CENTER FOR Hydrogen SAFETY
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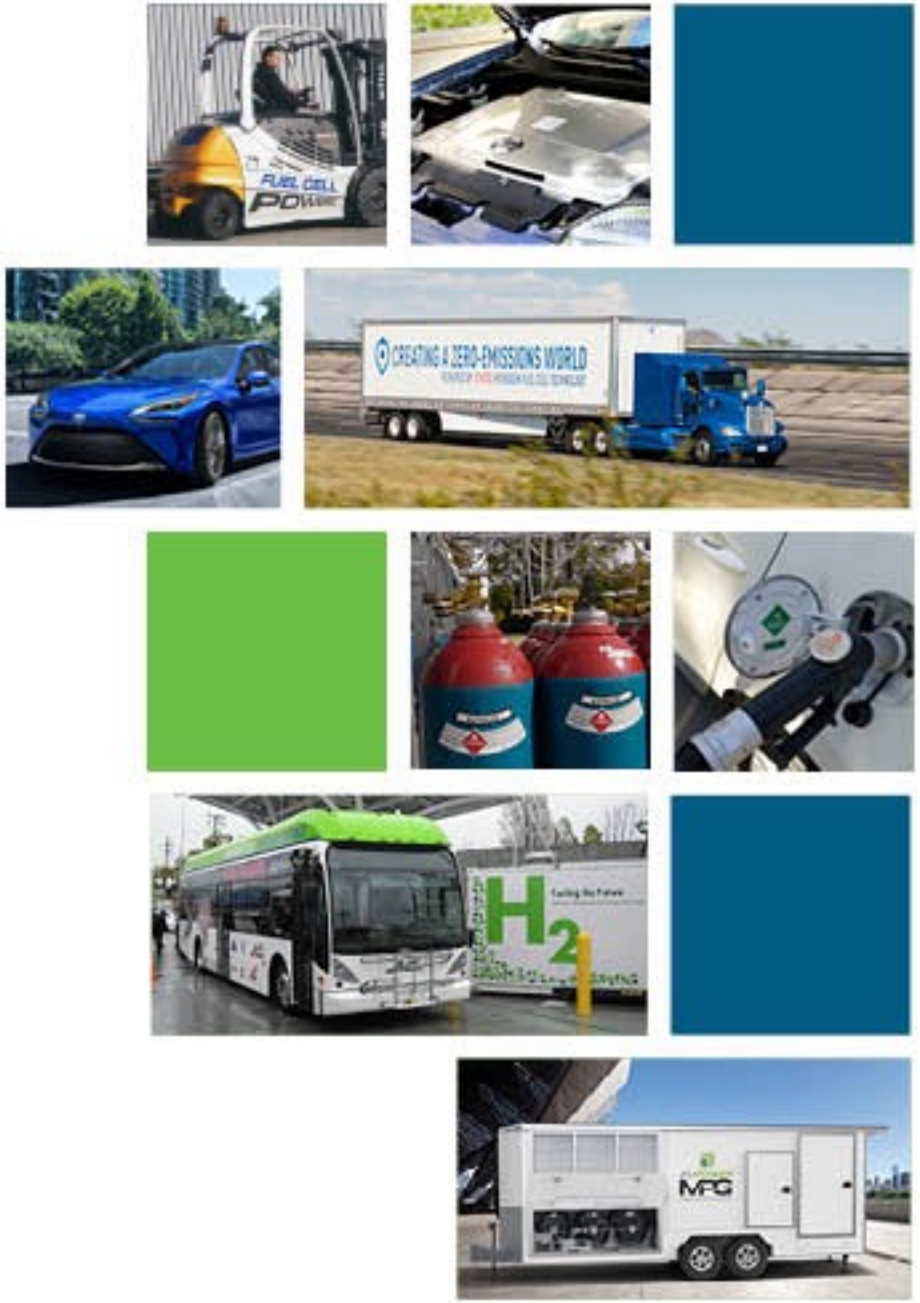


Liquid Hydrogen: Safety and Design Considerations

Harold Beeson, Ph.D
Thomas Witte, P.E.
Center for Hydrogen Safety, AIChE
January 26, 2023

About Tom

- 38 years of experience with GH2 and LH2 systems
- Managed Air Projects NA Gases Engineering Group
- Managed hydrogen transfill
- Developed global hydrogen processes, equipment, and procedures with large hydrogen supplier.
- H2 codes and standards Member for Compressed Gas Association (CGA) and National Fire Protection Association (NFPA)
- Involved in numerous hydrogen hazard system reviews
- Member of the Hydrogen Safety Panel

Thomas Witte, PE
Chemical Engineer

Witte Engineered Gases

About Harold

- PhD in Chemistry
- NASA for over 30 years
- NASA Safety Standard for Hydrogen Systems
- NASA Hydrogen Safety Training Instructor
- WHA International Since 2019
- Hydrogen Design and Safety Training
- Hydrogen Risk Analysis
- Failure investigation
- Member Hydrogen Safety Panel
- Member CHS
- Member ISO TC 197
- Husband to Margie, 3 daughters and 13 Grandchildren

Topics to be covered by Harold

- Hydrogen properties
- Fire and explosion hazards
- Materials
- Liquid hydrogen hazards
- Liquid hydrogen spill procedures
- Training

Hydrogen (H_2) Properties

- **Gaseous Hydrogen (GH_2)**
  - Fuel (i.e. flammable gas)
  - Colorless, odorless, tasteless gas
  - Non-corrosive, non-toxic
  - Simple asphyxiant
  - Lightest gas
- **Liquid Hydrogen (LH_2)**
  - Non-corrosive liquid fuel (i.e. flammable)
  - Cryogenic liquid at -423 °F (-252.8 °C | 20.3 K)
  - Burn hazard if contact with skin
  - At boiling temperature, all gases except He are solid
  - ~800 times more dense than GH_2 and 14x less dense than water
  - 1 vol. liquid expands to 848 vol. gas (23x more than water)

Hydrogen
1
H
1.0078

Image from wiki/Liquid_Hydrogen

The Problem

When hydrogen mixes with an oxidizer…

…the risk of ignition is high

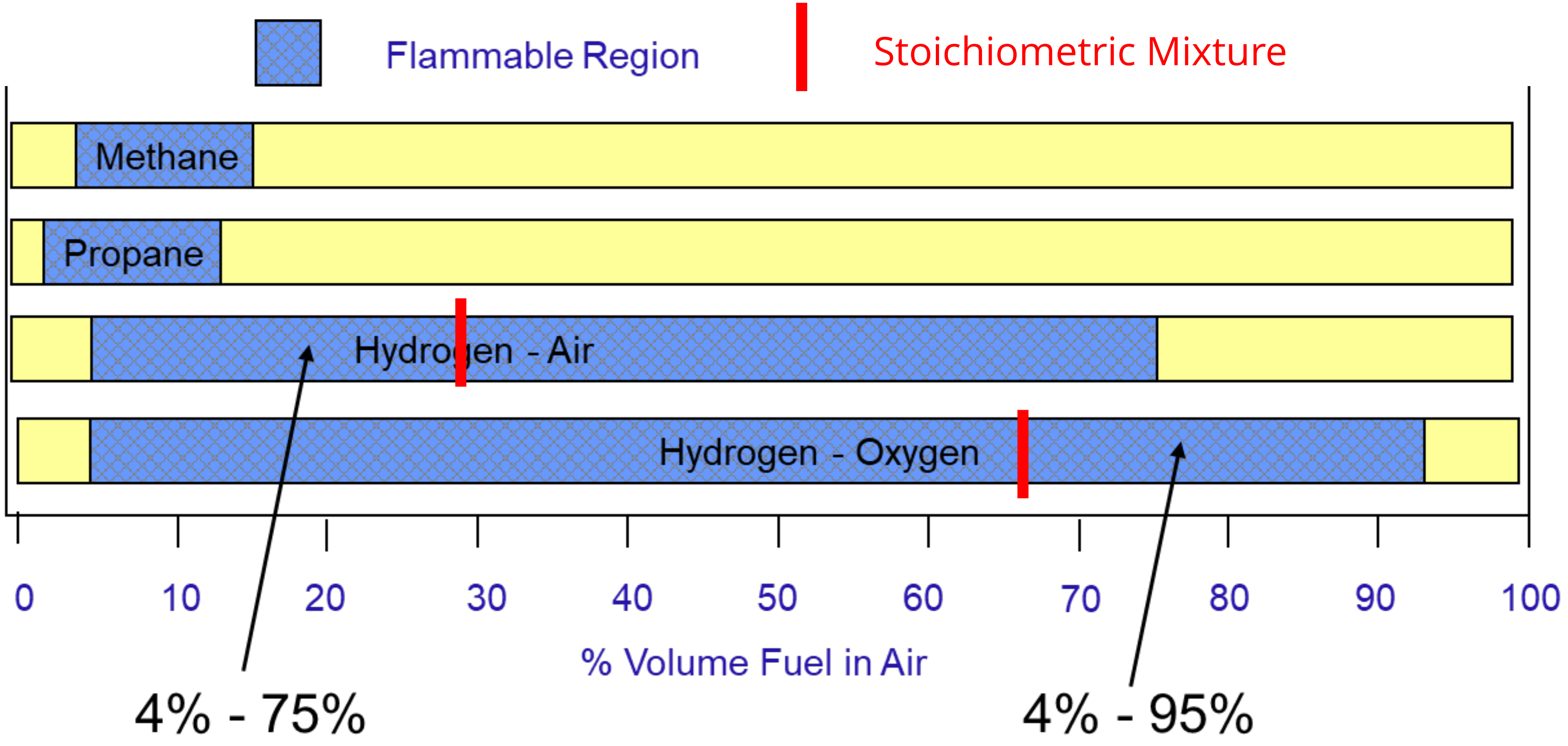
Unique Molecular Properties

Low Ignition Energy

Wide Flammability Range

In Comparison to Other Flammable Gases

At ambient pressure and temperature



In Comparison…

Min. Ignition Energy in Air @ 1 ATM	0.017 mJ (1.6×10^{-8} BTU)
Min. Ignition Energy in Oxygen @ 1 ATM	0.0012 mJ (1.1×10^{-9} BTU)

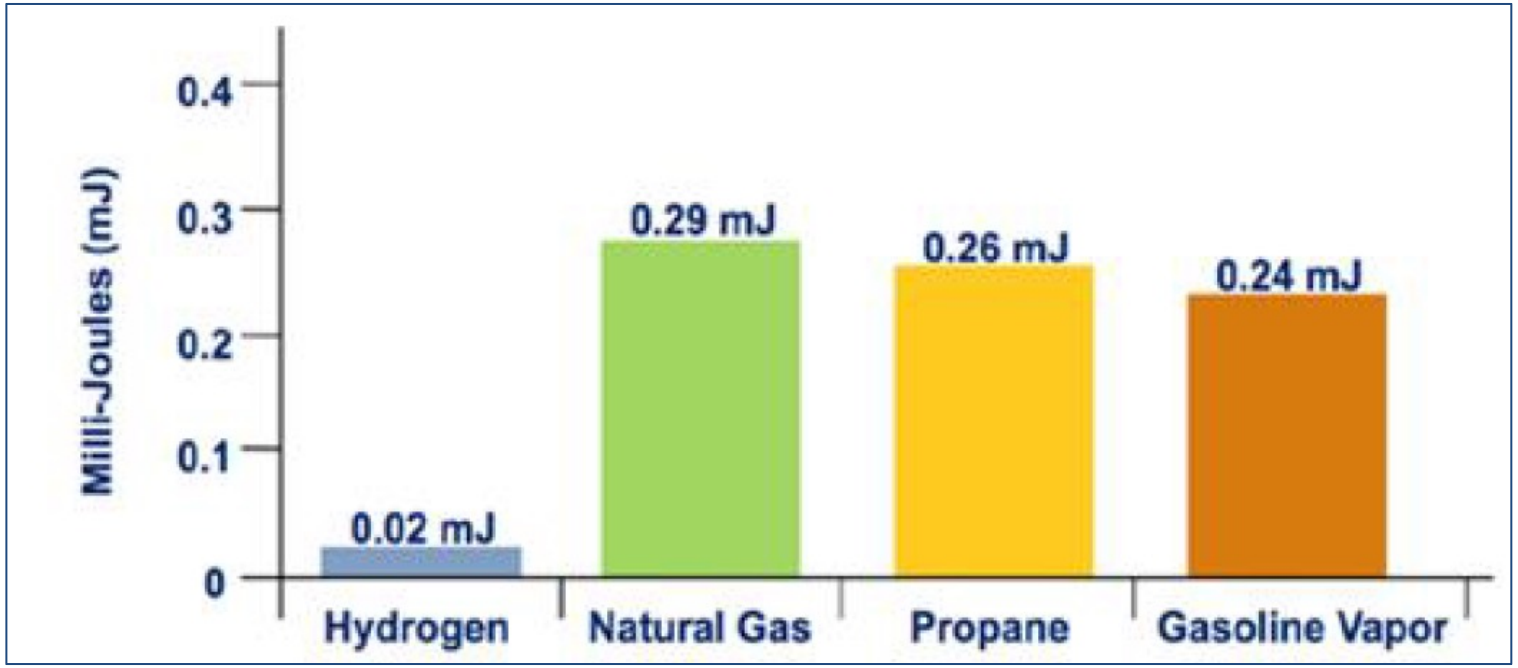
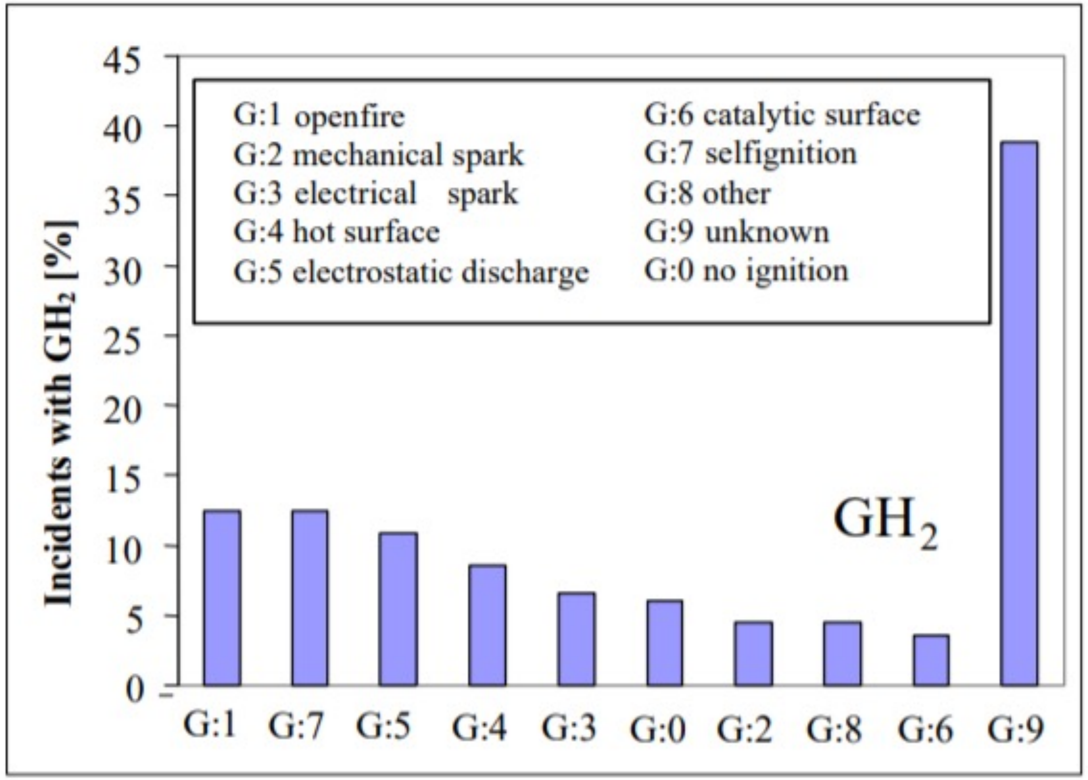


Image from H2Tools Hydrogen Compared to Other Fuels
https://h2tools.org/bestpractices/hydrogen-compared-other-fuels

Ignition Mechanism Statistics



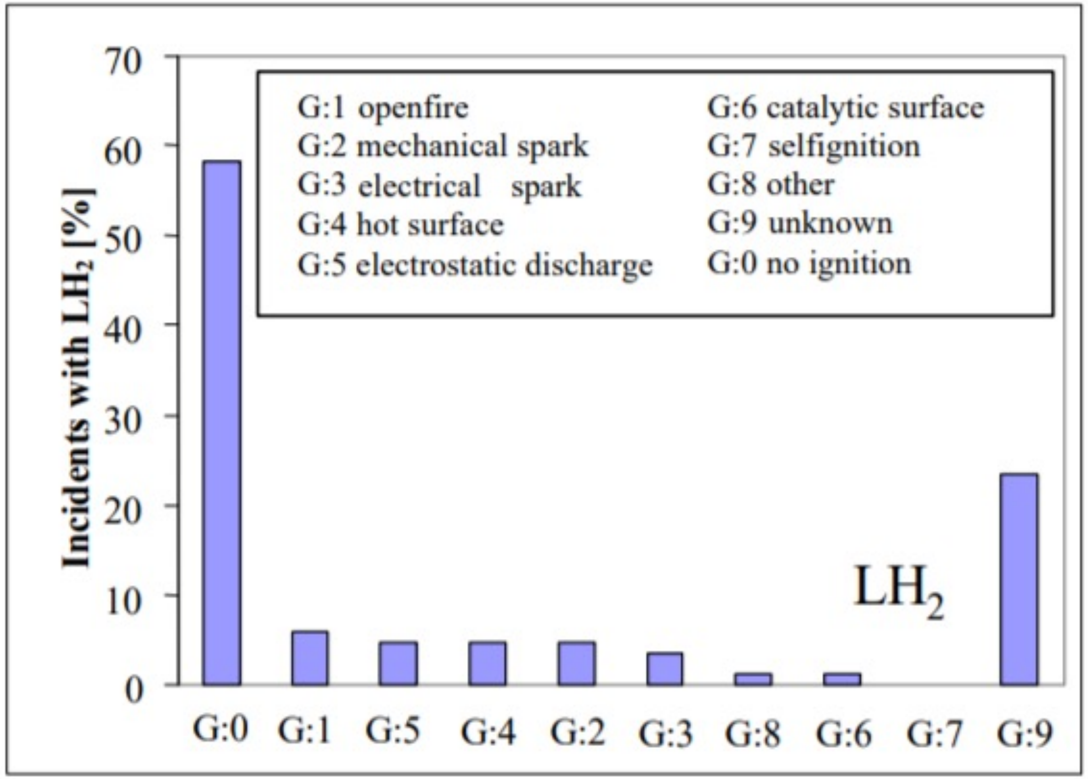


Image from: W. Breitung, Analysis Methodology for Hydrogen Behavior in Accident Scenarios 2016
Original data from: Kreiser et al. 1994

NIST H_2 Release in Garage

H_2 Concentration Near Ceiling	
16%	28.8%

- Concentration @ 15in: ~10%
- Burn down to 15 in. height
- Peak temp: 444 °C
- Deflagration speed: 7-10 m/s

- Concentration @ 15 in: ~23%
- Deflagration speed: 25 m/s
- Debris field extended 46 m (150 ft)

Examples of Preferred Materials List for LH_2

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Metals

Aluminum and alloys
Copper and alloys

Piping

- Stainless 304/304L
- Stainless 316/316L

Valves

- Forged, machined, and cast bodies (304/316 SS or brass) with extended bonnet

Fittings

Stainless steel bayonet type for vacuum jackets

Lubricants

Lubricants listed for GH2 service

Dry lubricants

PTFE

PTFE carbon

PTFE bronze

Fiberglass-PTFE graphite

Gaskets

Soft aluminum

Lead

Annealed copper between serrated flanges

Kel-F®/ Neoflon® (PCTFE)

Teflon® (PTFE)

Glass-filled Teflon® (PTFE)

O-rings

Teflon® (PTFE)

Kel-F®/ Neoflon® (PCTFE)

Stainless steel

Rupture Disk

Stainless 304/304 L

Stainless 316-316L

LH_2 Hazards

- At boiling temperature of LH_2, all gases except He become solid
  - Leaks can plug flow restrictions and/or be explosion hazards
- LH_2 has one of the highest expansion ratios of any cryogen
  - 1 vol. Liquid ➡ 848 vol. gas
  - Continuous venting required to prevent overpressure

Liquid Lockup

Video from Linde North America Training Course: Taking the Lead in Safety – Working with Hydrogen

Best Practices

- Although LH_2 vessels are designed to keep the liquid cold, boil off is inevitable
- Clear vent paths are important!
  - Trapped hydrogen will vaporize when warmed and generate overpressures in equipment if not vented
- Vent valves should not be open when not in use
  - Air intrusion may freeze, blocking relief
- Un-insulated piping, liquid, or cold vapor presents a burn risk to personnel
- System must be designed to be able to purge air and moisture
  - Use He as the inert gas

LH_2 Personal Protective Equipment

No exposure to liquid is expected

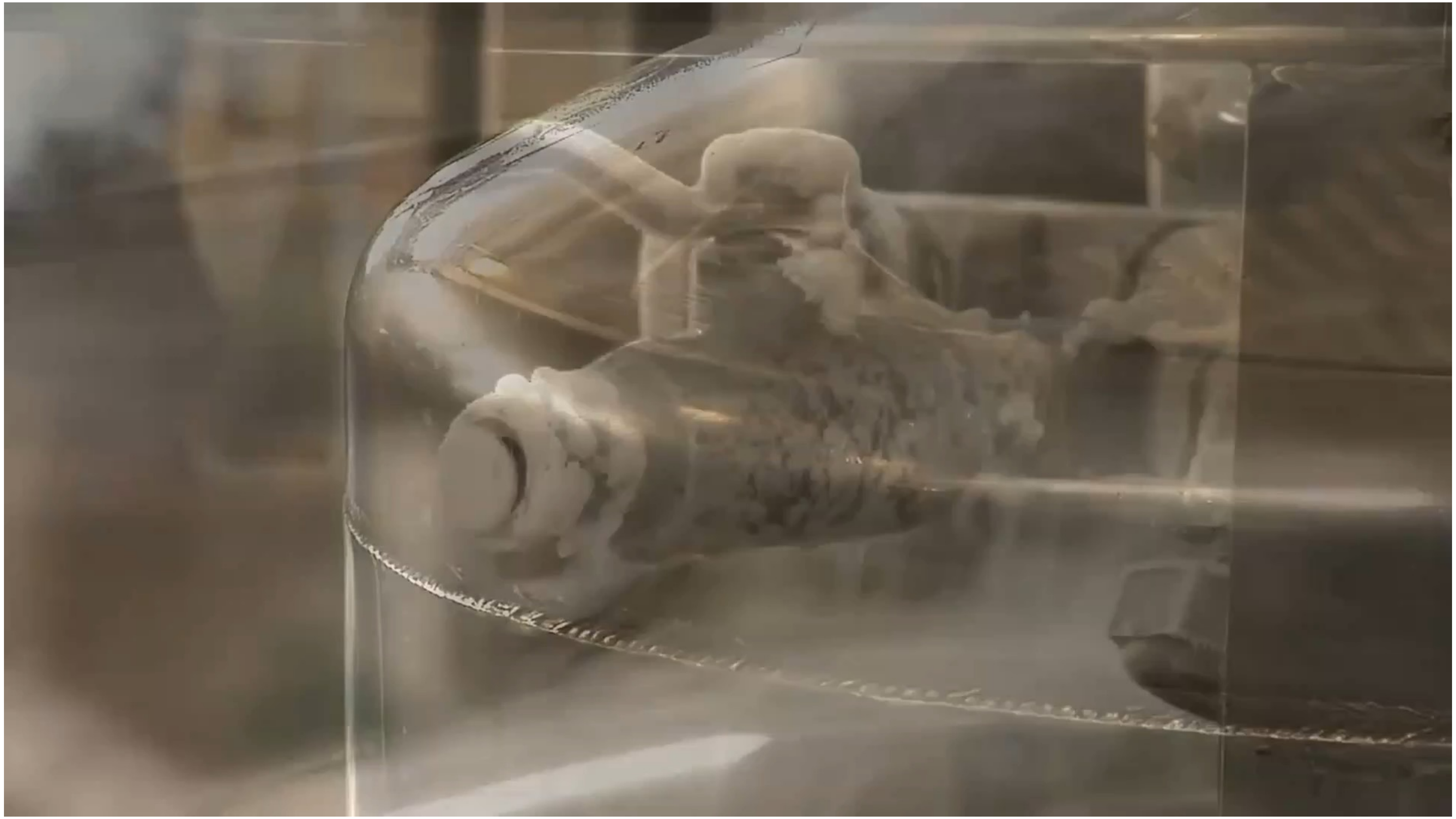
- Safety glasses
- Leather gloves
- Fire resistant clothing with long sleeves
- High-top leather boots

Possibility of liquid exposure

<u>ADD:</u>

- Face shield
- Insulated gloves

Low Temperature Results in Liquid Air Forming



Video from Linde North America Training Course: Taking the Lead in Safety – Working with Hydrogen

LH2 Leak / Spill Procedures

- LH_2 will rapidly boil or flash to a gas if exposed to ambient temperatures
- Leaks and spills will appear as fog clouds
  - Presents burn, asphyxiation, fire and/or explosion hazards
  - If possible, shut off H2 source
  - Evacuate area until liquid has evaporated and gas has dispersed below LFL
  - Be aware that the cold, dense H2 gas formed can remain close to the ground

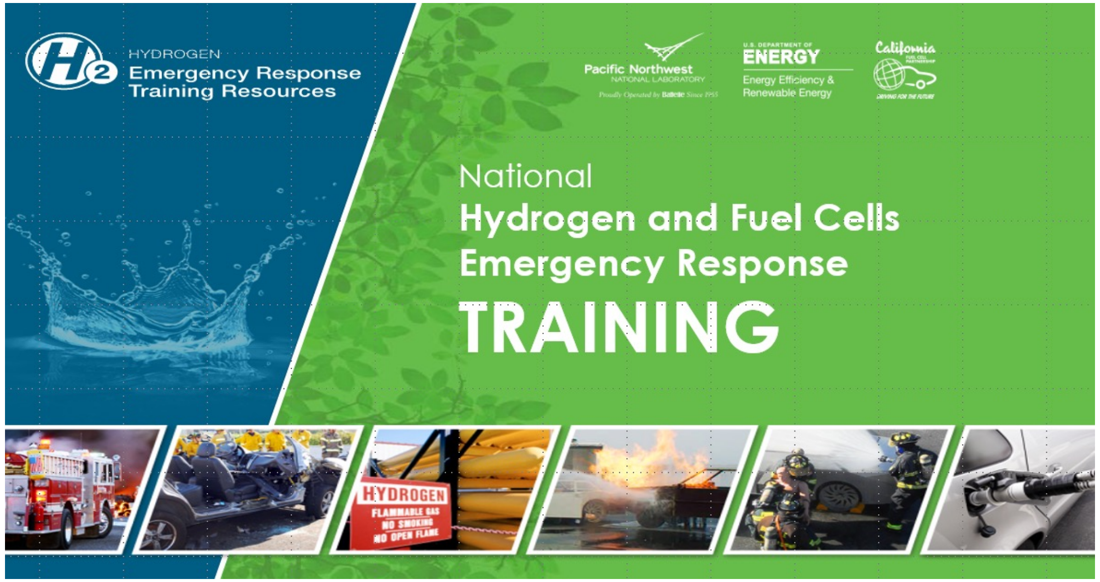
LH_2 Plume Dispersion Study

White Sands Test Facility, New Mexico

4 mph (6.4 km/h) wind	14 mph (22.5 km/h) wind
	

Training

- Training is critical for safe operation, maintenance, and emergency response.
- Include in training
  - Operations
  - Maintenance personnel
  - Site operators and personnel
  - Emergency responders is
- Training in proper maintenance procedures, including purging techniques, to assure air/hydrogen mixtures are minimized is key.
- Procedures should be planned and not developed at the final moment

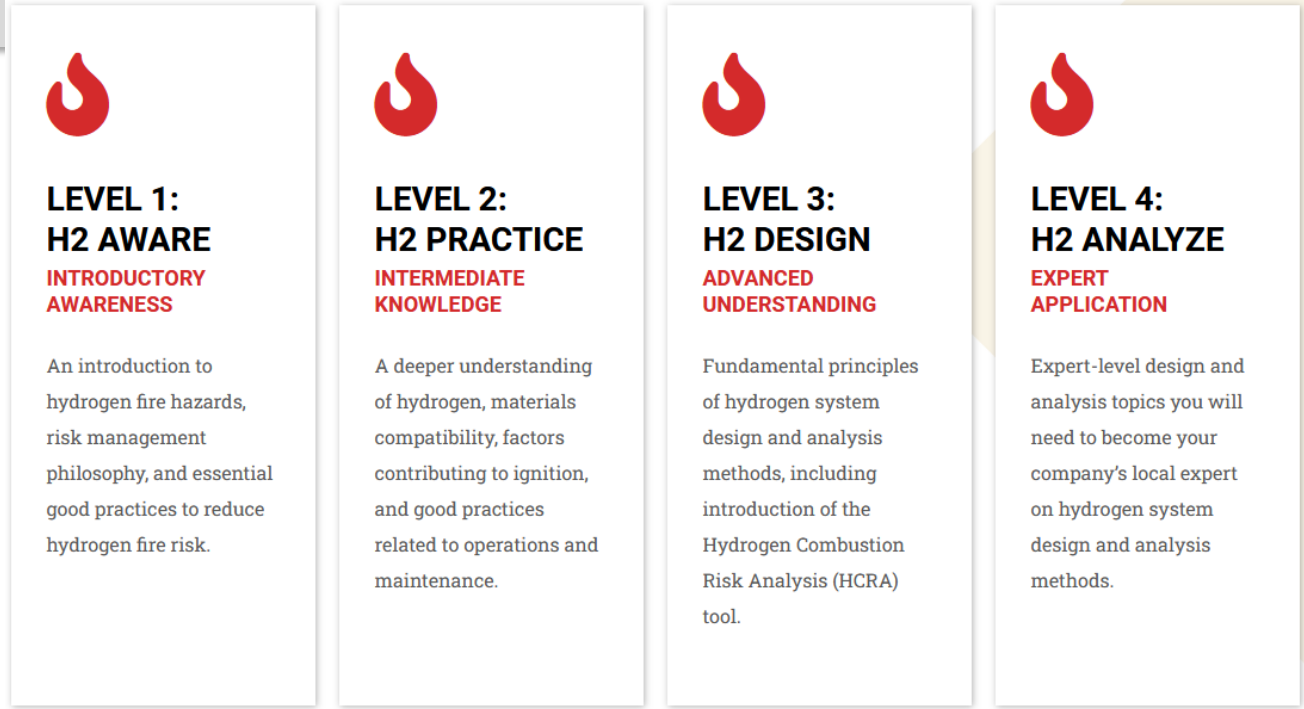


Available Training Center for Hydrogen Safety

- ELA201 Hydrogen as an Energy Carrier
- ELA202 Properties and Hazards of Hydrogen
- ELA203 Safety Planning for Hydrogen Projects
- ELA204 Safety Considerations for Hydrogen Facility Design and Construction
- ELA205 Safety Considerations for Hydrogen System Components
- ELA206 Safety Considerations for Liquid Hydrogen Systems
- ELA207 Material Compatibility Design Considerations for Hydrogen Systems
- ELA208 Hydrogen System Operation
- ELA209 Hydrogen System Maintenance and Inspection

Training and Hazard Analysis

Training with WHA International: https://wha-international.com/training/



In addition to training, we provide:

- Hydrogen systems design review
- Hydrogen component design review
- Risk analysis

Hydrogen Combustion Risk Analysis:

https://wha-international.com/hazard-analysis/hydrogen-combustion-risk-analysis-hcra

Agenda – LH2 System Design

- System
- Deliveries
- Design Scope
- Locating Systems
- Equipment
- Codes and Standard

System

- Delivered by LH2 delivery trailer into Cryogenic LH2 Tanks
- Cryogenic Liquid Tank
- Pumped and then vaporized OR
- Vaporized & compressed
- Stored onsite in intermediate storage
- Dispensed to the vehicle for fueling
- Safety Controls (LH2 only)

Liquid Hydrogen Delivery by Tanker Truck

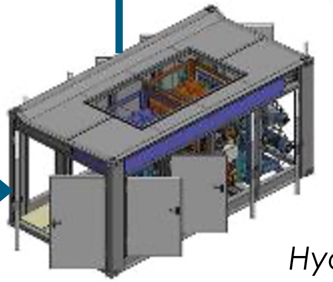
Liquid Hydrogen Storage Tank

EITHER

LH2 Pump

OR

Vaporizer



Hydrogen Compressor

Intermediate Storage

Hydrogen Dispenser

Deliveries

- Liquid Trailers
  - Medium to high usage – up to 25,000 kg/mo
  - Max pressure – 12 barg
- Pressure fill
- Pumped

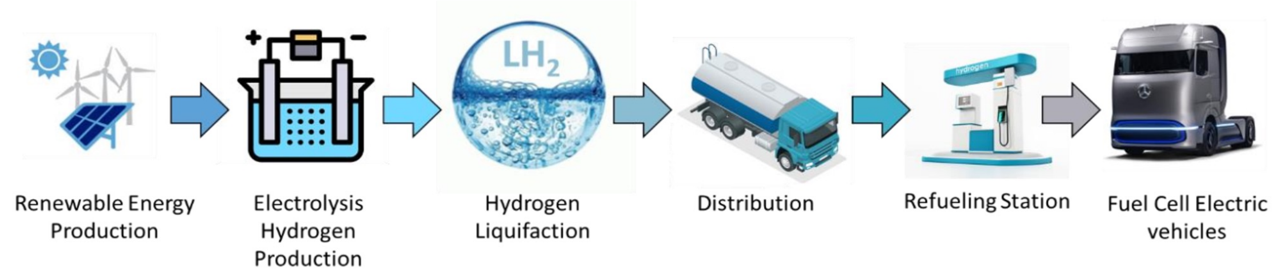


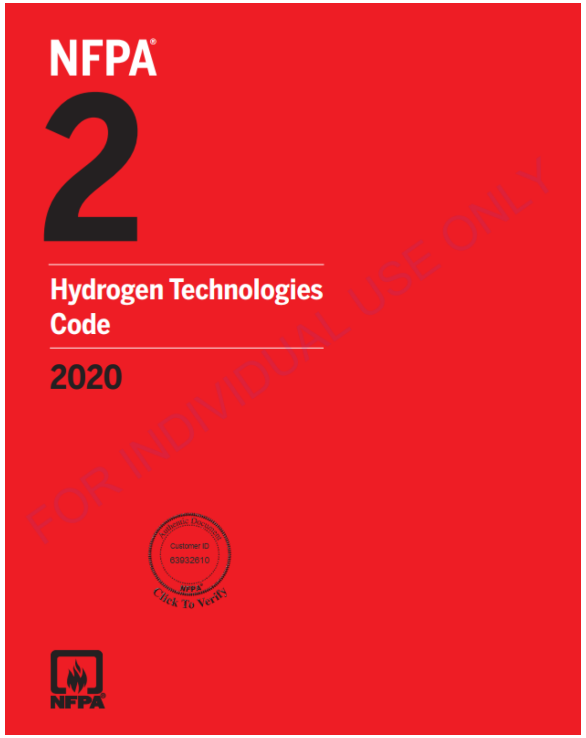
Figure 3: The green hydrogen path for LH2

Design Scope

- Pressure - less than 8 bar to pumps
- Monthly throughput - Tank size/vaporizers
- Flow rate – Size pipe sizes
- Temperature range -253 C (-423 F) to ambient temperature
- # fills and how fast - provides operating time and flow rate
    - Sizes pumps/cycles, vaporizer, piping and storage tubes
- Determine Vent Losses – Cryogens are typically “Use it or lose it”
    - Influence losses - Tank size, Pump cycles,
    - Recycle Compressor- reduces vent loss but a capital vs loss decision.

Locating Systems

- Safe Locations incorporate
  - Safety setback distances (possibly with fire barrier walls) to minimize
  - Understanding the surroundings Protection from damage from vehicular impact from delivery tankers or other vehicles.
- Setback distances are based on fire exposure not for deflagration or detonation
- Vehicle access



Equipment

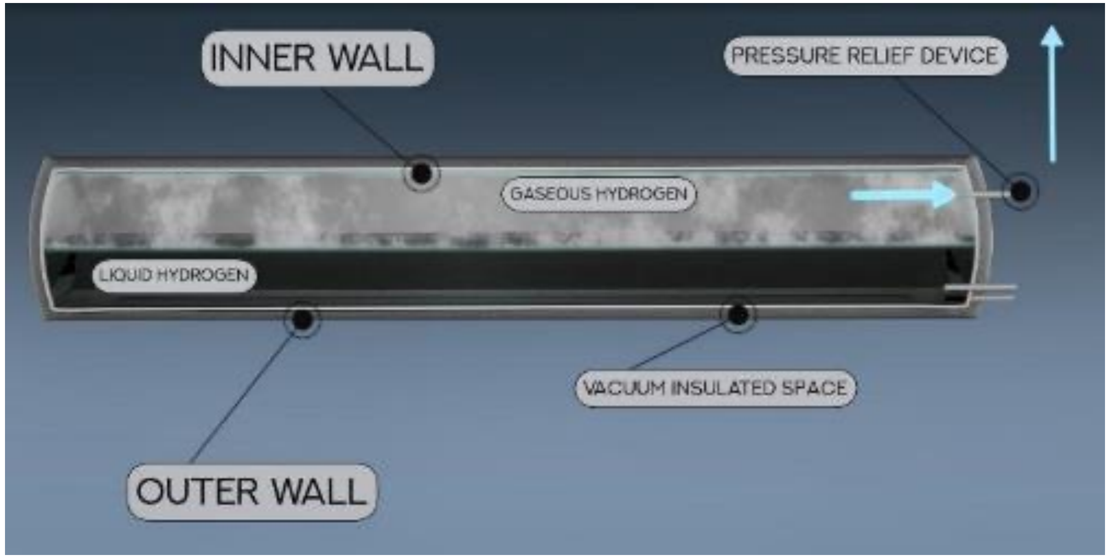
- Tank
- Vent Stack
- Vaporizers
- Pumps/Compressors
- Components
- Controls

Tank

- Double walled vessels
- Vacuum Insulated

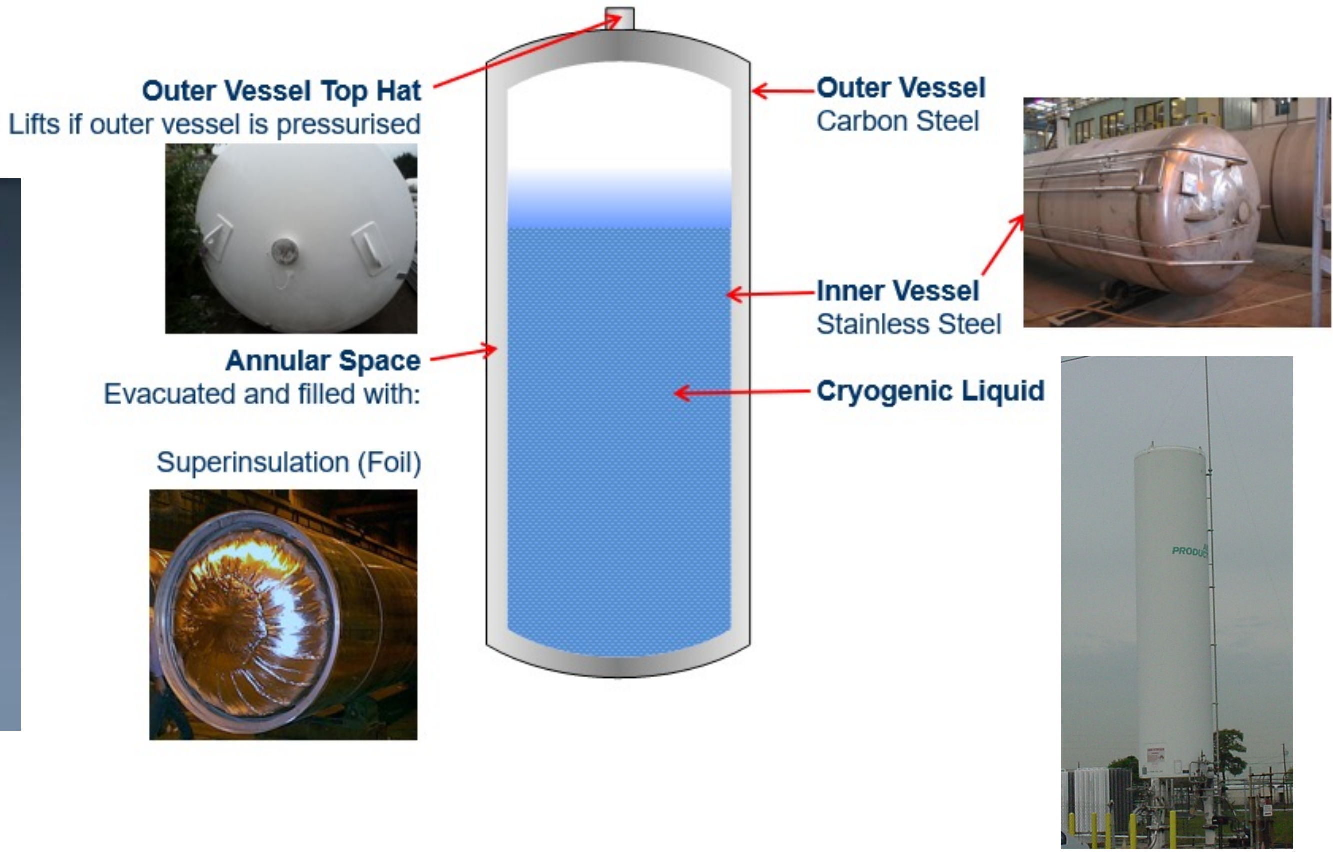
Double walled vessels

Vacuum Insulated



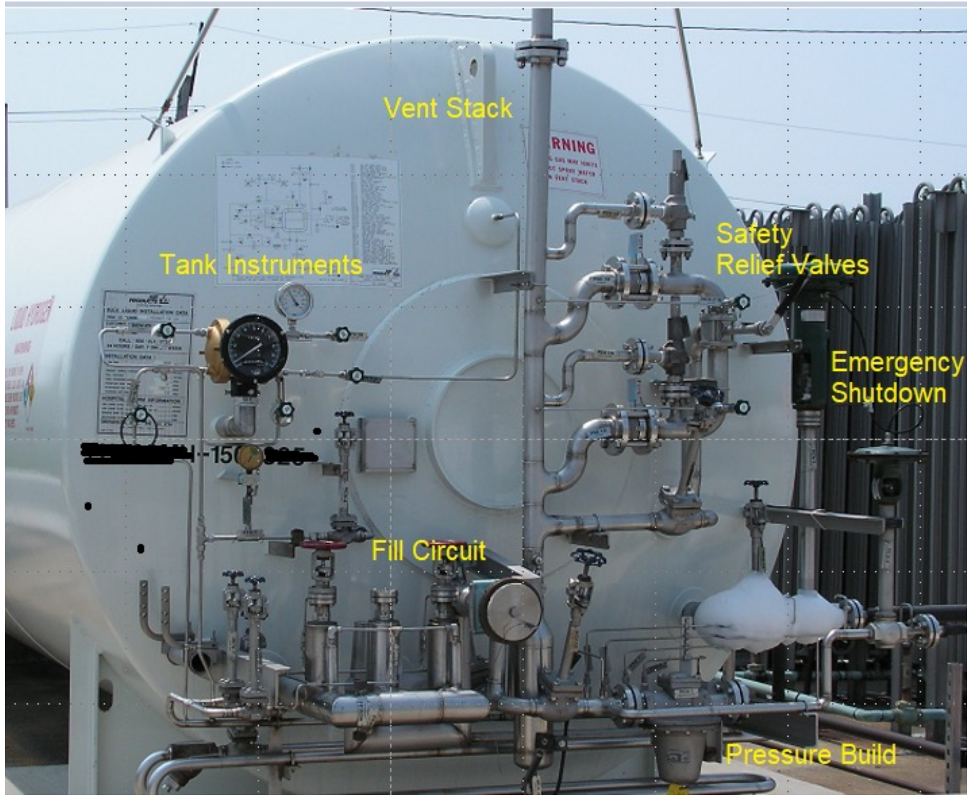
Typical Cryogenic Tank Construction

- Cryogenic tanks are double walled and vacuum insulated

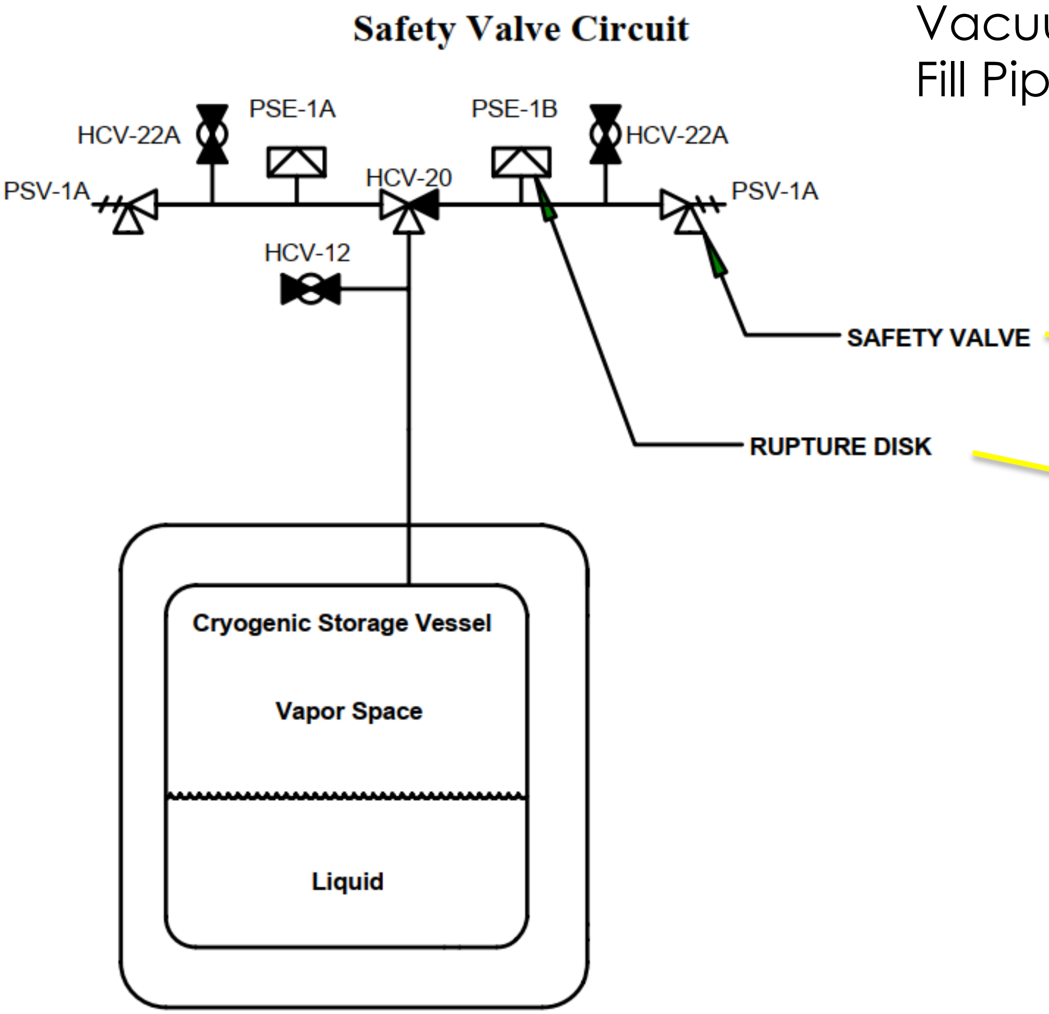


Tank Circuits

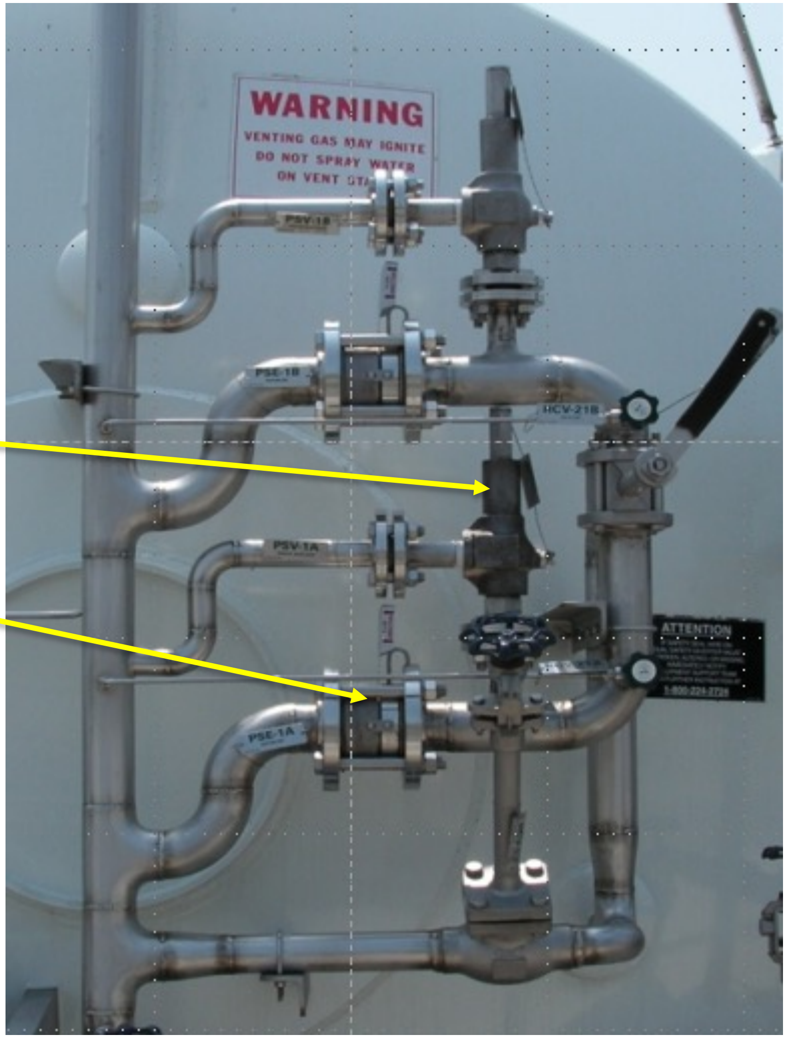
- Safety Relief
- Fill Circuit
- Pressure Build
- Instrumentation
- Tank Vacuum
- Safety Control (i.e. Emergency Shutdown)



Safety Relief Circuit



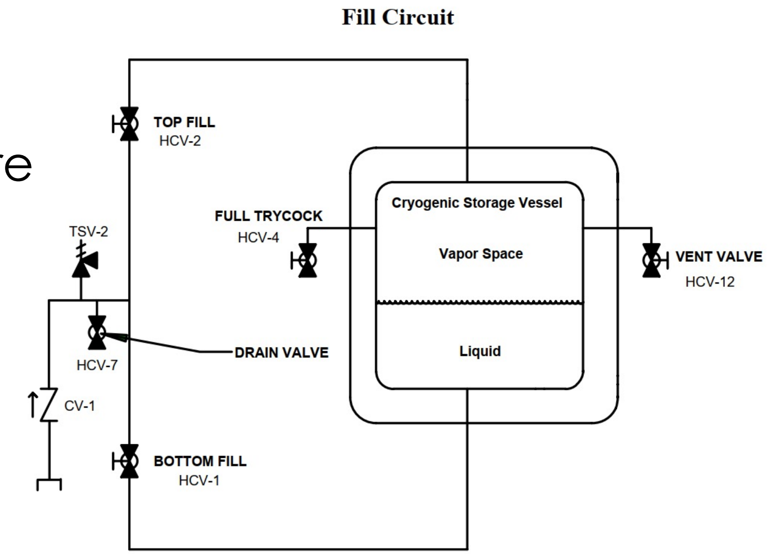
Vacuum Jacketed Fill Pipe

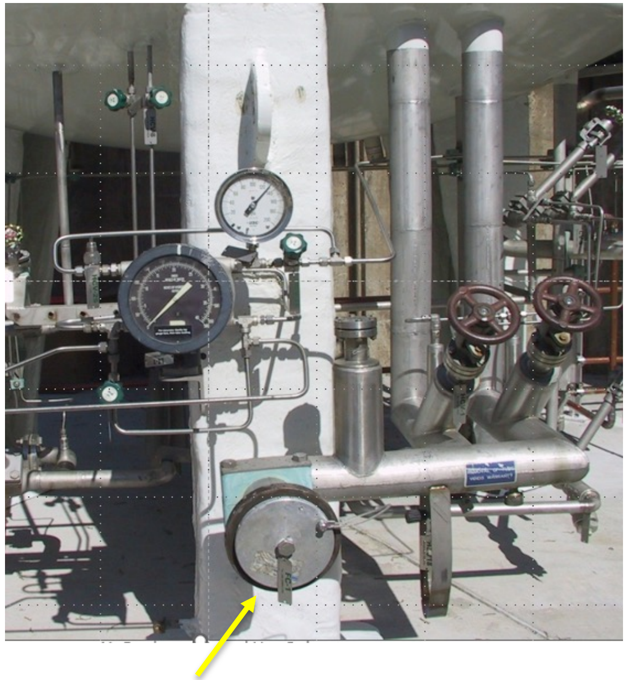


Fill Circuit

- Tank is filled to Level and with Trycock valve
  - Key item, it's a safety issue to overfill
- Top and Bottom Fill
  - Top Fill - to reduce pressure
  - Bottom Fill - to increase pressure

Vacuum Jacketed Fill Pipe

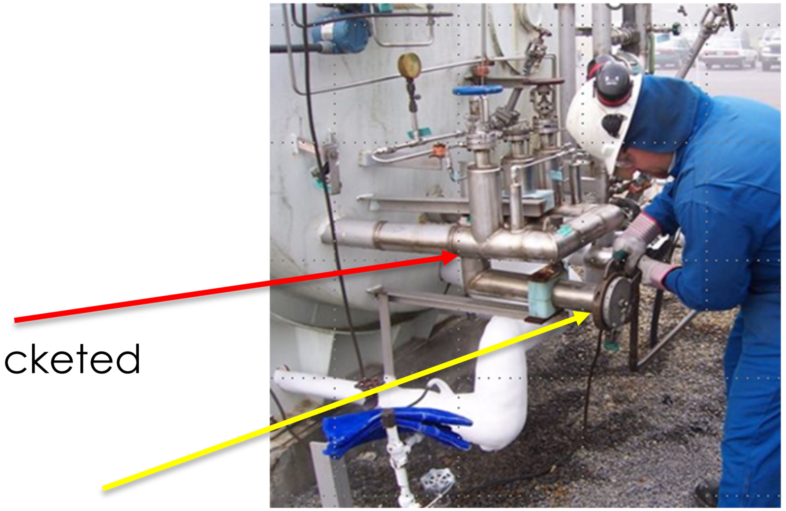




Fill Connection

Fill Piping

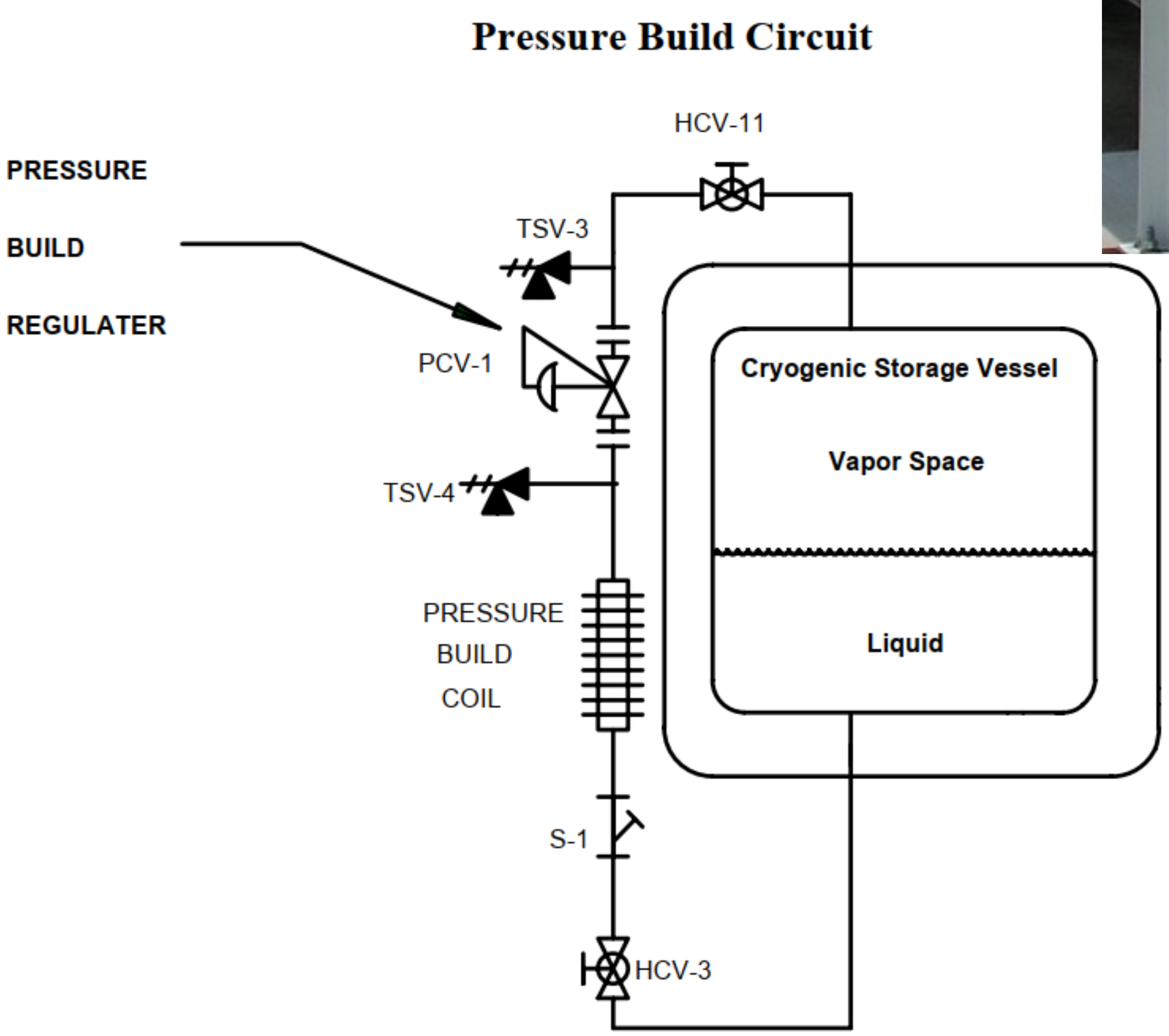
- Vacuum Jacketed Hose & Fill piping (Double wall)
- Fill Connection - Not standard
  - Bayonet, Vacuum Jacketed
    - Built for cryogenic temperatures
    - Reduce heat input and liquid air formation
    - NOT standardized
- Transfer Activity is manned by driver
  - Monitors Pressure and Liquid Level
  - Warm Hydrogen/Helium purging is needed at the beginning and end
  - Measuring Delivered Product - Flow meter or weight (scale nearby)



Vacuum Jacketed Fill Pipe

Fill Connection

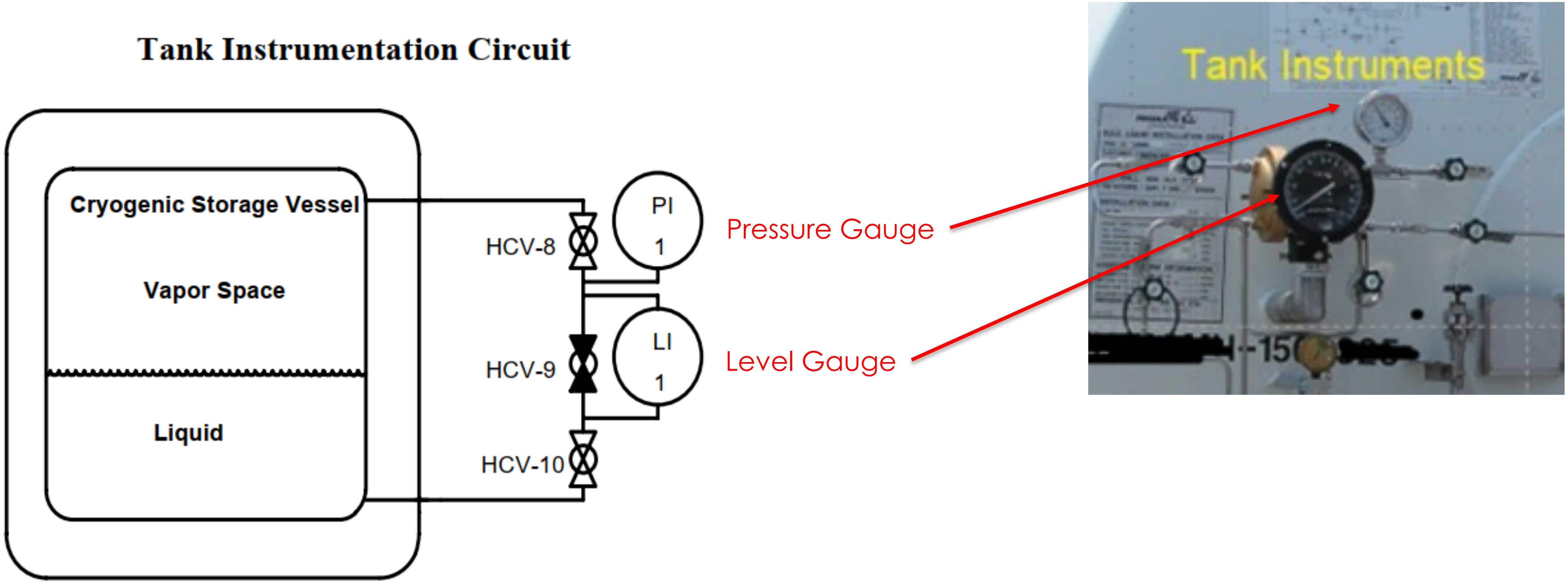
Pressure Build



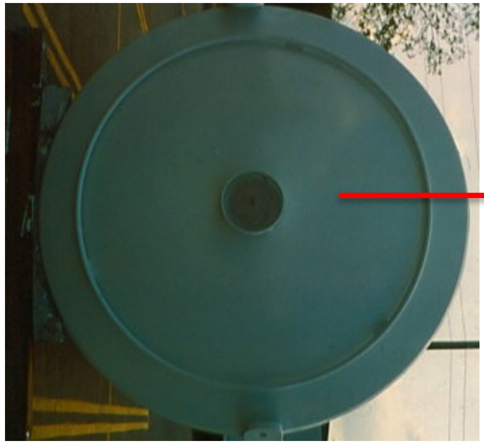
Pressure Build Heat Exchanger

Pressure Build Regulator PCV-1

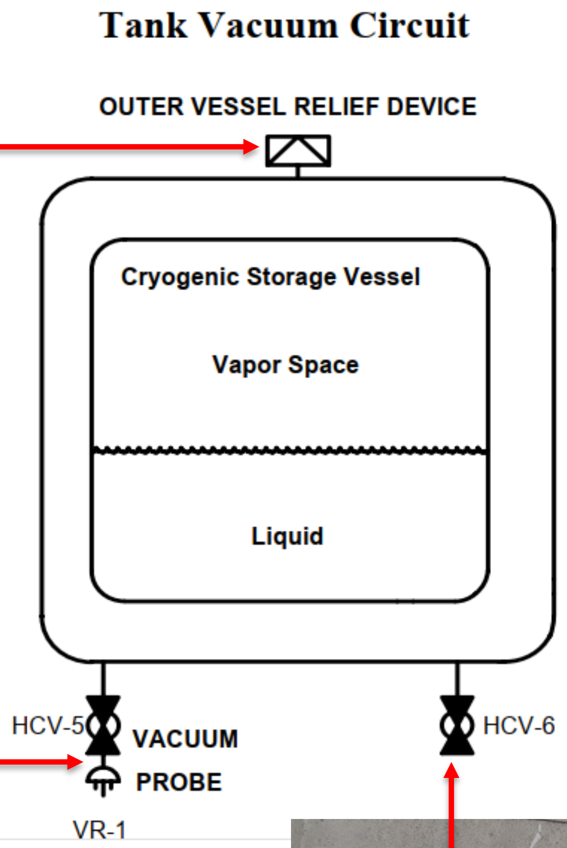
Instrumentation



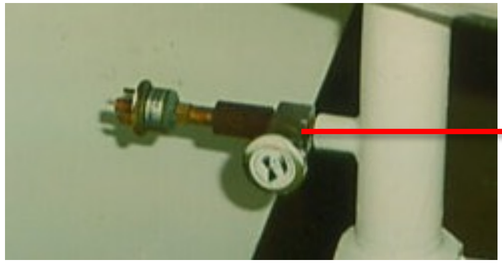
Vacuum Circuit



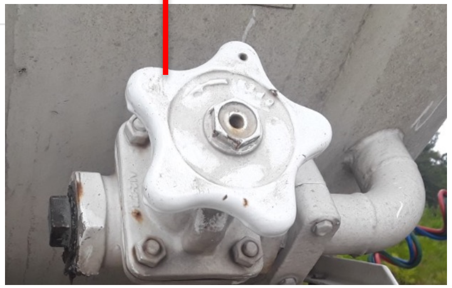
Relief
Device



Vacuum
Pump out



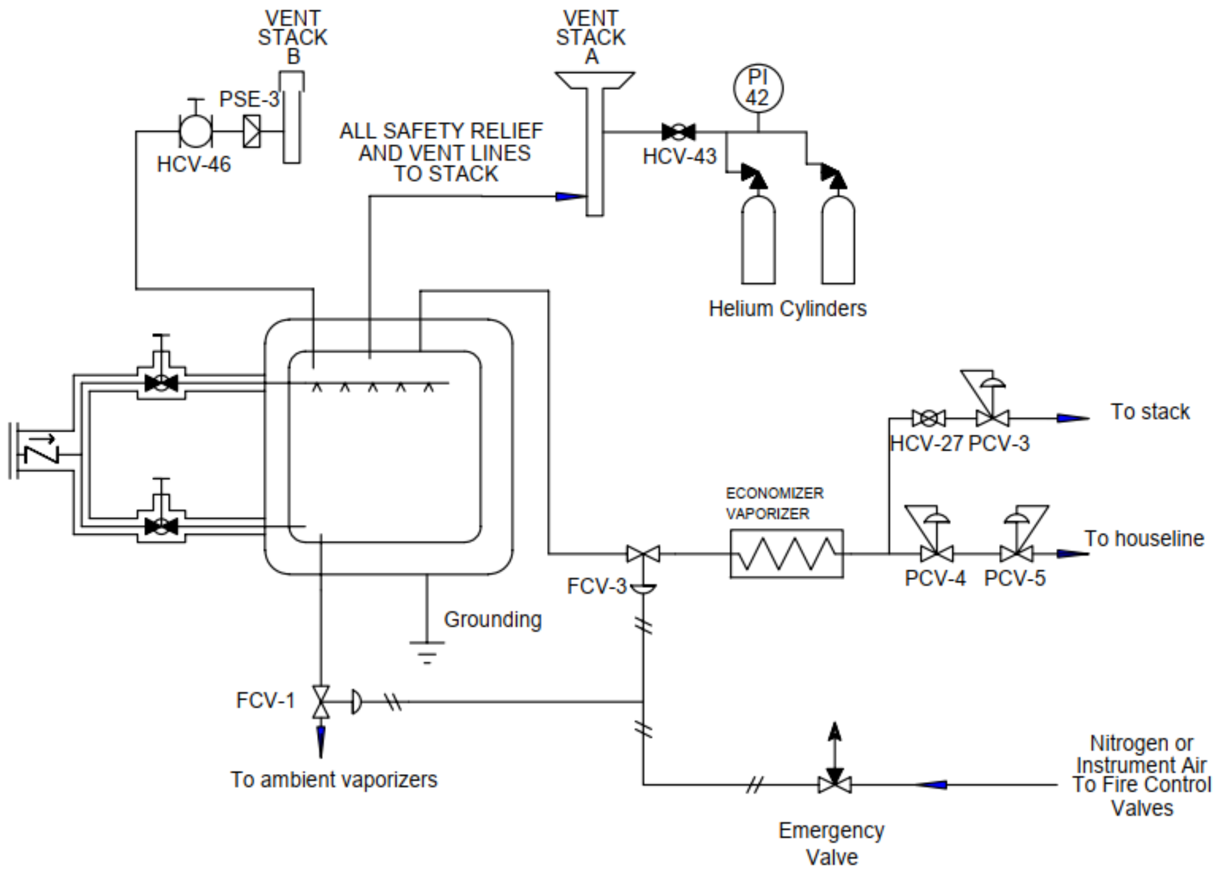
Probe to
Check Vacuum



Controls/ Emergency Shutdown

- Isolation valves (Estops)
- Vent component set to vent stack
- Secondary stack vent stack
- Equipment grounded and bonded
- Purge gas
- Electrical components designed for hydrogen (Atex or NFPA 70)

Hydrogen Tank Features

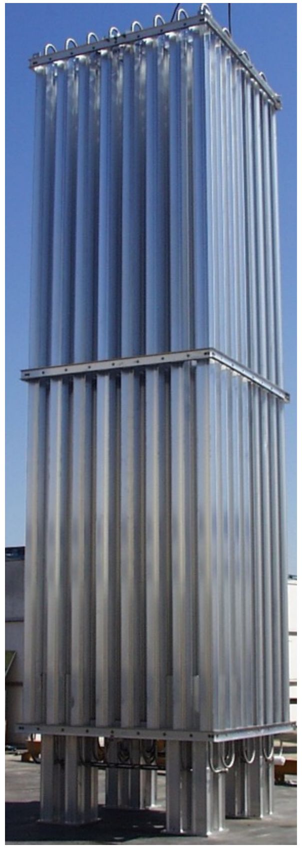


Liquid Hydrogen Venting

- More complex than GH2
- Elevated higher than GH2 to 25 ft
- Allows H2 to warm and disperse
- Cryopump air when cold inside (Moisture inside pipe)
- Liquid air condensation

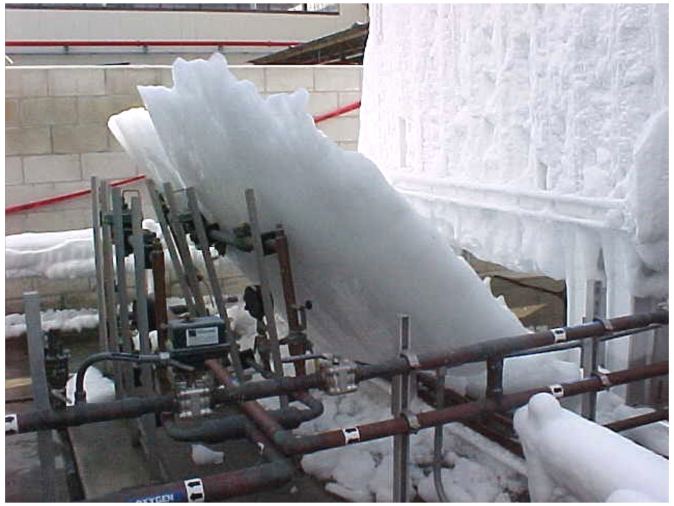
Vaporizers

- Convert LH2 to gas
- Warm to near ambient temperatures
- Can be overdrawn with too much flow in continuous service and/or cold wet weather
- Safety - Low temperature, fog, and ice issues



Vaporizer Safety Issue

- Falling Ice
- Fog
- Low Temperature



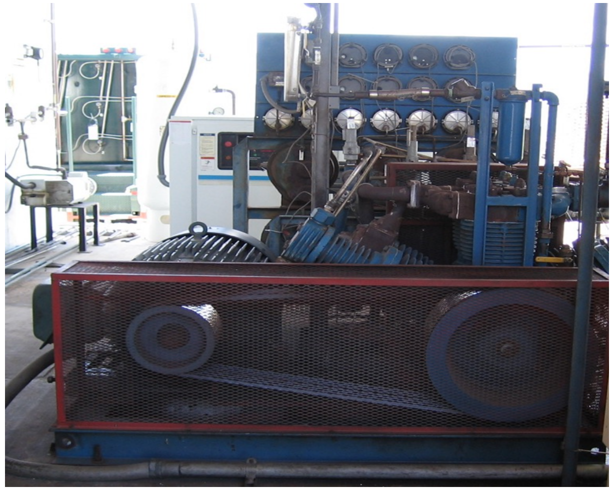
Vaporizer – Low Temperature

Compressors/ Pump

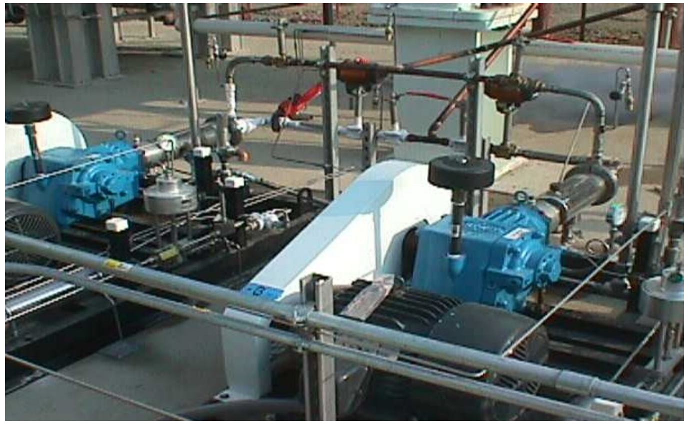
- Compressors - Gaseous hydrogen (GH2) pressure increase
- Compressors can be driven by electric motors or pneumatically

- LH2 Pump
  - LH2 pressure increase
  - Pumps are driven by electric motors. Electric motors have to meet electrical classification

Compressor



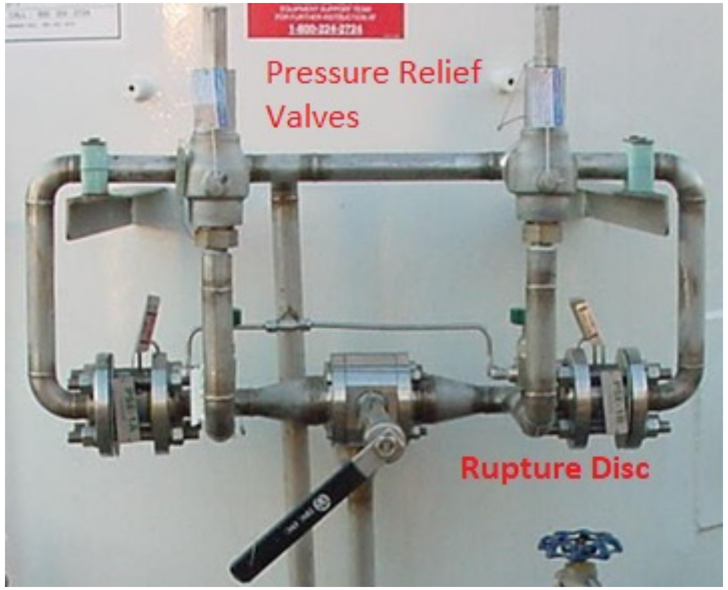
Pneumatic Gaseous Hydrogen Compressor



Cryo pumps

Component Design

- Relief Devices
- Expansion/ contraction design



Safety Controls

- Emergency Shutoff
- Low-Temperature Shutdown
- Pressure Relief Devices where liquid can expand and overpressure the system
- Pumps – High pressure and high temperature ~ -160 C (-256 F) shutdowns
- Compressors – high pressure and high temperature ~ 150 C (300 F)
- Electrical Classification – means to control ignition sources in flammable/explosive environments
  - Atex – Zone 1 or 2 (ATEX Directive for controlling explosive atmosphere (Europe)
  - NEC – Class 1, Division 1 or 2, Group B (National Electric Code (aka NFPA 70) (North America)
- Grounding and Bonding

Codes and Standards

- Asian Industrial Gas Association (AIGA)
- Compressed Gas Association (CGA)
  - H-5 – Standard for Bulk Hydrogen Supply Systems
  - H-3 Standard for Cryogenic Hydrogen Storage
  - G5.4 - Standard for Hydrogen Piping Systems at User Location
  - G5.5 – Hydrogen Vent Systems
- European Industrial Gas Association (EIGA)
  - Doc. 211/17 Hydrogen Vent Systems for Customer Applications
- National Fire Protection Association (NFPA)
  - NFPA 2 - Hydrogen Technologies Code
  - NFPA 70 (NEC) – Article 500

Codes, Standards & Regulation

- Global
  - ISO – International Standards Org
    - ISO 13984 Liquid hydrogen – Land vehicle fueling system interface
    - ISO 13985 Liquid hydrogen - Land vehicle fuel tanks
    - ISO/TR 15916 Basic consideration for the Safety Hydrogen Systems
  - Global Technical Regulations GTR 13 - Hydrogen and Fuel Cell Vehicles
  - United Nations
    - Work Party 29 Global Regulations on Pollution and the Environment Global Technical Regulations (GTR) - Hydrogen

Hydrogen Fuel Cell Codes & Standards (fuelcellstandards.com)

Thanks for Your Attention!

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CHS… Bringing together individuals and organizations to develop and share best safety practices and learnings

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