Hazards and Potential Consequences

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

Key acronyms

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

VCE = *vapor cloud explosion*

LFL = *lower flammable limit*

LOC = *limiting oxygen concentration*

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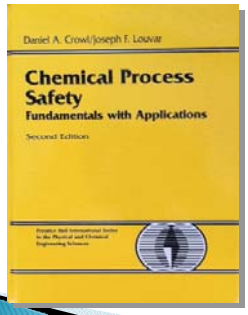
Resources

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**

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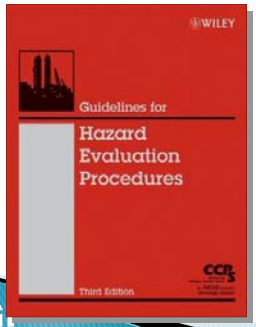
Resources

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

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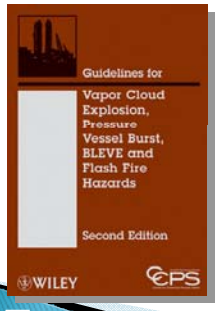
Resources

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



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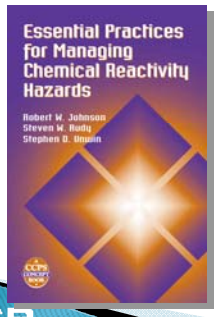
Resources

Johnson et al. 2003. *Essential Practices for Managing Chemical Reactivity Hazards,* NY: AIChE, 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

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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**

Types of process hazards & 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.

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Types of process hazards & potential consequences

- Toxicity and corrosivity hazards
- Simple asphyxiation hazards
- Combustion hazards
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Toxicity/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/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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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 colorless and odorless.

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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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 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 & potential consequences

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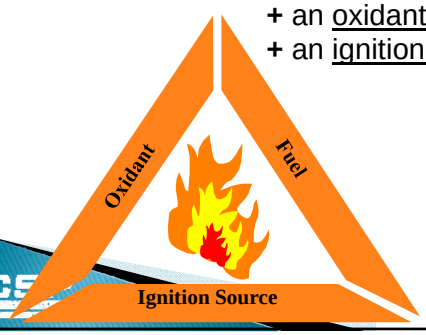
Combustion hazards

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

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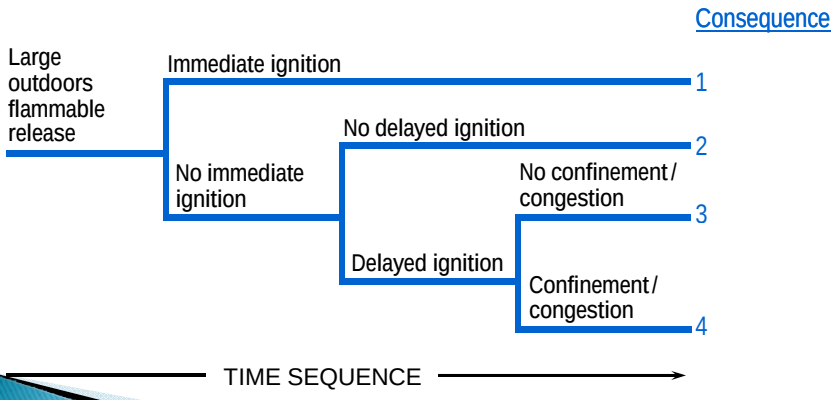
EXERCISE

Describe each of the four possible outcomes.



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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.

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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

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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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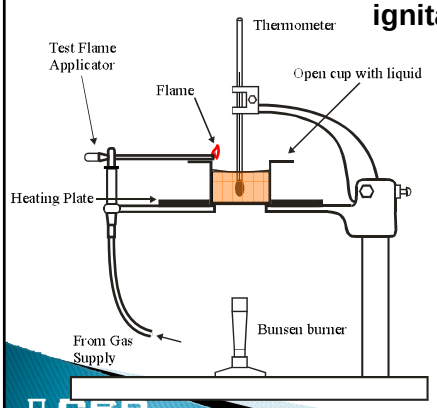
Flash point

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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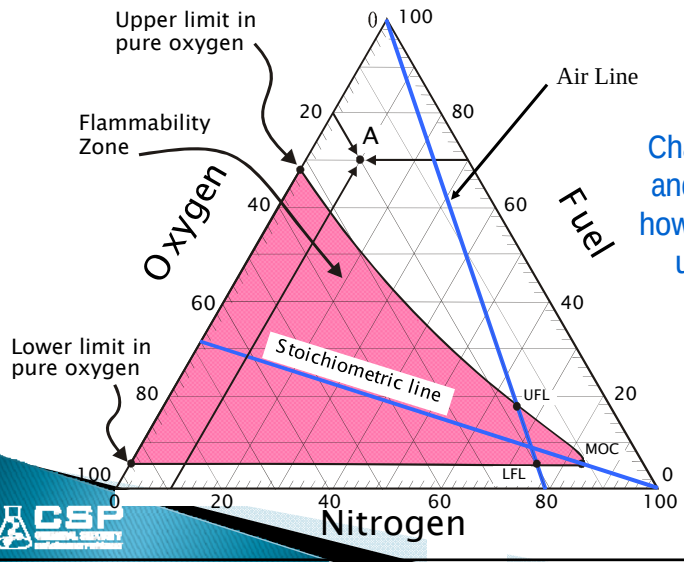
Flammability diagram



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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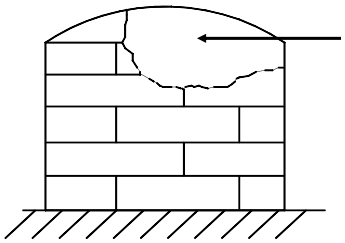
Inerting and purging

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**

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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

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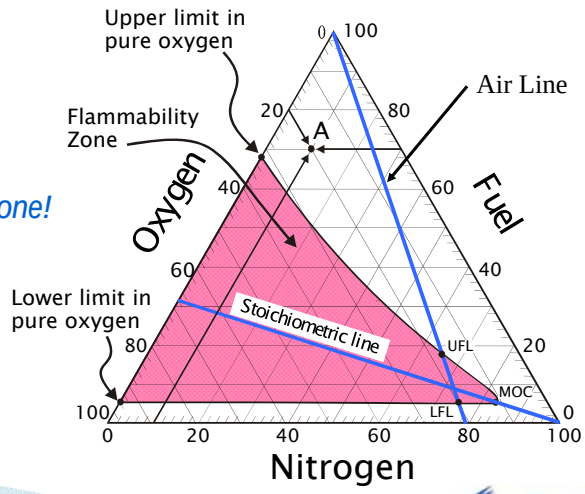
Flammability diagram

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
- Chemical Sources
  - Catalytic materials
  - Pyrophoric materials
  - Thermite reactions
  - Unstable chemical species formed in system
- Physical sources
  - Adiabatic compression
  - Heat of adsorption
  - Friction
  - Impact

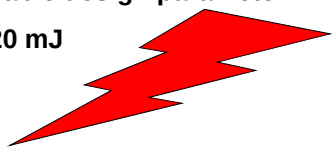
Minimum ignition energy

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.**

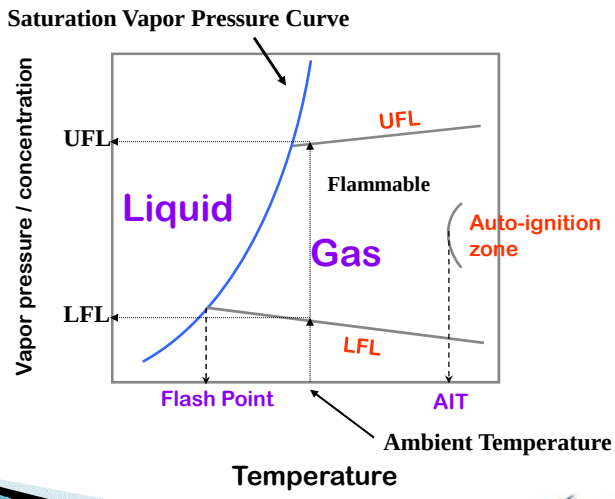
Example values:

	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**

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Types of process hazards & potential consequences

- Toxicity and corrosivity hazards
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- Other physical hazards

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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

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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**

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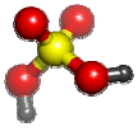

Some definitions

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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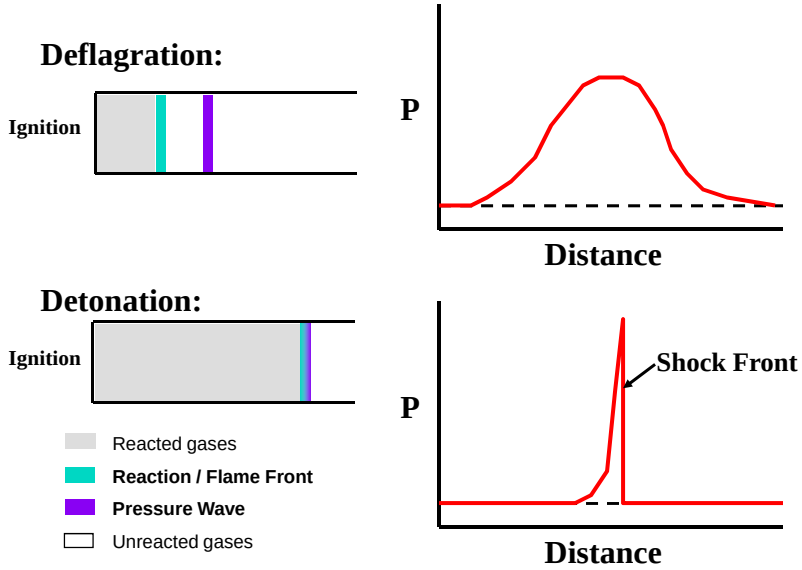
Deflagration *vs* Detonation



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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 <u>intended</u> reaction • Initiation of an <u>unintended</u> 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 ***See also:*** Day 3 presentation on Chemical Reactivity 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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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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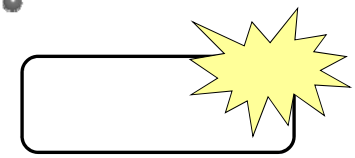
Bursting vessel explosion hazards



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:

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

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

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

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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>

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Bursting vessel explosion hazards

Consequences

Table 6-9 of Crowl and Louvar 2001 (p. 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

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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*

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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.

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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

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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*

CSP

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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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CCPS Process Safety Beacon

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

Messages for Manufacturing Personnel

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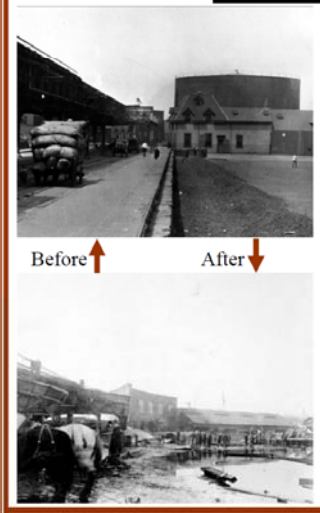
The Great Boston Molasses Flood of 1919

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.

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.

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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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Chemical SAFETY AND SECURITY TRAINING

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						

A "chemical interaction matrix" format

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															

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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Inherently Safer Design

Bandung, Indonesia
March 2012

SAND No. 2011-0720P

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

Key acronyms

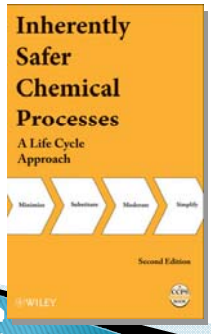
IS = *inherent safety*

ISD = *inherently safer design*

IST = *inherently safer technology*

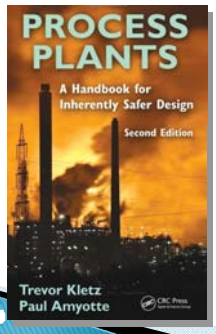
Inherent safety resources

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



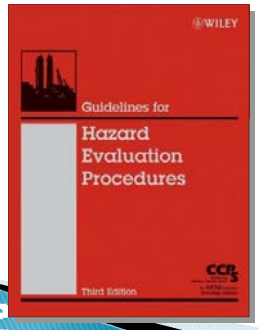
Inherent safety resources

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: AIChE.



- 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. Dept. of Homeland Security. July.

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"?
2.
3.
4.
5.
6.
7.

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*

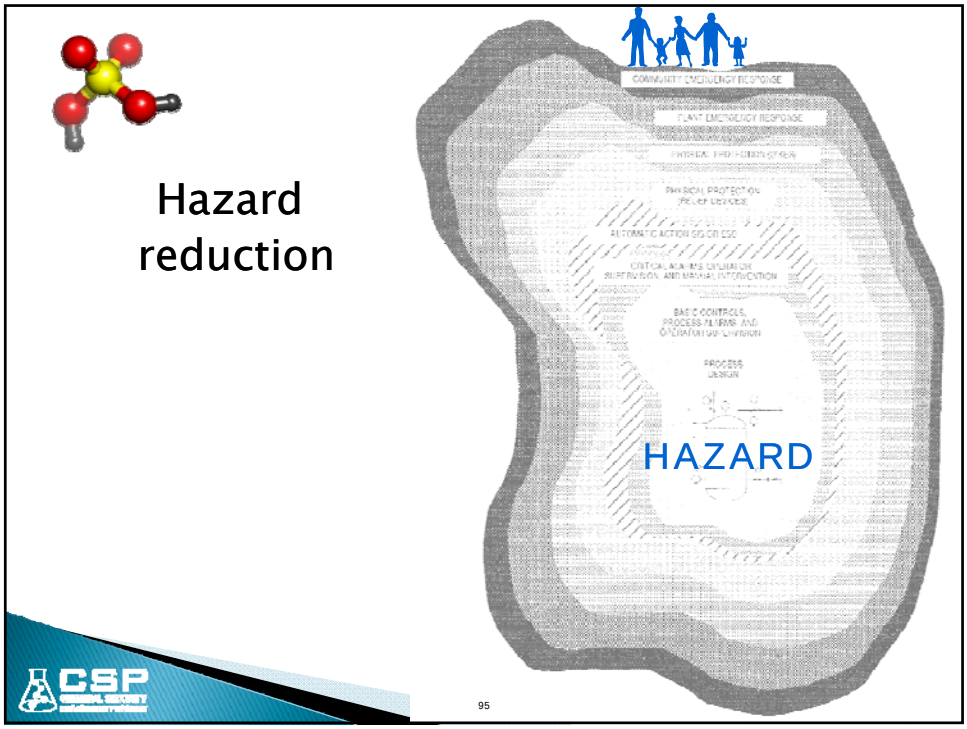
- A technology can only be described as *inherently safer* when compared to a different technology, including a description of the hazard or set of hazards being considered, their location, and the potentially affected population.
- A technology may be inherently safer than another with respect to some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

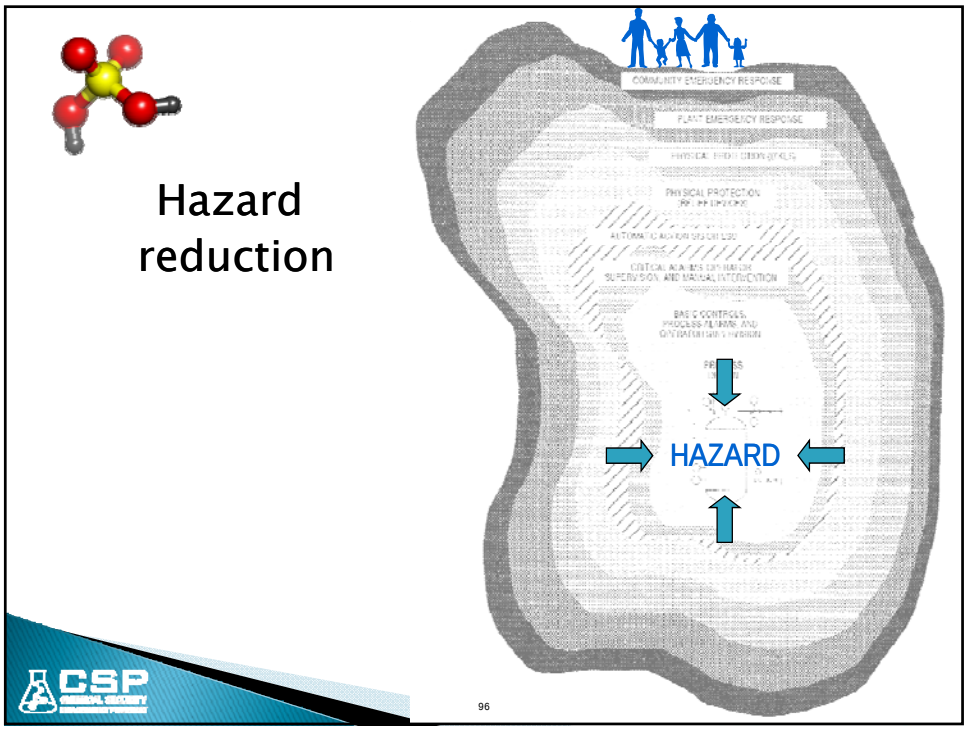
ISTs are based on an *informed decision process*

- 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)


Hazard reduction
COMMUNITY EMERGENCY RESPONSE
PLANT EMERGENCY RESPONSE
PHYSICAL PROTECTION (RELIEF DEVICES)
AUTOMATIC ACTION SYSTEMS
CRITICAL ALARMS OPERATOR SUPERVISION AND MANUAL INTERVENTION
BASIC CONTROLS, PROCESS ALARMS AND OPERATOR SUPERVISION
PROCESS DESIGN
HAZARD
CSP
95


Hazard reduction
COMMUNITY EMERGENCY RESPONSE
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CRITICAL ALARMS OPERATOR SUPERVISION AND MANUAL INTERVENTION
BASIC CONTROLS, PROCESS ALARMS AND OPERATOR SUPERVISION
HAZARD
CSP
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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

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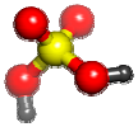
Inherently Safer Design

1. What is "inherent safety"?
2. Why is "inherent safety" important?
3.
4.
5.
6.
7.

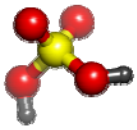


Inherently safer designs

permanently and inseparably

reduce or eliminate process hazards

that must be contained and controlled to avoid loss events.



Importance of inherent safety

- Ground-breaking 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

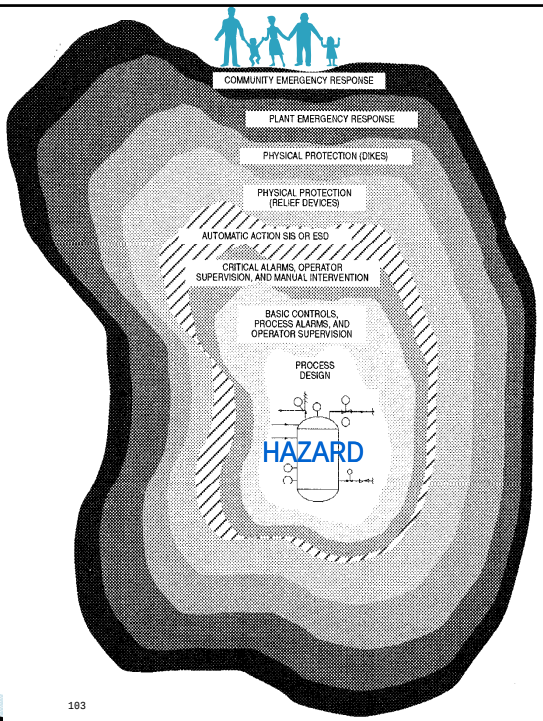
- Security corollary:

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

Importance of inherent safety

Those hazards that are <u>not</u> 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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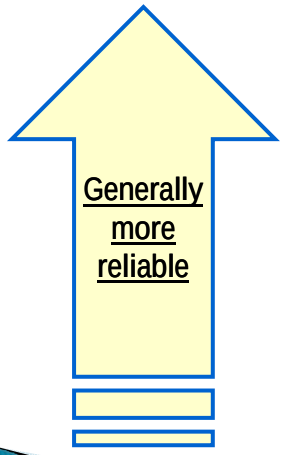
Inherent safety benefits

- 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

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.

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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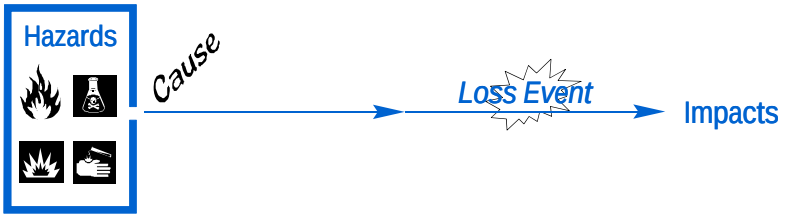
One more vantage point

… can reduce potential loss event impacts.



Inherently Safer Design

1. What is "inherent safety"?
2. Why is it important?
3. **What are the basic inherent safety strategies?**
4.
5.
6.
7.

Inherent safety strategies

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

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Inherent safety strategies

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

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Inherent safety strategies

Focus in this course:

Minimize

Substitute

Attenuate

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Inherent safety strategies

Focus in this course:

Minimize

Substitute

Attenuate

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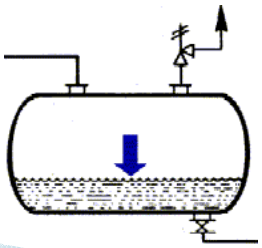
Part of formal IST definition

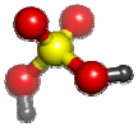
- IST is an iterative process that considers such options, including eliminating a hazard, reducing a hazard, substituting a less hazardous material, using less hazardous process conditions, and designing a process to reduce the potential for, or consequences of, human error, equipment failure, or intentional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

Minimize

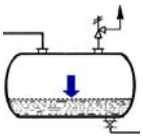
To *minimize* is to reduce the amount of potential energy present (i.e., get the system closer to a zero energy state),

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





Minimize

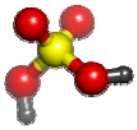


Some strategies for making a process inherently safer by *minimization*:

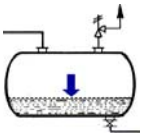
- Inventory reduction; e.g.,
  - less material stored
  - fewer tanks; just-in-time delivery
  - less vapor volume
  - generate on demand (chlorine, MIC, ammonia, hydrogen...)
  - receive by pipeline instead of by truck or rail
- Process intensification
- Process operation closer to ambient conditions

CSP

Chemical SAFETY AND SECURITY TRAINING



Minimize

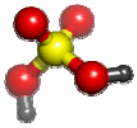


Some strategies for making a process inherently safer by *minimization*:

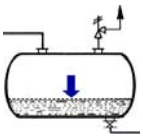
- Inventory reduction; e.g.,
  - less material stored ⇦ *requires administrative control*
  - fewer tanks; just-in-time delivery
  - less vapor volume
  - generate on demand (chlorine, MIC, ammonia, hydrogen...)
  - receive by pipeline instead of by truck or rail
- Process intensification
- Process operation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

CSP

Chemical SAFETY AND SECURITY TRAINING

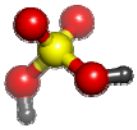


Minimize



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?
  -
  -

Inherent safety strategies

Focus in this course:

Minimize

Substitute

Attenuate

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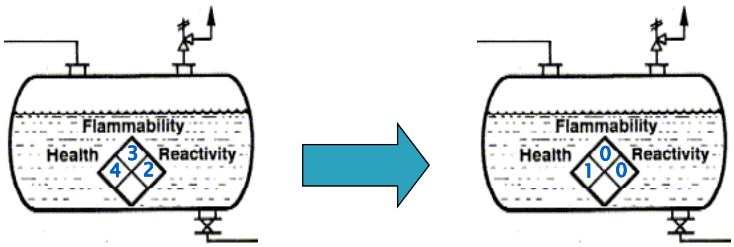
Part of formal IST definition

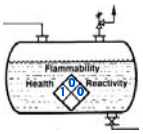
- IST is an iterative process that considers such options, including eliminating a hazard, reducing a hazard, substituting a less hazardous material, using less hazardous process conditions, and designing a process to reduce the potential for, or consequences of, human error, equipment failure, or intentional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

Substitute

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

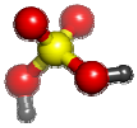


Substitute

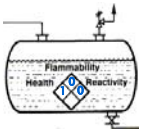


Some strategies for making a process inherently safer by *substitution*:

- 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

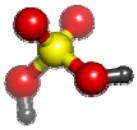


Some chlorine alternatives: Cl_2

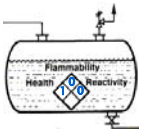
- Sodium hypochlorite
- Calcium hypochlorite
- Hydrogen peroxide
- Chlorine dioxide
- Bromine
- Mixed oxidants

CSP

Chemical SAFETY AND SECURITY TRAINING



Substitute



Some chlorine alternatives: Cl_2

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

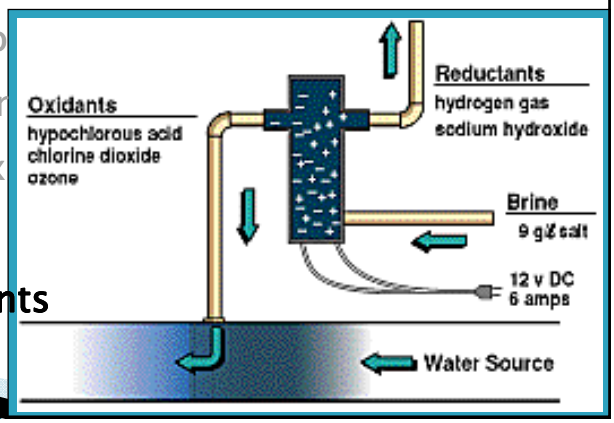
CSP

Chemical SAFETY AND SECURITY TRAINING

Substitute

Some chlorine alternatives: Cl_2

- Sodium hypochlorite
- Calcium hypo
- Hydrogen per
- Chlorine diox
- Bromine
- **Mixed oxidants**

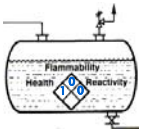


Substitute

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," www.epa.gov/ozone/snap/solvents/solvents.pdf

Inherent safety strategies

Focus in this course:

Minimize

Substitute

Attenuate

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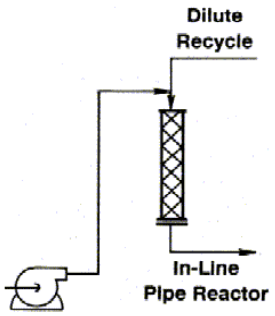
Part of formal IST definition

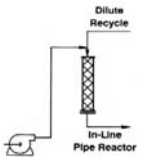
- IST is an iterative process that considers such options, including eliminating a hazard, reducing a hazard, substituting a less hazardous material, using less hazardous process conditions, and designing a process to reduce the potential for, or consequences of, human error, equipment failure, or intentional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

Attenuate

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



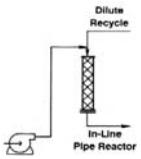
Attenuate



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

Note: 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?
5.
6.
7.

Part of formal IST definition

- IST is a philosophy, applied to the design and operation life cycle, including manufacture, transport, storage, use, and disposal.
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Inherent safety strategies

CCPS 2008:

Minimize
Substitute
Moderate
Simplify

Kletz and Amyotte 2010:

Intensify
Substitute
Attenuate
Limit Effects
Simplify

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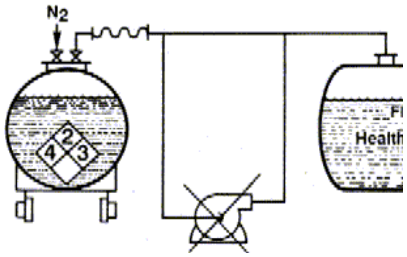
Simplify

To *simplify* is to eliminate unnecessary complexity.



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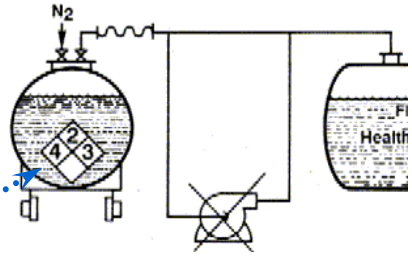
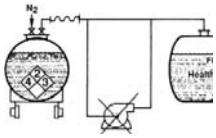


(Not "first-order" inherent safety, since the underlying hazard is still there.)

Simplify

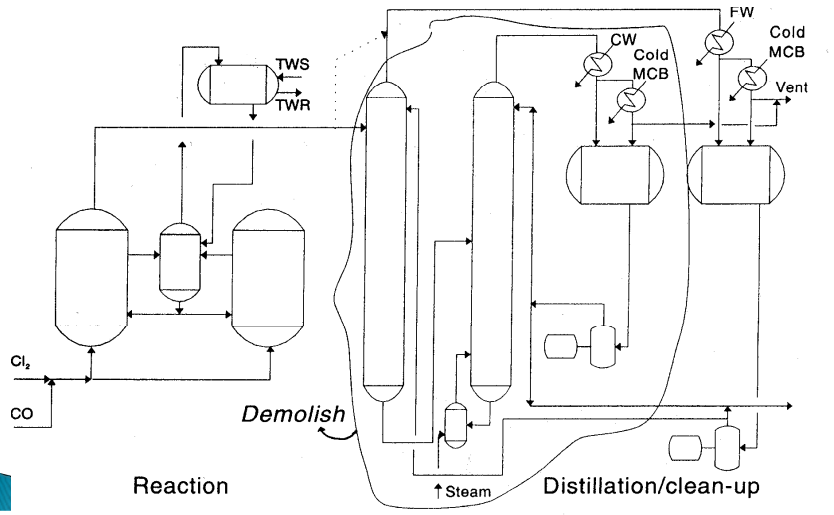


Some *simplification* strategies:

- **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**

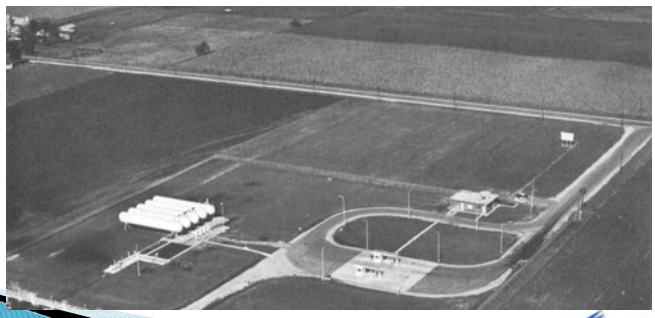
Simplification of Dow Phosgene Unit for MDI Production

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"?
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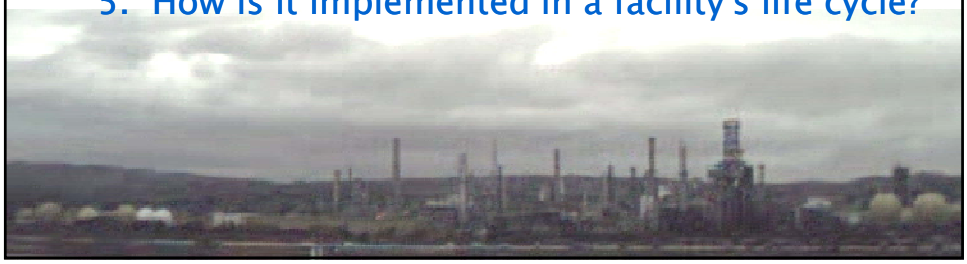
5. How is it implemented in a facility's life cycle?



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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 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.

CSP

Chemical SAFETY AND SECURITY TRAINING

Inherently Safer Design

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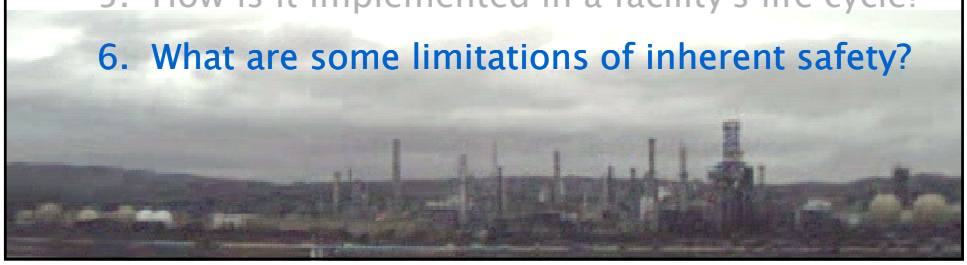
4. What are some other, related strategies?
5. How is it implemented in a facility's life cycle?
6. What are some limitations of inherent safety?



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

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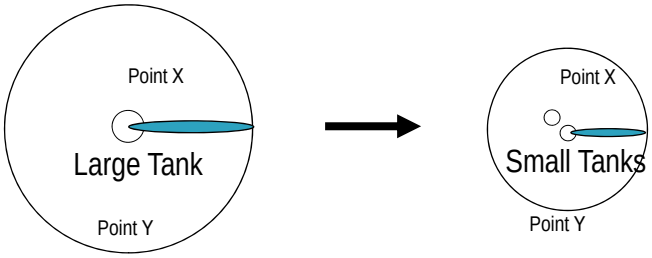
6. What are some limitations of inherent safety?
7. Class discussion and exercise

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 <u>inherently safer</u>

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*?