NASA Glenn Research Center Glenn Safety Manual Chapter 6 - Hydrogen BMS Document GRC-MQSA.001 Effective Date: 3/06

CHAPTER 6 – HYDROGEN

For further guidelines the reader should refer to <u>ANSI / AIAA G-095-2004</u>, Guide to Safety of Hydrogen and Hydrogen Systems.

6.1 SCOPE

The Glenn Safety Manual chapter on hydrogen is written to serve as a practical guide for the safe design and fabrication of systems for, and the safe use of, hydrogen at the Glenn Research Center. A summary of operational hazards along with hydrogen safety and emergency procedures is provided. These hydrogen standards and practices are for minimum safety requirements only. More extensive safety precautions should be employed where possible.

The intent is to provide safe, practical guidance that permits the accomplishment of experimental test operations at the Glenn Research Center and that is restrictive enough to prevent personnel endangerment and to provide reasonable facility protection. This chapter is intended to serve as a tutorial on operational hydrogen safety. Appendixes A and B detail, respectively, procedures for filling gaseous hydrogen tube trailers and procedures for cleaning hydrogen service systems.

These guidelines shall govern all aspects of hydrogen handling and usage at the Glenn Research Center. They shall govern whenever there is a conflict between information presented herein and information contained in a reference, except that these guidelines shall in no event be considered as relaxing any occupational safety or health standard imposed by regulation. Section 6.14 presents a list of references that contain rules and procedures to which adherence is mandatory.

6.2 DEFINITIONS

See the Glossary (Appendix C) for terms used in both the Oxygen and Hydrogen Chapters of the Glenn Safety Manual (Chapters. 5 and 6).

6.3 POLICY

6.3.1 Approach to Hydrogen Safety

<u>Safety programs</u>: Shall be directed toward minimizing the possibilities of accidents, reducing the severity of any accidents that occur, and establishing controls and safeguards for identified hazards.

<u>Inherent safety:</u> Hydrogen systems and operations shall be designed to be inherently devoid of hazards by observing the cardinal axioms of hydrogen safety: adequate ventilation, leak prevention, and appropriate elimination of ignition sources.

<u>Fail-safe design</u>: Redundant safety features shall be incorporated in the system design to prevent a hazardous condition when a component fails. In such incidents the system controls should rapidly shut down the equipment and allow only minimal leakage.

<u>Automatic safety devices:</u> Leak detection and ventilation shall be automatically controlled. Manual controls of pressure and flow rate shall be constrained by automatic limiting devices. Automation may be utilized in standardized test operations.

<u>Alarm, warning and shutdown devices:</u> Warning systems shall be installed to monitor those parameters of the storage, handling, and use of hydrogen that may endanger personnel and cause property damage. The warning and shutdown systems shall include sensors to detect abnormal conditions, measure malfunctions, indicate incipient failures, and introduce automatic shutdown when warranted. Data transmission systems for alarm and warning systems shall have sufficient redundancy to prevent any single-point failure from disabling the entire system.

<u>Hydrogen operations according to formal procedures:</u> Personnel involved in design and operations are required to carefully adhere to the safety standards for hydrogen handling and usage, and must comply with regulatory codes.

<u>Personnel training:</u> Personnel who handle hydrogen or who design equipment for hydrogen systems must become familiar with the physical and chemical properties of hydrogen as well as the specific hazardous properties of liquid and gaseous hydrogen. (Also see 6.3.3, Training)

Training should include detailed safety programs for recognizing human capabilities and limitations. Personnel must constantly re-examine procedures and equipment to be sure safety has not been compromised by changes in test methods, equipment deterioration, over-familiarity with the work, or work-related stress.

<u>Operator certification:</u> Operators shall be certified as "qualified" for handling liquid and gaseous hydrogen and "qualified" in the emergency procedures for handling leaks and spills in accordance with Section 6.9.2, Requirements for Personnel. Operators must be kept informed of changes in facility operations and safety procedures.

<u>Safety review:</u> Activities involving hydrogen use shall be permitted and be subject to an independent, third party Area Safety Committee review. Safety reviews shall be conducted in such typical areas of concern as effects of fluid properties, training, escape and rescue, fire detection, and firefighting. The safety reviews shall include review of the design, operating procedures, and in-service inspections. As part of obtaining a permit, hazards analyses shall be performed to identify conditions that may cause injury, death, or property damage.

6.3.2 Training

Personnel who handle/use liquid and gaseous hydrogen or who design equipment for hydrogen systems must become familiar with its physical, chemical, and hazardous properties. In addition, the following requirements apply:

- a. Personnel must know which materials are most compatible with hydrogen, what the cleanliness requirements of hydrogen systems are, how to recognize system limitations, and how to respond to failures. Designated operators shall be familiar with procedures for handling spills and with the actions to be taken in case of fire.
- b. Training should include detailed safety programs for recognizing human capabilities and limitations. Instruction on the use and care of protective equipment and clothing shall be provided. Regularly scheduled fire drills and safety meetings shall be instituted.
- c. Personnel must constantly reexamine procedures, hazards analyses and equipment to be sure safety has not been compromised by changes in test methods, over familiarity with the work, equipment deterioration, or stresses due to abnormal conditions. Hazards analyses shall be updated as changes are identified.
- d. Trained supervision of all potentially hazardous activities involving liquid hydrogen is essential. Everyone working with these materials must abide with the first aid procedures described in Appendix D. Personnel shall be instructed to call 911 (at Cleveland and at Plum Brook) for all emergency aid.

6.3.3 Protective Equipment

Note: See Chapter 15, Personal Protective Equipment for further supportive instruction. Protective clothing and equipment shall be included in personnel protective measures.

<u>Hand and foot protection</u>: Gloves for work near cryogenic systems must be of good insulating quality. They should be designed for quick removal in case liquid hydrogen gets inside. Because of the danger of a cryogenic splash, shoes should have high tops, and pant legs should be worn outside and over the shoe tops. Leather shoes are recommended.

<u>Head, face, and body protection</u>: Personnel handling liquid hydrogen shall wear splash protection. A face shield or a hood with a face shield shall be worn. If liquid hydrogen is being handled in an open system, an apron of impermeable material should be worn.

<u>Impermeable clothing</u>: Impermeable clothing with good insulating properties is effective in protecting the wearer from burns due to cryogenic splashes or spills. Impermeable clothing and gloves are not designed for immersion into cryogens.

Low static and fire resistant clothing: Specialized clothing is available to reduce the chance of ignition due to static charge and for protection against burns.

<u>Hydrogen vapors on clothing</u>: Any clothing that has been splashed or soaked with hydrogen vapors shall be removed and shall not be used until it is completely free of the gas.

Prior to entering a hydrogen test area, precautions must be taken to assure that the environmental level of hydrogen has stabilized to a safe and acceptable value below the lower explosive limit.

<u>Storage of protective equipment:</u> Facilities should be available near the hydrogen use or storage area for the proper storage, repair, and decontamination of protective clothing and equipment. Safety equipment shall be checked periodically to make sure it is operational.

6.3.4 Smoking Regulations

Smoking and open flames are prohibited within a minimum of 50 feet of a hydrogen system.

6.3.5 First Aid (See Paragraph 6.10 and Appendix D)

Call 911 for emergency first aid at Lewis Field or Plum Brook. Contact with liquid hydrogen or its cold boil off vapors can produce cryogenic burns (frostbite). Unprotected parts of the body should not be allowed to contact noninsulated pipes or vessels containing cryogenic fluids. The cold metal will cause the flesh to stick and tear.

Treatment of truly frozen tissue requires professional medical supervision since incorrect first aid practices almost always aggravate the injury.

6.4 PROPERTIES AND HAZARDS OF HYDROGEN

6.4.1 Selected Safety-Relevant Properties

Ortho and para hydrogen: The hydrogen molecule exists in two forms, distinguished by the relative rotation of the nuclear spin of the individual atoms in the molecule. Molecules with spins in the same direction (parallel) are called orthohydrogen, those with spins in the opposite direction (anti-parallel), parahydrogen. The two forms have slightly different physical properties but are chemically equivalent.

At or above room temperature, "normal" hydrogen is an equilibrium mixture of 75percent orthohydrogen and 25-percent parahydrogen. However, at cryogenic temperatures an equilibrium mixture contains predominately the para form. The liquefaction of normal hydrogen produces a liquid containing about 75-percent orthohydrogen, which slowly converts to a parahydrogen with the release of some heat. Catalysts are used to accelerate their conversion in production facilities, which produce almost pure parahydrogen in the liquid form.

Reference temperature	68°F	527.7° R	293.1° K
Standard pressure (1 atm) psia	14.69 kPa	101.325 abs	
Density (at 527.7° R & 1 atm)	.00523 lb/ft ³	83.7 g/m^3	
Specific Volume (at 527.7° R	$191.4 \text{ ft}^3/\text{lb}$	$0.0119 \text{ m}^{3}/\text{g}$	
& 1 atm)			
Specific Heat	Cp= 3.425 Btu/lb-R	Cp= 14.33 J/g-k	
	Cv= 2.419 Btu/lb-R	Cv= 10.12 J/g-k	
Velocity of Sound	4246 ft/sec	1294 m/sec	
	Low = 51596 Btu/lb	Low= 119.93 kJ/g	
Heat of Combustion	High = 61031Btu/lb	High= 141.86 kJ/g	
Flammability limits			
Hydrogen-air mixture	Lower= 4.0 % volume	Upper= 75 % volume	
Hydrogen-oxygen mixture	Lower= 4.0 % volume	Upper= 95 % volume	
Explosive limits			
Hydrogen-air mixture	Lower= 18.3 %	Upper= 59 % volume	
	volume		
Hydrogen-oxygen mixture	Lower= 15.0 %	Upper= 90 % volume	
	volume		
Minimum spark ignition			
energy at 1 atm			
In air	1.9 x 10 ⁻⁸ Btu	0.02 mJ	
In Oxygen	6.6 x 10 ⁻⁹ Btu	0.007 mJ	

Properties of gaseous (normal) hydrogen are as follows:

Properties of Liquid (para) hydrogen are as follows:

Boiling Point at 1 atm	-423.3° F	36.49° R	20.27 °K
Vapor Pressure @			
-402°F / 57.7° R	163.0 psia	1124.3 kPa	
-420° F / 39.7° R	23.7 psia	163.5 kPa	
-423° F / 36.5° R	14.7 psia	101.4 kPa	
-433° F/ 26.7° R	1.9 psia	13.1 kPa	
Density @			
36.49° R & 1 atm	4.42 lb/ft^3	70.79 kg/m^3	
Critical Density	1.99 lb/ft^3	31.49 g/m^3	
Critical Pressure	187.5 psia	1292.7 kPa	
Critical Temperature	-400.3° F	59.4° R	32.98° K
Triple Point Temperature	-434.8° F	24.84° R	13.80° K
Specific heat	Cp=2.32 Btu/lb-R	Cp= 9.69 J/g-K	
	Cv=1.37 Btu/lb-R	Cv= 5.74 J/g-K	
Heat of Vaporization	191.7 Btu/lb	445.59 J/g	
Heat of Fusion	25.1 Btu/lb	58.23 J/g	
LIQUID			
Temperature	36.49° R	20.27° K	

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Vapor Pressure	14.69 psia	101.28 kPa
Density	4.42 lbm/ft^3	70.79 kg/m^3
LIQUID AT TRIPLE POINT		
Temperature	24.84° R	13.8° K
Vapor Pressure	1.02 psia	7.04 kPa
Density	4.81 lbm/ft^3	77.04 kg/m^3
SLUSH - 50% MASS		
SOLID		
Temperature	24.84° R	13.8° K
Vapor Pressure	1.02 psia	7.04 kPa
Density	5.09 lbm/ft^3	81.50kg/m ³
SLUSH - 50% VOLUME		
SOLID		
Temperature	24.84° R	13.8° K
Vapor Pressure	1.02 psia	7.04 kPa
Density	5.11 lbm/ft^3	81.77 kg/m^3
SOLID AT TRIPLE POINT		
Temperature	24.84°R	13.8° K
Vapor Pressure	1.02 psia	7.04 kPa
Density	5.40 lbm/ft^3	86.50 kg/m^3

A more complete listing of the thermo physical properties of hydrogen is available in NASA SP-3089 (McCarty 1975) and NBS-NM-168 (McCarty et al.1981). Although both of these references cover a broad range of properties over a wide range of pressures and temperatures, chapter 3 of the latter provides an in-depth discussion of hydrogen combustibility properties that should be useful to a hydrogen system designer or user.

6.4.2 Typical Hydrogen Hazards

The major hazards associated with hydrogen are fires and explosions, and in the event of contact with the liquid or cold boil off vapor, frostbite and burns. <u>Deflagration and detonation</u>: Hydrogen gas can burn in two modes, as a deflagration or as a detonation.

In a deflagration, the ordinary mode of burning, the flame travels through the mixture at subsonic speeds. This happens, for instance, when an unconfined cloud of hydrogen-air mixture is ignited by a small ignition source. Under these circumstances, the flame will travel at a rate anywhere from ten to several hundred feet per second. The rapid expansion of hot gases produces a pressure wave. Witnesses hear a noise, often a very loud noise, and may say that an explosion occurred. The pressure wave from rapid unconfined burning may be strong enough to damage nearby structures and cause injuries to personnel.

In a detonation, the flame and the shock wave travel through the mixture at supersonic speeds. The pressure ratio across a detonation wave is considerably greater than that in a

deflagration. The hazards to personnel, structures, and nearby facilities are greater in a detonation.

A detonation will often build up from an ordinary deflagration that has been ignited in a confined or partly confined mixture. This can occur even when ignition is caused by a minimal energy source. It takes a powerful ignition source to produce detonation in an unconfined hydrogen-air mixture. However, a confined mixture of hydrogen with air or oxygen can be detonated by a relatively small ignition source.

The pressure ratio across a detonation wave in a hydrogen-air mixture is about 20, as indicated when the wave passes a detector mounted flush in a confining wall. (A pressure ratio of 20 means 300 psi if the mixture is at atmospheric pressure.) When the wave strikes an obstacle, the pressure ratio seen by the obstacle is between 40 and 60. Even larger pressure ratios occur in the region where a deflagration builds into a detonation.

<u>Leakage, diffusion, and buoyancy</u>: These hazards result from the difficulty in containing hydrogen. Hydrogen diffuses extensively, and when a liquid spill or large gas release occurs, a combustible mixture can form over a considerable distance from the spill location.

<u>Leakage</u>: Hydrogen, in both the liquid and gaseous states, is particularly subject to leakage because of its low viscosity and low molecular weight (leakage is inversely proportional to viscosity). Because of its low viscosity alone, the leakage rate of liquid hydrogen is roughly 100 times that of JP-4 fuel, 50 times that of water, and 10 times that of liquid nitrogen.

<u>Diffusion and buoyancy</u>: The diffusion rate of hydrogen in air is approximately 3.8 times faster than air in air. In a 500-gallon ground-spill demonstration experiment, liquid hydrogen diffused to a nonexplosive mixture after about 1 minute. Air turbulence increases the rate of hydrogen diffusion. The buoyancy of hydrogen tends to limit the spread of combustible mixtures resulting from a hydrogen release. Although hydrogen vapor is heavier than air at the temperatures existing after evaporation from a liquid spill, at temperatures above -418° F the hydrogen vapor becomes lighter than air, thereby making the cloud buoyant. (See <u>ANSI / AIAA G-095-2004</u>, Guide to Safety of Hydrogen and Hydrogen Systems, for more specific related information.)

6.4.3 Hazards of Handling and Storage

Safety is improved when designers and operational personnel are aware of accidents that are repeatedly associated with the handling and use of hydrogen. The release of liquid or gaseous hydrogen has resulted in fires and explosions. Such hazards are associated with the formation and movement of a flammable gas-air cloud upon hydrogen release. The dispersion of the cloud is affected by wind speed and wind direction.

<u>Storage tank failures:</u> Tank failures resulting in the release of hydrogen may be started by material failures, excessive pressures caused by heat leaks, or failures of the pressure-relief systems. Hydrogen embrittlement is a major material failure threat (see Sec. 6.6.3).

<u>Unloading and transfer leaks</u>: Deformed seals or gaskets, valve misalignment, or failures of flanges or equipment usually cause unloading and transfer leaks. A leak may cause further failures of construction materials including vacuum jacketed lines.

<u>Collisions during transportation</u>: Damage to hydrogen transportation systems have caused spills and leaks that resulted in fires and explosions.

6.4.4 Hazardous Properties of Gaseous Hydrogen

<u>Undetectability</u>: Hydrogen gas is colorless and odorless and not detectable by human senses.

<u>Flammability</u>: Mixtures of hydrogen with air, oxygen, or other oxidizers are highly flammable over a wide range of compositions. The flammability limits, in volume percent of hydrogen, define the range over which fuel vapors ignite when exposed to an ignition source of sufficient energy.

The flammable mixture may be diluted with either of its constituents until it is no longer flammable. Two limits of flammability are defined: the lower limit, the minimum amount of combustible gas that makes a mixture flammable; and the upper limit, the maximum amount of combustible gas in a flammable mixture.

The flammability limits based on the volume percent of hydrogen in air (at 14.7 psia) are 4.0 and 75.0. The flammability limits based on the volume percent of hydrogen in oxygen (at 14.7 psia) are 4.0 and 94.0. Reducing the pressure below 1 atmosphere tends to narrow the flammability range by raising the lower limit and lowering the upper limit. No mixture of hydrogen and air has been found to be flammable below 1.1 psia.

<u>Autoignition:</u> Temperatures of about 1050° F are usually required for mixtures of hydrogen with air or oxygen to autoignite at 14.7 psia; however, at pressures from 3 to 8 psia, autoignitions have occurred near hot hydrogen and flash fire. The primary hazard of using hot hydrogen (1050° to 6000° F) is that a large leak at temperatures above the autoignition temperature will almost always result in a flash fire. Other safety criteria are the same as for ambient temperature gaseous hydrogen. System construction materials must be suitable for use at the elevated temperatures.

<u>Ignition at low energy input:</u> Hydrogen-air mixtures can ignite with very low energy input, 1/10th that required igniting a gasoline-air mixture. For reference, an invisible spark or a static spark from a person can cause ignition.

Lack of flame color: Hydrogen-oxygen and hydrogen-pure air flames are colorless. (Any visible flame is caused by impurities.) Colorless hydrogen flames can cause severe burns.

6.4.5 Hazardous Properties of Liquid Hydrogen

All of the hazards that exist when gaseous hydrogen is present exist with liquid hydrogen because of the ease with which the liquid evaporates. However, there are additional hazards due to the properties of liquid hydrogen.

Low boiling point: Liquid hydrogen has a normal boiling point of -423° F at sea-level pressure. Any liquid hydrogen splashed on the skin or in the eyes can cause serious "burns" by frostbite.

Storage tanks and other containers should be kept under positive pressure to prevent air from seeping in. Condensed and solidified atmospheric air, or trace air accumulated in manufacturing, contaminates liquid hydrogen, thereby forming an unstable mixture. This mixture may detonate with effects similar to those produced by trinitrotoluene (TNT) and other highly explosive materials.

<u>Ice formation</u>: Vents and valves from storage vessels and dewars may be frozen closed by accumulations of ice formed from moisture in the air. Excessive pressure may then rupture the container and release a potentially hazardous quantity of hydrogen.

<u>Continuous evaporation</u>: The continuous evaporation of liquid hydrogen in a vessel generates gaseous hydrogen, which must be vented to a safe location.

<u>Trapped liquid:</u> If liquid hydrogen is confined, for example, in a pipe between two valves, it will eventually warm to the surroundings and cause a significant pressure rise. The pressure of a trapped volume of liquid hydrogen at 14.7 psia, when warmed to 70° F, rises to 28,000 psia.

<u>Cold gas leak</u>: At temperatures above -418.6° F, hydrogen gas is lighter than air at standard temperature and pressure (STP) and tends to rise. At temperatures just after evaporation from the liquid, the vapor is heavier than air and will remain close to the ground until the gas temperature rises.

6.4.6 Hazardous Properties of Slush Hydrogen

All of the hazards that exist with gaseous and liquid hydrogen exist with slush hydrogen. The combustibility properties of slush hydrogen should not present any greater hazard than those of liquid hydrogen, but there are additional hazards with slush hydrogen.

<u>Low vapor pressure</u>: The greatest hazard with slush hydrogen systems is the intrusion of air into the hydrogen storage container. Because the vapor pressure of slush hydrogen mixtures is only 1.02 psia, there is always a concern that atmospheric air will leak into the slush system.

<u>Volume expansion on melting and warming</u>: When the solid hydrogen in slush hydrogen melts and the colder liquid hydrogen warms up to temperatures above the triple point, the

volume of the hydrogen increases significantly. <u>A mixture of 50-percent solid (by mass)</u> slush expands more than 15 percent in reaching the density of liquid hydrogen at 36° <u>R</u> and 1 atm. <u>Sufficient ullage must be available to accommodate the expansion caused by</u> heat input to a slush hydrogen storage system over the expected storage time.

<u>Thermal acoustic oscillations</u>: Thermal acoustic oscillations can be caused by the entrance of the slush mixture into a warmer duct (typically into a gauge line or/and instrumentation tube). The subsequent warming and expansion forces the fluid back into the tank where cooling occurs. The cooling lowers the fluid pressure and causes a resurgence of the slush mixture into the tube. Repetition of this process drives an undamped pressure oscillation which pumps thermal energy into the bulk mixture.

<u>Solid particles in flow streams</u>: Slush hydrogen piping systems shall be designed to prevent solid particles from accumulating and then blocking valve seats, instrumentation ports, and relief valve openings.

<u>Slush hydrogen system air intrusion</u>: During operation, slush hydrogen systems shall be monitored continuously for the intrusion of air from the atmosphere. A detection warning system design and emergency operation plan shall be presented to the Area Safety Committee.

6.5 SYSTEM DESIGN AND OPERATION

All pressure vessels and systems shall be designed in accordance with the requirements in NPD 8710.5, "NASA Safety Policy for Pressure Vessels and Pressurized Systems."

6.5.1 Safety Approval Policy

Before hydrogen facilities, equipment, and systems are constructed, fabricated, and installed, the design safety shall be reviewed and approved by the Area Safety Committee. Hydrogen facilities, equipment, and systems that are or may need to be electrically classified, as hazardous locations shall obtain formal approval from the Safety Branch. Documentation that details the design of hazardous locations must be submitted to the Safety Branch for review prior to installation, fabrication, or construction. Approval will be documented by memo to the requestor with a copy filed in the Safety Branch and a copy sent to the Area Safety Committee. For guidelines on Hazardous Classified Locations see Chapter 8 of the GSM (8.8.18 Hazardous Classified Locations). The safety of hydrogen storage, handling, and use in systems is enhanced when the facility plans, equipment designs, materials, and cleaning specifications are reviewed and approved before construction begins.

6.5.2 Safety Review Requirements

Note: For hydrogen systems in quantities of 10,000 pounds or more, on site in one location, it is required to abide by the directives of 29 CFR 1910.119, Process Safety Management of highly hazardous chemicals.

<u>Analysis of hazards</u>: The Safety Permit request shall include a hazards or failure mode analysis identifying conditions that may cause death, injury, or damage to the facility and surrounding property.

<u>Assessment of final designs</u>: Reviews of the final drawings, designs, structures, and flow and containment systems shall include a safety assessment to identify potential system hazards and areas of compliance required by local, state, and federal agencies.

<u>Evaluation of operational procedures</u>: Operational procedures, along with instrumentation and control systems, shall be evaluated for their capacity to provide the required safety. It may be necessary to develop special procedures to counter hazardous conditions. Analysis or certification testing should verify equipment performance. The Area or Process Systems Safety Committee must review and approve the special procedures and verifications.

<u>Training and certification of operators</u>: Operators shall be adequately trained and certified prior to operations. Plans for hydrogen safety training shall be presented. See Section 6.9.2.

<u>Development of emergency procedures</u>: The safety of personnel at and near hydrogen systems shall be carefully reviewed, and emergency procedures shall be developed in the earliest planning and design stages. Advance planning for a variety of emergencies, such as fires and explosions, should be undertaken. The first priority is to reduce any risk to life.

6.5.3 Detection of Combustibles

Hydrogen detectors, where possible, shall be placed above possible leak points. The use of gathering hoods around the detectors is recommended. The hydrogen detection system must be compatible with systems for fire detection and suppression. Verification that the detection units shall not be or become ignition sources is extremely critical. Details are provided in Section 6.8.

Well-placed, reliable hydrogen detectors are imperative for a safe operating installation. Detection of liquid hydrogen leaks by observation alone is not adequate. Although a cloud of frozen air and moisture may be visible, such a cloud is not a reliable indicator of the presence of hydrogen.

The number and distribution of detection points and the time required to shut off the hydrogen at its source should be based on factors such as estimated leakage rates, ventilation, and room volume. In addition, the detection signal should actuate warning alarms should automatically affect shutoff whenever practicable and send an alarm to Emergency Dispatch at a designated percentage of the lower explosive limit (usually 20%).

Hydrogen detection systems shall be field calibrated at least every 6 months. A record of calibrations shall be maintained for each facility.

6.5.4 Buildings

Type of structure: In general, hydrogen should be stored, transferred, and handled outdoors where leaks are diffused and more easily diluted to noncombustible mixtures. However, if protection from the weather is required, the type of structure should be selected in the following order of preference:

- a. Roof without peaks; no sides (weather shelter or canopy)
- b. Well-ventilated roof; removable sides
- c. Well-ventilated "expendable" building
- d. Well-ventilated permanent building

The walls and roof should be lightly fastened and designed to relieve at a maximum internal pressure of 25 pounds per square foot without collapse of the structure. Doors shall be hinged to swing outward in an explosion. Any walls or partitions should be continuous from floor to ceiling and securely anchored. At least one wall shall be an exterior wall, and the room shall not open to other parts of the building.

Rooms and test cells with the potential to contain hydrogen shall be heated only by steam, hot water, or other indirect, passive means. Circulation fans shall have totally enclosed, non-spark producing induction motors, thermostats shall have non-spark producing contacts (enclosed) suitable for Class I, Division 2, Group B, use.

<u>Construction materials</u>: The building shall be constructed of noncombustible materials on a substantial frame. The windowpanes shall be shatterproof glass or plastic in frames. In addition, floors, walls, and ceilings should be designed and installed to limit the generation and accumulation of static electricity and shall have a fire resistance rating of at least 2 hours.

<u>Electrical equipment selection and installation</u>: Electrical equipment shall, at a minimum, be installed to conform to the "National Electric Code" requirements (NFPA 70) for Class I, Division 2, Group B. Special considerations shall be given to the selection of wire sizes, types, bonding techniques to prevent arcing, and mechanical damage protection.

Materials for electrical and electronic equipment should be selected in accordance with established specifications such as KSC STD E-0002, "Hazard Proofing of Electrically Energized Equipment."

Installing electrical equipment in purged boxes, using special types of nonarcing electric motors, and locking out specific electrical circuits when hydrogen is present are alternative ways of meeting code requirements.

Electrical wiring and equipment located within 3 feet of a point where hydrogen line connections are regularly made and disconnected, or within 3 feet of a point where hydrogen is vented shall be Class I, Division 1, Group B. Electrical wiring and equipment located from 3 feet to 25 feet of a point where connections are regularly made and disconnected, or within 25 feet of a liquid hydrogen storage container, shall be Class I, Division 2, Group B. See Section 6.7.3 for more information and special exceptions.

6.5.5 Test Chambers

<u>Ventilation</u>: Any test cell or chamber containing hydrogen system components must be adequately ventilated whenever hydrogen is in the system. The quantities of air, or other means of making the system inert, shall be sufficient to avoid an explosion and should be based on the largest credible volume of the leakage gases relative to the room volume and the time available for instituting corrective measures.

Adequate ventilation must be ensured before hydrogen enters the system, and such ventilation must remain adequate until the system is purged. Do not shut off ventilation as a function of an emergency shutdown procedure. The test cell control system should include interlocking features to prevent operation without adequate ventilation.

Safety-relief devices of containers in buildings should be vented to the outdoors at an appropriate elevation that will ensure area safety and where there are no obstructions (see Sec. 6.5.16). Vents must be located at least 50 feet from air intakes (OSHA standard, 29 CFR 1910.103). The discharge from outlet openings must be directed to a safe location (see Sec. 6.5.7).

Explosion venting must be provided in exterior walls or in the roof. The venting should be not less than 1 square foot per 30 cubic feet of room volume.

Hydrogen diffuses rapidly if not confined. At room temperature, hydrogen is the lightest of all gases, only 1/14th as heavy as air; consequently, it rises. Therefore, inverted pockets will trap hydrogen gas. Avoid covers, suspended ceilings, or places where pockets may form and trap hydrogen gas.

Forced air ventilators shall be powered only by devices approved for hydrogen service. Electric motors and drive belts used to open vents, operate valves, or operate fans must be designated as Class I, Division 1 or 2, Group B.

Adequate ventilation to the outdoors must be provided. Inlet openings should be located in exterior walls. Outlet openings should be located at the high point of the room in exterior walls or the roof. Inlet and outlet openings shall have a minimum total area of 1 square foot per 1000 cubic feet of room volume.

<u>Inert atmosphere:</u> Test cells or chambers that cannot be ventilated sufficiently to cope with potential hazards may be rendered nonhazardous by providing an inert atmosphere of nitrogen, carbon dioxide, helium, steam, or other nonreactive gas. In such cases it is desirable to have the chamber pressure higher than atmospheric pressure to avoid inward leakage of air. The design shall prevent any possibility of asphyxiation of personnel in adjacent areas or of personnel who accidentally enter the cell.

<u>Partial vacuum</u>: Oxidants may be restricted in a test chamber by using a partial vacuum. The vacuum should be sufficient to limit the pressure of an explosion to a value that the tank can withstand. In such a case the chamber must withstand 20 times the maximum operating pressure, except for heads, baffles, and other obstructions in a pipe run, which must withstand 60 times the maximum operating pressure. Because the reaction time during a detonation is so short, ultimate stress values may be used.

<u>Secondary fire protection systems</u>: Strong consideration should be given to the installation of deluge systems along the top of storage areas. These deluge systems should have both manual and automatic actuation capabilities.

Fire-extinguishing systems should be used to protect manifold piping, relief vents, and transfer pump facilities from secondary fires. In addition, rooms containing cryogenic and flammable fluids should be provided with secondary fire and explosion protection. These rooms should have a continuously operating exhaust system with a flow of about 1 cubic foot/minute/square foot (0.3 cubic meter/minute/square meter) of floor area. If a flammable gas is detected at 25 percent of the lower flammability limit, the exhaust capacity should be doubled.

6.5.6 Control Rooms

A blast-proof control room remote from the hydrogen test site is advisable. In any case, control rooms should provide a means to observe (directly or by closed-circuit television) the hydrogen systems. In control rooms where hydrogen use in adjacent test areas could create a hazardous situation, the following must be considered:

<u>Openings to test area</u>: Any control room window opening into a test cell where excessive pressures or ricocheting fragments could be present must be considered a hazard. If a window is required, it shall be made as small as practicable and shall be of bulletproof glass or the equivalent.

If wall openings and such cannot be sealed, any hydrogen-containing cell with openings to other rooms should be maintained at a negative pressure relative to the communicating rooms.

<u>Piping systems:</u> Hydrogen piping must not enter the control room. Any hydraulic or pneumatic control valve must have a double barrier between the hydrogen line and the control room. Manual isolation valves should be used for greater protection. Conduits shall be sealed at the test rig end and be designed to prevent purge gases from entering an occupied area.

Existing gaseous hydrogen transmission lines buried underground in the control areas shall be proof-tested and leak-checked periodically. Buried lines are not allowed for new facilities.

<u>Ventilation</u>: Inlet openings for room ventilation should be located near the floor level in exterior walls only. Outlet openings should be located at the high point of the control room in the exterior walls or the roof. Both the inlet and outlet vent openings must have a minimum total area of 1 square foot per 1000 cubic feet of room volume.

Title 29 CFR 1910.103 (b) (2) (ii) (d) (5) prohibits locating hydrogen systems of more than 3000 cubic feet within 50 feet of intakes for ventilation or for air-conditioning equipment and air compressors. Compliance with this standard is required.

There are stricter limits for liquid hydrogen; for all quantities, the minimum distance to air compressor intakes, air-conditioning inlets, or ventilating equipment shall be 75 feet measured horizontally.

Particular attention should be paid to the ventilation or air source for control rooms that may, in an emergency, be enveloped in hydrogen gas or the products of combustion. Undetected hydrogen is responsible for a large number of fires and explosions.

To ensure that inert gases are prevented from escaping into control room areas:

- a. Do not pipe inert gases into tightly sealed shelters if there is a possibility of accidental release and suffocation from lack of oxygen
- b. Seal purged electrical gear and conduits from personnel shelters
- c. Make sure that instrumentation and gas sampling systems cannot provide a leak path for inert gases to the control area

6.5.7 Hydrogen Vessels and Storage Systems

<u>General requirements</u>: The following are design requirements for the safe storage and use of hydrogen.

- a. All hydrogen vessels or containers other than piping shall comply with the following:
 - Storage or stationary containers shall be designed, constructed, and tested in accordance with appropriate requirements of Section VIII of the "ASME Boiler and Pressure Vessel Code" for unfired pressure vessels.
 - Portable containers shall be designed, constructed, tested and maintained in accordance with U.S. Department of Transportation specifications and regulations (49 CFR).
- b. All piping and systems shall conform to Section 6.5.10.
- c. Fixed storage vessels and propellant trailers shall be located in accordance with the appropriate quantity-distance tables as specified in Section 6.11.

- d. Amounts of hydrogen in test rigs and special vessels inside buildings should be kept at a minimum as approved by the Area Safety Committee (see Sec. 6.11).
- e. All hydrogen vessels shall be protected from potential sources of shrapnel. Barricades should be installed near the test area to protect the dewar from blast fragments or from disintegrating high-speed machinery. Housings for high rotational speed equipment may be designed as shrapnel shields between the rig and the vessel.
- f. Combustible materials shall be allowed in the hazardous areas only when they are required for test purposes. Otherwise, the onsite materials restrictions of NFPA 55 shall be followed.
- g. Piping carrying hydrogen to the test vessels from the dewars, trailers, and storage vessels should be installed above ground.
 - Hydrogen lines for new construction shall be installed above grade or in open trenches covered with grating.
 - Lines crossing under roadways shall be installed in concrete channels covered with an open grating.
 - Lines carrying liquid hydrogen should be insulated to prevent the condensation of atmospheric air.
- h. Hydrogen transport dewars and trailers shall be kept outdoors and located so that hydrogen cannot leak into any building.
- i. Hydrogen transport trailer parking areas shall be barricaded and have warning signs posted whenever a loaded hydrogen gas trailer or mobile dewar is present. Warning signs are required and shall state "Gas (or Liquefied) Hydrogen Flammable Gas No Smoking or Open Flame."
- j. Adequate lighting should be provided for nighttime transfer operations. The electrical wiring and equipment shall comply with established code requirements as specified in Section 6.7.3.
- k. Vessels shall be tagged and coded per ASME code.
- 1. Facility file records of tests on vessels, piping, and components shall be maintained as prescribed by the Glenn Pressure Systems Office certification procedures.

<u>Fixed storage systems for liquid hydrogen</u>: Surfaces exposed to the cryogen shall be constructed of materials that do not tend toward low-temperature embrittlement. Generally, face-centered-cubic metals and alloys such as aluminum, copper, nickel, and austenitic stainless steels are used. The outer wall or vacuum jacket may be fabricated from mild steels (see Sec. 6.6).

The tank outlet and inlet markings should designate whether the working fluid is vapor or liquid. The hazard potential of opening the system will differ significantly for pressurized vapors and liquids. Wherever possible, avoid storing liquid hydrogen in containers with bottom openings, thereby preventing an uncontrollable leak path if a valve or connector should fail.

Insulation shall be designed to have a vapor-tight seal in the outer jacket or covering, to prevent air condensation and oxygen enrichment within the insulation. Condensed air in the insulation system may expand explosively as it reverts to a gas when the liquid hydrogen is emptied from the tanks or pipes.

The roadways and surfaces of areas below hydrogen piping from which liquid air may drop shall be constructed of noncombustible materials such as concrete.

<u>Mobile storage systems for liquid hydrogen</u>: The design of mobile storage systems shall conform to the applicable specifications herein and to Department of Transportation (DOT) Hazardous Materials regulations, listed in Title 49, Code of Federal Regulations, Parts 100 to 185. In addition, dual rupture disks shall be required on trailers used for NASA liquid hydrogen operations.

<u>Fixed and mobile storage systems for gaseous hydrogen</u>: Large volumes of gaseous hydrogen shall be stored outdoors in mobile or fixed cylinders. Design guidelines for these systems are as follows:

- a. Use recommended materials as listed in Section 6.6.
- b. Do not make unrelieved penetrations to the sidewalls. If a pressure gauge is needed, consider entry through the forged heads.
- c. Include a passageway for regular visual inspection in larger diameter vessels.
- d. Do not use T-1 steel or cast iron.

Gas tube trailers shall have physically specific connecting fittings to prevent cross connection to the incorrect gas manifold. In addition to the manually operated main shutoff valves, these gas tube trailers should be equipped with remotely operated, normally closed safety shutoff valves that require maintained power to remain open. They shall automatically return to fully close upon the removal of the control power. The valve cabinets should be well ventilated, and the trailer valve cabinet doors should be fully opened when in service.

Common gas facilities for both fuels and oxidants are not recommended. If common facilities are absolutely necessary, however, the installation must have proper purging procedures, blocking valves, venting systems, and most importantly, personnel technically trained in gas handling. Use of common gas facilities for both fuels and oxidants will require a locally granted waiver.

Fixed storage vessels shall be located in accordance with the approved gaseous hydrogen quantity-distance tables (see Sec. 6.11).

<u>Vessel valves</u>: Valves and other components subjected to liquid hydrogen or cold gas flows shall be suitable for cryogenic service. All liquid hydrogen vessels and mobile dewars shall be equipped with automatic shutoff valves. Manually operated valves may be used under the following conditions:

- a. The loading operations and valves are attended by personnel using the buddy system, if this procedure has been approved by the Area Safety Committee
- b. The pressure of the dewar does not exceed its normally designed operating pressure.
- c. Vessels used as components of a test facility have remote-operating failsafe shutoff valves with manual override to be used if the power fails.
- d. For protection against the hazards associated with ruptures, rupture disks or relief valves are installed in all enclosures that contain liquid or that can trap liquids or cold vapors.

<u>Vessel supports for mobile dewars</u>: The design and construction of supports for inner vessels, as well as for piping systems, should meet structural and thermal operational requirements.

For over-the-road trailers (tank motor vehicles) all supports to inner vessels and to loadbearing outer shells should be attached by pads of materials similar to that of the inner vessel or outer shell, respectively, and by load rings or bosses designed to distribute the loads.

Trailers shall be provided with at least one rear bumper designed to protect the tank and piping in the event of a rear-end collision and to keep any part of another vehicle from striking the tank. The design should allow the force of a rear-end collision to be transmitted directly to the chassis of the vehicle. See NFPA 385 for other information on tank motor vehicles for flammable and combustible liquids.

<u>Transfer connections</u>: Connectors must be keyed, sized, or located so that they cannot be cross connected, thereby minimizing the possibility of connecting incompatible gaseous fluids or pressure levels. The connectors and fittings to be disconnected during operations should have tethered end plates, caps, plugs, or covers to protect the system from contamination or damage when it is not in use.

<u>Liquid hydrogen connections</u>: Vessels shall be connected to rigidly mounted test facility piping with supported and anchored flexible metal hose that is insulated for low-temperature service at the desired pressure. Other requirements for liquid hydrogen connections follow:

- a. Recommendations for flexible hoses include a maximum allowable slack of about 5 percent of the total length, per 29 CFR 1910.103. Flexible hoses pressurized to greater than 165 psia shall be restrained at intervals not to exceed 6 feet and should have an approved restraint device such as the Kellems hose containment grips attached across each union or hose splice and at each end of the hose. The restraint devices should be secured to an object of adequate strength to restrain the hose if it breaks.
- b. Sharp bends and twists should be avoided in the routing of flexible hose. A minimum of 5 times the outside diameter of the hose is considered acceptable as a bend radius.

- c. The pressure range of the transfer equipment should be rated equal to or greater than the tanker design pressure. Flexible hose delivering a high-pressure fluid (greater than 165 psia) should be secured at both ends.
- d. If condensation or frost appears on the external surface of the vacuum jacketed hose during use, the jacket vacuum should be checked. The hose should be removed from service and repaired if the vacuum is above 100 torr.
- e. Gasket materials used shall be suitable for this cryogenic service. Loose-fiber gasket material that can be readily fretted should not be used since the loose particles may contaminate the system. Properly sized gaskets shall be used.
- f. O-rings and O-ring grooves shall be matched properly for the design service conditions. (Reference: Parker Handbook Chart A5-2)

<u>Gaseous hydrogen connections:</u> Gaseous hydrogen connections from over-the-road tube trailers to facility supply systems shall conform to the specific safety design and material requirements specified by the Glenn Facilities Division. General requirements are as follows:

- a. Piping, tubing, and fittings shall be suitable for hydrogen service at the pressures and temperatures involved. Preferably, welding should make the joints in piping and tubing.
- b. Flexure installations 6 feet long or longer that are to be used at high pressures shall be designed with a restraint on both the hose and the adjacent structure at 6 feet intervals and at each end to prevent whiplash in the event of a burst.

<u>Vent systems:</u> All dewars and storage and flow systems shall be equipped with unobstructed vent systems designed to dispose of hydrogen safely and to prevent the entry and accumulation of atmospheric precipitation. (See Sec. 6.5.5 for information on ventilation and Sec. 6.5.16 for vent systems design.) In addition, note the following:

- a. Over-the-road dewar vent systems shall be connected to a building hydrogen vent system when the dewar is parked near a building (assuming proper vent system design per NFPA, etc...).
- b. Gas or liquid trapped in vessels or transfer lines by emergency shutdown conditions shall be released or vented in a safe manner.
- c. Cabinets and housings containing hydrogen control or operating equipment shall be adequately ventilated or purged.

6.5.8 Overpressure Protection of Storage Vessels and Systems

<u>General requirements:</u> Safety devices (safety relief valves and/or rupture disks) shall be installed on tanks, lines, and component systems to prevent damage by overpressure. Relief devices and the installation of such, shall meet the requirements of ASME code Section VIII, Pressure Vessels, and B31.3, Process Piping. Reference the American Petroleum Institute Standards and Recommended Practices, RP 520 Part 1 and Part 2, and RP 521. Also reference the Compressed Gas Association Standard S-1.3. These standards meet the ASME codes and provide additional guidance.

6.5.9 Protective Barricades, Dikes, and Impoundment Areas

<u>Purpose of barricade</u>: Barricades serve two purposes: to protect uncontrolled areas from the effects of a storage vessel rupture and to protect the storage vessel from the hazards of adjacent or nearby operations. Barricades are often needed in hydrogen storage areas to shield personnel, storage vessels, and adjoining areas from fragments if a rupture should occur where adequate separation distance is not available.

Barricades are mainly effective against fragments and only marginally effective in reducing overpressures at extended distances from the barricade. They should be located adjacent to the expected fragment source and in a direct line-of-sight between it and the facility to be protected.

If this is not possible, a barricade may be placed adjacent to the facility to be protected and in a direct line-of-sight between it and the expected fragment source.

Since pump facilities are usually required at hydrogen storage and use facilities, barricades shall be included in the design to provide protection against pump failures that could yield shrapnel. (See Sec.6.11.6 for more information.)

<u>Types of barricades:</u> The most common types of barricades are earthworks (mounds) and earthworks behind retaining walls (single revetted barricades). A mound is an elevation of naturally sloped dirt with a crest at least 3 feet wide. Single revetted barricades are mounds modified by a retaining wall on the side facing the potential hazard source.

<u>Barricade design</u>: The proper height and length of a barricade shall be determined by line-of-sight considerations. Barricades, when required, must block the line-of-sight between any part of equipment from which fragments can originate and any part of the protected items. Protection of a public roadway shall assume a 12-foot high vehicle on the road.

Barricades must not completely confine escaped hydrogen, or detonation rather than simple burning might result. One-cubic-meter liquid hydrogen spill tests conducted inside an open-ended (U-shaped) bunker without a roof-produced detonation of the hydrogenair mixture. Explosive limits of hydrogen in air are 18.3 to 59 percent by volume (Strehlow and Baker 1975; and Cloyd and Murphy 1965).

<u>Confinement of liquid and vapor</u>: A rapid liquid hydrogen spill (e.g., from the rupture of a storage vessel) results in a ground-level flammable cloud for a brief period. The quick change from a liquid to a vapor and the thermal instability of the cloud cause the hydrogen vapors to mix quickly with air, disperse to nonflammable concentrations, warm up, and become buoyant.

To control the travel of liquid and vapor due to tankage or piping spills, the facility should include impoundment areas and shields for diverting spills. The loading areas and the terrain below transfer piping should be graded toward an impoundment area, and the

surfaces within these areas should be cleaned of flammable materials. Crushed stone in the impoundment area can provide added surface area for liquid hydrogen dissipation.

Planned installations should eliminate possible confining spaces created by the equipment, tankage, and piping. Flames in and around a collection of pipes or structures can create turbulence that causes a deflagration to evolve into a detonation, even in the absence of gross confinement.

Where it is necessary to locate liquid hydrogen containers on ground that is level with or lower than adjacent storage containers for flammable liquids or liquid oxygen, suitable protective means should be employed (such as dikes, curbs, and sloped areas) to prevent accumulation of other liquids within 50 feet of the liquid hydrogen containers (NFPA 50B).

No sewer drains shall be located in an area where a liquid hydrogen spill could occur.

6.5.10 Piping Systems

<u>General requirements</u>: All pressure, vacuum, and vent piping for both gaseous and liquid hydrogen systems shall conform to the American Society of Mechanical Engineers, B31.3 "Process Piping".

Hydrogen systems shall also conform to the special requirements of NFPA 55, National Fire Protection Association, 2005, "Standard for the Storage, Use, and Handling of Compressed Gases and Cryogenic Fluids in Portable and Stationary Containers, Cylinders, and Tanks". Also reference CGA G-5.4, "Standard for Hydrogen Piping Systems at Consumer Locations" and <u>ANSI / AIAA G-095-2004</u>, "Guide to Safety of Hydrogen and Hydrogen Systems".

6.5.11 System Testing and Recertification

Plans for system testing and recertification must be developed during the system design process. See Chapter 7 of this Manual for requirements.

6.5.12 Contamination

Contamination must be prevented. The storage and piping systems, including system components, shall be designed and installed to allow for cleaning of the hydrogen system and for effective maintenance of a clean system. See Appendix B of this chapter for more information.

<u>Filters</u>: Filter placement should ensure effective collection of impurities in the system and accessibility for cleaning. The following are other guidelines for filter design:

- a. Filter elements should be made of noncalendered woven wire mesh.
- b. Sintered metal elements are not suitable because metal tends to spall and get into the system.
- c. As a general rule, the filter element should retain 100 percent of the particles greater than 0.0059 inches (150 micrometers) in diameter. Some systems, however, may require more stringent standards.

<u>Interconnected systems</u>: The passages in interconnected systems must be arranged so that cleaning or draining procedures can be developed to make sure that all piping, including dead-end passages and possible traps, is adequately cleaned.

<u>Pressure levels</u>: For interconnected systems operating at different pressure levels, adequate means shall be provided to prevent damage to the lower pressure system and its components. Spool pieces, nonstandard elbows, or tees are typically used to isolate the high- and low-pressure systems. Block and bleed valves and/or blind flanges may be required.

<u>Protection from contamination by other fluids</u>: Pressure-regulating valves, shutoff valves, and check valves do not adequately protect low-pressure systems connected to high-pressure systems. The low-pressure system must therefore have pressure-relief valves that are sized to handle the maximum high-pressure system flow. Discharge must be vented to an appropriate location (see Sec. 6.5.16).

If the pressure differences in the systems cannot be managed by relief valves to prevent leakage and if the hydrogen system is not in use, the hydrogen supply shall be disconnected and capped. Other measures may be necessary or useful in preventing contamination:

- a. Relief valves and burst disks are required for the protection of third piping systems supplied through valves from either the high- or low-pressure system.
- b. A double block and bleed valve design may help prevent system contamination by other fluids.
- c. Check valves shall not be used when bubble-free tightness is required; they can develop leaks during service. Two check valves in series have been found to be unreliable. In some cases, a single check valve has been more leak proof because the larger pressure drop closes the check valve more tightly.
- d. Leaking check valves in interconnected systems can contaminate bottled gases thereby jeopardizing the safety of laboratory operations. Suppliers of bottled gases specifically prohibit contaminating gases in their bottles. Check valves may, however, be used when system contamination is not important and where bottle pressures are not permitted to fall within 40 psig of the contaminating pressure. A safe pressure margin must be maintained.
- e. A check valve may be used in the vent line to limit air influx.

<u>Explosion hazards</u>: Explosion hazards in interconnected systems are caused by hydrogen leakage from one system into another. The design should recognize that leakage through valves is always a possibility; therefore

- a. Over pressurization safety systems shall be installed for protection
- b. The system shall be designed so that interconnected components can be separated and capped.

Protection from contamination by oxygen, air, or nitrogen: Contamination can occur with interconnected systems (e.g., nitrogen purge system connected to hydrogen systems). Check valves shall not be relied on to prevent contamination. Localized concentrations of solid oxygen particles can become detonable in liquid hydrogen; therefore eliminate oxidants from the hydrogen system and observe the following precautions:

- a. Store liquid hydrogen under pressure (4 to 25 psig) to reduce the amount of external contaminants entering the system.
- b. Keep the pressurizing hydrogen gas at least 99.6 percent pure. Know the levels of impurities, especially oxygen, to ensure that the hydrogen gas is a satisfactory pressurant.
- c. Keep all gas and liquid hydrogen transfer and handling equipment clean, dry, and purged.
- d. Do not recirculate hydrogen if dangerous contamination cannot be prevented with reasonable certainty.

If contamination should occur, see Section 6.9.14 for decontamination procedures.

6.5.13 Safe Disposal of Hydrogen

Hydrogen shall be disposed of by atmospheric venting of unburned hydrogen or by using a suitable approved burning system.

<u>Vent stacks:</u> Hydrogen systems and components must be equipped with venting systems that are satisfactory for normal operating requirements and that are protected against explosions. The vent stacks should be designed to keep air out of the stack and be placed to avoid contaminating the air intakes leading into nearby buildings.

<u>Vent stack quantities</u>: At Glenn Research Center, the guideline for the steady-state quantity of unburned hydrogen from a single roof vent should generally be limited to 0.25 pounds/second, released at least 15 feet above a roof peak. Multiple roof vents may be used at spacing of 15 feet and at locations across the prevailing wind. Significantly higher vent flows have safely and routinely been disposed of at Glenn. The Area Safety Committee may permit higher vent rates based on demonstrated safe experience or appropriate safety analysis.

At Plum Brook Station, the guideline for the steady-state quantity of unburned hydrogen is 0.5 pounds/second released from a single vent at least 15 feet above a roof peak.

<u>Vent stack designs</u>: Reference NASA Glenn drawings CF639138, CF639179, and CF303496 for typical 8-inch, 6-inch, and 4-inch vent designs. In the preferred design, each flow system would have its own vent stack because interconnecting vent discharges to the same vent stack could over pressurize parts of the vent system. An inadequate design could effectively change the release pressure on all relief valves and rupture disks connected to the vent system, and overpressure could reverse buckle burst disks in other parts of the system.

High-pressure, high-capacity vent discharges and low-pressure vent discharges shall not be connected to the same vent stack unless there is sufficient vent capacity to avoid over pressurizing the weakest part of the system. The discharge from vacuum pumps shall be ducted to specifically dedicated vents.

The vent systems shall be designed to carry vented hydrogen to safe-release locations above the roof and support the excess thrust load caused by venting the liquid, vapor, or gas. Vents for hydrogen, however, shall not be interconnected with vents for other fluids.

<u>Vent stack operations</u>: Small quantities of hydrogen may be disposed of outdoors through vent stacks at suitable heights. A check valve or other suitable device should be provided in the vent stack near the atmospheric discharge to limit the backflow of air. The vent piping shall be pre-purged to ensure that a flammable mixture does not develop in the piping when hydrogen is introduced. Nitrogen gas may be used as a purge and blanketing gas when process temperatures are above -321° F. For lower temperatures, helium gas should be used. Vent lines may need trace heating to prevent icing of relief devices.

Nonflare designed hydrogen vent stacks may still occasionally ignite. Possible ignition sources include corona discharge and lightning. The design location of hydrogen vent stacks must take into consideration that all of these stacks may ignite and burn. A system and procedure shall be in place to terminate a hydrogen fire on all nonflare designed vent stacks.

One cure, used at Kennedy Space Center and Plum Brook Station for nonflare standby vent stacks that often auto-ignited from atmospheric discharges, was to electrically isolate the top section (nominally 10 feet) of vent stack from the remainder of the system. Using a nonconducting gasket and bolt insulator sleeves at a flange joining the two sections allows the top section of the vent to electrically float at atmospheric potential and the lower section, at ground potential. An adjustable spark gap across the electrical isolation flange joint allows sparks to occur away from the venting hydrogen. (Also incorporate check valves and prepurge as identified in vent stack operations paragraph and any other positive considerations as may prove beneficial to this design).

Explosion venting: If the vent area is sufficiently large it may reduce the severity of hydrogen-air tank explosions. Explosion vents shall not be connected to gaseous hydrogen vent systems.

In general, it is not possible to provide effective venting against an explosion in pipes or long, narrow tanks. See NFPA 68, "Guide for Venting of Deflagration," for additional information.

<u>Burnoff flare stacks</u>: Larger quantities of hydrogen that cannot be handled safely by roof vent systems are best disposed of in a burnoff system in which the liquid or the gas is piped to a remote area and burned with air. These systems shall have pilot ignition warning systems in case of flameout and a means for purging the vent line.

Diffusion flames are most frequently used in flare stack operations; that is, combustion air from the open atmosphere mixes with hydrogen beyond the vent stack discharge, not with the hydrogen within the stack. Although disposing of hydrogen by flaring is essentially safe, hazards related to flame stability, flame blowoff, and flame blowout do exist. The following list contains important safety rules for disposing of hydrogen by burning:

- a. The safe disposal of hydrogen through flare stacks requires suitable flows. Atmospheric wind may modify stable performance because the wind not only aids air entrainment but also may direct the flammable mixture laterally from the stack rather than to substantial heights above the facility.
- Malfunctions in flare stacks, such as fires and explosions, have generally occurred at low flows with air forced downward from the atmosphere. Stack discharge velocities should be from 20 to 30 percent of the sonic velocity. Where the flow is too low to support stable combustion, a continuous purge or a slight positive pressure should be provided.
- c. Liquid or gas in flared venting systems should be piped at least 200 feet (61 meters) from the work and storage areas and burned with air.
 - Water pond burning (burn pond) may be used, under proper climatic conditions, for rapid releases of large quantities as well as for relatively long releases. The hydrogen is dispersed through a submerged pipe manifold to evolve into the atmosphere, where it is ignited and burned. The water serves as a seal to prevent backmixing of air into the distribution manifold and pipeline and provides some protection for the manifold from thermal radiation damage.
 - Ignitable substances such as trees and grass shall be removed from the vicinity of overland flare stacks.
- d. Burnoff flare stacks shall be designed and operated so they do not present a hazard to low-flying aircraft.

Hydrogen in a trailer traveling on a highway should be disposed of by venting it unburned in a safe location, away from populated areas and high enough to increase dispersion.

<u>Altitude exhaust systems:</u> Unburned hydrogen may be dumped into the altitude (vacuum) exhaust system only under certain conditions. Approval of the Process Systems Safety

Committee is required in all cases. Furthermore a special waiver from the Executive Safety Board is required before the following limits may be exceeded.

Lean mixture operations: It shall be permissible to introduce hydrogen-air mixture ratios leaner than 0.0068 by weight into the altitude exhaust system. (In calculating the hydrogen-air ratio, noncondensable inert gas that is added to the system may be considered as air.) This value is based on explosive limits and not on the lower limit of flammability. The 0.0068 ratios are about 50 percent of the lower explosive limit of hydrogen at standard pressure and temperature.

The preceding statement includes routine and emergency phases of altitude exhaust system operations including, but not limited to, hydrogen-rich experimental testing, engine blowout, failure to start, and hydrogen line failure within the exhaust system.

<u>Rich mixture operations:</u> Hydrogen-air mixture ratios richer than 0.0068 by weight may be introduced into an exhaust system provided that the entire system is capable of withstanding a detonation of the mixture. The system shall be capable of withstanding pressures 20 times the maximum system operating pressure; however, heads, baffles, elbows, and other types of obstructions must withstand 60 times the maximum system operating pressure.

Ultimate stress values may be used to calculate "design of system" pressures for rich mixtures because the pressure pulse is of such short duration.

<u>Burnoff ignition torches:</u> with burnoff ignition torches, controlled burning of free hydrogen before it can accumulate and detonate may enhance safe operation of hydrogen systems at sea level and within an altitude exhaust facility. This burnoff technique is effective at test cell pressures of greater than 4 psia.

6.5.14 Slush Hydrogen Systems

The primary considerations in the design of slush hydrogen systems are thermally protecting the fluid during handling and preventing air from intruding into the storage vessel.

Slush hydrogen systems shall be designed to operate so as to prevent air intrusion into the system (normally at 1.02 psia). Such systems must be designed to handle possible system blockage and wear from the solid particles of hydrogen contained in the flow stream. The structural design materials suitable for liquid hydrogen service are suitable for slush service.

6.6 MATERIALS

All structural materials shall be selected to provide safe performance with the least degradation of their mechanical properties.

6.6.1 Code Requirements

The materials for fixed-storage hydrogen containers shall be selected, and the containers designed, constructed, and tested, in accordance with the appropriate requirements of the ASME "Boiler and Pressure Vessel Code".

Materials specifications and thickness requirements for hydrogen system piping and tubing shall conform to the ASME B31.3, Process Piping. Piping or tubing for operating temperatures below 20° F (29.9°C) shall be fabricated from materials that meet the impact test requirements of Chapter III of ASME B31.3 when they are tested at the minimum operating temperature to which piping may be subjected in service.

6.6.2 Materials Selection

Selection of materials for liquid hydrogen use requires knowledge of the following:

- a. Hydrogen's unique properties and the effect of cryogenic temperatures on material behavior
- b. Specific requirements such as pressure, temperature, length of service, physical properties, fluid conditions, and critical performance requirements
- c. The mechanisms by which flaws can lead to failures

<u>Typical materials</u>: Table 6.1 lists typical recommended materials and their applications in liquid and gaseous service systems.

<u>Also</u> reference CGA G-5.4, "Standard for Hydrogen Piping Systems at Consumer Locations" and <u>ANSI / AIAA G-095-2004</u>, "Guide to Safety of Hydrogen and Hydrogen Systems".

6.6.3 Hydrogen Embrittlement

<u>Effect on mechanical properties</u>: Hydrogen service generally reduces the mechanical properties of structural materials. Such losses have been attributed to three independent primary factors: a critical, absorbed, localized hydrogen concentration; a critical stress intensity (crack length and applied or residual stress); and a susceptible path for hydrogen damage. Hydrogen effects on metals include the following:

- a. Environmental hydrogen embrittlement, present in metals and alloys plastically deformed in a high-pressure environment, which leads to increased surface cracks, losses in ductility, and decreases in fracture stress
- b. Internal hydrogen embrittlement, caused by absorbed hydrogen, which may cause failures in some metals with little or no warning
- c. Hydrogen reaction embrittlement, caused by absorbed hydrogen's reaction with the base metal, an alloy, or a contaminant, which typically results in very brittle hydrides that lower the metal's ductility

<u>Considerations in design</u>: Mechanical property loss can be prevented by such measures as coatings, elimination of stress concentrations, and additions of impurities to gas-phase hydrogen, oxidation treatments, grain size, specifications of inclusion morphology, and careful selection of alloys.

Available data are sometimes not sufficient to allow selection and application of any specific preventive measure, although the following recommendations can be made:

- a. Whenever practical, use aluminum alloys for hydrogen containment. Aluminum is one of the few metals with only minimal susceptibility to hydrogen attack.
- b. Use containers with thick walls of low-strength metals because they generally contain hydrogen more safely than containers fabricated from similar alloys treated for high strength.
- c. A metal or alloy exposed to cyclic stresses is almost certain to have lower resistance to fatigue if hydrogen is present; in the absence of data, always assume a fivefold increase in fatigue growth rates.
- d. Avoid the use of body-centered-cubic metals and alloys whenever practical. Do not use hydride-forming metals and alloys as structural materials for hydrogen service.

6.7 IGNITION SOURCES

6.7.1 Concept

Elimination of ignition sources is a second line of defense for safe operation with hydrogen. The general procedure is to eliminate all likely ignition sources.

<u>Eliminating risks</u>: Hydrogen leaks and accumulations occur despite safeguards against them. The optimum protection against unsafe conditions is the elimination of all likely ignition sources near the hydrogen hazard areas. However, escaped hydrogen is very easily ignited by unexpected means, and the presence of unknown ignition sources must be always expected. Therefore;

- a. Controls shall be established for limiting ignition sources in critical areas.
- b. Necessary ignition sources in hydrogen areas should be surrounded locally with inert gas and noncombustible heat sinks.
- c. Operating limits shall be established for all energized equipment, to minimize the temperature, energy, and duration of unavoidable ignition sources.

<u>Maintaining acceptable safety risks</u>: If ignition sources are a required part of the hydrogen test apparatus, provisions shall be made to maintain acceptable safety risks during any resulting explosion or fire. Burnoff ignition torches may enhance safe test operations under these conditions by mixture when it first reaches a flammable level. The accumulation and detonation of larger hydrogen accumulations is then prevented. See Section 6.5.16 for more information.

6.7.2 Potential Ignition Sources

Ignition of hydrogen-air mixtures usually results in ordinary combustion or deflagration, and thus, hazards from overpressure and shrapnel are less than from detonations (refer to Sec. 6.4.2).

The autoignition temperature, the minimum temperature for self-sustained combustion, is 1065° F (874° K) for a stoichiometric mixture of hydrogen and air. Compare this value with 481.4°F (523°K) for kerosene and 438.2°F (499°K) for aviation fuel such as an octane. Although the autoignition temperature of hydrogen is higher than those for most hydrocarbons, hydrogen's lower ignition energy makes the ignition of hydrogen-air mixtures more likely. The minimum energy for spark ignition at atmospheric pressure is about 0.02 millijoules.

<u>Electrical</u>: Electrical sparks are caused by sudden electrical discharges between objects having different electrical potentials (e.g., breaking electrical circuits or discharges of static electricity). Minimum values of electrical spark energy as a function of the volume percent of hydrogen are shown in Section 6.4.1. Thermal. Burning material or hot objects causes thermal ignition. Some examples are:

- a. Sparks, which are caused by hard objects coming into forcible contact with each other such as metal striking metal or stone, or stone striking stone (Sparks are particles of burning material that have been sheared off as a result of contact.)
- b. Objects at temperatures above 1065°F (847°K), which will ignite hydrogenair or hydrogen-oxygen mixtures at atmospheric pressure; substantially cooler objects (about 600°F, 590°K) cause ignition under prolonged contact at less than atmospheric pressure
- c. Open flames and smoking, which can easily ignite hydrogen mixtures

6.7.3 Limiting Electrical Ignition Sources

<u>Classification of hydrogen areas</u>: Areas where flammable hydrogen mixtures are normally expected to occur shall be classified as Class I, Division 1, Group B, in accordance with the "National Electric Code" (NEC).

Areas where hydrogen is stored, transferred, or used and where the hydrogen is normally contained shall be classified as Class I, Division 2, and Group B as a minimum. The "National Electric Code" (NFPA 70,) shall be consulted to determine if an area will be made safer by being classified as the more stringent Division 1 installation.

The Area Safety Committee may permit certain test cells where hydrogen is used to remain electrically unclassified if appropriate safety justification is presented. A rocket test cell firing into the open atmosphere might be an example. A waiver of the required Division 1 and 2 designations will be by special exception rather than as a rule and require approvals of the appropriate committee and Safety Branch.

<u>Explosion-proof enclosures</u>: A Division 1 installation differs from a Division 2 installation mainly in its degree of isolation from the electrical ignition sources in the system. A Division I installation relies heavily on explosion-proof enclosures for its isolation; such an explosion-proof enclosure is not gas tight. Explosion-proof equipment is equipment that has been qualified by a testing laboratory as being "explosion proof" for a specific gas. It means that:

- a. The enclosure is strong enough to contain the pressure produced by igniting a flammable mixture inside the enclosure, if code-required seals are properly used
- b. The joints and threads are tight enough and long enough to prevent issuance of any flames or any gases that would be hot enough to ignite a surrounding flammable mixture
- c. Guidelines for installing and using explosion-proof equipment are given in NFPA 70, KSC STD E 0012, and NFPA 496.

<u>Equipment for hydrogen areas:</u> All electrical sources of ignition shall be prohibited in classified areas, including open electrical arcing devices and heaters or other equipment that operates at elevated temperatures. This means one should use approved explosion-proof equipment (Class I, Division 1, Group B) or select non-arcing equipment approved for Division 2. Articles 500 and 501 of NFPA 70 cover equipment application and installation methods for these locations.

Intrinsically safe installations approved for hydrogen area service may be used if there is appropriate grounding, labeling, and wire separations in accordance with NFPA 70, Article 504, "Intrinsically Safe Systems," and ANSI/ISA RP 12.06.01 "Wiring Practices for Hazardous (Classified) Locations Instrumentation".

Another alternative to using explosion-proof equipment is to locate the equipment in an enclosure that is purged and then maintained at higher than ambient pressure with air or an inert gas. An indication of positive pressure shall be provided. See "Purged Enclosures for Electrical Equipment," NFPA 496.

Cost is minimized if electrical junction boxes are installed outside of the hazardous area. If systems are installed in the hazardous area, but not required during hazardous periods, they may be built with general-purpose equipment, provided that they are disconnected before the hazardous period begins. The conduits for such systems must be sealed in accordance with NEC requirements (NFPA 70) to contain hydrogen within the hazardous area and to exclude inert purge gases from control rooms and other occupied areas. Safety Committee and Safety Branch approval of this protection method is required.

See Section 6.5.4 for electrical equipment selection

<u>Classification of electric motors</u>: Electric motor classification rules and definitions are specified in NFPA 70, Article 501-8.

For Division 1 locations, a totally enclosed, fan-cooled motor can be used if an inert purge is used. Large electric motors are not generally manufactured in explosion-proof Division 1 configurations. However, electric motors of a non-arcing, nonsparking design (brushless, induction) are suitable for Division 2 locations if they meet the requirements of NFPA 70, Article 501-8.

In both Division 1 and 2 areas, surface temperatures of motors must not exceed 80 percent of the autoignition temperature of the surrounding gas. This means the motor case temperature must not exceed 867° F for motors used in hydrogen service areas at ambient pressure. Monitoring of motor case temperature may be advisable under some conditions of use.

<u>Grounding and bonding</u>: All transport, storage, and transfer system equipment and connections must be grounded. The offloading facility shall provide easily accessible grounding connections, and the connections shall be made before final operation. "National Electric Code" Article 100 (NFPA 70) defines the term "grounded" and lists the sizes of grounding conductors. The minimum size used for grounding fixed equipment in Class 1 areas shall be # 2 American wire gauge.

All of the metal components of a hydrogen system shall be electrically bonded and grounded in accordance with the "National Electric Code." This includes tanks, regulators, valves, pipes, vents, vaporizers, and receivers (mobile or stationary). Each flange should have bonding straps in addition to metal fasteners, which are primarily structural.

The resistance to ground shall be less than 10 ohms, and it shall be checked at least every 6 months to ensure this grounding is maintained. A facility record of these checks shall be maintained.

<u>Portable electrical equipment</u>: Portable electrical and electronic equipment shall be properly electrically classified for use in a classified hydrogen area. Portable radios, pagers, and hydrogen detectors are typical pieces of equipment that must meet this criterion.

6.7.4 Other Ignition Sources

<u>Lightning</u>: Lightning protection in the form of lightning rods, aerial cable, and ground rods shall be provided at all preparation, storage, and use areas. All equipment in buildings shall be interconnected and grounded to prevent induction of sparks between equipment during lightning strikes. This subject is developed further in NFPA 780, "Standard for Installation of Lightning Protection Systems." The area considered to be protected by lightning rods or aerial cable is the area within 30 degrees of either side of vertical.

<u>Static</u>: Static and electrostatic charges may be generated in flowing gases that contain solid or liquid particles as well as in flowing liquids and gases that are pure.

<u>Sparks</u>: Tests and experience indicate that in a liquid hydrogen atmosphere the energy required for ignition is so small that even spark-proof tools can cause ignitions. Therefore, all tools should be used with caution to prevent slipping, glancing blows, or dropping, all of which can cause sparks. Spark-proof and conductive floors, however, are not required.

Clothing made of nylon and other synthetic materials, and certain kinds of electrically insulated shoes have generated large static electrical buildups, which have produced significant electrical sparks.

Hot objects and flames: The following rules will aid in preventing ignition by hot objects and flames:

- a. Clearly marked exclusion areas shall be established around hydrogen facilities, and smoking shall be prohibited inside these exclusion areas.
- b. Except as they occur normally during tests, flames and objects with temperatures above 80 percent of the hydrogen ignition temperature (871° F; 739° K) shall be prohibited. Welding and cutting shall not be performed when hydrogen is present.
- c. Motor vehicles and equipment employing internal combustion engines shall be equipped with exhaust system spark arresters and hydrogen-safe carburetor flame arresters when they are operated in an established control area during hydrogen transfer.
- d. Flame arresters specifically designated for hydrogen applications shall be used to prevent open flames from contacting hydrogen-air atmospheres. A properly designed hydrogen flame arrester is very difficult to accomplish in practice because;
 - The small quenching distance of 0.024 inches (0.060 centimeters) for hydrogen makes it difficult to develop flame arresters and explosionproof equipment that can successfully disrupt a deflagration or detonation originating within the equipment
 - Flame arresters designed for hydrocarbon flames will not stop hydrogen flames, and flame arresters that are effective against hydrogen-air flames may not stop hydrogen-oxygen flames
- e. Vegetation shall not be within 25 feet (7.6 meters) of gaseous or liquid hydrogen systems.

6.8 DETECTION OF HYDROGEN LEAKS AND FIRE

6.8.1 Hydrogen Leak Detection Systems

<u>General requirements of a reliable system:</u> A reliable hydrogen detection and monitoring system shall give warning when the maximum acceptable condition has been exceeded. This acceptable condition must still be in the safe range, and the warning should indicate that a problem exists. Visual alarms should be designed into the system to indicate hazardous concentrations.

Note: Care must be given in selection of detectors to assure that they cannot become sources of ignition.

The system should locate the source of a hydrogen leak within the facility during test operations. The goals for test facility hydrogen gas detection systems should be:

- Detection of +/- 0.25 percent by volume of hydrogen in air
- Response time of 1 second at a concentration of 1 percent by volume
- Detection of 1 to 10 percent by volume of hydrogen in inert atmosphere

Portable detectors shall not be used as gas detectors for test installations that require remote location of personnel during the test period. Portable gas detectors are valuable for local leak detection.

<u>Design and calibration requirements</u>: In the design of a detection system, all possible hydrogen leak sources to be monitored shall be listed and evaluated. Valid justification shall be presented for deciding not to monitor a possible leak source.

A means to ensure that any leaking hydrogen passes the detectors at the installation must be part of the system design and installation. Consideration should be given to using hoods to route any leakage across the detector, which should be positioned to indicate area detection rather than point detection. Hydrogen leaks at exposed liquid hydrogen valves and outside containers or at exposed vacuum-jacketed liquid hydrogen lines may be allowed to diffuse into the atmosphere.

The detection system design shall ensure that the system's expected response time is rapid enough to be compatible with the fire detection or auxiliary safety system.

To ensure acceptable performance, periodic maintenance and field-recalibration of detectors shall be conducted every 6 months. Facility records of these recalibrations shall be maintained on site.

Hydrogen detector locations and alarm levels. The number and distribution of sampling points in hydrogen detection systems must be based on the possible rate of leakage, the amount of ventilation, and the size of the area. A single sampling point does not provide adequate sensing. Typical locations requiring detectors and the recommended performance requirements are presented here.

NOTE: At STP, 1 percent by volume of hydrogen in air is 25 percent of the lower flammability limit.

Facility test and transfer areas: In the area around hydrogen facilities, a 1-percent by volume hydrogen concentration at any point 3.28 feet (1 meter) or greater from the hydrogen equipment shall generate an ambient pressure warning. A 2-percent by volume concentration shall generate a high-level alarm. The performance of these detectors depends on the location of the sensors and the leak and on the direction of the wind. The number of sensors must be adequate for the area.

In vacuum-jacketed equipment, detectors are not necessary because liquid hydrogen leaks may be detected through loss of vacuum, formation of frost, formation of solid air, or a decrease in outer wall temperature.

Enclosure exhaust ports: For exhaust vents from enclosures containing hydrogen piping and storage systems, detectors should be located in the vent stream at ambient pressure and within 3 feet of the vent port. Examples of such are vent ports from purged boxes containing hydrogen valves, and ventilation discharge ducts from enclosed forceventilated test areas where hydrogen is used.

A detector shall warn of a 1-percent by volume gaseous hydrogen concentration in the purge exhaust from enclosed areas containing hydrogen systems. A 2-percent by volume gaseous hydrogen concentration, or higher, in the purge exhaust from enclosed areas would indicate a hydrogen leak and potential fire hazard within the enclosure. At this alarm level the hydrogen source shall be shut off.

Altitude (vacuum) chambers: Detectors in the altitude chamber shall generate an alarm if 1-percent by volume hydrogen concentration occurs when the chamber is not evacuated. A 4-percent by volume hydrogen concentration in the evacuated duct shall generate an alarm during altitude operation.

Leak detector accuracy and sensitivity cautions. The catalytic combustion devices currently available can be affected by large concentrations of helium gas. Ionizing handheld detectors cannot differentiate between gaseous helium and gaseous hydrogen, so a high helium concentration will give a high reading as if it were hydrogen. Furthermore, a nitrogen-rich environment can cause these detectors to give negative readings.

6.8.2 Fire Detectors

Hydrogen fires pose a special safety problem because the flames are essentially invisible. Therefore, thermal and optical sensors have been developed to detect burning hydrogen.

- a. Thermal fire detectors that can be classified as rate-of-temperature-rise detectors and heat detectors are not subject to frequent failure. To cover a large area or volume, many thermal detectors are required and they must be located at or very near the site of a fire.
- b. Optical sensors for detecting hydrogen fires operate in two spectral regions, ultraviolet and infrared. In general, different sensors and optical components must be used in each region. Closed-circuit infrared and ultraviolet remote-viewing systems, equipped with appropriate filters, have been used successfully.
- c. Linear heat detection systems consist of heat sensitive polymer insulation and inner conductors that move into contact with each other at any point along its length once a rated activation temperature is reached.

Fire detection systems should be installed in storage and use areas to warn whenever a worst allowable condition is exceeded. The fire detectors should give a rapid and reliable indication of the existence, location, and size of a hydrogen fire.

Automatic shutdown systems, triggered by multiple fire detectors and activated quickly enough to prevent large-scale damage, should be considered. Connecting an automatic shutdown system to a fire-detecting system may not always be effective since alarms may be triggered by reflections from allowable fires (burn ponds and flare stacks) and sunlight.

6.9 STANDARD OPERATING PROCEDURES

6.9.1 Policy

Standard operating procedures (SOP's), with checklists as required, shall be developed for common operations. The SOP's should be set by individuals directly involved with hydrogen operations and shall be approved during the safety permit review process. These procedures should be reviewed and updated periodically.

<u>Confined spaces:</u> (See chapter 16 of Glenn Safety Manual) Repairs, alterations, cleaning, or other operations in confined spaces in which hydrogen vapors or gases are likely to exist are not permitted until a detailed safety procedure is established. These procedures should:

- a. Specify, as a minimum, the evacuation or purging requirements necessary to ensure safe entry and the maximum hydrogen concentration limits allowed (10 percent of the lower flammability limit in the confined space)
- b. Require that an acceptable gas sample be taken before personnel are allowed to enter
- c. Require that persons engaged in operations be advised of possible hazards
- d. Provide for emergency rescue training
- e. Ensure that at least one trained person is always available in case of emergency

Before major work is performed on hydrogen vessels, they must be drained and purged of hydrogen. All pipelines leading to systems still containing hydrogen shall be disconnected, capped or blank flanged, and tagged. The following should be done before work begins:

- a. De-energize electric power supply to equipment within the vessel.
- b. Purge tanks of flammable vapors, and test to ensure the effectiveness of the purging operation.
- c. For major repairs or modifications, warm and purge the vacuum annulus. Purging of vacuum jackets is a unique procedure that requires careful planning and execution.

6.9.2 Requirements for Personnel

Training shall familiarize personnel with the physical, chemical, and hazardous properties of hydrogen and with the nature of the facility's major process systems (i.e., loading and storage; purge gas piping; control, sampling, and analyzing; alarm and warning signals; ventilation; and fire and personnel protection (see Sec. 6.10)).

The buddy system of the appropriate level must be followed. Chapter 22.2. (c) details the level normally accepted for GH2 operations and handling, although the two "qualified operators" that shall be present are required to <u>have an equal degree of knowledge</u>. This "qualified operator" policy applies to both hydrogen research test operations and hydrogen handling operations. However, no more than the minimum number of personnel necessary should be present in a hazard area (see Ch. 2). Qualified operators should demonstrate:

- a. Knowledge of the nature and properties of hydrogen in both the liquid and gaseous phases
- b. Knowledge of the materials that are compatible with both liquid and gaseous hydrogen
- c. Knowledge of proper equipment and proficiency in its operation
- d. Familiarity with the operation manuals of the operating equipment
- e. Proficiency in the use of protective equipment and clothing
- f. Proficiency in self aid, first aid, and proper emergency actions
- g. Recognition of normal operations and of symptoms that indicate a deviation from such operations
- h. Conscientiousness in following instructions and checklist requirements

6.9.3 Startup Examination and Inspection

<u>Examination</u>: The Test Site Engineering Operations organization is responsible for ensuring that the following are accomplished before system startup:

- a. Before initial operations, all storage and piping installations and their components shall be inspected to ensure compliance with the material, fabrication, workmanship, assembly, and test requirements established by NASA. Hydrogen system examinations shall be performed in accordance with the ASME "Boiler and Pressure Vessel Code," Section V.
- b. The completion of all required examinations and testing shall be verified. Verifications should include, but not be limited to, certifications and records pertaining to materials, components, heat treatment, examination and testing, and qualification of welding operators and procedures.
- c. Materials must be identified for all piping and components used in fabrications and assemblies subjected to liquid hydrogen temperatures. No substitutions for the materials and components specified in the engineering design are permitted without written approval from the facility project

engineer. During reassembly, cleanliness and dryness of all components shall be maintained.

<u>Test records</u>: Records shall be made on each system and piping installation during system checkout testing. These records should include date of test; identification of system, component, and piping tested; test method (e.g., hydrostatic, pneumatic, or sensitive leak test); test fluid; test pressure; hold time at maximum test pressure; test temperature; locations, types, and causes of failures and leaks in components and welded joints; types of repair; test records; and the name of the responsible safety design engineer or operations engineer.

Test records shall be retained by the responsible operating organization and may need to be incorporated in the system configuration management system.

6.9.4 Signals and Identification

<u>Safety signals</u>: Established uniform audible and visible safety signals are to be used at Glenn, and all personnel must know and obey them. The meanings of the signals shall be posted in all operational areas. These signals are specified in Chapter 19, Vehicle and Pedestrian Safety, Section 19.6 Safety Barricades.

<u>System identification</u>: The approved method of indicating the contents of a container or system is the printed word.

6.9.5 Checklists

Checklists are substantial aids to safe operations and therefore are required for all installations.

6.9.6 Allowable Hydrogen Leakage at Test Installations

Every reasonable effort should be made to eliminate leakage from installations where hydrogen is used. In practice, however, it is sometimes very difficult to completely eliminate leakage. Therefore, operations may be performed coincident with some leakage if the test installation is entirely out-of-doors or in a well-ventilated expendable building. Tolerable hydrogen leakage shall not exceed 25 percent of the lower explosive limit at a distance of 2 feet above the leakage source (no wind) and shall be permitted only when:

- a. The source of leakage is known and the leakage is stable (e.g., leakage from a crack may be unstable because the crack might widen)
- b. Plentiful ventilation is provided
- c. The leakage is unconfined and free to diffuse rapidly
- d. Ignition sources are eliminated
- e. Gas detection means are employed as stated in Section 6.8

- f. Leakage is determined at test temperatures and pressures or by using helium in conjunction with a mass spectrometer and by converting the reading to the equivalent quantity of hydrogen
- g. The facility's responsible engineering manager gives written approval of the operation

6.9.7 Clean Systems (see also Appendix B, Cleanliness Requirements)

Systems, including their components, for storing and piping liquid and gaseous hydrogen shall be appropriately cleaned for service, thereby ensuring the removal of contaminants and avoiding mechanical malfunctions, system failures, fires, or explosions. Effective cleaning will remove greases, oils, and other organic materials as well as particles of scale, rust, dirt, weld spatter, and weld flux.

The cleaning of liquid hydrogen systems is a specialized service that requires welltrained, responsible individuals to properly carry out the necessary procedures. Note the following guidelines:

- a. Some systems may require disassembly for suitable cleaning. Components that could be damaged during cleaning should be removed and cleaned separately.
- b. The compatibility of cleaning agents with all system construction materials must be definitely established. Cleaning methods include steam or hot water cleaning; mechanical descaling; vapor, solvent, or detergent degreasing; acid cleaning; and purging.
- c. Clean flexible hoses and pipe sections should be sealed and marked to indicate certified cleanliness. The ends should be closed with metal caps and then covered with a clean plastic bag or sheet and, where required, sealed with a tamper-proof seal tape.
- d. Systems should be rechecked periodically for cleanliness; the facility engineers should determine the schedule. Accumulations of wear debris and frozen contaminants are possible.
- e. Cleaning operations, agents, and their effects on construction materials are described briefly in Appendix B of this chapter.

6.9.8 Purging

Before a hydrogen system or vessel is loaded, it must be made inert. This may be accomplished by a vacuum purge, a positive pressure purge, or a flowing gas purge to ensure complete removal of any contaminant gases. These gases, when trapped in a liquid hydrogen system, solidify and introduce the possibility of contamination, fire, or explosion.

<u>Vacuum purge</u>: Vacuum purging is the most satisfactory method of making a system inert since it requires fewer operations and ensures the elimination of air or nitrogen pockets. The system is vented to the atmosphere, evacuated to a relatively low pressure,

repressurized with an inert gas to a positive pressure, and again re-evacuated. Before purging the system, the operator must be sure that the container or system will not collapse when the vacuum is applied.

Recommended steps for a vacuum purge are as follows:

- a. Evacuate the system to below 10 torr (1.333 kilopascals).
- b. Perform a pressure rise rate test under static conditions and ensure that the system is tight by observing the rate of pressure rise within the system. (A 1-torr/minute (133-pascals/minute) rise for a 5-minute period indicates good vacuum holding ability.)
- c. Backfill with nitrogen or helium to atmospheric pressure.
- d. Re-evacuate to 10 torr (1.333 kilopascals).

Two or more cycles of steps (c) and (d) may be required to achieve a contaminate concentration that is low enough (nominally 0.1 percent by volume). A theoretical determination of concentration can be found by multiplying the ratios of the absolute pressures for each purge cycle.

The system is now ready for hydrogen, and the vacuum may be broken with hydrogen gas.

<u>Positive pressure purge</u>: A positive pressure purge requires alternate pressurizing and venting of the system to progressively dilute air until a safe environment is obtained.

- a. Air in the system is diluted with an inert gas to a positive pressure within the working pressure range of the vessel. (Helium must be used for liquid hydrogen system purges; nitrogen will freeze at liquid hydrogen temperatures.) Venting to the atmosphere then displaces the mixture.
- b. The system is repressurized to the positive pressure, and the mixture is again vented to the atmosphere. A positive pressure must be maintained in the receiver during these procedures to prevent the backflow of air.
- c. Following a check to ensure the system oxygen level is below 0.1 percent by volume, liquid or gaseous hydrogen may be introduced into the container.

It may be necessary to repeat these steps to obtain a safe hydrogen environment. A theoretical determination of contaminant gas concentrations can be found by multiplying the ratios of the absolute pressures for each purge cycle.

<u>Flowing gas purge</u>: A flowing gas purge is the least likely method of ensuring a positively purged system. It requires the use of an inert gas flowing into one part of the system and out of another part of the system. Helium must be used for liquid hydrogen systems; nitrogen or helium may be used for gaseous hydrogen systems.

Considerations in a flowing gas purge are volume to be purged, gas flow rate, and purge duration. Turbulent flow or a sufficiently high flow rate must be achieved to thoroughly purge all parts of the system. This method should be used only for short lines.

<u>System purge sample</u>: A newly purged system should be sampled to ensure it is safe for loading hydrogen. Normally, this requires the oxygen level to be below 0.1 percent by volume. Since nitrogen can contaminate a liquid hydrogen system by condensing and freezing at liquid hydrogen temperatures, nitrogen concentrations below 0.1 percent by volume are recommended.

6.9.9 Gaseous Hydrogen Tube Trailers and Cylinders

<u>Gaseous hydrogen tube trailers:</u> Specific equipment and procedures are required for gaseous hydrogen tube trailers.

<u>Equipment requirements</u>: All Glenn-owned gaseous hydrogen tube trailers shall be fitted with remotely operated transfer shutoff valves of a Glenn standardized design and configuration. Only inert gas or dry air shall be used to operate these remote shutoff valves.

Transfer lines (trailer to facility) may be made of corrugated stainless steel, rubber, or Teflon hose, with the proper pressure rating, inside an external braid of stainless steel. Proper restraining cables and anchoring are required. A stainless steel tube with proper pressure rating may also be used. Forming the tube into a large loop provides for some flexibility in the connection.

<u>Operational procedures</u>: Specific operational procedures to connect, start up, and shut down Glenn gaseous hydrogen tube trailer systems are found in Appendix A of this chapter.

<u>Gaseous hydrogen cylinders</u>: To prevent the infiltration of air into gas cylinders, the cylinder pressures should not be allowed to fall below 150 psig.

<u>Mandatory procedures</u>: Specific operational procedures for the safe use of gaseous hydrogen cylinders are found in the Compressed Gas Association publication CGA Pamphlet G-5, Sections 4 and 5. CGA Pamphlet G-5 is hereby adopted as a part of this chapter.

<u>Safety rules</u>: These rules apply to all portable gas cylinders.

- a. Do not transport cylinders unless the valve is closed and covered with a protective bonnet.
- b. Never handle cylinders roughly.
- c. Secure cylinders in an upright position with a chain, cable, or strap.
- d. Store cylinders where they are not subjected to physical damage and where they are protected from direct sunlight.

- e. Do not use leaky or damaged cylinders; mark them "defective" and notify the Safety Branch.
- f. Never alter, repair, change, or disassemble a valve or safety disk on a cylinder.
- g. Use proper regulators on all cylinders. Tag regulators to indicate use.
- h. Do not use a wrench to open a cylinder valve. If it can't be opened by hand, tag it as a bad valve and return it to the supplier.
- i. Remove cylinders to a safe storage area when they are not being used.

6.9.10 Storage, Transfer, and Test Operations

A facility's Standard Operating Procedures shall include safe general operating procedures for the storage, transfer, and test areas (29 CFR 1910.103). In addition, the facility shall provide good illumination, lightning protection, alarm systems, and gas detection and sampling systems. (The hydrogen detection equipment should be calibrated for short response times and detection of 25 percent of the lower flammability limit.)

To limit spill quantities, transfer operations shall be monitored whenever practical and provisions should be made for a programmed automatic shutdown in case the loading or unloading system fails. Furthermore, to protect the unloading area in case of a leak or spill, no liquid hydrogen transfer shall begin unless there is a positive shut-off capability in the supply vehicle system.

As part of the transfer procedures at Lewis Field, the Safety Branch should be notified of the liquid hydrogen offloading location and time. At Plum Brook, Plant Protection should be notified. The responsible manager shall verify that a pretest briefing has been conducted, that approved procedures are used, that emergency escape routes are clear, and that the operational area is clean and free from combustible materials and ignition sources.

Contractor unloading procedures, along with vehicle schematics and descriptions of the piping systems that interact with the NASA facility, must be provided to ensure performance of necessary precautions and procedures during and after unloading operations. As an additional safeguard, checklists shall be made for the operations performed by the supplier and user of the liquid hydrogen.

6.9.11 Cold-Shock Conditioning

All vessels and lines to be used for cryogenic service should be cold-shocked before final leak testing. Cold shocking verifies the integrity of the system for use at cryogenic temperatures. It is especially important that the expansion and contraction from ambient to cryogenic cycling not impose excessive stresses on any component.

Only those liquid hydrogen systems determined to be strong enough to carry the extra nitrogen weight may be cold-shocked with liquid nitrogen.

Components may be function tested while immersed in liquid nitrogen, but fluid systems should be conditioned with liquid nitrogen (preferably) or hydrogen and function tested at operating conditions. After the system has been purged, vented, and warmed to ambient temperature, all connections and threaded fittings should be retorqued.

The entire system shall be inspected for evidence of cracking, distortion, or other anomaly, with special attention given to welds. After repairs, cold-shock tests shall be repeated prior to the final pressure test.

6.9.12 Liquid Hydrogen Tank Cooldown

When a warm liquid hydrogen tank is being filled, the tank vent should be connected to a stack to remove hydrogen vapors from the work area. The liquid flow shall be throttled carefully to satisfactorily handle the flashoff through the vent system and to limit stress development due to excessive cool down. Typical cool down hydrogen vapor flows are 0.5 to 1.0 pound/second (0.23 to 0.46 kilograms/second). Note: If a warm dewar needs to be filled, the commercial supplier often can deliver large amounts of cold gaseous hydrogen to the NASA dewar before liquid hydrogen is added, thereby helping to reduce dewar cool down stress.

The filling system must be controlled so that the maximum liquid flow rate into the vessel is less than the tank vent system venting capacity. High vent flow rates can result in vent fires caused by static discharge. They can also result in excessive pressure increases that cause the safety valves to open or the safety disk to rupture. Tank pressures shall not exceed tank design working pressure during any routine operation. Note: This process can be aided by limiting the liquid supply dewar pressure to a few PSIG above the tank being filled.

6.9.13 Optional Liquid Nitrogen Precool

An optional method of preparing a warm vessel or system to receive liquid hydrogen uses liquid nitrogen for precooling. The cooling process evaporates large amounts of the cooling liquid, so the vessel must be determined strong enough to carry the added load of nitrogen before this method is attempted. The following procedure is to be used:

- a. Evacuate the vessel or system to approximately 10 torr (1.333 kilopascals). If this vacuum cannot be tolerated, a warm, inert gas pressure purge should be carefully planned as an alternate procedure.
- b. Introduce the liquid nitrogen into the vessel or system, taking care to prevent air migration, which will cause contamination.
- c. Allow ample time to obtain all of the cooling possible from the liquid and the cold gas. Drain off the remaining liquid nitrogen.
- d. Remove the nitrogen atmosphere by purging the vessel with helium. Make sure all of the nitrogen is removed from the vessel; this is very difficult to accomplish. (Vacuum or pressure pulse purging can be used to remove gaseous nitrogen.)

e. Admit liquid hydrogen into the vessel or system.

6.9.14 Liquid Hydrogen Systems

The equipment and techniques employed in the storage, transfer, and use of liquid hydrogen are determined by the requirements of the user. Procedures shall be periodically reviewed through the safety permit process.

<u>General procedures</u>: The procedures for operating transfer and propellant system equipment will be determined by local designs and construction, the type of equipment, and the procedures prescribed by either the local engineering operations group or the equipment manufacturer. All personnel should be completely and thoroughly instructed before operating the equipment, and all valves, pumps, switches, and such, should be identified and tagged. A written operating procedure shall be used at each operational site.

When all filling and transfer connections have been properly made, all inlet and vent valves should be set and checked before the transfer operation is started. Local piping designs will determine the details of the foregoing operation. Inspections for possible contamination and for operating conditions of the equipment are recommended after extended use and after periods of extended shutdown.

<u>Composition acceptance tests:</u> Requirements for liquid hydrogen composition, sampling methods, and quality performance testing are listed in specification MIL P 27201B and ASTM F310 70. Composition acceptance tests should be performed on the deliverable hydrogen, in the filled transport dewar, in accordance with these specifications before it leaves the filling site.

Liquid hydrogen transfers: For safe transfer of liquid hydrogen, note the following:

- a. Dewars shall be connected to electrical ground, inspected generally for leaks and mechanical defects, and checked for pressure and vacuum. The connections shall be cleaned and purged. (Contamination must be avoided.)
- b. Surfaces should be monitored for condensed water or frost, since these may indicate leaks. Minor frost at bayonet connections is quite common and expected. Cold spots on vacuum jacketed piping at the annulus spacers are also common.
- c. All transfers must be made in closed systems. Liquid hydrogen shall not be transferred into an open-mouthed dewar or be allowed to come into contact with air, for it can become contaminated with solid air. All hydrogen transfers should be made against enough backpressure to prevent air ingestion.
- d. Liquid and gaseous hydrogen should not be transferred if there is an electrical storm or a fire near the facility.
- e. Procedures to prevent overloading liquid hydrogen trailers and storage tanks must be followed. Overloading reduces the ullage space and may result in

liquid hydrogen leakage during transportation (for trailers); excessive thermal cycling may cause the relief valves to become inoperable.

<u>Beware:</u> A major cause of leaks and spills in loading and unloading areas has been the accidental removal of mobile dewars or gas tube trailers before a transfer hose is disconnected.

<u>Ullage requirements for liquid hydrogen dewars:</u> Ullage or vapor space must be maintained above the liquid hydrogen surface for safety purposes. (Filling into this space constitutes unsafe overfilling.) The design capacity for this equipment includes an excess volume normally 10 percent above the rated full capacity as shown on the level gauge. For example, a full 13,000-gallon dewar contains 13,000 gallons of liquid hydrogen and has a 1,300-gallon vapor space. The ullage requirements for slush hydrogen are appreciably greater than 10%. Refer to 6.4.6 for additional related information.

Retention of this ullage serves to avoid possible hydrostatic rupture of the vessel, since the vapor in the ullage is readily compressible whereas the liquid is not. It provides an ebullition surface to enable de-entrainment of the liquid from the vent stream and helps prevent freeze-up and consequent malfunction of the overpressure protective devices. Since changes in temperature affect the density of liquid hydrogen, available ullage varies. DOT regulations allow pressure to increase from 1 atmosphere to 17 psig in transit. This represents an ullage volume increase of more than 5 percent.

In summary, without adequate ullage, it is possible to get liquid into the vent piping during venting operations or through sloshing effects during transit. This impairs the operation of these systems and creates hazardous conditions.

<u>System leak repair</u>: No leaks shall be repaired until all pressure in the appropriate systems has been bled. All tools and fittings should be cleaned appropriately before use.

<u>Contamination</u>: Contamination must be prevented. Liquefied or solidified gases can contaminate liquid hydrogen when it is exposed to air or other gases with a higher boiling point. Containers suspected of being contaminated must be removed from service immediately and must be tagged or otherwise identified as unfit for service. Arrangements with the group responsible for that container shall be made for special handling of the container.

<u>Condensation of contaminants during loading</u>: During loading of cryogenic hydrogen, water or any other condensable vapor may condense inside the system. In large systems, even contaminant levels measured in parts per million can produce a sizable frozen mass that could impede flow or system function.

Before a cryogenic system is loaded, all air, water, and condensable vapors shall be purged or evacuated from the system. Experimentation and sample analysis may be required to define the degree of purge or the number of evacuation cycles required. <u>Removing a liquid hydrogen vessel from service</u>: Any liquid remaining in tanks containing liquid hydrogen or cold hydrogen vapor shall be removed through the liquid transfer hose to a liquid disposal system or shall be allowed to boil off through the tank hydrogen pressure buildup coil. Venting must take place through an approved hydrogen vent stack.

Purging a liquid hydrogen tank after the liquid is removed requires the use of gaseous helium or gaseous nitrogen. The instrumentation, calibrating and operating valves and lines, self-pressurization valves (hydrogen pressure buildup coil), and rupture disk bypass valves should be open during purging and venting.

During the final venting the appropriate trailer valves shall be opened slightly to provide purge gas flow through the trailer connections and lines. A sample of the vented gas shall be taken from the trailer vent and from the empty try-cock valve to verify a hydrogen concentration of 1 percent or less by volume. A warm-up period should follow.

<u>Dewar decontamination</u>: Tanks and dewars should be decontaminated (derimed) periodically by draining the contents and letting the product container warm up to permit removal of all contaminants. The warm-up period shall be determined from the service history.

Contamination often occurs in roadable dewars, which are frequently filled and emptied. Large, fixed dewars generally do not require frequent decontamination unless they inadvertently become contaminated. The interval then depends on the degree of contamination, and engineering judgment must be used. The responsible managers shall make this decision.

To ensure decontamination, the container should be vacuum purged and vacuum static checked to 10 torr (1.333 kilopascals), if it is strong enough to withstand a vacuum. If the dewar is not strong enough, a warming or pressure purge will be necessary, and dew point and gas analyses should follow.

6.9.15 Removal of Dewars and Gas Trailers From Test Facilities

Dewars and gas trailers should be disconnected from the test equipment after rig operation and moved away from the test facility as soon as practical. However, in controlled areas where large dewars are used and disconnection may constitute a hazard, the dewars may remain connected between periods of research operation at the discretion of the appropriate Safety Committee. Gaseous hydrogen trailers, isolated from the system manifold, may also be left on site with the approval of the Safety Committee. When dewars and tube trailers are moved, the peak traffic hours should be avoided.

6.9.16 Substitution of Dewars and Change of Content

Substitutions of dewars and change of content are not permitted unless approved by the cognizant Safety Committee and the responsible engineering managers. With interchange

of equipment, purging must be complete and contents must be accurately marked on the dewar. Note that many liquid hydrogen dewars are not structurally capable of handling the heavier liquid nitrogen or oxygen. Critical issues such as load bearing capability, total heat leak, cleanliness, oil free condition, and overall system compatibility are but a few of the considerations that must be thoroughly reviewed when changing content and/or substituting dewars not designed specifically for gas intended to be utilized.

6.9.17 Slush Hydrogen

Procedures for handling slush hydrogen include those for gaseous and liquid hydrogen. However, additional procedures are required for slush hydrogen. Section 6.4.6 highlights the added hazards of slush operations.

<u>Preventing and monitoring air intrusion:</u> System designs and operational procedures shall be developed and shall always be followed to eliminate the possibility of air intrusion into slush hydrogen systems. Operating slush hydrogen systems shall be monitored continuously for the intrusion of air.

<u>Periodic system warm-up:</u> Slush hydrogen systems should periodically be warmed to above the boiling points of nitrogen and oxygen (above 200° R), and the residual gas should be analyzed. If nitrogen and oxygen are present, air has probably intruded and the system should be cleaned of any entrapped air.

The <u>ANSI / AIAA G-095-2004</u>, Guide to Safety of Hydrogen and Hydrogen Systems, provides an extensive discussion of operations with slush hydrogen.

6.10 PROTECTION OF PERSONNEL AND EQUIPMENT

The best single investment in safety is trained personnel. Full consideration for the safety of personnel at and near hydrogen facilities must start at the earliest planning and design stages.

Training should familiarize personnel with the physical, chemical, and hazardous properties of liquid and gaseous hydrogen and with the nature of the major processing systems in the facility. It should also provide operators with practice in handling hydrogen as well as in handling emergency spills and fires.

Operators shall be kept up to date on changes in facility operations and safety procedures.

6.10.1 Protective Clothing

All personnel who handle liquid hydrogen or who may be exposed to cryogenic vapors shall have eye and body protection. Any unprotected parts of the body must not be allowed to touch uninsulated pipes or vessels that contain liquid hydrogen, because the cold will cause the flesh to stick and tear. Any clothing that is splashed or becomes soaked with hydrogen vapors should be aired out. Face shields shall be required when the system is being operated under pressure, when lines or components are being connected or disconnected, and when the system is being vented, unless the vent system releases gases away from all personnel.

Proper gloves (e.g., leather) shall be worn when handling anything that comes in contact with cryogenic liquids or vapors. These gloves should fit loosely and come off easily. Adequate foot protection should be provided; open or porous shoes are not permitted. Trousers must be kept outside the boots or work shoes.

6.10.2 First Aid for Cryogen-Induced Injuries

Exposure to cryogenic gases/liquids: Cryogenic burns result when tissue comes into contact with cold gases, liquid, or their containers. The result may be merely skin chilling or true tissue freezing. Commonly, only small areas are involved and the injury is to the outer layers of the skin.

Small quantities of cryogenic material may evaporate from the skin before actual freezing occurs; this injury typically produces a red area on the skin. More significant injury is caused by true freezing, the formation of crystals within and around the tissue cells. Frozen tissue always assumes a yellowish-white color, which persists until thawing occurs.

Steps to prevent and emergency care for cryogen-induced injuries must be incorporated into safety standards and training programs for operations and emergency response. Personnel shall be knowledgeable about the risks of injury from cryogens.

<u>Treatment of frozen body tissue:</u> Treatment of truly frozen tissue requires medical supervision since incorrect first aid practices invariably aggravate the injury. In the field it is safest to do nothing other than cover the involved area, if possible, and transport the injured person to a medical facility.

NOTE: Attempts to administer first aid for this condition will often be harmful. Here are some important don'ts:

- a. Don't remove frozen gloves, shoes, or clothing except in a slow, careful manner (skin may be pulled off inadvertently). Unremoved clothing can easily be put into a warm water bath.
- b. Don't massage the affected part.
- c. Don't expose the affected part to temperatures higher than 112° F or lower than 100° F.
- d. Don't apply snow or ice to the affected area.
- e. Don't use safety showers, eyewash fountains, or other sources of water, because the temperature will almost certainly be incorrect therapeutically and will aggravate the injury.
- f. Don't apply ointments.

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Although safety showers may be provided, they should not be used for treatment of cryogen burns.

6.10.3 Access to Hazardous Areas

<u>Test-cell entry forbidden:</u> Test cells and buildings with combustible hydrogen mixtures in the atmosphere shall NOT be entered under any conditions. Furthermore, no personnel may enter a test cell when liquid hydrogen or propellant gaseous hydrogen is flowing in the cell.

<u>Test-cell entry conditions</u>: Every entry into an operating test cell must be considered dangerous. After conditions within the cell have been determined to be safe, only authorized personnel shall be granted entry and then only if the project operating engineer and the personnel who are entering determine such entry is necessary. The appropriate buddy system shall be employed, and entry shall be limited to essential personnel.

<u>Monitoring personnel in cells:</u> personnel outside the test cell shall know the presence of personnel in an operating test cell. Others shall monitor in-cell personnel continuously outside the cell, either by direct sight or closed circuit TV or by the two-man buddy system with periodic calls back to the control room.

<u>Warning personnel of hazards:</u> Personnel must be warned of the presence of combustible mixtures or low oxygen concentrations. Automatic warning systems shall operate both an audible and a visible alarm. Warning alarms shall be designed so that they are not ignition sources themselves.

Work in confined hydrogen areas: Unless a detailed safety procedure is established, work is not permitted in confined spaces in which hydrogen gas could exist. See Chapter 16 of this Manual.

6.10.4 Protective Shelters and Control Rooms

Structures close to the test facilities, which would normally house personnel during a test, shall be designed to adequately protect the occupants if the test facility should explode. The design shall be in accordance with the guidelines in Section 6.5, considering the following:

- a. Particular attention shall be paid to the ventilation or source of air for shelters that may, in case of emergency, be enveloped in hydrogen gas or the products of combustion.
- b. Inert gases shall not be piped into tightly sealed shelters if there is a possibility of accidental release, which could result in suffocation from lack of oxygen. Likewise, purged electrical gear and conduits shall be sealed from personnel shelters.
- c. Hydrogen shall not be piped into shelters or control rooms.

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d. In hydrogen test areas, barricades are often needed to shield personnel, dewars, and adjoining areas from blast waves and/or fragments. Barricades are needed to isolate liquid hydrogen storage areas that are too close to public property.

6.10.5 Safeguards in Inert Environments

Asphyxiation is a safety concern for personnel entering vessels containing inert environments. Acute asphyxia, as from breathing 100-percent inert gases, produces immediate unconsciousness without warning; it happens so quickly that individuals cannot help or protect themselves. Workers may fall as if struck down by a blow on the head and will die in a few minutes if not resuscitated.

To prevent asphyxiation, the contents of a vessel's atmosphere shall be checked before any personnel enter it. Any person entering a vessel shall wear a harness-type safety belt with a lifeline attached. The line must be tended by a watcher positioned outside the vessel at a point where the watcher can be in constant communication with the worker throughout the time the worker is in the vessel. In addition, the worker shall wear a supplied-air respirator if asphyxiation could occur (see Chapter 15 for proper respirator equipment).

Personnel shall never enter an enclosure or vessel, which may contain unsafe quantities of hydrogen or any other inert or toxic gas.

6.11 BLAST EFFECTS AND SEPARATION DISTANCES

6.11.1 Quantity-Distance Concept

Quantity-distances are based on the concept that the effects of fire, explosion, and detonation can be reduced to tolerable levels if the source of hazard is kept far enough from people and facilities. Tests, analyses, and experience are employed to determine the relationship between the effects of an accident and the quantity of material involved in the accident. From knowledge of the tolerance levels of people and structures, safe distances are determined. These distances are based entirely on the estimated damage that could result from an incident, without considering probabilities or frequency of occurrence. Baker et al. (1975) present information on methods for predicting yields and blast behavior of propellant explosions. Baker et al. (1975 and 1978) and KHB 1710.2 present information on fragmentation effects from explosions.

6.11.2 Quantity-Distance Policy

The quantity-distances are intended as a basic guide in choosing sites for hydrogen operations; they are based on the total quantity of propellants at a particular site and are intended to minimize damage to facilities and to protect personnel from injury. A hazard analysis shall be performed for each facility system or subsystem.

This analysis shall take into account the physical state of the hydrogen propellant (liquid or gas), whether oxidants are present in the system, and the quantities of propellants that could be involved.

The recommended separation distances shall be based on the references listed in the following section. Recommended distances may be impossible to achieve, but proper design can sometimes guarantee that only part of the total propellant supply or only one of the propellants will be involved in an accident.

6.11.3 Quantity-Distances for Liquid and Slush Hydrogen

Quantity-distances have been established for two different situations: (1) storage of liquid or slush hydrogen, in which case the main hazards are pressure rupture, fragmentation, and gas-phase burning of hydrogen in air; and (2) the use of liquid hydrogen in propulsion test systems together with liquid oxidizers, in which case the main hazards are rapid combustion or detonation of liquid hydrogen-oxidizer mixtures.

DOD quantity-distances. The DOD classifies bulk liquid hydrogen storage as a Group III hazard. The Department of Defense manual 6055.9, "Ammunition and Explosive Safety Standards," provides quantity-distance information and tables for liquid propellants. See Tables 6.2 to 6.4, preceding the appendixes of this chapter. These are found in the NASA document NSS 1740.12, Safety Standard for Explosives, Propellants, and Pyrotechnics.

NOTE: These tables apply only to liquid and slush propellants.

Table 6.2 gives not only the recommended quantity-distances between bulk liquid hydrogen storage and compatible propellants but those between both unprotected and protected inhabited buildings, public traffic routes, and incompatible propellants. These distances provide reasonable protection from fragments of tanks or equipment that is expected to be thrown about should a vapor-phase explosion occur.

NFPA quantity-distances for bulk liquid hydrogen storage: An alternate quantity-distance separation can be used, contingent on Safety Branch approval, only for bulk liquid hydrogen storage as specified in NFPA 55, National Fire Protection Association, 2005, "Standard for the Storage, Use, and Handling of Compressed Gases and Cryogenic Fluids in Portable and Stationary Containers, Cylinders, and Tanks". The stringent requirements of NFPA 55, Chapter 11, "Liquefied Hydrogen Systems," and either CGA Pamphlet S 1.2, for mobile vessels, or S-1.3, for stationary vessels, must be met to use these distances. These values are predicated on the installation of a CGA S 1.2 or 1.3 sized emergency vent system that will prevent a storage vessel rupture even when the vessel is surrounded by fire.

The NFPA quantity-distances do NOT apply to slush hydrogen.

<u>Liquid hydrogen use with oxidizers:</u> Where liquid hydrogen is used in conjunction with liquid oxidizers such as oxygen or fluorine, as in rocket engine static test operations, the

quantity-distances are based on blast hazards. The total weight of propellants (fuel plus oxidizer) that could be involved in accidental release must be related to an equivalent amount of TNT or similar highly explosive material that would produce the same blast wave overpressure.

Tables 6.3 and 6.4 should be used to determine the blast hazard separation distances. For example, a given total quantity of liquid hydrogen plus liquid oxidizer, accidentally released, can be expected to produce a blast wave characteristic of some smaller amount of a highly explosive material. To determine the equivalent amount of explosive, multiply the combined total weight of propellants by the explosive equivalent factor, and then use the results to determine the separation distance.

Distances to inhabited buildings and to public traffic routes for various quantities of equivalent propellant mixes are given in Table 6.4; and intraline distances, the distances to be maintained between similar propellant combinations within the facility complex, are also given in Table 6.4.

6.11.4 Mandated Quantity-Distances for Gaseous Hydrogen

The installation and location of gaseous hydrogen systems, both fixed and tube trailer, shall conform to the requirements in NFPA 55, which shall be considered an integral part of this chapter.

Required quantity-distances are based on the total volume of hydrogen involved. The location of a system shall be in the order of preference indicated in NFPA 55.

6.11.5 Fragmentation

Analytical predictions of fragment velocity distributions, fragmentation patterns, and lifting and rocketing fragment free flight ranges are contained in "Occupational Noise Exposure," (29 CFR 1910.95); and "Assembly and Analysis of Fragmentation Data for Liquid Propellant Vessels" (Baker et al. 1974). These references describe methods for determining the effects of fragments on concrete and steel walls.

6.11.6 Need For Barricades

Barricades are often needed in hydrogen test areas to shield personnel, dewars, and adjoining test areas from fragments. For maximum protection, barricades should be placed adjacent to the fragment source.

NOTE: A common misconception is that barricades significantly reduce the overpressures experienced at extended distances. Barricades serve only to stop fragments; after the blast wave passes the barricade, it re-forms with almost full strength.

Barricades may be needed to isolate liquid hydrogen storage areas close to public property. In addition, they are needed to protect uncontrolled areas from the possible

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rupture and fragmentation of a storage dewar and to protect the storage dewars against vandalism.

For additional design information on barricades, see Section 6.5.9. Also see "Workbook for Estimating Effects of Accidental Explosions in Propellant Ground Handling and Transport Systems" (Baker et al. 1978) and "Hazards of Chemical Rockets and Propellants," (CPIA 394 VOL 1).

6.12 EMERGENCY PROCEDURES

6.12.1 Basic Guidelines

If an uncontrolled leak, fire, or other emergency occurs, first call 911 or using a cell phone call 216-433-8888 at Lewis Field or 419-621-3222 at Plum Brook Station. Specific actions are listed here for such emergencies as leaks and spills, over pressurization, and transportation emergencies.

<u>Leaks and spills</u>: Fire is the principal danger from a spill or leak. To help reduce the danger of fire, make sure that storage, transfer, and use areas are well ventilated and that ignition sources are avoided.

If a spill occurs, do not allow personnel or vehicles into the area affected by the spill. Completely rope off the area and post signs. If rope or signs are not available, station a person upwind to warn personnel.

<u>Liquid</u>: If a liquid leaks or spills from the piping of a vessel or pumping system, remotely shut off the source of supply. After the equipment or piping has been thoroughly vented and purged, the system can be disassembled and the leak repaired.

<u>Gas:</u> Gas leaks are more frequently heard than seen. As soon as leaks are detected, immediately stop operations, shut off the source of the supply, and relieve the line (or system) of any pressure. Resume operations only after the repairs are completed.

<u>Accumulated combustible gas mixture</u>: If there is an accumulation of combustible gas in a test cell or area, do the following:

- a. Evacuate the area. Personnel shall stay out of areas where there are combustible gases.
- b. Shut off the gas and ventilate the area.
- c. Assess the situation and, if necessary, actuate the emergency shutdown switch. All hydrogen test rigs using electrically actuated valves should have an emergency shutdown safety switch that drives system valves with known safe positions to their safest positions.
- d. Do not actuate electrical or other devices having questionable nonsparking characteristics. Portable telephones and radios usually fall in this category. Metal dampers, sashes, doors, and such may create sparks when opened.

e. Call 911.

6.12.2 Controlling Leaks

Controllable leaks are relatively small leaks that do not result in a significant spill before block, shutoff, and relief valves can be enabled. Uncontrollable leaks are large and may cause major spills. In such circumstances, do the following:

- a. Take actions to ensure the safety of personnel (i.e., take precautions against fires and explosions).
- b. Call 911.
- c. Evacuate the area within 500 feet (152 meters) of the spill source.
- d. Cool down adjacent equipment to protect it from possible fire.

6.12.3 Hydrogen Gas Leaks From Cylinders

Only properly trained technicians shall be permitted to work on leaking hydrogen gas cylinders, and they shall use only approved solutions to test for leaks (e.g., Leak-tek). If a cylinder safety device leaks, no attempt should be made to tighten the safety device cap while the cylinder is under pressure. Follow this procedure:

- a. <u>Slowly</u> empty the contents of the cylinder in a safe location.
- b. Purge cylinder with inert gas and sample for safe level of GH2.
- c. Remove the safety device cap and examine the condition of the threads.
- d. Correct the damage.
- e. Pressurize with inert gas and leak-test.

6.12.4 Slush Hydrogen Emergencies

The most significant hazard associated with slush hydrogen is the intrusion of air into the hydrogen storage vessel. The emergency procedures that apply to liquid hydrogen apply for slush hydrogen use (see Sec. 6.12.1). Special additional emergency procedures for slush hydrogen air intrusion problems are detailed in <u>ANSI / AIAA G-095-2004</u>, Guide to Safety of Hydrogen and Hydrogen Systems.

6.12.5 Transportation Emergencies

<u>Tanker hazards:</u> Hazards can occur in transporting liquid hydrogen by highway tanker. Some of the likely places and causes are:

- a. During tanker preparation, testing, and filling at the producer's site
- b. During delivery of cargo at the user's site or preparation of the tanker for return
- c. Because of vehicle malfunction, road conditions, traffic situations, or driver error
- d. Because of cargo leakage en route

e. Because of vehicle mishaps resulting in cargo leakage or spillage

<u>Emergency procedures:</u> In the event of a transportation emergency, the first concern shall be to prevent death or injury; therefore, try to get the dewar off the road, preferably to an open location if possible. Shut off the tractor-trailer electrical system, post warning lights and signs, and keep people at least 500 feet (152 meters) away.

Do not try to put out a hydrogen fire while it is still being supplied with hydrogen. For vent fires a helium gas stack purge should be initiated prior to attempting to slowly shut off the hydrogen gas supply. For vent stack and other fires it would be prudent to depressurize vessel and shutdown pressure buildup coil. If a water hose is available, use it to keep metal parts cool until the fire burns itself out. Be careful when using water not to allow water to get down the vent stack because ice formation may take place and plug the vent. For tractor fires, a fire extinguisher should be used to put out engine, tire, or electrical fires that are not fed by hydrogen.

If there is no fire, fog may be visible near a cold leak. Stop or minimize the leak if it can be done safely. Remove all ignition sources. Since a flammable mixture may exist when fog is visible, and sometimes beyond the visible cloud, do not deliberately flare hydrogen leaks.

<u>Communications</u>: A tractor-trailer transporting liquid hydrogen should be equipped with a radio or telephone to allow the driver to communicate immediately about any difficulty. If physically able, the driver should remain in the general vicinity of the vehicle at all times. The first priority is reduction of any risk to the lives of emergency personnel and bystanders. The following are important:

- a. Drivers should be trained to take prompt protective measures and to be aware of the aid they can obtain from the Chemical Transportation Emergency Center (CHEMTREC) and other emergency information systems.
- b. The toll free CHEMTREC telephone number is 800-424-9300.
- c. Other emergency information sources include the Dow Chemical USA Distribution Emergency Response System (telephone 517-634-4400) and the Union Carbide Corporation Hazardous Emergency Leak Procedure (HELP), which provides information 24 hours a day. The HELP telephone number is 304-744-3487.

<u>Major accidents</u>: If a major accident makes it impossible to move the dewar off the road, post warnings and keep people away. Notify authorities first, and then notify home base. Keep ALL people, including firefighters, at a safe distance; an explosion could occur. If there is a large hydrogen fire in which the source of hydrogen cannot be shut off, do not allow firefighters to extinguish it. Have them use water streams from a safe distance to cool the container and surrounding equipment, and to put out secondary fires.

If there has been major damage to the vacuum shell or vent system, pressure may build up and cause the liquid hydrogen container to rupture explosively. Vacate the area and keep people at least 500 feet (152 meters) away. If the surface of the inner vessel or insulation is exposed, do not apply water; this acts as a heat source to the much colder hydrogen and aggravates the boiloff.

If frost spots appear on the outer jacket, liquid hydrogen may be contacting the jacket, which is usually made of carbon steel. This metal becomes brittle when cold and should not be struck or shocked, since it could break.

Overturned trailers: If an accident occurs in which the trailer is overturned:

- a. Request the aid of the local police and fire departments by dialing 911.
- b. Seek assistance from anyone to stop traffic and evacuate the area. Do not use flares to alert or control traffic; traffic should be detoured.
- c. Do not perform any procedures on an overturned trailer unless they are well thought out before action is taken. This activity carries a very high risk.
 - In the overturned trailer, the ullage space and the venting and pressure-relief devices are exposed to the liquid. It is possible, however, to reduce the tank pressure by venting gas through lines normally used for liquid flow.
 - The detailed liquid hydrogen tanker piping schematics indicate the lines and valves that allow such an operation.
- d. Vent the trailer, if necessary, but only after consultation with the home office.

<u>Emergency venting</u>: DOT regulations require the driver to avoid unnecessary delays during transportation. The pressure in the sealed dewar must be monitored. If it shows signs of approaching the relief valve setting, the truck must be driven to a remote and safe location and the pressure must be reduced through the manual blowdown valve. Observe the rate of pressure rise, and plan manual venting operations for the daylight hours, if possible.

Repeated emergency venting during transport is unusual; however, if it is necessary, do not proceed on the established route, but drive the tanker to a safe, open off-the-road area that is clear of power lines, buildings, and people. In choosing an area, consider the wind direction so that vented gas will be carried away safely.

Liquid hydrogen trailers are equipped with at least two safety valves. If the road safety valve relieves, pull off the road, and then either:

- a. Let the road safety valve relieve until it reseats, or
- b. Use the tank operating vent valve to reduce the pressure.

Regardless of which method is used, the tank should be vented as soon as possible to less than 25 psia (172 kilopascals). Before returning to the highway, reconnect the tank to the road safety valve. The information required for selecting either of the two safety valves should be on the trailer schematic located on the trailer operating cabinet door.

<u>Faulty relief valves:</u> Make no attempt to repair a relief valve leak while the valve is exposed to the tank pressure, because such procedures are hazardous. Special methods have been developed for replacing relief valves when the trailers are loaded with liquid hydrogen; however, such operations should be performed under the direction of a qualified pressure system mechanic.

<u>Rupture disk failure:</u> Procedures for handling rupture disk failure depend on the type of disk on the trailer.

<u>Single disk</u>: Many trailers have one rupture disk whose replacement requires that specific detailed procedures be carried out in a remote area, that firefighting equipment be present, and that protective clothing be worn.

<u>Dual rupture disk assembly</u>: If the trailer is equipped with a dual rupture disk assembly, the driver must be familiar with the type of three-way valve used to switch to the other rupture disk. The gas flow should stop when the switch to the new disk is completed. The ruptured disk should be replaced as soon as possible.

6.12.6 Assistance in Emergencies

Responsible test site and safety personnel shall monitor hydrogen operations to ensure that all safety precautions are taken during transfer, loading, testing, and disposal operations. In any emergency, assistance should be available from knowledgeable safetytrained personnel, including plant security, the Safety Branch Emergency Response and site personnel.

Site personnel trained in handling specific mishaps and accidents should be assigned definite tasks to perform in an emergency. The test site senior operations engineer should assign these tasks.

6.12.7 Firefighting Techniques

<u>Caution:</u> <u>Only highly trained firefighting and certified technical professionals should engage in this team activity.</u>

Training personnel can prevent catastrophic results of fires. Should a hydrogen fire occur:

- a. Prevent the fire from spreading and let it burn until the hydrogen is consumed (Use water to keep adjacent equipment cool, not to arrest the fire.)
- b. Be aware that if the fire is extinguished without stopping the hydrogen flow, an explosive mixture may form, causing a more serious hazard than the fire itself
- c. Firefighting professionals need to exercise extreme caution in fighting fires involving hydrogen. In the event of a test facility fire, the fire fighting should

be under the joint direction of the senior professional fire fighting officer and the senior test site engineer.

<u>Liquid hydrogen fire scenario</u>: The following are descriptions of the initial and final phases of a liquid hydrogen fire.

<u>Initial phase of fire</u>: When a storage tank ruptures, flames will occupy the volume around the ruptured tank. Spills of a few hundred gallons may cause a flash hot-gas ball about 50 feet (15.12 meters) in radius. Wind may change the shape to an ellipsoid almost entirely downwind of the rupture. Flame temperature will be approximately 3800° F (2370° K). Large amounts of liquid hydrogen will flash into vapor.

The hot-gas ball will radiate, but more slowly than in gasoline-air fires. Radiation effects on adjacent vessels and lines should not be severe, especially if they have reflective painting or surfaces.

Detonation of hydrogen-air mixtures in unconfined spaces is unlikely. However, the rapid burning of the initial cloud produces pressure waves that are sometimes strong enough to damage structures and injure personnel.

Final phase of fire: Because hydrogen fires are invisible and radiate less than ordinary fires, their presence is not as easily detected. The invisible flame may be many feet long and shift quickly with the slightest breeze. Therefore, personnel should wear protective clothing when fighting hydrogen fires. Note: When entering an area where a hydrogen fire is suspected, the use of a broom held out at arms length with bristles forward has proven to be a safe method of detecting small fires.

The only sure way of handling a hydrogen fire is to let it burn under control until the hydrogen flow can be stopped. If the hydrogen fire is extinguished and the hydrogen flow is not stopped, a hazardous combustible mixture begins to form immediately. It is very possible for the mixture to ignite with an explosion, causing more damage and restarting the fire.

The block or isolation valves located close to the hydrogen container should be closed by remote operations from a safe distance outside the local hazard area.

Although the hydrogen fire should not be extinguished until the hydrogen flow can be stopped, water sprays should be used to extinguish any secondary fire and to keep the fire from spreading.

- The hydrogen-containing equipment should be kept cool with water sprays to decrease the rate of hydrogen leakage and to prevent further heat damage. However, if the inner surface is exposed, water should not be applied.
- Some pressure-relief devices have frozen shut from water spray during liquid hydrogen fire fighting activities. Great caution must be exercised in using water since a frozen relief device can lead to vessel rupture.

Remotely controlled water spray equipment, if it has been installed, should be used instead of hoses to cool equipment and to reduce the spread of the fire. If it is necessary to use hoses, those using them should stay behind protective structures.

It is permissible to use carbon dioxide in the presence of hydrogen fires.

<u>Gaseous hydrogen fire scenario</u>: Gaseous hydrogen fires are not generally extinguished until the supply of hydrogen has been shut off, because of the anger of reignition or explosion. Hydrogen systems should be designed to allow the gas flow to be stopped. In a fire, water should be sprayed on adjacent equipment to cool it. Fog and solid stream nozzles are the most adaptable in controlling fires. In dealing with hydrogen cylinder fires, proceed as follows:

- a. Do not try to put out a fire unless the cylinder is out in the open or in a wellventilated area free of combustibles and ignition sources. Extreme care should be taken in attempting to extinguish the fire. The process may create a mixture of air and escaping hydrogen that, if reignited, may explode.
- b. Do not attempt to remove the burning cylinder but keep it and any surrounding cylinders and combustibles cool by spraying them with water.
- c. If a group of cylinders is burning, it is extremely important that the persons fighting the fire be at as great a distance from the fire as practicable and is protected against the possibility of flying debris. The efforts of firefighters in such instances should be divided between keeping the cylinders cool and preventing adjacent equipment and buildings from catching fire.

6.12.8 Protection from Exposure to Fire

Fires can damage objects by heat fluxes transmitted by radiation and convection. Radiation is a significant component of heat flux in hydrogen fires.

Water molecules are responsible for much of the infrared radiation from the hydrogen flame; therefore, atmospheric water vapor is very effective in absorbing this radiation. For example, a 1-percent concentration of water vapor in the atmosphere (corresponding to a relative humidity of about 43 percent at ambient temperature) will reduce the radiation flux at least two orders of magnitude at a distance of 328 feet (100 meters).

Water spray/mist is an effective means for attenuating radiation from a hydrogen flame. Comparisons of hydrogen fires with hydrocarbon fires show that, although smoke inhalation danger is lower with hydrogen fires, it remains a major cause of injuries and deaths in a hydrogen fire due to the burning of other nearby combustible material.. Safe limits for thermal-radiation-flux exposure levels for personnel and equipment cover a wide range and are listed in the Appendix of <u>ANSI / AIAA G-095-2004</u>, Guide to Safety of Hydrogen and Hydrogen Systems.

6.13 TRANSPORTATION OF HYDROGEN

Safety of personnel and facilities while hydrogen is being transported requires adherence to accepted standards and guidelines as well as mandatory compliance with existing regulatory codes.

6.13.1 Codes and Regulations

Various industrial and government organizations have published standards and guidelines for facility construction and for safe procedures to be followed in the various phases of producing, handling, transporting, and using of cryogenic fluids. Regulatory bodies such as the Department of Transportation (DOT), which includes the Federal Aviation Administration (FAA), the U.S. Coast Guard, and the Office of Hazardous Materials Transportation, have adapted pertinent published guidelines. Department of Transportation regulations, Title 49, Code of Federal Regulations, Parts 100 to 185 designate the rule-making and enforcement bodies of the DOT.

Transport dewars are to be marked in accordance with DOT regulations with both of the following legends: "FLAMMABLE GAS" and "LIQUID (or GAS) HYDROGEN," as appropriate.

6.13.2 Loading Area Requirements

Liquid hydrogen is delivered to Glenn facilities in tanker trailers. The contracts for supplying hydrogen state that personnel involved in the handling, transportation, and storage of hydrogen must be given appropriate safety training.

The safety operating procedures included in the safety documents at Glenn will be rigidly followed to protect personnel. Emergency procedures shall be detailed in the standard operating procedures of the applicable operating organization. Other requirements are as follows:

- a. No flame-producing devices shall be located within the control area. Sparkproducing and electrical equipment that is within 25 feet (7.6 meters) of the operation and is not hazard-proof shall be turned off and locked out. All tools used shall be in accordance with established safety procedures.
- b. The transfer and control areas must remain clear of personnel not directly involved in the operation. Loading and transfer of liquid or gaseous hydrogen should not begin during an electrical storm and, if underway, should be discontinued if a storm comes within 5 miles (8.05 kilometers) of the operation.
- c. In liquid hydrogen trailer transfer
 - There shall be no smoking or open flames within 150 feet (45 meters) of the loading or unloading of liquid hydrogen trailer.
 - The tractor ignition switch and light circuit must be turned off during loading and unloading operations.

- When the tractor is parked, the trailer wheel chocks must be in place with the emergency brakes set. Prior assurance checks of the area grounds, ground cable and attachment fixture should be facilitated as identified in 6.7.3 (every 6 months minimally). Prior to the static ground attachment, a hand held hydrogen detector shall be used to check for presence of hydrogen in the immediate area of operation.
- Before the trailer is used, all external or associated systems should be inspected (e.g., for cold spots on vacuum jackets or visible leakage).
- d. If a leak develops, the transfer must be stopped and the leak repaired. If a hydrogen fire occurs, the hydrogen sources must be closed as quickly as possible.
- e. Before any type of maintenance is performed, the system shall be depressurized and all liquid hydrogen lines disconnected, drained, vented, and purged; the operations area inspected; and the security of all systems verified.
- f. The atmosphere must be free of hydrogen in the air before motor vehicles are permitted to operate within the control transfer area. At a hydrogen alarm level of 20 percent of the lower explosive limit, vehicles shall be shut off, and personnel shall immediately leave the area of high hydrogen concentration.
- g. All transport dewar inlets and outlets, except safety relief devices, should be marked to designate whether they are covered by vapor or liquid when the tank is filled to the maximum permitted level. This is a DOT marking requirement.
- h. Each cargo tank must be protected by a primary system of one or more springloaded pressure-relief valves and by a secondary system of one or more rupture disks arranged to discharge upward and unobstructed to the outside of the protective housing. The rated capacity of each pressure-relief device must be set in accordance with Compressed Gas Association Pamphlet S 1.2.

6.13.3 Mandatory Transport Regulations

The following is a sample of mandatory regulations for safe tractor-trailer transportation of liquid hydrogen:

- a. Drivers shall be required to successfully complete the training and certification programs provided by the supplier. These programs should include instructions about the nature of loading and the procedures to be taken in an emergency.
- b. Two drivers are to be assigned when normal driving time exceeds 10 hours between the point of origin and the destination or between driver relay points.
- c. The maximum allowable travel time, the pressure used to determine the marked rated holding time (MRHT), and the appropriate filling density must be marked on the right side of the cargo tank near the front, in accordance with 49 CFR, Parts 100 to 185. The one-way travel time is derived from the MRHT of the cargo tank for liquid hydrogen at the pressure and filling density (in percent) marked on the tank.

- d. The trailer shall be equipped with a spring-loaded, fail-safe emergency brake system.
- e. The trailer shall be equipped with a dry chemical fire extinguisher. The rating should not be less than Underwriter's Laboratory and NFPA Codes of 10 BC; some special permits require a rating of 20 BC.
- f. Each tanker must have an installed brake interlock switching system that ties the tank venting system to the brake system of the trailer. The objective of such a control is to permit venting of the tanker when it is in a controlled park position. For the trailer to be moved without venting, the brake switch position must be moved from park to drive.

6.14 ADOPTED REGULATIONS

This chapter is based on the best information available. It draws heavily on material from the <u>ANSI / AIAA G-095-2004</u>, Guide to Safety of Hydrogen and Hydrogen Systems. Much additional information is taken from NFPA and CGA standards. Experience gained over the past 40 years with hydrogen systems at Glenn Research Center also contributed much to the development of the new safety chapter.

The following documents or portions thereof are referenced within this chapter as mandated regulations and shall be considered as part of the requirements of this chapter; however, whenever there is a conflict between information presented in a reference and information contained in this chapter, the chapter information shall govern.

- NPD 8710.5, "NASA Safety Policy for Pressure Vessels and Pressurized Systems."
- NFPA 55, National Fire Protection Association, 2005, Standard for the Storage, Use, and Handling of Compressed Gases and Cryogenic Fluids in Portable and Stationary Containers, Cylinders, and Tanks.
- CGA Pamphlet G-5, "Hydrogen."
- <u>ANSI / AIAA G-095-2004</u>, Guide to Safety of Hydrogen and Hydrogen Systems, provides an outstanding source of additional practical safety, design, and handling information on the use of hydrogen in gas, liquid, and slush forms. Many useful references are provided. Much valuable guideline information used in this chapter was extracted from the original drafts of NSS/FP 1740.11.

TABLES

Table 6.1 can be viewed at: <u>ANSI / AIAA G-095-2004</u>, Guide to Safety of Hydrogen and Hydrogen Systems.

TABLE 6.1. A SELECTION OF RECOMMENDED MATERIALS FOR TYPICALAPPLICATIONS, Page 152 – Table A5.2

Tables 6.2 through 6.4 can be viewed at: <u>NSS 1740.12</u>, Safety Standard for Explosives, Propellants, and Pyrotechnics.

TABLE 6.2. SAFE QUANTITY-DISTANCE RELATIONSHIPS FOR LH2 STORAGE, Page 7-12 - Table 7-5

TABLE 6.3. EXPLOSIVE EQUIVALENT FACTORS FOR LIQUID PROPELLANTS, Page 7-5 – Table 7-1

TABLE 6.4. Space Distances for Separation of Propellant Static Testing, Launching, and Storage Sites from other Facilities, Page 7-15 – Table 7-6.

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I Operational Requirements

Only qualified operators are to perform transfers.

While in storage or transport, a properly secured tube trailer shall have all valves in the closed position and the tailpieces and sample port capped.

A two-man buddy system shall always be in place. (See Chapter 22 - The Glenn Buddy System) and (See Section 6.9.2. Requirements of Personnel) for further in-depth information.

CAUTION: Eliminate all potential ignition sources from the area.

II Tube Trailer Fill

- a. Ground the trailer at the connector on the bumper. Make certain that there is a proper ground.
- b. Open and secure trailer doors with the latches provided.
- c. Chock/block trailer wheels. Also place at the front of the trailer a cone or stand with sign indicating that the trailer is connected to the manifold.
- d. Put up the required barricades and signs.
- e. Open the gauge isolation valve to ensure that the supply manifold has maintained pressure and is leak-free. (If the manifold has leaked to atmospheric pressure, cease operations and contact the cryogenic maintenance COTR for proper evaluation and repair.)
- f. Leak-check the trailer manifold piping (use Leak-tek and/or hand-held analyzer).
- g. Connect an approved transfer hose to the fill tailpiece and supply-side fitting (maintain cleanliness of caps).
- h. Secure the transfer hose restraining cables to the eyelets provided.
- i. Open all tube isolation valves.
- j. Vacuum evacuate or purge the transfer line as specified in the area where the fill or cascade is being accomplished. Leak-check the hose connections prior to completing the purge.
- k. After the transfer hose has been purged and checked, stand clear of the transfer hose and slowly open the trailer-mounted manual fill valve.
- 1. Require personnel to stand clear of transfer hose, then slowly open the main gas supply isolation fill valve (from source) to fill the trailer.

III Post-Fill Shutdown

- a. Close the main gas supply isolation valve (from source) to begin shutdown and disconnect operations.
- b. Close the trailer manual fill valve.
- c. Purge and vent the transfer hose to atmospheric pressure as specified in the area of use.
- d. Disconnect the transfer hose restraining cable from trailer side.
- e. Remove the transfer hose from the trailer and cap the hose and tailpiece ports.

NOTE: If a sample is required, follow the checksheet procedures as provided by the Chemical Analysis Branch. (Draw sample gas from the sample panel only.)

- a. Close all tube isolation valves (transfer is complete).
- b. Remove the ground and close the doors prior to moving the trailer.
- c. Remove barricades, warning signs, and wheel chocks.

IV Tube Trailer Withdrawal

- a. Ground the trailer at the connector located on the bumper. Make sure that the ground has been checked.
- b. Open and secure the trailer doors.
- c. Chock/block trailer wheels. Also place at the front of the trailer a cone or sign indicating trailer is connected to the manifold.
- d. Put up the required barricades and signs.
- e. Open the gage isolation valve to ensure that the supply manifold has maintained pressure and is leak free.
- f. Connect an approved transfer hose to the trailer withdrawal tailpiece and receiving station.
- g. Secure the transfer hose restraining cables to the eyelets provided.
- h. Open all trailer tube isolation valves.
- i. Leak-check the trailer manifold piping.
- j. Open receiving station main isolation valve.
- k. Pressure purge the transfer hose assembly and maintain 40 to 100 psi in transfer lines.
- 1. Leak-check transfer hose connections.
- m. Partially open trailer manual withdrawal valve.
- n. Withdraw personnel from area of transfer hoses.
- o. Open the trailer emergency shutoff valve from the remote location.
- p. Allow H2 receiving station pressure to reach trailer pressure; then close the trailer emergency shutoff valve.
- q. Leak-check transfer hose connections.
- r. Fully open trailer manual withdrawal valve.
- s. Open the trailer emergency shutoff valve from the remote location to withdraw hydrogen for use.

V Post-Withdrawal Shutdown

- a. From the remote location, close the emergency shutdown valve.
- b. Vent and purge the transfer hose to atmospheric pressure, as specified in the area of use.
- c. Close the manual withdrawal valve on the trailer.
- d. Close the receiving station main isolation valve to begin securing the system after use.
- e. Disconnect the transfer hose restraining cable.
- f. Remove the transfer hose from the trailer, and cap the hose and tailpiece ports.
- g. Close all tube isolation valves (the trailer is secure).
- h. Remove barricades, warning signs, and wheel chocks.
- i. Prior to relocating trailer, remove ground and close and secure trailer doors.

Contamination Control

Cleaning procedures shall be established and effective contamination controls developed to maintain the required cleanliness level for hydrogen systems.

Contamination of liquid hydrogen by solid air or oxygen-enriched air has resulted in serious explosions. Liquid hydrogen exposed to air can form slurries of solid oxygen and nitrogen that tend to be richer in oxygen than in air. These slurries can form explosive mixtures that can detonate with effects similar to those of TNT or other highly explosive materials.

Solid contaminants should be held to a minimum because they can contribute to the generation of static electricity in flowing systems. Explosions have occurred in filters contaminated with solid air; therefore, filter elements in liquid hydrogen servicing systems should be regenerated well before their capacity is reached. The warm-up and purge of liquid hydrogen transfer systems usually regenerates the filters.

An effective control program must specify the degree of cleanliness, materials, and configuration required. Gross cleaning procedures (blast, mechanical, washing) should be followed by precision cleaning methods (vapor degreasing and ultrasonic). Suitable cleaning agents and methods for verifying surface cleanliness should be identified. Contaminants in liquid and gaseous hydrogen systems must be kept under control, and personnel must be trained to ensure control is maintained.

Cleanliness Requirements (see also paragraph 6.9.7 Clean Systems)

All storage, transfer, and system components must be completely clean before being placed in service.

Liquid hydrogen systems must be free of any surface film, oxidant, grease, or oil. They must be free of all matter (e.g., rust, dirt, mill scale, weld spatter, and weld flux) that could jam or clog valves and flow passages.

Valve stem seals and seats shall be carefully inspected and cleaned if necessary. The system must be dry and free of foreign material.

A system or dewar that has been out of service for a significant time should be inspected and cleaned as appropriate.

Recommended Procedure

A recommended cleaning procedure for a warm hydrogen system or component includes flushing to remove all loose particles (e.g., sand, grit, rust, and weld spatter). First, flush with approved degreaser, dry, and then flush with demineralized water.

For liquid hydrogen systems only, the system should be cold-shocked with liquid nitrogen to break off attached particles. The particles then can be flushed with liquid nitrogen into filters. The filters should be cleaned separately.

The system should be dried by evacuation. If the system cannot withstand a vacuum, flowing hot nitrogen gas through it may dry it. The nitrogen gas temperature should be well above the boiling temperature of water.

Systems should be dried by three cycles of evacuation and purging through a cold trap before filling with hydrogen gas. Usually three cycles will dry a system so that the cold trap shows no further collection.

All openings in cleaned systems should be closed in an airtight manner with metal covers and suitable gaskets. Good practice dictates similar treatment or the use of plastic containers for pipes and systems that are yet to receive a final cleaning.

Cleaning Filters

Frequency of cleaning depends on the amount of system use and impurities in the fluid. The operators must monitor increases in pressure drops, and clean the filters as needed.

Filters are cleaned by disconnecting, warming, draining, flushing (with a solvent or ultrasonic cleaning), and then drying thoroughly. Filters must not be cleaned by back-flushing the system.

Periodic System Recheck

To ensure that the appropriate level of cleanliness is maintained, hydrogen systems should be periodically rechecked for contamination levels. Frequency of checking depends upon system use. The engineering organization responsible for a system should establish a cleanliness recheck schedule.

<u>Adiabatic compression:</u> Compression of a gas in an adiabatic system. Since energy cannot be transferred to or from the surroundings in an adiabatic system, the compressional energy increases the energy (temperature) of the compressed gas.

<u>Autogenous ignition</u>: The phenomenon in which a mixture of gases or vapors ignites spontaneously with no external ignition source. It is frequently called "autoignition" or "spontaneous ignition."

<u>Autoignition temperature:</u> The lowest temperature at which a fuel in contact with air or an oxidizer will self-heat to ignition without an external ignition source. The autoignition temperature for a monopropellant is the temperature at which it will self-heat to ignition in the absence of an oxidizer.

Blast wave: A shock wave in air, caused by the detonation of explosive material.

<u>Blast yield:</u> Energy released in an explosion. The amount of energy is inferred from measurements of the characteristics of blast waves generated by the explosion.

<u>Burn velocity</u>: The propagation velocity of a flame through a flammable mixture. Burning velocities are absolute velocities measured relative to the velocity of the unburned gas; flame velocities are measured in laboratory coordinates and are not absolute.

<u>Combustion wave:</u> A zone of burning, propagating through a combustible medium, that is capable of initiating chemical reaction in the adjacent unburned combustible layers.

<u>Critical diameter:</u> The minimum diameter required for a tube to produce a stable spherical detonation into an unconfined environment. This term is sometimes used by other authors to describe the minimum tube diameter for propagation of a flame or of a detonation confined in the tube.

<u>Deflagration</u>: A rapid chemical reaction in which the output of heat is enough to enable the reaction to proceed and accelerate without input of heat from another source. Deflagration is a surface phenomenon in which the reaction products flow away from the unreacted material along the surface at subsonic velocity. The effect of a true deflagration under confinement is an explosion. Confinement of the reaction increases pressure, rate of reaction, and temperature and may cause transition into a detonation.

<u>Detonation</u>: A violent chemical reaction of a chemical compound or mechanical mixture in which heat and pressure are emitted. A detonation is a reaction which proceeds through the reacted material toward the unreacted material at supersonic velocity. As a result of the chemical reaction, extremely high pressure is exerted on the surrounding medium, forming a propagating shock wave that originally is of supersonic velocity.

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<u>Detonation cells:</u> The cellular pattern left on a soot-coated plate by a detonation wave. The dimensions of a single cell (length and width) can be used to predict detonation limits and critical diameters.

<u>Detonation limits:</u> The maximum and minimum concentrations of vapor, mist, or dust in air or oxygen at which stable detonations occur. The limits are controlled by the size and geometry of the environment as well as the concentration of the fuel. "Detonation limit" is sometimes used as a synonym for "explosive limit."

<u>Detonation wave:</u> A shock wave that is sustained by the energy of a chemical reaction initiated by the temperature and pressure in the wave. Detonation waves propagate at supersonic velocities relative to the un-reacted fluid.

<u>Diffusion coefficient:</u> The mass of material diffusing across a unit area in unit time at a unit concentration gradient.

<u>Electrical arc/spark test:</u> Method of determining the susceptibility of metals to ignition in oxygen by using an electrical arc or spark. Arc energy input and oxygen pressure are the major variables.

<u>Explosion</u>: The sudden production of a large quantity of gas or vapor, usually hot, from a smaller amount of a gas, vapor, liquid, or solid. An explosion may be viewed as a rapid equilibration of a high-pressure gas with the environment; the equilibration must be so fast that the energy contained in the high pressure gas is dissipated as a shock wave. Depending on the rate of energy release, an explosion can be categorized as a deflagration, a detonation, or pressure rupture.

<u>Explosive reaction</u>: A chemical reaction wherein any chemical compound or mechanical mixture, when ignited, undergoes a very rapid combustion or decomposition, releasing large volumes of highly heated gases that exert pressure on the surrounding medium. Also, a mechanical reaction in which failure of the container causes the sudden release of pressure from within a pressure vessel.

<u>Explosive yield</u>: The amount of energy released in an explosion. Explosive yield is often expressed as a percent or fraction of the energy that would be released by the same mass of a standard highly explosive substance such as TNT.

<u>Flammability limits:</u> The maximum and minimum concentrations of a fuel (gas or vapor) in an oxidizer (gas or vapor) at which flame propagation can occur.

<u>Free air or free gas (STP)</u>: Air or gas measured at a temperature of 60° F (15.6° C) and a pressure of 14.7 psia (101.4 kPa).

<u>Hazardous (classified) location:</u> A location where fire or explosion hazards may exist because of flammable gases or vapors, flammable liquids, combustible dust, or easily ignitable fibers or flyings.

Ignitable mixture: A mixture that can propagate a flame away from the source of ignition.

<u>Ignition energy:</u> The amount of energy needed to initiate flame propagation through a combustible mixture. The minimum ignition energy is the minimum energy required for the ignition of a particular flammable mixture at a specified temperature and pressure.

<u>Ignition temperature</u>: The temperature required to ignite a substance by using an ignition source such as a spark or flame.

<u>Intrinsically safe system</u>: A circuit in which any spark or thermal effect is incapable of causing ignition of a mixture of flammable or combustible material in air under prescribed test conditions and which may be used in hazardous classified locations.

Lower explosive limit (LEL): The minimum concentration of a combustible/ flammable gas or vapor in air (usually expressed in percent by volume at sea level) that will explode if an ignition source is present.

<u>Lower flammable limit (LFL)</u>: The minimum concentration of a combustible/ flammable gas or vapor in air (usually expressed in percent by volume at sea level at temperatures up to 121° C) that will ignite if an ignition source is present.

<u>Shock wave:</u> A surface or sheet of discontinuity set up in a supersonic field of flow, through which the fluid undergoes a finite decrease in velocity accompanied by a marked increase in pressure, density, temperature, and entropy, as occurs in a supersonic flow about a body.

<u>Stoichiometric combustion:</u> The burning of fuel and oxidizer in the exact proportions required for a complete reaction to give a set of products.

<u>Unconfined vapor cloud explosion</u>: Explosion that results from a quantity of fuel having been released to the atmosphere as a vapor or aerosol, mixed with air, and then ignited by some source.

<u>Vapor explosion</u>: A shock wave produced by the sudden vaporization of a superheated liquid coming into contact with a cold liquid.

(TO BE POSTED AT TEST SITE)

Contact with liquid cryogens or there cold boiloff vapors can produce cryogenic burns (frostbite). Unprotected parts of the body should not be allowed to contact uninsulated pipes or vessels containing cryogenic fluids. The cold metal will cause the flesh to stick and tear. Treatment of frozen tissue requires medical supervision since incorrect first aid practices always aggravate the injury.

Exposure to Cryogenic Gases/Liquids

Cryogenic burns result when tissue comes into contact with cold gases, liquids, or their containers. Contact may result in skin chilling or true tissue freezing. Commonly, only small areas are involved, with injury to the outer layers of the skin.

Small quantities of cryogenic material may evaporate from the skin before actual freezing occurs. Such an injury typically produces a red area on the skin. More significant injury is caused by true freezing: the formation of crystals within and around the tissue cells. Frozen tissue always assumes a yellowish-white color, which persists until thawing occurs.

Treatment of Frozen Body Tissue

Treatment of frozen tissue requires medical supervision since incorrect first aid practices always aggravate the injury. In the field it is safest to do nothing other than cover the area, if possible, and to transport the injured person to a medical facility. Attempts to administer first aid for this condition will often be very harmful. Listed below are some important don'ts:

- a. Don't remove frozen gloves, shoes, or clothing except in a slow, careful manner (skin may be pulled off inadvertently).
- b. Don't massage the affected part.
- c. Don't expose the affected part to temperatures exceeding 112° F or temperatures lower than 100° F.
- d. Don't ever apply snow or ice.
- e. Don't use safety showers, eyewash fountains, or other sources of water because the water temperatures will almost certainly be incorrect and will aggravate the injury.
- f. Don't apply ointments.

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