ATTACHMENT A
HAZARDOUS GAS DESIGN

RECORD OF REVISIONS

Rev	Date	Description	POC	OIC
0	11/17/03	Initial issue at App A.	Tobin Oruch, FWO-DO	Gurinder Grewal, FWO-DO
1	10/27/06	Administrative changes only. Organization and contract reference updates from LANS transition. IMP and ISD number changes based on new Conduct of Engineering IMP 341. Other administrative changes.	Mike Clemmons, FME-DES	Kirk Christensen, CENG
2	9/29/14	Became Att A. Updated for 420.1C, 420.1-1A, and lessons learned. Other administrative changes.	Lowell Christensen, *ES-EPD*	Mel Burnett, *ES-DO*

Please contact the Chapter POC for upkeep, interpretation, and variance issues.

1.0 Introduction and Scope

A. This attachment specifies the design requirements that shall be implemented for compressed and liquefied gas systems. See ESM Chapter 17 Pressure Safety, P101-34 – Pressure Safety, and P101-5 - Cryogens for the requirements that shall be implemented for acquiring, handling, using, and disposing of compressed and liquefied gases in cylinders.

B. Variance to these requirements can be made in writing by the Engineering Standards Hazardous Process POC.

C. Hazardous gases (toxic, flammable, oxidizing, pyrophoric, asphyxiating) can be handled safely if the required precautions are taken; thus, the requirements that shall be implemented to determine the precautions shall include those pertaining to the quantity, concentration, toxicity, reactivity, and pressure of the gas and the adequacy of engineering controls.

The Laboratory Industrial Hygiene and Safety Manual (LIHSM) provides the minimum requirements for performing industrial hygiene and industrial safety functions at LANL to ensure consistency and compliance. These requirements are based on Title 10 of the Code of Federal Regulations (CFR) 851, Worker Safety and Health Program, federal regulations, consensus standards, and good industrial hygiene and safety practices. If conflicting requirements exist, the most stringent one applies.

The Chemical Management Procedure, P101-14, defines the chemical management requirements for the Los Alamos National Laboratory (LANL or the Laboratory) Hazardous Materials Lifecycle Management program. It defines processes to ensure protection of employees from health hazards associated with hazardous chemicals, and to keep exposures below Occupational Exposure Limits (OELs). It also provides direction to ensure that work with hazardous chemicals is conducted in a safe and responsible manner that protects workers, the public, and the environment, in accordance with Laboratory Integrated Work Management (IWM) and Environmental Management Systems,

ESM Chapter 17 Pressure Safety and the Pressure Safety Procedure, P101-34, establishes safety requirements to ensure that pressure systems are designed, fabricated, tested, inspected, maintained, repaired, and operated by trained and qualified personnel in accordance with applicable sound engineering principles, as required by 10 Code of Federal Regulations (CFR) 851, Worker Safety and Health Program, Appendix A, Section 4 (a), Pressure Safety.

2.0 Definitions

2.1 Acronyms

ANSI	American National Standards Institute
ASME	American Society of Mechanical Engineers
atm	atmosphere
C&LGSC	Cryogenic and Liquefied Gas Safety Committee
CGA	Compressed Gas Association
CGPF	Compressed Gas Processing Facility (TA-3-170)

DOT	US Department of Transportation
EIV	Emergency Isolation Valve
HCP	Hazard Control Plan
HSR	Health, Safety and Radiological Protection
K	kelvin
LANL	Los Alamos National Laboratory
MAWP	Maximum Allowable Working Pressure
NFPA	National Fire Protection Association
OIC	Office of Institutional Coordination
psia	pounds per square inch (absolute)
psig	pounds per square inch (gauge)
scf	standard cubic feet
TNT	tri-nitrotoluene
µJ	microjoule
vol %	percentage based on volume

2.2 Terms

Adequate ventilation—Ventilation that is adequate to prevent gas concentration from reaching 25% of the lower explosive limit. Ventilation can be either natural (gravity) or mechanical.

Autoignition temperature—The temperature at which a substance will self-ignite without any external sources of ignition.

Compressed gas—In general, a gas stored and used at pressures greater than nominal atmospheric pressure (14.7 psia at sea level and 11.3 psia in Los Alamos). Specific regulatory definitions include (1) a gas or mixture of gases having, in a container, an absolute pressure exceeding 40 psi at 70°F; (2) a gas or mixture of gases having, in a container, an absolute pressure exceeding 104 psi at 130°F, regardless of the pressure at 70°F; and (3) a liquid having a vapor pressure exceeding 40 psi at 100°F.

Cryogenic fluid (cryogen)—A liquid with a normal (i.e., at standard temperature and pressure) boiling point below approximately 120 K (–238°F, –150°C) that can be used as a low temperature refrigerant.

Deflagration—An explosion that propagates at subsonic speed.

Deflagration venting—Venting of overpressure from deflagrations in accordance with NFPA 68.

Detonation—An explosion that propagates at supersonic speed.

Electrically classified area—An area surrounding gas storage containers, piping, and distribution systems that is classified for the purpose of eliminating electrical sources of ignition. See NFPA 497.

Employee—Any Laboratory worker, including tenants, affiliates, visitors, vendors, contractors, subcontractors and their employees, who may work with hazardous gases.

Epitaxy—Growing a crystal film on the substrate of another mineral. In semiconductor manufacturing, epitaxy means growing semiconductor crystals on wafers.

Explosion proof apparatus—Apparatus enclosed in a case, including conduit, that is capable of containing an explosion of a specified gas or vapor inside without igniting that gas or vapor outside the case. Such apparatus is so listed by a nationally recognized testing laboratory.

Explosion suppression—Suppressing an incipient explosion by flooding an enclosure with a suppressant gas before the pressure developed is strong enough to cause any damage. Explosion suppression systems are covered by NFPA 69.

Explosion venting—(Also called deflagration venting) Relieving the pressure of a deflagration through a venting system that is weaker than the surrounding building or process equipment. Explosion venting systems are covered by NFPA 68.

Flammable gas—A gas that is flammable at atmospheric temperature and pressure in a mixture of 13% or less (by volume) with air or that has a flammable range with air wider than 12%, regardless of the lower limit.

Flammable gas system—A system for distributing flammable gases where needed, which includes storage containers, gas generators and distribution piping.

Fuel gas—Any gas burned in fuel-fired heating or process equipment, or in equipment for cutting, welding or other hot work.

Hazard control measures—A hierarchy of controls that includes engineering controls, administrative controls, or PPE to mitigate workplace hazards, including the hazards of working with flammable gas systems.

Hazard control plan—A document that, at a minimum, defines the work, identifies the hazards associated with the work, and describes the controls needed to reduce the risk posed by the work to an acceptable level. See SD100 Integrated Safety Management, System Description Document with embedded 10 CFR 851 Worker Safety and Health Program.

Hazardous—Such that it would cause harm to personnel or the environment. This is a broader definition than that for mixed waste in Chapter 10 proper.

Intrinsically safe apparatus—Apparatus that is incapable of igniting a specified gas or vapor at its most ignitable concentration with either the worst electrical fault or the worst combination of two faults. Such apparatus is appropriate for use in Division 1 areas. This apparatus is so listed by nationally recognized testing laboratories as meeting ANSI 4913.

Lecture bottle cylinder—A small portable cylinder (approximately 2 in. x 13 in. [5 cm x 33 cm]).

Liquefied gas—A gas that can be maintained in the liquid state at room temperature by elevating the pressure. A gas, other than in solution, which, when contained under the charge pressure, exists both as a liquid and as a gas at a temperature of 68°F.

Liquefied petroleum (LP) gas—Any material having a vapor pressure not exceeding that allowed for commercial propane that is composed predominantly of the following hydrocarbons, either by themselves or as mixtures: propane, propylene, butane (normal butane or isobutane), and butylenes.

MAPP gas—Methylacetylene-propadiene, stabilized. A fuel gas sometimes used in hot work.

Maximum allowable working pressure (MAWP)—The maximum pressure at which a system is safe to operate, which is the maximum setting for the primary pressure relief device.

Maximum operating pressure—The highest pressure expected during normal operation, which is usually 10% to 20% below the MAWP.

National codes and consensus standards—Documents published by nationally recognized organizations that reflect good engineering design practices and that are regularly revised to reflect changes in good practices. See ASME, CGA, and NFPA.

NFPA Health Hazard Rating 4—Materials that under emergency conditions can be lethal.

NFPA Health Hazard Rating 3—Materials that under emergency conditions can cause serious or permanent injury.

NFPA Health Hazard Rating 2—Materials that under emergency conditions can cause temporary incapacitation or residual injury.

Nonincendive apparatus—Apparatus that is incapable of igniting a specified gas or vapor at its most ignitable concentration with one electrical fault. Such apparatus is appropriate for use in Division 2 areas. This apparatus is so listed by nationally recognized testing laboratories as meeting ANSI 4913.

Oxidizing gas—A gas that can support and accelerate combustion of other materials.

Pressure relief system—A system designed to relieve excess internal pressure in any type of pressurized system. A pressure relief system includes pressure relief devices (i.e., safety valves, relief valves, and rupture disks) and piping or tubing to an approved release point.

Pressure system—Containers and pressure vessels; interconnecting hardware (including pipe and tubing); instrumentation; and devices such as valves, pressure relief equipment, and flare systems that contain fluids (i.e., liquids and gases). Small, one-of-a-kind, experimental pressurized devices and systems are included.

Pressure vessel—A container designed and built, when possible, in accordance with national codes and national consensus standards to hold gases or liquids at pressures greater than 15 psig. Pressure vessels not meeting national codes and consensus standards are "specialized pressure systems." Compressed gas cylinders and compressed gas storage tubes in tube trailers are pressure vessels built to national code requirements.

Portable cylinder—A compressed gas container, fabricated to the specifications of or authorized for use by the DOT or fabricated according to the "Rules for the Construction of Unfired Pressure Vessels," Section VIII, ASME Boiler & Pressure Vessel Code. DOT-specified cylinder sizes generally range from 5 in. in diameter x 32 in. in length (nominal 60 scf) to 9 in. in diameter x 55 in. in length (nominal 300 scf) in capacity.

Purged or pressurized apparatus—Apparatus that prevents vapors from accumulating by being purged or pressurized in accordance with NFPA 496. Different types of purged and pressurized systems are suitable for different electrical classifications.

Pyrophoric—A chemical with an autoignition temperature in air at or below 130°F (54.4°C).

Pyrophoric gas—A gas that spontaneously ignites in air at or below 130°F.

Semiconductor gas—Any of a number of gases commonly used in the semiconductor industry to make micro-electronic chips, e.g., silane, diborane.

Stored energy—A hazardous property of a system that is a function of pressure, the material pressurized (liquid or gas), and the system volume.

Note: Stored energy may be expressed in units of foot-pounds, joules, or TNT equivalence. A large-volume, low-pressure gas or vacuum system may involve a significant amount of stored energy, as would a high-pressure, low-volume system.

Work area—An indoor room or distinct space for testing, analysis, research, or similar activities that involve the use of chemicals.

3.0 Hazard Labeling

A. Compressed and liquefied gas cylinders containing hazardous gases shall be labeled with distinctive labels and signs that signify their contents, hazard warnings or target organ effects, and group ownership. When a gas is classified in more than one category, the most stringent labeling requirements shall be used. Gas distribution lines shall be labeled in accordance with ANSI A13.1, "Scheme for the Identification of Piping Systems." The LANL Compressed Gas Processing Center shall be contacted for assistance in obtaining required labels.

B. *Guidance: Gas cylinders with Compressed Gas Processing Center labels meet the HAZCOM and CHP labeling requirements except for group ownership.*

4.0 Quantity Limitations

Cylinders that are not necessary for immediate work activities shall be stored in a safe location outside the work area. The total number of lecture bottles in a work area shall be limited to 25. The maximum internal volume (water volume) of all portable compressed or liquefied gas cylinders containing hazardous materials or oxygen in use in a single work area shall not exceed the sum of the following:

4.1 Maximum Quantity of Flammable Gases

- For work areas ≤ 500-ft^2, the internal cylinder volume shall be ≤ 6.0-ft^3 (170-L).
- For work areas > 500-ft^2, the internal cylinder volume shall be ≤ 0.012-ft^3 per ft^2 (0.24-L per ft^2) of work area.

4.2 Maximum Quantity of Oxidizing Gases

- For work areas ≤ 500-ft^2, the internal cylinder volume shall be ≤ 6.0-ft^3 (170-L).
- For work areas > 500-ft^2, the internal cylinder volume shall be ≤ 0.012-ft^3 per ft^2 (0.24-L per ft^2) of work area.

4.3 Maximum Quantity of Liquefied Flammable Gases

- For work areas ≤ 500-ft^2, the internal cylinder volume shall be ≤ 1.2-ft^3 (34-L).
- For work areas > 500-ft^2, the internal cylinder volume shall be ≤ 0.0018-ft^3 per ft^2 (0.05-L per ft^2) of work area.

4.4 Maximum Quantity of NFPA 704 Health Hazard 3 or 4 Gases

- For work areas ≤ 500-ft^2, the internal cylinder volume shall be ≤ 0.3-ft^3 (8.5-L).
- For work areas > 500-ft^2, the internal cylinder volume shall be ≤ 0.0006-ft^3 per ft^2 (0.017-L per ft^2) of work area.

Table F1030.60-A1 provides internal cylinder volumes for various portable compressed and liquefied gas cylinders.

TABLE F1030.60-A1

TYPICAL INTERNAL VOLUME OF CYLINDERS

Nominal Dimensions Diameter × Length		Internal Volume (Water Volume)	
cm	in.	L	ft^3
23 × 132	9 × 52	43.8	1.54
30 × 109	12 × 43	609	2.15
38 × 137	15 × 54	126.3	4.46
38 × 117	15 × 46	109.6	3.87
25 × 122	10 × 48	55.7	1.97
36 × 150	14 × 59	126.3	4.46
25 × 140	10 × 55	49.0	1.73
30 × 135	12 × 53	85.0	3.00
20 × 122	8 × 48	29.5	1.04
20 × 135	8 × 53	38.7	1.37
51 × 305	20 × 120	438.9	15.50
25 × 130	10 × 51	42.4	1.54
25 × 122	10 × 48	54.5	1.92
23 × 142	9 × 56	48.7	1.72
20 × 69	8 × 27	16.7	0.59
18 × 48	7 × 19	8.5	0.30
20 × 64	8 × 25	15.3	0.54
23 × 56	9 × 22	15.3	0.54
16 × 85	7 × 38	15.7	0.55
15 × 53	6 × 21	6.9	0.24
13 × 61	5 × 24	6.7	0.24
23 × 33	9 × 13	6.9	0.25
15 × 53	6 × 21	6.9	0.25
18 × 43	7 × 17	6.7	0.24
10 × 36	4 × 14	2.3	0.08
8 × 32	3 × 12.5	0.93	0.033
5 × 38	2 × 15	0.44	0.016

5.0 Storage

A. Storage areas for compressed and liquefied gas cylinders shall be dry, <125°F, well ventilated, away from direct sunlight, and preferably fire-resistive (see Table F1030.60-A2).

B. Gas cylinders containing flammable, oxidizing, toxic, and other potentially incompatible gases shall be separated in accordance with Table F1030.60-A2. When a gas is classified in more than one category, all compatibilities shall be checked, and the most stringent separation requirements shall be used.

TABLE F1030.60-A2

REQUIREMENTS FOR SEPARATION OF GAS CYLINDERS BY HAZARD SHALL BE:

Gas Hazard Category	Nonflammable	Oxidizing	Flammable	Pyrophoric	Toxic
Toxic	C[a]	20 ft[b]	20 ft	20 ft	--
Pyrophoric	C	20 ft	20 ft	--	20 ft
Flammable	C	20 ft	--	20 ft	20 ft
Oxidizing	C	--	20 ft	20 ft	20 ft
Nonflammable	--	C	C	C	C

C = compatible. No separation required.

The 20-ft separation requirement may be reduced without limit when the incompatible gases are separated by a barrier of noncombustible material(s) at least 5 ft high that has a fire-resistance rating of at least 30 min.

C. Toxic or flammable gas cylinders shall not be installed or stored near windows, doors, or other openings to the work area(s). The minimum separation shall be 9 ft.

D. Toxic or flammable gas cylinders shall not be installed near ventilation intake ducts. The minimum separation shall be 30 ft.

E. Cylinders of all gases having a NFPA health hazard rating of 3 or 4 and cylinders of gases having a NFPA health hazard rating of 2 and having no physiological warning properties shall be kept in a continuously mechanically ventilated hood or enclosure.

F. Storage of toxic gases shall be evaluated to ensure the safety of building occupants and the public. The ISH-qualified person shall be contacted for assistance in identifying safe storage locations for toxic gases.

G. Compressed gas regulators that are not in service shall be stored in plastic bags, and the labels shall indicate the gas they regulate.

6.0 Flammable Gases

A. *Flammable gas design involves the following decisions:*

- *Selecting the form of gas supplies*
- *Locating the gas supplies*
- *Piping the supplies to the processes that use the gases*
- *Designing the processes that use the gases*
- *Classifying electrical areas and specifying the proper electrical equipment*
- *Determining the best suppression systems for protecting the hazards*

B. *Gas supplies can consist of the following:*

- Tanks
- Tube trailers
- Cylinder banks
- Individual cylinders

C. *In the case of hydrogen, gas generators can also be used. The best supply depends on the amount of gas to be used, the gas flow rate, locations available for locating the supply, and other factors.*

D. *The decisions involved in locating gas supplies include:*

- *The type of supply*
- *Distances to the nearest buildings/structures*
- *Distance from building openings*
- *Distance from air inlets*
- *Distance from combustible materials*
- *Distance from sources of ignition*
- *Whether the supply is inside or outside*

E. Flammable gas supplies at LANL shall normally be located outdoors. Exceptions include:

- Portable cutting and welding units
- One or two cylinders less than 100 scf kept in separate, ventilated fire resistive rooms with normally closed fire doors
- One-cylinder vented and sprinklered gas cabinets
- Hydrogen generators listed for indoor use

F. All gas cylinders shall be properly secured.

G. *Distances between gas supplies and building features are given in the NFPA codes addressing specific gases. Lacking other requirements, explosion overpressure circles can be calculated for input on locating supplies.*

H. *The features of the gas piping/distribution system include:*

- *Pipe material*
- *Size of pipes*
- *Types of fittings*
- *Types of control valves, regulators, relief valves and other devices*
- *Routing of pipe*
- *Locations of control valves*

I. Design safe processes giving consideration to the following features:

- Material holdup (i.e., the volume of material that process equipment and piping holds)
- Operating speeds, temperatures, pressures and flows
- What parts of the process are open or closed
- Determining where ventilation is needed
- Determining where inerting is needed
- Locating and sizing emergency vents
- What parameters are to be monitored
- What alarms to sound and at what settings
- What interlocks to provide and at what settings

J. In addition, each process shall be reviewed for proper electrical classification of areas. Given the electrical classification, the proper type of electrical equipment shall be specified. The following factors apply:

- What kind of electrical equipment is to be used (explosion-proof, intrinsically safe, purged, pressurized, etc.)
- Where the equipment is to be installed

K. Protecting processes using flammable gases includes selecting the type of fire protection system; buildings using piped systems of flammable gases shall be provided with conventional wet pipe sprinkler systems. Depending on the process, additional protection may be warranted.

1. Examples of additional protective systems include:

- Deluge/water spray systems (covered in NFPA 15)
- Foam systems (covered in NFPA 11, 11A and 16)
- Inerting of process vessels
- Explosion venting (covered in NFPA 68)
- Explosion suppression systems (covered in NFPA 69)

L. *Explosion venting can be provided for a building or room, or it can be provided for the process equipment itself. Explosion suppression systems sense an explosion pressure wave so fast that they can extinguish the flame before the explosion pressure wave is strong enough to cause any damage. These intricate systems are used where the importance of limiting damage from explosion in hazardous processes is paramount.*

7.0 Semiconductor Gas

A. *The term "semiconductor gases" is used here to mean the gases commonly used in the semiconductor industry to make micro-electronic chips. These gases are most frequently used in to "dope" chips with n- or p-type semiconductor material. They are also used in epitaxy, etching and cleaning.*

B. *Semiconductor gases are among the most hazardous gases used anywhere. They can be highly toxic, highly reactive, flammable, pyrophoric, or a combination of these. In addition to being used by the semiconductor industry, these gases are used in many facets of nanotechnology research, including at LANL. The American National Standards Institute's Nanotechnology Standards Panel (ANSI-NSP) has compiled an ANSI-NSP Nanotechnology Standards Database. This database is a free, comprehensive resource for individuals and groups seeking information about standards and other relevant documents related to nanomaterials and nanotechnology products and processes.*

C. *Common semiconductor gases and their properties include:*

- *Arsine – flammable and toxic*
- *Chlorine Trifluoride – flammable, extremely reactive, and corrosive*
- *Diborane – pyrophoric and toxic*
- *Dichlorosilane – flammable and corrosive*
- *Disilane – flammable*
- *Germane – flammable and toxic*
- *Phosgene – flammable and toxic*
- *Phosphine – pyrophoric and toxic*
- *Silane (silicon tetrachloride) – pyrophoric*

D. *The most comprehensive code for safe storage and use of semiconductor gases is NFPA 318, Protection of Cleanrooms. Some of the requirements in this code assumes the larger quantities of gases used in the semiconductor industry, but research facilities usually don't use that much gas. NFPA 45, Standard on Fire Protection for Laboratories Using Chemicals, addresses storage and use of gases at the laboratory scale, but this code may not properly account for all the elevated hazards of the semiconductor gases.*

E. Design semiconductor gas systems with sprinklered, ventilated, gas cabinets with controls to automatically shut off the gas supply upon sensing potentially unsafe conditions. These conditions shall include:

- Heat
- Smoke
- Presence of the gas where it would not be present under normal operating conditions

- Loss of cabinet ventilation
- Process upset

F. Design of systems using semiconductor gases shall use an appropriate combination of the elements from both NFPA 318 and NFPA 45. The appropriate combination depends on the risk the gases present. *Factors affecting the risk include the numbers of different types of gases, their amounts, where and how they are used, and the risk the gases present to the public, laboratory personnel, and operations.*

8.0 Hydrogen

8.1 Hazards of Using Hydrogen

A. Hydrogen is used at LANL for targets in high energy particle experiments, for temperature control systems, and for other laboratory experiments. Hydrogen is also used as a fuel gas. Using hydrogen involves hydrogen storage systems (tanks, tube trailers, cylinders), distribution systems (control and relief valves, regulators, piping and fittings), and process systems. In addition, hydrogen generators are becoming more common.

B. Hydrogen is a flammable gas that is colorless, odorless, tasteless, and nontoxic. It is the lightest gas known, having a specific gravity of 0.0695 (air = 1.0). Hydrogen diffuses rapidly in air and through porous materials. Compressed hydrogen gas can be stored at pressures exceeding 3000 psig.

C. Liquefied hydrogen is transparent, odorless, and not corrosive or significantly reactive. The boiling point at atmospheric pressure is –423°F. It is only 1/14 as dense as water.

D. Several unique properties contribute to the hazards associated with hydrogen systems. First, hydrogen is flammable over a wide range of concentrations. Second, the ignition energy for hydrogen is very low. Third, a single volume of liquid expands to about 850 volumes of gas at standard temperature and pressure when vaporized; therefore, high gas pressure can be created when liquid hydrogen is vaporized in a confined system. Finally, some materials (including metals and, in particular, carbon steel) are embrittled by hydrogen and shall not be used in hydrogen service.

E. Hydrogen burns in air with a pale blue, almost invisible flame. The temperature of burning hydrogen in air is high (3,718°F), and warm hydrogen gas rises rapidly because of its great buoyancy. The flammable limits of hydrogen-air mixtures depend upon pressure, temperature, and water-vapor content. Hydrogen forms a flammable mixture with air at ambient conditions over a wide range of concentrations, from 4 to 75 vol %.

F. The minimum ignition energy required for hydrogen (20 µJ) is about one-tenth the minimum ignition energy required for gasoline vapors. This minimum ignition energy can be provided when the static electricity accumulated by a person (10,000 to 20,000 µJ) is discharged. A high-pressure hydrogen leak will ignite from static electricity, from sparks from high-velocity rust particles, or other low-energy sources. At atmospheric pressure, the ignition temperature of hydrogen-air mixtures has been reported by the U.S. Bureau of Mines to be as low as 932°F. Auto-ignition occurs at 1,085°F.

G. Once hydrogen is ignited, the reaction can proceed either by deflagration (subsonic propagation) or detonation (supersonic propagation). Deflagration in a closed volume *can cause a pressure increase of almost 8 times the initial pressure. Detonation from a low energy ignition source is possible in well mixed and confined hydrogen-air mixtures of 18 to 60 vol %. Although hydrogen-air mixtures have the same calorific value per pound as TNT (trinitrotoluene), the rate of energy release is much slower for hydrogen-air mixtures. Hydrogen detonations, although rare, are characterized by pressure increases so rapid that pressure relief devices are usually ineffective.*

H. Hydrogen can burn or explode; it also presents the hazard of stored energy (pressure). Safe handling requires the measures that would be taken for any pressure container, as well as for any cryogen.

I. *Liquefied hydrogen presents the same hazards as any cryogen. Liquid hydrogen is no longer routinely handled at the Laboratory.* Special arrangements shall be made through the Compressed Gas Processing Facility (CGPF) to procure and receive liquid hydrogen. As with other cryogenic liquids, cryogenic hydrogen shall only be used or handled by personnel who are familiar with its properties and skilled in the procedures necessary for its safe use. Reference P101-5 – Cryogens.

J. The specific hazards that hydrogen presents to employees, property, and the public shall be considered in designing, installing and using hydrogen supply and distribution systems. These hazards shall also be considered in controlling processes handling hydrogen. As a flammable gas, using hydrogen safely requires specific loss control measures.

8.2 Physical and Chemical Properties of Hydrogen

Characteristic	**Value**
Color	None
Odor	None
Toxicity	Nontoxic
Density, liquid (boiling point)	4.4 lb/ft^3 (0.07 g/cm^3)
Boiling point (1 atm)	–423.2°F (–252.9°C)
Critical temperature (188.2 psia)	–400.4°F (–240.2°C)
Stoichiometric mixture in air	29 vol %
Flammability limits in air	4 to 75 vol %
Detonation limits in air	18 to 60 vol %
Minimum ignition energy in air	20 µJ
Minimum ignition temperature	932°F (500°C)
Autoignition temperature	1,085°F (585°C)
Volume expansion:	
Liquid (–252.9°C) to gas (–252.9°C)	1:53
Gas (from –252.9°C to 20°C)	1:16
Liquid (–252.9°C) to gas (20°C)	1:848

8.3 Outside Stored Hydrogen Systems

A. *Most systems using hydrogen store it in tanks, tube trailers or cylinder banks*. The storage containers shall always be outside, and away from exposures such as combustible materials, transformers, vehicle access ways, and any potential source of ignition.

B. The outside stored hydrogen system consists of the storage container(s) and the delivery piping up to and including the regulator. If the system holds over 400 scf of hydrogen, it shall meet all the requirements of both NFPA 50A and of the Compressed Gas Association (CGA). If it holds than 400 scf or less, it shall meet the applicable requirements of the CGA as a minimum.

C. If hydrogen storage containers are outside and in the open, no special electrical classification is required around the containers. If the containers are stored in gas cabinets, the cabinets shall be vented. The inside of the cabinets and around the cabinet vent shall be classified as Group B, division 2 for the distances specified in NFPA 50A.

D. If the hydrogen storage is in cylinders, cylinders in storage that are not connected to the manifold are not part of the system. Connected cylinders are part of the system whether or not they are required for operations. Cylinders shall comply with NFPA 55.

E. Occasionally, small hydrogen storage cylinders will be installed inside laboratory buildings near where the hydrogen is needed. In this case, the system capacity shall be less than 400 scf. The installation shall meet the applicable requirements of CGA and on NFPA 45. Adequate ventilation must be provided for the room where the cylinder is stored.

8.4 Hydrogen Generating Systems

A. Sometimes instead of having a stored hydrogen supply, a facility will elect to use a hydrogen generator. Requirements for hydrogen generators vary with the design of the generator. Some are designed for use outside and some inside. Some are enclosed and some are not.

B. Requirements for hydrogen generators shall be developed on a case-by-case basis. Consider the following areas:

- Whether the generator cabinet must be in a Class I, Division 2, Group B enclosure.
- Whether an inside generator enclosures requires fire-rated construction.
- What process safety interlocks shall be provided. Examples include a hydrogen sensor in the enclosure set to alarm and shut down the generator at 2 vol %.
- How the generator cabinet vent system is designed. Usually this would be for the greater of the storage system MAWP or 150 psig and in accordance with ASME B31.3. The relief vent valve shall be set to open at 90% or less of the design pressure. The vent system piping shall be sized to ensure that the backpressure at the relief discharge does not exceed 10% of the relief device set pressure. Use 300-series stainless steel for vent piping, and design the vent in accordance with CGA G-5.5.

- Where to locate vent stacks. Vent stack exit elevation shall be the greater of 10 ft above grade, or 2 ft above equipment, or 5 ft above roof tops. The vent stack exits shall be located outdoors at least 15 ft away from personnel areas, ignition sources, air intakes, building openings, and overhangs.
- Whether the power supply must be outside the enclosure. If so, it shall be connected to the generator in accordance with the NEC, including proper conduit sealing.
- Whether ventilation is required for the generator enclosure. If required, it shall enter the enclosure at floor level and leave at the roof/ceiling level. Natural ventilation is adequate. A minimum of 1 ft^2 of vent area per 1000 ft^3 of room volume is recommended. Ventilation system supply and exhaust shall be from the outside.

C. In all cases, piping, tubing, fittings, valves, accessory equipment, gaskets, and thread sealants shall be suitable for hydrogen service at the pressure and temperatures involved to maintain their integrity under the high temperatures of fire conditions.

8.5 Hydrogen System Piping and Valving Inside Buildings

A. The portion of a hydrogen distribution system considered to be inside the facility is everything downstream of the Emergency Isolation Valve (EIV). Since the EIV is upstream of the regulator, and must be outside, there is a small overlap between the outside stored hydrogen system and the inside distribution system.

B. The inside hydrogen distribution system shall comply with:

- Applicable CGA requirements
- ASME B31.3, Process Piping
- NFPA 45

C. All distribution piping shall be of metallic material appropriate for hydrogen service (usually stainless steel). Fittings shall be welded, except where change-out will be required. If change-out is expected to be frequent, Cajon VCR-type fittings shall be considered rather than compression fittings. Areas with welded fittings do not require special electrical classification, whereas areas with other fittings do. *Refer to the ASME 31.3 Piping Guide located in the ESM Mechanical Chapter for guidance.*

D. If the system is 400 scf or less, it shall comply with the "Storage” and “Piping” sections of NFPA 50A. If the system is greater than 400 scf, it shall comply with all of NFPA 50A.

E. If any cylinders are inside, they shall comply with NFPA 55.

8.6 Safety Controls for Processes Using Hydrogen

A. The following portions of hydrogen systems can present potential leakage points:

- *Fill connections*
- *Regulators*
- *Vents*

- *Relief valves*
- *Non-welded fittings*
- *Operational valves*

B. *Every potential leakage point is classified as Class I, Group B for electrical purposes. In cases where vapors are expected to be released under abnormal conditions, such as process upset, the area would be Division 2. In cases where vapors can be expected to be released routinely, the area would be Division 1.* In both cases this means the electrical equipment must be explosion proof per NFPA 497, purged or pressurized per NFPA 496, or intrinsically safe or non-incendive per ANSI 4913.

C. Parameters to be monitored shall include:

- Hydrogen concentration in areas where it might leak. Processes should be shut down at 25% LEL (1% hydrogen concentration by volume).
- Oxygen concentration in processes running above the upper explosive limit. Such processes should use inert gas purging for normal startup and shutdown, as well as for emergency shutdown.
- Process excess temperatures
- Other potentially dangerous process parameters, including pressure, flow and liquid levels

D. Adequate ventilation can be used to reduce the electrical area classification. For example, make and break connections can be put inside a ventilated cabinet so that the entire room does not have to be electrically classified. If this is done, the ventilation pressure or flow should be monitored and interlocked with the process.

E. Consideration shall be given to providing deflagration venting for process equipment in accordance with NFPA 68. Installing an explosion prevention system in accordance with NFPA 69 shall also be considered for important processes where explosions could have severe consequences.

9.0 References

ANSI Standards

ANSI 4913, Intrinsically Safe and Associated Apparatus

ASME Standards

ASME B31.3, Process Piping

ASME Boiler and Pressure Vessel Code, Section IX

CGA Standards

CGA G-5.4, Standard for Hydrogen Piping Systems at Consumer Locations

CGA G-5.5, Hydrogen Vent Systems

CGA S-1.1, Pressure Relief Device Standards--Part 1--Cylinders for Compressed Gases

CGA S-1.2, Pressure Relief Device Standards--Part 2--Cargo and Portable Tanks for Compressed Gases

CGA S-1.3, Pressure Relief Device Standards--Part 3--Compressed Gas Storage Containers

CGA SB-13, Use of regulators in compressed gas cylinders over 3000 psig

CGA V-1, Compressed Gas Association Standard for Compressed Gas Cylinder Valve Outlets and Inlet Connections

CGA V-9, Compressed Gas Association Standard for Compressed Gas Cylinder Valves

LANL

ESM Chapter 17 Pressure Safety

P101-34 – Pressure Safety

P101-5 – Cryogens

P101-14 – Chemical Management Procedure

NFPA Codes

NFPA 11, Standard for Low-Expansion Foam

NFPA 11A, Standard for Medium- and High-Expansion Foam Systems

NFPA 13, Standard for the Installation of Sprinkler Systems

NFPA 15, Standard for Water Spray Fixed Systems for Fire Protection

NFPA 16, Standard for the Installation of Foam-Water Sprinkler and Foam-Water Spray Systems

NFPA 45, Standard on Fire Protection for Laboratories Using Chemicals

NFPA 50A, Standard for Gaseous Hydrogen Systems at Consumer Sites

NFPA 50B, Standard for Liquefied Hydrogen Systems at Consumer Sites

NFPA 51, Design and Installation of Oxygen-Fuel Gas Systems for Welding, Cutting, and Allied Processes

NFPA 54, National Fuel Gas Code©

NFPA 55, Standard for the Storage, Use, and Handling of Compressed and Liquefied Gases in Portable Cylinders

NFPA 58, Storage and Handling of Liquefied Petroleum Gases

NFPA 59, Storage and Handling of Liquefied Petroleum Gases at Utility Gas Plants

NFPA 59A, Production, Storage, and Handling of Liquefies Natural Gas

NFPA 68, Guide for Venting of Deflagrations

NFPA 69, Standard on Explosion Prevention Systems

NFPA 70, National Electrical Code©

NFPA 77, Recommended Practice on Static Electricity

NFPA 85, Boiler and Combustion Systems Hazards Code

NFPA 86, Ovens and Furnaces

NFPA 86C, Industrial Furnaces Using a Special Processing Atmosphere

NFPA 318, Protection of Cleanrooms

NFPA 496, Standard for Purged and Pressurized Enclosures for Electrical Equipment

NFPA 497, Recommended Practice for the Classification of Flammable Liquids, Gases, or Vapors and of Hazardous (Classified) Locations for Electrical Installations in Chemical Process Areas

NFPA 704, Standard System for the Identification of the Hazardous Materials for Emergency Response

Other

American Chemical Society, 1998. "Living with the Laboratory Standard: A Guide for Chemical Hygiene Officers," Washington, DC.