Chemical Reactivity Hazards

Bandung, Indonesia
March 2012

SAND No. 2012-1608C
Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Introduction

Chemical reactivity hazard:

A situation with the potential for an <u>uncontrolled chemical reaction</u> that can result directly or indirectly in serious harm to people, property and/or the environment.

2

Introduction

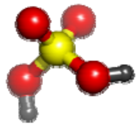
The worst process industry disasters worldwide have involved uncontrolled chemical reactions.

Examples?

-
-
-

Introduction

- *Problem:* Chemical reactivity hazards are more difficult to anticipate and recognize than other types of process hazards.
- **Inadequate recognition and evaluation of reactive chemical hazards was a causal factor in 60% of investigated reactive chemical incidents with known causes.** (U..S. Chemical Safety Board Hazard Investigation)



Very-short-course Syllabus

- Course texts
- Pretest
- Key concepts
- Extra-credit activities

Course Texts

Texts

CCPS Safety Alert 2001. ***Reactive Material Hazards: What You Need to Know.*** New York: AIChE. 10 pages.

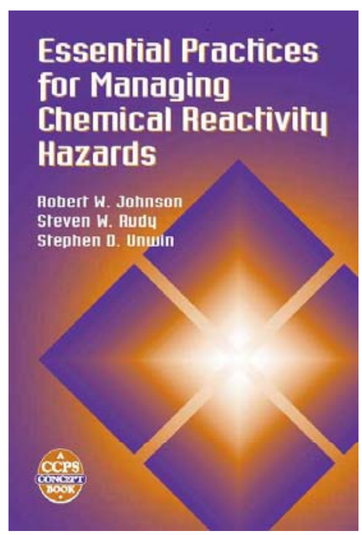
On course CD-ROM:

ccps-alert-reactive-materials.pdf

Texts

Johnson et al. 2003. ***Essential Practices for Managing Chemical Reactivity Hazards.*** New York: AIChE. 193 p.

Register for free access at www.knovel.com/ccps



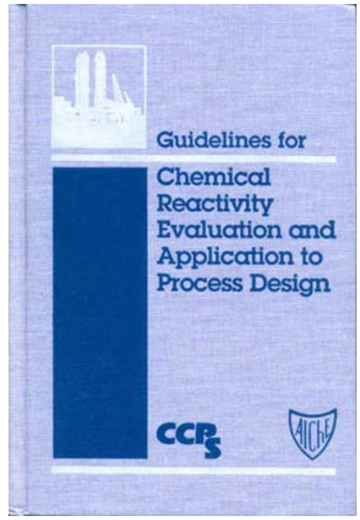
Texts

CCPS 1995.

Guidelines for Chemical Reactivity Evaluation and Application to Process Design.

New York: AIChE. 210 p.

AIChE members can access for free at www.knovel.com



Chemical SAFETY AND SECURITY TRAINING

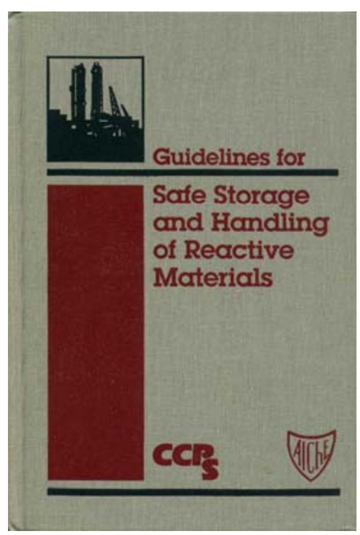
Texts

CCPS 1995.

Guidelines for Safe Storage and Handling of Reactive Materials.

New York: AIChE. 364 p.

AIChE members can access for free at www.knovel.com



Chemical SAFETY AND SECURITY TRAINING

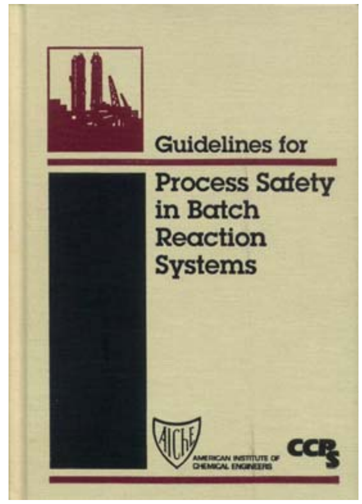
Texts

CCPS 1999.

Guidelines for Process Safety in Batch Reaction Systems.

New York: AIChE. 171 p.

Available from www.wiley.com



Texts

CSB 2002.

Improving Reactive Hazard Management.

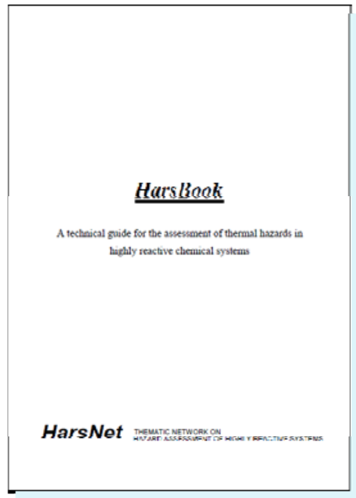
Washington, D.C.: U.S. Chemical Safety and Hazard Investigation Board. 150 p.

Download for free at www.csb.gov

Texts

HarsBook: A technical guide for the assess-ment of thermal hazards in highly reactive chemical systems.

HarsNet Thematic Network on Hazard Assessment of Highly Reactive Systems. 143 p.



Download for free at www.harsnet.net/harsbook/harsbook_02.htm

Chemical SAFETY AND SECURITY TRAINING

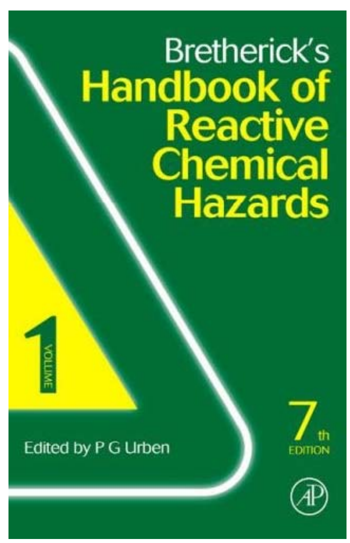
Texts

P.G. Urben (ed.) 2006.

Bretherick's Handbook of Reactive Chemical Hazards (2 vols).

Academic Press. 2680 p.

~US$500 from Amazon.com; also available electronically

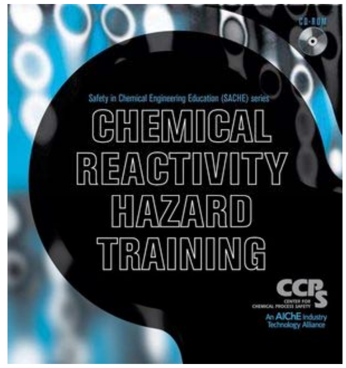


Chemical SAFETY AND SECURITY TRAINING

Software

CCPS 2006.
Chemical Reactivity Training CD-ROM.
New York: AIChE.

US$316 from wiley.com; free to all SAChE members (www.sache.org)



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Chemical SAFETY AND SECURITY TRAINING

Pretest

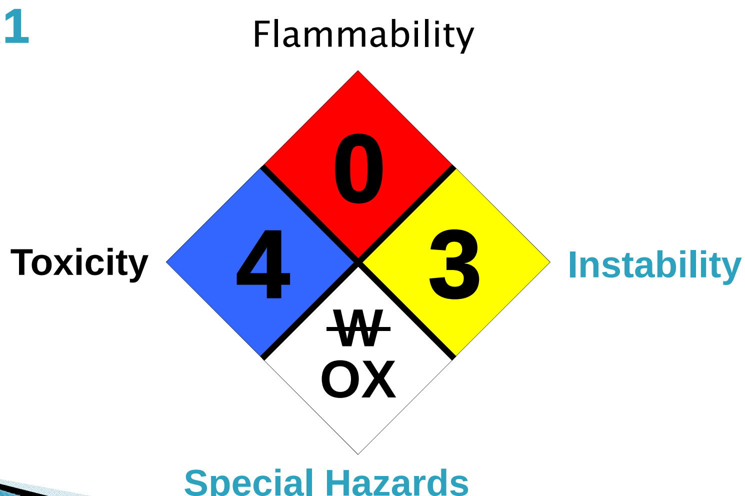
Pretest

Q1 *On the NFPA 704 'diamond', which color(s) or position(s) are associated with **chemical reactivity hazards**?*

Chemical SAFETY AND SECURITY TRAINING

Pretest

A1



Chemical SAFETY AND SECURITY TRAINING

Pretest

Q2 *Your new research calls for the piloting of a process involving* ***acetone cyanohydrin****.*

What should you do first?

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Chemical SAFETY AND SECURITY TRAINING

Pretest

A2 *First, find out the inherent hazards of acetone cyanohydrin.*

C_4H_7NO

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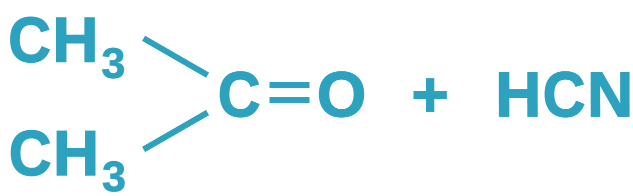
Chemical SAFETY AND SECURITY TRAINING

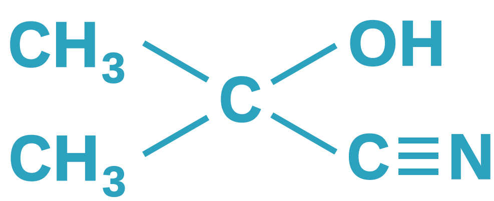
Pretest

A2 *First, find out the inherent hazards of acetone cyanohydrin.*



Pretest

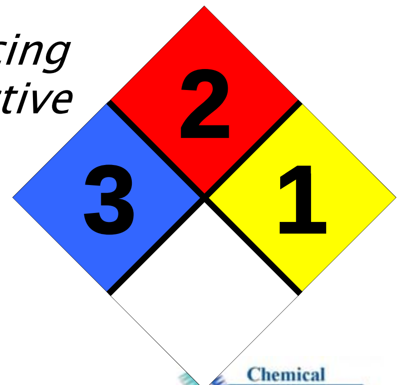
A2 *First, find out the inherent hazards of acetone cyanohydrin.*



Acetone cyanohydrin

NFPA 49

Severe health hazard; combustible; readily decomposes, producing HCN; not water-reactive or oxidizer; reacts with acids, alkalis, oxidizing materials, reducing agents



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Acetone cyanohydrin

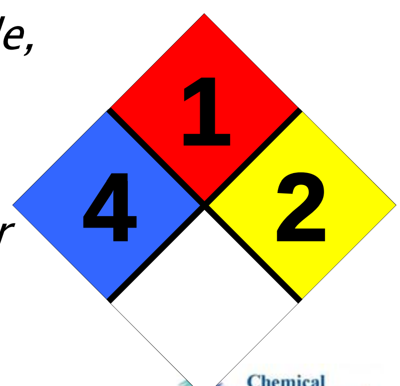
International Chemical Safety Card

Extremely toxic,

Class IIIB combustible,

unstable at elevated temperatures,

decomposes in water



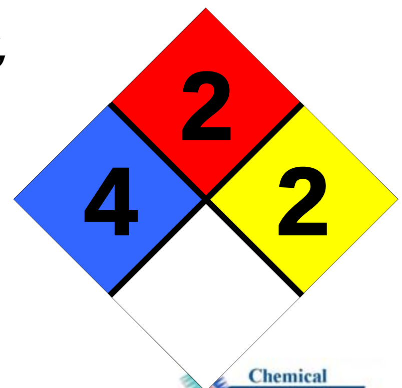
Chemical
SAFETY AND SECURITY TRAINING

Acetone cyanohydrin

WISER
(wiser.nlm.nih.gov)

HIGHLY FLAMMABLE: Easily ignited by heat, sparks or flames

DO NOT GET WATER on spilled substance or inside containers



Acetone cyanohydrin

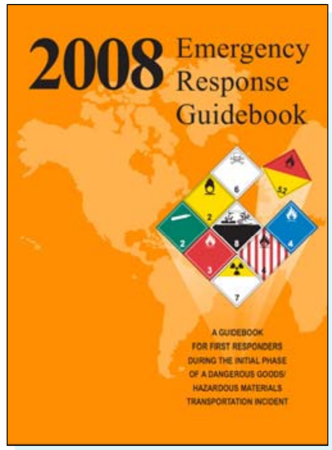
U.S. DOT

Class 6.1 Poisonous material

Acetone cyanohydrin

U.S. DOT Emergency Response Guidebook

"A water-reactive material that produces large amounts of HCN when spilled in water"



Acetone cyanohydrin

NOAA Chemical Reactivity Worksheet

Chemical Profile

Readily decomposes to acetone and poisonous hydrogen cyanide gas on contact with water, acids (sulfuric acid) or when exposed to heat. Should be kept cool and slightly acidic (pH 4-5) [Sax, 2nd ed., 1965, p. 388].

Slowly dissociates to acetone, a flammable liquid, and hydrogen cyanide, a flammable poisonous gas, under normal storage and transportation conditions. Rate of dissociation increased by contact with alkalis and/or heat.

Special Hazards

- *Water-reactive*
- *No rapid reaction with air*

Air and Water Reactions

Soluble in water. Readily decomposes on contact with water to form acetone and poisonous hydrogen cyanide.

General Description

A colorless liquid. Flash point 165°F. Lethal by inhalation and highly toxic or lethal by skin absorption. Density 7.8 lb / gal (less dense than water). Vapors heavier than air. Produces toxic oxides of nitrogen during combustion (© AAR, 1999).

Acetone cyanohydrin

NIOSH Pocket Guide to Chemical Hazards

www.cdc.gov/niosh/npg/search.html

Incompatibilities and reactivities:
Sulfuric acid, caustics

Note: *Slowly decomposes to acetone and HCN at room temperatures; rate is accelerated by an increase in pH, water content, or temperature.*

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Chemical SAFETY AND SECURITY TRAINING

Acetone cyanohydrin

CHRIS U.S. COAST GUARD

Chemical Hazards Response Information System (CHRIS)

Click on the desired CHRIS Code to view the chemical sheet:

CHRIS Code	Chemical Name	Description
ACY	ACETONE CYANOHYDRIN	Color: Colorless Odor: Mild, almond odor. Physical State Shipped: Watery liquid Characteristics In Water: Floats and mixes with water. Poisonous vapor is produced. IMO-UN Number: 6.1/1541 DOT ID Number: 1541 NFPA Hazard Classification: Health Hazard (Blue) - Flammability (Red) - Reactivity (Yellow) - Special (White) - View Synonyms

cameochemicals.noaa.gov

CSP

A

CHRIS

4. FIRE HAZARDS

4.1 **Flash Point:** 165°F C.C.
4.2 **Flammable Limits in Air:** 2.2%-12%
4.3 **Fire Extinguishing Agents:** Water spray, dry chemical, alcohol foam, carbon dioxide
4.4 **Fire Extinguishing Agents Not to Be Used:** Not pertinent
4.5 **Special Hazards of Combustion Products:** Toxic hydrogen cyanide is generated when heated
4.6 **Behavior in Fire:** Not pertinent
4.7 **Auto Ignition Temperature:** 1270°F
4.8 **Electrical Hazards:** I, D
4.9 **Burning Rate:** Currently not available
4.10 **Adiabatic Flame Temperature:** Currently not available
4.11 **Stoichometric Air to Fuel Ratio:** Currently not available
4.12 **Flame Temperature:** Currently not available
4.13 **Combustion Molar Ratio (Reactant to Product):** Currently not available
4.14 **Minimum Oxygen Concentration for Combustion (MOCC):** Not listed

5. CHEMICAL REACTIVITY

5.1 **Reactivity with Water:** No reaction
5.2 **Reactivity with Common Materials:** No reaction
5.3 **Stability During Transport:** Stable
5.4 **Neutralizing Agents for Acids and Caustics:** Not pertinent
5.5 **Polymerization:** Not pertinent
5.6 **Inhibitor of Polymerization:** Not pertinent

7. SHIPPING INFORMATION

7.1 **Grades of Purity:** 98-99%
7.2 **Storage Temperature:** Ambient
7.3 **Inert Atmosphere:** No requirement
7.4 **Venting:** Pressure-vacuum
7.5 **IMO Pollution Category:** A
7.6 **Ship Type:** 2
7.7 **Barge Hull Type:** 1

8. HAZARD CLASSIFICATIONS

8.1 **49 CFR Category:** Poison
8.2 **49 CFR Class:** 6.1
8.3 **49 CFR Package Group:** I
8.4 **Marine Pollutant:** No
8.5 **NFPA Hazard Classification:**

Category	Classification
Health Hazard (Blue)..........	4
Flammability (Red)............	2
Instability (Yellow)............	2

8.6 **EPA Reportable Quantity:** 10
8.7 **EPA Pollution Category:** A
8.8 **RCRA Waste Number:** P069
8.9 **EPA FWPCA List:** Yes

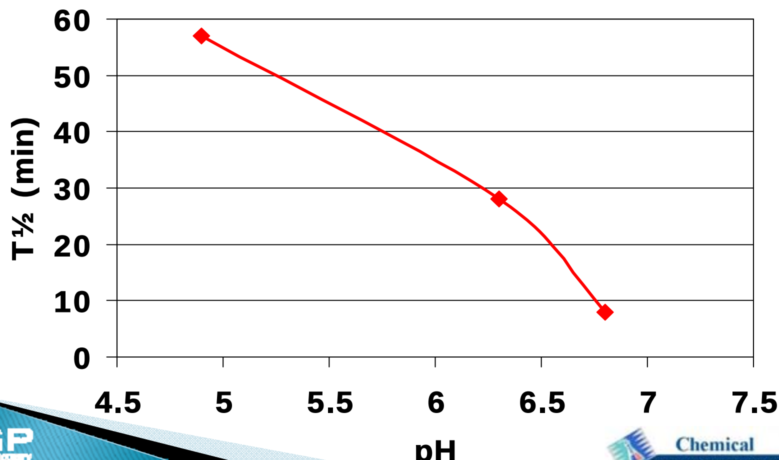
9. PHYSICAL & CHEMICAL PROPERTIES

9.1 **Physical State at 15° C and 1 atm:** Liquid
9.2 **Molecular Weight:** 85.11
9.3 **Boiling Point at 1 atm:** Decomposes (~74.4C)
9.4 **Freezing Point:** –5.8°F = –21°C = 252°K

Acetone cyanohydrin

SIDS: Stability in Water

(OECD Screening Information Dataset)



Acetone cyanohydrin

Conclusions:

- Extremely toxic; must keep contained and avoid all contact
- Combustible; must avoid flame, ignition
- Dissociates to produce highly toxic and flammable gases; dissociation increases with heat, moisture, alkalinity
- Must prevent spills into drains, etc.
- Must avoid incompatible materials

Key Concepts

Key Concepts

- Types of reactivity hazards
- Potential consequences
- Runaway reactions
- Contain and control measures
- Inherently safer systems

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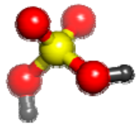


- Intentional chemical reactions
- Unintentional reactions
  - Materials reactive with common substances
    - Spontaneously combustible
    - Peroxide-forming
    - Water-reactive
    - Oxidizing
  - Self-reactive materials
    - Polymerizing
    - Decomposing
    - Rearranging
  - Reactive interactions
    - Incompatibilities
    - Abnormal conditions

Main Category	Subcategory	Adjective	Noun	
READILY SELF-REACTS with energy input such as by shock, pressure, or temperature (UNSTABLE MATERIALS)	POLYMERIZES		MONOMERS	
	DECOMPOSES	SHOCK-SENSITIVE	EXPLOSIVES	Toxic / flammable decomposition products
		THERMALLY SENSITIVE (Decomposes upon heating; may require pressure/confinement)	EXPLOSIVES	
			Other unstable or thermally sensitive materials	
		SENSITIVE TO OTHER STIMULUS (e.g. friction, spark, light, pressure)		
	REARRANGES	ISOMERIZING / TAUTOMERIZING / DISPROPORTIONATING		
	CONDENSES			
READILY REACTS WITH COMMON ENVIRONMENTAL SUBSTANCES	REACTS WITH ATMOSPHERIC NITROGEN			
	REACTS WITH ATMOSPHERIC OXYGEN	SPONTANEOUSLY COMBUSTIBLE (including hypergolic, pyrophoric)		
		FLAMMABLE / COMBUSTIBLE (includes explosible dusts; usually treated separately from reactives)		
		PEROXIDE FORMING		
	REACTS WITH WATER	WATER REACTIVE (DANGEROUS WHEN WET)	Rate of reaction can vary from slow to explosively violent	
	REACTS WITH ORDINARY COMBUSTIBLES	OXIDIZING	ORGANIC PEROXIDES	
			Other OXIDIZERS	
	REACTS WITH METALS			
READILY REACTS WITH OTHER CHEMICALS (INCOMPATIBLE MATERIALS)	REACTS WITH ACIDS			
	REACTS WITH BASES			
	REACTS WITH HYDROGEN (etc.)			

Chemical reactivity hazards

Some chemicals have more than one reactive property.

R–O–O–R

For example, organic peroxides can be any or all of:

- **Oxidizing**
- **Decomposing** (shock-sensitive / thermally unstable)
- **Flammable** or **combustible**
- **Interacting** (incompatible with many other chemicals)

Chemical reactivity hazards

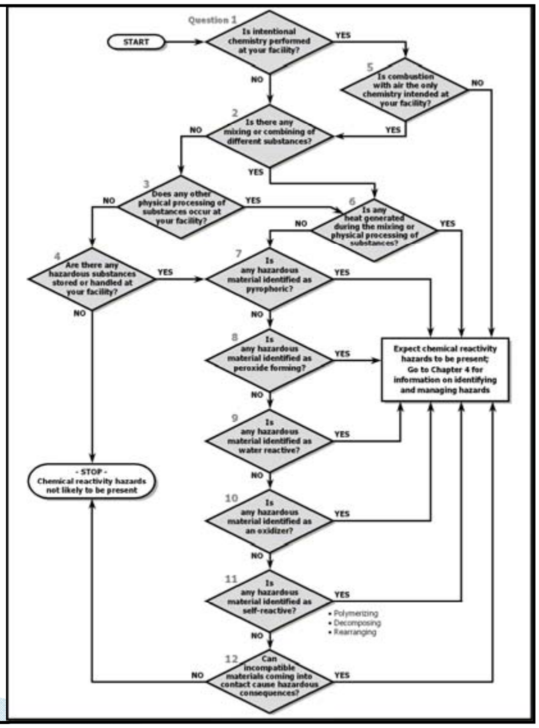
Some types of molecular structures tend to increase chemical reactivity, such as:

- Carbon-carbon double bonds not in benzene rings (ethylene, styrene...)
- Carbon-carbon triple bonds (e.g., acetylene)
- Nitrogen-containing compounds (NO_2 groups, adjacent N atoms...)
- Oxygen-oxygen bonds (peroxides, hydroperoxides, ozonides)
- Ring compounds with only 3 or 4 atoms (e.g., ethylene oxide)
- Metal- and halogen-containing complexes (metal fulminates; halites, halates; etc.)

Preliminary Screen for Chemical Reactivity Hazards

Summary Flowchart

Source: Johnson et al. 2003



Key Concepts

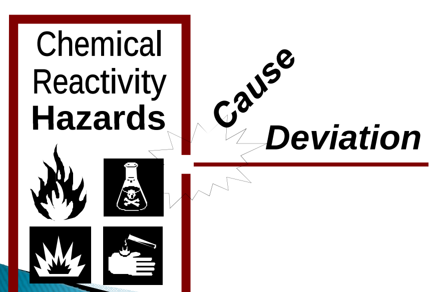
- Types of reactivity hazards
- **Potential consequences**
- Runaway reactions
- Contain and control measures
- Inherently safer systems

Normal situation

- Reactive materials contained
- Reactive interactions (incompatibilities) avoided
- Intended reactions controlled

Abnormal situation

- **Loss of containment**
- **Reactive interaction** (incompatibility)
- **Loss of reaction control**



Chemical reactivity loss events

From Johnson and Unwin, "**Addressing Chemical Reactivity Hazards in Process Hazard Analysis,**" 18th Annual International CCPS Conference, NY: AIChE, Sept. 2003.

Loss Event

- Fire
- Explosion
- Release

Chemical SAFETY AND SECURITY TRAINING

Loss events associated with reactivity hazards

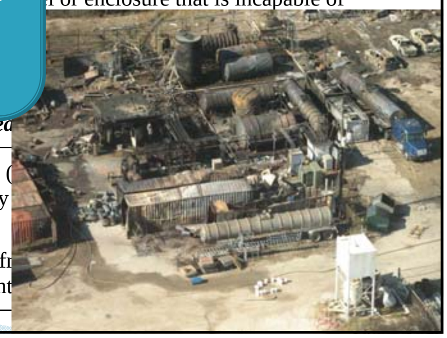
Hazard Type	Typical Uncontrolled Chemical Reaction Consequences
Intentional Chemistry	***Containment rupture explosion*** (uncontrolled reaction resulting in liquid/vapor heating or gas generation inside inadequately relieved vessel or enclosure that is incapable of withstanding peak pressure) ***Fire*** (e.g., excess heating or loss of cooling in unconfined configuration allows autoignition temperature to be attained) ***Toxic reaction products release*** (e.g., off-gas treatment system fails)
Spontaneously Combustible Materials	***Containment rupture explosion*** (self-ignition of vapor, dust or mist inside inadequately relieved vessel or enclosure that is incapable of withstanding peak pressure) ***Fire*** (e.g., self-ignition of flash fire, jet fire, pool fire, pile fire, or building fire) ***Toxic combustion gases release***
Peroxide Formers	***Condensed-phase explosion*** (e.g., explosive decomposition of unstable peroxide initiated by heat, friction, spark, or mechanical shock) ***Fire*** (e.g., follow-on effects from condensed-phase explosion, such as flammable liquid containment rupture and ignition)

Chemical SAFETY AND SECURITY TRAINING

Loss events associated with reactivity hazards

Hazard Type	Typical Uncontrolled Chemical Reaction Consequences
Intentional Chemistry	***Containment rupture explosion*** (uncontrolled reaction resulting in liquid/vapor hea g or gas generation inside inadequately relieved vessel or enclosu is incapable of withstanding peak pressure) F s of cooling in unconfined temperature to be attained) e.g., off-gas treatment system fails)
Spontaneously Combustible Materials	self-ignition of vapor, dust or mist l or enclosure that is incapable of ***Toxic combustion gases relea***
Peroxide Formers	***Condensed-phase explosion*** (unstable peroxide initiated by shock) ***Fire*** (e.g., follow-on effects fr flammable liquid containment

T-2 Incident
Jacksonville, Florida
December 2007



Hazard Type	Typical Uncontrolled Chemical Reaction Consequences
Water-Reactive Materials	***Explosively violent reaction*** (e.g., reaction of sodium with water) ***Containment rupture explosion*** (reaction with water resulting in liquid/vapor heating or gas generation inside inadequately relieved vessel or enclosure that is incapable of withstanding peak pressure, or flammable vapors generated by reaction with water ignited inside inadequately relieved vessel or enclosure that is incapable of withstanding peak pressure) ***Flash fire*** (e.g., ignition of unconfined flammable vapors generated by reaction with water) ***Toxic vapor release*** (toxic vapors generated by reaction with water, or decomposition reaction initiated by heat of reaction with water)
Oxidizers	***Fire*** (initiated or accelerated by presence of oxidizer) ***Condensed-phase explosion*** (initiation of detonable mixture of oxidizer with reducing substance) ***Containment rupture explosion*** (ignition or spontaneous ignition of oxidation reaction inside inadequately relieved vessel or enclosure that is incapable of withstanding peak pressure) ***Toxic combustion gases release*** • Note that many oxidizers are subject to decomposition, so also have ossible Self-Reactive Material consequences

Chemical
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Hazard Type	Typical Uncontrolled Chemical Reaction Consequences
Water-Reactive Materials	***Explosively violent reaction*** (e.g., reaction of sodium with water) ***Containment rupture explosion*** (reaction with water resulting in liquid/vapor heating or gas generation inside inadequately relieved vessel or enclosure that is incapable of withstanding peak pressure, or flammable vapors generated by reaction with water ignited inside inadequately relieved vessel or enclosure that is incapable of withstanding peak pressure) ***Flash fire*** (e.g., ignition of unconfined flammable vapors generated by reaction with water) ***Toxic vapor release*** (toxic vapors generated by reaction with water, or decomposition rea tion initiated by heat of reaction with water)
Oxidizers	***Fire*** (initiated or ac ed by presence of oxidizer) ***Condensed-p*** nable mixture of oxidizer with ***Containmen*** ntaneous ignition of oxidation rea essel or enclosure that is incapable ***Toxic combu*** • Note that m position, so also have p sible Self-

Bhopal
India
December 1984

Hazard Type	Typical Uncontrolled Chemical Reaction Consequences
Self-Reactive Materials (Polymerizing, Decomposing, Rearranging)	***Condensed-phase explosion*** (e.g., heat, friction, spark, or mechanical shock initiation of decomposition proceeding at detonation velocity) ***Containment rupture explosion*** (e.g., by self-reaction resulting in liquid/vapor heating, gas generation, or evolution and ignition of flammable vapors inside inadequately relieved vessel or enclosure that is incapable of withstanding peak pressure) ***Toxic vapor release*** (e.g., from toxic decomposition products or heat from self-reaction resulting in vaporization of toxic component) ***Flash fire*** (e.g., by ignition of flammable off-gases) ***Pile fire*** (e.g., by self-heating to autoignition temperature)
Incompatible Materials	***Condensed-phase explosion*** (e.g., by initiation of detonable mixture) ***Containment rupture explosion*** (e.g., by liquid/vapor heating, gas generation, or evolution and ignition of flammable vapors inside inadequately relieved vessel or enclosure that is incapable of withstanding peak pressure) ***Toxic vapor release*** (e.g., from toxic reaction products or from heating and vaporization of toxic component) ***Flash fire*** (e.g., by ignition of flammable off-gases) ***Hazardous material spill*** (e.g., loss of containment due to reaction with wrong material of construction)

Hazard Type	Typical Uncontrolled Chemical Reaction Consequences
Self-Reactive Materials (Polymerizing, Decomposing, Rearranging)	***Condensed-phase explosion*** (e.g., heat, friction, spark, or mechanical shock initiation of decomposition proceeding at detonation velocity) ***Containment rupture explosio***(e.g., by self-reaction resulting in liquid/vapor heating, gas gener... or evolution and ignition of flammable vapors inside inadeq... relieved vessel or enclosure that is incapable of withstanding pea...re) ***Toxic vapor*** ...sition products or heat from self-re... toxic component) ***Flash fire*** (... ases) ***Pile fire*** (e.... mperature)
Incompatible Materials	***Condensed-*** ... of detonable mixture) ***Containme*** ... l/vapor heating, gas generation, o... able vapors inside inadequately relieved vessel or enclosure that is incapable of withstanding peak pressure) ***Toxic vapor release*** (e.g., from toxic reaction products or from heating and vaporization of toxic component) ***Flash fire*** (e.g., by ignition of flammable off-gases) ***Hazardous material spill*** (e.g., loss of containment due to reaction ... wrong material of construction)

Toulouse
France
September 2001

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Incompatible materials

How would you define “chemical incompatibility”?

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52

ASTM E 2012

"Standard Guide for the Preparation of a Binary Chemical Compatibility Chart"

- Define scenario
- Define incompatibility
- Compile chart

www.astm.org

CSP

Chemical SAFETY AND SECURITY TRAINING

ASTM E 2012

"Standard Guide for the Preparation of a Binary Chemical Compatibility Chart"

- Define scenario
  - Quantities
  - Temperatures
  - Confinement
  - Atmosphere (air, nitrogen, inerted)
  - Contact time

CSP

Chemical SAFETY AND SECURITY TRAINING

ASTM E 2012

"Standard Guide for the Preparation of a Binary Chemical Compatibility Chart"

- Define scenario
- Define incompatibility

"In a general sense, chemical incompatibility implies that there may be undesirable consequences of mixing these materials at a macroscopic scale. These consequences might be, in a worst case, a fast chemical reaction or an explosion, a release of toxic gas, or, in a less severe case, an undesirable temperature rise that might take the mixture above its flash point or cause an unacceptable pressure increase in the system…. Consequently, a working definition of incompatibility needs to be formulated before compatibility judgments can be effectively and accurately made."

ASTM E 2012

"Standard Guide for the Preparation of a Binary Chemical Compatibility Chart"

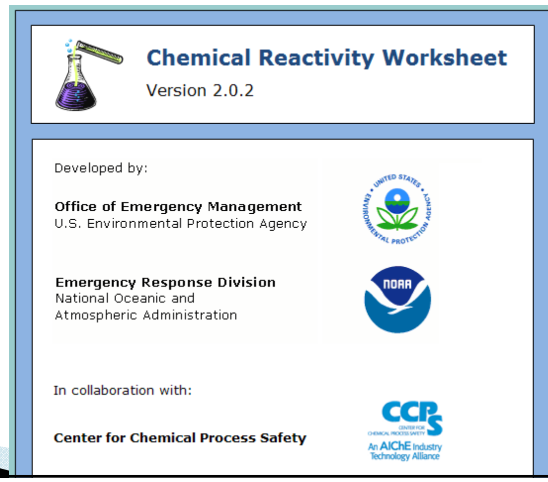
- Define scenario
- Define incompatibility
- Compile chart

NOAA Chemical Reactivity Worksheet

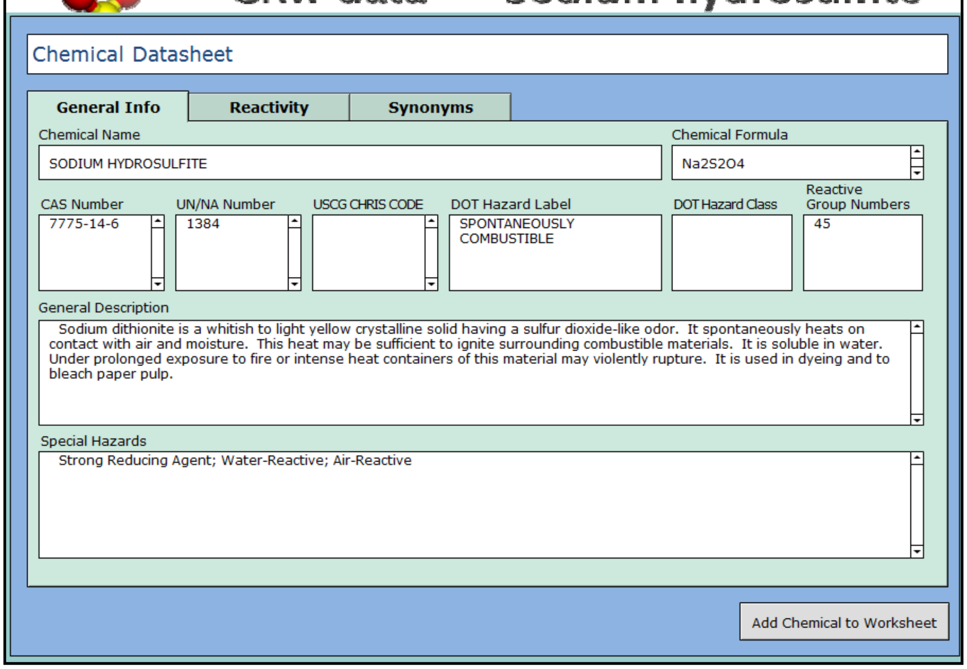
response.restoration.noaa.gov/crw

The NOAA Chemical Reactivity Worksheet predicts the results of mixing any binary combination of the 6,000+ chemicals in the CAMEO database, including many common mixtures and solutions.

For each substance, a general description and chemical profile are given, along with special hazards such as air and water reactivity.



CRW data – Sodium hydrosulfite



Chemical Datasheet

General Info | Reactivity | Synonyms

Chemical Name: SODIUM HYDROSULFITE

Chemical Formula: Na2S2O4

CAS Number	UN/NA Number	USCG CHRIS CODE	DOT Hazard Label	DOT Hazard Class	Reactive Group Numbers
7775-14-6	1384		SPONTANEOUSLY COMBUSTIBLE		45

General Description

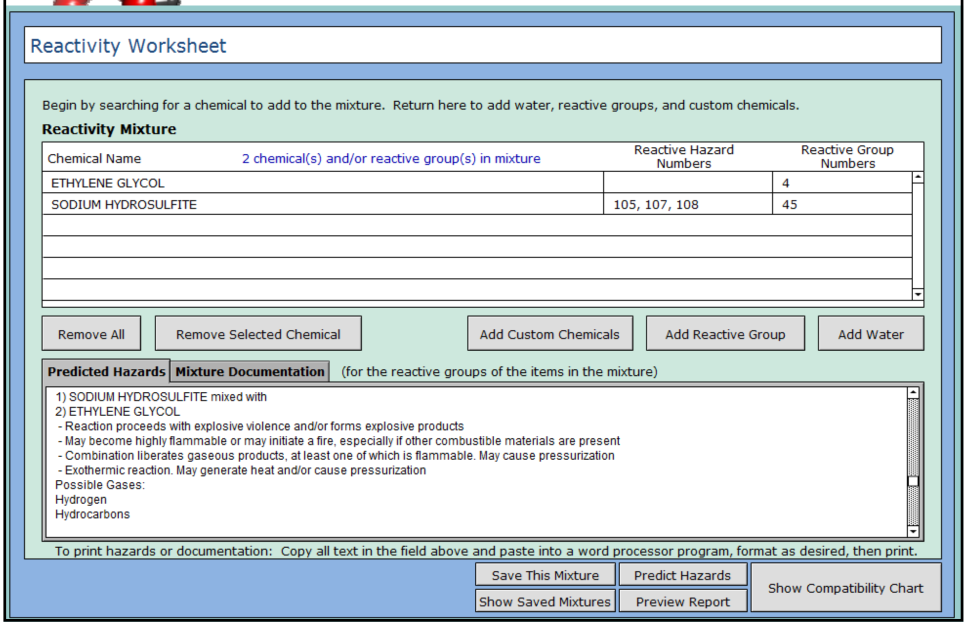
Sodium dithionite is a whitish to light yellow crystalline solid having a sulfur dioxide-like odor. It spontaneously heats on contact with air and moisture. This heat may be sufficient to ignite surrounding combustible materials. It is soluble in water. Under prolonged exposure to fire or intense heat containers of this material may violently rupture. It is used in dyeing and to bleach paper pulp.

Special Hazards

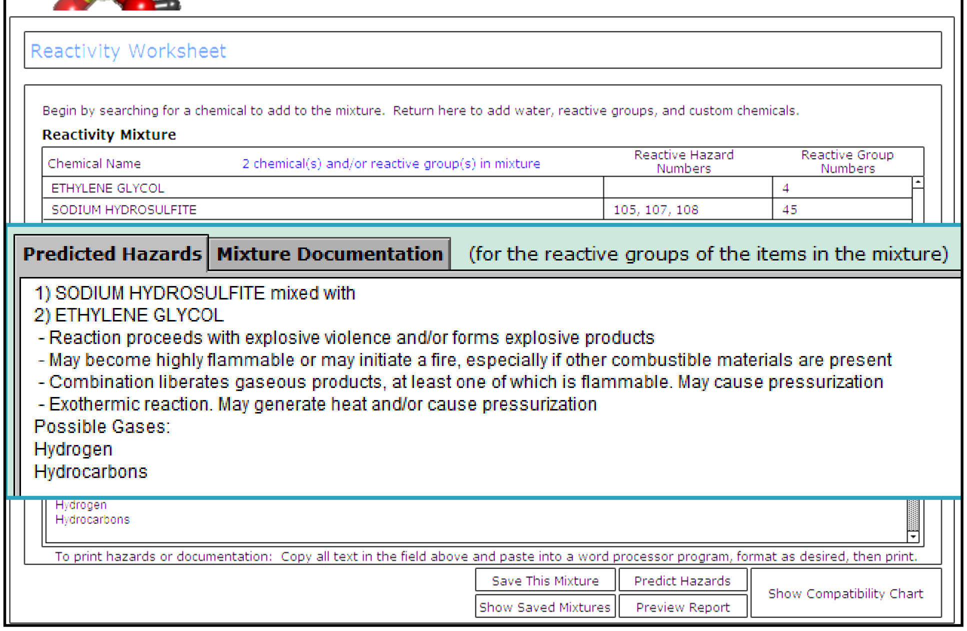
Strong Reducing Agent; Water-Reactive; Air-Reactive

Add Chemical to Worksheet

Sodium hydrosulfite + ethylene glycol

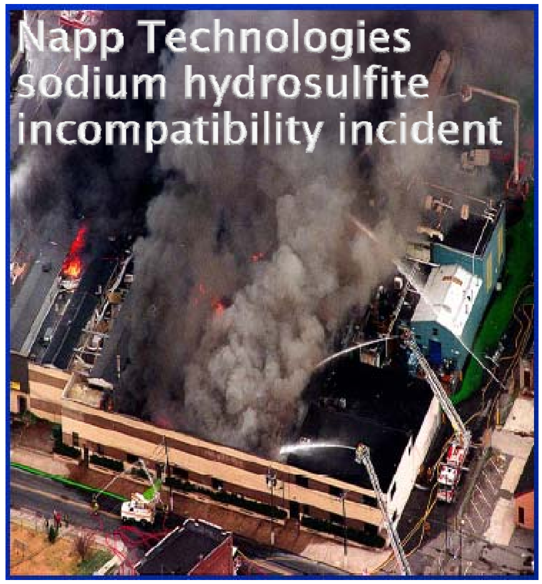


Sodium hydrosulfite + ethylene glycol



April 21, 1995

- 5 worker fatalities
- ~300 evacuated
- Facility destroyed
- Surrounding businesses damaged



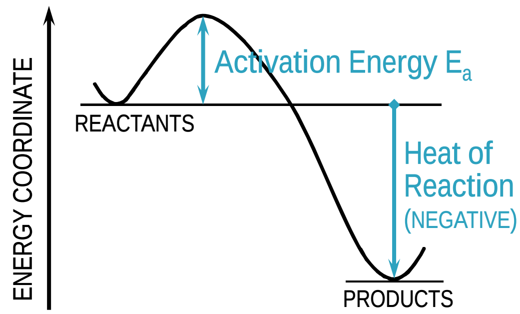
Ed Hill, The Bergen Record

Key Concepts

- Types of reactivity hazards
- Potential consequences
- **Runaway reactions**
- Contain and control measures
- Inherently safer systems

Chemical reactivity hazards

Energy diagram for exothermic reaction:



- Lower activation energy barrier | faster reaction
- Larger heat of reaction | more energy released

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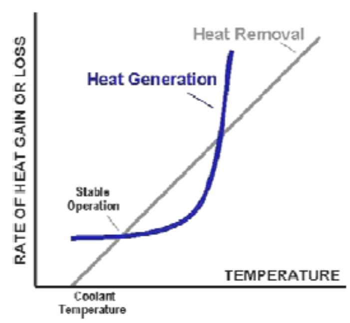
Chemical Safety and Security Training

Key term to understand:

"Runaway reaction"



For an exothermic chemical reaction: FIRST-ORDER KINETICS

- Reaction rate is exponential *f* (temperature) $k = A\ e^{(-Ea/RT)}$
- If reaction temperature increases, rate increases and more heat is released by exothermic reaction
- If this heat is not removed, it further increases the reaction rate
- Then even more heat is released, etc.
- Temperature can rise hundreds of °C per minute!
- Pressure is generated by product gases and/or liquid boiling
- Reactor may rupture if pressure not safely vented

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Chemical Safety and Security Training

U.S. CHEMICAL SAFETY AND HAZARD INVESTIGATION BOARD

INVESTIGATION REPORT

T2 LABORATORIES, INC.

RUNAWAY REACTION

(Four Killed, 32 Injured)

Chemical SAFETY AND SECURITY TRAINING

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Key Concepts

- Types of reactivity hazards
- Potential consequences
- Runaway reactions
- Contain and control measures
- Inherently safer systems

Chemical SAFETY AND SECURITY TRAINING

Foresee, Avoid, Control

- Anticipate chemical reactivity hazards
- Identify all reactive materials and all possible reactive interactions
- Do whatever it takes to fully understand intended and unintended reactions
  - Boundaries of safe operation
  - Calculations, literature, testing, experts
- Design and operate to avoid unintended reactions and control intended reactions

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Chemical SAFETY AND SECURITY TRAINING

Safe operation

(with respect to chemical reactivity hazards)

- Contain and control all chemical reactivity hazards throughout entire facility lifetime
- *OR* Reduce hazards or design safeguards such that even if hazard containment or control were lost, no injuries, property damage, environmental damage or business interruption would occur
- *OR* Eliminate chemical reactivity hazards

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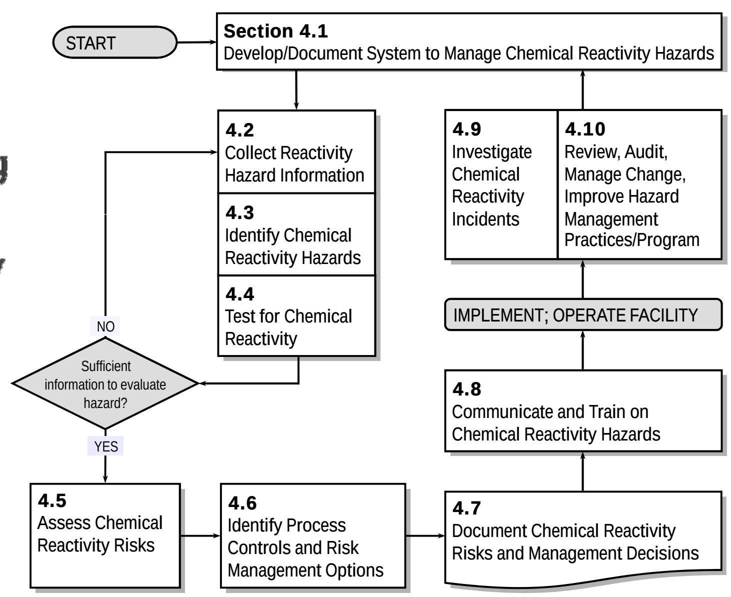
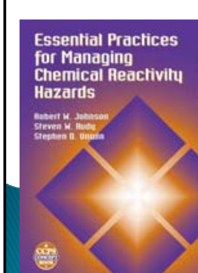
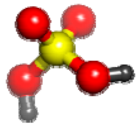
Managing chemical reactivity hazards

- More effort is required to identify and characterize the reactivity hazards
- This may require small-scale testing
- See flowchart on next page

Managing Chemical Reactivity Hazards

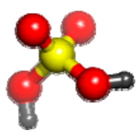


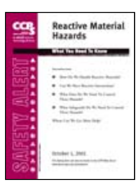




Key steps to avoid unintended chemical reactions

- Train all personnel to be aware of reactivity hazards and incompatibilities and to know maximum storage temperatures and quantities
- Design storage / handling equipment with all compatible materials of construction
- Avoid heating coils, space heaters, and all other heat sources for thermally sensitive materials
- Avoid confinement when possible; otherwise, provide adequate emergency relief protection
- Avoid the possibility of pumping a liquid reactive material against a closed or plugged line
- Locate storage areas away from operating areas in secured / monitored locations





Key steps to avoid unintended chemical reactions (continued)

- Monitor material and building temperatures where feasible with high temperature alarms
- Clearly label and identify all reactive materials, and what must be avoided (e.g., heat, water)
- Positively segregate and separate incompatible materials using dedicated equipment if possible
- Use dedicated fittings and connections to avoid unloading a material into the wrong tank
- Rotate inventories for materials that can degrade or react over time
- Pay close attention to housekeeping and fire prevention around storage/handling areas

Key steps to control intended chemical reactions

- *Scale up very carefully!* – Heat generation increases with the system **volume** (by the cube of the linear dimension), whereas heat removal capability increases with the **surface area** of the system (by the square of the linear dimension).
- Ensure equipment can handle the maximum pressure and maxiumum adiabatic temperature rise of uncontrolled reactions
- Use gradual-addition processes where feasible
- Operate where the intended reaction will be fast
- Avoid using control of reaction mixture temperature as a means for limiting the reaction rate
- Use multiple temperature sensors in different locations
- Avoid feeding a material above the reactor contents' boiling point

Design safer facilities

The following slides are a summary of D.C. Hendershot, "A Checklist for Inherently Safer Chemical Reaction Process Design and Operation," *CCPS International Symposium on Risk, Reliability and Security,* New York: AIChE, October 2002

Reaction Hazard Identification

1 Know the heat of reaction for the intended and other potential chemical reactions.

You should identify all potential reactions that could occur in the reaction mixture and understand the heat of reaction of these reactions.

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Reaction Hazard Identification

2 Calculate the maximum adiabatic temperature rise for the reaction mixture.

Use the measured or estimated heat of reaction, assume no heat removal, and that 100% of the reactants actually react.

Compare this temperature to the boiling point of the reaction mixture.

If the maximum adiabatic reaction temperature exceeds the reaction mixture boiling point, the reaction is capable of generating pressure in a closed vessel.

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Reaction Hazard Identification

3 Determine the stability of all individual components of the reaction mixture at the maximum adiabatic reaction temperature.

This might be done through literature searching, supplier contacts, or experimentation.

It will only tell you if any of the individual components of the reaction mixture can decompose at temperatures which are theoretically attainable.

Reaction Hazard Identification

4 Understand the stability of the reaction mixture at the maximum adiabatic reaction temperature.

Are there any chemical reactions, other than the intended reaction, which can occur at the maximum adiabatic reaction temperature?

Consider possible decomposition reactions, particularly those that generate gaseous products.

Understanding the stability of a mixture of components may require laboratory testing.

Reaction Hazard Identification

5 Determine the heat addition and heat removal capabilities of the pilot plant or production reactor.

Don't forget to consider the reactor agitator as a source of energy – about 2550 Btu/hour/hp.

Understand the impact of variation in conditions on heat transfer capability.

Reaction Hazard Identification

6 Identify potential reaction contaminants. In particular, consider possible contaminants that are ubiquitous in a plant environment, such as air, water, rust, oil and grease.

Think about possible catalytic effects of trace metal ions such as sodium, calcium, and others commonly present in process water and cleaners.

Determine if these materials will catalyze any decomposition or other reactions, either at normal conditions or at the maximum adiabatic reaction temperature.

Reaction Hazard Identification

7 Consider the impact of possible deviations from intended reactant charges and operating conditions.

For example, is a double charge of one of the reactants a possible deviation, and, if so, what is the impact?

Reaction Hazard Identification

8 Identify all heat sources connected to the reaction vessel and determine their maximum temperature.

Assume all control systems on the reactor heating systems fail to the maximum temperature. If this temperature is higher than the maximum adiabatic reaction temperature, review the stability and reactivity information with respect to the maximum temperature to which the reactor contents could be heated by the vessel heat sources.

Reaction Hazard Identification

9 Determine the minimum temperature to which the reactor cooling sources could cool the reaction mixture.

Consider potential hazards resulting from too much cooling, such as freezing of reaction mixture components, fouling of heat transfer surfaces, increase in reaction mixture viscosity reducing mixing and heat transfer, precipitation of dissolved solids from the reaction mixture, and a reduced rate of reaction resulting in a hazardous accumulation of unreacted material.

Reaction Hazard Identification

10 Consider the impact of higher temperature gradients in plant scale equipment compared to a laboratory or pilot plant reactor.

Agitation is almost certain to be less effective in a plant reactor, and the temperature of the reaction mixture near heat transfer surfaces may be higher (for systems being heated) or lower (for systems being cooled) than the bulk mixture temperature.

For exothermic reactions, the temperature may also be higher near the point of introduction of reactants.

Reaction Hazard Identification

11 Understand the rate of all chemical reactions.

It is not necessary to develop complete kinetic models with rate constants and other details, but you should understand how fast reactants are consumed and generally how the rate of reaction increases with temperature.

Thermal hazard calorimetry testing can provide useful kinetic data.

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Reaction Hazard Identification

12 Consider possible vapor-phase reactions.

These might include:

- combustion reactions
- other vapor-phase reactions such as the reaction of organic vapors with a chlorine atmosphere
- vapor phase decomposition of materials such as ethylene oxide or organic peroxide.

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Reaction Hazard Identification

13 Understand the hazards of the products of both intended and unintended reactions.

If you find an unexpected material in reaction equipment, determine what it is and what impact it might have on system hazards.

For example, in an oxidation reactor, solids were known to be present, but nobody knew what they were. It turned out that the solids were pyrophoric, and they caused a fire in the reactor.

Reaction Hazard Identification

14 Consider doing a Chemical Interaction Matrix and/or a Chemistry Hazard Analysis.

These techniques can be applied at any stage in the process life cycle, from early research through an operating plant.

Reaction Process Design

1 Rapid reactions are desirable.

In general, you want chemical reactions to occur immediately when the reactants come into contact.

The reactants are immediately consumed and the reaction energy quickly released, allowing you to control the reaction by controlling the contact of the reactants.

However, you must be certain that the reactor is capable of removing all of the heat and any gaseous products generated by the reaction.

Reaction Process Design

2 Avoid batch processes in which all of the potential chemical energy is present in the system at the start of the reaction step.

If you operate this type of process, know the heat of reaction and be confident that the maximum adiabatic temperature and pressure are within the design capabilities of the reactor.

Reaction Process Design

3 Use gradual addition or "semi-batch" processes for exothermic reactions.

The inherently safer way to operate exothermic reaction process is to determine a temperature at which the reaction occurs very rapidly. Operate the reaction at this temperature, and feed at least one of the reactants gradually to limit the potential energy contained in the reactor.

A physical limit to the possible rate of addition of the limiting reactant is desirable – e.g. a metering pump, small feed line or restriction orifice.

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Reaction Process Design

4 Avoid using control of reaction mixture temperature as a means for limiting the reaction rate.

If the reaction produces a large amount of heat, this control philosophy is unstable – an increase in temperature will result in faster reaction and even more heat being released, causing a further increase in temperature and more rapid heat release..... If there is a large amount of potential chemical energy from reactive materials, a runaway reaction results.

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Reaction Process Design

5 Account for the impact of vessel size on heat generation and heat removal capabilities of a reactor.

Heat generation increases with the volume of the system – by the cube of the linear dimension.

Heat removal capability increases with the square of the linear dimension.

Reaction Process Design

6 Use multiple temperature sensors, in different locations in the reactor for rapid exothermic reactions.

This is particularly important if the reaction mixture contains solids, is very viscous, or if the reactor has coils or other internal elements which might inhibit good mixing.

Reaction Process Design

7 Avoid feeding a material to a reactor at a higher temperature than the boiling point of the reactor contents.

This can cause rapid boiling of the reactor contents and vapor generation.

Key Concepts

- Types of reactivity hazards
- Potential consequences
- Runaway reactions
- Contain and control measures
- **Inherently safer systems**

Where chemical reactivity hazard(s) are identified, one of the first questions to ask should be:

"Can the reactivity hazards be eliminated or reduced?"

WHY?

Those hazards that are <u>not</u> eliminated or reduced to insignificance must be managed throughout the lifetime of the facility,

to avoid uncontrolled chemical reactions that can result directly or indirectly in serious harm to people, property or the environment.

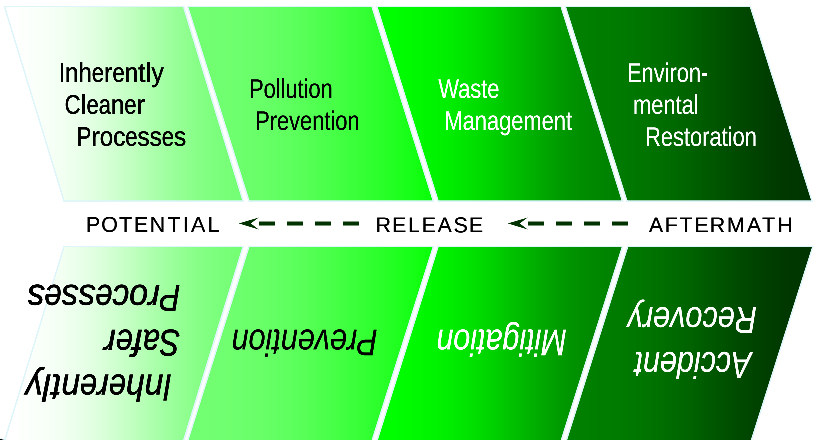
Eliminating or reducing the potential for uncontrolled chemical reactions makes a facility

"inherently safer"

If feasible, this has the possibility of affecting a facility in many different ways, such as:

- Reduce the need for engineered controls and safety systems (including both initial and ongoing inspection, testing and maintenance costs)
- Reduce labor costs and potential liabilities associates with ongoing legal compliance
- Eliminate the need for personal protective equipment associated with particular hazards
- Reduce emergency preparedness and response requirements
- Improve worker safety and health
- Improve neighborhood / community relations

Inherently safer processes



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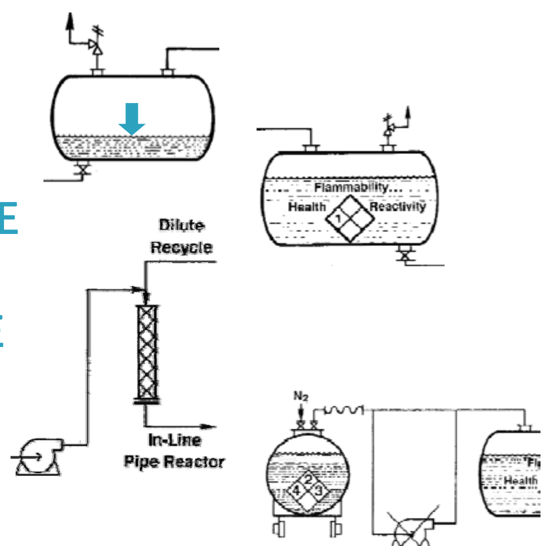
Inherently safer strategies

- MINIMIZE
- SUBSTITUTE
- MODERATE
- SIMPLIFY



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Safe operation

(with respect to chemical reactivity hazards)

- Contain and control all chemical reactivity hazards throughout entire facility lifetime
- *OR* **Reduce hazards** or design safeguards such that even if hazard containment or control were lost, no injuries, property damage, environmental damage or business interruption would occur
- *OR* **Eliminate chemical reactivity hazards**

Inherently safer systems

Case history:
Methyl isocyanate

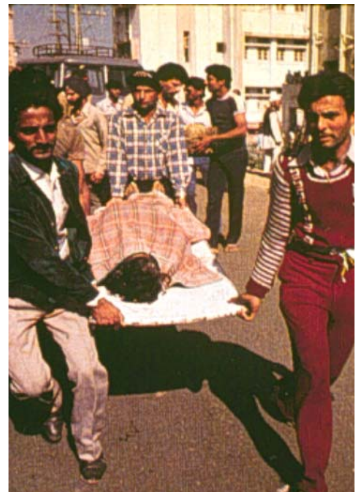
Bhopal

On December 4, 1984, approximately 40 metric tons of methyl isocyanate was released from the UCIL plant in Bhopal, India, resulting in an over 2,000 fatalities and many more injuries.

This was the worst disaster in chemical industry history.

The basic issue:

An uncontrolled chemical reaction occurred, resulting in devastating consequences.

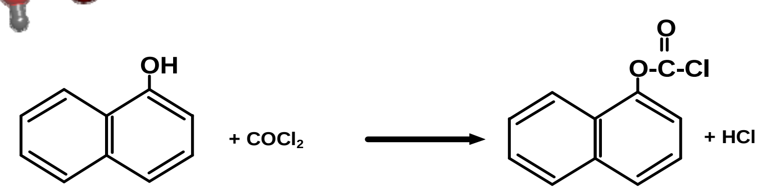


Time 12/17/84 (Tucci/Liaison)

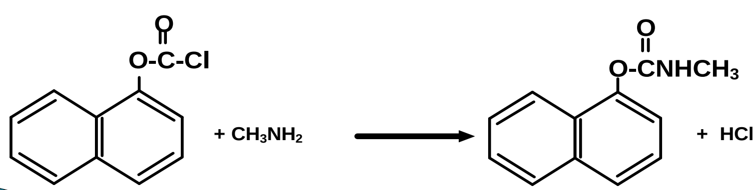
The two theories explaining the Bhopal tragedy both involve a significant amount of water getting into a 15,000 gal (56.5 m3) methyl isocyanate storage tank, resulting in an uncontrolled exothermic reaction that heated the MIC above its boiling point and led to the release of about 40 metric tons (~90,000 lb) of vaporized MIC from an elevated stack.

By comparison, the life-threatening concentration of MIC vapors in air is only 5 ppm (ERPG-3, 1 h exposure), which is only about 400 milligrams (~or about 0.001 lb by weight) of MIC in a room about the size of a medium to large bedroom or office (1200 ft3).

Non-MIC route



α- NAPHTHOL CHLOROFORMATE

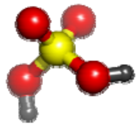


MIC generated on demand

- One company previously received and stored methyl isocyanate (MIC) in bulk liquefied form, as an ingredient for agricultural chemical products
- A process modification was made so that the MIC was generated as needed in vapor form, and piped directly to the process that consumed it

MIC generated on demand

- Average MIC inventory was reduced from thousands of pounds to about 2 pounds (1 kg) of vapor in the transfer line between generation and consumption
- The possibility of interrupting production (if a problem occurred in the process that generated MIC) was considered to be more than offset by the reduced vapor release risks



Exercise

What opportunities are there in your field of research or interest to consider reducing chemical reactivity hazards?

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Extra-Credit Activities

SAChE case histories

- Batch Polystyrene Reactor Runaway
- The Bhopal Disaster
- Methacrylic Acid Tankcar Explosion -video
- Explosion and Fire Caused By a Runaway Decomposition
- Rupture of a Nitroaniline Reactor
- Seveso Accidental Release
- T2 Runaway Reaction and Explosion

SAChE reactivity modules

Hazards awareness; hazard reduction

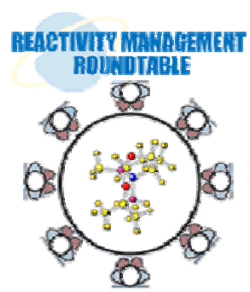
- An Introduction to Reactive and Explosive Materials (video)
- Acrylic Monomers Handling
- The Hazards of Hydroxylamine
- Chemical Reactivity Hazards (web-based)
- Introduction to Inherently Safer Design

SAChE reactivity modules

Emergency relief systems

- Design for Overpressure and Underpressure Protection
- Unit Operations Laboratory Experiment for Runaway Reactions and Vent Sizing
- Relief System Design for Single- and Two-Phase Flow
- Runaway Reactions -- Experimental Characterization and Vent Sizing
- Compressible and Two-Phase Flow with Applications Including Pressure Relief System Sizing

RMR



Reactivity Management Roundtable

Started in 2003

Most recent activity:

Reactivity Evaluation Software Tool

See description and download link at
www.aiche.org/ccps/ActiveProjects/RMR/index.aspx

DIERS Users Group

AIChE Design Institute for Emergency Relief Systems

DIERS

DIERS Users Group Meetings

See www.diers.net/diersweb/home.aspx for schedule and information

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Loss Prevention Symposium

46th Annual Loss Prevention Symposium

Houston, Texas, USA
April 2-6, 2012

Sessions include presentations on:

- Material hazard characteristics
- Case histories and lessons learned

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LPS'12 reactivity presentations

- A Mechanistic and Experimental Study of the Diethyl Ether Oxidation
- Phase Behavior of Poly-Substituted Mono-Nitrated Aromatic Compounds
- Global and Local QSPR Models to Predict the Impact Sensitivity of Nitro Compounds
- Thermal Safety of Ionic Liquids
- The CCPS Reactivity Evaluation Software Tool
- On the Catastrophic Explosion of the AZF Plant in Toulouse (September 21, 2001)

Safe Work Practices

SAND No. 2011-0785C
Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Overview

- Safe Work Practices
- Job Hazard Analysis
- Lockout-tagout (LOTO)
- Confined Space
- Line Breaking
- Hot Work

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Process Safety Management

Hazards

- Material hazards
- Energy hazards
- Chemical interaction hazards

Controls

- Job hazard analysis
- Operating procedures (OPs)
  - Safe Work Practices
    - Lockout-Tagout
    - Confined space
    - Line breaking
- Hot work permit

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Job Hazard Analysis

Job Hazard Analysis focuses on job tasks as a way to identify hazards before they occur. It focuses on the relationship between the worker, the task, the tools, and the work environment.

*Not the same as process hazard analysis.

Essential Steps in Job Hazard Analysis

- Involve your employees!
- List, rank, and set priorities for hazardous jobs
- Review your accident history/lessons learned
- Conduct a preliminary job review
- Outline the steps or tasks

What Jobs Need a Hazard Analysis?

- Jobs with the highest injury or illness rates
- Jobs with the potential to cause severe or disabling injuries or illness
- Jobs in which one simple human error could lead to a severe accident or injury;
- Jobs that are new to your operation or have undergone changes in processes and procedures; and
- Jobs complex enough to require written instructions

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The Job Hazard Analysis Asks Several Questions

- What can go wrong?
- What are the consequences?
- How could it happen?
- What are other contributing factors?
- What is the likelihood of an incident?

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Job Hazard Analysis Form

Job Hazard Analysis

Date: ____________ JHA Number: ________ Steps: 1 through 5

Location of Task: ____________________________________

Task Description: ____________________________________

Step 1 Description	Hazards	Preventive Measure(s)
Step 2 Description	Hazards	Preventive Measure(s)
Step 3 Description	Hazards	Preventive Measure(s)
Step 4 Description	Hazards	Preventive Measure(s)
Step 5 Description	Hazards	Preventive Measure(s)
Safe Job Procedures		

Exercise

Task Description: Worker reaches into metal box to the right of a grinding wheel machine, grasps a 15-pound casting and carries it to grinding wheel. Worker grinds 20 to 30 castings per hour.

- What are the hazards? Consider the equipment hazards, the material hazards, and ergonomic stressors.
- What controls can mitigate the hazards?

Credit: US Occupational Safety and Health Administration

Safe Work Practices

Safe Work Practices provide for the control of hazards during work activities

Safe Work Practices required by the US Process Safety Management Standard:

- Lockout –Tagout
- Confined space entry
- Line breaking
- Control over entry by maintenance contractors

They are generally written methods outlining how to perform a task with minimum risk to people, equipment, materials, environment, and processes.

They are issued

- to specific persons
- for a specific time period
- for a specific job

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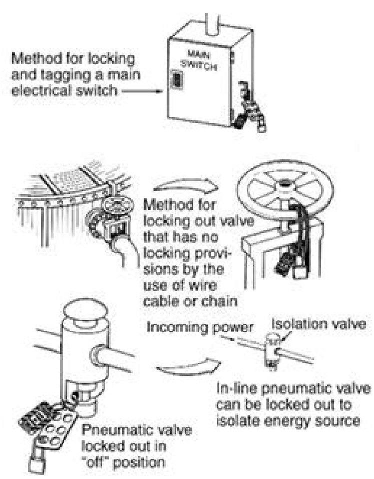
LOTO Addresses *All* Forms of Hazardous Energy

- Electrical energy *from generated elec*trical power, static sources, or electrical storage devices (batteries or capacitors)
- Kinetic (mechanical) energy – *in the* moving parts of mechanical systems
- Potential energy –*stored in pressure* vessels, gas tanks, hydraulic or pneumatic systems, and springs
- Thermal energy *(high or low temperature)* resulting from mechanical work, radiation, chemical reactivity, or electrical resistance



Credit: Lawrence Berkeley Laboratory

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LOTO Definition

Lockout-Tagout (LOTO) or lock and tag is a safety procedure which is used in industry and research settings to ensure that dangerous machines are properly shut off and not started up again prior to the completion of maintenance or servicing work.

OSHA 1910.147

LOTO U.S. Department of Labor Statistics

- Approximately 3 million workers are at risk of injury if LOTO is not properly implemented.
- LOTO prevents an estimated 120 fatalities and 50,000 injuries each year.
- Workers injured on the job from exposure to hazardous energy lose an average of 24 workdays for recuperation.
- United Auto Workers (UAW) reported that 20% of their fatalities between 1973 and 1995 were attributed to inadequate hazardous energy control procedures.

LOTO Incidents

- A worker attempted to prevent an elevator from moving by jamming the doors open with a wooden plank while the elevator was on the second floor and then turning off the outside panel switch on the main floor. Worker was killed when the elevator returned to the main floor.
- Worker turned off the power to a packaging machine and attempted to remove the jam. Residual hydraulic pressure activated the holding device and the worker's arm was caught in the packaging machine.
- A mechanic was repairing an electrically operated caustic pump and had turned off the pump toggle switch. A co-worker dragged a cable across the toggle switch and caustic liquid was sprayed on the mechanic.

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Steps to Safe LOTO

- Prepare for shutdown
- Shutdown machine or piece of equipment
- Isolate or block all hazardous energy sources for the equipment
- Apply lockout or tagout devices
- Release all stored energy
- Verify energy isolation
- Perform work

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Steps to Release from LOTO

- Make the work area safe
- Check the work area to ensure individuals are clear of the hazard area
- Remove locks, tags, and devices
- Notify affected workers
- Re-energize

Isolation of Energy

LOTO Practices-

•Only <u>one</u> key for each lock the worker controls

•<u>Only</u> the worker who installs lock can remove it

•Shift changes- New lock added <u>before</u> old one removed

•*Authorized employee* for group lockout device

•LOTO program

  •Energy control procedures

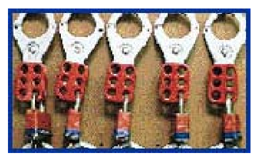
  •Training

  •Periodic inspections

•Alternatives (US regulation)

  •Cord & plug

  •Hot tap procedures

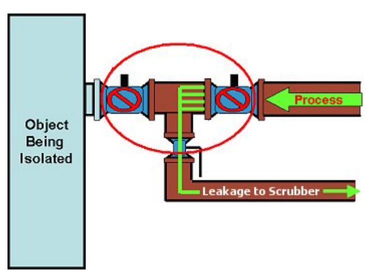


Dissipation or Control of Energy

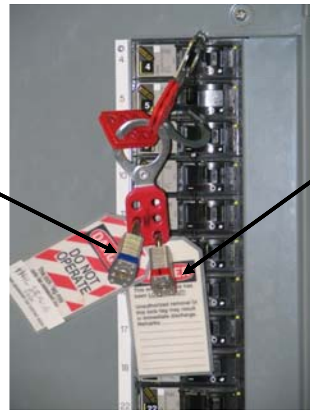
•Blind or blank piping

  •Lock and tag inline valves

•Remove stored energy-springs, hydraulics

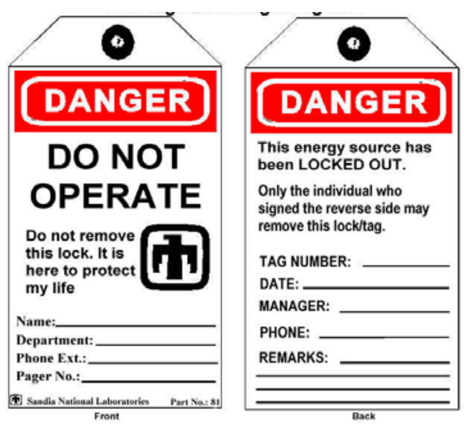


Each Company Assigns Unique Locks and Tags



LOTO Locks and Tags

Lock Self Adhesive Band , IDEAL Part Number 34-003



Other LOTO Devices

BALL VALVE LOCKOUTS - Brady Catalog #65666 & #65669 Panduit Catalog #PSL-BV1 & #PSL-BV2 (Similar)

GATE VALVE LOCKOUT - Brady Catalog #65560 to 65564

Circuit Breaker LOCKOUT...OPEN

Circuit Breaker LOCKOUT...LOCKED

CSP

Chemical SAFETY AND SECURITY TRAINING

Case Study

<u>Replacement of Nitrogen Pressure Vessel Seals</u>

A group of employees are assigned to replace the head seals on twelve large nitrogen pressure vessels (accumulator bottles) at a manufacturing facility. Each pressure vessel has an operating pressure of about 5,000 psig. Replacement of the seals on each vessel requires that its head be opened, releasing any vessel contents to the atmosphere. The vessels lack individual gauges to indicate internal pressure levels.

Credit: US Occupational Safety and Health Administration

CSP

Chemical SAFETY AND SECURITY TRAINING

Case Study

- Did the pressure within the nitrogen vessels constitute hazardous energy?
- Were the employees performing a servicing and/or maintenance operation that was subject to unexpected energization, start up, or release of hazardous energy?
- Would the group lockout or tagout provisions apply to this operation?

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Chemical SAFETY AND SECURITY TRAINING

Confined Space

Confined space is any space that has:

- Limited or restricted means of entry or exit;
- Is large enough for a person to enter to perform tasks and is not designed or configured for continuous occupancy

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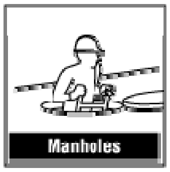
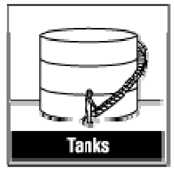
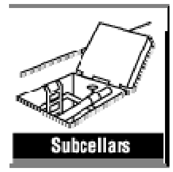
Chemical SAFETY AND SECURITY TRAINING

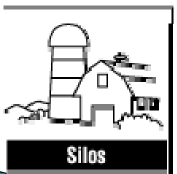
Confined Space

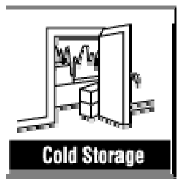


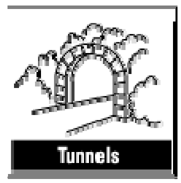


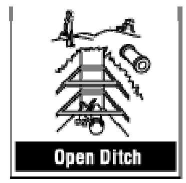


All of these spaces constitute a confined space…









Credit: Canadian Centre for Occupational Health and Safety

Permit-Required Confined Space

- Contains or has the potential to contain a hazardous atmosphere
- Contains a material that has the potential for engulfing the entrant
- Has an internal configuration that might cause an entrant to be trapped or asphyxiated by inwardly converging walls or by a floor that slopes downward and tapers to a smaller cross section
- Contains any other recognized serious safety or health hazards
- Work activities may introduce serious health & safety hazards
  - Welding
  - Spray paintings or coatings

Confined Space Incidents

60% of fatalities are of would-be rescuers!

- 2003-City engineer killed in landfill manhole when retrieving flow meter
- 2004-Mechanic dies from lack of oxygen in transport tank
- 2005-A utility cleanup worker for a brick manufacturer suffocated in a storage silo
- 2006-Welder dies during welding repair inside of cargo tank compartment

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Chemical SAFETY AND SECURITY TRAINING

Confined Space Permit

- Essential Elements of a CS Permit:
  - List potential hazards
  - List hazard controls
    - PPE, ventilation, barricades,
    - line blanking. LOTO
  - Communication equipment
  - Emergency & retrieval equipment
  - Pre-entry & continuous monitoring values
    - Oxygen, flammability, toxicity concentrations
  - Calibration/bump test information

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Chemical SAFETY AND SECURITY TRAINING

Confined Space Alternate Procedures

1. The *only* hazard posed by the space is an actual or potential atmospheric hazard controlled by mechanical ventilation.
   - Example: Underground communication vaults
2. No actual or potential atmospheric hazards, and all hazards are eliminated without entering the space.
   - Energy isolation-LOTO
   - Pipe or line isolation
   - Shielding of entrapment , mechanical hazards
   - Fall protection

Credit: Utah Safety Council

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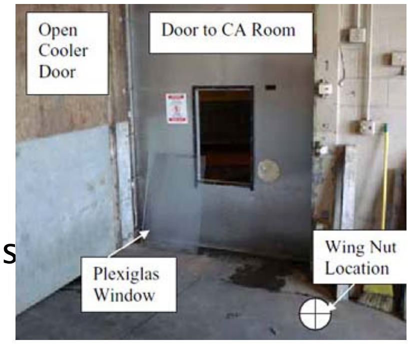
Chemical SAFETY AND SECURITY TRAINING

Atmospheric Hazards in Confined Spaces

- Oxygen Deficiency
- Oxygen Enrichment
- Flammable Vapors
- Flammable Gases
- Combustible Dust
- Toxic Vapors or Gases



Controlled Atmosphere Storage Room
Credit: US NIOSH

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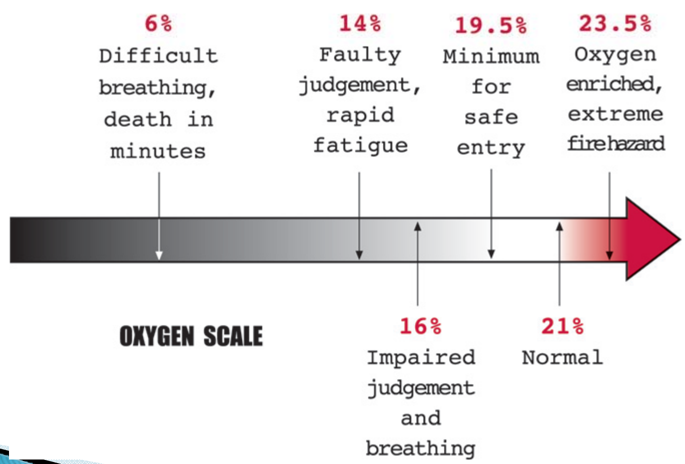
Chemical SAFETY AND SECURITY TRAINING

Oxygen Concentration



Atmospheric Testing of the Confined Space

1. Oxygen is tested first
   Combustible gas meters are oxygen-dependent and will not provide reliable readings when used in oxygen-deficient atmospheres.

2. Combustible gases and vapors are tested second
   The threat of fire and explosion is a more immediate acute hazard

3. Toxic atmospheres are tested last
   In most instances, the exposure limit for a toxic gas or vapor is less likely to be exceeded than the flammability limit over a short period of time.

Many modern direct-reading instruments provide simultaneous readings of multiple gases.

Example of Need to Air Sample for Toxics

- American Conference of Governmental Industrial Hygienists (ACGIH) short term exposure limit (STEL) to styrene exceeded
  - 186 parts per million (ppm) measured as STEL
  - ACGIH STEL is 40 ppm
  - Standard set to minimize the potential of irritation to the eyes and respiratory tract
- Task involved positioning and securing of uncured liner material in a sewer manhole.
- Lining expanded and off gassed styrene
- Manhole was under continuous ventilation
- Oxygen and flammable limits in acceptable range

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Chemical SAFETY AND SECURITY TRAINING

Confined Space Air Monitoring Poor Practices

- No monitoring checklist
- Using your senses to detect atmospheric hazards
- No training in gas detection monitoring
- No factory instrument calibration
- No daily "bump" test
- No pre-entry monitoring
- No continuous monitoring
- No attendant trained in monitoring

Credit: OC Environmental Services

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Chemical SAFETY AND SECURITY TRAINING

Emergency During Entry

•Entrants evacuated-entry aborts.
(Call rescuers if needed).
•Permit is *void*.
•Reevaluate program to correct/prevent prohibited condition.
•Occurrence of emergency (usually) is proof of deficient program.
•No re-entry until program (and permit) is amended.
(May require new program.)

Opening Lines and Vessels "Line Breaking" Definition

Line breaking means the intentional opening of a pipe, line, or duct that is or has been carrying flammable, corrosive, or toxic material, an inert gas, or any fluid at a volume, pressure, or temperature capable of causing injury.

US OSHA "Ammonia High Pressure Receiver Standard Operating Procedure" http://www.osha.gov/SLTC/etools/ammonia_refrigeration/receiving/receiver_sop.html

Hazards of Opening Lines and Vessels

- Hot or cold fluids
- Toxic release and exposure
  - Ammonia
  - Hydrogen Sulfide
- Fire and explosion
  - Hydrocarbons
  - Pyrophoric materials
  - Moisture sensitive materials
- Pressure release
  - Pipeline pigging
  - Steam

Credit: Reagan Safety

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Chemical SAFETY AND SECURITY TRAINING

Line Breaking Procedures & Permitting

- Operating procedures
- Scope includes both employees *and* contractors
- Permit
  - Identify the hazard
    - SDS, process information
    - Consider cleaning agents which may be reactive
  - Establish required controls
    - Barricades-warning signs, cones, flags
    - Safety equipment-pipe supports, fall protection, fire extinguisher, monitoring equipment
    - Isolate or control system hazards
      - Cool system
      - Depressurize system
      - Flush system
      - LOTO energy sources
    - Appropriate personal protective equipment (PPE)

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Chemical SAFETY AND SECURITY TRAINING

Line Breaking/Line Opening Procedures

- Additional considerations:
  - Replace broken, corroded and stripped bolts first
  - If transferring flammable chemical residue, bond the container to the pipe
  - Control access to area to authorized personnel
  - Log all isolation valves
  - Ensure personnel are trained and training documented
  - Prepare emergency plan

Credit: Reagan Safety

CSP — Chemical Safety and Security Training

Hot Work Definition

Hot work is work involving electric or gas welding, torch cutting, grinding, brazing, or similar flame or spark-producing operations.

OSHA 1910.252

CSP — Chemical Safety and Security Training

Hot Work Permit

- Fire prevention and protection requirements
- Implemented prior to beginning the hot work operations
- Date(s) authorized for hot work
- Identify the object on which hot work is to be performed
- Permit shall be kept on file until completion of the hot work operations.

WARNING!
HOT WORK IN PROGRESS
WATCH FOR FIRE!

PART 2

INSTRUCTIONS

1. Person doing Hot Work: Indicate time started and post permit at Hot Work location. After Hot Work, indicate time completed and leave permit posted for Fire Watch.
2. Fire watch: Prior to leaving area, do final inspection, sign, leave permit posted and notify Firesafety Officer.
3. Monitor: After 4 hours, do final inspection, sign and return to Firesafety Officer.

HOT WORK BEING DONE BY:

☐ EMPLOYEE ________ LIFE NO. ______
☐ CONTRACTOR ________ CO. ______

DATE | JOB NO.

LOCATION/BUILDING & FLOOR

NATURE OF JOB

NAME OF PERSON DOING FIRE WATCH

I verify the above location has been examined, and permission is authorized for this work.

SIGNED: (FIRE/SAFETY OFFICER)

DATE:

PERMIT EXPIRES	DATE	TIME AM PM

I verify that the List of Precautions is Understood and work will proceed only if precautions are followed:
Signed: (Supervisor) ________

FIRE WATCH SIGNOFF

Work area and all adjacent areas to which sparks and heat might have spread were inspected during the fire watch period and were found fire safe.

Signed: ________

FINAL CHECKUP

Work area was monitored following Hot Work and found fire safe.

Signed: ________

Required Precautions Checklist

MAY BE RETAINED AS RECORD OF HOT WORK ACTIVITY

- ☐ Available sprinklers, hose streams and extinguishers are in service/operable.
- ☐ Hot Work equipment in good repair.

Requirements within 35 ft (10m) of work

- ☐ Flammable liquids, dust, lint and oil deposits removed.
- ☐ Explosive atmosphere in area eliminated.
- ☐ Floors swept clean.
- ☐ Combustible floors wet down, covered with damp sand or fire-resistive sheets.
- ☐ Remove other combustibles where possible. Otherwise protect with fire-resistive tarpaulins or metal shields.
- ☐ All wall and floor openings covered.
- ☐ Fire-resistive tarpaulins suspended beneath work.

Work on walls or ceilings

- ☐ Construction is noncombustible and without combustible covering or insulation.
- ☐ Combustibles on other side of walls moved away.

Work on enclosed equipment

- ☐ Enclosed equipment cleaned of all combustibles.
- ☐ Containers purged of flammable liquids/vapors and monitored for vapor buildup.

Fire watch/Hot Work area monitoring

- ☐ Fire watch conractor/department will supply during and for 60 minutes after work, including any coffee or lunch breaks.
- ☐ Fire watch is supplied with suitable extinguishers, charged small hose.
- ☐ Fire watch is trained in use of this equipment and in sounding alarm (telephone, alarm box, radio).
- ☐ Fire watch may be required for adjoining areas, above, and below (see other precautions).
- ☐ Monitor Hot Work area for 4 hours after job is completed.

Other Precautions Taken

- ☐ False alarm with detection systems considered.
- ☐ ________

3195

Responsibility for Hot Work is Clearly Outlined

Permit Authorizing Individual – Inspects hot work site before starting

Hot Work Operators – Perform hot work operations

Fire Watch – is posted to monitor safe operations

Designated Area – Location approved for hot work operations.

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Chemical SAFETY AND SECURITY TRAINING

Fire Protection during Hot Work

- All entrances and exits clear
- Correct poor housekeeping practices
- Use appropriate shielding of flammable surfaces
- Keep work area free of unnecessary combustible materials
- Do not use flammable degreasing agents
- Monitor the atmosphere–<10 % of Lower Explosive Limit (LEL)

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Chemical SAFETY AND SECURITY TRAINING

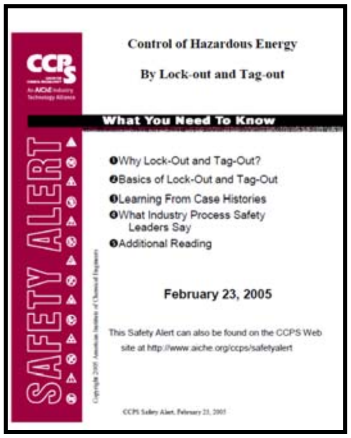
Fire Fighting Equipment and Procedures

- All workers should know the location of the fire fighting equipment in their area.
- Fire extinguishers are checked monthly
- Mark empty fire extinguisher with "empty" and never return empty extinguisher to its fire station.
- All fire extinguishers should be inspected on an annual basis by a certified company.
- All workers should receive training before using fire extinguishing equipment.
- If Fire Watch determines fire may grow beyond control– emergency services must be contacted

Hot Work Area is Controlled by Zoning

- Hot zone- inside permit space
- Warm zone – outside occupied by attendant personnel
- Cold or support zone – equipment and supplies
- Barricades and barriers
- Shields and railings

Resources: LOTO


Control of Hazardous Energy

By Lock-out and Tag-out

What You Need To Know

❶Why Lock-Out and Tag-Out?
❷Basics of Lock-Out and Tag-Out
❸Learning From Case Histories
❹What Industry Process Safety Leaders Say
❺Additional Reading

February 23, 2005

This Safety Alert can also be found on the CCPS Web site at http://www.aiche.org/ccps/safetyalert

CCPS Safety Alert, February 23, 2005

http://www.osha.gov/SLTC/controlhazardousenergy/index.html


NIOSH ALERT

Preventing Worker Deaths from Uncontrolled Release of Electrical, Mechanical, and Other Types of Hazardous Energy

WARNING!

Workers who install or service equipment and systems may be injured or killed by the uncontrolled release of hazardous energy.

http://www.cdc.gov/niosh/docs/99-110/pdfs/99-110sum.pdf

Personal Protective Equipment

SAND No. 2012-1421C

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000

Personal Protective Equipment (PPE)

- Limitations of PPE
- Hazard assessment
- Training
- Characteristics of PPE
- Protective clothing
- Gloves
- Eyewear
- Respirators
- Exercise

Limitations of PPE

- The least desirable control, but may be necessary if:
  - Engineering controls are being installed
  - Emergency response/spill cleanup
  - Non-routine equipment maintenance
  - To supplement other control methods
- Problems with PPE:
  - The hazard is still present with PPE
  - Use is very dependent on human behavior
  - Proper fitting is essential
- Can exposure be controlled by other means?

PPE Hazard Assessment

- Identify the hazard(s)
  - Chemical
  - Mechanical
  - Electrical
  - Light energy (lasers, welding)
  - Fire response
  - Hot processes
- Identify the potential exposure route
  - Inhalation
  - Skin contact
  - Eye contact

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PPE Hazard Assessment

- Identify the type of skin contact
  - Immersion
  - Spray
  - Splash
  - Mist
  - Vapor (gaseous)
- Consider the exposure time
  - Incidental contact
  - Continuous immersion
  - Unknown/emergency response

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Exercise

- List one work activity at your plant that uses PPE
- What is the hazard?
- What is the route of exposure? Inhalation, skin, eyes, or ?
- Are there ways to control exposure to this hazard other than PPE?
  - What other ways?

Training

Employees should be trained to know:

- When PPE is necessary
- What PPE is necessary
- How to properly don, doff, adjust and wear PPE
- Limitations of PPE
- Proper care, maintenance, useful life and disposal
- Involve workers in selection

http://www.free-training.com/OSHA/ppe/Ppemenu.htm

Training

Retraining is necessary when there is:

- A change in the hazards
- A change in the type of PPE required
- Inadequate employee knowledge or use of PPE

http://www.free-training.com/OSHA/ppe/Ppemenu.htm

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Chemical SAFETY AND SECURITY TRAINING

General Characteristics of PPE

Protective clothing and gloves:

- Act as a barrier to prevent contact with the skin
- Protect against
  - Toxics
  - Corrosives
  - Irritants
  - Sensitizers (allergens)
  - Thermal injury (burns)
  - Physical Trauma

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Chemical SAFETY AND SECURITY TRAINING

General Characteristics of PPE

Protective clothing and gloves

- When selecting consider:
  - Permeation
    - Breakthrough time
    - ASTM F739 Standard
  - Penetration
  - Degradation
  - Comfort
  - Heat stress
  - Ergonomics
  - Cost

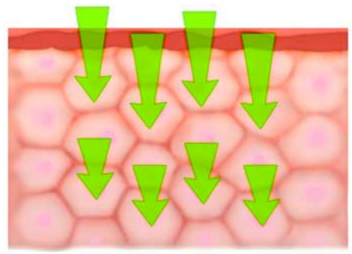

Photo credit: Permeation, http://www.cdc.gov/niosh/topics/skin/

Permeation Rate (PR)	Permeation Breakthrough (PB)	Permeation Degradation rate (DR)
E- Excellent; permeation rate of less than 0.9 mg/cm²/min	>Greater than (time - minutes)	E - Excellent; fluid has very little degrading effect.
VG - Very Good; permeation rate of less than 9 mg/cm²/min	< Less than (time - minutes)	G - Good; fluid has minor degrading effect.
G - Good; permeation rate of less than 90 mg/cm²/min		F - Fair; fluid has moderate degrading effect.
F - Fair; permeation rate of less than 900 mg/cm²/min		P - Poor; fluid has pronounced degrading effect.
P - Poor; permeation rate of less than 9000 mg/cm²/min		NR - Fluid is not recommended with this material.
NR - Not recommended; permeation rate greater than 9000 mg/cm²/min		† Not tested, but breakthrough time > 480 min DR expected to be Good to Excellent
		†† Not tested, but expected to be Good to Excellent based on similar tested materials

Protective Clothing

- Special Applications
  - Hot processes
  - High voltage/arc flash
    - NFPA 70E
  - Foundries/molten metal
  - Refineries
- Select flame resistant clothing
- Chemical resistant coating may be added to flame resistant clothing

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Chemical SAFETY AND SECURITY TRAINING

Gloves

- **Evaluate the work task**
  - **Chemical immersion or incidental contact?**
  - **Consider ergonomics/dexterity required**
- **Use glove charts**
  - **Charts recommend gloves for specific chemicals**
    - **Evaluate permeation rates and breakthrough time of selected glove for the specific task**
  - **Consider several glove manufactures data before final selection.**
    - http://www.mapaglove.com
    - http://www.ansellpro.com
    - http://www.bestglove.com/site/chemrest/

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Chemical SAFETY AND SECURITY TRAINING

The first square in each column for each glove type is color coded. This is an easy-to-read indication of how we rate this type of glove in relation to its applicability for each chemical listed. The color represents an overall rating for both degradation and permeation. The letter in each square is for Degradation alone…

- GREEN: The glove is very well suited for application with that chemical.
- YELLOW: The glove is suitable for that application under careful control of its use.
- RED: Avoid use of the glove with this chemical.

	LAMINATE FILM			NITRILE			UNSUPPORTED NEOPRENE			SUPPORTED POLYVINYL ALCOHOL			POLYVINYL CHLORIDE (Vinyl)			NATURAL RUBBER			NEOPRENE/ NATURAL RUBBER BLEND		
	BARRIER			SOL-VEX			29-865			PVA			SNORKEL			CANNERS AND HANDLERS*			CHEMI-PRO*		
CHEMICAL	Degradation Rating	Permeation: Breakthrough	Permeation: Rate	Degradation Rating	Permeation: Breakthrough	Permeation: Rate	Degradation Rating	Permeation: Breakthrough	Permeation: Rate	Degradation Rating	Permeation: Breakthrough	Permeation: Rate	Degradation Rating	Permeation: Breakthrough	Permeation: Rate	Degradation Rating	Permeation: Breakthrough	Permeation: Rate	Degradation Rating	Permeation: Breakthrough	Permeation: Rate
1. Acetaldehyde	■	380	E	P	—	—	E	10	F	NR	—	—	NR	—	—	E	7	F	E	10	F
2. Acetic Acid	■	150	—	G	270	—	E	60	—	NR	—	—	F	180	—	E	110	—	E	260	—
3. Acetone	▲	>480	E	NR	—	—	E	10	F	P	—	—	NR	—	—	E	10	F	G	10	G
4. Acetonitrile	▲	>480	E	F	30	F	E	20	G	■	150	G	NR	—	—	E	4	VG	E	10	VG
5. Acrylic Acid	—	—	—	G	120	—	E	390	—	NR	—	—	NR	—	—	E	80	—	E	65	—
6. Acrylonitrile	E	>480	E	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
7. Allyl Alcohol	▲	>480	E	F	140	F	E	140	VG	P	—	—	P	60	G	E	>10	VG	E	20	VG
8. Ammonia Gas	■	19	E	▲	>480	—	▲	>480	—	—	—	—	■	6	VG	—	—	—	■	27	VG
9. Ammonium Fluoride, 40%	—	—	—	E	>360	—	E	>480	—	NR	—	—	E	>360	—	E	>360	—	E	>360	—
10. Ammonium Hydroxide	E	30	—	E	>360	—	E	250	—	NR	—	—	E	240	—	E	90	—	E	240	—
11. Amyl Acetate	▲	>480	E	E	60	G	NR	—	—	G	>360	E	P	—	—	NR	—	—	P	—	—
12. Amyl Alcohol	—	—	—	E	30	E	E	290	VG	G	180	G	G	12	E	E	25	VG	E	45	VG
13. Aniline	▲	>480	E	NR	—	—	E	100	P	F	>360	E	F	180	VG	E	25	VG	E	50	G
14. Aqua Regia	—	—	—	F	>360	—	G	>480	—	NR	—	—	G	120	—	NR	—	—	G	180	—
15. Benzaldehyde	▲	>480	E	NR	—	—	NR	—	—	G	>360	E	NR	—	—	G	10	VG	G	25	F
16. Benzene, Benzol	▲	>480	E	P	—	—	NR	—	—	E	>360	E	NR	—	—	NR	—	—	NR	—	—
17. Benzotrichloride	—	—	—	E	>480	E	NR	—	—	—	—	—	—	—	—	NR	—	—	NR	—	—
18. Benzotrifluoride	—	—	—	E	170	G	F	—	—	E	—	—	G	<10	F	P	50	G	—	—	—
19. Bromine Water	—	—	—	E	>480	E	E	>480	E	—	—	—	—	—	—	—	—	—	—	—	—
20. 1-Bromopropane	▲	>480	E	■	23	F	■	<10	P	▲	>480	E	■	<10	F	■	<10	P	■	<10	P

General Types of Glove Material

Laminated Gloves: 4H®, Silver Shield®

- Useful for a wide range of chemicals.

  NOT HYDROGEN FLUORIDE!

- Can use with a nitrile over glove to improve dexterity.

Butyl Rubber

- Highest permeation resistance to gas or water vapors.
- Uses: acids, formaldehyde, phenol, alcohols.

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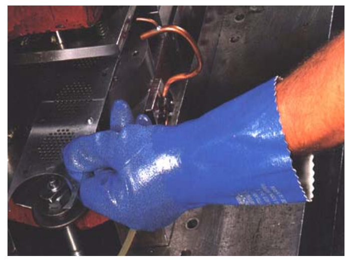
SAFETY AND SECURITY TRAINING

General Types of Glove Material

Neoprene
- Protects against acids, caustics.
- Resists alcohols, glycols.

Nitrile
- Good replacement for latex
- Protects against acids, bases, oils, aliphatic hydrocarbon solvents and esters, grease, fats
- NOT ketones
- Resists cuts, snags, punctures and abrasions



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Latex Allergy

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Proper Steps for Removing Gloves


1


2


3


4


5


6

Eye and Face Protection

- Each day, 2000 U.S. workers have a job-related eye injury that requires medical treatment.
- Nearly *three out of five* U.S. workers are injured while failing to wear eye and face protection.

NIOSH. (2010). http://www.cdc.gov/niosh/topics/eye/

Types of Eye Hazards

Hazard Type	Common related tasks	Protective Eyewear
Impact	Chipping, grinding, machining, abrasive blasting, sawing, drilling, riveting, sanding,…	Safety glasses with sideshields Goggles
Heat	Furnace operations, smelting, pouring, casting, hot dipping, welding, …	Face shield with infrared protection
Chemicals	Pouring, spraying, transferring, dipping acids, solvents or other injurious chemicals	Goggles Faceshield
Particles/ Dust	Woodworking, metal working, and general dusty conditions	Safety glasses with sideshields
Optical Radiation	Welding, torch-cutting, brazing, and laser work	Welding helmet Laser glasses -Must protect for specific wavelength of ultraviolet or infrared radiation.

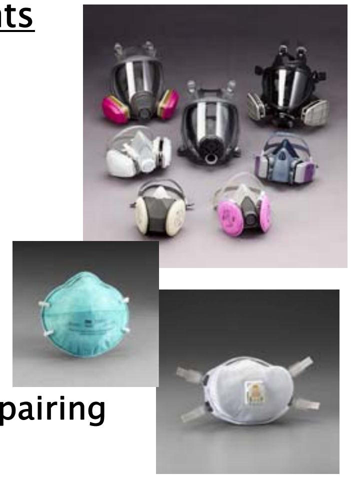
Examples of Eye & Face Protection


- Goggles
- Face shield
- Safety glasses
- Welding helmet
- Hooded faceshield



Respiratory Protection

- U.S. Respirator Requirements
- Written program
- Hazard assessment
  - Air monitoring
- Medical clearance
- Fit testing
- Respirator selection
- Procedures
  - Cleaning, maintenance, repairing
- Training (annual refresher)



Basic Types of Respirators

- Air purifying (APR)
  - Half Face
  - Full Face
  - Powered APR (PAPR)
- Air supply
  - Air line
  - SCBA

Air Purifying Respirators (APR)

- Work area must have at least 19.5% oxygen
- The contaminant must have adequate warning properties. Ex. ammonia
  - Never use APR in oxygen deficient atmospheres
- APRs work by filtering, absorbing, adsorbing the contaminant or chemical reaction.
  - Filters, cartridges, canisters
- The contaminant concentration must NOT exceed the maximum use concentration.
- Some cartridges have "end of service life" indicators or can use change schedules

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Types of APR Cartridges

Cartridge	Description
	Organic Vapor
	Organic Vapor and acid gases
	Ammonia, methylamine and P100 particulates filter

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End of Service Life Indicators (ESLI)

There are very few NIOSH-approved ESLI's:

- ammonia
- carbon monoxide
- ethylene oxide
- hydrogen chloride
- hydrogen fluoride
- hydrogen sulfide
- mercury
- sulfur dioxide
- toluene-2,4-diisocyanate
- vinyl chloride

APR Filter Efficiency

National Institute of Occupational Safety and Health
Filter Efficiencies

Filter Class	
N95	Filters at least 95% of airborne particles. Not resistant to oil.
N99	Filters at least 99% of airborne particles. Not resistant to oil.
N100	Filters at least 99.97% of airborne particles. Not resistant to oil.
R95	Filters at least 95% of airborne particles. Somewhat resistant to oil.
P95	Filters at least 95% of airborne particles. Strongly resistant to oil.
P99	Filters at least 99% of airborne particles. Strongly resistant to oil.
P100	Filters at least 99.97% of airborne particles. Strongly resistant to oil

Assigned Protection Factors (APF)

- Level of workplace respiratory protection that a respirator or class of respirators is expected to provide.
- Each specific *type* of respirator has an Assigned Protection Factor (APF).
- Select respirator based on the exposure limit of a contaminant and the level in the workplace.

Maximum Use Concentration (MUC)
= APF x Occupational Exposure Limit
(e.g. PEL, TLV)

Assigned Protection Factors

Type of Respirator	Half Face Mask	Full Facepiece	Helmet/ Hood	Loose-Fitting Facepiece
Air-Purifying	10	50	-	-
PAPR	50	1,000	25/1,000	25
Supplied-Air or Airline				
– Demand	10	50	-	-
– Continuous flow	50	1,000	25/1000	25
– Pressure demand	50	1,000	-	-
SCBA				
– Demand	10	50	50	-
– Pressure Demand	-	10,000	10,000	-

Assigned Protection Factors

Workplace air sampling indicates the exposure to benzene is 15 parts per million (ppm). The exposure limit is 0.5 ppm (ACGIH TLV).

What respirator should you choose?

Maximum Use Concentration (MUC) = APF x OEL

Half Face Mask: MUC = 10 x 0.5 ppm = 5 ppm

PAPR (LFF): MUC = 25 x 0.5 ppm = 12.5 ppm

Full Face Respirator: MUC = 50 x 0.5 ppm = 25 ppm

Filtering Facepieces

Filtering Facepiece Use

Respiratory Fit Testing

- Qualitative
  - Irritant smoke
    - stannic chloride
  - Isoamyl acetate
    - banana oil
  - Saccharin
  - Bitrex
- Quantitative
  - Portacount

Respirator Fit Test

Positive / Negative pressure fit test

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Supplied Air

- Supplies breathing air to worker
  - SCBA
  - Airline
- Must use Grade D Air
- Many limitations

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Breathing Air Quality and Use

- Compressed breathing air must be at least Type 1 – Grade D [ANSI/CGA G-7.1-1989]:
  - Oxygen content = 19.5 – 23.5%
  - Hydrocarbon (condensed) = 5 milligrams/cubic meter or less
  - CO ≤ 10 parts per million (ppm) or less
  - CO_2 of 1,000 parts per million (ppm) or less
  - Lack of noticeable odor
- Compressors may be equipped with in-line air-purifying sorbent beds and filters.

Maintenance & Storage Procedures

- Disposable filtering face-piece:
  - Dispose after use
- Air purifying respirators:
  - Discard cartridges based on expiration date, end-of-service life indicator or calculated service life
  - Clean
  - Dry
  - Place in sealable bag (write your name on bag)
  - Contact Safety Office for repairs
- SCBA:
  - Inspected monthly
  - Accessible and clearly marked

Discussion

- A contractor has been hired to sweep out a work area that contains lead dust. The plant safety officer has recommended that the worker don a full-face air purifying respirator with a HEPA filter (P100) during this activity.
- Later that week the plant safety officer observes the worker sweeping without wearing the respirator. When asked why he is not wearing the respirator, the worker states "it is too uncomfortable to wear."
- What approach should the safety officer take to ensure the worker wears a respirator?

PPE Exercise

- Worker A needs to transfer 10 liters of acetone into a hazardous waste drum.
- The safety officer has determined that due to the use of ventilation, the air concentration of acetone is below the exposure limit.
- The worker may have incidental skin contact with the acetone during pouring.
- Prolonged skin exposure to acetone causes dry and cracked skin, but acetone is not normally absorbed through the skin.
- There is also a possibility that the acetone may splash in the worker's face during pouring.

What PPE should Worker A wear?

PPE Exercise

- Worker B is walking back from the break room when he notices a yellow cloud of chlorine coming towards him from the chlorine storage area. He also notices that some of the chlorine has come into contact with water under one of the tanks and formed chlorine hydrate.
- He alerts the emergency response team who arrive at the emergency staging area.
  - Chlorine is a corrosive and toxic gas by inhalation.
  - Chlorine hydrate is corrosive to the skin and eyes.
  - The airborne concentration of chlorine is unknown in this situation.

  What PPE should the emergency response team use?

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PPE Exercise

- Worker C is tasked with adding zinc oxide pigment into a mixing bath by hand.
- This task will take 15 minutes.
- Worker C performs this task once every day.
- The safety officer has determined that the airborne concentration during this task is 20 milligrams/cubic meter.
- The short term exposure limit (15 minutes) for zinc oxide is 10 milligrams/cubic meter .
- Zinc oxide powder is mildly irritating to the skin and eyes, but not toxic or corrosive.

What PPE should Worker C wear?

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Process Equipment Inspection and Testing

Bandung, Indonesia
March 2012

Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Key acronyms

MI = *mechanical (asset) integrity*

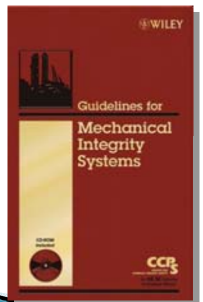
ITM = *inspections, testing, maintenance*

PM = *preventive maintenance*

MMS = *maintenance management system*

Resource

CCPS 2006. Center for Chemical Process Safety, *Guidelines for Mechanical Integrity Systems*, NY: AIChE.



Chapter
- **1** Introduction
- **2** Management responsibility
- **3** Equipment selection
- **4** Inspection, testing and preventive maintenance
- **5** MI training program
- **6** MI program procedures
- **7** Quality assurance
- **8** Equipment deficiency management
- **9** Equipment-specific integrity management
- **10** MI program implementation
- **11** Risk management tools
- **12** Continuous improvement of MI programs

Resource CD included

Process Safety Beacon

CCPS 20 YEARS — An AIChE Industry Technology Alliance

http://www.aiche.org/ccps/safetybeacon.htm

Messages for Manufacturing Personnel

Sponsored by CCPS Supporters

April 2006

Mechanical Integrity

BEFORE

The flange on the left is badly corroded and the bolts are in very poor condition - a leak waiting to happen. Fortunately, the poor condition was noted during a plant inspection and the flange was replaced (as shown on the right).

The picture on the left shows a corroded control valve. Could you count on this valve to operate when you need it? The picture on the right shows the replacement valve, which, if properly maintained and tested, is much more likely to function correctly when needed.

AFTER

This picture shows an improvised pipe support made from scaffolding, springs and clamps.

Did you know?

- In 2004, process safety incidents reported to the Canadian Chemical Producers Association indicate that 25% were caused by problems with process equipment mechanical integrity.
- Further analysis of the same data shows that mechanical integrity failure is a cause of up to 50% of the incidents in several years between 1998 and 2003.
- ALL OF US are the first line of defense for plant integrity issues like the ones shown here. We are in the plant every day and have the opportunity to see and report these problems.

What You Can Do

- Plan regular plant tours to look for mechanical integrity problems – such as corroded equipment, piping and valves, inadequate piping support, small drips or wet spots around flanges.
- Listen as well as look! For example, does that pump sound different? If so, perhaps maintenance should check it in case there is something wrong.
- But, don't wait for "official" plant safety tours and inspections. Be constantly aware of visual and other signs of equipment mechanical integrity problems.
- If you see or hear something that concerns you, report it promptly and follow-up to make sure steps are taken to correct the situation.

"You can see a lot just by looking!" (Yogi Berra, New York Yankees)

Three basic MI activities

1. Design and build reliability into process equipment and controls
2. Inspect / test / maintain the integrity of the equipment and controls
3. Successfully correct failures and performance degradations as they occur

Three basic MI activities - By whom?

1. Design and build reliability into process equipment, controls [ENGINEERING/CONSTRUCTION]
2. Inspect / test / maintain the integrity of the equipment and controls [PLANT MAINTENANCE]
3. Successfully correct failures and performance degradations as they occur [PLANT MAINTENANCE]

Three basic MI activities

1. Design and build reliability into process equipment, controls
2. Inspect / test / maintain the integrity of the equipment and controls
3. Successfully correct failures and performance degradations as they occur

Focus of this module

Equipment Inspections and Testing

1. Understand the importance of plant equipment PM
2. Determine what needs to be maintained
3. Put in place a system of how it will be maintained
4. Determine how often tasks need to be performed
5. Equip with maintenance procedures and training
6. Document ITMs
7. Correct identified deficiencies

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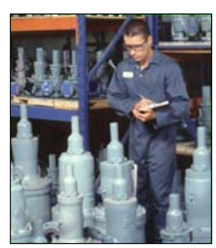
8. Equipment-specific issues

Equipment Inspections and Testing

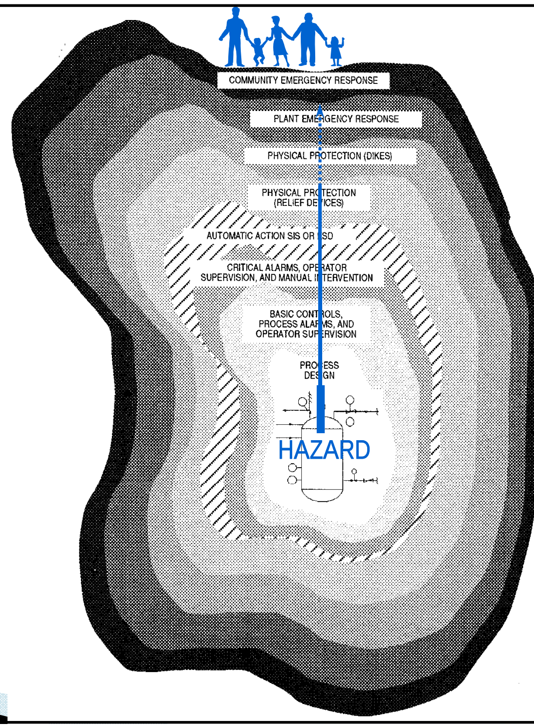
1. Understand the importance of plant equipment PM



"Layers of Protection" between hazards and receptors

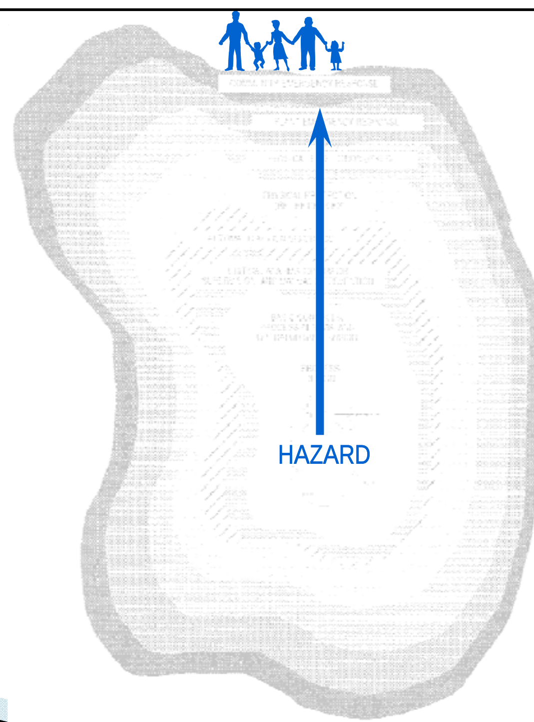
=

"Defense In Depth"



"Layers of Protection" between hazards and receptors

MUST BE MAINTAINED TO BE EFFECTIVE



Process Safety Beacon

http://www.aiche.org/CCPS/Publications/Beacon/index.aspx

Messages for Manufacturing Personnel

Sponsored by CCPS Process Safety Incident Database (PSID)

Mechanical Integrity

May 2009

A compressed air tank failed, blowing the bottom off of the tank (1) and sending fragments flying into a concrete wall, puncturing the wall (2). Investigation following the incident revealed several serious problems with the condition of the tank, including severe corrosion and rust at the bottom of the tank (3), where it failed, and an improper weld repair (4) which had been made to the tank at some time in the past. Although the weld repair did not contribute to this incident, it is a symptom of improper maintenance and inspection, and could have caused a tank failure. Fortunately, nobody was in the area when the tank failed, and there were no injuries.

What can you do?

- Look at vessels, piping, and other equipment as you walk through your plant, and report anything which appears to be corroded or improperly maintained. Include visual inspection of piping, vessels, compressed gas cylinders, and other equipment in routine safety inspections. Follow up and make sure that problems are corrected.
- Understand the equipment inspection and maintenance program in your plant, and understand your role in ensuring that all activities are completed as required.
- When you do mechanical work that requires removal of insulation from equipment, take the opportunity to look at the condition of the equipment and report any corrosion or other problems that you observe. Corrosion under insulation may be hidden, but mechanical work which requires removal of the insulation provides an opportunity to observe problems.
- Make sure that all welds and other repairs follow all required standards, and meet the original design specifications for the equipment.
- Assure that all pressure vessels in your plant, including portable tanks and tanks which are a part of "packaged systems" (for example, compressors, refrigeration units, compressed air systems, etc.), are included in the plant mechanical integrity inspection program and are being inspected by qualified pressure vessel inspectors. This may include inspection for internal corrosion at an appropriate frequency.
- Make sure that compressed air tanks and other portable compressed gas cylinders are stored in dry locations to prevent external rust and corrosion.

Watch out for damaged or corroded equipment!

Maintain contain & control measures

Contain
& Control

Operational Mode: Normal operation

Objective: Maintain normal operation; keep hazards contained and controlled

Examples of *Contain & Control*:
- 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

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"Swiss cheese model"

Contain & control measure failures result in a higher frequency of initiating causes and a proportionally higher risk of a major incident.

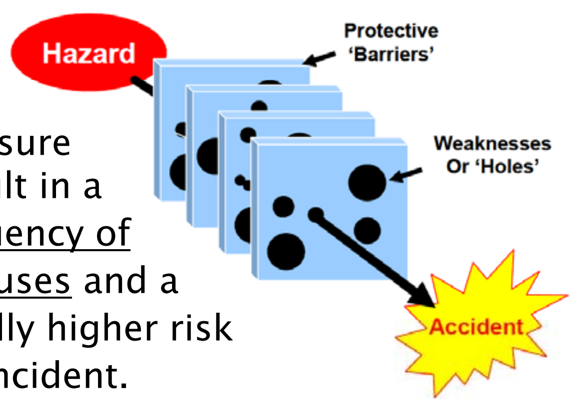

Image credit: CCPS, "Process Safety Leading and Lagging Indicators," New York: American Institute of Chemical Engineers, January 2011, www.aiche.org/ccps.
"Swiss cheese model" originally proposed by James Reason, U. Manchester, 1990.

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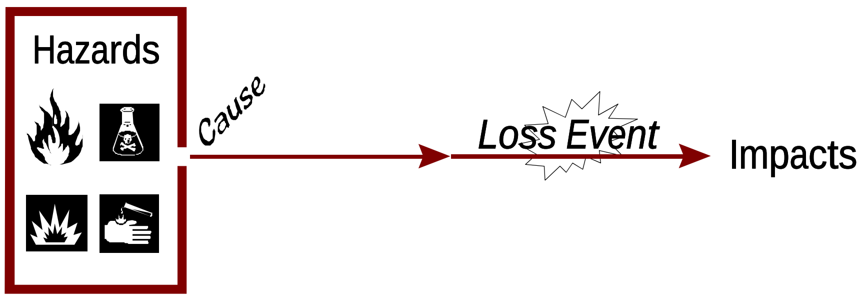
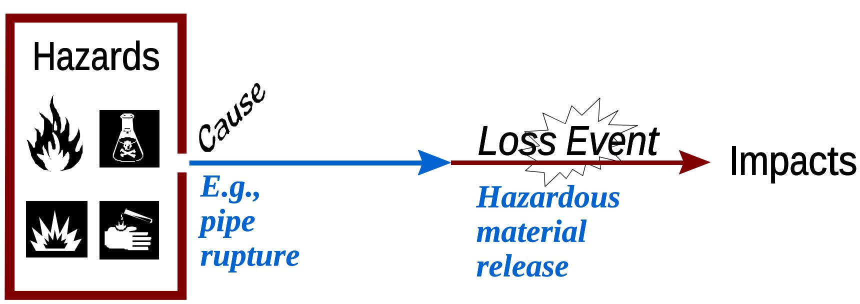
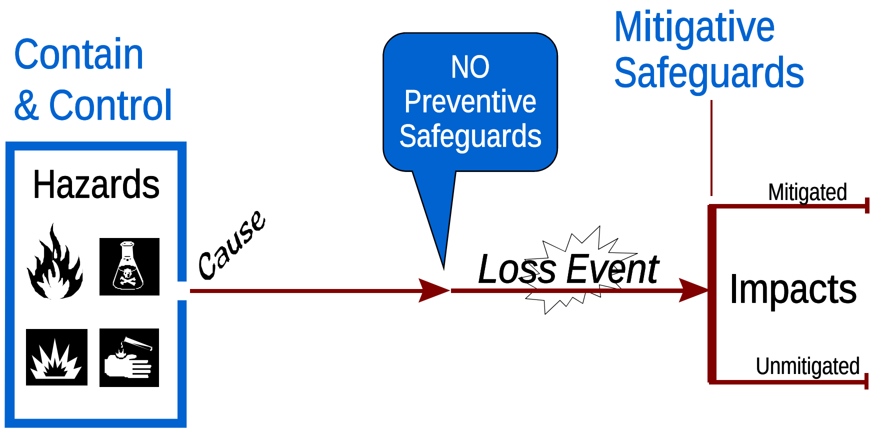
Typical loss-of-containment incident



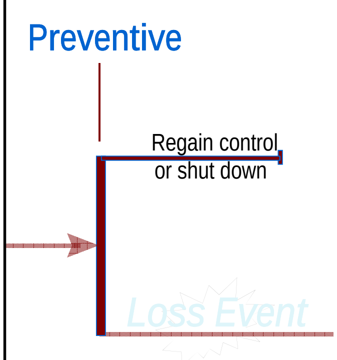
Typical loss-of-containment incident



Vitally important: Integrity of primary containment system!



Maintain preventive safeguards



Operational Mode: Abnormal operation

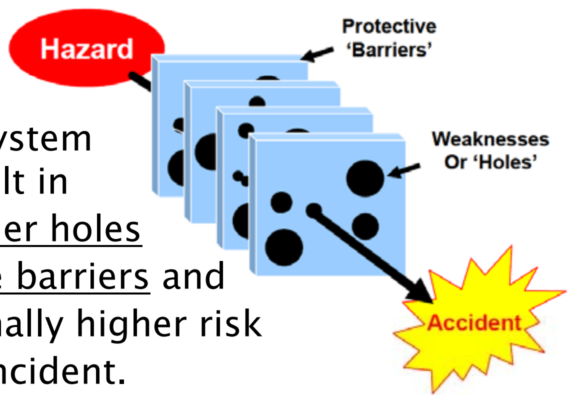
Objective: Regain control or shut down; keep loss events from happening

Examples of Preventive Safeguards:

- Operator response to alarm
- Safety Instrumented System
- Hardwired interlock
- Last-resort dump, quench, blowdown
- Emergency relief system

"Swiss cheese model" revisited

Preventive safeguard system failures result in <u>more or larger holes in protective barriers</u> and *a* proportionally higher risk of a major incident.



Quantification of safeguard reliability

Probability of Failure on Demand (PFD)

$$PFD_{Total} = PFD_{Sensor} + PFD_{LogicSolver} + PFD_{FinalElement}$$

$$PFD_{Sensor} = 1 - \exp(-\lambda \cdot \tau)$$

where λ = *failure frequency*

τ = *failure duration*

Quantification of safeguard reliability

For random failures of repairable components:

failure duration = 1/2 (*inspection interval*)

$$PFD_{Sensor} = 1 - \exp(-\lambda \cdot \tau)$$

where λ = *failure frequency*

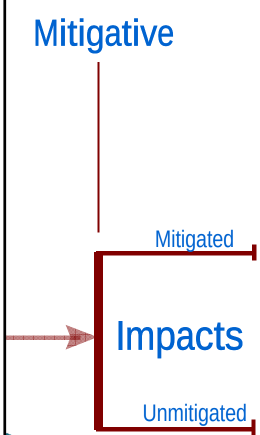
τ = *failure duration*

Quantification of safeguard reliability

For a sensor with a failure frequency λ = 0.1 / yr:

Test interval	Failure duration	Sensor PFD
Monthly	0.04 yr	0.004
Annually	0.5 yr	0.05
Every 5 years	2.5 yr	0.22
Never	½ (plant lifetime)	0.9 to 1.0

Maintain mitigative safeguards



Operational Mode: Emergency

Objective: Minimize impacts

Examples of Mitigative Safeguards:

- Sprinklers, monitors, deluge
- Emergency warning systems
- Emergency response
- Secondary containment; diking/curbing
- Discharge scrubbing, flaring, treatment
- Shielding, building reinforcement, haven
- Escape respirator, PPE

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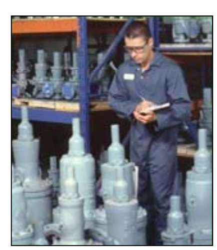
Equipment Inspections and Testing

1. Understand the importance of plant equipment PM
2. Determine what needs to be maintained



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What equipment needs to be maintained?

From a *hazard* perspective:

all equipment that contains or controls MAJOR HAZARDS, or safeguards against loss events if their loss of containment or control does occur.

- Toxic/corrosive/asphyxiating materials
- Flammable/combustible materials
- Reactive/thermally sensitive materials
- Intentional chemical reactions
- Potential chemical incompatibilities
- Physical hazards (high pressure, liquefied gas…)

What equipment needs to be maintained?

From a *consequence* perspective:

all equipment that, if it failed, would result in MAJOR LOSS OR INJURY, or would eliminate a safeguard against the major loss or injury consequence.

- Severe personnel injury or fatality
- Significant environmental damage
- Significant community impact
- (Major property damage or product loss)
- (Major business interruption)

What equipment needs to be maintained?

Typical examples:

- Fixed equipment
  - Process tanks / vessels
  - Process piping + piping system components (valves, check valves…)
  - Relief and vent systems
- Rotating equipment
  - Pumps
  - Compressors

- Instruments & electrical
  - Controls
  - Shutdown systems
  - Power systems
- Emergency equipment
  - Detection, suppression, fire protection systems
  - Diking and drainage
  - etc.

What equipment needs to be maintained?

What about utilities?
(steam, cooling water, nitrogen, compressed air, etc.)

- Include all utilities that, if system components (including piping) fail, could cause a major incident or is used to protect against a major incident.
- Examples:
  - Water used to cool an exothermic chemical reaction
  - Nitrogen used to exclude oxygen from the head space of a tank containing a flammable liquid
  - Compressed air used to close a safety shutdown valve
  - Steam / process heat exchanger

What equipment needs to be maintained?

Aids in determining what must be inspected / tested / maintained:

- Codes and standards
  - E.g., all pressure vessels, all emergency reliefs
  - E.g., combustion safeguards
- Manufacturers' recommendations
- Process hazard analyses
  - Look at all equipment-failure initiating causes
  - Look at all safeguards credited as being in place, including e.g. check valves, sensors / alarms

What equipment needs to be maintained?

Outcome of this step:

"Critical Equipment List"

- Inventory of all equipment and controls to be included in the mechanical integrity program
- Grouped by equipment type
- Listed using unique identifiers e.g. serial numbers and specific process / location
- Computerize in a database (or spreadsheet)

Centrality of critical equipment list to MI

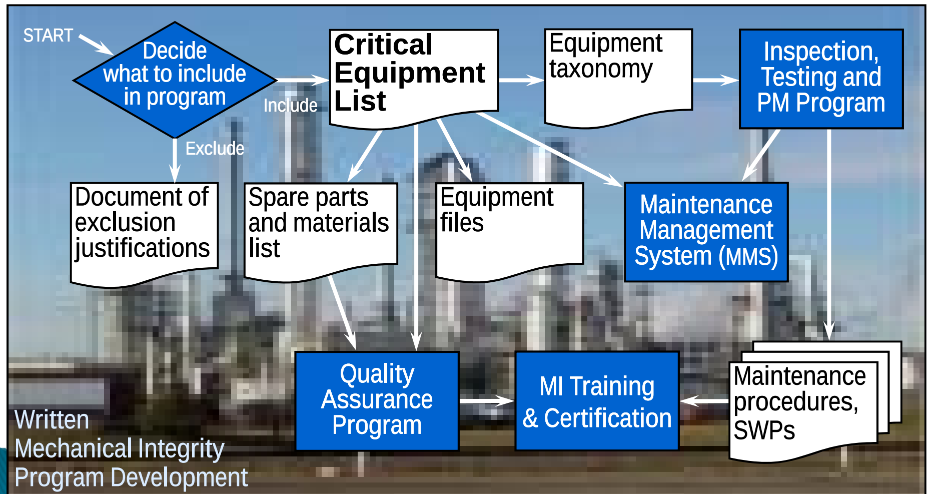
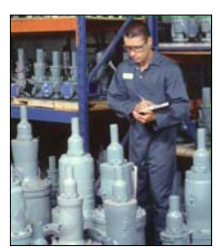


Image Credit: DHS Chemical Sec... ...ness Training

Equipment Inspections and Testing

1. Understand the importance of plant equipment PM
2. Determine what needs to be maintained
3. Put in place a system of how it will be maintained

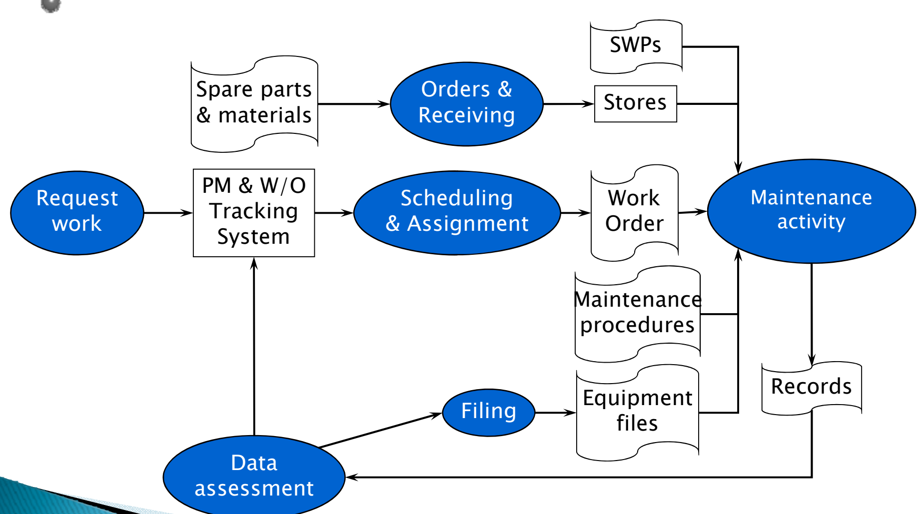


How will it be maintained?

NECESSARY INGREDIENTS

- True management commitment
- Documented program description
  - What is to be maintained
  - Who is to do it (qualifications, responsibilities)
  - How it is to be done (requirements, procedures)
  - How often it is to be done (frequencies, changes)
- Maintenance management system
  - Work order system
  - Activity scheduling
  - Spare parts inventory, quality control

MI program implementation overview



Equipment Inspections and Testing

1. Understand the importance of plant equipment PM
2. Determine what needs to be maintained
3. Put in place a system of how it will be maintained
4. Determine how often tasks need to be performed

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How often must ITMs be performed?

PRINCIPLES:

- ITM frequencies must be pre-established
- Some frequencies are experience-adjusted
- ITMs must be performed according to schedule

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How often must ITMs be performed?

PRINCIPLES:

- ITM frequencies must be pre-established
  - Frequencies will vary by equipment type
  - Initial frequencies come from various sources
    - Authority having jurisdiction
    - Codes and standards
    - Manufacturers' recommendations
    - Calculated values to meet reliability requirements

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How often must ITMs be performed?

PRINCIPLES:

- ITM frequencies must be pre-established
- Some frequencies are experience-adjusted
  - Problems found: Do ITMs more often
  - Good experience: Do ITMs less often if allowed

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How often must ITMs be performed?

PRINCIPLES:

- ITM frequencies must be pre-established
- Some frequencies are experience-adjusted
- ITMs must be performed according to schedule
  - System to schedule and execute ITMs is needed
  - Adequate resources must be available
  - *Management commitment and priority is required!*

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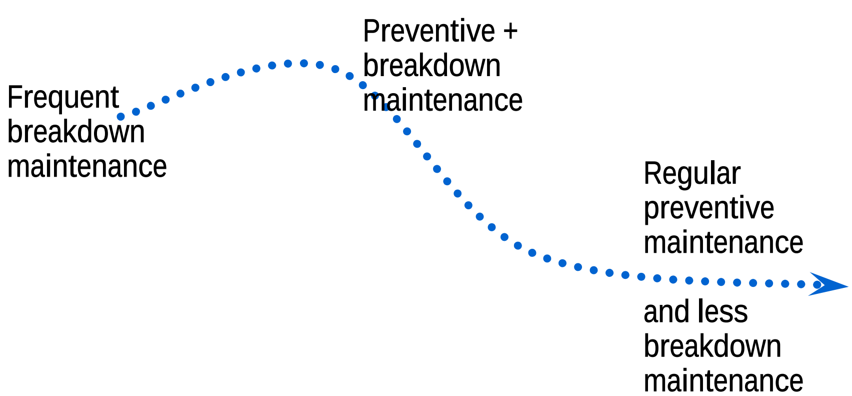
Getting over the hump



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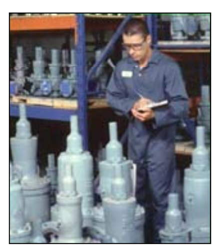
DISCUSSION

What are some advantages in having less breakdown maintenance and more regular preventive maintenance?

Equipment Inspections and Testing

1. Understand the importance of plant equipment PM
2. Determine what needs to be maintained
3. Put in place a system of how it will be maintained
4. Determine how often tasks need to be performed
5. **Equip with maintenance procedures and training**



Maintenance procedures and training

PRINCIPLES:

- Prepare written procedures to maintain equipment
  - Basic craft skills are assumed
  - Unique activities may require one-time procedures
  - Make procedures consistent with RAGAGEPs
  - Use standardized procedure format

Maintenance procedures and training

PRINCIPLES:

- Prepare written procedures to maintain equipment
- Train maintenance personnel to safely perform ITMs
  - Ensure basic craft skills by hiring, testing and training
  - Include safety procedures and safe work practices
  - Include awareness of process hazards and potential consequences
  - Establish necessary qualifications to perform critical and specialized tasks
  - Train and re-train in consistently performing tasks according to the written procedures

Equipment Inspections and Testing

1. Understand the importance of plant equipment PM
2. Determine what needs to be maintained
3. Put in place a system of how it will be maintained
4. Determine how often tasks need to be performed
5. Equip with maintenance procedures and training
6. Document ITMs

Document ITMs

ITM documentation will be equipment-specific.

Examples:

- Storage tank external visual inspection checklist
- Piping system thickness measurement locations (TMLs), test description and measurement results
- Compressor vibration monitoring charts, results

Document ITMs

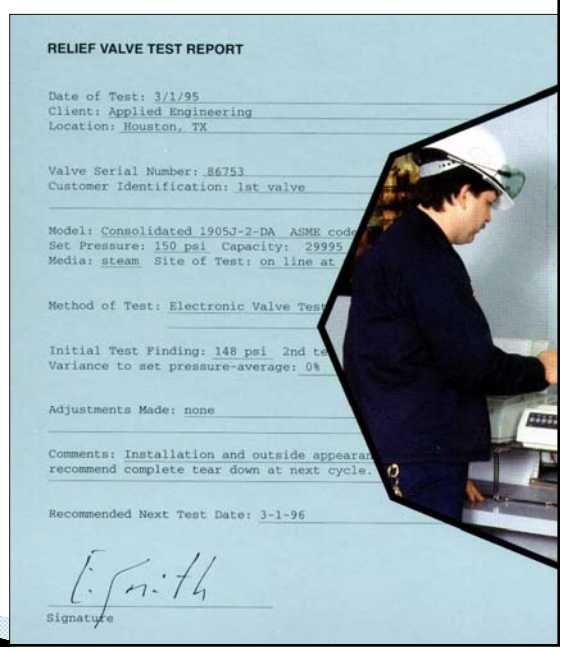
ITM documentation will be equipment-specific.

COMMON ELEMENTS:

- Date of the ITM activity
- Person's name who performed it
- Serial number or other unique equipment identifier
- Description of the ITM activity
- ITM results
  - "As-found" condition
  - "As-left" condition

Additionally:

- Document any incipient problems
- Provide sufficient detail to inform any decision on increasing or decreasing ITM frequency



RELIEF VALVE TEST REPORT

Date of Test: 3/1/95
Client: Applied Engineering
Location: Houston, TX

Valve Serial Number: 86753
Customer Identification: 1st valve

Model: Consolidated 1905J-2-DA ASME cod
Set Pressure: 150 psi Capacity: 29995
Media: steam Site of Test: on line at

Method of Test: Electronic Valve Tes

Initial Test Finding: 148 psi 2nd te
Variance to set pressure-average: 0%

Adjustments Made: none

Comments: Installation and outside appeara
recommend complete tear down at next cycle.

Recommended Next Test Date: 3-1-96

Signature

Equipment Inspections and Testing

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7. Correct identified deficiencies

Working definitions

Deficiency

= departure outside predetermined acceptable limit

Failure

= no longer performing intended function

Working definitions

Deficiency

= departure outside predetermined acceptable limit

Example:

- A restricting orifice is taken out and inspected once every 6 months
- The predetermined acceptable limit for orifice enlargement due to erosion is that the orifice diameter must be no larger than 10 mm
- If the orifice diameter is > 10 mm, a deficiency exists

Working definitions

Deficiency

Failure

Example:

- A spring-operated relief valve can fail to open due to corrosion or inlet blockage
- The same relief valve can fail to hold pressure and open prematurely due to a broken spring

(One component, two different *failure modes*)

Working definitions

Deficiency

= departure outside predetermined acceptable limit

Failure

= no longer performing intended function

Note: All failures are deficiencies, but not all deficiencies are failures

Deficiency corrections

OPTIONS:

- BEST: Correct deficiency before re-starting while system is shut down (e.g., replace corroded pipe)
- OK: Correct deficiency right away while system is in operation, if it can be done safely (e.g., switch over to on-line spare pump, fix bad pump, switch back)
- OK: Wait to correct deficiency until next scheduled shutdown AND put extra control measures in place (e.g., exclude personnel from area; do extra level checks)
- NOT OK: Operate with deficient equipment

Deficiency corrections

ALL TOO COMMON:

- Hire an inspector
- Receive the inspection report
- The report documents equipment deficiencies and the inspector's recommended actions
- The report gets filed without any action taken

*Make sure your MI program 'closes the loop' on **correcting identified deficiencies**!*

CSP

Chemical SAFETY AND SECURITY TRAINING

Equipment Inspections and Testing

1. Understand the importance of plant equipment PM
2. Determine what needs to be maintained
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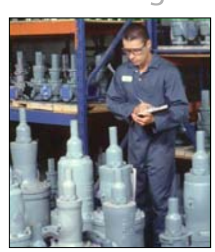
8. Equipment-specific issues



CSP

Chemical SAFETY AND SECURITY TRAINING

CCPS Center for Chemical Process Safety
Process Safety Beacon
http://www.aiche.org/CCPS/Publications/Beacon/index.aspx
Messages for Manufacturing Personnel

CCPS Sponsors, the Beacon Committee, and volunteer Beacon translators wish all Beacon readers a happy, prosperous ***and safe*** New Year 2010.

Corrosion and Erosion

January 2010

Mechanical integrity is one of the biggest challenges for an effective process safety management program. Think about it – in your plant, there may be hundreds of vessels, thousands of feet of pipe, and hundreds of pumps, compressors, instruments, and other equipment. All of it must be kept in good operating condition to ensure safe, reliable, and profitable operation. Management of corrosion and erosion of process piping and equipment must be a major component of any effective mechanical integrity program.

The pictures show some examples of corrosion and erosion problems which were identified in plant inspections. (1) and (2) – external corrosion of pipes in a plant; (3) – close up of erosion damage to the face of a flange; (4) – close up of eroded body and seat of a gate valve; (5) – erosion damage on the body of a valve.

Do you know?

• ***Corrosion*** is the deterioration of metal by electro-chemical reaction with substances or microbes in its environment. These substances can be process materials contained in a vessel, pipe, or other equipment, or materials in the outside environment – for example, water, salt, or contaminants in the atmosphere. The rusting of steel is an example of corrosion.

• ***Erosion Corrosion*** is the degradation of material surface due to mechanical action, often by impinging liquid, abrasion by a slurry, or particles, bubbles, or droplets suspended in fast flowing liquid or gas.

• Corrosion has been responsible for major losses in the process industries. For example, in 2006, part of a major oil field had to be shut down for several months because of multiple oil spills resulting from severe pipeline corrosion.

What can you do?

• Understand mechanical integrity programs in your plant, and your role in ensuring that these programs are effective.

• Observe pipes, vessels, and other equipment when you are working in the plant. Look for stains on the outside of insulated lines and other signs of damaged or corroded equipment. Follow up to make sure that repairs are made.

• If you are taking equipment or piping apart, look for evidence of corrosion damage – for example, corrosion under insulation, internal corrosion in pipes or other equipment, damage to flanges or valves.

• When replacing pipes, valves, or other equipment, be careful to use the same material of construction.

• Understand the corrosion and erosion corrosion properties of the materials in your plant, and what you must do to minimize corrosion problems.

Watch out for corrosion and keep the chemicals inside the equipment!

Equipment-specific issues

- Fixed equipment
- Relief and vent systems
- Rotating equipment
- Instruments & electrical
- Emergency systems

See CCPS 2006 for more details

Fixed equipment

Primary objective:

Detect weaknesses in, or deterioration of, primary containment system integrity

(tanks, vessels, piping, heat exchangers, etc.)

- Internal / external corrosion
- Erosion
- Pitting
- Embrittlement
- Fatigue
- Etc.

Fixed equipment

- Mechanisms often chemical-dependent
  - Hydrogen embrittlement
  - Stress-corrosion cracking
  - Etc.
- Mechanisms also may be process-specific
  - Pressure-dependent
  - Temperature-dependent

Fixed equipment

- Inspections and tests generally require specialized equipment and techniques
  - Thickness measurements
  - Weld inspections
  - etc.
- Trained and certified inspectors
- Codes, standards usually apply

Fixed equipment

Important considerations:

- Corrosion under insulation
- Internal inspections
- Connected utilities
- Deficiency corrections

Fixed equipment

Some types of equipment imperfections to detect:

- **Imperfections arising prior to commissioning and not detected before startup**
  - Equipment inadequately designed for proposed duty
    - Wrong materials specified,
    - Pressure ratings of vessel or pipework inadequate,
    - Temperature ratings inadequate, etc.
  - Defects arising during manufacture
  - Equipment damage or deterioration in transit or during storage
  - Defects arising during construction
    - Welding defects, misalignment, wrong gaskets fitted, etc.

Fixed equipment

(continued)

- **Imperfections due to equipment deterioration in service**
  - Normal wear and tear on pump or agitator seals, valve packing, flange gaskets, etc.
  - Internal and/or external corrosion, including stress corrosion cracking
  - Erosion or thinning
  - Metal fatigue or vibration effects
  - Previous periods of gross maloperation; e.g., furnace operation at above the design tube skin temperature ("creep")
  - Hydrogen embrittlement

Fixed equipment

(continued)

- **Imperfections arising from routine maintenance or minor modifications not carried out correctly**
  - Poor workmanship
  - Wrong materials
  - Etc.

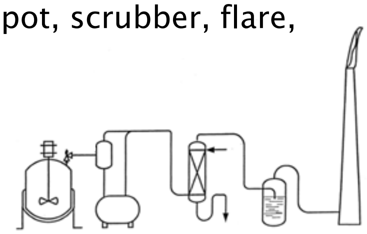
Reference: *Guidelines for Vapor Release Mitigation* (New York: American Institute of Chemical Engineers, 1988)

Relief and vent systems

Primary objectives:

Ensure relief and vent system will work when called upon to relieve excess internal pressure or vacuum; treat relief effluent

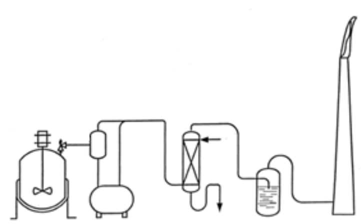
(relief valve, rupture disk, vent valve, header, cyclone separator, knockout pot, scrubber, flare, thermal oxidizer, etc.)



Relief and vent systems

Important considerations:

- Always maintain relief capability while operating
- Detect plugging
- Maintain scrubber/quench fluid levels, potency
- Verify correct reinstallation



Rotating equipment

Primary objectives:

Maintain continuous operation of rotating equipment; ensure availability of standby rotating equipment

(pumps, compressors, etc.)

Rotating equipment

Primary ITM activities:

- Vendor-specified PMs (lube, oil level checks, etc.)
- Routine visual inspections
- Incipient failure detection (vibration analysis, oil analysis, etc.)
- Periodic switchover to standby systems

Instruments & electrical

Primary objectives:

Maintain continuous operation of controls and power systems; ensure availability of standby and emergency shutdown systems

(valves, sensors, controllers, power supplies, etc.)

Instruments & electrical

Primary ITM activities:

- Vendor-specified PMs (valve stroking, etc.)
- Routine inspections and readings (voltages, etc.)
- Scheduled functional tests
  - Safety shutdown systems: Ensure full functional tests, from sensor to final control element
  - May require testing part of the system at a time

Emergency equipment

Primary objectives:

Ensure availability of emergency systems and integrity of passive mitigation systems

(detection, suppression, fire protection systems; diking and drainage; etc.)

Emergency equipment

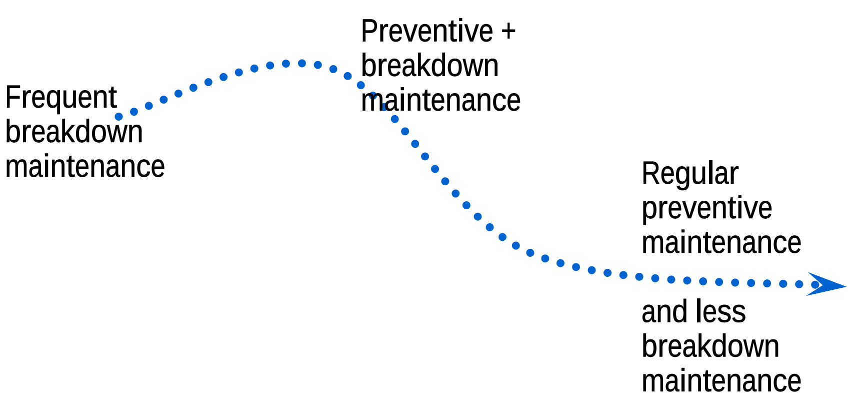
Primary ITM activities:

- Routine inspections (diking integrity, drain valve closed and locked, fire extinguisher checks, etc.)
- <u>Scheduled functional tests</u>
  - Firewater system flow tests
  - Deluge system tests
  - Detectors and suppression system tests
  - Etc.

DISCUSSION

- What are some major challenges to having a proper inspection and testing program?
- How can these be overcome?

Getting over the hump



Equipment Inspections and Testing

1. Understand the importance of plant equipment PM
2. Determine what needs to be maintained
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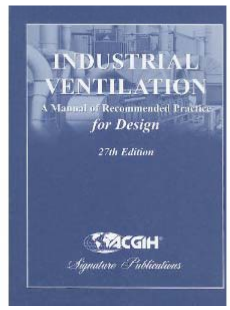
8. Equipment-specific issues

Industrial Ventilation

SAND No. 2012-1603C
Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Industrial Ventilation

- Definitions
- Common Terminology
- Purpose
- Hazard Assessment
- General Ventilation
- Local Exhaust Ventilation
- Ventilation Evaluation
- Troubleshooting
- Exercises



American Conference of Governmental Industrial Hygienists (ACGIH) Ventilation Manual 27th Edition
http://www.acgih.org/store/ProductDetail.cfm?id=1905

Definitions

- <u>Heating, ventilating and air conditioning</u> (HVAC):refers to the distribution system for heating, ventilating, cooling, dehumidifying and cleansing air.
- <u>Replacement/Supply air</u>: refers to replacement air for HVAC and local exhaust ventilation.
- <u>General ventilation</u>: refers to ventilation that controls the air environment by removing and replacing contaminated air before chemical concentrations reach unacceptable levels.
  - <u>Local exhaust ventilation</u> (LEV): refers to systems designed to enclose, or capture and remove contaminated air at the source.

Common Terminology

Q = volume of air in cubic meters

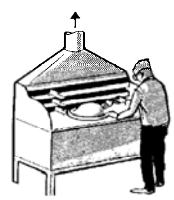
V = velocity of air in meters per second
- Duct velocity–velocity required to transport the contaminant
- Face velocity–velocity on the front of an enclosing hood
- Capture velocity–velocity required to capture contaminant at point of generation

A = cross sectional area of hood opening in square meters

X = distance of ventilation from the source in meters

Purposes of Industrial Ventilation

- Protect workers from health hazards
  - *Dilute, capture, or contain* contaminants
- Protect workers from hot processes
  - *Ovens, foundries*
- Protect the product
  - *Semiconductor*
  - *Electronics*
  - *Pharmaceuticals*



Slot Hood

Canopy Hood

Purposes of Industrial Ventilation

- Emergency ventilation
  - Standalone fans
  - Detectors connected to ventilation or scrubber systems
  - Safe room
    - Positive pressure
- Enclosed vented rooms or cabinets
  - Gas cabinets
- Comply with health and safety regulations

Photo credit: Emergency Responder Products

Photo credit: Advanced Specialty Gas Equipment

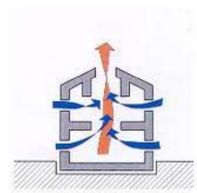
Hazard Assessment

- What are the airborne contaminants?
  - Particles
  - Solvent vapors
  - Acid mists
  - Metal fumes
- How do to the workers interact source contaminant?
- Are workers exposed to air contaminants in concentrations over an exposure limit?
  *Requires air monitoring of the task
- Dilution or local exhaust ventilation?

Picture Credit : International Labor Organization

General Ventilation

- Natural Ventilation:
  - Useful for hot processes
  - Chimney effect
  - Windows and doors kept open



- Example: a warehouse opens the create natural ventilation

  Q = 0.2 AV

  A = square meters (area of open doors)

  V = wind speed in kilometers/hour

  Q = estimates the flow rate through the building (m/s)

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Chemical SAFETY AND SECURITY TRAINING

General Ventilation

Dilution Ventilation

- Heat control
- Dilution of odors, flammables
- Not for control of toxics

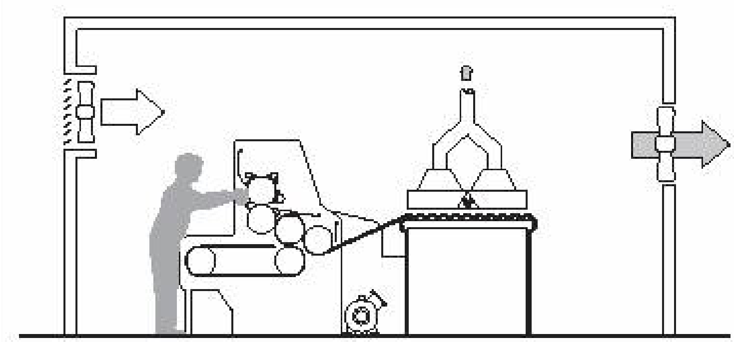
Principles

- Contaminant emissions must be widely dispersed
- Exhaust openings must be near contaminant source
- The worker must not be downstream of contaminant
- Air flow over worker should not exceed 3.5 meters/sec

CSP

Chemical SAFETY AND SECURITY TRAINING

General Ventilation

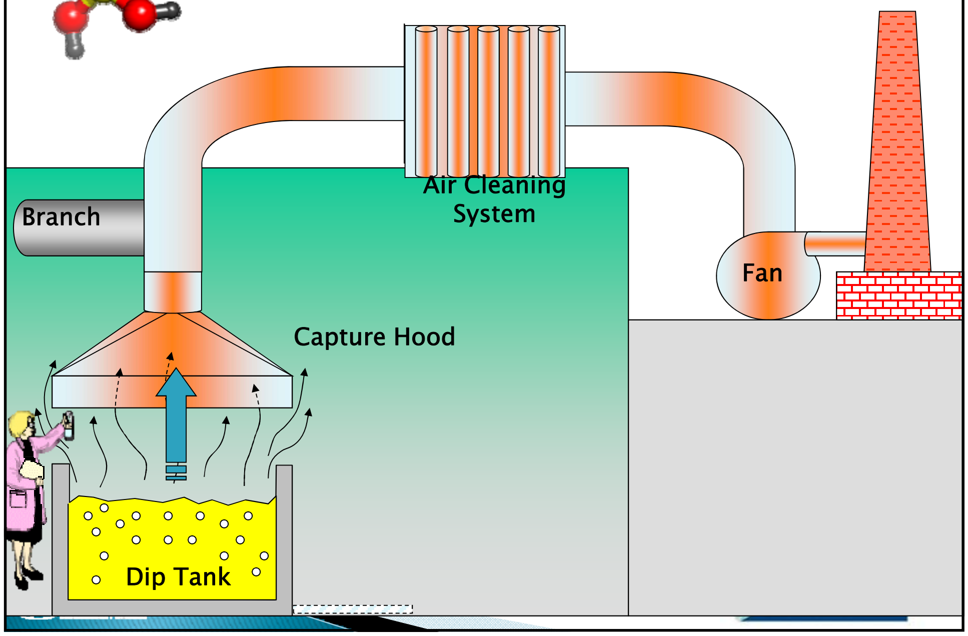


General ventilation for cleaning a printing press

Local Exhaust Ventilation (LEV)

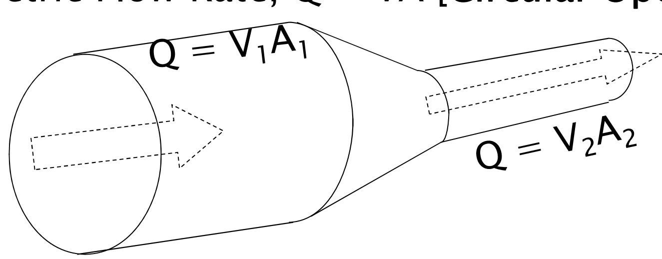
- Use when contaminant concentration cannot be controlled by dilution ventilation or other controls
- Select the type of LEV from hazard assessment
  - Which type is best to capture the contaminant?
    - Enclosed or capture hood?
    - Consider worker's needs
  - What duct transport velocity is required to carry the contaminant? Heavy particles?
  - What face or capture velocity is required?
- Select duct material for the contaminant
- Ensure enough replacement air/adequate fan size

Local Exhaust Ventilation



Local Exhaust Ventilation

Volumetric Flow Rate, Q = VA **[Circular Opening]**

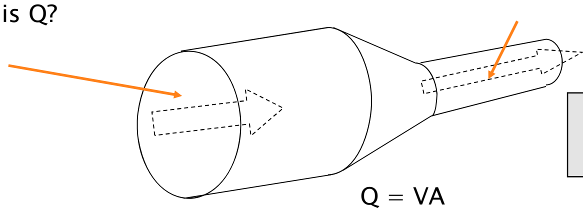


Q = Volumetric flow rate, in cubic meters/second
V = Average velocity, in meters/second
A = Cross-sectional area in square meters

Local Exhaust Ventilation

Duct diameter = 1 meter
V = 600 meters/second
What is Q?

Duct diameter = 0.5 meter
What is the duct velocity (V)?



For circular ducts
$A = \pi d^2/4$

$Q = VA$

$Q = (600\ m/s)(\pi[1m]^2/4)$

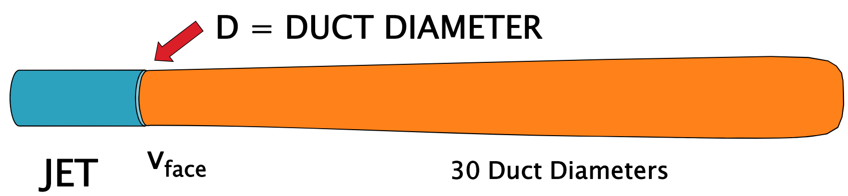
$Q = 471$ meters^3/second

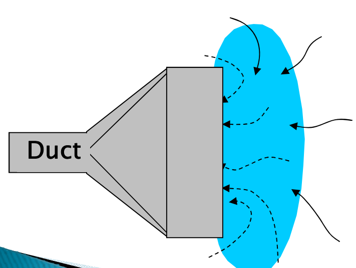
$Q = VA$

471 meters^3/s $= V (\pi[0.5m]^2/4)$

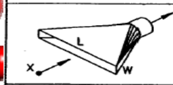
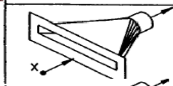
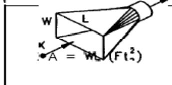
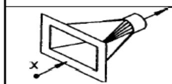
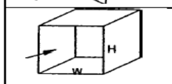
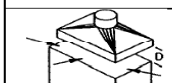
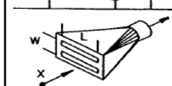
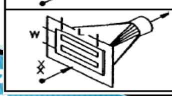
V = 2400 meters/second

Local Exhaust Ventilation





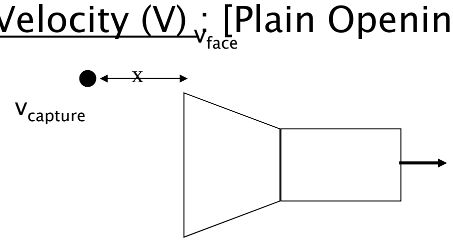
Capture of contaminant is only effective within <u>one (1) duct diameter</u>

HOOD TYPE	DESCRIPTION	ASPECT RATIO, W/L	AIR FLOW
	SLOT	0.2 OR LESS	$Q = 3.7\ LVX$
	FLANGED SLOT	0.2 OR LESS	$Q = 2.6\ LVX$
	PLAIN OPENING	0.2 OR GREATER AND ROUND	$Q = V(10X^2 + A)$
	FLANGED OPENING	0.2 OR GREATER AND ROUND	$Q = 0.75V(10X^2 + A)$
	BOOTH	TO SUIT WORK	$Q = VA = VWH$
	CANOPY	TO SUIT WORK	$Q = 1.4\ PVD$ SEE FIG. VS-99-03 P = PERIMETER D = HEIGHT ABOVE WORK
	PLAIN MULTIPLE SLOT OPENING 2 OR MORE SLOTS	0.2 OR GREATER	$Q = V(10X^2 + A)$
	FLANGED MULTIPLE SLOT OPENING 2 OR MORE SLOTS	0.2 OR GREATER	$Q = 0.75V(10X^2 + A)$

ACGIH Ventilation Manual

Local Exhaust Ventilation

Capture Velocity (V) : [Plain Opening]



$Q = V\ (10x^2 + A)$
X = distance of source from hood face

Recommended Capture Velocities

CONDITION	EXAMPLES	CAPTURE VELOCITY Range in meters/second
No velocity, Quiet air	Evaporation from tanks, degreasers	0.25 – 0.5
Low velocity, moderately still air	Spray booths, container filling, welding, plating	0.5 – 1.0
Active generation into rapid air motion	Spray painting (shallow booths), crushers	1.0 – 2.5
High initial velocity into very rapid air motion	Grinding, abrasive blasting, tumbling	2.5 – 10.1

ACGIH Ventilation Manual

Recommended Duct Velocities

CONTAMINANT	EXAMPLES	DUCT VELOCITY Meters/second
Vapors, gases, smoke	Vapors, gases, smoke	5.0 – 10.1
Fumes	Welding	10.1 – 12.7
Very fine dust	Cotton lint	12.7 – 15.2
Dry dusts & powders	Cotton dust	15.2 – 20.3
Industrial dust	Grinding dust, limestone dust	17.8 – 20.3
Heavy dust	Sawdust, metal turnings	20.3 – 22.9
Heavy/moist dusts	Lead dusts, cement dust	> 22.9

ACGIH Ventilation Manual

Local Exhaust Ventilation

- Canopy hood:
  - Best for controlling hot processes
  - Not good for capturing dusts, or vapors
  - Not good where cross-drafts exist
  - Worker must not put head under canopy

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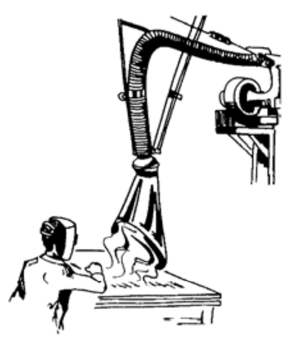
Chemical SAFETY AND SECURITY TRAINING

Local Exhaust Ventilation

- "Elephant trunk":
  - Good for welding fumes, small process tasks, machining, disconnecting process lines
  - Place close to contaminant
  - Ensure adequate capture velocity at distance from contaminant
  - *Flanged* opening captures contaminant better

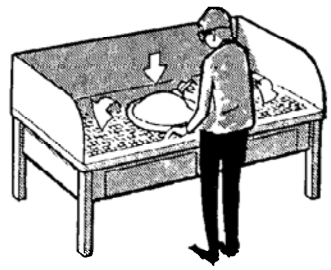


CSP

Chemical SAFETY AND SECURITY TRAINING

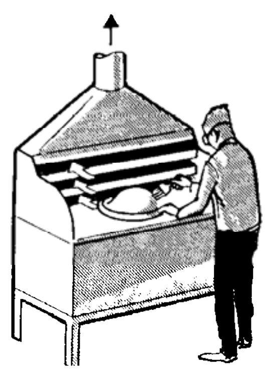
Local Exhaust Ventilation

- Downdraft hood:
  - Vapors pulled down through grill
  - Capture velocity depends on source distance from grill
  - Not for hot operations



Local Exhaust Ventilation

- Slot ventilation:
  - Best for liquid open surface tanks
    - Acid baths
    - Plating tanks
  - Pulls air across the tank away from worker
  - Side enclosures prevent cross drafts
  - Push-Pull design is optional (push jet)



Local Exhaust Ventilation

- Fume hood:
  - Laboratory use
  - Best for small amounts of chemicals
  - Sash must be kept at set level
  - NO storage of equipment in the hood!

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Local Exhaust Ventilation

- Enclosures:
  - Example:
    - Paint booths
  - Control of exposure to liquid aerosols and vapors
  - Flammability hazard
  - Must have scheduled filter changeout
  - Operator must be upstream

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Chemical SAFETY AND SECURITY TRAINING

Local Exhaust Ventilation

- Other vented enclosures
  - Glove boxes
  - Furnaces/ovens
  - Abrasive blasting

Photo credit: Borel Furnaces and Ovens

Photo credit: U. S. Department of Labor. OSHA

Local Exhaust Ventilation

Exhaust Systems:

- Do not place exhaust stack near air intakes
  - Re-entrains contaminants into the building
- Do not use rain caps
- Stack height depends on:
  - Contaminant temperature
  - Building height
  - Atmospheric conditions
  - Discharge velocity
  - Ideal discharge velocity is 15 meters per second

Ventilation System Evaluation

- **Evaluate capture velocity**
  - **Quantitatively-anemometers, velometers**
  - **Qualitatively-smoke tubes,**
    - **Visualizes air movement**
    - **Use water vapor for clean rooms**

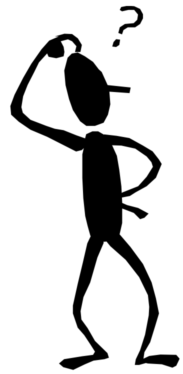
Photo Credit: All Products Inc.

Ventilation System Evaluation

- Air velocity measurements
  - Measure air velocities (meter/sec) at a number of points
  - Average the results and determine volumetric flow rate: $Q = VA$
  - All instruments must be calibrated periodically
  - Types:
    - Swinging vane velometer
    - Hot-wire anemometer

Troubleshooting

- Wrong hood for process
  - Example: canopy hood for toxics
- Insufficient capture velocity
- Insufficient duct velocity
  - ~14 meters/second for vapors
  - ~18 meters/second for dust
- Too much air flow = turbulence
- Traffic or competing air currents
- Insufficient make up air
  - Negative pressure
  - Can't open doors



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Exercise

- What is the preferred ventilation system for the following situation?
  - Dilute non-toxic odors in the warehouse

A) General ventilation
B) Local exhaust ventilation

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Exercise

- What is the preferred ventilation system for the following situation?
  - Acid processing bath with open surface area

A) Lab fume hood
B) Slot ventilation
C) Elephant trunk
D) Canopy hood
E) Paint booth

Exercise

- What is the preferred ventilation system for the following situation?
  - Welding table

A) Lab fume hood
B) Slot ventilation
C) Elephant trunk
D) Canopy hood
E) Paint booth

Exercise

- What is the preferred ventilation system for the following situation?
  - Chemical analysis of small samples for quality control

A) Lab fume hood
B) Slot ventilation
C) Elephant trunk
D) Canopy hood
E) Paint booth

Exercise

- What is the preferred ventilation system for the following situation?
  - Spray painting a large piece of equipment

A) Lab fume hood
B) Slot ventilation
C) Elephant trunk
D) Canopy hood
E) Paint booth

US Standards & Guidelines

ACGIH
American Conference of Governmental Industrial Hygienists
Industrial Ventilation, A Manual of Recommended Practice

AIHA
American Industrial Hygiene Association
Standard Z9.2, Fundamentals Governing the Design and Operation of Local Exhaust Ventilation Systems

ASHRAE
American Society of Heating, Refrigeration and Air Conditioning Engineers
Standard 62.1-2010*, *Ventilation for Acceptable Indoor Air Quality

OSHA
Occupational Safety and Health Administration
Ventilation, 29 Code of Federal Regulations 1910.94
http://osha.gov/

Hazard and Risk Analysis

SAND No. 2011-0991 C
Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Key acronyms

PHA = process hazard analysis

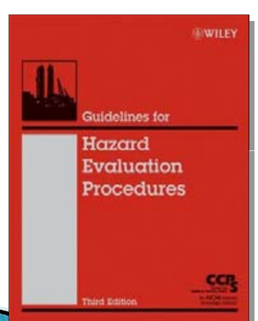
HAZOP = hazard and operability [study]

FMEA = failure modes & effects analysis

LOPA = layer of protection analysis

Hazard and risk analysis resources

CCPS 2008a. Center for Chemical Process Safety, *Guidelines for Hazard Evaluation Procedures,* Third Edition, NY: American Institute of Chemical Engineers.

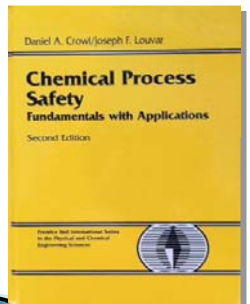


Chapter 4 • Non-Scenario-Based Hazard Evaluation Procedures
- 4.1 Preliminary Hazard Analysis
- 4.2 Safety Review
- 4.3 Relative Ranking
- 4.4 Checklist Analysis

Chapter 5 • Scenario-Based Hazard Evaluation Procedures
- 5.1 What-If Analysis
- 5.2 What-If/Checklist Analysis
- 5.3 Hazard and Operability Studies
- 5.4 Failure Modes and Effects Analysis
- 5.5 Fault Tree Analysis
- 5.6 Event Tree Analysis
- 5.7 Cause-Consequence Analysis and Bow-Tie Analysis
- 5.8 Other Techniques

Hazard and risk analysis resources

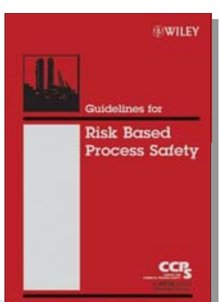
D.A. Crowl and J.F. Louvar 2001. *Chemical Process Safety: Fundamentals with Applications,* 2nd Ed., Upper Saddle River, NJ: Prentice Hall.



Chapter 10 • Hazards Identification
Chapter 11 • Risk Assessment

Hazard and risk analysis resources

CCPS 2007a. Center for Chemical Process Safety, *Guidelines for Risk Based Process Safety*, NY: American Institute of Chemical Engineers.



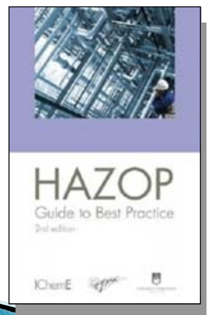
Chapter 9 • Hazard Identification and Risk Analy

9.1 Element Overview
9.2 Key Principles and Essential Features
9.3 Possible Work Activities
9.4 Examples of Ways to Improve Effectiveness
9.5 Element Metrics
9.6 Management Review

Hazard and risk analysis resources

B. Tyler, F. Crawley and M. Preston 2008.

HAZOP: Guide to Best Practice, 2nd Edition, Institution of Chemical Engineers, Rugby, UK.



Hazard and Risk Analysis

- Basic risk concepts
- Experience-based vs predictive approaches
- Qualitative methods (What-If, HAZOP, FMEA)
- Order-of-magnitude and quantitative methods
- Analysis of procedure-based operations
- Team meeting logistics
- Documenting hazard and risk analyses
- Implementing findings and recommendations

Hazard and Risk Analysis

- Basic risk concepts

Hazard versus Risk

Fundamental definitions:

HAZARD
Presence of a material or condition that has the potential for causing loss or harm

RISK
A combination of the severity of consequences and the likelihood of occurrence of undesired outcomes

Source: R.W. Johnson, "Risk Management by Risk Magnitudes," *Chemical Health & Safety* 5(5), 1998

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RISK

Constituents of risk:

- Likelihood and
  - Severity

of Loss Events

$$Risk = f(Likelihood, Severity)$$

RISK

General form of risk equation:

$$Risk = Likelihood \cdot Severity^{n}$$

Most common form:

$$Risk = Likelihood \cdot Severity$$

RISK

Example units of measure:

$$Risk = Likelihood \cdot Severity$$

$$\frac{\text{injuries}}{\text{year}} = \frac{\text{loss events}}{\text{year}} \times \frac{\text{injuries}}{\text{loss event}}$$

$$\frac{\text{\$ loss}}{\text{year}} = \frac{\text{loss events}}{\text{year}} \times \frac{\text{\$ loss}}{\text{loss event}}$$

Costs versus *Risks*

Another way of understanding risk is to compare *risks* with *costs*:

Costs	Risks
Near certain; expected	Uncertain; unexpected; probabilistic
Cost estimates are usually available	Risk estimates are usually not available
Higher-precision estimates	Lower-precision estimates, if available
Predictable benefits if cost incurred	Negative consequences if outcome realized
Incurred every year over life of project	Liability incurred only if outcome realized

Source: R.W. Johnson, "Risk Management by Risk Magnitudes," *Chemical Health & Safety* 5(5), 1998

Costs + Risks

- *Costs* are certain, or expected, liabilities
  e.g., 30,000 km/year, 10 km/L, $1.00/L = $3,000/year
- *Risks* are uncertain liabilities
  e.g., $10,000 collision, 1/20 year = $500/year
- Costs + Risks = Total Liabilities
  $3,000/year + $500/year = $3,500/year

What Is a "Process Hazard Analysis"?

A *Process Hazard Analysis* (PHA) is a structured team review of an operation involving hazardous materials/energies, to identify previously unrecognized hazards, identify opportunities to make the operation inherently safer, identify loss event scenarios, evaluate the scenario risks to identify where existing safeguards may not be adequate, and document team findings and recommendations.

What Is a "Process Hazard Analysis"?

A *Process Hazard Analysis* (PHA) is a structured team review of an operation involving hazardous materials/energies, to:

- identify previously unrecognized hazards,
- identify opportunities to make the operation inherently safer,
- identify loss event scenarios,
- evaluate the scenario risks to identify where existing safeguards may not be adequate, and
- document team findings and recommendations.

Already addressed

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What Is a "Process Hazard Analysis"?

Process Hazard Analysis (PHA) is a structured team review of an operation involving hazardous materials/energies, to:

- identify previously unrecognized hazards,
- identify opportunities to make the operation inherently safer,
- identify loss event scenarios,
- evaluate the scenario risks to identify where existing safeguards may not be adequate, and
- document team findings and recommendations

Focus of this module

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Hazard and Risk Analysis

- Basic risk concepts
- Experience-based vs predictive approaches

Experience-based approaches

- Some PHA methods determine the adequacy of safeguards without assessing scenario risks
- This is done on the basis of collective past experience
- Compare process with recognized and generally accepted good engineering practices (RAGAGEPs)

Experience-based approaches

- Effective way to take advantage of past experience
- Concentrates on protecting against events expected during lifetime of facility
- Low-probability, high-consequence events not analyzed
- Not good for complex or unique processes

Experience-based approaches

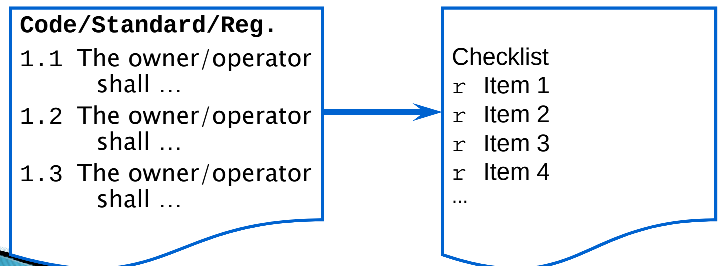
Example experience-based approaches:

- Safety Review
- Checklist Analysis

Experience-based approaches

Example experience-based approaches:

- Safety Review
- Checklist Analysis



Experience-based approaches

Example experience-based approaches:

- Safety Review
- Checklist Analysis
  - Code / standard / regulatory requirements checklist
  - See Crowl and Louvar 2001, pages 433-436, for a checklist of process safety topics

Predictive studies

- Supplement adherence to good practice
- Qualitative to quantitative
- Able to study adequacy of safeguards against low probability / high severity scenarios
- All predictive studies are scenario-based approaches

Scenario – definition

Scenario:

An unplanned event or incident sequence that results in a loss event and its associated impacts, including the success or failure of safeguards involved in the incident sequence.

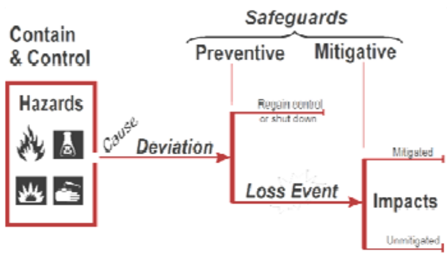
- CCPS 2008a

Scenario necessary ingredients:

- Initiating cause

  AND

- Loss event or safe outcome



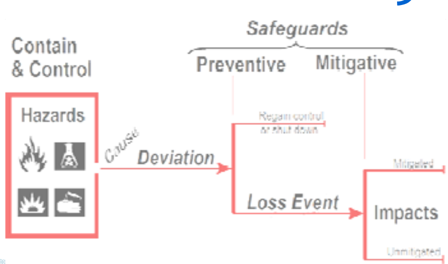
Scenario necessary ingredients:

- Initiating cause

  AND

- Loss event or safe outcome

"Cause - consequence pair"



Example of a simple scenario:

While unloading a tankcar into a caustic storage tank, the tank high level alarm sounded due to the person unloading not paying close attention to the operation.

The operator noticed and responded to the alarm right away, stopping the unloading operation. Normal production was then resumed.

- What is the *initiating cause*?
- What is the *consequence?*

Example of a more complex scenario:

A reactor feed line ruptures and spills a flammable feed liquid into a diked area, where it ignites. A fire detection system initiates an automatic fire suppression system, putting the fire out.

The loss of flow to the reactor causes the temperature and pressure in the reactor to rise. The operator does not notice the temperature increase until the relief valve discharges to the relief header and stack. At that point, the emergency shutdown system is activated and the plant is brought to a safe state.

Predictive studies

Objective of scenario-based approaches:

- Identify and analyze all failure scenarios
  - Not generally possible just by inspection
  - Systematic approach needed
  - In reality, many scenarios eliminated by common sense and experience
    - Negligible likelihood (WARNING: Truly negligible?)
    - Unimportant consequence

Predictive studies

Some scenario-based approaches:

- What-If Analysis
- What-If / Checklist Analysis
- Hazard and Operability (HAZOP) Study
- Failure Modes and Effects Analysis (FMEA)
- Fault Tree Analysis (FTA)
- Event Tree Analysis (ETA)

Hazard and Risk Analysis

- Basic risk concepts
- Experience-based vs predictive approaches
- Qualitative methods (What-If, HAZOP, FMEA)

What-If Analysis

What If...?

What-If Analysis

Concept: Conduct thorough, systematic examination by asking questions that begin with "What if..."

- Usually conducted by a relatively small team (3-5 persons)
- Process divided up into "segments" (e.g., unit operations)
- Review from input to output of process
- Question formulation left up to the team members

What-If Analysis

- Question usually suggests an initiating cause.

  "What if the raw material is in the wrong concentration?"

- If so, postulated response develops a scenario.

  "If the concentration of oxidant was doubled, the reaction could not be controlled and a rapid exotherm would result..."

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What-If Analysis

Answering each "What if …" question:

1 Describe potential consequences and impacts
2 If a consequence of concern, assess cause likelihood
3 Identify and evaluate intervening safeguards
4 Determine adequacy of safeguards
5 Develop findings and recommendations (as required)
6 Raise new questions

Move to next segment when no more questions are raised.

Adequacy of safeguards

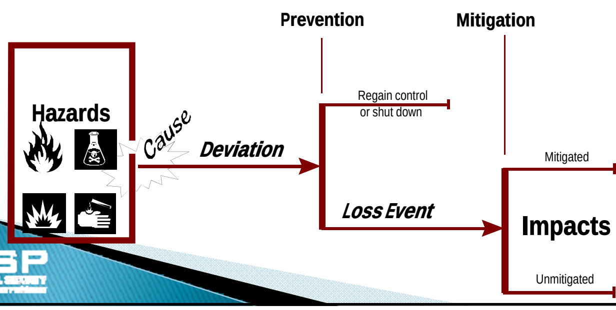
- Determining the adequacy of safeguards is done on a scenario-by-scenario basis
- *Scenario risk* is a function of:
  - Initiating cause frequency
  - Loss event impact
  - Safeguards effectiveness
- If the *scenario risk* is found to be too high, safeguards are considered inadequate
  - Qualitative judgment
  - Risk matrix
  - Risk magnitude

See SVA Overview for matrix and magnitude approaches.

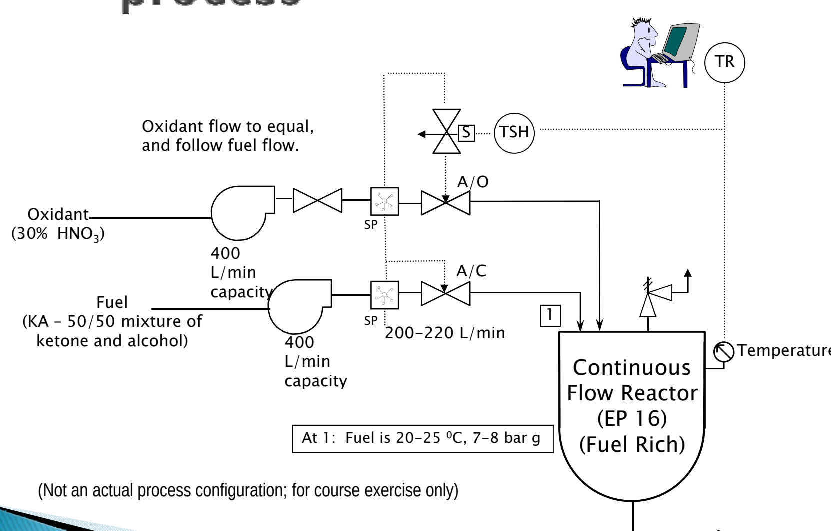
Safeguards

Evaluating the effectiveness of safeguards must take into account:

- *Fast* enough?
- *Independent*?
- *Effective* for this scenario?
- *Reliable* enough?



Example: Continuous process

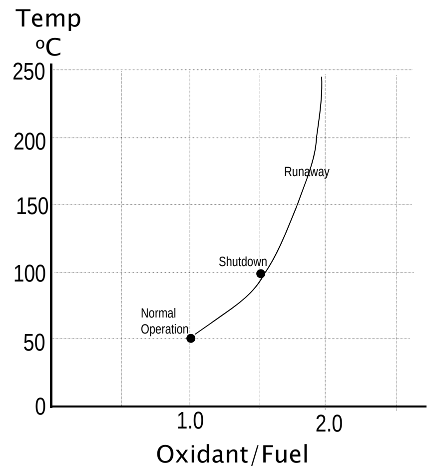


(Not an actual process configuration; for course exercise only)

Example: Continuous process (continued)

EP 16 produces adipic acid by an exothermic (heat-releasing) reaction of an oxidant (30% nitric acid) and a fuel (mixture of ketone and alcohol). An oxidant-to-fuel ratio greater that 2.0 in the reactor causes the reaction to run away (rapid temperature and pressure build-up). The high temperature shutdown system is intended to protect the reactor by stopping the oxidant flow if the reactor temperature reaches 100 °C.

NOTE: RELIEF VALVE CANNOT CONTROL RUNAWAY REACTION.



PROCESS SEGMENT:	SCOPE:	What-If Analysis
REVIEW DATE:	INTENT:	

What If ...	Consequences	Safeguards	Finding/Recommendation Comments

PROCESS SEGMENT:	SCOPE:	What-If Analysis
REVIEW DATE:	INTENT:	

What If …	Consequences	Safeguards	Finding/Recommendation Comments

PROCESS SEGMENT:	SCOPE:	What-If Analysis
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What If …	Consequences	Safeguards	Finding/Recommendation Comments

Hazard and Operability Study

HAZOP

HAZOP Study

- Developed within process industries
- Team-based approach
- Needs well-defined system parameters
- Used as hazard and/or operability study method
  - Safety issues dominate for existing process
  - Operability issues prevail for new designs
  - Many issues relate to both safety and operability

HAZOP Study

Premise:

- No incidents when system operates as intended ("normal operation")
- Failure scenarios occur when system deviates from intended operation ("abnormal situation")

HAZOP sequence

- Establish review scope
- Identify study "nodes"
- Establish Node 1 design/operation intent
- Identify Deviation 1 from Node 1 intent
- Identify causes, loss events, safeguards
- Decide whether action is warranted
- Repeat for every node and deviation

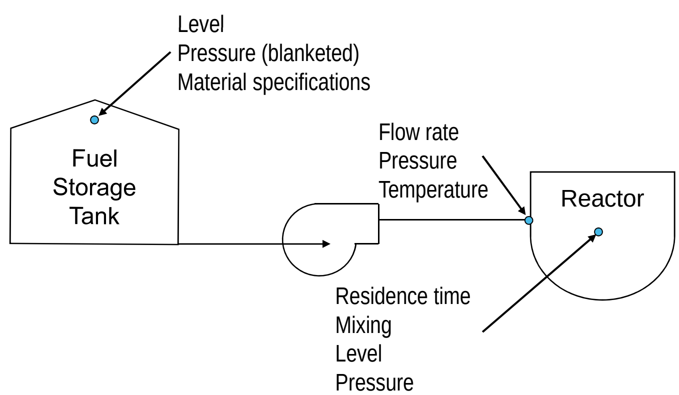
Study nodes

A node is a specific point in a process or procedure where deviations are studied.

Typical study nodes:

- Process vessel
- Transfer line
  - Strictly: Wherever a process parameter changes
  - At end of line (vessel interface)
  - Line may include pump, valves, filter, etc.
- Procedural step

Study nodes



Design/operational

INTENT

The intent describes the design / operational parameters defining normal operation.

- Functions
- Limits
- Compositions
- Procedural steps

It answers one of these questions:

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

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

Design/operational intent

A complete design/operational intent includes:

- Equipment used
- All functions or operations intended to be achieved in this part of the process
- All intended locations/destinations
- Quantitative limits for all pertinent process parameters
- Intended stream composition limits

Design/operational intent

Example:

The intent of a reaction vessel might be to:

Contain and control the complete reaction of 1000 kg of 30% A and 750 kg of 98% B in EP-7 by providing mixing and external cooling to maintain 470-500 °C for 2 hours, while venting off-gases to maintain < 1 bar g pressure.

Typical design intents

Storage tank

- Contain between 40 and 300 cubic meters of 50% caustic at atmospheric pressure and ambient temperature.

Transfer line

- Transfer 40 to 45 L/min of [pure] acetone from drum to mixer at room temperature.

Rotary kiln incinerator design intent

Contain and control the thermal incineration of incoming wastes (up to 4.76 t/h, 33.32 to 66.64 GJ/h heat load) to allow achievement of at least a 99.9% destruction and removal efficiency of organics in the incineration process by providing temperature (1000 to 1400 ^{o}C upstream of the secondary injection air point), residence time (at least 2 s for gases), and oxygen (9 to 13%, measured at the downstream end of the combustion zone) at a slight negative pressure (-100 Pa gage upstream of the secondary air injection point). Additional controlled variables are kiln rotation speed (0.05 to 0.5 rpm) and up to 15% Cl_2, up to 3% S, up to 50% H_2O, and up to 30% inerts entering the kiln.

HAZOP Guide Words

Guide Words are applied to the design intent to systematically identify deviations from normal operation.

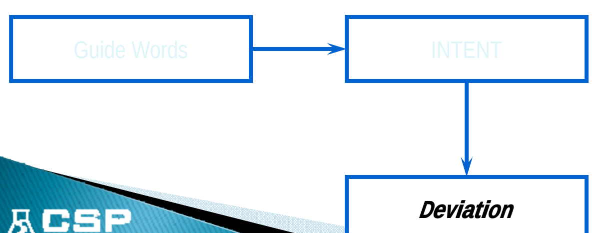
- NONE
- MORE OF
- LESS OF
- PART OF
- AS WELL AS
- REVERSE
- OTHER THAN

HAZOP Guide Words

Guide Word	Meaning
NONE	Negation of intent
MORE OF	Exceed intended upper limit
LESS OF	Drop below intended lower limit
PART OF	Achieve part of intent
AS WELL AS	Something in addition to intent
REVERSE	Logical opposite of intent occurs
OTHER THAN	Something different from intent

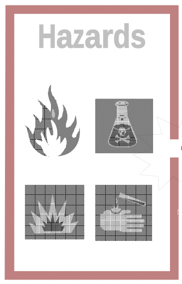
Deviations from Intent

- Do not begin developing deviations until intent is fully described, documented and agreed upon
- List of deviations can be started as soon as intent is established



Deviations

A *deviation* is an abnormal situation, outside defined design or operational parameters.



Cause

Deviation

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

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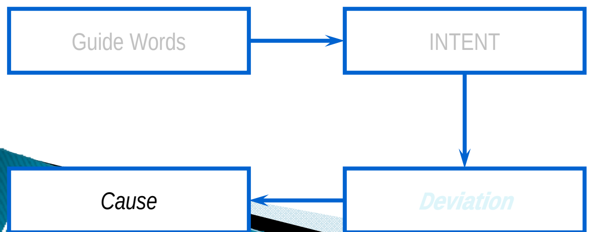
HAZOP Deviations Guide

Design Intent	NO / NONE	MORE OF	LESS OF
Apply each guide word to intent. A complete design intent for each line/vessel/node includes: • All functions and locations • Controlled variables' SOCs • Expected compositions • Equipment used E.g., the intent of a reaction step might be to "Contain and control the complete reaction of 1000 kg of 30% A and 750 kg of 98% B in EP-7 by providing mixing and external cooling to maintain 470-500 ºC for 2 hours, while venting off-gases to maintain < 1 bar g"	Containment lost Procedure step skipped No [function] No transfer No agitation No reaction	Procedure started too late Procedure done too long Too much [function] Too much transferred Too much agitation High [controlled variable] High reaction rate High flow rate High pressure High temperature	Procedure started too soon Procedure stopped too soon Not enough [function] Not enough transferred Not enough agitation Low [controlled variable] Low reaction rate Low flow rate Low pressure Low temperature
PART OF	AS WELL AS	REVERSE	OTHER THAN
Part of procedure step skipped Part of [function] achieved Part of [composition] Component missing Phase missing Catalyst deactivated	Extra step performed Extra [function] Transfer from more than one source Transfer to more than one destination Extra [composition] Extra phase present Impurities; dilution	Steps done in wrong order Reverse [function] Reverse flow Reverse mixing	Wrong procedure performed Wrong [function] achieved Transfer from wrong source Transfer to wrong destination Maintenance/test/sampling at wrong time/location

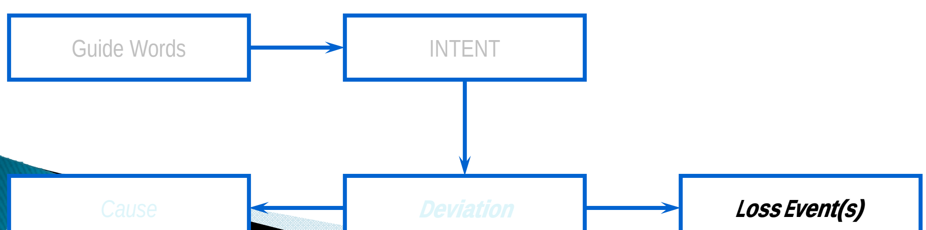
Initiating causes

- Identify deviation cause(s)
  - Must look backward in time sequence
  - Only identify <u>local</u> causes (i.e., in current study node)
  - Most deviations have more than one possible cause



Loss events

- Determine cause and deviation consequences, assuming failure of protection safeguards
- Take scenario all the way to a loss consequence
- Consequences can be anywhere and anytime



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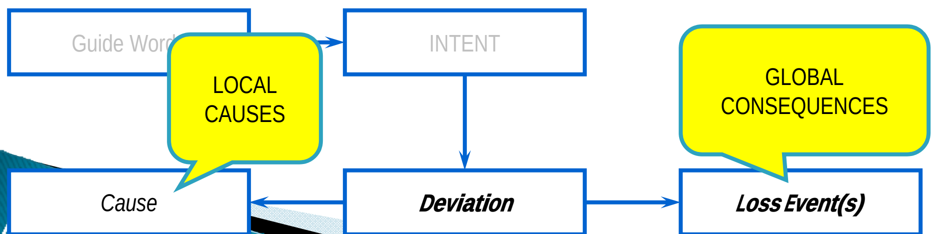
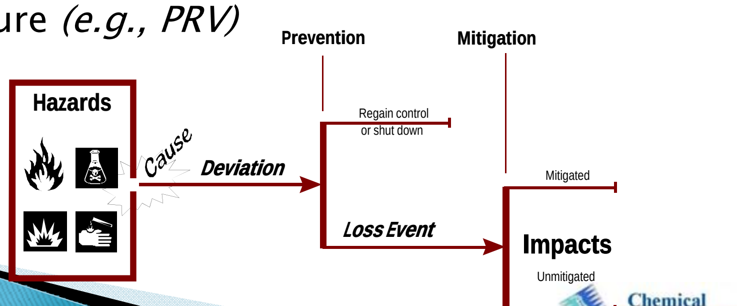


Safeguards

- Document preventive safeguards that intervene between the specific Cause–Consequence pair
- Note that different Consequences are possible, depending on safeguard success or failure *(e.g., PRV)*



	NODE:	HAZOP Study
REVIEW DATE	SCOPE: INTENT:	

Guide Word	Deviation	Cause	Consequences	Safeguards	Finding/Recommendation Comments

	NODE:	HAZOP Study
REVIEW DATE	SCOPE: INTENT:	

Guide Word	Deviation	Cause	Consequences	Safeguards	Finding/Recommendation Comments

	NODE:	HAZOP Study
REVIEW DATE	SCOPE: INTENT:	

Guide Word	Deviation	Cause	Consequences	Safeguards	Finding/Recommendation Comments

	NODE:	HAZOP Study
REVIEW DATE	SCOPE: INTENT:	

Guide Word	Deviation	Cause	Consequences	Safeguards	Finding/Recommendation Comments

Node 1	Fuel Transfer Line			HAZOP Study
Review Date:	SCOPE: From fuel supply to EP16 inlet, including fuel pump and fuel flow control loop INTENT: Feed fuel (50/50 KA mix) at 50-55 gpm, 20-25 C and 100-120 psig from fuel supply system to reactor EP-16			
Guide Word, Deviation	**Cause**	**Consequences**	**Safeguards**	**Finding/Rec. #** Comments
NONE No feed of KA to EP16	Pump stops	High oxidant-to-fuel ratio in reactor; temperature increase in reactor; reaction rate increase; pressure increase in reactor; runaway reaction; vessel rupture explosion, with resulting blast effects causing severe injuries or fatalities to persons nearby and NOx plume drifting off-site	[] Cascade control system stops oxidant flow automatically [] Operator response to high temperature reading (close manual oxidant valve); adequate time to respond, but valve is in same general area as EP16 [] SIL1 high-high temperature trip system shuts off oxidant feed; off same temperature sensor as temperature recorder	1, 2 PRV not designed to relieve runaway reaction
NONE No feed of KA to EP16	Fuel flow control valve fails closed or commanded to close	High oxidant-to-fuel ratio in reactor; temperature increase in reactor; reaction rate increase; pressure increase in reactor; runaway reaction; vessel rupture explosion, with resulting blast effects causing severe injuries or fatalities to persons nearby and NOx plume drifting off-site	[] Operator response to high temperature reading (close manual oxidant valve); adequate time to respond, but valve is in same general area as EP16 [] SIL1 high-high temperature trip system shuts off oxidant feed; off same temperature sensor as temperature recorder	1, 2 PRV not designed to relieve runaway reaction
NONE No feed of KA to EP16	Line blocked upstream of pump	High oxidant-to-fuel ratio in reactor; temperature increase in reactor; reaction rate increase; pressure increase in reactor; runaway reaction; vessel rupture explosion, with resulting blast effects causing severe injuries or fatalities to persons nearby and NOx plume drifting off-site	[] Cascade control system stops oxidant flow automatically [] Operator response to high temperature reading (close manual oxidant valve); adequate time to respond, but valve is in same general area as EP16 [] SIL1 high-high temperature trip system shuts off oxidant feed; off same temperature sensor as temperature recorder	1, 2 PRV not designed to relieve runaway reaction

Failure Modes and Effects Analysis

FMEA

FMEA

- Originally developed for aerospace / military systems
- Good for systems with little human interaction
- Focus is primarily on independent equipment failures and their effects on the larger system

FMEA level of resolution

Level of resolution determines detail in FMEA table:

- Subsystem level
- Equipment (component) level
- Component parts

Equipment failure modes

EXAMPLE OF EQUIPMENT FAILURE MODES FOR FMEA

Equipment Description	Failure Modes
Pump, normally operating	a. Fails on (fails to stop when required) b. Transfers off c. Seal rupture/leak d. Pump casing rupture/leak
Heat exchanger, high pressure on tube side	a. Leak/rupture, tube side to shell side b. Leak/rupture, shell side to external environment c. Tube side, plugged d. Shell side, plugged

DISCUSSION

What are some common failure modes for the following components?

- Safety relief valve
- Float switch

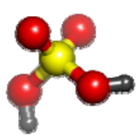
Which of the failure modes are *revealed* and which are *latent*?

Completing the FMEA table

- Complete in deliberate, systematic manner
  - Begin at process boundary (usually input)
  - Evaluate each item in order of flowsheet
  - Complete each item before continuing
- Table entries:
  - Equipment identification
  - Equipment description (type, operation configuration, service characteristics)
  - Failure modes (all are listed)
  - Effects (scenario elements)
  - Safeguards
  - Findings and recommendations

REVIEW DATE	System:				FMEA
	P&ID:				
Component ID	Component Description	Failure Mode	Immediate to Ultimate Effects	Safeguards	Finding/Recommendation Comments

REVIEW DATE	System:				FMEA
	P&ID:				
Component ID	Component Description	Failure Mode	Immediate to Ultimate Effects	Safeguards	Finding/Recommendation Comments



Hazard and Risk Analysis

- Basic risk concepts
- Experience-based vs predictive approaches
- Qualitative methods (What-If, HAZOP, FMEA)
- Order-of-magnitude and quantitative methods

Order-of-magnitude & quantitative methods

- Layer of Protection Analysis (LOPA)
- HAZOP/LOPA
- Fault Tree Analysis (FTA)

- Event Tree Analysis (ETA)
- Human Reliability Analysis (HRA)
- Consequence Analysis
- Others

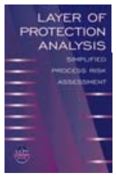
CSP — Chemical Safety and Security Training

Layer of Protection Analysis

LOPA

CSP — Chemical Safety and Security Training

LOPA references



CCPS 2001. Center for Chemical Process Safety, *Layer of Protection Analysis: Simplified Process Risk Assessment,* NY: American Institute of Chemical Engineers.

IEC 61511-3, Annex F (Informative), Layer of protection analysis (LOPA)

What is a *LOPA*?

LOPA

A *Layer of Protection Analysis*

- is a simplified method of risk assessment,
- intermediate between a qualitative process hazard analysis and a quantitative risk analysis,
- using simplifying rules to evaluate scenario impacts, initiating cause frequency, and independent layers of protection,
- to provide an order-of-magnitude risk estimate.

What is a *LOPA*?

Impacts

ANALYSIS TYPE	IMPACT MEASURE
Qualitative hazard evaluations	Qualitative impact categories (e.g. L/M/H)
Layer of Protection Analysis (LOPA)	Order-of-magnitude impact categories
Quantitative risk analyses (QRAs)	Quantitative total impact assessment

LOPA

What is a *LOPA*?

A *Layer of Protection Analysis*

- is a simplified method of risk assessment,
- intermediate between a qualitative process hazard analysis and a quantitative risk analysis,
- using simplifying rules to evaluate scenario impacts, initiating cause frequency, and independent layers of protection,
- to provide an order-of-magnitude risk estimate.

What is a *LOPA*?

"LOPA typically uses order-of-magnitude categories for initiating event frequency, consequence severity, and the likelihood of failure of independent protection layers (IPLs) to approximate the risk of a scenario."

– CCPS 2001, p. 11

LOPA scenarios

LOPA scenarios are unique initiating event / loss event (cause-consequence) pairs.

- Scenarios are not identified by the LOPA analyst(s)
- Scenarios are first identified by other means
  - HAZOP Study
  - Safety Integrity Level (SIL) determination
  - Incident investigation
  - Management of change
- Scenarios are then selected for LOPA
  - Screening of hazard evaluation scenarios
  - Scenario(s) of interest to current situation

Initiating causes

- "Initiating events" is term usually used in LOPA
- Same definition as for HAZOP Studies
- One initiating event per scenario
- A company may establish default initiating event frequency categories for LOPA usage
  - e.g. CCPS 2001, p. 71; see table footnote
  - e.g. see next two pages

Initiating cause frequencies

Example set of initiating event categories for LOPAs:

Frequency*	Example
-1	Pump stops
-1	Sensor or final control element fails
-2	Fail-closed valve fails open
-2	Relief valve opens prematurely
-2	Unloading hose failure
-3	Piping system rupture
-4	Atmospheric tank mechanical failure
-5 to **-6**	Pressure vessel mechanical failure

*Initiating event frequency magnitude

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Initiating cause frequencies

Examples given in ANSI/ISA-84.00.01-2004 Part 3:

Frequency*	Description	Examples
> -2	High - Can reasonably be expected to occur within the expected plant lifetime	Process leak Single instrument or valve failure Human error that could result in material release
-2 to **-4**	Medium - Low probability of occurrence within the expected plant lifetime	Single failures of small process lines or fittings
< -4	Low - Very low probability of occurrence within the expected plant lifetime	Spontaneous failure of single tanks or process vessels

*Initiating event frequency magnitude

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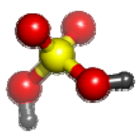
Loss-of-containment reference

Table 2. Default Equipment Leak Frequencies

Equipment Type	Leak Frequency (per year except as noted) 1/8" to 1/2" hole	1/2" to 2" hole	2" to 8" hole	Rupture	Notes
Process piping[a]	3E-6 / (Dp x Dh), where Dp = pipe diam. (in.), Dh = hole diam (in.)				Frequency is per foot of pipe length per year
Pressure vessel	2E-4	1E-4	1E-5	1E-5	
Atmos tank	5E-3	1E-3	1E-4	2E-5	
Pump, centrif.	2E-2	4E-4	--	1E-4	For single seals[b]
Pump, recip.	7E-2	2E-3	--	1E-3	For single seals[c]
Compressor, centrifugal	5E-3	1E-3	--	3E-5	
Compressor, reciprocating or screw	5E-2	3E-3	--	5E-4	For medium-sized compressors[d]
Heat exch., shell	1E-3	2E-4	4E-5	2E-5	
Loading hoses	2E-2	--	--	2E-3	Based on 100 loadings/year per hose[e]

(a). The algorithm includes leaks in the pipe as well as leaks in connections such as welds and flanges in the line. The frequency includes hole sizes a factor of two above and below the hole size input to the equation.
(b). For double sealed pumps divide the ¼" hole frequency by 3
(c). For double sealed pumps divide the ¼" hole frequency by 3
(d). There is a large variation (factor of ~ 30) between small and large reciprocating compressors. Some rates are so large that a plant may have observed enough failures to develop site-specific data that can be used to replace the data above.
(e). For other usages, ratio as follows: Rate = Rate reported above x $[(\# \text{ loadings/year})/100]^{0.5}$

From M. Moosemiller 2009, "Development of Algorithms for Predicting Ignition Probabilities and Explosion Frequencies," 43rd Annual Loss Prev Symposium.



Procedure-based operations

For procedure-based operations where the initiating event is an operational error:

Initiating event frequency
=
Frequency of performing operation
*
Probability of error per operation

PHA EXERCISE

The Upper West Central Midland water treatment plant uses chlorine from 68 kg cylinders.

One cylinder is moved from storage to hookup twice a week.

While transporting a cylinder from storage, a cylinder that does not have its protective cap in place is dropped.

The valve strikes a concrete step and breaks off, resulting in a rocketing cylinder and a Cl_2 release.

What is the initiating event frequency?

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IPL definition

Independent Protection Layer (IPL):

- A device, system or action that is capable of preventing a scenario from proceeding to its undesired consequence, regardless [i.e., independent] of the initiating event or the action of any other protection layer associated with the scenario.
- The effectiveness and independence of an IPL must be auditable.

– CCPS 2001 Glossary

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Possible IPLs

Use same thinking as for HAZOP Study *safeguards*.

- BPCS (if criteria met)
- Operator response to critical alarm
- Safety Instrumented Function (SIF)
- Emergency relief system
- Mitigative safeguards (sometimes)

IPL effectiveness

- Must detect the abnormal situation
- Must decide to take the correct protective action (may be done automatically or in software)
- Must be capable of bringing the system to a safe state
- Must do all of the above quickly enough, before the loss event occurs
- All necessary components must work reliably

Quantification of IPL effectiveness

From ANSI/ISA-84.00.01-2004 Part 3, Annex F:

Typical protection layer PFDs

Protection layer	Probability of failure on demand
Control loop	0.1
Human performance (trained, no stress)	1E-2 to 1E-4
Human performance (under stress)	0.5 to 1.0
Operator response to alarms	0.1
Vessel pressure rating above maximum challenge from internal and external pressure sources	1E-4 or better, if vessel integrity is maintained (i.e., corrosion is understood, inspections and maintenance is performed on schedule)

See also CCPS 2001 Tables 6.3 and 6.4; CCPS 2008a Table 7.4

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Quantification of IPL effectiveness

Probability of Failure on Demand (PFD)

$$PFD_{IPL} = PFD_{Sensor} + PFD_{LogicSolver} + PFD_{FinalElement}$$

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LOPA calculations

Basic scenario risk equation:

Risk = Scenario Frequency ⁎ Scenario Impact

Initiating event frequency ⁎ PFD_{IPL1} ⁎ PFD_{IPL2} ⁎ PFD_{IPL3} …

Conditional modifiers

Three common *conditional modifiers:*

- Probability of ignition | release
- Probability of person(s) in effect area | loss event
- Probability of injury or fatality | person(s) in area

Conditional modifiers

Three common *conditional modifiers:*

- P_{ign}
- P_{loc}
- P_{inj}

- These are risk reduction factors but not IPLs
- Each factor and its value is scenario-specific

LOPA calculations

Scenario risk eqn. with conditional modifiers:

*Risk = Scenario Frequency * Scenario Impact*

$$\text{IE freq.} * PFD_{IPL1} * PFD_{IPL2} * PFD_{IPL3} \ldots * P_{ign} * P_{loc} * P_{inj}$$

"Typical spreadsheet that can be used for the LOPA"

#	Impact event description	Severity level	Initiating cause	Initiation likelihood	PROTECTION LAYERS					Intermediate event likelihood	SIF integrity level	Mitigated event likelihood	Notes
					General process design	BPCS	Alarms, etc.	Additional mitigation restricted access	IPL additional mitigation dikes, pressure relief				
1	Fire from distillation column rupture	S	Loss of cooling water	0.1 / yr	0.1	0.1	0.1	0.1	PRV 01	1E-7 / yr	1E-02	1E-9 / yr	High press. causes column rupture
2	Fire from distillation column rupture	S	Steam control loop failure	0.1 / yr	0.1		0.1	0.1	PRV 01	1E-6 / yr	1E-02	1E-8 / yr	High press. causes column rupture
3	etc.												
.													

ANSI/ISA-84.00.01-2004 Part 3 Report

Risk decisions • Options

Objective: All evaluated scenarios meet level of risk tolerable to the organization.

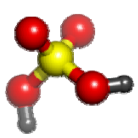
Approaches:

- Comparison with tolerable risk criteria
- Expert judgment *(not recommended by itself)*
- Relative risk reduction of competing alternatives
- Cost-benefit analysis of competing alternatives

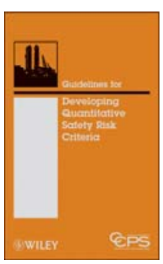
Matrix approach – Two risk regions

SCENARIO LIKELIHOOD	MAG.	RISK-REDUCTION PRIORITY				
1 / year Expected to occur occasionally or periodically	0	A	A	A	A	A
1/10 yrs, or 10% per yr Likely to occur more than once during plant lifetime	-1	A	A	A	A	A
1% likelihood per year Might occur once during plant lifetime	-2	C	A	A	A	A
1/1,000 likelihood per yr Unlikely/not expected to occur during plant lifetime	-3	C	C	A	A	A
1/10,000 likelihood per yr Remote likelihood; would be surprising and unexpected	-4	C	C	C	A	A
1/100,000 per yr Not expected to be possible, or almost inconceivable	-5	C	C	C	C	A
		3	4	5	6	7

SEVERITY MAGNITUDE



Risk decisions • Resource



CCPS 2009. Center for Chemical Process Safety, *Guidelines for Developing Quantitative Safety Risk Criteria*, New York: American Institute of Chemical Engineers.

Who performs LOPAs?

- Hazard evaluation team (HAZOP/LOPA)
- Single LOPA expert, with input
- Dedicated site or corporate LOPA team
- Third party, with input

HAZOP/LOPA

HAZOP/
LOPA

HAZOP/LOPA

- HAZOP Study using order-of-magnitude frequencies, impacts and probabilities
- Conditional modifiers used as risk-reduction factors and documented same as safeguards
- Done by HAZOP Study team
- Reference: R.W. Johnson, "Beyond-Compliance Uses of HAZOP/LOPA Studies," *Journal of Loss Prevention in the Process Industries 23*(6), November 2010, 727-733.

HAZOP/LOPA Example

Dev.	Cause	F	Consequences	S	Safeguards	Risk
No C_2H_4 Flow	FCV-1 fails closed	**-1**	Unreacted chlorine to furnace; possible failure of furnace tubes from chlorine contact damage; hot chlorine vapor release from furnace	4	[1] Alarm, shutdown on PT-1 low pressure [2] Detection of loss of ethylene flow by 2/h reactor sampling before furnace tube(s) fail	0

From Johnson, 2010

Node 3	Flasher Bottoms Draw-off	HAZOP Study
Review Date:	SCOPE: TK-301 bottom outlet line, PU-301A/B, HE-323, to valve at blowdown tank inlet or valve at aromatics gas header battery limits INTENT: To prevent heavies buildup, transfer liquid heavies (C30's+) to blowdown tank or to aromatics gasoline header at 325 350 °F; suction pressure 8-20 psig, discharge 30-40 psig; 0.5 to 1.5 gpm, to maintain 10-30% level in TK-301	

GuideWord/ Deviation	Cause	Freq	Consequences	Severity On	Severity Off	Severity Bus	Safeguards	Protec Factor	Scenario Freq	Scenario Sev	Scenario Risk	Action Priority	Rec # Comments
NONE No Flow to Blowdown Tank or Header	Line rupture between TK-301 and FV-4113	-3	Release heated crude DCPD, including contents of TK-301	3	3	4	No protection safeguards	0	-3	3.3	**0.3**	C	Prevention: MI tests, inspections Mitigation safeguards: HC detectors
NONE No Flow to Blowdown Tank or Header	Line rupture between TK-301 and FV-4113	-3	Fire	4	3	5	Ignition source control	0.5	-3.5	4.0	**0.5**	**B**	Mitigation safeguards: HC detectors, fire monitors, Nomex Safeguards considered adequate
NONE No Flow to Blowdown Tank	Line rupture downstream of FV-4113	-3	Release restricted flow of liquid heavies, including backflow from blowdown tank	2	0	4	No protection safeguards	0	-3	2.0	**-1.0**	C	Would likely take longer to detect
NONE No Flow to Blowdown Tank	Line rupture downstream of FV-4113	-3	Fire	3	0	4	Ignition source control	2	-5	3.0	**-2.0**	C	
NONE No Flow to Header	Line rupture downstream of FV-4113	-4	Release restricted flow of liquid heavies, including backflow from header	3	3	4	No protection safeguards	0	-4	3.3	**-0.7**	C	**13** Transfer now goes to blowdown tank
NONE No Flow to Header	Line rupture downstream of FV-4113	-4	Fire	4	3	5	Ignition source control	1	-5	4.0	**-1.0**	C	**13**

Order-of-Magnitude HAZOP Study

Fault Tree Analysis

Fault Tree Analysis

FTA

- Developed due to FMEA's inadequacy to analyze complex systems
- Able to handle concurrent events
- Integrates mechanical, human, process, external events
- Usually not a team-based approach

Fault Tree Analysis

FTA

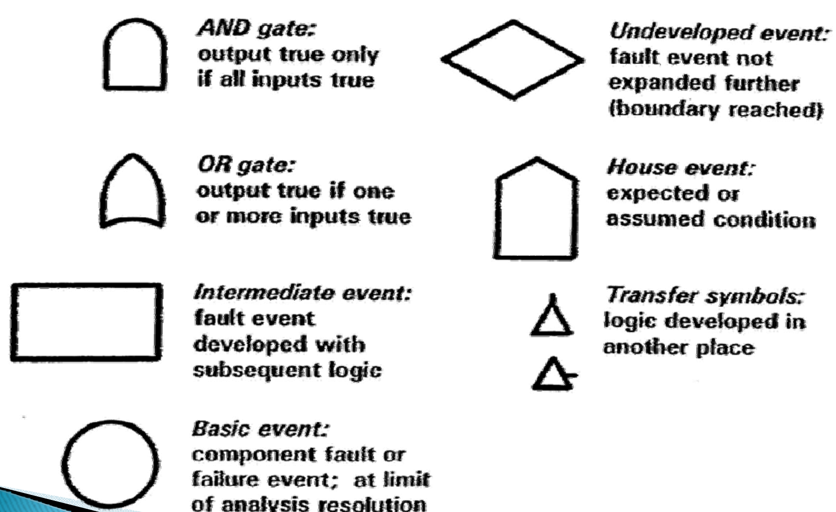
- Risk analysis "power tool"
  - Resource-intensive
  - Logic models can get very large
  - Quantitative studies can take 3-6 months
  - Used in nuclear power risk assessments
  - Used for analyzing complex control systems
- Deductive, graphical logic modeling method

Fault Tree Analysis

"TOP" Event

- Establishes scope of analysis
- Should be a physical, irreversible loss event
  - Example: vessel rupture explosion
- FTA is NOT a system-wide review
  - Only analyzes events contributing to TOP event

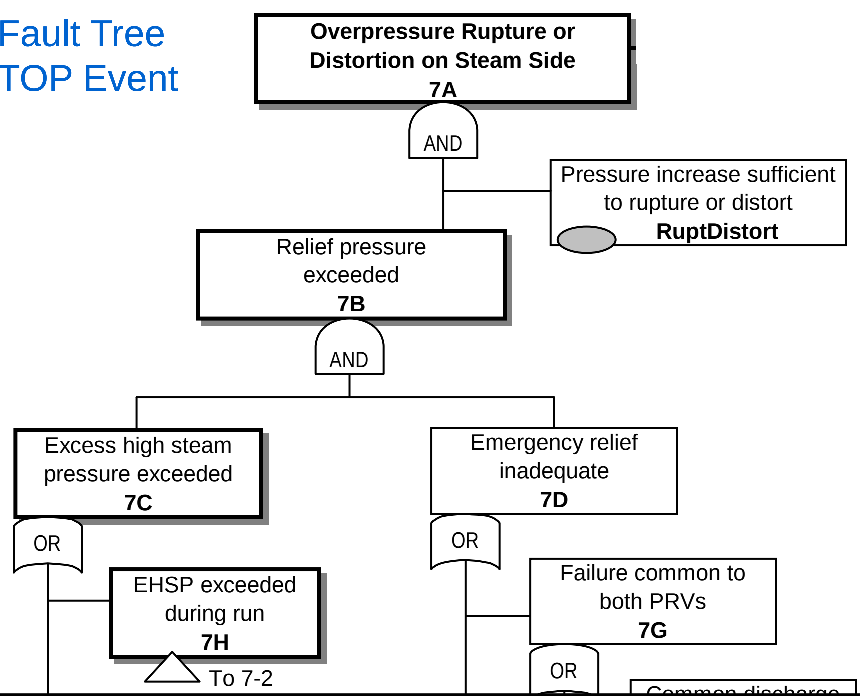
Fault tree symbols

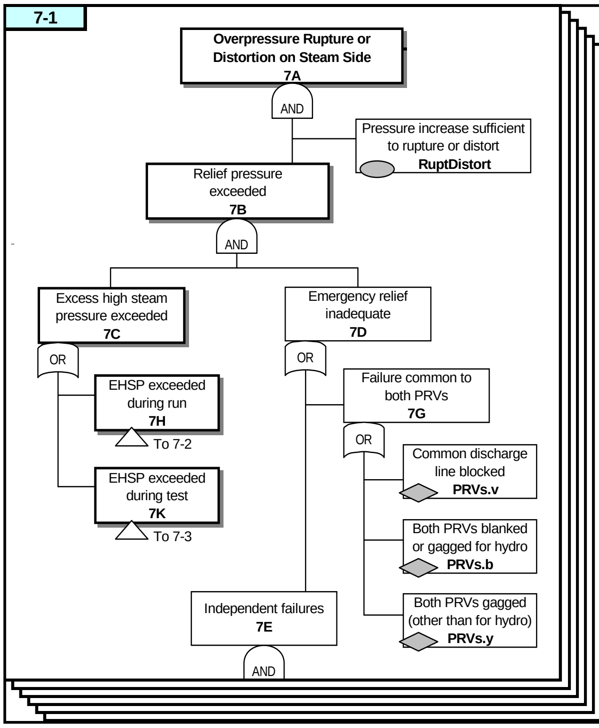


Fault tree construction

- Trace event sequence backwards in time
- No gate-to-gate connections
- Include all necessary and sufficient conditions
- Trace all branches back to basic events or boundaries

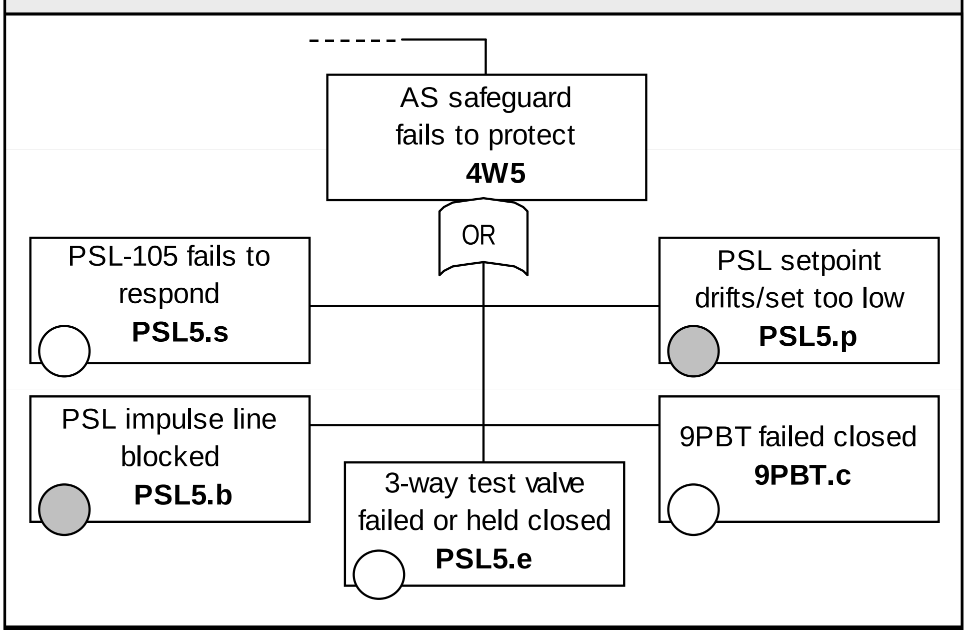
Fault Tree TOP Event





Reference: Kauffman et al., "Combustion Safeguards Test Intervals - Risk Study and Industry Survey," presented at AIChE Loss Prevention Symposium, Houston, April 2001.

Combustion air low pressure switch



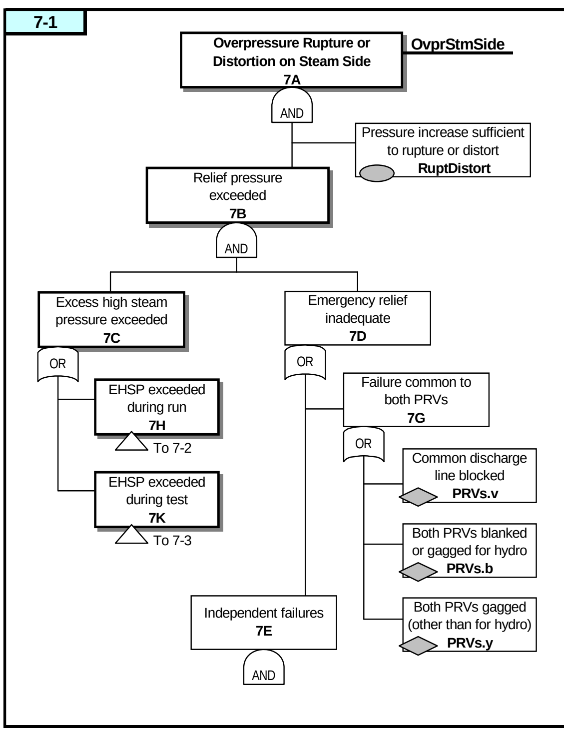
Fault tree solution

The Fault Tree is a Boolean algebra expression of the system.

Solving the expression yields *minimal cut sets*.

- Minimal cut sets are all nonredundant scenarios that lead to the TOP event
- Common mode failures must have same ID
- Solution usually done by computer

Quantifying basic event frequencies and probabilities yields a TOP event frequency.



Type	Name	Freq (/yr)	Dur (h)	Prob
Conseq	OvprStmSide	1.3E-06		
AND	7A	1.3E-06		
	RuptDistort			1
AND	7B	1.3E-06		
OR	7C	0.0071		
OR	7D			0.00018
	7H	0.0006		
	7K	0.0065		
OR	7E			8.E-05
OR	7G			1E-04
OR	7F1			0.0091
OR	7F2			0.0090
	PRVs.v			0
	PRVs.b			0.0001
	PRVs.y			0
	PRV1.v	0.004	4400	0.00201
	PRV1.s	0.009	4400	0.005
	PRV1.b	0.004	4400	0.00201
	PRV1.y			0.0001
	PRV2.v	0.004	4400	0.00201
	PRV2.s	0.009	4400	0.005
	PRV2.b	0.004	4400	0.00201
	PRV2.y			0

Notes:

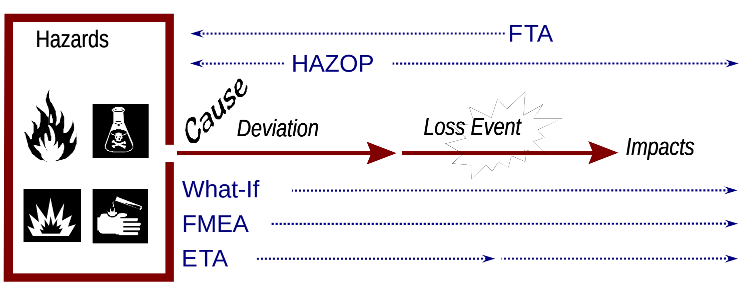
1. hydro = hydrotest
2. PRV settings: PRV1, 180 psig; PRV2, 185 psig
3. PRVs tested once/year, by either bench testing or testing in place

FTA EXERCISE

Draw the next level down for this TOP Event:

Flash fire

Summary of scenario-based approaches



PHA method selection guide

HAZOP	What-If/Checklist	FMEA	FTA	ETA
By deviation	By checklist item	By component	By loss event	By cause
Best for process operations	*Best for relatively standard operations*	*Best for mechanical and electrical systems*	*Best for complex systems/operations*	*Best to study one or only a few causes*
Good for continuous and procedure-based operations	Good for continuous and procedure-based operations	Good for continuous operations	Good for continuous operations; possible for procedure-based	Good to analyze administrative and engineering controls
Higher level of effort	Lower level of effort	Higher level of effort	Highest level of effort	Higher level of effort
Can analyze complex processes with multiple safeguards	*Mostly appropriate for simpler operations*	*Best analyzes processes with single-point failures*	*Can analyze complex processes with multiple safeguards*	*Can analyze complex processes with multiple safeguards*
Distinguishes between causes and safeguards	Does not distinguish between causes and safeguards	Does not distinguish between causes and safeguards	Distinguishes between causes and safeguards	Distinguishes between causes and safeguards
Only looks at causes that could lead to deviations	Only studies causes from checklist and what-if questioning	Looks at all failure modes of all components	Only studies causes and safeguards related to top event	Looks at all safeguards protecting against cause

Hazard and Risk Analysis

- Basic risk concepts
- Experience-based vs predictive approaches
- Qualitative methods (What-If, HAZOP, FMEA)
- Order-of-magnitude and quantitative methods
- **Analysis of procedure-based operations**

Procedure-based operations

- Batch processes
- Continuous processes:
  - Start-up
  - Shutdown
  - Production changes
- Receipt and unloading of chemicals
- Loading of product
- Sampling
- Maintenance

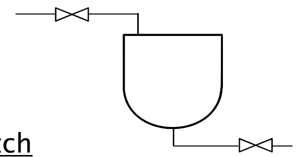
Why analyze procedure-based operations?

- Typical petrochemical facility time distribution:
  < 10% of the time in "abnormal operations"
- IChemE analysis of 500 process safety incidents:
  53% of the incidents occurred during "abnormal operations" (startup, shutdown, responding to avoid a shutdown)

References:
S.W. Ostrowski and K.Keim, "A HAZOP Methodology for Transient Operations," presented at Mary Kay O'Connor Process Safety Center International Symposium, October 2008

I.M. Duguid, "Analysis of Past Incidents in the Oil, Chemical and Petrochemical Industries," ICHemE *Loss Prevention Bulletin 144,* 1999

Batch vs continuous processes



Batch

- Transient process parameters
- Many operations are time-dependent
- Manual operations / control common
- Only part of system in use at any time

Continuous

- Steady-state process parameters
- Operations do not generally have time-dependencies
- Process control is usually automatic
- Entire system almost always in use

Chemical SAFETY AND SECURITY TRAINING

PHA of continuous operations

- Address continuous flows from input to output
- Address startup, shutdown and transient steps as procedure-based operations

Chemical SAFETY AND SECURITY TRAINING

PHA of procedure-based operations

Procedures usually follow these general steps:

1. Prepare vessel
2. Charge vessel
3. Reaction with monitor/control
4. Discharge
5. Purge

Which step is most like a continuous operation?

PHA of procedure-based operations

Suggested approach:

- Select study nodes as for continuous process
- Group procedures by nodes
- Conduct procedure-based PHA
- When procedure completed, do equipment-based PHA as for a continuous process

PHA of procedure-based operations

- PHA of procedure-based operation follows order of procedural steps
- All rules of continuous HAZOP Study apply
  - Local causes
  - Global consequences
  - All safeguards pertinent to cause-consequence pairs
- Consequence and safeguards considered at each succeeding step, until consequence occurs

Three approaches

- What-If Analysis of each operating step
- Two-Guide-Word Analysis
  - OMIT (all or part of the step is not done)
  - INCORRECT (step is performed wrong)
    - Operator does too much or too little of stated task
    - Wrong valve is closed
    - Order of steps is reversed
    - Etc.
- HAZOP Study of each step or group of steps
  - All seven guide words used
  - Extra guide word of "MISSING" sometimes used

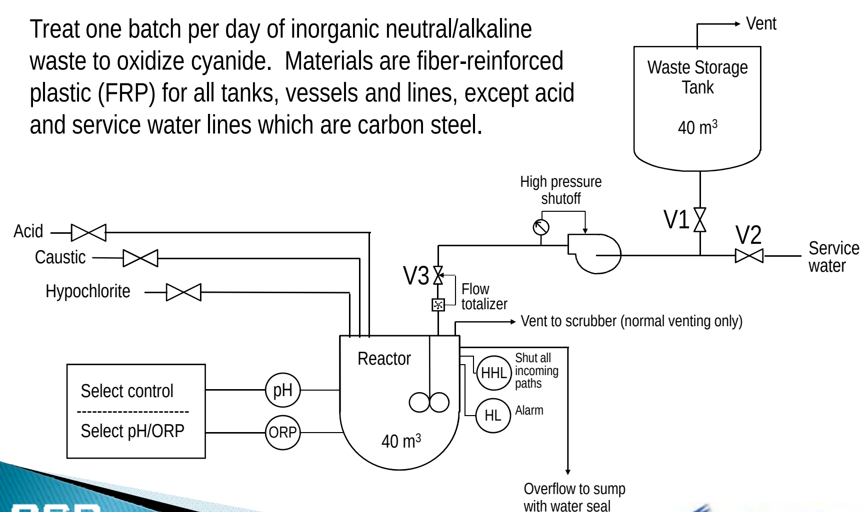
DISCUSSION

Give one or two examples of a deviation from a procedural step for each HAZOP guide word.

NONE	
MORE OF	
LESS OF	
PART OF	
AS WELL AS	
REVERSE	
OTHER THAN	

Example batch process

Treat one batch per day of inorganic neutral/alkaline waste to oxidize cyanide. Materials are fiber-reinforced plastic (FRP) for all tanks, vessels and lines, except acid and service water lines which are carbon steel.



Example batch process

1. Charge reactor with 5.3 m^3 of cyanide waste.
2. Add 24.8 m^3 service water to dilute waste to 0.3% (initially at 1.7%).
3. Add caustic (NaOH) on pH control to bring pH to 11.5.
4. Add sodium hypochlorite (NaOCl) on ORP control.
5. React with agitation for 6 hours; caustic and NaOCl to remain on auto-addition to maintain pH and ORP.
6. Send sample of reactor contents to lab to test for cyanide oxidation.
7. If lab approves, continue.
8. Add sulfuric acid (93%) on pH control to bring pH to 2.5.

Potential consequences:
- Concentration > 0.3% releases HCN during oxidation.
- Addition of acid before oxidation is complete releases all available CN^- as HCN.
- Excess NaOCl releases chlorine gas when acid is added.

"Actual procedure" for Step 1

1. Charge reactor with 5.3 m^3 of cyanide waste.

1.1 OPEN valve V1 to create path from cyanide waste storage tank to reactor.

Note: Valve V3 automatically opens when a flow totalizer value is set.

1.2 ENTER flow totalizer value of 5.3 via controller keyboard.

1.3 START waste transfer pump.

1.4 VERIFY pump automatically stops when 5.3 m^3 is transferred.

1.5 CLOSE valve V1 at waste storage tank.

PHA GROUP EXERCISE

- Divide into teams and conduct PHA of Step 1
- Use one or more of the three procedure-based approaches
- Be prepared to present your most important findings and any problems with, or comments on, your selected approach

PROCESS SEGMENT:	SCOPE:		What-If Analysis
REVIEW DATE:	INTENT:		
What If …	**Consequences**	**Safeguards**	**Finding/Recommendation** Comments
1. Charge reactor with 5.3 m3 of cyanide waste. 1.1 OPEN valve V1 to create path from cyanide waste storage tank to reactor.			

PROCESS SEGMENT:	SCOPE:	What-If Analysis
REVIEW DATE:	INTENT:	

What If …	Consequences	Safeguards	Finding/Recommendation Comments

PROCESS SEGMENT:	SCOPE:	What-If Analysis
REVIEW DATE:	INTENT:	

What If …	Consequences	Safeguards	Finding/Recommendation Comments

	NODE:	HAZOP Study
REVIEW DATE	SCOPE: INTENT:	

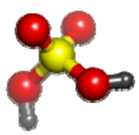
Guide Word	Deviation	Cause	Consequences	Safeguards	Finding/Recommendation Comments
1. Charge reactor with 5.3 m3 of cyanide waste. 1.1 OPEN valve V1 to create path from cyanide waste storage tank to reactor.					

	NODE:	HAZOP Study
REVIEW DATE	SCOPE: INTENT:	

Guide Word	Deviation	Cause	Consequences	Safeguards	Finding/Recommendation Comments

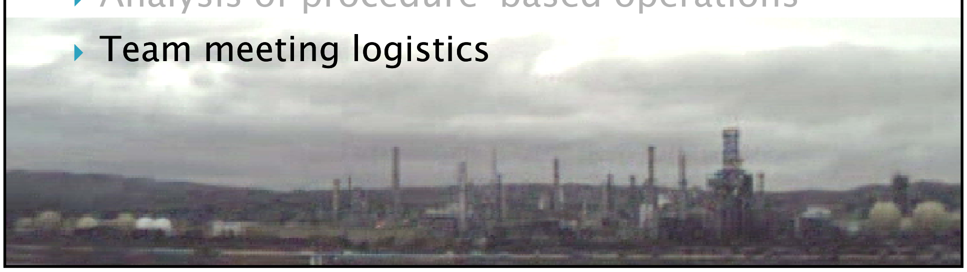
	NODE:	HAZOP Study
REVIEW DATE	SCOPE:	
	INTENT:	

Guide Word	Deviation	Cause	Consequences	Safeguards	Finding/Recommendation Comments



Hazard and Risk Analysis

- Basic risk concepts
- Experience-based vs predictive approaches
- Qualitative methods (What-If, HAZOP, FMEA)
- Order-of-magnitude and quantitative methods
- Analysis of procedure-based operations
- Team meeting logistics



Team meeting logistics

The following are common to all PHA team reviews:

- Team composition
- Preparation
- First team review meeting
- Final team review meeting

PHA team composition

5 to 7 team members optimum

- Team leader (facilitator) – hazard analysis expertise
- Scribe – responsible for PHA documentation
- Key members – should have process/engineering expertise, operating and maintenance experience
- Supporting members – instruments, electrical, mechanical, explosion hazards, etc.

PHA preparation

At initial scheduling of review and designation as team leader:

- Become familiar with the plant's PSM procedures
- Determine exact scope of PHA
- With PSM Coordinator, select one or more PHA methods that are appropriate to the complexity of the process
  (Different techniques can be used for different parts of the process)

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PHA preparation

~ 6 weeks before start date of team review:

- Compile process safety information for process to be studied
- Obtain procedures for all modes of operation
- Gather other pertinent information
- Determine missing or out-of-date information
- Make action plan for updating or developing missing information prior to the start of the team reviews

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PHA preparation

~ 4 weeks before expected start date:

- Confirm final selection of review team members
- Give copy of PHA Procedures to scribe; emphasize the necessity for thorough documentation
- Estimate the number of review-hours needed to complete PHA team review, or check previous estimate
- Establish an initial schedule of review sessions, coordinated with shift schedules of team members

PHA timing

Plan PHA team review in half-day sessions of 3 to 3½ hours duration.

- *Optimum:* 1 session/day, 4 sessions/week
- *Maximum:* 8 sessions/week

- Schedule sessions on a long-term plan
- Schedule at set time on set days
- PHA team reviews usually take one or two days to get started, then ~ ½ day per typical P&ID, unit operation or short procedure

PHA preparation

~ 2 to 3 weeks before start date:

- Obtain copies of all incident reports on file related to the process or the highly hazardous materials in the process
- Reserve meeting room
- Arrange for computer hardware and software to be used, if any
- Divide up process into study nodes or segments
- Develop initial design intent for each study node, with the assistance of other review team members as needed

PHA preparation

During the week before the start date:

- Select and notify one person to give process overview
- Arrange for walk-around of facility, including any necessary training and PPE
- Secure projector and spare bulb
- Arrange for refreshments and lunches

PHA preparation

Immediately before each meeting:

- Check out meeting room and facilities, including heating/air conditioning
- Set up computer and projection equipment
- Lay out or tape up P&IDs and plant layout diagrams

First team review meeting

1 Attendance

- Go over emergency exits, alarms and evacuation procedures
- Introduce team members and their background / area of expertise
- Ensure all required team members are present
- Document attendance for each half-day session
- Emphasize need for punctuality and minimal interruptions

First team review meeting

2 Scope and objectives

- Go over exact boundaries of system to be studied
- Explain purpose for conducting the PHA

First team review meeting

3 Methodology

- Familiarize team members with methodology to be used
- Explain why selected methodology is appropriate for reviewing this particular process

First team review meeting

4 Process safety information

- Review what chemical, process, equipment and procedural information is available to the team
- Ensure all required information is available before proceeding

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First team review meeting

5 Process overview

- Prearrange for someone to give brief process overview, covering such details as:
  - Process, controls
  - Equipment, buildings
  - Personnel, shift schedules
  - Hazardous materials, process chemistry
  - Safety systems, emergency equipment
  - Procedures
  - What is in general vicinity of process
- Have plant layout drawings available

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First team review meeting

6 Unit tour

- Prearrange for tour through entire facility to be included in team review
- Follow all safety procedures and PPE requirements
- Have team members look for items such as:
  - General plant condition
  - Possible previously unrecognized hazards
  - Human factors (valves, labeling, etc.)
  - Traffic and pedestrian patterns
  - Activities on operator rounds (gauges, etc.)
  - Emergency egress routes

First team review meeting

7 Review previous incidents

- Review all incident and near-miss reports on file for the process being studied
- Also review sister-plant and industry-wide incidents for the type of process being studied
- Identify which incidents had potential for catastrophic on-site or off-site / environmental consequences
- Make sure detailed assessment (e.g., HAZOP Study) covers all previous significant incidents

First team review meeting

8 Review facility siting

- Discuss issues related to whether buildings intended for occupancy are designed and arranged such that people are adequately protected against major incidents
- Various approaches are possible:
  - API Recommended Practices 752, 753
  - Topical review (e.g., CCPS 2008a page 291)
  - Checklist review (e.g., Appendix F of W.L. Frank and D.K. Whittle, *Revalidating Process Hazard Analyses*, NY: American Institute of Chemical Engineers, 2001)

First team review meeting

9 Review human factors

- Discuss issues related to designing equipment, operations and work environments so they match human capabilities, limitations and needs
- Human factors are associated with:
  - Initiating causes (e.g., operational errors causing process upsets)
  - Preventive safeguards (e.g., operator response to deviations)
  - Mitigative safeguards (e.g., emergency response actions)

First team review meeting

9 Review human factors (continued)

- Various approaches are possible:
  - Ergonomic studies
  - Topical review of positive and negative human factors (e.g., CCPS 2008a pages 277-279)
  - Checklist review (e.g., Appendix G of W.L. Frank and D.K. Whittle, *Revalidating Process Hazard Analyses*, NY: American Institute of Chemical Engineers, 2001)

First team review meeting

10 Identify and document process hazards

- See earlier module on Hazards and Potential Consequences
- Also an opportunity to address inherent safety issues

Final team review meeting

To do during the final team review meeting:

- Ensure entire scope of review has been covered
- Read through all findings and recommendations to
  - Ensure each finding and recommendation is understandable to those needing to review and implement them
  - Consolidate similar findings
- Ensure all previous significant incidents have been addressed in the PHA scenarios

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Chemical SAFETY AND SECURITY TRAINING

Hazard and Risk Analysis

- Basic risk concepts
- Experience-based vs predictive approaches
- Qualitative methods (What-If, HAZOP, FMEA)
- Order-of-magnitude and quantitative methods
- Analysis of procedure-based operations
- Team meeting logistics
- Documenting hazard and risk analyses

PHA report

Goal: Record the results such that study is understandable, can be easily updated, and supports the team's decisions.

- System studied
- What was done
- By whom
- When
- Findings and recommendations
- PHA worksheets
- Information upon which the PHA was based

Report disposition

- Draft report
  - prepared by scribe
  - reviewed by all team members
  - presented to management, preferably in a face-to-face meeting
- Management input considered by review team
- Final report
  - prepared by scribe
  - reviewed by all team members
  - accepted by management
  - kept in permanent PHA file

Hazard and Risk Analysis

- Basic risk concepts
- Experience-based vs predictive approaches
- Qualitative methods (What-If, HAZOP, FMEA)
- Order-of-magnitude and quantitative methods
- Analysis of procedure-based operations
- Team meeting logistics
- Documenting hazard and risk analyses
- Implementing findings and recommendations

Implementing findings & recommendations

What is the most important product of a PHA?

1. The PHA report
2. A deeper understanding gained of the system
3. Findings and recommendations from the study

Implementing findings & recommendations

What is the most important product of a PHA?

1. The PHA report
2. A deeper understanding gained of the system
3. Findings and recommendations from the study
4. The actions taken in response to the findings
   and recommendations from the study

Implementing findings & recommendations

- Findings and recommendations are developed throughout team review
  - Analysis of hazards; inherent safety options
  - Facility siting review
  - Human factors review
  - HAZOP, What-If, etc.
- <u>Basis</u> for determining whether finding or recommendation is warranted:
  - CHECKLIST REVIEW: Code/standard is violated
  - PREDICTIVE ANALYSIS: Scenario risk is too high (also if code/standard is violated)

Implementing findings & recommendations

Wording of findings and recommendations:

- Be as general as possible in wording of finding, to allow flexibility in how item is resolved

Install reverse flow protection in Line 112-9 to prevent backflow of raw material to storage	instead of	Install a Cagey Model 21R swing check valve in the inlet flange connection to the reactor

- Describing the concern as part of the finding will help ensure the actual concern is addressed
- Use of words such as these warrants follow-up to ensure the team's concern was actually addressed:
  - CONSIDER…
  - STUDY…
  - INVESTIGATE…..

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PHA risk-control actions

Example risk-control actions:

- Alter physical design or basic process control system
- Add new layer of protection or improve existing layers
- Change operating method
- Change process conditions
- Change process materials
- Modify inspection/test/maintenance frequency or method
- Reduce likely number of people and/or value of property exposed

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PHA action item implementation

"The employer shall establish a system to promptly address the team's findings and recommendations; assure that the recommendations are resolved in a timely manner and that the resolution is documented; document what actions are to be taken; complete actions as soon as possible; develop a written schedule of when these actions are to be completed; communicate the actions to operating, maintenance and other employees whose work assignments are in the process and who may be affected by the recommendations or actions."

- OSHA PSM Standard, 29 CFR 1910.119(e)(5) and U.S. EPA RMP Rule, 40 CFR 68.67(e)

1 – Document findings & recommendations

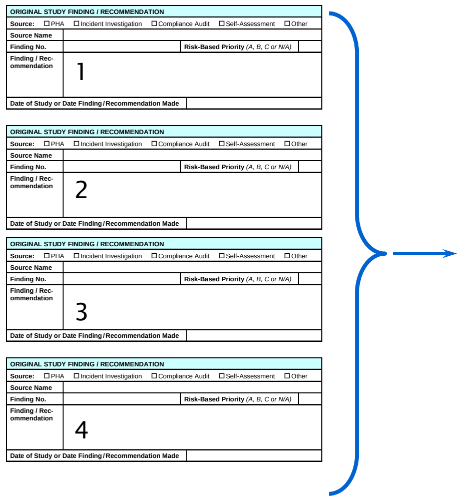
Example form:

ORIGINAL STUDY FINDING / RECOMMENDATION			
Source: ☐ PHA ☐ Incident Investigation ☐ Compliance Audit ☐ Self-Assessment ☐ Other			
Source Name			
Finding No.		**Risk-Based Priority** *(A, B, C or N/A)*	
Finding / Rec-ommendation			
Date of Study or Date Finding / Recommendation Made			

2 – Present findings & recommendations

PHA team

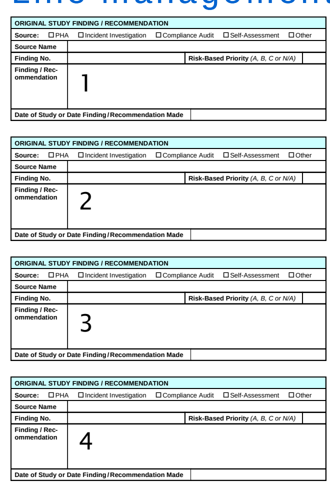
Line management



2 – Present findings & recommendations

PHA team

Line management



3 – Line management response

For each PHA team finding/recommendation:

ACTION COMMITTED TO BY MANAGEMENT		
Specific Action To Be Taken		
To Be Completed By		*Time extension requires management approval*
Responsible Person		

Suggestions:

- Use database or spreadsheet
- Flag imminent and overdue actions
- Periodically report overall status to top management

Example

ORIGINAL STUDY FINDING / RECOMMENDATION			
Source:	☒ PHA ☐ Incident Investigation ☐ Compliance Audit ☐ Self-Assessment ☐ Other		
Source Name	Formaldehyde Unloading PHA		
Finding No.	PHA-UF-11-01	**Risk-Based Priority** *(A, B, C or N/A)*	B
Finding / Recommendation	*Safeguards against formaldehyde storage tank overfilling are considered to be inadequate due to the signals for the controlling level indication and the high level alarm both being taken off of the same level transmitter. Options for consideration: Take manual level reading before unloading into the tank to cross-check adequate capacity for unloading; add separate high level switch for the high level alarm.*		
Date of Study or Date Finding/Recommendation Made	1 March 2011		

ACTION COMMITTED TO BY MANAGEMENT		
Specific Action To Be Taken	The following steps are to be taken to adopt and implement finding PHA-UF-11-01: (1) Add a separate high level switch on the formaldehyde storage tank, using a different level measurement technology than the controlling level sensor. (2) Add the new level switch, in addition to the high level alarm, to the MI critical equipment list and schedule for regular functional testing. (3) Until the new level switch is installed, implement a temporary procedural change to take manual level readings before unloading into the tank to cross-check adequate capacity for unloading, ensuring proper PPE is specified and used for performing the manual level readings.	
To Be Completed By	1 September 2011	*Time extension requires management approval*
Responsible Person	I. M. Engineer	

4 – Document final resolution

Document how each action item was implemented.

FINAL RESOLUTION		
Resolution Details *(attach drawings, procedures, etc.)*		
Associated MOC(s)		
DATE COMPLETED		
Date Communicated		
How Communicated		*Attach documentation of the communication(s)*

Communication of actions

Communicate actions taken in response to PHA findings and recommendations.

TO WHOM?

- To operating, maintenance and other employees whose work assignments are in the process and who may be affected by the recommendations or actions

Communication of actions

HOW?

- Train through plant training program when needed
  - Use appropriate techniques
  - Verify understanding
- Otherwise inform, such as by
  - Safety meetings
  - Beginning-of-shift communications
  - E-mail
- Document communications

Communication of actions

WHAT?

- Physical changes
- Personnel or responsibility/accountability updates
- Operating / maintenance procedures
- Emergency procedures; Emergency Response Plan
- Safe work practice procedures
- Control limits or practices

DISCUSSION

WHY?

What are two or more reasons why it is important to communicate PHA action items to affected employees?

-
-
-
-

Final word

The task of the PHA team is to identify where action is needed, not to redesign the system.