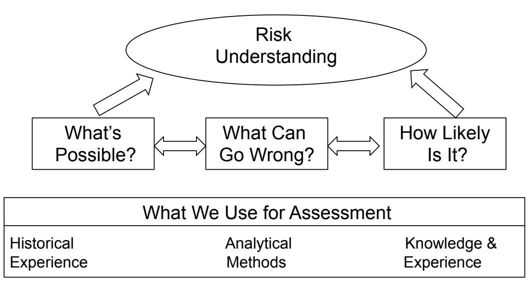
Process Safety Management of Highly Hazardous & Explosive Chemicals

NC OSHA PSM Training
Process Hazards

What Should We Expect to See at An Employer?

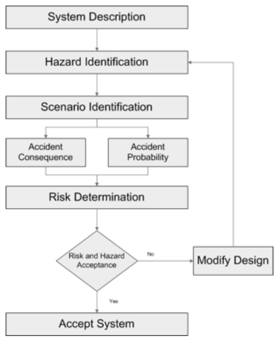
A Good Understanding of the Process Hazards & Risks



We Must Know Safe Operation Envelope

- **Safe operation envelope is determined/developed/ defined entirely by an assembly of:**

1. **Chemical/Physical Hazards**
2. **Reactivity Hazards**
3. **Properties of materials**
4. **Corrosivity Hazards**
5. **Process technology**
6. **Equipment design**



HIRA Logic Diagram Source: CCPS Boot Camp Training

Chemical Hazards

Process Hazards Elements

Hazards We Must Understand & Consider

What Are the Hazards?

5 |

Process Hazards Inventories we Must Consider

- Flammable Liquids
- Combustible Liquids
- Unstable Materials
- Corrosive Materials
- Asphyxiates
- Highly Reactive Materials
- Toxic Materials
- Combustible Dusts

Physical Conditions We Must Consider

- High Temps
- Cryogens
- High Pressure
- Vacuum
- Pressure & Temperature Cycling
- Vibration
- High Voltage
- Radiation

Pressure Vessel Hazards & Safeguards

CSB – Without Safeguards

Chemical Hazards

Process Hazard Initiating Causes

What Can Cause It to Happen?

Initiating Causes
Containment Failures (LOPC)

- Pipes
- Ducts
- Tanks & Vessels
- Flex Hoses
- Sight Glasses
- Gaskets / Seals

Initiating Causes
Equipment Failure

- Pumps
- Compressors
- Agitators
- Valves
- Instrumentation
- Control Failures
- Trips / Vents / Reliefs
- Corrosion

Corrosion

NDK Crystal

Initiating Causes
Loss of Utilities

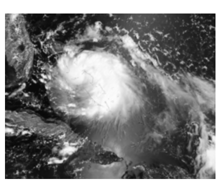
- Power
- Nitrogen Blankets or Purges
- Water
- Refrigeration
- Heat
- Steam
- Ventilation

Initiating Causes
Human Factors

- Operations
- Maintenance
- Safe Work Practices

Initiating Causes
External Events

- Vehicle / Equipment Impact
- Weather Events
- Earthquakes
- Adjacent Operation Hazard Exposure
- Vandalism / Sabotage / Terrorism



Chemical Hazards

Process Hazard Incident Outcomes

What Would be the Result?

Incident Outcomes Release or Discharge

- Pool Fires
- Jet Fires
- Flash Fires
- Fireballs

What Can Go Wrong?

- Flash Fire
  - Occurs when a cloud of flammable gas is ignited in air
  - Progresses rapidly and engulfs the entire cloud
  - May generate slight overpressure
  - Can ignite pool fires or jet fires
  - May develop into an explosion in confined location

What Can Go Wrong?

- Fireball
  - Combustion of a large, fuel-rich vapor cloud
  - Intense radiation is released over a brief time span, generally 10 to 15 seconds
  - Burning takes place from the outside in
  - Fireball rises due to thermal buoyancy
  - Size and duration of a fireball determined by the flammable mass released

What Can Go Wrong?

- Explosion Definitions
  - **Explosion**: a very sudden release of energy resulting in a shock or pressure wave
  - **Shock, Blast or Pressure Wave**: pressure wave that causes damage
  - **Deflagration:** reaction wave speed is less than the speed of sound
  - **Detonation:** reaction wave speed is greater than the speed of sound
  - **Fundamental or Laminar Burning Velocity**: burning rate which is an inherent characteristic of a specific gas at T and P
  - **Flame Speed:** rate of expansion of flame front in a combustion reaction

What Can Go Wrong?

- Pressure Piling
  - Usually occurs in multiple vessels connected by piping
  - Ignition in one vessel or a pipe could send accelerated flame front to a second vessel which results in a higher ultimate pressure in the second vessel
  - Could result in transition from deflagration to detonation

What Can Go Wrong?

- Types of Explosions
  - Vapor cloud explosion
  - BLEVE
  - Mist/Aerosol/Dust Explosion
  - Physical explosion from overpressure

What Can Go Wrong?

- Vapor Cloud Explosions
- **Within Refining and Petrochemicals over the last 50 years there have been 250 VCEs. This is compared to hundreds of millions of safe operating years.**
  - **There is a VCE within industry every 10 weeks**
  - **There is a major VCE within industry (Multiple fatalities) every 3 years**

What Can Go Wrong?

- Vapor Cloud Explosion
  - High energy release associated with rapid burning of a flammable vapor/air mixture
  - Subsonic flame progression (deflagration)
  - Usually followed by fire
  - Requires large mass of flammable vapor or flashing liquid
  - **Physical confinement is required to produce overpressure**
  - **Overpressure is a function of degree of congestion**
  - **For the same congestion level, High Reactive fuels will develop a stronger explosion than low reactive fuels (acetylene, hydrogen, ethylene).**
  - Only the quantity of material within the cloud in a confined area is involved in the explosion
  - A one to two minute delayed ignition is usually required (immediate ignition: fire only)
  - Wind may cause vapor cloud to drift into a confined area (also disperses the cloud and reduces flammable mass)

What Can Go Wrong?

- BLEVE – Boiling Liquid Expanding Vapor Explosion
  - Flame impingement on a vessel results in mechanical failure followed by the sudden release of the process fluid
    - Below liquid level, wall is cool
    - Above liquid level, wall heats and weakens
    - Physical rupture - shrapnel
    - Rapid release of superheated liquid
    - If flammable – fireball with intense radiation
    - Vapor explosion possible with overpressure
    - Pool fire – residual liquid

What Can Go Wrong?

- BLEVE Videos – You Tube

Combustible Dust

Combustible Dusts

- **Chemical Safety Board (CSB) Dust Incident Study 2006**
  - 281 combustible dust incidents (over 25 year period ending in 2005)
  - 119 fatalities, 718 injuries, millions of dollars in lost facilities and productivity
  - Included 7 catastrophic dust explosions in the past decade
  - Did not include Imperial Sugar

Combustible Dust

1/29/03 - West Pharmaceutical – Kinston, NC

6 fatalities, 38 injuries, and destroyed the facility

Combustible Dust

2/30/03 - CTA Acoustics – Corbin, KY

7 fatalities, 37 injuries

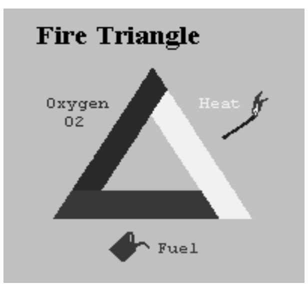
Combustible Dust

2/7/08 - Imperial Sugar – Port Wentworth, GA

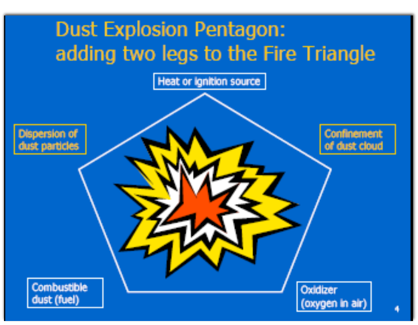
14 fatalities and numerous injuries

Combustible Dust

Fire Triangle – a Review

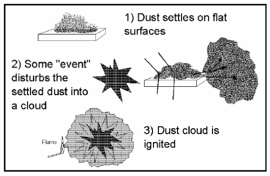


Combustible Dust



Combustible Dust

- Primary event initiates
  - Usually localized issue
  - Can still have large impact
- Secondary event
  - Catastrophic losses
  - Made possible through dust accumulations
    - Suspended ceilings
    - Floors, tables, ceiling beams, etc.



Combustible Dust

- **Hazard Management Options**
  - Depends largely on physical properties of dust (fines)
  - “Break a Leg” of the pentagon
    - Fuel (accumulations of 1/32” over surface area of at least 5% of the floor area (up to 1000 ft^2), including overhead beams, joists, ducts, tops of equipment, etc.)
    - Ignition source (bonding/grounding, elimination of non-conductives, insulators, electrical classification, limited free flow product, equipment maintenance, foreign metal elimination)
    - Oxygen (oxygen exclusion)
    - Dispersion (metered feeding, housekeeping)
  - If you can’t break a leg –
    - Deflagration containment
    - Relief and Isolation
    - Suppression systems

Combustible Dust

- **Physical Properties**
  - **Flammable, Explosive, Combustible** – for dusts, all the same
  - **MIE – Minimum Ignition Energy** - Predicts the ease and likelihood of ignition of a dispersed dust cloud
  - **MEC – Minimum Explosive Concentration** - Measures the minimum amount of dust, dispersed in air, required to spread an explosion. Analogous to LFL. NOT RECOMMENDED AS A BASIS OF SAFETY
  - **LOC – Limiting Oxygen Concentration** - Determines the least amount of oxygen required for explosion propagation through the dust cloud.
  - **Resistivity –** Indicates amount of time established charge would take to dissipate
  - **Kst –** Measures the relative explosion severity compared to other dusts

Combustible Dust

- **Combustible Dust RAGAGEP**
  - **NFPA 654 – Standard for the Prevention of Fires and Dust Explosions from the Manufacturing, Processing, and Handling of Combustible Particulate Solids**
  - NFPA 484 – Standard for Combustible Metals, Metal Powders, and Metal Dusts
  - NFPA 664 – Standard for the Prevention of Fires and Explosions in Wood Processing and Woodworking Facilities
  - NFPA 68 – Guide for Venting of Deflagrations
  - NFPA 85 – Boiler and Combustion Systems Hazards Code
  - NFPA 69 – Standard on Explosion Prevention Systems
  - NFPA 499 – Recommended Practice for the Classification of Combustible Dusts and of Hazardous (Classified) Locations for Electrical Installations in Chemical Process Areas
  - FM Global Safety Data pamphlet FM 7-76

Combustible Dust Hazards

CSB - Understanding Combustible Dust Explosions and Hazards

Incident Outcomes…What Happens if We Don't Control the Hazards

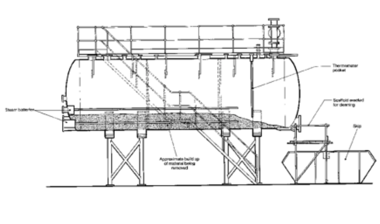
Explosions/Fires/Catastrophes

Incident Outcomes Explosions

- Confined Explosions
- Unconfined – Vapor Cloud Explosions
- Vessel Rupture Explosions
- BLEVE's
- Dust Explosions
- Detonations

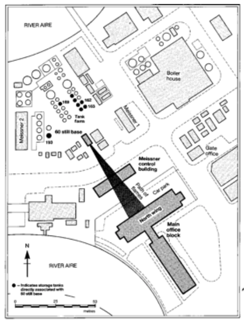
What Can Go Wrong?

- Hickson & Welch, Castleford, UK 1992



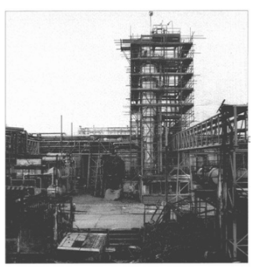
What Can Go Wrong?

- Hickson & Welch



What Can Go Wrong?

- Hickson & Welch



Tesoro's Anacortes Explosion

Incident Outcomes Impacts

- Toxic, Corrosive, Thermal
- Overpressure / Under pressure
- Missiles

Chemical Hazards

Process Hazard Initiating Causes

Who Can It Affect?

Who Does It Affect?

- Workforce – Inside the Fence
- Community – Outside the Fence
- Environment – Large & Small Effects
- Production
- Company Assets
- License to Operate

Chemical Hazards
Operating Envelope

What is It?
Is It Important to Know?

Chemical Hazards Information

- **Chemical & Physical Data**

- Toxicity – Acute & Chronic
- Routes of Entry
- Appearance
- Physical state
- Molecular weight
- Vapor pressure
- Viscosity
- Freezing point
- Particle size distribution
- Melting point
- Solubility in water
- Odor and odor threshold
- Specific gravity
- Surface tension

- Heat of vaporization
- Critical temperature/pressure
- Heat capacity
- Heat of combustion,
- Electrical conductivity and dielectric constant
- Vapor density versus air
- pH
- Flammability and Combustibility
  - Boiling point,
  - Flash point,
  - LFL
  - UFL
  - Minimum Oxygen Concentration

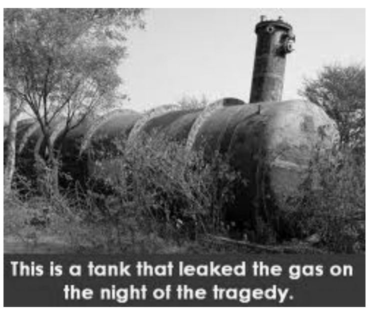
Chemical Reactivity Hazards

Chemical Reactivity Hazards

❑

Chemical Reactivity Hazards

❑



Chemical Reactivity Hazards

❑

- Water entered tank containing 42 tons of methyl isocyanate
  - Exothermic reaction: temp increased to over 200ºC
  - Accelerated by iron from non-SS pipelines
  - Tank vented to atmosphere
  - Tank was filled beyond recommended level
  - Safety devices undersized
  - Plant was in densely populated area

Chemical Reactivity Hazards

-
  - Immediate death toll ca. 3800
  - Govt estimate (2006) – 558,000 injuries with 38,000 temporary partial and 3900 severely and permanently disabling injuries
  - Area still contaminated
  - Civil court cases still active in US; Indian criminal courts convicted CEO of manslaughter and others of death by negligence
  - Facility was sold in 1994, and Union Carbide was bought by Dow in 2001. Indian officials are seeking additional compensation from Dow and requesting Dow's sponsorship of the 2012 London Olympics be revoked.

Chemical Reactivity Hazards

- **US Chemical Safety & Hazard Investigation Board Report – 2002**
  - 167 incidents in US 1980-2001
  - 48 resulted in ≥ 1 fatalities
  - 108 total fatalities
  - 50 incidents had public impact
  - Over 50% of the incidents involved chemicals not covered by OSHA PSM standard
  - Ca. 60% involved chemicals that were not rated for stability by NFPA diamond, or which were listed as "no special hazard" – 0 rating in NFPA system

Chemical Reactivity Hazards

***Chemical reactivity hazards* can result from any chemical reaction with the potential to release heat, pressure, or toxic reaction products in quantities too high to be absorbed or contained by the environment and equipment that hold the reacting mixture**

Chemical Reactivity Hazards

- Prime Causes
  - Process Chemistry
    - No appreciation of heat of reaction (*Increases in reactor sizes make reaction more adiabatic)*
    - Decomposition of raw material/ intermediate/ product
    - Unstable by-products
    - Batch vs. semi-batch
    - Concentrations too high
    - Catalysis by materials of construction

Chemical Reactivity Hazard

- **Prime Causes (continued)**
  - Mischarging:
    - Too much
    - Too fast
    - Wrong order
  - Agitation
    - Too fast
    - Too slow
    - None or delayed
  - Raw material quality
    - Water contamination
    - Impurities
    - New specs

Chemical Reactivity Hazards

- **Process Safety Goals**
  - Chemists and engineers develop intrinsically safe, environmentally sound processes

    ELSE

  - Determine and establish safe operating limits and ensure process is controlled within them

Vent sizing is last line of defense!

Chemical Reactivity Hazards

- **Basics of Managing Chemical Reactivity Hazards**
  - Identify chemical reactivity hazards (intended and unintended)
  - Understand / evaluate the consequences of possible uncontrolled reactions
  - Implement inherent safety strategies to eliminate or reduce the hazards
  - Establish safe operating limits
  - Carry out Process Hazard Analysis
  - Implement preventive and protective measures

Chemical Reactivity Hazards

- **Process Safety Data Requirements**
  - Intended Chemistry (Synthesis Reactions)
    - Heat of reaction / mixing
    - Maximum temperature which can be reached by the synthesis reaction under *adiabatic* conditions: Process temperature + *Adiabatic Temperature Rise (ATR)*
    - Maximum heat generation rate, % reagent accumulation, effect of mixing on accumulation (effect of mixing on reaction rate)
    - If there is gas generation during the synthesis / mixing total gas release and gas release rate, and if necessary gas analysis

Chemical Reactivity Hazards

- **Process Safety Data Requirements**
  - Decompositions and Secondary Reactions (Unintended Chemical Reactions)
    - Thermal stability of reagents / starting materials, intermediates, reaction mixtures, distillation bottoms, products
    - Heat of reaction
    - Exothermic and/or gassy reaction/decomposition *onset temperature*
    - Heat generation rates
    - Gas generation rates
    - Total gas generation

Chemical Reactivity Hazards

- **Must consider the impact of possible deviations**
-
  - **Loss of utilities** - e.g., loss of cooling water, loss of power, loss of steam, loss of nitrogen
  - **Varying composition** – e.g., too much reactant, too little reactant, incorrect addition order, incorrect additions
  - **Mechanical failure** – loss of agitation, loss of vacuum, valve failure / wrong position
  - **Inadvertent mixing** including inadvertent installation of improper material of construction
  - **Measurement/Data Error** – failed or dry thermocouple, gauge error
  - **Human error** - incorrect set point, wrong addition, incorrect temperature

Chemical Reactivity Hazards

- Compatibility Matrices
- **Example Compatibility Chart for an Acetic Anhydride Handling Facility**

Will These Two Materials React?	Acetic Acid	Acetic Anhydride	Cooling Water	Sulfuric Acid	50% Caustic	Lube Oil	Cleaning Solution
Acetic Acid							
Acetic Anhydride	*Reactive*						
Cooling Water	*Not reactive*	*Reactive*					
Concentrated Sulfuric Acid	*Reactive*	*Reactive*	*Reactive*				
50% Caustic	*Reactive*	*Reactive*	*Reactive*	*Reactive*			
Lube Oil	*Not reactive*	*Not reactive*	*Not reactive*	*Reactive*	*Reactive*		
Cleaning Solution	*Find out what the cleaning solution contains, then determine reactions*						

CCPS Reactive Material Hazards Safety Alert, October 2001

Chemical Reactivity Hazards

- **API Development and Engineering Process Safety Lab (PSL)**
  - Designs and performs testing (coordinates / oversees testing with external resources as needed)
  - Evaluates data
  - Collaborates with R&D chemist / engineer to assess the alternative chemicals, chemistries and process conditions to improve the inherent safety of the process
  - Recommends safe operating limits through working with R&D chemist / engineer and manufacturing representatives

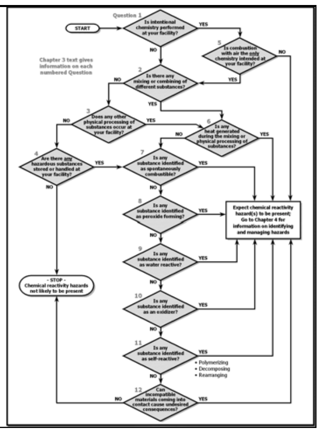
Chemical Reactivity Hazards

Chemical reactivity hazards can be manifest through:

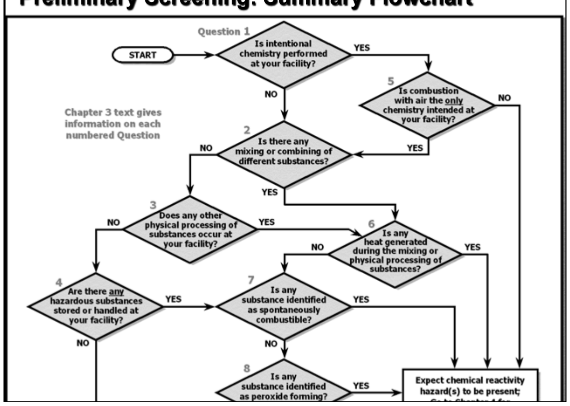
- Materials which become chemically unstable for a variety of reasons,
- Intended chemical reactions that runaway for a variety of reasons
- Unintended chemical reactions that take place due to accidental mixing of chemicals that are normally separate

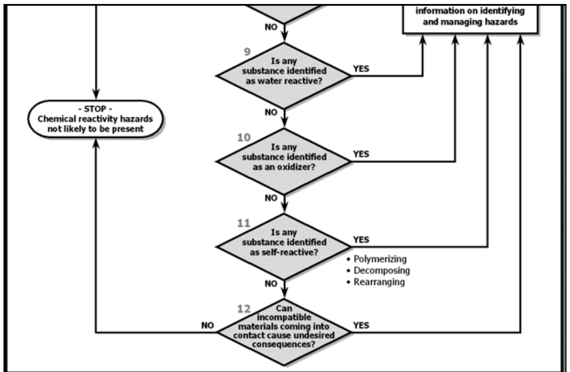
Preliminary Screening for Chemical Reactivity Hazards

Summary Flowchart



Preliminary Screening: Summary Flowchart





Summary Flowchart (continued)

FACILITY:			COMPLETION DATE:
COMPLETED BY:			APPROVED BY:
Do the answers to the following questions indicate chemical reactivity hazard(s) are present? ____________			
AT THIS FACILITY:		*YES, NO* or *NA*	BASIS FOR ANSWER; COMMENTS
Question 1. Is intentional chemistry performed?			
2. Is there any mixing or combining of different substances?			
3. Does any other physical processing of substances occur?			
4. Are there any hazardous substances stored or handled?			
5. Is combustion with air the only chemistry intended?			
6. Is any heat generated during the mixing or physical processing of substances?			
7. Is any hazardous material identified as spontaneously combustible?			
8. Is any hazardous material identified as peroxide forming?			
9. Is any hazardous material identified as water reactive?			
10. Is any hazardous material identified as an oxidizer?			
11. Is any hazardous material identified as self-reactive?			
12. Can incompatible materials coming into contact cause hazardous consequences, based on the following analysis?			
SCENARIO	CONDITIONS NORMAL?*	*R, NR* or *?***	INFORMATION SOURCES; COMMENTS
1			
2			
3			

*Does the contact/mixing occur at ambient temperature, atmospheric pressure, 21% oxygen atmosphere, and unconfined? (IF NOT, DO NOT ASSUME THAT PUBLISHED DATA FOR AMBIENT CONDITIONS APPLY)

**R = Reactive (incompatible) under the stated scenario and conditions
NR = Non-reactive (compatible) under the stated scenario and conditions
? = Unknown; assume incompatible until further information is obtained

Example Form for Documenting Chemical Reactivity Hazard Screening

Chemical Reactivity Hazards

CSB Video - T2 Laboratories Jacksonville, FL

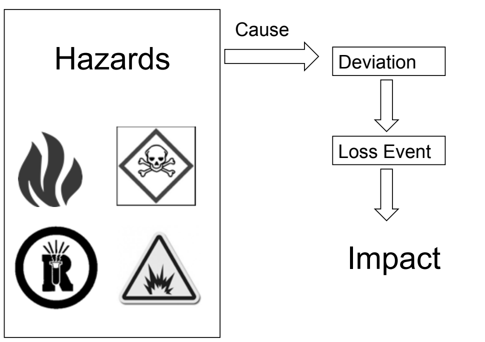
Now That We Understand the Hazards

What Can Go Wrong?

How Bad Is It?

How Likely is It to Occur?

We Will Cover This in the PHA Section…But Here is a Taste.



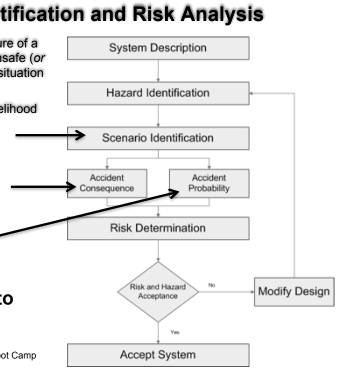
Hazard Identification and Risk Analysis

- Hazard: The inherent nature of a substance or a potentially unsafe (*or any undesired*) condition or situation
- Risk: Consequence X Likelihood

1.
wrong?

2. How bad is it?

3. How likely is it to occur?



HIRA Logic Diagram Source: CCPS Boot Camp Training

Managing Risk

- Determine Risk Tolerance
- Evaluate Current Risk
- The Effect of Mitigation

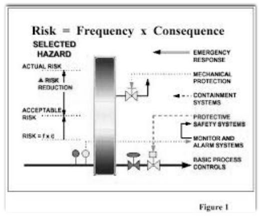
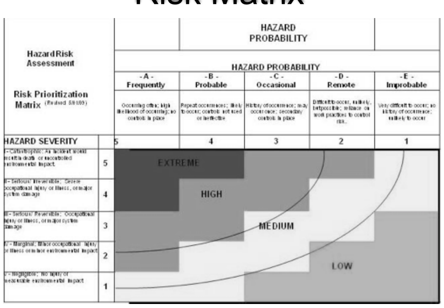


Figure 1

Risk Ranking
How Bad Is It?
How Do We Quantify It?

Risk Matrix



Process Safety Management of Highly Hazardous & Explosive Chemicals

NC OSHA PSM Training
Process Hazards