Safe Use of Hydrogen and Hydrogen Systems

NASA Safety Training Center
Course Outline

- Introduction
- Why Study Hydrogen Safety?
- The Hydrogen Hazard
- Addressing the Hydrogen Hazard
- Component Design
- PEM Fuel Cell/Electrolyzer Issues
- Hydrogen Facility Design
- Hydrogen Hazards Analysis Approach
- Summary
Introduction

• Attendees
  – Name
  – What do you do with hydrogen?

• Instructors
  – Harold Beeson
  – Kevin Farrah
  – Max Leuenberger
  – Miguel Maes
  – Larry Starritt
  – Stephen Woods
Administrative Details

- Facility safety considerations
- Restrooms
- Breaks
- Questions and answers
- Course evaluations
Course Objectives

• To familiarize you with $H_2$ safety properties
• To enable you to identify, evaluate, and address $H_2$ system hazards
• To teach you safe practices for
  - Design
  - Materials selection
  - $H_2$ system operation
Course Objectives (cont.)

- Physical principles and empirical observations on which these safe practices are based
- How to respond to emergency situations involving H₂
- How to visualize safety concepts through in-class exercises
- Identify numerous parameters important to H₂ safety
We Will Show

Hydrogen can be handled safely...

...while stressing appropriate precautions
Course Materials

- Course slides
- 29CFR1910.103, *Hydrogen*

*Also available on the NASA Technical Standards Program [http://standards.msfc.nasa.gov/]
Disclaimer

• The use, or misuse, of this material is the responsibility of the attendee
• If you have an incident
  – Do not blame the course instructors
  – Do not blame anyone else
  – Get good video

Course instructors assume no responsibility
Course Limitations

- Imprecise quantification
- Technical judgment required
- No unique solutions given
- No endorsements implied
- Examples are illustrations only
Technical Judgment

• Overlapping roles
  – What must you know?
  – What must others know?
• How does this information affect me?

Bottom line: You must think
What is Judgment?

• Recognition of
  – Need
  – Limitations
  – Implications and consequences of actions
• Conservative approach
• Searching for hazards
Remember...

- Every situation is unique
- You are responsible
Battery Box Explosion
Old JSC Water Immersion Facility
(January 29, 1972)

• Watertight portable battery supply with 2 lead-acid cells had been charged overnight
• H₂ gas vent valve closed, not open
• Valve installed to purge H₂ at direction of previous hazards analysis
• Manually operated switch on lid (magnetic switch contacts internal to box)
In a seemingly conventional application such as this sealed battery box...
... the box lid killed one worker and severely injured another before puncturing a 35-ft-high concrete ceiling
Tube Trailer Accident

O₂ inadvertently leaked into this H₂ tube trailer (modifications made without review)
The mixture detonated at ~550 psi
Tube Trailer Accident (cont.)
Tubes and shrapnel were hurled 1250 ft, and several employees were burned.
LH Vent Line Incident Survey

H$_2$ Vent Line Explosion
H$_2$ Vent Line Explosion

Duct Fails Along Weld
H₂ Vent Line Explosion (cont.)
H$_2$ Vent Line Explosion (cont.)
H$_2$ Vent Line Explosion (cont.)

Hydrogen flames do not take corners well
H$_2$ Vent Line Explosion (cont.)
Hydrogen Balloon Accident

- Carlsbad, NM 2002 fireworks display
- Poor judgment used in constructing and deploying a balloon filled with hydrogen and oxygen
- One firefighter injured, and public “unnecessarily put at risk”
Why study hydrogen safety?
Why Study H₂ Safety?

• Because accidents occur!
  – In the ‘70s Over 400 industry accidents (Factory Mutual 4A7NO.RG)
  – 96 NASA mishaps (‘74 - Ordin, NASA TM X-71565)
  – See the DOE Hydrogen Incidents Database [http://www.h2incidents.org/]

• Despite H₂’s safe use for over 100 years
  – Town gas was 50% H₂

• Public perception is caution & danger
  – High school chemistry class experiment
  – Hydrogen bomb
Hydrogen Uses

- **Chemicals** 23%
  - Sorbitol production
  - General pharmaceutical
- **Electronics** 23%
  - Polysilicon production
  - Epitaxial deposition
  - Fiber optics
- **Metals** 19%
  - Annealing/heat treating
  - Powder metallurgy
- **Propulsion** 17%
- **Food, float glass, other** 18%
  - Fats/fatty acids
  - Blanketing
Hydrogen Production

- Primary source
  - Light hydrocarbons

- \( \text{GH}_2 \) production (USA)
  - 35 billion SCFD (Air Products 2002)

- \( \text{LH}_2 \) operating capacity
  - 136 tons per day (USA 1986)

- \( \text{LH}_2 \) demand
  - 82 tons per day (USA 1986)
Accidents occur...

...but looks can be deceiving
Tanker Truck Fire
LH$_2$ Trailer Accidents
# LH$_2$ Transportation - Reality

<p>| | |</p>
<table>
<thead>
<tr>
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<tbody>
<tr>
<td>Miles driven</td>
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<td>Deliveries</td>
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<td>Hydrogen releases</td>
<td>0</td>
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<tr>
<td>and accidents</td>
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</table>

Air Products data (1967-1989)
Lessons Learned from Previous Incidents

General Mishap Causes
Lessons Learned from Previous Incidents (cont.)

Detailed Mishap Causes

<table>
<thead>
<tr>
<th>Causes</th>
<th>Percent of Total Mishaps</th>
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<tbody>
<tr>
<td>A</td>
<td>20</td>
</tr>
<tr>
<td>B</td>
<td>16</td>
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<td>C</td>
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<td>D</td>
<td>8</td>
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<td>E</td>
<td>4</td>
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<tr>
<td>F</td>
<td>4</td>
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<tr>
<td>G</td>
<td>4</td>
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<td>H</td>
<td>3</td>
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<tr>
<td>I</td>
<td>2</td>
</tr>
<tr>
<td>J</td>
<td>2</td>
</tr>
<tr>
<td>K</td>
<td>1</td>
</tr>
<tr>
<td>L</td>
<td>1</td>
</tr>
<tr>
<td>M</td>
<td>1</td>
</tr>
</tbody>
</table>

- A: Valve Malfunctions and/or Valve Leaks
- B: Leaking Connections
- C: Safety Disk Failures
- D: Unsatisfactory Materials, Embrittlement
- E: High Venting Rates
- F: Cryopumping
- G: Air in System
- H: Bellows Failure
- I: Battery-Restricted Ventilation
- J: Tank Rupture
- K: Highway-Traffic Accidents
- L: Vacuum Loss
- M: Line Rupture
Hindenburg Misconception
Hindenburg Misconception (cont.)

What has been seen
Theory

- Researchers concluded \( \text{H}_2 \) not to blame
  - Film footage analysis shows explosion to be inconsistent with hydrogen fire, which only burns upward, with no visible flame
  - Gasbags coated with gelatin
  - Al powder mixed with doping solution made to stretch and waterproof outer hull
- 1930s fabric samples tested in modern laboratories proved to still be combustible
The Hydrogen Hazard

Safety-related Properties

and

What You Need to Know
The Hydrogen Hazard

• General properties
• Primary hydrogen hazards
  – Combustion
  – Pressure hazards
  – Low temperature
  – Hydrogen embrittlement
  – Exposure and health
Physical Properties

Hydro (water) + genes (forming) = Hydrogen

- **Forms:** Atomic Hydrogen, Molecular Hydrogen
- **Isotopes:** Protium (1 amu), Deuterium (2 amu), Tritium (3 amu)
- **Molecular Hydrogen States**
  - Orthohydrogen – protons have parallel spins
  - Parahydrogen – protons have anti-parallel spins
  - Normal hydrogen – thermal equilibrium mix of both
    - 300 K: 25% parahydrogen
    - 77 K: 50% parahydrogen
    - 20 K: 99.8% parahydrogen
- **States:** Gas, Liquid, Slush, and Solid
Energy Properties

- Heat of combustion (mass)
  - (HHV) 61,062 Btu/lb
  - (LHV) 51,560 Btu/lb

- Volumetric energy density
  - (HHV) 318.1 Btu/scf

- 1 kg H2 ~ 1 gallon of gasoline

- Hydrogen mass to volume conversions
  - 1 kg H2 = 423 scf = 11.13 Nm³ (normal m³)
Gaseous Hydrogen Properties

- **Description**
  - Colorless, odorless, tasteless

- **General Properties**
  - Flammable,
  - Non-irritating, nontoxic, asphyxiating
  - Non-corrosive
  - Lightest gas, buoyant, can escape earth

- **Physical Properties**
  - GH2 density @ NTP: 0.0838 kg/m³ (1/15th air)
  - GH2 specific gravity: 0.0696 (Air = 1.0)
  - Viscosity: 33.64 x 10^{-3} kg/m hr (1/2 air)
  - Diffusivity: 1.697 m²/hr (4x NG in air)
  - Thermal Conductivity: 0.157 kcal/m hr K (7 x air)
Liquid Hydrogen Properties

Description - Noncorrosive, colorless liquid

Normal boiling point 20.268 K, 101.325 kPa

Density @ NBP

- Vapor: 1.338 kg/m³
- Liquid: 70.78 kg/m³

LH₂ specific gravity, NBP 0.0710 (H₂O = 1.0)

Pressure to maintain NBP: 172 MPa

Density @ NBP

- Vapor: 845.1 kg/m³
- Liquid: 0.0710 (H₂O = 1.0)

Triple point: 13.8 K, 7.04 kPa

Thermal expansion: 0.0164 K⁻¹

Liquid density in NTP gas (per vol liquid @ NBP)

Equivalent vol gas @ NTP

LH₂ specific gravity, NBP

Vapor density @ NBP

Normal boiling point

Description - Noncorrosive, colorless liquid
# Thermal Expansion Coefficients of Some Cryogens

<table>
<thead>
<tr>
<th>Liquid</th>
<th>Thermal Expansion Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water(^b)</td>
<td>0.0007</td>
</tr>
<tr>
<td>Oxygen</td>
<td>0.0044</td>
</tr>
<tr>
<td>Argon</td>
<td>0.0044</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.0057</td>
</tr>
<tr>
<td>Neon</td>
<td>0.0144</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>0.0164(^c)</td>
</tr>
<tr>
<td>Helium</td>
<td>0.2100</td>
</tr>
</tbody>
</table>

\(^a\) Source: Edeskuty and Stewart 1996. Data for NBP.

\(^b\) Included for comparative purpose.

\(^c\) 23.4 times that for water.
Hydrogen Combustion Requirements

• Hydrogen mixed with an oxidizer to form a flammable mixture

• Ignition energy source (but may not be necessary for sensitive mixtures)

• Combustion can involve any of these
  – Fire
  – Deflagration
  – Detonation

• Confinement can lead to flame acceleration and overpressure

Note: Both deflagration and detonation can appear as an explosion to the human senses
Fire

• Rapid chemical reaction that produces heat and light
• Stationary flame with the flammable mixture fed into the reaction zone (plume or jet)

• Characterized by sustained burning, as manifested by any or all of the following
  – Light
  – Flame
  – Heat
  – Smoke
Deflagration

- Flame moving through a flammable mixture as a subsonic wave, with respect to the unburned mixture
  - Slow deflagration occurs in the open or with confinements that don’t favor flame acceleration
    - Laminar burning (2 – 3 m/s)
    - Non accelerating confinements (less than 100 m/s)
  - Flame acceleration up to choked flow (approaches sound speed in unburned gases, 400 – 800 m/s)
  - Deflagration-to-detonation transition (DDT): accelerated flames trip to detonation by turbulence or reflection of shock waves.
Deflagration in Open Air Following 5 Gallon LH2 Spill
Detonation

- Exothermic chemical reaction coupled to shockwave that propagates through a detonable mixture.
  - Shockwave velocity is supersonic with respect to the unburned gases.
  - After initiation, thermal energy of reaction sustains shockwave, which compresses unreacted material to sustain reaction.
Explosion

- Rapid equilibration of pressure between a system and the surroundings, such that a shockwave is produced
- May occur through
  - Mechanical failure of vessels containing high-pressure fluids
  - Rapid chemical reaction producing a large volume of hot gases
Hydrogen Combustion
Related Properties

- Wide flammability range
- Low ignition energy
- Small quenching distance
- Rapid diffusion
- Small molecule

- Buoyant in air (above 23 K)
- High ignition temperature
- High flame velocity
- Low flame emissivity

Remember: Hydrogen must be mixed with an oxidizer [air, O₂, Cl, F, N₂O₄, etc.] to burn
# Combustion Properties*

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flammability limits in NTP air</td>
<td>3.9 - 75.0 vol%</td>
</tr>
<tr>
<td>Flammability limits in NTP oxygen</td>
<td>3.9 - 95.8 vol%</td>
</tr>
<tr>
<td>Detonability limits in NTP air</td>
<td>18.3 - 59.0 vol%</td>
</tr>
<tr>
<td>Detonability limits in NTP oxygen</td>
<td>15 - 90 vol%</td>
</tr>
<tr>
<td>Minimum ignition energy in air</td>
<td>0.017 mJ</td>
</tr>
<tr>
<td>Autoignition temperature</td>
<td>858 K</td>
</tr>
<tr>
<td>Quenching gap in NTP air</td>
<td>0.064 cm</td>
</tr>
<tr>
<td>Diffusion coefficient in NTP air</td>
<td>0.061 cm²/s</td>
</tr>
<tr>
<td>Flame velocity</td>
<td>2.70 m/s</td>
</tr>
<tr>
<td>Flame emissivity</td>
<td>0.10</td>
</tr>
</tbody>
</table>

* Data is for parahydrogen but is applicable to ortho or normal hydrogen
Flammability Limits in Air

- Methane
- Propane
- Hydrogen
Combustion Hazards

**Triangle**

- **Fuel**
- **Ignition**
- **Oxidizer**

- **Fire Triangle**

- **Hydrogen**
- **Oxygen**
- **Air**

- **Combustion Hazards**
  - Electric Spark
  - Electric Arc
  - Heat
Fire Concerns

• Without Confinement:
  – High flame temperature (in air): 2045 °C (3713 °F)
  – Difficult to sense except by direct exposure, unless detection is used

• With Confinement
  – Can lead to high pressures (factor 1 – 8x)
  – Mechanical pressure relief for confined volumes is adequate
Deflagration Concerns

- **Slow Deflagration**: the concerns are the same as for fire [concentrations > 8 % v/v]
- **Accelerated flames and choked propagation**:
  - Concentrations > 12% v/v
  - Confinement characterized by L/W ratios > 8
  - Rapid propagation (400 – 800 m/s)
  - Pressure piling: pressurization of unburned gases
  - Dynamic pressures ranging from those produced by confined fire to a factor of 15x initial pressure
- **DDT**: transition to detonation due to turbulence and superposition of reflected shockwaves [Note: may begin with pressures formed by pressure piling]
- **Protection of vessels by mechanical relief devices** marginal for fully accelerated flames
### Deflagration Pressures

<table>
<thead>
<tr>
<th>Volume %</th>
<th>$T_o$ (K)</th>
<th>$P_o$ (kPa)</th>
<th>$T_f^a$ (K)</th>
<th>$P_f^a$ (kPa)</th>
<th>$T_o$ (K)</th>
<th>$P_o$ (kPa)</th>
<th>$T_f$ (K)</th>
<th>$P_f$ (kPa)</th>
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<tbody>
<tr>
<td>H$_2$</td>
<td>5</td>
<td>298</td>
<td>101.3</td>
<td>707.9</td>
<td>234.7</td>
<td>273</td>
<td>101.3</td>
<td>684.3</td>
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<tr>
<td></td>
<td>25</td>
<td>298</td>
<td>101.3</td>
<td>2159.2</td>
<td>643.8</td>
<td>273</td>
<td>101.3</td>
<td>2141.9</td>
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<td>50</td>
<td>298</td>
<td>101.3</td>
<td>1937.9</td>
<td>590.0</td>
<td>273</td>
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<td>1917.7</td>
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<td>75</td>
<td>298</td>
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<td>1165.7</td>
<td>375.6</td>
<td>273</td>
<td>101.3</td>
<td>1142.6</td>
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<td>Hydrogen/Air</td>
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<td>298</td>
<td>101.3</td>
<td>694.2</td>
<td>230.1</td>
<td>273</td>
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<td>671.6</td>
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<td>365.9</td>
<td>273</td>
<td>101.3</td>
<td>1132.8</td>
</tr>
</tbody>
</table>

$^a$ $T_f$ and $P_f$ are the final temperature and pressure that would occur in the fixed volume (2 m$^3$) when thermodynamic equilibrium occurred.
Detonation Concerns

• A detonation is potentially the worst-case event resulting from ignition of a combustible H\textsubscript{2}/oxidizer mixture
  – High velocity 1500 m/s
  – Large pressure ratio 15 – 120 x
  – Pressure relief No
Detonation Concerns (cont.)
Factors that Influence Detonation

• Percentage of H₂
  – Detonation limits in air*: 18.3-59 vol%
  – Detonation limit in oxygen*: 15-90 vol%

• Initial temperature, pressure, composition, and presence of diluents or inhibitors

• Strength (energy) of ignition source

• Degree of confinement

* Approximate percentages are based upon moderate initiation energies, better determinations are based on cell size information
### Detonation Pressures and Temperatures

<table>
<thead>
<tr>
<th>Volume % H₂</th>
<th>T₀</th>
<th>P₀</th>
<th>T₁/T₀</th>
<th>P₁/P₀</th>
<th>T₀</th>
<th>P₀</th>
<th>T₁/T₀</th>
<th>P₁/P₀</th>
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<tbody>
<tr>
<td></td>
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<td>kPa</td>
<td></td>
<td></td>
<td>K</td>
<td>kPa</td>
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<td>Hydrogen/Air</td>
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<td>4.880</td>
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<td>10.1</td>
<td>8.327</td>
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**a** T = temperature  
**b** P = pressure
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<tr>
<th>Property</th>
<th>Hydrogen</th>
<th>Gasoline</th>
<th>Comparison</th>
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<tr>
<td>MIE (in air)</td>
<td>17</td>
<td>240</td>
<td>+/-</td>
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<tr>
<td>Flammability range</td>
<td>4-75</td>
<td>1.5-7.6</td>
<td>+/-</td>
</tr>
<tr>
<td>Diffusion coefficient</td>
<td>0.61</td>
<td>0.05</td>
<td>+/-</td>
</tr>
<tr>
<td>Buoyant velocity</td>
<td>nonbuoyant</td>
<td>1-2.9</td>
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</tr>
<tr>
<td>PROPERTY</td>
<td>HYDROGEN</td>
<td>GASOLINE</td>
<td>COMPARISON</td>
</tr>
<tr>
<td>--------------------------------</td>
<td>----------</td>
<td>----------</td>
<td>------------</td>
</tr>
<tr>
<td>Minimum Ignition Energy in air, µJ</td>
<td>17</td>
<td>240</td>
<td>-</td>
</tr>
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<td>Autoignition Temperature in air, K</td>
<td>858</td>
<td>530</td>
<td>+</td>
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<td>Flammability Range, vol % in air</td>
<td>4-75</td>
<td>1.5-7.6</td>
<td>+/-</td>
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<tr>
<td>Detonability Range, vol % in air</td>
<td>18.3-59.0</td>
<td>1.1-3.3</td>
<td>+/-</td>
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<td>Flame Temperature, K</td>
<td>2323</td>
<td>2470</td>
<td>=</td>
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<tr>
<td>Flame Velocity, m/s</td>
<td>2.7-3.5</td>
<td>0.4</td>
<td>+/-</td>
</tr>
<tr>
<td>Flame Emissivity</td>
<td>0.10</td>
<td></td>
<td>+/-</td>
</tr>
<tr>
<td>Thermal Energy radiated from flame to surroundings, %</td>
<td>17-25</td>
<td>30-42</td>
<td>+</td>
</tr>
<tr>
<td>Diffusion Coefficient in NTP air, cm²/s</td>
<td>0.61</td>
<td>0.05</td>
<td>+/-</td>
</tr>
<tr>
<td>Diffusion Velocity in air at NTP, cm/s</td>
<td>&lt;2.0</td>
<td>&lt;0.17</td>
<td>+/-</td>
</tr>
<tr>
<td>Buoyant velocity in NTP air, m/s</td>
<td>1.2-9</td>
<td>nonbuoyant</td>
<td>+/-</td>
</tr>
<tr>
<td>Quenching Distance at 101.3 kPa absolute, mm</td>
<td>0.64</td>
<td>2</td>
<td>-</td>
</tr>
<tr>
<td>Vaporization rate (steady state) of liquid pools without burning, cm/min</td>
<td>2.5-5.0</td>
<td>0.005-0.02</td>
<td>+/-</td>
</tr>
<tr>
<td>Burning rates of spilled liquid pools, cm/min</td>
<td>3.0-6.6</td>
<td>0.2-0.9</td>
<td>+/-</td>
</tr>
</tbody>
</table>

- denotes hydrogen more hazardous than gasoline with respect to this property
+ denotes gasoline more hazardous than hydrogen with respect to this property
= denotes hazard is about equal for hydrogen and gasoline with respect to this property
+/-. denotes that the hazard for hydrogen could be more or less than gasoline with respect to this property depending on the circumstances
Summary of Possible Combustion Consequences

• **Fire**
  – Heating (thermal & UV energy radiated from flame)
  – Promoted combustion (direct contact with flame)
  – Burns (thermal & UV)

• **Deflagration and Detonation**
  – Effects of fire
  – Blast (overpressure)
  – Fragments
Formation of Combustible Mixtures

- Identify sources of hydrogen and oxidizers
  - Boil-off and venting
  - Batteries, fuel cells, electrolyzers
  - Chemical processes, radioactive decay
- Leaks and spills
  - External leakage
  - In-leakage
  - Leakage between system components
- Secondary accumulation
- Internal contamination
Possible Leak/Spill Causes

- Operator error
- Temperature
- Pressure
- Deformation and vibration
- Mechanical stress
- Mechanical damage
- Corrosion, wear,
  - Low temperature
  - Hydrogen
  - Embrittlement
  - Expansion/contraction
  - Diffusion/permeation
- Materials
Internal Contamination Causes

- Improper purging
- Contaminated fluids
  - Pressurization gas
  - Pump oils
  - Buildup of impurities
- In-leakage
  - Occurs from outside to inside of a system
  - Cryopumping
- Internal leakage
  - Occurs from one part of system to another
Ignition Sources

- Electrical
- Mechanical
- Thermal
- Chemical
Electrical Ignition Sources

- Static discharge
- Static electricity (two-phase flow)
- Static electricity (flow with solid particles)
- Electric arc
- Lightning

- Charge accumulation
- Electrical charge generated by equipment operation
- Electrical short circuits
- Electrical sparks
- Clothing (static electricity)
Mechanical Ignition Sources

- Mechanical impact
- Tensile rupture
- Friction and galling
- Mechanical vibration
- Metal fracture
Thermal Ignition Sources

- Open flame
- Hot surface
- Personnel smoking
- Welding
- Exhaust from combustion engine
- Resonance ignition

- Explosive charge
- High-velocity jet heating
- Shock wave from tank rupture
- Fragment from bursting tank
Chemical Ignition Sources

- Catalysts
- Reactants
For more combustion hazards information:


Pressure, low-temperature, and hydrogen embrittlement implications.
H₂ Properties Related to Overpressure Hazards

- Large liquid-to-gas expansion ratio
- Low heat of vaporization
- Large thermal difference
- Significant potential energy of compressed gas
Overpressure Hazard Sources

- Pressurization system failure
- Pressure relief system failure
- Fire from an external source
- Inadequate venting
- Ortho- to para-hydrogen conversion
- Overfilling
- Liquid-to-gas phase change

Overpressure Hazard Sources

- Pressurization system failure
- Pressure relief system failure
- Fire from an external source
- Inadequate venting
- Ortho- to para-hydrogen conversion
- Overfilling
- Liquid-to-gas phase change
## Physiological Effects of Blast Overpressure

<table>
<thead>
<tr>
<th>Max. Overpressure (kPa)</th>
<th>Effect on personnel</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>Knock personnel down</td>
</tr>
<tr>
<td>35</td>
<td>Eardrum damage</td>
</tr>
<tr>
<td>100</td>
<td>Lung damage</td>
</tr>
<tr>
<td>240</td>
<td>Threshold for fatalities</td>
</tr>
<tr>
<td>345</td>
<td>50% fatalities</td>
</tr>
<tr>
<td>450</td>
<td>99% fatalities</td>
</tr>
</tbody>
</table>
Low-temperature Hazards

- Cold fluids
  - Contaminant solidification
- Cold surfaces
  - Oxygen enrichment of air
  - Cryogenic burn (frostbite)
- Low-temperature embrittlement
  - Containment materials
  - Nearby materials
N₂/O₂ Phase Diagram Showing O₂ Enrichment

The diagram illustrates the phase diagram for N₂/O₂ mixtures, highlighting the atmospheric composition, vapor, dew line, boiling or bubble line, and liquid phases. The diagram shows the relationship between temperature (K) and oxygen concentration (% O₂) with nitrogen concentrations (N₂). The phases are indicated by points A and B, with A representing the atmospheric composition and B representing the boiling or bubble line. The diagram also indicates the transition from liquid to vapor as temperature increases.
Oxygen Enrichment Effect (Polyethylene)
H$_2$ Attack of Metals

Mechanical properties can be significantly reduced by H$_2$ embrittlement
- Tensile strength
- Ductility
- Fracture toughness
- Crack behavior

Failures have resulted

Use less susceptible materials
Types of H₂ Embrittlement

• Environmental embrittlement
  – Observed in metals and alloys plastically deformed in H₂ environment (especially high pressure)
  – Maximum effect from 200 - 300K

• Internal embrittlement
  – Caused by absorbed H₂
  – Maximum effect from 200 - 300K
Types of $H_2$ Embrittlement (cont.)

- $H_2$ reaction embrittlement
  - Absorbed $H_2$ chemically combines with metal to form a brittle hydride
  - Lowers materials ductility
  - Occurs readily at elevated temperature
  - Methane can form with carbon in steels
## H₂ Exposure and Ultimate Strength

<table>
<thead>
<tr>
<th>Material (notched sample)</th>
<th>Exposure (at 80 ºF)</th>
<th>Strength [MPa (psi)]</th>
<th>Change (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4140 (low strength)</td>
<td>69 MPa N₂ 69 MPa H₂</td>
<td>1660 (241,000) 1407 (204,000)</td>
<td>-15.2</td>
</tr>
<tr>
<td>4140 (high strength)</td>
<td>69 MPa N₂ 41 MPa H₂</td>
<td>2946 (362,000) 834 (121,000)</td>
<td>-66.6</td>
</tr>
<tr>
<td>C1025</td>
<td>69 MPa N₂ 69 MPa H₂</td>
<td>730 (106,000) 552 (80,000)</td>
<td>-24.4</td>
</tr>
<tr>
<td>K Monel PH</td>
<td>69 MPa N₂ 69 MPa H₂</td>
<td>1731 (251,000) 779 (113,000)</td>
<td>-55.0</td>
</tr>
<tr>
<td>K Monel (annealed)</td>
<td>69 MPa N₂ 69 MPa H₂</td>
<td>993 (114,000) 724 (105,000)</td>
<td>-27.1</td>
</tr>
</tbody>
</table>
Factors & Mechanisms Involved

- Operating environment
  - Temperature, pressure, exposure time

- Material
  - Physical and mechanical properties, stress state, stress concentrations, surface finish, microstructure, cracks

- Hydrogen
  - Purity, concentration
Factors & Mechanisms Involved (cont.)

• Susceptibility to embrittlement generally increases with increasing
  – Tensile stress
  – Alloy ultimate strength
  – H₂ purity
• Electrical discharge machining increases potential for H₂ embrittlement
Health Hazards

- Burns
  - Direct contact with flame
  - Thermal energy radiated from flame
  - UV exposure
- Asphyxiation
  - Hydrogen
  - Purge gas ($N_2, He$)
- Hypothermia
Health Hazards (cont.)

• Cryogenic burn (frostbite)
  – Similar to thermal burns produced from contact with cryogen or cold surfaces
  – Can result in permanent eye damage
  – Cryogen vapor can freeze skin or eyes faster than liquid contact, even faster than metallic contact
Cryogenic Burns

Third-degree cryogen burn (frostbite) to fingers

Second-degree thermal burn to hand
What You Need to Know

Summary

- General properties
- Primary hydrogen hazards
  - Combustion
  - Pressure hazards
  - Low temperature
  - Hydrogen embrittlement
  - Exposure and health
Addressing the H₂ Hazard

Safety Management and Standards
Start with Safety Management

- Minimize consequences
- Use safe principles and practices
- Perform reviews
- Be prepared for emergency situations
Managing a Hazard

Ignore it?

Control it?

Eliminate it?

Avoid it?
Cornerstones

Safe Use of Hydrogen

Follow proper principles, practices, and procedures...

... by properly trained and motivated personnel
Federal Regulations

- 29CFR1910.103, Hydrogen
- 49CFR Subtitle B, Vol 2, Ch 1, Parts 171-180, Transportation

* See osha.gov for latest CFR references
### HYDROGEN CFR INFORMATION

<table>
<thead>
<tr>
<th>Chemical Formula</th>
<th>H₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Common name</td>
<td>Hydrogen</td>
</tr>
</tbody>
</table>
| Hazard material description and proper shipping name | GH₂ | Hydrogen, compressed<sup>a</sup>
|                  | LH₂ | Hydrogen, refrigerated liquid (<i>cryogenic liquid</i>)<sup>a,b</sup> |
| Shipping identification number | GH₂ | UN1049<sup>a</sup> |
|                  | LH₂ | UN1966<sup>a</sup> |
| Shipping hazard class or division | GH₂ | 2.1<sup>a</sup> |
|                  | LH₂ | 2.1<sup>a</sup> |
| Shipping packing group | None given<sup>a,c</sup> |
| Shipping labels required | GH₂ | FLAMMABLE GAS<sup>a</sup> |
|                  | LH₂ | FLAMMABLE GAS<sup>a</sup> |
| Shipping special provisions | None given<sup>a</sup> |
| Shipping packaging authorization exceptions | GH₂ | See 49CFR173.306<sup>a</sup> |
|                  | LH₂ | See 49CFR173.316<sup>a</sup> |
| Shipping non bulk packaging requirements | GH₂ | See 49CFR173.302<sup>a</sup> |
|                  | LH₂ | See 49CFR173.316<sup>a</sup> |
| Shipping bulk packaging requirements | GH₂ | (See 49CFR173.302 and 173.314)<sup>a</sup> |
|                  | LH₂ | (See 49CFR173.318 and 173.319)<sup>a</sup> |
| Shipping quantity limitations for passenger aircraft or railcar | GH₂ | Forbidden<sup>a</sup> |
|                  | LH₂ | Forbidden<sup>a</sup> |
| Shipping quantity limitations for cargo aircraft only | GH₂ | 150 kg<sup>a</sup> |
|                  | LH₂ | Forbidden<sup>a</sup> |
| Vessel shipping stowage requirements | GH₂ | E<sup>a,d</sup> |
|                  | LH₂ | D<sup>a,e</sup> |
| Vessel shipping stowage provisions | GH₂ | 40<sup>a,f</sup>, 57<sup>a,g</sup> |
|                  | LH₂ | 40<sup>a,f</sup> |
| Process Safety Management Threshold Quantity | ≥10,000 lb<sup>b</sup> |

**NOTES:**

<sup>a</sup> 49CFR172.101

<sup>b</sup> Punctuation marks and words in italics are not part of the proper shipping name, but may be used in addition to the proper shipping name.<sup>a</sup>

<sup>c</sup> Class 2 materials do not have packing groups.<sup>a</sup>

<sup>d</sup> “E” means the material may be stowed “on deck” or “under deck” on a cargo vessel, but is prohibited on a passenger vessel.<sup>a</sup>

<sup>e</sup> “D” means the material must be stowed “on deck” on a cargo vessel, but is prohibited on a passenger vessel.<sup>a</sup>

<sup>f</sup> Storage provision “40” means: “Stow ‘clear of living quarters’” (49CFR176.84).

<sup>g</sup> Storage provision “57” means: “Stow ‘separated from’ chlorine” (49CFR176.84).

<sup>h</sup> 29CFR1910.119
Guidelines and Voluntary Consensus Standards*

- **Standards**
  - NFPA 55, Standard for the Storage, Use, and Handling of Compressed Gases and Cryogenic Fluids in Portable and Stationary Containers, Cylinders, and Tanks. [*Supersedes NFPA 50 A and 50 B*]
    - NFPA 50A, GH2 Systems at Consumer Sites
    - NFPA 50B, LH2 Systems at Consumer Sites

- **Consensus Guides**

* Approved standards and guidelines are available through the NASA Technical Standards Program available on the web [http://standards.msfc.nasa.gov/]
Industry Resources

• Accepted industry practice
  – CGA G-5, Hydrogen
  – CGA G-5.5, Hydrogen Vent Systems
  – CGA G-5.4, Standard for Hydrogen Piping Systems at Consumer Locations
  – CGA G-5.6, Hydrogen Pipeline Systems

• Industry resource documents
  – CGA H-2 Guidelines for the Classification and Labeling of Hydrogen Storage Systems with Hydrogen Absorbed in Reversible Metal Hydrides
  – CGA H-3 Cryogenic Hydrogen Storage
  – CGA H-4 Terminology Associated with Hydrogen Fuel Technologies
  – CGA P-12 Safe Handling of Cryogenic Liquids

• Industry positions
  – CGA PS-17 CGA Position Statement on Underground Installation of Liquid Hydrogen Storage Tanks
  – CGA PS-20 CGA Position Statement on the Direct Burial of Gaseous Hydrogen Storage Tanks
  – CGA PS-21 Position Statement of Adjacent Storage of Compressed Hydrogen and Other Flammable Gases
  – CGA PS-25 Recommendations for aerial storage
  – CGA PS-26 The Use of Carbon Fiber, Fully Wrapped Composite Storage Vessels in Stationary Gaseous Hydrogen Fueling Systems (proposed)
Guidelines and Voluntary Consensus Standards (cont.)

- **Storage vessels**
  - ASME, *International Boiler and Pressure Vessel Code, Section VIII, Pressure Vessels*
  - API Standard 620, *Design and Construction of Large, Welded, Low-pressure Storage Tanks*

- **Piping**
  - ASME B31.3, *Process Piping*
  - CGA G-5.4, *Standard for Hydrogen Piping Systems at Consumer Locations*
  - CGA G-5.6, *Hydrogen Pipeline Systems*
Safety Responsibility

• Management is responsible for
  – Establishing and enforcing safety policy
  – Ensuring that all applicable statutory and regulatory requirements are identified, documented, and adhered to in H₂ use

• Ultimately, everyone involved with H₂ system or operation is responsible for safety
Authority Having Jurisdiction

- Management shall define, designate, and document the entity (AHJ) that is empowered to implement and enforce safety policies and procedures
- The AHJ may be a person, a group, an office, an organization, or a federal, state, or local governing body
Organizational Policies and Procedures

• Required to control handling/use of H$_2$
• Should be
  – Formal (written)
  – Approved and enforced by upper level management
  – Available to, and understood by, all personnel involved in H$_2$ activities
  – Applicable to all phases of system operations
Hydrogen Safety Achieved by

- Inherent safety
- Approved operating procedures
- Trained personnel
- Design, safety, hazard, and operational reviews
- Approved quality control and maintenance programs
Inherent Safety

- Inherent safety vs. inherent hazards
- Involves
  - Fail-safe design
  - Automatic safety design
  - Caution and warning devices
  - Control of H₂ quantity
  - Siting of H₂ facilities
Delta Clipper

Flight Test 5
June 27, 1994
Approved Operating Procedures

- Required for facility or system operation and for routine task performance
- Prepared/reviewed by appropriate personnel
- Performed by trained personnel
- Reviewed appropriately to ensure that changes to processes, equipment, and operating conditions have been properly considered
Approved Operating Procedures (cont.)

- Help mitigate hazards
- **Teach how to prevent, detect, and respond to H₂ leaks**
- Outline
  - Adequate ventilation guidelines
  - Suitable maintenance and emergency procedures
Trained Personnel

• Training and refreshers are mandatory
  – Taught by approved instructors
  – Tailored to specific facility or system
  – Centered on H₂’s physicochemical properties and their safety implications
• Human limitations necessitate feedback
  – Student input improve subsequent training
• Certify for critical operations
Design, Safety, Hazard, and Operational Reviews

- Should be made of a system/facility before $H_2$ wetting
- Should be regularly conducted to ensure continual safe use of $H_2$
QC and Maintenance Programs

• All materials and components should be subject to a comprehensive inspection and be quality-controlled

• Maintenance program must be approved and sustained as needed
  – Inspected at least annually
  – Maintained by qualified personnel according to approved procedures
  • Inspection should be performed only if equipment is made safe for such maintenance
Maintenance Examples

- Lubrication
- Instrumentation calibration
- Cleaning and painting
- Operational verification of relief and check valves

- Replacement of filter elements
- Repair or replacement of
  - Damaged or faulty components
  - Components subject to wear (seals, seats, bearings)
Minimize consequences
Minimize Severity of Consequences

• Minimize quantity involved
• Control the area
• Use
  – Good housekeeping practices
  – Personnel protection
  – Operational requirements
  – $H_2$ and $H_2$ fire detection
  – Alarms and warning devices
Minimize Quantity Involved

• Minimize storage, transport, transfer, and end-use quantity
  – Mitigates consequences of accidents
  – Reduces siting requirements and area control requirements
    • Siting requirements based on quantity involved and type of use
### QUANTITY COVERED BY VARIOUS STANDARDS AND CODES

<table>
<thead>
<tr>
<th>CODE, STANDARD</th>
<th>FLUID</th>
<th>QUANTITY COVERED</th>
</tr>
</thead>
<tbody>
<tr>
<td>29CFR 1910.103 (HSS.1-2; A-53 - A-54)</td>
<td>GH₂</td>
<td>Does not apply to a system having a total content of less than 11 m³ (400 ft³). No maximum quantity specified. QD Requirements apply to any quantity.</td>
</tr>
<tr>
<td>NFPA 50A</td>
<td>GH₂</td>
<td>No min or max quantity specified. Does not apply to single systems using containers having a total content of less than 11 m³ (400 ft³) at 101.3 kPa (14.7 psia) and 294.1 K (70 °F). Applies where individual systems, each having a total content of less than 11 m³ (400 ft³) at 101.3 kPa (14.7 psia) and 294.1 K (70 °F), are located less than 1.5 m (5 ft) from each other. QD requirements apply to any quantity.</td>
</tr>
<tr>
<td>29CFR 1910.103 (HSS.1-2; A-55 - A-56)</td>
<td>LH₂</td>
<td>No min or max quantity specified. Does not apply to portable containers having a total content less than 150 L (39.63 gal). QD requirements apply to 150 L (39.63 gal) to 113,550 L (30,000 gal).</td>
</tr>
<tr>
<td>NFPA 50B</td>
<td>LH₂</td>
<td>No min or max quantity specified. Does not apply to portable containers having a total content less than 150 L (39.63 gal). QD requirements apply to 150 L (39.63 gal) to 283,875 L (75,000 gal).</td>
</tr>
<tr>
<td>29CFR 1910.119 (HSS.1-2)</td>
<td>any form</td>
<td>≥ 4536 kg (10,000 lbm)</td>
</tr>
<tr>
<td>NSS 1740.12 (NSS.A-56 - A-62)</td>
<td>LH₂</td>
<td>0 - 4.536 x 10⁶ kg (1 x 10⁷ lbm)</td>
</tr>
</tbody>
</table>
Control the Area

• Determine
  – Who can enter, and for how long
  – What can enter, especially ignition sources
  – What kind of activities are allowed in the area
Good Housekeeping Practices

• Weeds or similar combustibles are not permitted within 25 ft of LH$_2$ equipment (29 CFR 1910.103, Hydrogen)
• Access and evacuation routes are to be kept clear of equipment
• Conductive and nonsparking floors are to be kept clean of dirt
Personnel Protection

• Limit or, if possible, eliminate personnel exposure to cryogenic or flame temperatures
• Protect personnel from exposure to
  – Thermal radiation from H₂ fire, including intentionally flared H₂
  – Oxygen-deficient atmospheres of H₂ or inert purge gases (N₂, He)
Personnel Protection (cont.)

- Ensure personnel wear protective equipment to minimize injury if exposed
  - Quickly remove an injured person from a danger zone
- Insulate cold surfaces
Personnel Protection (cont.)

- Operations involving a cryogenic fluid require eye and hand protection
- Face shield when connecting and disconnecting lines/components
- Cotton/Nomex clothing
- Closed-toe shoes
- Hearing protection as appropriate
- Hard hats as appropriate
Operational Requirements

- Buddy system
- System/facility training
- Hydrogen training
- Emergency planning
- Don’t innovate!
H$_2$ and H$_2$ Fire Detection

• Human senses cannot normally detect H$_2$
  – Colorless and odorless
• Personnel should use portable H$_2$ detectors
• Detectors should be permanently installed where leaks can occur
  – Valves, joints


H₂ and H₂ Fire Detection (cont.)

- H₂ flame nearly invisible in daylight
- H₂ flame emissivity is low
  - Difficult to feel
- Personnel should use portable fire detectors
Alarms and Warning Devices

• Warning devices should provide an alarm for potentially hazardous situation, preferably before it happens
  – Abnormal condition, malfunction, incipient failure
• Alarm can be audible, visible, or both
Warning System Examples

- Pressure extremes
- Hydrogen in building ventilation intake
- Flare flameout
- Loss of vacuum insulation
- Valve position
- Pump speed extremes
- Hydrogen leak
- Filter differential pressure
- Fire
Use safe principles and practices
Use a Safe, Proven Approach

• Principles
  – Eliminate ignition sources
  – Use fail-safe design
  – Use redundancy in critical areas

• Practices
  – Control storage and transfer
  – Prevent unwanted air and fuel mixtures
  – Prevent overpressures
Storage and Transfer Operations

- Be alert for leaks
- Keep storage and transfer areas clear of nonessential personnel
  - Buddy system
  - Establish area control
- Cancel or discontinue operations in electrical storms
- Isolate, vent, and purge to remove H$_2$ or air
Eliminate Ignition Sources

- Control smoking, open flames, welding, use of mechanical tools
- Bonding and grounding
- Wear proper clothing
- Use lightning protection
- Use conductive machinery belts
- Use explosion-proof or purged enclosures for electrical equipment

But assume an ignition source is present
Prevent Unwanted Fuel/Air Mixtures

- Purging
- Leak free systems
- Hydrogen venting and disposal
- Ventilation
- Maintain positive pressures
Prevent Unwanted Fuel/Air Mixtures

This demonstration simulates the explosion of a battery box apparatus used at the Johnson Space Center in February 1972. The accident resulted in one fatality and severe hand injuries to a second worker.
Purging

• Purge equipment with inert gas before and after using $\text{H}_2$
  – Purge oxidizer before introducing $\text{H}_2$
  – Purge $\text{H}_2$ before introducing oxidizer
• Use $\text{GN}_2$ if temperature is $>80 \text{ K}$; if colder, use He
• Turn off $\text{N}_2$ purge to vent stack before venting cold $\text{H}_2$
  – Otherwise, $\text{N}_2$ will solidify
Purge Gas Systems

- Needed for purge, pressurization gases
- $\text{H}_2$ volumes should be capable of being purged and vented
- Inert gas subsystems should be protected from $\text{H}_2$ contamination
  - Use higher pressure, check valves, or a double block-and-bleed arrangement
# Improper Purging Causes Mishaps

<table>
<thead>
<tr>
<th>Purging Mishaps</th>
<th>No.</th>
<th>(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mishaps identified with purging problems</td>
<td>24*</td>
<td>25</td>
</tr>
<tr>
<td>Effects of mishaps due to purging problems</td>
<td></td>
<td></td>
</tr>
<tr>
<td>release into atmosphere</td>
<td>14</td>
<td>58</td>
</tr>
<tr>
<td>Release into system containers</td>
<td>10</td>
<td>42</td>
</tr>
<tr>
<td>Effects of release into atmosphere</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ignition</td>
<td>13</td>
<td>93</td>
</tr>
<tr>
<td>Non-ignition</td>
<td>1</td>
<td>7</td>
</tr>
<tr>
<td>Effect of release into system containers</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ignition</td>
<td>10</td>
<td>100</td>
</tr>
</tbody>
</table>

* 25% of total mishaps
Purging Techniques

- Evacuation and backfill
- Pressurization and venting
- Flow-through
Leak-free Systems

• Minimize number of joints and fittings
• Threaded fittings discouraged
  – Back-braze or seal weld
• Leak-check with N₂, then He
Dispose of Hydrogen Properly

- Venting
  - Low flow
- Flaring
  - Flare stack
  - Burn pond
Vent Fires

• Lightning a common cause of vent fires

  Procedure for extinguishing vent fire
  – Add inert gas flow, such as He
  – Stop $H_2$ flow
  – Continue inert gas flow until metal cools
  – Restart $H_2$ venting
  – Stop inert gas flow
Ventilation

- Ventilation must preclude formation of flammable mixture
  - Ventilate to below 1/4 of LFL
- Need to couple with $\text{H}_2$ detection
- Limited effectiveness on complex geometries
Maintain Positive Pressures

• Preclude air inclusion into system
  – Critical if system is not purged when idle
• Preclude contamination of purge and vent systems
Prevent Overpressure

Typical volumes that require pressure relief
Use Redundancy in Critical Areas

- Pressure relief
- Isolation
- Detection
Perform reviews
Reviews

• Design
• Safety
• Hazard
  – Requirements
  – Hazards analysis protocol
• Operational
Design Review

- Typically four types
  - Concept
  - Preliminary
  - Final
  - Certification

- Made for new facility, or significant modification of existing facility

- Should be made by qualified personnel of various fields of expertise
Safety Review

• Facility safety reviews made for
  – Construction
  – Operation
  – Maintenance
  – Final disposition

• Includes
  – System safety analyses
  – Failure modes and effects analyses
Hazard Review

• Covers
  – Component and system design
  – Operating conditions and procedures
  – Protective measures
  – Emergency procedures

• Performed
  – For components and systems
  – Regularly and as needed by qualified technical personnel
Hazard Review Requirements

- 29CFR1910.103, *Hydrogen*
- Federal Clean Air Act
- Emergency preparedness
Hazard Review Requirements (cont.)

- Identify hazardous operations
- Assess/analyze risk to personnel, equipment, and facilities
- Eliminate or control hazards
- Follow an approved hazardous operating procedure or permit
- Certify personnel who perform or control hazardous operations
Hazard Review Requirements (cont.)

- Mitigate hazards in order of priority
  - Design components and systems appropriately
  - Install safety, caution, and warning devices
  - Develop administrative controls
  - Provide protective clothing and equipment
Hazards Analysis Protocol

• Systematically and objectively*
  – Identify hazards
  – Determine their risk level
  – Provide mechanism for their elimination or control

* See NASA Reference Publication 1358, System Engineering “Toolbox” for Design-Oriented Engineers
* See NASA TM-2003-212059, Guide for Hydrogen Hazards Analysis on Components and Systems
Hydrogen Hazards Analysis Process

Define Scope of Analysis
Select Hazards Team Members

Compile Component/System Information

Decide on Component Analysis Strategy

Determine Component Hazards Scenarios

Assess Possible Combustible Mixture Formation

Assess Possible Ignition Mechanisms

Assess Possible Combustion Mechanisms

Fire  Deflagration  Detonation

Analyze Possible Secondary Effects

Assess Reaction Effects

Complete Report

Component By Component
## Component Hazards Chart

Assess Probability Rating for:

<table>
<thead>
<tr>
<th>Component/Operational Mode</th>
<th>Failure Modes</th>
<th>Flammable Mixture Formation</th>
<th>Ignition</th>
<th>Fire Deflagration</th>
<th>Secondary Effects</th>
<th>Overall Effects</th>
</tr>
</thead>
<tbody>
<tr>
<td>Valve # ---</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rating</td>
<td>0 – 4</td>
<td>0 – 4</td>
<td>0 – 4</td>
<td>0 – 4</td>
<td>N/R</td>
<td>A - D</td>
</tr>
</tbody>
</table>

**Ratings**
- 0 = Almost impossible
- 1 = Remote
- 2 = Unlikely
- 3 = Probable
- 4 = Highly probable

**Reaction Effects**
- A = Negligible
- B = Marginal
- C = Critical
- D = Catastrophic
Operational Reviews

- Operating procedures
- Operator training
- Test readiness
- Operational readiness inspection
- Emergency procedures
Be prepared for emergency situations
Emergency Response

- Primary aim is to protect life and prevent injury
- Principal danger from a leak or spill is fire
- H$_2$ flame limits are difficult to detect
  - Flame may be invisible in daylight
    - Inadvertent flame entry
Emergency Leak Procedures

- Isolate source, vent, purge, and repair
- Avoid ignition sources
- Exclude people and vehicles from leak area
- Do not deliberately flare a leak
Emergency Fire Procedures

- Let $H_2$ burn until supply can be cut off
- Use water to stop fire from spreading
- Do not spray water on vent systems or relief valves
- Remove a burning vessel from nearby vessels if it can be done safely
Avoid Asphyxiation

- Avoid areas near spills
- Oxygen monitoring
- Tank entry (H₂, N₂, He)
  - Ensure fresh air supply
  - Monitor atmosphere in tank
  - Entry plan, with emergency plans
  - Safety precautions
## Anoxia Symptoms

<table>
<thead>
<tr>
<th>% O₂ at 1 atm total pressure (vol basis)</th>
<th>At rest symptoms</th>
</tr>
</thead>
<tbody>
<tr>
<td>15 - 19</td>
<td>Decreased ability to perform tasks; may induce early symptoms in persons with heart, lung, or circulatory problems</td>
</tr>
<tr>
<td>12 - 15</td>
<td>Respiration deeper, pulse faster, poor coordination</td>
</tr>
<tr>
<td>10 - 12</td>
<td>Giddiness, poor judgement, lips slightly blue</td>
</tr>
<tr>
<td>8 - 10</td>
<td>Nausea, vomiting, unconsciousness, ashen face, fainting, mental failure</td>
</tr>
<tr>
<td>6 - 8</td>
<td>100% die in 8 min; after 6 min 50% die and 50% recover with treatment, 100% recover with treatment in 4-5 min</td>
</tr>
<tr>
<td>4</td>
<td>Coma in 40 s, convulsions, respiration ceases, death</td>
</tr>
</tbody>
</table>
Summary

- Safe use of $\text{H}_2$ is achievable
  - Comply with regulations
  - Management commitment
  - Apply proven principles and practices
    - Minimize consequences
    - Design for inherent safety
    - Review designs, safety, and operations
    - Use approved operating procedures
    - Proper maintenance
    - Use PPE and appropriate detection
    - Prepare for emergency situations
  - Train and motivate personnel
"That's why I never walk in front."
Component Design

Component and Material Considerations
Hydrogen Component Design

- System components
  - CGA G-5.4, *Standard for Hydrogen Piping Systems at Consumer Locations*
- Materials selection
- Liquid Hydrogen Component Considerations
System Components

- Joints and connections
- Valves
- Pressure relief devices
- Instrumentation and controls
- Filters
- Hydrogen detectors
- Fire detectors
Material considerations
Material Considerations

• Use proper materials
  – Metals
  – Nonmetals
• Understand temperature effects
  – Hydrogen embrittlement
• Dissimilar materials used together
• Permeability and porosity
<table>
<thead>
<tr>
<th>Material</th>
<th>GH₂</th>
<th>LH₂</th>
<th>SLH₂</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum and its alloys</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td></td>
</tr>
<tr>
<td>Austenitic stainless steels with &gt; 7% nickel (such as, 304, 304L, 308, 316, 321, 347)</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Some make martensitic conversion if stressed above yield point at low temperature.</td>
</tr>
<tr>
<td>Carbon steels</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>Too brittle for cryogenic service.</td>
</tr>
<tr>
<td>Copper and its alloys (such as, brass, bronze, and copper-nickel)</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td></td>
</tr>
<tr>
<td>Gray, ductile, or cast iron</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>Not permitted for hydrogen service.</td>
</tr>
<tr>
<td>Low-allow steels</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>Too brittle for cryogenic service.</td>
</tr>
<tr>
<td>Nickel and its alloys (such as, Inconel® and Monel®)</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
<td>Susceptible to hydrogen embrittlement</td>
</tr>
<tr>
<td>Nickel steels (such as, 2.25, 3.5, 5, and 9% Ni)</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>Ductility lost at LH₂ and SLH₂ temperatures.</td>
</tr>
<tr>
<td>Titanium and its alloys</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
<td>Susceptible to hydrogen embrittlement</td>
</tr>
<tr>
<td>Asbestos impregnated with Teflon®</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Avoid use because of carcinogenic hazard.</td>
</tr>
<tr>
<td>Chloroprene rubber (Neoprene®)</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>Too brittle for cryogenic service.</td>
</tr>
<tr>
<td>Dacron®</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>Too brittle for cryogenic service.</td>
</tr>
<tr>
<td>Fluorocarbon rubber (Viton®)</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>Too brittle for cryogenic service.</td>
</tr>
<tr>
<td>Mylar®</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>Too brittle for cryogenic service.</td>
</tr>
<tr>
<td>Nitrile (Buna-N®)</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>Too brittle for cryogenic service.</td>
</tr>
<tr>
<td>Polyamides (Nylon®)</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>Too brittle for cryogenic service.</td>
</tr>
<tr>
<td>Polychlorotrifluoroethylene (Kel-F®)</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td></td>
</tr>
<tr>
<td>Polytetrafluoroethylene (Teflon®)</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td></td>
</tr>
</tbody>
</table>
Understand H₂ Embrittlement Effects

- Extremely embrittled
  - 410 SS, 1042 steel, 17-7 PH SS, 4140, 440C, Inconel 718
- Severely embrittled
  - Ti-6Al-4V, Ti-5Al-2.5Sn, AISI 1020, 430F, Ni 270, A515
- Slightly embrittled
  - 304 ELC SS, 305 SS, Be-Cu Alloy 25, Ti
- Negligibly embrittled
  - 310 SS, 316 SS, 1100 Al, 6061-T6 Al, 7075-T73 Al, OFHC Cu, A286
Address $\text{H}_2$ Embrittlement

- Increased material thickness
- Surface finish
- Welding technique
- Material selection
- Conservative design stress (avoid yielding)
<table>
<thead>
<tr>
<th>Application</th>
<th>LH₂ or SLH₂</th>
<th>Typical materials</th>
</tr>
</thead>
<tbody>
<tr>
<td>Valves</td>
<td>Forged, machined, and cast valve bodies (304 or 316 stainless steel, or brass) with extended bonnet, and with other materials inside</td>
<td>Appropriate industrial products&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Fittings</td>
<td>Stainless steel bayonet type for vacuum jackets</td>
<td>Appropriate industrial products&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>O-rings</td>
<td>Stainless steel, Kel-F®️, or Teflon®️</td>
<td>Appropriate industrial products&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Gaskets</td>
<td>Soft Aluminum, lead, or annealed copper between serrated flanges; Kel-F®️️; Teflon®️️; glass-filled Teflon®️️</td>
<td>Appropriate industrial products&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Flexible hoses</td>
<td>Convoluted vacuum jacketed 316 or 321 stainless steel</td>
<td>Stainless steel braided with Teflon-lining</td>
</tr>
<tr>
<td>Rupture disk</td>
<td>304, 304L, 316, or 316L stainless steel</td>
<td>304, 304L, 316, or 316L stainless steel</td>
</tr>
<tr>
<td>Piping</td>
<td>304, 304L, 316, or 316L stainless steel</td>
<td>300 series stainless steel (316 preferred&lt;sup&gt;b&lt;/sup&gt;)</td>
</tr>
<tr>
<td>Dewars</td>
<td>No lubricants used in some applications.&lt;sup&gt;b&lt;/sup&gt; Lubricants listed for GH₂ are compatible but will become solid at low temperatures. Dry lubricants, such as PTFE, PTFE carbon, PTFE bronze, fiberglass-PFTE graphite.&lt;sup&gt;e&lt;/sup&gt; Graphite and molybdenum disulfide permit only very limited service life for bearings.&lt;sup&gt;f&lt;/sup&gt;</td>
<td>Dupont Krytox 240AC, Fluoramics OXY-8, Dow Corning DC-33, Dow Corning FS-3452, Bray Oil Braycote 601, General Electric Versilube, Houghton Cosmolube 5100, Braycote 640 AC, Dupont GPL 206, Halocarbon Series 63, oil, and Kel-F®️️ oil</td>
</tr>
<tr>
<td>Lubricants</td>
<td>No lubricants used in some applications.&lt;sup&gt;b&lt;/sup&gt; Lubricants listed for GH₂ are compatible but will become solid at low temperatures. Dry lubricants, such as PTFE, PTFE carbon, PTFE bronze, fiberglass-PFTE graphite.&lt;sup&gt;e&lt;/sup&gt; Graphite and molybdenum disulfide permit only very limited service life for bearings.&lt;sup&gt;f&lt;/sup&gt;</td>
<td>Dupont Krytox 240AC, Fluoramics OXY-8, Dow Corning DC-33, Dow Corning FS-3452, Bray Oil Braycote 601, General Electric Versilube, Houghton Cosmolube 5100, Braycote 640 AC, Dupont GPL 206, Halocarbon Series 63, oil, and Kel-F®️️ oil</td>
</tr>
</tbody>
</table>


<sup>b</sup> A number of standard industrial products are available covering a wide range of temperatures and pressures in a variety of compatible materials.

<sup>c</sup> Metal O-rings have proven satisfactory when coated with a soft material and when used on smooth surfaces. Type 321 stainless steel, with a coating of teflon or silver, should be used in stainless steel flanges with stainless bolting. Teflon®️ coated aluminum should be used in aluminum flanges with aluminum bolting. Using similar materials avoids the leakage possibility from unequal contraction of dissimilar metals. (Lewis Hydrogen Safety Manual, December 10, (1959) pp. 3-18)

<sup>d</sup> Threaded joints should be avoided in LH₂ or SLH₂ systems. If they must be used, the male and female threads should be tinned with a 60% lead-40% tin solder, then heated to provide a soldered joint with pipe thread strength. (Lewis Hydrogen Safety Manual, December 10, (1959) pp. 3-15)


<sup>g</sup> Carbon steel meeting ANSI/ASME B31.3 standards may be used for GH₂ service above 244 K (-20 °F.) (Lewis Safety Manual, Chapter 6 “Hydrogen Propellant,” NASA Technical Memorandum 104438, November (1992): pp. 6-35.)

<sup>h</sup> McPherson, B., Private communication (1996).
LH₂ Component Considerations
Lines and Fittings

- Use vacuum jacketed lines
- Do not use thread sealant in LH₂ systems
- “Cold shock” and retighten lines and fittings
- Use metal convoluted flexible hoses
Thermal Insulation

- LH₂ systems normally insulated
  - Reduce heat input and boiloff
  - Prevent liquid air formation
  - Prevent cold surface contact by personnel

- Cold GH₂ systems may need to be insulated
Thermal Insulation

• Insulation should have selfextinguishing fire rating
• Concern with foam insulation over air condensation with oxygen enrichment
  – Involves factors such as open cell vs closed cell, cell size, interstitial gas, joints and gaps
Vents

- Vents must be sized to allow for flow under all conditions
  - Normal flow
  - Cool down
- Vents should be at least rated for 150 psig per CGA G5-5
- Precautions must be taken to prevent cryopumping and moisture collection
Relief Devices

- Both normal flow and cooldown need protection.
- Sudden pressure decrease on relief valve actuation will cause sudden boiling.
- Avoid thermal cycling on rupture discs.
- Moisture collected in relief valve will freeze and prevent valve from operating.
Vacuum Subsystem

- Maintain insulating vacuum
- Remove unwanted $H_2$ or other gases by purging
  - Beware that vacuum pump with ballast valve could develop combustible mixture within the pump or its exhaust
Vacuum Subsystem (cont.)

• Vacuum pump exhaust must be connected to a proper vent
  – To vent $\text{H}_2$ gas
  – To vent oil vapors (mechanical pump)

• Leak in an evacuating system can result in system being contaminated with air
Summary

• Careful consideration should be given to
  – Each part of every component
  – Operating conditions
  – How each component is used in an H$_2$ system

• Special considerations are required for LH$_2$ systems
Initial Thoughts on Hydrogen Combustion Issues for Fuel Cell/Electrolyzer System Design

* Proton Exchange Membrane
Prevents the hydrogen and oxygen from mixing.

Transfers protons (H⁺) from Anode to Cathode.

Electrons travel from Anode to Cathode through external load.

Anode (Catalytic Electrode)
\[ 2H_2 \rightarrow 4H^+ + 4e^- \]

Cathode (Catalytic Electrode)
\[ 4H^+ + O_2 + 4e^- \rightarrow 2H_2O \]

Overall Reaction:
\[ 2H_2 + O_2 \rightarrow 2H_2O \]
Understand Combustion Potential

• Understand possibilities
  – \( \text{H}_2 + \text{O}_2 \)
  – \( \text{H}_2 + \text{air} \)
  – \( \text{H}_2 + \text{other oxidizers} \)

• Primary focus on \( \text{H}_2 \)-wetted volumes
  – Interstack spaces & stack headers
  – Gas separators
  – Filters, heat exchangers, pumps
  – Lines and fittings
Secondary Analysis Required

- Secondary focus on regions exposed following exposure
  - External to components and system
  - Internal to gauges
- Separate $O_2$ hazards analysis required
  - Possibility of $O_2$/material combustion
  - “Kindling chain” processes
  - Requires additional expertise
Approaches to Combustion Control

- Exploit physical combustion limits
  - Fire and deflagration
    - Choose dimensions < quenching gap
    - Avoid flammable mixture compositions
  - Detonation
    - Choose dimensions < critical cell size
    - Avoid detonable mixture compositions
  - Deflagration-to-detonation transition
    - Design channel lengths < ~0.5 m
    - Avoid detonable mixture compositions
Approaches to Combustion Control (cont.)

• Control combustible atmosphere formation
  – Composition <1% H₂
  – Detection
    • H₂ sensors in air, or O₂ sensors in H₂
  – Multiple fault tolerance

• Buffer H₂ from oxidizers with purges

• Postfailure safing

• Monitor cell performance for pinholes
Approaches to Combustion Control (cont.)

- Minimize ignition sources
  - Beware of component power use
    - Indicates ignition potential
  - Reduce conductive debris
  - Isolate potential surfaces
  - Control accumulation of catalytic fines
Other Considerations

• Consider material compatibility
• H₂ embrittlement
• Consider H₂ in solution
• Choose SS lines over plastic
• Avoid combustible seal materials

• Design for worst-case containment
  – Detonation $p_{\text{initial}} \times \sim(15 \text{ to } 20) \times 3$ (reflection) $\times$ safety factor
  – Deflagration $p_{\text{initial}} \times \sim(1 \text{ to } 8) \times$ safety factor
Henry never knew what hit him.
General Facility Design

- General considerations
- Facility siting
- Piping and storage
- Venting, flaring, and dispersion
- Buildings and test chambers
General considerations
Goals of Facility Safety

- Protection of the public and workers most important
- Value of equipment
- Importance of mission
- Public perception
- Environment
A Safe Facility

- Safety considered in design and construction
  - As foolproof as possible
- Safety and hazard analyses
  - Inputs from designers, operators, safety engineers
- Good maintenance
- Safety committee oversight
Safe Operation

- Training
  - Initial and periodic
- SOPs and checklists
Facility siting
Facility Siting

- Site location preferences
- Quantity-distance requirements
- Exclusion areas
- Barricades, dikes and impoundments
Site Location Preferences

- Driven by application and quantity
  - Laboratory scale operations (small quantities)
  - Non-propellant
  - Propellant
- Laboratory scale
  - Determined by site AHJ
  - OSHA regulation: \( \text{GH}_2 < 11.3 \text{ m}^3 \) (400 ft\(^3\)), \( \text{LH}_2 < 150 \text{ L} \) (39.6 gal)
- Non-propellant
  - Industry like applications for \( \text{GH}_2 \) or \( \text{LH}_2 \)
  - Primary hazard is inadvertent release into air and subsequent fire
  - Must consider standard exposures [powerlines, drains, etc.]
Simulated Spill
1500 Gal LH2 in 30 seconds
## Preferred Order for Locating GH$_2$ Storage Systems

<table>
<thead>
<tr>
<th>Nature of Location</th>
<th>GH$_2$ Volume</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>&lt;3K ft$^3$ (85 m$^3$)</td>
</tr>
<tr>
<td>Outdoors</td>
<td>I</td>
</tr>
<tr>
<td>In separate building</td>
<td>II</td>
</tr>
<tr>
<td>In special room</td>
<td>III</td>
</tr>
<tr>
<td>Inside buildings, exposed to other</td>
<td>IV</td>
</tr>
<tr>
<td>occupancies, but not in special room</td>
<td></td>
</tr>
</tbody>
</table>
NFPA Gaseous Hydrogen Separation Distances

- Identifies exposures,
  - Walls by material, openings, fire ratings
  - Presence of flammable/combustible liquids (above and below ground), combustible materials
  - Places of public assembly, sidewalks, parking, property lines
- Provides a breakdown by quantity: <3000 ft³ (85 m³), 3000 ft³ (85 m³) – 15,000 ft³ (425 m³), >15,000 ft³ (425 m³)
- For example: >15,000 ft³ (425 m³)
  - 25 ft to unsprinklered building
  - 50 ft to flammable gases other than hydrogen
  - 50 ft to places of public assembly
- See NFPA 55, Standard for the Storage, Use, and Handling of Compressed Gases and Cryogenic Fluids in Portable and Stationary Containers, Cylinders, and Tanks [supersedes NFPA 50 A]
# Preferred Order for Locating LH₂ Storage Systems

<table>
<thead>
<tr>
<th>LH₂ Volume, L (gal)</th>
<th>Nature of Location</th>
</tr>
</thead>
<tbody>
<tr>
<td>150-189 (40-50)</td>
<td>Outdoors I</td>
</tr>
<tr>
<td>190-1136 (51-300)</td>
<td>In separate building II</td>
</tr>
<tr>
<td>1137-2271 (301-500)</td>
<td>In special room III</td>
</tr>
<tr>
<td>&gt;2271 (&gt;600)</td>
<td>Inside buildings, exposed to other occupancies, but not in special room IV</td>
</tr>
</tbody>
</table>

- Not permitted
**NFPA Liquid Hydrogen Separation Distances**

- Identifies exposures,
  - Walls by material, openings, fire ratings
  - Intakes for compressors, AC, or ventilation
  - Presence of flammable/combustible liquids (above and below ground), combustible materials
  - Places of public assembly, sidewalks, parking, property lines
- Provides a breakdown by quantity 75 ft (gallons): 39.65 – 3,500, 3501 – 15,000, 15,001 – 75,000.
- For example: 15,001 – 75,000 gallons
  - 100 ft to unsprinklered building
  - 75 ft to liquid oxygen
  - 100 ft to all classes of flammable & combustible liquids
  - 75 ft to places of public assembly
- See NFPA 55, Standard for the Storage, Use, and Handling of Compressed Gases and Cryogenic Fluids in Portable and Stationary Containers, Cylinders, and Tanks [supersedes NFPA 50 B]
Siting for Propellant Applications

- Propellant applications are determined by the potential for mixing fuel and oxidizer.
- Typical applications include:
  - Launch pads
  - Static test stands, cold-flow test operations
  - Bulk storage, rest storage, & run tankage
  - Pipelines
- Amounts < 45 kg (100 lbs) explosive equivalent (fuel + oxidizer) are controlled by the AHJ.
LH$_2$-LOX Range Safety Test
Siting for Propellant Applications

- Distances are much larger than NFPA
  - 75,000 lb ~100,000 gal
  - 1200 ft to inhabited buildings
  - 1200 ft to public traffic
  - 130 ft to intragroup storage
- NASA adheres to DOD Ammunition and Explosive Safety Standard [6055.9]
- Latest range safety test data: Correlation of Liquid Propellants NASA Headquarters RTOP, WSTF-TR-001-01-02
Facility Siting
Exclusion Areas

• Create an exclusion area with controls
  – Limit access to personnel with required training and proper protective equipment
  – Ensure equipment is not an ignition source
  – Operate according to approved procedures
    • Post known hazards
  – Minimum exclusion area = Q-D requirements
Facility Siting
Barricades

• Use barricades to protect
  – From shrapnel and fragments
  – $\text{H}_2$ facility from other hazards
  – Nearby facility from $\text{H}_2$ facility

• Use earth mounds and blast mats

• Ensure it does not provide confinement sufficient for detonation
Facility Siting
Dikes and Impoundments

• Use to contain spills
• Can limit vaporization rate
  – Possibly smaller combustion cloud, but longer time to vaporize
• Use crushed stone for added surface area to increase vaporization rate in an impoundment can
• Ensure they do not provide confinement sufficient for detonation
Piping and storage
Storage Vessels

• Design

• Design and siting
  – NFPA 50A, *GH₂ Systems at Consumer Sites*
  – NFPA 50B, *LH₂ Systems at Consumer Sites*

• Hazards analysis
Storage Vessel Design

- Equip with shutoff valve
  - Automatic operation preferred
- Provide for approved vent and pressure relief systems
- Provide barriers to potential failure of rotating equipment, such as pumps
Storage Vessel Installation

• Ensure that LH$_2$ vessels are
  – Insulated
    • Limits vaporization and condensation of air
    • Should be self-extinguishing
  – Periodically warmed to remove solid contaminants
  – Electrically bonded at all joints
  – Grounded and properly labeled
    • Contents, capacity, MAWP
  – Surrounded by a 15-ft clear space
Piping Siting

- Be located in accordance with appropriate standards
  - 29CFR1910.103, NFPA 55 [Supersedes NFPA 50 A and B]
- Not located beneath electric power lines
- New piping should not be buried
- Protect from potential failure of rotating equipment and from vehicles
Piping Design and Fabrication

• Design, fabricate, and test to ASME B31.3 and CGA G-5.4

• Provide appropriate
  – Flexibility (expansion joints, loops, offsets)
  – Supports, guides, and anchors
  – Relief devices
  – Electrical bonding across all joints
  – Grounding
  – Labeling (contents, flow direction)
Venting, flaring, and dispersion
Vent/Flare and Dispersion

• Vent or flare according to approved methods
• Ensure H$_2$ vent system velocity is in satisfactory range
• Provide purge capability
  – Use N$_2$ or He, depending on temperature
Vent/Flare and Dispersion (cont.)

- Prevent air and precipitation from entering vent/flare system
  - Use molecular seal or flapper
- Ensure relief device connection to manifold does not affect relief pressure
H₂ flare stack with gas (molecular) seal
Siting

- Locate roof vents so that $\text{H}_2$ does not get into building air intakes
  - Roof vent located 16 ft above roof can be used to vent up to 0.5 lb/s
- Dispose of large quantities of $\text{H}_2$ by flaring
  - Flare stack or burn pond
Disposal Factors

- $\text{H}_2$ quantity/extent in combustible cloud
- Thermal radiation from flame
- Site conditions
  - Size of exclusion area
  - Building locations
  - Personnel control
  - Weather
Dispersion Test Results

White Sands Test Facility, New Mexico
Fall 1980

Liquid Hydrogen was spilled to study hydrogen plume dispersion. Release rate was 1500 gallons/30 seconds into a 30 foot diameter spill pond. Three tests show the effect of increasing wind speed for the following conditions:
Flammable Mixture and Visible Cloud
Combustible Cloud Length

![Graph showing the relationship between Combustible Cloud Length and Hydrogen Release Rate (g/s)]
H₂ Mass in Combustible Cloud

![Graph showing the relationship between Hydrogen Release Rate (g/s) and Hydrogen Mass in Combustible Cloud (kg). The graph includes lines labeled A, B, C, and D, representing different conditions: GHT, 1 m/s; GHT, 3 m/s; DAY, 1 m/s; and DAY, 3 m/s.]
Combustible Cloud Mixture

Combustible Cloud Maximum Rise (m)

Night, 1 m/s
Night, 3 m/s
Day, 1 m/s
Day, 3 m/s

Hydrogen Release Rate (g/s)
Buildings and test chambers
Buildings and Test Chambers

- Minimize personnel injury and facility damage in case of H$_2$ fire or explosion
- Construct with lightweight, noncombustible materials according to 29CFR1910.103, Hydrogen
Building Design

- Avoid peaks in ceilings
- Use shatterproof glass or plastic in window frames
- Ensure a 2-h fire resistance rating for walls, floors, and ceilings
- Provide explosion venting in exterior walls or roof
- Provide heat by steam, hot water, or other indirect means
Building Ventilation

• Ensure structures containing $H_2$-wetted systems are ventilated
  – Ventilation rate should dilute $H_2$ leak to 25% of LFL (1% by volume) or less
• Establish ventilation before introducing $H_2$ into the system
• Ensure ventilation does not shut down during emergency shutdown procedure
Building Ventilation (cont.)

• Ensure building air intake is installed if \( \text{H}_2 \) vented nearby
  – Sensors activate alarms and automatic air shutoff if \( \text{H}_2 \) detected

• Install \( \text{H}_2 \) sensors in building outlet vents if \( \text{H}_2 \) used inside

• Avoid suspended ceilings and inverted pockets or ensure adequate ventilation
Facility support infrastructure
Facility Support Infrastructure

- Inert gas subsystem
- Electrical subsystem
- Cooldown
- Transportation
Inert Gas Subsystem

- Used to provide purge and pressurization gases
- Ensure that all H$_2$-containing volumes are capable of being purged and that purge gas is vented
- Protect inert gas subsystems from H$_2$ contamination
  - Higher pressure, check valve, double block and bleed arrangement
Positive GH$_2$ Shutoff Systems
Electrical Requirements

• Must conform to NFPA 70, National Electrical Code
  – If within 3 ft of where connections are regularly made and disconnected
    • NFPA 70, “Class I, Group B, Division 1” locations, which rely heavily on explosion-proof or an inert-gas-purged enclosures
  – If within 25 ft of where connections are regularly made and disconnected, or within 25 ft of an LH₂ storage container
    • NFPA 70 “Class I, Group B, Division 2” locations
Definition of Explosion-proof

• Enclosure must be strong enough to withstand any internal pressures caused by an explosion and tight enough to prevent the issuance of flames.

• Does not mean that equipment has to be gas-tight.

Explosion-proof electrical equipment is required in “Class I” hazardous locations per NEC.
NEC Definitions

• Class I: Location in which flammable gases or vapors exist in quantities sufficient to render the resultant atmosphere explosive or ignitable

• Group B: Atmospheres containing hydrogen or gases or vapors of equivalent hazards such as manufactured gas
NEC Definitions

• Division 1: Locations where hazardous concentrations of flammable gases or vapors exist
  – Continuously, intermittently or periodically under normal conditions
  – Frequently because of repair/maintenance operation or because of leakage
  – Due to breakdown or faulty operation of equipment or processes, which might also cause electrical equipment failure
NEC Definitions

• Division 2: Locations in which flammable volatile liquids or gases are handled, processed, or used
  – Normally confined to closed containers or systems from which they can escape only by accidental rupture or breakdown of such containers or systems or by abnormal equipment operation
Electrical Considerations

- Use a purged enclosure as an alternative to explosion-proofing
- Provide lightning protection in all areas where there is H₂
- Bond and ground mobile H₂ supply units before discharge
Personnel Electrical Protection

• Ensure personnel are grounded before working on an $\text{H}_2$ system
  – Use antistatic clothing
• Ensure personnel use conductive machinery belts
• Provide adequate illumination for all $\text{H}_2$ areas
Cooldown Model
Two-phase Flow Regimes

- Plug
- Stratified
- Wave
- Slug
- Annular
- Dispersed (Almost all liquid)
- Bubble
Cooldown Issues

• Large stresses can result from
  – Large circumferential and radial temperature gradients
  – Large thermal contraction, especially in long lines

• Two-phase flow can cause random cooling
  – Liquid flow will cool faster than comparable gas flow
Cooldown Issues (cont.)

- Stratified flow can cause high stress from large circumferential temperature gradients
- Maintain minimum flow during cool-down to avoid pipe bowing
- Vent appropriately the resultant gases
- Design pipe properly to accommodate required gas flow-through
Cooldown Issues (cont.)

- Establish min/max cool-down limits
  - Too slow can result in stratified, 2-phase flow and pipe bowing
  - Too fast can result in large radial temperature gradients
    - Flange: inner wall is cooled quickly while the outer wall remains near ambient temperature
Maximum $H_2$ Flow Rate
Minimum $\text{H}_2$ Flow Rate
Transportation

- Transport H₂ according to 49CFR

  - On cargo ships, GH₂ may be stowed on or below deck; but LH₂ may only be stowed below deck, but LH₂ may only be stowed on deck.
  - On cargo aircraft, GH₂ may be stowed on or below deck.
  - Up to 150 kg (GH₂ only) permitted on a cargo aircraft.
  - Air or passenger railcars or ships is prohibited.

Transportation
Facility safety subsystems
Facility Safety Subsystem

- Use leak- and fire-detection elements
- Include
  - Fire protection
  - Fire fighting
Facility Fire Protection

- Use
  - Automatic or manual process shutdown systems
  - Sprinklers
  - Deluge systems
  - Water spray systems
  - Dry-chemical extinguishing systems
  - Halon systems

- Large H₂ systems
  - Storage, grouped piping, and pumps shall be completely covered by a water-spray system according to 29CFR1910.163, *Fixed extinguishing systems, water spray and foam*
Facility Fire Protection (cont.)

- Consider installing deluge systems along the top of storage areas, especially LH$_2$
- Provide fire hydrant or 2 in. dia hose bib adjacent to all LH$_2$ storage areas
  - Also used for wash down
- Keep water from entering H$_2$ vents
Facility Fire Fighting

• Shut off $\text{H}_2$ supply before attempting to extinguish an $\text{H}_2$ fire
  – Preclude reignition of combustible cloud
• Spray water on adjacent equipment to keep it cool
• Extinguish small $\text{H}_2$ fires with
  – Dry chemical or $\text{CO}_2$ extinguishers, $\text{N}_2$, or steam
Summary

• Keep safety as the primary H₂ facility consideration, from concept through disposal
• Adhere to proven practices and principles
• Follow approved procedures followed for all operations
Summary (cont.)

• Control
  – Ignition sources
  – Formation of combustible mixture

• Minimize exposure to the hazard
  – Siting, quantity of H₂ involved, number of people exposed

• Be alert to changes in operating conditions
Hydrogen Hazards Analysis

Prerequisites and Approach
Overview

- Why perform hazards analysis?
- Prerequisites for hazards analysis
- Hazards analysis approach
- Sample analysis
- Summary
Why Perform a Hazards Analysis?

- Systematically and objectively
  - Identify hazards
  - Determine their risk level
  - Provide mechanism to evaluate for the elimination or control of hazards

- Use to
  - Improve designs
  - Evaluate safety of operations
  - Analyze failures

- Formal hazards analysis specifies protocol for evaluation and documentation
Hazards Analysis Prerequisites

- Understand analysis scope
- Have detailed design information
  - Up-to-date schematics
  - All vendor information
  - Identify all materials exposed to H₂
- Assemble necessary expertise
- Have information necessary to evaluate all leak paths
Hazards Analysis Overview

- H$_2$ hazards analysis based on NASA WSTF protocol
- Before team analysis
  - System owners set agenda/scope
  - Facilitators compile system information
- Sequester team from distractions
- Decide on analysis strategy
  - Component similarity
  - Materials similarity
  - According to system sequence
Hazards Analysis Overview (cont.)

- Conduct component-level assessment
  - Determine failure modes and causes
  - Classify failure modes
- Determine failure effects on components and systems

Flowchart:

1. Define Scope of Analysis
   - Select Hazards Team Members
2. Compile Component/System Information
3. Decide on Component Analysis Strategy
4. Determine Component Hazards Scenarios
5. Assess Possible Combustible Mixture Formation
6. Assess Possible Ignition Mechanisms
7. Assess Possible Combustion Mechanisms
   - Fire
   - Deflagration
   - Detonation
8. Analyze Possible Secondary Effects
9. Assess Reaction Effects
10. Complete Report

Team Analysis
Failure Effects Consideration

- Evaluate probability
  - Combustible mixture formation
  - Ignition sources
  - Types of combustion events [fire, deflagration, detonation]
- Evaluate secondary effects
- Evaluate total reaction effects
Questions to Consider

• What failure modes involve \( \text{H}_2 \)?
• Where can combustible mixtures form?
• What ignition sources exist?
• What combustion mechanisms are active?
• What are the combustion effects?
• What are the overall risks to system, users, mission, or business?
Sample Analysis

• The following circuit depicts part of a system used to recover water from a hydrogen gas – water mixture exiting from an electrolyzer
  – The water is critical for spacecraft operations
  – The hydrogen is vented overboard.

• The focus of the sample analysis is on the back-pressure regulator component
System Schematic
Component Schematic
## Hazards Analysis Chart

<table>
<thead>
<tr>
<th>Component</th>
<th>STEP 1</th>
<th>STEP 2</th>
<th>STEP 3</th>
<th>STEP 4</th>
<th>STEP 5</th>
<th>STEP 6</th>
<th>STEP 7</th>
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<tr>
<td>Differential-backpressure regulator into recirculation loop</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>3</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Differential-backpressure regulator into the vacuum enclosure</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>3</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
1. The following leak paths are considered:

A) A small internal leak across the valve which does not drop the separator outlet pressure will not create an H$_2$ hazard in the water line.
B) A leak across the bellows will cause gaseous H$_2$ to flow into the water recirculation loop and will be analyzed separately.
C) Leaks externally into the vacuum enclosure can occur at the manifold seal or adjusting cap seal.
D) A large internal leak which is not sensed by the delta P sensor, or when sensed solenoid valve fails open (both second point failure) could cause H$_2$ from the phase separator to enter the recirculation loop. Two failures to be considered are 1) if a large internal leak across this valve which does drop the separator outlet pressure and cause H$_2$ to enter the water line or 2) if the valve fails open. Both failures will be detected by either the separator differential pressure sensor or the gas detector. Hydrogen gas will be isolated by a solenoid valve before a combustible mixture is formed. If a second failure occurs where the solenoid valve fails open or leaks internally, then a combustible mixture could form in the recirculation loop or downstream.

Because of the H$_2$ embrittlement properties of Inconel 17-4 and 17-7PH and the 304L, and the fact that these materials are used in bellows and springs, it is recommended that a fatigue analysis be conducted to determine the life of the parts. After assembly the component attached to the manifold is proofed to 1.5 times MDP and then tested for leaks at MDP using helium.
2. Cap leakage from the exterior can result in pressurizing the vacuum enclosure to 0.25 psia. If this is followed by a component failure resulting in H2 leaking into the vacuum enclosure, this will result in a potentially combustible mixture. The shutdown pressure inside the vacuum enclosure is 0.25 psia.

*It is recommended that under these conditions the vacuum enclosure is vented when pressure >0.25 psia so that total pressure remains <0.43 psia which is where H2 and O2 are not flammable for spark energies similar to those inside the vacuum enclosure (see Fuels Handbook).*

3. Electrical ignition sources are present but insulation, grounding, and other protective measures are designed in to reduce the risk of arcing or sparking. At 0.25 psia, the system is shut down. Bleed resistors are present to drain any residual charge. In the absence of electrical component failure there is insufficient energy to ignite this mixture.

4. Given the presence of two failures to give a flammable mixture and the small ignition sources, the probability of deflagration inside the vacuum enclosure is remote.

5. Catastrophic failure of the system is defined as loss of system function. Component failure results in system function loss.

6. A large internal leak (initial failure) not sensed by the \(\Delta P\) sensor or when the solenoid valve fails open (both second point failures) could cause H2 from the phase separator to enter the recirculation loop. A leak across the bellows will cause GH2 to flow into the water recirculation loop. The effect of these failures will be analyzed separately. Leaks externally into the vacuum enclosure can occur at the manifold seal or adjusting cap seal. After assembly the component attached to the manifold is proofed to 1.5 times MDP and then tested for leaks at MDP using helium.
7. Leakage from the exterior can result in pressurizing the vacuum enclosure to a pressure of 0.25 psia. If this is followed by a failure of the component resulting in leaking of H₂ into the vacuum enclosure, this will result in a potentially combustible mixture. The shut down pressure inside the vacuum enclosure is 0.25 psia.

*It is recommended that under these conditions that the vacuum enclosure is vented when the pressure exceeds 0.25 psia so that the total pressure remains below 3 kPa (0.43 psia) which is where drop has shown that H₂ and O₂ are not flammable for spark energies similar to those inside the vacuum enclosure (See Fuels Handbook).*

8. Electrical ignition sources are present but insulation, grounding and other protective measures are designed in to reduce the risk of arcing or sparking. At 0.25 psia the system is shut down. Bleed resistors are present to drain any residual charge. Therefore, in the absence of failure of electrical components there is insufficient ignition energy to ignite a 0.25 psia mixture.

9. Given the presence of two failures to give a flammable mixture and the small ignition sources, the probability of deflagration inside the vacuum enclosure is remote.

10. Catastrophic failure of the system is defined as loss of system function. Failure of the component results in loss in function of the system.
Analysis Results

- Single failure required for formation of combustible mixture in first instance
  - Enclosure (normal) and component leakage
  - System is controlled with pressure sensor
- Electrical ignition sources present but small
- Deflagration will occur, but likelihood is low
- Reaction effect is a function of application and is catastrophic as defined by user
Analysis Results (cont.)

- Two failures required for formation of combustible mixture
  - Large internal leak not sensed by delta pressure sensor, or sensed but solenoid valve fails open
- Electrical ignition sources present, but small

- Deflagration will occur, but likelihood is low
  - propagation in bubbly flow
- Reaction effect is a function of application and is catastrophic as defined by user
Summary

• Hazards analysis approach
  – Systematically and objectively identify hazards and evaluate risk
  – Tool to help control hazards, improve designs

• Requires
  – Understanding the scope of the analysis
  – Complete information
  – Necessary expertise

• Successfully applied to several key systems
Course Summary

- $\text{H}_2$ use is important
- $\text{H}_2$ use involves hazards/risks
- $\text{H}_2$ can be used safely
  - Thinking
  - Planning
  - Training
  - Being prepared
We Have Studied

- Hydrogen’s safety related properties
- Hazards associated with H₂ use
- How to deal with hazards and emergency situations
- Typical components and materials for use with H₂
- H₂ facility guidelines
- Hazards analysis approach
Safety in the Use of Hydrogen

- Proper system design
  - Critical component redundancy
  - Fail-safe policy
- Proven practices and principles
- Personnel training and certification
- Design, safety, hazard, and operational reviews
- Careful system operation
- Approved operating procedures and checklists
- Personal protective equipment
- Quality control and maintenance programs
In Summary

• A core body of knowledge exists
• It has been used to provide safe H₂ uses
• Use conservative approach
• Recognize hazards and limitations
• Search for hazards
• Don’t take chances or shortcuts

THANKS