# Safe Use of Hydrogen and Hydrogen Systems

## NASA Safety Training Center


Revision Sept. 06

# Course Outline

# 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 $H_2$
- How to visualize safety concepts through in-class exercises
- Identify numerous parameters important to $H_2$ safety

# We Will Show

Hydrogen can be handled safely…


…while stressing appropriate precautions

# Course Materials

- Course slides
- ANSI/AIAA G-095-2004, *Guide to Safety of Hydrogen and Hydrogen Systems**
- 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…

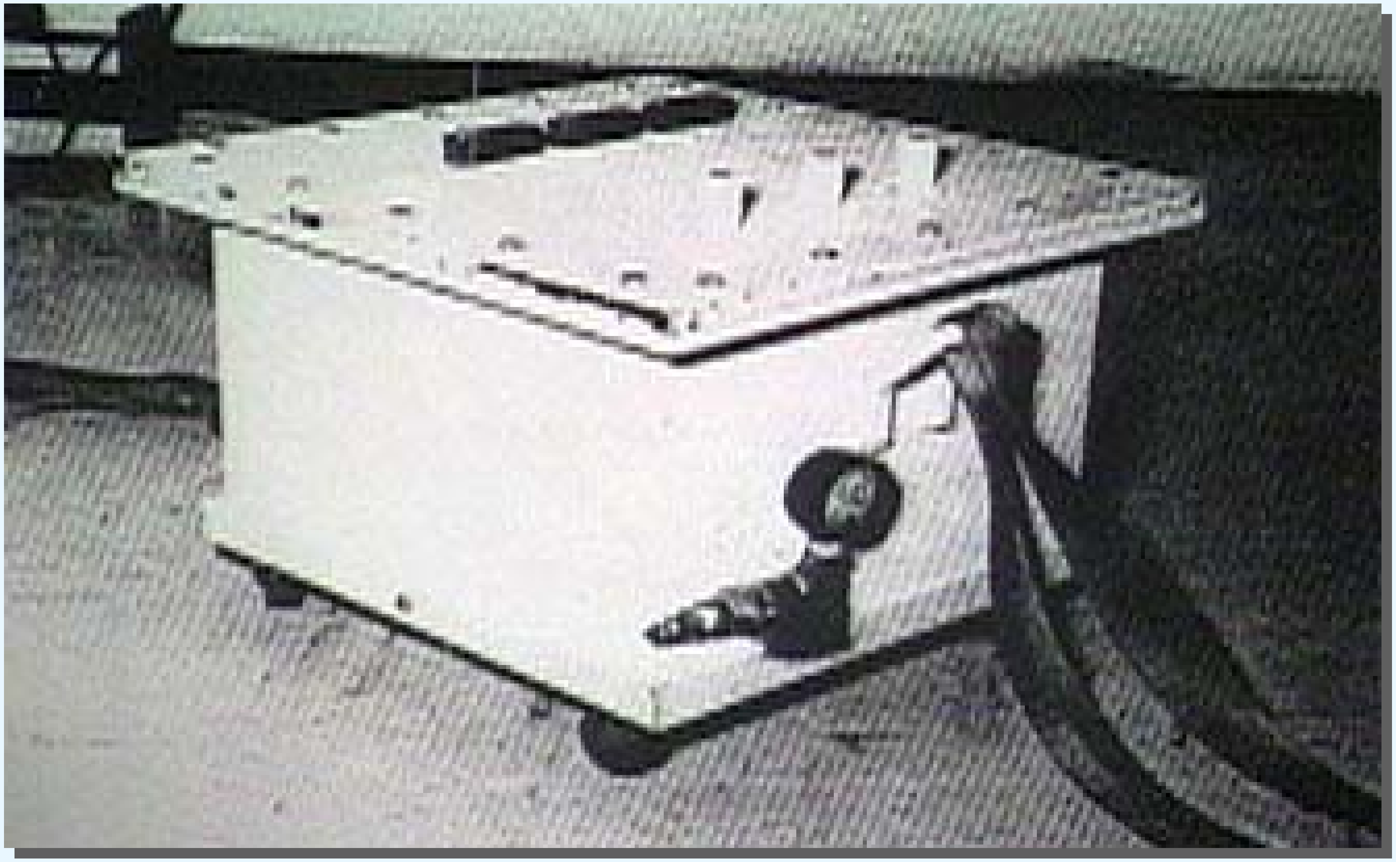
- Every situation is unique
- You are responsible

# Battery Box Explosion

## Old JSC Water Immersion Facility

### (January 29, 1972)

- Watertight portable battery supply with 2 lead-acid cells had been charged overnight
- $H_2$ gas vent valve closed, not open
- Valve installed to purge $H_2$ 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

$O_2$ inadvertently leaked into this $H_2$ tube trailer (modifications made without review)

# Tube Trailer Accident (cont.)

The mixture detonated at ~550 psi

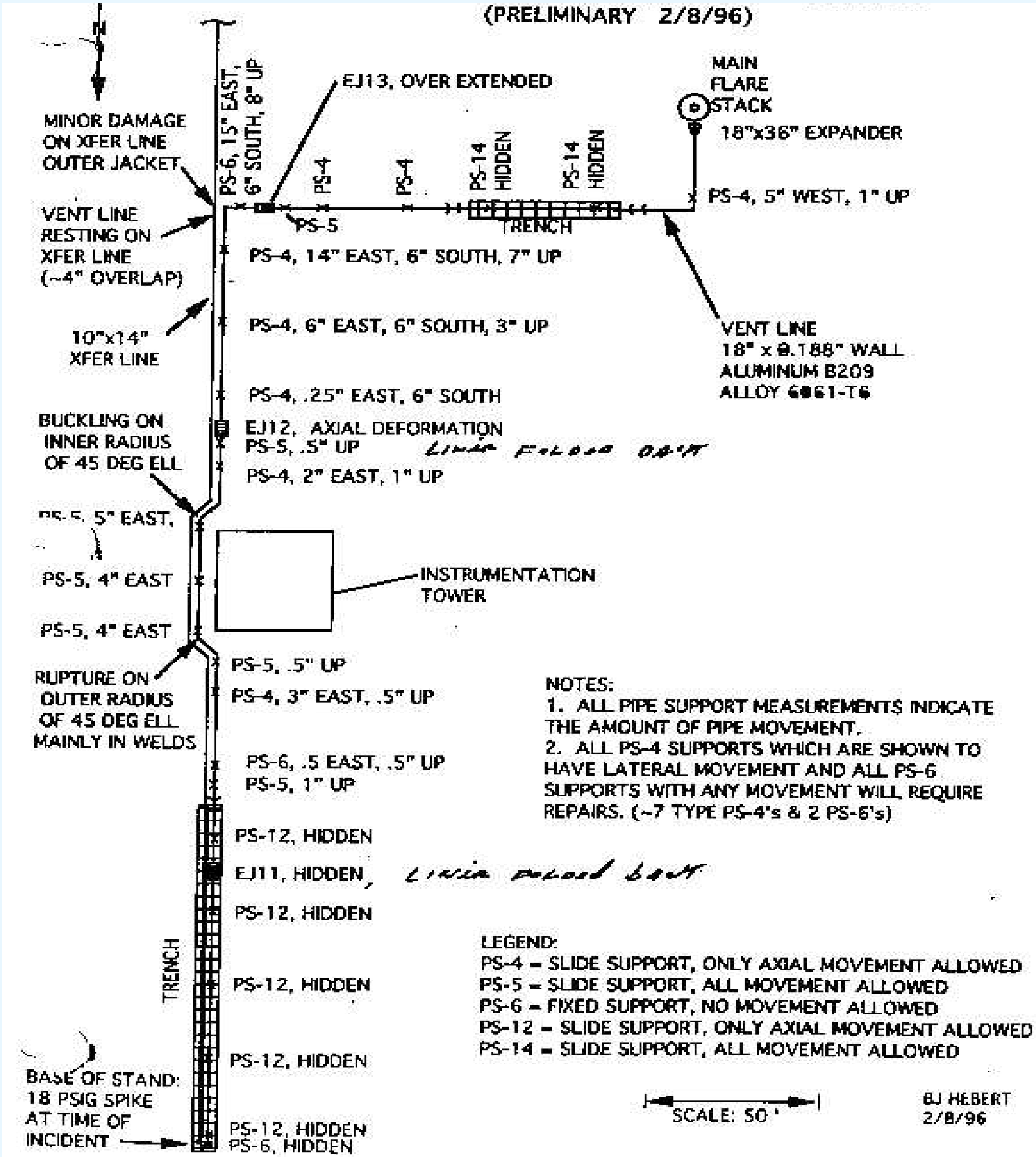
# Tube Trailer Accident (cont.)

# Tube Trailer Accident (cont.)

Tubes and shrapnel were hurled 1250 ft, and several employees were burned

# $H_2$ Vent Line Explosion

## LH Vent Line Incident Survey

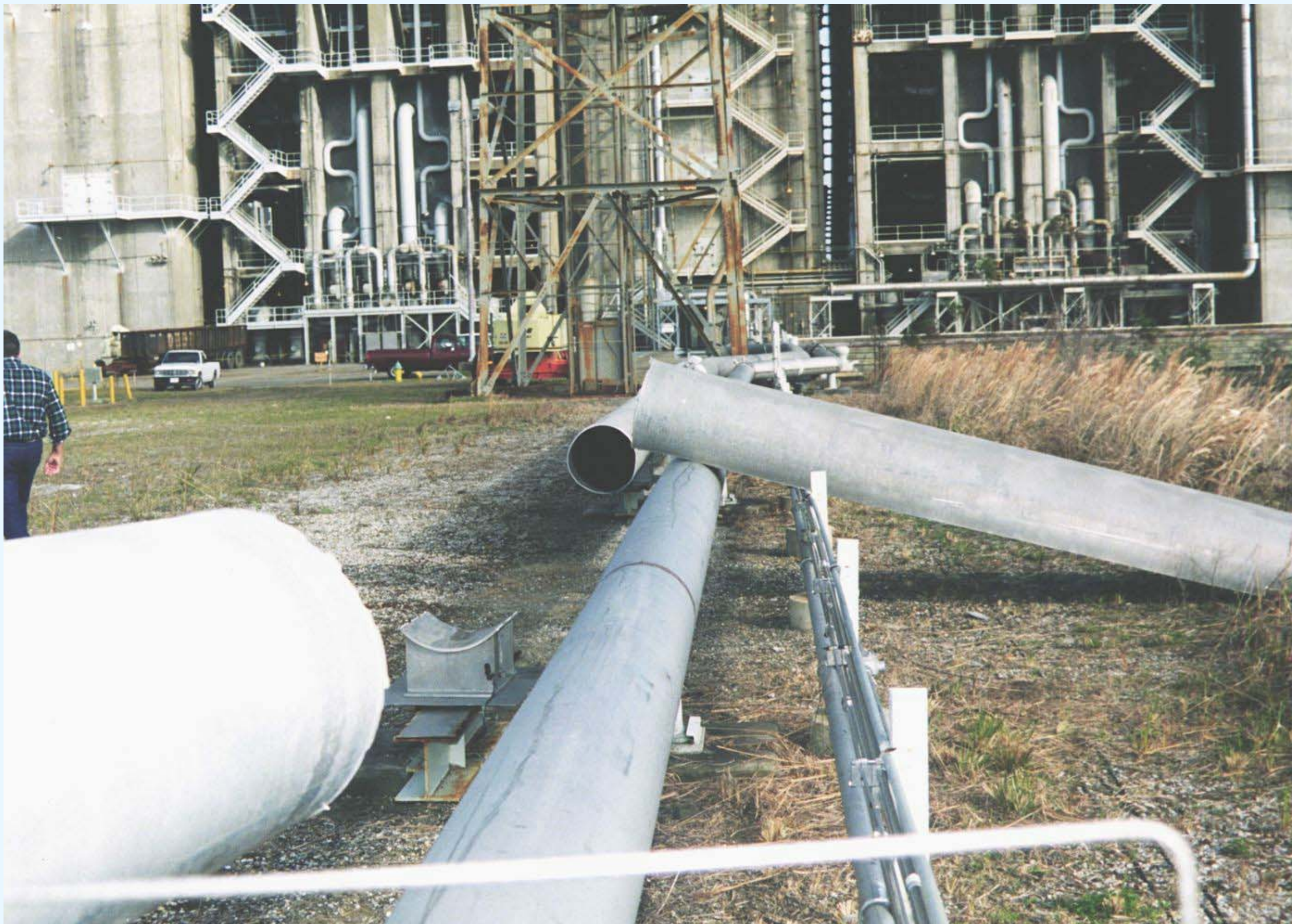



# $H_2$ Vent Line Explosion

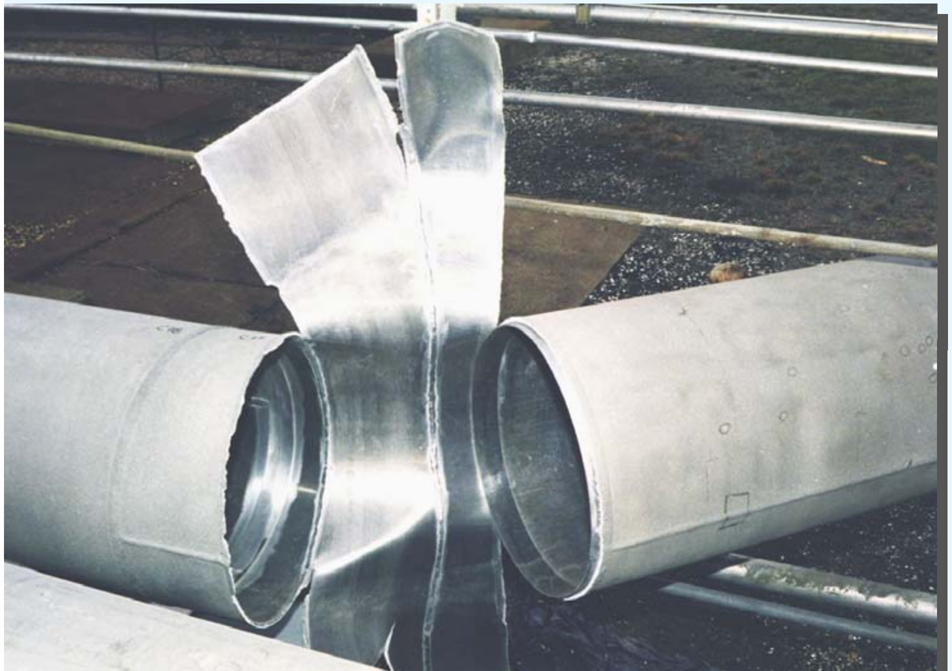
Duct Fails Along Weld

# $H_2$ Vent Line Explosion (cont.)

# $H_2$ Vent Line Explosion (cont.)

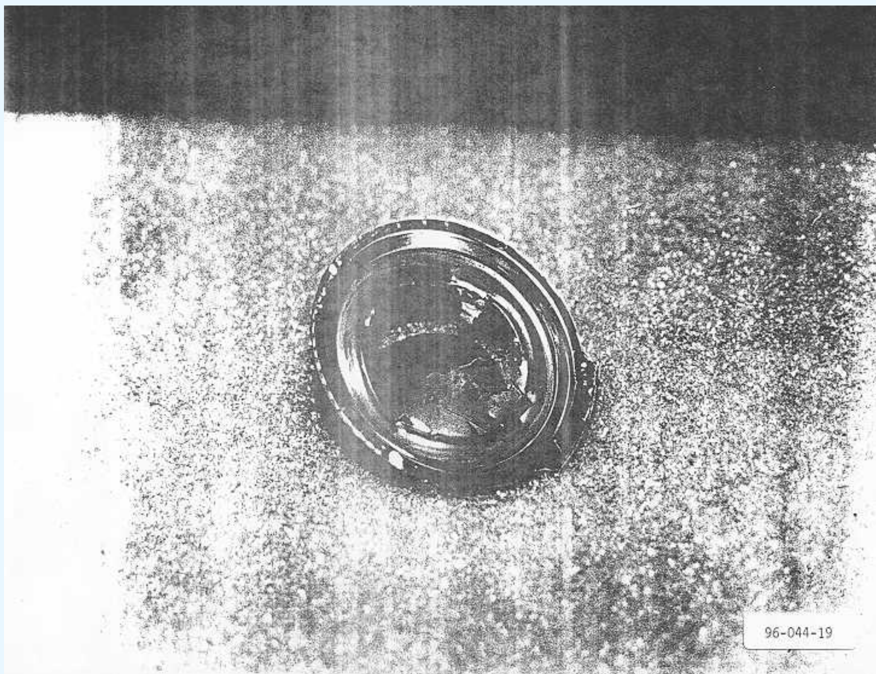


# $H_2$ Vent Line Explosion (cont.)



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 $H_2$ 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 $H_2$’s safe use for over 100 years
  - Town gas was 50% $H_2$
- 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

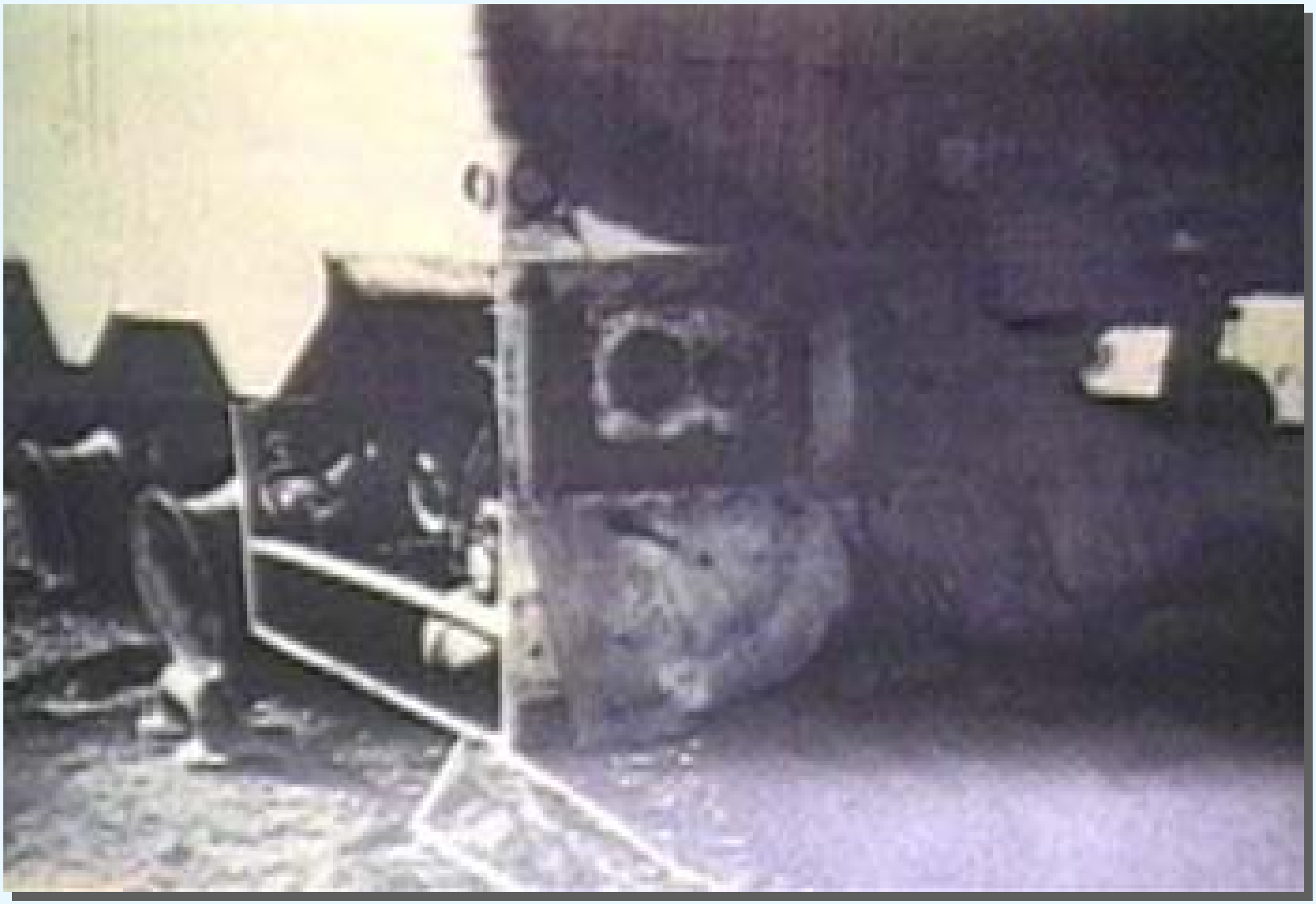
- Primary source
  - Light hydrocarbons
- $GH_2$ production (USA)
  - 35 billion SCFD (Air Products 2002)
- $LH_2$ operating capacity
  - 136 tons per day (USA 1986)
- $LH_2$ demand
  - 82 tons per day (USA 1986)

# Accidents occur…

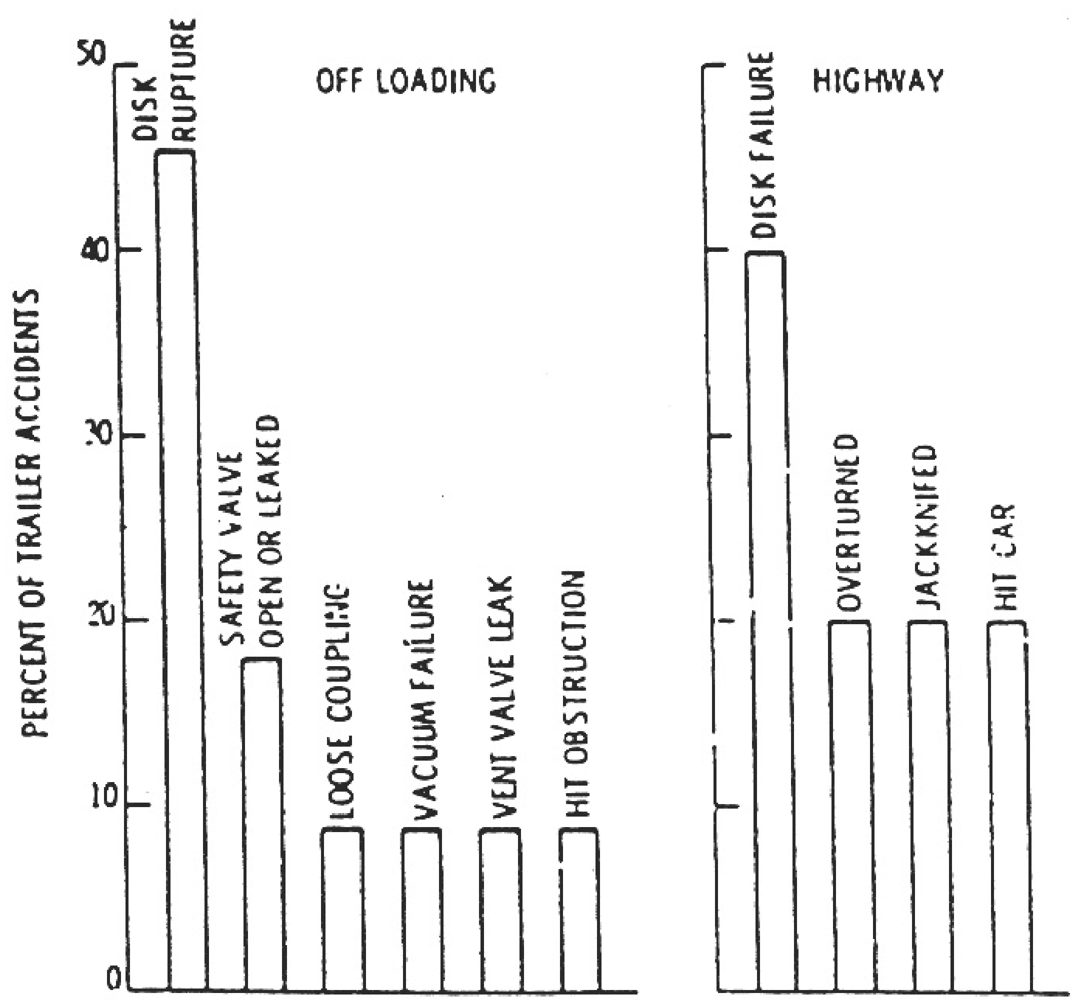
…but looks can be deceiving

# Tanker Truck Fire

# Tanker Truck Fire (cont.)



# $LH_2$ Trailer Accidents

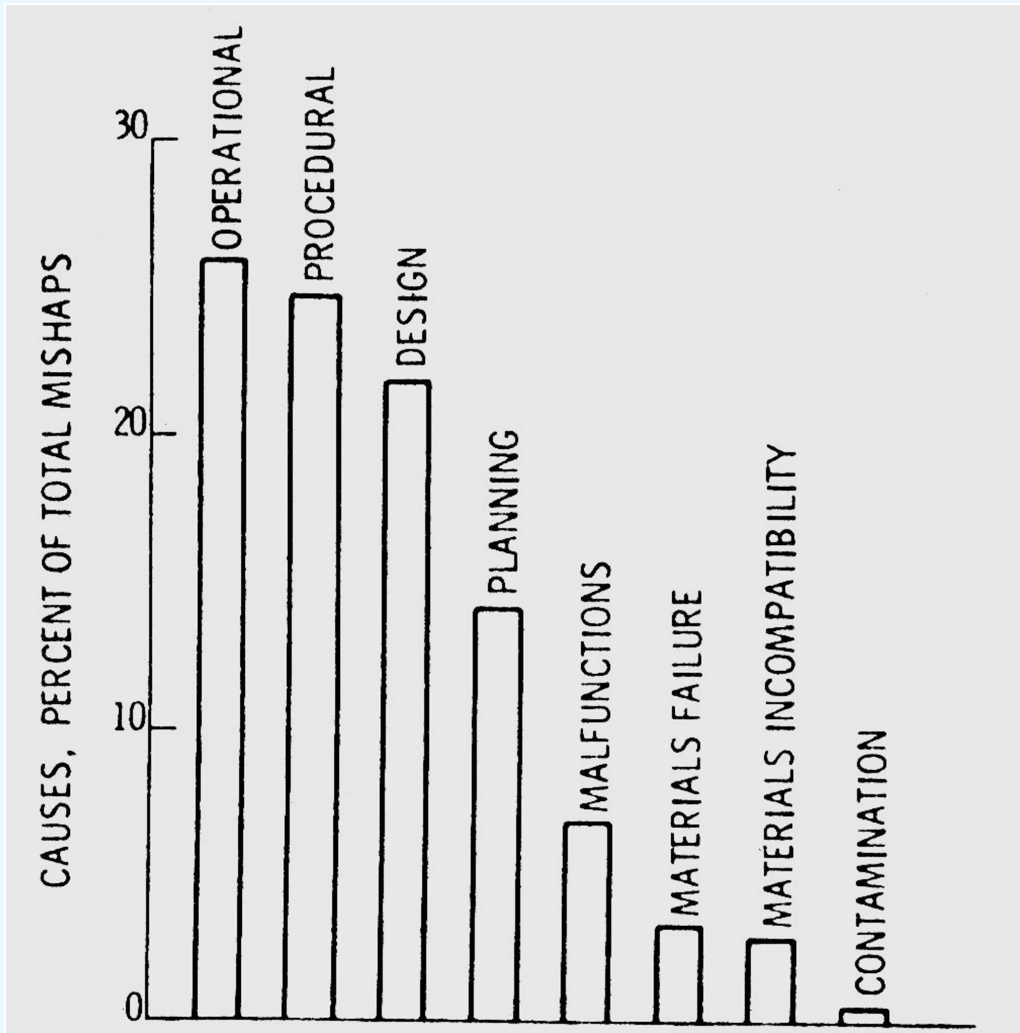


# $LH_2$ Transportation - Reality

| | |
|---|---|
| Miles driven | 87,600,000 |
| Trips | 76,200 |
| Deliveries | 135,000 |
| Hydrogen releases and accidents | 0 |

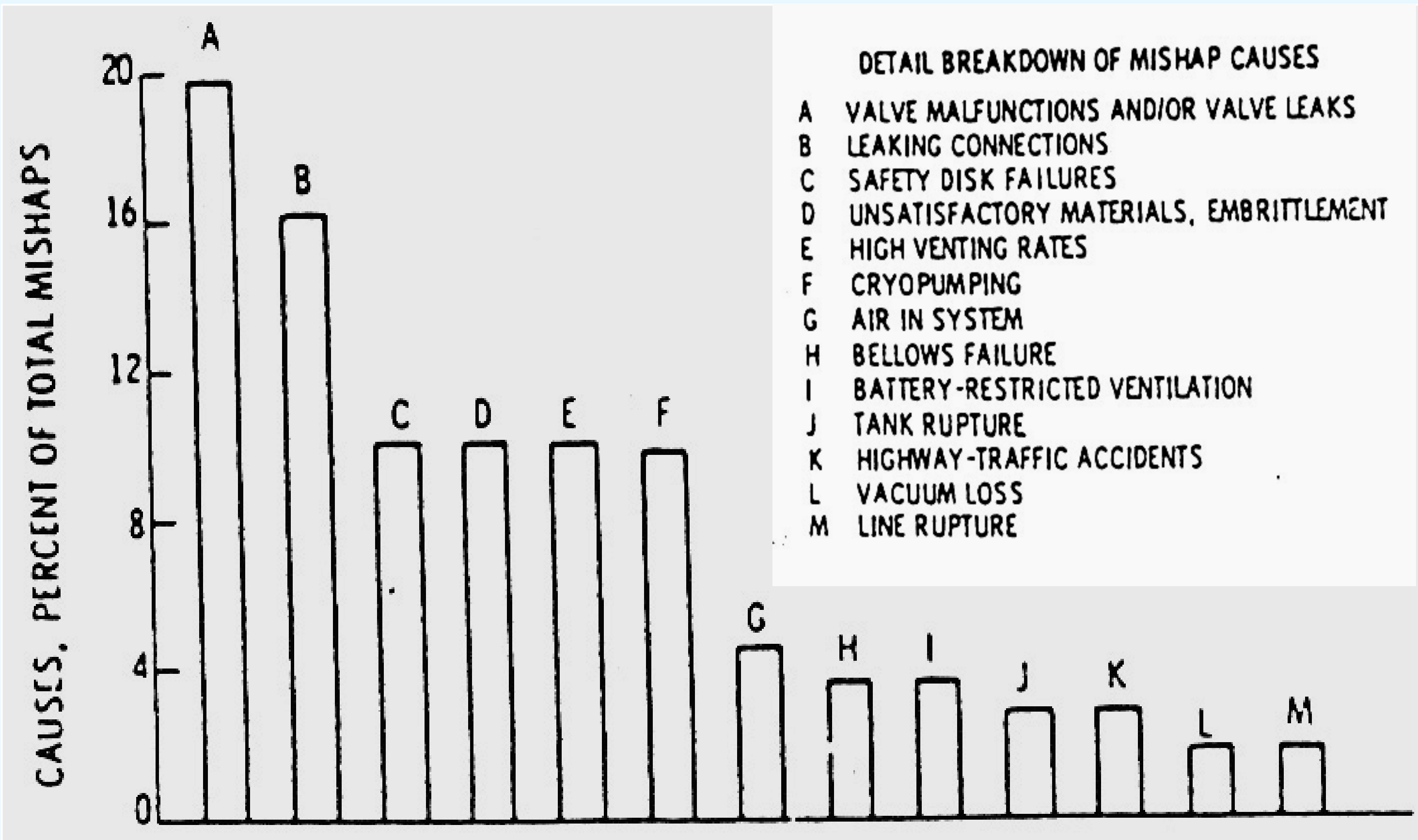
Air Products data (1967-1989)

# Lessons Learned from Previous Incidents




General Mishap Causes

# Lessons Learned from Previous Incidents (cont.)




Detailed Mishap Causes

# Hindenburg Misconception

# Hindenburg Misconception (cont.)

What has been seen

# Theory

- Researchers concluded $H_2$ 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

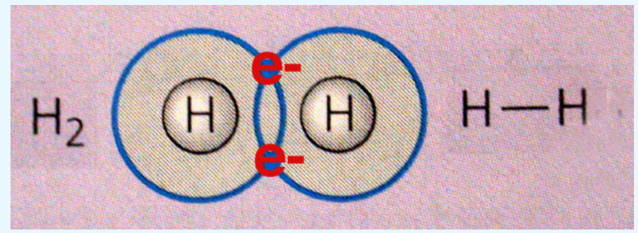
# The Hydrogen Hazard

- General properties
- Primary hydrogen hazards
  - Combustion
  - Pressure hazards
  - Low temperature
  - Hydrogen embrittlement
  - Exposure and health

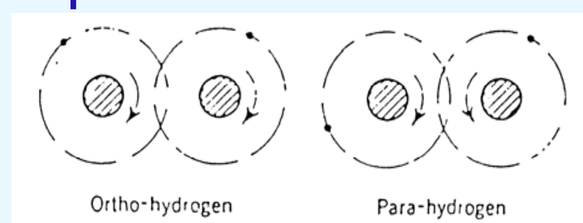
# Physical Properties

***Hydro (water) + genes (forming) = Hydrogen***

- Forms: Atomic Hydrogen, Molecular Hydrogen
- Isotopes: Protium (1amu),
  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 $Nm^3$ (normal $m^3$)

# Gaseous Hydrogen Properties

- Description
  - Colorless, odorless, tasteless
- General Properties
  - Flammable,
  - Non-irritating, nontoxic, asphyxiant
  - Non-corrosive
  - Lightest gas, buoyant, can escape earth
- Physical Properties

| | | |
|---|---|---|
| – GH2 density @ NTP | 0.0838 kg/m3 | (1/15$^{th}$ air) |
| – GH2 specific gravity | 0.0696 | (Air = 1.0) |
| – Viscosity | 33.64 x $10^{-3}$ kg/m hr | (1/2 air) |
| – Diffusivity | 1.697 $m^2$/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) |
| Equivalent vol gas @ NTP (per vol liquid @ NBP) | 845.1 |
| Pressure to maintain NBP liquid density in NTP gas | 172 MPa |
| Triple point | 13.8 K, 7.04 kPa |
| Thermal expansion | 0.0164 $K^{-1}$ |

# Thermal Expansion Coefficients of Some Cryogens[a]

| Liquid | Thermal Expansion Coefficient |
|---|---|
| Water[b] | 0.0007 |
| Oxygen | 0.0044 |
| Argon | 0.0044 |
| Nitrogen | 0.0057 |
| Neon | 0.0144 |
| Hydrogen | 0.0164[c] |
| Helium | 0.2100 |

[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

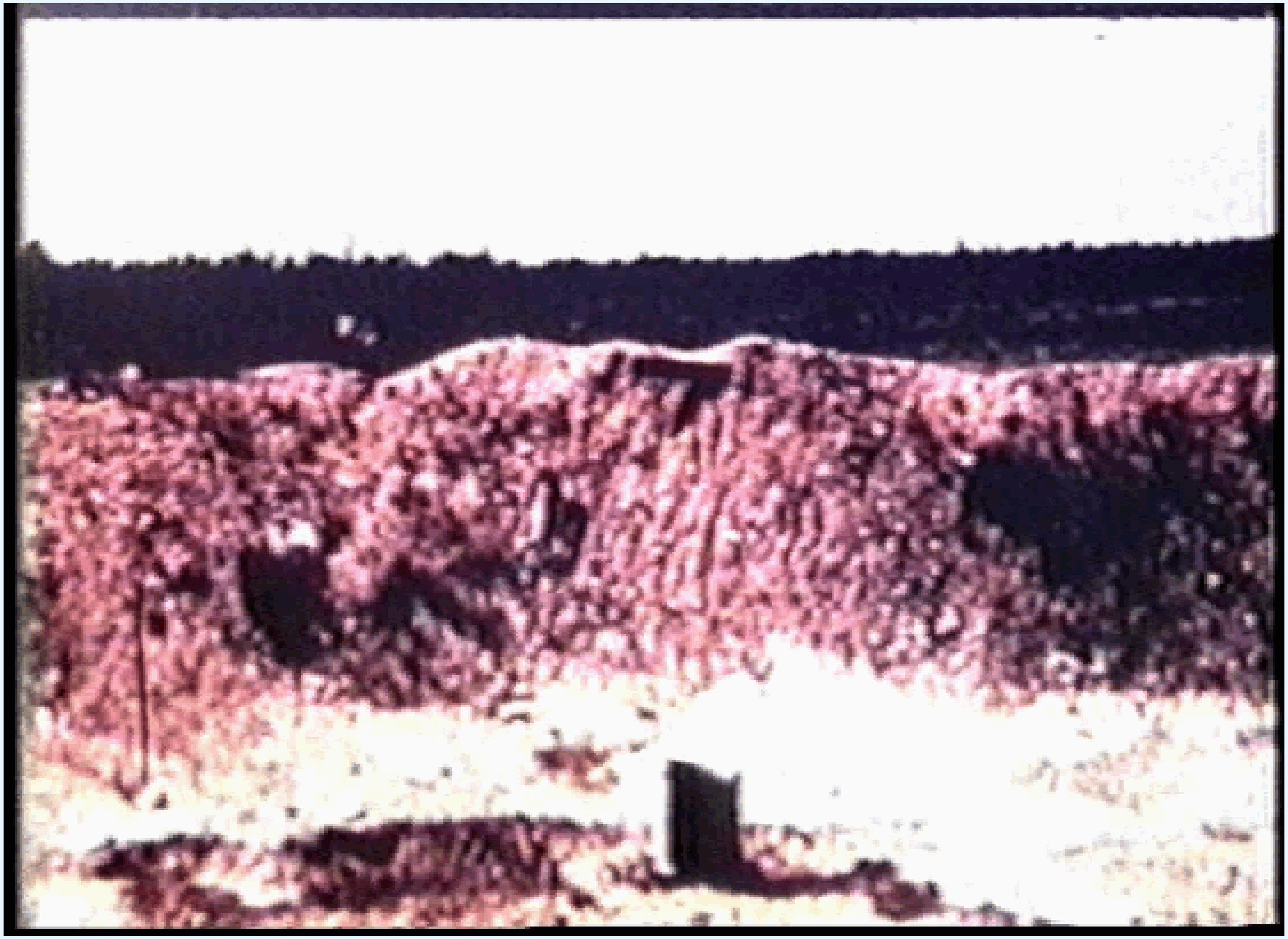
# Fire

- 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

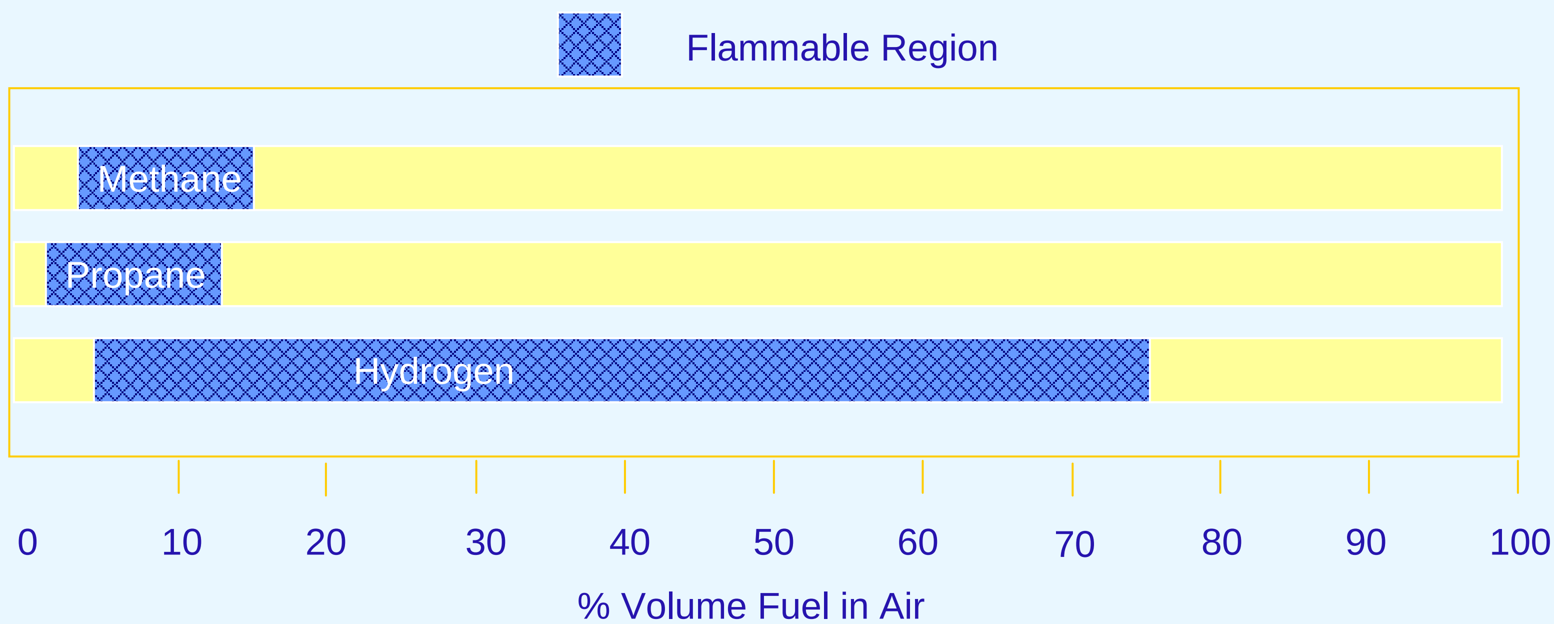
**Remember: Hydrogen must be mixed with an oxidizer [air, $O_2$, Cl, F, $N_2O_4$, etc..] to burn**

# Combustion Properties*

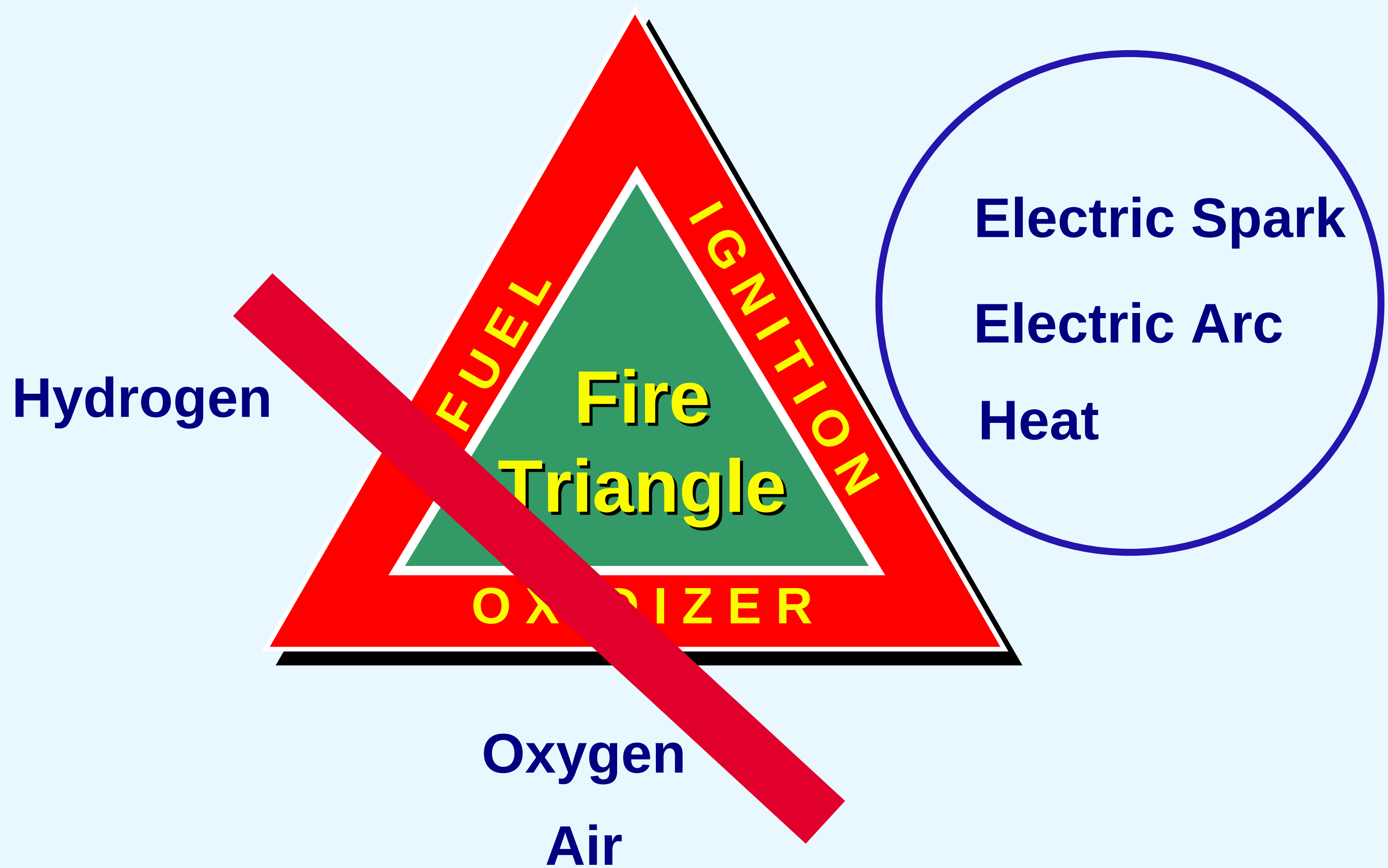
| | |
|---|---|
| Flammability limits in NTP air | 3.9 - 75.0 vol% |
| Flammability limits in NTP oxygen | 3.9 - 95.8 vol% |
| Detonability limits in NTP air | 18.3 - 59.0 vol% |
| Detonability limits in NTP oxygen | 15 - 90 vol% |
| Minimum ignition energy in air | 0.017 mJ |
| Autoignition temperature | 858 K |
| Quenching gap in NTP air | 0.064 cm |
| Diffusion coefficient in NTP air | 0.061 $cm^2/s$ |
| Flame velocity | 2.70 m/s |
| Flame emissivity | 0.10 |

* Data is for parahydrogen but is applicable to ortho or normal hydrogen

# Flammability Limits in Air



# Combustion Hazards



# Fire Concerns

- Without Confinement:
  - High flame temperature (in air): 2045 ºC (3713 ºF)
  - 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

| Volume % $H_2$ | $T_o$ (K) | $P_o$ (kPa) | $T_f$ [a] (K) | $P_f$ [a] (kPa) | $T_o$ (K) | $P_o$ (kPa) | $T_f$ (K) | $P_f$ (kPa) |
|---|---|---|---|---|---|---|---|---|
| **Hydrogen/Air** | | | | | | | | |
| 5 | 298 | 101.3 | 707.9 | 234.7 | 273 | 101.3 | 684.3 | 247.6 |
| 25 | 298 | 101.3 | 2159.2 | 643.8 | 273 | 101.3 | 2141.9 | 697.0 |
| 50 | 298 | 101.3 | 1937.9 | 590.0 | 273 | 101.3 | 1917.7 | 637.3 |
| 75 | 298 | 101.3 | 1165.7 | 375.6 | 273 | 101.3 | 1142.6 | 401.9 |
| **Hydrogen/Oxygen** | | | | | | | | |
| 5 | 298 | 101.3 | 694.2 | 230.1 | 273 | 101.3 | 671.6 | 243.0 |
| 25 | 298 | 101.3 | 2134.5 | 639.1 | 273 | 101.3 | 2118.3 | 692.2 |
| 50 | 298 | 101.3 | 2913.0 | 808.5 | 273 | 101.3 | 2908.3 | 880.0 |
| 75 | 298 | 101.3 | 3003.4 | 837.5 | 273 | 101.3 | 2999.2 | 911.6 |
| 90 | 298 | 101.3 | 1899.2 | 581.4 | 273 | 101.3 | 1878.6 | 612.2 |
| 95 | 298 | 101.3 | 1132.8 | 365.9 | 273 | 101.3 | 1132.8 | 399.4 |

[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 $H_2$/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 $H_2$
  - 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

| Volume % $H_2$ | $T_o$ [a] (K) | $P_o$ [b] (kPa) | $T_1/T_o$ | $P_1/P_o$ | $T_o$ (K) | $P_o$ (kPa) | $T_1/T_o$ | $P_1/P_o$ |
|---|---|---|---|---|---|---|---|---|
| **Hydrogen/Air** | | | | | | | | |
| 18.3 | 298 | 101.3 | 7.657 | 12.154 | 298 | 10.1 | 7.580 | 12.111 |
| 25 | 298 | 101.3 | 9.257 | 14.605 | 298 | 10.1 | 8.870 | 14.223 |
| 50 | 298 | 101.3 | 8.706 | 13.713 | 298 | 10.1 | 8.482 | 13.555 |
| 59 | 298 | 101.3 | 7.678 | 12.144 | 298 | 10.1 | 7.601 | 12.119 |
| **Hydrogen/Oxygen** | | | | | | | | |
| 5 | 298 | 101.3 | 3.118 | 4.880 | 298 | 10.1 | 3.119 | 4.882 |
| 25 | 298 | 101.3 | 9.034 | 14.289 | 298 | 10.1 | 8.660 | 13.896 |
| 50 | 298 | 101.3 | 11.646 | 17.857 | 298 | 10.1 | 10.537 | 16.616 |
| 75 | 298 | 101.3 | 12.111 | 18.671 | 298 | 10.1 | 10.834 | 17.250 |
| 90 | 298 | 101.3 | 8.576 | 13.584 | 298 | 10.1 | 8.327 | 13.393 |

[a] T = temperature

[b] P = pressure

# Hydrogen/Gasoline Comparison

| Property | Hydrogen | Gasoline | Comparison |
|---|---|---|---|
| MIE<br>(in air) | 17 | 240 | - |
| Flammability range<br>(vol % in air) | 4-75 | 1.5-7.6 | +/- |
| Diffusion coefficient<br>($cm^2/s$ in NTP air) | 0.61 | 0.05 | +/- |
| Buoyant velocity<br>(m/s in NTP air) | 1-2.9 | nonbuoyant | +/- |

HYDROGEN AND GASOLINE COMPARISON

| PROPERTY | HYDROGEN | GASOLINE | COMPARISON |
|---|---|---|---|
| Minimum Ignition Energy in air, μJ | 17 | 240 | - |
| Autoignition Temperature in air, K | 858 | 530 | + |
| Flammability Range, vol % in air | 4-75 | 1.5-7.6 | +/- |
| Detonability Range, vol % in air | 18.3-59.0 | 1.1-3.3 | +/- |
| Flame Temperature, K | 2323 | 2470 | = |
| Flame Velocity, m/s | 2.7-3.5 | 0.4 | +/- |
| Flame Emissivity | 0.10 | | +/- |
| Thermal Energy radiated from flame to surroundings, % | 17-25 | 30-42 | + |
| Diffusion Coefficient in NTP air, $cm^2/s$ | 0.61 | 0.05 | +/- |
| Diffusion Velocity in air at NTP, cm/s | <2.0 | <0.17 | +/- |
| Buoyant velocity in NTP air, m/s | 1.2-9 | nonbuoyant | +/- |
| Quenching Distance at 101.3 kPa absolute, mm | 0.64 | 2 | - |
| Vaporization rate (steady state) of liquid pools without burning, cm/min | 2.5-5.0 | 0.005-0.02 | +/- |
| Burning rates of spilled liquid pools, cm/min | 3.0-6.6 | 0.2-0.9 | +/- |

- 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

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

# 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

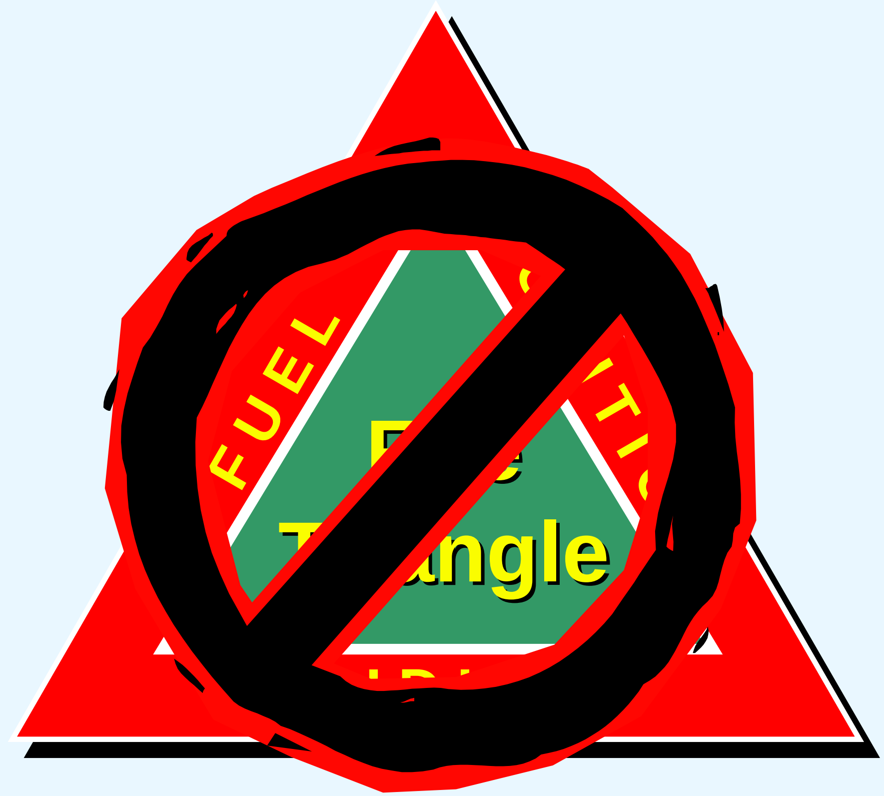
# Thermal Ignition Sources

- 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:**

*  (Rivkin, Carl, H.  *The NFPA Guide to Gas Safety*. National Fire Protection Association, Quincy, MA 2005

*  Benz, Frank J., Craig V. Bishop, Michael Pedley. *Ignition and Thermal Hazards of Selected Aerospace Fluids*. RD-WSTF-0001, Johnson Space Center White Sands Test Facility, Las Cruces NM 88004, October 14, 1988.

## *Pressure, low-temperature, and hydrogen embrittlement implications*

# $H_2$ 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 parahydrogen conversion
- Overfilling
- Liquid-to-gas phase change

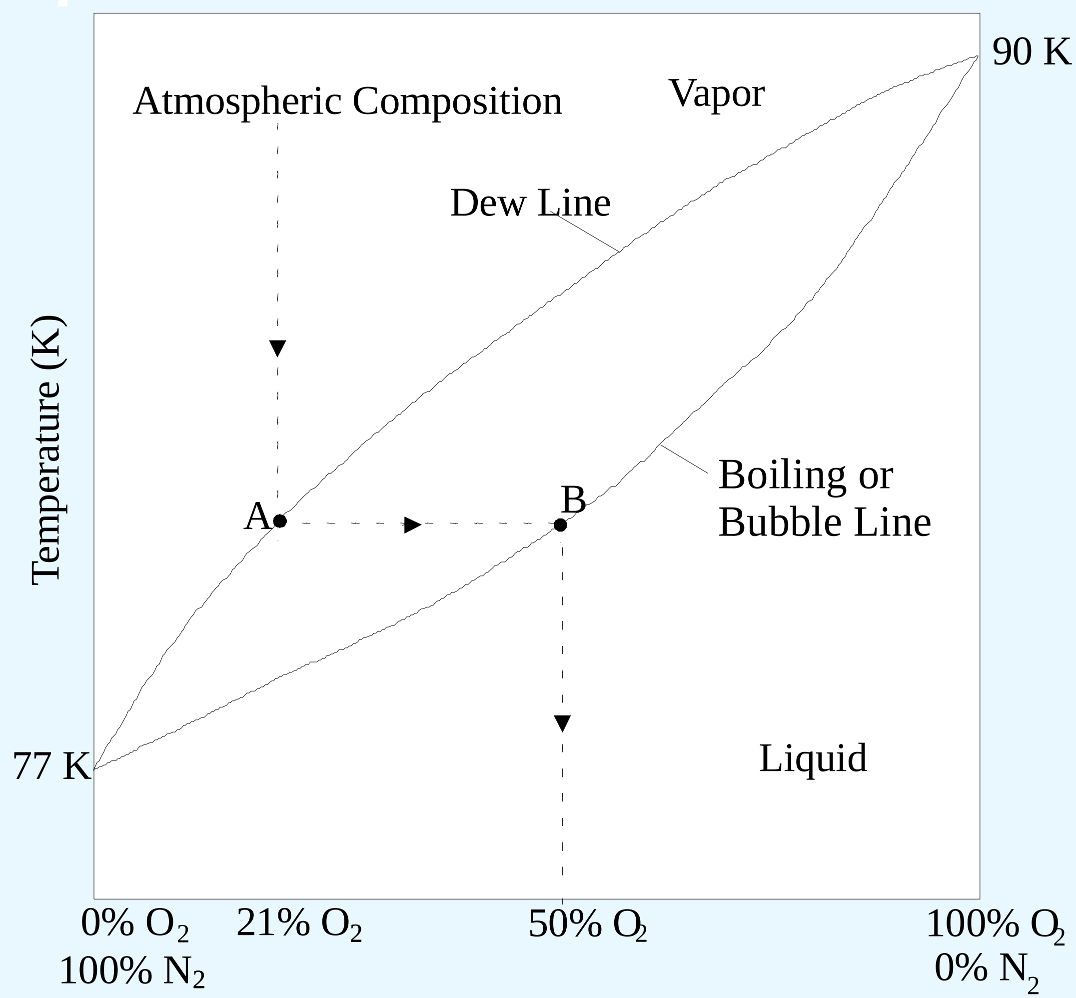
# Physiological Effects of Blast Overpressure

| Max. Overpressure | | Effect on personnel |
|---|---|---|
| (kPa) | (psi) | |
| 7 | 1 | Knock personnel down |
| 35 | 5 | Eardrum damage |
| 100 | 15 | Lung damage |
| 240 | 35 | Threshold for fatalities |
| 345 | 50 | 50% fatalities |
| 450 | 65 | 99% fatalities |

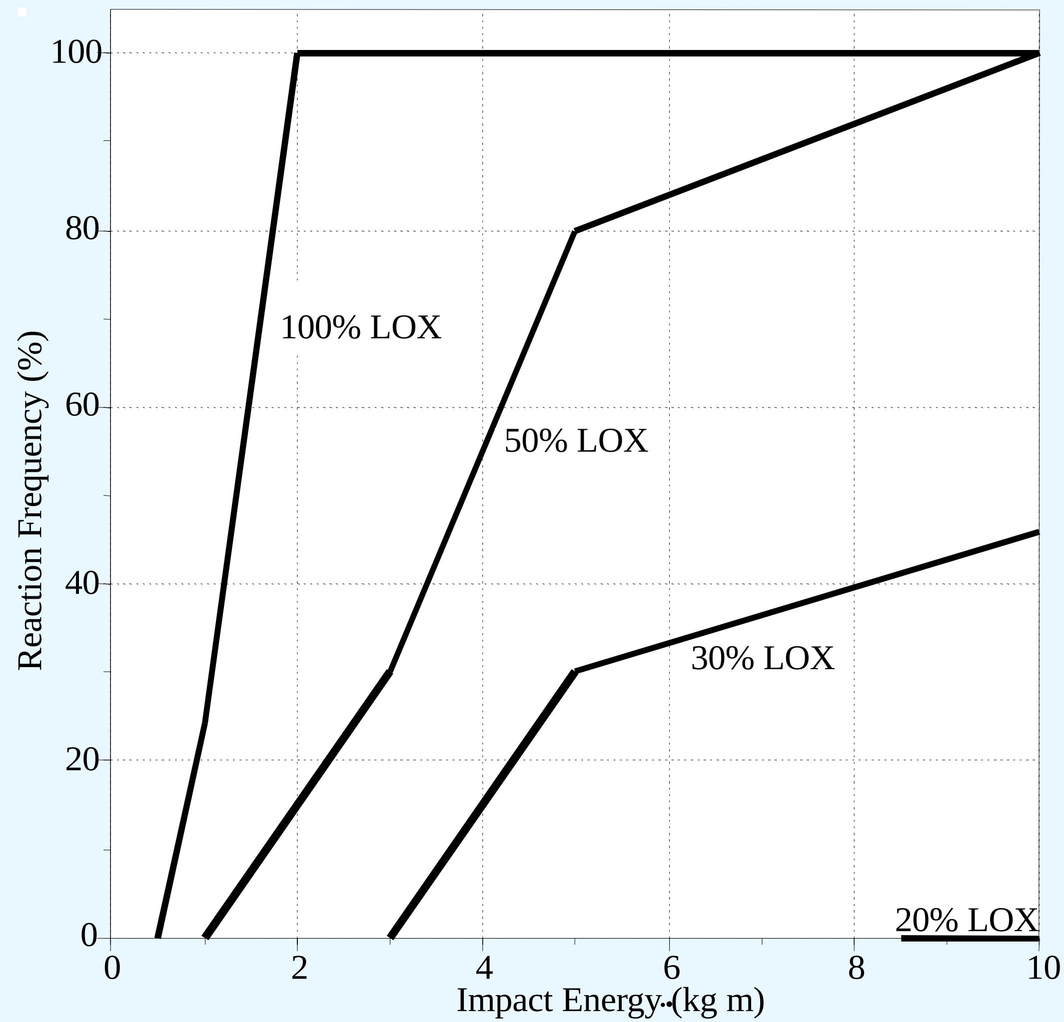
# Low-temperature Hazards

- Cold fluids
  - Contaminant solidification
- Cold surfaces
  - Oxygen enrichment of air
  - Cryogenic burn (frostbite)
- Low-temperature embrittlement
  - Containment materials
  - Nearby materials

# $N_2/O_2$ Phase Diagram Showing $O_2$ Enrichment



# 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 $H_2$ Embrittlement

- Environmental embrittlement
  - Observed in metals and alloys plastically deformed in $H_2$ environment (especially high pressure)
  - Maximum effect from 200 - 300K
- Internal embrittlement
  - Caused by absorbed $H_2$
  - 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

# $H_2$ Exposure and Ultimate Strength

| Material (notched sample) | Exposure (at 80 ºF) | Strength [MPa (psi)] | Change (%) |
|---|---|---|---|
| 4140 (low strength) | 69 MPa $N_2$ | 1660 (241,000) | -15.2 |
| | 69 MPa $H_2$ | 1407 (204,000) | |
| 4140 (high strength) | 69 MPa $N_2$ | 2946 (362,000) | -66.6 |
| | 41 MPa $H_2$ | 834 (121,000) | |
| C1025 | 69 MPa $N_2$ | 730 (106,000) | -24.4 |
| | 69 MPa $H_2$ | 552 (80,000) | |
| K Monel PH | 69 MPa $N_2$ | 1731 (251,000) | -55.0 |
| | 69 MPa $H_2$ | 779 (113,000) | |
| K Monel (annealed) | 69 MPa $N_2$ | 993 (114,000) | -27.1 |
| | 69 MPa $H_2$ | 724 (105,000) | |

# 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
  - $H_2$ purity
- Electrical discharge machining increases potential for $H_2$ embrittlement

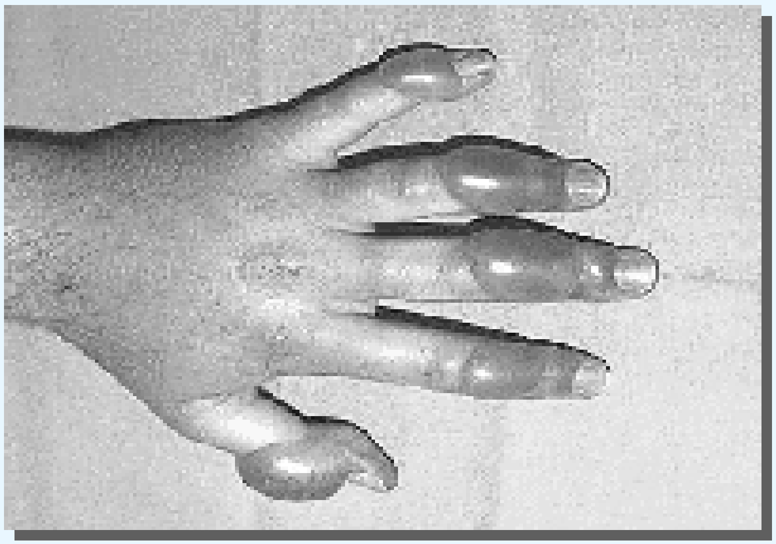
# Health Hazards

- 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



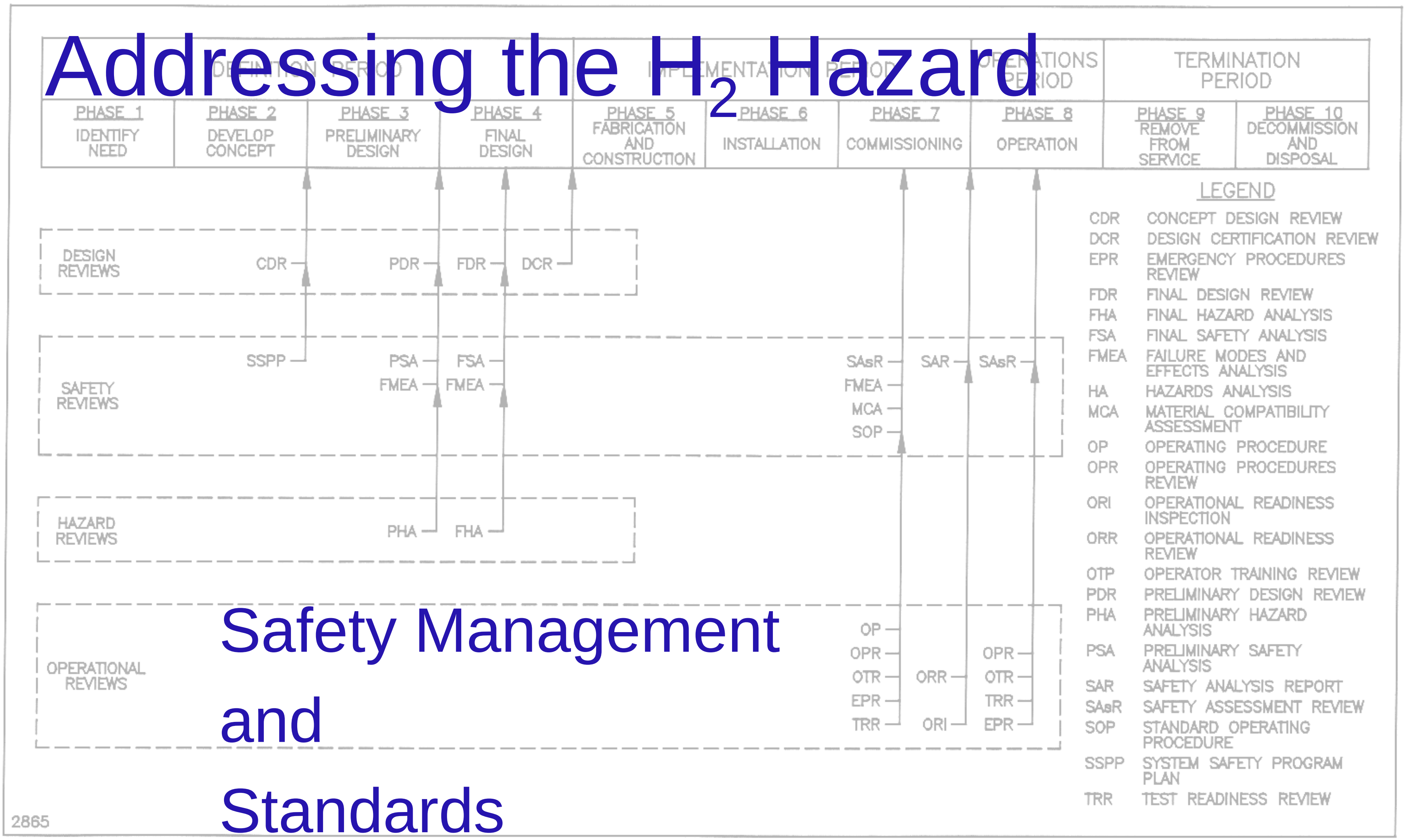
**Third-degree cryogen burn (frostbite) to fingers**

**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 $H_2$ Hazard




Safety Management

and

Standards

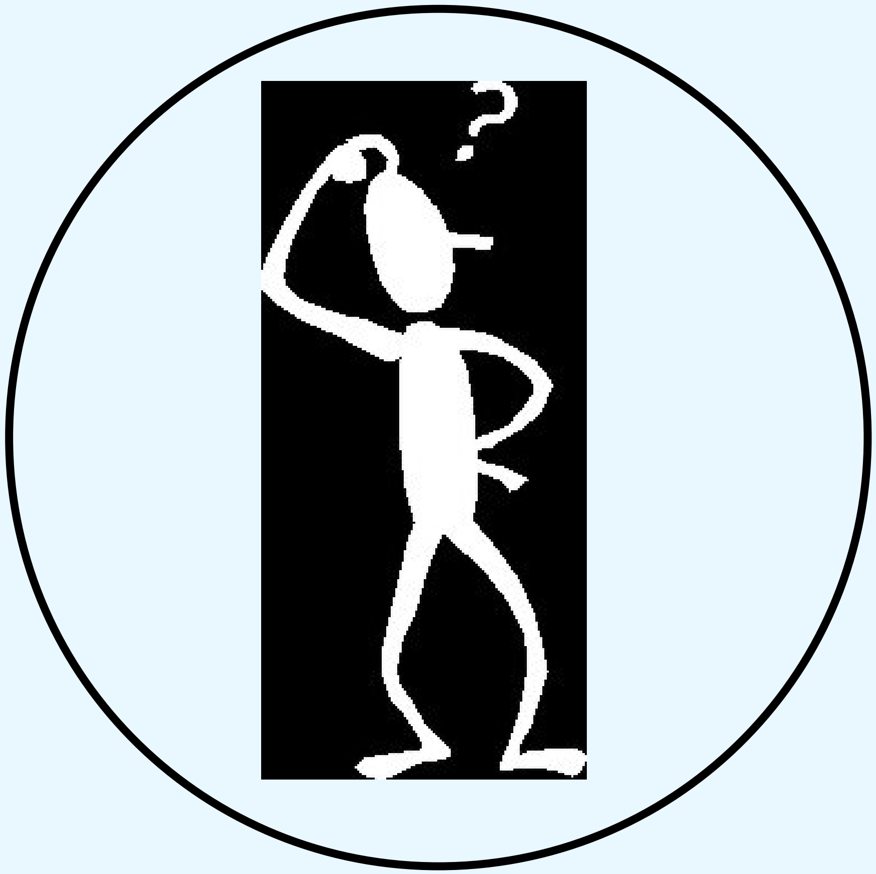
# Start with Safety Management

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

# Managing a Hazard

Ignore it?

Eliminate it?



Control 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*
- 29CFR1910.119, *Process Safety Management of Highly Hazardous Chemicals*
- 49CFR Subtitle B, Vol 2, Ch 1, Parts 171-180, *Transportation*

* *See osha.gov for latest CFR references*

## HYDROGEN CFR INFORMATION

| | | |
|---|---|---|
| Chemical Formula | | $H_2$ |
| Common name | | Hydrogen |
| Hazard material description and proper shipping name[a] | $GH_2$ | Hydrogen, compressed[a] |
| | $LH_2$ | Hydrogen, refrigerated liquid (*cryogenic liquid*)[a, b] |
| Shipping identification number[a] | $GH_2$ | UN1049[a] |
| | $LH_2$ | UN1966[a] |
| Shipping hazard class or division[a] | $GH_2$ | 2.1[a] |
| | $LH_2$ | 2.1[a] |
| Shipping packing group[a] | | None given[a, c] |
| Shipping labels required[a] | $GH_2$ | FLAMMABLE GAS[a] |
| | $LH_2$ | FLAMMABLE GAS[a] |
| Shipping special provisions[a] | | None given[a] |
| Shipping packaging authorization exceptions[a] | $GH_2$ | See 49CFR173.306[a] |
| | $LH_2$ | See 49CFR173.316[a] |
| Shipping non bulk packaging requirements[a] | $GH_2$ | See 49CFR173.302[a] |
| | $LH_2$ | See 49CFR173.316[a] |
| Shipping bulk packaging requirements[a] | $GH_2$ | (See 49CFR173.302 and 173.314)[a] |
| | $LH_2$ | (See 49CFR173.318 and 173.319)[a] |
| Shipping quantity limitations for passenger aircraft or railcar[a] | $GH_2$ | Forbidden[a] |
| | $LH_2$ | Forbidden[a] |
| Shipping quantity limitations for cargo aircraft only[a] | $GH_2$ | 150 kg[a] |
| | $LH_2$ | Forbidden[a] |
| Vessel shipping stowage requirements[a] | $GH_2$ | E[a,d] |
| | $LH_2$ | D[a,e] |
| Vessel shipping stowage provisions[a] | $GH_2$ | 40[a,f], 57[a, g] |
| | $LH_2$ | 40[a, f] |
| Process Safety Management Threshold Quantity[h], lb | | ≥10,000 lb[h] |

**NOTES:**

[a] 49CFR172.101

[b] 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.[a]

[c] Class 2 materials do not have packing groups.[a]

[d] "E" means the material may be stowed "on deck" or "under deck" on a cargo vessel, but is prohibited on a passenger vessel.[a]

[e] "D" means the material must be stowed "on deck" on a cargo vessel, but is prohibited on a passenger vessel.[a]

[f] Stoage provision "40" means: "Stow 'clear of living quarters'" (49CFR176.84).

[g] Stoage provision "57" means: "Stow 'separated from' chlorine" (49CFR176.84).

[h] 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
  - ANSI/AIAA G-095-2004 Guide to Safety of Hydrogen and Hydrogen Systems [Required by NASA]

* 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*
  - CGA P-28 *Risk Management Plan Guidance Document for Bulk Liquid Hydrogen Systems*
- 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 $H_2$ use
- Ultimately, everyone involved with $H_2$ 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 $H_2$ quantity
  - Siting of $H_2$ facilities

# Delta Clipper

# 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 $H_2$ 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 $H_2$'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**

| CODE, STANDARD | FLUID | QUANTITY COVERED |
|---|---|---|
| | | |
| 29CFR 1910.103<br>(HSS.1-2; A-53 - A-54) | $GH_2$ | Does not apply to a system having a total content of less than 11 $m^3$ (400 $ft^3$).<br>No maximum quantity specified.<br>QD Requirements apply to any quantity. |
| NFPA 50A | $GH_2$ | No min or max quantity specified.<br>Does not apply to single systems using containers having a total content of less than 11 $m^3$ (400 $ft^3$) at 101.3 kPa (14.7 psia) and 294.1 K (70 ºF).<br>Applies where individual systems, each having a total content of less than 11 $m^3$ (400 $ft^3$) at 101.3 kPa (14.7 psia) and 294.1 K (70 ºF), are located less than 1.5 m (5 ft) from each other.<br>QD requirements apply to any quantity. |
| 29CFR 1910.103<br>(HSS.1-2; A-55 - A-56) | $LH_2$ | No min or max quantity specified.<br>Does not apply to portable containers having a total content less than 150 L (39.63 gal).<br>QD requirements apply to 150 L (39.63 gal) to 113,550 L (30,000 gal). |
| NFPA 50B | $LH_2$ | No min or max quantity specified.<br>Does not apply to portable containers having a total content less than 150 L (39.63 gal).<br>QD requirements apply to 150 L (39.63 gal) to 283,875 L (75,000 gal). |
| 29CFR 1910.119<br>(HSS.1-2) | any form | ≥ 4536 kg (10,0000 $lb_m$) |
| NSS 1740.12<br>(NSS.A-56 - A-62) | $LH_2$ | 0 - 4.536 x $10^6$ kg (1 x $10^7$ $lb_m$) |

# 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 (29CFR 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 $H_2$ fire, including intentionally flared $H_2$
  - Oxygen-deficient atmospheres of $H_2$ or inert purge gases ($N_2$, 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

# $H_2$ and $H_2$ Fire Detection (cont.)

- $H_2$ flame nearly invisible in daylight
- $H_2$ 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


DIDN'T WASH HANDS
MEN

# 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**

SOURCE: HSS.2-15, 4-9

# 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 $H_2$
  - Purge oxidizer before introducing $H_2$
  - Purge $H_2$ before introducing oxidizer
- Use $GN_2$ if temperature is >80 K; if colder, use He
- Turn off $N_2$ purge to vent stack before venting cold $H_2$
  - Otherwise, $N_2$ will solidify

# Purge Gas Systems

- Needed for purge, pressurization gases
- $H_2$ volumes should be capable of being purged and vented
- Inert gas subsystems should be protected from $H_2$ contamination
  - Use higher pressure, check valves, or a double block-and-bleed arrangement

# Improper Purging Causes Mishaps

| | Purging Mishaps | |
|---|---|---|
| | No. | (%) |
| Mishaps identified with purging problems | 24* | 25 |
| Effects of mishaps due to purging problems | | |
| release into atmosphere | 14 | 58 |
| Release into system containers | 10 | 42 |
| Effects of release into atmosphere | | |
| ignition | 13 | 93 |
| Non-ignition | 1 | 7 |
| Effect of release into system containers | | |
| ignition | 10 | 100 |

* 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 $N_2$, 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

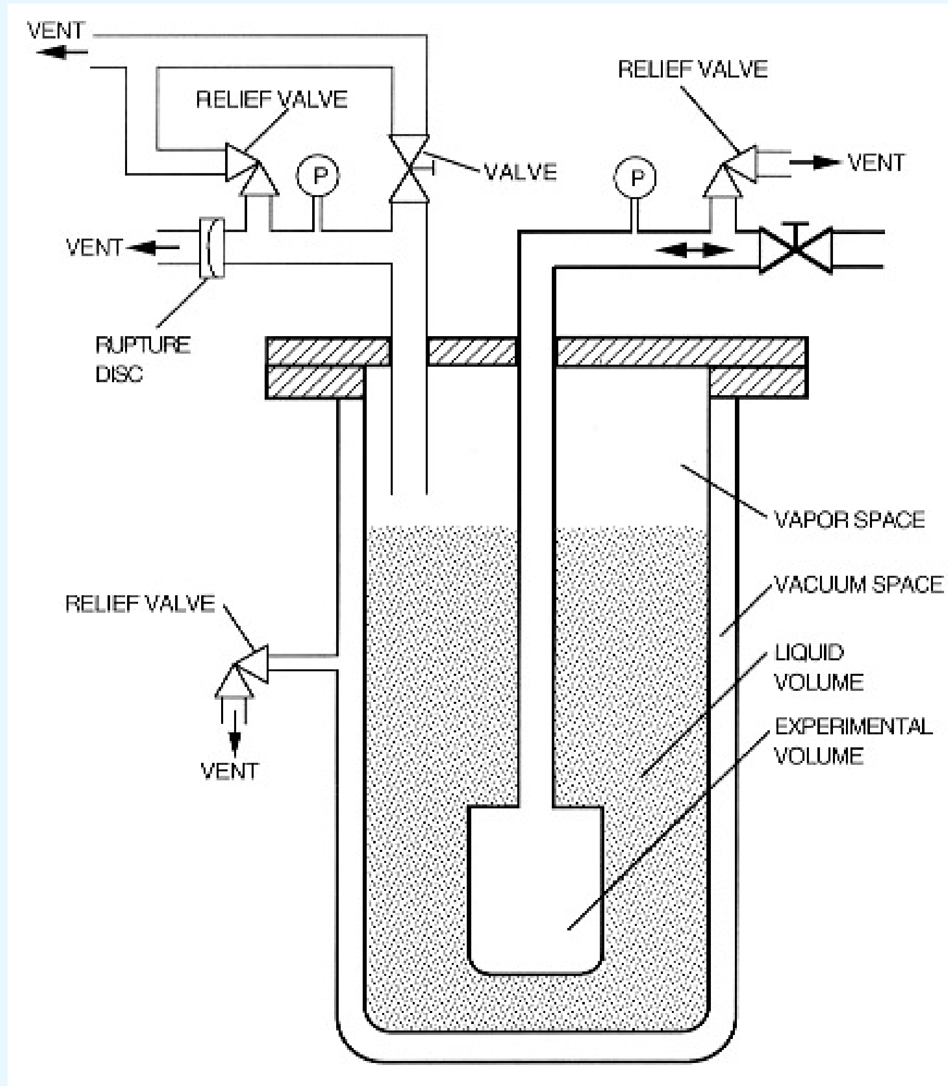
- Ventilation must preclude formation of flammable mixture
  - Ventilate to below 1/4 of LFL
- Need to couple with $H_2$ detection
- Limited effectiveness on complex geometries

# 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



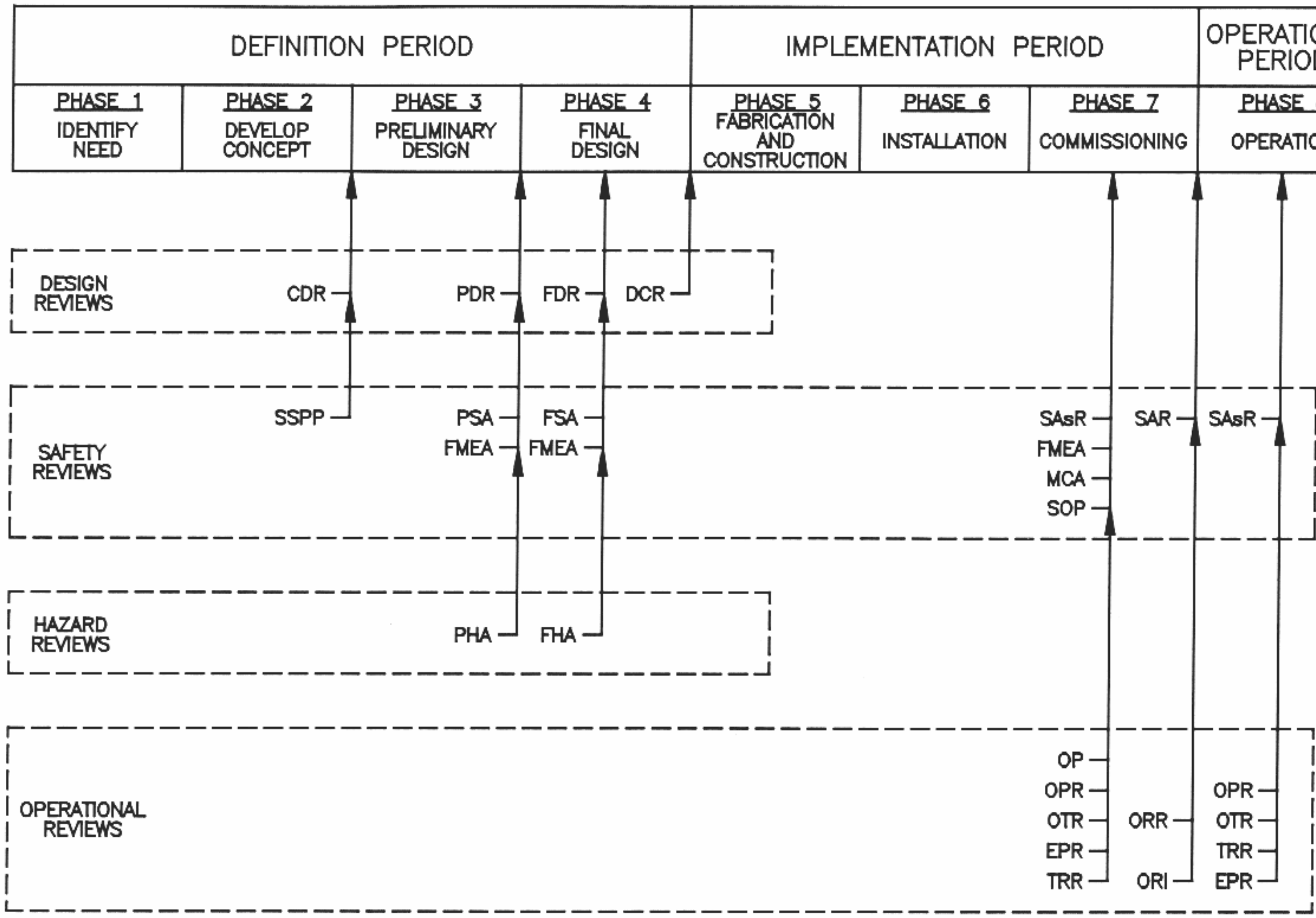
# Use Redundancy in Critical Areas

- Pressure relief
- Isolation
- Detection

*Perform reviews*

# Reviews

- Design
- Safety
- Hazard
  - Requirements
  - Hazards analysis protocol
- Operational




## LEGEND

| | |
|---|---|
| CDR | CONCEPT DESIGN REVIEW |
| DCR | DESIGN CERTIFICATION REVIEW |
| EPR | EMERGENCY PROCEDURES REVIEW |
| FDR | FINAL DESIGN REVIEW |
| FHA | FINAL HAZARD ANALYSIS |
| FSA | FINAL SAFETY ANALYSIS |
| FMEA | FAILURE MODES AND EFFECTS ANALYSIS |
| HA | HAZARDS ANALYSIS |
| MCA | MATERIAL COMPATIBILITY ASSESSMENT |
| OP | OPERATING PROCEDURE |
| OPR | OPERATING PROCEDURES REVIEW |
| ORI | OPERATIONAL READINESS INSPECTION |
| ORR | OPERATIONAL READINESS REVIEW |
| OTP | OPERATOR TRAINING REVIEW |
| PDR | PRELIMINARY DESIGN REVIEW |
| PHA | PRELIMINARY HAZARD ANALYSIS |
| PSA | PRELIMINARY SAFETY ANALYSIS |
| SAR | SAFETY ANALYSIS REPORT |
| SAsR | SAFETY ASSESSMENT REVIEW |
| SOP | STANDARD OPERATING PROCEDURE |
| SSPP | SYSTEM SAFETY PROGRAM PLAN |
| TRR | TEST READINESS REVIEW |

2865

# 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

- 29CFR1910.119, *Process safety management of highly hazardous chemicals*
- 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

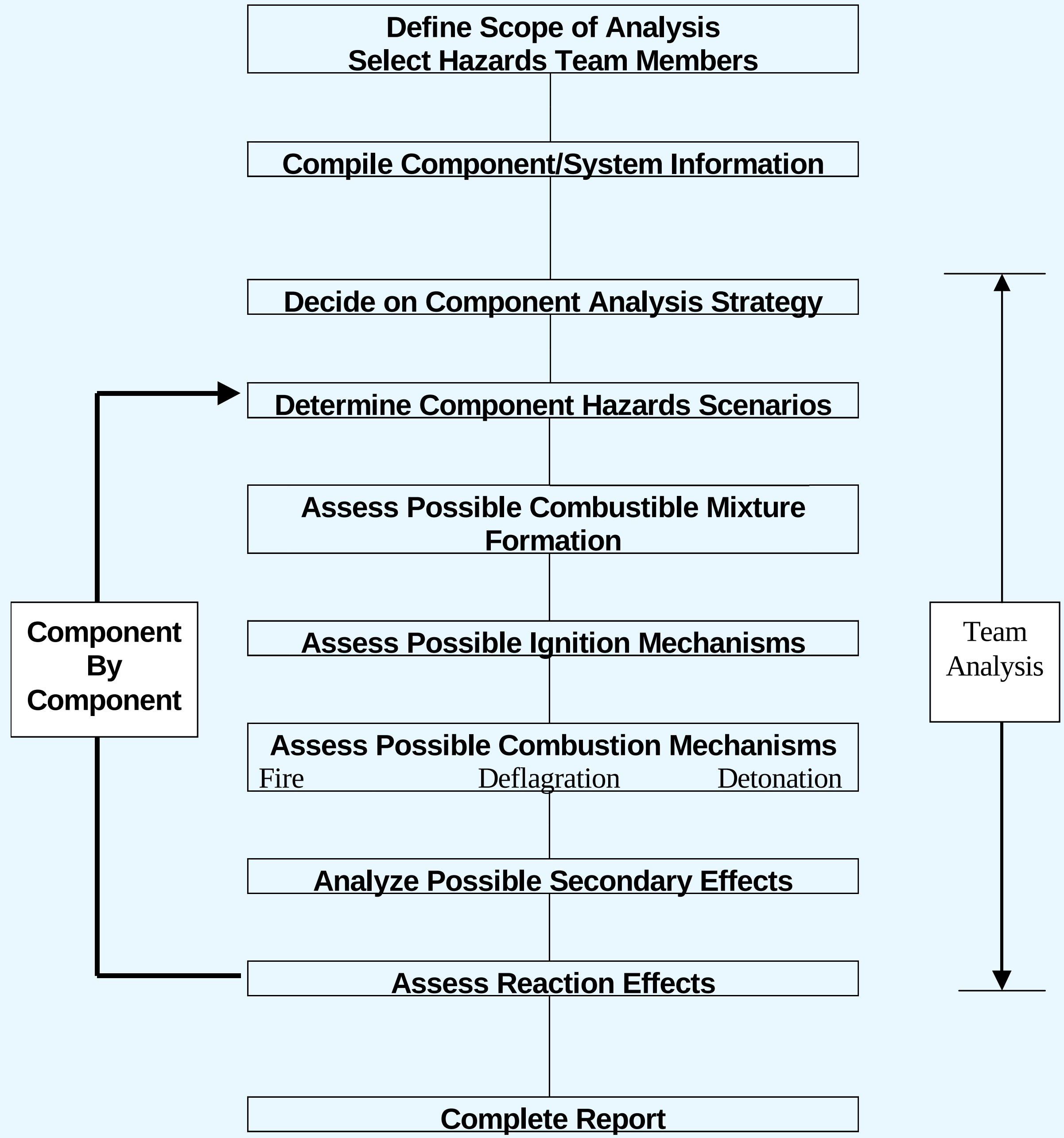
# Hazards Analysis Protocol

- 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



# Component Hazards Chart

| | Assess Probability Rating for: | | | | | |
|---|---|---|---|---|---|---|
| Component/ Operational Mode | Failure Modes | Flammable Mixture Formation | Ignition | Fire Deflagration Detonation | Secondary Effects | Overall Effects |
| Valve # --- | | | | | | |
| Rating | 0 – 4 | 0 – 4 | 0 – 4 | 0 – 4 | N/R | A - D |

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 ($H_2$, $N_2$, He)
  - Ensure fresh air supply
  - Monitor atmosphere in tank
  - Entry plan, with emergency plans
  - Safety precautions

# Anoxia Symptoms

| % $O_2$ at 1 atm total pressure (vol basis) | At rest symptoms |
|---|---|
| 15 - 19 | Decreased ability to perform tasks; may induce early symptoms in persons with heart, lung, or circulatory problems |
| 12 - 15 | Respiration deeper, pulse faster, poor coordination |
| 10 - 12 | Giddiness, poor judgement, lips slightly blue |
| 8 - 10 | Nausea, vomiting, unconsciousness, ashen face, fainting, mental failure |
| 6 - 8 | 100% die in 8 min; after 6 min 50% die and 50% recover with treatment, 100% recover with treatment in 4-5 min |
| 4 | Coma in 40 s, convulsions, respiration ceases, death |

# Summary

- Safe use of $H_2$ 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."

# 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

| Material | Service | | | Remarks |
| --- | --- | --- | --- | --- |
| | $GH_2$ | $LH_2$ | $SLH_2$ | |
| Aluminum and its alloys | Yes | Yes | Yes | |
| Austenitic stainless steels with > 7% nickel (such as, 304, 304L, 308, 316, 321, 347) | Yes | Yes | Yes | Some make martensitic conversion if stressed above yield point at low temperature. |
| Carbon steels | Yes | No | No | Too brittle for cryogenic service. |
| Copper and its alloys (such as, brass, bronze, and copper-nickel) | Yes | Yes | Yes | |
| Gray, ductile, or cast iron | No | No | No | Not permitted for hydrogen service. |
| Low-allow steels | Yes | No | No | Too brittle for cryogenic service. |
| Nickel and its alloys (such as, Inconel® and Monel®) | No | Yes | Yes | Susceptible to hydrogen embrittlement |
| Nickel steels (such as, 2.25, 3.5, 5, and 9 % Ni) | No | No | No | Ductility lost at $LH_2$ and $SLH_2$ temperatures. |
| Titanium and its alloys | No | Yes | Yes | Susceptible to hydrogen embrittlement |
| Asbestos impregnated with Teflon® | Yes | Yes | Yes | Avoid use because of carcinogenic hazard. |
| Chloroprene rubber (Neoprene®) | Yes | No | No | Too brittle for cryogenic service. |
| Dacron® | Yes | No | No | Too brittle for cryogenic service. |
| Fluorocarbon rubber (Viton®) | Yes | No | No | Too brittle for cryogenic service. |
| Mylar® | Yes | No | No | Too brittle for cryogenic service. |
| Nitrile (Buna-N®) | Yes | No | No | Too brittle for cryogenic service. |
| Polyamides (Nylon®) | Yes | No | No | Too brittle for cryogenic service. |
| Polychlorotrifluorethylene (Kel-F®) | Yes | Yes | Yes | |
| Polytetrafluorethylene (Teflon®) | Yes | Yes | Yes | |

# Understand $H_2$ 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 $H_2$ Embrittlement

- Increased material thickness
- Surface finish
- Welding technique
- Material selection
- Conservative design stress (avoid yielding)

| Application | Typical materials | |
|---|---|---|
| | $LH_2$ or $SLH_2$ | $GH_2$ |
| Valves | Forged, machined, and cast valve bodies (304 or 316 stainless steel, or brass) with extended bonnet, and with other materials inside | Appropriate industrial products[b] |
| Fittings | Stainless steel bayonet type for vacuum jackets | Appropriate industrial products[b] |
| O-rings | Stainless steel[c], Kel-F®, or Teflon® | Appropriate industrial products[b] |
| Gaskets | Soft Aluminum, lead, or annealed copper between serrated flanges; Kel-F®; Teflon®; glass-filled Teflon® | Appropriate industrial products[b] |
| Flexible hoses | Convoluted vacuum jacketed 316 or 321 stainless steel | Stainless steel braided with Teflon-lining |
| Rupture disk assembly | 304, 304L, 316, or 316L stainless steel | 304, 304L, 316, or 316L stainless steel |
| Piping | 304, 304L, 316, or 316L stainless steel | 300 series stainless steel (316 preferred[h])<br>Carbon steel[g] |
| Dewars | 304, 304L, 316, or 316L stainless steel | Not applicable |
| Lubricants | No lubricants used in some applications.[h] 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.[e] Graphite and molybdenum disulfide permit only very limited service life for bearings. [f] | 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 6.3 oil, and Kel-F® oil |

[a] Adapted from Table 6.1, Recommended Materials for Hydrogen Systems, in "Hydrogen Propellant," Chapter 6 in *Lewis Safety Manual*, NASA Technical Memorandum 104438, November (1992): pp. 6-70.

[b] A number of standard industrial products are available covering a wide range of temperatures and pressures in a variety of compatible materials.

[c] 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)

[d] Threaded joints should be avoided in $LH_2$ or $SLH_2$ 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)

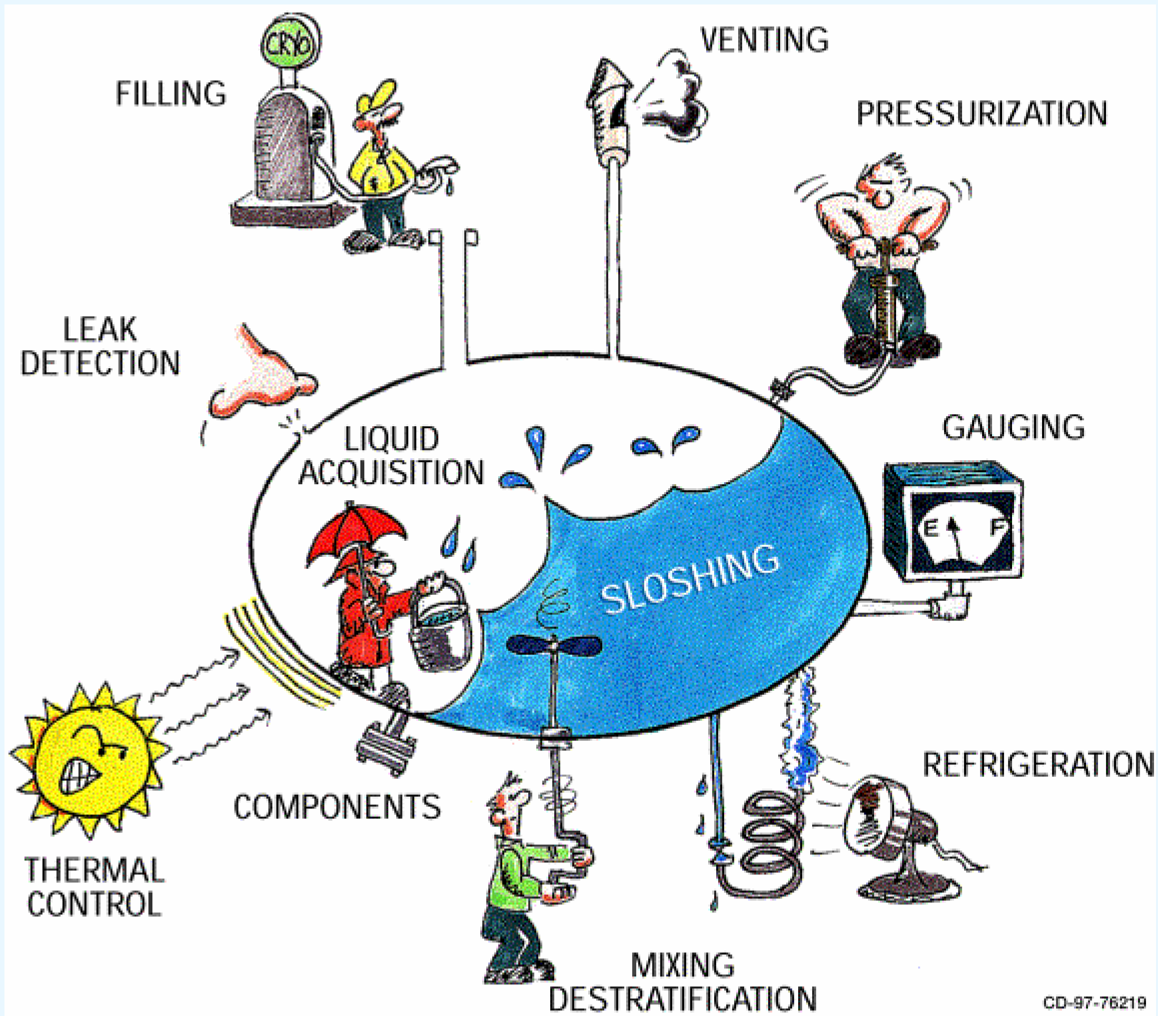
[e] W. Peschka, *Liquid Hydrogen, Fuel of the Future*, Springer-Verlag Wien, New York, (1992): pp. 197.

[f] D. A. Wigley, "The Properties of Nonmetals," In *Mechanical Properties of Materials at Low Temperature*, Chapter 4, pp. 225, Plenum Press, New York 1971

[g] Carbon steel meeting ANSI/ASME B31.3 standards may be used for $GH_2$ service above 244 K (-20 °F.) (Lewis Safety Manual, Chapter 6 "Hydrogen Propellant," NASA Technical Memorandum 104438, November (1992): pp. 6-35.)

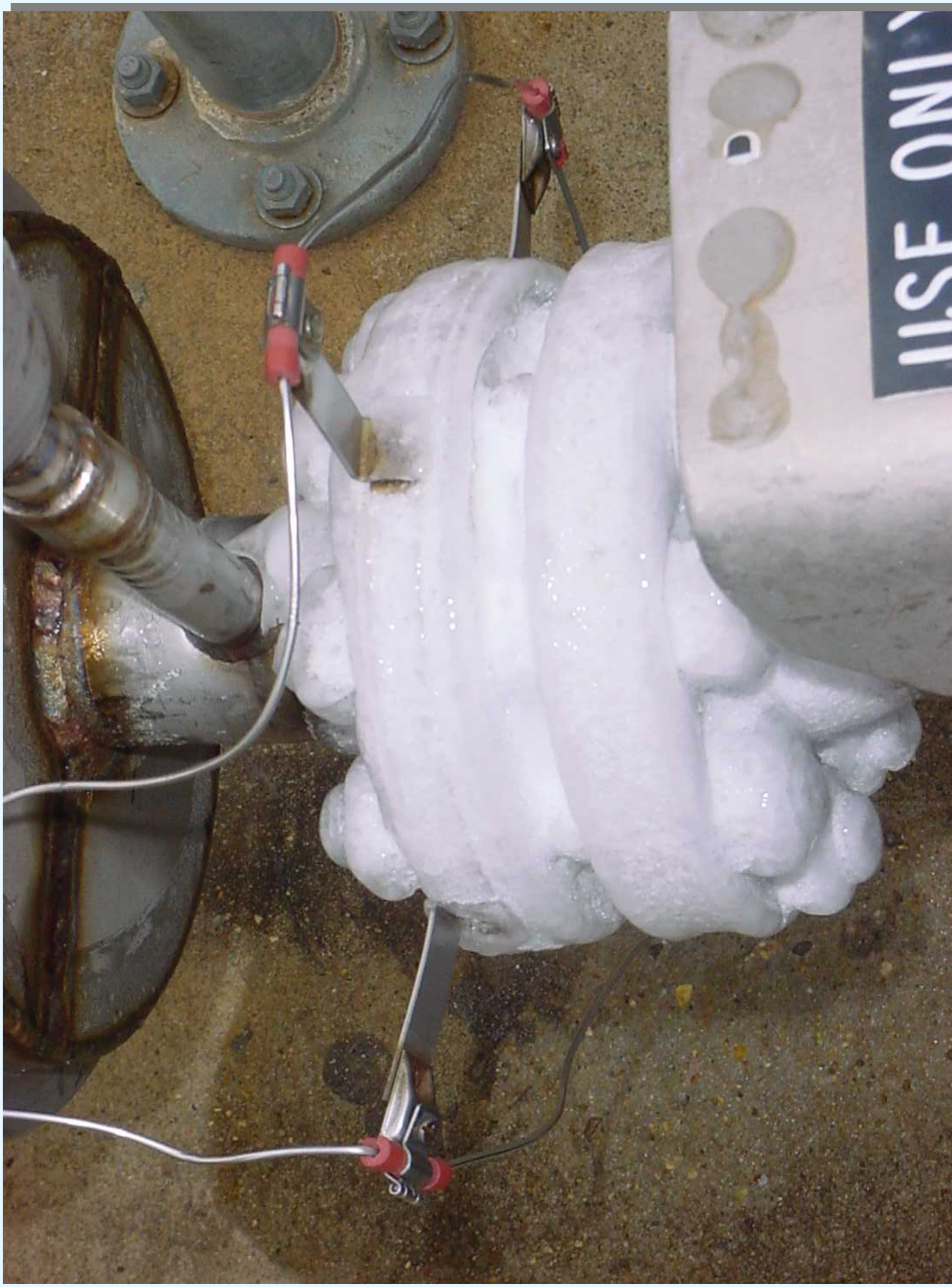
[h] McPherson, B., Private communication (1996).

# $LH_2$ Component Considerations



# Lines and Fittings

- Use vacuum jacketed lines
- Do not use thread sealant in $LH_2$ systems
- “Cold shock” and retighten lines and fittings
- Use metal convoluted flexible hoses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# Thermal Insulation

- $LH_2$ systems normally insulated
  - Reduce heat input and boiloff
  - Prevent liquid air formation
  - Prevent cold surface contact by personnel
- Cold $GH_2$ 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

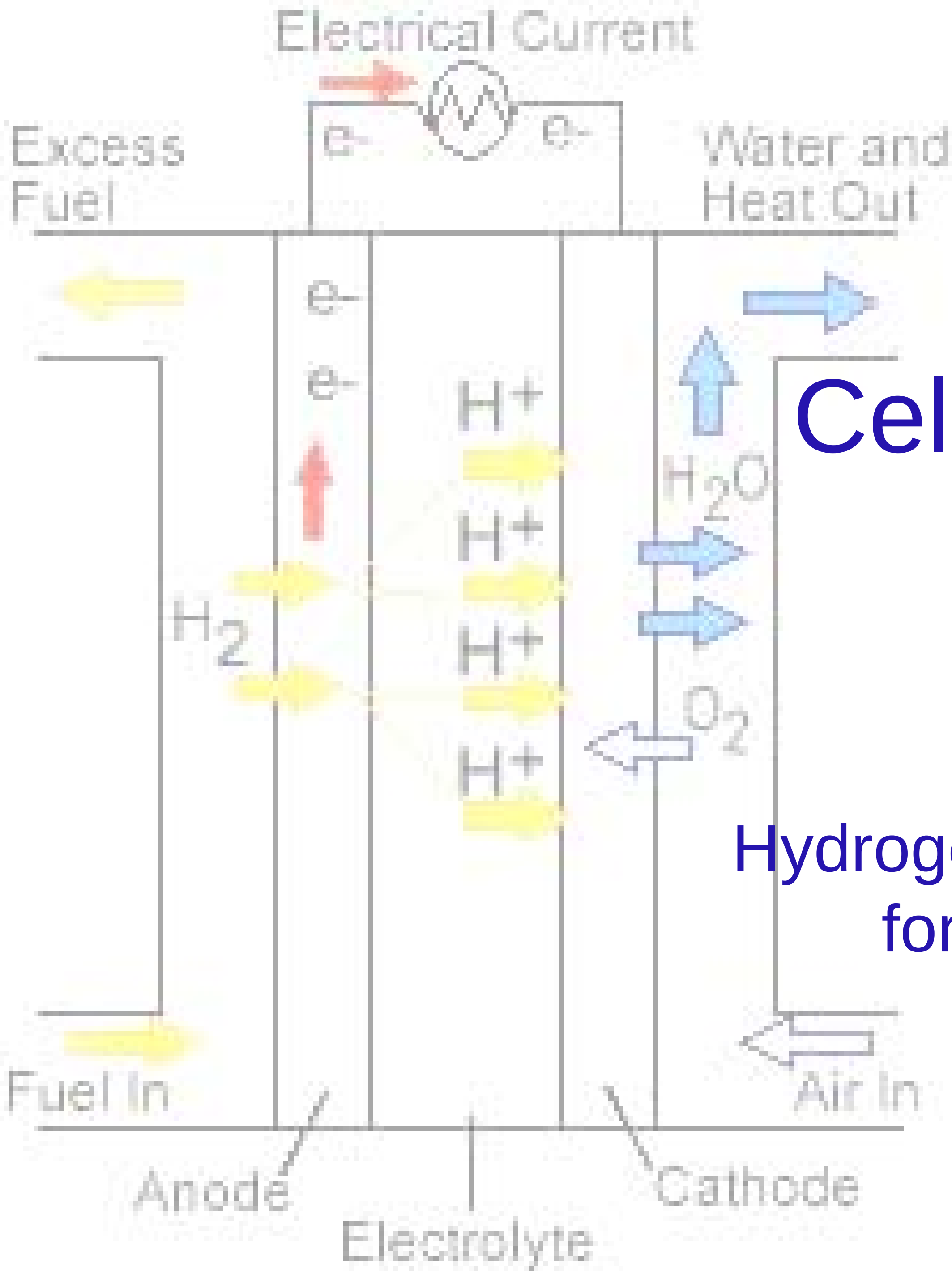
- Maintain insulating vacuum
- Remove unwanted $H_2$ or other gases by purging
  - Beware that vacuum pump with ballast valve could develop combustible mixture within the pump or its exhaust

# Vacuum Subsystem (cont.)

- Vacuum pump exhaust must be connected to a proper vent
  - To vent $H_2$ 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

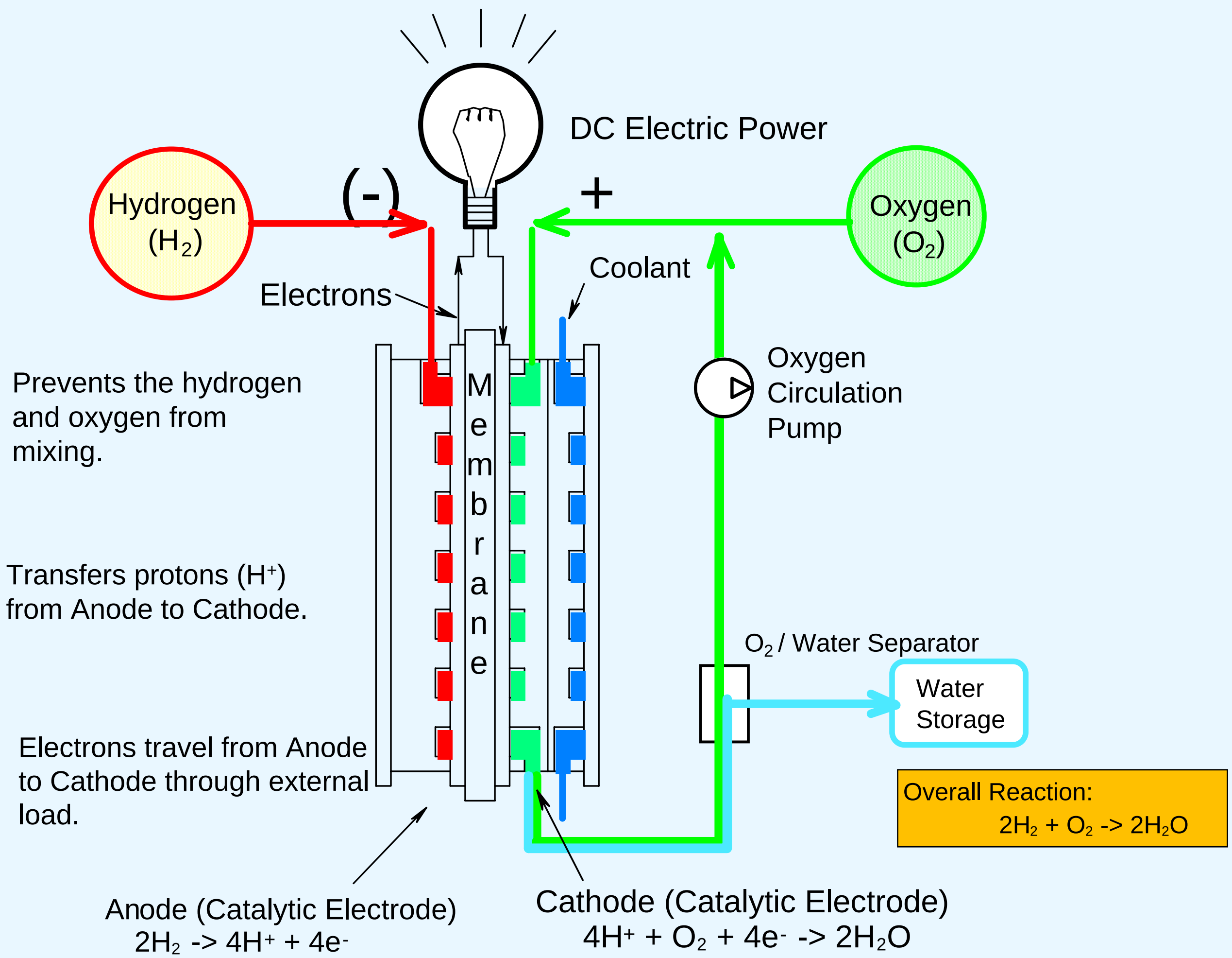



# PEM* Fuel Cell/Electrolyzer Issues

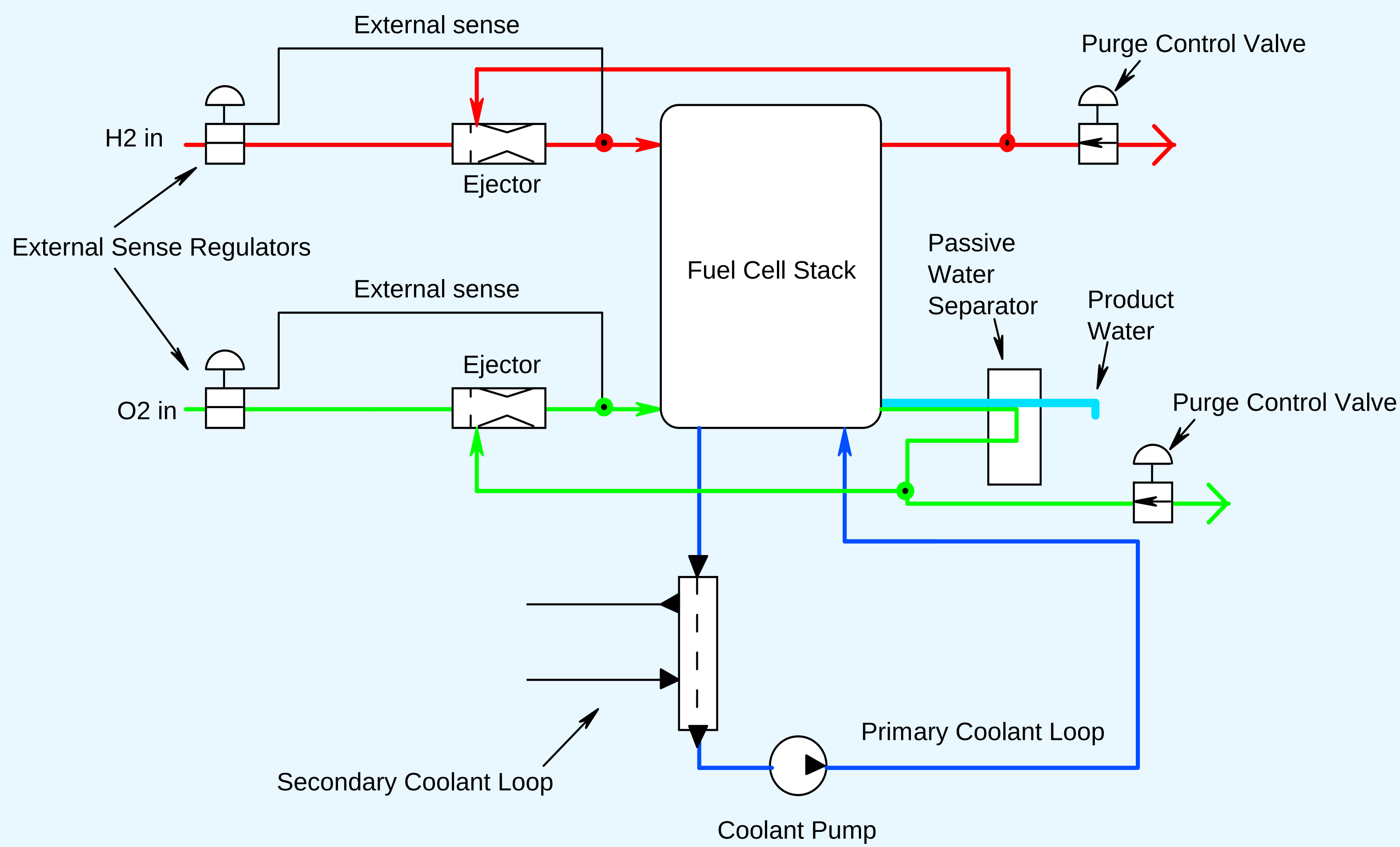
Initial Thoughts on
Hydrogen Combustion Issues
for Fuel Cell/Electrolyzer
System Design

* Proton Exchange Membrane

# PEM Fuel Cell Concept



# System Schematic



# Understand Combustion Potential

- Understand possibilities
  - $H_2 + O_2$
  - $H_2$ + air
  - $H_2$ + other oxidizers
- Primary focus on $H_2$-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% $H_2$
  - Detection
    - $H_2$ sensors in air, or $O_2$ sensors in $H_2$
  - Multiple fault tolerance
- Buffer $H_2$ from oxidizers with purges
- Postfailure safing
- Monitor cell performance for pinholes

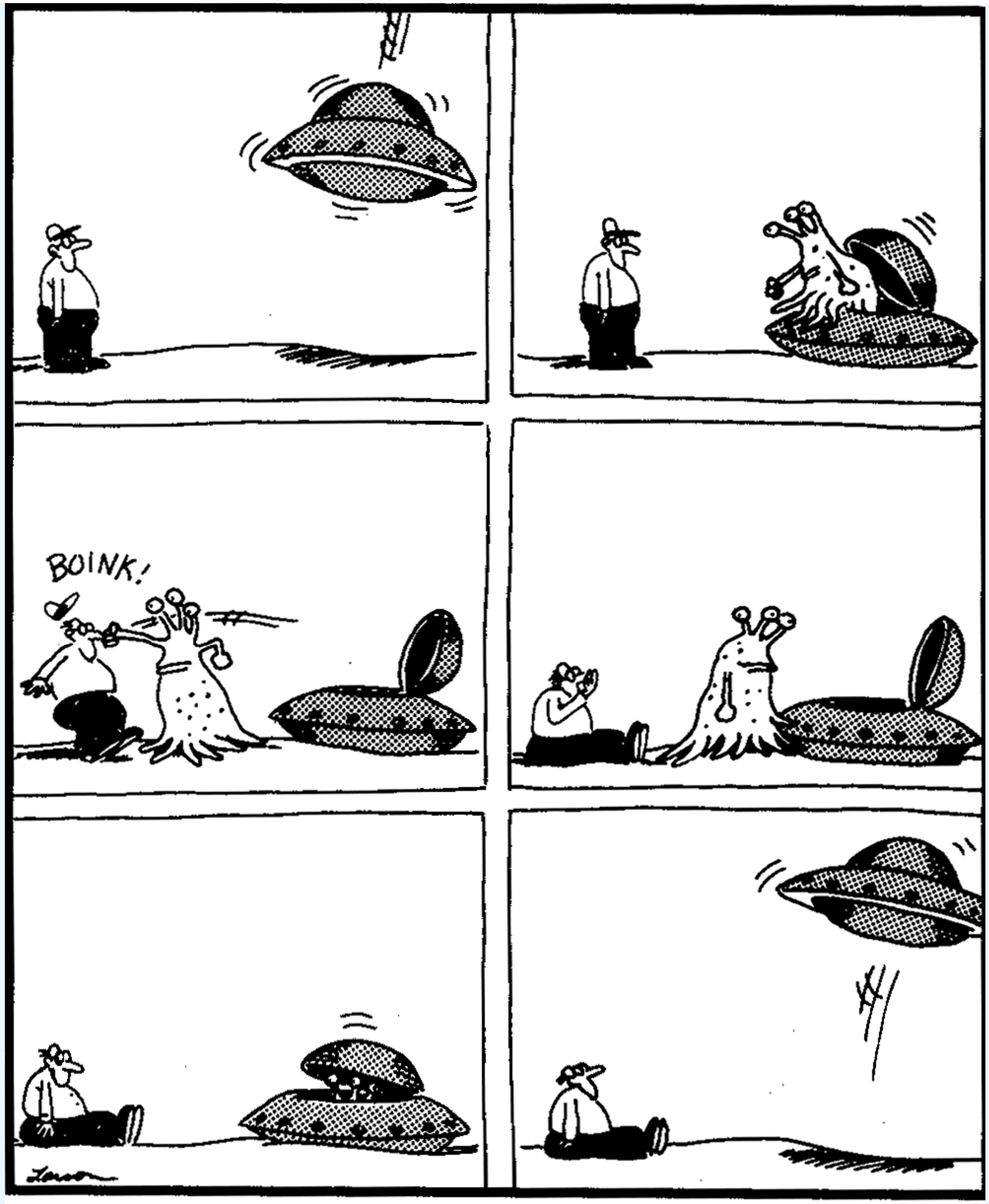
# Approaches to Combustion Control
(cont.)

- 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
- $H_2$ embrittlement
- Consider $H_2$ in solution
- Choose SS lines over plastic
- Avoid combustible seal materials

- Design for worst-case containment
  - Detonation $p_{initial}$ x ~(15 to 20) x 3 (reflection) x safety factor
  - Deflagration $p_{initial}$ x ~(1 to 8) x 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: $GH_2$ < 11.3 m3 (400 ft3), $LH_2$ < 150 L (39.6 gal)
- Non-propellant
  - Industry like applications for $GH_2$ or $LH_2$
  - 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

| Nature of Location | $GH_2$ Volume <3K $ft^3$ (85 $m^3$) | 3 to 15K $ft^3$ (85 to 425 $m^3$) | >15K $ft^3$ (425 $m^3$) |
|---|---|---|---|
| Outdoors | I | I | I |
| In separate building | II | II | II |
| In special room | III | III | Not permitted |
| Inside buildings, exposed to other occupancies, but not in special room | IV | Not permitted | Not permitted |

# 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 $ft^3$ (85 $m^3$), 3000 $ft^3$ (85 $m^3$) – 15,000 $ft^3$ (425 m3), >15,000 $ft^3$ (425 $m^3$)
- For example: >15,000 $ft^3$ (425 $m^3$)
  - 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 $LH_2$ Storage Systems

| | $LH_2$ Volume, L (gal) | | | |
|---|---|---|---|---|
| Nature of Location | 150-189 (40-50) | 190-1136 (51-300) | 1137-2271 (301-500) | >2271 (>600) |
| Outdoors | I | I | I | I |
| In separate building | II | II | II | Not permitted |
| In special room | III | III | Not permitted | Not permitted |
| Inside buildings, exposed to other occupancies, but not in special room | IV | Not permitted | Not permitted | 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]
  - [http://www.ddesb.pentagon.mil/DoD6055.9-STD%205%20Oct%202004.pdf]
- 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
  - $H_2$ facility from other hazards
  - Nearby facility from $H_2$ 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
  - ASME, *International Boiler and Pressure Vessel Code*, Section VIII, Pressure Vessels
- Design and siting
  - 29CFR1910.103, *Hydrogen*
  - NFPA 50A, *$GH_2$ Systems at Consumer Sites*
  - NFPA 50B, *$LH_2$ Systems at Consumer Sites*
- Hazards analysis
  - 29CFR1910.119, *Process safety management of highly hazardous chemicals ($\geq$10,000 lb)*

# 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

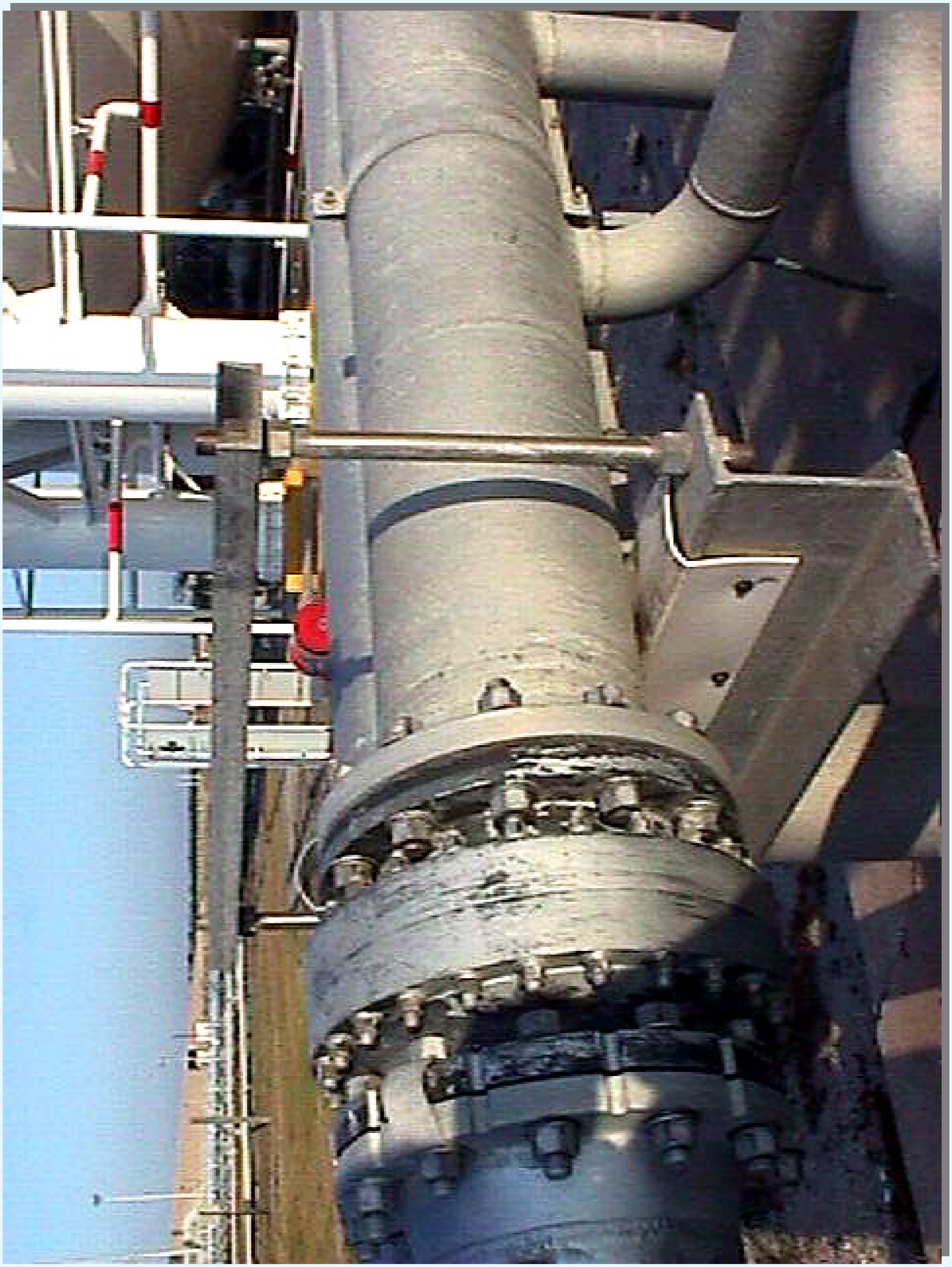
- Ensure that $LH_2$ vessels are
  - Insulated
    - Limits vaporization and condensation of air
    - Should be self-extinguishing
  - Periodically warmed to remove solid contaminants
  - Electrically bonded at all joints
  - Grounded and properly labeled
    - Contents, capacity, MAWP
  - Surrounded 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)

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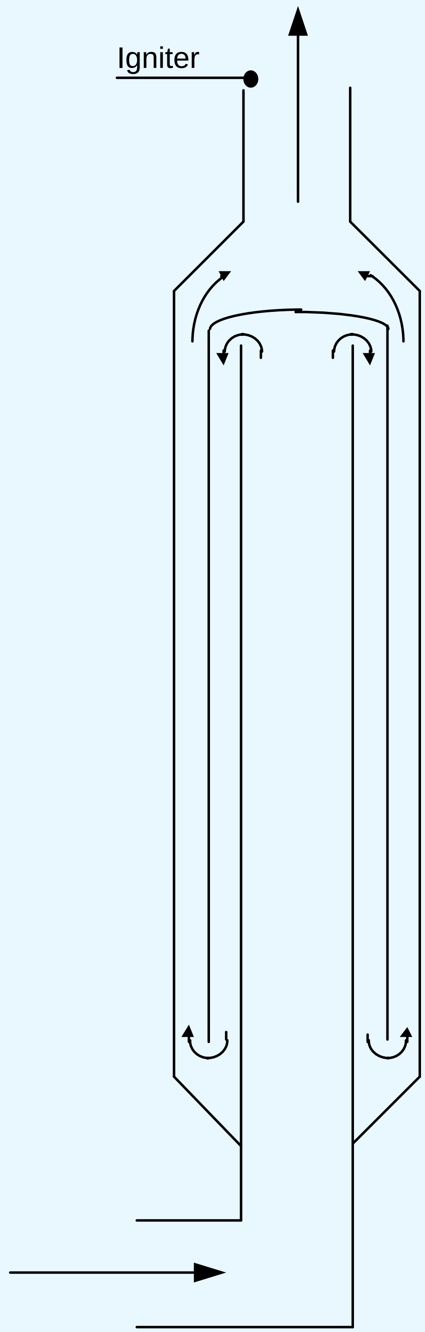
## *Venting, flaring, and dispersion*

# 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




# $H_2$ flare stack with gas (molecular) seal

# Siting

- Locate roof vents so that $H_2$ 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 $H_2$ by flaring
  - Flare stack or burn pond

# Disposal Factors

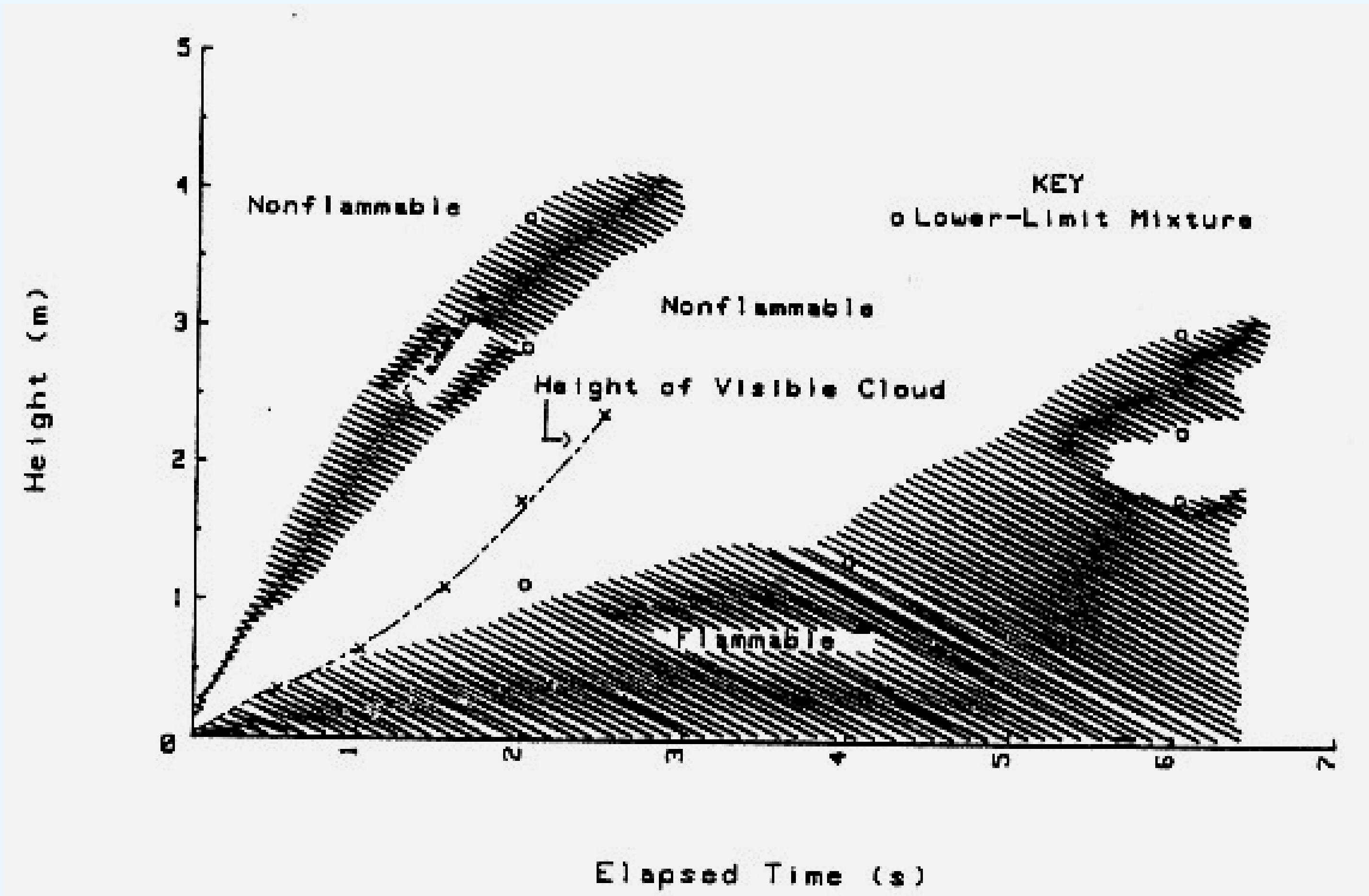
- $H_2$ quantity/extent in combustible cloud
- Thermal radiation from flame
- Site conditions
  - Size of exclusion area
  - Building locations
  - Personnel control
  - Weather

# Dispersion Test Results

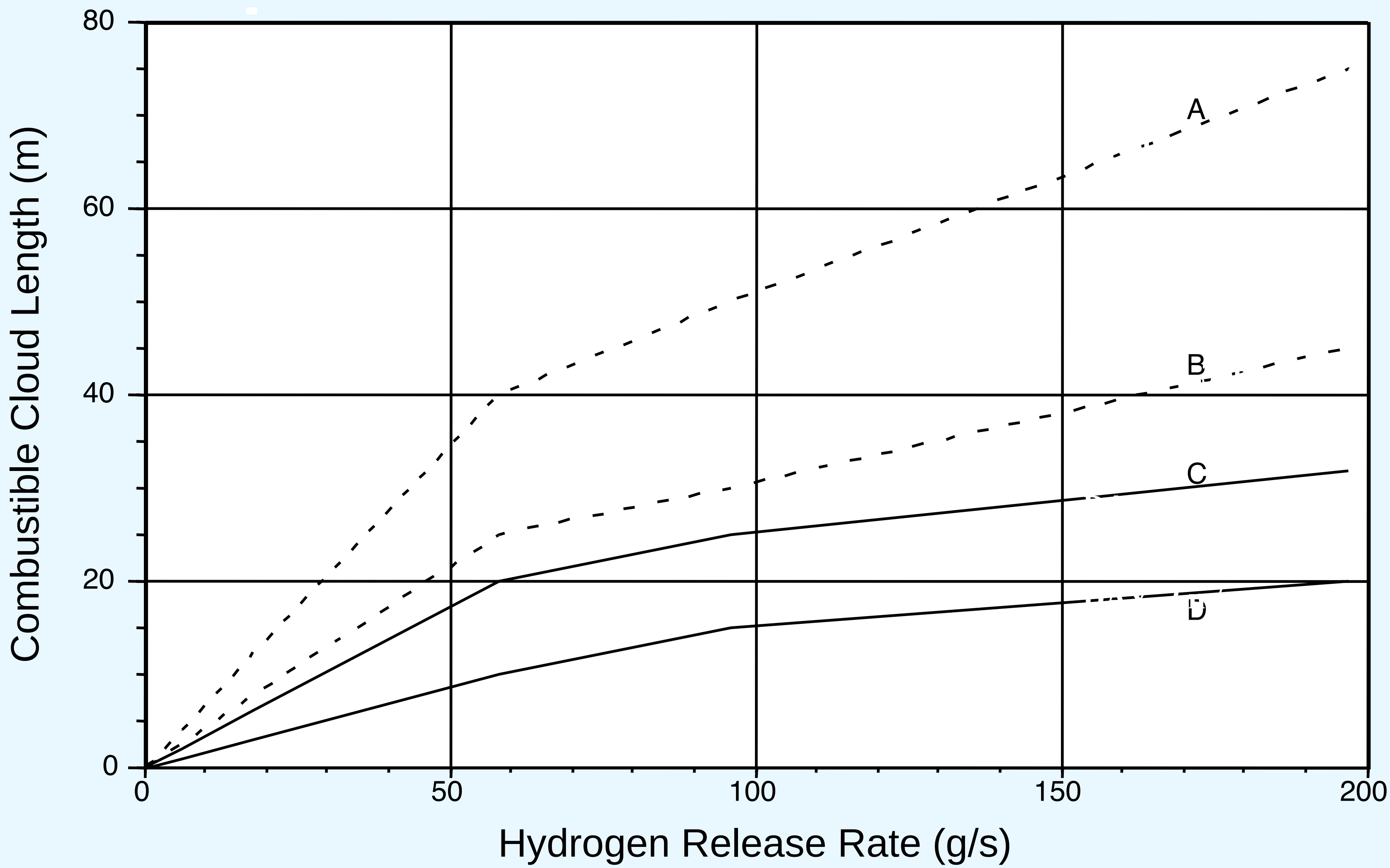
White Sands Test Facility, New Mexico
Fall 1980

**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:**

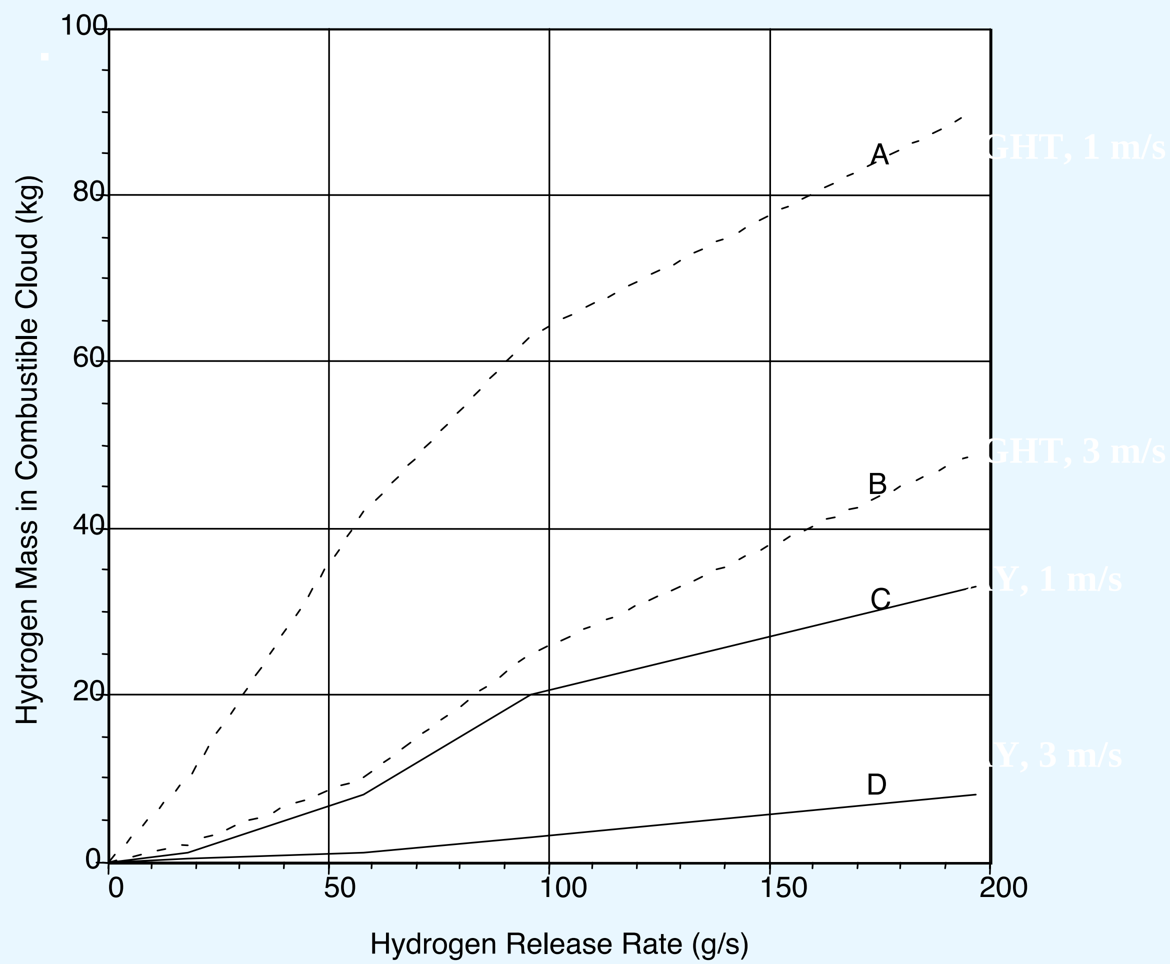
# Flammable Mixture and Visible Cloud



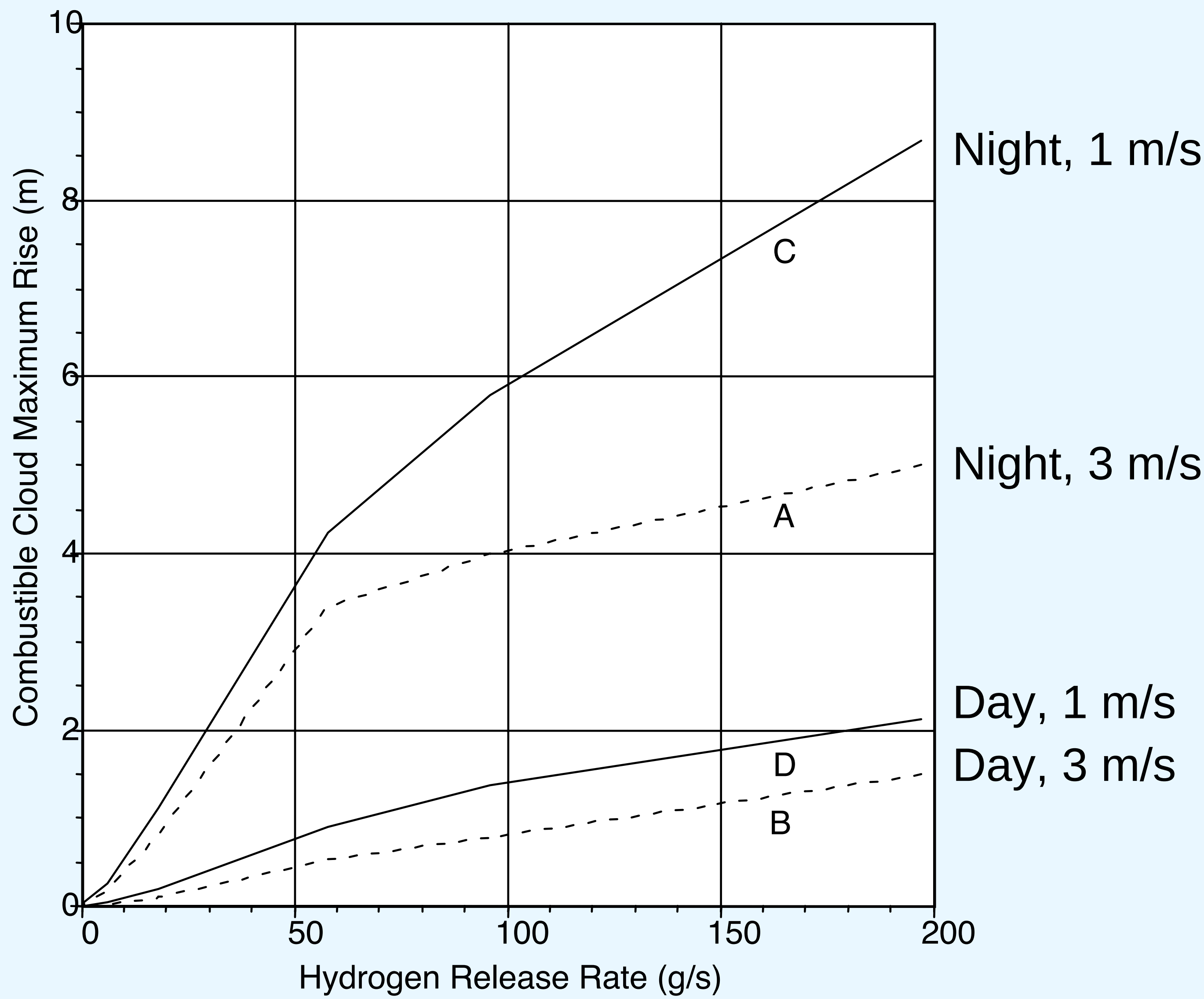
# Combustible Cloud Length



# $H_2$ Mass in Combustible Cloud



# Combustible Cloud Mixture



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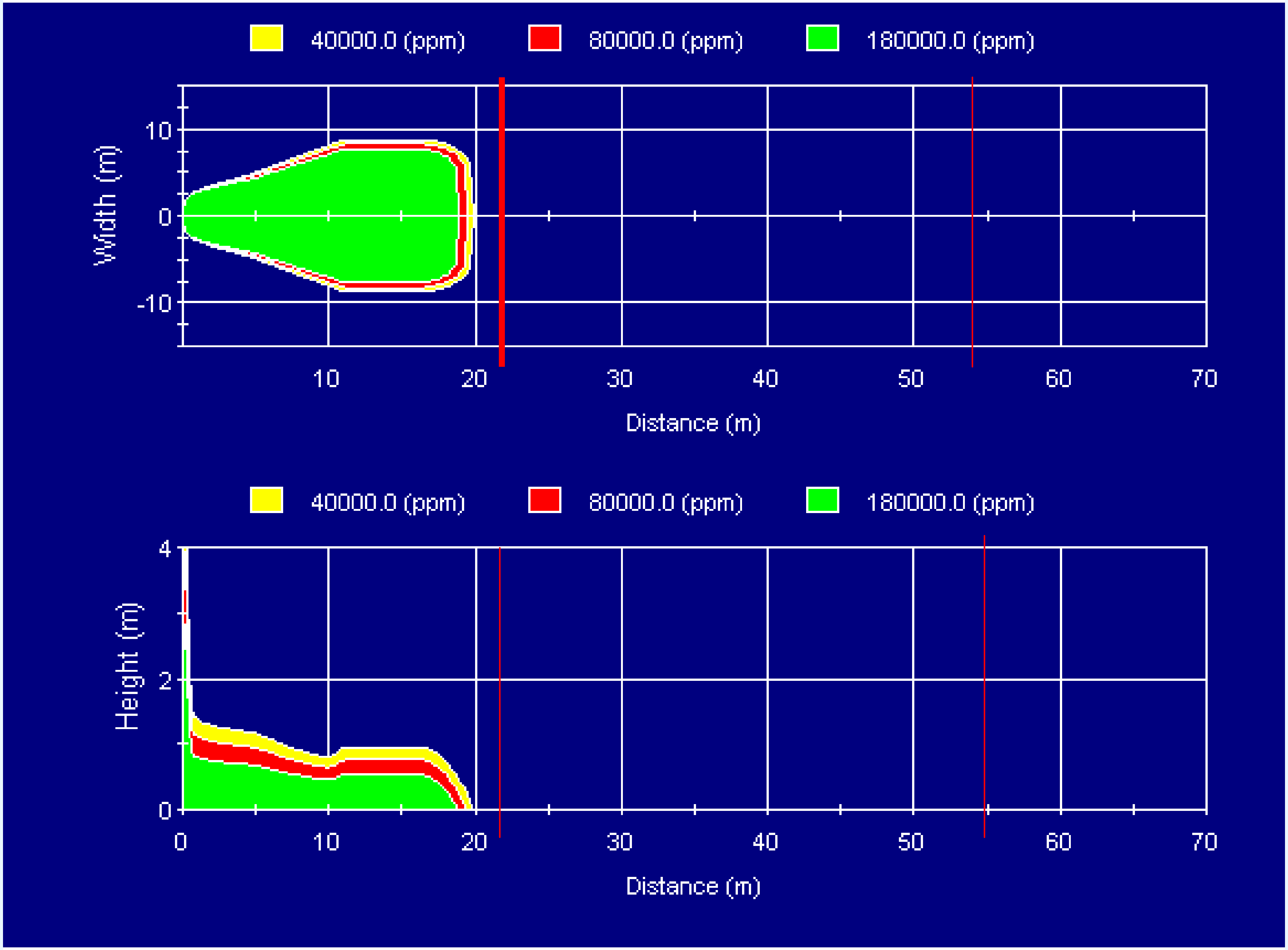

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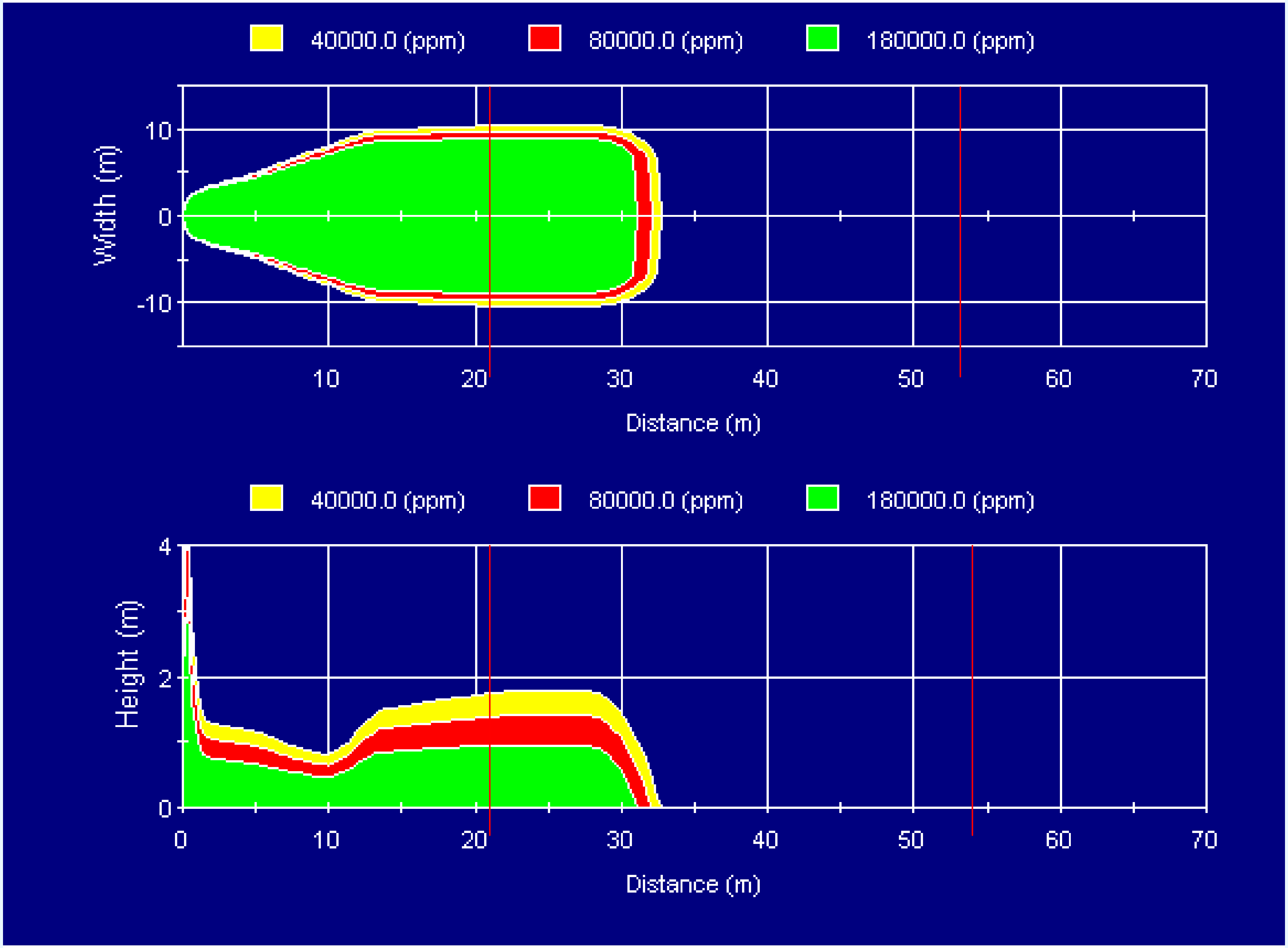

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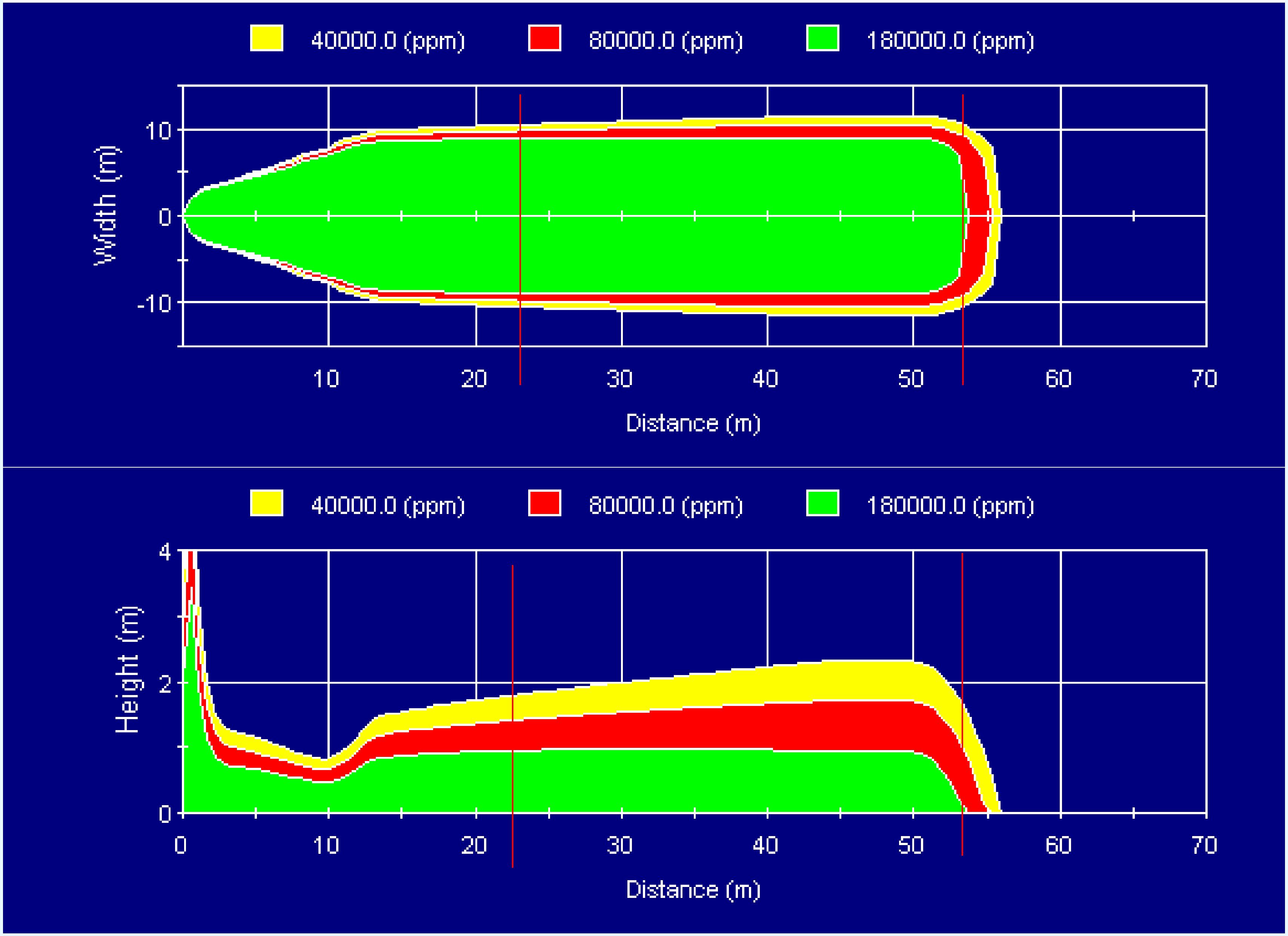

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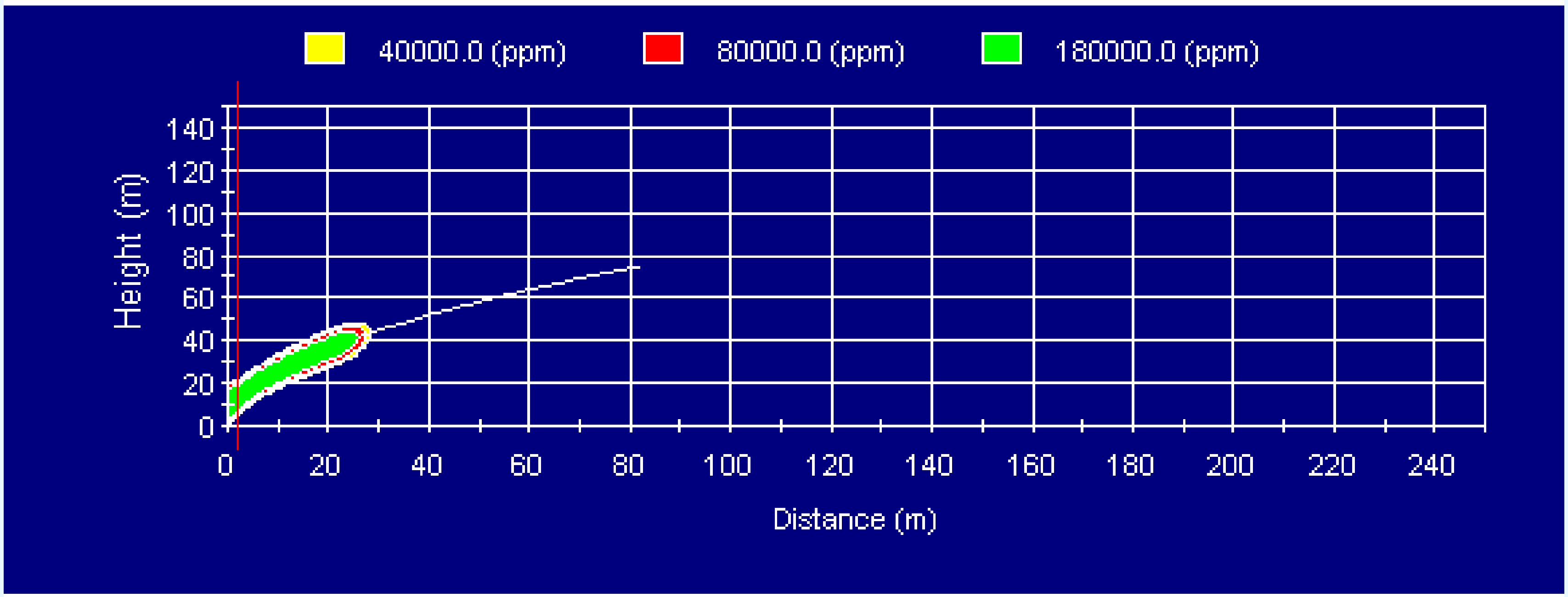
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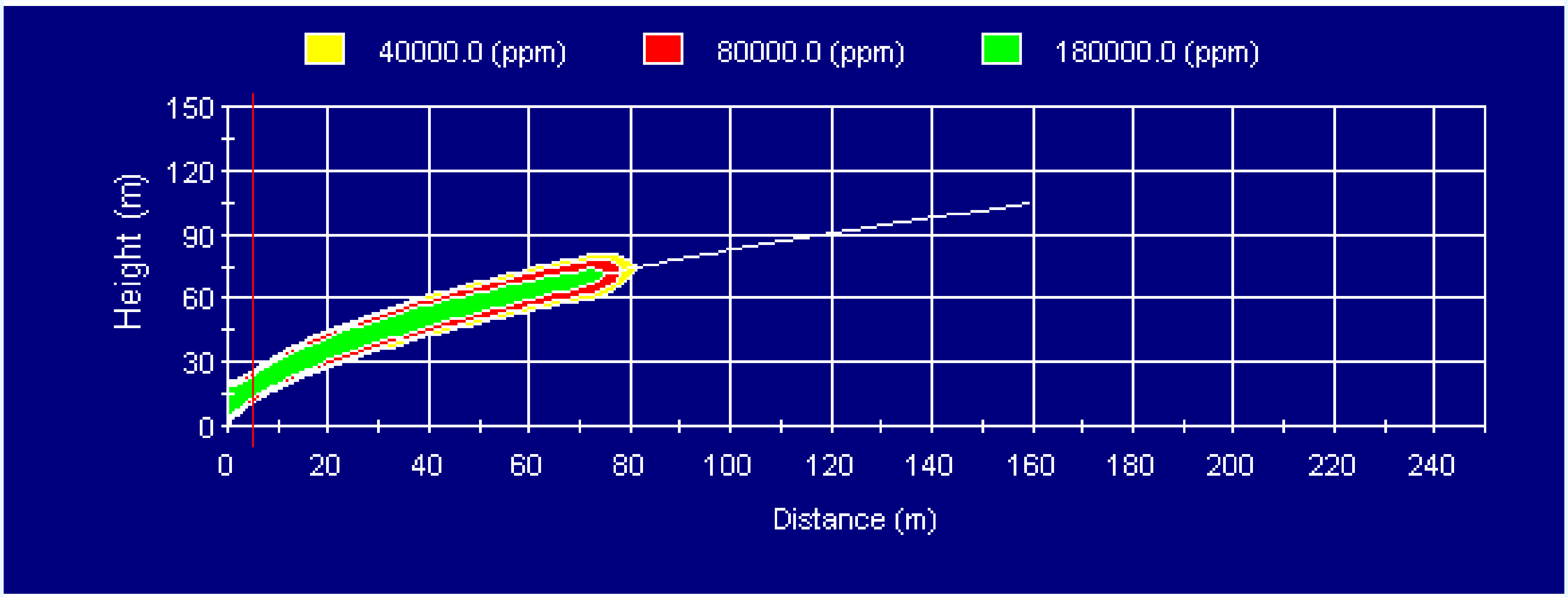
# Time 0:38



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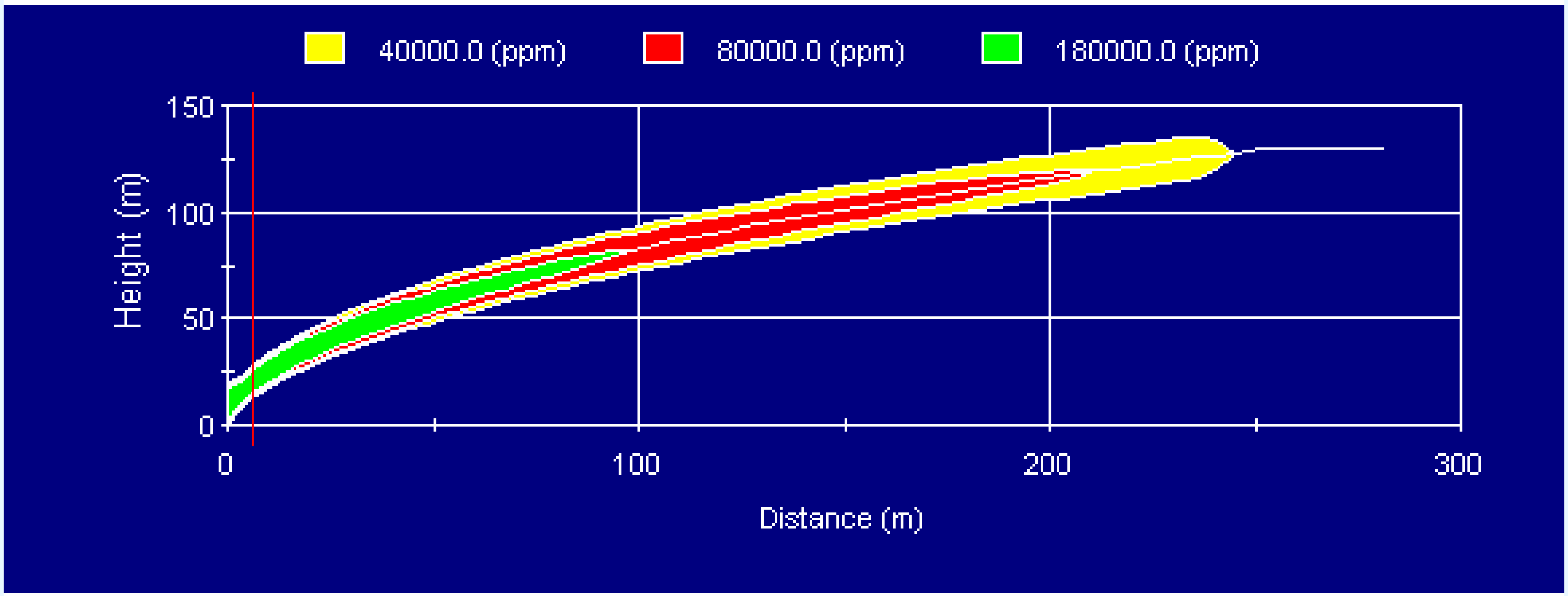
Distance (m)

# Time 1:14



40000.0 (ppm)
80000.0 (ppm)
180000.0 (ppm)
Height (m)
150
100
50
0
0
100
200
300
Distance (m)

## *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 $H_2$ vented nearby
  - Sensors activate alarms and automatic air shutoff if $H_2$ detected
- Install $H_2$ sensors in building outlet vents if $H_2$ used inside
- Avoid suspended ceilings and inverted pockets or ensure adequate ventilation

*Facility support infrastructure*

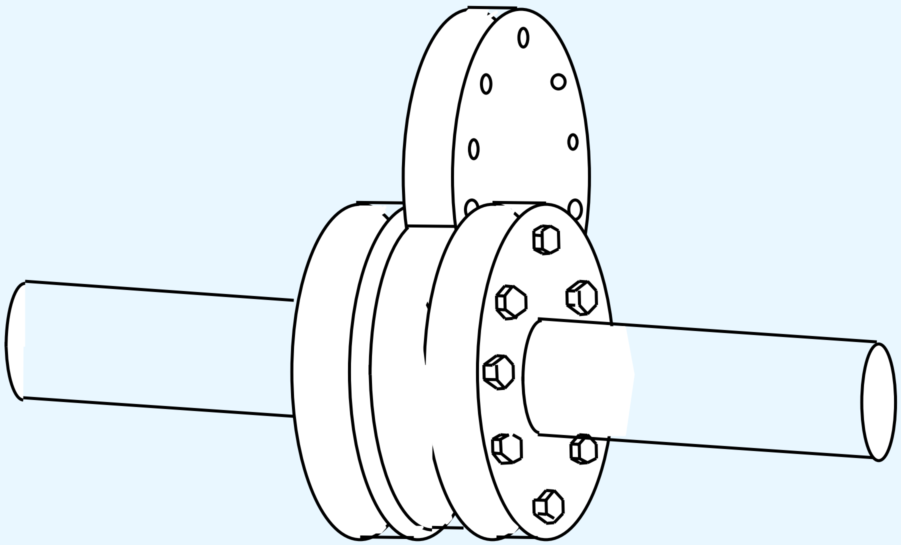
# Facility Support Infrastructure

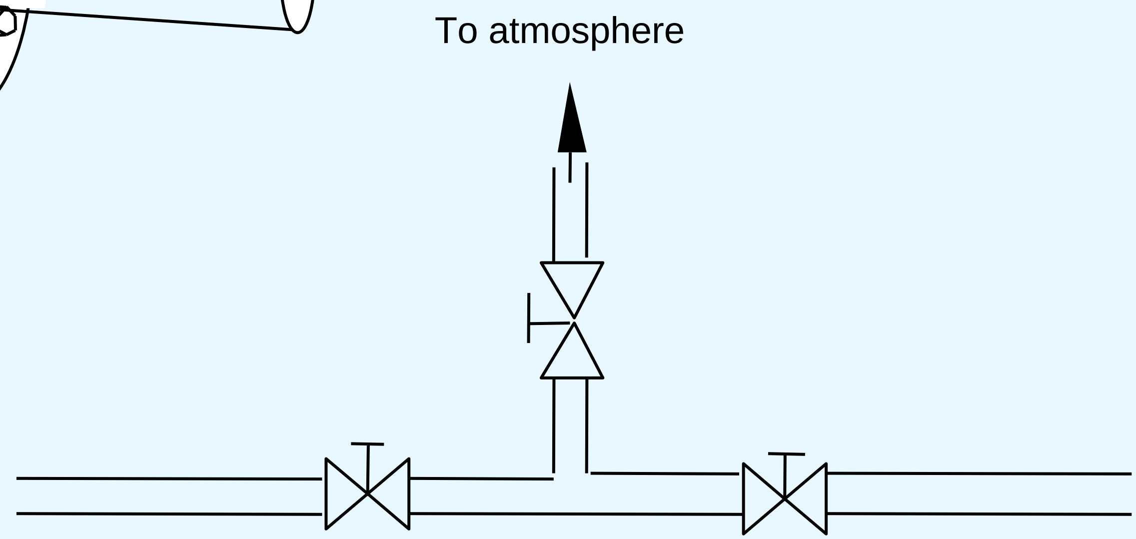
- Inert gas subsystem
- Electrical subsystem
- Cooldown
- Transportation

# 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 $LH_2$ 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

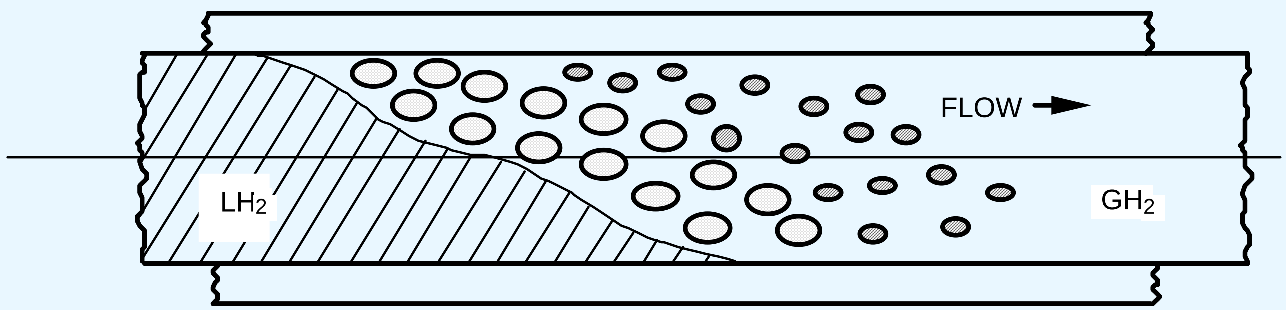
# Electrical Considerations

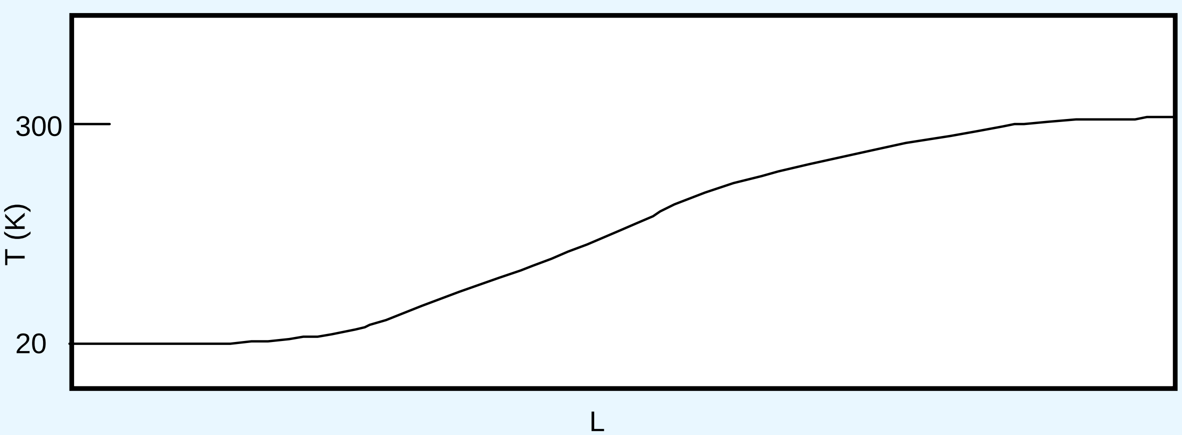
- Use a purged enclosure as an alternative to explosion-proofing
- Provide lightning protection in all areas where there is $H_2$
- Bond and ground mobile $H_2$ supply units before discharge

# Personnel Electrical Protection

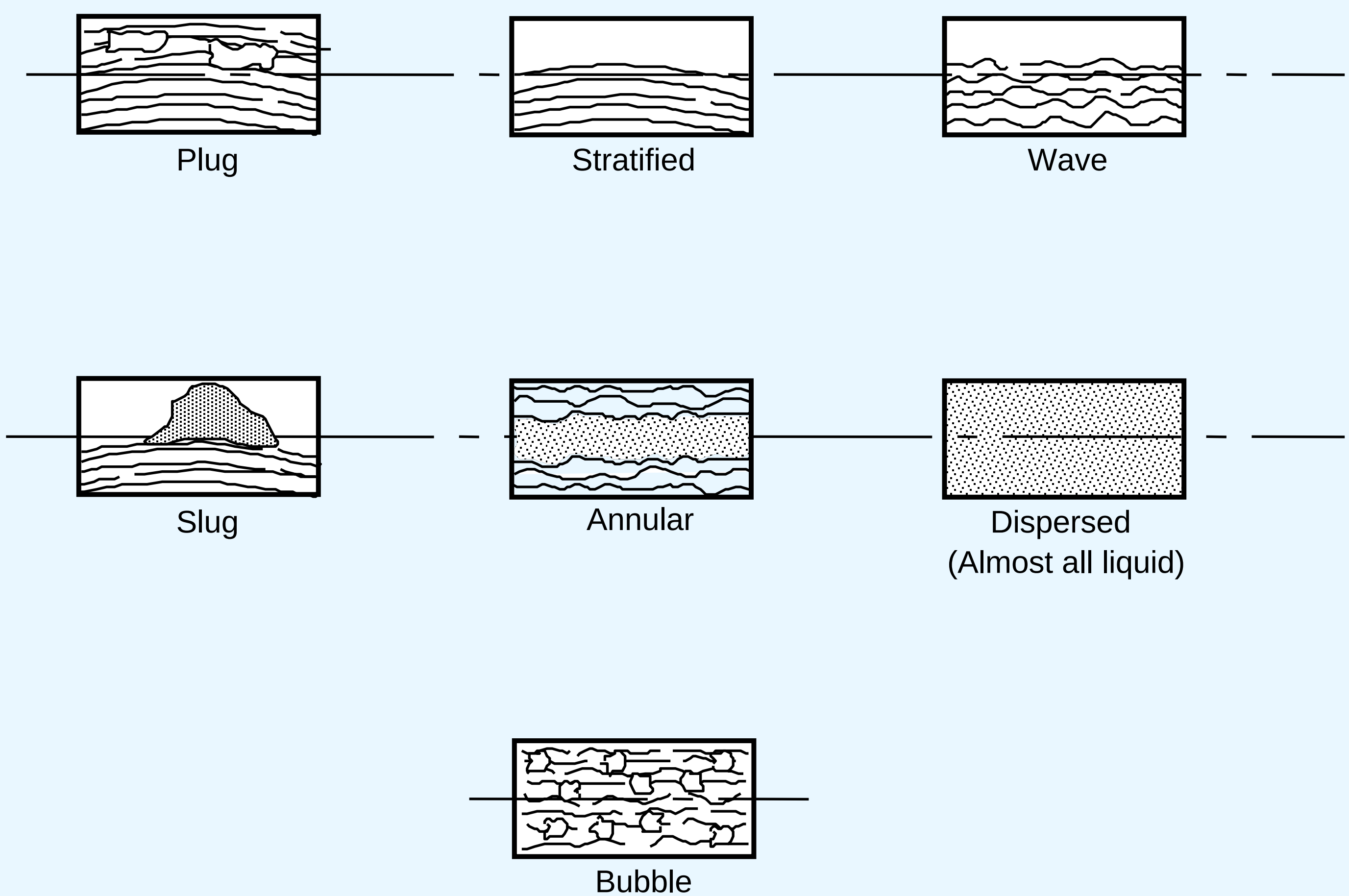
- Ensure personnel are grounded before working on an $H_2$ system
  - Use antistatic clothing
- Ensure personnel use conductive machinery belts
- Provide adequate illumination for all $H_2$ areas

# Cooldown Model



# Two-phase Flow Regimes



# 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

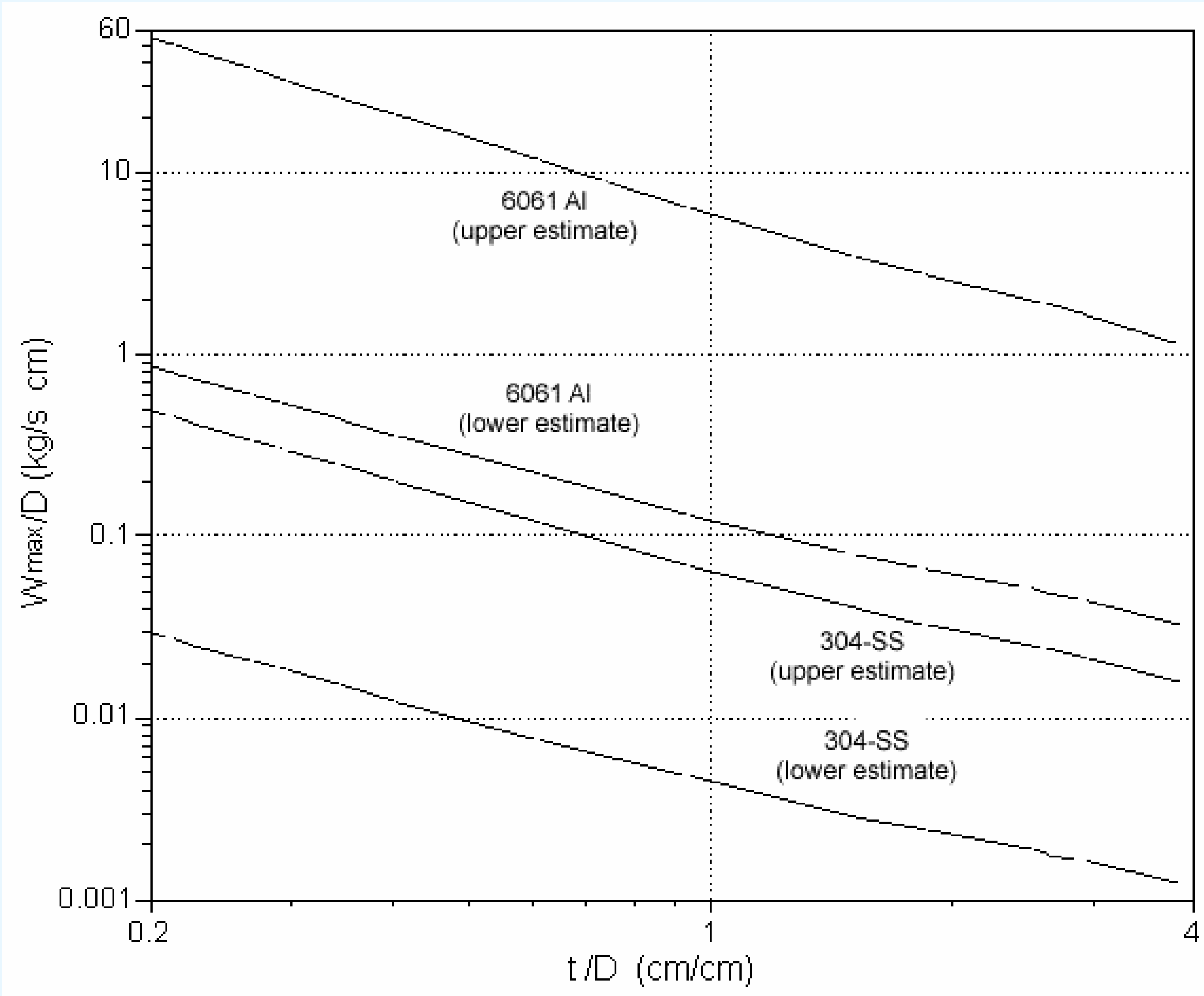
# Cooldown Issues (cont.)

- 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

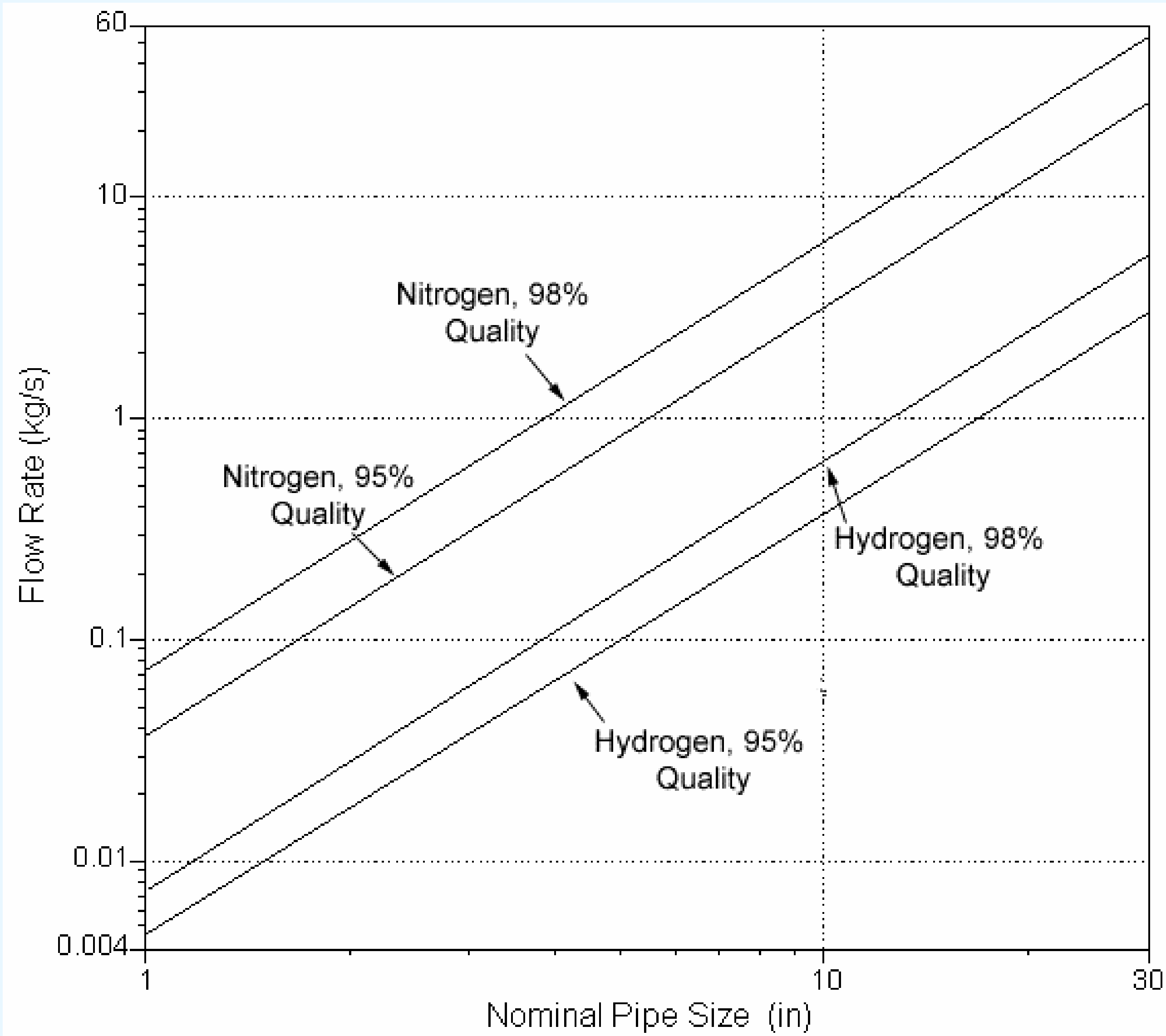
# Cooldown Issues (cont.)

- 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 $H_2$ Flow Rate



# Transportation

- Transport $H_2$ according to 49CFR
  - $H_2$ transportation aboard a passenger aircraft, railcar, or ship is prohibited
  - Up to 150 kg ($GH_2$ only) permitted on a cargo aircraft
  - On cargo ships, $GH_2$ may be stowed on or below deck, but $LH_2$ may only be stowed on deck

## *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 $H_2$ 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 $H_2$ supply before attempting to extinguish an $H_2$ fire
  - Preclude reignition of combustible cloud
- Spray water on adjacent equipment to keep it cool
- Extinguish small $H_2$ fires with
  - Dry chemical or $CO_2$ extinguishers, $N_2$, or steam

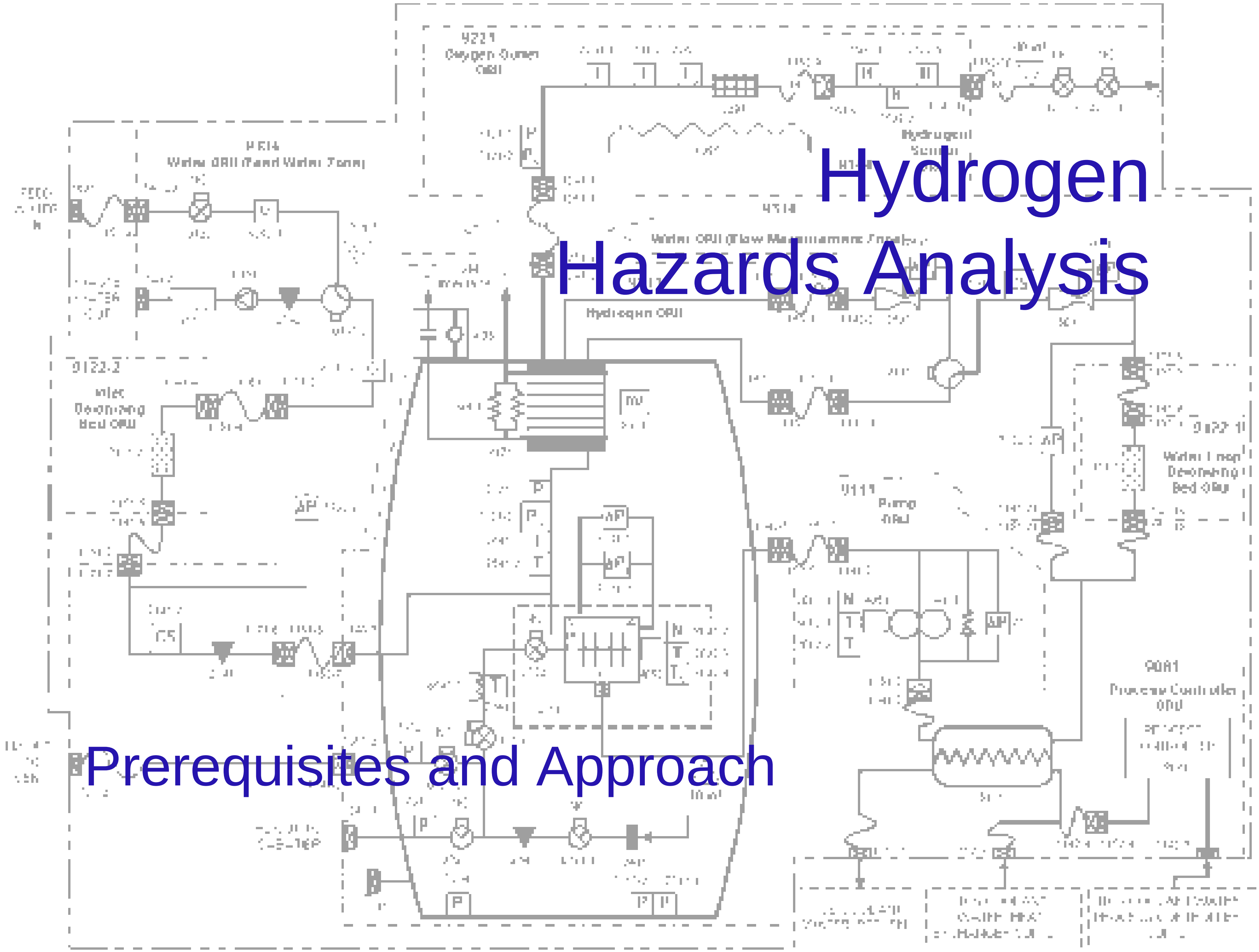
# Summary

- Keep safety as the primary $H_2$ 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 $H_2$ 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

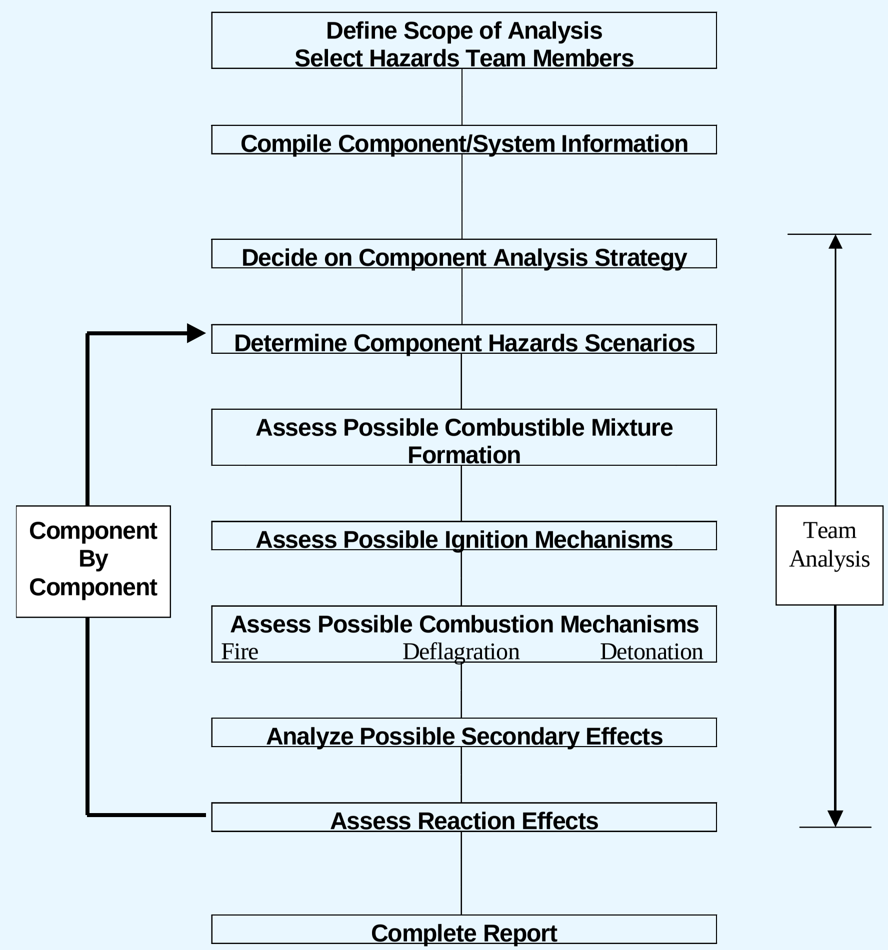
- Understand analysis scope
- Have detailed design information
  - Up-to-date schematics
  - All vendor information
  - Identify all materials exposed to $H_2$
- Assemble necessary expertise
- Have information necessary to evaluate all leak paths

# 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

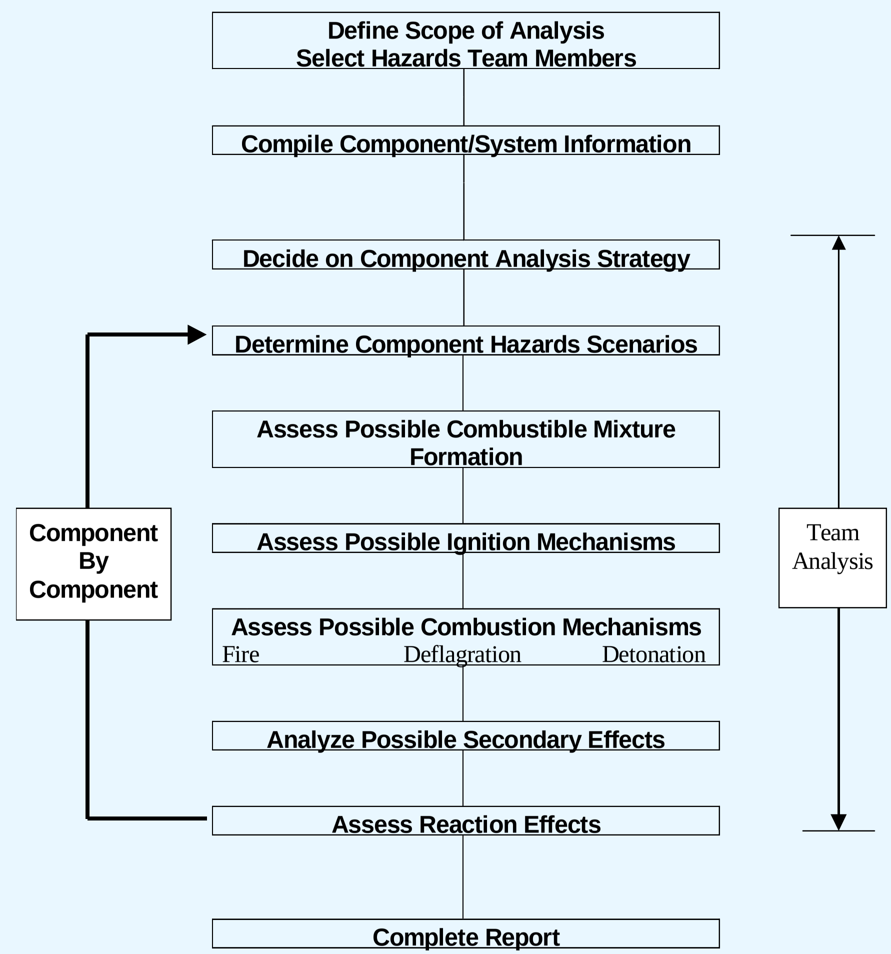
# Hazards Analysis Overview (cont.)

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



# Failure Effects Consideration

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



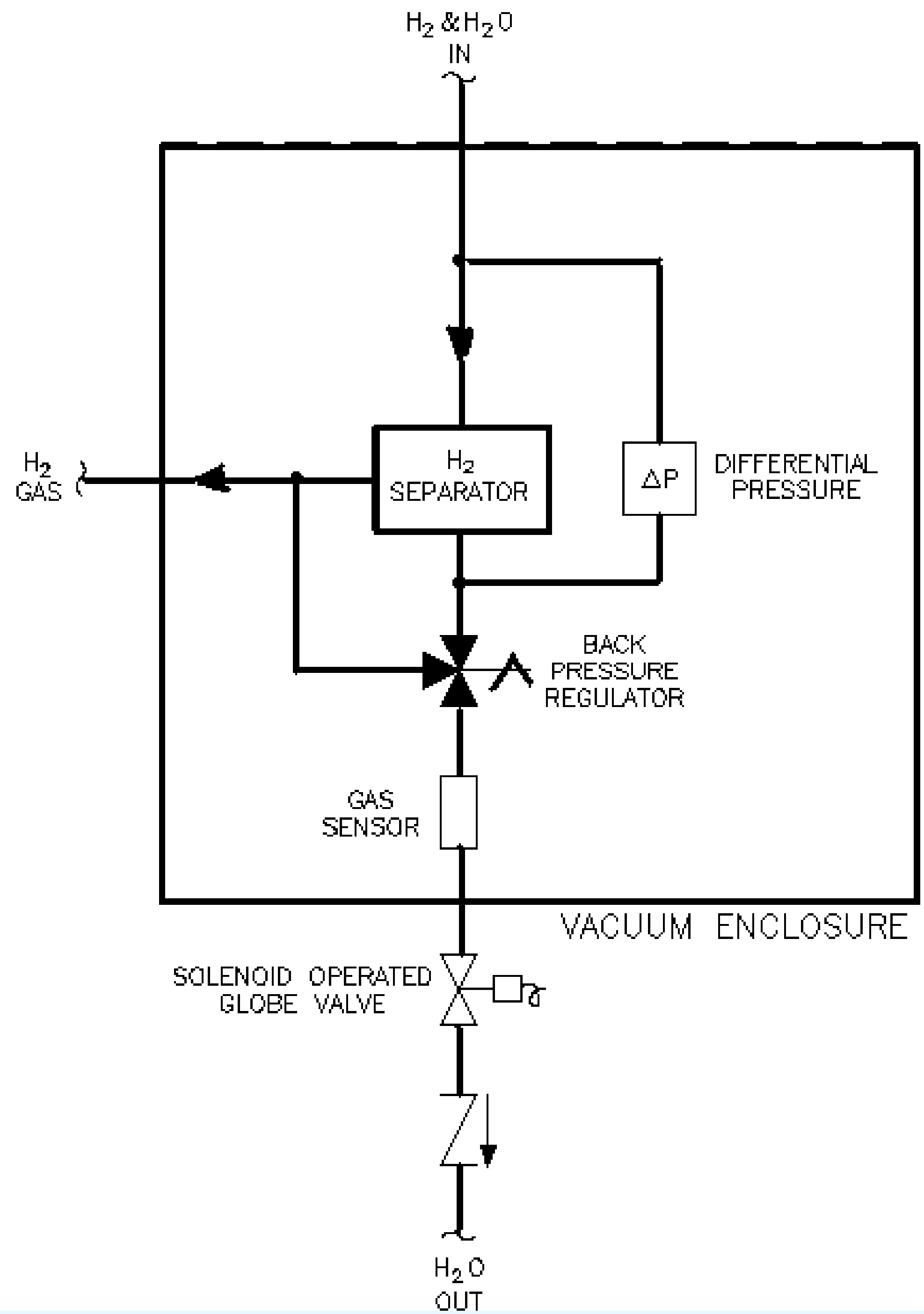
# Questions to Consider

- What failure modes involve $H_2$?
- 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?

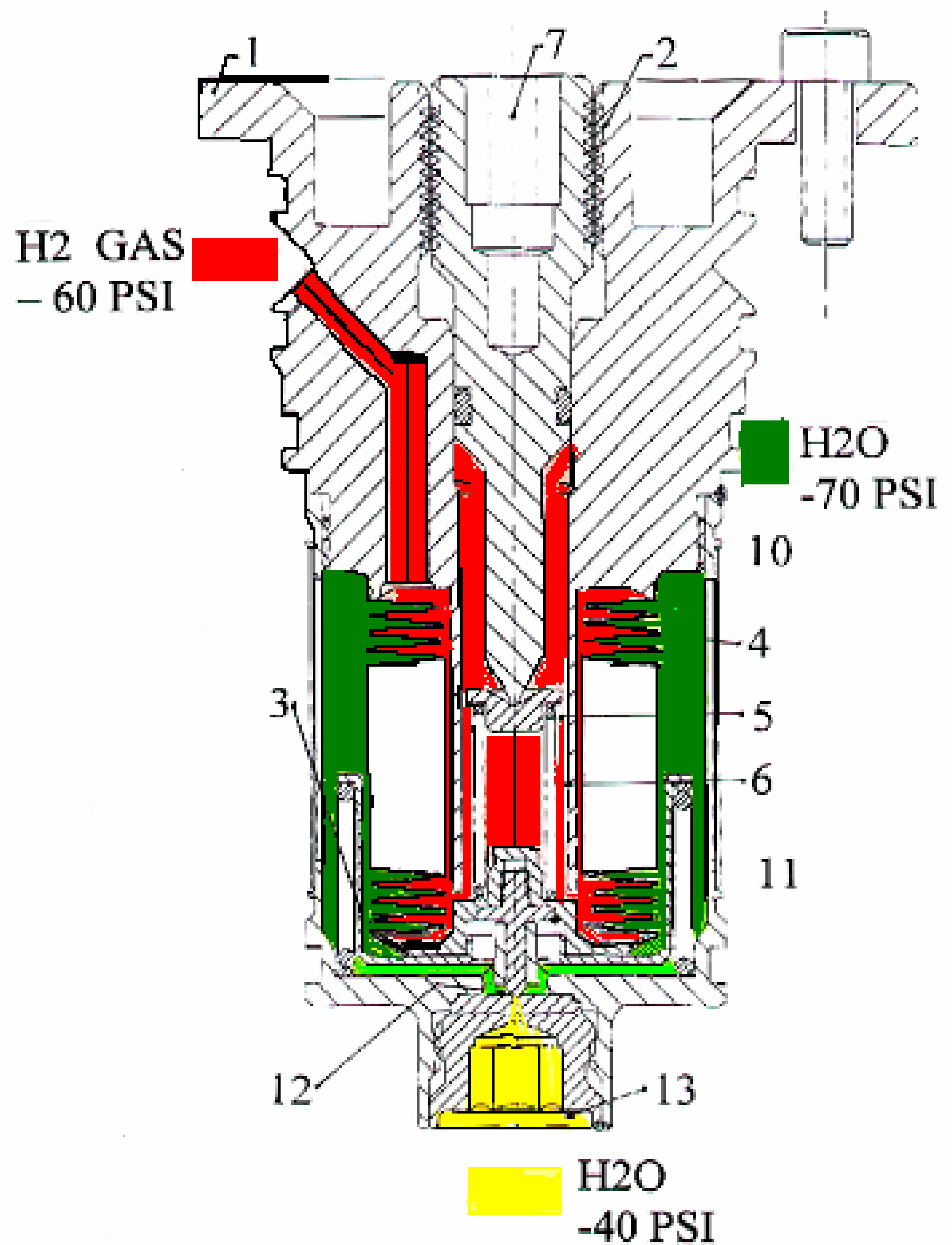
# Sample Analysis

- 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

| STEP 1 | STEP 2 | | | STEP 3 | | | | STEP 4 | | | | STEP 5 | | | | STEP 6 | STEP 7 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 |
| | Probability of Failure in These Modes | | | Probability of Combustible Mixture From These Events | | | | Probability of Ignition From These Sources | | | | Probability of These Consequences | | | | | |
| Component | Noncatastrophic | Catastrophic | Other | External Leakage | In leakage | Contamination | Other | Electrical | Mechanical | Thermal | Other | Fire | Deflagration | Detonation | Other | Secondary Effect | Reaction Effect |
| Differential -backpressure regulator into recirculation loop | **1**[1] | **0** | **0** | **3**[2] | **0** | **0** | **0** | **1**[3] | **0** | **0** | **0** | **0** | **1**[4] | **0** | **0** | **N** | **D**[5] |
| Differential-backpressure regulator into the vacuum enclosure | **1**[6] | **0** | **0** | **3**[7] | **0** | **0** | **0** | **1**[8] | **0** | **0** | **0** | **0** | **1**[9] | **0** | **0** | **N** | **D**[10] |

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 17-4and 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 $H_2$ 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 $H_2$ and $O_2$ 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 resisters 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 $H_2$ from the phase separator to enter the recirculation loop. A leak across the bellows will cause $GH_2$ 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 $H_2$ 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 resisters 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

## Facts and Reminders

# Course Summary

- $H_2$ use is important
- $H_2$ use involves hazards/risks
- $H_2$ can be used safely
  - Thinking
  - Planning
  - Training
  - Being prepared

# We Have Studied

- Hydrogen's safety related properties
- Hazards associated with $H_2$ use
- How to deal with hazards and emergency situations
- Typical components and materials for use with $H_2$
- $H_2$ 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 $H_2$ uses
- Use conservative approach
- Recognize hazards and limitations
- Search for hazards
- Don’t take chances or shortcuts

**THANKS**