Silane Safety/Lessons Learned and Accident Prevention

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Eugene has a BS in Chemical Engineering and an MS in Environmental Engineering, all from New Jersey Institute of Technology.

He has over 30 years of Specialty Gas Experience in Production, Laboratory, R&D, Engineering, Safety positions at Matheson, Exxon Research, Solkatronic Chemicals and Scientific Gas Products. Had increasing management responsibilities during his career and held an Executive Management position as Vice President of Corporate Development and Technology for Solkatronic Chemicals for 10 years prior to the Air Products acquisition in 1999. He had responsibility for EHS, Engineering, Information Technology, Research and Development, and Quality. Most recently he was Director of Compound Semiconductor Technology in the Electronics Division and is now Director of ER and Disposal Technology in the Product Safety Group.

He is active in a number of industry associations, Compressed Gas Association (CGA), Asia Industrial Gas Association (AIGA), National Fire Protection Association (NFPA) and the Semiconductor Environmental Health and Safety Association (SESHA)

He also developed and manages the Emergency Response Equipment and Training group since 1990. He is the Course Director for a 3 day Specialty Gas Emergency Response course, which has trained over 4000 customers, government agencies and employees since 1990. He has trained over 750 Firefighters in Compressed Gas Safety and Emergency Response. He has taught at a number of Fire Academies worldwide, including New York and Singapore

He has made numerous presentations worldwide on Emergency Response, Product Safety, Gas Technology and Environment over the last 20 years.

He has 4 US patents for Gas Safety Devices and 2 pending for new Purification Technology

Dr. Vasilis Fthenakis

Vasilis Fthenakis is a senior chemical engineer and the head of the National Photovoltaic Research Center at Brookhaven National Laboratory www.pv.bnl.gov. He is also a professor of earth and environmental engineering at Columbia University where he founded and directs the Center for Life Cycle Analysis. www.clca.columbia.edu

Fthenakis has authored a book on Prevention and Control of Accidental Releases of Hazardous Gases and about 200 papers on energy-related safety and environmental topics. He serves in several expert panels, two journal editorial boards, and frequently consults the PV and chemical industries.

Gas Cabinet Testing, May 2006

Color is 0.033 sec/frame

Black/White is 0.002 sec/frame

Flames for 0.010-0.012 sec

BROOKHAVEN NATIONAL LABORATORY

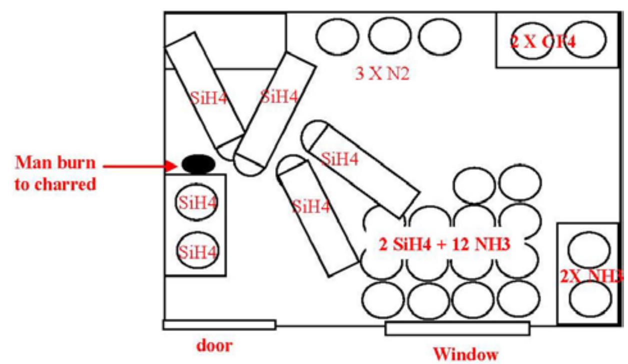
Silane Gas Cabinet Release Test

- High pressure Silane was vented into the gas cabinet through a ¼” tube.
- The cabinet was ventilated at 300 cfm.
- Silane was released without ignition, mixing with air in the cabinet.
- The metastable mass was ignited by an abrupt shutoff of Silane flow.
- The ignition was at the valve outlet
- Reaction is a rapid deflagration
- Obstructions will increase mixing forming a larger steady state metastable mass
- It can be dangerous to approach a silane leak that is not burning, especially if there is any confinement

Taiwan, Silane Explosion, Nov. 23, 2005

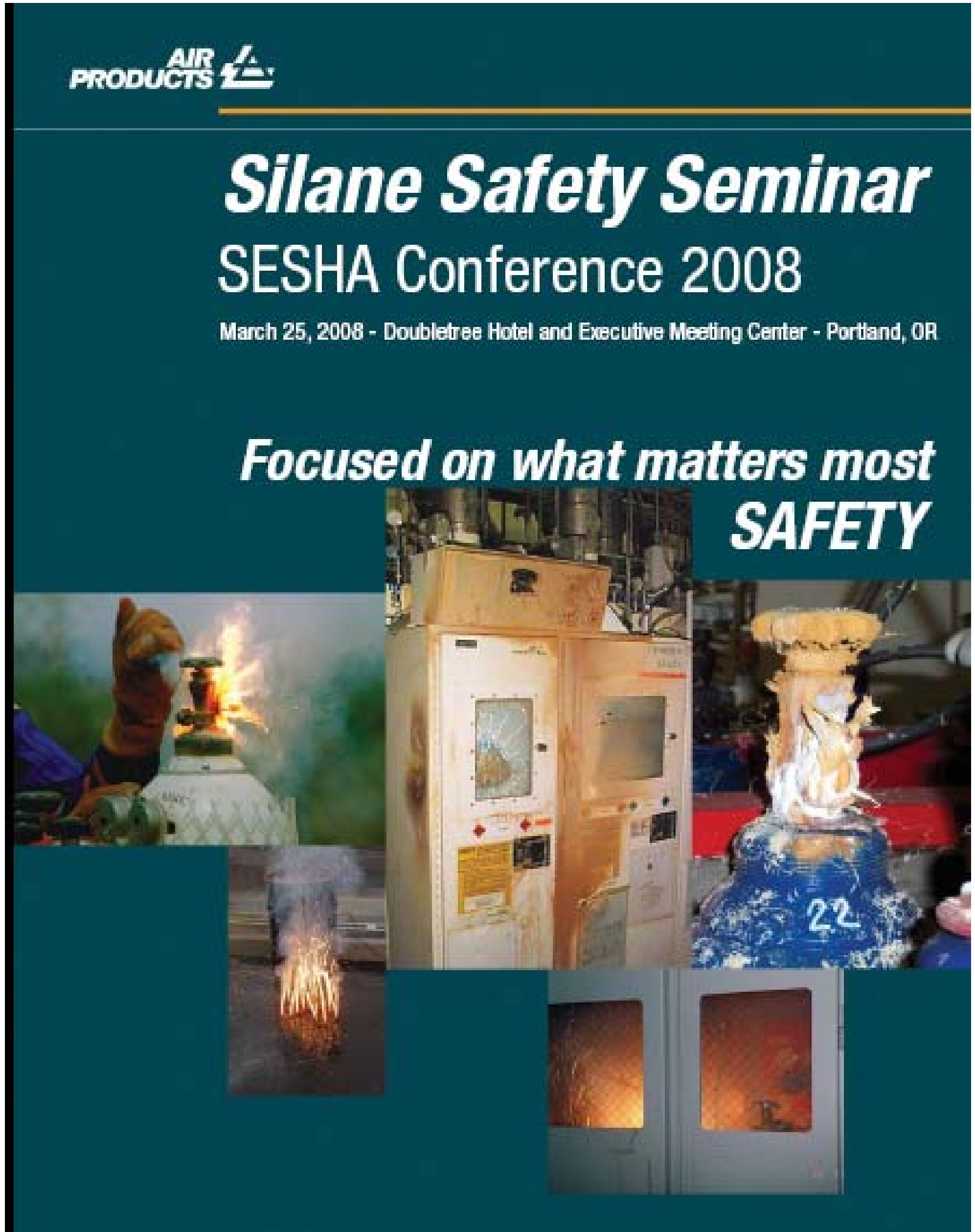
During a cylinder change Silane was released from a full cylinder unignited. The metastable mixture ignited, fatally injuring the operator and rupturing the cabinet.

Other silane and Ammonia cylinders in the gas room also started to release their contents



Silane Safety Seminars

- APCI Spearheaded worldwide effort to improve the industry understanding of silane through a series of silane safety seminars.
- APCI led the effort to organize the first Silane Safety seminar in Asia in Taiwan
- Presentations or seminars on silane have been conducted or are planned for all regions of the world
- Links with major trade shows has resulted in outstanding attendance


AIR PRODUCTS
Silane Safety Seminar
SESHA Conference 2008
March 25, 2008 - Doubletree Hotel and Executive Meeting Center - Portland, OR
Focused on what matters most
SAFETY

Introduction

- Silane has been involved in a number of severe incidents over the last 40 years of use. This presentation will review key incidents and how Silane behaved in the incident. While Silane is pyrophoric gas with a wide flammable range, releases into the air may not always ignite immediately or sometimes not at all. Understanding this behavior can help improve safety in the design and operation of systems as well as improve the response procedure to an incident.
- As reported by numerous studies (FM Global, Intel, Hazards Research, etc) conducted on Silane ignition of Silane is influenced by a variety of environmental and release conditions.
- Of interest is the study by Emeleus and Stewart on the upper and lower explosion limits of silane and oxygen. showed that silane and oxygen in a 1 : 2.3 mol ratio at a total pressure of *ca.* 0.6 bar do not react appreciably even when kept at 70^{o}C for many days. Yet at a slightly higher partial pressure of silane or at a slightly higher temperature an explosion occurred immediately.

History of Silane Use

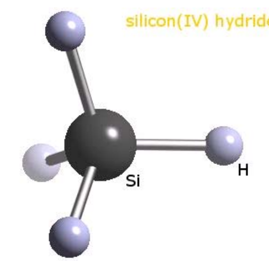
- The Semiconductor Industry started to use Silane in small quantities in 1968.
- During this time there were many small Silane manufacturing processes at a number of gas companies. The manufacturing method was a batch reaction of Trichlorosilane or Silicon Tetrachloride in a molten Lithium Aluminum Hydride salt bath
- As a new compound there was a lot of concern with safety. Considerable study on the safe fill density in the early days only 1 kg
- During transportation there were numerous fires due to valves vibrating open and no secondary valve outlet seal on the valve

Silane Release Behavior

- The greatest hazard of Silane is its unpredictable behavior when released to the air
  - No ignition
  - Immediate Ignition
  - Delayed Ignition
- Silane can easily be released without ignition. FM Global found that Silane did not ignite in 11 out of 12 release tests at 33 psig from 1/8” line. Even at 7.8 psig. For a ¼” line the lowest pressure with no ignition was 70 psig.
- Silane when released at high velocities may not immediately ignite
- Smaller the diameter of the release tube the lower the pressure at which no ignition would occur

Silane, Chemical & Physical Properties

- Silane is a compressed gas which is pyrophoric
- Silicon Tetrahydride, SiH_4
- CAS# 7803-62-5
- UN# 2203
- Molecular Weight 32.11
- Compressed Gas which is filled by weight due to high compressibility
- Gas Density of 0.083 lb/ft^3, 1.33 gm/l @ 70^{o}F (21^{o}C)
- Boiling Point, 1 atm. -169.6^{o}F (-112^{o}C)
- Freezing Point, 1 atm. -299^{o}F (-184^{o}C)
- Critical Temperature 19.9^0 F (-7^{0}C)
- Critical Pressure 632 psia (43 atm)
- Liquid Density @ 10^{o}F (-12^{o}C) 21.1 lbs/ft^3 (338 gm/l)

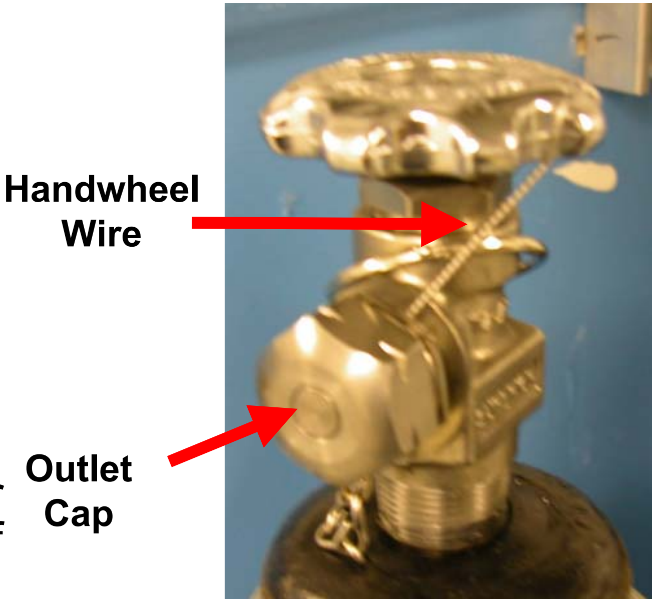


Silane ER Information

- Silane has a vapor specific density heavier than air.
  - 1.12
- Gas Specific Volume @ 70°F (21°C)
  - 12 ft^3/lb (750 cc/gm)
- Autoignition
  - -50°C (-58°F) to -100°C (-148°F) Note: Can vary depending on source of data
- Flammability (LFL -UFL)
  - 1.37 - 96% In a fire Silane will oxidize to amorphous Silicon Dioxide
- Thermal Stability
  - Silane is thermally stable up to 788°F (420°C)
- Water Solubility
  - Silane is slightly soluble in water
- Odor
  - While Silane has reported to have a repulsive odor, the more common odor reported has been none and the distinctive "Ozone" like odor after combustion
- Latent Heat of Vaporization -170°F (-112.5°C)
  - 166.8 btu/lb (388 kJ/kg) at Boiling Point

Leaking Silane Cylinder Valve

- During the early days, numerous incidents were reported of a Silane release when the vaportight outlet cap on a cylinder valve was loosened
- The reactions were reported to be a fire, minor “pops” to explosions. The “pops” can occur when a small amount of Silane trapped behind the valve cap or pigtail is released. In a few cases they have been severe enough to cause eardrum rupture.
- A severe explosion was reported to have occurred in the US in 1977. A piggyback trailer containing 20 cylinders of Silane and 28 drums of antifreeze exploded as the train was moving at 70 mph. A 5 kg cylinder leaked into the trailer and exploded at some point. The sides and roof of the trailer were blown out. 17 cylinders and 4 drums were thrown out of the trailer.
- This and another incident led to improved procedures for inspection, handwheel wiring, gastight outlet caps. Also block and bracing



Valve Crossport Leakers

Recent Silane Incidents

- In the last 20 years, a number of major incidents have occurred with Silane use.
- Release and detonation of gas cabinet
- Release and detonation of duct
- Release and Fire
- Explosion of Cylinder
- Reaction of Solid Byproducts
- Pressure Relief Device Leak
- Aluminum Cylinder rupture

Some Causes

- Connection Leaks
- Failure to cap line during maintenance
- Check valve failure
- Regulator Diaphragm failure
- Improper PRD design
- Cylinder contamination with Nitrous Oxide
- Operator removes wrong cylinder

SiH_4 Leak from Elastomer Gasket

- Silane cylinder on standby
- DISS connection with PTFE Gasket
- PTFE gasket coldflowed and leaked
- Fire from leakcheck hole.
- Sprinkler activated

Connection Leak

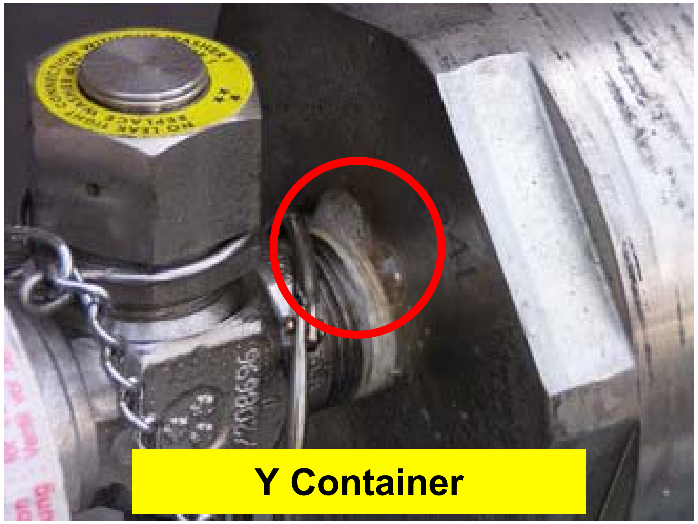
- The most vulnerable part of a Silane system is where there is a mechanical connection that is removed periodically or physically stressed. The most common leak points are the cylinder connection or the pigtail connection to the gas **panel.**
  - Physical impact
  - Wrong Gasket
  - Used Gasket
  - Corroded Bead
  - Not enough or too much torque
  - Forgot to tighten
  - Cold Flow (PTFE Gasket)
  - Work Harden (CGA 350)
  - Low leakcheck pressure

Silane Leak/Release Behavior

- Small Silane leaks
  - without visual indication (smoke, solids, flames)
  - Popping Sound
  - Solids Formation
  - Fire continuous flame or Puffs
- Medium & Large Releases can
  - Immediately Ignite
  - Not Ignite
    - With Delayed Ignition
    - Ignition At Abrupt Shutoff
    - Unknown Ignition Source
    - Not at all

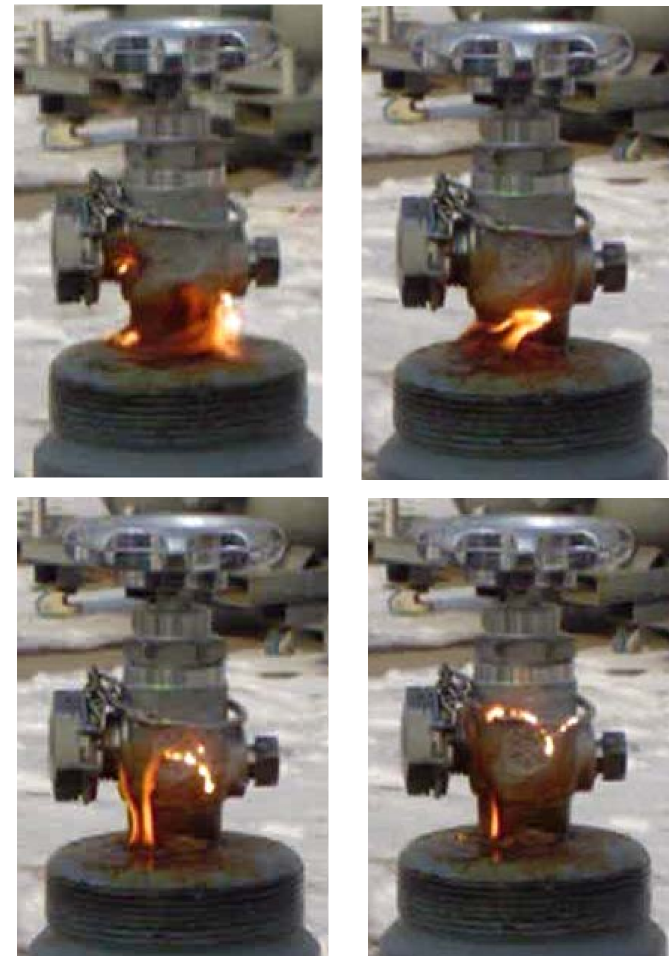
Small Leak no Visual Indication

- Very small Silane leaks may give no visual indication of a leak. These are detected only with the use of a hydride specific leak detector or soap solution.
- Concentrations of 8-15 ppm have been reported



Small Leak with Popping Sounds

- Some small releases have also been discovered by reports of a popping sound
- Sometimes when soap solution is applied to a small leak, it can accumulate enough Silane in a bubble, releasing it with a pop and fire

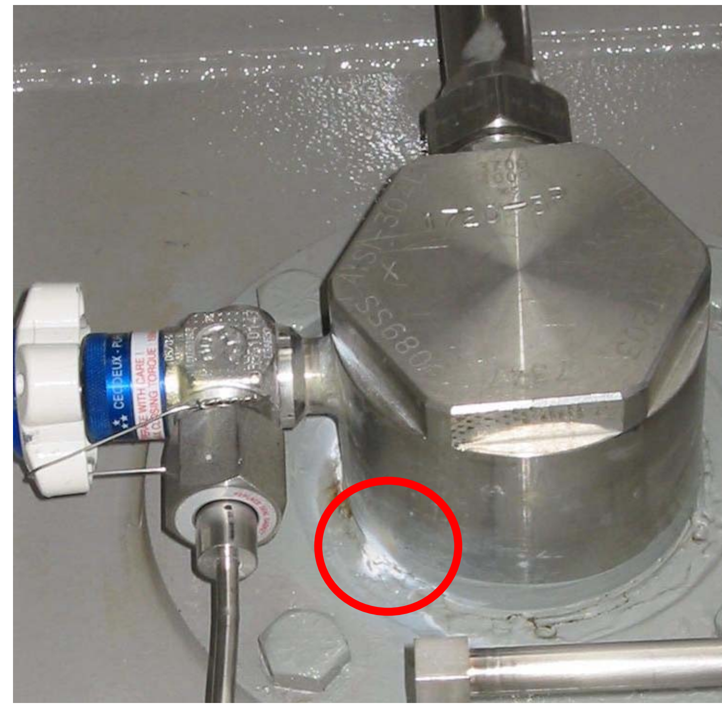


Small Leak with Solids Formation

- Some small releases oxidize to form pure Silicon Dioxide which is white
- There are no flames or popping

Solids Plugging

- Sometimes these seal themselves even at full cylinder pressures of 1450 psig
- 0 ppm using a hydride leak detector
- Leak will start again if solids are removed. It will not however become worst

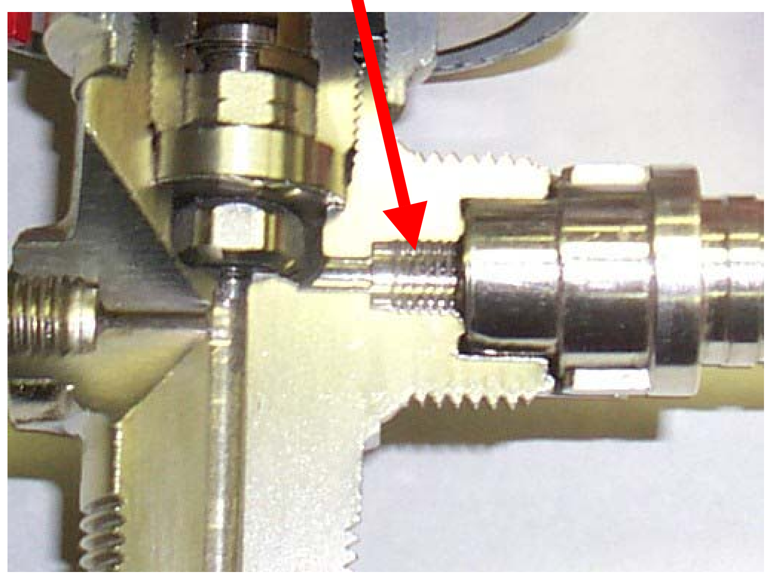


Leaks and Fire

- **Most Silane leaks will immediately ignite**

RFO (Restrictive Flow Orifice)

- The use of a RFO in the cylinder valve can reduce the release rate dramatically and increase the chances of ignition

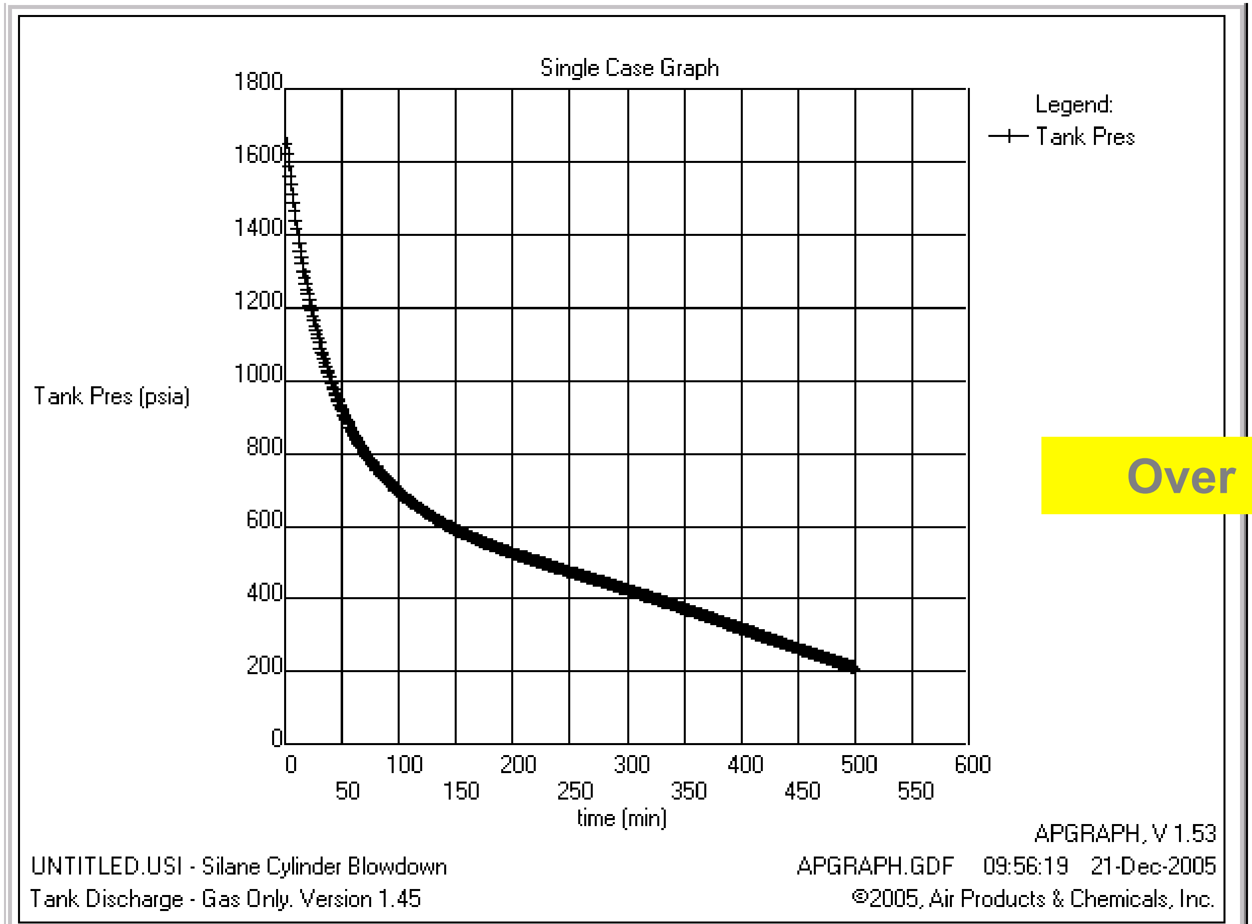


DISS Leak with and without RFO (0.010", 0.25mm)

Ceoduex Valve with RFO (0.010”, 0.25mm) and Without

- 0.5 m vs 3 m flame
- 2.5 cfm (70.8 lpm) vs 333 cfm (9430 lpm) silane flow
- A 15 kg cylinder with RFO will take over 10 hours (see following graph) to empty while without, it will be 6-7 minutes

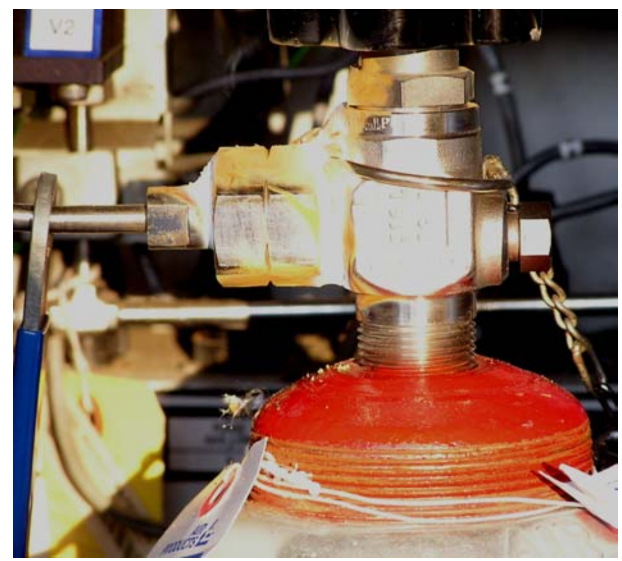
Worst Case Leak, 15 kg Cylinder with a 0.010” (0.25 mm) RFO



Over 10 hours!

Leak and Fire

- **The burning Silane can quickly develop a solid mass around the leak point which can quickly plug the leak if it is a low flowrate release.**

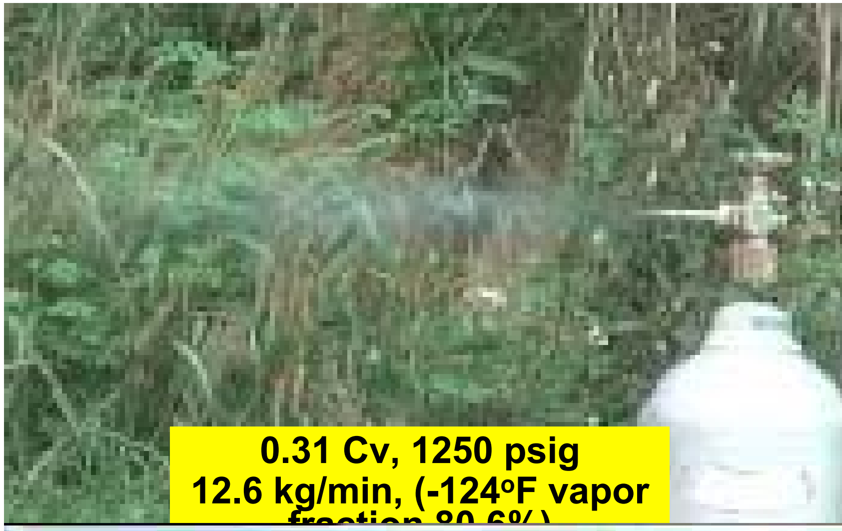


Leak without ignition

- Under certain conditions, Silane can leak and not ignite.
- Ignition at abrupt flow shutoff. This could result in a open air deflagration
- Ignition a few seconds after release

Leak without Ignition

- High pressure releases causes condensation of Silane at -110^{o}C



Open air "Pop". Ignition at Abrupt Shutoff

- Numerous theories on what would cause a release to suddenly ignite.
- Dr. Tamanini's testing determined that one was abrupt shutoff of the flow
- The pictures are the 4 frames in sequence from a cylinder valve wide open with Silane pressure of 1250 psig. Within 0.033 sec of shutoff, it popped

Open Air Releases

- Large unobstructed jets of Silane can incorporate enough air to create a large metastable mixture of Silane and Air which can have a bulk ignition
- Some ignite 1-2 seconds after the release

Open Air Release with Obstruction Creates Even Larger Amounts of Metastable Mixtures

- Release for 17.5 secs from 1/8” (3.175 mm) dia orifice then bulk ignition
- Approx 6” away from obstruction
- Cylinder Pressure of 1260 psig
- Overpressure significantly greater than unobstructed flow

Confinement and Metastable Mass

- **In confinement a Silane release can create an even larger metastable mass due to obstructions**
- **The greater the degree of confinement, the greater the overpressurization from the Silane/Air reaction**

Parameter	Product Pressure	Constant Volume	Constant Detonation
Final Pressure (atm)	1.00	10.21	19.81
Final Temperature (°K)	2725.8	3069.6	3192.1
Gas Density (g/cc)	1.34×10^{-3}	1.19×10^{-3}	2.21×10^{-3}
Sonic Velocity (m/s)	914.3	981.7	1008.8
Detonation Velocity (m/s)			1864.2
Pressure Ratio	1.00	10.21	19.81
Density Ratio	0.112	1.00	1.85

Table 2. Stoichiometric Combustion Parameter in air

Silane Release Into Gas Cabinet

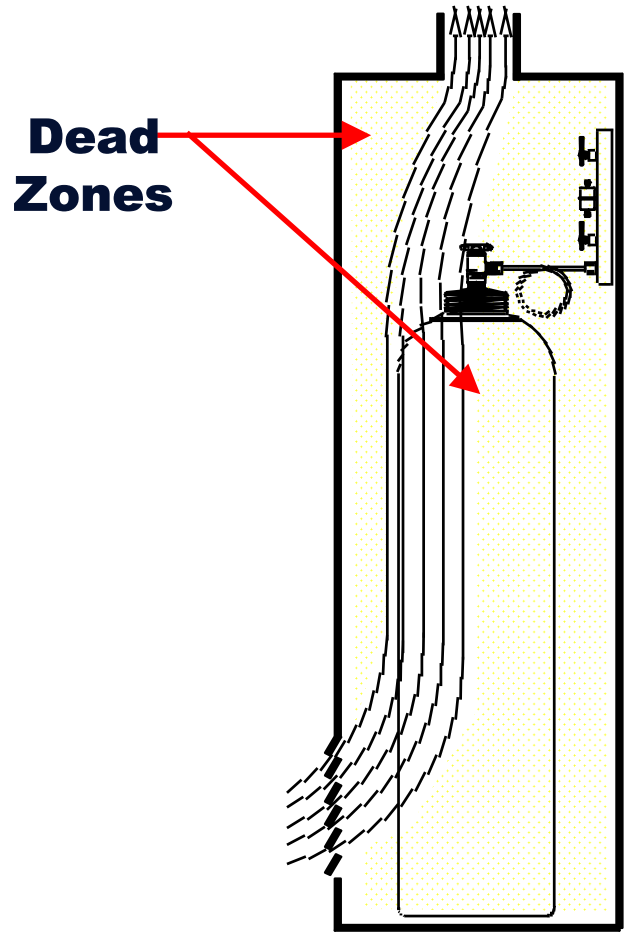
- In 1976, a German company had a Silane release into a gas cabinet which did not immediately ignite. This suddenly detonated and killed a researcher
- After this incident IBM funded a number of studies by Hazards Research and Battelle
  - Merryman, E. L. & Levy, A., “The Rates of Hydrogen Release In Silane-Air Systems”, Battelle Report to IBM, Nov 20, 1980
  - Cruice, W. J. & Grelecki, C., “Effects of Releases of Silane Mixtures in Ambient Air”, Hazards Research Corporation, Report # 4007 to IBM, Dec. 15, 1978
  - Cruice, W. J. & Grelecki, C., “Sensitivity of Silane To Thermal and Shock Initiation”, Hazards Research Corporation, Report # 3750 to IBM, July 19, 1977
  - Cruice, W. J. & Dolch, T. J.,“Temperature of Silane/Air Flames in Exhaust Ducts”, Hazards Research Corporation, Report # 4881 to IBM, June 19, 1981
  - Cruice, W. J., “Leakage of Silane in Gas Cabinets and Ducts”, Hazards Research Corporation, Report # 5038 to IBM, May 11, 1982
  - “An Investigation Of The Oxidative and Explosive Properties of Silane-Air Mixtures:”, Battelle Report to IBM, April 11, 1983

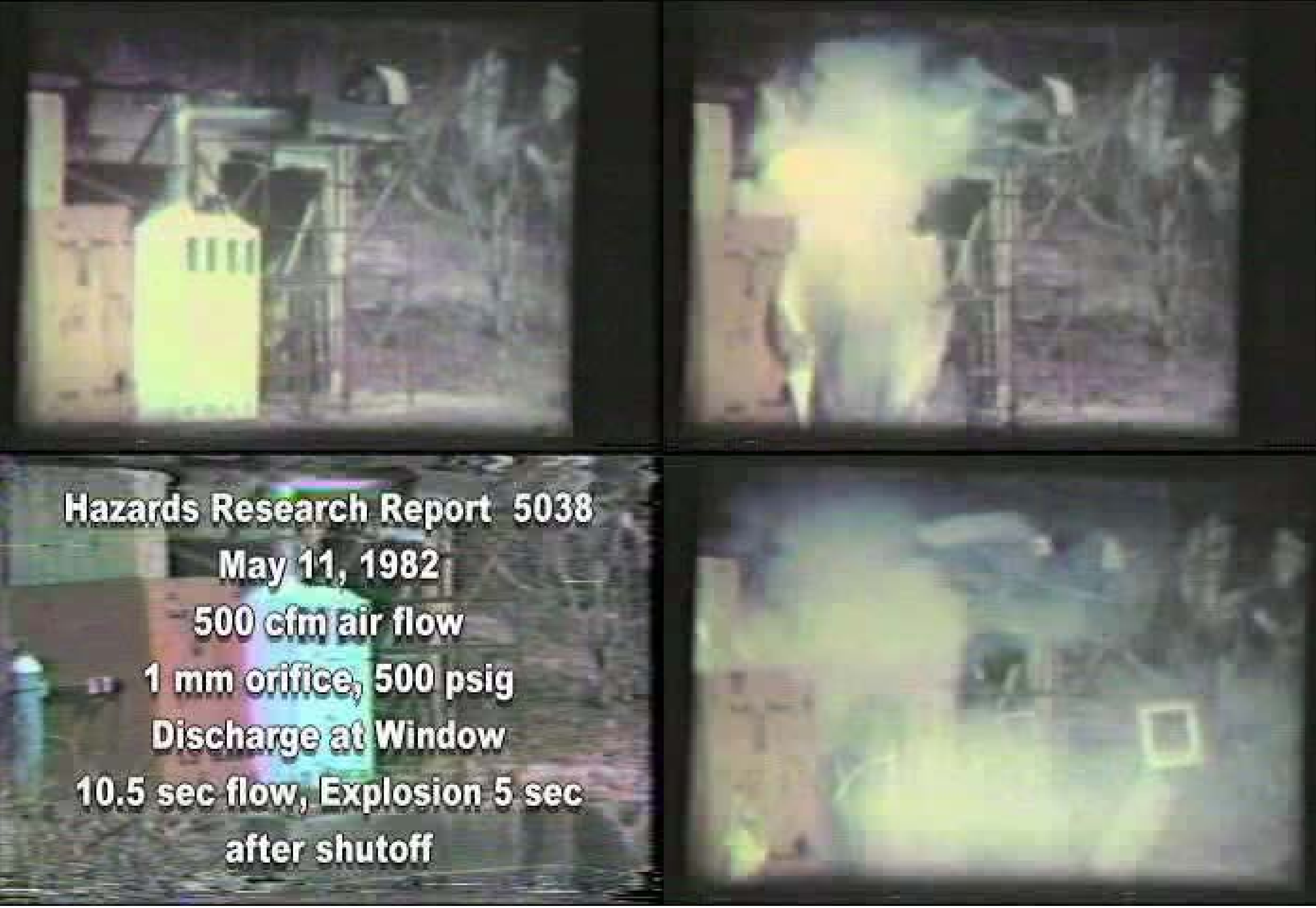
Gas Cabinet Explosions

- Incidents reported where Silane was released into a gas cabinet without immediate ignition and exploded after a delay
  - Germany, 1976 – 1 fatality
  - Japan, 1989, 1 fatality & 1 injury
  - Japan, Dec. 13, 1990 – 1 fatality & 3 injuries
  - US, Jan 1992 – 1 injury
  - Japan, Dec. 21, 1996 – 1 fatality
  - US Dept of Energy, Date Unknown – no injuries
  - US, 2003, no injuries
  - Taiwan, Nov 23, 2005 – 1 fatality
  - India, March 2007 – 1 fatality

Hazards Research Gas Cabinet Testing, 1982

- **Hazards Research in New Jersey was able to simulate the 1976 incident where they released pure silane at two different points (at 8" duct inlet, window level) into a 2 cylinder gas cabinet (17 ½" x 36" x 85") while it was being ventilated at 500 cfm. Silane was discharged at pressures of 50 and 500 psig through 0.38, 1 and 4 mm (0.015", 0.040" and 0.160") orifices. The 0.38" burned at all conditions. The 1 mm discharging at 500 psig had a violent detonation after a few seconds of release. Cabinet disappeared in 1/18 of a second. This was duplicated with a second cabinet. In the first, the discharge at 50 psig was stopped after 16 seconds when it "popped", blowing open the doors. The second test at 500 psig was stopped after 10.5 seconds of flow. 5 seconds after shutdown the cabinet blew apart with pieces flying over 100 ft. The pressure rise rate was well above 100,000 psi/sec indicative of a gas phase detonation. (Hazards Research Corp Report #5038 to IBM "Leakage of Silane in Cabinets and Ducts" May 11, 1982)**




Hazards Research Report 5038
May 11, 1982
500 cfm air flow
1 mm orifice, 500 psig
Discharge at Window
10.5 sec flow, Explosion 5 sec
after shutoff

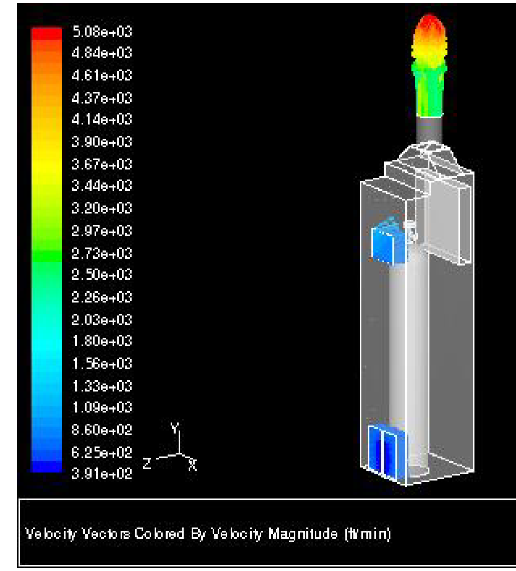
Silane Metastable Mass

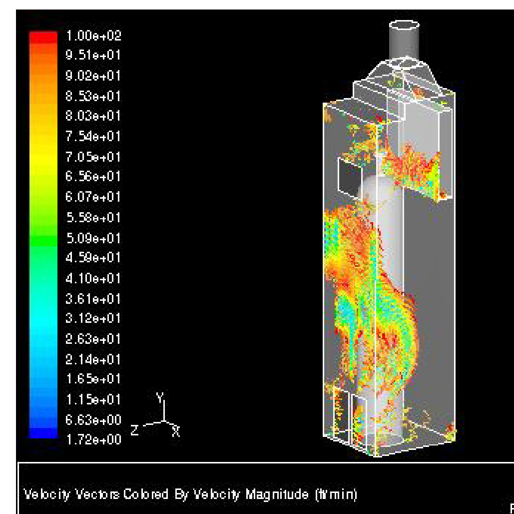
- Larger the orifice and higher the pressure, the greater the amount of metastable mass in a open jet
- Obstructions create dramatically higher mixing and mass
- Table below assumes 1200 psig release pressure

Orifice dia "	Release	Estimated Mass, kgs
1	Open Jet	7.22
0.75	Open Jet	3.14
0.5	Open Jet	0.96
0.125	Open Jet	0.016
0.125	Obstructed	0.362

Gas Cabinet Design

- To better understand release behavior we launched a project to use CFD (Computational Flow Dynamics) to review our gas cabinet designs
- This has led to a better understanding of baffles and other objects in the cabinet
- Collaboration with the FM Global Inc. R&D team to see if we can develop a mathematical model to predict overpressure in a gas cabinet release. This would combine testing data from their 1996 studies with AP MRC CFD analysis





FM Global Testing, 1996

Flame Temperatures

- At lower flammability limit < 3 % silane
  - flame temperature ~ 800 °F
  - will not ignite paper
- At stoichiometric mix with air 9.51 % silane
  - Flame is white and smoke is white
  - most efficient ratio of fuel to air
  - flame temperature ~ 4400 °F
  - will melt metal

By-Products of Oxidation

$SiH_4 + O_2 \longrightarrow SiO_2 + 2H_2$

$SiH_4 + 2O_2 \longrightarrow SiO_2 + H_2O$

$SiH_4 + O_2 \longrightarrow SiH_2O + H_2O$

$SiH_4 + \frac{1}{2} O_2 \longrightarrow SiH_2O + H_2$

$SiH_2O + O_2 \longrightarrow SiO_2 + H_2O$

Depending on available oxygen oxidation may be incomplete. Brown smoke and a dull orange flame is an indication of incomplete oxidation

Hazards of By-Products

- Brown Dust is reactive & pyrophoric
  - Typically silicon oxyhydride SiH_2O
  - Can also absorb Hydrogen
- White Dust
  - silicon dioxide SiO_2

Reactivity of Silane

- Delayed reaction with oxidizer gases like N_2O, NF_3, requires a ignition source (Gollub 1988 & Osaka University 1991)
- Immediate reaction with strong oxidizer gases like ClF_3, Cl_2 & F_2
- Oxygen reaction can be delayed or immediate
- Other Oxidizers like Nitric Acid (HNO_3), Hydrogen Peroxide (H_2O_2)
- Reacts with some of the Chlorofluorocarbons
  - Halocarbon 12 (Dichlorodifluoromethane) & Halocarbon 22 (Chlorodifluoromethane)
  - fire extinguishers, cleaning agents, refrigeration units and lubricants may contain these materials
  - contact with these materials may result in a fire or explosion

U.S. Silane Codes and Standards

- NFPA 318 & 55 *(National Fire Protection Agency)*
- IFC Chapters 18, 27, 30 & 41*(International Fire Code)*
- FM Global 7-7 *(Factory Mutual)*
- ANSI/CGA-G-13 *(American National Standards Institute / Compressed Gas Association)*
- UFC *(Uniform Fire Code)**
- *Also must comply with*
  - *Local Codes*
  - *Authority Having Jurisdiction*

*Obsolete

Summary of Air Products Internal Safety Requirements for Silane

(note: Any exceptions to these requirements require a Hazop / Safety Review to ensure equivalent protection is in place)

U.S. Requirements

All Silane Systems

- UV / IR detector
- Gas Monitor
- Exhausted Enclosure for indoor equipment
- Dedicated purge system
- High pressure (not liquid bulk) purge source
- Overpressure protection
- Process vent dedicated to silane
- Dedicated purge system
- Electrical Hazardous area protection
- Inert Coax Monitoring (recommended)
- Trickle purged vent header
- Overpressure protection
- Process vent
- Vacuum system
- Backflow protection
- Isolation valves
- Pressure indication
- Compatible materials
- Equipment and Hazard labels

Additional Requirements for Enclosed Systems

- Access port or view port for distribution systems
- Access port for source systems
- Exhaust Monitor
- Automatic Door and Window Closers
- Ventilation at least 250 times potential leak rate
- One silane cylinder per cabinet
- 150 ft/min minimum air velocity across open window
- 200 ft/min average air velocity across open window

Additional Requirements for Source Systems

- RFO in source container valve
- 0.010 inch max diameter for cylinders
- Sprinkler
- Captured Bonnet Relief Vents
- ASO valve located on Cylinder
- Excess Flow Protection
- Metal Separation plate between silane cylinders
- Remote Emergency Stop
- Remote, barricaded, or delayed start for bulk systems
- 12 gauge sheet metal for enclosures
- Pressure regulation
- Controller
- Cylinder restraints
- Provisions for Seismic Anchoring
- All-Welded pigtail
- Automated purging
- High Pressure Leak Test (recommended)

Scope and Purpose of CGA G-13

- Addresses the hazards in handling silane
- Covers storage, use and cylinder filling facilities
- Prescribes controls for installation of silane systems
- Recommends methods for storage & transfer of silane
- Provides guidance for siting, design of equipment, safety systems & installation of silane storage and gas delivery/filling systems
- Provides guidance on operational steps
- Does NOT cover user facilities and gas distribution after the gas cabinets or VMB's

Key elements of CGA G-13 that are not in other standards

- Separation distances based on experiments
- Comprehensive guidance for bulk delivery systems
- Covers all applications, not just semiconductor, and includes manufacturers filling facilities
- Comprehensive – design guideline, siting, life safety, gas properties…
- Focus on silane systems only
- Written in "Code Language"

CGA G-13 is a Comprehensive Standard

- Physical properties of silane
- Packaging
- Outdoor storage & use (Strongly encouraged)
- Indoor storage & use (Allowed but discouraged)
- System design – cylinder & bulk
- Piping
- Gas & flame detection
- Fire protection systems
- Ventilation systems

CGA G-13 a a Comprehensive Standard (cont)

- Venting and treatment of silane
- Purge gas systems
- Electrical requirements
- Supervisory controls/life safety
- Detailed references
- Personnel protection (PPE, training, operations, maintenance)
- Thermal radiation and overpressure modeling

Bulk Silane Supply Hazards Assessment

Hazards Assessment Damage Criteria

- Explosion Overpressure Damage
  - 1.5 psi - Instrument Damage
  - 3.5 psi - Damaged Pipe Supports, Block Walls Fail
  - 6.0 psi - Horizontal Pressure Vessel Support Damage, Process Piping Displaced or Broken
  - 15 psi - Tankage Overturned or Destroyed
- Thermal Radiation Tolerances
  - 38 kw / sq m - Sprinklered Tankage
  - 25 kw / sq m - Buildings (No Windows, Fireproof Doors)
  - 10 kw / sq m - Vegetation
  - 6 kw / sq m - Escape Routes
  - 2 kw / sq m - Plastic Cables
  - 1.5 kw / sq m - Stationary Personnel

Setback distances to protect the public and workers

- From radiant energy or overpressure

Appendix C—Thermal radiation
(Normative)

Thermal radiation kW/m^2	Exposure	Minimum distance to exposure ft (m)							
		Cylinders [1)] $\le 600\ ft^3$ $(17\ m^3)$		Cylinders 601 to 2500 ft^3 $(71\ m^3)$		Cylinders 2501 to 10 000 ft^3 $(283\ m^3)$		450 L cylinder [2)] $\le 10\ 000\ ft^3$ $(283\ m^3)$	
		ft	(m)	ft	(m)	ft	(m)	ft	(m)
1.6	Location where personnel with protective clothing are allowed to be continuously exposed [19].	16	(5)	30	(9)	50	(15)	60	(18)
4.7	Heat intensity where emergency actions lasting up to three minutes is required [19].	12	(4)	20	(6)	30	(9)	50	(15)
6.3	Heat intensity in areas where emergency actions lasting up to 1 minute is required [19].	10	(3)	16	(5)	25	(8)	45	(14)

Appendix D—Overpressure
(Normative)

Over-pressure Psi (kPa)	Minimum distance to exposure ft (m)													
	PRD with ≤ 0.375 in (10mm) orifice				PRD with > 0.375 in (10mm) to ≤ 0.5 in (13 mm) orifice				PRD with > 0.5 in (13mm) to ≤ 1 in (25 mm) orifice					
	1000 psig (6900 kPa)		1600 psig (11 030 kPa)		1000 psig (6900 kPa)		1600 psig (11 030 kPa)		600 psig (4140 kPa)		1000 psig (6900 kPa)		1600 psig (11 030 kPa)	
	ft	(m)	ft	(m)	ft	(m)	ft	(m)	ft	(m)	ft	(m)	ft	(m)
0.5 (3)	105	(32)	175	(53)	140	(43)	225	(69)	175	(53)	275	(84)	450	(137)
1 (7)	65	(20)	110	(34)	80	(24)	145	(44)	110	(34)	180	(55)	300	(91)
2 (14)	40	(12)	65	(20)	50	(15)	90	(27)	65	(20)	100	(30)	165	(50)

Table 3—Minimum distance from cylinder sources in storage or use to outdoor exposures

Type of exposure	Minimum distance to exposures for different storage volumes or nests [1] [2] [3]							
	Cylinders [4] $\leq$ 600 ft^3 (17 m^3)		Cylinders [5] 601 ft^3 to 2500 ft^3 (71 m^3)		Cylinders [5] 2501 ft^3 to 10 000 ft^3 (283 m^3)		450 L cylinders[6] $\leq$ 10 000 ft^3 (283 m^3)	
	ft	(m)	ft	(m)	ft	(m)	ft	(m)
Places of public assembly, property line that is able to be built upon.	20	(6)	30	(9)	50	(15)	60	(18)
Public street and sidewalk	20	(6)	30	(9)	50	(15)	60	(18)
Buildings of nonrated construction [7]	15	(5)	25	(8)	25	(8)	40	(12)
Buildings of nonrated construction [8]	20	(6)	25	(8)	25	(8)	40	(12)
Buildings with 2 hr fire rating and no openings within 25 ft (8 m)	5	(1.5)	5	(1.5)	5	(1.5)	5	(1.5)
Buildings with 4 hr fire rating and no openings within 25 ft (8 m)	0	(0)	0	(0)	0	(0)	0	(0)
Compatible compressed gas cylinder storage or other silane nests[7]	9	(3)	9	(3)	12	(4)	30	(9)
Compatible compressed gas cylinder storage or other silane nests[8]	20	(6)	20	(6)	20	(6)	40	(12)
Incompatible compressed gas cylinders and materials	20	(6)	20	(6)	20	(6)	40	(12)
Flammable and/or combustible liquid storage above ground [7]								
(a) 0 gal to 1000 gal (3785 L)	10	(3)	10	(3)	25	(8)	25	(8)
(b) In excess of 1000 gal (3785 L)	25	(8)	25	(8)	50	(15)	50	(15)
Flammable and/or combustible liquid storage above ground [8]								
(a) 0 gal to 1000 gal (3785 L)	20	(6)	20	(6)	25	(8)	25	(8)
(b) In excess of 1000 gal (3785 L)	25	(8)	25	(8)	50	(15)	50	(15)

[1] The distances are based on permissible exposure to thermal radiation. See Appendix C for thermal radiation data.

[2] The distances specified are allowed to be reduced to 5 ft (1.5 m) when protective walls are provided in accordance with 6.3.2 or reduced to zero feet when in accordance with 6.2.6.2.

[3] Volume shown in liters refers to the water volume of the cylinder.

[4] For cylinders with an internal volume of 1.8 ft^3 (50 L) or less in storage or for those in use when separated to prevent flame impingement as required by 6.4.4.

[5] For cylinders with an internal volume of 1.8 ft^3 (50 L) or less in storage only.

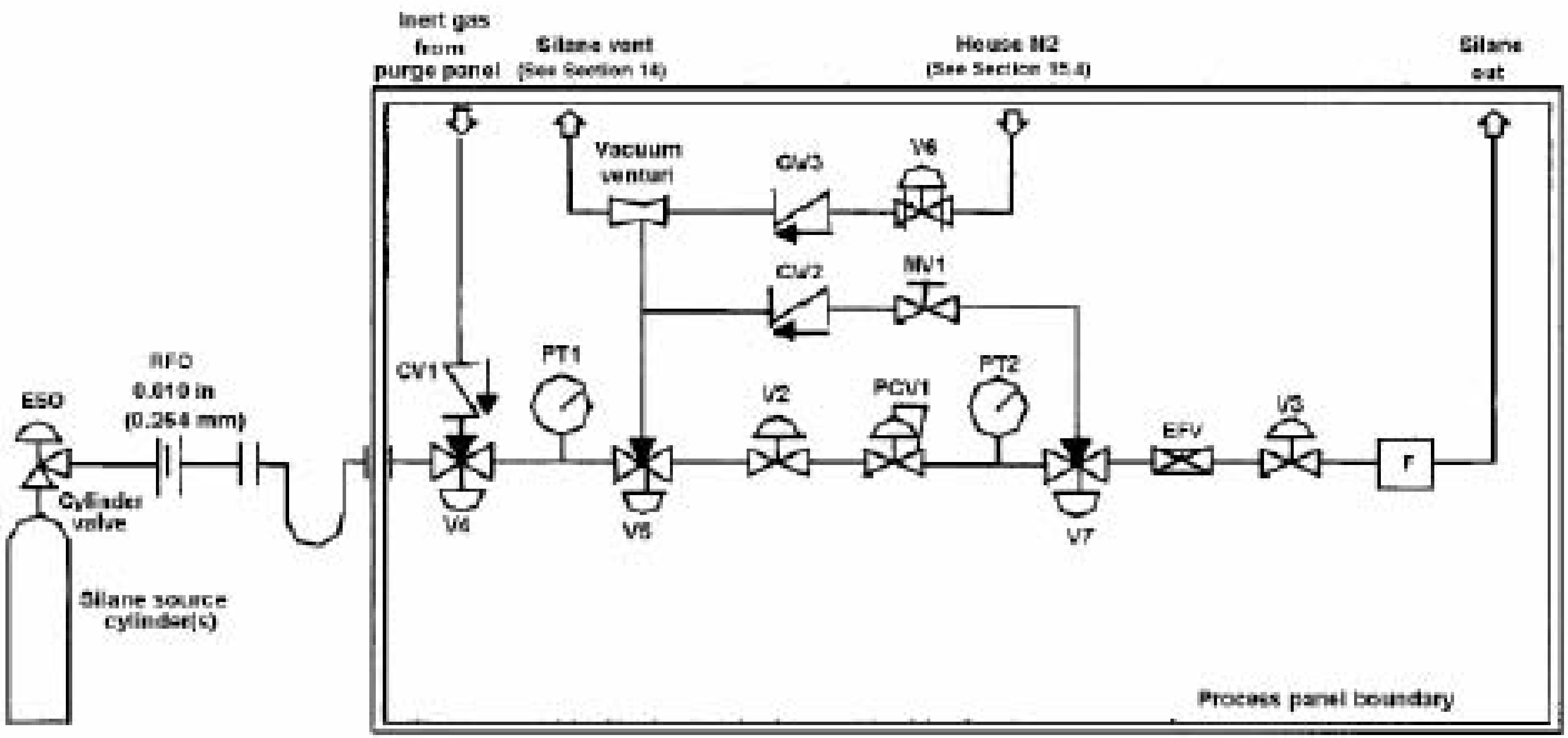
[6] For cylinders with an internal volume greater than 1.8 ft^3 (50 L) and not exceeding 16 ft^3 (450 L) in storage or use.

[7] Silane packaged in steel cylinders or fiber overwrapped aluminum cylinders or silane stored in proximity to compatible gases packaged in steel or aluminum fiber overwrapped cylinders.

[8] Silane packaged in aluminum cylinders or silane stored in proximity to compatible gases packaged in aluminum cylinders.

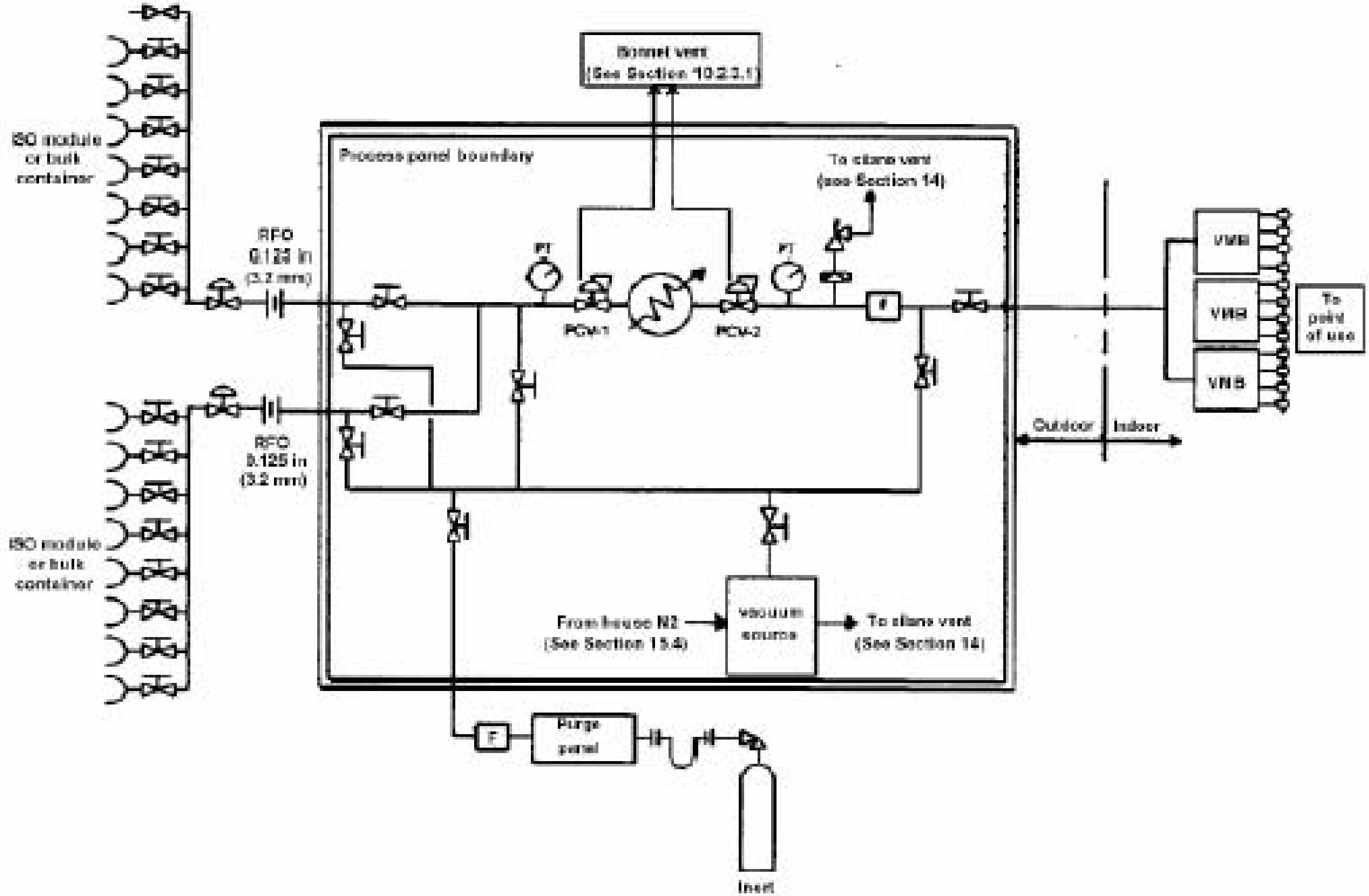
8.1.2 Process gas panel

Process gas panels shall be used to regulate the downstream pressure of gas from the silane source cylinder(s) to a VMB or point of use. General requirements for process gas panel piping systems, RFO, emergency shutoff system (ESO) valves, and components are specified in Section 10. See Figure 5.



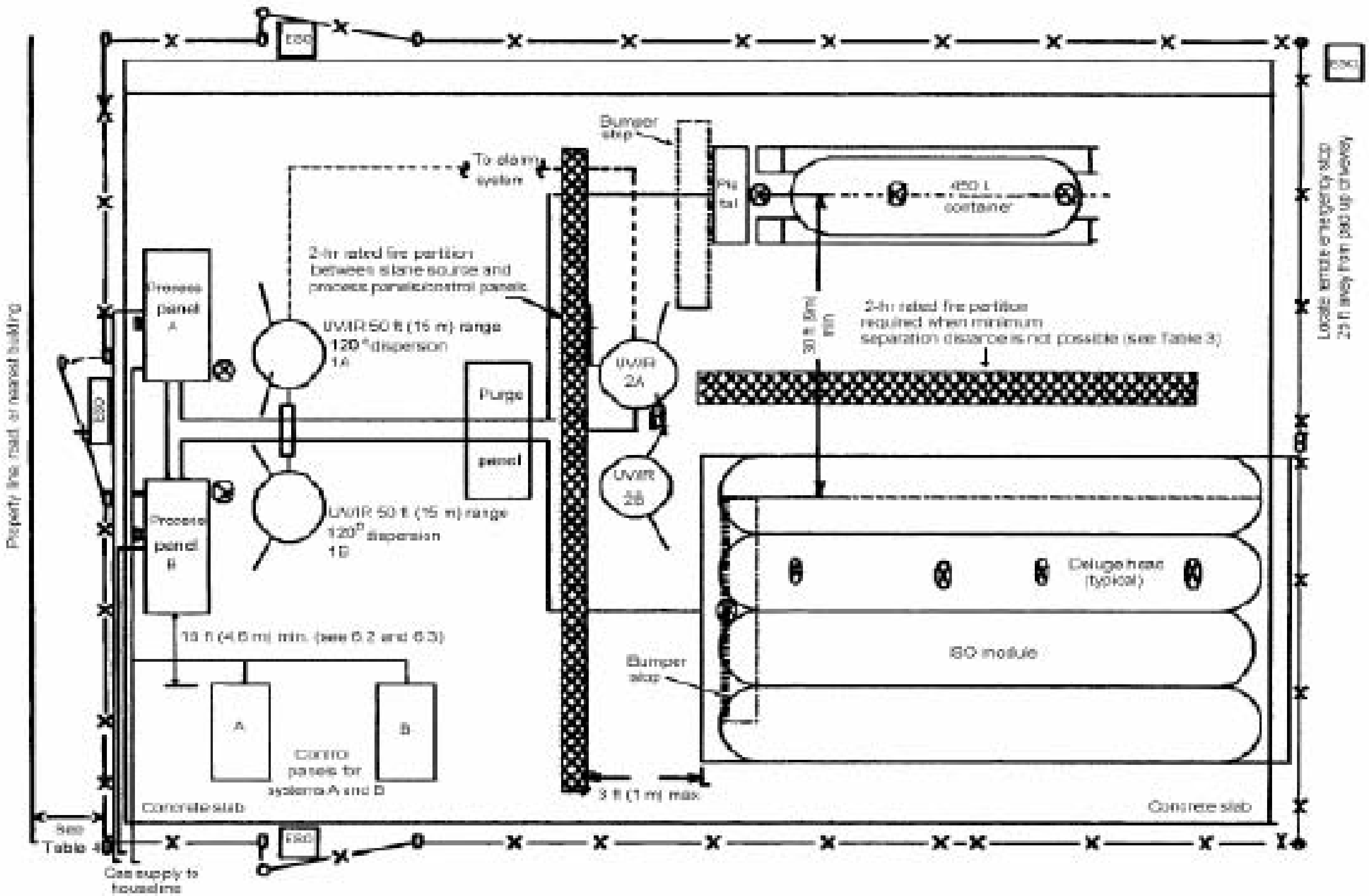
NOTE—The ESO valve is allowed to be located on the cylinder or on the pigtail close coupled to the cylinder. Figure 5 has been provided to illustrate the concepts described in the text of the standard. The figure is schematic in nature. It is neither to be interpreted as a design document nor is it intended to restrict alternate designs. For instrument nomenclature, see Figure 1.

Figure 5—Typical silane process gas panel



NOTE—The vacuum source is either a vacuum pump system or a vacuum venturi system. Figure 8 has been provided to illustrate the concepts described in the text of the standard. The figure is schematic in nature. It is neither to be interpreted as a design document nor is it intended to restrict alternate designs. For instrument nomenclature, see Figure 1.

Figure 8—Typical bulk system process flow diagram



NOTE—Figure 4 has been provided to illustrate the concepts described in the text of the standard. The figure is schematic in nature. It is neither to be interpreted as a design document nor is it intended to restrict alternate designs. For instrument nomenclature, see Figure 1.

Figure 4—Typical bulk source container layout (unattended operations)

Key Bulk Silane System Safeguards

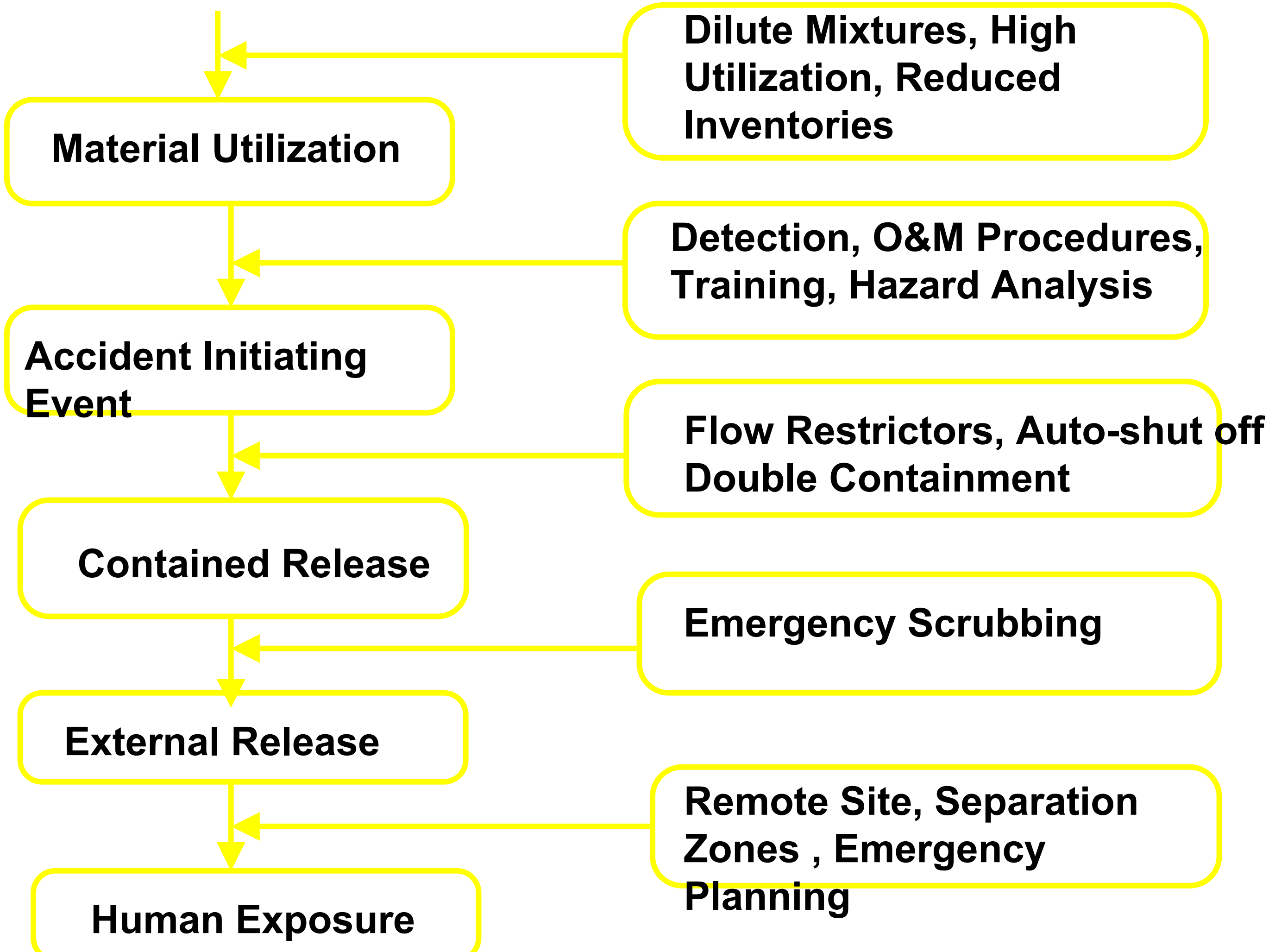
- Fire Separation Walls
- Natural Ventilation with outdoor location
- Deluge system
- Remote Shutdown
- Flame detection
- Security and limited access
- High pressure leakcheck

Evolution of CGA G-13

- Regional version to be published by the Asia Industrial Gases Association
- Regional version to be published by the European Industrial Gases Association
- Regional version under review by the Japan Industrial and Medical Gases Association
- Revision of CGA G-13 is now underway with a PINS formed submitted to ANSI

Multi-layer Protection Strategy for PV Manufacturing Facilities

HAZARD DEVELOPMENT PREVENTION/MITIGATION LAYERS



Process Hazard Analysis (PHA)

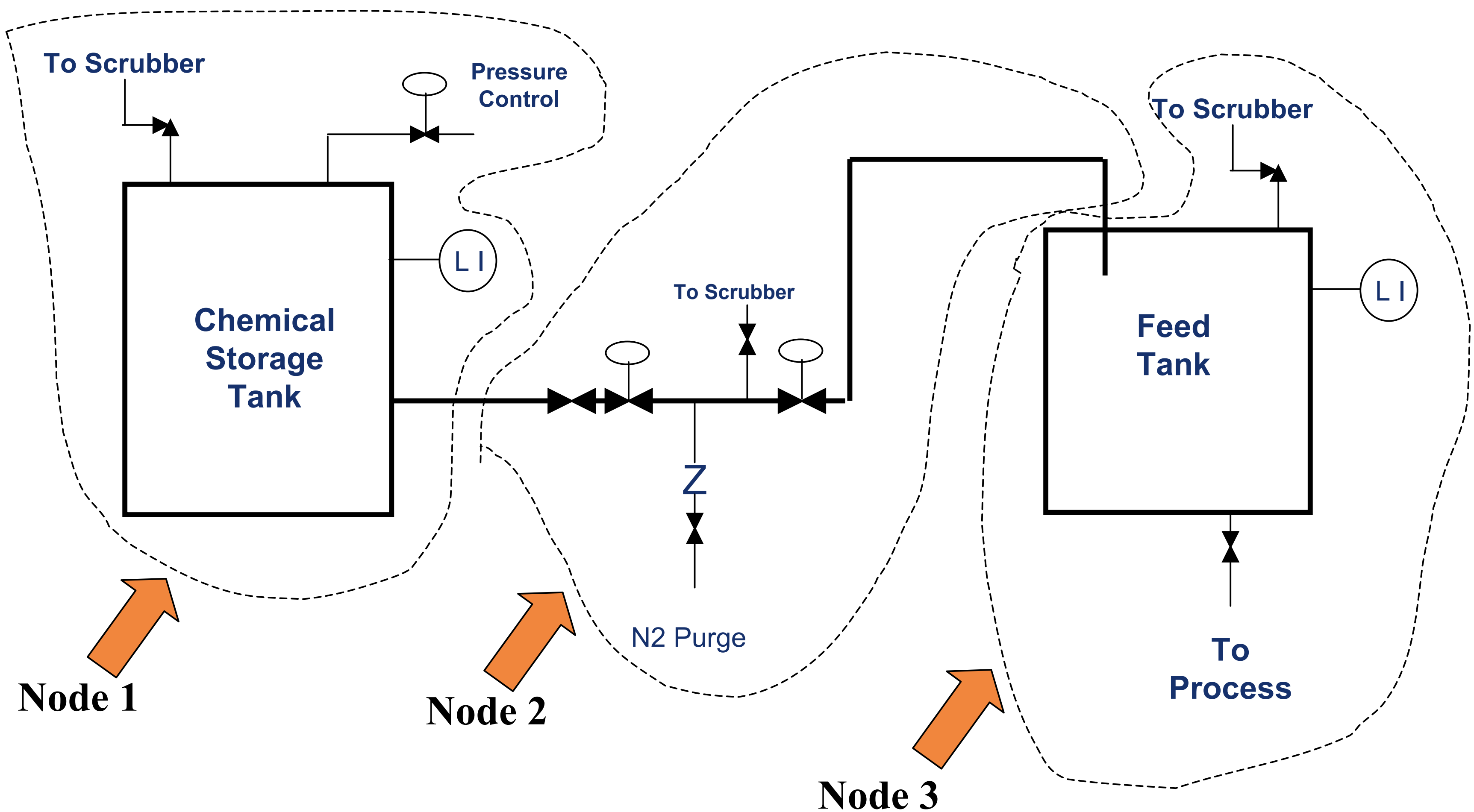
- **Focus** on equipment, instrumentation, utilities, human factors & external factors that might impact the process.
- **Goal**

  Identify potential system interactions and failures that could result in an accident.
- **Types of Methods**
  - Flexible, fast methods when quantities of hazardous materials are low (e.g., Checklist, What if)
  - Rigorous methods in the development stages of a project and during manufacturing as processes are scaled up (e.g., HAZOP, FMEA, FTA)

Hazard and Operability Studies

- Used as a method of studying hazard and/or operability by exploring the effects of any deviations from design conditions
- Team-based approach
- Needs well-defined system parameters
  - Start with PIDs
  - Break the design into manageable sections with definite boundaries (nodes)

System Divided Into Nodes



Systematic Review Sequence

- **Identify study** “nodes” **on PIDs**
- **Establish Node 1 design/operation** intent
- **Identify** Deviation 1 **from Node 1 intent**
- **Identify** causes**,** loss events**,** protection
- **Decide whether** action **is warranted**
- Repeat **for every node & deviation**

HAZOPs

"Scenarios"

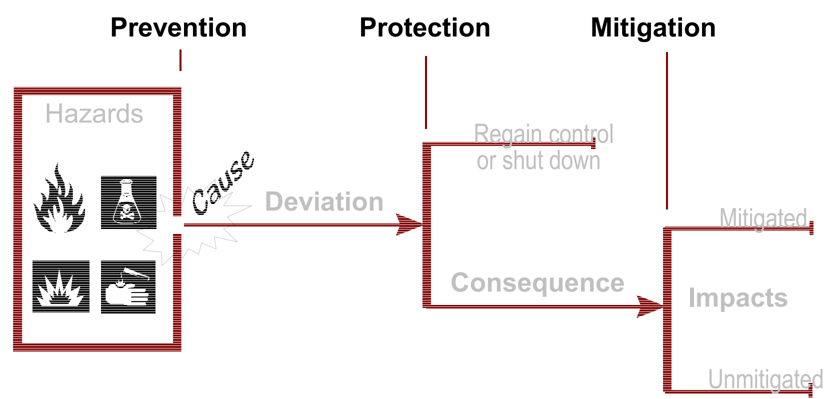
- *What Can Go Wrong?*
- *How Likely?*
- *How Severe?*
- *So What?*

Objective

- Identify <u>all</u> failure scenarios
  (accident initiating events)
  - **Not generally possible just by inspection**
  - <u>Systematic approach</u> **needed**

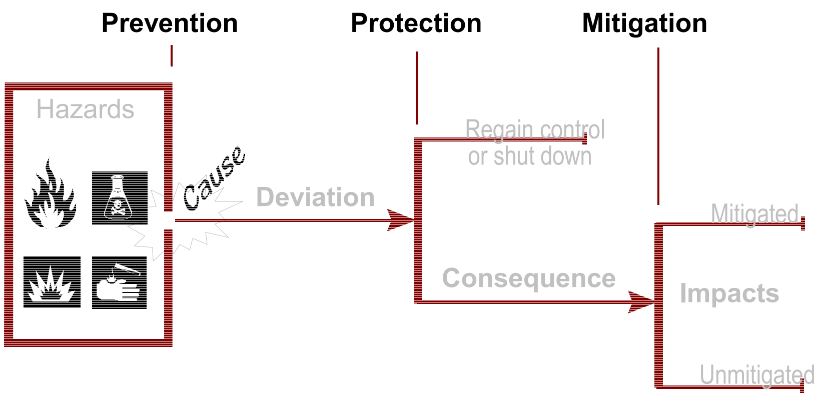
HAZOP Scenario Development

- Node
- Intent
- Deviation
- Cause
- Consequence ***(Loss Event)***
- Protection ***(safeguards)***



HAZOP Scenario Development

- Node
- Intent
- Deviation
- Cause
- Consequence ***(Loss Event)***
- Protection ***(safeguards)***



Design / Operational

INTENT

The intent describes the design / operational parameters defining normal operation

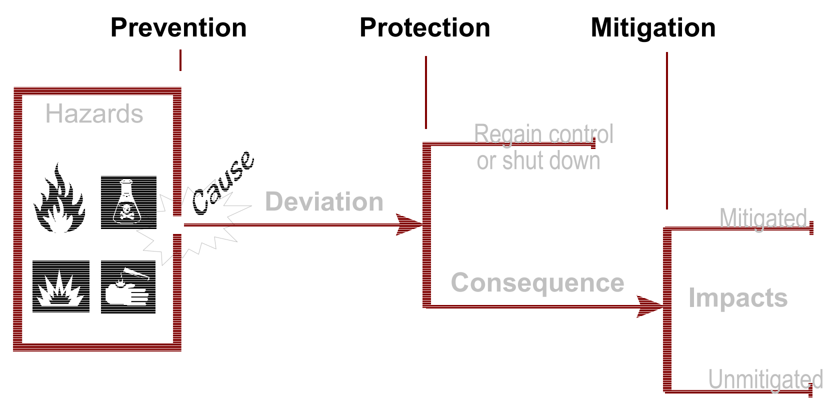
- Functions
- Limits
- Compositions
- Procedural steps

"What is this part of the process designed to do?"

"What is supposed to be done at this point in time?"

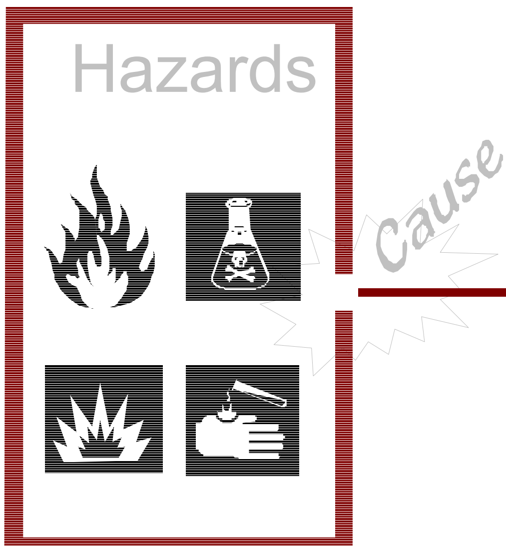
HAZOP Scenario Development

- Node
- Intent
- Deviation
- Cause
- Consequence ***(Loss Event)***
- Protection ***(safeguards)***



Deviations

A deviation **is an <u>abnormal situation</u>, outside defined design or operational parameters.**



Deviation

- No Flow
- Low Temperature
- High Pressure *(exceed upper limit of normal range)*
- Less Material Added
- Excess Impurities
- Transfer to/from Wrong Tank
- Wrong Connection
- Loss of Containment
- etc.

Determine Parameter Deviations

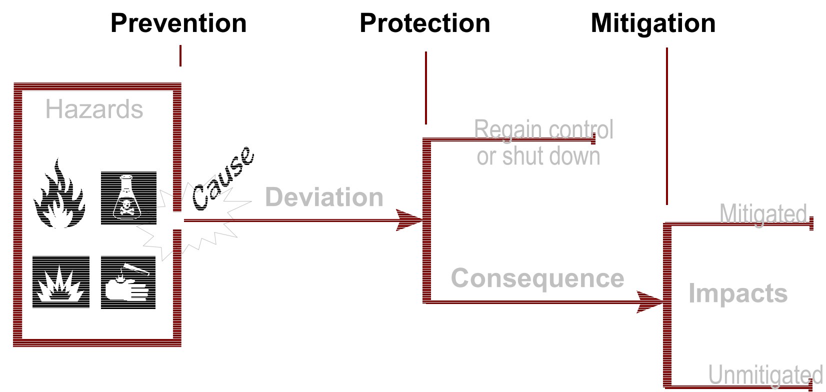
Parameters	***Guidewords***
Flow	**More**
Level	**Less**
Pressure	**No**
Temperature	**Reverse**
Information	**Other Than**

Parameters and Deviations

	Node 1	Node 2	Node 3	Node 4	Node 5	
Flow	More Less No	Reverse				
Level	More Less No	N/A				
Pressure	Less No					
Temp	Less					

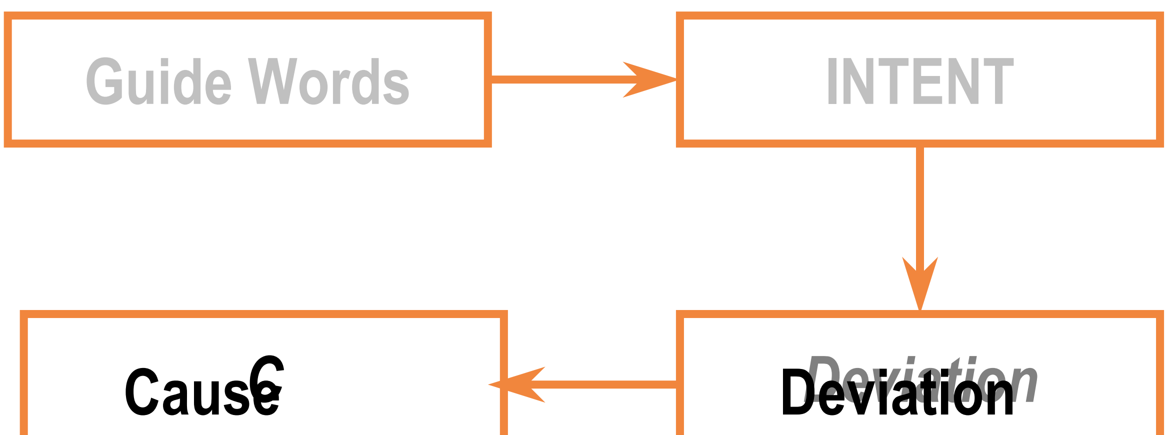
HAZOP Scenario Development

- Node
- Intent
- Deviation
- Cause
- Consequence ***(Loss Event)***
- Protection ***(safeguards)***



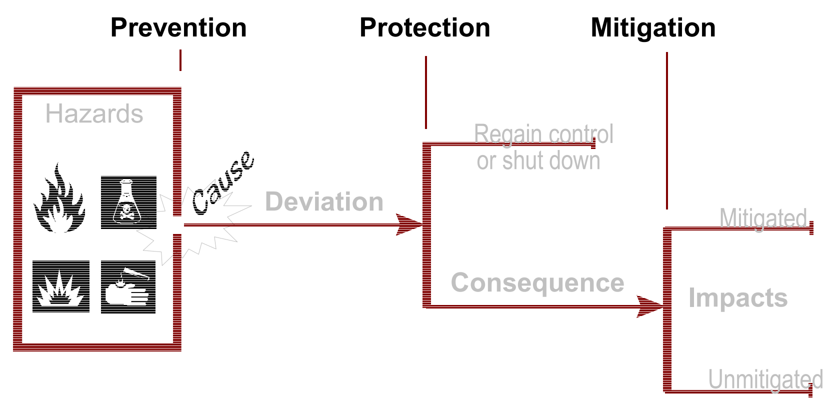
Scenario Development: Causes

- Identify deviation cause(s)
  - Must look backward in time sequence
  - Only identify causes in local node
  - Most deviations have more than one possible cause



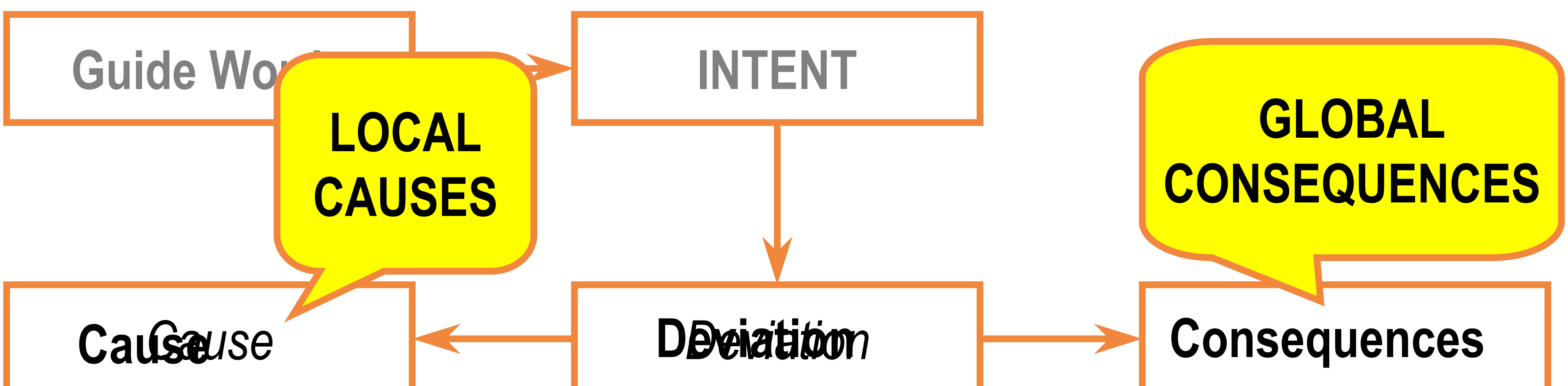
HAZOP Scenario Development

- Node
- Intent
- Deviation
- Cause
- Consequence ***(Loss Event)***
- Protection ***(safeguards)***



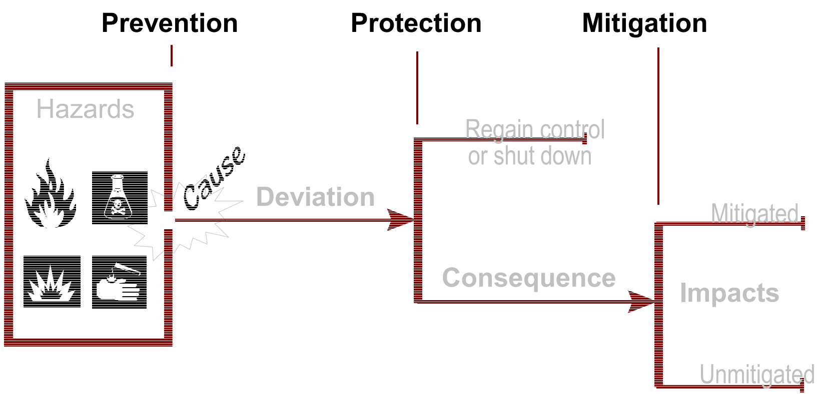
Scenario Development: Consequences

- Determine cause and deviation consequence
- Take scenario all the way to a loss consequence
- Consequences can be <u>anywhere</u> and <u>anytime</u>

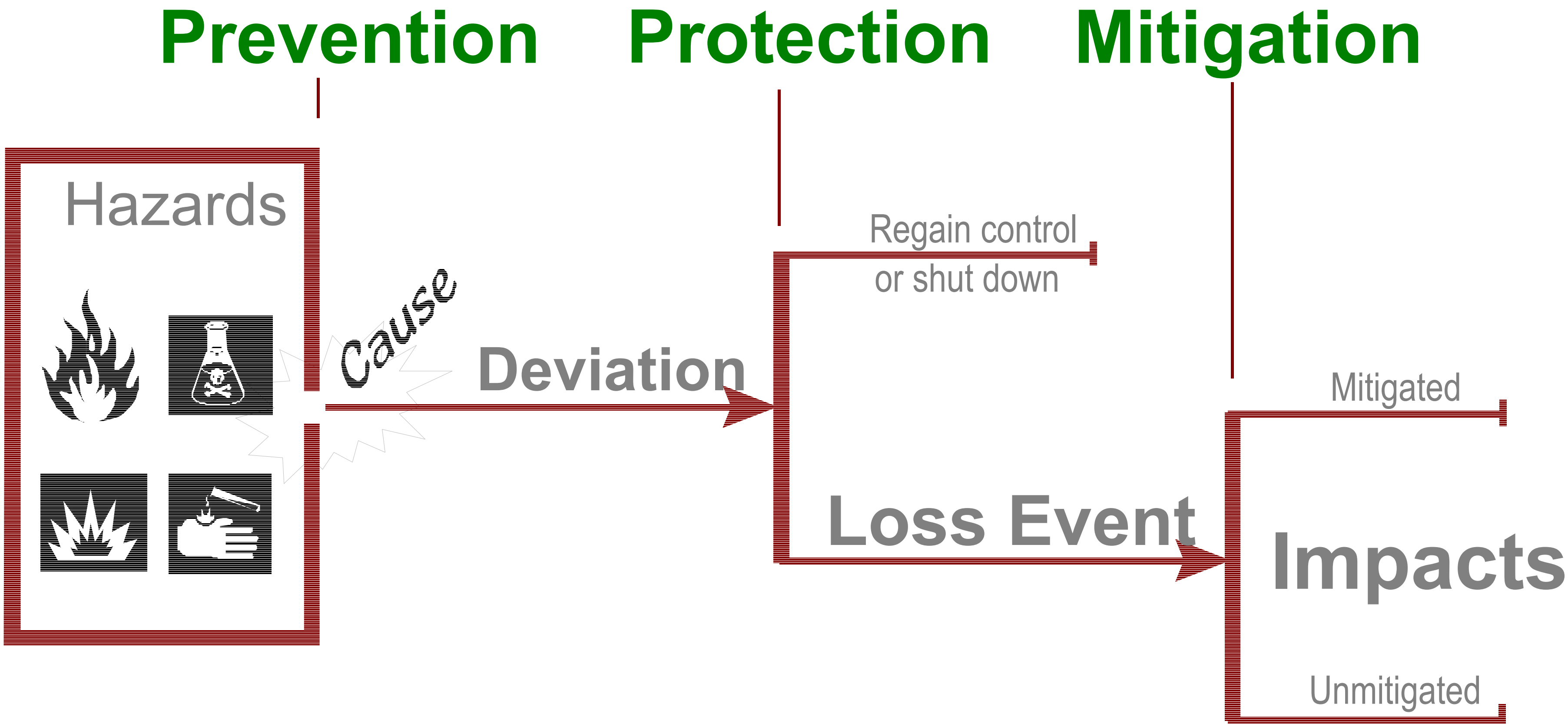


HAZOP Scenario Development

- Node
- Intent
- Deviation
- Cause
- Consequence ***(Loss Event)***
- Protection ***(safeguards)***



Three Types of Safeguards



Prevention Safeguards

Prevention

Operational Mode: Normal operation

Objective: Maintain normal operation; keep hazards contained and controlled

Examples of Prevention Safeguards:

- **Basic process control system**
- **Inspections, tests, maintenance**
- **Operator training**
  - **How to conduct a procedure or operate a process correctly and consistently**
  - **How to keep process within established limits**
- **Guards, barriers against external forces**
- **Management of change**

HAZOP Recap

- HAZOP is a qualitative hazard evaluation method
- It uses a rigorous, intensive brainstorming approach to identify hazards & the qualitative causes and consequences of accident scenarios related to these hazards
- In addition, it identifies the various protections already part of the design which may prevent the accident from progressing to consequences.

Fault Tree Analysis

- A graphical representation of the pathways which can lead to a foreseeable, undesirable event.
- The pathways interconnect contributory event or conditions, using standard logic symbols.
- Failure probabilities can be entered and propagated through the system to evaluate probability of the foreseeable, undesirable event.

Fault Tree Analysis

Fault Tree Analysis is best applied to cases with:

- **Already identified undesirable events. (A MUST !!)**
- **Large threats of loss (high risk).**
- **Numerous potential contributors to mishaps.**
- **Complex or multi-element systems or processes.**

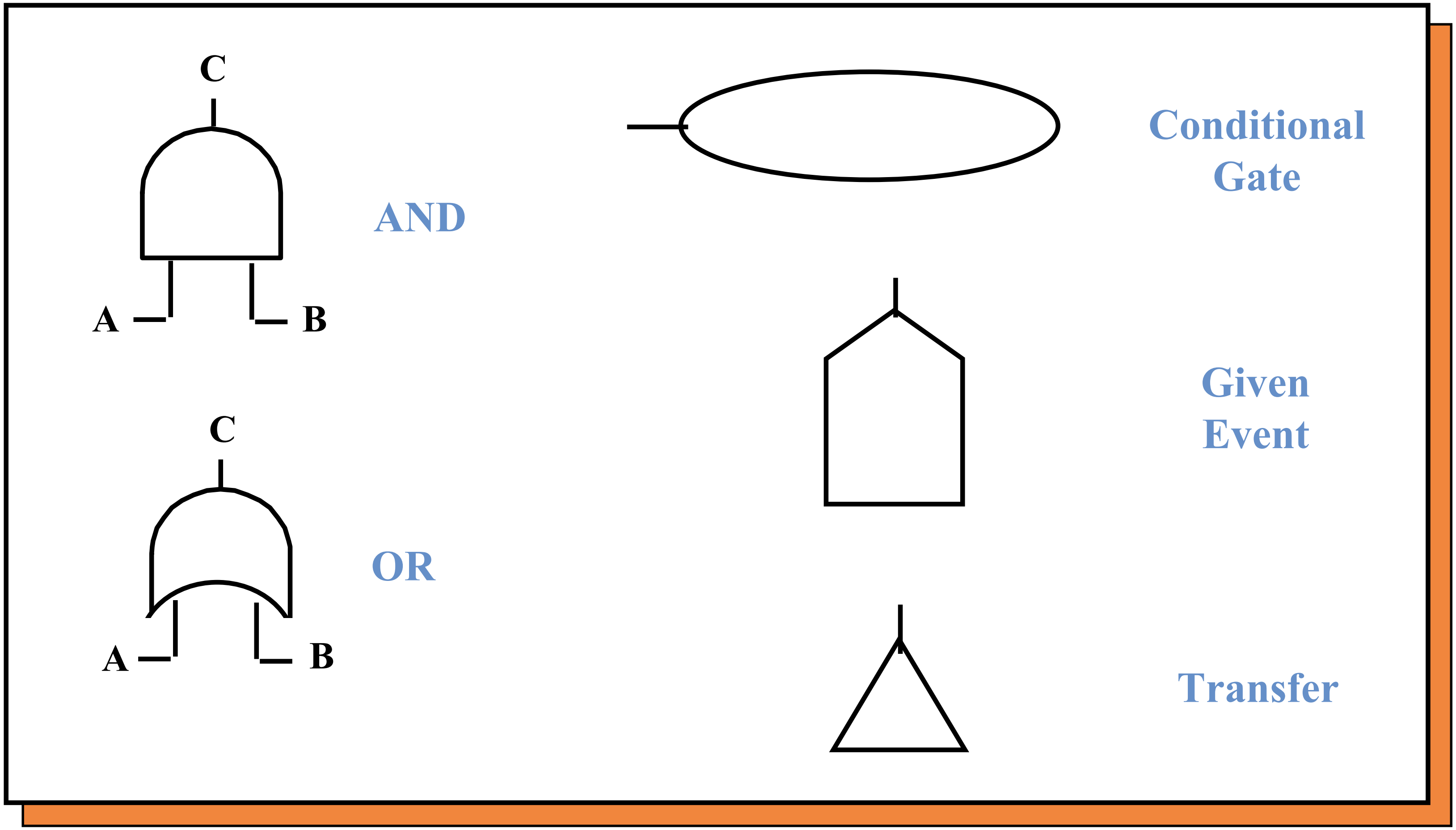
Fault Tree Analysis

A Fault Tree Analysis produces:

- **Graphic display of chain of events leading to failure.**
- **Identification of those potential contributors to failure which are critical.**
- **Qualitative/quantitative insight into probability of failure.**

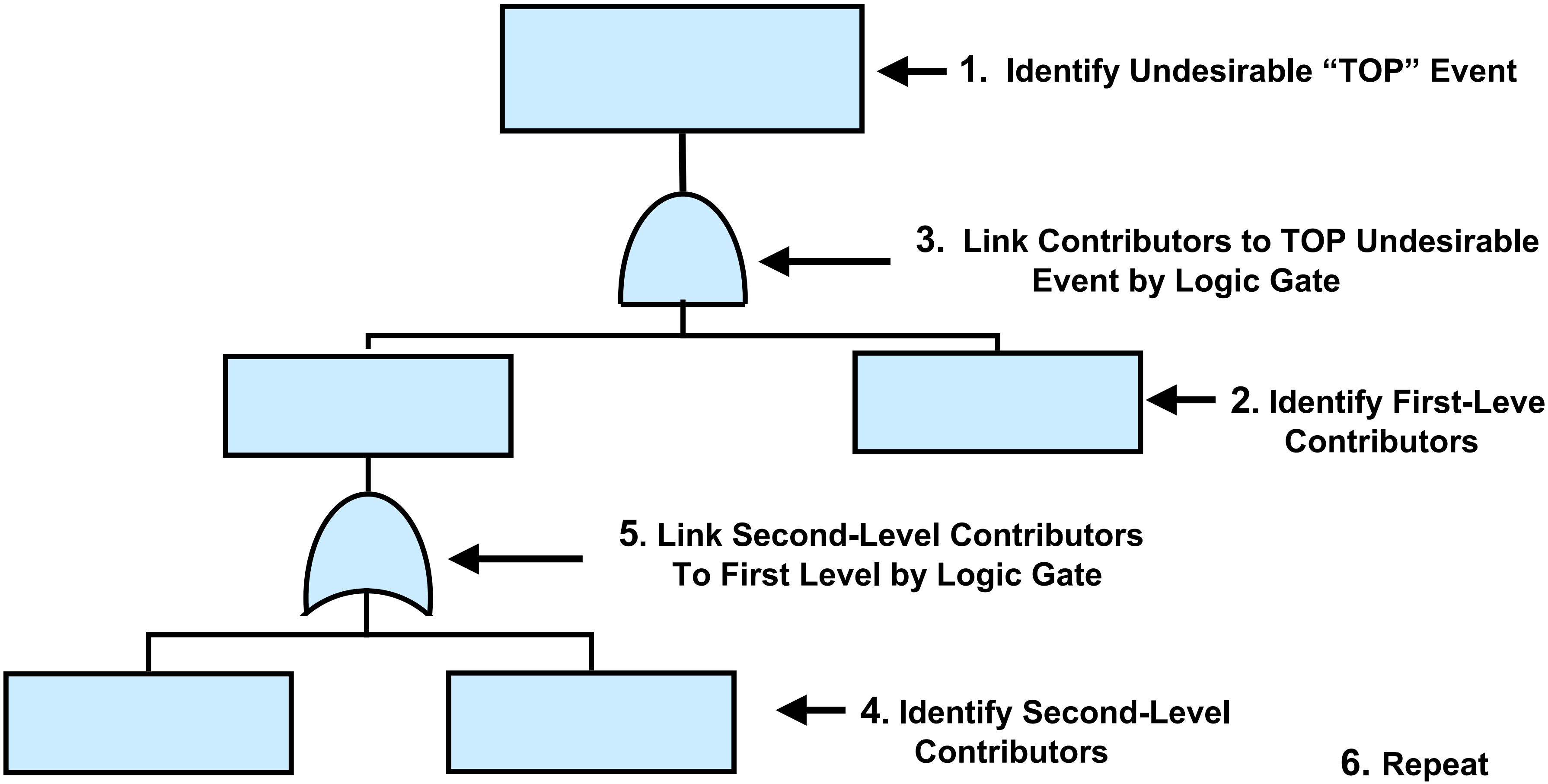
Fault Tree Analysis

Basic Symbols



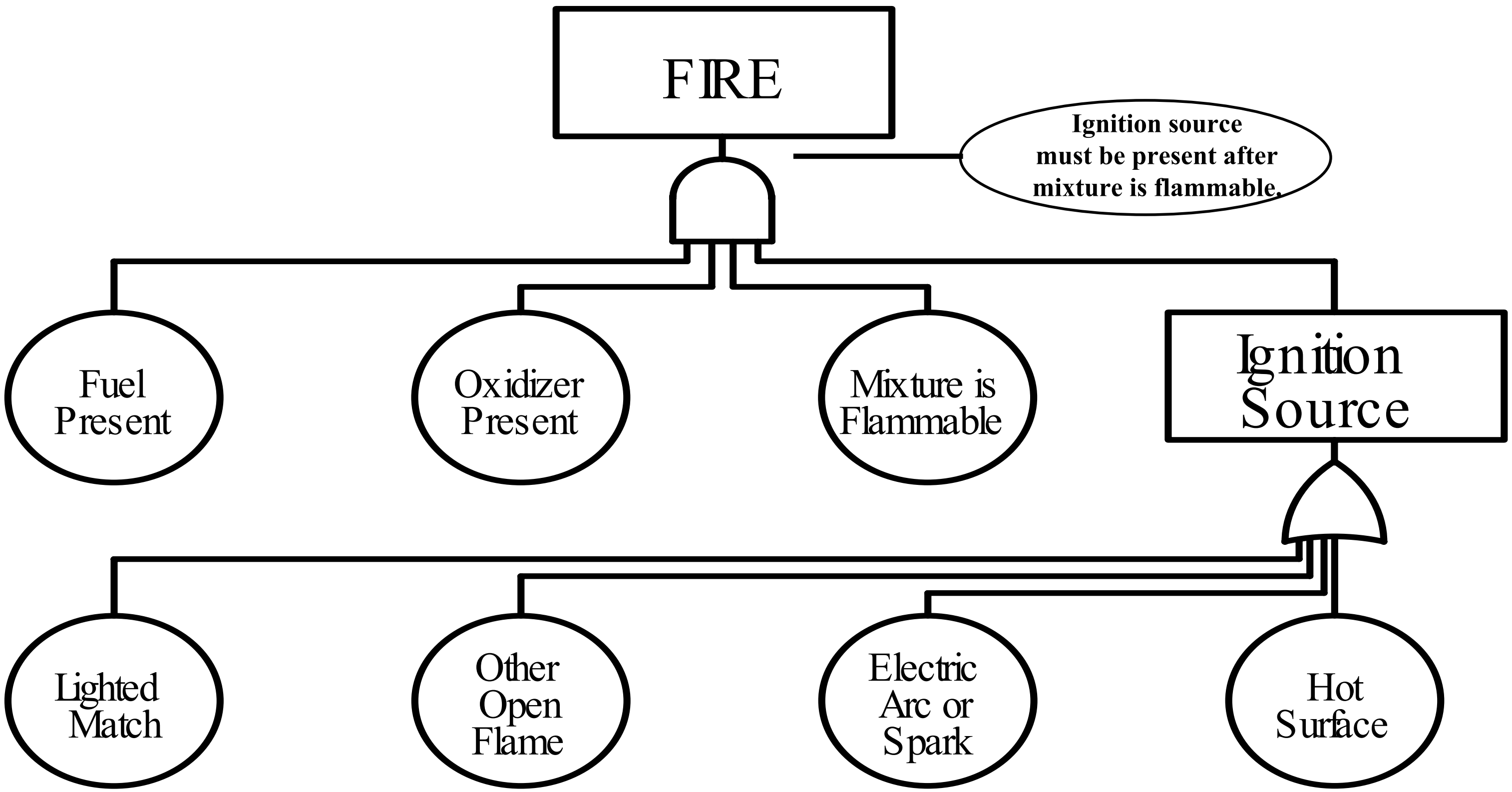
Fault Tree Analysis

Constructing the Tree



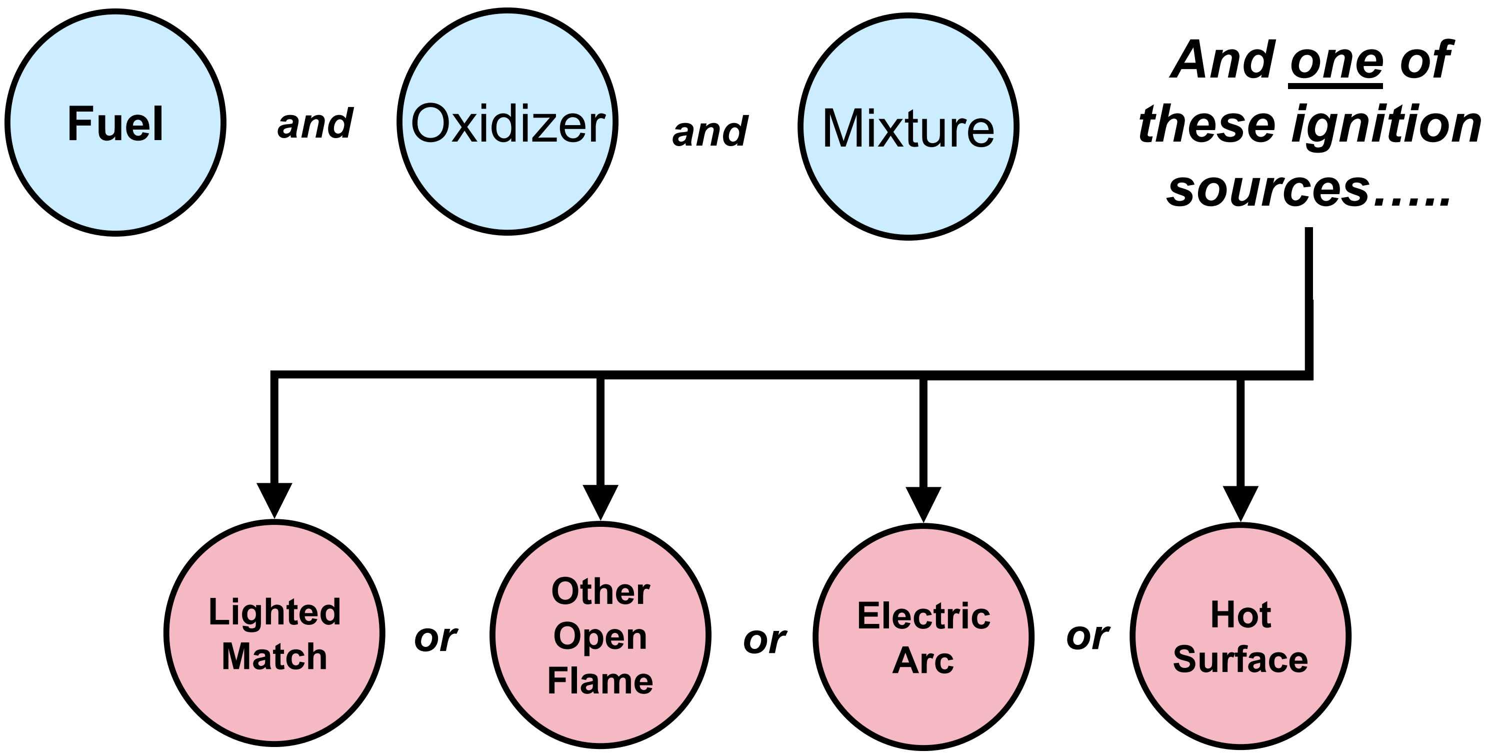
Fault Tree Analysis

Example Tree

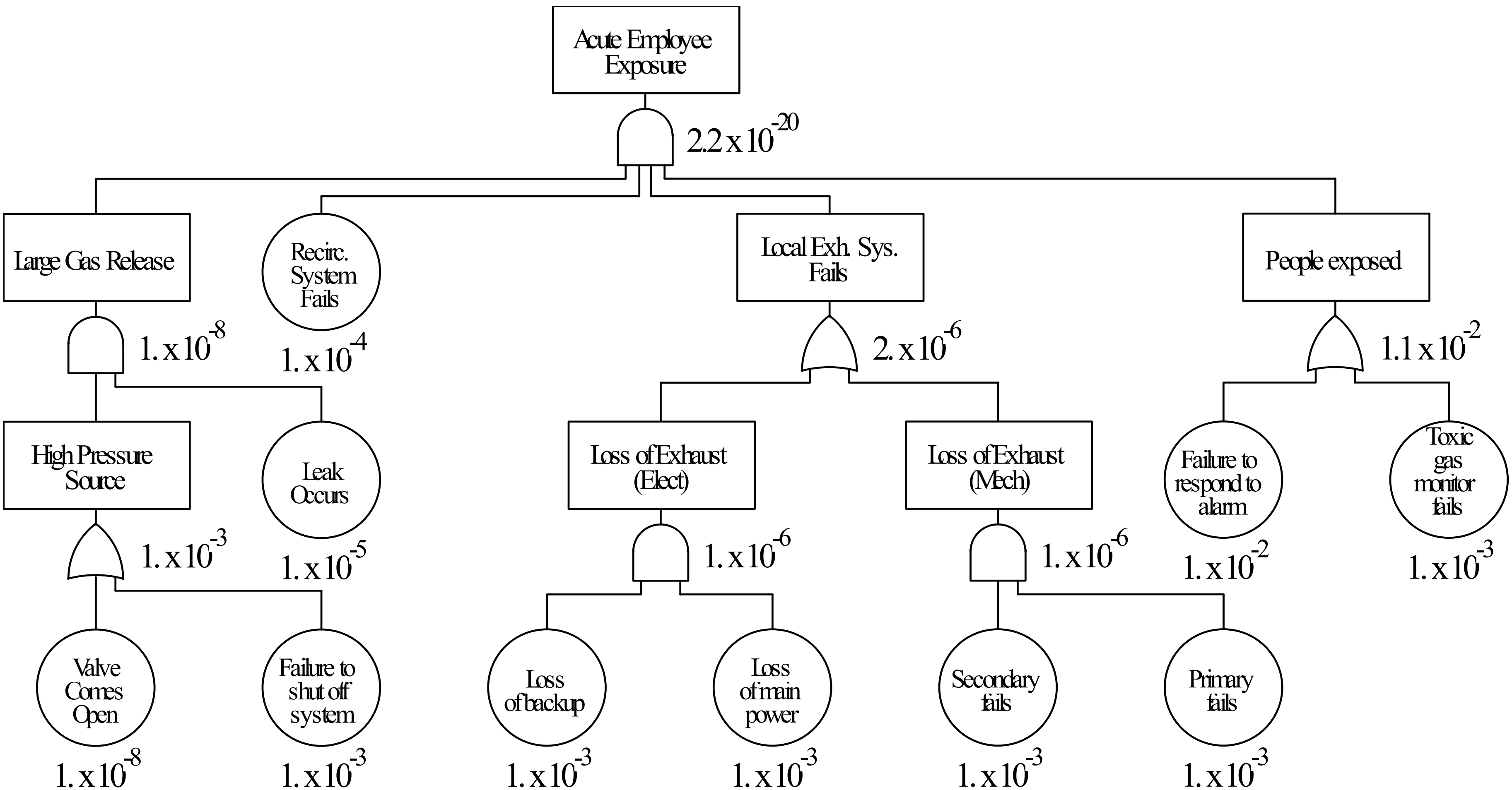


Fault Tree Analysis

Cut Sets for Example Tree

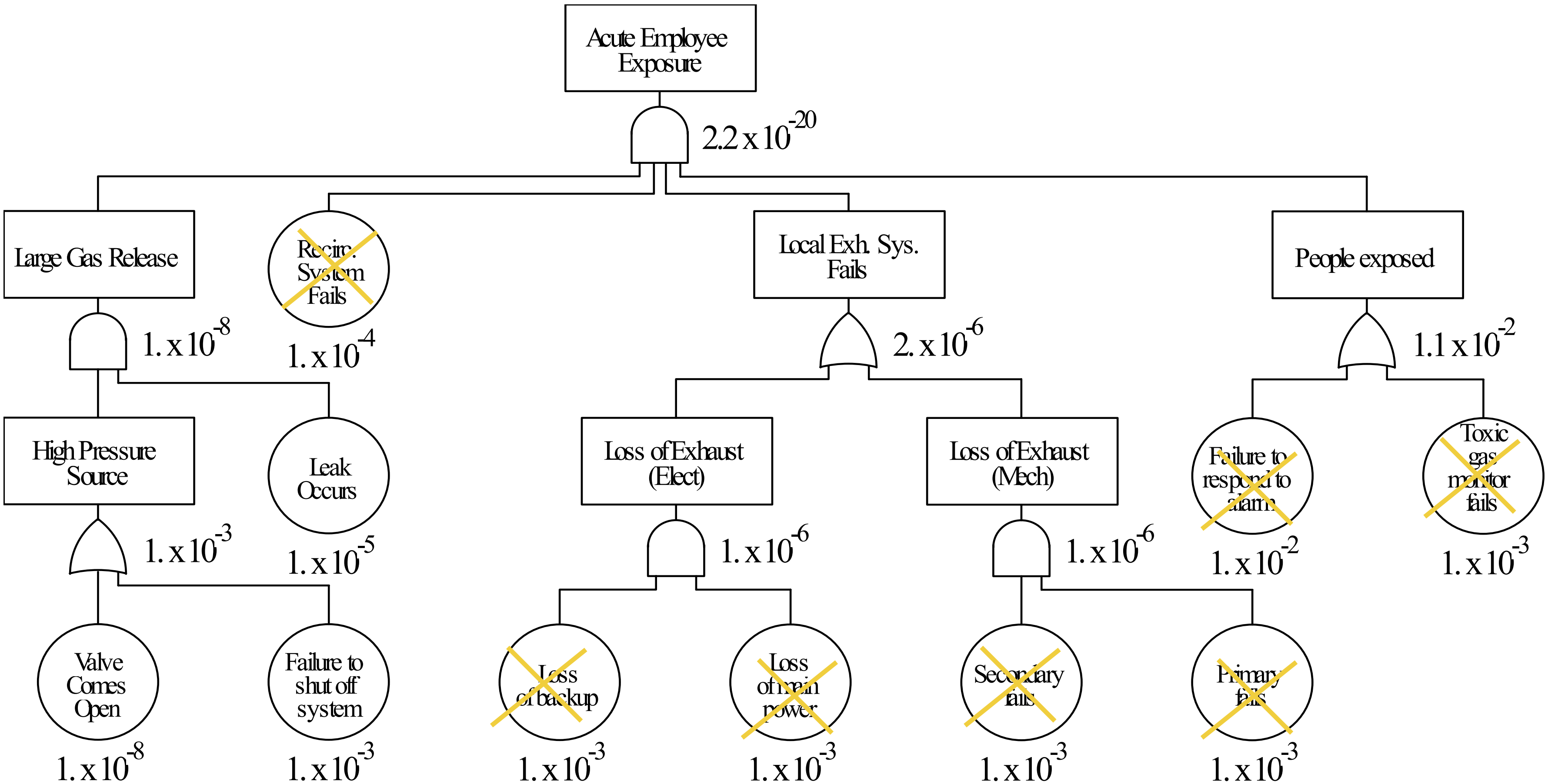


Hazardous Gas Cylinder Fault Tree



Hazardous Gas Cylinder Fault Tree

Common Cause Failure, Total Loss of Power



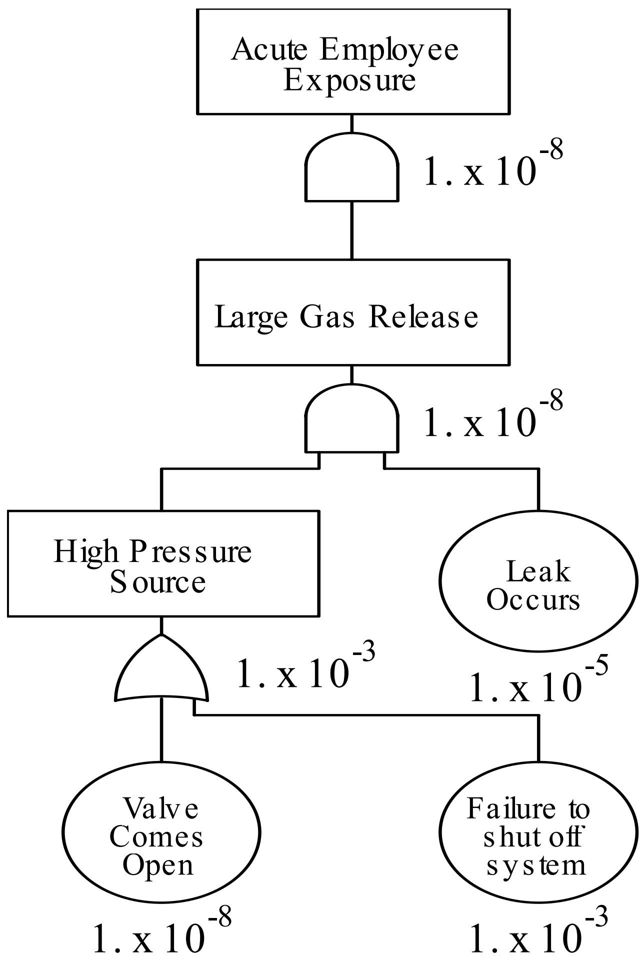
AIR PRODUCTS

Silane Safety
IEEE Conference 2008

BROOKHAVEN NATIONAL LABORATORY

Hazardous Gas Cylinder Fault Tree

Common Cause Failure, Total Loss of Power



Increase in relative risk:

10^{-20} vs. 10^{-8}

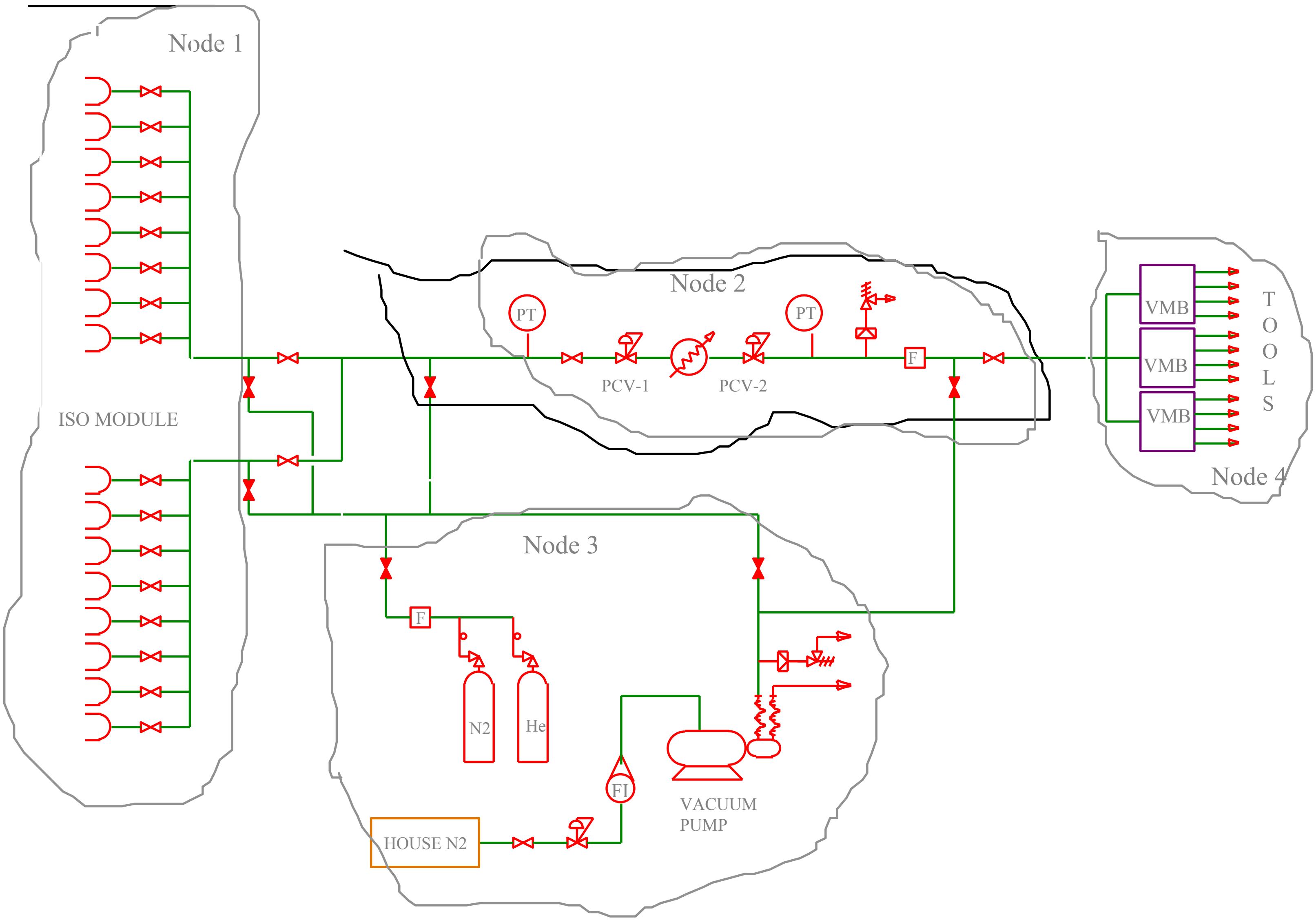
CGA Bulk Silane Release Study

Sponsors

- SEMATECH
- AIR PRODUCTS & CHEMICALS INC.
- ADVANCED SILICON MATERIALS INC. (ASMI)
- BOC GASES
- PRAXAIR
- MATHESON
- AIR LIQUIDE
- SOLKATRONIC CHEMICALS
- CONSOLIDATED PRECISION CORP. (CPC)
- WELDSHIP CORP.

THEORETICAL WORK

- PROCESS HAZARD ANALYSIS
- FAULT TREE ANALYSIS
- CONSEQUENCE ANALYSIS
  - DISPERSING MODELING
  - JET FLAME MODELING



SCHEMATIC OF BULK SILANE DELIVERY SYSTEM

PROCESS HAZARD ANALYSIS (PHA)

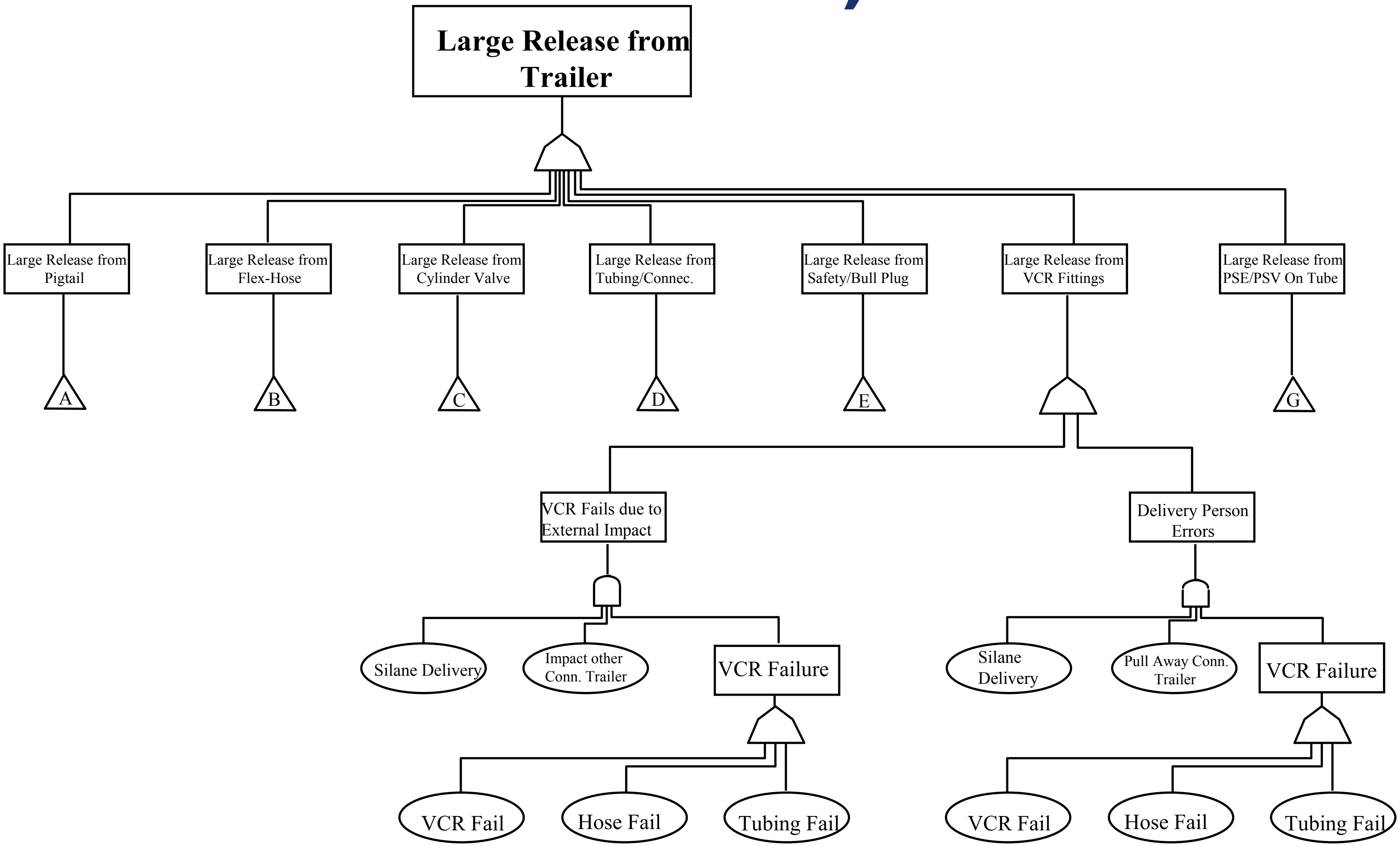
- NODE 1: STORAGE & SUPPLY
  - ONE TRAILER IMPACTS SECOND TRAILER IN PLACE
  - FLAME IMPINGEMENT ON VALVE ASSEMBLY
  - DIAPHRAGM VALVE FAILURE
- NODE 2: REDUCE SUPPLY PRESSURE
  - FAILURE OF PRESSURE TRANSMITTER
  - REGULATOR FAILURE, 2400 PSI N2
- NODE 3: EVACUATE DURING HOOKING/UNHOOKING
  - FAILURE OF VCR FITTING DUE TO IMPACT

FAULT TREE ANALYSIS (FTA)

Release No.	Description	Frequency
1	Instantaneous release of silane from one tube; spurious rupture of the tube due to defects	1.6E-05/yr
2	Small continuous release from the trailer	3.46E-02/yr
3	Large continuous release from trailer	1 .44E-02/yr
4	Small continuous release from PCFM	0.15/yr
5	Large continuous release from PCFM	7.87E-02/yr
6	Trailer tube fireball	3.4E-05/yr
7	Impact on other systems	1 .46E-02/yr

Table 4. Silane Release Frequency Based on FTA

FAULT TREE (Large continuous Release from Trailer)



CONSEQUENCE ANALYSIS

- Dispersion Modeling
  - 2-Dimensional model
  - Equation of mass, momentum and energy
  - Gaussian similarity profiles for velocity, density, conc.
  - Overpressure footprints using Factory Mutual guidelines
  - Explosion dynamics codes; obstacles on turbulence and overpressure

- Jet Flame Hazard Assessment
  - Multiple point source flame jet model
  - API guideline for estimating thermal flux

When is the FTA Effort Justified?

- High Potential Consequences
  - Consequence analysis should be done first
- Undesirable Consequences/Complex Systems
  - Even the process of constructing logic diagrams can improve understanding & can identify design or facility modifications which increase safety
- FTA can provide an estimate of the benefits of proposed modifications

Thank you

for more information see

www.airproducts.com/electronics
www.pv.bnl.gov