# Safety Aspects of Hydrogen at Low and High Velocity

## Materials Innovations in an Emerging Hydrogen Economy

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# OUTLINE

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CLASSICAL $H_2$ APPLICATIONS

NEW EMERGING $H_2$ APPLICATIONS

HAZARDS

- Explosive Risks, Indeterminate Atmospheres, $H_2$ Stratification
- Concurrent Hazards, Jets and Jet Fires

STORAGE & DELIVERY IN CLASSICAL $H_2$ APPLICATIONS

STORAGE & DELIVERY IN NEW EMERGING $H_2$ APPLICATIONS

MAIN STANDARDS AND GUIDEBOOKS

CONCLUSIONS

# CLASSICAL $H_2$ APPLICATIONS

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Food and Beverages – to hydrogenate edible liquid fats and oils into margarine and other semi-solid products.

Chemicals – to hydrogenate non-edible oils for soap, creams, plastic and other chemical processes and for the production of bulk, intermediates and specialty chemicals. A mixture of hydrogen and carbon monoxide is used for the large-scale production of methanol, ammonia and oxo-products like higher alcohols and aldehydes.

Pharmaceutical – to produce pharma intermediates, feedstock or reactants, reaction cooling, fermentation and process enhancement.

Electronics – to enhance heat transfer, used as ultra high purity (UHP) for controlled atmospheres in semiconductor manufacturing to increase productivity and protect against impurities.

Energy – to enhance heat transfer for cooling high speed turbine power generators and nuclear reactors and as a fuel for the growing fuel cell energy generation market.

Oil and Gas – to remove organic sulphur from crude oil, fuel oil and gasoline to enhance its performance.

Glass – used with nitrogen to prevent oxidation of molten tin in the float glass lines and improve glass quality.

# CLASSICAL $H_2$ APPLICATIONS

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Iron and Steel and Non-Ferrous Metals – for quenching and as a protective atmosphere for heat treatment at very high temperature such as in stainless steel manufacturing, also to support plasma welding and cutting.

Examples:

Annealing of Copper Strip Coils in 70%H2+30%N2 atmosphere in bell type furnaces.

Annealing Steel Strip and Wire Coils in 100%H2 atmosphere in bell type furnaces.

Annealing of Stainless Steel Wire in 80%H2+20%N2 atmosphere in continuous strand furnaces.

Brazing of Stainless Steel Parts in 70%H2+30%N2 atmosphere in continuous belt furnaces.

Sintering of Stainless Steel Powder in 100%H2 atmosphere in continuous belt furnaces.

Cooling for HPGQ (High Pressure Gas Quenching) in Vacuum Furnaces after LPC (Low Pressure Carburizing) of Carburizing Steels and Solution Treating of Austenitic Stainless Steels (in process of development).

Aerospace –fuel gas for launching spacecraft (maximum BTU/lb or KJ/kg of any fuel) and backup power systems for spacecraft.

# EMERGING $H_2$ ENERGY APPLICATIONS

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As a transportation and portable fuel, hydrogen has some interesting advantages:

• like all fuels, the reaction with oxygen releases energy and produces heat and products of combustion but unlike any other fuel the only POC is water.

• when PEM fuel cells consume hydrogen they produce up to 70% direct electrical power and only 30% waste heat as compared to IC engines that get only 30% efficiency (and 70% waste heat.

•the highest energy density with respect to mass of any fuel: 1 kg of hydrogen has the same energy of 2.4 kg of rocket (jet) fuel. This is very important for transportation applications where the vehicle must fight the forces of gravity.

• there are many pathways to producing hydrogen: reformation of natural gas or other fossil or bio fuels, electrolysis of water, as well as potential biological or photochemical methods currently under investigation.

As a transportation and portable fuel, hydrogen has one challenging disadvantage:

• even liquid hydrogen stored at 5 psig (34.5 kPa or 0.345 bar) will require 3.8 x the volume of the energy equivalent of gasoline. Compressed hydrogen is even less dense.

*Fuel tank package weight and volume is the most challenging aspect* of using hydrogen as a transportation fuel as the next slide makes quite clear.

# Why go to 700 bar?

## Density of liquid & compressed hydrogen

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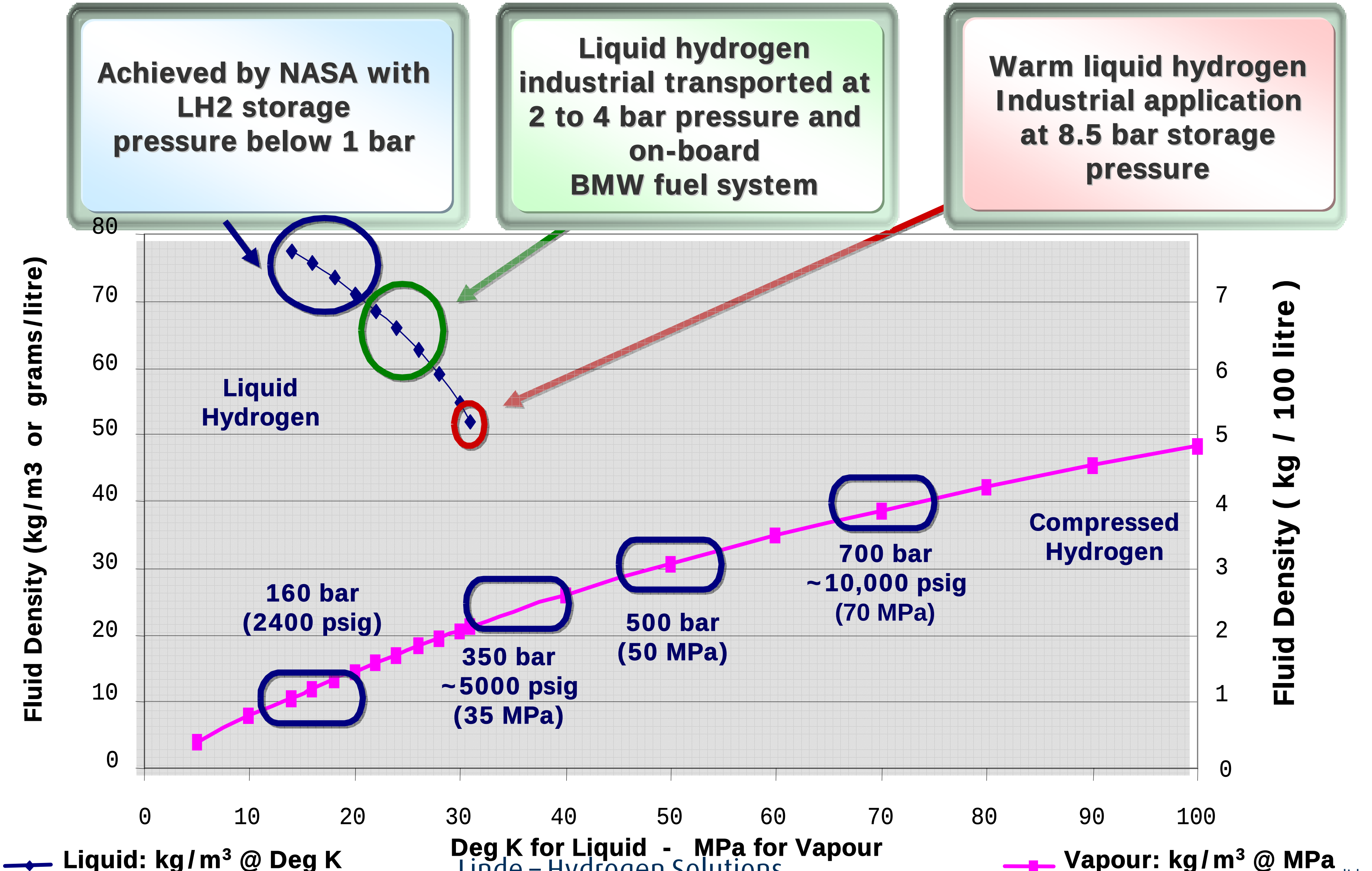

# NEW EMERGING $H_2$ ENERGY APPLICATIONS
# Fuel for portable power: tools and vehicles

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## Fuel Cell Powered Utility Vehicles

## Handheld Devices

## Back Up Power for Cell Phone Sites

Our present carbon-based energy system uses the internal combustion engine (ICE) as its main energy conversion device: either spark ignition or compression ignition. In the hydrogen cycle a fuel cell (HFC) chemically combines hydrogen and oxygen to produce water vapor and electricity at efficiencies approaching 70%.

The electric current produced by the HFC can be used to power an electric motor. The car in a hydrogen economy will be an electric car, but very different from the battery-powered cars proposed from the early days of the automotive industry.

Oil and natural gas can run through pipelines to move from one part of the country to another, but there are only a few hydrogen pipelines today and new pipelines are costly infrastructure investments. Today in the US, the most efficient means of delivering hydrogen to users is via a network of liquid hydrogen plants and road transport.

There is a growing array of compact on-site hydrogen production plants to serve large hydrogen customers with a steady, continuous demand. Liquid hydrogen storage is a cost effective backup and peak shaving system to support on-site plants and new applications.

# Fuel Cell Powered Utilty Vehicles

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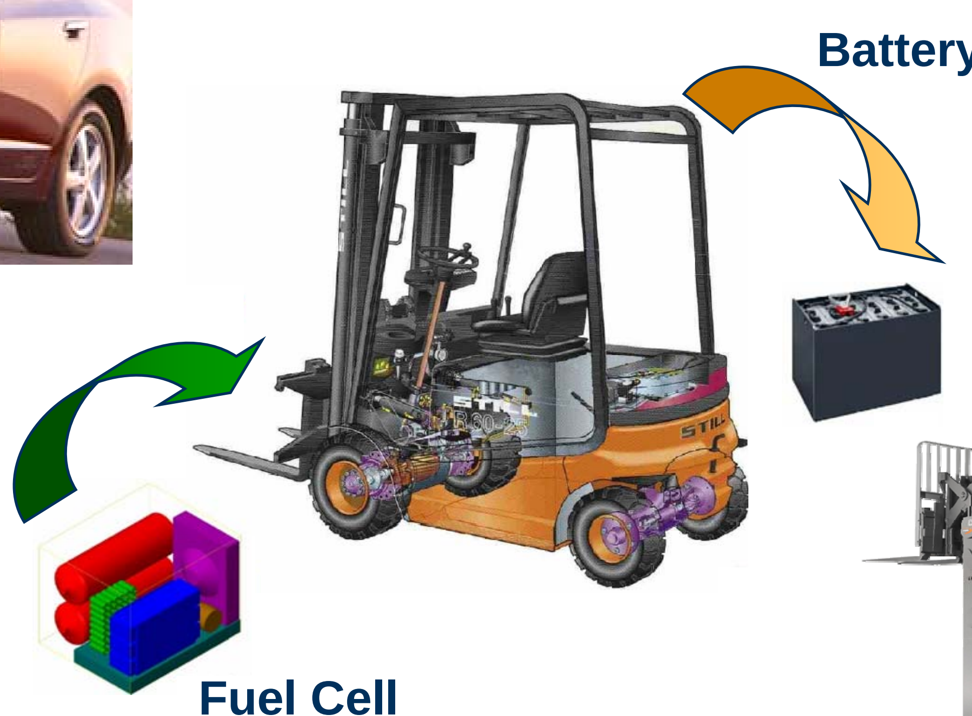
Vehicle Fueling at 25 or 35 MPa
(3600 or 5000 psig, SAE Stds)




# Micro Fuel Cells for Consumer Devices , and ...
# Fuel Cell Backup Power for Cell Phone Towers

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Micro fuel cells and hydride storage is coming to your airplane (1jan09)

Backup power using H2 fuel cells is a big market opportunity now!

# Hazards Associated with Hydrogen

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**ASPHYXIATION -** H2 leaked into enclosed spaces can reduce the concentration of O2 in air to levels which could cause death. H2 is not toxic.

**TISSUE DAMAGE –** Liquid Hydrogen is very cold -423 $^oF$ (-253 $^oC$). Contact with LH2 and cold vapor can cause grave tissue damage.

**FIRE -** H2 can be ignited by electrical sparks, heat, open flames, and static electricity. H2 has a wide range of flammable concentrations in air and a low ignition energy. H2 burns with an almost invisible flame

**EXPLOSION -** is a sudden increase in volume and release of energy in an extreme manner usually with generation of high temperature.

**Detonation:** may occur when hydrogen leaks are confined in such a way that hydrogen and oxygen are mixed in a specific, explosive, range and then ignited, resulting in supersonic flame speeds and enormous shock waves.

**Deflagrations** are characterised by subsonic flame velocity where a pressure pulse associated with rapid flame propagation acts on the elements of confinement and surrounding environment. Deflagrations happen when a major release of hydrogen first ignites. The shock wave is proportional to the mass of rich hydrogen in free air prior to ignition. A wave of oxygen streaming towards the flame front is followed by a outward shock wave of steam and heated air.

# EXPLOSIVE RISKS
# FLAMMABILITY RANGES OF COMPONENTS IN FURNACE ATMOSPHERE

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| Gas | $H_2$ | CO | $CH_4$ | $NH_3$ | $CH_3OH$ |
|---|---|---|---|---|---|
| % Volume in Air | 4.0 | 12.5 | 5.3 | 15.0 | 6.7 |
| | 74.0 | 74 | 14 | 28.0 | 36 |

Low density $H_2$ can accumulate to form explosive mixtures with air, on the top of the vertical furnaces & retorts, in roof spaces and/or other higher enclosed areas.

Solutions:

Dispose of atmosphere gases completely, preferably by combustion

Ventilate roof spaces. Natural ventilation is safer than forced ventilation by electric fan.

# MANAGING EXPLOSIVE RISKS WITH CONTROLLED ATMOSPHERE FURNACES

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Prevent air getting into the furnace.

Maintain a positive furnace pressure

Take precautions during the introduction or removal of flammable atmosphere into or from the furnace to make sure that it does not mix with air below the self ignition temperature

Do not relay on human operations alone, design safety systems,

Maintain the safety systems to schedule

Train competent personnel

Verify and apply the requirements of the NFPA 86, 2007 Edition

## EXPLOSIVE RISKS – FURNACE ATMOSPHERES
## INDETERMINATE ATMOSPHERES & H2 STRATIFICATION

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**Indeterminate atmospheres** are those that contain components (like $H_2$) that in their pure state are flammable but in the mixture used (diluted with non-flammable gases like $N_2$ or Ar) **are not reliably and predictably flammable**

N2 + 2% $H_2$ to 6% $H_2$ atmospheres are not flammable. However, nitrogen + hydrogen gases in a gravity field in vertical containers, retorts, without circulation, could stratify due to their big difference in molecular weights and densities. For example:

| Gas | $H_2$ | $N_2$ |
|---|---|---|
| Molecular Weight | 2.016 | 28.013 |
| Density [Kg/m$^3$] at 21.1 ºC & 1 atm | 0.0834401 | 1.1605 |
| Densitiy [lb/ft$^3$] at 70 ºF & 1 atm | 0.005209 | 0.07245 |

# MANAGING EXPLOSIVE RISKS – FURNACE ATMOSPHERES

A burn-off pilot flame-torch or glow-plugs should be installed where $N_2$ + $H_2$ or $H_2$ (or another flammable gas) is coming out from the furnace. Pilots should remain lit under inert atmosphere.

Make sure that the fan works and circulates the atmosphere in furnaces (ex: bell type furnaces).

After more than five inner volume changes by $N_2$ purging and after removing the retort from the base, a flame torch should be used to make sure that no hydrogen is left on the top of the retort of the bell type furnace.

As long as the retort is anchored and sitting on the base in a vertical position, no welding should be performed.

Note: $H_2$ is much lighter than air and therefore dissipates rapidly when released or leaked.

Some metals can become brittle when exposed to hydrogen, so design of safe hydrogen systems should be performed by specialist in the field. Hydrogen embrittlement is particularly problematic at pressures greater than 100 bar (1500 psig)

# EXAMPLE OF CONCURRING HAZARDS, NFPA 86, 2007 EDITION

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## Ex: Low Temperature Protection of Piping, may be a Case of Concurring Hazards

In case of a 100% $H_2$ furnace atmosphere and carbon steel piping downstream the $N_2$ vaporizer. If using a shutoff device, no $N_2$ for purging would be available for purging $H_2$ out of the furnace, in case of an emergency.

NFPA 86, 2007 Edition, 12.1.9.2: Pressure vessels and receivers shall be constructed of materials compatible with the lowest possible temperature of special processing atmospheres, or controls shall be provided to stop the flow of gas when the minimum temperature is reached.

A low temperature shutoff device used as prescribed in 12.1.9.2 shall not be installed so that closure of the device can interrupt the main flow of inert safety purge gas to connected furnaces containing indeterminate special processing atmospheres. *(Linde Note: No temperature shutoff device is recommended for the vaporizer on the nitrogen purging supply line.)*

If closure of a low temperature shutoff device creates any other hazard, an alarm shall be provided to alert furnace operators or other affected persons of this condition.

# SOLUTIONS TO CONCURRING HAZARDS
# NFPA 86, 2007 EDITION

Dedicated emergency ambient air vaporizer – *The emergency ambient air vaporizer is connected in parallel with the process vaporizer. It is used only when the low temperature shutoff valve has been actuated, indicating that the process vaporizer has been overdrawn.*

Low liquid level gauge on the bulk storage tank – *The bulk storage tank will have a liquid nitrogen level gauge that will indicate when the minimum amount of nitrogen remains to purge all applicable furnaces with 5 volume changes of nitrogen.*

Visible and audible alarm at the furnace operator station – *The visible and audible alarm panel serves to alert the furnace operator that the low temperature shutoff valve has been activated, and nitrogen is flowing through the emergency vaporizer.*

Low pressure switch *is installed to indicate a drop in the nitrogen supply pressure. It is tied in to visible and audible alarm panel to indicate that nitrogen is flowing through the emergency purge vaporizer instead of the process vaporizer.*

# SOLUTIONS TO CONCURRING HAZARDS
# NFPA 86, 2007 EDITION

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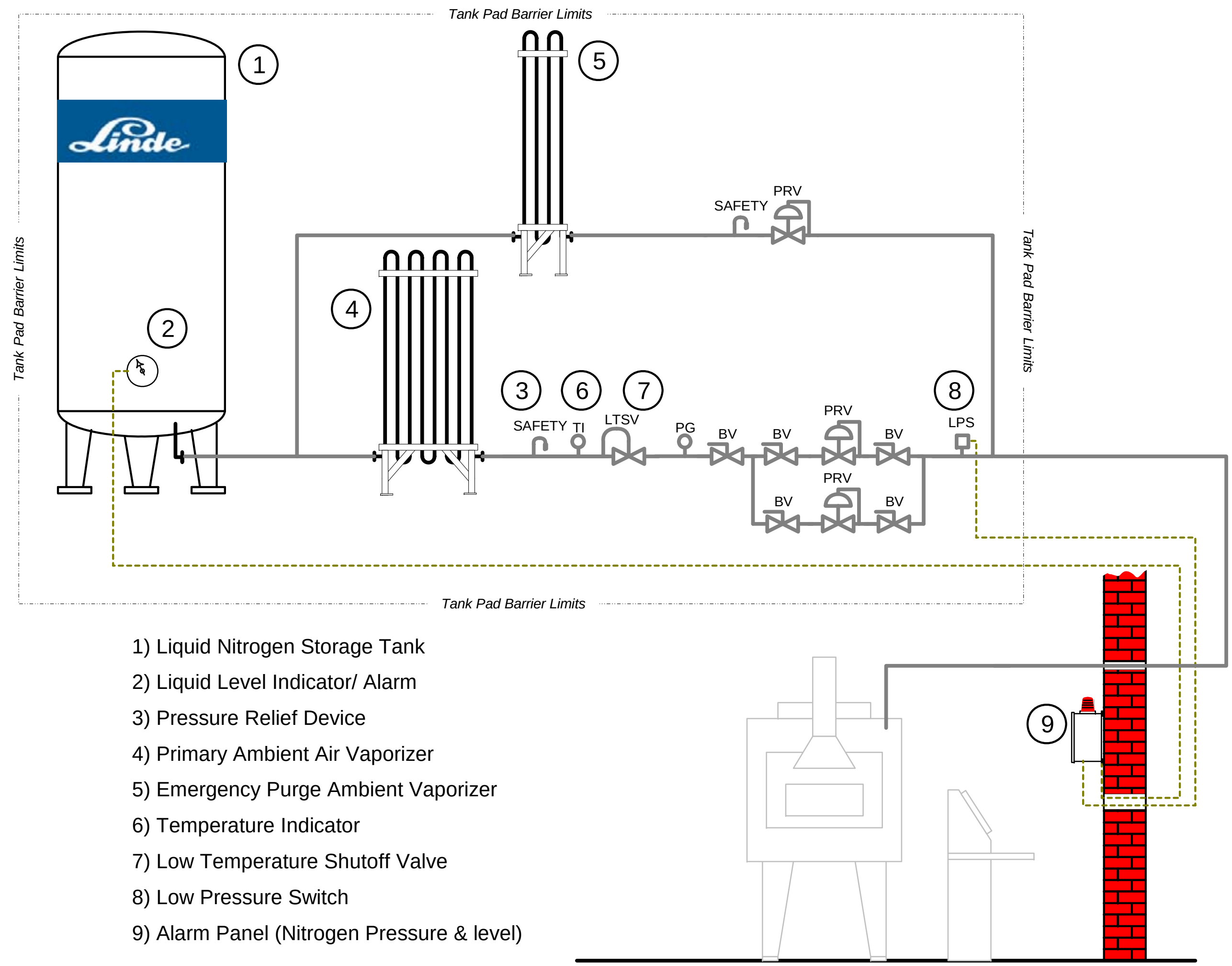


1) Liquid Nitrogen Storage Tank
2) Liquid Level Indicator/ Alarm
3) Pressure Relief Device
4) Primary Ambient Air Vaporizer
5) Emergency Purge Ambient Vaporizer
6) Temperature Indicator
7) Low Temperature Shutoff Valve
8) Low Pressure Switch
9) Alarm Panel (Nitrogen Pressure & level)

# Fueling fork lift trucks and other utility vehicles
## A brief review of the developing standards for safe fueling

# Pressure Ratings Comparison : ASME , DOT, NGV

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| | ASME (steel) | DOT (steel) | NGV (composite) |
|---|---|---|---|
| **Service Pressure** | Up to MAWP | At 70 deg F | At 15 deg C |
| **Maximum fill pressure** | Up to MAWP (90 to 95% of MAWP is typ.) | 1.00 to 1.10 x service pressure (as stamped) | 1.25 x service pressure |
| **Need for periodic inspection** | None, except PRD every 5 years | Hydrostatic or ultrasonic test every 5 years | Annual visual inspection |
| **Lifetime** | Unlimited | Unlimited | Currently limited to 15 years |

# Pressure Ratings for vehicle tanks fueling at 25, 35 and 70 MPa

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Dispensing systems shall be equipped to stop fuel flow automatically when a fuel supply container reaches the temperature-corrected fill pressure.

| | | | | |
|---|---|---|---|---|
| **Service Pressure** | **MPa**<br>**psig** | **25**<br>**3626** | **35**<br>**5076** | **70**<br>**10153** |
| **Max Hot Fill Pressure (1.25 x SP)** | **MPa**<br>**psig** | **31.25**<br>**4532** | **43.75**<br>**6345** | **87.5**<br>**12691** |
| **Overpressure Limit (1.40 x SP) : Max PRD setpoint** | **MPa**<br>**psig** | **35**<br>**5076** | **49**<br>**7107** | **98**<br>**14214** |

Dispensing systems shall be equipped with an overpressure protection device (PRD) set at no greater than 140 percent of the service pressure of the fueling nozzle it supplies.

The vehicle tank is protected with a **thermally activated PRD**, but during filling, the **dispenser must also protect the tank with a pressure activated PRD**

# Responsibilities of the dispenser system for the vehicle tank

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**The dispensing system** must be listed, labeled, or approved to insure that the fills are protective of the safety of the temperature, pressure and flow rate of the on-board fuel system during fueling **(MI: 4-3.9.1 (e))**

**Dispenser control system.** The dispensing device shall provide a means to prevent over pressurization of the on-board storage container and in accordance with the following:

1. The maximum pressure of the vehicle fuel storage system **shall not exceed 125% of the on-board storage container service pressure.**

2. The on-board storage container and its integral appurtenances **shall not exceed 185oF** (85C) during the fueling operation.

3. The hydrogen content of the on-board storage container **shall not exceed the gas density of hydrogen at the service pressure and 59oF** (15C).

4. An over-pressure relief device **[Pressure Relief Valve (PRV)] shall be provided for the dispenser, set at no greater than 140% of the service pressure** of the on-board, vehicle fuel storage container

**HIPOC proposal to ICC #F234**

The compressed hydrogen vehicle fueling dispenser has a number of critical safety functions with respect to safe fueling and the pressure vessel on-board the vehicle:

— Dispensing systems shall be equipped to stop fuel flow automatically when a fuel supply container reaches the temperature-corrected fill pressure (the gas density of hydrogen at service pressure and 15 degrees C),

— The maximum pressure of the vehicle fuel storage system shall not exceed 125% of the vehicle storage tank service pressure.

— Dispensing systems shall be equipped with an overpressure protection device set at no greater than 140% of the service pressure of the fueling nozzle it supplies.

CGA H-5 Hydrogen Installation Standard – 2008 -Section 8.10

# The dispenser must manage the increased target pressure as the vehicle storage tank heats up during a fill

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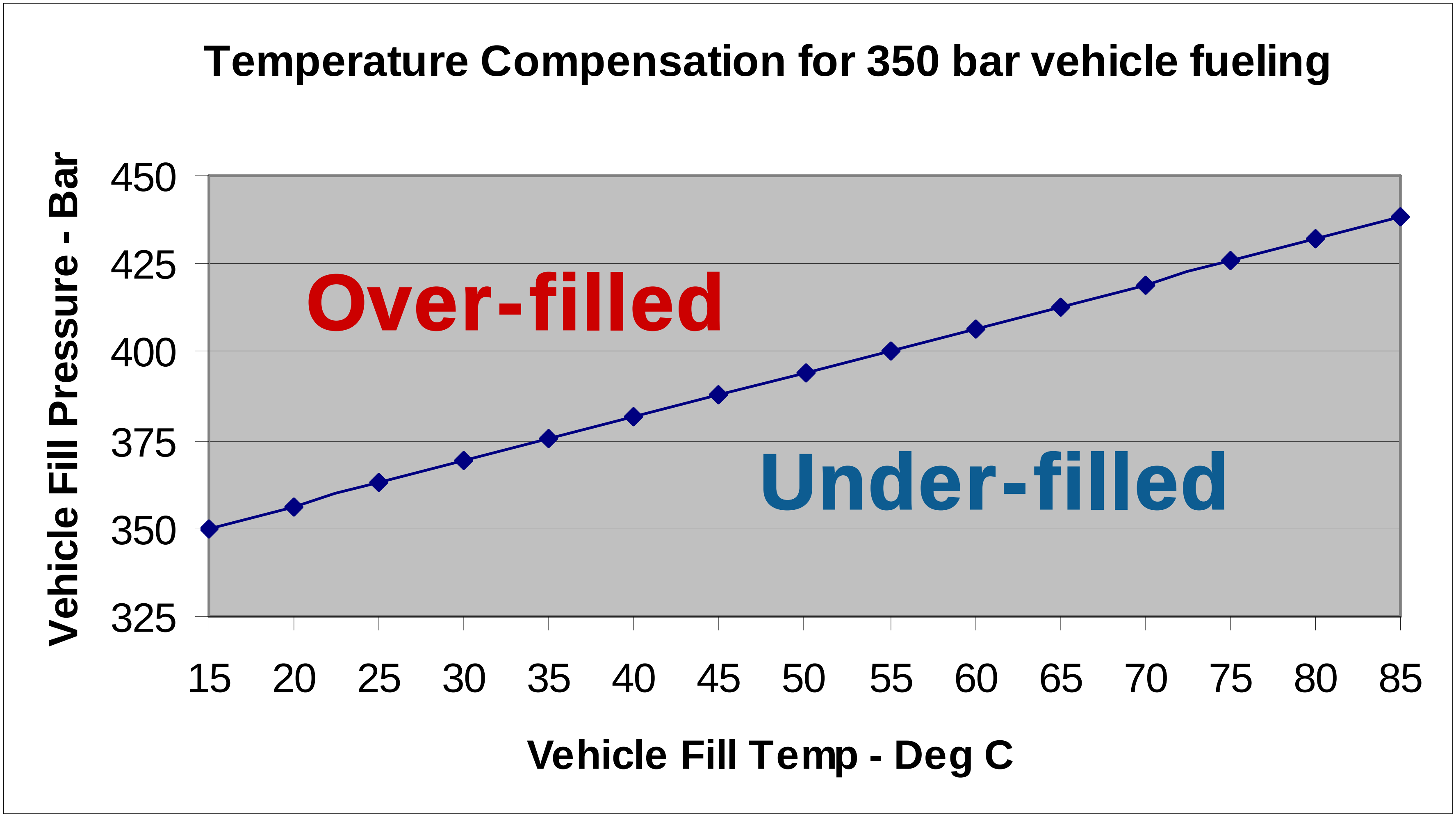


350 bar target Density = 24.022 g/liter

# If you're filling a big vehicle inside a small room, you need ventilation

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*MI 4-3.9.(g)* **A ventilation system shall be installed for the dispensing area.** The ventilation system shall be capable of delivering ventilation air as provided in section 4.3.7. **The ventilation system shall operate prior to dispenser operation, during fueling, and for at least 1 minute after fueling has been completed**. The ventilation flow rate shall be monitored. Failure or reduction of the ventilation flow rate below the required flow rate shall shut down the dispensing system.

*Exception: A dispensing area ventilation system is not required when the fuel delivery per refueling event is less than those listed in table 4-3.9.*

| Room Size (m3) | **Maximum fuel delivery per refueling event that does not require room ventilation (kg)** |
|---|---|
| **1000** | **0.8** |
| **2000** | **1.7** |
| **3000** | **2.5** |
| **4000** | **3.3** |
| **5000** | **4.2** |

# The area around the dispenser is being defined as a Class 1 Div 2 area.

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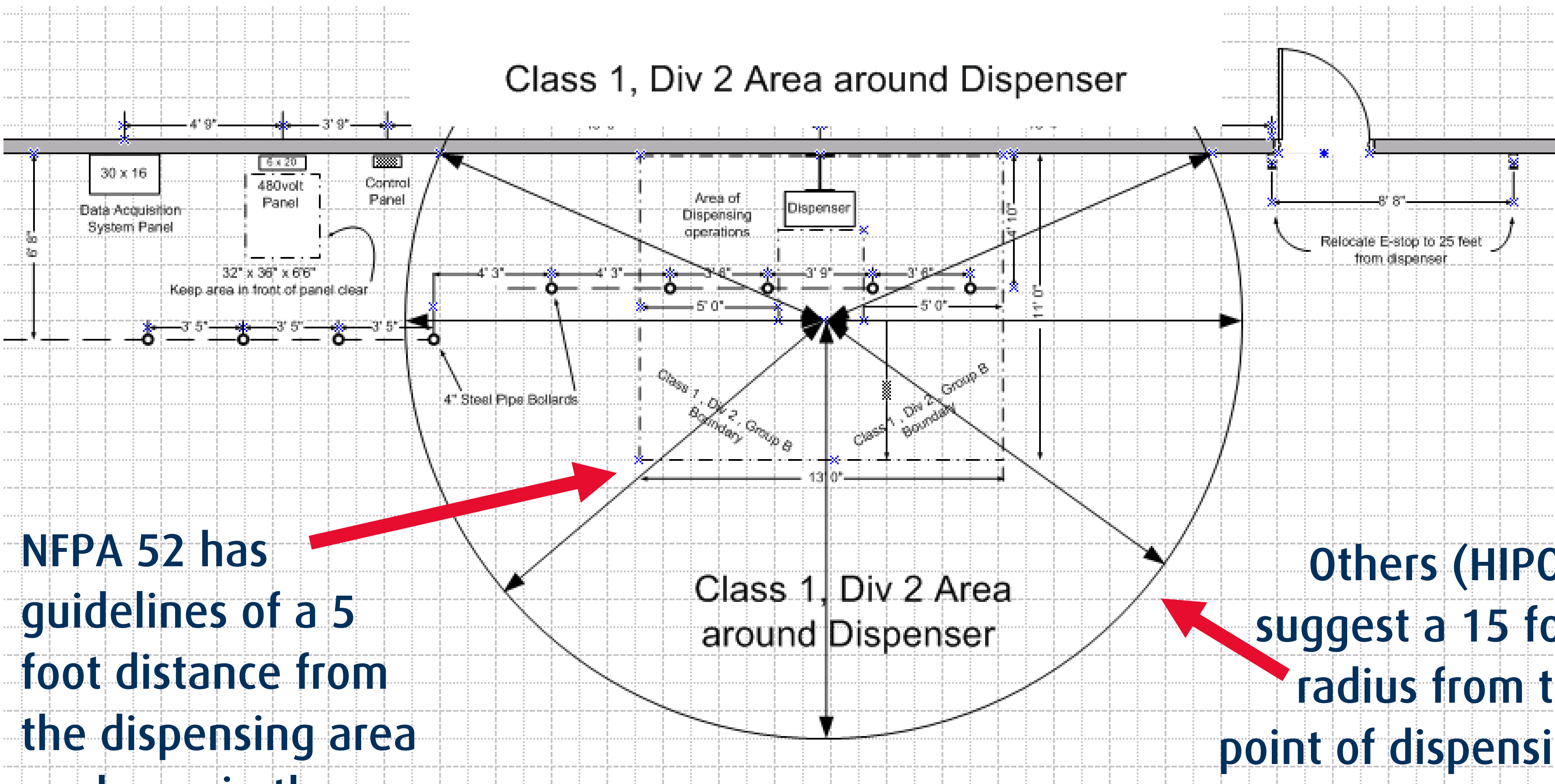


NFPA 52 has guidelines of a 5 foot distance from the dispensing area as shown in the inner box

Others (HIPOC) suggest a 15 foot radius from the point of dispensing area as shown in the outer circle

Interior walls, doors, and window openings within 15 feet (4.6 meters) of the dispenser shall be constructed of non combustible materials.  No storage of combustibles

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# Dispenser Leak Management:
# Hose, nozzle and receptacle tightness testing

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**During each fueling event, the dispenser will test the hose and the dispenser nozzle to vehicle receptacle for leaks: before fueling and at least once again during the fueling event**

**CGA – H-5 Hydrogen Installation Code – 2008 – section 8.10**

"The dispenser shall be equipped with a leak detection system capable of identifying a leak from the dispensing system outside the dispenser housing including the interface to the vehicle by conducting a pre-fill pressure test. The leak detection must be capable of detecting a minimum leak rate of **1.9 grams/minute** and shall actuate when a leak is detected"

CGA H-5, the new hydrogen installation standard from the Compressed Gas Association, includes best practice guidelines for developers of fueling stations for road vehicles at traditional fueling islands as well as and details of indoor fueling of utility vehicles with hydrogen. http://www.cganet.com/

# OTHER STANDARDS AND GUIDEBOOKS

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Material Safety Data Sheets. PDF files from Air Liquide, Linde (formerly BOC) and Praxair are all available under the "Technical Resources" tab of the Hydrogen and Fuel Cell Safety Report at www.hydrogensafety.info/resources/mdss/index.html.

Emergency Response Guidebook(ERG2004). Developed by the US Department of Transportation, Transport Canada, and the Secretariat of Communications and Transportation of Mexico (SCT) For additional information or to download the Guidebook, please visit hazmat.dot.gov/pubs/erg/gydebook.htm.

The California Fuel Cell Partnership Emergency Response Guide - Fuel Cell Vehicles and Hydrogen Fueling Stations. This document covers light duty fuel cell vehicles, fuel cell transit buses, and hydrogen fueling stations. It can be found online at www.fuelcellpartnership.org/resource-ctr_ermaterials.htm.

ISO TR 15916: Basic Considerations for the Safety of Hydrogen Systems. The aim of this document is to promote the acceptance of hydrogen technologies by providing key information to regulators and by educating the general public on hydrogen safety issues. It is available for purchase through ISO and several national standard organizations, including ANSI.

Regulators' Guide to Permitting Hydrogen Technologies. This guide currently includes an overview, and modules on Permitting Stationary Fuel Cell Installations and Permitting Hydrogen Motor Fuel Dispensing Facilities. A description of this guide, and links to the documents can be found at www.hydrogensafety.info/resources/regulators.html.

# OTHER STANDARDS AND GUIDEBOOKS
## Sourcebook for Hydrogen Applications

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Sourcebook for Hydrogen Applications
New technologies, such as the fuel cell, will lead to widespread use of hydrogen as an energy carrier, particularly in transportation. These emerging applications will require hydrogen system designs different from those for established industrial applications. For hydrogen vehicles, onboard hydrogen storage, hydrogen refueling systems and prototype vehicle designs and propulsion technologies are being demonstrated. The Sourcebook for Hydrogen Applications is a unique searchable CD ROM application that provides information to facilitate designing, building, and operating hydrogen systems for these new applications.

The Sourcebook also provides the user with an extensive listing of the Codes and Standards for the U.S., Canada, and other International certifying bodies, a complete look at fuel Cell technology, a robust listing of suppliers and vendors for hydrogen technologies, and an interactive hydrogen sourcebook for kids.

The Sourcebook can be purchased from Tisec at
www.tisec.com/products/hydrogen_sourcebook/hydrogen_sourcebook.htm.

# CONCLUSIONS

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The major weapons in the fight to minimise the dangers of using $H_2$ in classical and emerging applications are:

•Awareness of the risks and the design of atmosphere systems to minimise the dangers. The first can be developed by adequate training of both management and operators and the second, by the application of the highest safety standards available.

•No safety regulations, standards or publications could guarantee the elimination of accidents. Technology and equipment in both classical and emerging applications are under constant development.

•There is no substitute for competent engineering judgement, continuous and adequate training and application of the most updated safety standards.

# THANK YOU FOR YOUR ATTENTION

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# ACRONYMS USED IN THIS PRESENTATION

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| ACRONYM | WHAT IT MEANS |
|---|---|
| ANSI | American National Standards Institute |
| ASME | American Society of Mechanical Engineers |
| CGA | Compressed Gas Association |
| DOT | Department of Transportation Regulations, US Dept of Transportation |
| ERG | Emergency Response Guidebook, US Dept of Transportation |
| HFC | Hydrogen Fuel Cell |
| HPGQ | High Pressure Gas Quenching |
| HIPOC | Hydrogen Industry Panel On Codes |
| IC | Internal Combustion |

# ACRONYMS USED IN THIS PRESENTATION

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| ACRONYM | WHAT IT MEANS |
|---|---|
| ICC | International Code Counsel |
| ICE | Internal Combustion Engine |
| ISO | Internal Organization for Standards |
| LPC | Low Pressure Carburizing |
| MAWP | Maximum Allowable Working Pressure |
| NFPA | National Fire Protection Association |
| NFPA 86 | NFPA Standard for Ovens and Furnaces |
| NGV | Natural Gas Vehicle |
| PEM | Proton Exchange Membrane |
| POC | Product Of Combustion |
| PRD | Pressure Relief Device - also Pressure Relief Valve (PRV) |
| SP | Service Pressure |
| UHP | Ultra High Purity |
| UHP H2 | Ultra High Purity H2 used in semiconductor manufacturing |