AIR LIQUIDE

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The Effects of Purity and Pressure on Hydrogen Embrittlement of Metallic Materials (ID 149)

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Overview

- Introduction to Hydrogen Embrittlement (HE)
  - Causes and Mechanisms
  - Scope of Research
- Results and Data
  - Test Methods
  - Effects of Pressure
  - Effects of H_2 gas purity
- Issues to Address

Hydrogen Embrittlement in Steels

- Loss of ductility and deformation capacity in the presence of hydrogen
- Strongly affects high-strength steels
- Maximum embrittlement at room temperature (~20°C)
- Causes hydrogen transport by dislocations

Hydrogen Embrittlement in Steels

- **Factors affecting HE**
  - ✓ Environment
  - ✓ Material properties and surface condition

- **Possible Mechanisms of HE**
  - ✓ Stress-induced hydride formation
  - ✓ Hydrogen-enhanced localized plasticity (HELP)
  - ✓ Hydrogen-induced decohesion

Environment

- Gas purity
- Pressure
- Temperature
- Exposure time (affects diffusion in internal HE)
- Stress and strain rates

Material Properties related to HE

- Chemical composition of metal
- Heat treatment, welding
- Microstructure
- Cracks, corrosion pits, and other surface defects

Scope of Research

- **Metals**
  - ✓ Carbon, Low alloy, and Stainless Steels
  - ✓ Aluminum and Copper

- **Focusing on three aspects of HE for steels**
  - ✓ Effective testing methods for HE
  - ✓ Effects of H_2 gas pressure (700-1000 bar)
  - ✓ Effects of H_2 gas purity

Hydrogen Embrittlement

- Austenitic alloys suffer less embrittlement than ferritic alloys
- Martensitic specimens are very sensitive to HE
- Steels often become less ductile, but strength is not significantly reduced by HE
- Aluminum and copper alloys have shown high resistance to HE in tensile testing

TESTING METHODS

Testing for HE

- Need to simulate in-service stresses of pressure vessels -external HE effects
- High sensitivity
- Capable of being reproduced
- Small cells for lower cost and easy cleaning

Tensile Tests

- Compare behavior under pressurized hydrogen vs. inert gas
- Provide data for changes in ductility-elongation and %RA

$$\%RA = \frac{A_i - A_f}{A_i} x100\%$$

- Tensile stresses are uniaxial

Fracture Mechanics

- **Wedge Opening Load (WOL)**
  - ✓ Test of threshold stress intensity factor, K_{TH}
  - ✓ Crack growth

Maximum acceptable crack growth: 0.25mm [1]

- **Compact Tension (CT)**
  - ✓ Fatigue crack growth rate, da/dN
  - ✓ K_{TH}

Acceptable criteria: K_{TH}>(60/950) x R_m (MPa-m0.5), where R_m is UTS of metal [1]

  - ✓ Plane-strain fracture toughness, K_{IC}

Disk Tests

- **Disk rupture**
  - ✓ Provides strength comparison in H_2 and He environments
  - ✓ Creates triaxial stress state
- **Delayed rupture**
- **Disk fatigue test**
  - ✓ Good for simulating life of a pressure vessel

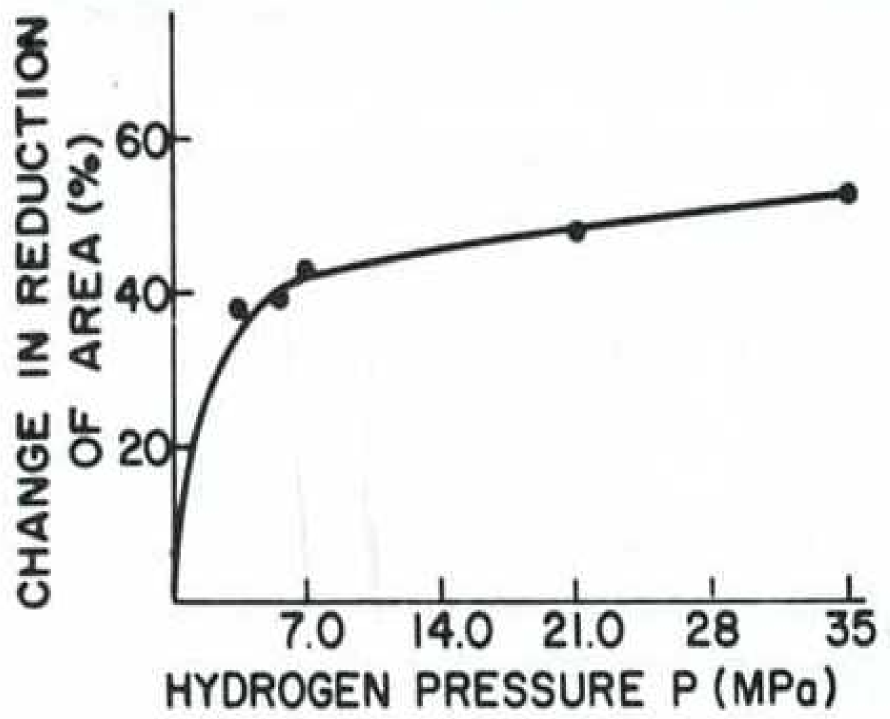
EFFECTS OF HYDROGEN GAS PRESSURE

Pressure Effects

- HE generally increases with partial hydrogen pressure
- Some tests showed maximum HE at a certain pressure level
  - ✓ ~100 bar for carbon and low alloys where UTS<1000 MPa
  - ✓ ~25 bar for AISI 321 stainless steel [2]

HE Test Results

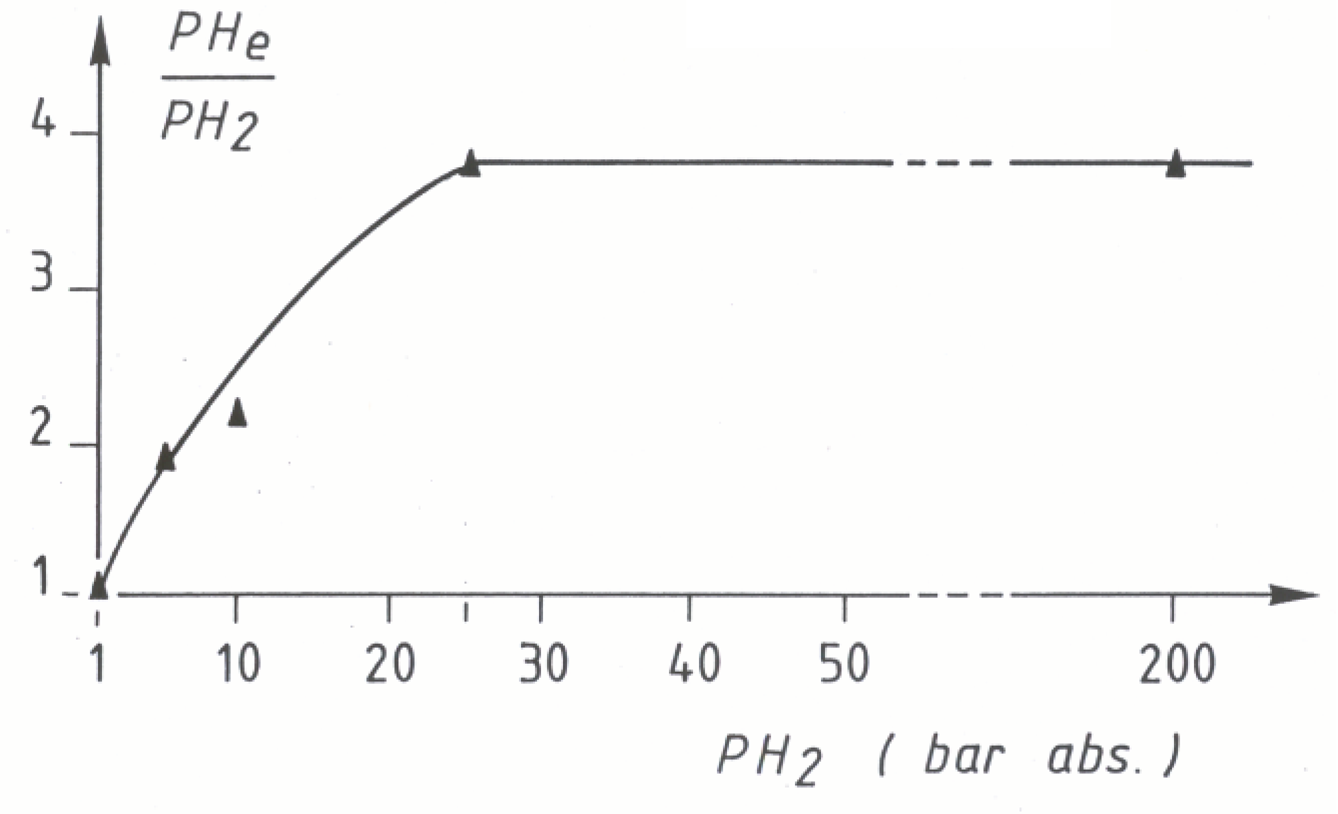
HEE observed in double-notched tensile specimens.



Large ductility loss with increase of hydrogen pressure for carbon steel [3]

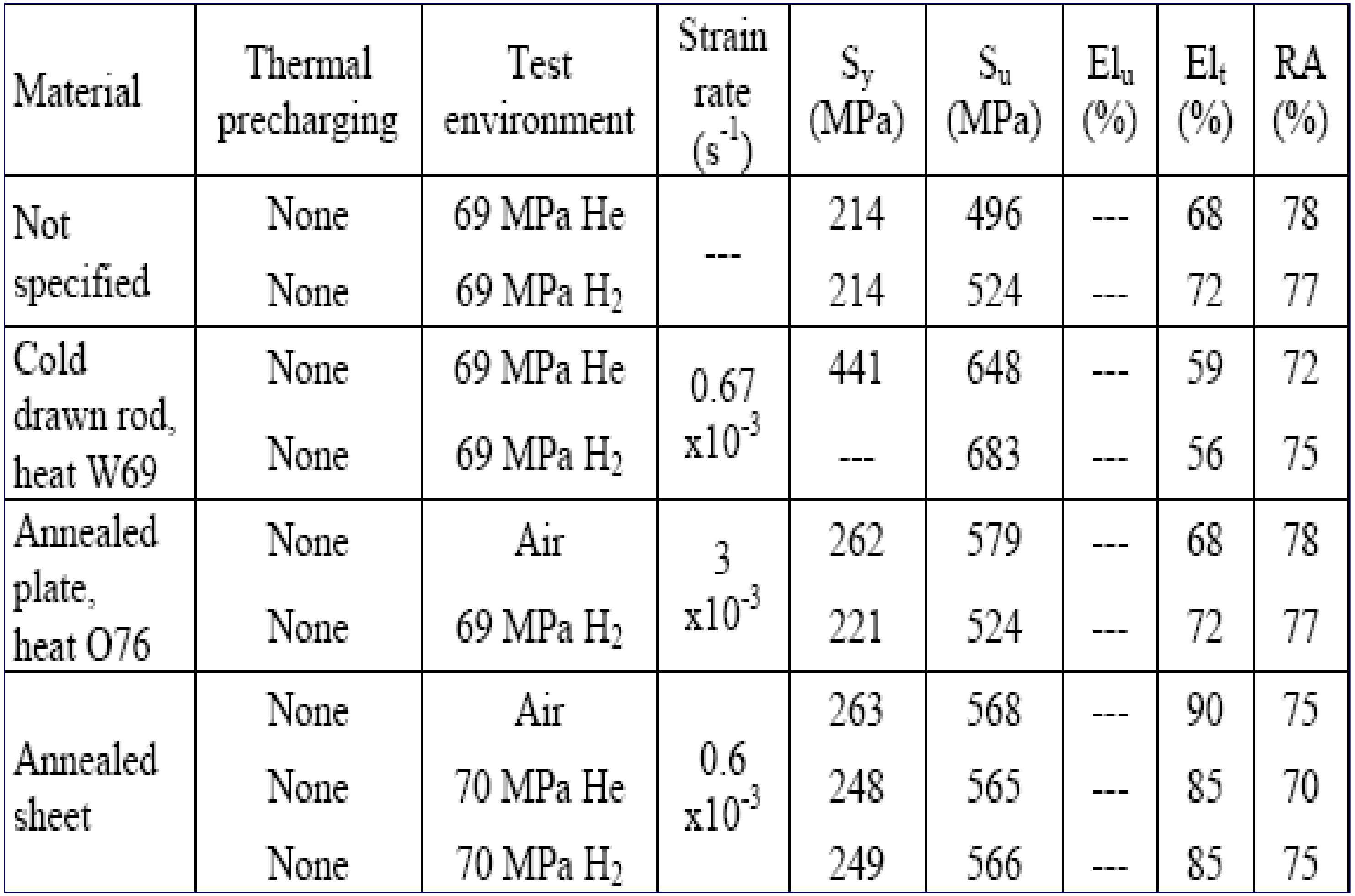
HE Test Results – Disk test

- **Hydrogen pressure**



Influence of H_2S partial pressure for AISI 321 steel

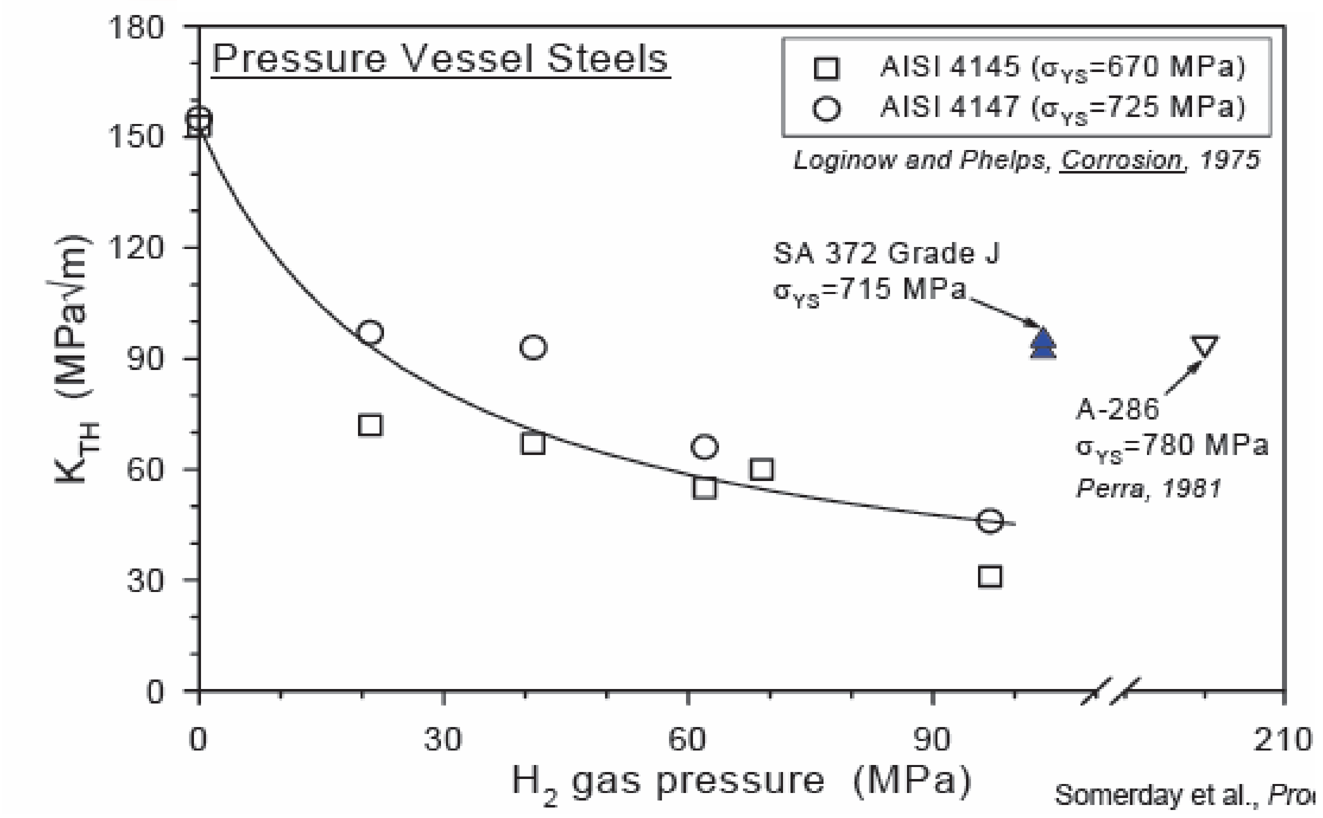
316 Stainless Steel



Material	Thermal precharging	Test environment	Strain rate (s^{-1})	S_y (MPa)	S_u (MPa)	El_u (%)	El_t (%)	RA (%)
Not specified	None	69 MPa He	---	214	496	---	68	78
	None	69 MPa H_2		214	524	---	72	77
Cold drawn rod, heat W69	None	69 MPa He	0.67 $x10^{-3}$	441	648	---	59	72
	None	69 MPa H_2		---	683	---	56	75
Annealed plate, heat O76	None	Air	3 $x10^{-3}$	262	579	---	68	78
	None	69 MPa H_2		221	524	---	72	77
Annealed sheet	None	Air	0.6 $x10^{-3}$	263	568	---	90	75
	None	70 MPa He		248	565	---	85	70
	None	70 MPa H_2		249	566	---	85	75

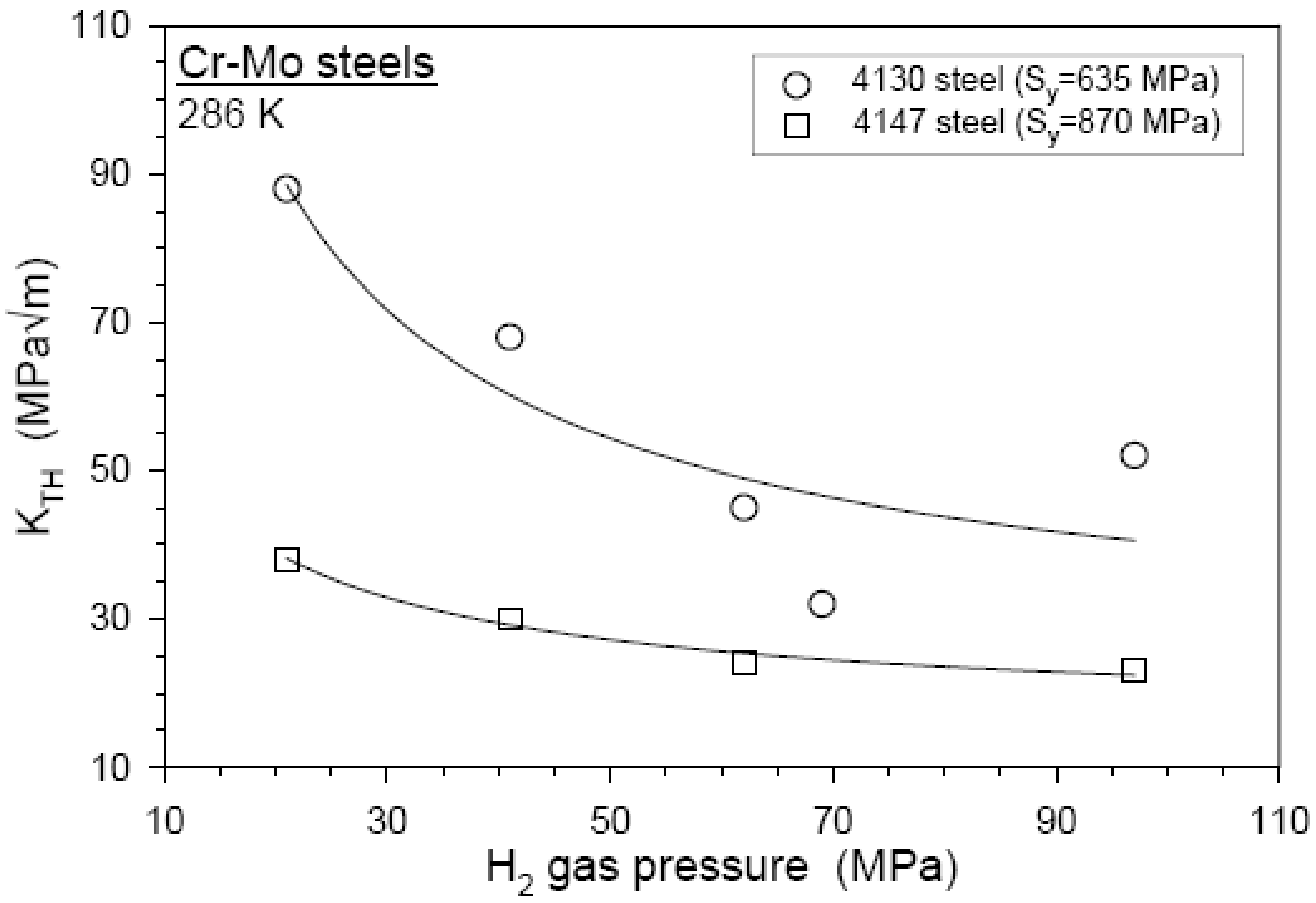
Successful performance of 316 steel in tensile tests with high pressure hydrogen [4]

Pressure Test Results



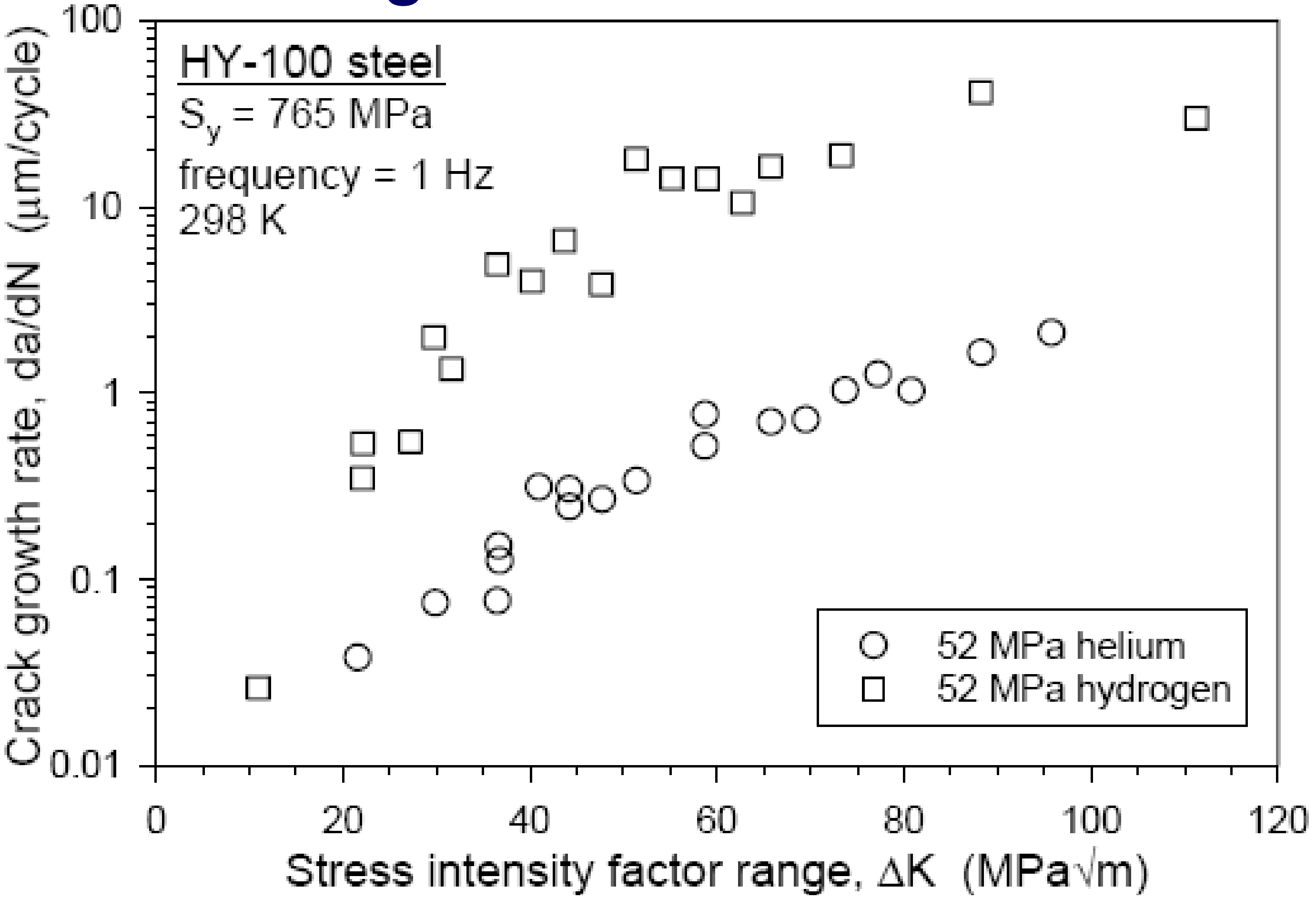
Somerday et al., *Pro*

Cracking threshold significantly decreases as hydrogen pressure increases for low alloy steel [4]

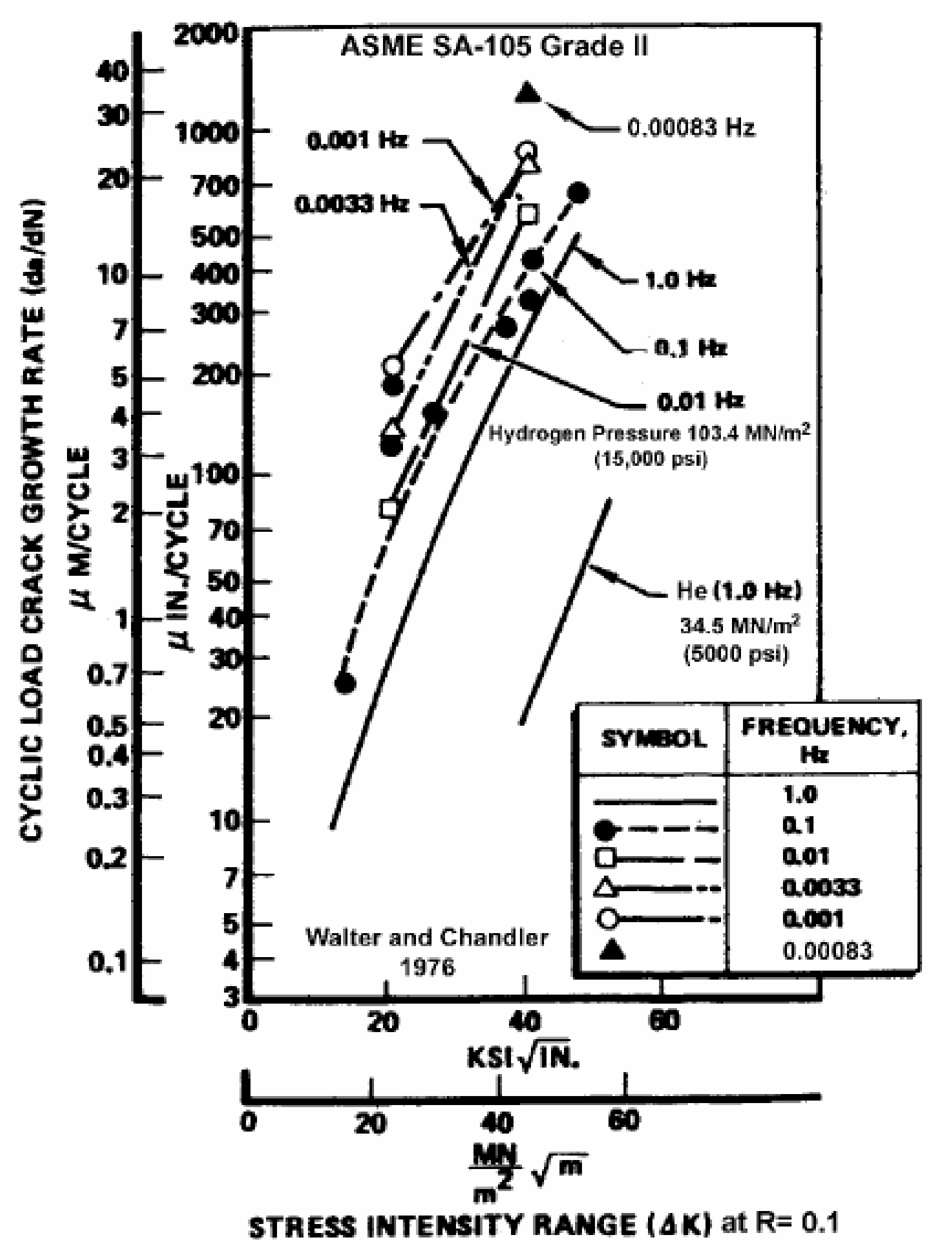


HE effects on type 4147 appear to level off at pressures higher than 60 MPa [4]

Effects of 52 MPa hydrogen on fatigue crack growth for HY-100 Steel



HY-100 showed significantly increased crack growth rate in 52 MPa hydrogen [4]



In tests performed at 103.4 MPa on SA-105 steel, fatigue crack growth was slower at higher frequencies [5]

Results of High Pressure Tests

- Losses in ductility increase with pressure, although several steels reached maximum embrittlement at a threshold pressure
- Fracture toughness and resistance to crack propagation decrease
- Strength of the material is usually not significantly affected

Effects of High Pressure Hydrogen

- Fatigue resistance decreases at higher pressures
- A286 and 316 stainless steels have shown the most resistance to HE
- Aluminum and copper alloys appear to be resistant to HE
- More fatigue testing at high pressure needs to be performed on these materials

EFFECTS OF HYDROGEN GAS PURITY

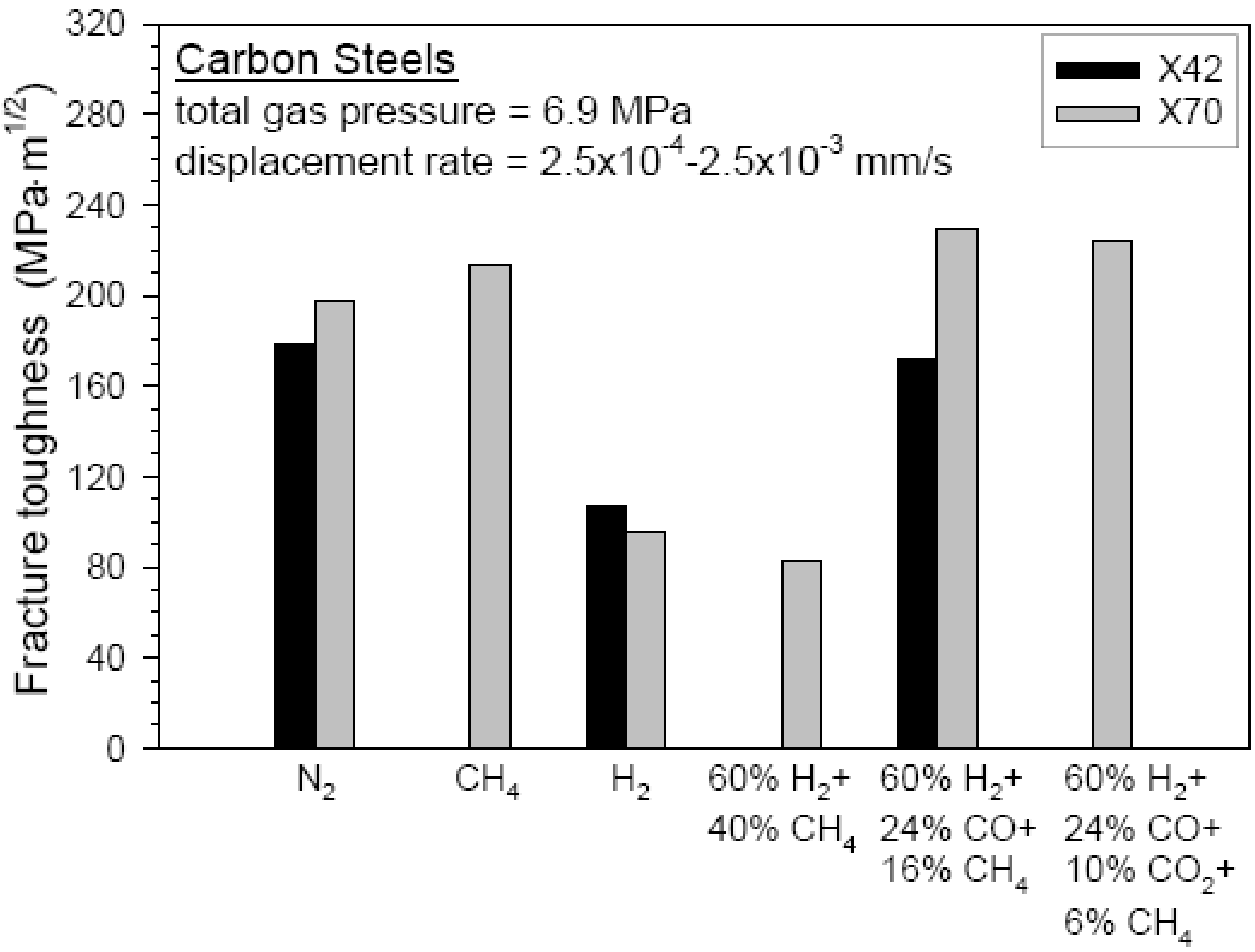
Impurities Affecting HE

HE Inhibitor	No Effect	Embrittling Effect
O_2	CH_4	H_2S
SO_2	N_2	CO_2

H_2O has demonstrated both embrittling and inhibiting effects

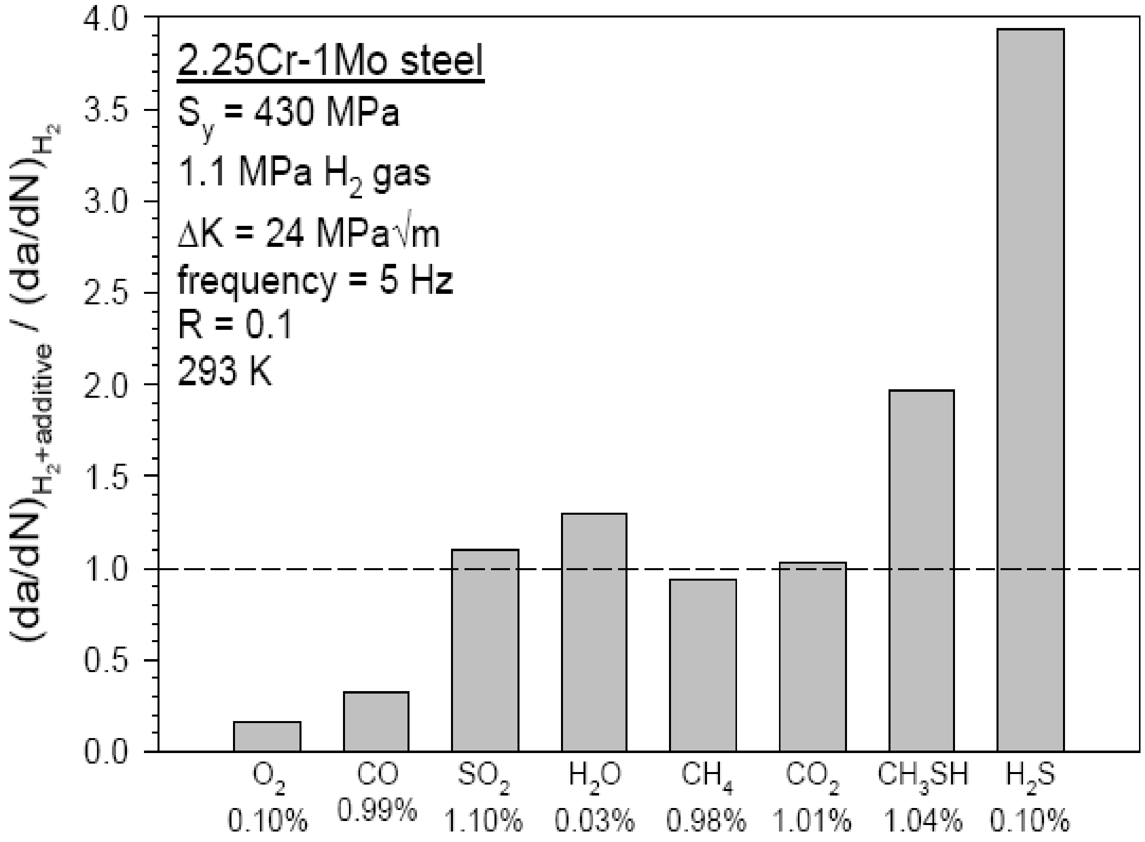
Impurity Effects

- Oxygen has shown inhibiting effects in delayed disk rupture
- Varying results for impurities such as CH_4 and CO_2
- H_2S has consistently accelerated HE



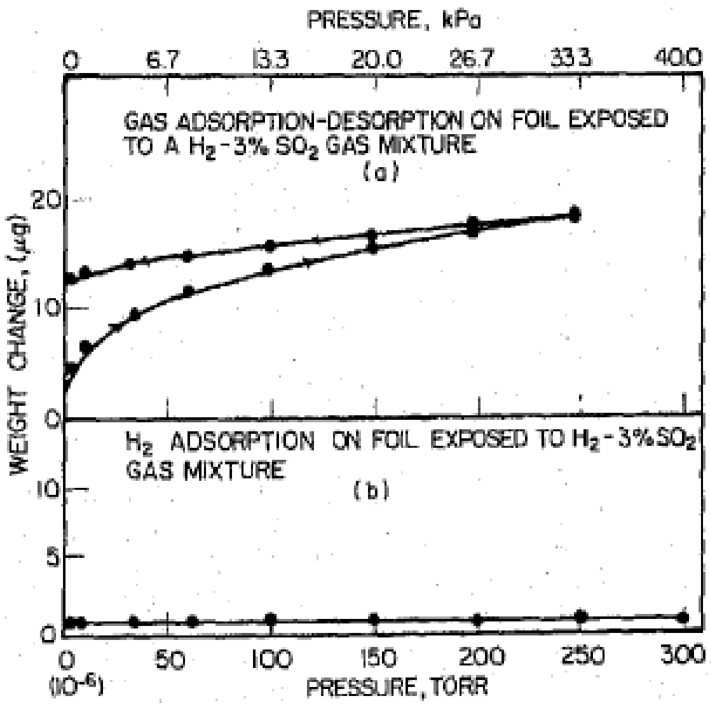
Effects of gas impurity on HE for carbon steels [4]

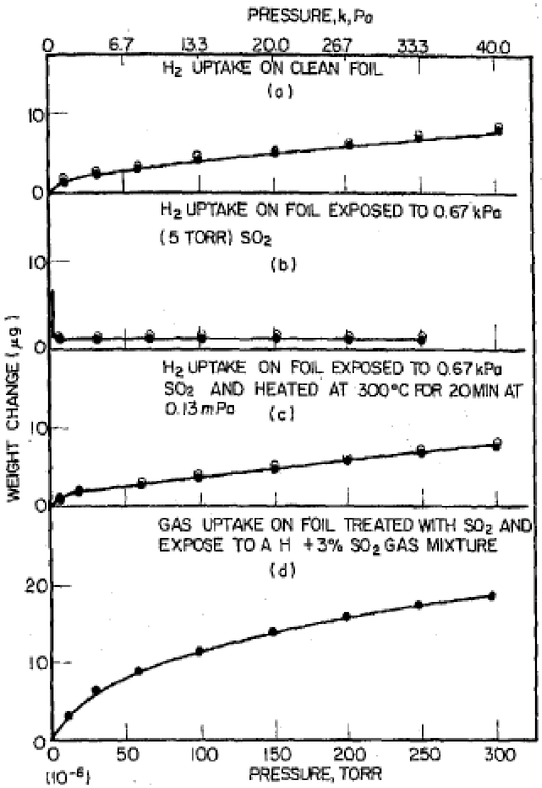
Impurity effects on fatigue crack growth



Comparison between pure gas and H_2 with additives [4]

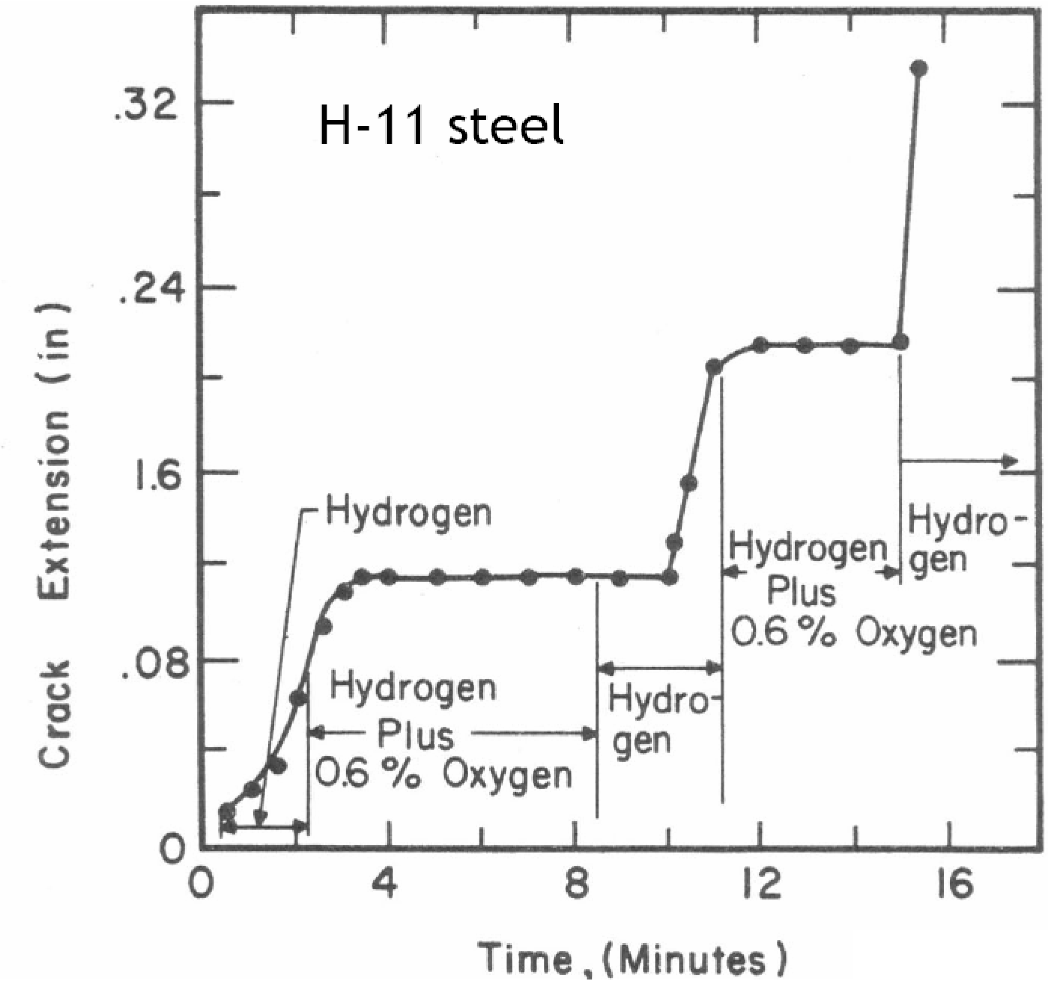
Inhibiting effects of SO_2





Sulfur dioxide exhibited inhibitory effects as a pretreatment for steel sheet [6]

Inhibiting effects of oxygen on crack growth in H-11 steel



Results from Impurity Tests

- O_2 consistently acts as an inhibitor
- H_2S has consistently accelerated HE
- Pretreating with SO_2 had inhibiting effects during pretreatments
- More data and information is needed regarding purity at higher pressures

Areas for Further Research

- More information needed about threshold pressures at which maximum embrittlement occurs
- Fatigue data for metals demonstrating good HE resistance (A286, 316, Al and Cu alloys)
- More information needed about effects of inhibitors
  - ✓ Resolve conflicting claims
  - ✓ Specific concentrations for mixtures
  - ✓ Inhibiting at higher pressures

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1. ISO 11114-4: Transportable gas cylinders, compatibility of cylinder and valve materials with gas contents, 2006.
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