Safety Analysis Report

For the Use of Hazardous Production Materials in Photovoltaic Applications at the National Renewable Energy Laboratory

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Safety Analysis Report

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2/24/92

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ABSTRACT: To ensure the continued safety of SERI's employees, the community, and the environment, NREL commissioned an internal audit of its photovoltaic operations that used hazardous production materials (HPMs). As a result of this audit, NREL management voluntarily suspended all operations using toxic and/or pyrophoric gases. This suspension affected seven laboratories and ten individual deposition systems. These activities are located in Building 16, which has a permitted occupancy of Group B, Division 2 (B-2). NREL management decided to do the the following. 1) Exclude from this SAR all operations which conformed, or could easily be made to conform, to B-2 Occupancy requirements. 2) Include in this SAR all operations that could be made to conform to B-2 Occupancy requirements with special administrative and engineering controls. 3) Move all operations that could not practically be made to conform to B-2 Occupancy requirements to alternate locations. In addition to the layered set of administrative and engineering controls set forth in this SAR, a semiquantitative risk analysis was performed on 30 various accident scenarios. Twelve presented only routine risks, while 18 presented low risks.. Considering the demonstrated safe operating history of NREL in general and these systems specifically, the nature of the risks identified, and the layered set of administrative and engineering controls, it is clear that this facility falls within the DOE Low Hazard Class. Each operation can restart only after it has passed an Operational Readiness Review, comparing it to the requirements of this SAR, while subsequent safety inspections will ensure future compliance.

<u>NREL Approvals:</u>
NREL Director	NREL Deputy Director
Basic Sciences Director 2/24/92	Photovoltaics Director
Director of Technical Services	Safety and Security Office Manager

<u>DOE Signatures:</u>	
Recommended for Approval by:	NREL Area Manager 2/26/92
Approved by:	Assistant Secretary, Conservation and Renewable Energy 3/5/92

Preserving our environment, protecting health and safety, and assuring the Nation's energy security are primary responsibilities of the U.S. Department of Energy (DOE). To ensure that these objectives are accomplished, DOE has been supporting programs to develop new energy technologies that are protective of the environment while aggressively implementing new health and safety policies and activities.

The National Renewable Energy Laboratory (NREL) is responsible for implementing and managing research, development, and demonstration programs for renewable energy systems. Introduction of the advanced systems under development by NREL will help ensure our energy security in the 21st century. As progress in technology development continues, it is also important that environment, health, and safety continue to be protected. For this reason, NREL was asked to prepare the attached Safety Analysis Review (SAR). The objectives of the SAR preparation and review process assure that:

1. Potential hazards are systematically identified;
2. Potential consequences are analyzed;
3. Reasonable measures to eliminate, control, or mitigate hazards have been identified;
4. There is documented management authorization of the DOE operation based on an objective assessment of the safety analysis.

Based on independent critical review of this SAR and of the NREL programs by the DOE Tiger Teams, I am convinced that the operation of the NREL programs can meet the dual objectives of developing advanced photovoltaic energy systems in an environmentally compatible way.

I commend NREL for the thoughtful and detailed critical review contained in this SAR. Furthermore, I believe that the concepts and details outlined in this SAR should also be of broader interest to other Federal and private organizations engaged in the handling of toxic and hazardous gases and liquids.

J. Michael Davis, P.E.
Assistant Secretary
Conservation and Renewable Energy

EXECUTIVE SUMMARY

INTRODUCTION

This Safety Analysis Review (SAR) is prepared in conformance with U.S. Department of Energy (DOE) Order No. 5481.1B. It addresses the hazards and risks involved with handling highly toxic or pyrophoric gases and liquids in NREL's Building 16. The SAR presents a detailed discussion of the potential accidents, their consequences, and their probabilities of occurrence. A collection of mandatory engineering and administrative controls is used to reduce the risks to health and property to acceptable levels. This ensures that all highly toxic and pyrophoric operations in Building 16 operate in a safe manner.

Under the DOE National Photovoltaic (PV) Program, NREL sponsors potentially high-payoff research and development (R&D) which industry is neither able nor willing to undertake. This R&D effort is in the area of renewable energy technologies. NREL is responsible for most of the R&D and manufacturing technology development, and some of the systems and market development task areas, under the national PV program. NREL's specific internal PV-related research activities in Building 16 are conducted in advanced material technologies. These include amorphous silicon thin-film, polycrystalline thin-film, and high-efficiency crystalline solar cells. To produce these cells, many chemicals are used; some, if improperly used, can present dangers to life and property.

Because of DOE's increased concerns about the dangers presented by DOE facilities, and because of NREL's interest in ensuring that its own facilities were operating in an environmentally conscious way, an internal audit of its PV R&D program was conducted in April of 1991. As a result of an extensive audit, NREL management elected to voluntarily suspend all of its PV R&D using toxic and pyrophoric gases until a thorough evaluation had been made. Immediately following the suspension, NREL initiated four successive activities:

- 1) All toxic and pyrophoric gas sources were returned to their respective manufacturers.
- 2) A task force was appointed to evaluate the internal audit findings.
- 3) Discussions were held with the DOE area office, where it was decided that an SAR would be prepared prior to resuming these R&D activities.
- 4) A committee was formed to develop an SAR identifying and analyzing the risks of those R&D activities.

The laboratories that suspended their operations are all located within Building 16 and were involved in fabricating amorphous silicon (190 and 369), gallium arsenide (103, 222, 368, and 458), and copper indium diselenide films (285). In addition, a laboratory using small amounts of tungsten hexafluoride for electrochromic research also ceased operation.

This SAR explores the hazards associated with these operations, as well as the controls in place to reduce the risks to health and property to those established by regulatory limits. It is concerned only with resuming the operation of a subset of the activities conducted in Building 16; that is, only seven laboratories out of the 87 located in building. All the other activities in the building present only routine risks and are not included in this SAR.

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FACILITIES

Building Description

Building 16 is a four-story leased office and laboratory building located in Denver West Office Park. The building area is 24,300 sq. ft. on each of the first three floors and 18,600 ft² on the fourth floor: 91,500 sq. ft. total. Toxic and hazardous gases have been used in laboratories 103, 190, 222, 285, 368, 369, and 458. These laboratories account for a total of approximately 4,200 sq. ft. This is 4.6% of the total area of the building.

Hazardous Gas Detection

All laboratories using toxic or highly toxic gases are monitored for those gases using a central monitoring system. All laboratories using flammable gases in excess of 400 ft³(STP) are monitored for those gases using a central monitoring system. Laboratories using flammable gases in quantities less than 400 ft³ are monitored locally using a monitor contained within the laboratory. All laboratories using corrosive gases are monitored using a central monitoring system. The monitoring facility for Building 16 is located in the center area of the third floor (16/323). It contains all toxic gas monitors, hydrogen and corrosive gas monitors.

Security Systems

All NREL buildings are monitored by a continuously manned central security station located in Building 17. In addition to security, the station also monitors fire alarms. All security systems are on emergency power. Access to Building 16 is controlled 24 hours per day. From 7:30 a.m. to 5:30 p.m., any NREL employee with a valid NREL badge can access the building. Only building occupants, Safety and Security Office (SSO), and Facilities Branch personnel are allowed off-hours access to Building 16.

PRINCIPAL HAZARDS

The principal hazards associated with Building 16 arise from using and handling toxic and pyrophoric solids, liquids, or gases. These materials are commonly referred to as Hazardous Production Materials (HPMs); however, it should be pointed out that these systems are not production-scale operations, and the quantities of HPMs used are very small. These are all used in reactors to produce solid semiconductor devices by a variety of chemical vapor deposition methods. These materials are listed in Table E-1 and have been routinely used in this facility, without major incident (injury, illness, or equipment loss > \$10k), since 1984.

During normal operation, the principal potential sources of human exposure to these chemicals include handling and transportation to laboratories, gas or liquid cylinder change-out, gas distribution during normal system operation, ventilation failure, failure of effluent treatment, and waste disposal. Other principal sources for exposure include fire, explosion, and natural phenomena. Other hazards associated with operating this facility are similar to those encountered in most chemical laboratories; they include solvents, heavy metals, organic compounds, flammable liquids, and compressed gases.

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TYPICAL HAZARDOUS PRODUCTION MATERIALS USED IN BUILDING 16 OPERATIONS

HPM Name	Type of Hazard(s)	HPM Name	Type of Hazard(s)
Arsine	Highly Toxic Gas	Diethylzinc	Pyrophoric Liquid
Phosphine	Highly Toxic & Pyrophoric Gas	Trimethylindium	Pyrophoric Solid
Hydrogen Selenide	Highly Toxic	Diethylsilane	Flammable Liquid
Tungsten Hexafluoride	Toxic & Corrosive Gas	Lightly Doped Mixtures	Flammable Gas
Molybdenum Hexafluoride	Toxic & Corrosive Gas	Hydrogen	Flammable Gas
Silicon Tetrafluoride	Toxic & Corrosive Gas	Methane	Flammable Gas
Tertiarybutylarsine	Pyrophoric & Highly Toxic Liquid	Hydrogen Chloride	Corrosive Gas
Tertiarybutylphosphine	Pyrophoric Liquid	Oxygen	Gaseous Oxidizer
Trimethylgallium	Pyrophoric Liquid	≤1% Silane in Helium	Compressed Gas
Trimethylaluminum	Pyrophoric Liquid		

Table E-1

REGULATIONS AND CODES

Except where noted, each of these systems in Building 16 is designed, built, and operated in compliance with the standards and codes discussed in this section. These include NREL internal standards as well as local, state, and federal regulations and codes.

The internal standards and procedures developed at NREL and adopted by NREL management include NREL ES&H Policies and Procedures; SERI Standards for the Safe Handling, Use, and Monitoring of Toxic Gases; SERI Emergency Response Procedures to the MDA Toxic Gas Monitor; the SERI Laboratory Chemical Hygiene Plan; and the NREL Corrective Action Plan to the Tiger Team Assessment. These standards and procedures are revised as required by changes in operations, facilities, the codes, the management structure, or other relevant concerns. Critical to the continuing safety of personnel in this building is an ongoing safety assessment of operations. Separate protocols, known as safe operating procedures (SOPs), are developed for each deposition system using hazardous chemicals. These SOPs cover all safety aspects of operating these systems. To ensure that these SOPs remain relevant and effective, they are reviewed and approved annually by NREL line management and the NREL SSO.

The federal government regulates the handling and use of toxic or hazardous compressed gases in the workplace through statutory and regulatory programs administered by the Department of Labor Occupational Health and Safety Administration (DOL OSHA) and the U.S. Environmental Protection Agency (EPA). NREL complies with regulatory requirements of OSHA, which regulates matters affecting the health and safety of employees in the workplace.

EPA develops and promulgates guidelines, procedures, standards, and regulations to protect the environment based on currently available data. In principal, there are a large number of statutes and regulations relevant to NREL operations. The three most important are the Resource Conservation and Recovery Act (RCRA), the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA), and the Superfund Amendment Reauthorization Act - Title III. Because many of these regulations are triggered only when specified material-specific

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quantity limits are exceeded or when regulated disposal procedures are not in compliance, they do not necessarily apply to their handling in Building 16 daily operations (which is a generator, not a disposal facility). In practice, the quantities of materials present in Building 16 are below all thresholds identified in applicable statutes and regulations; even if the contents of an entire laboratory were accidentally released.

In Colorado, the Colorado Department of Health (CDH) protects public health and the environment by collecting health and environmental data, developing plans to address health problems, managing and enforcing regulatory programs, investigating complaints and responding to emergencies. The State of Colorado along with the EPA enforces RCRA.

The HPM operations addressed in this SAR are located in Building 16 in the Denver West Office Park. The Denver West Office Park is located in the unincorporated Jefferson County, whose County Building Department has adopted the Uniform Building Code (UBC), Uniform Mechanical Code (UMC), Uniform Plumbing Code (UPC), Uniform Fire Code (UFC), and National Electric Code (NEC). Under the UBC, Building 16 is classified as a Group B, Division 2 (B-2) occupancy. In a B-2 occupancy, the quantity of toxic and hazardous materials present is limited. The quantities of those hazard classes relevant to NREL operations are presented in Table E-2. In an effort to ensure compliance with the Uniform Codes, NREL has implemented a variety of activities. These include improvements to the facility, rigorous engineering and administrative controls placed on HPM operations, and increased controls on the other operations in Building 16. Examples of such improvements include; upgrading of the existing sprinkler system, installation of sprinklers in the remainder of the building, installation of a new fully addressable smoke detection system, and installation of most -- if not all -- required controls to address mishap conditions anticipated under the requirements of today's codes. It should be noted that NREL has enjoyed a long history of providing a safe work environment, even before these modifications were proposed.

1988 UBC/UFC EXEMPT AMOUNTS PER CONTROL AREA

HPM	GAS	LIQUID	SOLID	NOTES
Highly Toxic	20* ft ³	1 lb	1 lb	Gas Cabinets
Toxic	20†* ft ³	1 lb	1 lb	Gas Cabinets
Pyrophoric	10 ft ³	1 lb	1 lb	Sprinklered Building
Flammable	750 ft ³	30 gal	25 lb	
Corrosive	650 ft ³	500 gal	5000 lb	

† = Note that this value has been increased to 650 ft³ in the 1991 UFC.

All amounts at STP.

Table E-2

RISKS INVOLVED

A semiquantitative risk analysis is presented in this SAR, rather than a more comprehensive probabilistic safety analysis similar to those used by nuclear power plants or large production facilities, because of the small scale of the R&D activities and because of the dynamic nature of the programs.

As a first step in this risk analysis, a series of accidents was identified based on industry experience and the expert judgement of NREL, Brookhaven National Laboratory (BNL), and

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others. To develop estimates of event probabilities for these accidents, NREL and industry experiences and failure rate data were used. Event probabilities are divided into six different classes: Impossible, Extremely Remote, Remote, Occasional, Reasonably Probably, and Frequent. In these assignments, it is recognized that the failure of individual components in isolation may not result in the accidental release of a hazardous material. Often, a release may occur only after a series of components fail. Because of the frequent need for a series of components to fail, the probability estimates provided here are conservative; that is, they likely overestimate the occurrence of the identified accident.

In a similar way, hazards or consequences are divided into four different classes: Negligible, Marginal, Critical, and Catastrophic. Estimates of potential consequences were based on past experiences, published literature, and more detailed numeric calculations developed for each accident scenario. In these calculations, it has been assumed that the defined transient occurs in the absence of other passive or active hazard management control systems. For example, a leak in a hydrogen selenide gas cylinder fitting during cylinder change-out could present very serious health hazards if the change-out team is not using self contained breathing apparatus (SCBA). But in reality, and as discussed below, multiple active and passive controls exist. Consequently, the consequence estimates will almost always be conservative; that is, they will overestimate the potential hazard.

Accident event probabilities and consequences were combined to develop a semiquantitative measure of risk. An analogy can be made to a multiplication table; risk = probability x consequence. The risk is determined by looking up its value based on the intersection of the probability and consequence. These values are divided into four final classes: Routine Risk, Low Risk, Moderate Risk, and High Risk. This means that an event with a critical consequence would be considered to be a low risk if the probability of that event occurring is remote or extremely remote. Similarly, an event with a critical consequence would be considered to be a high risk if the probability of that event occurring is reasonably probable or frequent. Events classified as "Routine Risk" are no different from those experienced by any individual in his or her daily life. "Low Risk" events are those that may have an impact within a facility and little or no impact to adjacent facilities or to health or the environment. "Moderate Risk" events are those with considerable potential impacts within the facility or to people or the environment, but at most only minor impacts off site. "High Risk" events are those with the potential for on-site and off-site impacts to large numbers of persons or for a major impact to the environment. Although it is still difficult to evaluate the acceptability of any option, it is clear that the need for additional controls increases, and the possible acceptability of any option declines, as the risk increases.

Table E-3 summarizes the results of this risk analysis. Of the 30 potential transients identified, none are classified as moderate or high risk; all are classified as routine or low risk. In light of this, and the likelihood that the dangers they present have been overestimated, the technical risks from the proposed activities are acceptable.

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RISK ANALYSIS TABLE

NUMBER	TRANSIENT DESCRIPTION	PROBABILITY						CONSEQUENCE				RISK			
		I	ER	R	O	RP	F	N	M	C	CA	R	L	M	H
6.2.1.1.	Quantity in Excess of B-2 Occupancy Ordered				•			•				•			
6.2.2.1.	Leak in Cylinder			•						•			•		
6.2.3.1.	Intra-Laboratory Transportation Accident		•						•			•			
6.3.1.1.	Cross-threading of Valve CGA Fitting and Failure of Helium Leak Check		•						•			•			
6.3.1.2.	Missing Washer in HCl or H ₂ Se Cylinder			•					•			•			
6.3.1.3.	Forgetting Washer/Gasket in a Gasketed Gas Connection			•						•			•		
6.3.1.4.	Attempt to Open Sticky Cylinder Cap Using a Wrench as a Lever			•						•			•		
6.3.2.1.	Toxic/Pyrophoric Liquid Bubbler Put in Backwards			•				•				•			
6.3.2.2.	Toxic/Pyrophoric Liquid Bubbler Leak Outside Delivery System				•				•				•		
6.4.1.1.	Leak of Air in Vacuum Pump			•					•				•		
6.4.1.2.	Leak in Pyrophoric Gas Distribution System into Gas Cabinet or System Enclosure			•					•				•		
6.4.1.3.	Leak in Toxic Gas Distribution System into Gas Cabinet or System Enclosure			•						•			•		
6.4.1.4.	Leak in Distribution System Between Gas Cabinet and Deposition System and Failure of Secondary Containment (Coaxial Tubing or Ducting Raceway)		•							•			•		
6.4.1.5.	Faulty Seals Connecting Reactor Vessel to System				•				•				•		
6.4.1.6.	Rupture of Quartz Reactor Vessel			•					•				•		
6.4.1.7.	Hydrogen Leak in Gas Cabinet			•						•			•		
6.4.1.8.	Hydrogen Leak in Purifier			•					•				•		
6.4.2.1.	Loss of Process Control with Potential for Episodic Release of AsH ₃ , PH ₃ and/or H ₂ Se			•					•				•		
6.4.2.2.	Loss of Process Control and Simultaneous Failure of "Scram" Unit, Exhaust Scrubber, or Cylinder Valve		•						•			•			
6.4.2.3.	Loss of Exhaust Ventilation					•		•				•			
6.4.3.1.	Liquid-type Effluent Scrubber Blockage					•		•				•			
6.4.3.2.	Excessive Oxygen in Carbon Drum Effluent Scrubber and Buildup of Unreacted Hydrides and/or Metalorganics			•						•			•		
6.4.3.3.	Effluent Removal Fails due to Loss of System Vacuum				•			•				•			
6.4.3.4.	Burn Box (CDO) Flame Goes Out				•			•				•			
6.4.4.1.	Loss of Containment of Carbon Drum Contents			•					•				•		
6.4.4.2.	Operator Exposed to Toxic By-Product Materials			•				•				•			
6.4.4.3.	Caustic Spill of Sodium Hydroxide Disposal (pH 13.8)				•				•				•		
6.5.1.1.	Fire			•					•				•		
6.5.2.1.	Seismic Activity			•						•			•		
6.5.3.1.	High Winds and Tornadoes			•				•				•			
TOTALS		0	4	18	6	2	0	8	14	8	0	12	18	0	0

PROBABILITY

I: Impossible
ER: Extremely Remote
R: Remote
O: Occasional
RP: Reasonably Probable
F: Frequent

CONSEQUENCE

N: Negligible
M: Marginal
C: Critical
CA: Catastrophic

RISK

R: Routine
L: Low
M: Moderate
H: High

Table E-3

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ENGINEERING AND ADMINISTRATIVE CONTROLS

Each of the following topics refers to a specific section of the SAR. The numbers following the section titles, in parentheses, are the section numbers in the SAR.

HPM Gas Distribution Systems (5.4.1.)

There are comprehensive design requirements of gas distribution systems for toxic (and highly toxic) gases, flammable gases, dopant gases (low concentrations of toxic gases), and corrosive gases. All NREL HPM gas distribution systems meet these minimum standards.

Distribution Systems for Pyrophoric Liquids and Solids (5.4.2.)

The Metal-Organic Chemical Vapor Deposition (MOCVD) systems require a small amount of pyrophoric liquids and solids to dope III-V semiconductors. Larger quantities of pyrophoric or toxic liquids may be used as alternative chemical sources to replace highly toxic gases. To provide an equivalency to the code requirements, each laboratory using pyrophoric liquids and solids in excess of the one pound, in use, exempt quantity (NREL internal limit is two pounds), has added dry chemical fire suppression in the reactor enclosure. These dry chemical fire suppression systems are installed by qualified fire protection contractors. Additionally, each laboratory using pyrophoric liquids and solids in conjunction with flammable gases has centralized flammable gas detection. This over-engineered system is proposed primarily to reduce the combined risk of hydrogen as a fuel, and small quantities of pyrophoric materials as an ignition source.

Distribution Systems for Highly Toxic Liquids and Solids (5.4.3.)

One of the liquid organometallic source materials for proposed use in Building 16 is tertiarybutylarsine (TBA); in addition to being pyrophoric, it is also highly toxic. All precautions from the section on pyrophoric liquids already apply. Additional precautions are taken to mitigate the hazards of toxic liquids (e.g., the use of SCBA, special gloves, capture traps, and special administrative controls on return and/or disposal).

Reaction Vessels and Deposition Chambers (5.4.4.)

A variety of engineering controls are required for reaction vessels and deposition chambers. These include physical pressure relief and/or secondary pressure reduction, automatic valve closure of inlet gases upon triggering system fail-safe, manual override to ensure positive gas shut-off on long lines, and reactor and associated plumbing containment within a ventilated equipment enclosure.

Effluent Removal (5.4.5.)

Effluents are considered waste products and are treated. This section includes strict engineering controls, including safety interlocks for automatically shutting down systems, for three basic types of effluent removal systems: liquid scrubbers, burn boxes, and adsorption beds with controlled oxidation.

Exhaust Systems (5.4.6.)

The maximum allowable discharge concentration of HPM gases, at the point of discharge, must not exceed one-half the Immediately Dangerous to Life and Health (IDLH) level for a specific material. A mix of the following options (varying for each laboratory) will be used to meet this requirement:

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1) Ventilation dilution is used where there is enough exhaust flow to adequately dilute the entire source at the specified release rate.

2) If the exhaust ventilation flow is too low to sufficiently dilute the HPM gases, an approved type of treatment system is used. Such treatment systems include exhaust ventilation scrubbers or scram units installed on the toxic gas lines.

3) An alternative to the treatment systems is to use these gases with the cylinder valve closed at all times. This necessarily implies that all runs are conducted with only the gas remaining in regulator and line. The engineering controls associated with this option are that all such cylinders must be supplied with pneumatically operated cylinder valves that are controlled by a circuit to allow only momentary operation (not to exceed a 10-second open period per valve operation).

Safety Interlocks (5.4.7.)

Safety interlocks are used to minimize the chance of a harmful accident by sensing abnormal conditions in the primary system(s) and triggering a fail-safe mode. This mode can be activated by either a safety interlock tied to a sensor, a deliberate shut-off of the system, or a power failure. The system must be reset manually by the operator to resume operations. Sensors include those for toxic gas, hydrogen, reactor over-pressure, loss of exhaust ventilation, loss of critical nontoxic gas flows, over-pressure at effluent removal system inlet, and other anomalous scrubber conditions (loss of scrubber solution recirculation, adsorption bed over-temperature, flame snuff-out, etc.).

Storage Facilities (5.4.9.)

An HPM container is considered to be in service if it is properly installed in an HPM handling system and will be used within the next 90 days. All other cylinders are considered to be in storage or in the process of exchange. There will be no storage of toxic, highly toxic, pyrophoric, or corrosive gaseous or liquid HPMs in Building 16. The only place these materials will be stored is in the bunker to the northeast of the Field Test Laboratory Building (FTLB). This facility is subject to strict administrative and engineering controls.

Emergency Response Team Stations (5.6.5.)

The NREL Emergency Response Team (ERT) is trained to respond in the case of a variety of emergency situations. ERT stations are centrally located in Building 16, and one station is located in Building 17. The following items are included in these stations: SCBA(s), spill control equipment, personal protective clothing, and at least one fire extinguisher (more if different classes of extinguishers are required for that area).

SOPs (5.5.1.)

An SOP is prepared and approved for each system. It contains comprehensive information about the safe operation of the system for which it was written, and it is stored in a standardized, central location along with Material Safety Data Sheets (MSDSs), chemical inventories, etc.

Responsibilities (5.5.2.)

The responsibilities of the various personnel involved with the use, handling, and monitoring of HPMs are outlined. Specific responsibilities are provided for research division directors; research branch managers; research program managers; HPM users; all personnel who transport toxic gases; all personnel who are involved with, or otherwise assist in, changing toxic gas

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cylinders; all personnel involved with purchasing toxic gases; SSO personnel; and Facilities Branch personnel.

Procuring HPMs (5.5.3.)

In line with the control area of Building 16, aggregate quantities of chemicals does not exceed B-2 limits. This policy is strictly enforced for all operations within Building 16, not just those operations covered in this SAR. All purchase requests for HPMs will be processed through the SSO and will receive an authorization signature from that section. A table will be provided to the NREL Procurement Office with all known controlled HPMs and all known safe production materials in general use at NREL. If an item is not specifically on the latter list, it will be considered a controlled HPM; the SSO must be contacted prior to its purchase.

The NREL limit on pyrophoric liquids is 2 lb per control area, which is adequate for our research needs. This is intermediate between the 1 lb in-use limit and the 4 lb in-storage limit allowed in Tables 9-A and 9-B of the Uniform Building and Fire Codes.

Transporting HPMs (5.5.4.)

HPM containers are received at and shipped from the FTLB receiving/shipping dock. HPM containers will be located in that building just long enough for receiving purposes and to perform a leak check using a portable leak detector (specific to the material in the container). Leaking cylinders will not be accepted. Only trained Shipping and Receiving personnel are allowed to transport HPM containers between the receiving area, the outside HPM storage facility, and individual laboratories. All HPMs are transported using 2-person change-out teams. A portable monitor, capable of monitoring for the material being transported, is used when transporting all highly toxic HPMs and hydrogen. Transporting hazardous materials through areas of the building occupied by office personnel is done in transport systems using secondary containment. These procedures reduce the chances of the cylinder valve head shearing, a fire during transport, or accidental valve opening. Incompatible materials are not transported on the same cart or truck.

Training (5.5.5.)

Because many people are responsible for HPMs, and because the extent of their involvement varies from position to position, the training requirements of the various personnel differ. The training requirements for the following personnel are addressed in this SAR: HPM users, personnel who assist in the change-out of HPM containers, anyone who is responding to the MDA room in the case of an alarm (including personnel from the SSO and Facilities Branch), Shipping and Receiving personnel who actually transport HPMs, the building landlord, the building fire marshal, fire marshal assistants, and SSO personnel.

Inspections and Audits (5.5.7.)

All laboratories are regularly inspected by line management. All laboratories containing systems using HPMs are thoroughly inspected quarterly for issues specific to the use of these materials. Additional specific inspections of systems and safety interlocks must be performed by principal operators annually or upon changes to the system. All ventilated enclosures associated with systems using HPMs are inspected on an annual basis. Inspections include ventilation measurements and smoke testing. A copy of the records of these inspections are kept in the SOP for each system.

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Oxygen availability in the SSO (5.6.6.)

Many of the toxic gases, such as arsine, cause hemolysis. Because of this, a readily available supply of breathing oxygen is kept in the ES&H area located in Building 16.

SUMMARY

There are several hazardous materials for proposed use within the facility. Because of the large number of administrative and engineering controls in place to ensure the continued safe handling and use of these materials (as specified in Section 5 of this SAR), the building is considered to be a low risk facility. This is true even with the operations described in this SAR fully operational.

The responsibility of complying with the law rests with the building occupant. The authority having jurisdiction over activities conducted in Building 16 is the Lakewood-Bancroft Fire Authority. NREL has submitted a document entitled "UBC Interpretation and Application for NREL Occupancy of Denver West Building 16" to the Lakewood-Bancroft Fire Authority. This document addresses the total occupancy of Building 16, not just the laboratories affected by the SAR, as it relates to the use of some areas of the building for offices and some for laboratories. The Lakewood-Bancroft Fire Authority concurs with this document that NREL can have mixed usage (which is not the same as mixed occupancy) of the building for its operations, provided that specific items within the UBC and UFC are met (fire separation, limitation of quantities of hazardous materials, etc.). NREL meets these requirements.

In this SAR, operations in Building 16 have been carefully evaluated to identify the maximum credible accidents and their associated event probabilities and consequences. In Section 3, a worst case (almost not credible, but presented for screening purposes only) accident analysis is presented. In this Section, the instantaneous release of the entire contents of hydrogen selenide (2.4 ft³), arsine (10 ft³), and phosphine (5.7 ft³) cylinders (assuming no flow restriction that we know are present) are evaluated by PVPUFF to determine the downgradient atmospheric concentrations. In all three cases, the estimated peak concentrations are below the IDLH values. The estimates are based on a 5 minute averaging period. Were a 30 minute averaging period used for which the IDLH value is based, the estimated concentrations would be much less.

Of the 30 potential accidents identified, none present High or even Moderate Risks, 18 present Low Risks and 12 present Routine Risks; these are summarized in Table 12. It is important to note here, that both accident event probabilities and consequences are larger than would actually be expected, because they are based on the fundamental assumption that all administrative, engineering and personal safety controls have failed. Given the redundancies and backups discussed in the earlier sections, this is a gross oversimplification. Because all identified accidents are either Low or Routine, and because of the inherent and very conservative assumption that all safety controls will fail for the identified consequences to occur, this facility clearly falls within the DOE Low Hazard Class.

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GLOSSARY

ACGIH	American Conference of Government Industrial Hygienists
ANSI	American National Standards Institute
ATW	Automatic Tube Welder
AWS	American Welding Standards
B-2 occupancy	Business Occupancy (stores, office buildings, print shops, etc.)
BNL	Brookhaven National Lab
CAS	Chemical Abstract Service
CDH	Colorado Department of Health
CDO	Controlled Decomposition and Oxidation
CERCLA	Comprehensive Environmental Response, Compensation and Liability Act
CGA	Compressed Gas Association
Container	Any vessel of 60 United States gallons or less capacity used for transporting or storing hazardous materials.
Control Area	A space within a building (a maximum of 8 per building) where the exempt amounts may be stored, dispensed, used or handled.
Cylinder	A pressure vessel designed for pressures higher than 40 pounds per square inch, absolute and having a circular cross section.
DEZ	diethyl zinc
DOE	Department of Energy
DOL OSHA	Department of Labor Occupational Health and Safety Administration
DOT	Department of Transportation
DSM	Debit Shipping Memo
EHS	Extremely Hazardous Substances
EPA	Environmental Protection Agency
ERPG	Emergency Response Planning Guidelines
ERT	Emergency Response Team
ES&H	Environmental Safety and Health
Explosive	A chemical that causes a sudden, almost instantaneous release of pressure, gas and heat when subjected to sudden shock, pressure, or high temp.s.0
Flammable gas	A gas which is flammable in a mixture of $\leq 13\%$ by volume in air, or which has a flammable range with air $> 12\%$, regardless of the lower limit.
FTLB	Field Test Laboratory Building (At NREL, on the permanent site.)
H-6 occupancy	Hazardous Occupancy: Semiconductor Fabrication
Highly Toxic	A chemical or substance with an LC50 in air of ≤ 200 parts per million by volume of gas or vapor, or ≤ 2 milligrams per liter of mist, fume or dust, when administered by continuous inhalation for one hour to albino rats weighing between 200 and 300 grams each.
HMeX	Hazardous Materials Expert (A hazardous materials database marketed by Larry Fluor, Inc. to compare chemical inventory to the Uniform Codes.)
HPM	Hazardous Production Material is a substance that has a degree-of-hazard rating in health, flammability or reactivity of Class 3 or 4 as ranked by UFCS No. 79-3 and which is used directly in research or production processes which have as their end product materials which are not hazardous.
ID	identification
IDLH	Immediately Dangerous to Life and Health is a concentration of air-borne contaminants which represents the maximum level from which one could escape within 30 minutes without any escape-impairing symptoms or irreversible health effects. Established by NIOSH.
kW	kilowatt
LC50	Median Lethal Concentration
LCHP	Laboratory Chemical Hygiene Plan
LFL	Lower Flammability Limit
LFPM	Linear Feet Per Minute
LL	Landlord-Usually a senior NREL Administrator responsible for a building
LOC	Level of Concern
MDA	trade name of the toxic gas monitor
MHz	megahertz

GLOSSARY

MOCVD	Metal Organic Chemical Vapor Deposition
MSDS	Material Safety Data Sheet
NAS	National Academy of Science
NEC	National Electric Code
NFPA	National Fire Protection Association
NIOSH	National Institute for Occupational Health
NRC	National Research Council
NREL	National Renewable Energy Laboratory
ORR	Operational Readiness Review
PECVD	Plasma Enhanced Chemical Vapor Deposition
PEL	Permissible Exposure Limit
PO	Purchase Order
ppb	parts per billion (1 in 1,000,000,000)
ppm	parts per million (1 in 1,000,000)
PR	Purchase Request
psi	pounds per square inch
PSIA	pounds per square inch, absolute
PSIG	pounds per square inch, gauge
PV	Photovoltaic
PVPUFF	Gaussian Puff Dispersion Model
Pyrophoric	A chemical that will ignite spontaneously in air at or below a temperature of 130 °F
QA	Quality Assurance
R&D	Research and Development
RCRA	Resource Conservation and Recovery Act
REL	Recommended Exposure Limit
RF	Radio Frequency
RQ	reportable quantity
S&R	Shipping and Receiving
SAR	Safety Analysis Report
SARA	Superfund Amendment Reauthorization Act
SCBA	Self Contained Breathing Apparatus
sccm	standard cubic centimeters per minute
SERI	Solar Energy Research Institute (now NREL)
SL	Safety Limit
slpm	standard liters per minute
SOP	Safe Operating Procedure
SSO	Safety and Security Office
STEL	Short Term Exposure Limit
TBA	Tertiary Butyl Arsine
TBP	Tertiary Butyl Phosphine
TLV	Threshold Limit Value (see page 7, under gas detection)
TLV	Threshold Limit Value
TMA	trimethyl aluminum
TMG	trimethyl gallium
TMI	trimethyl indium
Toxic	A chemical or substance with 200 ppm < the LC50 in air < 2,000 ppm by volume of gas or vapor, or more than two milligrams per liter but not more than 20 milligrams per liter of mist, fume or dust, when administered by continuous inhalation for 1 hour to albino rats between 200 and 300 g each.
TPQ	Threshold Planning Quantity
TWA	Time Weighted Average
UBC	Uniform Building Code
UFC	Uniform Fire Code
UFCS	Uniform Fire Code Standards
UMC	Uniform Mechanical Code
UPC	Uniform Plumbing Code

1. INTRODUCTION

Under the U.S. Department of Energy (DOE) National Photovoltaic (PV) Program, the National Renewable Energy Laboratory (NREL) PV Program sponsors long-term, potentially high-payoff research and development (R&D) in PV energy technology. The aim of this R&D is to provide a technology base from which the private sector can choose options for further development and competitive application in domestic electrical markets. The NREL PV Program is responsible for most of the R&D, manufacturing technology development, and some of the systems and market development task areas under the DOE PV program. This Safety Analysis Report (SAR) is prepared in conformance with U.S. Department of Energy (DOE) Order No. 5481.1B. It addresses, and is restricted to the hazards and risks involved with handling highly toxic or pyrophoric gases and liquids in NREL's Building 16. To our knowledge, this type of SAR for handling highly toxic or pyrophoric gases and liquids has not been prepared before.

NREL's internal research activities in PV are conducted in advanced material technologies. These include amorphous silicon (a-Si:H) thin-films, polycrystalline thin-films (including copper indium diselenide (CuInSe_2), cadmium telluride, and their alloys), and high-efficiency crystalline materials (including silicon, gallium arsenide (GaAs), gallium phosphide, indium phosphide (InP), and their alloys). Transferring the results of this R&D to private industry in a timely and effective manner is a major objective of NREL's PV program. NREL's success in R&D was confirmed by the receipt of four R&D 100 awards in 1990, one of which was for development of a GaAs heterostructure solar cell device.

In a major international safety conference sponsored by NREL in 1988, Dr. L. O. Herwig, a high-ranking spokesman for the DOE PV Program stated, *"Our concern and attention in {the area of safe PV development} must be continuous and ingenious, since the approach to acceptable personal and public risk is largely an inductive methodology.ES&H considerations must receive the best efforts of all participants in designing, siting, and constructing facilities; selecting source materials, fabrication methods, and operating procedures; evaluating potentially hazardous conditions; educating the participants and outside community services and leaders; and communicating openly within the photovoltaic community about ES&H approaches and experiences."* [1]

NREL is proud of its safety record. In over eight years of R&D, NREL has experienced only two minor incidents related to the use of toxic and hazardous gases, neither of which resulted in property loss or personal injury. The excellent safety performance of NREL's PV program is attributed to a number of factors. First, NREL has always been involved in the activities of the Semiconductor Safety Association (a professional organization committed to the sharing of lessons learned and disseminating ES&H information on the entire range of activities involved in this emerging commercial technology). Second, NREL has historically required Safe Operating Procedures (SOPs) to be developed and approved by management prior to conducting its R&D activities. Third, NREL organized a "Toxic Gas Safety Panel" in 1986 to serve as an advisory review panel to NREL management and staff in matters concerning the safe use of toxic gases. This panel provides a forum for sharing internal and external expertise and eventually developed consensus internal standards [2] for the safe use of toxic and hazardous gases and for handling emergencies [3].

As Dr. Herwig stated [1], NREL's attention to safety in PV R&D must be "continuous and ingenious." Now, rather than after an accident, is the time to look for ES&H improvements in NREL's R&D activities. To do otherwise might jeopardize the success of PV energy's penetrating the U.S. electrical markets and contributing in a meaningful way toward a more balanced energy supply.

With the above objective in mind, NREL conducted an internal audit of its PV R&D program in April of 1991. To ensure that the audit was rigorous and objective, the consulting service of Mr. Larry Fluer, a toxic gas expert of international prominence, was secured. Mr. Fluer conducted a two day audit and prepared a report presenting his findings. In this report, Mr. Fluer raised a number of issues and concerns [4]. As a result of these findings, NREL immediately and voluntarily suspended all of its PV R&D using toxic and hazardous gases in Building 16. This response, while not required by the findings of the audit, were viewed by NREL management to be in the spirit of heightened safety awareness.

While Mr. Fluer did not note any imminently dangerous situations, which would have meant immediately stopping those operations, he did highlight several issues which should be corrected in the future. These include: 1) the use and storage of materials exceeding the amounts allowed under Uniform Building Code (UBC) permitted occupancy of Group B, Division 2 (B-2 or B-2 Occupancy); 2) the lack of redundant engineering controls in some instances; 3) insufficient attention to scrubbing and treatment systems; and 4) a lack of strict adherence to NREL's internal safety standard. (Appendix I3 provides a written response each of Fluer's 55 recommendations, provided in Section 5 of his report. Either Section numbers from the SAR are provided, which directly address a particular recommendation, or a written response is provided.) While many of the findings could be rectified by relatively easy system configuration modifications, other concerns were not so easily resolved; these were primarily facility-related in nature. He stated that the internal standards [2] were quite comprehensive and were in agreement with the broad concepts of good practice specified by the codes and practiced by users of these materials. He also noted that the MDA Emergency Response Procedure [3] was well done.

Immediately following the suspension of the PV R&D activities, NREL initiated four major responses:

- All toxic and hazardous gas cylinders were returned to their respective manufacturers.
- A task force was appointed to evaluate the internal audit findings.
- Discussions were held with the local DOE area office where it was decided that a Safety Analysis Review should be prepared prior to the resumption of suspended R&D efforts.
- A committee was formed to develop the SAR, identifying and analyzing the risks of those R&D activities that were proposed to resume operations.

The laboratories that suspended their operations include two involved in the fabrication of a-Si:H films and solar cells (only one of which is under consideration to resume operations in Building 16), four involved in the fabrication of GaAs and its alloys, and one involved in CuInSe₂ research. These encompass a significant fraction of NREL's PV research, but only about 5% of Building 16's laboratory space. In addition, a laboratory using small amounts of tungsten hexafluoride for electrochromic research also suspended operations. This document is concerned with resuming all of the above operations, except for one of the a-Si:H laboratories, which is to be moved off site. Henceforth in this document, the operations to be resumed in Building 16 are referred to as either "the systems," "the laboratories," or "the operations."

This document represents the culmination of three months of intensive effort by NREL's PV R&D program personnel, aided by ES&H experts from the Brookhaven National Laboratory (BNL), to identify administrative, engineering, and personnel measures that ensure occupational and public safety, while allowing for meaningful

R&D opportunities within existing facilities. This SAR follows the guidelines and preferred practices outlined by DOE for line organizations responding to the requirements of DOE Order 5481.1B.

At this point, the only suspended operations moved to an alternate facility involve the use of concentrated silane. These operations are not included in the scope of this SAR. If any future R&D activities present risks which NREL or DOE deem to be unacceptable for Building 16, those operations would also be relocated.

DOE Order 5481.1B was established to provide uniform requirements for the preparation and review of safety analyses for U.S. Department of Energy operations. In this guidance DOE notes that consideration should be given to categorizing the hazards into three classes: Low, Moderate and High. DOE defines these classes in the following way:

1. Low - Those which present minor on-site and negligible off-site impacts to people or the environment;
2. Moderate - Those which present considerable potential impacts to people or the environment, but at most only minor off-site impacts; and,
3. High - Those with the potential for on-site or off-site impacts to large number of persons or for major impacts to the environment.

In this SAR, operations in Building 16 have been carefully evaluated to identify the maximum credible accidents and their associated event probabilities and consequences; these are summarized in Table 12. Of the 30 potential accidents identified, none present High or even Moderate Risks, 18 present Low Risks and 12 present Routine Risks. It is important to note here, that both accident event probabilities and consequences are larger than would actually be expected, because they are based on the fundamental assumption that all administrative, engineering and personal safety controls have failed. Given the redundancies and backups discussed in the earlier sections, this is a gross oversimplification. Because all identified accidents are either Low or Routine, and because of the inherent and very conservative assumption that all safety controls fail for the identified consequences to occur, this facility clearly falls within the DOE Low Hazard Class.

This view is shared by an outside agency as well. NREL recently contracted the services of Fire Mark Limited, a Boulder-based fire hazard consulting firm, to conduct a fire hazard and life safety analysis of Building 16 [5]. In the executive summary to that report, Mr Harvey states: "*Fire Mark Limited strongly believes that, with the implementation of the recommendations found at the end of this report, {these recommendations are straight forward and in accord with this SAR in every instance} Building 16 will be at least as safe, in normal operation, as any other business use (B-2) building. We further believe that, with the implementation of the recommendations found at the end of this report, Building 16 meets, and many times exceeds, the intent of the Uniform Building Code, the Uniform Fire Code, and the National Fire Protection Association standards, if not the letter in every sense.*"

Section 2 gives a brief description of the site and general building facilities and the laboratories involved in this SAR (all figures for Section 2 have been placed at the end of the section); Section 3 summarizes the hazards presented by the operations; Section 4 lists federal, state, and local regulations and guidelines; Section 5 presents the operational safety limits and hazard controls placed upon the operations; Section 6 is a semi-quantitative risk analysis of several potential accident scenarios; Section 7 includes the references used to prepare this document; and Section 8 lists the appendices.

2. SITE AND BUILDING DESCRIPTION

2.1. Building Description

Building 16 is a four story office and laboratory building located at 1607 Cole Boulevard in Golden, Colorado. It is one of NREL's three buildings, in a cluster, located in a group of buildings known as the Denver West Office Park (see Fig. 1). The permitted UBC occupancy is B-2. Building 16 was constructed by Denver West in 1978 and has been leased by NREL from Denver West since its completion.

2.2. Floor Plan

The approximate Building 16 area is 24,300 ft² on each of the first three floors and 18,600 ft² on the fourth floor; 91,500 ft² total. Hazardous production material (HPM) gases were used in laboratories 103, 190, 222, 285, 368, 369, and 458. These laboratories, which voluntarily suspended operations, account for a total of approximately 4,200 ft² (see Fig. 2); this accounts for only 4.6% of the area of the total building. In this SAR, it is proposed to resume R&D operations with highly toxic gases, flammable gases, and pyrophoric materials in laboratories 103, 222, 368, and 458. Laboratory 285 will resume operations with highly toxic and flammable gases. Laboratories 190 and 369 will resume operations using toxic/corrosive and flammable gases. (See Figs. 3a, 3b, 3c, 3d, 3e, and 3f.) All operations using silane in concentrations in excess of 1% will move off-site. A separate document will be written for those operations.

2.3. Heating, Ventilation and Air Conditioning

Both ASHRAE and ACGIH regulations are used as guidance for all heating, ventilation and air conditioning installations in Building 16.

The make-up air for Building 16 is drawn from the roof and run through the make-up air fan systems which provide heating and cooling. There are also several "under the soffit" intakes for individual hoods. There are four independent air handling units which are interconnected for back-up purposes, that also provide make-up air. The make-up air fan systems are located on the fourth floor and distribute air to the building through galvanized steel duct work. The duct work runs down from the fourth floor in two building shafts, with branch ducts to distribute air to each floor.

Make-up air is delivered to each laboratory through a variable volume box. The variable volume box is controlled by a system that maintains the laboratories at 0.03" of water pressure below the corridor pressure. Should an accidental release of chemical contaminants occur in the laboratory, they would be isolated to the laboratory, since air flows from the corridor into the laboratories. Building make-up air is also distributed to fan-coil units located in the ceiling space above each particular zone. A zone may be a group of offices, a laboratory, or a corridor. The fan-coils in interior zones provide cooling only. The fan-coils in exterior zones provide heating and cooling.

Local exhaust ventilation is provided to each HPM laboratory by an exhaust fan (or fans) dedicated to each laboratory. The exhaust fan draws air from the reactor, gas cabinet and fume hood, through stainless steel or polyvinylchloride coated galvanized duct work, and discharges the air to the outside through the exterior wall (see Fig. 4 for a typical exhaust system plan). The exhaust fans are located above the ceiling, at the exterior wall, in a "exhaust spandrel enclosure" (see Fig. 5). The enclosure is open to the outside so that if there were any leakage from the fan, it would be to the outside

ambient, not into the building. Air is not drawn from the laboratories to be returned to laboratories or any where else in the building. All make up air for the exhaust systems comes from the outdoors; there is no recycled air in the laboratories.

All the exhaust fans serving the laboratories are on standby power. The exhaust fans are interlocked with the make-up air volume box so that if an exhaust fan failure were to occur, the make-up air would be shut down, preventing a positive pressure in the space. Table 1 summarizes the pre-SAR corrective action ventilation rates for each of the laboratories. Any changes to these values would be add more ventilation to the laboratory overall (e.g. more gas cabinets). All additional ventilation will comply with those requirements set forth in Section 5.4.6.7. for gas cylinder cabinets and Section 5.4.6.9. for system enclosures. The Operational Readiness Review will ensure that these requirements are met.

LABORATORY VENTILATION RATES

Laboratory Number	Laboratory Description	Equip Encl. (cfm)	GC #1 (cfm)	GC #2 (cfm)	GC #3 (cfm)	Total Vent. (cfm)	Lab Area (ft ²)	Lab Vol. (ft ³)	Vent/ Lab Area	Air Exc/ hour
103	MOCVD	200	250	150		2500	890	8010	2.8	19
190 - "HV"	high vac. sys.	990	125	115		6600	1020	9180	6.5	43
190 - "A"	a-Si PECVD	1529	526	260						
190 - "E"	Electrochromics	516	233	290	260					
222	MOCVD	400	270	321		2000	330	2970	4.8	32
285	Selenization	1000	400	400		1800	495	4455	3.6	24
368	MOCVD	236	80	130		2800	630	5670	4.4	30
369	a-Si hot wire	1047	441			2800	551	4959	5.1	34
458	MOCVD	685	246	259		1200	235	2115	5.1	34

Equip Encl. = Equipment enclosure

GC = Gas cabinet

Total Vent. = Total ventilation being exhausted from the laboratory (includes fume hoods)

Vent/Lab Area = Laboratory exhaust in cubic feet per minute (cfm) per laboratory area (ft²)

Air Exc/hour = Air exchanges per hour, based on laboratory volume and ventilation rate

Table 1

2.4. Fire Protection

Building 16 is of noncombustible construction (steel and concrete), with the exception of the roof. The building is UBC Type III-1 hour construction. At the date of this SAR, only the fourth floor and the attic between the fourth floor and the roof are sprinkled. However, by the time of the ORR the entire building will be sprinkled. The building is divided by an "area separation wall" (see Fig. 2). Because of the area separation wall, Building 16 may be considered two separate buildings, per UBC 505.(e), and be divided up into eight "control areas" (two per floor with four floors). Over the past few months much effort has been made to ensure that a proper one-hour separation has been maintained between all control areas. All breaches and wall penetrations have been repaired.

Each laboratory is separated from the rest of the building by a one hour fire wall that extends from deck to deck. False ceilings in the building are made of fiber tile, which meet DOE General Design Criteria for flame spread and smoke contribution ratings. Fire alarm pull stations are located throughout the building and in all exit paths. Fire extinguishers are located in all laboratories. A smoke detection system is

installed throughout the building, including all of the laboratories. Gas cylinder cabinets are equipped with fast acting sprinkler heads connected to the domestic water system. The ventilation duct work in all laboratories is noncombustible. Flammable gas detection is required in cases where the quantity of flammable gases used are in excess of 400 ft³.

To provide an equivalency to the code requirements, each laboratory using pyrophoric liquids and solids in excess of the one pound, in use, exempt quantity (NREL internal limit is two pounds), has added dry chemical fire suppression in the reactor enclosure. These dry chemical fire suppression systems are installed by qualified fire protection contractors. Additionally, each laboratory using pyrophoric liquids and solids in conjunction with flammable gases has centralized flammable gas detection. This over-engineered system is proposed primarily to reduce the combined risk of hydrogen as a fuel, and small quantities of pyrophoric materials as an ignition source.

2.5. Gas Detection

Continuous gas detection is required within laboratories for hazardous gases as outlined in UFC Article 80.303-B.9. All laboratories using toxic or highly toxic gases are monitored for those gases, using a central monitoring system. All laboratories using flammable gases in excess of 400 ft³ or laboratories using both pyrophoric materials and flammable gases are monitored for those gases, using a central monitoring system. All laboratories using corrosive gases, where the physiological warning properties for the gas are at a higher level than the permissible exposure limit (PEL) for the gas (UFC Section 51.105(e)3), are monitored for those gases, using a central monitoring system. All of UFC Section 51 is included as Appendix C2. Standby power is provided to the monitors as per the Uniform Code requirements. (Continuous gas detection is defined as a monitoring system where the analytical instrument is maintained in continuous operation, and sampling is performed without interruption [i.e., 24 hours a day, seven days a week]. Analysis may be performed on a cyclical basis, at intervals not to exceed 30 minutes.)

There are basically three recognized guidelines for obtaining exposure levels; the OSHA (Occupational Safety and Health Administration) Permissible Exposure Limit (PEL), the National Institute for Occupational Safety and Health (NIOSH) Recommended Exposure Limit (REL), and the American Conference of Government Industrial Hygienists (ACGIH) Threshold Limit Value (TLV). For the gases involved with this SAR all three levels (when available) are identical. Most of the monitoring industry makes reference to the ACGIH TLV. Therefore, in this document, all monitoring references are made to the TLV. However, should one of the above organizations change their exposure value, the lowest reported value will be used as a monitoring guideline.

The MDA Toxic Gas Monitor has been selected as the standard, central monitoring system for toxic gas detection within NREL. It consists of a number of ports (8 to 16 depending on the unit) which pump an air sample through a specially treated tape (Chemcassette®). If there are any gases present which react with the treatment on the Chemcassette®, the color of the tape changes. An optical detector senses how much of that gas was in the air sample by the degree of discoloration in the Chemcassette® and a print out a reading.

These MDA units are capable of detecting three different levels of gas concentrations: a high level, a low level, or a time-weighted average (TWA) of anything below the low level alarm set point. The high level alarm is programmed to activate at

the lower of these values; 5 x the TLV, 0.5 x the Immediately Dangerous to Life and Health (IDLH) level, or the Short Term Exposure Limit (STEL). (Note, only phosphine has a STEL established, which is 1 ppm.) The low level alarm is programmed to activate at the TLV. The TWA value is constrained by the lower detectable limit and is printed out every eight hours. The MDA point monitoring the work place ambient for toxic gases is set to alarm at one half the TLV for that gas. See Section 5.6.1. for more details on toxic gas monitoring.

In keeping with Section 51.105(e)3 of the UFC, the flammable gas alarm is programmed to be activated at a detected flammable gas concentration of 20% of the lower flammability limit (LFL) for that gas (4% for hydrogen). Note that this Code requires the use of continuous detection in those areas where concentrations are expected to exceed 20% of the LFL. The operations which fall under this SAR requirement do not have an expected buildup of any concentration and therefore are put under higher constraints than the Code requires.

The alarm on the corrosive gas monitor is activated at the TLV for the particular corrosive gas being monitored in ventilated spaces. The point monitoring the work place ambient for corrosive gases is set to alarm at one half the TLV for that gas. See Section 5.6.3. for more details on toxic gas monitoring.

2.6. Plumbing

The plumbing in Building 16 is conventional, meeting the requirements of the Uniform Plumbing Code and handles only water and sanitary wastes. All hazardous wastes are disposed of as per NREL policy, which complies with RCRA procedures.

Emergency shower and eye-wash stations are located in the corridors adjacent to each laboratory. The installation and travel distances to the safety shower/eye-washes meet the requirements of American National Standards Institute (ANSI) Z358.1-1990.

2.7. Security System

Access to Building 16 is controlled 24 hours per day. From 7:30 a.m. to 5:30 p.m., any NREL employee with a valid NREL badge can access the building by inserting his or her badge into a magnetic card reader located at either of the two main entrances. During off-hours, a four digit personal identification number must be entered, in addition to the use of the magnetic badge. Only building occupants and personnel from the Safety and Security Office (SSO), Security Services, and the Facilities Branch have their personal identification number programmed into the system to allow such off-hours access to Building 16.

All NREL buildings are monitored by a continuously manned central security station located in Building 17. The security station also monitors fire alarms, toxic gas (MDA) alarms, and the NREL emergency telephone. All security systems are on standby power.

2.8. Environment, Safety and Health

NREL has a formal Environment, Safety and Health (ES&H) program, based on professional support provided by the NREL Safety and Security Office, DOE and CE Environment, Safety and Health personnel, and Laboratory wide ES&H Policies and Procedures. Formal ES&H Policies and Procedures define the responsibilities of all NREL employees, the interactions off SSO to other NREL organizational units, and the details of each ES&H activity. These documents are described further in Section 4.3. on NREL Standards and Requirements.

Necessary and appropriate ES&H activities are conducted in support of the Laboratory (e.g. ongoing Medical Surveillance, air monitoring of contaminants, fire protection appraisals, periodic inspections, waste disposal audits, etc.) and all risks presented by Building 16 operations can be accommodated by existing ES&H programs and personnel. Under the direction of an Office Manager the SSO is divided into the following functional units:

2.8.1. Security Services

Security Services provides security oversight at all NREL facilities through formal programs, security systems, and protective force personnel. Staffed by a manager, supervisor, administrative assistants, and NREL protective force officers, with supplementary officers provided by a contract security service. Security specific to Building 16 is described in Section 2.7..

2.8.2. Medical Services

Medical Services maintains a Medical Surveillance Program through a clinic located in the NREL occupied Building 16 of the Denver West Office Park. It is staffed by a Program Administrator/Certified Occupational Health Nurse and a contracted Board Certified Occupational Health Physician. Specifics of an employee's medical surveillance are tailored to their activities and potential exposures. Such surveillance includes placement and routine physical examinations, physician case review, work-site surveys, review of Safe Operating Procedures (SOPs) and counselling. Complete confidential medical records are maintained. All medical monitoring and tests are transcribed into employees medical records. When applicable, Industrial Hygiene monitoring data is transcribed into employees medical records. (All positive test data showing exposure or potential exposure is transcribed into employees medical records. Negative test data is not necessarily included in medical records, but is kept by the S&H Section. Not all Industrial Hygiene monitoring data can be associated with specific individuals.) Procedures are in place for employee notification of monitoring results.

2.8.3. Environmental Section

The Environmental Section monitors NREL's compliance with all applicable environmental regulations and provides guidance and support for compliance activities. Staffed by an Environmental Scientist, a NEPA Coordinator, and a Waste Coordinator.

2.8.4. Safety and Health Section

The Safety and Health Section provides guidance and support for all aspects of employee and public safety and health. This includes necessary regulatory compliance. Laboratory wide coverage is provided by an Industrial Hygienist and two Safety Engineers. Three ES&H Representatives are individually assigned to specific NREL Divisions.

2.9. Laboratories

Laboratories utilizing HPMs, as shown in Figs. 2, 3a, 3b, 3c, 3d, 3e, and 3f, are located on the floors listed in Table 2a. Table 2b lists the types of HPM monitoring required in each of these laboratories. The chemical names for the formulas and abbreviations used in this section can be found later in Tables 3a and 3b.

LOCATION OF LABORATORIES USING HPMs

FLOOR	ROOM #	LABORATORY TYPE	SOURCE MATERIALS
1	103	GaAs (MOCVD)	toxics, pyrophorics, & corrosives
1	190	Electrochromics & a-Si	toxic/corrosive gases & flammables
2	222	GaAs (MOCVD)	toxic & pyrophoric liquids & gases
2	285	Selenization	toxic & flammable gases
3	368	GaAs (MOCVD)	toxics, pyrophorics, & corrosives
3	369	a-Si (Hot Wire)	toxic/corrosive gases & flammables
4	458	InP (MOCVD)	toxic & pyrophoric liquids & gases

Table 2a

HPM MONITORING REQUIRED IN THESE LABORATORIES

ROOM #	LABORATORY TYPE	TOXIC	FLAMMABLE	CORROSIVE
103	GaAs (MOCVD)	Yes	Yes	No
190	Electrochromics & a-Si	Yes	No	Yes
222	GaAs (MOCVD)	Yes	Yes	No
285	Selenization	Yes	No	No
368	GaAs (MOCVD)	Yes	Yes	No
369	a-Si (Hot Wire)	Yes	No	Yes
458	InP (MOCVD)	Yes	Yes	No

Table 2b

The following sections provide general descriptions of each of the laboratories covered by this SAR. With the exception of the system in laboratory 222, each of the deposition systems found in these laboratories has been designed and built in-house. There are not manufacturers specifications, nor formal blueprints for any of these systems. This is true even for the Spire system located in 222. The systems are research apparatus and undergo design changes frequently (~ once/year).

However, some general construction rules do apply. All system construction must conform to those requirements outlined in Section 5 of this SAR. In general the following design criteria apply as specified. 1) All HPM is transported through small diameter stainless steel tubing (1/8", 1/4", and 3/8"; almost exclusively 1/4") from the HPM source to the system reactor. 2) All gaseous and liquified gaseous HPM sources are located in gas cylinder cabinets (as required by Section 5.4.1.23.). 3) Liquid HPM sources are located in the reactor enclosures or separate enclosures, not gas cylinder cabinets. 4) MOCVD and selenization reactors are made of quartz and usually run at close to atmospheric pressures. 5) PECVD reactors for a-Si:H deposition are made of stainless steel vacuum components (6-way crosses or cubes) and may have one or more glass or quartz viewports. These systems are typically run at pressures $\leq$ one torr (atmosphere is 760 torr). 6) PECVD reactors for electrochromic deposition consist of small quartz bell jars ($\leq$ 5 liters) and are run at pressures $\leq$ ten torr. 7) Both types of PECVD systems require at least one vacuum pump as a part of the process; MOVCD systems do not. These vacuum pumps are located within the system or reactor enclosure. 8) Each of these systems has what is usually referred to as a gas distribution manifold (mass flow controllers, process valves, tubing, filters, etc.) located within the system or reactor enclosure. 9) The effluent from each reactor is treated before being exhausted from the laboratory. The type of treatment depends on the types of HPM being used and is done according to Section 5.4.5. 10) The fan that

provides the exhaust ventilation for each system provides ventilation for both the system enclosure and the gas cylinder cabinets for that system.

2.9.1. Laboratory 103

Laboratory 103 contains a metalorganic chemical vapor deposition (MOCVD) system, and is located on the first floor of Building 16, in the south wing. The laboratory has an exterior wall and about 890 ft² of floor space. The room is used to house a single MOCVD system and some miscellaneous film characterization equipment. The MOCVD system is located in the southern half of laboratory 103 (see Fig. 6) and consists of: 1) a vented noncombustible enclosure containing the main growth chamber, appropriate gas flow controls, and organometallic bubblers; 2) five approved gas cabinets used for storing gases (flammable, toxic, and corrosive) and a reactor effluent "burn box" (see App. M3) system; and 3) controlling electronics and a radio frequency (RF) induction heating power supply.

The principal activity in this laboratory is the epitaxial growth of III-V semiconductor compound films, using a variety of organometallic sources (liquid and solid metal alkyls), toxic gases (hydrides), and flammable gases (dopant mixtures and hydrogen). These films are subsequently used for fabricating lattice-matched two-junction solar cells of Ga_{0.5}In_{0.5}P on GaAs, with band gaps of 1.85 eV and 1.42 eV, respectively.

During a typical process run, a mixture of gases and vapors is carried by hydrogen over a single crystal substrate, heated by RF induction to 600-750°C. Hydrogen gas flows of 3-6 standard liters per minute (slpm) are typical, while flow rates for the hydride, dopant, and organometallic sources are much smaller: 20-50 standard cubic centimeters per minute (sccm), 10-500 sccm, and 10-150 sccm, respectively. HCl gas is used purely for cleaning and etching, with typical flows of 10-20 sccm. Delivery pressure is regulated to 30 pounds per square inch (psi) upstream of the mass flow controllers, while downstream components, including the reactor, are at atmospheric pressure. Unused reactants and by-products exiting the reaction chamber are directed into a burn box, which is itself located within an exhausted enclosure. The exhaust from this box is filtered with a prefilter and High Efficiency Particulate (HEPA) filter to remove arsenic oxide and other less hazardous oxides.

Organometallic liquids (TMA-0.11 lbs, TMG-0.11 lbs, TBA-0.88 lbs, TBP-0.88 lbs, and DEZ-0.06 lbs) and solids (TMI-0.22 lbs) are used as sources for dopant atoms. These sources come supplied in stainless steel containers, which are subsequently kept at constant temperature through the use of temperature controlled baths. These baths are housed in the main reactor enclosure, with the associated compressor units beside or beneath the enclosure. The toxic gases AsH₃ (10 ft³; a liquified gas at 205 psi) and PH₃ (5.7 ft³; a liquified gas at 593 psi) are used as additional sources for the group V constituent. Each gas is stored in its own double-cylinder gas cabinet with an accompanying purge gas cylinder (Ar or N₂; 260 ft³). Additional gases include HCl (53 ft³; a corrosive liquified gas at 613 psi), Se/Si dopant mixture gases (≤ 1000 ppm H₂Se in H₂ { 30 ft³; 2200 psi}; ≤ 1000 ppm SiH₄ or Si₂H₆ in H₂ { 30 ft³; 2200 psi}), and hydrogen (200 ft³; 2200 psi). The HCl cylinder shares a two-cylinder gas cabinet with a purge gas (Ar or N₂; 260 ft³), while the flammable dopant mixtures and hydrogen share a three-cylinder gas cabinet with a purge gas (Ar or N₂; 260 ft³).

Although the organometallic liquids offer the advantage of quick dissipation and easier containment in the event of spillage, and consequently reduced exposure potential for buildings and homes surrounding the site, their use presents several key

disadvantages: 1) most of these liquids exhibit pyrophoric tendencies, and in the case of TBA, toxic characteristics; 2) their process capability for fabricating high-efficiency solar cells is unproven (unlike AsH₃ and PH₃); and 3) they are nearly 10 times more expensive than the conventional gas sources. However, industry has expressed an interest in these alternate sources due, to the high toxicity of other gas sources. For these reasons, comparative studies of both toxic gases and liquid/solid alternatives would be of interest to the III-V solar cell community.

2.9.2. Laboratory 190

Laboratory 190, formerly the a-Si:H fabrication laboratory, contains a plasma-enhanced chemical vapor deposition (PECVD) system and a converted a-Si:H deposition system. The laboratory is located on the first floor of Building 16, in the north wing. It is the largest gas processing laboratory in Building 16, has no exterior walls, and occupies about 1020 ft² (see Fig. 7).

The PECVD system is a commercial apparatus designed to deposit novel thin-films or perform plasma-initiated modifications to an existing surface via high vapor pressure reactants. Essential components of the system include a rotary vane mechanical pump filled with an inert halocarbon oil, a 13.56 MHz RF-powered reaction chamber, a substrate platen capable of ~350°C, a gas delivery control manifold, an automatic throttle-valved exhaust, and an exhaust scrubber. The entire system is housed in a ventilated Plexiglass hood. The system is equipped with state-of-the-art safety devices, such as flow limiting orifices, emergency shut-off valves, and MDA monitoring points (see Fig. 7).

A typical process sequence utilizes a very low (≤ 20 sccm) flow rate of WF₆ or MoF₆, with a similar amount of O₂ and H₂ in a room temperature RF plasma discharge for 2 to 10 minutes. The resulting reaction deposits thin-films of tungsten trioxide and molybdenum trioxide for electrochromic research. Unreacted toxic by-products are then processed through a water-spray scrubber before exhausting to the laboratory exhaust duct work. The PECVD system also uses non-toxic gaseous sources for thin-film synthesis in other areas. For example, ethylene and perfluoroethylene are used to synthesize diamond-like carbon films.

The toxic ~3 psi WF₆ and MoF₆ liquid sources (lecture bottles, 5 ft³ and 3 ft³ total each, respectively) are stored within a gas cylinder cabinet. The flammable ethylene (30 ft³) is stored with the hydrogen (100 ft³) cylinder in a separate gas cabinet.

The hazards associated with the converted system could include the use of a toxic gas (SiF₄), flammable gases (H₂, CH₄), a flammable liquid (diethylsilane), solid selenium and compressed gases (N₂, Ar). Other hazards include: electrical and electronic equipment (shock hazard); pressurized and evacuated volumes (explosion and implosion hazard); the generation of RF power; use of ultraviolet light; cleaning with acids, bases, organic solvents, and alcohols; etc.

In addition to these systems, laboratory 190 contains two vacuum systems for metalization and high vacuum experiments.

2.9.3. Laboratory 222

Laboratory 222 is located in the south wing of the second floor of Building 16. This laboratory has an exterior wall and occupies about 330 ft². The laboratory houses a commercial MOCVD reactor built by Spire Corporation, which was installed in 1986. The MOCVD system consists of: 1) a vented noncombustible enclosure containing the

reactor, appropriate gas flow controls, and organometallic bubblers; 2) two separately vented gas cabinets used for storing flammable and toxic gases; 3) an approved graphite absorption drum used to trap waste products; and 4) controlling electronics and a 15 kW RF induction heating power supply. The layout for this laboratory is shown in Fig. 8.

The principal activity in this laboratory is the epitaxial growth on GaAs of III-V (GaAs and AlGaAs) semiconductor compound films, using a variety of organometallics (liquid and solid metal alkyls), toxic gases (hydrides), and flammable gases (dopant mixtures and hydrogen). The primary uses for these films include: 1) fabricating photoelectrochemical electrodes for hydrogen fuel production, and 2) fundamental studies of confinement effects in single quantum wells and superlattices.

During a typical process run, a mixture of gases and vapors is carried by hydrogen over a single crystal substrate, heated by RF induction to 600-750°C. Hydrogen gas flows of 10-20 slpm are typical. Flow rates for the hydrides, dopant mixtures, and organometallics are much lower (typically around 1-20 sccm). Film growth is carried out in the reaction chamber at atmospheric pressure. Unused reactants and by-products exiting the reaction chamber are prefiltered by a stainless steel mesh and then directed into a 55 gal drum containing 150 lbs of activated carbon (Calgon, Inc.). This carbon effectively traps all unreacted AsH₃ and reaction by-products for oxidation at a later time (controlled under a N₂ purge). The outlet of the drum is monitored continuously to insure that no AsH₃ passes into the exhaust ducting.

The types and amounts of organometallic solids and liquids to be used are identical to those used in laboratory 103. Arsine is also be used in this laboratory (10 ft³). Neither PH₃ nor HCl are used. The AsH₃ cylinder (a liquified gas at 200 psi) is be kept in its own two-cylinder gas cabinet with a dedicated N₂ purge gas cylinder (230 ft³; 2400 psi). Two H₂ cylinders (each 216 ft³; 2200 psi) are stored in a vented cabinet in a room adjacent to the laboratory (room 219). A flammable, diluted, non-toxic dopant gas cylinder (25 ft³; 2200 psi) and a N₂ purge cylinder (230 ft³; 2400 psi) is stored in a four-cylinder gas cabinet. The organometallics are be stored directly in the MOCVD cabinet. A liquid nitrogen dewar (which provides purge gas for the system) and two N₂ cylinders (which run various venturi pumps) are located in a room adjacent to laboratory 222.

Future plans include the addition of organometallic sources TMI, TBA, and TBP. The latter two are used to investigate the feasibility of liquid replacements for AsH₃ and PH₃.

2.9.4. Laboratory 285

Laboratory 285, the selenization laboratory, is located on the second floor of Building 16, in the north wing. The laboratory has no exterior walls and occupies 495 ft² of floor space. The selenization system consists of: 1) a vented polycarbonate unistrut enclosure containing the main growth chamber, appropriate gas flow controls, and effluent waste scrubber; 2) two approved gas cabinets; and 3) a control panel. In addition, the laboratory also contains a commercial Addax Rapid Thermal Anneal (50 kW) unit and a commercial sputtering vacuum system. Neither of these are used to process HPM. The laboratory layout is shown in Fig. 9.

The selenization process involves the chemical conversion of pure metal (Cu/In/Ga) layers into their respective selenide forms (Cu_xSe, In_xSe, Ga_xSe, and Cu(In,Ga)Se₂), by a thermal process utilizing the highly toxic gas H₂Se. Selenization is the industry process-of-choice (as identified by a recent Electric Power Research Institute report) for manufacturing high efficiency, low cost polycrystalline solar cells

based on CuInSe_2 . First-time in-house attempts in laboratory 285 have already yielded very respectable 6% efficient devices.

During a typical process, a mixture of H_2Se , H_2 , and an inert carrier gas, Argon, is directed into a narrow-gap quartz reactor over the metallic layer structures, heated with infrared lamps to a temperature of 400°C . Gas flow rates of 1-10 sccm for H_2Se , 0-150 sccm for H_2 , and 0-500 sccm for Ar are common. Unused reactant and by-products are then directed into a NaOH solution mist scrubber, after which it passes into the exhaust duct system. The scrubber has a tested 100% scrubbing efficiency at process conditions. The system layout, including gas cylinder location, system enclosure, and exhaust duct work is also shown in Fig 9. The entire system is ventilated to the exhaust duct work.

The H_2Se and H_2 cylinders are kept in separate ventilated gas storage cabinets. The H_2Se lecture bottle (lb-size) consists of 0.5 lbs (2.42 ft^3) of pure H_2Se , stored as a liquid under its own vapor pressure (125-150 psi at 25°C). The H_2 source is a K-size cylinder containing approximately 216 ft^3 at 2400 psi. Both sources have a dedicated purge N_2 tank (K size, 230 ft^3 , 2400 psi) within their respective cabinets. Although H_2Se in very dilute form ($<1000\text{ ppm}$ in Argon) can be classified as a non-toxic gas, it is not desired for two reasons: 1) the necessity for extremely long (hours) process runs, and 2) much higher tank pressures (1800 psi). It is believed that the combination of lower pressure source and much shorter process time presents a more desirable process scenario.

2.9.5. Laboratory 368

Laboratory 368 is located on an exterior corner of the third floor of Building 16, in the north wing, and occupies 630 ft^2 . In the southwest corner of the laboratory there is an MOCVD growth system similar to the one in laboratory 103. The remainder of the laboratory is used to house characterization and maintenance equipment. Both the reactors in 103 and 368 are operated by the same working group, and are used for epitaxial growth of $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$ and GaAs solar cells (see Fig. 10). The previous discussion for laboratory 103 applies in its entirety to laboratory 368.

2.9.6. Laboratory 369

Laboratory 369 is located on the third floor of Building 16, in the north wing. This laboratory contains an a-Si deposition system, has an exterior wall, and occupies 551 ft^2 . The exact location of the system within the laboratory is shown on the floor plan (see Fig. 11). The system is comprised of three gas cylinder cabinets, a scrubber, an electronics rack, and the stainless steel deposition system and pumps (which are housed in a vented Plexiglass enclosure).

The deposition technique used is called the hot filament assisted chemical vapor deposition, or hot wire, technique. In this technique, a thin tungsten wire is heated to a temperature of 2000°C . Silicon source gases are then let into the system and, due to the low chamber pressures used, the gas molecules come into contact with the heated filament many times. These gases are catalytically decomposed on the surface of the filament, and the resulting silicon fragments are in turn re-evaporated onto a heated substrate, thus depositing a film. The unused gases and the reactant by-products are then heavily diluted with an inert gas and sent through a liquid NaOH scrubber. This hot wire deposition process has several advantages compared to the standard PECVD (glow discharge) deposition process, including: 1) higher deposition rates at lower input gas flows, and 2) a lower amount of hydrogen incorporation. The improved process efficiency of this technique, compared to conventional PECVD processes, reduces the overall amounts of reactant gases required, and consequently improves the

safety aspects of this process. The hot wire technique is therefore being aggressively investigated to see what further improvements can be made.

Undiluted pyrophoric SiH_4 is used in this process. Rather, the use of a heavily diluted silane ($\leq 1\%$ SiH_4 in He ; 257 ft^3 , 2200 psi) is proposed. This material has been classified by the Department of Transportation (DOT) as a compressed gas only. In addition, the liquid source diethylsilane (0.50 lb) will be investigated. Low flow rates (< 50 sccm) for all sources are used. This source is a flammable liquid, and is neither pyrophoric nor toxic (no TLV has been established as of 1990). While each of these options has significant drawbacks, which include reduced deposition rates (1% diluted silane) and the possibility of C inclusion in films (diethylsilane), these alternatives to silane are considered to be worth pursuing at this time. If good a-Si:H material can be made using these "safe" source materials, that alone would be an important contribution to the amorphous silicon community, especially due to the increased emphasis on safety issues in today's environment.

In addition to the above sources, other gases to be used include diluted silicon tetrafluoride (3 ft^3 , 10-25% dilution in H_2), methane (30 ft^3 ; a flammable gas), and H_2 (30 ft^3 ; a flammable gas). While silicon tetrafluoride cannot, by itself, be detected by an MDA, one of its by-products, HF, is a corrosive gas and can be detected. Therefore, central monitoring is performed for HF.

2.9.7. Laboratory 458

Laboratory 458, a MOCVD laboratory, is located on the fourth floor of Building 16, in the north wing. This laboratory has no exterior walls and occupies 235 ft^2 . The laboratory is used to house a single, home-built MOCVD system that operates at atmospheric pressure (see Fig. 12). No other experimental activities take place here. The room is in the only previously sprinkled area of the building. The laboratory is bordered by two hallways and two adjacent laboratories. A large viewing window exists in the wall between laboratories 458 and 459, such that activities in laboratory 458 can be observed without entering the room.

The MOCVD reactor is set up to grow InP and related III-V compound semiconductors for the fabrication of new types of high-efficiency solar cells. A large fraction of the research conducted in this laboratory is funded by external agencies, and has resulted in a number of PV devices with record performance levels, and in a number of invention disclosures and patents. Most notably, two types of concentrator tandem solar cells have been fabricated, each with an efficiency exceeding 30%.

The types and amounts of organometallic solids and liquids to be used are identical to those used in laboratory 103, with the following exceptions: 0.22 lbs of the TMG liquid source, and no TBA or TBP is used. In addition, 1000 ppm H_2S in H_2 is used.

Additional details related to system design and operation and growth procedures are similar to those described for the MOCVD system in laboratory 103 (discussed earlier).

2.10. Remote Storage Facility

Storage of toxic, highly toxic, pyrophoric, or corrosive gaseous, solid or liquid source materials is prohibited in Building 16. There are no permanent facilities within NREL for indoor storage of these materials. The only place these materials are stored is the bunker, which is located over four hundred feet to the north/east of the Field Test Laboratory Building (FTLB). This bunker is of Type I-FR construction. It was

originally constructed by Camp George West, a military facility, for ammunition storage. The bunker is divided up into four separate rooms or areas each of which has its own exhaust fan. It occupies an approximate total area of 500 ft². The bunker, and the area surrounding it, is non-occupied space and is accessed only when a HPM container is either brought to or removed from this location. The bunker is located approximately 200 ft from the FTLB.

2.11. Quality Assurance

NREL is committed to adopting and carrying out the standards of excellence embodied in the NREL Quality Assurance Manual and the requirements of this procedure. A quality assurance program provides maximum benefit when it covers all aspects of equipment calibration, use, record keeping and maintenance. The SSO has written a draft Quality Assurance Plan as it pertains to ES&H. This is included as an attachment in Appendix I5. NREL recently established a Quality Assurance Office. Staff from this office are currently drafting a laboratory wide Quality Assurance Plan which incorporates the new DOE Order on QA for research. Section 5 embodies all aspects of Quality Assurance as it relates to these systems.

**SERI LEASED FACILITIES
AT DENVER WEST**

NO SCALE

Figure 1
16

BUILDING 16

Figure 2

BLDG. 16
LARGE WING
1ST FLOOR
PLOTTED 7/12/90

Figure 3a
18

BLDG 16
SMALL WING
1ST FLOOR

Figure 3b
19

BLDG 16
LARGE WING
2ND FLOOR
NO SCALE

Figure 3c
20

BLDG 16
LARGE WING
4TH FLOOR
NO SCALE

Figure 3f
23

BLDG. 16
SMALL WING
1ST FLOOR
PARTIAL PLAN

Figure 4
24

Figure 5
 25

MDA Toxic Gas Points
 ① System Enclosure
 ② Main Vent
 ③ Ambient

Figure 6
Laboratory 103
 MOCVD Laboratory

Hazardous Gas Classification

- Toxic
- ▨ Flammable
- ▤ Corrosive
- ▩ Pyrophoric
- ▧ Oxidizer

Figure 7
Laboratory 190
Electrochromics Experiment

MDA Toxic Gas Points
1 Gas Cabinets
2 Ambient
3 Enclosure Exhaust

Hazardous Gas Classification

	Toxic		Flammable		Corrosive
	Pyrophoric		Oxidizer

MDA Toxic Gas Points

- ① System Enclosure
- ② Gas Cabinet
- ③ Charcoal Scrubber
- ④ Ambient

Figure 8
Laboratory 222
MOCVD Laboratory

Hazardous Gas Classification

	Toxic		Flammable		Corrosive
	Pyrophoric		Oxidizer

Figure 9
Laboratory 285
 Hydrogen Selenization Laboratory

Hazardous Gas Classification

	Toxic		Flammable		Corrosive
	Pyrophoric		Oxidizer

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Hazardous Gas Classification

- Toxic
- Flammable
- Corrosive
- Pyrophoric
- O

 Oxidizer

[†] 1% Silane in He is not considered hazardous.

Figure 11

Laboratory 369

Amorphous Silicon Laboratory

MDA Toxic Gas Points

- ① Main Vent
- ② Ambient

MDA Toxic Gas Points

- ① Gas Cabinets
- ② System Enclosure
- ③ System Enclosure
- ④ Ambient

Figure 12
Laboratory 458
 MOCVD Laboratory.

Hazardous Gas Classification

	Toxic		Flammable		Corrosive
	Pyrophoric		Oxidizer		

3. IDENTIFICATION OF HAZARDS

3.1. Background and General Information

Many production materials that are potentially hazardous are used in PV R&D. For the past fifteen years, most of the semiconductor and solar cell industries have used highly toxic (arsine, phosphine, diborane) and pyrophoric (phosphine, silane) hydrides as source materials. The industry response to the potential dangers involved in handling these HPMs has combined the use of elaborate containment and sophisticated monitoring systems. In recent years, liquid alternative sources, such as TBP and TBA, have become available. The liquid nature of these compounds significantly reduces dispersion related hazards. While they are mildly pyrophoric, the small amount of liquid involved, and their rapid oxidation in air, provide for much simplified containment.

The principal hazard associated with operations in Building 16 is exposure to hazardous chemicals during the use and handling of toxic and/or pyrophoric solids, liquids or gases. Small quantities of these chemicals are used in reactors to produce solid semiconductor devices by a variety of chemical vapor deposition methods. These processes are all research sized operations and use only a fraction of the quantity of chemicals used by industry. Extensive ventilation and fire safety modifications to the existing leased facility were made in 1984, and there have been a number of safety improvements in the subsequent years. These modifications have made the Building generally safer by reducing the chance of employee exposure due to improper ventilation. During the 9 years that these facilities have been used for toxic and pyrophoric gas operations, there has been no known accidental release of hazardous material to the external environment above 1/2 OSHA Immediately Dangerous to Life and Health level (IDLH). The principal sources of exposure to these HPM include:

- (1) Handling and transportation to laboratories.
- (2) Gas or liquid cylinder change-out.
- (3) Gas distribution during normal system operation.
- (4) Ventilation failure.
- (5) Failure of effluent treatment.
- (6) Waste disposal.

Other hazards associated with the operation of this facility are similar to those encountered in most chemical laboratories, including solvents, heavy metals, organic compounds, flammable liquids, compressed gases, and high temperature furnaces.

3.2. Specific Hazards Associated With These Systems

Tables 3a and 3b list the chemicals proposed for use in the laboratories for which this SAR is written. Table 3a includes those chemicals that are unique to these systems, whereas Table 3b includes those chemicals also used in other laboratories in Building 16. The chemicals are grouped according to their UBC/UFC hazard class, dark horizontal lines separate these groupings. The B-2 exempt quantities of chemicals according to the 1988 Edition of the UFC (Tables 9-A and 9-B of Article 80 of the UFC are included as Appendix C1), which have been adopted by the local jurisdiction, are listed in parentheses in column 2. The maximum amount in each laboratory is given

in the remaining columns. Solid vertical lines separate the control areas. Note that some chemicals fall in both hazard classes. In these cases they are included in both when figuring the maximum amounts per hazard class. This does not necessarily mean that a control area will necessarily use this maximum. It may rather choose to limit the amount used to be within the UBC.

SPECIALIZED CHEMICALS (HPMs) PER CONTROL AREA

Chemical Name (Formula)/Abbrev.	UBC/UFC Hazard Class (Exempt qty.)	Lab 103 (qty)	Lab 190 (qty)	Lab 222 (qty)	Lab 285 (qty)	Lab 368 (qty)	Lab 369 (qty)	Lab 458 (qty)
1. Arsine (AsH ₃)	Highly Toxic Gas (20 ft ³)	10 ft ³		10 ft ³		10 ft ³		10 ft ³
2. Hydrogen Selenide (H ₂ Se)					2.4 ft ³			
3. Phosphine (PH ₃)	Pyrophoric Gas (20 ft ³)	5.7 ft ³				5.7 ft ³		5.7 ft ³
4. Tungsten Hexafluoride (WF ₆)	Toxic Gas (20 ft ³) Corrosive Gas (650 ft ³)		5 ft ³					
5. Molybdenum Hexafluoride (MoF ₆)			3 ft ³					
6. Silicon Tetrafluoride (SiF ₄)							3 ft ³	
7. Tertiarybutylarsine (C ₄ H ₁₁ As)/TBA	Highly Toxic Liquid (1 lb)	0.88 lb		0.88 lb		0.88 lb		
8. Tertiarybutylphosphine (C ₄ H ₁₁ P)/TBP	Pyrophoric Liquid (1 lb)	0.88 lb		0.88 lb		0.88 lb		
9. Trimethylgallium ((CH ₃) ₃ Ga)/TMG		0.11 lb		0.11 lb		0.11 lb		0.22 lb
10. Trimethylaluminum ((CH ₃) ₃ Al)/TMA		0.06 lb		0.06 lb		0.06 lb		0.06 lb
11. Diethylzinc ((C ₂ H ₅) ₂ Zn)/DEZ		0.06 lb		0.06 lb		0.06 lb		0.06 lb
12. Trimethylindium ((CH ₃) ₃ In)/TMI	Pyrophoric Solid (1 lb)	0.22 lb		0.22 lb		0.22 lb		0.22 lb
13. Diethylsilane ((C ₂ H ₅) ₂ Si)	Flammable Liquid (30 gal)					0.22 lb		
14. Lightly Doped H ₂ Mixtures	Flammable Gas (1500 ft ³)	60 ft ³		25 ft ³		60 ft ³		60 ft ³
15. Hydrogen (H ₂)		432 ft ³	176 ft ³	200 ft ³	216 ft ³	200 ft ³	30 ft ³	200 ft ³
16. Methane (CH ₄)			76 ft ³		50 ft ³		30 ft ³	
17. Hydrogen Chloride (HCl)	Corrosive Gas (650 ft ³)	53 ft ³				53 ft ³		
18. Oxygen (O ₂)	Oxidizer (1,500 ft ³)				244 ft ³			
19. ≤1% Silane in Helium (SiH ₄ / He)	Compressed Gas (NA)						257 ft ³	

Table 3a

COMMON LABORATORY CHEMICALS PER CONTROL AREA

Chemical Name (Formula)/Abbrev.	UBC/UFC Hazard Class (Exempt qty.)	Lab 103 (qty)	Lab 190 (qty)	Lab 222 (qty)	Lab 285 (qty)	Lab 368 (qty)	Lab 369 (qty)	Lab 458 (qty)
20. Inorganic Arsenides (As, As ₂ O ₃ , As ₂ O ₅)	Carcinogen	0.5 lb		1 lb		0.5 lb		
21. Carbon Tetrachloride (CCl ₄)	Suspected Carcinogen	0.1 gal	1 pt			0.1 gal		
22. Gallium Arsenide (GaAs)		≤2 lb		≤2 lb		≤2 lb		≤2 lb
23. Hydrofluoric Acid (HF)	Corrosive Liquid (500 gal)	1 gal	1 gal	0.4 gal		1 gal	1 gal	
24. Aqua Regia (3:1 HCl:HNO ₃)		1 gal		4 gal		1 gal		
25. Sulfuric Acid (H ₂ SO ₄)		1 gal	0.5 gal					
26. Nitric Acid (HNO ₃)		1 gal	1 gal			1 gal	1 gal	
27. Acetic Acid (CH ₃ CO ₂ H)		1 gal	1 gal				2 gal	
28. Sodium Hydroxide (NaOH)					15 gal			
29. Sodium Hydroxide (NaOH)	Corrosive Solid (5000 lbs.)				2.2 lb			
30. Trichloroethylene (ClCH:CCl ₂)	Flammable Liquid Class I-B (120 gal)	0.5 gal	1 gal	0.5 gal		0.5 gal	1 gal	
31. Acetone (CH ₃ COCH ₃)		0.5 gal	1 gal			0.5 gal	1 gal	
32. Methanol (CH ₃ OH)		0.25 gal	1 gal	1 gal		.25 gal	1 gal	
33. Ethanol (C ₂ H ₅ OH)		0.5 gal		1 gal				
34. Methyl Ethyl Ketone (CH ₃ CH ₂ COCH ₃)			0.5 gal					
35. Isopropyl Alcohol {CH ₃ CH(OH)CH ₃ }	Flammable Liquid Class I-C (180 gal)	0.5 gal	1 gal		0.1 gal	0.5 gal	1 gal	

Table 3b

Tables 4a and 4b provide more details about the specific hazards presented by those materials which are unique to these systems (#'s 1-19, in these two tables, and in Table 3a). As in Tables 3a and 3b, the chemicals are grouped according to their hazard class. The tables do not include those chemicals which are considered to be of common use within some of the other laboratories in Building 16. Those chemicals (from Table 3b) are typical solvents, acids, bases, and alcohols.

The Material Safety Data Sheets (MSDSs) for the chemicals found in Tables 4a and 4b can be found in Appendix M1. These MSDSs provide even more specific and detailed information than what can be found in Tables 4a and 4b.

DESCRIPTION OF HAZARDS ASSOCIATED WITH HPMs USED BY THESE SYSTEMS

Chemical Name (formula)	UBC/UFC Hazard Class (exempt qty)	TLV/ IDLH/ §LC50	Odor/ Threshold (ppm)	*Flam in Air (%) or Pyro Auto T (°C)	Toxic Effects		Lethal Dose Human	Special Precautions §§MDA LDL
					Acute	Systemic		
1. Arsenic (AsH ₃)	Highly Toxic Gas (20 ft ³)	50 ppb/ 6 ppm/ 20 ppm	garlic-like/ 1-2 ppm	flammable (4.5-64%)	headache, dizziness, weakness, nausea, vomiting	hemolytic agent, nerve/blood poison, delay in symptoms	250 ppm/ 30 minutes	• Toxic gas plumbing • Toxic gas monitoring • Oxygen available in ES&H • Housed in gas cabinet 5 ppb
2. Hydrogen Selenide (H ₂ Se)		50 ppb/ 2 ppm/ 2 ppm	garlic-like/ 0.3 ppm olfactory fatigue	flammable ** (NE)	dizziness, nausea, eye/nose irritation, CNS effects	allergen, lung/liver damage	deadly poison/ NE	• Toxic gas plumbing • Toxic gas monitoring • Housed in gas cabinet 10 ppb
3. Phosphine (PH ₃)	Highly Toxic (20 ft ³) and Pyrophoric Gas (10 ft ³)	0.3 ppm/ 200 ppm/ 20 ppm	garlic-like or decaying fish/ 2 ppm	pyrophoric (40 - 50°C)	headache, nausea, vomiting, stomach cramps, diarrhea	lungs, kidney convulsions	2,000 ppm/ 5 minutes	• Toxic gas plumbing • Toxic gas monitoring (STEL= 1ppm) • Housed in gas cabinet 5 ppb
4. Tungsten Hexafluoride (WF ₆)	Toxic Gas (20 ft ³) and Corrosive Gas (650 ft ³)	3 ppm/ NE/ 210 ppm	adequate physiological warning/ NE	neither	severe pain, redness, swelling and tissue destruction from HF acid burns	chemical pneumonitis and pulmonary edema, acid burns	NE	• Corrosive gas plumbing • Corrosive gas monitoring • Housed in gas cabinet 700 ppb of HF
5. Molybdenum Hexafluoride (MoF ₆)		3 ppm/ NE/ 210 ppm	adequate physiological warning/ NE	neither	irritation to respiratory tract, severe skin burns	fluorosis, kidney, liver	NE	• Corrosive gas plumbing • Corrosive gas monitoring • Housed in gas cabinet
6. Silicon Tetrafluoride (SiF ₄)		1.25 ppm/ NE/ 450 ppm	very pungent/ NE	neither	headache, nausea, vomiting, stomach cramps, eye irritation	lung damage	NE	• Corrosive gas plumbing • Corrosive gas monitoring • Housed in gas cabinet 700 ppb of HF
7. Tertiary-butylarsine (C ₄ H ₁₁ As)	Highly Toxic and Pyrophoric Liquid (1 lb)	0.5 mg/m ³ / NE/ 140 ppm	***NA	pyrophoric (NE)	NE	carcinogen	NE	• Highly toxic liquid plumbing • Housed in ventilated enclosure
8. Tertiarybutylphosphine (C ₄ H ₁₁ P)	Pyrophoric Liquid (1 lb)	NE/ NE/ >1000 ppm	NA	pyrophoric (NE)	NE	NE	NE	• Pyrophoric liquid plumbing • Housed in ventilated enclosure
9. Trimethyl gallium [(CH ₃) ₃ Ga]		NE/ NE/ NE	NA	pyrophoric (NE)	NE	NE	NE	• Pyrophoric liquid plumbing • Housed in ventilated enclosure

† TLV = Threshold Limit Value

* Flammability in Air value given in %; Pyrophoric Autoignition Temperature given in °C

** NE = Not Established

‡ IDLH = Immediately Dangerous to Life and Health level

*** NA = Not Applicable

§ LC50 = median lethal concentration

§§MDA LDL = MDA Lower Detection Limit

Table 4a

DESCRIPTION OF HAZARDS ASSOCIATED WITH HPMs USED BY THESE SYSTEMS (continued)

Chemical Name (formula)	UBC/UFC Hazard Class (exempt qty)	†TLV/ ‡IDLH/ §LC50	Odor/ Threshold (ppm)	*Flam in Air (%) or Pyro Auto T (°C)	Toxic Effects		Lethal Dose Human	Special Precautions
					Acute	Systemic		
10. Trimethyl aluminum [(CH ₃) ₃ Al]	Pyrophoric Liquid (1 lb)		***NA	pyrophoric (NE)	severe burns to eyes, skin, lungs	**NE	NE	<ul style="list-style-type: none"> • Pyrophoric liquid plumbing • Housed in ventilated enclosure • Keep away from water and H₂ compounds
11. Diethylzinc [(C ₂ H ₅) ₂ Zn]			NA	pyrophoric (NE)	coughing, wheezing, laryngitis, headache, nausea	nervous system disturbances	NE	<ul style="list-style-type: none"> • Pyrophoric liquid plumbing • Housed in ventilated enclosure
12. Trimethyl-indium [(CH ₃) ₃ In]	Pyrophoric Solid (1 lb)		NA	pyrophoric (NE)				<ul style="list-style-type: none"> • Flammable gas plumbing • Pyrophoric solid plumbing • Housed in ventilated enclosure
13. Diethyl-silane [(C ₂ H ₅) ₂ Si]	Flammable Liquid (30 gal)			flammable (NE)				<ul style="list-style-type: none"> • Flammable gas plumbing • Housed in ventilated enclosure
14. Lightly Doped H ₂ Mixtures			NA	flammable (4 - 8%) (585°C)			Non-lethal	<ul style="list-style-type: none"> • Dopant gas plumbing • Housed in gas cabinet • Hydrogen monitoring
15. Hydrogen (H ₂)	Flammable Gas (750 ft ³)		NA	flammable (4 - 80%)	nausea, dizziness and headache	NE	Non-lethal	<ul style="list-style-type: none"> • Flammable gas plumbing • Housed in gas cabinet • Hydrogen monitoring
16. Methane (CH ₄)			oil-like	flammable (5 - 16%)	simple asphyxiant, faulty judgement, depression of senses	NE	Non-lethal	<ul style="list-style-type: none"> • Flammable gas plumbing • Keep from ignition sources & oxidizers
17. Hydrogen Chloride (HCl)	Corrosive Gas (650 ft ³)	5 ppm 100 ppm 3,120	noxious	neither	irritating to skin and eyes, headache, nausea, vomiting	lungs, skin	1300 ppm	<ul style="list-style-type: none"> • Corrosive gas plumbing • Housed in gas cabinet
18. Oxygen (O ₂)	Gaseous Oxidizer (1,500 ft ³)		NA	oxidizer	hyperoxia, nausea, dizziness			
19. ≤1% Silane in Helium (SiH ₄ / He)	Compressed Gas			neither				

† TLV = Threshold Limit Value ‡ IDLH = Immediately Dangerous to Life and Health level § LC50 = median lethal concentration
* Flammability in Air value given in %; Pyrophoric Autoignition Temperature given in °C
** NE = Not Established *** NA = Not Applicable

Table 4b

The total of 1.99 lb of pyrophoric liquid per MOCVD system is intermediate between the 1 lb in-use limit and the 4 lb in-storage limit for sprinkled B-2 buildings. The use of this amount with appropriate local fire suppression and containment (refer to Section 5.4.2.) is justified for three reasons. First, the use of these liquids allows NREL to experiment with materials that could potentially replace arsine and phosphine. The bulk of this requested amount (1.76 lb or 89% of the pyrophoric liquid total) consists of the toxic gas substitute liquids TBP and TBA. If these operations continued with toxic gases only, the total amount of pyrophoric liquid would only be 0.22 lb, which is well below the exempt limit of 1 lb. Second, the fire hazard associated with TBP and TBA is not as high as it is for some pyrophoric materials (e.g., TMA). In fact, according to the manufacturer, TBP and TBA pass only one of the two tests needed for pyrophoric classification. The result of a spill would thus be a smoldering liquid, not a violent burst of flame. Finally, these quantities represent a reasonable compromise between keeping the quantity on hand low, and not changing containers so frequently that a spill becomes reasonably probable. As with any hazardous chemical, the operation most likely to result in an accidental release is the change of the supply container. The quantities given above should last about 2 months and 5 months, respectively, for TBP and TBA. The optimum change-out frequency of TBA is longer because of its highly toxic nature.

3.3. Hazards Presented by Worst Case Accident Scenarios

Hazards to the public outside of the laboratory are not anticipated. A worst case (almost not credible, but presented for screening purposes only) accident analysis is presented. In this case, the instantaneous release of the entire contents of hydrogen selenide (2.4 ft³), arsine (10 ft³), and phosphine (5.7 ft³) cylinders (assuming no flow restriction that we know are present) are evaluated by PVPUFF (see Appendix A3, Tables 1-3) to determine the down-gradient atmospheric concentrations. In all three cases, the estimated peak concentrations are below the IDLH values. These estimates are based on a 5 minute averaging period. Were a 30 minute averaging period used for which the IDLH value is based, the estimated concentrations would be much less. In the worst of these cases the ambient concentration 100 m downwind of the stack was one half of the IDLH concentration for arsine.

This dispersion model probably overestimates the off-site exposure. There are two basic reasons for this. First, it assumes a two dimensional model (distance above ground and linear distance from the building). This means it does not allow for any side-to-side dispersion which of course would happen in an actual release. Thus, the concentration reaching the receptor point is overestimated. Second, the worst case stated above is for a 5 minute exposure although the IDLH concentration refers to 30 minutes. The average concentrations during longer exposure times would be even lower.

It should be noted that using the IDLH in this case is an appropriate measure of exposure. The IDLH represents the maximum concentration, which in the absence of or failure of a respirator, a healthy adult could escape within 30 minutes without experiencing any escape-impairing (e.g., severe eye irritation) or irreversible health effects. In this context, concentrations approaching or exceeding the IDLH values may be viewed as presenting a risk to health, if the exposure continues at this level for an extended period (i.e. 30 minutes). As stated above, the exposure concentrations predicted by the model are much lower than the corresponding IDLH levels. Therefore, no serious irreversible health effects would be expected.

3.4. Hazards Presented by Natural Phenomena

NREL recently contracted the services of Fire Mark Limited, a Boulder-based fire hazard consulting firm, to conduct a fire hazard and life safety analysis of Building 16 [5]. As a part of this report, Mr. Harvey performs an analysis on the potential hazards presented by natural phenomena. (This entire section has been reproduced in Appendix I4.)

Mr. Harvey has looked at the impact of earthquakes, flooding, and tornados on the Building sprinkler systems, smoke detection, fire alarms, standpipes, special hazards, and NREL operations. With the possible exception of flooding, an extreme act of nature could result in major disruption to the building support systems. However, all such destruction to the Building would cause these systems to fail-safe and thus the major amount of hazardous material which could realistically be released would be the amount remaining in the gas distribution lines. This would be a small amount, not presenting an appreciable risk.

Given the nature of the activities in Building 16 and its physical location (i.e., elevated relative to local topographic relief) and layout (i.e., all gas systems above ground), the impacts of some external events can be quickly dismissed for various reasons. First there are some events (i.e., extraterrestrial activity, flood and volcanic activity) that are expected to occur so infrequently (i.e., probability cannot be distinguished from zero) that they are unimportant. Second, other events (i.e., severe winter storm, and nearby accidents) have been dismissed because they would not effect the integrity of the HPM control systems. Finally, lightening is not further considered because Building 16 is adequately grounded and because backup power is available for all critical gas control (e.g., gas detectors and ventilators) systems. Thus, only fire, seismic activity, and wind and tornadoes are considered further. These are analyzed in detail in Section 6.5.

The primary danger from seismic activity, and wind and tornadoes, would be if the Buildings floors started to crash down, rupturing HPM gas cylinders themselves. As described in Section 3.3. above, this would not pose a serious threat to the community. Realistically, the physical hazard of the Building collapsing would be more of concern to the Building occupants than a HPM gas release. It is conceivable that such a scenario (tornado or major earthquake) would result in a critical to catastrophic consequence to those Building occupants who were able to avoid the physical hazards presented by the transient. However, due to the extremely remote probability of such an occurrence, the risk presented is low (see Fig. 14, page 115).

4. REGULATIONS AND CODES

Each of these systems is designed, built and operated in compliance with the following standards and codes. The internal standards and procedures were developed by the NREL Toxic Gas Safety Panel and adopted by NREL management. These standards and procedures are revised as required by changes in operations, facilities, management structure or other relevant concerns. The codes are revised every three years and even though it has been three years since some of these codes have been adopted, it will probably be an extended period before the 1991 codes are adopted by local jurisdictions.

Critical to the continuing safety of personnel in this facility is an ongoing safety assessment of operations. Separate protocols, known as SOPs, are developed for each deposition system using these hazardous chemicals. These SOPs cover all safety aspects of the operation of these individual systems and are detailed in Section 5.5.1. of this SAR. In order to ensure these SOPs remain relevant and effective they are reviewed and approved annually by NREL line management and the NREL SSO.

4.1. Federal Regulations

The federal government regulates the handling and use of toxic or hazardous compressed gases in the work-place through statutory and regulatory programs administered by the Department of Labor, OSHA, and the U.S. Environmental Protection Agency (EPA). Frequently, federal statutes or regulations incorporate, in whole or in part, standards developed by standards organizations such as the Compressed Gas Association, the National Fire Protection Association, and the ANSI. Key regulatory requirements imposed by OSHA and EPA are highlighted below. More detailed discussion of these issues can be found elsewhere (e.g., [6], [7], [8]).

4.1.1. OSHA

The federal government regulates matters affecting the health and safety of employees in the work-place through the Occupational Safety and Health Act, enforced by the Department of labor. There are many provisions in this Act, that are directly relevant to the use of compressed gases. They include:

CFR 1910.101 - In plant handling, storage and use of compressed gases shall be in accordance with CGA Pamphlet P-1, "Safe Handling of Compressed Gases in Containers."

CFR 1910.132 - The employer (NREL) shall provide and maintain protective equipment wherever necessary by reasons of the hazards of the process equipment that might cause injury or impair functioning of any part of the body through absorption, inhalation or physical contact. Protective equipment, may include, but not be limited to safety apparatus (e.g., ventilating hoods) and personal protective devices (e.g., eye protection and respiratory equipment).

CFR 1910.1000 - Worker exposures shall be limited to prescribed permissible and short-term exposure levels.

CFR 1910.1450 - In recognition of the fact that small laboratories differ from industrial operations in their use and handling of hazardous chemicals, OSHA has recently promulgated additional rules for controlling occupational exposures to hazardous chemical in laboratories. Among the requirements of these new regulations

are guidelines for employee training and information transfer, medical consultation and examination, hazard identification, respirator use and record keeping requirements.

4.1.2. EPA

EPA protects the environment and public health by regulating the discharge of materials to the environment. In principal, there are a large number of statutes and regulations relevant to the NREL operations. The three most important are the Resource Conservation and Recovery Act (RCRA), Comprehensive Environmental Response, Compensation and Liability Act (CERCLA), and the Superfund Amendment Reauthorization Act (SARA) - Title III. Because many of these regulations are triggered only when specified material-specific quantity limits are exceeded or when regulated disposal procedures are not in compliance, they do not necessarily apply to their handling in Building 16 daily operations (which is a generator, not a disposal facility). Nevertheless, for completeness, a background discussion of these requirements is presented.

4.1.2.1. RCRA

EPA regulates the disposal of solid and hazardous wastes under the authority of RCRA. RCRA is a regulatory statute designed to provide "cradle-to-grave" control of hazardous wastes by imposing management requirements on generators and transporters of hazardous wastes. NREL does not generate large quantities of wastes but still is subject to RCRA requirements and does comply with all applicable RCRA requirements {see 40 CFR 261.5, 262.34(d)-(f)}. NREL has the appropriate EPA ID numbers to dispose of hazardous waste.

4.1.2.2. CERCLA

CERCLA was enacted by Congress to respond to releases of hazardous substances to the environment through either accidental spills or chronic releases. Most of CERCLA focuses on the clean-up of abandoned hazardous waste sites. The part that applies to NREL involves the reporting of releases. In Section 102 the EPA Administrator is given the authority to promulgate regulations establishing quantities of hazardous substances that must be reported, if released to the environment. CERCLA is enforced by the EPA. Under these authorities, releases of CERCLA hazardous substances, in quantities equal to or greater than their reportable quantity (RQ), are subject to reporting to the National Response Center located in Washington, DC. Such releases are also subject to state and local reporting under Section 304 of Title III. CERCLA hazardous substances, and their reportable quantities, are listed in 40 CFR Part 302, Table 302.4. On January 23, 1989, all Section 302 chemicals not already listed under CERCLA were proposed for listing, and on August 30, 1989, adjusted RQs (not included in this document) were proposed for these chemicals. The CERCLA RQ column shows the RQs (in pounds) for chemicals that are CERCLA hazardous substances. An asterisk ("*") following the RQ indicates that no reporting of releases is required if the diameter of the pieces of the solid metal released is 100 micrometers (0.004 inches) or greater. The last column in Table 5 clearly shows that the total amount of chemicals per control area is below any reporting requirements should a release occur. However, NREL would still report an accidental release.

4.1.2.3. SARA

SARA - Title III (also known as the Emergency Planning and Community Right to Know Act) outlines significant planning requirements for facilities handling hazardous materials. Title III has four major sections: emergency planning (Sections 301-303), emergency notification (Section 304), community right-to-know reporting

requirements (Sections 311-312) and toxic release reporting - emissions inventory (Section 313). Under Section 312, the presence of extremely hazardous substances (EHSs) in quantities in excess of the Threshold Planning Quantity (TPQ), requires certain emergency planning activities to be conducted. The extremely hazardous substances and their TPQs are listed in 40 CFR Part 355, Appendices A and B. Table 5 summarizes the SARA Title III data and compares the chemical quantities likely to be used or produced as a by-product of the research activities underway in Building 16.

The chemicals in Table 5 are ordered by Chemical Abstract Service (CAS) registry number. Categories of chemicals, which do not have CAS registry numbers, but which are cited under these statutes, are placed at the end of the list. For chemicals that are solids, there may be two TPQs given (e.g., 500/10,000). In these cases, the lower quantity applies for solids in powder form with particle size less than 100 microns, or if the substance is in solution or in molten form. Otherwise, the 10,000 pound TPQ applies.

Releases of reportable quantities (RQ) of EHSs are subject to reporting under Section 304 of Title III. If a final RQ has not been assigned under CERCLA to a chemical listed under Section 302, a statutory RQ of one pound applies for Section 304 reporting. The EHS RQ column lists the one-pound statutory RQ for EHSs not listed under CERCLA. Emissions or releases of chemicals listed under Section 313 must be reported annually as part of SARA Title III's community right-to-know provisions. The rule containing these chemicals was published on February 16, 1988 (53 FR 4500) (40 CFR 372).

The notation "313" in the column for Section 313 indicates that the chemical is subject to reporting under Section 313 under the name listed. An "X" in this column indicates that the same chemical with the same CAS number appears on another list with different chemical names.

4.1.3. DOT

The United States DOT has set specific standards for the transportation of an extremely wide variety of materials, including the chemicals relevant to this SAR. In general terms, the requirements of the DOT include placarding of vehicles, documentation of shipments, and emergency response procedures.

Materials are identified by a four digit identification (ID) number. Each chemical has a unique ID number. This number must accompany each shipment and be posted on the outside of the vehicle by use of placards. These placards must be posted on either the end of the vehicle or on both sides. The ID number for a material in transport may be displayed either on the placards or on orange panels on tank trucks which must also have a placard stating the hazard classification.

A standardized form (shipping paper) must accompany all shipments of hazardous materials, which may be used or generated by these operations. The requirements of this form are that it allow for the entry of the shipping name of the hazardous material (e.g. Acetone), the quantity or number of containers of the material (5 gal), its classification (flammable liquid), its ID number (1090), and a reportable quantity notation or RQ-number (5,000 gallons) for use in reporting spill incidents to the National Response Center. The form must also have NREL's name on it, along with an emergency contact phone number. Whenever hazardous materials are shipped, this form must be fully completed and accompany the shipment in the cab of the motor vehicle.

**CONSOLIDATED CHEMICAL LIST
SUBJECT TO REPORTING REQUIREMENTS
2/13/91**

Section 304

CAS Number	Chemical Name	Sec. 302 (ENS) TPQ (lb)	EHS RQ (lb)	CERCLA RQ (lb)	Sec 313	RCRA Code	SERI Max. Per Control Area (lb)
64-19-7	Acetic acid			5,000			4
67-56-1	Methanol			5,000	313	U154	1
67-63-0	Isopropyl alcohol				313		1
67-64-1	Acetone			5,000	313	U002	1
74-85-1	Ethylene				313		
78-93-3	Methyl ethyl ketone			5,000	313	U159	
78-93-3	Methyl ethyl ketone (MEK)			5,000	X	U159	1/2
127-18-4	Tetrachloroethylene			100	313	U210	
127-18-4	Perchloroethylene			100	X	U210	
1303-28-2	Arsenic pentoxide	100/10,000		1		P011	1/2
1303-32-8	Arsenic disulfide			1			
1303-33-9	Arsenic trisulfide			1			
1310-73-2	Sodium hydroxide			1,000			15
1314-56-3	Phosphorus pentoxide	10	1				1/4
1327-53-3	Arsenic trioxide	100/10,000		1		P012	
7440-23-3	Sodium			10			
7440-38-2	Arsenic			1*	313		
7446-08-4	Selenium dioxide			10			
7448-56-4	Selenium sulfide			10			
7647-01-0	Hydrogen chloride	500		5,000	X		5 lb
7664-93-9	Sulfuric acid	1,000		1,000	313		1
7697-37-2	Nitric acid	1,000		1,000	313		1
7782-49-2	Selenium			100*	313		
7783-06-4	Hydrogen sulfide	500		100		U135	
7783-07-5	Hydrogen selenide	10	1				1/2
7784-42-1	Arsine	100	1				
	Arsenic Compounds			***	313		
	Beryllium Compounds			***	313		
	Cadmium Compounds			***	313		
	Copper Compounds			***	313		
	Selenium Compounds			***	313		

* No reporting of releases is required if the diameter of the pieces of the solid metal released is equal to or exceeds 100 micrometers (0.0004 inches).

*** Indicates that no RQ is assigned to this generic or broad class, although the class is a CERCLA hazardous substance. See 50 Federal Register 13456 (April 4, 1985).

Table 5

The DOT has also established general guidelines for emergency response to hazardous materials. This guidance was developed for use by first responders; such as fire-fighters, police, emergency services personnel and in certain respects for use in the transportation industry. It is a guide for initial action to be taken to protect those who are responding and the general public from a leak, upset or spill. It is used as general guidance, primarily during the initial phases of an incident. Currently there are only 76 guides for 2,000 materials.

4.2. State and Local Regulations

In Colorado, the Colorado Department of Health (CDH) protects public health and the environment by collecting health and environmental data, developing plans to address health problems, managing and enforcing regulatory programs, investigating complaints and responding to emergencies. It also enforces RCRA.

NREL's photovoltaic research laboratories are located in Building 16 in the Denver West Office Park. The Denver West Office Park is located in unincorporated Jefferson County. The Jefferson County Building Department has adopted the UBC, Uniform Mechanical Code (UMC), Uniform Plumbing Code (UPC), UFC, and the National Electric Code (NEC). Denver West and NREL follow these codes.

4.2.1. Uniform Fire Code

The Lakewood fire jurisdiction has recently been consolidated with that of Bancroft and it is now known as the Lakewood-Bancroft Fire Authority. It has the responsibility of regulatory overview of these facilities and the fire protection services. The district enforces the 1988 UFC; however, they do not consistently issue the required permits.

In an effort to ensure compliance with the UFC, NREL has implemented a variety of activities. These include improvements to the facility, rigorous engineering and administrative controls placed on HPM operations, and increased controls on the other operations in Building 16. Examples of such improvements include; upgrading of the existing sprinkler system, installation of sprinklers in the remainder of the building, installation of a new fully addressable smoke detection system, and installation of most -- if not all -- required controls to address mishap conditions anticipated under the requirements of today's codes. NREL staff (SSO, Facilities, and research personnel) will work with the Lakewood-Bancroft Fire Authority to ensure they understand the scope, location, and duration of the proposed HPM research activities. If they so desire, the NREL emergency drills in which the Lakewood-Bancroft Fire Authority participates each year, can involve laboratories using HPMs.

The UFC prescribes regulations governing conditions hazardous to life and property from fire and explosion, providing for the issuance of permits and establishing a bureau of fire prevention. Article 80 of the UFC provides specific requirements for the prevention, control and mitigation of dangerous conditions related to hazardous materials.

4.2.2. Uniform Building Code

The basic premise of the Uniform Building Code (UBC) is that there must be a general correlation between the level and type of "risk" associated with activities or substances to be housed in a building and the level and type of safety features which must be provided in the construction of the building. The UBC classifies the different types of activities and substances housed in the different areas of a building into various

categories, known as "occupancy" classifications, based upon similarities in the level and type of perceived "risk" associated with them. In simplistic terms, as the "risk" associated with the "occupancies" housed within a building increases, so does the number and stringency of code provisions with which the building must comply. The UBC is enforced by Jefferson County Building Department.

Building 16 was constructed as an "office" building which is covered by chapter 7 of the UBC - Group B occupancies. Division 2 covers office building, printing plants, etc. The occupancy is abbreviated to be called a B-2. Section 702(b)3. Laboratories and vocational shops states "laboratories...and similar areas containing hazardous materials shall be separated from each other and other portions of the building by not less than one-hour fire resistive occupancy separation. When the quantity of hazardous materials in such uses does not exceed those listed in Table No. 9-A or 9-B, the requirements of Section 905 (light, ventilation and sanitation) and 908 (special hazards) shall apply. When the quantities of hazardous materials in such uses exceeds those allowed by Table No. 9-A or 9-B, the use shall be classified as the appropriate Group H Occupancy." Except for one case, the quantities of toxic and/or hazardous materials used per control area in building 16 do not exceed those listed in Table No. 9-A or 9-B, so the occupancy remains a B-2 and the appropriate requirements are met.

The one exception to meeting the requirements of Tables 9-A and 9-B is the possible use of nearly twice the quantity of pyrophoric liquid allowed by the code. However, at this time there are not firm plans for any of the operations to exceed the UBC limit. NREL has proposed an internal limit of two pounds (UBC limit is one pound) on pyrophoric liquids if and when a researcher would substitute TBA for arsine (highly toxic gas). This substitution is desirable from a safety standpoint, because a liquid is easier to contain and control than a gas. NREL addresses this by using alternate materials and methods of construction (see Sections 3., 5.5.3., and 5.4.2.) and additional internal fire suppression as allowed by Section 105 of the code. Section 105 states "the provisions of this code are not intended to prevent the use of any materials or methods of construction not specifically prescribed by this code, provided any alternate has been approved and its use authorized by the building official." NREL will obtain this approval prior to restarting this type of operation.

4.2.3. National Fire Protection Association (NFPA)

NFPA 45 - Standard on Fire Protection for Laboratories Using Chemicals - applies to laboratory buildings, laboratory units, and laboratory work areas in which hazardous chemicals are handled or stored. The standard is very comprehensive in that it addresses how a laboratory is classified, designed and constructed, fire protection requirements, ventilation systems, chemical storage, handling and disposal, compressed and liquified gases, and laboratory operations. NFPA 45 addresses all hazards found in the NREL labs, including toxic gases and flammable liquids, but it does not address pyrophoric materials.

Laboratory unit classification is based on the amount of flammable and combustible liquids within the work area. The NREL laboratories are classified as Class C (low hazard) which is the lowest classification. A Class C laboratory is allowed 4 gallons of flammable and combustible liquid (2 gallons class I) per 100 square feet of laboratory unit excluding quantities in storage cabinets, or 8 gallons (4 gallons class I) per 100 square feet including storage cabinets.

4.3. NREL Standards and Requirements

NREL has a variety of internal policies and procedures which govern the continued safety of its operations. The policies and procedures which are most closely related to the systems are referenced below. These documents are in good agreement with industry standards and practices. Note that some of these documents were named while the Laboratory was named the Solar Energy Research Institute (SERI) and thus the titles retain this nomenclature.

4.3.1. SERI Environment Safety and Health Policies and Procedures

This document outlines the basic responsibilities for all staff members with regard to thirteen different aspects of ES&H. These thirteen areas include:

- Outlining the individual responsibilities of employees, subcontract personnel, managers, and the SSO manager with respect to ES&H.
- Outlining the organizational responsibilities of employees, subcontract personnel, managers, the SSO, and the Facilities Branch with respect to ES&H. This includes Technical Safety Panels and the NREL ES&H Committee.
- Describing the personal protective equipment which NREL makes available to its employees and subcontract personnel to reduce the potential for physical injury and/or illness. Such items include: safety shoes, safety glasses, hard hats, gloves, hearing protection, special goggles, respirators, and face shields.
- Requirements for the completion of certain ES&H reports to address hazards (Safety Analysis Reviews), unusual or unplanned events (Unusual Occurrence Reports), government property loss and/or work-related injury or illness (Individual Accident/Incident Reports).
- Requirements for ES&H training to enable employees and subcontract personnel to recognize the risks associated with their work, or the work environment, so that appropriate precautions can be taken to minimize injury or property loss.
- An outline of the emergency response capabilities and emergency response mechanism to preserve life and protect property and the environment.
- An outline of how NREL manages its operations in a manner that protects, maintains, and, if necessary, restores environmental quality; minimizes potential threats to the environment and the public health; and complies with environmental laws and regulations and DOE policies.
- An outline of how NREL establishes engineering controls and procedures to be used by the institute in the fire protection program. These emphasize both the prevention and immediate suppression of fires in an effort to reduce, to the maximum extent possible, the severity of loss resulting from fires.
- An outline of how NREL provides an industrial hygiene program designed to preserve the health of employees and subcontract personnel through the identification, evaluation, and control of potential health hazards in the work-place.
- Requirements for the organizational elements within NREL to comply with general safety requirements, whether their activities are covered by SOPs or not, to ensure the safest work conditions and environment possible.

- An outline of how NREL provides an occupational medicine program designed to promote and maintain the highest degree of physical, mental, and emotional well-being of employees and to prevent or reduce potential exposure of employees and subcontract personnel to health hazards in the work environment.
- An outline of how NREL provides a radiation safety program that outlines uniform requirements and assigns responsibilities for safely using radioactive materials and/or radiation producing machines for research purposes at the institute.
- Requirements for SOPs for activities that included, but may not be limited to, the use of certain hazardous materials, systems, or devices. These requirements provide a method for systematically evaluating the environmental, safety, and/or health hazards that may occur during the course of conducting experimental research or associated support activities at NREL.

4.3.2. SERI Standards for the Safe Handling, Use and Monitoring of Toxic Gases

This document [2] is a compilation of ideas that were discussed by the NREL Toxic Gas Safety Panel and those ideas which were passed on to the panel by other staff members. The document was adopted by NREL management as policy in October of 1989 and is considered a model document by many in the industry.

It is comprised of three main sections: Engineering/System Design Standards; Administrative Standards; and Personal Protective Equipment Standards. It is not an exhaustive document, but was considered as a minimum set of standards which users must meet.

4.3.3. SERI Emergency Response Procedures to the MDA Toxic Gas Monitor

This document [3] is intended as a complete guideline for the appropriate response to a toxic gas release. The introduction outlines the overall duties and responsibilities of all the different personnel who may respond to a toxic gas alarm. The remainder of the document is a step by step explanation of the response procedures for different release levels. These release levels include a catastrophic release, a high level release, a low level release, and a less than low level release. The definition of what characterizes each type of release is given at the beginning of each section. The last section includes some guidelines for other uses of the toxic gas monitor (e.g. changing gas cylinders).

If a problem arises with a particular piece of equipment, it is the responsibility of the researcher in charge of that equipment to ensure the safety of self and of fellow personnel. Therefore, this document has been prepared as an A-Z approach to assist the researcher from the time an alarm is sounded in the laboratory to the time everything is declared safe. Other personnel who may be involved in some of steps of these procedures need to be familiar with this document as well. This includes personnel from the SSO and Facilities Branch, Fire Marshalls, and building Landlords(chosen from the senior scientific administration). A copy of this document is provided in Appendix II.

4.3.4. SERI Laboratory Chemical Hygiene Plan (LCHP)

The purpose of the SERI LCHP [9] is to provide NREL management and Staff with the guidance and information needed to fulfill the requirements of the OSHA Laboratory Standard, 29 CFR 1910.1450, Occupational Exposures to Hazardous Chemicals in Laboratories. This procedure applies to all NREL employees, visiting

scientists, and contractors that use, generate, store, or dispose of small quantities of hazardous chemicals within the definition of "laboratory scale" and "laboratory use". A copy of this document is provided in Appendix I2.

Each laboratory is a "Designated Work Area" and is required to comply with the requirements outlined in Section 5.2 of the SERI LCHP - Special Procedures for Extremely Hazardous Substances.

4.3.5. NREL Emergency Preparedness Manual

NREL Emergency Preparedness Manual has been developed in accordance with DOE Order 5500.1A, Emergency Management System, to provide predetermined response actions to emergencies that arise from environmental causes (storm, earthquake, flood, etc.), internal activities (fire, explosion, accident, failure or malfunction of equipment, sabotage, etc.), or external activities such as national emergency, or civil disturbance. The purpose of the manual is to protect the health and well being of NREL employees and the public, prevent damage to physical property, and prevent damage to the environment during and after emergency situations.

The manual is comprised of two different sections. The first section is entitled NREL Emergency Response Guides. The second section is entitled NREL Emergency Preparedness Plan (EPP) and is comprised of the NREL plan itself.

The NREL Emergency Response Guides has been developed for individuals who have been assigned specific responsibilities in the event of an actual emergency. By utilizing clearly labeled indexing tabs, the document provides these individuals with an easy to reference sequence of response actions for various types of emergencies. The types of emergencies addressed by the Response Guide include; Fire/Explosion, Injury/Illness, Chemical/Radioactive Material Spill, Security Occurrence, Loss of Utilities, Natural Disaster, Transportation Emergency, and the Activation of the Emergency Operations Center. Basically, the Response Guide is utilized as follows:

- The NREL Emergency Extension (x 1234) is dialed to trigger a response action to an actual emergency.
- Based on the type of emergency reported, the Emergency Extension operator/guard will then tab to the corresponding section in the Response Guides and collect the information on the emergency information questionnaire which is included in each section.
- The operator/guard will then begin notifying the appropriate agencies or individuals as listed on the call list included in that section.
- The individuals assigned specific responsibilities in the event of an actual emergency can then tab to the section that corresponds to the type of emergency to which they are responding and perform the appropriate response actions.

The second portion of the manual, the NREL EPP, provides in depth information regarding NREL's emergency preparedness, emergency organization, floor plans, and training requirements. It includes individualized EPPs for NREL, the DOE Area Office, the Denver West Buildings occupied by NREL, the FTLB/BTRF area, the Biotechnology Annex area, the SERF, the TFG, Facilities Internal Agency, Medical Internal Agency, Public Affairs Internal Agency, Safety Internal Agency, and Security Internal Agency. It also includes a listing of acronyms and definitions; as well as, a section on reporting requirements.

5. OPERATIONAL SAFETY LIMITS/HAZARD CONTROLS

Operational Safety Limits are auditable boundaries of operation which are not to be exceeded during normal operation to insure safety. They define the conditions, safety boundaries, and administrative controls needed to ensure that the facility operates within the defined guidelines. This section outlines the measures in place when the laboratories restart their operations. Administrative and Engineering Controls as well as Personal Protective Equipment Standards are described in this section.

5.1. Operational Readiness Review

All laboratory operations subject to the requirements set forth in this SAR must undergo an Operational Readiness Review (ORR) before resumption of operations can be authorized. An ORR Panel has been assigned to perform the ORRs. This Panel has developed a Review Plan as a guidance document for its activities. The ORR Panel and their Review Plan are applicable only to the NREL laboratories specified in this SAR.

The objective of the ORR Panel is to ensure that all necessary requirements of this SAR have been met before laboratory operations are authorized to restart. These activities must be performed in a timely, organized and impartial manner. Panel members are appointed by the NREL Operational Safety Committee.

The following concepts have been established as necessary components of the Review Plan and will be followed by the Panel as closely as possible:

- A separate ORR will be performed for each laboratory/research activity. Authorization to restart operations will be recommended by the ORR Panel for each individual laboratory as it successfully completes the ORR process.
- It is the responsibility of the research staff involved with individual research operations to request an ORR for their activities. It is recommended that they request a preliminary review which will cover all aspects of the final ORR. However, the purpose of this review is to assist the research staff in identifying items that would not pass the final review. The final review should be conducted when the laboratory is nearly ready to resume operations. ORR requests should be made to the ORR Coordinators. Schematics of HPM distribution systems and safety interlock systems should be included with the review requests.
- The ORR process will address the physical and procedural requirements established in this SAR for both laboratory and specific support departments.
- Comprehensive ORR Checklists will be made available to the research and support staffs to facilitate self-assessment prior to the ORR.
- The ORR Panel will be divided into subgroups that are responsible for specific portions of the review process.
- The ORR Panel members will not perform reviews of laboratories/research activities in which they are routinely involved.
- Necessary and appropriate communications will be maintained with all NREL personnel as the ORR progresses. Special emphasis will be placed on communication with Building 16 occupants. This includes pre-review and post-review meetings.
- Conditions may be encountered during the ORR process that were not anticipated when this SAR was written. The ORR Panel will develop interpretations and/or clarifications to this SAR when necessary. This guidance will be submitted to appropriate personnel to ensure it meets the SAR's original intent. Appropriate personnel could include the authors of this SAR, the Toxic Gas Safety Panel, the Safety and Security Office, or other management as deemed necessary.
- If the requirements set forth in this SAR have been met, the ORR Panel will submit a recommendation to authorize resumption of operations to the appropriate Division

Director. After assessing the recommendation the Division Director can authorize restart of work or can return the recommendation to the ORR Panel for revision or further review.

- If after the Final Review there are open items that present an unacceptable risk, the ORR Panel will submit a report of open items to the research staff and require another review.
- If there are open items that do not present unacceptable risks, the ORR panel will submit a Conditional Recommendation to authorize resumption of operations, which may include operational restrictions. If the Division Director concurs with a conditional restart of operations, the conditional recommendation and restrictions will be submitted to the Laboratory Director for approval. The Division Director will establish time lines for resolution of open items and operations will be suspended if time lines are not met.

When ORRs have been completed for all activities subject to the requirements set forth in this SAR, the ORR Panel will conclude their operations and disband. Original documents authorizing resumption of laboratory activities will be retained by the appropriate Divisions and a copy of the ORR will be available in each laboratory. Copies of all ORR documents will be retained by the Safety and Health Section.

5.2. Approval of SAR

Following extensive internal review by the NREL ES&H Committee, NREL Toxic Gas Safety Panel, and Line Management, the SAR will be submitted to the Director for internal approval. The final version must be formally submitted to DOE for approval with authorization to commence research activities.

5.3. Definitions

5.3.1. Engineering Design Related Features

Design Features are those components, systems or other engineered features (e.g. redundant controls and automatic fail-safe devices) which are intended to maintain the facility within the boundaries established by this SAR. Design features usually have a margin of safety built in.

A Safety Limit (SL) is a parameter placed on observable and measurable variables that is directly related to performance and integrity of the operation. If the value of the variable were to reach this limit, no impact to the health and safety of personnel would occur and no permanent damage to equipment would occur. However, operation above a safety limit would not be permitted since the margin of safety would be reduced to an unacceptable level.

Typically there would also be a set point below the safety limit where normal operations would take place. This set point provides sufficient margin for alarms and for corrective action by automatic protective action controls, before the safety limit is reached. An example of such a set point is a vacuum switch used on the PECVD deposition chambers. The typical set point for this switch is 5 torr, where the normal operating pressure is less than one torr; and of course atmosphere is 760 torr. This obviously provides a more than adequate margin of safety.

5.3.2. Administrative Controls

Administrative Controls are used in addition to design features and safety limits to augment the control of the hazard. These typically take the form of additional

requirements imposed upon the facility to ensure that the operation is maintained within the conditions of the SAR. These include, but are not limited to:

1. Minimum staffing requirements.
2. Minimum training requirements.
3. Verification program for status and configurations of critical components and systems.

Recognizing that no activity is without some degree of risk, and that routine risks are accepted without question by the vast majority of persons (e.g., machine shops which do not handle hazardous materials, cars for personal transportation), the applicability of this SAR is limited to operations that involve hazards that are not routinely encountered in the course of everyday living by the majority of the general public.

5.3.3. Hazardous Substances

The definitions of toxic and highly toxic specified by OSHA are mandated for use by all suppliers and manufacturers in the "Right to Know" legislation which was codified into 29 CFR 1910.1200 in the early- to mid-1980's. For gases, the definitions of interest are as follows:

A chemical or substance is classified as toxic if it has a median lethal concentration (LC50) in air more than 200 parts per million but not more than 2,000 parts per million by volume of gas or vapor, or more than two milligrams per liter but not more than 20 milligrams per liter of mist, fume or dust, when administered by continuous inhalation for one hour (or less if death occurs within one hour) to albino rats weighing between 200 and 300 grams each.

A chemical or substance is classified as highly toxic if it has a median lethal concentration (LC50) in air of 200 parts per million by volume or less of gas or vapor, or 2 milligrams per liter or less of mist, fume or dust, when administered by continuous inhalation for one hour (or less if death occurs within one hour) to albino rats weighing between 200 and 300 grams each.

Another classic approach to indicate the relative risk of a chemical or substance in air is a reference text published by the National Institute of Occupational Safety and Health. It is summarized in Table 6. (National Institute of Occupational Safety and Health, The Industrial Environment - Its Evaluation and Control, Washington, D.C.: U.S. Governmental Printing Office, pg 63)

A Hazardous Production Material (HPM) is defined as a solid, liquid, or gas that has a degree of hazard ranking in health, flammability, or reactivity of 3 or 4 as ranked by UFC Standard 79-3 and which is used directly in research, laboratory or production processes which have as their end product materials which are not hazardous (UFC Section 51.102).

RELATIVE RISKS OF CHEMICALS/SUBSTANCES IN AIR

Descriptive Term	LC ₅₀ (ppm rat) [†]
extremely toxic	<20
highly toxic	20 - 200
moderately toxic	200 - 2,000
slightly toxic	2,000 - 20,000
practically non-toxic	20,000 - 200,000
relatively harmless	>200,000

[†] = using a modified Haber Factor for time, non-hazardous as per CGA DRAFT - inhalation rat 1 hour

Table 6

5.4. Engineering/System Design Controls

Each of these systems is designed, built and operated in compliance with the standards and codes set forth in Section 4 of this SAR. A summary of the more relevant rules and regulations is set forth in this section.

All the systems addressed in this SAR comply with these requirements. This means that all relevant controls, safety systems, interlocks, etc. must be in place and operational before operation of these systems is allowed. The ORR will be performed to ensure this is the case initially. Subsequent safety inspections will ensure compliance in the future.

It is one of the primary purposes of the following requirements to guard against having a single point failure which would place anyone into a situation which is immediately dangerous to life or health. Therefore, the action required when one of the controls, safety systems, interlocks, etc fails is to safely affect repairs as soon as possible; before the next run is performed. It is unlikely that any single point failure would require emergency response procedures to be implemented. However, the Emergency Response Procedures to the MDA Toxic Gas Alarm (Appendix I1) should be followed should such an event occur.

5.4.1. HPM Gas Distribution Systems

This section deals with engineering/system design controls required of HPMs found in the gaseous state. Specifically, the design requirements of gas distribution systems for toxic (and highly toxic) gases, flammable gases, dopant gases, and corrosive gases.

Gas distribution systems are designed so that they are modular, serviceable, and above all else, safe. If a system is modular, each module or section can be tested more quickly than an entire system. If a system is not easily serviceable, then it will require major dismantling for service. This can lead to unsafe practices or accidents.

The minimum standards applied at NREL for a HPM gas delivery system are summarized in Tables 7a and 7b. Any approved HPM gas distribution system design meets these minimum standards, while the use of new or additional safety items is encouraged. The first column of the table briefly describes specific gas handling requirements. The last four columns of the table reflect whether a particular HPM gas is subject to the corresponding requirements. Each of the specific gas handling requirements is more fully described in the text following the table. (Note that in this

section only, the phrase "toxic gas" refers to both toxic and highly toxic gases. This is because the requirements for gas distribution systems for both toxic and highly toxic gases are the same. Requirements are not; however, the same for other controls. For example, there is a clear distinction in the exempt amounts per control area; the exempt amount is 20 ft³ for each. Therefore, they are tabulated separately.)

Standardized purge panels are not required from one system to the next. All the requirements for the safe distribution of these materials are here in this section. We do not have a single individual, or single team of individuals, whose job it is to go from system to system to change cylinders (requiring standardization). Each research group associated with an individual system is trained and experienced with that system, has developed detailed procedures for changing cylinders, and is adequately supported by fellow staff members so that any purge panel which fulfills these requirements is deemed adequate.

MINIMUM STANDARDS FOR HPM GAS DELIVERY SYSTEMS

SAR Requirement	Toxic Gases	Flam-mable	Dop-ants	Cor-rosive
1. No sharing of this type of HPM gas lines is permitted.	Yes	Yes	Yes	Yes
2. Components are compatible with the gases being used.	Yes	Yes	Yes	Yes
3. High pressure components can take 2x (120%) the maximum cylinder press.	Yes	(Yes)	(Yes)	Yes
4. Low pressure components can take full cyl. press. or press. relief is provided.	Yes	Yes	Yes	Yes
5. Flow limiting orifices are provided if needed to meet 1/2 IDLH reqs	Yes	No	Yes	Yes
6. An excess flow, automatic shut off device is installed.	Yes	Yes	Yes	Yes
7. A normally closed, pneumatic valve is installed on high press. side.	Yes	Yes	Yes	Yes
8. Purging assemblies have proper vents, connected to effluent removal system.	Yes	No	No	No
9. A check valve is installed on the purge gas side of purging assemblies.	Yes	†	Yes	†
10. Purging assembly valves are of the packless stem and 1/4 turn type.	Yes	†	Yes	†
11. Common purge gas manifolds between non-compatible HPMs is prohibited.	Yes	Yes	Yes	Yes
12. Purge gas cylinders are contained in a gas cylinder cabinet.	Yes	No	No	Yes
13. The regulator is of the tied diaphragm design.	Yes	Yes	Yes	Yes
14. Regulator bonnets, if present, are connected to scrubbers or safe vents.	Yes	No	No	No
15. Low pressure isolation valves are of the packless stem variety.	Yes	Yes	Yes	Yes

† = Yes, if purging assemblies are installed (installation is optional).

Table 7a

MINIMUM STANDARDS FOR HPM GAS DELIVERY SYSTEMS (continued)

SAR Requirement	Toxic Gases	Flam-mable	Dop-ants	Cor-rosive
16. The flow control device is able to take full cyl. press. or press. relief provided	Yes	Yes	Yes	Yes
17. The gas delivery valves are of the packless stem variety.	Yes	Yes	Yes	Yes
18. There is at least one manual valve in each line, in the cyl. cabinet.	Yes	Yes	Yes	Yes
19. There is at least one manual valve for all lines, on the reactor side (>15'-source)	Yes	Yes	Yes	Yes
20. The tubing is seamless, type 316L stainless steel.	Yes	Yes	Yes	Yes
21. All tubing is in a ventilated chase or race way.	Yes	No	No	No
22. Compression fittings are forbidden in this type of HPM gas line.	Yes	No	Yes	Yes
23. All new welds are performed following NREL procedures.	Yes	Yes	Yes	Yes
24. All welds & connections are both inboard and outboard leak tested.	Yes	Yes	Yes	Yes
25. At least one NC pneumatic valve is for all lines, on the reactor side.	Yes	Yes	Yes	Yes
26. There is a standardized panic button to stop all flow of this gas.	Yes	Yes	Yes	Yes
27. Filters can not contain adhesives, resins, or binders.	Yes	No	Yes	No
28. Gas cyl. through low press. isolation valves are located in gas cyl. cabinets.	Yes	Yes	Yes	Yes
29. The entire gas line is completely purged after each use.	No	No	No	Yes

Table 7b

Each of the following gas handling requirements applies to all four types of HPM gases defined above. Exceptions are noted within specific requirements.

- 5.4.1.1. Separate workstations/systems may not share HPM gas lines.
- 5.4.1.2. Components are compatible with gases being used.
- 5.4.1.3. For corrosive and toxic gases, components upstream from the regulator (high pressure side) are able to withstand two times the maximum cylinder pressure or ten times the normal operating pressure, whichever is greater. For flammable and dopant gases, components upstream from the regulator (high pressure side) are able to withstand 120% of the maximum cylinder pressure.
- 5.4.1.4. Components downstream from the regulator (low pressure side) are able to withstand the maximum cylinder pressure or be provided with physical pressure relief and/or secondary pressure reduction. The physical pressure relief is attached to an appropriate effluent removal system.
- 5.4.1.5. Except for flammable gases, properly sized flow limiting orifices must be provided by the gas supplier in the gas cylinder or cylinder valve if required to

meet 1/2 IDLH requirements at point of discharge from the building in worst case release scenarios (UFC Article 80 Section 304.6.D.iv.). Otherwise, flow limiting orifices can be located either in the CGA connection or a flow limiting device directly connected to the CGA connection.

- 5.4.1.6. An excess flow, automatic shut off device is installed as close to the cylinder as possible (at CGA). For pure hydrogen manifolds, this device must of a type which cannot be locked in the open or bypass mode. (Panels which are purged must have the excess flow valve locked open for thorough purging.)
- 5.4.1.7. A normally closed pneumatic valve is installed as close to the cylinder as possible. This valve is interlocked to all of the appropriate safety features for the system (e.g. panic button, MDA alarm, effluent removal system, ventilation monitor, and other system features).
- 5.4.1.8. For toxic gases, a purging assembly is installed with a proper vent (vacuum pump, venturi eductor, etc.) connected to appropriate effluent removal systems.
- 5.4.1.9. Purging assemblies are installed with a check valve on purge gas side.
- 5.4.1.10. Valves on the purging assembly are of the packless stem variety and be of the quarter turn design or otherwise provide some type of clear visual indication of their status.
- 5.4.1.11. The use of a common purge gas manifolding between non-compatible HPMs is prohibited. The only purge gas manifolding which is allowed is for HPM with identical classification under the codes (e.g. hydrogen and methane, hydrogen and lightly doped hydrogen, etc.)
- 5.4.1.12. When purge gas cylinders are connected to high pressure components (upstream of the regulator), they are considered to be a part of the HPM gas distribution system (in the event of operator and/or component failure) and therefore are contained in a gas cylinder cabinet. This is not true for flammable gases where the requirement for purge gases is that they be located in close proximity to a flammable gas monitoring point.
- 5.4.1.13. Regulators are of the tied diaphragm design.
- 5.4.1.14. For toxic gases only, if the regulator has bonnet vents, they are connected to appropriate scrubbers or dilution venting.
- 5.4.1.15. The low pressure isolation valve is of the packless stem variety.
- 5.4.1.16. The flow control device is able to withstand full cylinder pressure or pressure relief and/or secondary pressure reduction is provided. Physical pressure relief is exhausted through an appropriate effluent removal system.
- 5.4.1.17. The gas delivery valves are of the packless stem variety.
- 5.4.1.18. There exists at least one manual valve in each gas line, within the cylinder cabinet, in order to manually verify that gas flow from the cylinder out of the cabinet can be terminated.
- 5.4.1.19. If reactors are located more than 15 feet from a HPM source (length of line outside of gas cabinet), then in order to ensure positive gas shut off and to have a

manual override of electro/pneumatic controls, all gaseous HPM sources are plumbed through at least one manual valve, as close to the reactor as practical.

- 5.4.1.20. The tubing is seamless, type 316L stainless steel.
- 5.4.1.21. For toxic gases, all tubing outside of gas cabinets and ventilated system enclosures is enclosed in a ventilated chase or race way (or the use of coaxial tubing can be employed) providing secondary containment, with this ventilated volume being monitored for the appropriate HPM.
- 5.4.1.22. No compression fittings can exist in a HPM (except flammables) gas distribution system; VCR or weld fittings only. Pipe threads are allowed from a safety aspect, but may not be desirable based on a purity point of view.
- 5.4.1.23. All new welds are made following the NREL procedures listed below:
 - 5.4.1.23.1. Only persons trained and listed as qualified users on the automatic tube welder Safe Operating Procedure may operate the weld machine.
 - 5.4.1.23.2. Master sample welds of acceptable quality are kept with the weld machine to serve as reference samples.
 - 5.4.1.23.3. A log book is kept with the weld machine which specifies the user name, date and duration of use, any adjustments or tip changes made, and measurements of weld gap, sample weld undercut, face reinforcement, weld root concavity, and root reinforcement.
 - 5.4.1.23.4. Sample welds are required at the start of any project, repeated at the beginning of each work week for an ongoing project, and after any adjustment of the weld gap or weld head components. Sample test pieces may either be butt welds of stainless steel tubing or ATW-tubing welds.
 - 5.4.1.23.5. The above mentioned sample welds are destructively tested by sawing the tube lengthwise in half through the weld and filing or grinding as necessary to remove sawing burrs and distortions. The weld is visually checked for depth and penetration, joint contamination, joint soundness, surface oxidation and discoloration. Measurements taken from the sample are recorded in the log book. Each sample weld is inspected visually, with the unaided eye, following the guidelines outlined below (AWS D10.9-80 [10]).
 - 5.4.1.23.6. Each sample weld is inspected visually prior to assembly of the test pieces, to assure that the proper materials are being used, that the parts have been cleaned, and that the end preparation is correct.
 - 5.4.1.23.7. Each sample weld is inspected visually after fit-up, to check the joint clearances, as per manufacturers specifications.
 - 5.4.1.23.8. Each sample weld is inspected visually during welding for cracks, porosity, undercut, incomplete fusion, surface roughness, and poor crater conditions. Each weld bead is inspected as-deposited and after any normal mechanical operations such as brushing, filing, or grinding, prior to depositing subsequent passes. Grinding may be used when necessary on starts and stops and to remove local defects from bead-to-bead, but dressing of the complete sample weld is limited to the removal of weld reinforcement. If production welding is done from the outside of the pipe only, no repair of the root of the sample weld from the inside of the pipe is permitted.

- 5.4.1.23.9. Each sample weld is inspected visually after welding has been completed, to detect any surface defects. This includes ensuring that: the specified base metal and filler metal have been used, the weld is free of cracks, all craters are filled to the full cross section of the weld and are free of cracks upon completion of the welding, the face of the weld is at least flush with the outside surface of the pipe, and the weld merges smoothly with the base metal. The depth of weld undercut shall not exceed 1/32" (0.8 mm), irrespective of length. The weld reinforcement shall not exceed 3/32" (2.4 mm) along the face.
- 5.4.1.23.10. The root of the weld is examined to insure complete joint penetration and no cracks, nor incomplete fusion. A concave root surface is permitted within the following limits, provided the total weld thickness is equal to or greater than that of the base metal; the maximum root surface concavity is 1/32" (0.8 mm) and the maximum root reinforcement is 1/16" (1.6 mm).
- 5.4.1.23.11. The AWS D10.9-80 [10] guideline for undercut (1/32" recess from outer face of tubing) is used to determine acceptability of welds not destructively tested.
- 5.4.1.23.12. 100% of all ATW welds are leak checked, as per Section 5.4.1.24.
- 5.4.1.24. The integrity of all welds and connections must be tested by inboard techniques before the line is used, after any modifications to the line, and at least every two years (corrosive lines annually) if the line has not been altered. Inboard testing also occurs after each cylinder/container change-out on the components of the HPM distribution system from the connection to the HPM container (CGA) through first component securely anchored to the gas cabinet or other rigid structure. Outboard leak checking of all welds and connections using one of the two techniques listed below is also required before first use and after any modifications (not including cylinder changes). Components of the distribution line from the gas cylinder up to the secondary pressure regulator or over-pressure relief mechanism are subject to the more stringent requirements that outboard leak checking with components pressurized with helium is required before the first use and after any modifications (not including cylinder changes). A CGA cap or plug may be used instead of an actual gas cylinder for tests prior to first use, following modifications, or periodic checks.
- 5.4.1.24.1. An inboard leak test is performed by evacuating the line and introducing helium at all connections, valves, joints, welds, and fittings, while monitoring a mass spectrometer (mass spec.) to detect any helium which may enter the line. The leak rate must not exceed 5×10^{-8} sccm of helium. (More stringent leak rates may be required for purity considerations.) The line can be evacuated using the system vacuum pump(s), the pump(s) on a helium leak detector, or other pumping systems designed for this purpose. Devices such as residual gas analyzers and helium leak detectors all employ the use of mass spec. technology to detect helium. What ever type of mass spec. device is employed, must be capable of detecting a leak rate of 5×10^{-8} sccm of helium and be tested with a helium leak standard of known value to before testing the line in order to ensure that the equipment is functioning.
- 5.4.1.24.2. An outboard leak test - probe method is performed by pressuring a line to the maximum achievable pressure (100%). This would be the cylinder pressure of the gas being used in the line up to the regulator, the maximum delivery pressure of the primary regulator up to the secondary regulator or pressure relief device (or rating of pressure relief device if it is lower), and 120% of normal operating pressure for the remainder of the line Exception: Reaction

vessels are tested at their normal operating pressure or atmospheric pressure, whichever is greater. A gas specific detector probe must be used around all connections, valves, joints, welds, and fittings to detect any leaking gas. The preferred test gas is helium, used in conjunction with a helium leak detection probe; however, hydrogen used in conjunction with a portable hydrogen monitor is acceptable. The SSO shall be notified prior to tests using hydrogen gas above 100 psig. During or prior to initial testing, the pressure shall be gradually increased in steps until the test pressure is reached, holding the pressure at each step long enough to equalize piping strains.

- 5.4.1.24.3. An outboard leak test - pressure decay method is performed by pressuring a line to the maximum achievable pressure, as described in Section 5.4.1.24.2. and then isolating the line from the pressure source. The line is then held at pressure for a minimum (not less than one hour) amount of time to ensure that the leak rate does not exceed the maximum total leakage rate as determined by the following calculation [11]:

$$\text{Max. Leak Rate (sccm)} = 0.0283 \times \text{TLV (ppm)} \times \text{Exhaust Rate (cfm)}.$$

The minimum amount of time the line must remain pressurized can be calculated from the volume of the line and the minimum pressure drop which can be accurately observed.

- 5.4.1.24.4. It is the responsibility of the principal operator for each system to prepare and retain the records of all leak checks on HPM lines for at least 5 years after the test. These records must include the date of the test, identification of the line(s) tested, the method of the test, the data from the test, any required interpretation of the data, the testers name, and the testers signature.
- 5.4.1.25. There exists at least one normally closed pneumatic valve for all HPM gas lines, on the reactor side of the distribution system, which shuts down flow of gas into the reactor. This valve(s) is interlocked to all of the appropriate safety features for the system (e.g. panic button, MDA alarm, effluent removal system, ventilation monitor, and other system features).
- 5.4.1.26. There exists a standardized panic button (common design, color, type and labeling within NREL), at the system, which puts the system into fail-safe mode - shutting off all HPM gas flows both at the source and into the reactor.
- 5.4.1.27. Except for flammable and corrosive gases, filters must not contain adhesives, resins, or binders which are incompatible with the gases being used.
- 5.4.1.28. All gas cylinders containing HPM gases, flow limiting orifices, excess flow valves, normally closed pneumatic valves, purging assemblies, regulators, and low pressure isolation valves are located in approved gas cylinder cabinets, as per Section 5.4.6.6..
- 5.4.1.29. To prevent damage and early failure of gas handling components, the lines carrying hydrogen chloride must be purged after each use from the cylinder fitting on. The cylinder valve is only open momentarily to charge the pigtail before each use, then closed during etching operation and purged upon completion of etching.
- 5.4.1.30. Additional requirements on HPM gases.
- 5.4.1.30.1. No silane over 1% concentration is allowed inside of the building. This is below the LFL and pyrophoric limit for silane. The manufacturer ships this

mixture as a compressed gas, when diluted in an inert gas. The LC₅₀ is 9,600 ppm. This means that the LC₅₀ for a 1% mixture is 960,000 ppm. This makes the mixture relatively harmless according to the National Institute of Occupational Safety and Health (see Table 6).

- 5.4.1.30.2. The aggregate amount of toxic gas per control area for the laboratory conforms to necessary levels for exempt status per control area. Both toxic and highly toxic gases each are allowed 20 ft³ when contained within approved gas cabinets (see administrative controls - Section 5.5.3.).

Examples of toxic gases for proposed use in Building 16 are tungsten hexafluoride and silicon tetrafluoride. Examples of highly toxic gases for proposed use in Building 16 are arsine, phosphine (also pyrophoric), and hydrogen selenide.

- 5.4.1.30.3. The aggregate amount of flammable gas per control area for the laboratory conforms to necessary levels for exempt status per control area. For flammable gases this equals 1500 ft³ when contained within approved gas cabinets (see administrative controls - Section 5.5.3.).

Examples of flammable gases for proposed use in Building 16 include: hydrogen, hydrogen mixtures (lightly doped with other gases to form nontoxic mixtures), deuterium, methane, etc. A total of 200-500 ft³ of flammable gas, consisting of one to two cylinders of pure hydrogen of 220 ft³ (maximum) each and one or two hydrogen mixtures (>99% hydrogen) of 30 ft³ (maximum) each are used by each MOCVD system. Each of the other laboratories (a-Si, selenization, and electrochromics) has a maximum of 220 ft³ of hydrogen and <100 ft³ of methane. These quantities are significantly under the B-2 limit of 1500 ft³ per control area for flammable gases in gas cabinets, allowing other operations in the building to use flammable gases provided each control area complies with the exempt amount.

- 5.4.1.30.4. The aggregate amount of dopant gas per control area for the laboratory conforms to necessary levels for exempt status per control area. For dopant gases in a flammable gas balance, this equals 1500 ft³ when contained within approved gas cabinets (see administrative controls - Section 5.5.3.). The term dopant gas necessarily refers to gas mixtures which are of neither toxic nor highly toxic concentrations.

Examples of dopant gases for proposed use in Building 16 include very dilute mixtures (1000 ppm or less) of a dopant compound in hydrogen or an inert gas such as nitrogen or argon. Typical dopant compounds are hydrogen selenide, silane, disilane, diethylzinc, and diethyltellurium. Although these compounds are toxic in their pure form, the resulting mixtures are significantly less hazardous and are treated as nontoxic according to the code definitions and DOT shipping regulations. Therefore, there are no limits on the amount which can be kept in a B-2 building beyond flammable gas limits for those dopant mixtures which are flammable if diluted in a flammable balance. The presence of these dopant mixtures and appropriate precautions is included in the individual system's SOP.

- 5.4.1.30.5. The aggregate amount of corrosive gas per control area for the laboratory conforms to necessary levels for exempt status per control area. For corrosive gases this equals 1300 ft³ when contained within approved gas cabinets (see administrative controls - Section 5.5.3.).

Examples of corrosive gases for proposed use in Building 16 include; hydrogen chloride and tungsten hexafluoride (also toxic). Hydrogen chloride gas is used to clean reactor components between growth runs in the systems in laboratories 103 and 368. Each of these systems uses 5 lb. (53 ft³) of pure hydrogen chloride gas, which is well under the B-2 limit of 1300 ft³ of corrosive gas in gas cabinets per control area. The primary hazard associated with this gas is its corrosive nature, particularly when combined with water vapor. The TLV-TWA ceiling for hydrogen chloride is 5 ppm, and the IDLH is 100 ppm. Hydrogen chloride is delivered liquified at a pressure of 613 psi, is nonflammable and is classified by the uniform fire code as a nontoxic, corrosive gas. Tungsten hexafluoride is used in laboratory 190 in a PECVD process making electrochromic devices. This laboratory uses 5 ft³ in small quantities per run. Hydrogen selenide is used in laboratory 285 for selenization of CuInSe₂ films, with 2.4 ft³ of gas in the system.

5.4.2. Distribution Systems for Pyrophoric Liquids and Solids

The MOCVD systems in Building 16 require a small amount of pyrophoric liquids and solids to produce III-V semiconductors. Larger quantities of pyrophoric or toxic liquids may be used as alternative chemical sources replacing toxic gases. Since it is not known whether these chemicals produce material of sufficient quality for our research, these sources must be tested (in small quantities) before they can be finally accepted for regular use (see administrative controls - Section 5.5.3.2.).

The specific liquid compounds and approximate quantities per MOCVD system are: Tertiarybutylphosphine (TBP) 0.88 lb., Tertiarybutylarsine (TBA) 0.88 lb., Trimethylgallium (TMG) 0.22 lb., Trimethylaluminum (TMA) 0.22 lb, and Diethylzinc (DEZ) 0.06 lb. In addition, each system uses 0.22 lb of Trimethylindium (TMI), a pyrophoric solid. Although these materials are pyrophoric, they do not burn with an intense flame nor generate intense heat.

Stainless steel bubblers each containing less than the amount of material listed above may be used in each system. (See Appendix M2 for specifications of a typical bubbler.) These bubblers are on the low pressure side of the system and use a carrier gas to transport the chemical vapor to the system's reactor. The amounts allowable under the B-2 limits is one pound in a sprinkled building. Therefore, we propose to provide additional safety features to those required by the code within the reactors using pyrophoric liquids (especially as described in Section 5.4.2.4. below).

To mitigate the hazards associated with pyrophoric liquids, the following precautions are followed:

- 5.4.2.1. Each laboratory using pyrophoric materials in excess of the exempt amount must have an automatic dry-chemical fire suppression system installed in the reactor housing.
- 5.4.2.2. This fire suppression system has been designed by an expert in fire protection systems, to meet the appropriate fire codes, and has been approved by the local fire jurisdiction.
- 5.4.2.3. Liquid-tight containment tray/basin is provided under the system's main plumbing and bubblers.
- 5.4.2.4. All containers of pyrophoric liquids and solids must be housed in enclosures with fire resistant walls on all sides.

- 5.4.2.5. Flammable materials are minimized inside the system enclosures.
- 5.4.2.6. Where available, vertical bubblers with non-interchangeable (female in male out, different sized fittings, etc.) connections are employed to minimize installation errors. Color coding and other administrative procedures are used where such bubblers are not available (for TBP and TBA).
- 5.4.2.7. Before bubbler removal from the systems, carrier lines must be adequately purged or pumped down.
- 5.4.2.8. A container of absorbant clay or sand is kept readily available in the laboratory for containment of small organometallic spills and fire control.

5.4.3. Distribution Systems for Highly Toxic Liquids and Solids

One of the liquid organometallic source materials for proposed use in Building 16 is tertiarybutylarsine (TBA), which in addition to being pyrophoric is also highly toxic. One stainless steel bubbler containing ~ 0.88 lb of material may be used in each system. These bubblers are on the low pressure side of the system and use a carrier gas to transport the chemical vapor to the system's reactor. The amounts allowable under the B-2 limits are 1 lb per control area (see administrative controls - Section 5.5.3.).

Since this material is also listed under Section 5.4.2., all precautions from that section already apply. In addition, the following precautions are used to mitigate the hazards of toxic liquids:

- 5.4.3.1. Self Contained Breathing Apparatus (SCBA) is worn and a portable MDA monitor is employed during bubbler changes.
- 5.4.3.2. Disposable gloves are worn when handling used bubblers when they are outside the growth systems. If there is a probability of significant particulate formation, respiratory protection are also employed.
- 5.4.3.3. Sufficient ventilation flow with appropriate interlocks is incorporated into the growth systems.
- 5.4.3.4. The effluent from the system exhaust is treated to remove its toxic components.
- 5.4.3.5. Administrative procedures are set up to insure the safe return of unused bubblers. (Cyanamid, the manufacturer of tertiarybutylarsine, accepts return of bubblers whether they are used or unused.)
- 5.4.3.6. Minimum storage of these materials is maintained. Extra bubblers are kept only during the short time of bubbler replacement.
- 5.4.3.7. Capture traps are installed both downstream and upstream of the material bubbler. These traps protect against forcing toxic liquid into inappropriate parts of the system in case of accidental over-pressure of the bubbler or backwards installation of the bubbler. Alternatively, the liquid is purchased in a bubbler which does not contain a dip tube.

5.4.4. Reaction Vessels and/or Deposition Chambers

- 5.4.4.1. Physical pressure relief and/or secondary pressure reduction is provided in order to protect the reactor from over-pressure.

- 5.4.4.2. Automatic valve closure of inlet gases with a pressure transducer controlled interlock provides for protection of the reactor. (Requires all gaseous HPM sources to be plumbed through at least one normally closed pneumatic valve, as close to the reactor as practical.)
- 5.4.4.3. If reactors are located more than 15 feet from a HPM source (length of line outside of gas cabinet), then in order to ensure positive gas shut off and to have a manual override of electro/pneumatic controls, all gaseous HPM sources are plumbed through at least one manual valve, as close to the reactor as practical.
- 5.4.4.4. The reactor, and associated plumbing, are contained in a ventilated equipment enclosure as per Section 5.4.6.8..

5.4.5. Effluent Removal

In this section the word effluent is used to mean those materials which flow from the system reactor. These materials are generally considered waste products and are treated. The word effluent is not considered to be the flow of HPM in an episodic or catastrophic release from the system or source. Such an event is covered in Section 5.4.6.15. under exhaust systems.

- 5.4.5.1. An approved (by the SSO) type of effluent removal system (liquid scrubber, burn box - plus (see App. M3), or adsorption bed with controlled oxidation) is installed to remove HPM from normal operation effluent streams.
- 5.4.5.2. Toxic gases and hazardous reaction products of toxic gases must not be expelled into the environment under any normal operating processes.
- 5.4.5.3. Where the reactor pressure may be different from the inlet pressure of the effluent removal system, the latter inlet pressure is monitored and an interlock to automatically shut down the system, upon over-pressure, is installed.
- 5.4.5.4. Secondary gas flows (nitrogen, argon, oxygen mixtures, etc.) necessary for effluent removal are monitored and an interlock to automatically shut down the system, upon flow reduction and/or loss of flow, is installed.
- 5.4.5.5. Other required safety interlocks (scrubber solution flow and level, adsorption bed temperature, flame snuff out, etc.) are in place on the effluent removal system and interlocked to automatically shut down the system upon failure.
- 5.4.5.6. Effluent removal systems must receive preventative and routine maintenance as per a maintenance schedule laid out specifically for each system (see Section 5.5.6.2. - under Administrative Controls).
- 5.4.5.7. Waste materials generated by effluent removal systems (charcoal canisters or drums, HEPA filters, scrubber solution, etc.) are disposed of as hazardous waste through the SSO. Documentation of materials used on the effluent removal system are maintained in the laboratory and provided to the SSO upon delivery for disposal. Documentation must also be kept on the disposal of these materials (see Section 5.5.6.1. - under Administrative Controls).
- 5.4.5.8. "Burn Boxes" or Controlled Decomposition and Oxidation systems must not present a fire/explosion hazard should a large release of flammable gas occur (as they provide an ignition source). Therefore, they are located in a ventilated enclosure separate from the system enclosure and gas cabinets.

- 5.4.5.9. Effluent removal systems which use adsorption beds are purged with a non-explosive gas mixture in order to minimize the possibility of runaway exothermic reactions. If air is used to oxidize the effluents, the bed must be pre-purged with an inert gas in order to displace any hydrogen which may be present. Otherwise, the purge gas must have an oxygen concentration below that of air (21%). As per Section 5.4.7.1.9., the flow of the purge gas is interlocked with the temperature of the adsorption bed. If the temperature goes over a pre-set, safe value, the flow of gases into the bed is automatically terminated.
- 5.4.5.10. Systems which use vacuum pumps as a means of passing process gases from the reactor to the effluent removal system must provide a means of bypassing the primary pump, should it fail. This can best be done by providing a second pump on the system which can be easily used to pump process gases from the reactor, delivering them to the effluent removal system. Alternately, a tee and closed valve at both the pump inlet and in the plumbing of the effluent removal system must be provided in order to install an auxiliary pump on the system, without breaking into plumbing containing HPM.

5.4.6. Exhaust Systems

- 5.4.6.1. All exhaust systems utilize pull style ventilation, creating a negative pressure in the duct relative to the building ambient outside of the duct.
- 5.4.6.2. All exhaust systems discharge outside of the building with no recirculation.
- 5.4.6.3. All exhaust systems run continuously.
- 5.4.6.4. There exists adequate air movement across all portions of ventilated enclosures, duct work, and gas cabinets in order to minimize dead pockets. Horizontal surfaces are minimized (see Sections 5.5.7.6.1. & 5.5.7.6.2. on smoke testing).
- 5.4.6.5. The exhaust from all ventilated enclosures, ducts and gas cabinets is monitored to ensure the ventilation system is functional at all times. This monitor must ensure that a system is put into the fail-safe mode upon a failure of the corresponding ventilation.
- 5.4.6.6. All gas cylinders containing toxic, highly toxic, dopant, pyrophoric and corrosive gases; as well as, the corresponding plumbing for those gases (including flow limiting orifices, excess flow valves, normally closed pneumatic valves, purging assemblies, regulators, and low pressure isolation valves) are located in approved gas cylinder cabinets (see Section 5.4.6.7.).
- 5.4.6.7. All gas cylinder cabinets must meet the following criteria:
 - 5.4.6.7.1. Constructed of at least 11 gauge steel and be of one piece construction.
 - 5.4.6.7.2. It is externally exhausted, with intake air located within 12" of the floor.
 - 5.4.6.7.3. There is a self closing, limited access port or window.
 - 5.4.6.7.4. The minimum average velocity of ventilation at the face of an access port is at least 200 LFPM, with the port open.
 - 5.4.6.7.5. A minimum of 150 LFPM at any point in the access port is maintained, when the port is open.

- 5.4.6.7.6. The cabinet must have installed an internal, automatic fire sprinkler.
- 5.4.6.7.7. The cabinet is equipped with self closing doors.
- 5.4.6.7.8. All windows are wire reinforced or shatterproof.
- 5.4.6.7.9. There is a means of securely strapping or chaining the cylinders.
- 5.4.6.7.10. No more than three HPM gas cylinders can be contained in a single gas cabinet.
- 5.4.6.7.11. Only those materials/gases which are completely compatible are allowed within the same gas cylinder cabinet .
- 5.4.6.7.12. No ignition source or electrical wiring which is not Class 1, Division 1 rated is allowed inside of a gas cabinet.
- 5.4.6.7.13. The purge gas cylinder for a given toxic, highly toxic, pyrophoric, dopant, or corrosive gas cylinder is located within a gas cabinet.
- 5.4.6.7.14. If a purge gas cylinder is not located within the same gas cylinder cabinet as the source it is used to purge, the plumbing interconnecting the two cabinets is continuous (not containing any welds or connections).
- 5.4.6.7.15. Manifolding of purge lines is only allowed within individual gas cabinets.
- 5.4.6.7.16. It is preferred (not required) that gas cabinets have transition (tapered) tops.
- 5.4.6.7.17. Gas cabinets are to be used solely for the purpose of housing in-use HPM containers and their associated distribution systems. The use of gas cabinets as a catch all for unused materials, hazardous waste, HPM storage, etc. is forbidden.
- 5.4.6.7.18. The portion of the toxic and highly toxic gas distribution systems which require access while wearing SCBA must be designed for operation from a standing position. Installations which require operators to crouch or kneel to change cylinders or operate controls are not permitted.
- 5.4.6.8. All system reactors, secondary pressure reduction, physical pressure relief, flow control devices, delivery valves, etc. are housed in a ventilated enclosure.
- 5.4.6.9. Ventilation to all system enclosures must provide a minimum average face velocity of 100 LFPM, inward, with the largest access door/window open.
- 5.4.6.10. No part of a system containing toxic gases can be located outside of a ventilated enclosure, gas cabinet, or vented secondary containment (coaxial tubing or ventilated race way).
- 5.4.6.11. Toxic gas laboratories are at a negative pressure relative to hallways.
- 5.4.6.12. There is exhausted from the laboratory a minimum of one cubic foot per minute of air per square foot of laboratory floor area.
- 5.4.6.13. In the event of a building fire alarm, or other emergency, the laboratory ventilation must exhaust only. Therefore, the make-up or supply air flow must be easily stopped from a location outside of the laboratory. A manual control switch

for the ventilation is installed in an approved location outside of the laboratory as per UFC 51.105(d)3.

- 5.4.6.14. Each laboratory described in this SAR must have separate and independent exhaust ventilation system/fans from other laboratories and areas in the building.
- 5.4.6.15. The maximum allowable discharge concentration of toxic gases, at the point of discharge, must not exceed one-half the IDLH for a specific material. The following options are available for the researcher to meet this requirement.
 - 5.4.6.15.1. Ventilation dilution of a total accidental release of a toxic gas cylinder is allowed provided there exists a sufficient exhaust flow to adequately dilute the entire source at the specified release rate. For a toxic gas cylinder, the maximum flow rate of release shall be calculated based on assuming the total release from the cylinder is five minutes for a non-liquified source and thirty minutes for a liquified source (as per UFC Table 80.303-B). When cylinders are equipped with approved excess flow or reduced flow valve, the worst case release is determined by the maximum achievable flow from the valve as determined by the valve manufacturer or the gas supplier (UFC 80.303.D.iv). Reduced flow and excess flow valves shall be permanently marked by the manufacturer to indicate the maximum design flow rate. Such marking shall indicate the flow rate for air under standard conditions.
 - 5.4.6.15.2. If the exhaust ventilation flow is not adequate to sufficiently dilute the quantity of toxic gases used, an approved type of treatment system is employed. Treatment systems (exhaust ventilation scrubbers, "scram" units (see App. M&)) installed on the toxic gas lines, etc.) used to process all exhaust ventilation to be discharged from gas cabinets, exhausted enclosures or separate storage rooms, is sized to meet this 1/2 IDLH requirement. When more than one gas is emitted to the treatment system, the treatment system shall be designed to handle the worst case release based on the release rate, the quantity and the IDLH for each of the gases used. Examples of gas cabinet scrubbers can be found in Appendix M5 (dry chemical) and Appendix M6 (wet scrubber). An example of a scram unit can be found in Appendix M7. (It should be noted that scram units counteract catastrophic releases by diverting the toxic gas stream from the high pressure side of the gas cabinet manifold to a neutralizing bed capable of absorbing the entire cylinder contents. Scram units do not treat the exhaust air directly, and require that the cylinder valve be open in order to actually neutralize all the toxic gas. They have been accepted as providing equivalent protection for UFC requirements in some jurisdictions.)
 - 5.4.6.15.3. An alternative to the use of treatment systems is to use these gases with the cylinder valve closed at all times. This necessarily implies that the run is conducted with the gas in regulator and line only and this administrative control must be followed at all times. In order to implement this option, strict adherence to administrative and engineering controls is followed. Administrative controls on procurement are found in Section 5.5.3. The engineering controls are that all such cylinders must be supplied with pneumatically operated cylinder valves and that valve is controlled by a circuit which allows only momentary operation of the cylinder valve not to exceed a 10 second open period per valve operation. An example of such a pneumatic cylinder valve can be found in Appendix M4.
- 5.4.6.16. If unclassified electrical components are present in the reactor enclosures, ventilation is sufficient to keep flammable gas concentration below one-tenth the

lower flammability limit (LFL) in a worst case leak, determined by either an excess flow valve in the gas cabinet - if it cannot be bypassed - or the flow through a reduced flow orifice. The LFL for hydrogen is 4% by volume (or mole fraction).

5.4.7. Safety Interlocks

The engineering controls described in this section minimize the chance of a harmful accident by sensing abnormal conditions in the primary system(s) and triggering a fail-safe mode. This mode can be activated by a safety interlock, a deliberate shutoff of the system, or a power failure and requires a manual reset by the operator in order to resume operations. Sensors that monitor anomalous conditions within a hazardous production system are required as a redundant control to prevent the release or potential for release of hazardous materials into the environment.

5.4.7.1. All interlocks which are critical to the safety of the system initiate automatic shut down of the system - putting it into the fail-safe mode - and activate both an audible and a visual alarm. Some common interlocks follow:

- 5.4.7.1.1. High level MDA alarm (for toxic gases).
- 5.4.7.1.2. Hydrogen alarm in room ambient (where hydrogen is used in excess of 400 ft³ or in conjunction with pyrophoric materials).
- 5.4.7.1.3. Reactor over-pressure.
- 5.4.7.1.4. Loss of exhaust ventilation flow.
- 5.4.7.1.5. Loss of pneumatic pressure.
- 5.4.7.1.6. Loss of critical nontoxic gas flows.
- 5.4.7.1.7. Manual red panic button activation.
- 5.4.7.1.8. Over-pressure at effluent removal system inlet.
- 5.4.7.1.9. Other anomalous scrubber conditions; such as, loss of scrubber solution recirculation, adsorption bed over-temperature, flame snuff out, etc.
- 5.4.7.1.10. Panic buttons are installed which put the system into a fail-safe mode, one of which shall be located outside the laboratory. These panic buttons are of standardized design, shape and design.
- 5.4.7.1.11. Loss of power.
- 5.4.7.1.12. The MDA goes off line or becomes inoperable, leaving the lab without monitoring. (The green light also goes out in this case.)

5.4.7.2. The fail-safe mode of these systems is characterized by the following:

- 5.4.7.2.1. All power to operate HPM valves is through a drop out relay wiring arrangement so that once the fail-safe mode is initiated it must be manually reset by the operator in order to resume operations. This is so that the system doesn't auto restart in an undetermined mode upon correction of the situation which put the system into fail-safe.

- 5.4.7.2.2. In the event of power loss to the gas distribution systems, the solenoids that control gas valves are deactivated and the valves revert to their normal condition.
- 5.4.7.2.3. All valves that regulate the flow of toxic, highly toxic, flammable, corrosive and pyrophoric materials are normally closed so that the flow of hazardous materials is stopped in a non-energized mode. These valves include, as a minimum, the normally closed pneumatic valves at the source and near the reactor.
- 5.4.7.2.4. All valves that regulate the critical flow of safety gases, which must keep flowing in the fail-safe mode, (such as to keep effluent system functioning, purging of parts of the system, etc.) are normally open so that the flow of these materials continues in a non-energized mode.
- 5.4.7.3. All audio alarms on safety interlocks are audible from all locations within the laboratory.
- 5.4.7.4. All visual alarms for safety interlocks are clearly labeled to identify the anomalous situation which activated the alarm and shutdown.

5.4.8. General Laboratory

- 5.4.8.1. Doors to laboratories conform with UBC Section 3305(h)1.
- 5.4.8.2. The following items are on the standby generator:
 - 5.4.8.2.1. Exhaust ventilation.
 - 5.4.8.2.2. Critical emergency alarms.
 - 5.4.8.2.3. Critical safety control systems.
 - 5.4.8.2.4. Effluent removal systems.
 - 5.4.8.2.5. Critical vacuum or process pumps.
- 5.4.8.3. Appropriate fire extinguishers are readily available within the laboratories.
- 5.4.8.4. Each toxic gas laboratory, as well as the entire building, contain smoke detection systems which activate the building fire alarm.
- 5.4.8.5. Each laboratory using pyrophoric materials must have automatic fire sprinklers installed. The water supply is obtained from either the sprinkler system riser or, where hydraulically adequate, from the domestic water supply. Regardless of the supply, a check valve must be installed in the supply line, immediately after the supply tee is attached.

5.4.9. Storage Facilities

Storage of toxic, highly toxic, pyrophoric, or corrosive gaseous, solid or liquid source materials is prohibited in Building 16. There are no permanent facilities within NREL for indoor storage of these materials. The only place these materials are stored is the bunker, which is located over four hundred feet to the north/east of the Field Test Laboratory Building (FTLB). This bunker is of Type I-FR construction. It was originally constructed by Camp George West, a military facility, for ammunition

storage. The bunker is divided up into four separate rooms or areas each of which has its own exhaust fan. It occupies an approximate total area of 500 ft². The bunker, and the area surrounding it, is non-occupied space and is accessed only when a HPM container is either brought to or removed from this location.

The main purpose of this facility is to provide interim storage for HPM containers as they are being switched out. Ideally, an HPM distribution system would be purged out and the used container removed from the system just in time for the new container to be installed on the system. The vendor could then return with the used container on the same trip as when the new container is delivered. In practice; however, this ideal change-out procedure is rarely realized. That is where this storage facility is to be utilized. If the new HPM container arrives before the used container is removed from the distribution system, the new container could be stored in the bunker until the researcher is ready to receive it (typically a day or two). Similarly, if the old HPM container is removed from the distribution system before the vendor arrives with the new container (or pick up the old container for return), the old container could be stored in the bunker until the vendor arrives for pick-up. In this case the new container would be delivered directly to the laboratory and it would not need to be stored in the bunker.

It should be noted that this storage facility/bunker does not meet the letter of the UFC requirements for hazardous materials storage facilities. However, its use as a "short term" storage facility is warranted for a variety of reasons. The UFC requirements on storage facilities are intended for such facilities that are storing large quantities of hazardous materials (i.e. in excess of Tables 9-A and 9-B of the UBC/UFC). Section 5.4.9.19.4. clearly insures that the aggregate amount of materials in this facility remain below those of Tables 9-A and 9-B. The remote location of this facility, along with its unoccupied function, do not warrant that many of these requirements be met by the letter. Such occurrences are clearly described in notes (*italicized*) to the appropriate requirement which follow.

- 5.4.9.1. To understand the regulation of this storage facility, some definitions must be provided. The definitions of "in use", "in storage", and "in a state of exchange" are provided below.
 - 5.4.9.1.1. A HPM container is considered to be in service if it is properly installed on a HPM handling system, within a laboratory, and has a projected use within the next 90 days. All other cylinders are considered to be in condition of storage or exchange.
 - 5.4.9.1.2. Both a new HPM container, until it is installed on the system, and an old HPM container, after it has been removed from the system and until it is picked up for return to the vendor/manufacturer, are considered to be in a state of exchange.
 - 5.4.9.1.3. The condition of storage of a HPM container is defined internally as the keeping of any such container where it is not in service or in a state of exchange.
- 5.4.9.2. The only place HPMs can be stored is the bunker (outdoor storage facility) to the north/east of the FTLB. This facility is for "short term" storage only (Sections 5.4.9.3. and 5.4.9.4.). Storage of HPMs in Building 16 is prohibited.
- 5.4.9.3. This outdoor storage facility is used just for "short-term" storage of HPM containers being returned or received to/from the supplier. The use of this facility for long term (> 90 days) storage is prohibited.

- 5.4.9.4. Any HPM container left in this storage facility for 90 days will automatically be returned to the supplier. The requestor/user will be notified of the action, but their permission is not required for return. (See Section 5.4.9.19. for documentation procedures related to keeping track of the duration of storage.)
- 5.4.9.5. This storage facility/bunker can be used for such storage only after a fully approved Safe Operating Procedure (SOP) has been developed for its use.
- 5.4.9.6. This outdoor storage facility is in an area which is secured against unauthorized entry. This security is characterized by the following:
 - 5.4.9.6.1. It is located in a remote location of the permanent site, away from the publicly accessible Denver West Office Park. This site has one entrance from a public road and is posted as government land, forbidding unauthorized access.
 - 5.4.9.6.2. A chain link fence surrounds this facility and the gate is locked with a chain and padlock.
 - 5.4.9.6.3. Each of the four doors, to the separate storage areas, is secured with a padlock.
- 5.4.9.7. This outdoor storage facility is used as a storage facility for only HPMs. Other types of storage and general use is prohibited.
- 5.4.9.8. Segregation of HPMs by different class hazard classifications is provided in the storage area by the use of the separate storage rooms within the facility. The first room is to be used for Oxidizers and Corrosives, the second room is used for Poisons, the third room is used for Non-Flammables, and the fourth room is used for Pyrophorics and Flammables. Each of the four rooms is clearly marked as to identify the hazard class of the materials stored within and is appropriately placarded as per UFCS 70-3 (NFPA 704).

NOTE: The UFC, Section 80.301.(n), states that storage in excess of the exempt amounts specified in Sections 80.302 through 80.315 {quantities which exceed those in Tables 9-A and 9-B} shall either be: 1) segregated from incompatible hazardous materials by $\geq 20'$, or 2) be isolated by a noncombustible partition extending not less than 18" above and to the sides of the stored material, or 3) stored in separate hazardous material storage cabinets or gas cabinets. Because the storage plan (Section 5.4.9.19.) requires the aggregate quantity in this storage facility be below the Table 9-A and 9-B exempt quantities, this amount of segregation is deemed adequate. In other words, it is not required that tungsten hexafluoride (both a toxic and a corrosive) be separated from hydrogen chloride (a corrosive) by means of additional gas cabinets within the corrosive room.

- 5.4.9.9. All HPM gas cylinders in this storage facility are individually secured by means of a cylinder strap or chain.
- 5.4.9.10. All containers for liquid or solid HPMs are placed in secondary containment (fire proof spill trays).

NOTE: The UFC, Section 80.301.(l), states that areas used for storage of solid and liquid hazardous materials shall be provided with a means of spill control to able to retain the spill from the largest single container. This can be more than accommodated by spill trays as the maximum quantity of such a container would be one pound. It must also be able to contain a twenty minute discharge from the fire suppression system. This facility is not equipped with a fire suppression system. Because it a

remote, unoccupied, unheated building fire suppression is not provided. These trays are also used as an equivalent measure to having liquid tight floors, where required. The quantities present, nature of any release (rapidly oxidizing), and the fact there is not any occupancy of the facility do not warrant the expense of liquid tight floors.

5.4.9.11. The attachment of a HPM container to any type of HPM distribution system, or any other intentional dispensing of HPM, within or around this facility is prohibited.

5.4.9.12. Gas detection is used when entering and at all times when occupying the HPM storage facility. Portable, hand held detectors do qualify, provided they detect the appropriate gases contained in the facility.

NOTE: The UFC, Section 80.303.(a).9, for indoor storage of compressed gases, requires continuous detection. Because of the remote location, unoccupied condition, and solitary function of this facility it is more reasonable to consider it an exterior storage facility. Such a facility is not required to have continuous gas monitoring. Note also, that in Section 3.3 it was demonstrated that a worst case release in Building 16 would not pose a serious health risk at a receptor site 100 meters distant. The nearest occupied space to this facility exceeds this distance.

5.4.9.13. The buddy system is used when entering and at all times when occupying the HPM storage facility. Personnel are not permitted access to this facility alone. All personnel must carry a two-way NREL Radio when entering the premises.

5.4.9.14. Access to an individual storage room within the facility is permitted only if it is known that the exhaust fan for that room is operational. If the fan is not operational, the appropriate Facilities and SSO personnel must be contacted to affect repairs and declare the room clear to enter.

5.4.9.15. Off hours access to this facility is prohibited.

5.4.9.16. Two SCBA are provided at the Shipping and Receiving area, in the FTLB, for use when responding to emergency situations at the HPM storage facility. Only trained personnel are allowed to use the SCBA.

NOTE: The UFC, Section 80.303.(b).5, for exterior storage of compressed gases, requires that the SCBA be located near the area of storage, in a location that provides safety to those expected to don the apparatus. This would exclude it from the interior of the fenced off area. Additionally, any location in the immediate area would subject the equipment to extremes in temperature, calling into question its integrity. Thus, the most logical location for such equipment is at the FTLB.

5.4.9.17. A manual alarm pull station is provided at the building exterior. Activation of this alarm sounds a local alarm which is clearly audible from the nearest occupied building (the FTLB).

5.4.9.18. The following signs shall be clearly posted at this facility. They shall be in English and not be obscured, obstructed, or removed. They must be of adequate size and use colors and lettering which make them easily readable.

5.4.9.18.1. On the gate or other area close to the first point of access, a sign is posted which conveys the following message: "Restricted Access; Authorized Personnel Only! Off-hours access is prohibited."

- 5.4.9.18.2. On the gate or other area close to the first point of access, a sign is posted which conveys the following message: "NO Smoking, Use of Open Flames, or High-Temperature Devices within 25 feet of this facility!"
- 5.4.9.18.3. Each of the four rooms is clearly marked as to identify the hazard class of the materials stored within (1-Pyrophorics, 2-Pyrophorics and Highly Toxics, 3-Toxics or Highly Toxics, and 4-Corrosives) and is appropriately placarded as per UFCS 70-3 (NFPA 704).
- 5.4.9.18.4. A sign must be clearly posted which indicates the location of the storage plan for the facility (Section 5.4.9.19.). It must be posted in close proximity to the storage plan.
- 5.4.9.18.5. A sign must be clearly posted in close proximity to the alarm pull station (Section 5.4.9.17.) which conveys the following message: "Very Loud, Local Alarm! This alarm does not summon the fire department."
- 5.4.9.19. A storage plan must be posted at the exterior to the storage facility. This storage plan must be protected from the elements. As a minimum, it must contain the following elements.
 - 5.4.9.19.1. Indicate the intended storage arrangement, including the location and dimension of the rooms.
 - 5.4.9.19.2. Each container placed in the facility should be logged in with following information; name of person making entry, name of contents in container, quantity of contents in container, name of user/requestor, the PR and/or PO number under which the container was purchased, the date container entered facility, and any identifying container numbers (e.g. NREL bar codes, cylinder serial number, etc.). All of the above information must be provided.
 - 5.4.9.19.3. Each container removed from the facility should be logged out by providing the name of the person removing the container, the date of removal, and the location to where the container is moved.
 - 5.4.9.19.4. Each new entry into the log must be compared to the Table 9-A and 9-B exempt amounts to ensure that the aggregate quantities of HPMs in the facility do not exceed these levels. If a new container exceeds these quantities, the SSO must be contacted to initiate the appropriate action.
 - 5.4.9.19.5. Each time the facility is entered, the log must be checked for any HPM container which has remained in the facility for 90 days. Such containers must be returned to the supplier. The PR and/or PO number of the container must be provided to the procurement office so the process of return can be initiated.
 - 5.4.9.19.6. Applicable editions of Tables 9-A and 9-B (exempt quantities of HPMs) from the UBC/UFC.
 - 5.4.9.19.7. The SOP for this facility may be kept in this location as well.
- 5.4.9.20. As per Section 5.5.4.5., secondary containment is required for all transportation of HPMs. Because of the low volume of use of HPMs at NREL, these secondary containment vehicles are not in everyday use. Therefore, they are readily available to serve as a means of containing "leakers" should one be detected. It should be pointed out that because of Section 5.4.9.11., HPM

containers are not opened at this facility. Therefore, the only means of a leak developing is through the original container and the probability of this is extremely remote. Section 5.5.3.17. clearly indicates that the container would be inspected for leaks upon delivery, which is before it would be placed in this facility.

5.5. Administrative Controls/Standards

The topic of administrative standards considers the minimum requirements for operators of systems using HPM and their managers. These standards are followed at all times while a system is operational.

5.5.1. Safe Operating Procedures (SOPs)

An SOP is prepared and approved for each system. It is stored in a standardized, central location in which Material Safety Data Sheets (MSDSs), chemical inventories, etc. are also kept. Each SOP contains the following information:

- 5.5.1.1. A brief description of the processes and experiments performed with the system on the cover/sign off page (abstract).
- 5.5.1.2. A statement of location of the system within the building.
- 5.5.1.3. The Institutional management organizations responsible for the system.
- 5.5.1.4. Details of the system, including, but not limited to, a system schematic and a discussion of how the system complies with these and other standards (e.g. a copy of the Operational Readiness Review for that system).
- 5.5.1.5. A description/listing of the hazards present.
- 5.5.1.6. Statements of hazard precautions and/or controls. This section must address all of those hazards listed in the previous section.
- 5.5.1.7. A description of all applicable emergency responses. This necessarily includes reference to, but is not limited to, "The Emergency Response Procedures to the MDA Toxic Gas Alarm."
- 5.5.1.8. General operating procedures. This must include general start-up, run and shut-down procedures. Additionally, it must include special procedures or precautions for the cleaning of reactors and deposition products. (Note: exact step-by-step procedures are not applicable to these systems due to the fact that each individual step may, and probably does, vary from run to run. These are systems devoted to research, not production. There are; however, general procedures which do correlate to all runs. It is these procedures which must be included in the SOP. Depending on the complexity of these procedures they may or may not be written down in the form of a checklist for operators to check off for each run. This is left up to the discretion of the person responsible for each system.)
- 5.5.1.9. Procedures for the changing of HPM sources. (See Section 5.5.6.4. for requirements on HPM source change out procedures.) This would include a description of the required duties of all personnel involved in a HPM source change out.

- 5.5.1.10. A preventative maintenance schedule, if applicable. Maintenance records do not need to be kept in the SOP, but reference to where these records are kept should be made.
- 5.5.1.11. A list of all authorized personnel (system operators). These persons are required to read the SOP and sign off that they did indeed read the SOP and understood it.
- 5.5.1.12. A list of all personnel authorized to assist in other activities related to the operation of the system; e.g. changing HPM sources, monitoring the system for short times, etc.
- 5.5.1.13. A list of the specific management chain responsible for the particular system.
- 5.5.1.14. A section outlining the type of training received by those persons affected by the particular SOP. Included is a current training log for those personnel.
- 5.5.1.15. Emergency information, including off hours telephone numbers of those included in the SOP.
- 5.5.1.16. A list to the references used in the preparation of the SOP.
- 5.5.1.17. Attachments as needed.
- 5.5.1.18. Appendices as needed.
- 5.5.1.19. Addendums as needed.
- 5.5.1.20. Each laboratory must establish, update, and maintain the following (these do not have to be a part of the SOP, but the a reference to their location must be provided in the SOP):
 - 5.5.1.20.1. A hazardous materials/gases log. Minimum information required on this log would include: the material name, date of receipt, quantity, hazard classification, supplier name & phone numuer, and date of removal from laboratory.
 - 5.5.1.20.2. A training log indicating the safety course status of all users in the laboratory.
 - 5.5.1.20.3. A record designed to monitor the efficiency of effluent treatment systems; i.e., pH solution monitoring of liquid scrubbers.
 - 5.5.1.20.4. A maintenance log discussing the status of system modifications and subsequent leak checks performed.
 - 5.5.1.20.5. A record of ventilation tests, measurements, and certifications received by personnel from either the SSO or the Facilities Branch.
 - 5.5.1.20.6. A record of audit/inspections performed on the safety interlocks associated with each system (see Appendix S5 for a sample log).

5.5.2. Responsibilities

Section 4-2 (III) of the Institute Environment, Safety and Health Policies and Procedures provides a general outline of the responsibilities of employees, subcontract personnel, managers, the SSO, and the Facilities Branch. In addition to these

responsibilities referenced above, the following personnel are responsible for those items as indicated.

- 5.5.2.1. Line managers must ensure that each system has been thoroughly analyzed for safety prior to the acquisition of equipment or HPM source materials, assembly, or use. This would include:
 - 5.5.2.1.1. Review of SOPs prepared for systems using HPM on an annual basis.
 - 5.5.2.1.2. Ensure that SOPs include the information described in Section 5.5.1, above.
 - 5.5.2.1.3. Ensure that a SOP is prepared, and approved, prior to the operation of any new systems.
 - 5.5.2.1.4. Confirm that each system in their management chain actually does meet the minimum engineering/system design standards, and that the safety devices, equipment, and procedures outlined in the SOP are being used.
 - 5.5.2.1.5. Ensure that all inspections of laboratories containing systems which use HPM are conducted as per those guidelines in Section 5.5.7.
 - 5.5.2.1.6. Enforce the safety standards as described in this document, in the Institute Environment, Safety and Health Policies and Procedures, and any specialized guidelines described in an SOP.
 - 5.5.2.1.7. Ensure that the maximum allowable quantities of toxic gases (defined in Section 5.5.3.) are not exceeded for those areas under their control.
 - 5.5.2.1.8. Ensure that all employees under their direction fulfill the minimum mandatory training requirements, as defined in Section 5.5.5.
 - 5.5.2.1.9. Ensure that toxic waste products and by-products are disposed as per those procedures specified in Section 5.5.6.1.
 - 5.5.2.1.10. Make accommodations for regular preventative maintenance as it relates to those safety issues set forth in Section 5.5.6.2.
 - 5.5.2.1.11. Ensure that all employees under their direction operate systems using toxic gases in accordance with the operating procedures established within the SOP for that system.
 - 5.5.2.1.12. Ensure that all employees follow the procedures for changing HPM source materials.
 - 5.5.2.1.13. Ensure that all positions are properly staffed with competent and well-trained personnel. This includes ensuring that there be enough personnel available in order to operate, maintain, service, and repair these systems in a safe manner (meeting minimum staffing requirements).
 - 5.5.2.1.14. Ensure that all contractors which are hired to service, or otherwise work on, these systems are properly trained and supervised in order to maintain their safety and the safety of the laboratory and building occupants.

5.5.2.2. Research Division Director

The Research Division Directors must lead the division in attaining excellence in the research, development, and commercialization of renewable energy and related technologies. This must be done concurrently with directing the division's ES&H activities and assuring compliance with all policies, procedures, and legal requirements. Their Primary Responsibilities include:

- 5.5.2.2.1. Manage line organizations and programs and assure compliance with NREL policies and procedures.**
- 5.5.2.2.2. Assure sound human resources management (including succession planning).**
- 5.5.2.2.3. Communicate with DOE, other clients, and within NREL.**
- 5.5.2.2.4. Lead the development and implementation of the Division's ES&H Management Plan; assure compliance with this Plan and all NREL ES&H policies and procedures.**
- 5.5.2.2.5. Direct the technical transfer, commercialization of technology, and external relations activities.**
- 5.5.2.2.6. Assure technical excellence throughout the division.**
- 5.5.2.2.7. Direct the division's business development activities.**
- 5.5.2.2.8. Participate in NREL strategic planning; lead the division long range and strategic planning activities.**
- 5.5.2.2.9. Lead and guide the division objectives and activities in response to institutional priorities.**
- 5.5.2.2.10. Lead and guide the research activities within the Division such that they comply with the Institute's Quality Assurance (QA) program.**

5.5.2.3. Research Branch Manager

The Research Branch Managers must lead branch staff and manage resources in the development and maintenance of excellence in R&D of renewable energy and related technologies. This must be done concurrently with leading the implementation of Branch environment, safety and health activities and ensuring compliance with appropriate policies and procedures and legal requirements. Their Primary Responsibilities include:

- 5.5.2.3.1. Manage personnel matters through high quality staffing, career planning, training, performance evaluation, salary administration, staff development and Equal Employment Opportunity compliance.**
- 5.5.2.3.2. Direct and plan research activities, assign staff, and, as appropriate conduct research in support of programs.**
- 5.5.2.3.3. Develop and maintain effective communication with branch staff and other NREL personnel.**
- 5.5.2.3.4. Promote and maintain a safe work environment for Branch staff; implement and enforce compliance with ES&H policies and procedures, including**

development of SOPs for all laboratories under the Branch's jurisdiction and assuring that all staff have completed ES&H training requirements for program or project assignments.

5.5.2.3.5. Lead the branch business development and technology transfer activities.

5.5.2.3.6. Assure technical excellence, product quality, and compliance with quality assurance standards: and acquire first class personnel, facilities, and equipment.

5.5.2.3.7. Participate in division and institute strategic planning.

5.5.2.4. Research Program Manager

The Research Program Managers must lead and manage program activities in support of the client's goals to advance and commercialize renewable energy and related technologies. This must be done while directing support of NREL's ES&H program by assuring that program specific ES&H requirements are included in program plan document(s). Their Primary Responsibilities include:

5.5.2.4.1. Lead overall program planning, and management to meet the client's program goals and objectives.

5.5.2.4.2. Serve as primary client interface and program spokesperson to ensure program continuity and growth.

5.5.2.4.3. Identify, plan, and **fund** program-specific ES&H and QA activities and training requirements and document compliance in program files.

5.5.2.4.4. Communicate and negotiate with branch managers the scope of work and resources for each work package.

5.5.2.4.5. Lead commercialization of program technology.

5.5.2.5. HPM Users

HPM Users are to adhere to the safety standards as described in this document, in the Institute Environment, Safety and Health Policies and Procedures, and any specialized guidelines described in an SOP. This would include:

5.5.2.5.1. They are to not exceed the maximum allowable quantities of toxic gases defined in Section 5.5.3.

5.5.2.5.2. They must receive the minimum mandatory training requirements, as defined in Section 5.5.5.

5.5.2.5.3. Dispose of toxic waste products and by-products as per those procedures specified in Section 5.5.6.1.

5.5.2.5.4. Conduct regularly scheduled preventative maintenance as it relates to those safety issues set forth in Section 5.5.6.2., and keep the appropriate documentation of such maintenance.

5.5.2.5.5. Perform those inspections described in Sections 5.5.7.3.-5.5.7.7.

- 5.5.2.5.6. Operate systems using toxic gases in accordance with the operating procedures established within the SOP for that system and Section 5.5.1.
- 5.5.2.5.7. Strictly adhere to and follow the procedures for changing gas cylinders, Section 5.5.6.4.
- 5.5.2.5.8. Employees who are not responsible for working with these systems and are not authorized within the SOP, are not allowed to operate or otherwise work on these systems without first receiving the proper training and authorization from line management. Employees who are authorized operators must ensure that unauthorized personnel do not work on or otherwise operate these systems.
- 5.5.2.5.9. Ensure that all contractors which are hired to service, or otherwise work on, these systems are properly trained and supervised in order maintain their safety and the safety of the laboratory and building occupants.
- 5.5.2.6. Shipping and Receiving Personnel

All personnel who transport toxic gases must do so in accordance with the guidelines established in Section 5.5.4. and DOT guidelines.
- 5.5.2.7. Personnel who Change Toxic Gas Cylinders

All personnel who are involved with, or otherwise assist in, the changing of toxic gas cylinders must comply with the guidelines established in Section 5.5.6.4.
- 5.5.2.8. Procurement Office

All personnel involved with the purchasing of toxic gases must comply with the guidelines established in Section 5.5.3.
- 5.5.2.9. SSO

Provide resources and guidance to ensure proper use of HPMs and compliance with applicable standards.

 - 5.5.2.9.1. Monitor developments in the area of HPM use and provide information and guidance on internal and external codes, standards, policies, etc.
 - 5.5.2.9.2. Participate in the review and approval process for new and revised SOPs, and monitor annual SOP reviews to ensure they are initiated and documented in accordance with NREL policy.
 - 5.5.2.9.3. Participate in inspections of HPM use areas.
 - 5.5.2.9.4. Perform or coordinate the performance of environmental monitoring.
 - 5.5.2.9.5. Serve as the primary interface with regulatory agencies.
 - 5.5.2.9.6. Provide training as specified in Section 5.5.5., within the capabilities of the SSO personnel.
 - 5.5.2.9.7. Monitor the activities of contractors that are working on or in the vicinity of HPM systems, ensure that contractor personnel are properly informed and trained, and issue NREL Work Permits as necessary and appropriate.

- 5.5.2.9.8. Ensure that hazards unique to HPM use are addressed in NREL emergency response procedures.

5.5.2.10. Security Services

Provide monitoring of HPM use areas during non-business hours, with appropriate response to emergencies.

- 5.5.2.10.1. Ensure that Security personnel are trained regarding the hazards of HPM, the toxic gas alarms, and emergency response and notification procedures.
- 5.5.2.10.2. Perform routine patrols of HPM use areas during non-business hours.
- 5.5.2.10.3. Respond to toxic gas alarms or observed emergencies in accordance with established procedures.

5.5.2.11. Facilities Branch

Provide and maintain the support systems necessary for the use of HPMs.

- 5.5.2.11.1. Ensure that necessary building systems are provided for HPM use areas, and that the systems are maintained in a reliable condition.
- 5.5.2.11.2. Facilities Branch personnel are responsible for the operation, calibration, maintenance and service of all HPM monitoring devices (specifically the toxic gas, corrosive gas, and hydrogen monitors), as per Section 5.5.6.3.. This includes the documentation of maintenance and all other QA requirements.
- 5.5.2.11.3. Provide appropriate personnel on-call to respond to support system malfunctions during non-business hours.
- 5.5.2.11.4. Ensure that Facilities Branch personnel working in HPM use areas have received appropriate training.
- 5.5.2.11.5. Ensure that Emergency Notification Lists are updated promptly upon receipt of changes from the research branches.
- 5.5.2.11.6. Coordinate design and construction activities with in-house and external personnel, including design and pre-construction meetings, notifications, etc.

5.5.3. Procurement of HPM

Because of the potential dangers associated with the HPMs used on these systems, the procurement of materials is controlled. This is done in order to ensure that the quantities of HPM in Building 16 do not exceed those permitted.

- 5.5.3.1. Except in one case, the quantities of HPM do not exceed B-2 limits defined in Tables 9-A and 9-B of the UFC and UBC. (These tables are reproduced in their entirety in Section 80.402 of Appendix C1.) The only exceptions to these values are for pyrophoric liquids, explained in detail in Section 5.5.3.2.
- 5.5.3.2. The NREL limit on pyrophoric liquids is 2 pounds per control area. The total of 1.99 lb pyrophoric liquid is intermediate between the 1 lb in-use limit and 4 lb in-storage limit for sprinkled B-2 buildings. (Note: An exemption, based on providing additional safety features, issued by the fire marshal is being sought to allow these materials to be present.)

- 5.5.3.3. The exempt amount of pyrophoric gas is 10 ft³ per control area. Permitted in sprinkled buildings only. No amount is allowed in unsprinkled buildings. The amount may be doubled when dispensed or used in closed containers or systems (which is the case for these operations). Therefore, the exempt amount for the control areas containing these systems is 20 ft³.
- 5.5.3.4. It is possible to be under the exempt amounts defined above and still have more toxic gas in a single container than the ventilation can adequately dilute to meet the 1/2 IDLH requirements, as defined in Section 5.4.6.15. This is especially true of some highly toxic gases. The first line of control is to only order quantities of these materials which can be adequately diluted with the existing ventilation. (If operations cannot be performed with these quantities, then other engineering and/or administrative controls must be implemented as described in Section 5.4.6.15.) Calculations to determine these maximum quantities per cylinder (to meet the 1/2 IDLH requirements) are as follows (for cylinders without flow limiting orifices):

Maximum Quantity per Cylinder (ft³) =

$$\frac{1/2 \text{ IDLH (ppm)} \times \text{release time (min \{see below\})} \times \text{exhaust flow (ft}^3\text{/min)}}{1,000,000 \text{ (ppm)}}$$

For a toxic gas cylinder, the maximum flow rate of release shall be calculated based on assuming the total release from the cylinder is five minutes for a non-liquified source and thirty minutes for a liquified source.

A copy of the above calculation must accompany all purchase requests for toxic gas cylinders without flow limiting orifices. If the maximum amount ordered exceeds the maximum quantity per cylinder (as calculated above), then a memo must be attached which explains what engineering and/or administrative controls are in place to ensure compliance with the 1/2 IDLH requirements (e.g. gas cabinet scrubbers, scram units, etc.).

- 5.5.3.5. If cylinders are equipped with an approved excess flow or reduced flow valve, the worst case release is determined by the maximum achievable flow from the valve as determined by the valve manufacturer or the gas supplier. In this case the maximum quantity per cylinder is determined by control area limits above, Sections 5.5.3.1.-5.5.3.3..

To conform with Article 80 requirements, a calculation is be performed to see if adequate dilution occurs from the ventilation system, in order to meet the 1/2 IDLH requirement.

Maximum Allowable Flow from Cylinder Valve (ft³/min) =

$$\frac{1/2 \text{ IDLH (ppm)} \times \text{exhaust flow (ft}^3\text{/min)}}{1,000,000 \text{ (ppm)}}$$

A copy of the above calculation must accompany all purchase requests for toxic gas cylinders with flow limiting orifices. If the maximum achievable flow from the valve (as specified by the manufacturer) exceeds the maximum allowable flow calculated above, then a memo must be attached which explains what engineering and/or administrative controls are in place to ensure compliance with the 1/2 IDLH requirements (e.g. gas cabinet scrubbers, scram units, etc.).

- 5.5.3.6. In the event of a fire, or other catastrophic event, it is necessary to keep to a minimum the number of HPM containers in all areas of NREL. Therefore, only the number of HPM containers for which there is a current use are allowed in the building. If a HPM container does not have a projected use within the next three months, that container must be shipped by the Shipping and Receiving personnel to the HPM storage area. If a HPM container doesn't have a projected use within the next six months, that cylinder must be returned to the manufacturer/vendor by contacting the NREL buyer.
- 5.5.3.7. When a HPM container is received from the vendor, it must be immediately either put into the outdoor HPM storage facility or delivered to the requestor. The requestor has until the close of the following work week to put the HPM container into service, after it is received. If a HPM container cannot be put into service within this time frame, the cylinder must be taken to the HPM storage facility for temporary storage until it can be put into service. Both the new HPM container, until it is installed, and old HPM container, after it has been removed and until it is picked up for return to the vendor/manufacturer, are considered to be in a state of exchange.
- 5.5.3.8. All paperwork to return sources removed from service is completed at the same time the new source was ordered.
- 5.5.3.9. Any in service HPM container that is not used within the 90 days must be moved to the outdoor storage facility/bunker.
- 5.5.3.10. Any HPM container that is not be used within 180 days must be returned to the manufacturer/vendor. (Section 5.5.3.9. requires that any HPM container that is not used within 90 days must be moved to the bunker. Section 5.4.9.4. requires that any HPM container left in the bunker for 90 days is automatically returned to the vendor. Thus, if a container is known not to have a use within 180 days, it should be immediately returned to the vendor.)
- 5.5.3.11. No more than three HPM cylinders can be housed in a single gas cylinder cabinet. This includes those cylinders which are in a cabinet "temporarily" while waiting to be either shipped to the storage area or returned to the vendor.
- 5.5.3.12. All toxic, highly toxic, and pyrophoric gases are purchased from a supplier who has their own Emergency Response Team. These suppliers must have these teams available so that if there is a problem with one of their cylinders (i.e., a leaking cylinder valve), they can have this team help assist NREL personnel in returning the cylinder to that supplier. Most major gas supply companies have such a team. When inquiring about the price and availability of these gases, this information must be obtained. The SSO has a partial listing of which companies meet this requirement.
- 5.5.3.13. HPM gases are purchased in containers which are returnable to the supplier. Many lecture bottles are bought with the contents and therefore constitute a significant disposal problem. The purchase of lecture bottles in this manner is prohibited. Gas cylinders which are purchased from suppliers, with the intent of returning the cylinders for future refills, are allowed, provided that provisions can be made concerning the ultimate use, storage, resale or disposal of these cylinders. (Note to requestors: keep track of your PR and PO numbers for subsequent return of cylinders to manufacturers.)

5.5.3.14. All purchase requests for HPMs are processed through the SSO and receive an authorization signature from its manager. The SSO personnel must ensure the following:

5.5.3.14.1. The requestor is trained properly to receive such materials.

5.5.3.14.2. The purchase of the requested quantity of the specific HPM does not exceed the exempt amounts per control area as specified in Sections 5.5.3.1.-5.5.3.3. (To aid in checking against the code requirements of a program, THE HAZARDOUS MATERIALS EXPERT (HMeX), developed by L. Fluer, Inc., is used to assess the chemical inventory and compare it area by area against the code.)

5.5.3.14.3. If a toxic, highly toxic, or pyrophoric gas is ordered, the supplier is one that has an emergency response team which can be called upon to come to the aid of the responding personnel should a cylinder have a "problem."

5.5.3.14.4. If the material being ordered is a HPM gas, the container is one that is returnable to the supplier.

In the interest of time, it would be prudent if the requestor went directly to the SSO to receive authorization, before routing the purchase request to the Procurement Branch.

5.5.3.15. When ordering HPM cylinders with reduced flow and excess flow valves, they must be permanently marked by the manufacturer to indicate the maximum design flow rate. Such marking shall indicate the flow rate for air under standard conditions.

5.5.3.16. Shipping and Receiving personnel do not deliver replacement HPMs until the Debit Shipping Memo (DSM) for its predecessor has come through, or in the case of hydrogen, to deliver only if an empty is ready or by written permission of the SSO. This requires that DSMs are processed expeditiously.

5.5.3.17. All incoming HPM containers are monitored for leaks, with the appropriate portable leak detector, before accepting shipment. Any HPM containers which arrive with a detectable leak is not accepted from the shipper and immediately returned to the supplier/vendor.

5.5.3.18. HPM containers for use in Building 16 are not to be taken into the interior of the Shipping and Receiving area, or anywhere else within the FTLB. Upon arrival, during inspection, during transfer to secondary containment (if required), and before being transported to Building 16 (or the outside storage facility/bunker) the container must remain outside of the FTLB envelope.

5.5.3.19. Two tables, provided to the NREL procurement office, one with all known controlled HPMs and one with all known safe production materials in general use at NREL are to be used to ensure that the required signatures are obtained from the SSO before the procurement process begins. If an item is not specifically on the latter list, it shall be considered controlled HPM and the appropriate signatures from the SSO must be obtained prior to purchase.

5.5.4. Transportation of HPM

HPM containers are received and shipped from the FTLB receiving/shipping dock. HPM containers are located in that building just long enough for receiving

purposes and to perform a leak check using a portable leak detector, specific to the material in the container. Leaking cylinders are not accepted as per Section 5.3.3.17. The HPM containers which are received are then either sent to the user or to the outdoor storage facility as per Sections 5.3.3.7.

- 5.5.4.1. Only trained Shipping and Receiving personnel are allowed to transport HPM containers between the receiving area, the outside HPM storage facility, and individual laboratories. All HPMs shall be transported over public roads by trained Shipping and Receiving personnel in properly placarded vehicles approved for transporting hazardous materials. Applicable DOT and internal transportation regulations (under development) are followed.
- 5.5.4.2. All HPMs are transported, at all times, using the buddy system; at least two trained personnel are present.
- 5.5.4.3. A portable monitor, capable of monitoring for the material being transported, is used when transporting all highly toxic HPMs and hydrogen.
- 5.5.4.4. At any time during the transportation of HPMs, if a leak is detected, the Emergency Notification System is activated by dialing x1234. This way personnel from the SSO, the Emergency Response Team, and the researcher responsible for the purchase of the material can all be contacted in order to respond. This requires that two communication (radio) be available to Shipping and Receiving personnel, should they be removed from telephone communications.
- 5.5.4.5. All transportation of HPMs into Building 16 is done in transport systems using secondary containment as described below. These procedures reduce the incidence of cylinder valve head shearing, effects of a fire during transport, or accidental valve opening. See Appendix M3 for a description of secondary containment specifications.
 - 5.5.4.5.1. Pyrophoric liquid and solid source materials are transported in their original packing containers (which is in itself secondary containment) in concert with a fire resistant delivery vehicle.
 - 5.5.4.5.2. Toxic gases, corrosive gases, and gas mixtures categorized as a toxic gas are transported to the laboratories in a secondary containment vehicle designed to contain leaks from toxic gas cylinders (Solkatronic Model 5501 or equivalent -- see Appendix M3) and provide indication if a leak has occurred within the unit (e.g. a pressure gauge).
 - 5.5.4.5.3. Pure hydrogen cylinders are delivered on a normal gas hand truck provided that they have valve protective caps and are checked for hydrogen leaks before being brought into the Building.
- 5.5.4.6. The cylinder has both the protective Compressed Gas Association (CGA) cap and the cylinder valve cap.
- 5.5.4.7. At no time can a toxic gas cylinder be transported in an automobile or the cab of a truck.
- 5.5.4.8. Carts and trucks used to transport toxic gases are designed to provide a stable base for the cylinders and a means of restraining the cylinders from accidental dislodgement. All cylinders are individually restrained.

- 5.5.4.9. Carts and trucks used to transport toxic gases are not left unattended or obstruct any part of an exit.
- 5.5.4.10. Incompatible materials are not transported on the same cart or truck.
- 5.5.4.11. Before a toxic gas cylinder is accepted from the vendor, it is checked for leaks with a portable leak detector. After a toxic gas cylinder has been received by the Shipping and Receiving personnel, they notify the purchaser of the arrival of that cylinder. If the purchaser is not ready to use or exchange that cylinder within 24 hours, the Shipping and Receiving personnel will transport that cylinder to the outside toxic gas storage area. The cylinder remains there until the purchaser makes provision for it to be delivered to the purchaser's laboratory. Shipping and Receiving personnel are not to deliver toxic gas cylinders to the purchaser until they established a specific time when that delivery will be made.
- 5.5.4.12. Shipping and Receiving personnel only transport the cylinder to the laboratory. Once it is in the laboratory it is the responsibility of the purchaser. The purchaser, or other authorized person, has to be present in order for the delivery to be made. If no one is in the laboratory at the time of the delivery, the delivery is not made.
- 5.5.4.13. Once the purchaser has taken responsibility for the cylinder, that person must first properly secure the cylinder in an approved toxic gas cabinet. The purchaser must then make sure that the contents of the cylinder are known and obtain a current MSDS for those gases if one isn't already available in that laboratory. When the cylinder is placed into service it is done so in accordance with Section 5.5.6.4. and the guidelines specified within the SOP for the system on which the cylinder is to be connected. If the cylinder is to be transported between laboratories, it is done so in accordance with those provision set forth in the rest of this section.

5.5.5. Training

Because many people are responsible for HPMs, and the extent of their involvement varies from position to position, the training requirements of the various personnel differ. Table 8 summarizes what the minimum training requirements are specifically for people who are involved with HPMs within NREL. This table is a subset of the more extensive NREL training program.

Training activities are administered by Training Services (a group within the Human Resource Office) with a view towards; developing and administering training to provide the highest level course consistent with cost; enhancing employees' knowledge of health and safety issues; providing employees with skills-enhancement training; and bringing NREL employees up to date with DOE and OSHA guidelines. Courses are offered for both mandated and optional courses and cover Safety and Health, Security, Human Resource Development, as-well-as specialized areas. Courses in Quality Assurance, Management, and Technical Training will be added as they are developed.

A description of these abbreviations used in Table 8 follows. A "HPM User" is defined as someone who actually handles, processes, or in any way uses HPMs within a laboratory. A "HPM chngr" is someone who assists in the change out of HPM containers, but otherwise does not operate HPM systems. A monitor is defined as anyone who is authorized to watch a system while the principle operator steps out of the laboratory momentarily. This person is provided with emergency shut-down procedures. "SSO/Fac." is defined as anyone who responds to the MDA room in the case of an alarm. This would include personnel from the SSO and Facilities Branch.

"S&R" are those Shipping and Receiving personnel who actually transport HPMs. The column titled "LL & Fire" consists of the Building Landlord, Building Fire Marshall, and Fire Marshall Assistants. They must be familiar with the Emergency Response Procedures to know what type of conditions warrant building evacuation. The Security column are those Security Services personnel who need the specialized training contained in the last two rows of the table.

The table indicates what training is required from the standpoint of that person's involvement with HPMs; as well as, some typical training that is required for a particular position. Additional training for some individuals may also be requested. The ORR will ensure that training requirements for each individual listed are met.

TRAINING REQUIREMENTS FOR PERSONNEL INVOLVED WITH HPM

TRAINING TO BE RECEIVED	Freq. (#/yr)	HPM User	HPM chngr	Mon-itor	SSO/ Fac.	S&R	LL & Fire	Sec-urity
SCBA	1	Yes	Yes	No	Yes	No	No	No
Fire Extinguisher	1	Yes	Yes	No	Yes	Yes	No	No
MDA Operation and Emergency Response Proc.	1	Yes	Yes	Yes	Yes	Yes*	Yes*	No
Toxic Gas Safety	1	Yes	Yes	Yes	Yes	Yes*	No	No
First Aid	†	Yes	Yes	No	Yes	No	No	No
CPR	1	Yes	Yes	No	Yes	No	No	No
Compressed Gas Safety	‡	Yes	Yes	No	No	Yes	No	No
Electrical Safety	‡	Yes	No	No	Yes	No	No	No
Simulated Emergency Exercises	1	Yes	Yes	Yes	Yes	Yes*	Yes	No
Use of Emergency Notification Phone List	1	No	No	No	No	No	No	Yes
Reading of Remote MDA Printer in 17/1	1	No	No	No	No	No	No	Yes

† = First Aid training is required once every three years.

‡ = Compressed Gas and Electrical Safety training are required at least once, but not necessarily on a recurring basis.

* = Some of the training may have to be specialized for a particular group.

Table 8

5.5.6. Miscellaneous Procedures

5.5.6.1. There are a variety of process wastes produced in the handling of HPMs. These could include wastes from effluent removal systems, residual material in reactors, purifiers, system components, etc. These wastes, and all disposable materials contaminated in the cleaning of these wastes, are enclosed in appropriate containment. The SSO can provide information on what types of containers to use for various materials. They can also supply containers and a form to fill out in order to record what types of material are in the container. None of this material can be disposed of by merely having it hauled away with the trash.

5.5.6.1.1. The SSO is notified when hazardous waste has been generated or collected and they indicate what procedure to follow when disposing of this waste. In most cases they pick up the container(s) and dispose of them through a certified disposal agency.

- 5.5.6.1.2. In all normal operating conditions, no hazardous materials are released into a sewer, storm drain, landfill site, ditch, upon the ground, onto a street or sidewalk, or into the atmosphere.
- 5.5.6.1.3. It is up to the individual generating toxic, poisonous, or hazardous wastes to ensure that its disposal complies with NREL, local, state, and Federal waste disposal laws. Therefore, researchers who generate waste products or by-products which are of unsafe or of unknown health risk, must contact the SSO for disposal.
- 5.5.6.1.4. Line management periodically checks on employee compliance.
- 5.5.6.1.5. The SSO is responsible for reporting an accidental release in excess of the CERCLA RQ to the National Response Center, Washington, D.C. (see Section 4.1.4.)
- 5.5.6.1.6. Burn boxes use filters to prevent arsenic oxide particles from being exhausted with ventilation air. Arsenic oxide is a carcinogen and therefore personnel engaged in changing these filters should wear proper protective gear. Specifically, personnel must use a negative pressure respirator with cartridges for particulates, lab coats, disposable gloves, sleeve coverings, and head coverings. When changing the HEPA filter, a complete disposable coverall and head covering should be used instead of a lab coat. The procedure used in changing either filter is that the opening of the filter casing is covered with a plastic bag, and the operator reaches through the bag to grab the filter and pull it into the bag. Personnel have been monitored during filter changes to test for exposure to arsenic. No arsenic was detected by vacuum-pumped filters mounted to the shoulders of the operators' lab coats or mounted next to the opening of the filter casing. Based on these findings, the above personnel protection is adequate, since the procedure technically requires no protective gear to be performed below OSHA's PEL for arsenic and arsenic oxide. All laboratories using arsenic-containing compounds are monitored for arsenic contamination with periodic wipe samples as well.
- 5.5.6.2. A preventative maintenance schedule for each toxic gas system is prepared and followed. Important safety equipment associated with a system using HPMs is checked for functionality on a regular basis. Preventative maintenance requirements of systems vary from system to system. However, the following steps are taken for all systems:
 - 5.5.6.2.1. Components which are integral to the safe operation of a system have a preventative maintenance schedule planned out and this schedule is followed.
 - 5.5.6.2.2. A copy of this schedule is kept in the SOP (see Appendix S4 for an example of a preventative maintenance schedule).
 - 5.5.6.2.3. Items which might be considered essential preventative maintenance include the changing of scrubber solution, changing of adsorption bed material, changing pump oil on key pumps, changing or cleaning of various filters, etc. The determination of whether something is just maintenance or essential preventative maintenance related to safety is left to the discretion of the primary user(s). The primary user(s) must have a good idea as to what type of maintenance should be considered essential before the system is put into operation. These must be identified in the SOP.

5.5.6.3. A preventative maintenance schedule for all toxic gas monitoring and support systems is strictly followed.

5.5.6.3.1. As a minimum the MDA Toxic Gas Monitor must receive the following routine maintenance:

<u>MAINTENANCE OPERATION</u>	<u>FREQUENCY OF MAINTENANCE</u>
• Replace Chemcassette®	Weekly.
• Calibrate Optics	Weekly.
• Check Flow Rates	Weekly.
• Check Printer Paper	Monthly.
• Inspect/Clean Optic Block	Quarterly.
• Inspect/Clean Fan Filter	Quarterly.
• Replace Sample Line Filters	Annually.
• Test Continuity of Sample Lines	Annually.
• Replace Sample Point Valves	Annually.
• Check Power Supply Output	Annually.

A copy of this schedule is kept by the Facilities Branch and is included in their maintenance/work schedule. All maintenance of the MDA must be kept under the control of the Facilities Branch, as is currently the case. No one outside of the Facilities Branch is permitted to perform any changes, alterations, modifications, or adjustments to the MDA system.

5.5.6.3.2. When hydrogen monitors are on-line, a similar schedule is developed and kept by the Facilities Branch to be included in their maintenance/work schedule. All maintenance of the hydrogen monitor is kept under the control of the Facilities Branch. No one outside of the Facilities Branch performs any changes, alterations, modifications, or adjustments to the hydrogen monitor.

5.5.6.3.3. When the corrosives monitor is on-line, a similar schedule is developed and kept by the Facilities Branch to be included in their maintenance/work schedule. All maintenance of the corrosives monitor is kept under the control of the Facilities Branch. No one outside of the Facilities Branch performs any changes, alterations, modifications, or adjustments to the corrosives monitor.

5.5.6.4. The following items are accounted for in the changing of toxic or highly toxic HPM containers. (Sections marked with a ☆ also apply to all other HPM containers.)

5.5.6.4.1. ☆ HPM gas cylinders are changed using the buddy system; at least two authorized and trained personnel are present.

5.5.6.4.2. SCBA is worn by both the people in the laboratory who are changing the cylinder.

5.5.6.4.3. ☆ Absolutely no one else shall be allowed to enter the laboratory while a HPM container is being changed, unless they are there to assist in the changing of the cylinder and have donned SCBA. Appropriate signs are posted outside of laboratory entrances as notification that hazardous operations are occurring within the laboratory.

- 5.5.6.4.4. An additional person is at the HPM monitoring unit which is monitoring the laboratory where the HPM container is being changed. The person at the HPM monitoring unit must keep monitoring closely for even small leaks which may occur during the changing of a container.
- 5.5.6.4.5. The Facilities Branch is notified that a HPM container is going to be changed. They have a representative put the HPM monitoring unit into a mode of operation where specific, and strategic, points can be monitored during the changing of the cylinder to ensure the most rapid sampling times possible. Note that this likely requires that other research personnel, who may be sharing the same HPM monitoring unit, will have to be contacted about the interruption of the monitor. This would require those people who are changing a container to do so at a time when the other research personnel using a particular monitor are not running or doing any activity requiring uninterrupted monitoring.
- 5.5.6.4.6. Research personnel will never reset a HPM monitoring unit in order to return it to the normal mode of operation. This must always be done by a representative from the Facilities Branch in order to ensure that everything is operating correctly.
- 5.5.6.4.7. ☆ Always use the correct CGA, or other correct container, connection.
- 5.5.6.4.8. ☆ Be sure there is no chance of contamination from other gas sources.
- 5.5.6.4.9. ☆ Never use excessive force when installing a new cylinder. (If two components do not fit together well, make absolutely sure that they are compatible components.)
- 5.5.6.4.10. ☆ Never tamper with or bypass the safety relief devices installed on gas cylinders or regulators.
- 5.5.6.4.11. ☆ A checklist for the changing of HPM containers is prepared for each system and strictly followed. As a minimum, the following points must be included for all HPM except flammable gases. Because the buddy system is used in changing toxic gas cylinders, one person will actually do the steps outlined on the checklist, while the other person checks off the steps as they are performed. This is done to ensure that none of the steps are skipped inadvertently. The second person should also operate any portable HPM monitor that may be available for the HPM being changed. The elements of a checklist are listed below. Copies of this check list are made available for the changing of HPM containers. (See Appendix S1 for a sample checklist for changing highly toxic gas cylinders.)
- 5.5.6.4.12. ☆ Evacuate the laboratory of all personnel not involved with changing the toxic gas cylinder. Post "Do Not Enter" signs on the entrances to the laboratory.
- 5.5.6.4.13. Ensure that someone is monitoring an appropriate HPM monitor.
- 5.5.6.4.14. ☆ Close the valve(s) on the old container and adequately pump and/or purge the gas line.
- 5.5.6.4.15. ☆ Close any other valves which must be closed before removing the old container.

- 5.5.6.4.16. Turn the delivery pressure adjusting screw, on the regulator, fully counter-clockwise. (This is the no, or zero, delivery pressure position.)
- 5.5.6.4.17. Don SCBA (required for all HPM gases, except flammables and corrosives).
- 5.5.6.4.18. Cap CGA and attach cylinder valve cap and appropriate safety straps. Remove the old container.
- 5.5.6.4.19. Remove cylinder valve cap and CGA cap from the new cylinder after placing it inside of an approved gas cabinet.
- 5.5.6.4.20. Check the cylinder valve to ensure that it is closed before removing the CGA cap.
- 5.5.6.4.21. When removing the CGA cap, the cylinder must be facing away from the person changing the cylinder. (This is in case there has been a leak of gas through the valve which has collected behind the CGA cap. If the cylinder valve was closed tightly and a gas release is detected when removing the CGA cap, the cylinder must not be placed into service. Both the manufacturer/vendor and SSO should be contacted immediately. See Section 5.5.3.17. for procedures concerning leaking cylinders.)
- 5.5.6.4.22. Install the new cylinder, remove SCBA and re-pump and/or purge the gas line. HPM monitoring can be suspended until the container valve is about to be opened.
- 5.5.6.4.23. ☆ Helium leak check the line after the new cylinder has been installed, but before the container is opened. Leak testing of the CGA connection is required.
- 5.5.6.4.24. Don SCBA and resume watching of the appropriate HPM monitoring unit before opening the container valve(s).
- 5.5.6.4.25. ☆ Slowly open other valves which need to be opened. (Include a detailed procedure of what valves to open and close and in what sequence.) Check for leaks of toxics using portable detector along gas lines.
- 5.5.6.4.26. When all clear, remove SCBA.
- 5.5.6.4.27. Monitor appropriate HPM monitoring unit for at least 15 minutes after the container has been opened.
- 5.5.6.5. Cylinder changing techniques for dopant gases and corrosive gases shall be the same as for toxic gases except that SCBA shall not be required. Pure hydrogen cylinders may be changed without purging. Leak checking of the CGA fitting with portable hydrogen monitoring is adequate.
- 5.5.6.6. All HPM gas cylinders must have both the proper CGA plug (two piece construction on toxic and high toxic cylinders) and the protective cylinder valve cap in place when being moved within a laboratory. Exception: Pure hydrogen cylinders may be transported without CGA plugs.
- 5.5.6.7. Secondary containment, as per Section 5.5.4.5., is used to transport HPM containers between laboratories or buildings.

- 5.5.6.8. There are number of places from which a HPM container can leak: through the valve seat; through the valve stem; through the connection where the valve is attached to the container; etc. Because there exists a finite probability that a HPM container will leak, it is necessary to monitor all HPM containers at all times when people might be present in that area. If a monitor detects a leak, and that leak is identified as coming from the container, the procedure to be followed varies depending upon where the HPM container is located and who is in possession of that container.
- 5.5.6.8.1. When a HPM container arrives at NREL, it is checked for leaks with a portable HPM detector before the shipment is accepted from the vendor. If the container is found to have a leak, the immediate area is to be evacuated and someone is appointed to ensure that no one enters that area. The SSO is notified as to the location and condition of the container. Acceptance of shipment must be refused and the container must be returned to the vendor. Additionally, the person who purchased the container should be contacted and informed of the events which have transpired.
- 5.5.6.8.2. If a HPM container is determined to be leaking while in possession of Shipping and Receiving personnel, either in storage or in transit, they must: evacuate the immediate area; appoint someone to ensure that no one enters that area; notify the SSO about the condition and location of the container; and be able to identify the container and the purchaser of the container. Personnel from the SSO work with the purchaser of the container and the vendor in order to get the container returned. If the leak is discovered outside, the container must not be removed from its secondary containment. The container, with the secondary containment, is taken to the outside storage facility until follow-up occurs. If the leak is discovered inside a building, personnel from the SSO ensure that properly trained personnel, with SCBA if necessary, move the container into an approved area and that the proper safeguards are taken. The leaking container must remain in secondary containment until it is either returned to the vendor or the secondary containment is attached to a proper treatment system and the hazard adequately reduced.
- 5.5.6.8.3. If a HPM container is determined to be leaking while in possession of personnel from the research staff they must: evacuate the immediate area; appoint someone to ensure that no one enters that area; notify the SSO about the condition and location of the container; be able to identify the container; and respond to the leak in accordance with the guidelines established in the "Emergency Response Procedures to the MDA Toxic Gas Alarm.". Personnel from the SSO work with the purchaser (or user) of the container and the vendor in order to get the container returned. The leaking container must remain in an approved gas cabinet until the container is to be returned to the vendor. If the leaking container is properly installed on the system when the leak is discovered, it must remain attached until the vendor is contacted and informs the user as to how to proceed.
- 5.5.6.9. Anyone operating a system using HPMs must do so in accordance with the operating procedures established within the SOP for that system. Those procedures must incorporate the following items:
- 5.5.6.9.1. Never use toxic gases outside of normal business hours; 8:00 am to 5:00 pm, Monday through Friday.

- 5.5.6.9.2. Never leave a system, with toxic gases flowing, unattended. (If you need to leave the laboratory, even for a moment, find someone who is adequately trained to watch the system in your absence.)
- 5.5.6.9.3. Always check for the green MDA run light (Section 5.6.1.4.) before starting a run. This light must be illuminated or the system(s) in that laboratory is in the fail-safe mode and the run cannot be started.
- 5.5.6.9.4. All equipment enclosure doors and openings are closed.
- 5.5.6.9.5. If a fire alarm sounds, the system is shut down before evacuation.
- 5.5.6.9.6. Check on quantities of secondary or critical nontoxic gas sources before starting a run, to ensure an adequate supply.
- 5.5.6.9.7. Make sure effluent removal systems are operational and adequately purged.
- 5.5.6.9.8. No runs can be performed with safety interlocks bypassed. (Special permission must be obtained through the signature authority for the SOP in order to run with bypassed safety interlocks.)
- 5.5.6.9.9. Tagout of non-functioning items must be done in accordance with the Institute Electrical Lockout & Tagout Desk Procedures (NREL ES&H Policies and Procedures, Section 10 on Industrial Safety)

5.5.7. Inspections and Audits

This section refers to two different types of inspections. Those conducted by line management as routine safety inspections (Section 5.5.7.1.) and those conducted by principal operators as regular inspections of systems to ensure the continued safe operation of those systems (Sections 5.5.7.3.-5.5.7.7.).

- 5.5.7.1. All laboratories are regularly inspected by line management (at the Branch and Division level). All laboratories containing systems using HPMs must be thoroughly inspected quarterly for issues specific to the use of these materials.

Each time an inspection is conducted a different aspect of system safety should be checked (if not all facets). Below is a possible schedule of things to be checked on quarterly inspections. If followed, this schedule would allow for the inspection of the key factors concerning the safe handling of HPMs over the course of a year. Included in this proposed schedule are those items which could be easily checked, in a minimal amount of time. (These inspections are merely follow-ups to the major compliance inspection performed during the ORR.) Note that adequate documentation and follow-up is required on all inspections. All inspection reports must include a statement on what action was taken on findings from previous inspections so that deficiencies don't "fall through the cracks."

All items which are considered to be "administrative controls" must be adequately documented in order to provide those personnel on inspections accurate records to judge whether or not such controls have been implemented. The absence of such documentation shall be interpreted as noncompliance and appropriate disciplinary action shall be taken; including, but not limited to, the tagging out of the system in question.

FIRST INSPECTION: Check SOP for the following:

- Appropriate signatures within last year.
- Training requirements are current as recorded in the training log.
- List of authorized personnel is current.
- Required inspections or tests of safety features were performed.

SECOND INSPECTION: Check the system for actual compliances with standards. Randomly pick items from the ORR and ensure that compliance is met. Any deficiencies in these requirements force the system to be tagged out immediately. The tag cannot be removed until a follow-up inspection is conducted and all deficiencies are found to be corrected.

THIRD INSPECTION: Perform a verbal quiz of principal operators as to what they would do in a hypothetical emergency situation. Questions could be formulated out of the "Emergency Response Procedures to the MDA Toxic Gas Alarms." Appropriate responses must follow these procedures. Documentation must be kept of these quizzes and only those who pass are allowed to continue the operation of systems. Those who do not adequately answer the questions are not allowed to operate HPM systems until they can satisfy the inspectors that they are competent to do so.

FOURTH INSPECTION: Have the principal operator demonstrate that the various safety interlocks on the system are operational. For example, over pressure the chamber with an inert gas and see if toxic gas lines are deactivated. Any deficiencies in such interlocks force the system to be tagged out immediately. The tag cannot be removed until a follow-up inspection is conducted and all interlocks are found to be functioning correctly.

- 5.5.7.2. Before these systems are put back into operation, the Toxic Gas Safety Panel conducts a thorough and complete audit of all systems using HPMs. This audit consists of using the Operational Safety Limits/Hazard Controls section of this SAR, to ensure that all systems fulfill NREL requirements for equipment as defined within. Any deficiencies are to be reported to the principle operator and the appropriate line management. The exact completion date of these audits is set by the Building Landlord. Individual researchers may request and receive written approval of system designs before and during the system modification process.
- 5.5.7.3. Inspections of HPM distribution systems, by principle operators, must be performed as set forth in Section 5.4.1.24. Additionally, periodic inspections of each component, connection, and weld on each line must be conducted visually for external problems (abrasions or other damage). The components of the HPM distribution system from the connection to the HPM container (CGA) through first component securely anchored to the gas cabinet or other rigid structure are checked for leaks with a portable monitor, or an extension put on a stationary HPM monitor, after each cylinder/container change-out is complete and the container has been opened. Accurate records of inspections of HPM distribution systems are kept by the principal operator.
- 5.5.7.4. Inspections of reactors/deposition chambers, by principle operators, are performed every time they are opened, reassembled, or modified.
- 5.5.7.4.1. Many operators routinely monitor the reactor tubes/deposition chambers as a part of the general operating procedures. For example, those systems that

operate under vacuum often monitor the "base pressure" of the chamber with some type of high vacuum gauge. If that base pressure changes considerably, the operator is readily aware that there may exist some type of breach in the integrity of the reactor.

- 5.5.7.4.2. Systems that do not have a means of accurately monitoring a base pressure must have some means of checking the integrity of the reactor before toxic gases are introduced into the reactor. For instance, a reactor can be left at a certain level of pressure (either by establishing a vacuum or by filling with an inert gas, depending on which type of pressure can be readily measured) and then close all the valves on the reactor for a period of time. The leak rate of the chamber can then be calculated and compared to previous leak rates to make sure everything is functioning normally. Alternatively, o-ring seals could be checked with a portable gas monitor.
- 5.5.7.5. Effluent removal systems probably require the most frequent inspections in order to ensure that they function efficiently. Any compressed gases which are necessary for the proper operation of the effluent removal system, must be checked to ensure there is an adequate supply, before starting each run. In addition to checking safety interlocks on a regular basis (see Section 5.5.7.7.), there exists some unique items for inspection and/or maintenance on each particular type of system.
 - 5.5.7.5.1. Liquid scrubbers must have a characteristic indicator of the efficacy of the scrubbing solution checked at least twice a month. More frequently if process loads can degenerate the solution in a shorter period of time. Characteristic indicators of scrubber solution can vary from process to process; however, some of the more common indicators include: pH; an empirical determination (based on the loading of scrubber, the chemical reaction responsible for scrubbing, and the amount of scrubbing chemical present in the solution); density; etc. The frequency of changing scrubbing solution can be determined by these regular inspections of the solution.
 - 5.5.7.5.2. Burn Box - Plus type systems equipped with condensation coils or filters, which collect oxidation particulates, must have those items cleaned or replaced on a regular basis which is dictated by the process demands. Regular inspection of the particulate collection components indicates the frequency of maintenance
 - 5.5.7.5.3. Adsorption beds with controlled oxidation, must have the adsorption medium changed on a regular basis. By monitoring the effectiveness of the adsorption bed, the frequency of changing medium can be determined. Note that the lifetime of a charcoal bed is likely to be 3-5 years.
- 5.5.7.6. All ventilated enclosures associated with systems utilizing HPMs must be inspected on an annual basis. A copy of the records of this inspection must be kept in the system SOP. When ventilated enclosures are referred to, this includes all system enclosures, gas cabinets, ducts between gas cabinets and system enclosures, ducts containing effluent removal plumbing, etc. As a minimum, the following items must be tested and the results recorded.
 - 5.5.7.6.1. Smoke Testing from Ambient: Smoke must be released around all openings to ventilated enclosures and the flow should be inward. All doors and openings should be in the position they would be under normal operating conditions.

- 5.5.7.6.2. **Smoke Testing Enclosures:** Smoke should be released in all corners and obscure locations within ventilated enclosures and there should exist an air flow such that the smoke is taken out of the enclosure through the appropriate duct work. Smoke should never be able to escape from the enclosure into the working environment.
- 5.5.7.6.3. **Air Velocity Testing of Enclosures:** All doors and openings should be in the position they would be in under normal operating conditions (i. e., when toxic HPM are flowing). Then the linear inward air velocity should be measured at all openings to enclosures and at the access ports to the gas cabinets with the access ports open. (Note: The minimum required linear inward air velocity at these locations is 150 LFPM.)
- 5.5.7.6.4. The SSO certifies and record that exhaust requirements (face velocity) for gas cabinets, system enclosures, and the total room are met. Certification information is tagged/displayed on all gas cabinets and enclosures and a record provided to each principle operator. Any deficiencies in the above tests are corrected immediately.
- 5.5.7.7. All safety interlocks, as described in Section 5.4.7., must be tested to ensure that they are operating properly at least once a year. This is especially critical for those interlocks which place the system in a fail safe mode. If any safety interlocks are not working correctly, the system must be tagged out of service until the appropriate repairs are made. Accurate records of these tests are maintained.

5.5.8. Information Exchange (Signage)

Because of the severely hazardous nature of these gases, as well as the new "Right to Know" laws in place, there is a certain amount of information which must be readily available to both employees and management. All signs referred to in this section shall not be obscured or removed. They shall be in English and use only symbols in addition to English text (except where permitted by the Uniform Fire Code Standard No. 79-3). The signs are to be durable; not handwritten on a piece of paper. As a minimum, the information outlined in this section is made available as indicated.

- 5.5.8.1. Contained within each SOP for systems using toxic gases is a training log sheet of all people who are associated with that system. This would include principle operators, personnel authorized to "watch" the system, personnel authorized to assist in the changing of toxic gas cylinders, etc. This log would necessarily include a column listing all required training for a particular individual and additional columns to indicate the date of when this training was last received. This training log is easily accessible within the SOP for periodic inspection (see Appendix S2 for a sample of a training log). Records for individuals can be obtained from employees' Branch Managers.
- 5.5.8.2. Section 5.5.1.5. requires that a description of all the hazards associated with a particular system be included in the SOP for that system. In addition to this, a log of all HPMS is kept in the laboratory. This log would necessarily include a column listing all the HPMS contained in the laboratory, a column to record how many containers of each are present, a column to record the location of each container, a column to record the date of when that container was received, and a column to record the date of when that container was returned to the vendor. This log is updated each time a new cylinder of toxic gas is received or returned. See Appendix S3 for an example of an acceptable log. (The SSO has installed an information rack in every laboratory. There are three compartments; Chemical

Inventory, SOPs, and ES&H Information. This log is to be kept in the Chemical Inventory section of this information rack.)

- 5.5.8.3. The following information must be readily available within all laboratories using HPMs.
 - 5.5.8.3.1 MSDSs for all HPM chemicals and gases used in association with HPM systems is kept in the laboratory. They can be kept in the information racks, added to the SOP, or in both places.
 - 5.5.8.3.2. A copy of the "Emergency Response Procedures to the MDA Toxic Gas Monitor" must be kept in an easily accessible place; preferably in the plastic ES&H information racks provided in each laboratory.
 - 5.5.8.3.3. A copy of this SAR will be kept in each HPM laboratory.
 - 5.5.8.3.4. A copy of the flow chart summarizing the "Emergency Response Procedures to the MDA Toxic Gas Monitor" (Section VIII) must be posted in a central location which can be easily viewed. Logical places to post this flow chart would be by all phones in the laboratory and by the MDA Toxic Gas Alarms.
 - 5.5.8.3.5. A copy of the SOP for each system is kept in an easily accessible location, near each system.
- 5.5.8.4. It is the responsibility of the Facilities Branch personnel to ensure that everything associated with the MDA Toxic Gas Alarm, the hydrogen monitor, and the corrosives monitor, in the HPM monitoring room (which is under their control), be clearly identified by use of labels and/or posters.
 - 5.5.8.4.1. Each HPM monitoring point must be clearly labeled so as to identify the location of that point, the set point levels for that point, and the type of HPM for which it is set.
 - 5.5.8.4.2. Each line for a monitoring point must be numbered, corresponding to the channel which is monitoring that point, at a location before that line enters the HPM monitoring unit.
 - 5.5.8.4.3. The following information from the "Emergency Response Procedures to the MDA Toxic Gas Monitor" must be made readily available, by the posting of copies of the following items in an easily accessible location within the HPM monitoring room: the Flow Chart of Procedures (Section VIII), the chart Defining the Release Levels (Section IX), and the Printer Enable Commands (Section XI). Finally, multiple copies of the MDA Alarm Checklist (Section X) must be readily available in the MDA room.
 - 5.5.8.4.4. A list containing the names of principle operators, authorized personnel (back-up contacts), and line management for all systems using the MDA Toxic Gas Monitors is to be posted in the MDA room. Accompanying these names must be the day time extension(s) where these people can be located; as well as, their night time emergency contact numbers.
- 5.5.8.5. Equipment and alarms are adequately labeled for easy identification.
- 5.5.8.6. All piping and equipment containing HPM are labeled with highly visible labels (standardized for all HPM systems) containing information about the contents and

the direction of flow. Signage must conform to 1991 SEMI Facility Standards and Safety Guidelines S1-90.

- 5.5.8.7. Long lengths of piping require a label every 30 ft.
- 5.5.8.8. Visible hazard identification signs (as specified in the Uniform Fire Code Standard No. 79-3) shall be placed at entrances to locations where hazardous materials and toxic gases are contained. Entrances to these areas shall be clearly identify those areas as possessing HPM.
- 5.5.8.9. Emergency notification contact lists are clearly posted near all entrances to areas containing HPM. These notification lists are kept current.
- 5.5.8.10. All systems using HPM are clearly identified. As a minimum, the official name of the system is on a sign with the following statement: "Caution: this system uses (name specific HPMs)!"
- 5.5.8.11. All safety alarms associated with this system are clearly identified; e.g. chamber over-pressure, low scrubber solution flow rate, no nitrogen purge gas flow, reduced exhaust ventilation, etc. No alarms associated with systems using toxic gases, whether visual or audible, are to exist without proper labeling.
- 5.5.8.12. All panic buttons which put HPM systems into a fail-safe mode are of a standard design and clearly labeled as to their function.
- 5.5.8.13. While toxic gas cylinders are being changed the entrances to the laboratory are secured and signs clearly posted forbidding entrance.
- 5.5.8.14. All outdoor storage facilities for toxic gases must have signs clearly posted which read as follows: "Toxic gases stored in this area; Do NOT Enter without using a toxic gas monitor!", "Authorized and trained personnel only!", and "NO Smoking, Use of Open Flames, or High-Temperature Devices within 25 feet of this facility!".
- 5.5.8.15. Documentation is provided that ensures an individual system has been audited for compliance with the requirements of this SAR; particularly the engineering/system design standards outlined in Section 5.4. All existing systems must make the necessary changes to comply with these requirements before they are allowed to resume operations.
- 5.5.8.16. HPM gas cylinders with reduced flow orifices must be permanently marked by the manufacturer to indicate the maximum design flow rate. Such marking shall indicate the flow rate for air under standard conditions.

5.6. Personal Protective Equipment Standards

The topic of personal protective equipment standards considers the minimum requirements within NREL to ensure the personal safety of employees who are involved with the handling of HPMs. While most of the standards addressed in Section 5.4. are involved in protection of employees, those topics are specifically involved with the regulation of system requirements. This section deals with items which are necessary in addition to the requirements placed upon systems and laboratories.

Table 9 summarizes the monitoring requirements, found in the next three subsections, for the continuous monitoring of toxic, flammable and corrosive gases.

HPM GAS MONITORING

Monitoring Requirement	Toxic	H ₂	Corr
1. Continuous monitoring required	Yes	†	‡
2. High level alarm set point (x TLV)	5*	0.2§	1
Initiates fail-safe of systems in that lab	Yes	Yes	Yes
Activates audible alarm in laboratory	Yes	Yes	Yes
Activates flashing lights at entrances	Yes	Yes	Yes
Activates the bell at monitoring room	Yes	Yes	Yes
Activates audible alarm in SSO & Reception Desk	Yes	Yes	Yes
Prints out value at remote printer, 17/1	Yes	Yes	Yes
3. Low level alarm set point (x TLV)	1	N/A	N/A
Initiates fail-safe of systems in that lab	No	"	"
Activates audible alarm in laboratory	Yes	"	"
Activates flashing lights at entrances	No	"	"
Activates the bell at monitoring room	No	"	"
Activates audible alarm in SSO & Reception Desk	Yes	"	"
Prints out value at remote printer, 17/1	Yes	"	"
4. Green run light located in laboratories	Yes	No	No
De-energizing puts systems into fail-safe	Yes	N/A	N/A
Alarm or maintenance de-energizes light	Yes	N/A	N/A
5. Standardized, central location for alarms in labs	Yes	Yes	Yes
6. Location of monitoring points controlled	Yes	Yes	Yes
Minimum of two points per laboratory required	Yes	Yes	Yes
Minimum of one ambient point required in lab	Yes	Yes	Yes
Points in ducts must be ≥8 dia. from junctions	Yes	Yes	Yes
All systems in each lab must be monitored	Yes	Yes	Yes
7. Monitoring accessories are labeled by Facilities Branch	Yes	Yes	Yes
Sign on flashing light, reset buttons	Yes	Yes	Yes
Sign on high level audible alarms	Yes	Yes	Yes
Sign on low level audible alarms	Yes	N/A	N/A
Sign on green run lights	Yes	N/A	N/A
Signs on each monitor	Yes	Yes	Yes
8. Color of flashing lights outside of lab entrances	Blue	Red	Yell.
Clearly indicate "DANGER KEEP OUT"	Yes	Yes	Yes
Other required signage is clearly posted	Yes	Yes	Yes
Are located in standardized spots for each lab	Yes	Yes	Yes
Do not auto reset when alarm bells are silenced	Yes	Yes	Yes
Require manual reset from affected area	Yes	Yes	Yes
9. Monitors are on the standby generator	Yes	Yes	Yes
10. Facilities Branch maintains monitoring units	Yes	Yes	Yes
11. Research staff must notify Facilities Branch of changes in operations which affect monitoring req.s	Yes	Yes	Yes
12. Monitoring units shall be set in sequential mode	Yes	Yes	Yes
13. Back-up stand alone monitors required in labs	Yes	No	No
14. Back-up stand alone monitors required in 17/1	Yes	No	No

† = if used with pyrophorics or in excess of 400 ft³

‡ = if cannot be sensed below the PEL

* = 5 x the TLV, 0.5 x the IDLH level, or the STEL; which ever is lower.

§ = factor of LFL, not TLV

Table 9

5.6.1. The MDA Toxic Gas Monitor

The MDA Toxic Gas Monitor has been selected as the standard, central monitoring system for toxic gas detection within NREL. It consists of a number of ports (8 to 16 depending on the unit) which pump an air sample through a specially treated tape (Chemcassette®). If there are any gases present which reacts with the treatment on the Chemcassette®, the color of the tape changes. An optical detector senses how much of that gas was in the air sample by the degree of discoloration in the Chemcassette® and print out a reading. There are three possible levels of detectable gas concentrations. There are two programmable levels at which either a high level (5.6.1.2.) or low level (5.6.1.3.) alarm is activated. The third condition exists if the concentration is below the low level alarm set point. The presence of the gas is picked up on a time weighted average which is printed out every eight hours. It should be noted that there is a lower detectable limit (LDL) that differs with each gas. This LDL affects the sensitivity of the time weighted average. See Table 4a for these detection limits.

5.6.1.1. Continuous Toxic Gas Monitoring

All areas where toxic and highly toxic gases, in any quantity, are used are continuously monitored. (Continuous monitoring is defined as a gas detection system where the analytical instrument is maintained in continuous operation and sampling is performed without interruption. That is 24 hours a day, seven days a week. Analysis may be performed on a cyclical basis at intervals not to exceed 30 minutes.)

5.6.1.2. High Level Alarm on MDA Toxic Gas Monitor

The high level alarm is programmed to activate at the lower of these values; 5 x the TLV, 0.5 x the IDLH level, or the STEL. (Note, only phosphine has a STEL established, which is 1 ppm.) Some gases (e.g. phosphine) may saturate the chemical reaction on the Chemcassette® before this high level is reached. In this case the high level set point will be the saturation level (see Section XII of the "Emergency Response Procedures to the MDA Toxic Gas Alarm"). If more than one gas is used in a laboratory, the set points is determined by the lowest levels on the correlation scale for different gas reactions with Chemcassette® (see Section XIII of the "Emergency Response Procedures to the MDA Toxic Gas Alarm").

- 5.6.1.2.1. Automatic shut down occurs only on the systems located within the laboratory with the "release", not all systems that are monitored by the same unit.
- 5.6.1.2.2. The high level alarm on the MDA activates the MDA alarm bell (very loud) located in each laboratory using toxic gases.
- 5.6.1.2.3. Flashing blue lights on the outside of each laboratory entrance are activated, see Section 5.6.1.8.
- 5.6.1.2.4. The bell is also activated outside of the HPM monitoring room.
- 5.6.1.2.5. All alarm conditions on the MDA Toxic Gas Monitors (high and low levels) activate a special low level buzzer (sonalert) in the laboratory from where the detected release occurred, in the SSO area, in the Facilities Branch area and at the guard station in building 17/1.
- 5.6.1.2.6. There is a print out the level of the detected release and the MDA point(s) registering the release at a remote printer, at the guard station in building 17/1.

5.6.1.3. Low Level Alarm on MDA Toxic Gas Monitor

The low level alarm, for all points located in ventilated spaces, the MDA is programmed to be activated at the TLV for the gas being monitored. The low level alarm, for the point monitoring the work-place ambient, is programmed to be activated at one half of the TLV for the gas being monitored. If more than one gas is used in a laboratory, the set points is determined by the lowest levels on the correlation scale for different gas reactions with Chemcassette® (see Section XIII of the "Emergency Response Procedures to the MDA Toxic Gas Alarm").

- 5.6.1.3.1. The low level alarm on the MDA must activate the MDA alarm buzzer located in the laboratory with the "release," but not initiate automatic system shut down of systems or activate the flashing blue lights outside of the laboratory entrances. This low level buzzer does not sound when there is a high level alarm.
 - 5.6.1.3.2. All alarm conditions on the MDA Toxic Gas Monitors (high and low levels) activate a special low level buzzer (sonalert) in the SSO area, in the Facilities Branch area and at the guard station in building 17/1.
 - 5.6.1.3.3. There is a print out the level of the detected release and the MDA point(s) registering the release at a remote printer, at the guard station in building 17/1.
- #### 5.6.1.4. MDA Toxic Gas Monitor Green Run Light

All laboratories using the MDA Toxic Gas Monitor have a green "run light" installed in a central location. The purpose of this light is to indicate when the MDA unit is fully operational.

- 5.6.1.4.1. This light is illuminated whenever the MDA unit monitoring that laboratory is operating properly. Because a researcher should never start a run without being monitored, all systems are powered through a drop out relay which is in turn powered by the same circuit as this run light. This means that when the run light is de-energized, the systems on that monitor are automatically put into the fail-safe mode.
 - 5.6.1.4.2. If the system is in an alarm mode or is under maintenance this light is automatically turned off. If the unit is being calibrated, the Chemcassette® is being changed, or any other type of maintenance is being performed, or if the unit is in an alarm condition, this light becomes de-energized. Because this puts the systems it is monitoring in the fail-safe mode, all researchers being monitored by a particular unit must be provided with as much notice of the time of maintenance as possible.
- #### 5.6.1.5. Standardized Location of MDA Accessories

The high level MDA alarm bell, low level MDA alarm buzzer, and the green MDA run light are centrally located, and within close proximity to one another, within each laboratory.

5.6.1.6. Location of Monitoring Points

The requirements on the number and location of the points follows. The location of the MDA Toxic Gas Monitoring points is controlled by the Facilities Branch. If a researcher would like to have a point moved to a new location, or modified in any way,

he/she must write a formal memo to the Facilities Branch, routed through the SSO, requesting approved changes.

- 5.6.1.6.1. There are at least two monitoring points in the laboratory, one in the ambient air of the work area and one in the air being exhausted from each toxic gas workstation located within the laboratory.
- 5.6.1.6.2. Ambient monitoring points are centrally located and in the vicinity of where operators are working.
- 5.6.1.6.3. Any monitoring point located in an exhaust duct is at least 8-10 duct diameters downstream of the last junction, if possible, in order to allow sufficient mixing before sampling system discharge.
- 5.6.1.6.4. If more than one system is in a laboratory and they are exhausted using different duct work, a point must be in each system enclosure or the exhaust ducts to those enclosures. Each system must be adequately monitored.

5.6.1.7. Signage/Labeling Within HPM Laboratories

It is the responsibility of the Facilities Branch to ensure that all components associated with all toxic gas monitoring are clearly identified by use of labels and/or posters. Within the laboratories the signage would include:

- 5.6.1.7.1. The flashing lights outside of the laboratory entrances are labeled as described in Sections 5.6.1.8. The reset button, inside of the laboratory, for these flashing lights must be labeled with the following information: "TOXIC GAS ALARM. FLASHING LIGHTS RESET BUTTON".
- 5.6.1.7.2. The high level audio alarms must be labeled with this information: "TOXIC GAS HIGH LEVEL ALARM! If alarm sounds, evacuate the area and call x1234". Personnel trained in the "Emergency Response Procedures to the MDA Toxic Gas Alarm" will know how to perform the additional emergency procedures.
- 5.6.1.7.3. The low level audio alarms must be labeled with this information: "TOXIC GAS LOW LEVEL ALARM! If alarm sounds evacuate area and call x1234."
- 5.6.1.7.4. The green HPM monitor "run" lights must be labeled with the following information: "TOXIC GAS MONITOR STATUS! Experiments using toxic gases can only be conducted if this light is illuminated."
- 5.6.1.7.5. Each line for a monitoring point must be numbered corresponding to the channel on the toxic gas monitoring unit which is monitoring that point. This number must be on the actual line and not on any filter or end connector.

5.6.1.8. Signage/Labeling on Flashing Lights Outside of Laboratory Entrances

Outside of each entrance to the laboratory containing toxic gases, there are flashing blue lights which indicate a high level alarm condition. This includes entrances between laboratories and to hallways.

- 5.6.1.8.1. These flashing blue lights clearly indicate that a message which reads "DANGER KEEP OUT". These lights must start flashing when a high level alarm is activated in that area.

- 5.6.1.8.2. In addition to the warning lights and the "DANGER KEEP OUT" sign, there must be a sign located nearby which conveys the following messages; "Toxic gas alarm in this laboratory. if alarm sounds and/or blue lights are flashing DO NOT ENTER. Notify emergency contacts (x1234) This alarm does not summon the fire department." This sign can be modified to reflect any other HPM gas detection alarm indicators which may be present. As a general note, these lights are activated whenever the standby generator is tested or there has been any other power outage.
- 5.6.1.8.3. All warning lights are in similar locations at each laboratory entrance and are readily noticeable. If more than one type of gas detection alarm light is present, the toxic gas alarm lights are the top most indicator if arranged in a "stack" or in the "Health Hazard" location of the safety diamond if the enunciator panel is arranged with this type of indicator.
- 5.6.1.8.4. The warning lights are triggered by suitable relays that prevent the lights from being extinguished when the alarm bells are silenced or the MDA is reset.
- 5.6.1.8.5. The lights require manual resetting from the affected area or laboratory. This includes both a reset push button located within the affected area or laboratory and a key switch located outside of the affected area or laboratory. The push button could be reset by research personnel after it has been determined that it is safe to reenter the laboratory. The key switch would allow personnel from the Facilities Branch to reset the flashing lights without reentering the laboratory. This is required when a power outage may cause the MDA units to be reset and the flashing lights become activated.

5.6.1.9. Standby Generator

MDA toxic gas monitors are on the standby generator.

5.6.1.10. Responsibility for Upkeep, Maintenance, and Calibration of Toxic Gas Monitors

The Facilities Branch personnel have sole responsibility for the day-to-day upkeep, maintenance, and calibration of the MDA units. This includes the replacing of Chemcassette® and printer tape. They also have the sole responsibility of programming the set points into the units. The maintenance requirements are logged on computer and maintenance personnel have been trained in system upkeep by the equipment manufacturer.

5.6.1.11. Responsibilities of Research Staff Requesting Changes to MDA Units

It is the responsibility of the research staff to notify the Facilities Branch and SSO of any changes in the type of toxic gas being used in their laboratory so that the MDA monitors can be set correctly. Any requests for the changing of the programming of the set points on the MDA must be in writing with specific levels for specific gases indicated. A formal memo to the Facilities Branch, routed through the SSO, must be written, requesting approved changes. Additional justification of why those gases were chosen may be required if there is a deviation from those guidelines established in Sections 5.6.1.2.-5.6.1.3. (See Appendix I1 for more information on these responsibilities.)

5.6.1.12. Programming Mode (sequential) of Monitors

When the units are programmed they shall be set in the sequential monitoring mode, as opposed to the parallel mode, for all normal operations. If a special, short-

term circumstance dictates a need for parallel mode monitoring, only a member of the Facilities Branch should re-program the machine after receiving approval from the SSO. As soon as the need for this type of monitoring is complete, the unit must be returned to its normal sequential mode. (Note: When changing from sequential to parallel, the Facilities Branch representative must verify proper parallel flow balancing.)

5.6.1.13. Back-up Stand Alone Monitors Required in Toxic Gas Laboratories

It is required that all laboratories, which are being monitored by the MDA Toxic Gas Monitor, have a stand alone monitor readily accessible. The only requirements on this monitor are that it be sensitive to the toxic gases present in that particular laboratory and that it has real time detection capabilities (e.g. MDA TLD-1 or Matheson Hand Held Detector). The purpose of this detector is not to be a substitute for the MDA units, but rather for use in special circumstances. For instance, if during a run the MDA is shut down for a short period of time, this monitor could be used so that the run may continue. Another example would be if portable detection is necessary in order to find a leak (of course SCBA would be worn).

5.6.1.14. Back-up Stand Alone Monitor Required at Reception Desk in 17/1

Additionally, at least one stand alone monitor and support supplies (e.g. chemical keys, Chemcassettes®, etc.) must be kept in the area of the remote printer (Building 17 Guard Station); a building where there are no HPMs. If one type of monitor detects all the types of toxic gases at NREL, no additional detectors are necessary. However, the capability to detect all of the toxic and highly toxic gases is needed. This monitor(s) would be used in after hours emergency responses when back-up or additional monitoring capabilities are needed.

5.6.2. Hydrogen Monitoring

As an added safety measure, flammable gas detection is required within each laboratory where both flammable gases and pyrophoric materials are used at the same time or where flammable gases are used in excess of 400 ft³.

As of the writing of this SAR the only laboratories affected by this requirement are those using MOCVD systems where both hydrogen and pyrophoric materials are used in the same laboratory. All laboratories using other flammable gases (i.e. methane) do not use appreciable quantities; and therefore, this requirement is written specifically for hydrogen detection. However, if other flammable gases are put into use which would be subject to these monitoring requirements, all the points listed in this section for hydrogen monitoring must be employed for those gases as well.

This over-engineered system is proposed primarily to reduce the combined risk of hydrogen as a fuel and small quantities of pyrophoric materials as an ignition source within some of the toxic gas laboratories.

At this time, NREL has not installed a standard, centralized monitor for hydrogen detection. If all engineering and administrative controls are ready to receive an ORR, except the installation of this monitoring system, the researcher may request a variance to the centralized hydrogen monitor based on an equivalency. Said researcher must adequately show that the intent of this requirement, if not the letter, is met by a local hydrogen monitor within the laboratory. However, once the centralized unit is put on-line, such systems must utilize this system and comply with this SAR with regard to hydrogen monitoring. The hydrogen monitor is chosen is an MDA unit and is compatible with existing equipment. It is to be installed the HPM monitoring facility (16/323) and meets the following requirements.

5.6.2.1. Continuous Hydrogen Monitoring

Continuous hydrogen detection is required within all laboratories where both hydrogen and pyrophoric materials are used at the same time or where hydrogen is used in excess of 400 ft³. (Continuous monitoring is defined as a gas detection system where the analytical instrument is maintained in continuous operation and sampling is performed without interruption. That is 24 hours a day, seven days a week. Analysis may be performed on a cyclical basis at intervals not to exceed 30 minutes.)

5.6.2.2. Hydrogen Alarm

The hydrogen alarm is programmed to be activated at a detected hydrogen concentration of 20% of the lower flammability limit (LFL) which is 4% for hydrogen. The following occurs when a the hydrogen alarm is activated.

- 5.6.2.2.1. Automatic shut down occurs only on the systems located within the laboratory with the "release", not all systems that are monitored by the same unit.
- 5.6.2.2.2. The hydrogen alarm must activate the hydrogen alarm bell located in each laboratory using hydrogen monitor.
- 5.6.2.2.3. Flashing red lights on the outside of each laboratory entrance are activated.
- 5.6.2.2.4. The bell is also activated outside of the HPM monitoring room.
- 5.6.2.2.5. The alarm on hydrogen monitors activates a special low level buzzer in the SSO area.
- 5.6.2.2.6. There is a print out of the detected release and the hydrogen detector registering the release at a remote printer, at the guard station in 17/1.

5.6.2.3. Standardized Location of Alarm

The hydrogen alarm bell is centrally located within each laboratory.

5.6.2.4. Location of Monitoring Points

The requirements on the number and location of the points follows. The locations of the hydrogen monitoring points are controlled by the Facilities Branch. If a researcher would like to have a point moved to a new location, or modified in any way, he/she must write a formal memo to the Facilities Branch, routed through the SSO, requesting approved changes.

- 5.6.2.4.1. There must be at least two monitoring points in each laboratory using hydrogen, one at the hydrogen cylinder(s) location and one in the exhaust duct at a point which is downstream from all system components containing hydrogen.
- 5.6.2.4.2. Ambient monitoring points must be centrally located and in the vicinity of where operators are working.
- 5.6.2.4.3. Any point located in an exhaust duct must be at least 8-10 duct diameters downstream of the last junction if possible in order to allow sufficient mixing before sampling system discharge.

- 5.6.2.4.4. If more than one system is in a laboratory and they are exhausted using different duct work, a point must be in each of the system enclosures or the exhaust ducts to those enclosures.

5.6.2.5. Signage/Labeling Within HPM Laboratories

It is the responsibility of the Facilities Branch to ensure that all components associated with all hydrogen monitor alarms are clearly identified by use of labels and/or posters. Within the laboratories the signage would include:

- 5.6.2.5.1. The flashing lights outside of the laboratory entrances are labeled as described in Sections 5.6.2.6. The reset button for these flashing lights must be labeled with the following information: "HYDROGEN ALARM. FLASHING LIGHTS RESET BUTTON".
- 5.6.2.5.2. The high level audio alarms must be labeled with this information: "HYDROGEN ALARM! If alarm sounds, evacuate the area and call x1234". Personnel trained in the "Emergency Response Procedures to the MDA Toxic Gas Alarm" know how to perform the additional emergency procedures.
- 5.6.2.5.3. Each line for a monitoring point is numbered corresponding to the channel on the hydrogen monitoring unit which is monitoring that point. This number should be on the actual sample head.

5.6.2.6. Signage/Labeling on Flashing Lights Outside of Laboratory Entrances

Outside of each entrance to the area containing hydrogen, there must be flashing red lights which indicate an alarm condition. This includes entrances between laboratories and to hallways.

- 5.6.2.6.1. These flashing red lights clearly indicate a message which reads "DANGER KEEP OUT". These lights must flash when a hydrogen alarm is activated in that area.
- 5.6.2.6.2. In addition to the warning lights and the "DANGER KEEP OUT" sign, there must be a sign located nearby which conveys the following messages; "Hydrogen alarm in this laboratory. if alarm sounds and/or red lights are flashing DO NOT ENTER. Notify emergency contacts (x1234) This alarm does not summon the fire department." This sign can be modified to reflect any other HPM gas detection alarm indicators which may be present.
- 5.6.2.6.3. All warning lights are in similar locations at each laboratory entrance and are readily noticeable. If more than one type of gas detection alarm light is present, the hydrogen alarm lights are the second from the top indicator if arranged in a "stack" or in the "Fire Hazard" location of the safety diamond if the enunciator panel is arranged with this type of indicator.
- 5.6.2.6.4. The warning lights are triggered by suitable relays that prevent the lights from being extinguished when the alarm bells are silenced or the hydrogen monitor is reset.
- 5.6.2.6.5. The lights require manual resetting from within the affected area or laboratory.
- 5.6.2.7. Standby Generator

Hydrogen monitors must be on the standby generator.

5.6.2.8. Responsibility for Upkeep, Maintenance, and Calibration of Hydrogen Monitors

The Facilities Branch personnel have sole responsibility for the day-to-day upkeep, maintenance, and calibration of the hydrogen detection units. This includes the replacing of electrodes and printer tape. They also have the sole responsibility of programming the set points into the units. The maintenance requirements are logged on computer and maintenance personnel have been trained in system upkeep by the equipment manufacturer.

5.6.2.9. Responsibilities of Researcher Staff Requesting Changes to Hydrogen Monitors

It is the responsibility of the research staff to notify the Facilities Branch and SSO of any changes in the type of flammable gases being used in their laboratory so that additional flammable monitors can be obtained if necessary. Any requests for the changing of the programming of the set points on the hydrogen monitor must be in writing with specific levels indicated. A formal memo to the Facilities Branch, routed through the SSO, must be written, requesting approved changes.

5.6.2.10. Programming Mode (sequential) of Monitors

When the units are programmed they shall be set in the sequential monitoring mode, as opposed to the parallel mode, for all normal operations. If a special, short-term circumstance dictates a need for parallel mode monitoring, only a member of the Facilities Branch should re-program the machine after receiving approval from the SSO. As soon as the need for this type of monitoring is complete, the unit should be returned to its normal sequential mode. (Note: When changing from sequential to parallel, the Facilities Branch representative must verify proper parallel flow balancing.)

5.6.3. Corrosive Gas Monitoring

Gas detection is required for HPM gases where the physiological warning properties for the gas are at a higher level than the permissible exposure limit (PEL) for the gas: UFC Section 51.105(e)3. This is not the case for hydrogen chloride, but is true for hydrogen fluoride; and therefore tungsten hexafluoride which is monitored by looking for hydrogen fluoride.

At this time, NREL has not chosen a standard, centralized monitor for corrosive gas detection. When one is chosen and purchased it is located in the HPM monitoring facility (3rd floor electrical room). The one that is chosen must be capable of meeting the following requirements.

5.6.3.1. Continuous Corrosive Gas Monitoring

All laboratories where corrosive HPM gases are used where the physiological warning properties for the gas are at a higher level than the PEL, must be continuously monitored. (Continuous monitoring is defined as a gas detection system where the analytical instrument is maintained in continuous operation and sampling is performed without interruption. That is 24 hours a day, seven days a week. Analysis may be performed on a cyclical basis at intervals not to exceed 30 minutes.)

5.6.3.2. Corrosive Gas Alarm

The alarm on the corrosive gas monitor, for points located in ventilated spaces, is activated at the TLV for the particular corrosive gas being monitored. The point monitoring the work place ambient for corrosive gases is programmed to alarm at one half the TLV for that gas.

The following occurs when a corrosive gas alarm is activated.

- 5.6.3.2.1. Automatic shut down occurs only on the systems located within the laboratory with the "release", not all systems that are monitored by the same unit.
 - 5.6.3.2.2. The corrosive gas alarm activates the corrosive gas alarm bell (very loud) located in each laboratory using corrosive gases.
 - 5.6.3.2.3. Flashing yellow lights on the outside of each laboratory entrance is activated, see Section 5.6.3.6.
 - 5.6.3.2.4. The bell is also activated outside of the HPM monitoring room.
 - 5.6.3.2.5. All alarm conditions on the corrosive gas monitors activate a special low level buzzer in the SSO area.
 - 5.6.3.2.6. There is a print out of the detected release and the corrosive gas detector registering the release at a remote printer, at the guard station in 17/1.
- 5.6.3.3. Standardized Location of Alarm

The corrosive gas alarm bell is centrally located within the laboratories.

5.6.3.4. Location of Monitoring Points

The requirements on the number and location of the points follows. The locations of the corrosive monitoring points are controlled by the Facilities Branch. If a researcher would like to have a point moved to a new location, or modified in any way, he/she must write a formal memo to the Facilities Branch, routed through the SSO, requesting approved changes.

- 5.6.3.4.1. There must be at least two monitoring points in the laboratory, one in the ambient air of the work area and one in the air being exhausted from each corrosive gas workstation located within the laboratory.
 - 5.6.3.4.2. Ambient monitoring points must be centrally located and in the vicinity of where operators are working.
 - 5.6.3.4.3. Any point located in an exhaust duct must be at least 8-10 duct diameters downstream of the last junction if possible in order to allow sufficient mixing before sampling system discharge.
 - 5.6.3.4.4. If more than one system is in a laboratory and they are exhausted using different duct work, a point must be in each of the system enclosures or the exhaust ducts to those enclosures.
- 5.6.3.5. Signage/Labeling Within HPM Laboratories

It is the responsibility of the Facilities Branch to ensure that all components associated with all corrosive gas alarms are clearly identified by use of labels and/or posters. Within the laboratories the signage would include:

- 5.6.3.5.1. The flashing lights outside of the laboratory entrances are labeled as described in Section 5.6.3.6. The reset button for these flashing lights must be labeled with the following information: "CORROSIVE GAS ALARM, FLASHING LIGHTS RESET BUTTON".

- 5.6.3.5.2. The high level audio alarms must be labeled with this information: "CORROSIVE GAS ALARM! If alarm sounds, evacuate the area and call x1234". Personnel trained in the "Emergency Response Procedures to the MDA Toxic Gas Alarm" will know how to perform the additional emergency procedures.
- 5.6.3.5.3. Each line for a monitoring point must be numbered corresponding to the channel on the HPM monitoring unit which is monitoring that point. This number must be on the actual line and not on any filter or end connector.
- 5.6.3.6. Signage/Labeling on Flashing Lights Outside of Laboratory Entrances
- Outside of each entrance to the laboratory containing corrosive gases, there must be flashing yellow lights which indicate a corrosive gas alarm condition. This includes entrances between laboratories and to hallways.
- 5.6.3.6.1. These flashing yellow lights clearly indicate that a message which reads "DANGER KEEP OUT". These lights must start flashing when a corrosive gas alarm is activated in that area.
- 5.6.3.6.2. In addition to the warning lights and the "DANGER KEEP OUT" sign, there must be a sign located nearby which conveys the following messages; "Corrosive gas alarm in this laboratory, if alarm sounds or yellow lights are flashing DO NOT ENTER. Notify emergency contacts (x1234) This alarm does not summon the fire department." This sign can be modified to reflect any other HPM gas detection alarm indicators which may be present.
- 5.6.3.6.3. All warning lights must be in similar locations at each laboratory entrance and be readily noticeable. Corrosive gas alarm lights must be located below any other gas alarm lights which might be present if arranged in a "stack" or in the "reactivity" location of the safety diamond if the enunciator panel is arranged with this type of indicator.
- 5.6.3.6.4. The warning lights must be triggered by suitable relays that prevent the lights from being extinguished when the alarm bells are silenced or the corrosive gas monitor is reset.
- 5.6.3.6.5. The lights require manual resetting from within the affected area or laboratory.
- 5.6.3.7. Standby Generator
- The corrosive gas monitors must be on the standby generator.
- 5.6.3.8. Responsibility for Upkeep, Maintenance, and Calibration of Corrosive Gas Monitors

The Facilities Branch personnel have sole responsibility for the day-to-day upkeep, maintenance, and calibration of the corrosive gas monitoring units. This includes the replacing of Chemcassette® or electrodes, and printer tape. They also have the sole responsibility of programming the set points into the units. The maintenance requirements are logged on the computer and maintenance personnel have been trained in system upkeep by the equipment manufacturer.

5.6.3.9. Responsibilities of Research Staff Requesting Changes to Corrosive Gas Monitoring

It is the responsibility of the research staff to notify the Facilities Branch and SSO of any changes in the type of corrosive gas being used in their laboratory so that the corrosive gas monitors can be set correctly. Any requests for the changing of the set points on the corrosive gas monitors must be in writing with specific levels for specific gases indicated.

5.6.3.10. Programming Mode (sequential) of Monitors

When the units are programmed they shall be set in the sequential monitoring mode, as opposed to the parallel mode, for all normal operations. If a special, short-term circumstance dictates a need for parallel mode monitoring, only a member of the Facilities Branch should re-program the machine after receiving approval from the SSO. As soon as the need for this type of monitoring is complete, the unit should be returned to its normal sequential mode. (Note: When changing from sequential to parallel, the Facilities Branch representative must verify proper parallel flow balancing.)

5.6.4. HPM Monitoring Room/Facilities

The HPM monitoring facility for Building 16 is located on the third floor, in the center area (16/323). It currently contains all MDA toxic gas monitors and will contain the hydrogen and corrosive gas monitors. This facility must meet the following criteria.

- 5.6.4.1. The MDA units, flammable gas monitors, and corrosive gas monitors are centrally located with respect to those areas being monitored (≤ 250 ft).
- 5.6.4.2. Both the flammable and corrosive gas monitors should be from the same manufacturer (MDA), or be completely compatible with the toxic gas monitors, in order to ensure familiarity and standardization of monitoring systems.
- 5.6.4.3. The HPM monitoring facilities are provided with emergency lighting, in accordance with NFPA 70-12 and others.
- 5.6.4.4. The HPM monitoring facilities are provided with a telephone.

5.6.5. Emergency Response Team (ERT) Stations

The Institute Emergency Response Team is trained to respond in the case of a variety of emergency situations. In order that there be adequate equipment readily available to them, at all times, ERT stations are fully equipped at all times. The following items are included in these stations.

- 5.6.5.1. ERT stations must be equipped with a minimum of two self contained breathing apparatus (SCBA).
 - 5.6.5.1.1. These SCBA units are fully charged at all times and have all of the necessary attachments kept with the cylinders.
 - 5.6.5.1.2. Control of these units are managed by the SSO. Any use of a SCBA unit is reported immediately to SSO personnel.
 - 5.6.5.1.3. Only in an actual emergency, or with express permission from SSO, should SCBA gear be used from the central location on each floor. For routine

maintenance purposes (such as changing gas cylinders) SCBA equipment should be obtained from the SSO Personnel.

- 5.6.5.2. ERT stations must be equipped with appropriate spill control equipment for the area in which it is located.
- 5.6.5.3. ERT stations must be equipped with at least one fire extinguisher, more if different classes of extinguishers are required for that area.
- 5.6.5.4. ERT stations must be equipped with appropriate personal protective clothing and gloves for the area in which it is located (e.g. fire resistant for handling pyrophoric liquid spills, etc.).
- 5.6.5.5. ERT stations must be centrally located in Building 16; as well as, one such station located in building 17 for use in catastrophic or after hour emergency response situations.

5.6.6. Oxygen Availability

Some of the toxic gases, such as arsine, are hemolytic agents. Because of this, there must be a readily available supply of breathing oxygen kept in the SSO area. If someone has been exposed to a toxic gas that person should be put on oxygen, if it is practical to do so, before emergency personnel arrive to transport that person to a hospital facilities. Oxygen should only be administered by qualified SSO personnel.

5.7. Environmental Protection

There are a variety of engineering controls, administrative policies and procedures, and equipment requirements defined in this document. Many of these requirements have the protection of the environment as their top priority. Others have environmental protection as a coequal priority with safety and health considerations. Because the requirements which deal with environmental issues are interspersed through out the document, the major ones have been collected in this Section.

5.7.1. Transportation

In order to ensure that hazardous materials are not released into the work place or the environment, secondary containment is used to transport HPM containers between laboratories or buildings. A portable monitor, capable of monitoring for the material being transported, is used when transporting all highly toxic HPMs and hydrogen. See Section 5.5.4. for more details on the transportation requirements for HPMs.

5.7.2. Work Place Monitoring

In order to ensure a safe work environment for all NREL personnel, continuous gas detection is required within laboratories using hazardous gases. All laboratories using toxic or highly toxic gases are monitored for those gases, using a central monitoring system (see Section 5.6.1). All laboratories using flammable gases in excess of 400 ft³ or laboratories using both pyrophoric materials and flammable gases are monitored for those gases, using a central monitoring system (see Section 5.6.2). All laboratories using corrosive gases, where the physiological warning properties for the gas are at a higher level than the PEL for the gas, are monitored for those gases, using a central monitoring system (see Section 5.6.3). (Continuous gas detection is defined as a monitoring system where the analytical instrument is maintained in continuous operation, and sampling is performed without interruption (i.e., 24 hours a

day, seven days a week}. Analysis may be performed on a cyclical basis, at intervals not to exceed 30 minutes.)

5.7.3. Safety Interlocks

These systems employ a variety of engineering controls which minimize the chance of a harmful accident by sensing abnormal conditions in the primary system(s) and triggering a fail-safe mode. This mode can be activated by a safety interlock, a deliberate shutoff of the system, or a power failure and requires a manual reset by the operator in order to resume operations. Sensors that monitor anomalous conditions within a hazardous production system are required as a redundant control to prevent the release or potential for release of hazardous materials into the environment.

All interlocks which are critical to the safety of the system or the protection of the environment initiate automatic shut down of the system - putting it into the fail-safe mode - and activate both an audible and a visual alarm. Some common interlocks include; toxic gas alarm, hydrogen alarm, reactor over-pressure, loss of critical nontoxic gas flows, over-pressure at effluent removal system inlet, or other anomalous scrubber conditions. See Section 5.4.7. for more details.

5.7.4. Effluent Removal

Toxic gases and hazardous reaction products of toxic gases must not be expelled into the environment under any normal operating processes. These materials are known as process effluents. Effluents are those process materials which flow from the system reactor, under normal operating conditions. These materials are generally considered waste products and are treated. (The word effluent is not considered to be the flow of HPM in an episodic or catastrophic release from the system or source. Such a release is covered in the next section.) An approved (by the SSO) type of effluent removal system (liquid scrubber, burn box - plus, or adsorption bed with controlled oxidation) is required to remove HPM from normal operation effluent streams (see Section 5.4.5.).

Waste materials generated by effluent removal systems (charcoal canisters or drums, HEPA filters, scrubber solutions, etc.) are disposed of as hazardous waste through the SSO. See Section 5.4.5.7. for documentation requirements and Section 5.5.6.1. for Administrative Controls.

5.7.5. Waste Disposal

There are a variety of process wastes produced in the handling of HPMs. These could include wastes from effluent removal systems, residual material in reactors, purifiers, system components, etc. None of this material can be disposed of by merely having it hauled away with the trash. The following procedures must be followed when hazardous wastes are generated (see Section 5.5.6.1.):

The SSO is notified when hazardous waste has been generated or collected and they indicate what procedure to follow when disposing of this waste. In most cases they will pick up the container(s) and dispose of them through a certified disposal agency.

It is up to the individual generating toxic, poisonous, or hazardous wastes to ensure that its disposal complies with NREL, local, state, and Federal waste disposal laws. Therefore, researchers who generate waste products or by-products which are of unsafe or of unknown health risk, must keep in close contact with the SSO.

5.7.6. Catastrophic Release Controls

As per UFC Article 80 Section 304.6.D.iv., the maximum allowable discharge concentration of HPM gases, at the point of discharge, must not exceed one-half the IDLH level for a specific material. A mix of the following options (varying for each laboratory) is used to meet this requirement. See Section 5.4.6.15 for more details about

1) Ventilation dilution is employed where there is enough exhaust flow to adequately dilute the entire source at the specified release rate.

2) If the exhaust ventilation flow is too low to sufficiently dilute the HPM gases, an approved type of treatment system is employed. Such treatment systems include exhaust ventilation scrubbers or scram units (Appendix M7) installed on the toxic gas lines.

3) An alternative to the treatment systems is to use these gases with the cylinder valve closed at all times. This necessarily implies that all runs are conducted with only the gas remaining in regulator and line. The engineering controls associated with this option are that all such cylinders must be supplied with pneumatically operated cylinder valves that are controlled by a circuit to allow only momentary operation (not to exceed a 10-second open period per valve operation).

5.7.7. Accidental Releases to Environment

The SSO is responsible for reporting an accidental release in excess of the CERCLA RQ to the National Response Center, Washington, D.C. (see Section 4.1.4.); The Local Emergency Planning Commission (Jefferson County); State Health Department; State Emergency Planning Commission; DOE Chicago and DOE Headquarters. Additionally, any releases into the domestic sewer would be reported to the Pleasantview Sanitation District.

6. ACCIDENT RISK ANALYSIS

6.1. Introduction

In this section, risk is technically defined as the possibility of suffering harm from a hazard. A complete technical analysis of risk describes (1) a hazard, that is, a dangerous substance or action that can cause harm to life, environment or property; (2) the event or events (also known as transients) that create the possibility of harm; and, (3) an estimate of the likelihood that the harm will occur. In Fig. 13, a conceptual framework is given for combining these data into a coherent technical analysis. An event is defined as an occurrence involving equipment performance or human action, or an occurrence external to a system that causes system upset.

Fig. 13

A risk analysis can range from a simple qualitative description of the risk to a full blown quantitative probabilistic risk assessment like those conducted for nuclear power plants. The different types of analyses available are described elsewhere (e.g., [12], [13]). The effort to produce these analyses can range from minutes for the first type of

approach to many man-years for the later alternative. In practice, the level-of-effort required for any risk analysis increases as the risk increases; the larger the risk (perceived or actual) the more comprehensive the analysis should be. Often, these types of analyses are conducted in a step-wise fashion. That is, simple analyses are first prepared. If the risks are deemed important enough, more sophisticated analyses are then prepared.

In this SAR, a semi-quantitative risk analysis is presented because of the small scale of the R&D activities and because of the dynamic nature of the programs. The approach draws in part on a framework described elsewhere [14]. The primary accidents or transients examined were identified by staff from NREL and BNL based on their past experiences and knowledge, and the published literature.

To develop estimates of event probabilities for these accidents, NREL and industry experiences and failure rate data (see Appendix A1) were used. Event probabilities are divided into six different classes: Impossible, Extremely Remote, Remote, Occasional, Reasonably Probable, and Frequent. More descriptive information on each of the classes is given in Table 10 [15]. In these assignments, it is recognized that failure of individual components in isolation may not result in the accidental release of a hazardous material. Often a release may occur only after a series of components fail. Therefore, the probability estimates provided here are conservative; that is, they likely overestimate the occurrence of the identified accident.

EVENT PROBABILITY CLASSIFICATION TABLE

PROBABILITY (Probability that the potential consequence occurs.)		
LEVEL	ANNUAL PROBABILITY	POTENTIAL CONSEQUENCES
A	Frequent >1.0	Likely to occur many times during the life cycle of the system (test/activity/operation).
B	Reasonably Probable 1.0 to 10^{-1}	Likely to occur several times during the life cycle of the system.
C	Occasional 10^{-2} to 10^{-1}	Likely to occur sometime during the life cycle of the system.
D	Remote 10^{-4} to 10^{-2}	Not likely to occur in the life cycle of the system, but possible.
E	Extremely Remote 10^{-6} to 10^{-4}	Probability of occurrence cannot be distinguished from zero.
F	Impossible $< 10^{-6}$	Physically impossible to occur.

Table 10

In a similar way, hazards or consequences are divided into four different classes (see Table 11 [15]): Negligible, Marginal, Critical, and Catastrophic. Estimates of potential consequences were based on past experiences, published literature, and more detailed numeric calculations (see Appendix A2). In these calculations, it has been assumed that the defined transient occurs in the absence of other passive or active hazard management control systems. For example, a leak in a hydrogen selenide gas cylinder fitting during cylinder change-out could present very serious hazards to health if the change-out team is not using self contained breathing apparatus. In reality, and as discussed below, multiple active and passive controls exist. Consequently, the

consequence estimates will almost always be conservative; that is they will overestimate the potential hazard.

HAZARD (CONSEQUENCE) CLASSIFICATION TABLE

CONSEQUENCE		
CATEGORY	DESCRIPTION (EST. \$ LOST)	POTENTIAL CONSEQUENCES
I	Catastrophic (equip. loss > \$10 ⁶)	May cause death or system loss.
II	Critical (\$10 ⁵ to \$10 ⁶)	May cause sever injury or occupational illness, or minor system damage.
III	Marginal (\$10 ⁴ to \$10 ⁵)	May cause minor injury or occupational illness, or minor system damage.
IV	Negligible (< \$10,000)	Will not result in injury, occupational illness, or system damage.

Table 11

In Fig. 14 [15], a matrix is presented that combines probability and consequence into a semi-quantitative measure of risk. These are then divided into four final classes: Routine Risk, Low Risk, Moderate Risk, and High Risk. Events classified as "Routine Risk" are no different from those experienced by any individual in his or her daily life. "Low Risk" events are those that may have an impact within a facility and little or no impact to adjacent facilities or to health or the environment. "Moderate Risk" events are those that present considerable potential impacts within the facility or to people or the environment, but at most only minor impacts off site. "High Risk" events are those with the potential for on-site and off-site impacts to large numbers of persons or for major impacts to the environment. In this analysis, risk for each event was defined using Fig. 14 based on the previously assigned classifications for Probability and Consequence. Although it is still difficult to evaluate the acceptability of any option, it is clear that the need for additional controls increases, and the possible acceptability of any option declines, as the risk increases.

Fig. 14

6.2. Procurement/Transportation

6.2.1. Purchasing

6.2.1.1. Transient: Quantity in Excess of B-2 Occupancy Ordered

Accident Description: Receipt of Excessive Quantity of Hazardous or Toxic Material

Probability - Occasional

This event is due to mechanical failure of a cylinder or valve and the valve cap. Mishandling during loading, or an accident during shipping or off-loading at the receiving dock are examples of the initiating events associated with this accident. As with most other transients described below, the probability of this transient occurring is based on multiple events, i.e., accident occurring and cylinder integrity breaching. The probability of an accident occurring due to mishandling has not been estimated, but should be very small because of the use of NREL employees who are trained and equipped to handle and transport these materials.

Although there are no numeric data readily available to support this evaluation, this event is likely to occur sometime in the lifetime of the system (assumed here for this accident and all others to be three years), because of the large number of individuals involved, and lack of institutional control over some key personnel (i.e., vendor and shipper). As shown in Appendix A1, Table A12, the general rate of human error of commission (e.g., misreading a label) is about 10^{-3} per demand.

Consequence - Negligible

Receipt at the shipping dock of an excessive quantity of hazardous or toxic material, by itself will not result in injury, occupational illness or system damage. Damage to life or property can only arise at a later stage in the material's handling life cycle at NREL. Even in these situations, multiple events must simultaneously occur for damage to arise, (e.g., excessive inventory and leak in a gas cabinet.) Hence, the consequences of this transient alone are negligible.

Risk - Routine (See Fig. 14)

Controls:

See Section 5.5.3..

6.2.2. Receipt

6.2.2.1. Transient: Leak in Cylinder

Accident Description: Leaking Cylinder.

Probability - Remote

This event is due to mechanical failure of a cylinder, gross mishandling during loading/off-loading, or an accident during shipping are examples of the initiating events associated with this accident. The probability of an accident occurring due to mishandling has not been estimated, but is expected to be remote because of the high-level of knowledge of handling of the materials by the vendors, contract carriers, and NREL personnel.

On average, it can be crudely estimated that there are 340 accidents per 100 million miles traveled, for the vehicle transporting these materials from the point of production to the FTLB. If we assume for discussion purposes that there are a total of 100 cylinder shipments to NREL and that each shipment involves a one-way distance of 100 miles, we calculate that the probability of an accident occurring is:

$$100 \text{ vehicle miles/shipment} \times 100 \text{ shipments} \times 340 \text{ accidents}/10^8 \text{ vehicle miles} = 0.00034 \text{ accidents [16].}$$

Loosely translated this suggests that this event is not likely to occur in the life cycle of the system, but is possible. Furthermore, the probability of this accident occurring is likely to be much smaller than the calculation suggests because of the added need to breach the integrity of the gas cylinder which is not evaluated here.

Consequence - Critical

Leaking of a full or "empty" compressed gas cylinder after off-loading at the FTLB, may result in death or severe injury; potential consequences are, therefore, determined to be critical. In the literature, there is at least one example of such an event occurring from the shipment of an "empty" cylinder of arsine [17]. After off-loading, all cylinders are inspected according to OSHA, DOT and NREL guidelines. Hence, if a leak was initiated at the loading dock or remained undetected, the effects could be marginal.

Risk - Low (See Fig. 14)

Controls:

Each cylinder is inspected before receipt for leaks; both visually and with a portable leak detector. Any cylinder which, for any reason, is suspected of leaking will not be accepted by NREL personnel. This ensures that the supplier still has responsibility for the cylinder and must take immediate action. Once the cylinder has been received by NREL personnel, it is placed in secondary containment for transport to the appropriate location. The secondary containment is equipped with a visual indicator (pressure gauge) should a leak develop while in transport. In this case the secondary containment would not be opened and Emergency Notification System would be activated. The use of secondary containment ensures that the contents of the cylinder is not vented into the unventilated space of a delivery truck and thus significantly reduces the potential consequences of having a leaking cylinder.

6.2.3. Transportation on Public Roads (FTLB to Building 16)

6.2.3.1. Transient: Intra-Laboratory Transportation Accident

Accident Description: Rupture cylinder/container

Probability - Extremely Remote

Similar to Accident 6.2.2.1., this event is due to mechanical failure of a cylinder or valve and the valve cap. Mishandling during loading, or an accident during shipping or off-loading at the receiving dock are examples of the initiating events associated with this accident. As with most other transients described below, the probability of this transient occurring is based on multiple events, i.e., accident occurring and cylinder integrity breaching. The probability of an accident occurring due to mishandling has not been estimated, but should be very small because of the use of NREL employees who are trained and equipped to handle and transport these materials. In parallel with the previous discussion (6.2.2.1.), we can crudely estimate the probability of an accident occurring in the transport of the cylinder from the FTLB to Building 16. In these calculations we assume for discussion purposes that there are a total of 100 cylinder shipments to NREL and that each shipment involves a one-way distance of 1 mile. Based on these assumptions, we calculate that the probability of an accident occurring is:

$1 \text{ vehicle mile/shipment} \times 100 \text{ shipments} \times 340 \text{ accidents}/10^8 \text{ vehicle miles} = 0.00034 \text{ accidents [16].}$

Loosely translated this suggests that this event is not likely to occur in the life cycle of the system, but is possible. Furthermore, the probability of the defined accident occurring (i.e., leak of cylinder) is likely to be significantly less than that calculated because of the combined need to breach the integrity of the double containment system which is not evaluated here. For these reasons, we believe that the possibility of this accident occurring is extremely remote.

Consequence - Marginal

Leaking of a full or "empty" compressed gas cylinder within the enclosed and unventilated space of a delivery truck may result in death or severe injury. However, because all cylinders are transported for a very short distance, it is not likely that gases will build to concentrations as high as described in the previous accident (6.2.2.1.). Consequently, the consequences of this event are marginal.

Risk - Routine (See Fig. 14)

Controls:

In addition to those controls listed for Transient 6.2.2.1 (the inspection of cylinders previous to receipt with portable gas detectors and the use of secondary containment), all cylinder shipments must conform with DOT regulations (Section 4.1.6.) and all Shipping and Receiving personnel must be properly trained (Section 5.5.5.). In general terms, the requirements of the DOT include placarding of vehicles, documentation of shipments, and emergency response procedures.

6.3. Installation of Hazardous Production Materials

6.3.1. Gas Cylinder Change-Out

6.3.1.1. Transient: Cross-threading of Valve CGA Fitting and Failure of Helium Leak Check

Accident Description: Leak at time of cylinder change

Probability - Extremely Remote

In the preparation of this SAR, gas vendors were contacted and asked about the observed rate of return of gas cylinders due to cross-threading. Jim Mayer of Linde, Dallas [18], indicated that they had processed more than 500 cylinders per month for the last five years, using stainless steel CGA connections, and have not had any cylinders returned that had clearly been cross-threaded. One cylinder was returned with some thread damage, but he was not sure of how the threads were damaged. "{Cross-threading} is just not a problem of any consequence in this industry, especially for stainless steel 350 CGA connectors." Based on these empirical data, we believe that this occurrence is not likely to occur in the life cycle of the system, but is possible. In addition, for this accident to occur, not only must the valve be cross-threaded during cylinder change-out, but the operator must fail to helium check the connection. Due to the combined set of events which must occur, the overall probability of this event is further reduced to extremely remote.

Consequence - Marginal

The leakage rate in this transient depends on the pressure in the cylinder and the opening of the built-in flow restrictor. A fully opened valve on a hydrogen selenide cylinder at 125-150 psi, equipped with a 7 mil flow restrictor, will release gas at maximum flow rate of 1.15 slpm. Assuming leakage into the gas cabinet at a rate of one tenth of the maximum flow due to the fact that the cylinder could be near empty and connected to the gas handling system, we calculated (Equation 2b, Table A2-3, Appendix A2) that hydrogen selenide concentrations of 20-40 ppm could build-up within a purged cabinet (the IDLH for H₂Se is 2 ppm. A release of arsine from a 205 psi cylinder, through a 6 mil orifice, would release gas at a maximum flow rate of 1.7 slpm; leakage of one tenth of this mass would generate concentrations of 23-50 ppm in the cabinet (IDLH=6 ppm). For phosphine releases, under the same assumptions, the maximum flow is 6.9 slpm and the concentration would build to 100-200 ppm which is at or below the IDLH level of 200 ppm. Even though the concentrations of arsine and hydrogen selenide exceed the IDLH, the consequences are only marginal because they occur outside the occupied work space. In the external environment, these materials are further diluted to safe levels by atmospheric dispersion processes.

Risk - Routine (See Fig. 14)

Controls:

SCBA are worn during toxic cylinder changes. The SCBA provides the operator's first line of control. The operator should be able to stop or at least minimize gas releases manually.

Training of personnel in this procedure will minimize chance of failure and enhance reaction to failure. All SOPs include a cylinder change-out check list to be followed during this procedure. Two operators for change-out of toxic cylinders ensures backup control and assistance.

Limited material quantity coupled with standard flow limiting orifices will reduce the amount and rate of release of compressed gases. A release in this scenario would take place within a ventilated gas cabinet. All gases except arsine and hydrogen selenide would conform to the 1/2 IDLH release limit. For those cylinders not able to conform to the 1/2 IDLH release limit or are pyrophoric, one of two additional controls is required: 1) positive cylinder valve control is interlocked to toxic gas monitor; or 2) gas cabinet exhaust scrubber must be present.

Nontoxic flammable gases present only standard compressed gas and fire hazards. All gas cabinets containing flammable gases are sprinkled.

6.3.1.2. Transient: Missing Washer in HCl or H₂Se Cylinder

Accident Description: Leak at time of Charging

Probability -Remote

This event is due to human or operator error introduced by the cylinder change-out team in NREL. As shown in Appendix A1, Fig. A1, human error was responsible for about 20% of the 100 major incidents analyzed by Marsh and McLenn Protection Consultants [16]. Human error can be an important event initiator. In this accident, not only must the operator fail to install a washer, but the change-out team must also fail to helium check the system. The probability of this type of error occurring cannot be now defined in strict numeric terms. Because cylinder change-outs at NREL is conducted by a team consisting of at least two members using a checklist who will also helium test the system, it is possible, but not likely that this transient will occur in the life cycle of the system.

Consequence - Critical

Assuming a leakage rate of one half of the maximum flows given in the previous paragraph, and a release into a purged gas cabinet, hydrogen selenide could build-up to 100-210 ppm (100 times the IDLH concentration-see Table A2-3). The consequences of such a transient could be critical. The consequences with such a transient for HCl would be considerably less, because it is not acutely toxic and is classified only as a corrosive.

Risk - Low (See Fig. 14)

Controls:

Changing of pure H₂Se (highly toxic) and HCl (corrosive) cylinders are performed in ventilated gas cabinets while wearing SCBA. Immediately after installing the cylinder, the CGA fittings are leak checked (inboard) prior to opening the cylinder valve. In the event the washer is missing, this leak check procedure will notify the gas user that the washer is missing before the valve is opened. At this point, the user can insert the missing washer. In addition, cylinder change procedures, as stated in the

SOP, for these materials specify that a washer must be used with these CGA fittings (660 and 330) and purchase procedures require that vendors supply washers with these cylinders. Toxic gas users are also required to check for any toxic gas leaks around the CGA connection after opening the cylinder valve with the use of the portable MDA monitor. Additional engineering controls include flow limiting orifices in the cylinders, fixed MDA monitoring points in the gas cabinet exhaust, excess flow valves in the gas distribution system, and normally closed pneumatic valves which put the gas distribution systems into the fail-safe mode under a variety of automatic safety abnormalities.

6.3.1.3. Transient: Forgetting Washer/Gasket in a Gasketed Gas Connection

Accident Description: Leak when charging the gas distribution system.

Probability - Remote

This event is due to human or operator error introduced by the cylinder change-out team in NREL or by the operator when making modifications to the gas distribution system. As shown in Appendix A1, Fig. A1, human error was responsible for about 20% of the 100 major incidents analyzed by Marsh and McLenn Protection Consultants [16]. Human error can be an important event initiator. In this event, not only must the operator fail to install a washer, but he/she must also fail to helium check the system. The probability of this type of error occurring cannot be now defined in strict numeric terms. It is possible, but not likely, that this transient will occur in the life cycle of the system.

Consequence - Critical

Assuming a leakage rate of one half of the maximum flows given previously, and a release into a ventilated enclosure or gas cabinet, hydrogen selenide could build-up to 100-210 ppm (100 times the IDLH concentration); arsine could build to a concentration of 120-240 ppm (40 times the IDLH), and phosphine concentration could build to 500-1000 ppm (5 times the IDLH) level. The consequences of such transients could be critical for all these gases.

Since the leak is contained within a ventilated space, the user is wearing SCBA, and the leak is small in nature, there is no danger to the individual opening the cylinder. The nature of this leak is also very small and will not result in a catastrophic release. (Normally, the gasket provides a flowing seal compressed between two metal surfaces. In the absence of the gasket, there is still sealing action and the resulting leak is small.)

Risk - Low (See Fig. 14)

Controls:

HPM gas distribution systems are located in ventilated spaces, where the exhausted air is monitored by the appropriate HPM gas detector. In the event that the operator fails to use a gasket and fails to perform the required leak check procedure, a leak will occur at the gasketed connection. This leak is detected by either the portable MDA monitor or the fixed monitor in the exhaust ventilation. Additional engineering controls include flow limiting orifices in the cylinders, excess flow valves in the gas distribution system, and normally closed pneumatic valves which put the gas distribution systems into the fail-safe mode under a variety of automatic safety abnormalities.

6.3.1.4. Transient: Attempt to Open Sticky Cylinder Cap Using a Wrench as a Lever

Accident Description: Incorrect opening of cylinder valve without cylinder CGA connection made.

Probability - Remote

This transient is due to operator error and has occurred elsewhere (e.g., BNL). Thus, this transient is possible, but unlikely to occur in the life cycle of the system.

Consequence - Critical

The consequences of this type of accident could be critical. The exact consequence depends on the material released, location of release, and size of release. In Building 16, possible hazards include fire, explosion or acute toxicity.

Risk - Low (See Fig. 14)

Controls:

The personnel involved in cylinder changing operations must receive compressed gas training (Section 5.5.5.) which includes a section on using the correct tools for each particular task. All personnel changing HPM gas cylinders have access to a specialized tool for providing a mechanical advantage when loosening a cylinder cap. This tool is especially designed to grab only the cylinder cap without reaching far enough into the cap to contact the valve. In addition to compressed gas training, personnel changing cylinders are wearing SCBA, removing cylinder valve caps in ventilated gas cabinets and following system specific procedures to ensure their safety.

It should be pointed out that all HPM cylinders are shipped with a CGA plug or cap. Should the cylinder valve be opened while removing the cylinder valve cap, this cap or plug would prevent a full cylinder discharge and very likely prevent any release what so ever. Once the cylinder valve cap is removed, the procedure calls for checking to ensure the cylinder valve is closed before removing the CGA plug or cap. Both the person changing the cylinder and the "buddy" who is checking off the steps on a checklist would have to skip this step for there to be a release in excess of the quantity which could build up between the valve stem tip and the CGA plug or cap.

6.3.2. Liquid Bubbler Change-Out

6.3.2.1. Transient: Toxic/Pyrophoric Liquid Bubbler Put in Backwards

Accident Description: Toxic or pyrophoric liquid forced into the system lines.

Probability - Remote

This event is due to human error introduced by the cylinder change-out team in NREL. As discussed, human error can be an important event initiator. Because cylinder change-outs at NREL are conducted by a team sensitive to this event, and schematics for this procedure are posted at each laboratory, the probability of this event occurring is remote.

Consequence - Negligible

This transient results in the direct flow of pure liquid TBA, TBP or other metalorganic into the system tubing, or in the case of toxic TBA, into a trap

immediately downstream of the bubbler. The quantity of metalorganic flowing through the deposition system and into the effluent stream would not increase significantly beyond routine that encountered during routine operations. The effluent control system is capable of handling both routine and accidental flows.

Risk - Routine (See Fig. 14)

Controls:

Asymmetric vertical bubblers are standard on MOCVD systems and will provide the first line of control. The inlet/outlet is unique avoiding the possibility of incorrect installation. A diagram in the vicinity of the bubbler is an added check for the operators. If better designs are provided by vendors in the future, they can be incorporated into existing growth systems.

Capture traps upstream and downstream of the bubbler provide a second line of control. Material in the traps can then be handled safely and controllably.

SCBA and protective clothing are worn during toxic bubbler changes and provides the operators control against personal exposure. Use of the buddy system ensures that backup control and assistance are available. Training coupled with SOP familiarity will minimize operator error.

The very first line of control is that the actual quantities of pyrophoric chemicals is very small (UBC exempt quantity is only one pound). For those systems with over one pound (NREL limit is two pounds) dry chemical fire suppression in the system enclosure are triggered by detectors in the enclosure. Additionally, liquid tight system floors and fire resistant enclosure will provide spill control if any liquid is forced out of the system.

Vermiculite, a clay based material, or sand are available in each laboratory to assist in manual containment of any release outside the gas delivery system.

Proper personal hygiene will minimize operator exposure to reacted materials (such as arsenic oxide).

6.3.2.2. Transient: Toxic/Pyrophoric Liquid Bubbler Leak Outside Delivery System

Accident Description: Toxic or pyrophoric liquid released due to valve failure or operator error.

Probability - Occasional

This event is due principally to mechanical error. Failure of the entire mechanical distribution system can only be quantified using more systematic fault or event tree type analyses. System and component failure rate data are summarized in Appendix A1, Table A1-1. As shown, the probability of piping components failures range from the extremely remote (e.g., pipe wall rupture = 10^{-6} faults per year) to reasonably probable (e.g., gasket leak = 10^{-2} faults per year). Due to the fact that there are several possible initiating events for this transient we believe that the identified transient might occur sometime in the life cycle of the gas handling systems. However, it should be noted that in the lifetime of these MOCVD systems (four systems with an average life cycle of six years) this transient has not occurred at NREL.

Consequence - Marginal

The bubblers (see Appendix M2) are not equipped with flow restrictors; under worst case conditions the whole content of a bubbler (1 lb of TBA or TBP, 0.22 lb of TMG, 0.11 of TMA) could be spilled within the MOCVD housing and on the floor. Because of their high vapor pressures, spilled liquid TBA or TBP would vaporize within 2-5 minutes. The estimated concentration of TBA in the enclosure, assuming a ventilation rate of 685 cfm (laboratory 458), is 537 to 672 ppm (Equations 5 and 2b, Table A2-3, Appendix A2). The probability of losing the total contents of the bubbler is however extremely remote; it may be more reasonable to assume that only a fraction of the liquid would leak out. If one tenth of the total mass leaks out, the concentration in the enclosure would build up to 32-40 ppm. These material rapidly oxidize thereby significantly reducing the toxicity of any release. If this material leaks from the enclosure into the laboratory where the ventilation rate is 1200 cfm, it would be diluted below the IDLH level.

TBA is extremely flammable; its auto-ignition temperature is not accurately known but it is somewhat below 54.5°C. It may not auto-ignite in a ventilated enclosure, but will rapidly oxidize. Precautions are needed that no ignition sources, including hot surfaces, exist inside the enclosure. Fumes from TBA fires can be hazardous, but are significantly less hazardous than the original chemical. Deposited arsenic oxide particles can present hazards to workers attempting to clean up in the aftermath of a fire. Hazards to the public outside of the laboratory are not anticipated since simulations using a Gaussian puff atmospheric dispersion model PVPUFF (see Appendix A3) show that ambient level concentrations at 100 m would be lower than the IDLH levels for arsine and phosphine. In these simulations we assumed releases from stacks 5 m off the ground, 1 min sampling time, and either stable atmospheric conditions with 1 m/s wind speed, or neutral atmospheric conditions and 5 m/s winds, or unstable conditions and 10 m/s wind. In the worst of these cases the ambient concentration 100 m downwind of the stack was $1.3 \times 10^{-2} \text{ g/m}^3$ which is one half of the IDLH concentration for arsine. The arsine and phosphine IDLHs were used as triggering levels because no IDLH levels exist for either TBA or TBP. If the LC₅₀ (lethal concentration in 50% of the test animals) of 70 ppm for TBA is used, even lower consequence level would be predicted. Thus, the consequences of this transient are marginal.

Note: 1 min sampling times are centered at the maximum of the Gaussian plume. Therefore, real exposure concentrations are less than that estimate which is the worst possible case. The ambient ground level concentrations are for some cases (e.g., stable conditions) increasing with down wind distance until they reach a peak concentration, because the gas is released from 5 m and it does not descent to the ground immediately, but farther downwind.

Risk - Low (See Fig. 14)

Controls:

Bubblers will only be uncapped if they are within a system enclosure.

SCBA and protective clothing are worn during toxic bubbler changes and provide the operators control against personal exposure. Two operator change-out ensures backup control and assistance if required. Adequate training coupled with SOP familiarity will minimize operator error.

The very first line of control is that the actual quantities of pyrophoric chemicals is very small (UBC exempt quantity is only one pound). For those systems with over one pound (NREL limit is two pounds) dry chemical fire suppression in the system enclosure are triggered by detectors in the enclosure. Additionally, liquid tight system

floors and fire resistant enclosure will provide spill control if any liquid escapes from the system.

Vermiculite, a clay based material, or sand are available in each laboratory to assist in manual containment of any release outside the gas delivery system.

Proper personal hygiene and personal protective equipment will minimize operator exposure to reacted materials (such as arsenic oxide).

6.4. Operation

6.4.1. Gas Distribution

6.4.1.1. Transient: Leak of Air in Vacuum Pump

Accident Description: Fire in vacuum pump

Probability - Remote

This event is due to a mechanical failure in a vacuum pump. As shown in Appendix A1, Table A1-1 the probability of a pump failing is about 10^{-3} faults per year. Consequently, the occurrence of the identified event is possible, but not likely to occur in the life cycle of the system.

Consequence - Marginal

Leak of air in the vacuum pump carrying a pyrophoric gas or vapor could result to a fire in the pump. The fire should be localized and of small intensity, but it could generate hazardous fumes and endanger the people who are present in the room. The consequences of this transient are marginal.

Risk - Low (See Fig. 14)

Controls:

The first level of control deals with periodic inspection and maintenance of the pumps. Not only is the pump oil changed and the pump visually inspected at specified intervals, but both the inlet and exhaust pressures are monitored before each toxic gas run, and an increase in either value compared to the normal value would mean either that the pump oil needs to be changed, or that there is a leak around the pump housing. In the latter case, leak testing would be necessary to establish that no leaks exist. Were there a leak in the vacuum pump during a deposition, causing a fire in the pump, the pump would undoubtedly stop and the chamber pressure would begin to rise. When this pressure would pass a preset valve, the second level of control, a system interlock, would turn off gas flow into the system, leaving only a small amount of toxic gas in the system. Since the pump has valves on both the upstream and downstream sides, the pump can be removed from the system by workers wearing SCBA gear, while monitoring any toxic gas release by the MDA monitor, and replaced by another pump. The rest of the toxic gas contained in the system can then be scrubbed in the usual manner.

6.4.1.2. Transient: Leak in Pyrophoric Gas Distribution System into Gas Cabinet or System Enclosure

Accident Description: Fire or possible release of toxic gas.

Probability - Remote

This event is due principally to mechanical error. Failure of the entire mechanical distribution system can only be quantified using more systematic fault or event tree type analyses. System and component failure rate data are summarized in Appendix A1, Table A1-1. As shown, the probability of piping component failures range from extremely remote (e.g., pipe wall rupture = 10^{-6} faults per year) to reasonably probable (e.g., gasket leak = 10^{-2} faults per year). Of these initiating events, however, in the lifetime of the NREL MOCVD systems (four systems with an average life cycle of four years) this transient has not occurred. Therefore, this transient is not likely to occur in the lifetime of the system, but is possible.

Consequence - Marginal

The maximum flow of phosphine from an open valve into the distribution system is 6.9 slpm. Table A2-3 lists concentrations corresponding to this flow; this flow is reduced to 0.5 slpm by an excess flow valve connected to the cylinder outlet. The concentration can build to 75-150 ppm (IDLH = 200 ppm) when purging of the cabinet is functioning and to a maximum of 4% if the leak remains undetected for about one hour and purging is not functioning. In the latter worst case scenario phosphine may ignite if the gas cabinet is relatively warm ($>40^{\circ}\text{C}$); however, no ignition is anticipated at the low concentrations encountered in purged cabinets.

Even if ignition were to occur, a 7 liter/min phosphine leak (through a typical flow limiting orifice) would generate about 290 BTU/min. A full cylinder would burn for about 18 minutes, generating 5,700 BTUs total. (The heat of combustion for phosphine is 31 kJ/gram; it is 49 kJ/gram for methane.) The flame front from such a phosphine leak would extend approximately 6". A typical domestic heating furnace is rated at about 100,000 BTU/hr = 1,667 BTU/min. This means a typical furnace in a home puts out over five times the heat, over a much longer period of time, than a leaking phosphine cylinder. The burner on such a furnace is housed in a thin metal enclosure, while the phosphine cylinder is housed in a thick metal gas cylinder cabinet. Thus, the consequences of this event are marginal.

Risk - Low (See Fig. 14)

Controls:

Large gas leaks in the gas distribution system are handled by a number of controls. The gas cabinets are ventilated, thus preventing the gas from entering the laboratory. Automatic shutdown of the gas flow from the cylinder can be initiated by a variety safety interlocks, including the following: If the MDA monitoring system detects a high level gas concentration ($5 \times \text{TLV}$), it automatically closes a normally closed, air-operated valve on the cylinder. A redundant, normally closed valve located immediately downstream of the cylinder is also closed. Loss of exhaust ventilation also triggers automatic shut down of the gas distribution system.

There are additional controls which will help mitigate this situation. 1) The gas flow can also be terminated at the cylinder manually by the operator if a malfunction is observed and not detected by the MDA system (e.g., if all of the gas is consumed while burning). The valves mentioned above are also used in this case. 2) If the cylinder valve is closed after charging the pigtail, then only a small amount of gas will escape from the system in any case. This is a recommended procedure. 3) If installed in the system, a "scram" unit can also be activated manually or automatically to neutralize the contents of the cylinder supplying the leaking gas. This procedure is followed if the gas flow cannot be terminated at the cylinder. 4) An excess flow valve connected to the

cylinder outlet will close if the leak rate exceeds 0.5 slpm. 5) In the case of a catastrophic hardware failure (e.g. a regulator gauge blowing out in conjunction with a failure of an excess flow valve), the flow-limiting orifice in the cylinder valve controls the rate of the escaping gas.

Small leaks are controlled by all items listed above with the exception of 4 and 5. The auto-shutdown control features discussed above ensure that only a small amount of gas is released to the environment in the event of a leak. Fail-safe shutdown of the system also ensures that all carrier gas flows to pyrophoric liquid/solid sources (e.g., organometallics) are terminated.

A cabinet exhaust scrubber are used to contain the leaking gas if the system is run with the source cylinder valve open and a "scram" unit is not included.

Fires caused by the leaking pyrophoric vapors are handled by the following control features: 1) The gas cabinets, system enclosure and exhaust ducts are composed of approved, fire-resistant materials; 2) Gas cabinets have built-in, heat-activated sprinkler systems that keep the gas cylinders cool during a fire; 3) Built-in, automatically activated dry-chemical fire suppression systems are included in areas of the system where pyrophoric organometallic sources are housed; 4) If a fire spreads from inside the gas cabinets or system enclosure and into the laboratory, the following controls are present: sprinklers or dry-chemical fire suppression system installed in the laboratory ceiling, one hour rated fire walls enclosing the laboratory and a building smoke detection and fire alarm system for evacuation of personnel.

Finally, systems are also leak checked periodically (see Section 5.4.1.24), so gasket leaks are most likely found and corrected before a catastrophic leak pathway develops, or in the case of components on the high pressure side of the distribution system, before the components are exposed to pyrophoric gas.

6.4.1.3. Transient: Leak in Toxic Gas Distribution System into Gas Cabinet or System Enclosure

Accident Description: Release of toxic gas.

Probability - Remote

This event is due principally to mechanical error. Failure of the entire mechanical distribution system can only be quantified using more systematic fault or event tree type analyses. System and component failure rate data are summarized in Appendix A1, Table A1-1. As shown, the probability of piping component failures range from extremely remote (e.g., pipe wall rupture = 10^{-6} faults per year) to reasonably probable (e.g., gasket leak = 10^{-2} faults per year). Of these initiating events, however, in the lifetime of the NREL MOCVD systems (four systems with an average life cycle of four years) this transient has not occurred. Therefore, this transient is not likely to occur in the lifetime of the system, but is possible.

Consequence - Critical

The maximum flow of arsine from an open valve into the distribution system is 1.7 slpm; this flow is limited to less than 0.5 slpm by an excess flow valve connected to the cylinder outlet. This valve actually shuts off all flow (closes) when the flow through the device exceeds this predetermined value. The concentration can build to 70-140 ppm (IDLH = 6 ppm) when purging of the cabinet is functioning and to a maximum of 3.6% in the unlikely event that the leak remains undetected for about one

hour and purging is not functioning (Table A2-3, basis = 1.7 slpm flow). The consequences of this transient are critical.

Risk - Low (See Fig. 14)

Controls:

Large gas leaks in the gas distribution system are handled by a number of controls. The gas cabinets are ventilated, thus preventing the gas from entering the laboratory. Automatic shutdown of the gas flow from the cylinder can occur by any of the following means. 1) If the gas is detected by the MDA monitoring system, it triggers an interlock which closes a normally closed, air-operated valve on the cylinder. A redundant, normally closed valve located immediately downstream of the cylinder is also closed in this case. 2) The gas flow can also be terminated at the cylinder manually by the operator if a malfunction is observed and not detected by the MDA system. The valves mentioned above are also used in this case. 3) If the cylinder valve is closed after charging the pigtail, then only a small amount of gas will escape from the system in any case. This is a recommended procedure. 4) If installed in the system, a "scram" unit can also be activated manually or automatically to neutralize the contents of the cylinder supplying the leaking gas. This procedure is followed if the gas flow cannot be terminated at the cylinder. 5) An excess flow valve connected to the cylinder outlet will close if the leak rate exceeds 0.5 slpm. 6) In the case of a catastrophic hardware failure (e.g. a regulator gauge blowing out in conjunction with a failure of an excess flow valve), the flow-limiting orifice in the cylinder valve controls the rate of the escaping gas.

Small leaks are controlled by all items listed above with the exception of 5 and 6. The auto-shutdown control features discussed above ensure that only a small amount of gas is released to the environment in the event of a leak.

A gas cabinet exhaust scrubber is used to capture the leaking gas if the system is run with the source cylinder valve open and a "scram" unit is not included.

Finally, systems are also leak checked periodically (see Section 5.4.1.24), so gasket leaks are most likely found and corrected before a catastrophic leak pathway develops, or in the case of components on the high pressure side of the distribution system, before the components are exposed to pyrophoric gas.

6.4.1.4. Transient: Leak in Distribution System Between Gas Cabinet and Deposition System and Failure of Secondary Containment (Coaxial Tubing or Ducting Raceway)

Accident Description: Tubing carrying toxic or pyrophoric gas from gas cabinet to growth system enclosure ruptures, and outer tubing wall or enclosed ducting also ruptures, allowing toxic gas into ambient air. If gas is pyrophoric, the leak may spontaneously ignite.

Probability - Extremely Remote

This event is most likely due to human error which produces a physical breaching of the gas line and secondary containment system. This accident could be caused by construction related activities in the laboratory by NREL scientific staff or their subcontractors. It is also possible, but extremely unlikely that there could be a mechanical failure within the system itself due to over-pressure, stress, etc. Estimation of the probability of such transients is difficult because of the human operator error associated with this transient. However, we believe that the probability of this transient

occurring cannot be distinguished from zero for two principal reasons. First, access to these facilities is controlled and there is no construction permitted when the process tools are pressurized and in use. Second, the probability of independently initiated mechanical rupture is quite small ($<10^{-6}$ faults per year).

Consequence - Critical

With an excess flow valve in the outlet of the cylinder, the flow of either phosphine or arsine would be automatically terminated should the flow exceed the predetermined value of 0.5 slpm. A release up to this flow rate into a room with a ventilation rate of 2800 cfm will result in concentrations of up to 20 ppm for either hydrogen selenide or arsine, concentrations which are a few times higher than the IDLH levels. For phosphine the concentration could build-up to 50 ppm which is 1/4 of the IDLH(extrapolated from Table A2-3) but still many times higher than the OSHA PEL of 0.3 ppm. The consequences of this transient could be critical for hydrogen selenide and arsine, marginal for phosphine.

Risk - Low (See Fig. 14)

Controls:

The first line of control against a leak in the distribution system is the proper design and installation as per Section 5.4.1., which includes procedures for leak checking each line before allowing toxic gases are introduced. Systems are also laid out to give a minimum length of tubing between gas cabinets and reactor enclosures, and to use a minimum number of welds and fittings in this interconnect.

The second line of control is the gas manifold in the gas cabinet, which has been designed with redundant controls to prevent downstream system failures and reduce the release rate of gas in case of a line rupture. Gas panels contain redundant regulators to greatly reduce the possibility that the line is pressurized above 35 psi, which is well below the working pressure of stainless steel tubing (5100 psi for 1/4" OD, 0.035" wall tubing).

Each gas line also contains an excess flow valve, which will close and therefore shut off gas flow in the event of the flow surge accompanying a line rupture. If the excess flow valve should fail, the flow limiting orifice in the gas cylinder valve will still limit the maximum leak rate through the tubing. This flow limiting orifice prevents the gas release from reaching levels where a flame fed by a pyrophoric gas leak would have sufficient fuel value to ignite equipment within greater than one foot of the line. (The fuel value of phosphine is within 10% of the fuel value of natural gas.) For systems which operate with the cylinder valve closed, the maximum release is further limited to the amount of gas in the manifold, typically about 1 standard liter or 0.035 ft³.

The final level of control is toxic gas detection in ambient air and room ventilation. A high level alarm in the ambient air is triggered before the gas concentration reaches the IDLH, and automatically closes the shutdown valve in the gas manifold upstream of the distribution system. The gas panel also contains a manual valve which could be closed by personnel responding in SCBA. The room ventilation helps to disburse the leak and is especially effective when either the excess flow valve closes, the automatic shutdown valve, or the cylinder valve is closed. In these cases, the toxic gas volume release is limited to what would be diluted to below the IDLH in less than one room air change, or less than approximately three minutes for the laboratories involved.

6.4.1.5. Transient: Faulty Seals Connecting Reactor Vessel to System

Accident Description: Release of toxic gas/possible fire.

Probability - Occasional

Several gas lines are connected to each reactor vessel. This event may be due to operator or human error when the system is initially installed. The operator may install an inappropriate seal and fail to helium check the integrity of the system. Alternatively, elastomer seals may also harden and crack over time. On a comparative basis, the probability of operator error is about 10^{-3} (see Appendix A1, Table A1-2) for any single event; the probability of multiple events (i.e., installing an incorrect gasket and failing to leak test) is smaller, but not completely independent because the same operator may be involved in both events. The failure rate for gaskets is about 10^{-2} faults per year. For these reasons, this transient might occur in the life cycle of the system.

Consequence - Marginal

In the event of faulty seal at the reactor vessel, the flow of toxic gas would be limited by the flow controller and be restricted to the system enclosure. Systems using arsine, hydrogen selenide or phosphine have mass flow controllers with maximum ranges less than 100 sccm (10 sccm for the hydrogen selenide system). For an exhaust system of 2000 cfm, the maximum concentration of any gas at release point to atmosphere is 1.8 ppm for arsine and phosphine and 0.18 ppm for hydrogen selenide. These values are well below 1/2 the IDLH for the respective gases. The actual release is expected to be several times lower since the most common o-ring failure mode is a slow leak which still presents significant resistance to escaping gases rather than catastrophic failure. Even for a catastrophic failure, the release is reduced due to typical flows being lower than the maximum range and due to cracking of some of the gases (about 50%) in the reaction vessel. Because the worst case release in such a case is below 1/2 the IDLH and this release source is required to be contained within a ventilated enclosure, the consequences of this transient are considered to be marginal.

Risk - Low (See Fig. 14)

Controls:

All fittings and associated seals to the reactor vessel are checked for contamination, wear and aging before each experiment. The system operator is responsible for tightening and checking seals carefully before flowing toxic source materials. Elastomer seals (e.g., o-rings) are changed on a periodic basis to prevent vapor leakage due to hardening and cracking. The reactor vessel components are carefully checked for any damage before each use. Prior to flowing hazardous gases, the reactor vessel can be checked for leaks by flowing a detectable, non-toxic, non-pyrophoric gas (e.g., hydrogen or helium) through the reactor while using an appropriate detector. Systems which use vacuum to provide the pressure to seal the o-rings are equipped with a vacuum switch interlock, by which low vacuum condition automatically stops HPM gas flows and puts the system under inert gas purge.

Gas leaks in the reactor vessel are handled by a number of controls. The system enclosure is ventilated and kept closed during system operation, thus preventing gases from entering the laboratory. Automatic shutdown of the gas flow to the reactor vessel can occur by any of the following means: 1) If the leak is caused by pressurization of the reaction vessel due to exhaust blockage, a reaction vessel interlock will shutdown all flow of HPM and alert the operator of malfunction with audio and visual signals; 2)

If leaking gas is detected by the MDA monitoring system, it triggers an interlock which closes sets of normally closed, air-operated valve on all source gas cylinders; 3) The gas flows can also be terminated manually by the operator if a malfunction is observed and not detected by the MDA system; 4) If the gas cylinder valves are closed after charging their respective pigtail assemblies, then only a small amount of gas will escape from the reactor vessel in any case. This is a recommended procedure. The fail-safe, auto-shutdown control features required for all systems ensure that only a small amount of gas is released to the environment in the event of a leak. Fail-safe shutdown of the system also ensures that all carrier gas flows to pyrophoric liquid/solid sources (e.g., organometallics) are terminated. After shutdown, the small quantity of toxic/pyrophoric vapors remaining in the reactor vessel (<100 sccm) is quickly and easily removed via ventilation of the system enclosure.

Fires caused by leaking pyrophoric vapors from the reactor vessel are handled by the following control features: 1) The ventilated system enclosure and exhaust ducts are composed of approved, fire-resistant materials; 2) Built-in, automatically activated dry-chemical fire suppression systems are included above the reactor vessel work area; 3) If a fire spreads from inside the system enclosure and into the laboratory, the following controls are present: sprinklers or dry-chemical fire suppression system installed in the laboratory ceiling, one hour rated fire walls enclosing the laboratory and a building smoke detection and fire alarm system for evacuation of personnel.

6.4.1.6. Transient: Rupture of Quartz Reactor Vessel

Accident Description: Release of toxic vapors with possible fire and/or explosion

Probability - Remote

This event is due to the spontaneous failure of the reactor vessel or the chamber seal. Mechanical failure of the reactor itself is likely to be a very rare event. EPA data on vessel component failures rates, for example, suggest that there are about 10^{-6} faults per year for vessel shell failure. Seals will probably fail more frequently. For this reason, this transient is possible, but is not likely to occur in the life cycle of the system.

Consequence - Marginal

Rupture of the reactor would result in a subsequent leak of the reactor contents into the reactor enclosure. This enclosure is vented and the leaked gases would be carried out to the stack. If a rupture of the reactor is accompanied by a compromise in the integrity of the reactor enclosure, hazardous concentrations could be formed in the work space. The presence of pyrophorics and hydrogen in the reactor creates an additional concern since air leaked in the reactor could cause the ignition of the pyrophoric/flammable mixture. If this were to happen, a flame at the breach in the reactor vessel would occur. This flame would be small due to the limited fuel supply, and would be easily contained. The consequences of this transient are therefore classified as marginal.

Risk - Low (See Fig. 14)

Controls:

If the quartz chamber were to rupture, or a seal to the chamber fail, during a process run, the flow of toxic and flammable gases is effectively limited by limiting the mass flow controller settings for these gases. To minimize the possibility of fire and/or explosion at the point of failure, proper ventilation is provided around all chambers

such that any release will immediately be diluted into the ventilation for the system enclosure at which point the toxics and flammables are effectively diluted.

MDA detection points located within the system enclosure and in the exhaust ventilation are also interlocked (at 5 times TLV levels) to automatically shut down the gas supplies in the event of detecting leaks due to chamber failure. Systems in which the possibility for over-pressure (>1 atm) exists (due to unintentional line blockage downstream of the reactor) also require a pressure interlock capable of automatically shutting down all inlet gas supplies in the event of such an occurrence.

6.4.1.7. Transient: Hydrogen Leak in Gas Cabinet

Accident Description: Leak at the hydrogen CGA connection or in the hydrogen manifold resulting in ignition of hydrogen inside the gas cabinet.

Probability - Remote

This event is due to a mechanical failure of a manifold or connection due to such factors as over-pressure, vibration, misalignment or thermal expansion and contraction. As shown in Appendix A1, Table A1-1 the probability of an automated valve failing to operate or remain open is quite high ($\sim 10^{-1}$ faults per year). These failures, however, will not result in a leak in the gas distribution cabinet. The probability of a leak from the manifold and associated connectors to the gas cabinet is substantially smaller. Consequently, it is possible, but not likely that this transient will occur in the life cycle of the system.

Consequence - Critical

The consequences of a hydrogen leak in a gas cabinet could be critical since the maximum initial flow out of a cylinder at 2500 psi, with a valve opening of 0.25" is approximately 25,000 slpm (4.9 lb/min). The flow decreases as pressure decreases, and in less than five minutes the cylinder will empty and saturate the gas cabinet. Fire and/or explosion are then possible.

A worst case scenario involves the release of hydrogen through a wide open valve at maximum cylinder pressure, when the cylinder is not connected, to any flow restricting lines. This includes potential leaks through a cylinder 0.25" open valve were considered. At $P=2000$ psig, Cylinder size 1A, 216 ft³ under STP, max flow release flow rate would be 25,000 lpm = 4.9 lb/min

We have estimated, based on the equations presented in App. A2, the concentration build-up in a) gas cabinets and ii) in lab were estimated with and w/o ventilation functioning. Comparing these concentrations with the LEL of H₂ which is 4.1%, we can see that it only takes a fraction of a minute for such concentrations to build up to the LEL even with adequately functioning ventilation. We consider LEL to be a dangerous level although ignition can not happen without an ignition source present (hydrogen auto-ignition temperature is 752°F). Although the explosiveness lower limit of hydrogen is not known, we can say that given the very rapid concentration built-up resulted by a worst case release, (see Table A 2.7), if an ignition source is present, explosion is possible.

To prevent such an event, cylinder change safety procedures should be strictly enforced.

Risk - Low (See Fig. 14)

Controls:

The most likely cause of leaking hydrogen in a gas cabinet is operator failure to properly tighten the CGA connection during a cylinder change. Therefore, this connection must be checked with a hydrogen detector after every cylinder change.

An excess flow valve at the CGA connection would stop the flow of hydrogen downstream in the event of a serious leak. A significant leak upstream (at the CGA connection) would be detected by the operator when the valve is opened.

Smaller leaks would be contained by the gas cabinet and diluted by the exhaust flow to prevent the buildup of a flammable hydrogen mixture. In the event of ventilation failure, a system wide interlock is triggered and the flow of hydrogen would be immediately stopped at the source.

No ignition source or electrical wiring is allowed inside a gas cabinet; this minimizes sources of ignition.

If a large leak were to develop with subsequent ignition, the cabinet would contain the fire and an internal sprinkler system would be activated to reduce damage.

6.4.1.8. Transient: Hydrogen Leak in Purifier

Accident Description: Leak and ignition of hydrogen inside the purifier

Probability - Remote

The hydrogen purifier may leak due to human error in the connection of the system or to mechanical failure of the unit itself. At the time of system installation, the operator may install an inappropriate seal and fail to helium check the integrity of the system. The probability of operator error is about 10^{-3} (see Appendix A1, Table A1-2) for any single event; the probability of multiple events (i.e., installing an incorrect gasket and failing to leak test) is smaller, but not completely independent. The mechanical failure rate for the hydrogen purifier is not known. However, the Matheson Unit to be used contains two significant safety features which reduce the likelihood that this event will occur. The two safety features which provide automatic shutdown in the event of certain unsafe conditions are: 1) A sensitive hydrogen detector in the cabinet responds to minute leaks at levels less than one-tenth the lower flammability level by stopping inlet hydrogen flow, removing power and initiating audio/visual alarms; 2) An over-temperature sensor reacts at 137°F by removing power and stopping inlet hydrogen flow.

Consequently, multiple human or mechanical failures must occur for this transient to take place. Thus, this transient is not likely to occur in the life cycle of the system.

Consequence - Marginal

The maximum flow to the purifiers are 11 slpm in laboratories 103 & 368 and 20 slpm in laboratory 222. Leakage of these flows into the ventilated laboratories would not result to concentrations above 0.2% (Table A2-4). This is well below the flammability range of hydrogen in air of 4 to 75% by volume. Therefore, it does not pose a high risk to workers. The consequences of this transient could be negligible to marginal.

Risk - Low (See Fig. 14)

Controls:

The hydrogen purifiers have detectors which activate a shutoff valve at the purifier inlet when a leak is sensed. A central MDA hydrogen detector is located in the laboratory which monitors the laboratory air and shuts off hydrogen in the gas cabinet should the purifier interlock fail.

A large leak triggers the excess flow valve and shuts off the flow at the CGA connection.

The hydrogen inventory is kept below 500 ft³ and is contained in the gas cabinet. This isolates the source from a potential accident and minimizes the chance for critical damage.

6.4.2. Ventilation

6.4.2.1. Transient: Loss of Process Control with Potential for Episodic Release of AsH₃, PH₃, and/or H₂Se

Accident Description: Regulator and/or mass flow controller fails, with the potential that large quantities of toxic gas will flow through the reactor.

Probability - Remote

This event is due principally to mechanical failure of the gas distribution controllers. Sudden changes in flow rate can occur by changes in either line pressure or the mass flow controller. As noted in several of the previous descriptions, the failure rate for automated valves (e.g., within mass flow controllers) is about 10⁻¹ to 10⁻² faults per year. A similar failure rate for regulators is assumed. In the NREL systems, redundant regulators and/or physical pressure relief are used. Therefore, a single mechanical failure cannot account for a large scale release. Consequently, this transient is only possible with multi-point failures and is not likely to occur in the life cycle of the system.

Consequence - Marginal

If the regulator fails when the cylinder valve is open, excess material will flow through the reactor and pass into the effluent scrubber. The maximum flow of hydrogen selenide, arsine or phosphine into the reactor would be 0.5 slpm, given that cylinders are equipped with flow restricting orifices and that excess flow valves are at the cylinder outlet. Under these conditions, the maximum mass flow rate in a reactor is 0.004 lb/min. The effluent scrubber for each reactor is capable of treating such a flow. For burn box effluent scrubbers employing a single H₂ flame, the flame front would extend about 3"(12") beyond a 0.5" nozzle for the orifice-limited flow of 1.6 slpm (7 slpm) for AsH₃ (PH₃). Such a flame front is easily contained with appropriate metal baffles, and presents minimal fire hazard.

Should the failure result in the release of a detectable amount of toxic gas, the primary catastrophic release treatment system (either a closed gas cylinder valve, "Scram" units, or gas cabinet exhaust treatment systems) will limit the release of toxic gas to small amounts. Specifically, most of the experiments require minimal quantities of toxic gases per unit operation. This quantity is typically less than that contained in the connecting manifold/regulator which is less than 1 standard liter. Consequently, the operation can be performed with the cylinder valve closed. This means that a complete loss of process control with no other controls would release less than 1 liter of toxic gas through the reactor and into the environment. Positive cylinder valve closure can be

assured through administrative controls and/or hardware interlocks. For systems that cannot operate with the system valve closed, "scram" units can provide an alternative control. These "scrams" are attached to the manifold immediately downstream of the cylinder valve. In the event of process control failure, a connecting valve is automatically opened and the contents of the cylinder are dumped into the "scram" where they are neutralized by a proprietary compound. Alternately, gas cabinet exhaust ventilation can be passed through an appropriately sized scrubber.

Because the release of toxic gas is small or zero, and the system is in a ventilated enclosure, the consequences of this transient are marginal.

Risk -Low (See Fig. 14)

Controls:

The first line of control would be redundant pressure regulators. This would ensure that pressure sensitive components of the reactor manifold would not be exposed to the high (<300 psi) cylinder pressures.

Flow limiting orifices and excess flow valves would limit the consequences of the failure of mass flow controllers and regulators.

In the case of a catastrophic hardware failure (e.g. a regulator gauge blowing out), the excess flow valves provide the same effective protection as operating with the cylinder valve closed. That is, they automatically close upon sensing excess flow. If the excess flow valve fails in conjunction with the catastrophic hardware failure, the flow-limiting orifice in the cylinder valve controls the rate of the escaping gas.

6.4.2.2. Transient: Loss of Process Control and Simultaneous Failure of Cylinder Valve, "Scram" Unit, or Ventilation/Gas Cabinet Exhaust Scrubber

Accident Description: Regulator and/or mass flow controller fail and cylinder valve, "Scram" unit, or ventilation exhaust scrubber fails to operate

Probability - Extremely Remote

For this transient to occur, both the gas control system and additional safety features must fail simultaneously. This could conceivably arise from a "common mode" failure. General examples of common mode failure include fire (Transient 6.4.4.4.) or loss of electrical power to both systems due to failure of a common electrical busbar, although loss of electrical power would put the system into the fail-safe mode. In the absence of a common mode failure, it is extremely unlikely that this transient will occur.

Consequence - Marginal

If the regulator or mass flow controller fail, excess material will flow through the reactor and pass into the scrubber. The maximum flow of hydrogen selenide, arsine or phosphine into the reactor would be 0.5 slpm, given that cylinders are equipped with flow restricting orifices and that excess flow valves are at the cylinder outlet. Under these conditions, the maximum mass flow rate in a reactor is 0.004 lb/min. The effluent treatment systems are capable of neutralizing such a flow. If the loss of process control is accompanied by component rupture or effluent scrubber failure along with failure of the safety systems already listed, it is possible that most of this material would pass untreated to the atmosphere. Assuming a pseudo-continuous release from a height 5 m off the ground the estimated (by a Gaussian plume model) ambient

concentrations 100 m downwind were below the IDLH of 2 ppm for all possible meteorological conditions(see App. A3). Ventilation would continue to protect laboratory personnel from exposure to toxic gas.

Risk - Routine (See Fig. 14)

Controls:

Redundant pressure regulators, flow limiting orifices, and excess flow valves would effectively limit the flow of the toxic gas to quantities that would be treatable with the effluent scrubber.

6.4.2.3. Transient: Loss of Exhaust Ventilation

Accident Description: Loss of ventilation while toxic gases are flowing through the system

Probability - Reasonably probable

This transient may be due to loss of belt on fan, tripping of breaker for fan, temporary power loss and the resulting transfer time to standby power, motor burn-out, or other fan failure resulting in ventilation loss. Such mechanical failures are expected and occur occasionally. Systems are not operated during normal scheduled maintenance on ventilation systems.

Consequence - Negligible

There exists a safety interlock for these systems which puts them into the fail-safe mode upon ventilation loss. Such fail-safe mode shuts off all HPM gas flows and contains all HPMs within the system plumbing. Additionally, effluent removal systems remain operational during ventilation loss. Therefore, any HPM gases still flowing through the system is treated. Therefore, should loss of ventilation occur, laboratory personnel will not be subjected to any situation which will result in injury, occupational illness, or system damage.

Risk - Routine (See Fig. 14)

Controls:

As per Section 5.4.7.1.4. of this SAR, the exhaust ventilation for these systems must be monitored for ventilation flow. Upon loss or reduction of ventilation, the system is interlocked to automatically shut down and go into fail-safe mode. Both an audible and visual alarm is activated to inform the operator of the anomalous situation. The fail-safe mode requires a manual reset, by the operator, so that the system does not auto-restart in an undetermined state upon the correction of the anomalous situation. Also for this transient, it is assumed that the system is actually running, which means that an operator is present to manually shut-down the system should the safety interlock fail.

There are many other safety features on the system which are designed to keep to an absolute minimum the amount of HPM which may escape from the system. These features include: stringent leak testing, excess flow control, monitoring for toxic and flammable gases, etc.

At any given moment during operation, there is a small amount of process gases in the system. Therefore, when the system goes into the fail-safe mode there is only a

small concentration of HPM in the reactor, plumbing and effluent removal system which need to be processed through the system. The HPM sources are isolated upon fail-safe.

The Facilities Branch personnel have a comprehensive preventative maintenance program designed to minimize the occurrence of a fan failure. Additionally, the safety ventilation interlocks are inspected annually to ensure that they are functioning properly.

6.4.3. Effluent treatment

6.4.3.1. Transient: Effluent Scrubber Failure- Liquid Type Scrubber Blockage

Accident Description: Blockage of scrubber inlet or exhaust

Probability - Reasonably Probable

The effluent scrubber could fail due to several reasons, for example, loss of fluid, neutralization of scrubber fluid, loss of flow, etc. These events could be initiated by mechanical failure of the flow controllers, exhaust system or monitors, or operator error due to inattention or placement of inappropriate fluids in the scrubber. Liquid scrubbers require much maintenance. For this reason alone, it is reasonably probable that the liquid scrubber could fail to work during the life cycle of the system.

Consequence - Negligible

If the scrubber system fails to work properly, unscrubbed effluent would be emitted through the exhaust stack. This type of scrubber is used only in the hydrogen selenide system. Under standard operational flow rates, with the H₂Se flow limited to 10 sccm (0.04 g per min) and with a mass flow controller, the concentrations at the stack would be 0.18 ppm for H₂Se, well below 1/2 the IDLH. Thus, the consequences of this transient are negligible.

Risk - Routine (See Fig. 14)

Controls:

There are two controls to place this transient in the above mentioned category. First, each scrubber has a manual plunger, which is moved back and forth several times before each toxic gas deposition to remove any potential blockages to the scrubber inlet. The second control deals with system interlocks. If blockage of the process gas line through the scrubber were to occur during a deposition, the scrubber would emit an audio alarm, and at the same time flow of the process gases into the system would be shut off by a system interlock, leaving only a small amount of gas in the system to be exhausted. At this point, it is likely that the blockage occurred near the inlet, which might be loosened by manually moving the scrubber plunger in and out several more times. Should this loosen the obstruction, the process gas remaining in the system can be scrubbed through the scrubber as usual. Should this not loosen the obstruction, or if the obstruction occurred at the scrubber exhaust, the scrubber, gas dilution, and the pumps should be turned off, and the exhaust line from the system should be connected directly to the building exhaust, bypassing the scrubber. Unfortunately, this will exhaust a small amount of toxic gas into the vented enclosure. This hookup is accomplished by evacuating all non-essential laboratory personnel, making these connections by researchers using SCBA gear, and monitoring the amount of toxic gas released by the MDA toxic gases monitor. The remaining portion of the small amount of gas left in the system can then be exhausted by turning the pumps back on and

increasing the amount of diluent gas going into the system exhaust to further reduce toxic gas concentration, as monitored by MDA.

6.4.3.2. Transient: Effluent Scrubber Failure- Carbon Drum Type Scrubber Exposed to Excessive Oxygen and Buildup of Unreacted Hydrides and/or Metalorganics

Accident Description: Highly exothermic reaction in drum; ignition of carbon; possible explosion; fire and/or loss of containment of drum contents.

Probability - Remote

This event is due to operator failure to routinely oxidize the carbon drum, and the mechanical failure of the temperature monitor interlocked to the gas distribution system. As noted previously, the general rate of human error of commission is about 10^{-3} faults per year (see Appendix A1, Table A1-2). Similarly, the failure rate for temperature controllers is about 0.3 failures per year (see Appendix A1, Table A1-1). Since, at least two independent initiating events must occur before such an accident will take place, this transient is possible, but is not likely to occur in the life cycle of the system.

Consequence - Critical

There have been several incidents involving fires in carbon adsorption drums. Fluer also refers to the possibility of explosion in such a device [4]. Since the device is, currently, only a few feet from the reactor, the consequences of such a transient could be critical. If a drum explodes there could be a significant hazard to workers and the facility.

Risk - Low (See Fig. 14)

Controls:

The primary control is to oxidize the drum on a routine basis with a non-explosive mixture of oxygen and nitrogen. The drum is oxidized after each growth run. Dry air is admitted only after the drum has been purged with nitrogen. This removes residual hydrogen and makes the occurrence of an explosion very unlikely. In addition, continuous oxidation when the system is in standby (about 1 liter per minute of hydrogen flowing) is performed. For this, a low oxygen content is used: 1% to 2%.

To prevent the ignition of the carbon, the temperature in the drum is monitored. There are reports in the literature of carbon temperatures regularly reaching nearly 200°C; in our experience, we have never observed a temperature in the drum of more than 45°C. Even so, the temperature monitor is interlocked to shut down the system if the temperature rises above 50°C.

6.4.3.3. Transient: Effluent Removal Fails due to Loss of System Vacuum

Accident Description: Process gas vacuum pump failure resulting in losing the ability to pump gases through the system to the effluent removal system.

Probability - Occasional

This transient is due to the mechanical failure of the vacuum pump. As shown in Appendix A1, Table A1-1, the failure rate for "Process Machinery Components" that result in "major leaks" is about 10^{-3} faults/year. Consequently, this transient is likely to occur sometime in the lifetime of the system. Only the hydrogen selenide system is subject to this mode of failure.

Consequence - Negligible

Loss of reactor vacuum should not result in an occupational hazard since the reactor and the distribution system are airtight and can safely contain the material until the flow is cut-off. The pressure to the inlet of the vacuum pump could raise temporarily, but still this should not necessarily result in a leak. The consequences are, therefore, negligible.

Risk - Routine (See Fig. 14)

Controls:

As per Section 5.4.7.1.3. of this SAR, the reactor is equipped with a pressure transducer which senses when the pressure exceeds a pressure limit which triggers shut down. Both an audible and visual alarm is activated to inform the operator of the anomalous situation. The fail-safe mode requires a manual reset, by the operator, so that the system doesn't auto-restart in an undetermined state upon the correction of the anomalous situation. (The safety limits described above are system dependant variables. Because each system is different, and some of the operators have not yet determined what value is appropriate for their system, these limits will be evaluated in detail during the ORR. Sufficient detail must be provided at that time, before the systems are allowed to operate.)

As per Section 5.4.5.10. of this SAR, systems which use vacuum pumps as a means of passing the effluent from the reactor to the effluent removal system must provide either a second pump on the system which can be easily used to pump processes gases from the reactor or a tee and closed valve at both the pump inlet and the plumbing going to the effluent removal system so that an axillary pump can be installed on the system without breaking into plumbing containing HPM, should the primary pump fail.

There are many other safety features on the system which are designed to keep to an absolute minimum the amount of HPM which may escape from the system should such a loss of vacuum occur. These features include: stringent leak testing, effluent removal systems, excess flow control, monitoring for toxic and flammable gases, etc. Therefore, should the loss of process vacuum occur the laboratory personnel will not be subjected to any situation which will result in injury, occupational illness, or system damage.

At any given moment during operation, there is a small amount of process gases in the system. Therefore, when the system goes into the fail-safe mode there is only a small concentration of HPM in the reactor, plumbing and effluent removal system which need to be processed through the system. The HPM sources are isolated upon fail-safe.

The laboratory personnel have a preventative maintenance program designed to minimize the occurrence of a vacuum pump failure (see Section 5.5.6.2.). Additionally, the reactor interlocks are inspected annually to ensure that they are functioning properly.

6.4.3.4. Transient: Effluent Scrubber Failure- Burn Box Type (CDO) Flame Goes Out

Accident Description: Flame goes out allowing untreated reactor effluent into ventilated enclosure containing burn box. The additional hazards and controls for reactor pressurization and resulting seal faults or rupture if caused by clogging of flame tube are discussed in Items 6.4.1.5 and 6.4.1.6..

Probability - Occasional

Moskowitz et al.[6] have analyzed the causes and qualitative probability of failure of a CDO unit due to loss of flame. In the system analyzed using Hazard Operability and Fault Tree Analysis techniques, the causes of this transient included loss of fuel, loss of power, loss of combustion air, and loss of instrument air. Single component failures are potentially significant because of their relatively large likelihood of occurring; the probability of a multiple component failure is often smaller. Because there are several types of failures that could trigger this event, it is likely to occur sometime in the life cycle of the system.

Consequence - Negligible

If the flame goes out in the CDO, the effluent gas would pass through the device, diluted at the outlet with 2000 cfm of air, and purged to the atmosphere. With the toxic gas flow rates into the CDO kept below 100 sccm, and the hydrogen flow rate kept below 20 slpm, the concentrations of arsine or phosphine would be about 2 ppm, and the hydrogen concentration would be about 0.04%. These concentrations are below 1/2 the IDLH for both arsine and phosphine. The actual release is expected to be lower due to typical flows being lower than the maximum range and due to cracking of some of the gases (about 50%) in the reaction vessel.

With excess flow and over-pressure protection on the hydrogen supply to the reactor, the maximum concentration of hydrogen in the main ducting following a burn box snuff out is 100 times below the LFL of 4% hydrogen in air, based on 20 slpm hydrogen flow and 2000 cfm ventilation. Thus the hydrogen released by extinguishing the flame is not a hazard. The consequences of this transient are therefore negligible.

Risk - Routine (See Fig. 14)

Controls:

The first line of control for this accident scenario is the use of flame sensors in the burn box which are interlocked to stop the toxic gas flows in case of flame failure and to set off audio and visual alarms to alert the operator of a malfunction. The MDA monitor point in the exhaust ducting serves as a redundant sensor for proper effluent functioning, and will initiate shutdown with alarms if before effluent reaches 1/2 the IDLH of the gases involved.

The second line of control is the proper maintenance and sizing of the flame tubes to prevent clogging. Although each system varies in the amount of material processed by the burn box, it can be expected that use of 1/2" quartz tubing cleaned or changed once a year will reduce the probability of tube clogging to extremely remote. Experience has shown that flame tubes fed by vent lines which carry organometallics, not toxic gases, are the only lines which clog. Because the organometallics are almost completely cracked and deposited out in the reactor tube, the reactor exhaust has never clogged in several years of operation on three systems.

6.4.4. Waste Disposal

6.4.4.1. Transient: Loss of Containment of Carbon Drum Contents

Accident Description: Drum or seals broken; operator exposed to arsenic oxide solids which are suspected carcinogens.

Probability - Remote

This event could be caused by an accident during the movement of the drum from the point of use to the point of disposal. Alternatively, oxidation by-products may build up pressure within the sealed drums and blow-out the inlet or outlet caps. Probability classification of either initiating event is difficult. Based on current experience at NREL, this transient is possible, but is not likely to occur in the life cycle of the system.

Consequence - Marginal

If the drum leaks during operation or transfer to disposal, some out-gassing would occur. Out-gassing while the drum is in its steel enclosure would be safely vented out. The consequences of out-gassing during transportation are marginal.

Risk - Low (See Fig. 14)

Controls:

The drum is made of stainless steel; rupture is nearly impossible. The lid is held on with a heavy duty ring clamp which would be very unlikely to break if the drum were dropped. The most likely occurrence is that the inlet and outlet caps could be blown off.

When the drum is to be disposed, the inlet and outlet ports are capped. However, there exists the possibility that the drum may still be oxidizing, and the oxidation by-products may build up enough pressure to force off the caps. This might release arsenic oxide solids into the ambient, although the chance that an unprotected worker would be exposed is very small.

The control is to oxidize the drum for a lengthy period prior to disposal (on the order of two weeks).

6.4.4.2. Transient: Operator Exposed to Toxic By-product Materials

Accident Description: Operator drops HEPA or prefilter during change-out while not wearing the required personal protective equipment and not following bag-out procedure. Arsenic containing particles are released into the air, presenting a carcinogenic hazard.

Probability - Remote

This event is due to multiple human errors involving disregard of established written procedures. As a result, this event is possible, but not likely to occur during the life cycle of the system.

Consequence - Negligible

The dropping of a contaminated pre-filter or HEPA filter during change-out operations could result in the mobilization of a very small quantity of arsenic containing particles to the air. Under routine circumstances, the operator would already be wearing respiratory protection to clean the laboratory using prescribed protocols. Even in the absence of the use of such equipment, the potential dose to the operator should be quite small. This is because the filters are changed regularly so that air flow is not inhibited, thus the amount of material present on the filters is less than 5 grams. Only a small fraction of that material could be mobilized by this transient and inhaled. For comparative purposes, the PEL for air born arsenic is $10 \mu\text{g}/\text{m}^3$ and the TLV-TWA for arsenic is $0.2 \text{ mg}/\text{m}^3$.

Risk - Routine (See Fig. 14)

Controls:

The first line of controls against operator exposure is the low level of possible contamination. The filter change frequency schedule prevents large quantities of contaminants from accumulating on any one filter. Tests during a routine filter change operation have shown no detectable amounts of airborne arsenic particles and very small increases in surface contamination directly below a filter which snagged on a misplaced support rod. Thus, even if the operator fails to wear personal protective equipment, the exposure for this accident scenario is expected to be well below the OSHA limits for daily, routine operations.

The second line of control is training of personnel so that they are properly attired and follow procedures. The system SOP includes a detailed description of what is required (particle respirator, disposable gloves, laboratory coat, disposable sleeves and head covering, etc.). The SOP procedure also requires removal of filters from the duct case directly into a containment bag. Filter changes are a two-person operation, so compliance with SOP instructions is monitored.

Finally, all of the laboratories using arsenic compounds are routinely tested for contamination to assure that procedures are not allowing release of arsenic into the air or accumulation on surfaces.

6.4.4.3. Transient: Caustic Spill of Sodium Hydroxide Disposal (pH 13.8)

Accident Description: Contact with caustic contaminated with Selenium, Phosphorous, Boron, Germanium, or Silicon

Probability - Occasional

This event is due to human error. As a result, this event it is likely to occur sometime in the life cycle of the system.

Consequence - Marginal

Spilled sodium hydroxide can present eye, dermal and inhalation hazards to workers. Because of the observable presence of these spilled materials, the response should be rapid and properly implemented. If the workers fail to don proper protective equipment, accidental exposure to these materials could cause minor injury.

Risk - Low (See Fig. 14)

Controls:

Each operator has system specific procedures for disposing of the caustic scrubber solution. In addition to following these procedures, the operator must wear the appropriate personal protective equipment including eye protection, gloves and other required splash protection.

6.5. External Events

In this SAR, external events are defined as those transients whose cause is beyond the direct control of Building 16 activities, but could impact on HPM control systems used during normal and emergency operations. In a general way, external events may include seismic activity, high winds and tornadoes, external floods,

transportation and nearby facility accidents, lightning, severe winter storms, external fires (e.g., forest and grass fires), extraterrestrial activity (e.g., meteorite strikes and satellite falls), and volcanic activity (Kennedy et al., 1990). Given the nature of the activities in Building 16 and its physical location (i.e., elevated relative to local topographic relief) and layout (i.e., all gas systems above ground), the impacts of some external events can be quickly dismissed for various reasons. First there are some events (i.e., extraterrestrial activity, flood and volcanic activity) that are expected to occur so infrequently (i.e., probability cannot be distinguished from zero) that they are unimportant. Second, other events (i.e., severe winter storm, and nearby accidents) have been dismissed because they would not effect the integrity of the HPM control systems. Finally, lightening is not further considered because Building 16 is adequately grounded and because backup power is available for all critical gas control (e.g., gas detectors and ventilators) systems. Thus, only fire, seismic activity, and wind and tornadoes are considered further.

6.5.1. Fire

6.5.1.1. Transient: Fire

Accident Description: Fire in Building

Probability - Remote

Over the past 12 years of operation, NREL has had no major fires in the building nor experienced fires from nearby structures or prairie. Based on these empirical observations, the occurrence of a fire is possible, but unlikely to occur in the life-cycle of the system.

Consequence - Marginal

The added risk from the presence of the toxic gases (chronic exposure to carcinogens and suspected carcinogens) is marginal compared to the other risks presented by the fire itself (loss of property and/or life). These materials oxidize very quickly and should they be released due to a fire in the building would most likely be consumed by the fire (self produced scrubber). The toxicity of these oxidized by-products is significantly reduced from that of the original chemical.

Risk - Low (See Fig. 14)

Controls:

There is a building wide fire alarm system which notifies all employees that the building should be evacuated. The Fire Evaluation of Building 16, by an outside consultant [5], indicated that "The cumulative limit of flame spread in Building 16, taking all the above considerations into account, is found to be at one room or less. **This is a very strong L value.** Its strength is, however, based almost entirely on the strength of the building, the lack of continuity of its fuels, and the attitude of its population." In addition to this evaluation of Building 16 each gas cabinet containing HPM gases is connected to automatic sprinklers, and the laboratories containing pyrophoric materials are sprinkled (as is the entire building) and equipped with fire detection interlocked to the building fire alarm.

6.5.2. Seismic Activity

6.5.2.1. Transient: Seismic Activity

Accident Description: Earthquake of 100, 500 or 1000 Year Return Period

Probability: Remote

Kennedy [19] and Coats and Murray [20] present background data on the return periods of earthquakes of differing magnitudes for all DOE sites. The data for Rocky Flats, located within 15 miles of Building 16, show that the best estimate of the peak acceleration for 100, 500 and 1000 year return period earthquakes are about 75, 125 and 140 cm/sec² (Coats and Murray 1984). This is roughly equivalent to G forces or UBC Zone Factors (Z) of 0.075, 0.13 and 0.15, respectively. Compared to other areas of the U.S. the incidence of earthquake activity is low.

Consequence: Critical

Building 16 is minimally designed to meet the Jefferson County Z Factor of 0.075; this is equivalent to a 100 year return period earthquake. In contrast, the DOE Z Factor design requirements for General and Low Hazard Facility Use Classifications are 0.13 and 0.15, respectively. Thus, at first glance, Building is below the DOE guidelines for General and Low Hazard Categories. However, some relief in the guidelines is permitted for existing facilities due to the difficulty in upgrading such a facility and due to the fact the facility may have a short operating lifetime. Both of these circumstances exist for Building 16. In addition, Building 16 was designed to comply with a more restrictive wind speed limit of 100 - 120 mph [21]. Furthermore, Building 16 was constructed with eight independent fire control zones. The fire zones are separated by fire walls. The design of Building 16 to a high wind speed of 100 - 120 mph and the presence of multiple fire zones add structural integrity to the Building. Thus, Building 16 likely complies in spirit and in principle with the larger Z factor required by DOE for General and Low Hazard facilities.

If the structural integrity of the HPM systems were challenged by a 100, 500 or 1000 year return period earthquake, we can still hypothesize the likely consequences of such a transient. In such an event, the most likely transient of interest would be the mechanical shearing of a gas distribution line; gas cylinders in gas cabinets are mechanically secured and distribution systems are equipped with fail-safe valves. The consequences of this event would be similar, but smaller in magnitude because of the increased ventilation due to window breakage, to Accident 6.4.1.4 - Leak in Distribution System Between Gas Cabinet and Deposition System.

Risk - Low (See Figure 14)

Controls:

Large gas leaks in the gas distribution system are handled by a number of controls. The gas cabinets are ventilated, thus preventing the gas from entering the laboratory. Automatic shutdown of the gas flow from the cylinder can occur by any of the following means. 1) If the gas is detected by the MDA monitoring system, it triggers an interlock which closes a normally closed, air-operated valve very near the cylinder. Redundant, normally closed valves, in various locations downstream of the cylinder, are also closed in this case. 2) The gas flow can also be terminated at the cylinder manually by the operator if a malfunction is observed and not detected by the MDA system. The valves mentioned above are also used in this case. 3) If the cylinder valve is closed after charging the pigtail, then only a small amount of gas will escape from the system in any case. This is a recommended procedure. 4) If installed in the system, a "scram" unit or gas cabinet exhaust scrubber can also be activated manually or automatically to neutralize the contents of the cylinder supplying the leaking gas.

This procedure is followed if the gas flow cannot be terminated at the cylinder. 5) An excess flow valve connected to the cylinder outlet will close if the leak rate exceeds 0.5 slpm. 6) In the case of a catastrophic hardware failure (e.g. a regulator gauge blowing out in conjunction with a failure of a excess flow valve), the flow-limiting orifice in the cylinder valve controls the rate of the escaping gas.

Small leaks are controlled by all items listed above with the exception of 5 and 6. The auto-shutdown control features discussed above ensure that only a small amount of gas is released to the environment in the event of a leak.

Systems are also leak checked periodically (see Section 5.4.1.24), so gasket leaks are most likely found and corrected before a catastrophic leak pathway develops, or in the case of components on the high pressure side of the distribution system, before the components are exposed to pyrophoric gas.

Finally, the likely hood of a high pressure portion of the gas distribution system being sheared due to seismic activity is remote. This is because the cylinders are secured in the gas cabinet and all high pressure components of the gas distribution system are also secured within the same gas cabinet. The cabinet may be ripped away from the rest of the system (where low pressure gas may exist in a line), but each individual gas cabinet would be thrown about independently; somewhat protecting the contents of the cabinet.

6.5.3. High Winds and Tornadoes

6.5.3.1. Transient: High Winds and Tornadoes

Accident Description: Occurrence of 50 Year Mean Recurrence Wind Event

Probability: Remote

The American National Standards Institute (see Institute for Disaster Research 1988) has compiled wind information for design load provisions. They note that in the Denver area the annual probability of a wind speed in excess of 80 mph is 0.02 (i.e., a 50 year mean recurrence interval). However, in the mountainous terrain proximate to Building 16, wind speed may be accelerated. The highest recorded wind speed in the Golden area is 97 mph (on an elevated mesa, above and within one mile of Building 16) [22].

Consequence: Negligible

The critical point is that Building 16 is designed to meet the Jefferson County UBC design wind-speed requirement of 100 - 120 mph. This is also equivalent to the recommended basic wind speed design load requirements of 109 mph for DOE General and Low Hazard Facilities. Thus, given the occurrence of a 50 year recurrent wind event, there should be no structural damage to the Building and consequently no breaching of the structural integrity of the HPM systems.

There are no UBC or DOE design requirements (for General and Low Hazard Facilities only) for tornadoes. Nevertheless, past experience suggests that buildings designed to resist the ANSI standard wind loads are able to resist, without significant damage, approximately 50% of the recorded tornadoes (Institute for Disaster Research, 1988). If a tornado struck Building 16, collateral damage and risk to life and property from structural damage would be of far greater importance than from the breaching of the HPM system.

Risk - Routine (See Figure 14)

Controls: Not applicable.

6.6. Summary

The operations in Building 16 have undergone a rigorous accident and associated risk assessment as described in this section. Of the 30 potential accidents assessed, none present High or even Moderate Risks, 21 present Low Risks and 9 present Routine Risks. These accidents, their Probabilities of Occurrence, Hazard Class, and Risk are outlined in Table 12. As shown in the risk assessment, the risks from all the postulated accidents are classified as "low" or "routine."

It is important to note here, that both accident event probabilities and consequences are larger than would actually be expected, because they are based on the fundamental assumption that all administrative, engineering and personal safety controls have failed. Given the redundancies and backups discussed in the earlier sections, this is a gross oversimplification. Because all identified accidents are either Low or Routine, and because of the inherent and very conservative assumption that all safety controls will fail for the identified consequences to occur, this facility clearly falls within the DOE Low Hazard Class.

RISK ANALYSIS TABLE

NUMBER	TRANSIENT DESCRIPTION	PROBABILITY						CONSEQUENCE				RISK			
		I	ER	R	O	RP	F	N	M	C	CA	R	L	M	H
6.2.1.1.	Quantity in Excess of B-2 Occupancy Ordered				•			•				•			
6.2.2.1.	Leak in Cylinder			•						•			•		
6.2.3.1.	Intra-Laboratory Transportation Accident		•						•			•			
6.3.1.1.	Cross-threading of Valve CGA Fitting and Failure of Helium Leak Check		•						•			•			
6.3.1.2.	Missing Washer in HCl or H ₂ Se Cylinder			•					•			•			
6.3.1.3.	Forgetting Washer/Gasket in a Gasketed Gas Connection			•						•			•		
6.3.1.4.	Attempt to Open Sticky Cylinder Cap Using a Wrench as a Lever			•						•			•		
6.3.2.1.	Toxic/Pyrophoric Liquid Bubbler Put in Backwards			•				•				•			
6.3.2.2.	Toxic/Pyrophoric Liquid Bubbler Leak Outside Delivery System				•				•				•		
6.4.1.1.	Leak of Air in Vacuum Pump			•					•				•		
6.4.1.2.	Leak in Pyrophoric Gas Distribution System into Gas Cabinet or System Enclosure			•					•				•		
6.4.1.3.	Leak in Toxic Gas Distribution System into Gas Cabinet or System Enclosure			•						•			•		
6.4.1.4.	Leak in Distribution System Between Gas Cabinet and Deposition System and Failure of Secondary Containment (Coaxial Tubing or Ducting Raceway)		•							•			•		
6.4.1.5.	Faulty Seals Connecting Reactor Vessel to System				•				•				•		
6.4.1.6.	Rupture of Quartz Reactor Vessel			•					•				•		
6.4.1.7.	Hydrogen Leak in Gas Cabinet			•						•			•		
6.4.1.8.	Hydrogen Leak in Purifier			•					•				•		
6.4.2.1.	Loss of Process Control with Potential for Episodic Release of AsH ₃ , PH ₃ and/or H ₂ Se			•					•				•		
6.4.2.2.	Loss of Process Control and Simultaneous Failure of "Scram" Unit, Exhaust Scrubber, or Cylinder Valve		•						•			•			
6.4.2.3.	Loss of Exhaust Ventilation					•		•				•			
6.4.3.1.	Liquid-type Effluent Scrubber Blockage					•		•				•			
6.4.3.2.	Excessive Oxygen in Carbon Drum Effluent Scrubber and Buildup of Unreacted Hydrides and/or Metalorganics			•						•			•		
6.4.3.3.	Effluent Removal Fails due to Loss of System Vacuum				•			•				•			
6.4.3.4.	Burn Box (CDO) Flame Goes Out				•			•				•			
6.4.4.1.	Loss of Containment of Carbon Drum Contents			•					•				•		
6.4.4.2.	Operator Exposed to Toxic By-Product Materials			•				•				•			
6.4.4.3.	Caustic Spill of Sodium Hydroxide Disposal (pH 13.8)				•				•				•		
6.5.1.1.	Fire			•					•				•		
6.5.2.1.	Seismic Activity			•						•			•		
6.5.3.1.	High Winds and Tornadoes			•				•				•			
TOTALS		0	4	18	6	2	0	8	14	8	0	12	18	0	0

PROBABILITY

I: Impossible
ER: Extremely Remote
R: Remote

O: Occasional
RP: Reasonably Probable
F: Frequent

CONSEQUENCE

N: Negligible
M: Marginal
C: Critical
CA: Catastrophic

RISK

R: Routine
L: Low
M: Moderate
H: High

Table 12

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8. LIST OF APPENDICES (Actual Appendices are located in a separate document.)

Appendix A1	Failure Rate Data
Appendix A2	Estimating Concentrations from Gas/Vapor Releases in Gas Cabinets & Laboratories
Appendix A3	PVPUFF: Gaussian Puff Dispersion Model
Appendix C1	UFC Article 80 - Hazardous Materials
Appendix C2	UFC Article 51 - Semiconductor Fabrication Facilities Using Hazardous Production Materials to the MDA Toxic Gas Alarm
Appendix I1	Emergency Response Procedures to the MDA Toxic Gas Alarm
Appendix I2	NREL Chemical Hygiene Plan
Appendix I3	NREL Comments to Fluer Recommendations
Appendix I4	Excerpts on Natural Disaster from Harvey Report
Appendix I5	SERI ES&H Office Quality Assurance Plan
Appendix M1	MSDSs (M1.1-M1.19, save M1.14) for HPMs listed in Table 3a of the SAR
Appendix M2	Manufacturer Specifications for Metalorganic Bubbler
Appendix M3	Manufacturer Specifications for Secondary Containment for Gas Cylinders
Appendix M4	Manufacturer Specifications for Pneumatically Operated Cylinder Valve
Appendix M5	Manufacturer Specifications for Dry Chemical Gas Cabinet Scrubber
Appendix M6	Manufacturer Specifications for Fume Scrubber
Appendix M7	Manufacturer Specifications for Vent Gas Scrubber/Scram System
Appendix M8	Burn Box - Plus Schematic Design for Effluent Treatment
Appendix S1	Sample Checklist for Hazardous Gas Cylinder Changing Procedures
Appendix S2	Sample Training Log
Appendix S3	Sample Toxic Gas Inventory Log
Appendix S4	Sample Preventative Maintenance Log
Appendix S5	Sample Safety Interlock/Alarm Inspection Log

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