Chemical
SAFETY AND SECURITY TRAINING

Hazards and Potential Consequences

SAND No. 2011-0720P

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.

Sandia National Laboratories

Key acronyms

BLEVE = *boiling-liquid-expanding-vapor explosion*

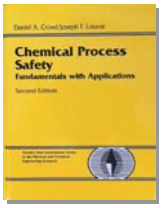
VCE = *vapor cloud explosion*

LFL = *lower flammable limit*

LOC = *limiting oxygen concentration*

Hazards / consequences resources

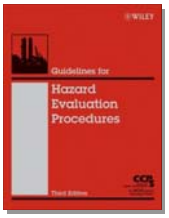
D.A. Crowl and J.F. Louvar 2001. ***Chemical Process Safety: Fundamentals with Applications, 2nd Ed.,*** **Upper Saddle River, NJ: Prentice Hall.**



Chapter
- **2 • Toxicology**
- **4 • Source Models**
- **5 • Toxic Release and Dispersion Models**
- **6 • Fires and Explosions**
- **10 • Hazards Identification**

Hazards / consequences resources

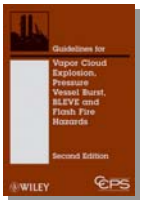
CCPS 2008a. Center for Chemical Process Safety, ***Guidelines for Hazard Evaluation Procedures, Third Edition*****, NY: American Institute of Chemical Engineers.**



Chapter 3 • Hazard Identification Methods
- 3.1 Analyzing Material Properties and Process Conditions
- 3.2 Using Experience
- 3.3 Developing Interaction Matrixes
- 3.4 Hazard Identification Results
- 3.5 Using Hazard Evaluation Techniques to Identify Hazards
- 3.6 Initial Assessment of Worst-Case Consequences
- 3.7 Hazard Reduction Approaches and Inherent Safety Reviews

Hazards / consequences resources

CCPS 2010. **Center for Chemical Process Safety, *Guidelines for Vapor Cloud Explosion, Pressure Vessel Burst, BLEVE and Flash Fire Hazards, 2nd Edition*, NY: American Inst. of Chem. Engineers.**



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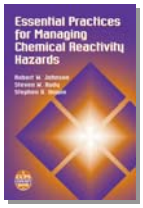
Hazards / consequences resources

Johnson et al. 2003. ***Essential Practices for Managing Chemical Reactivity Hazards,*** **NY: American Institute of Chemical Engineers,** accessible free after registration on www.knovel.com**.**



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Identification of Hazards and Potential Consequences

- ***Process hazard*** **defined**
- **Types of hazards and potential consequences**
- **Approaches and methods for systematically identifying process hazards**
- **Chemical hazard data**

US Chemical Safety Board

Identification of Hazards and Potential Consequences

- ***Process hazard*** **defined**

US Chemical Safety Board

Process hazard definition

***Presence** of a*
stored or connected
***material or energy** with*
inherent characteristics
*having the **potential** for*
causing loss or harm.

Identification of Hazards and Potential Consequences

- *Process hazard* defined
- **Types of hazards and potential consequences**

US Chemical Safety Board

Types of process hazards and potential consequences

- Toxicity and corrosivity hazards
- Asphyxiation hazards
- Combustion hazards
- Detonation hazards
- Chemical reactivity hazards
- Rapid phase transition hazards (BLEVEs)
- Bursting vessel explosion hazards
- Other physical hazards

These are not mutually exclusive categories.

Types of process hazards and potential consequences

- **Toxicity and corrosivity hazards**
- Simple asphyxiation hazards
- Combustion hazards
- Detonation hazards
- Chemical reactivity hazards
- Rapid phase transition hazards (BLEVEs)
- Bursting vessel explosion hazards
- Other physical hazards

Toxicity and corrosivity hazards

Nature of hazard	Potential exposure of people to materials having toxic and/or corrosive properties
What is required	Presence or generation of toxic/corrosive material + mechanism for physical contact
Typical examples	Chlorine used for water treatment; hydrogen sulfide as hydrocarbon impurity; sulfuric acid used for pH control
Consequences	Contact with toxic / corrosive material can cause various health effects, depending on material characteristics, concentration, route of exposure and duration of contact (see Day 1 information)

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Toxicity and corrosivity hazards

Video example	www.youtube.com; search term **Seward ammonia spill**
Area of effect	Liquid releases usually very localized; toxic vapor releases can extend many km
How calculated	• Toxic release dispersion models can be used to calculate release rates, downwind and cross-wind distances with various meteorological conditions • Some models can also calculate indoors concentration as a function of time
Free program	http://www.epa.gov/emergencies/content/cameo/aloha.htm

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Types of process hazards and potential consequences

- Toxicity and corrosivity hazards
- **Asphyxiation hazards**
- Combustion hazards
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- Chemical reactivity hazards
- Rapid phase transition hazards (BLEVEs)
- Bursting vessel explosion hazards
- Other physical hazards

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Asphyxiation hazards

- **An *asphyxiant* is a gas that can cause unconsciousness or death by suffocation (*asphyxiation*).**
  - ***Chemical asphyxiants* chemically interfere with the body's ability to take up and transport oxygen**
  - ***Physical asphyxiants* displace oxygen in the environment**
- ***Simple asphyxiants* have no other health effects**
- **Most simple asphyxiants are <u>colorless</u> and <u>odorless</u>.**

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Physical asphyxiation hazards

- **Common industry asphyxiant: Nitrogen** N_2
- **Other simple asphyxiants:**
  - **Hydrogen** H_2
  - **Argon, helium, neon** Ar
  - **Hydrocarbon gases (e.g., methane, ethane, ethylene, acetylene, propane, propylene, butane, butylene)** CH_4
  - **Carbon dioxide** CO_2

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Physical asphyxiation hazards

What is required	Reduced-oxygen atmosphere + situation allowing breathing of the atmosphere
Typical examples	Entry into vessel inerted with nitrogen; oxygen depletion by rusting over time; oxygen depletion by combustion; natural gas leak into enclosed room or area
Video	http://www.csb.gov/videoroom/detail.aspx?vid=11&F=0&CID=1&pg=1&F_All=y
Boundaries	• US OSHA: oxygen deficiency exists if concentration is less than 19.5% • ACGIH®: deficiency exists below 18% oxygen at 1 atm (equivalent to a partial pressure pO_2 of 135 torr)

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Types of process hazards and potential consequences

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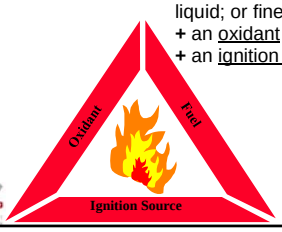
Combustion hazards

Nature of hazard	Potential for uncontrolled release of the heat of combustion upon rapid oxidation of a combustible material
What is required	A fuel (pyrophoric or flammable gas; pyrophoric, flammable or combustible liquid; or finely divided combustible solid) + an oxidant (usually atmospheric O_2) + an ignition source (unless pyrophoric)



Combustion hazards

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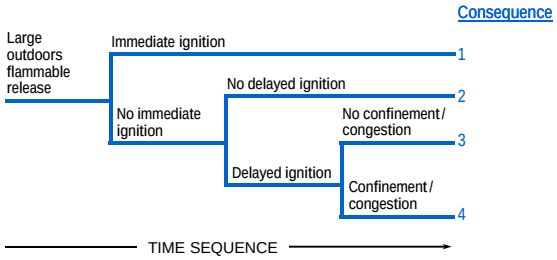
Possible consequences	• **Flash fire**, **pool fire** and/or **jet fire** • **Confined vapor explosion** • **Vapor cloud explosion** • **Dust or mist explosion** • Toxic combustion products

EXERCISE

Describe each of the four possible outcomes.



Combustion hazards - Some definitions

Combustion	A propagating rapid oxidation reaction.
Oxidation	In this context, a reaction in which oxygen combines chemically with another substance.
Oxidizer	Any material that readily yields oxygen or other oxidizing gas, or that readily reacts to promote or initiate combustion of combustible materials.
Explosion	A rapid or sudden release of energy that causes a pressure discontinuity or blast wave.

Some definitions (continued)

Spontaneously combustible	Capable of igniting and burning in air without the presence of an ignition source.
Pyrophoric	Capable of igniting spontaneously in air at a temperature of 130°F (54.4°C) or below.
Hypergolic	Hypergolic behavior is characterized by immediate, spontaneous ignition of an oxidation reaction upon mixing of two or more substances.

Reference: Johnson et al. 2003

Combustion hazards

Area of effect: Small fires usually have very localized effects; a large fire or a combustion-related explosions can destroy an entire facility and affect nearby surroundings

How calculated: Available combustion energy:

Mass of combustible x heat of combustion *or*
Mass rate of combustion x heat of combustion

E.g., Ethanol pool fire in a 50 m^2 dike:

[Pool area x burning rate x liquid density] x heat of combustion
= (50 m^2) (0.0039 m/min) (789 kg/m^3) (26900 kJ/kg) = 4×10^6 kJ/min

Note: Only ~ 20% of this will be released as thermal radiation.

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Combustion hazards

Free program: www.epa.gov/emergencies/content/cameo/aloha.htm

(can be used to calculate release rates, extent of a flammable vapor cloud, and vapor cloud explosion effect distances)

Online reference: Gexcon Gas Explosion Handbook, www.gexcon.com/handbook/GEXHBcontents.htm

Other references: **CCPS 2010; Crowl and Louvar 2001**

(See also the Chemical Data Sources at the end of this presentation)

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Flammability limits

LFL **Lower flammability limit**

Below LFL, mixture will not burn, it is too lean.

UFL **Upper flammability limit**

Above UFL, mixture will not burn, it is too rich.

- **Defined only for gas mixtures in air**
- **Both UFL and LFL defined as volume % fuel in air**

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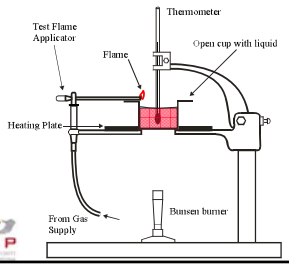
Flash point

Flash Point **Temperature above which a liquid produces enough vapor to form an ignitable mixture with air**



(Defined only for liquids at atmospheric pressure)

Example values

	LFL	UFL
Methane	5%	15%
Propane	2.1%	9.5%
Butane	1.6%	8.4%
Hydrogen	4.0%	75%

	Flash point
Methanol	12.2 °C
Benzene	-11.1 °C
Gasoline	-40 °C
Styrene	30.5 °C

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Limiting oxygen concentration

Limiting oxygen concentration (LOC):

Oxygen concentration below which combustion is not possible, with any fuel mixture, expressed as volume % oxygen.

Also called: Minimum Oxygen Concentration (MOC)
Max. Safe Oxygen Concentration (MSOC)

Examples:

	LOC (volume % oxygen)
Methane	12 %
Ethane	11 %
Hydrogen	5 %

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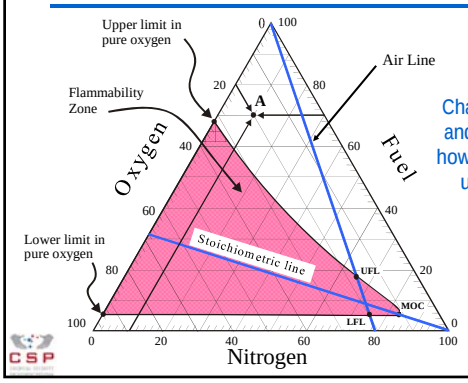
Flammability diagram



Chapter 6 of Crowl and Louvar shows how to prepare and use flammability diagrams

Design Criteria

1. **Avoid flammable mixtures**
2. **Eliminate ignition sources**

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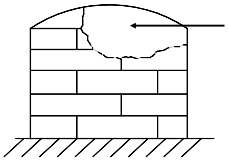
Inerting and purging

Purpose: To reduce the oxygen or fuel concentration to below a target value using an inert gas (e.g., nitrogen, carbon dioxide)



E.g., reduce oxygen concentration to **< LOC**

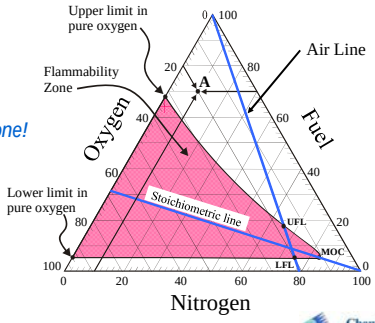
Inerting and purging options

- **Vacuum Purge** - evacuate and replace with inert
- **Pressure Purge** - pressurize with inert, then relieve pressure
- **Sweep Purge** - continuous flow of inert
- **Siphon Purge** - fill with liquid, then drain and replace liquid with inert
- **Combined** - pressure and vacuum purge; others

See Chapter 7 of Crowl and Louvar for details

Flammability diagram

OBJECTIVE:
***Stay out** of Flammability Zone!*



Ignition sources

- **Obvious (e.g., flames, welding, hot surfaces)**
- **Spontaneous ignition at moderate temp's**
- **Electrical sources**
  - **Powered equipment**
  - **Static electricity**
  - **Stray currents**
  - **Radio-frequency pickup**
  - **Lightning**
- **Physical sources**
  - **Adiabatic compression**
  - **Heat of adsorption**
  - **Friction**
  - **Impact**
- **Chemical Sources**
  - **Catalytic materials**
  - **Pyrophoric materials**
  - **Thermite reactions**
  - **Unstable chemical species formed in system**

Minimum ignition energy

Minimum ignition energy (MIE) — The electrical energy discharged from a capacitor that is just sufficient to ignite the most ignitable mixture of a given fuel-mixture under specific test conditions.

Typical values: **(wide variation expected)**

Vapors	**0.25 mJ**
Dusts	**about 10 mJ**

- **Dependent on test device, so not a reliable design parameter**
- **Static spark that you can feel: about 20 mJ**

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Autoignition temperature

Autoignition Temperature (AIT): **Temperature above which adequate energy is available from the environment to start a self-sustaining combustion reaction.**

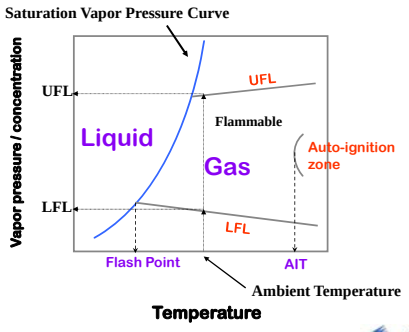
Example values:

	AIT
Methane	632 °C
Ethane	472
1-Pentene	273
Toluene	810
Acetaldehyde	185

There is great variability in reported AIT values! Use lowest reported value.

See Appendix B of Crowl and Louvar 2002 for a table of AITs

Flammability relationships



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Ignition source control

- **Identify ignition sources**
  - **Continuous ignition sources; e.g., fired equipment**
  - **Potential/intermittent ignition sources; e.g., traffic**
- **Identify what could be ignited**
  - **Flammable atmospheres**
  - **Potentially flammable atmospheres**
  - **Likely leak/release locations**
  - **Avenues to unexpected locations; e.g., drains, sumps**
- **Analyze for adequate control**

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DISCUSSION

Which of these two design criteria can be more easily and reliably attained?

1 **Avoid flammable mixtures**

2 **Eliminate ignition sources**

Types of process hazards and potential consequences

- Toxicity and corrosivity hazards
- Asphyxiation hazards
- Combustion hazards
- **Detonation hazards**
- Chemical reactivity hazards
- Rapid phase transition hazards (BLEVEs)
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- Other physical hazards

Detonation hazards

Nature of hazard	Potential for generating a damaging blast wave by extremely fast chemical reaction
What is required	One of two typical mechanisms: (1) Direct initiation of a solid or liquid explosive material or mixture, or (2) Acceleration of a propagating gas-phase reaction to detonation velocity
Typical examples	(1) TNT; picric acid; unstable peroxides; commercial explosives (2) Vapor cloud explosion; flame acceleration in a long pipeline containing a flammable mixture

Detonation hazards

Possible consequences	• **Blast wave** (sometimes more than one) • Shrapnel (usually small fragments) • Toxic decomposition products See calculation example for Bursting vessel explosion hazards
Video	www.youtube.com; search term **Pepcon explosion**

Detonation hazards - Some definitions

Deflagration	A chemical reaction propagating at less than the speed of sound relative to the unreacted material immediately ahead of the reaction front.
Detonation	A chemical reaction propagating at greater than the speed of sound relative to the unreacted material immediately ahead of the reaction front.
Deflagration-to-Detonation Transition (DDT)	Increase in the propagating velocity of a chemical reaction until the velocity exceeds the speed of sound relative to the unreacted material immediately ahead of the reaction front.

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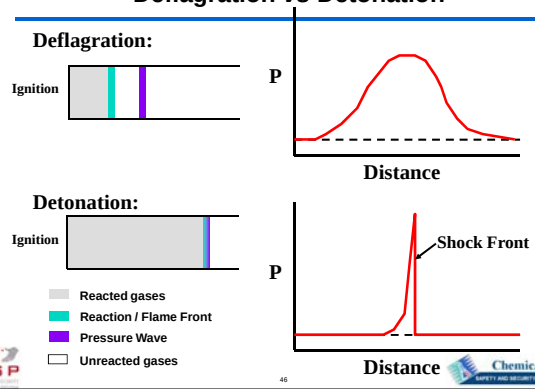
Deflagration *vs* Detonation



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Types of process hazards and potential consequences

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Chemical reactivity hazards

Nature of hazard	Potential for an uncontrolled chemical reaction that can result in loss or harm
Also known as	*Reactive chemical hazards*
What is required	Any situation where the energy and/or products released by a chemical reaction are not safely absorbed by the reaction environment
Typical examples	• Loss of control of an intended reaction • Initiation of an unintended reaction
Consequences	Fire, explosion, toxic gas release and/or hot material release

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Chemical reactivity hazards

Video	"Introduction to Reactive and Explosive Materials"
Types of chemical reactivity hazards	• Water-reactive • Oxidizing • Spontaneously combustible / pyrophoric • Peroxide forming • Polymerizing • Decomposing • Rearranging • Interacting (i.e., incompatible)
Reference	Johnson et al. 2003

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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)

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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, etc.)
- 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.)

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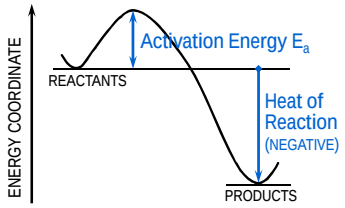
Chemical reactivity hazards

Energy diagram for exothermic chemical reaction:



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

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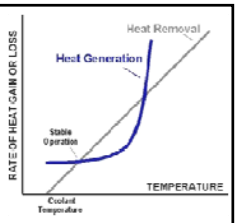
Key term to understand:

"Runaway reaction"



For an exothermic chemical reaction:

FIRST-ORDER KINETICS

$$k = A\, e^{(-E_a/RT)}$$

- Reaction rate is exponential *f* (temperature)
- 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

Chemical reactivity hazards

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

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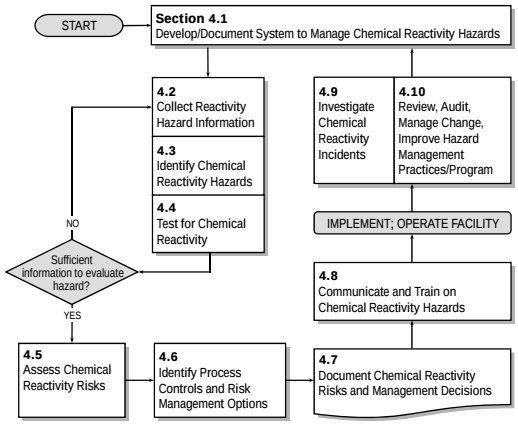
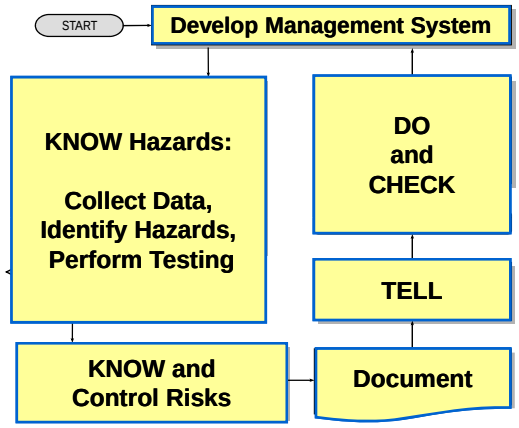
Flowchart for Implementing Chemical Reactivity Hazard Management (Johnson et al. 2003)



Flowchart for Implementing Chemical Reactivity Hazard Management (Johnson et al. 2003)



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

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Chemical reactivity hazards

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

Source: CCPS Safety Alert, "Reactive Material Hazards: What You Need to Know", 2001

Chemical reactivity hazards

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

For more details see D.C. Hendershot, "A Checklist for Inherently Safer Chemical Reaction Process Design and Operation," CCPS International Symposium, NY: AIChE, October 2002

Types of process hazards and potential consequences

- Toxicity and corrosivity hazards
- Asphyxiation hazards
- Combustion hazards
- Detonation hazards
- Chemical reactivity hazards
- **Rapid phase transition hazards (BLEVEs)**
- Bursting vessel explosion hazards
- Other physical hazards

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Rapid phase transition hazards

Nature of hazard	Near-instantaneous phase transition from liquid to gas, with large volume increase
Also known as	Boiling-liquid-expanding-vapor explosion (BLEVE)
What is required	Any liquefied gas stored under pressure above its boiling point
Typical example	Propane storage tank engulfed in fire with flame impinging on vapor space of tank, weakening the metal to point of failure
Consequences	Blast energy from both phase transition and bursting vessel; large tank fragments; huge fireball also if flammable liquid

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Rapid phase transition hazards

Videos	www.youtube.com; search term **BLEVE**
Area of effect	Can be 1 km or more, depending on size of storage tank(s)
How calculated	Calculate each mechanism separately and determine which has greatest effect; multiple mechanisms increases severity: • Bursting vessel explosion • Phase transition volume expansion • Missiles / flying debris • Fireball thermal radiation if flammable • Follow-on ("domino") effects
Reference	**CCPS 2010**

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Types of process hazards and potential consequences

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Bursting vessel explosion hazards

Nature of hazard	Near-instantaneous release of energy stored by a compressed vapor or gas
Also known as	Containment overpressurization; Vessel rupture explosion
What is required	Vapor or gas at elevated pressure inside some form of containment
Typical examples	Overpressurization of a reaction vessel from an unrelieved runaway reaction; ignition of flammable vapors in a tank
Consequences	Blast energy from bursting vessel; large vessel fragments thrown; expelling of remaining tank contents; follow-on effects

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Bursting vessel explosion hazards

Videos	www.csb.gov; several examples in Video Room, including **Explosion at T2 Labs**
Area of effect	Highly dependent on amount of stored energy at time of rupture
How calculated	Calculate each mechanism separately and determine which has greatest effect; multiple mechanisms increases severity: • Bursting vessel explosion (gas/vapor volume expansion) • Missiles / flying debris • Release of vessel contents • Follow-on ("domino") effects
References	**CCPS 2010; Crowl and Louvar 2002**

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Bursting vessel explosion hazards

One equation used for calculating blast energy:

$$W_e = R_g T\left[\ln\left(\frac{P}{P_E}\right) - \left(1 - \frac{P_E}{P}\right)\right]$$

Maximum Mechanical Energy

where W_e is the energy of explosion, P is absolute gas pressure in vessel, P_E is abs. ambient pressure, T is absolute temperature.

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Bursting vessel explosion hazards

Another equation used for calculating blast energy:

$$W_e = \frac{(P - P_E)\,V}{\gamma - 1}$$

Brode's Equation

where W_e is the energy of explosion, P is absolute gas pressure in vessel, P_E is abs. ambient pressure, V is vapor volume, and γ is the ratio of specific heats

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Bursting vessel explosion hazards

EXAMPLE

- The vapor space of a 30 m^3 flammable liquid storage tank is nitrogen-inerted.
- The nitrogen regulator fails open, exposing the tank vapor space to the full 4 bar gauge nitrogen supply pressure. The tank relief system is not sized for this failure case.
- If the tank ruptures at 4 bar gauge when it is nearly empty of liquid, how much energy is released?

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Bursting vessel explosion hazards

Data

P = 4 bar gauge = 400 Pa gauge = 501325 Pa abs

P_E = 0 bar gauge = 0 Pa gauge = 101325 Pa abs

V = 30 m^3

γ = 1.4 for nitrogen (dimensionless)

Bursting vessel explosion hazards

Calculation

Using Brode's equation:

$$W_e = \frac{(501325\ \text{N/m}^2 - 101325\ \text{N/m}^2) \cdot 30\ \text{m}^3}{1.4 - 1}$$

$$W_e = 3 \times 10^7\ \text{N-m} = 3 \times 10^7\ \text{Joules}$$

Bursting vessel explosion hazards

Comparison

TNT (trinitrotoluene) has a heat of explosion of 4686 J/g, so a blast energy of 3×10^7 J is equivalent to

3×10^7 / 4686 = 6400 g TNT = **6.4 kg TNT**

Bursting vessel explosion hazards

Consequences

Figure 6-23 in Crowl and Louvar 2001 (page 268) gives a correlation of scaled overpressure vs scaled distance.

If a control room building is 30 m away from the storage tank, the scaled distance is

$$z_e = 30\ \text{m} / (6.4\ \text{kg TNT})^{1/3} = 16.2$$

From Figure 6-23, the scaled overpressure p_s = 0.1, and the resulting overpressure is (0.1)(101 kPa) = <u>10 kPa</u>

Bursting vessel explosion hazards

Consequences

Table 6-9 of Crowl and Louvar 2001 (page 267) indicates that 10 kPa is sufficient to e.g.

- break windows
- cause serious damage to wood-frame structures
- distort the steel frame of clad buildings

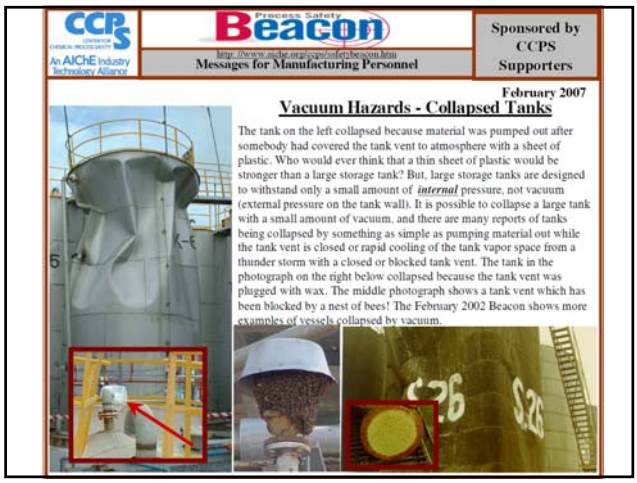
Types of process hazards and potential consequences

- Toxicity and corrosivity hazards
- Simple asphyxiation hazards
- Combustion hazards
- Detonation hazards
- Chemical reactivity hazards
- Rapid phase transition hazards (BLEVEs)
- Bursting vessel explosion hazards
- **Other physical hazards**

Other physical hazards

Physical hazard	Typical examples
Hydraulic pressure	High-pressure hydraulic fluid: *Jet spray from pinhole leak can cause severe cuts*
Vacuum	Contained sub-atmospheric pressure: *Pumping out of a tank or condensing steam with inadequate venting can cause tank implosion*

A railcar steam cleaning team went to lunch - but before they left, they put the manway back on the car on a cool and cloudy day. The steam condensed and created a vacuum.



CCPS Center for Chemical Process Safety — An AIChE Industry Technology Alliance

Process Safety Beacon

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

Messages for Manufacturing Personnel

Sponsored by CCPS Supporters

February 2007

Vacuum Hazards - Collapsed Tanks

The tank on the left collapsed because material was pumped out after somebody had covered the tank vent to atmosphere with a sheet of plastic. Who would ever think that a thin sheet of plastic would be stronger than a large storage tank? But, large storage tanks are designed to withstand only a small amount of ***internal*** pressure, not vacuum (external pressure on the tank wall). It is possible to collapse a large tank with a small amount of vacuum, and there are many reports of tanks being collapsed by something as simple as pumping material out while the tank vent is closed or rapid cooling of the tank vapor space from a thunder storm with a closed or blocked tank vent. The tank in the photograph on the right below collapsed because the tank vent was plugged with wax. The middle photograph shows a tank vent which has been blocked by a nest of bees! The February 2002 Beacon shows more examples of vessels collapsed by vacuum.

Other physical hazards

Physical hazard	Typical examples
Elevated temperature	High gas, liquid or surface temperature: *Contact with hot surface or leaking hot material can cause severe burns; prolonged exposure to high area temperature can cause heat exhaustion*
Cryogenic temperature	Liquid nitrogen; flashing liquefied gas: *Skin contact can cause cryogenic burns*

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Chemical Safety and Security Training

Other physical hazards

Physical hazard	Typical examples
Mass storage	Very large liquid storage tanks, silos: *Catastrophic failure can lead to fatalities*

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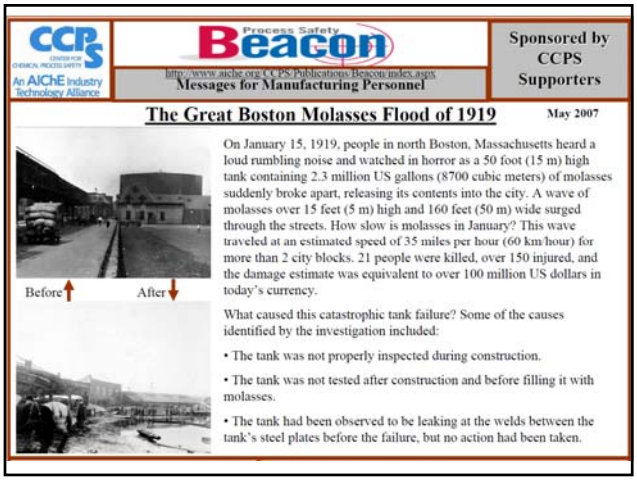
Chemical Safety and Security Training



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Process Safety Beacon

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

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The Great Boston Molasses Flood of 1919

May 2007

On January 15, 1919, people in north Boston, Massachusetts heard a loud rumbling noise and watched in horror as a 50 foot (15 m) high tank containing 2.3 million US gallons (8700 cubic meters) of molasses suddenly broke apart, releasing its contents into the city. A wave of molasses over 15 feet (5 m) high and 160 feet (50 m) wide surged through the streets. How slow is molasses in January? This wave traveled at an estimated speed of 35 miles per hour (60 km/hour) for more than 2 city blocks. 21 people were killed, over 150 injured, and the damage estimate was equivalent to over 100 million US dollars in today's currency.

Before ↑ After ↓

What caused this catastrophic tank failure? Some of the causes identified by the investigation included:

- The tank was not properly inspected during construction.
- The tank was not tested after construction and before filling it with molasses.
- The tank had been observed to be leaking at the welds between the tank's steel plates before the failure, but no action had been taken.

CCPS Process Safety Beacon (continued)

Do you know?

- You might think that an incident that occurred over 80 years ago is not relevant to today's industry. But, we still have catastrophic failures of storage tanks today (see pictures below), and for similar reasons.
- A large quantity of any liquid, even a non-hazardous material such as molasses or water, can be dangerous if rapidly released in large quantities, simply because of its volume and mass.

What You Can Do

- If you observe leakage, corrosion, or other indication of potential failure in a storage tank, report it immediately to management.
- Make sure that any new tank, or one being returned to service following repair or inactivity, is properly inspected and tested before filling.
- Ensure you know the operating capacities of your tanks and double check the level before filling.
- Don't throw out your old incident reports. Read them again, and remember the lessons. We can learn a lot from things that happened a long time ago.

January 1988 – Floreffe, Pennsylvania, USA, tank failure releases over 4 million US gallons (15,000 cu. m) of diesel oil into the Monongahela River.

January 2000 – Cincinnati, Ohio, USA, tank failure releases 365,000 gallons (1400 cu. m) of fertilizer solution into the Ohio River.

Remember the lessons of the past!

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Other physical hazards

Physical hazard	Typical examples
Obscuring vapor cloud	Acid gases, titanium tetrachloride, cryogenic liquids: *Dense vapors, dust or condensed humidity can obscure vision and lead to e.g. vehicle collisions*

$TiCl_4 + 2H_2O \rightarrow TiO_2 + 4HCl$

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Identification of Hazards and Potential Consequences

- "Process hazard" defined
- Types of hazards and potential consequences
- **Approaches and methods for systematically identifying process hazards**

US Chemical Safety Board

Approaches and methods for systematically identifying process hazards

Some "HAZID" approaches and methods:

- **Analyze material properties**
- **Analyze process conditions**
- **Use company and industry experience**
  - **Knowledge of the process chemistry**
  - **Experience at a smaller scale e.g. pilot plant**
  - **Examination of relevant previous incidents**
  - **Use relevant checklists e.g. CCPS 2008a Appx B**
- **Develop chemical interaction matrices**

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Approaches and methods for systematically identifying process hazards

Typical hazard identification results:

- List of flammable/combustible materials
- List of toxic/corrosive materials and by-products
- List of energetic materials and explosives
- List of explosible dusts
- List of hazardous reactions; chemical interaction matrix
- Fundamental hazard properties e.g. flash point, toxic endpoint
- Others e.g. simple asphyxiants, oxidizers, etc.
- Total quantities of each hazardous material
- List of chemicals and quantities that would be reportable if released to the environment
- List of physical hazards (e.g., pressure, temperature, etc.) associated with a system
- List of contaminants and process conditions that lead to a runaway reaction

Reference: CCPS 2008a, Table 3.4

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One format for a "hazard inventory"

Last Updated:	PROCESS HAZARDS

CHEMICAL PROCESS HAZARDS						Inherent Safety:
Chemical, Concentration*	Quantity Stored or Rate Processed	Volatility	Health Hazards	Flammability; Fire Hazards	Chemical Reactivity; Other Hazards	Recommendation No.

*Include materials that may have dust or mist explosion hazards, as well as toxicity, fire, explosion, and other reactivity hazards

PHYSICAL PROCESS HAZARDS						Inherent Safety:
Contained and Controlled Process Energy	Location Within or Connected To Process	Units of Measure	Range	Design	Comment	Recommendation No.
Pressurized Gas						
Hydraulic Pressure						
Vacuum						
Thermal Energy						
Radiant Energy						
Cryogenic Liquid						
Liquefied Gas						
Kinetic Energy; Material Movement						
Potential Energy; Mass Storage or Elevated Material						

One format for a "chemical interaction matrix"

Last Updated:	CHEMICAL REACTIVITY MATRIX

Abbreviation	Meaning
NR	Not reactive; no conditions identified for this process that would result in a chemical reaction between these materials
NS	No scenario identified that would result in this combination of materials coming into contact in this process
?	Unknown whether chemical reaction would occur between these materials at conditions found in this process
corr	One material corrosive to the other if these materials are combined
ht	Heat generation by chemical reaction or heat of solution; may cause pressurization if these materials are combined
R	Energetic chemical reaction, flammable gas generation, and/or toxic gas generation if these materials are combined
H#, F#, I#, W, OX	NFPA **H**ealth rating (0-4), **F**lammability rating (0-4), **I**nstability rating (0-4), vigorously or violently water reactive (**W**), oxidizer (**OX**)

Material	Abbv																												
		F_ H_ I_																											
			F_ H_ I_																										
				F_ H_ I_																									
					F_ H_ I_																								
						F_ H_ I_																							
							F_ H_ I_																						
								F_ H_ I_																					
									F_ H_ I_																				
										F_ H_ I_																			
											F_ H_ I_																		

Chemical interaction potentials based on scenarios and reactivity data listed [on separate page]

Reactivity represents only binary combinations. See ASTM E 2012, "Standard Guide for the Preparation of a Binary Chemical Compatibility Chart," for methodology and example.

Identification of Hazards and Potential Consequences

- "Process hazard" defined
- Types of hazards and potential consequences
- Approaches and methods for systematically identifying process hazards
- **Chemical hazard data**

US Chemical Safety Board

Chemical hazard data

Some sources of chemical hazardous property data:

- **Safety Data Sheets from chemical supplier**
- **Chemical-specific sources** (e.g., Chlorine Institute)
- **Many books and handbooks** (e.g., Sax, Brethericks)

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Chemical hazard data

Some internet-accessible data sources:

- **International Chemical Safety Cards**
  www.ilo.org/legacy/english/protection/safework/cis/products/icsc/dtasht/index.htm
- **CAMEO Chemicals**
  cameochemicals.noaa.gov
- **Chemical Reactivity Worksheet**
  response.restoration.noaa.gov/CRW
- **NIOSH Pocket Guide to Chemical Hazards**
  www.cdc.gov/niosh/npg
- **Wireless Information System for Emergency Responders**
  wiser.nlm.nih.gov

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DISCUSSION

- **Select a familiar type of simple chemical process**
- **Identify what *process hazards* are present; i.e., generate a hazard inventory**
- **Discuss what could happen if the hazards were not contained and controlled**

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Tea Break

Chemical
SAFETY AND SECURITY TRAINING

Inherently Safer Design

SAND No. 2011-0721P
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.

Key acronyms

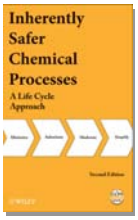
IS = *inherent safety*

ISD = *inherently safer design*

IST = *inherently safer technology*

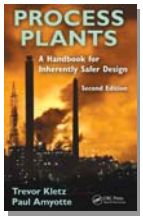
Inherent safety resources

CCPS 2008c. Center for Chemical Process Safety, ***Inherently Safer Chemical Processes: A Life Cycle Approach, 2nd Edition***. NY: American Institute of Chemical Engineers.



Inherent safety resources

T.A. Kletz and P. Amyotte 2010. ***Process Plants: A Handbook for Inherently Safer Design, 2nd Edition***. Boca Raton, Florida: CRC Press.



Inherent safety resources

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

- Inherent safety reviews
- Appendix A4: Inherently Safer Process Checklist

Inherent safety resources

DHS 2010. **"Final Report: Definition for Inherently Safer Technology in Production, Transportation, Storage, and Use." Prepared by CCPS for U.S. Department of Homeland Security. July 2010.**

On course CD-ROM

Inherently Safer Design

1. **What is "inherent safety"?**
2. **Why is it important?**
3. **What are the basic inherent safety strategies?**
4. **What are some other, related strategies?**
5. **How is it implemented in a facility's life cycle?**
6. **What are some limitations of inherent safety?**
7. **Class discussion and exercise**

Inherently Safer Design

1. **What is "inherent safety"?**

Formal definition

Inherently Safer Technology (IST), also known as ***Inherently Safer Design*** (ISD), **permanently eliminates or reduces hazards to avoid or reduce the consequences of incidents.**

DHS 2010

Formal definition (continued)

- IST is a philosophy, applied to the design and operation life cycle, including manufacture, transport, storage, use, and disposal.
- IST is an iterative process that considers such options, including eliminating a hazard, reducing a hazard, substituting a less hazardous material, using less hazardous process conditions, and designing a process to reduce the potential for, or consequences of, human error, equipment failure, or intentional harm.

ISTs are *relative*

- A technology can only be described as *inherently safer* when compared to a different technology, including a description of the hazard or set of hazards being considered, their location, and the potentially affected population.
- A technology may be inherently safer than another with respect to some hazards but inherently less safe with respect to others, and may not be safe enough to meet societal expectations.

ISTs are based on an *informed decision process*

- Because an option may be inherently safer with regard to some hazards and inherently less safe with regard to others, decisions about the optimum strategy for managing risks from all hazards are required.
- The decision process must consider the entire life cycle, the full spectrum of hazards and risks, and the potential for transfer of risk from one impacted population to another.
- Technical and economic feasibility of options must also be considered.

"The essence
of the inherently safer approach
to plant design
is the **avoidance of hazards**
rather than their control
by added-on protective equipment."

T. A. Kletz, *Plant Design for Safety: A User-Friendly Approach* (NY: Hemisphere, 1991)

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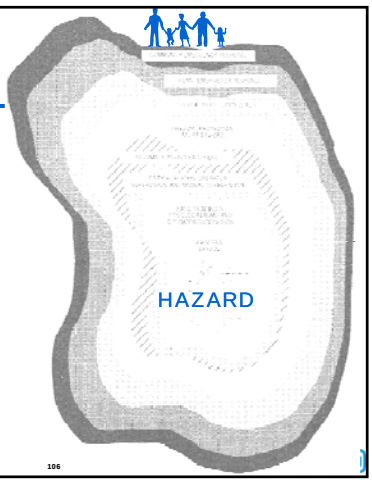
Hazard reduction



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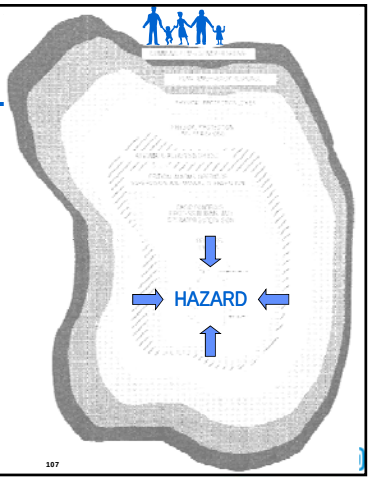
Hazard reduction



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Inherently cleaner, safer plants

Environ-mental Restoration	Waste Management	Pollution Prevention	Inherently Cleaner Processes

AFTERMATH >>>>> RELEASE >>>>> HAZARD

Accident Recovery	Mitigation	Prevention	Inherently Safer Processes

CSP

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Chemical

Inherently Safer Design

1. What is "inherent safety"?
2. **Why is "inherent safety" important?**

Inherently safer designs

permanently and inseparably reduce or eliminate process hazards that must be contained and controlled to avoid loss events.

Importance of inherent safety

- **Seminal paper by Trevor Kletz:**

"What you don't have, can't leak"

(*Chemistry and Industry,* 6 May 1978, pp 287-292)

Importance of inherent safety

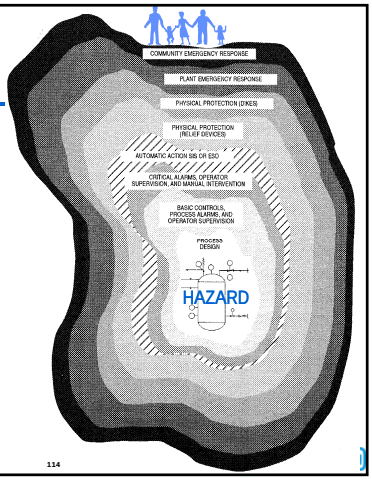
- **Security corrollary:**

What you don't have can't be stolen, ignited or intentionally released.

Importance of inherent safety

Those hazards that are not eliminated or reduced to insignificance must be managed throughout the lifetime of the facility, to avoid process incidents that can result in loss and harm.

"Layers of Protection" are needed to protect against hazards that are not eliminated



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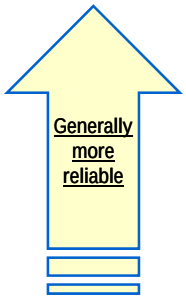
Possible inherent safety benefits

- **Reduce** the need for engineered controls and safety systems (including initial and ongoing ITM costs)
- **Reduce** labor costs and potential liabilities associated with ongoing regulatory compliance
- **Eliminate** the need for personal protective equipment associated with particular hazards
- **Reduce** emergency preparedness and response requirements
- **Improve** neighborhood / community relations

RECALL: Part of formal IST definition

- Overall safe design and operation options cover a spectrum from **inherent** through **passive**, **active** and **procedural** risk management strategies.
- There is no clear boundary between IST and other strategies.

Four types of process safety strategies



- **Inherent** - Hazard reduction
- **Passive** - Process or equipment design features that reduce risk without active functioning of any device
- **Active** - Engineering controls
- **Procedural** - Administrative controls

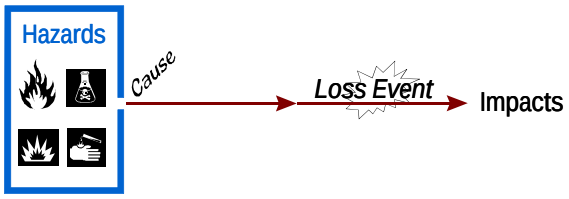
DISCUSSION

What are a couple of examples of each strategy?

- **Inherent** - Hazard reduction
- **Passive** - Process or equipment design features that reduce risk without active functioning of any device
- **Active** - Engineering controls
- **Procedural** - Administrative controls

One more vantage point

Reducing the underlying hazards...



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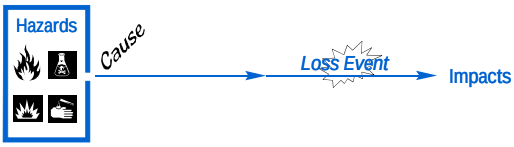
One more vantage point

… can reduce potential loss event impacts.



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Inherently Safer Design

1. What is "inherent safety"?
2. Why is it important?
3. **What are the basic inherent safety strategies?**

Basic inherent safety strategies

CCPS 2008:	*Kletz and Amyotte 2010:*
Minimize	Intensify
Substitute	Substitute
Moderate	Attenuate
Simplify	Limit Effects
	Simplify

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Basic inherent safety strategies

CCPS 2008:		*Kletz and Amyotte 2010:*
Minimize	⟷	Intensify
Substitute	⟷	Substitute
Moderate	⟷	Attenuate
Simplify	⟷	Limit Effects
		Simplify

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Basic inherent safety strategies

Focus in this course:

Minimize
Substitute
Attenuate

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Basic inherent safety strategies

Focus in this course:

Minimize

Substitute

Attenuate

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RECALL: Part of formal IST definition

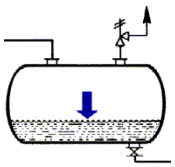
- IST is an iterative process that considers such options, including **eliminating a hazard, reducing a hazard**, substituting a less hazardous material, using less hazardous process conditions, and designing a process to reduce the potential for, or consequences of, human error, equipment failure, or intentional harm.

Minimize

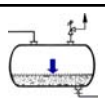
To *minimize* is to reduce the amount of potential energy present

(i.e., get the system closer to a zero energy state),

thus reducing the potential impacts if containment or control of the hazard is lost.



Minimize



Some strategies for making a process inherently safer by *minimization*:

- **Inventory reduction; e.g.,**
  - **less material stored**
  - **fewer tanks; just-in-time delivery**
  - **less vapor volume**
  - **generate on demand** (chlorine, MIC, ammonia, hydrogen...)
  - **receive by pipeline instead of by truck or rail**
- **Process intensification**
- **Process operation closer to ambient conditions**

Minimize

Some strategies for making a process inherently safer by *minimization*:

- Inventory reduction; e.g.,
  - less material stored ⟸ *requires administrative control*
  - fewer tanks; just-in-time delivery
  - less vapor volume
  - generate on demand (chlorine, MIC, ammonia, hydrogen...)
  - receive by pipeline instead of by truck or rail
- Process intensification
- Process operation closer to ambient conditions

Minimize

Ultimate case:

- Elimination of the hazard; e.g.,
  - Eliminating use of a particular hazardous material
  - Operating the system at a zero energy state with respect to a particular hazard
  - Shutting down the process
  - Using a toll manufacturer (risk *transfer*)

DISCUSSION

- An inherent safety review recommends eliminating intermediate storage of a hazardous raw material:

Raw Material Manufacture → Raw Material Usage

- What are the inherent safety benefits?
  -
  -
- What are the possible drawbacks?
  -
  -

Basic inherent safety strategies

Focus in this course:

Minimize

Substitute

Attenuate

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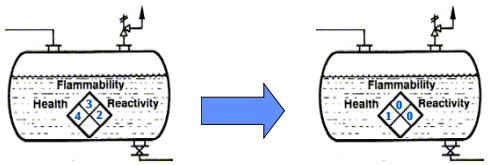
RECALL: Part of formal IST definition

- IST is an iterative process that considers such options, including eliminating a hazard, reducing a hazard, **substituting a less hazardous material,** using less hazardous process conditions, and designing a process to reduce the potential for, or consequences of, human error, equipment failure, or intentional harm.

Substitute

To *substitute* is to replace with a less hazardous material or condition.



Substitute

Some strategies for making a process inherently safer by *substitution*:

- **Commercially available alternatives**
- **Alternative raw material or intermediate that can be transported and stored more safely**
- **Alternative chemistry**
  - Propylene oxidation process instead of Reppe process for manufacture of acrylic esters
  - Biosynthesis routes

Substitute

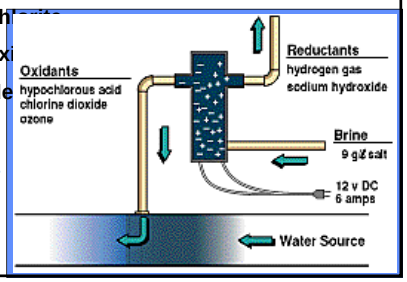
Some chlorine alternatives:

- **Sodium hypochlorite**
- **Calcium hypochlorite**
- **Hydrogen peroxide**
- **Chlorine dioxide**
- **Bromine**
- **Mixed oxidants**

Substitute

Some chlorine alternatives:

- Sodium hypochlorite
- Calcium hypochlorite
- Hydrogen peroxide
- Chlorine dioxide
- Bromine
- Mixed oxidants



Substitute

Oleum alternative:

- Sulfur burning to generate SO_3 on demand

Substitute

Solvent substitutes:

- Water-based paints, adhesives
- Aqueous cleaning systems
- Less volatile solvents; higher flash point
- Dibasic esters for paint stripping

Web resources are available

- E.g., "Substitutes in Non-Aerosol Solvent Cleaning," http://www.epa.gov/ozone/snap/solvents/solvents.pdf

Basic inherent safety strategies

Focus in this course:

Minimize

Substitute

Attenuate

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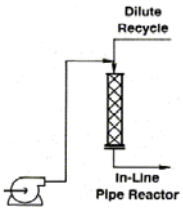
RECALL: Part of formal IST definition

- IST is an iterative process that considers such options, including eliminating a hazard, reducing a hazard, substituting a less hazardous material, **using less hazardous process conditions,** and designing a process to reduce the potential for, or consequences of, human error, equipment failure, or intentional harm.

Attenuate

To *attenuate* (or *moderate*) is to handle a material under less hazardous process conditions.



Attenuate

To *attenuate* (or *moderate*) is to handle a material under less hazardous process conditions.

<u>Note</u>: Available energy may be the same, but potential loss event impacts can be reduced

Attenuate

Some strategies for making a process inherently safer by *attenuation*:

- **Dilution**
  - **E.g., using in aqueous instead of anhydrous form**
  - **Using in solution such that the solute would boil off before a runaway reaction temperature was achieved**
  - **Lower concentration of benzoyl peroxide in paste**
  - **Mixing coal dust with rock dust**
- **Refrigeration**
  - **E.g. storing anhydrous ammonia as a refrigerated liquid instead of as a liquefied gas**

Inherently Safer Design

1. What is "inherent safety"?
2. Why is it important?
3. What are the basic inherent safety strategies?
4. **What are some other, related strategies?**

RECALL: Part of formal IST definition

- IST is a philosophy, applied to the design and operation life cycle, including manufacture, transport, storage, use, and disposal.
- IST is an iterative process that considers such options, including eliminating a hazard, reducing a hazard, substituting a less hazardous material, using less hazardous process conditions, and **designing a process to reduce the potential for, or consequences of, human error, equipment failure, or intentional harm**.

Basic inherent safety strategies

CCPS 2008:	*Kletz and Amyotte 2010:*
Minimize	Intensify
Substitute	Substitute
Moderate	Attenuate
Simplify	Limit Effects
	Simplify

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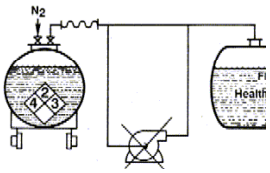
Simplify

To *simplify* is to eliminate unnecessary complexity.



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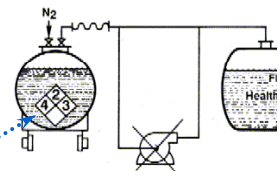
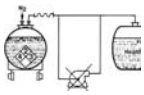


(Not "first-order" inherent safety, since the underlying hazard is still there.)

Simplify

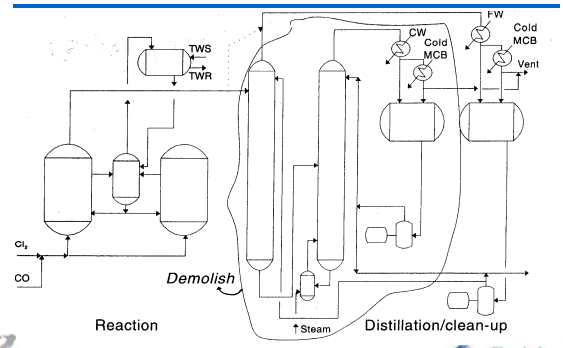


Some *simplification* strategies:

- Use simpler equipment arrangement
  - E.g., gravity flow
  - Natural convection
- Eliminate interconnections to reduce the likelihood of inadvertent mixing
- Minimize number of flanges, connections, and other potential leak locations

Simplification of Dow Phosgene Unit for MDI Production

R. Gowland, "Applying Inherently Safer Concepts to a Phosgene Plant Acquisition," *Process Safety Progress 15*(1), 57



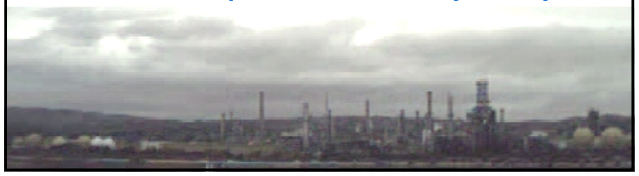
Limit Effects

The greatest opportunity to limit effects is generally by increasing the *distance* between the potential loss event location and the people, property and environment that could be affected.

CGA, *Handbook of Compressed Gases*

Inherently Safer Design

1. What is "inherent safety"?
2. Why is it important?
3. What are the basic inherent safety strategies?
4. What are some other, related strategies?
5. **How is it implemented in a facility's life cycle?**



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- IST is an **iterative process** that considers such options, including eliminating a hazard, reducing a hazard, substituting a less hazardous material, using less hazardous process conditions, and designing a process to reduce the potential for, or consequences of, human error, equipment failure, or intentional harm.

Two basic IS activities

1. **Design and build inherent safety into a process**
2. **Continually look for ways to reduce or eliminate hazards throughout the process life cycle**

Two basic IS activities - By Whom?

1. **Design and build inherent safety into a process**
   [INHERENT SAFETY REVIEWS / R&D / ENGINEERING]
2. **Continually look for ways to reduce or eliminate hazards throughout the process life cycle**
   [INHERENT SAFETY REVIEWS / PHAs / ENGINEERING]

Inherent safety reviews

Most effective life cycle phases to review a process process for opportunities to make it inherently safer (CCPS 2008a):

- **R&D**
- **Conceptual design**
- **Detailed engineering**
- **Routine operation**

(Members of review team will vary depending on life cycle phase)

Inherent safety reviews

Typical inherent safety review steps (CCPS 2008a):

1. **Collect and review background information**
2. **Identify / define / document the major hazards**
3. **Review the process flow schematic**
   - **Look at each process step and hazardous material**
   - **Identify creative ways to improve the process by applying inherently safer principles to reduce or eliminate hazards**
4. **Document the review and follow-up actions**

Inherent safety reviews

Good resource for IS reviews (CCPS 2008a, Appx. A4):

"An Inherently Safer Process Checklist"

1 Intensification / Minimization

1.1 Do the following strategies reduce inventories of hazardous raw materials, intermediates, and/or finished products?
- Improved production scheduling
- Just-in-time deliveries
- Direct coupling of process elements
- Onsite generation and consumption

1.2 Do the following actions minimize in-process inventory?
- Eliminating or reducing the size of in-process storage vessels
- Designing processing equipment handling hazardous materials for the smallest feasible inventory
- Locating process equipment to minimize the length of hazardous material piping runs
- Reducing piping diameters

1.3 etc.

Inherently Safer Design

1. What is "inherent safety"?
2. Why is it important?
3. What are the basic inherent safety strategies?
4. What are some other, related strategies?
5. How is it implemented in a facility's life cycle?
6. **What are some limitations of inherent safety?**

CAUTION

Inherently Safer* does not necessarily mean *lower risk!

- Process change may introduce new hazards
  - E.g., hydrogen gas generated by hydrolysis
- Loss event likelihood may be affected
  - E.g., Supplying from many small cylinders instead of one large cylinder increases frequency of connecting and disconnecting cylinders
- Loss event severity can also be affected
  - E.g., total containment increases burst pressure

DISCUSSION

Situation: You need to travel from a city at one part of the country to the most distant large city.

Your options: Travel by land or travel by commercial airline.

- Which option is *inherently safer* ?
- Which option has *lower risk* ?

Airline travel

HAZARDS:

- **Potential energy** (34,000 ft altitude; heavy objects in overhead bins)
- **Kinetic energy** (600 mph; other planes; rotating turbines/propellers)
- **Chemical energy** (fuel in tanks; hazmats in cargo; fire potential)
- **Temperature** (cold air outside; hot coffee inside)
- **Pressure** (low pressure outside)
- **Reduced oxygen**
- **Increased radiation**
- **Other people** (security threats; drunken or angry passengers)

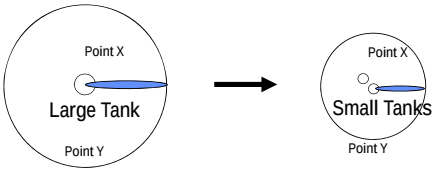
Inherently Safer Design

1. What is "inherent safety"?
2. Why is it important?
3. What are the basic inherent safety strategies?
4. What are some other, related strategies?
5. How is it implemented in a facility's life cycle?
6. What are some limitations of inherent safety?
7. **Class discussion and exercise**

DISCUSSION: Volatile toxic liquid storage

Situation: One stakeholder wanted one large storage tank, another stakeholder wanted two smaller storage tanks.

Second stakeholder's rationale: Worst-case impact is half as serious.



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EXERCISE

1 Select a familiar type of simple chemical process from your industry

2 Identify at least three specific ideas for making the process inherently safer

3 Discuss whether any of the approaches might actually increase safety or security risk

WRAP-UP DISCUSSION

- What are some major challenges to implementing inherent safety principles?
- How might these be overcome?

WRAP-UP DISCUSSION

- Do inherent safety principles also apply to *facility security*?

Chemical
SAFETY AND SECURITY TRAINING

Process Equipment Inspection and Testing

SAND No. 2011-0798C
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.

Key acronyms

MI = *mechanical (asset) integrity*

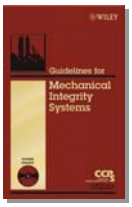
ITM = *inspections, testing, maintenance*

PM = *preventive maintenance*

MMS = *maintenance management system*

Resource

CCPS 2006. Center for Chemical Process Safety, ***Guidelines for Mechanical Integrity Systems***, NY: American Institute of Chemical Engineers.



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

CCPS 20 — An AIChE Industry Technology Alliance

Process Safety Beacon

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

Messages for Manufacturing Personnel

Sponsored by CCPS Supporters

Mechanical Integrity

April 2006

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.

BEFORE

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)

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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

8. Equipment-specific issues

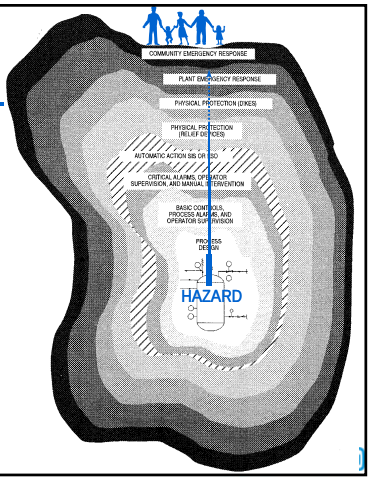
Equipment Inspections and Testing

1. Understand the importance of plant equipment PM

"Layers of Protection" between hazards and receptors

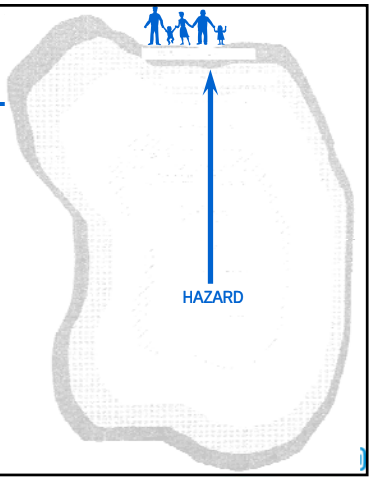
=

"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

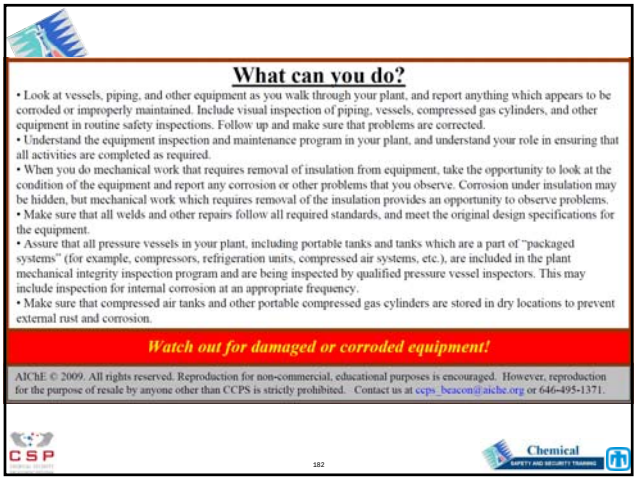
Messages for Manufacturing Personnel

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!

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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

"Swiss cheese model"

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

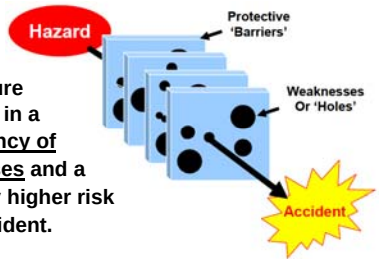
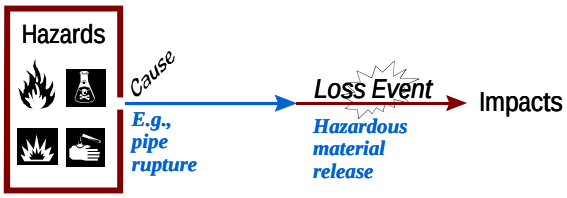


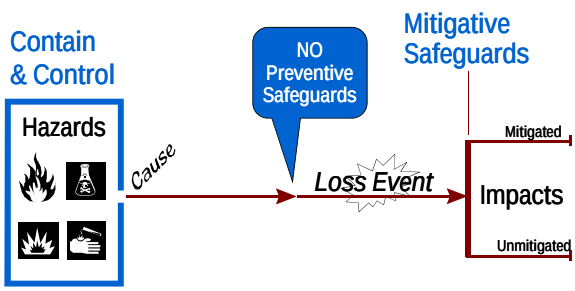
Image credit: CCPS, "Process Safety Leading and Lagging Indicators," New York: American Institute of Chemical Engineers, December 2007, www.aiche.org/ccps. "Swiss cheese model" originally proposed by James Reason, U. Manchester, 1990.

Typical loss-of-containment incident

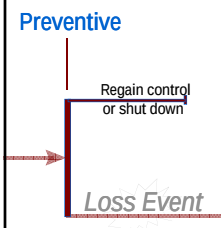
Typical loss-of-containment incident



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

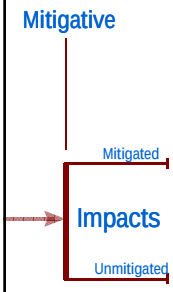
τ = failure duration

Quantification of safeguard reliability

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

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**

Equipment Inspections and Testing

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

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

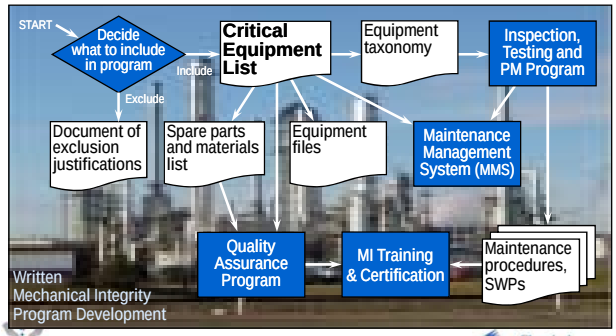


Image Credit: DHS Chemical Security Awareness Training

Equipment Inspections and Testing

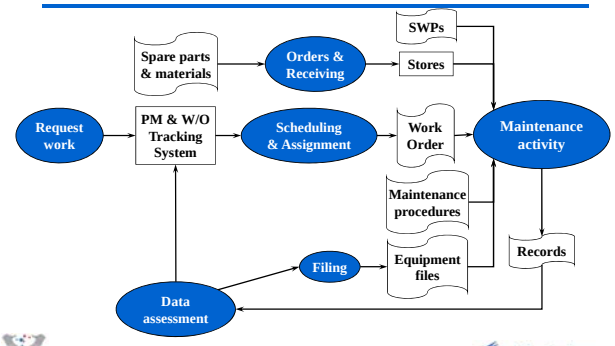
1. Understand the importance of plant equipment PM
2. Determine what needs to be maintained
3. **Put in place a system of how it will be maintained**

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**

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

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

How often must ITMs be performed?

PRINCIPLES:

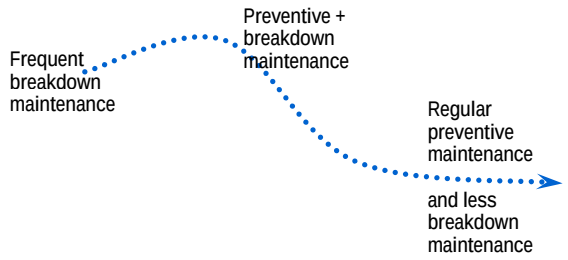
- ITM frequencies must be pre-established
- **Some frequencies are experience-adjusted**
  - Problems found: Do ITMs <u>more often</u>
  - Good experience: Do ITMs <u>less often</u> if allowed

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!***

Getting over the hump



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**

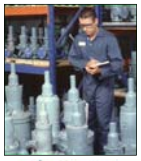
Maintenance procedures and training

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

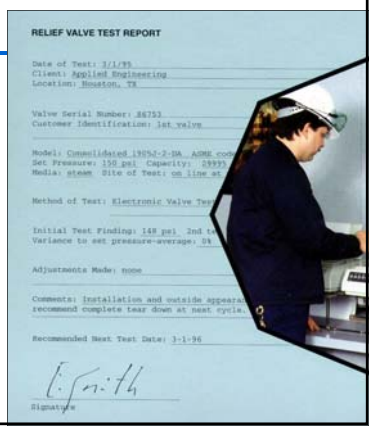
ITM documentation will be equipment-specific.

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



Equipment Inspections and Testing

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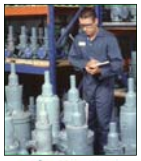

Working definitions

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!

Equipment Inspections and Testing

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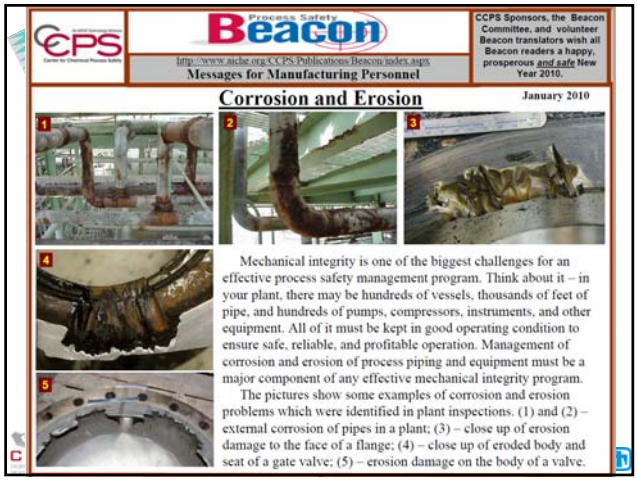
6. Document ITMs
7. Correct identified deficiencies

8. **Equipment-specific issues**



CCPS Process Safety Beacon

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

Messages for Manufacturing Personnel

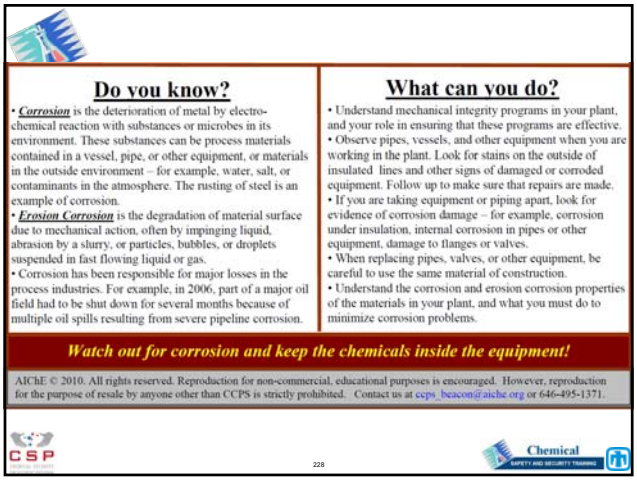
CCPS Sponsors, the Beacon Committee, and volunteer Beacon translators wish all Beacon readers a happy, prosperous and safe New Year 2010.

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!

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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.

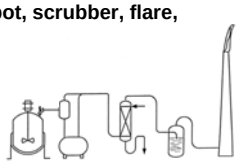
Reference: *Guidelines for Vapor Release Mitigation*
(New York: American Institute of Chemical Engineers, 1988)

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

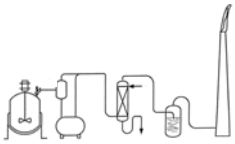
(relief valve, rupture disk, vent valve, header, cyclone separator, knockout pot, scrubber, flare, thermal oxidizer, etc.)



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.)**
- **<u>Scheduled functional tests</u>**
  - **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

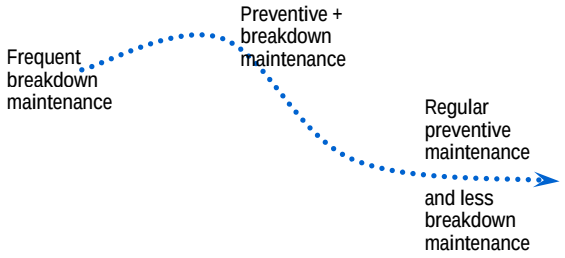
Primary ITM activities:

- **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



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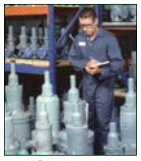

Chemical
SAFETY AND SECURITY TRAINING

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.
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Key acronyms

PHA = *process hazard analysis*

HAZOP = *hazard and operability [study]*

FMEA = *failure modes & effects analysis*

LOPA = *layer of protection analysis*

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Hazard and risk analysis resources

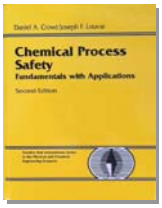
CCPS 2008a. Center for Chemical Process Safety, *Guidelines for Hazard Evaluation Procedures, Third Edition*, NY: American Institute of Chemical Engineers.

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

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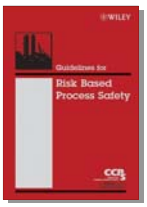
Hazard and risk analysis resources

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 Analysis
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

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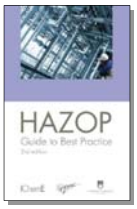
Hazard and risk analysis resources

B. Tyler, F. Crawley and M. Preston 2008.
***HAZOP: Guide to Best Practice, 2nd Edition*,**
Institution of Chemical Engineers, Rugby, UK.



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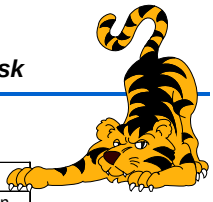
Hazard and Risk Analysis

- **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 vs *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 vs *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

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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.**

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Already addressed

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- **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 <u>collective past experience</u>**
- **Compare process with recognized and generally accepted good engineering practices (RAGAGEPs)**

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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**

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Experience-based approaches

Example experience-based approaches:

- **Safety Review**
- **Checklist Analysis**

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Experience-based approaches

Example experience-based approaches:

- Safety Review
- **Checklist Analysis**

Code/Standard/Reg.

1.1 The owner/operator shall …

1.2 The owner/operator shall …

1.3 The owner/operator shall …

→

Checklist

- r Item 1
- r Item 2
- r Item 3
- r Item 4

…

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

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Scenario necessary ingredients:

- Initiating cause

AND

- Loss event or safe outcome

"Cause - consequence pair"

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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?*

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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.

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Predictive studies

Objective of scenario-based approaches:

- Identify and analyze <u>all</u> 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

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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)

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Hazard and Risk Analysis

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

What-If Analysis

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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)
- Process divided up into "segments" (e.g., unit operations)
- Review from input to output of process
- Question formulation left up to the team members

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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.

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Adequacy of safeguards

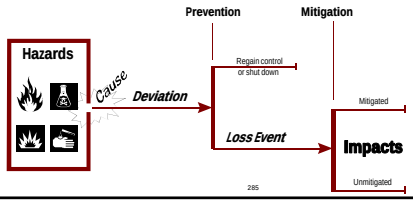
- Determining the adequacy of safeguards is done on a scenario-by-scenario basis
- *Scenario risk* is a function of:
  - Initiating cause frequency
  - Loss event impact
  - Safeguards effectiveness
- If the *scenario risk* is found to be too high, safeguards are considered inadequate
  - Qualitative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



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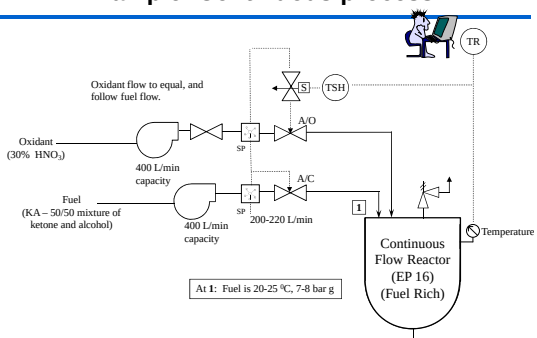
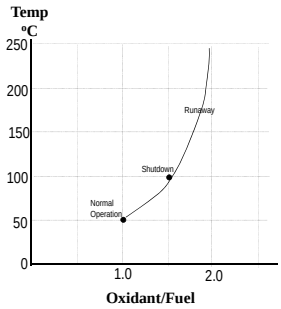
Example: Continuous process



(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.



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PROCESS SEGMENT:	SCOPE:		What-If Analysis
REVIEW DATE:	INTENT:		
What If …	**Consequences**	**Safeguards**	**Finding/Recommendation** Comments

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PROCESS SEGMENT:	SCOPE:		What-If Analysis
REVIEW DATE:	INTENT:		
What If …	**Consequences**	**Safeguards**	**Finding/Recommendation** Comments

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PROCESS SEGMENT:	SCOPE:		What-If Analysis
REVIEW DATE:	INTENT:		
What If …	**Consequences**	**Safeguards**	**Finding/Recommendation** Comments

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Hazard and Operability Study

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HAZOP Study

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

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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

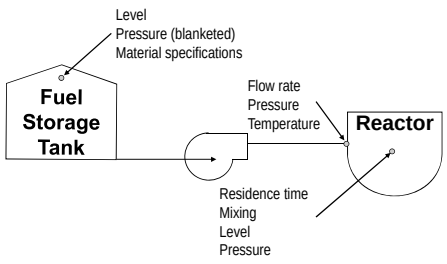
Study nodes

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 ºC 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 °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.

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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

Guide Words → INTENT

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

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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**

Guide Words → INTENT → ***Deviation***

Deviations

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

Cause

Deviation

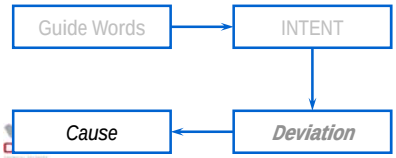
- No Flow
- Low Temperature
- **High Pressure** ***(exceed upper limit of normal range)***
- Less Material Added
- Excess Impurities
- Transfer to Wrong Tank
- Loss of Containment
- etc.

HAZOP Deviations Guide

Design Intent *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"	NO / NONE	MORE OF	LESS OF
	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

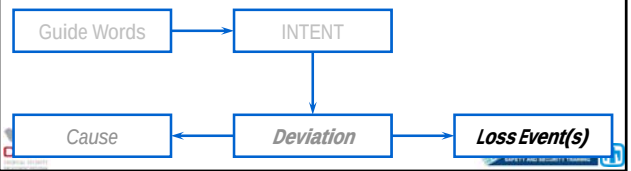
Initiating causes

- **Identify deviation cause(s)**
  - **Must look backward in time sequence**
  - **Only identify local 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**



Loss events

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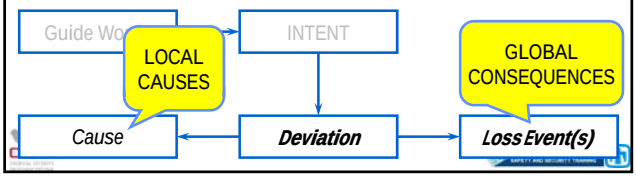
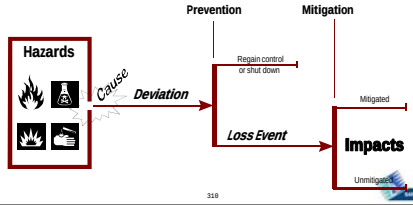


Safeguards

- 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

REVIEW DATE	NODE: SCOPE: INTENT:	HAZOP Study

Guide Word	Deviation	Cause	Consequences	Safeguards	Finding/Recommendation Comments

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REVIEW DATE	NODE: SCOPE: INTENT:	HAZOP Study

Guide Word	Deviation	Cause	Consequences	Safeguards	Finding/Recommendation Comments

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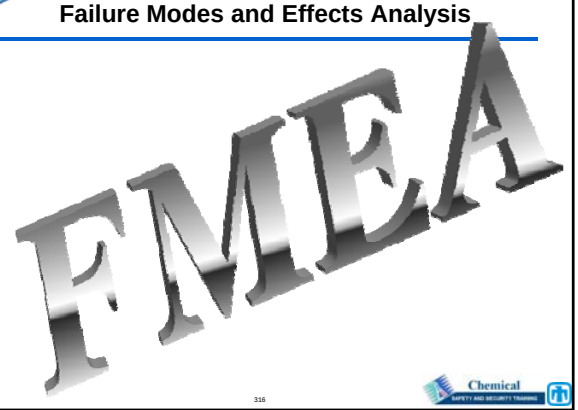
Node 1 Review Date:	Fuel Transfer Line SCOPE: From fuel supply to EP16 inlet, including fuel pump and fuel flow control loop INTENT: Feed fuel (50/50 KA mix) at 50-55 gpm, 20-25 C and 100-120 psig from fuel supply system to reactor EP-16			HAZOP Study
Guide Word, Deviation	**Cause**	**Consequences**	**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



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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
- Check valve
- Float switch
- Agitator

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: | P&ID: | FMEA

Component ID	Component Description	Failure Mode	Immediate to Ultimate Effects	Safeguards	Finding/Recommendation Comments

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REVIEW DATE | System: | P&ID: | FMEA

Component ID	Component Description	Failure Mode	Immediate to Ultimate Effects	Safeguards	Finding/Recommendation Comments

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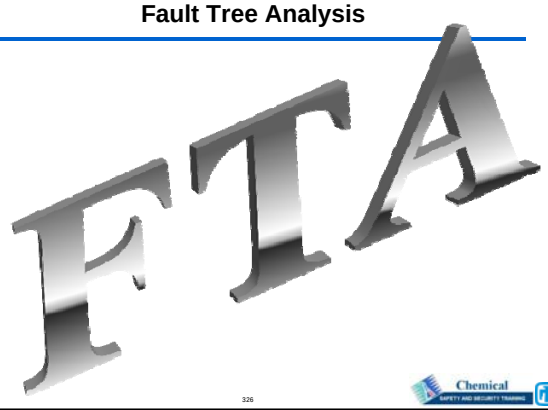
Hazard and Risk Analysis

- 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

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

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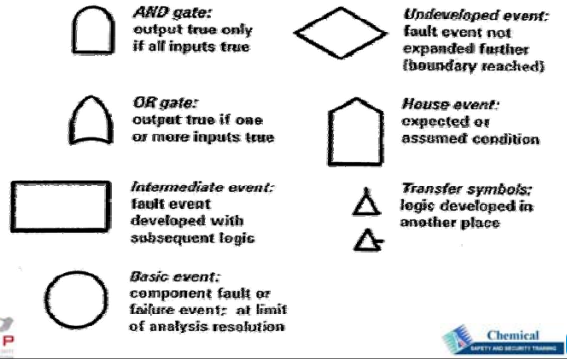
Fault tree symbols



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

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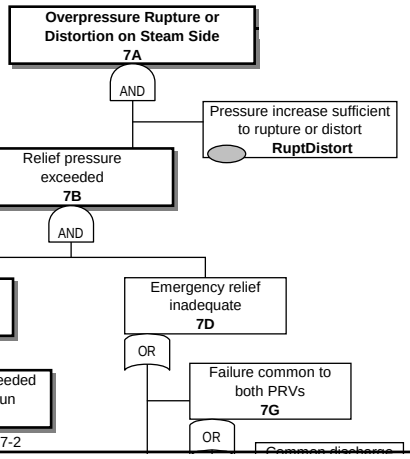
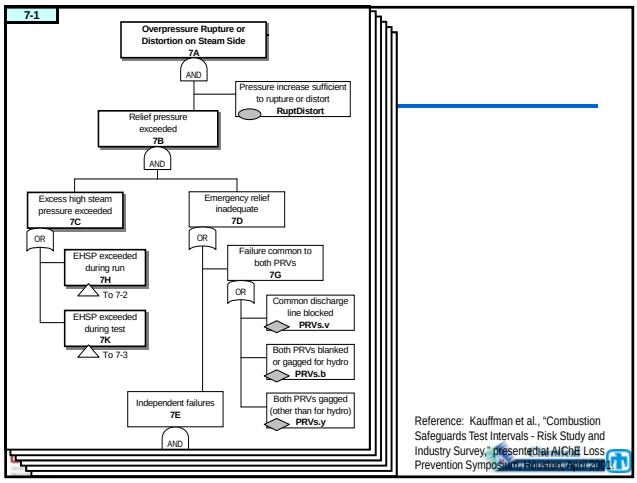
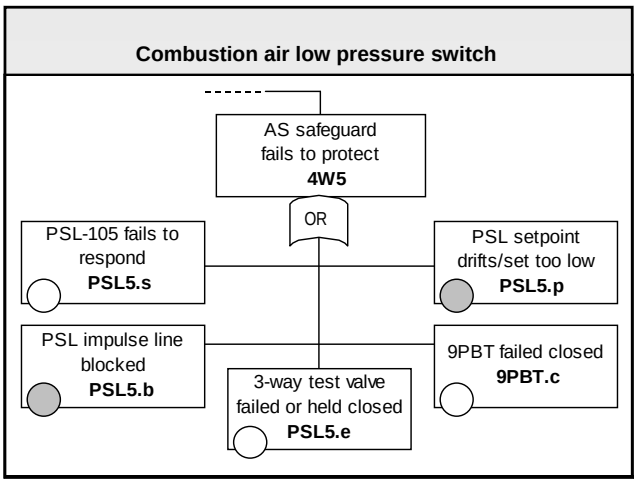
Fault Tree TOP Event







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.

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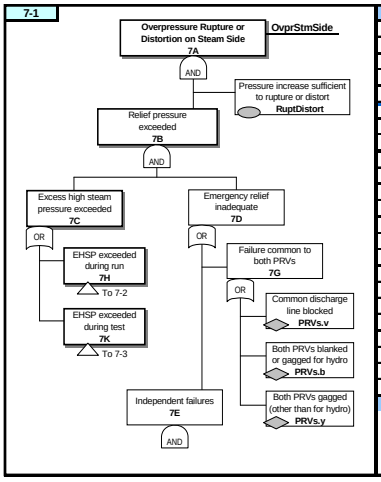


Type	Name	Freq (/yr)	Dur (h)	Prob
Conseq	OvprStmSide	1.3E-06		
AND	7A	1.3E-06		
	RuptDistort			1
AND	7B	1.3E-06		
OR	7C	0.0071		
OR	7D			0.00018
	7H	0.0006		
	7K	0.0065		
OR	7E			8.E-05
OR	7G			1E-04
OR	7F1			0.0091
OR	7F2			0.0090
	PRVs.v			0
	PRVs.b			0.0001
	PRVs.y			0
	PRV1.v	0.004	4400	0.00201
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

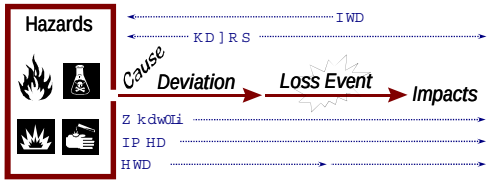
1. hydro = hydrotest
2. PRV settings: PRV1, 180 psig; PRV2, 185 psig
3. PRVs tested once/year, by either bench testing or testing in place

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

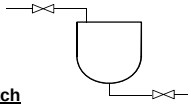
- Batch processes
- Continuous processes:
  - Start-up
  - Shutdown
  - Production changes
- Receipt and unloading of chemicals
- Loading of product
- Sampling
- Maintenance

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

PHA of continuous operations

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

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

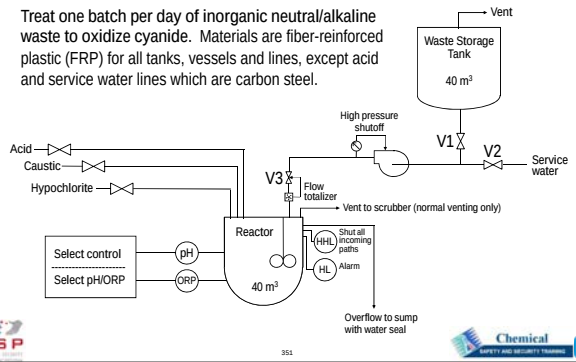
Give one or two examples of a deviation from a procedural step for each HAZOP guide word.

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

Tea Break

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.



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Example batch process

Procedure:

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.

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"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.

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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**

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PROCESS SEGMENT:

REVIEW DATE:

SCOPE:

INTENT:

What-If Analysis

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.			

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PROCESS SEGMENT:

REVIEW DATE:

SCOPE:

INTENT:

What-If Analysis

What If …	Consequences	Safeguards	Finding/Recommendation Comments

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PROCESS SEGMENT:

REVIEW DATE:

SCOPE:

INTENT:

What-If Analysis

What If …	Consequences	Safeguards	Finding/Recommendation Comments

REVIEW DATE

NODE:

SCOPE:

INTENT:

HAZOP Study

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.					

REVIEW DATE

NODE:

SCOPE:

INTENT:

HAZOP Study

Guide Word	Deviation	Cause	Consequences	Safeguards	Finding/Recommendation Comments

REVIEW DATE

NODE:

SCOPE:

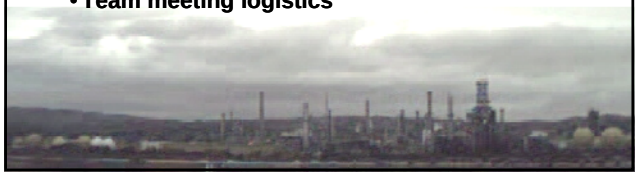
INTENT:

HAZOP Study

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**

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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.**

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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

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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

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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

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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

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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

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First team review meeting

2 **Scope and objectives**

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

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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

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

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

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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)

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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)

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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)

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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

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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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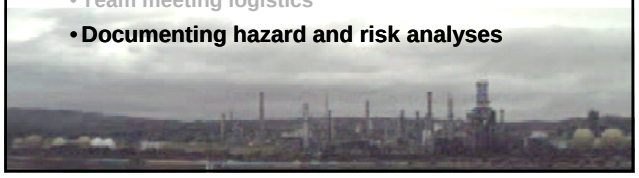
Hazard and Risk Analysis

- 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

<u>Goal</u>: 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

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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

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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

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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**

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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.
- Basis 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…
  - _____…

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

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:

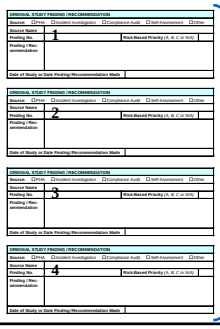
ORIGINAL STUDY FINDING / RECOMMENDATION			
Source: ☐ PHA ☐ Incident Investigation ☐ Compliance Audit ☐ Self-Assessment ☐ Other			
Source Name			
Finding No.		**Risk-Based Priority** *(A, B, C or N/A)*	
Finding / Rec-ommendation			
Date of Study or Date Finding/Recommendation Made			

Note that this can also be used for incident investigation and compliance audit findings.

2 - Present findings & recommendations

PHA team

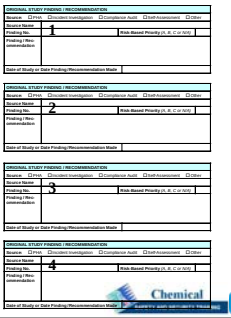
Line management



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	[date]	*Time extension requires management approval*
Responsible Person	[person or position]	

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 / Rec-ommendation	*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		

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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)*

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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**

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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**

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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

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DISCUSSION

WHY?

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

-
-
-
-

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Final word

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

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