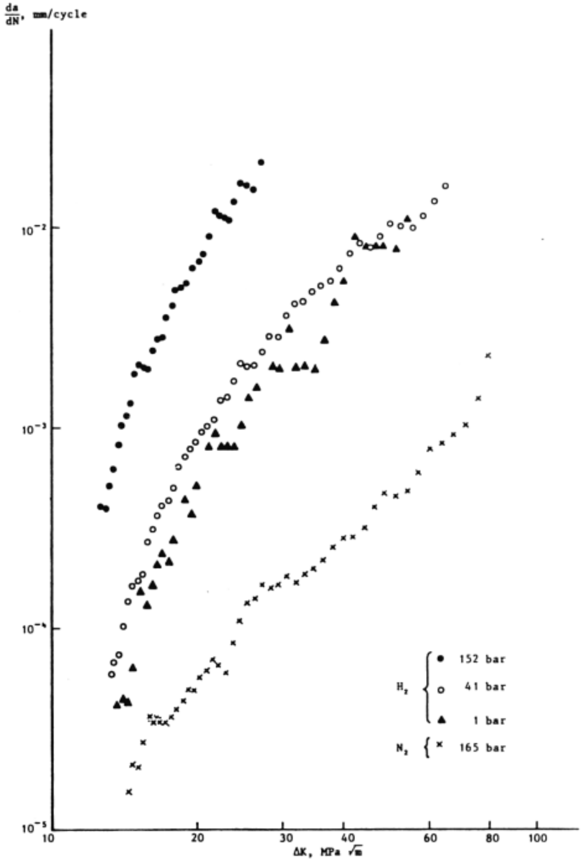
Influence of Hydrogen and Oxygen Impurity Content in a Natural Gas / Hydrogen Blend on the Toughness of an API X70 Steel – Briottet et al. ASME PVP 2018

Hydrogen Pipeline Integrity

Fatigue

- Similarly to fracture toughness, fatigue in hydrogen is also time-dependant.
- Increasing H exposure results in **higher fatigue crack growth rates**.
- Hydrogen effects more visible at greater ΔK / K_{max}.





THE EFFECT OF HYDROGEN PRESSURE ON THE FATIGUE CRACK GROWTH RATE IN HIGH STRENGTH 1% CrMo STEEL - TESTS PERFORMED AT 1 Hz

Suresh, S. and Ritchie, R.O. *Mechanistic Dissimilarities Between Environmentally-Influenced Fatigue Crack Propagation at Near-Threshold and High Growth Rates in Lower Srength Steels.* Berkeley, CA : Lawrence Berkeley National Laboratory, 1981

Barthelemy, H. and Pressouyre, G. *Hydrogen Gas Embrittlement of Steels, Synthesis of a Subtask of the CEC Hydrogen Energy Programme (1975-1983)* . Luxembourg : Commission of the European Communities, 1985

TESTING REQUIREMENTS & PROTOCOLS

Hydrogen Pipeline Integrity

In H environment: Fracture toughness

Two main approaches for testing H effects on fracture toughness:

1. Rising load fracture toughness -- recommend by ISO 11114-4
2. Threshold stress intensity factor KIH – recommended by ASME B31.12 and ISO 11114-4

NIST High Pressure H2 Test Chamber - https://www.nist.gov/image/materialstestinghighpressurehydrogentestchamberjpg

Hydrogen Pipeline Integrity

In H environment: Fracture toughness

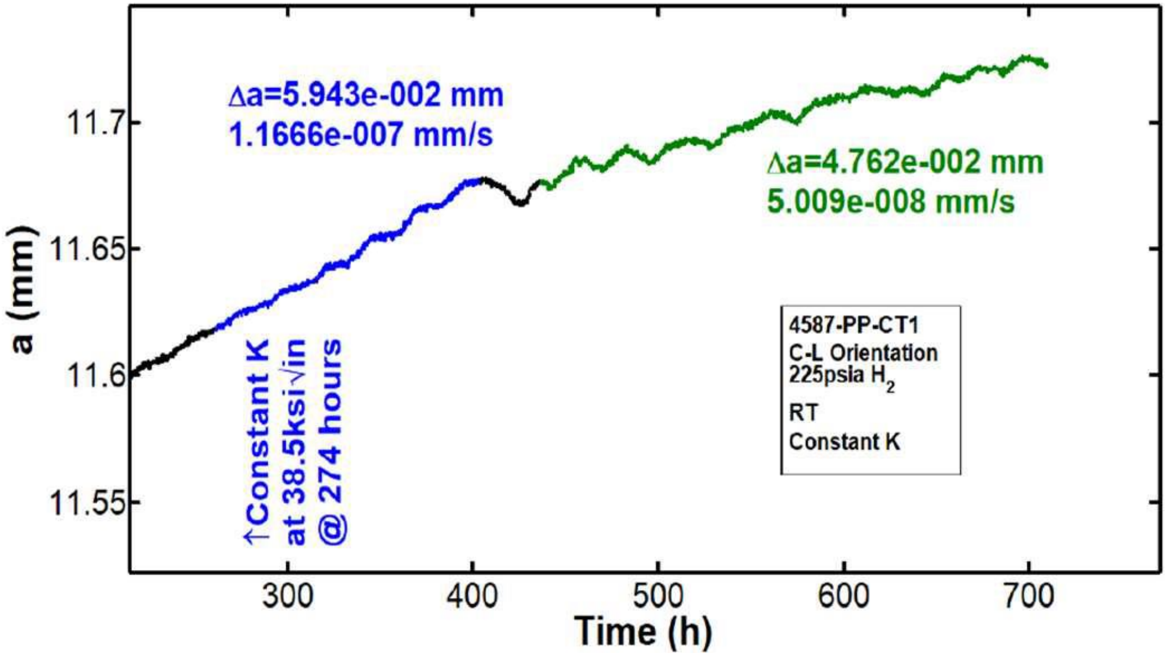
Advantages and disadvantages of fracture toughness test types:

	Rising load fracture toughness	**Threshold stress intensity factor KIH**
Advantages	• Produces a measurable toughness value J, K, CTOD.	• Results do not depend on H kinetics • Referenced in ASME B31.12
Disadvantages	• Fracture toughness depends on H kinetics • Results dependant on loading rate	• Pass/fail test outcome • Specimen might not fail • Long testing time • Several tests needed • Not quantitative

Hydrogen Pipeline Integrity

In H environment: da/dt

da/dt has been observed at relatively low Kmax (38 ksi.in$^{1/2}$ = 42 MPa.m$^{1/2}$)



Bezensek et al., Fracture and Fatigue Crack Growth Performance of a Vintage X60 Pipeline Material in Gaseous H2 and Comparison with Wet Sour Service, ASME PVP2023-105972

Calculated stress intensity factors for a 3 x 50 mm crack in 1973 X60 DN1200 Pipe, WT 14.1 – 22.3 mm

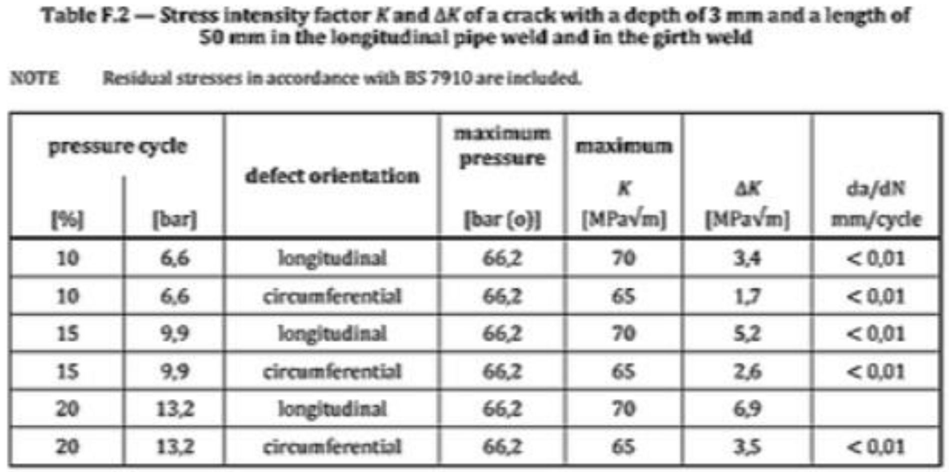


Table F.2 — Stress intensity factor K and ΔK of a crack with a depth of 3 mm and a length of 50 mm in the longitudinal pipe weld and in the girth weld

NOTE Residual stresses in accordance with BS 7910 are included.

pressure cycle		defect orientation	maximum pressure	maximum K	ΔK	da/dN
[%]	[bar]		[bar (o)]	[MPa√m]	[MPa√m]	mm/cycle
10	6,6	longitudinal	66,2	70	3,4	< 0,01
10	6,6	circumferential	66,2	65	1,7	< 0,01
15	9,9	longitudinal	66,2	70	5,2	< 0,01
15	9,9	circumferential	66,2	65	2,6	< 0,01
20	13,2	longitudinal	66,2	70	6,9	
20	13,2	circumferential	66,2	65	3,5	< 0,01

PD CEN/TR 17797:2022 Gas Infrastructure – Consequence of Hydrogen in the Gas Infrastructure and Identification of Related Standardisation Need in the Scope of CEN/TC 234

Hydrogen Pipeline Integrity

In H environment: da/dt

- da/dt is real (in the lab.)
- It does not happen all the time, appears to be due to the pre-conditioning and stress state around the crack tip
- Unpublished evidence that sometimes it arrests
- No agreed standard test protocols
- No evidence that it has happened in pipelines in service
- Full scale tests currently ongoing
- Implications for pipelines are unknown
- Currently the topic of a lot of research

Conclusions

- Codes are not mature enough to follow prescriptively
- No clear relationship between in-air and in-hydrogen material properties
- Likely that extensive programmes of material qualification in gaseous hydrogen will be required
- Significant amounts of current code developments / research.

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