# International Codes, Standards and Experience Applicable to Storage of $H_2$, Natural Gas and Blends of $H_2$ with Natural Gas in High Pressure Cylinders

Presentation to:

## International Technical Forum on Hydrogen, Natural Gas, and Hydrogen-Natural Gas Vehicles and Infrastructure: Testing and Certification of Pressurized Storage Tanks

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# Hydrogen Embrittlement?


1972 Hydrogen car had a 400 bar transducer failure.
Was it HE? Good transducer design saved Frank's life!

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# Why add $H_2$ to CNG?

- Reduce emissions
- Increase efficiency
- Introduce hydrogen energy in a cost-effective way
- Open a market for renewable $H_2$ energy

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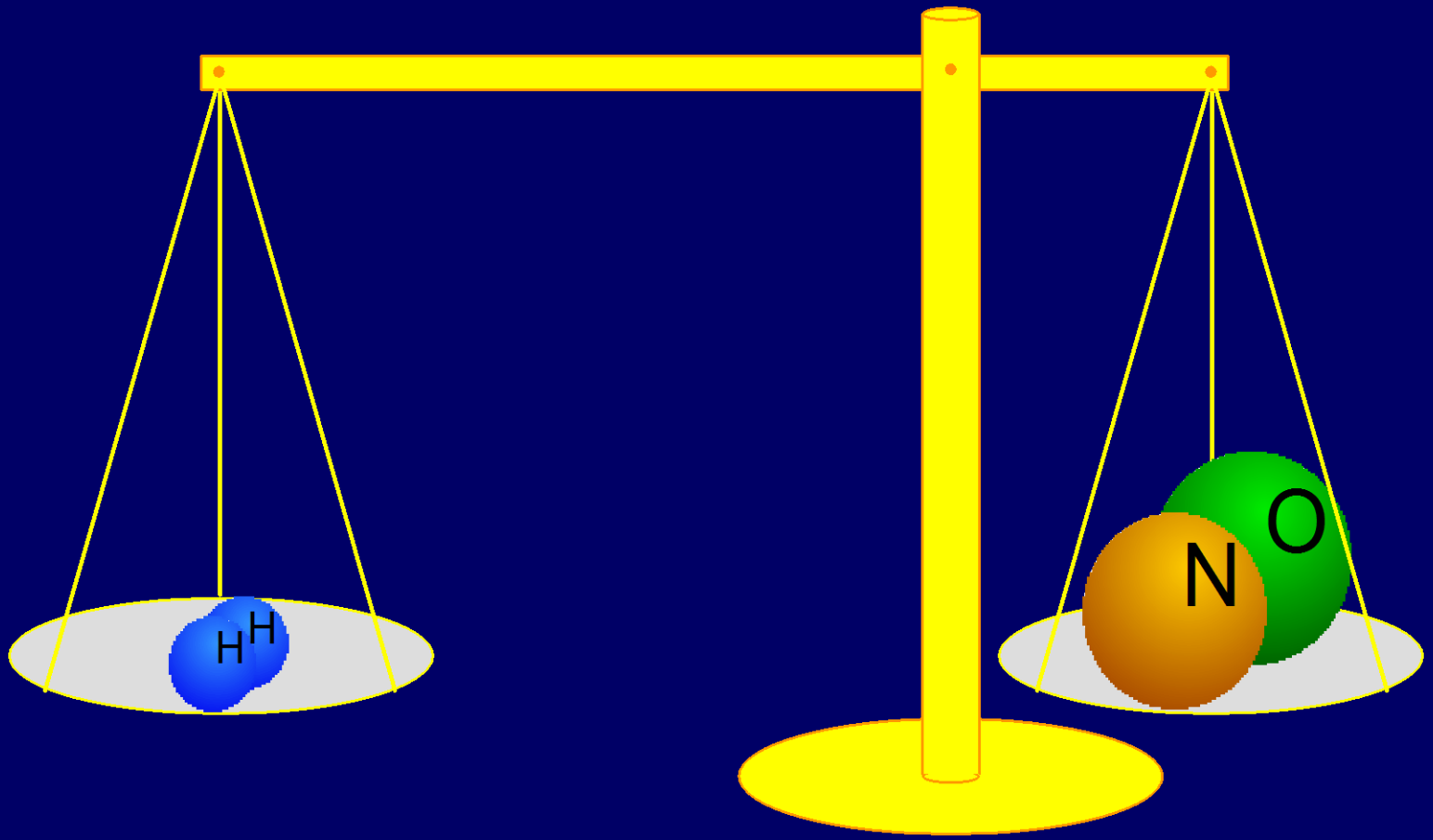
# LEVERAGED USE OF HYDROGEN IN INTERNAL COMBUSTION ENGINES

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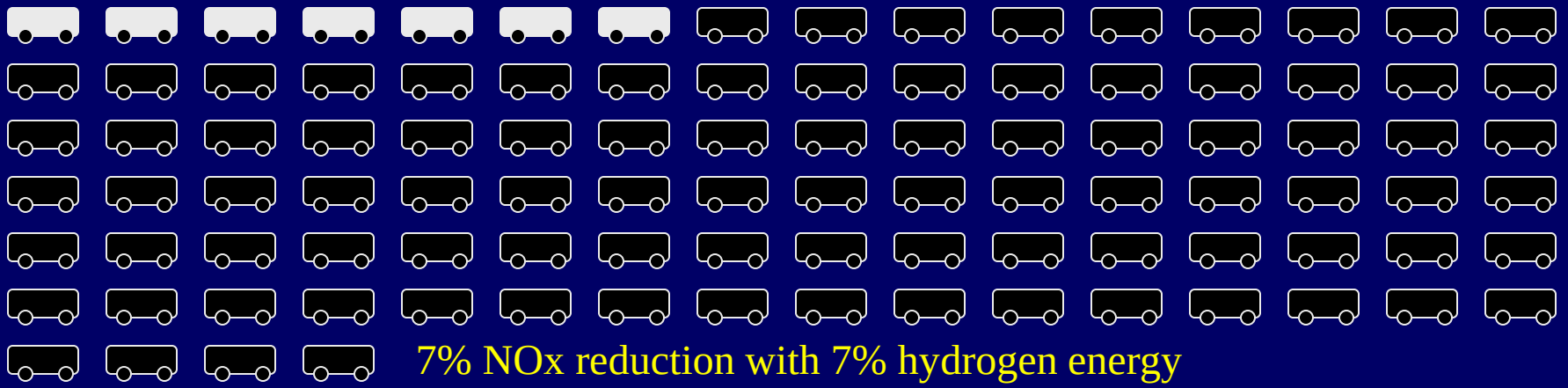
# What is the Best Use of 7% Hydrogen Energy?

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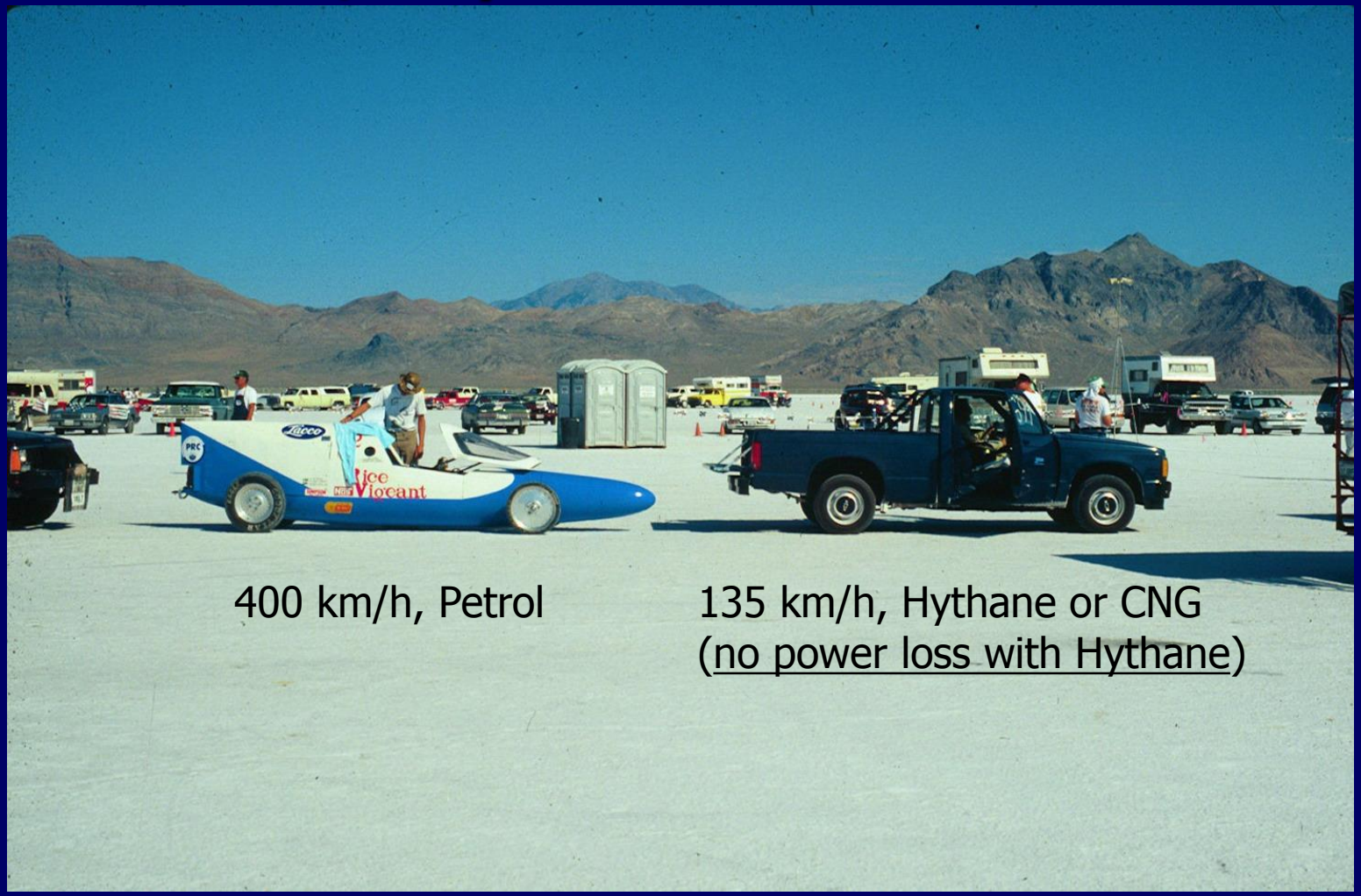
# 135 km/h, Hythane or CNG




400 km/h, Petrol

135 km/h, Hythane or CNG
(no power loss with Hythane)

World Speed Record Trials, Bonneville, August, 1991

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# Hythane is Mostly Methane

- 80 mol%, 93 energy%, 97 mass% $CH_4$
- Flame characteristics are more like $CH_4$
- Ignition energy is similar to $CH_4$
- $CH_4$ is a poison against $H_2$ embrittlement
- Hythane may be odorized like natural gas
- Hythane flames are not invisible


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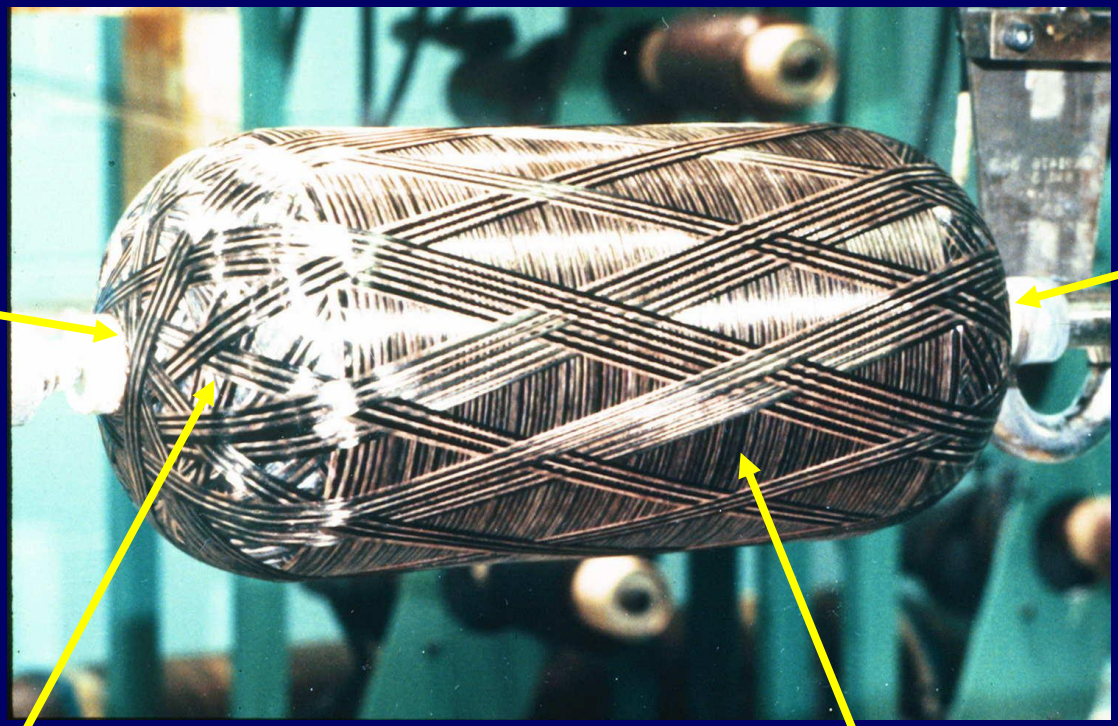
# Cylinder Types:



Type 4:
Type 3 with polymer liner (metal ends)

Type 1:
Metal tank only

Type 3:
Fully-wrapped with metal liner

Type 2:
Girth wrap on metal liner

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# Evolution of Type 1 Standards

- Hydrogen cylinder failures in 1970s
- Flurry of research through the 1980s
- 1990s cylinder manufacturing standards eliminated the problems

Most CNG cylinders in the world are Type 1


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# HYDROGEN CYLINDERS AND TRANSPORT VESSELS

## IGC Doc 100/03/E

Revision of TN 26/81

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# Hydrogen Embrittlement History

"…The French were the first to realize that hydrogen cylinders, as opposed to cylinders for other compressed gases, had to meet specific requirements. Based on the experience, which had been gained with similar steels in oil-field applications, the performance of the material in hydrogen was improved by limiting the maximum ultimate tensile strength and by closely controlling the alloy composition and heat treatment."


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# Hydrogen Quality

"…As a general rule, the higher the hydrogen gas purity (especially with respect to oxygen content), the higher is the potential susceptibility of steels … to hydrogen embrittlement."

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# Latest ISO $H_2$ Cylinder Standards

- 9809-1 Gas cylinders — Refillable seamless steel gas cylinders — Design, construction and testing —
  Part 1: Quenched and tempered steel cylinders with tensile strength less than 1100 MPa

- 11114-1 Transportable gas cylinders —Compatibility of cylinder and valve materials with gas contents —
  Part 1: Metallic materials

- 11114-4 Transportable gas cylinders —Compatibility of cylinder and valve materials with gas contents —
  Part 4: Test methods for selecting metallic materials resistant to hydrogen embrittlement


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# ISO 11114-4
## Test methods for selecting metallic materials resistant to hydrogen embrittlement

### Introduction

"It is widely recognized that compressed hydrogen and some hydrogen bearing gases can have an embrittling effect on metallic materials, especially steels. This embrittling effect has resulted in the failure of hydrogen cylinders (including some bursts) that has led gas cylinder users and manufacturers to adopt specific measures."

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# ISO 11114-4 (continued)

"The adoption of these measures has eliminated all known failures of hydrogen cylinders from this embrittlement phenomenon."


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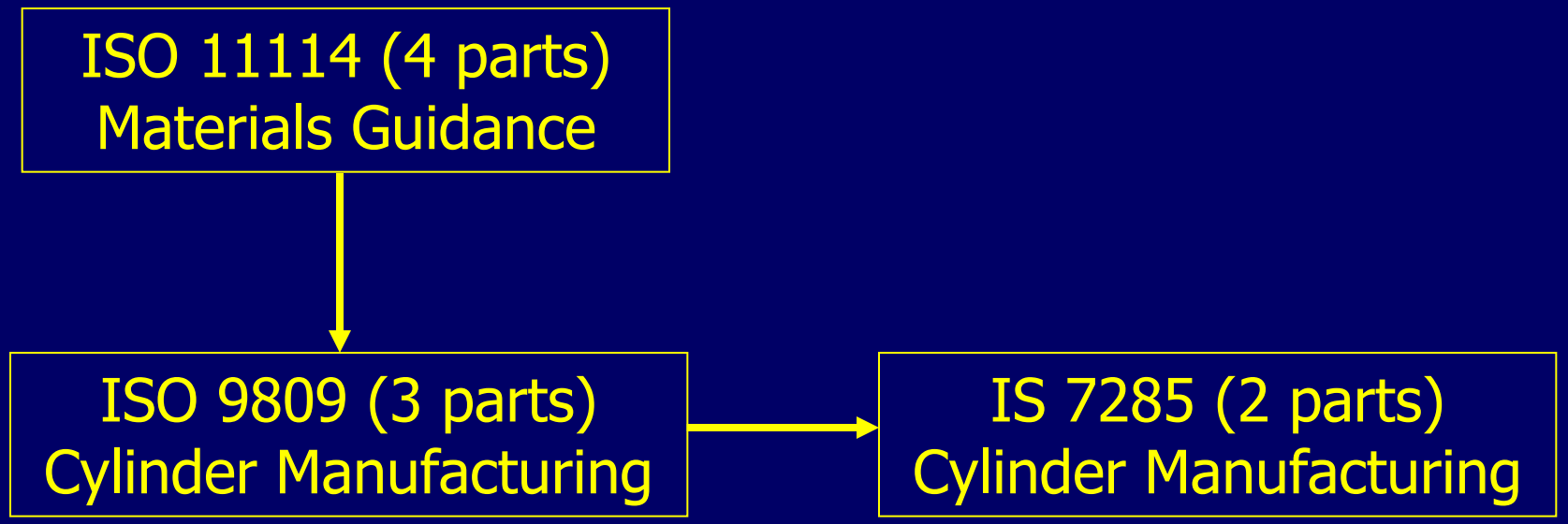
# China GB-5099 "Seamless Steel Gas Cylinders"

- 1000 $N/mm^2$ Tensile Limit for Most Gases
- 880 $N/mm^2$ for "Stress-Corrosive" Gases
- Sulphur Limit is 0.035%

# Relationship of Cylinder Manufacturing Standards




**ISO 9809-1 (<1100 MPa UTS)**
"**7.2.2** Where there is a risk of hydrogen embrittlement (see ISO 11114-1) the maximum value of the tensile strength…"

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# "Risk of Hydrogen Embrittlement" Defined:

"The requirements of this part of ISO 11114 are not applicable if at least one (Frank's underline) of the following conditions for the intended gas service is fulfilled[1]:

--the working pressure of the filled embrittling gas is less than 20% of the test pressure of the cylinder (1.5 x working P)

--the partial pressure of the filled embrittling gas of a gas mixture is less than 5 MPa (50 bar)…

[1]In such cases the cylinders may be designed as for ordinary (non-embrittling) gases."

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# US Dept. of Transportation 3AA Hydrogen Cylinder


Proof Test Date on this Cylinder, May 1946

Cylinders like this have been used safely around the world for over 100 years.

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# Typical Composition of Natural Gas

Table downloaded from http://www.naturalgas.org/overview/background.asp

| | | |
|---|---|---|
| Methane | $CH_4$ | 70-90 vol% |
| Ethane | $C_2H_6$ | 0-20 vol% |
| Propane | $C_3H_8$ | |
| Butane | $C_4H_{10}$ | |
| Carbon Dioxide | $CO_2$ | 0-8 vol% |
| Oxygen | $O_2$ | 0-2000 ppm |
| Nitrogen | $N_2$ | 0-5 vol% |
| Hydrogen Sulfide | $H_2S$ | 0-5 vol%* |
| Rare Gases | Ar, He… | Trace |

*$H_2S$ must be removed from CNG

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# Poisons Against Hydrogen Embrittlement*

- $H_2$ impurities inhibit hydrogen embrittlement (HE)
- $CH_4$, $C_4H_{10}$, $CO_2$ and especially $O_2$ inhibit HE
- Natural gas is mostly HE poisons
- $H_2$ is a dilute additive to natural gas in Hythane

*Richter, J. and Deimel, P., "Hydrogen Embrittlement of Pipeline Steels", International Energy Agency, Hydrogen Task VII, Storage, Conversion and Safety, Deutsche Forschungs- und Versuchsanstalt für Luft- und Raumfahrt, Cologne, Germany, 1984.

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# ISO 11114-4 Confirms Necessity of Pure $H_2$ for HE:

**"5 Test methods**
**5.1 Disc test (method A)**
**5.1.1 Principle of test**
…The embrittling effect of hydrogen is evidenced by comparing the hydrogen rupture pressures $P_{H2}$ with the helium rupture pressures $P_{He}$, helium being chosen as a reference gas…

NOTE 1 Hydrogen rupture pressures also depend on the hydrogen purity. Oxygen and water vapour can partially inhibit the hydrogen embrittlement effect.

**5.1.2.2 Cell and other apparatus**
…This permits the evacuation of the installation and a check of the hydrogen purity and freedom from either oxygen ($O_2$<1 ppm) or water vapour ($H_2O$<3 ppm)…"

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# Coal Gas is a Precedent for Hythane

- Coal gas is 30-50% $H_2$
- Other gases (CO, $CH_4$ , $O_2$) poison HE
- Indian Gas Cylinder Rules, 23 (3) are only concerned about impurities:

"…the (coal) gas shall be free from hydrogen sulphide and other sulphurous impurities as far as practicable. The moisture shall be less than 0.02 g/$m^3$ of gas at normal temperature and pressure."

Nothing is said about the hydrogen content of coal gas.

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# Three Reasons to Allow Hythane use in Type 1 Steel Cylinders

- The $H_2$ partial pressure in 200 bar Hythane falls below the limits in ISO 11114-4, so any certified ISO 9809-1 steel cylinder is OK for Hythane.

- The abundance of natural gas HE poisons in Hythane makes HE impossible at ambient temp.

- Coal gas (>30% $H_2$) is a precedent for allowing Hythane in steel cylinders.

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# India's First Public Hythane Station


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# WHAT SHALL WE DO?

- Ignore ISO guidance?
- Wait for more research?
- Stop making Hythane progress?
- Go ahead to make hydrogen progress via Hythane?


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# 21 Years, 12 Vehicles, 0 Fires
# 0 Accidents, 0 Materials Problems


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