

A Professional Process Safety Firm

Technology

Inherently Safer Design: Case Studies and Examples

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Inherent - "...existing in something as a *permanent* and *inseparable* element, quality, or attribute."

- American College Dictionary



Hazard

- An inherent physical or chemical characteristic that has the potential for causing harm to people, the environment, or property.
- Hazards are intrinsic to a material, or its conditions of use.



Chemical Process Safety Strategies

- Inherent
- Passive
- Active
- Procedural



- Eliminate or reduce the hazard by changing the process or materials which are non-hazardous or less hazardous
- Integral to the process or plant cannot be easily defeated or changed without fundamentally altering the process or plant design



Technology Inherently Safer Example

- Substituting water for a flammable solvent (latex paints compared to oil base paints)
- More to follow



 Minimize hazard using process or equipment design features which reduce frequency or consequence without the active functioning of any device



Characteristics of Passive Devices

- They work because they exist they don't have to "do anything"
- Often confused with inherent safety
- Robust if maintained, but passive devices are subject to failure
 - Deterioration, lack of maintenance
 - Overwhelmed (beyond design capacity)



Technology Passive Safety Device Example

- Containment dike around a hazardous material storage tank
 - Reduces consequence by confining spill to a defined area
 - Does not require active functioning of anything to perform its job
 - The hazard (spilled flammable or toxic material) still exists, so a dike is not an "inherent safety" feature
 - Can fail dikes can crack, leak, be full of water, etc., or a catastrophic tank failure might result in liquid overtopping the dike wall



- Controls, safety instrumented systems (SIS), pressure relief valves and rupture disks
- Generally involve multiple active elements
 - Sensor to detect hazardous condition
 - Logic device to decide what to do
 - Control element to implement the appropriate action



Characteristics of Active Safety Systems

- May require many systems and devices to detect and react to multiple potential incident scenarios
- High initial cost to implement
- Ongoing maintenance and operation costs
 - Must be tested throughout the life of the plant to confirm that they are still working as designed



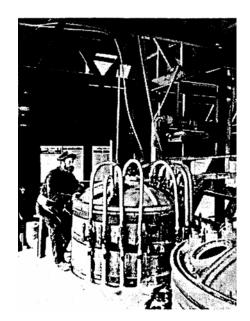
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Active Device Examples - Prevention or Mitigation

- Prevention
 - Stop an incident before it occurs
 - High level alarm to shut off a feed pump and prevent overfilling a tank
- Mitigation
 - Reduce the consequences of an incident after it occurs
 - Sprinkler systems to extinguish a fire

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- Standard operating procedures, safety rules and standard procedures, emergency response procedures, training
- EXAMPLE
 - An operator is trained to observe the temperature of a reactor and apply emergency cooling if it exceeds a specified value





Dust or powder handling example

- Fine powder in a combustible dust conveying operation
- Organic non-conductive polymer maximum explosion pressure of ~120 psig when burned in a confined space in air starting at atmospheric pressure
- Ignitable by static sparks, metal to metal sparks



Technology Some possible approaches

- Inherent
 - Larger particles granules or pellets (eliminate dust explosion hazard)
- Passive
 - Build equipment to greater than 120 psig pressure rating



Technology Some possible approaches

- Active
 - Inerting (assuming an active system to maintain inert atmosphere)
 - Explosion venting
 - Explosion suppression systems
- Procedural
 - Procedures to maintain electrical grounding and bonding of equipment
 - Procedures to avoid getting metal objects into the system (spark hazard)
 - Other ways to control ignition sources

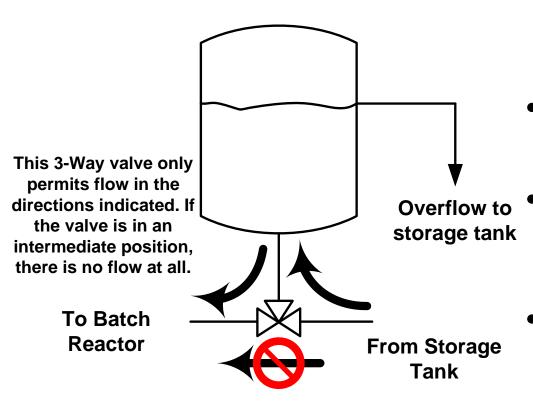


Technology Inherently safer design and risk

- Reduce risk by reducing or eliminating the hazard
 - Eliminate or reduce potential consequence part of the risk equation
- Reduce risk by reducing the ability of the system to allow a potential accident scenario to occur
 - Reduce the frequency part of the risk equation
 - Reduce frequency by equipment features which are a part of the process itself
 - Not "inherent" if it involves add-on safety devices
 - More controversial interpretation



Example of inherent frequency reduction



- If the material in the feed tank is overcharged to the downstream batch reactor, a runaway reaction can occur
- The charge tank holds exactly the correct charge, and overflows to the supply tank if overfilled
- The tank would have to be filled and emptied many times to get sufficient raw material into the reactor for a runaway
- If you do this, the consequence is the same, but the likelihood (frequency) is inherently lower – it is really difficult to overcharge the batch reactor



Inherently Safer Design Strategies

- Minimize
- Moderate
- Substitute
- Simplify



- Use small quantities of hazardous substances or energy
 - Storage
 - Intermediate storage
 - Piping
 - Process equipment



These types of reactors often have a much smaller inventory of material than a batch reactor for the same reaction:

- Continuous stirred tank reactors (CSTR)
- Tubular reactors
- Loop reactors
- Reactive distillation systems



Example – a nitration process



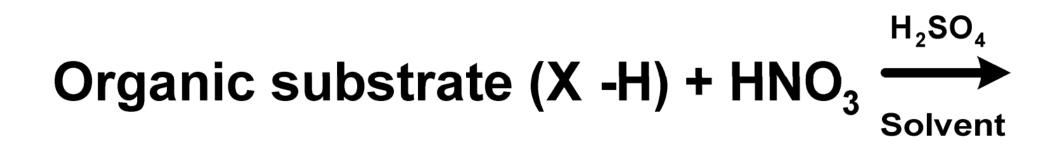
Technology Understand your process!

- Basic chemical engineering know what physical and chemical parameters are important in the process
 - Mass transfer
 - Heat transfer
 - Mixing
 - Chemical reaction

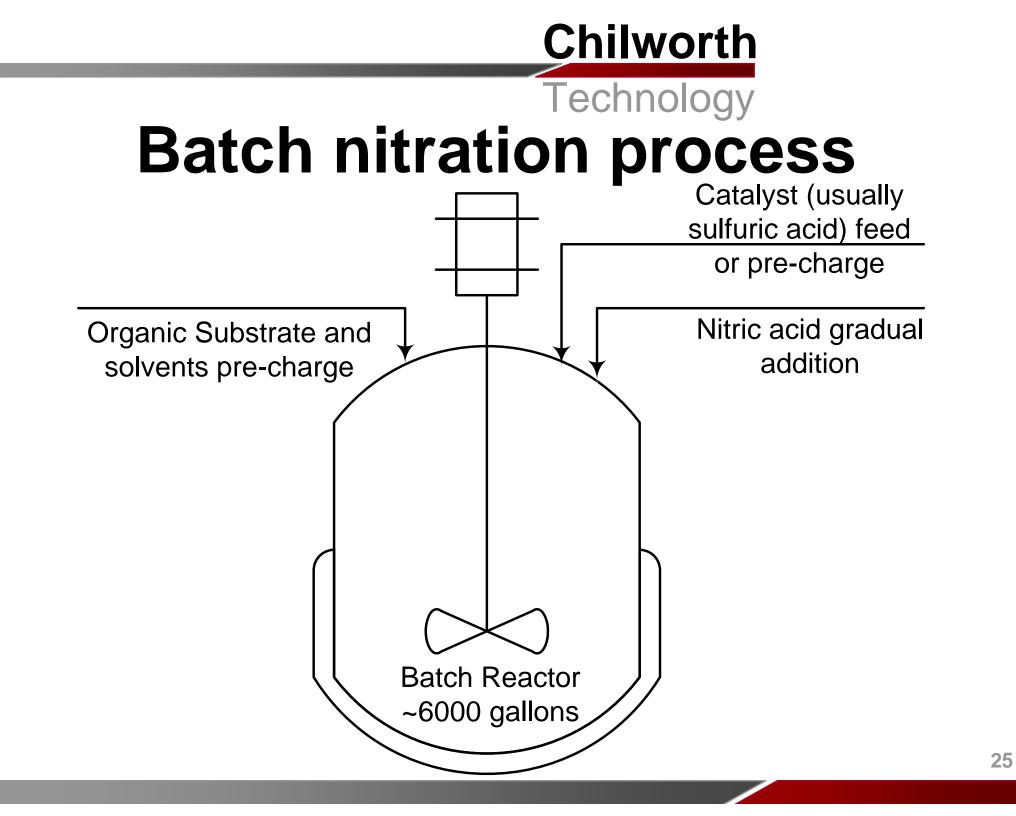
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Minimize – A batch nitration process



Nitrated Product (X -NO₂) + H₂O





What controls the nitration reaction?

- Bulk mixing of the nitric acid feed into the reaction mass
- Mass transfer of nitric acid from the aqueous phase to the organic phase where the reaction occurs
- Removal of the heat of reaction

To design a smaller reactor, focus on these characteristics.

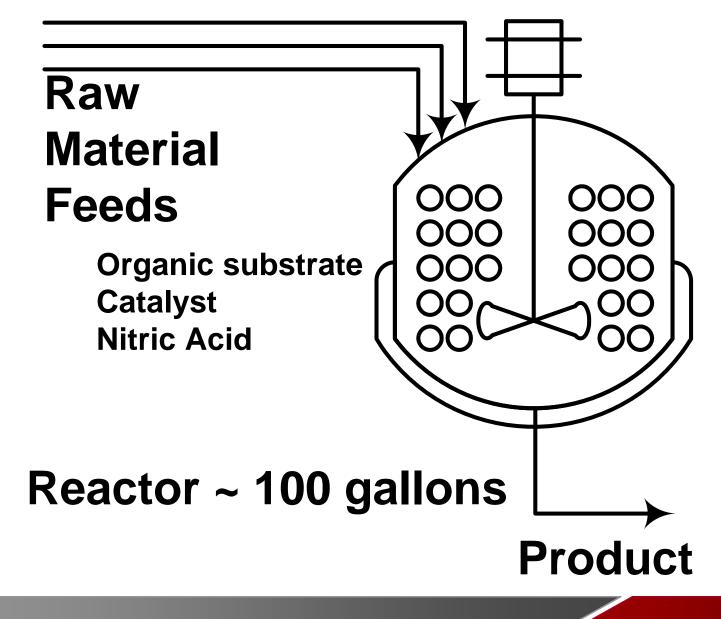


Technology To minimize reactor size

- Good bulk mixing of materials
- Large interfacial surface area between the aqueous and organic phase to maximize mass transfer
 - create smaller droplets of the suspended phase
- Large heat transfer area in the reactor

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Technology CSTR Nitration Process



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Technology Other Unit Operations

- Distillation
- Heat transfer
- Extraction



- Tray design to minimize liquid inventory
- Internal baffles in column base to minimize inventory
- Reduce diameter of column base
- Minimize reflux accumulators and reboiler inventory
- Internal reboilers and reflux condensers
- Packing design to minimize liquid inventory



Heat transfer

Type of exchanger

Surface compactness (sq. m. heat transfer area/ cu. m. exchanger volume)

70-500
120 - 1,000
65 - 3,300
150 - 5,900
1,000 - 5,000
20,000



- Continuous extractors in place of batch "kettle operations"
- Combined "mixer-settlers"
- Mechanically enhanced extraction columns
- Centrifugal extractors



Minimize - Material storage and transfer

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Storage and Transfer

- General principals
 - Storage of hazardous raw materials should be minimized
 - But consider the conflicting hazards
 - Transportation hazards
 - Potential increased frequency of plant shutdown
 - Pipes should be large enough to do the required job, and no larger
 - Intermediate storage is it really needed?

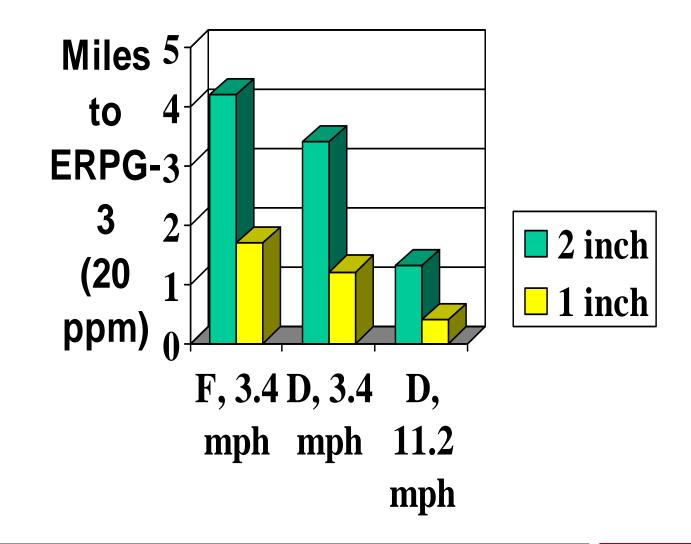


Technology Minimize pipeline inventories

- Minimize line size
 - A 2 inch pipe contains 4 times as much material as a 1 inch pipe
 - But consider the mechanical integrity of smaller pipe
- Minimize line length
 - Facility siting
 - Equipment location within a facility
 - Line routing

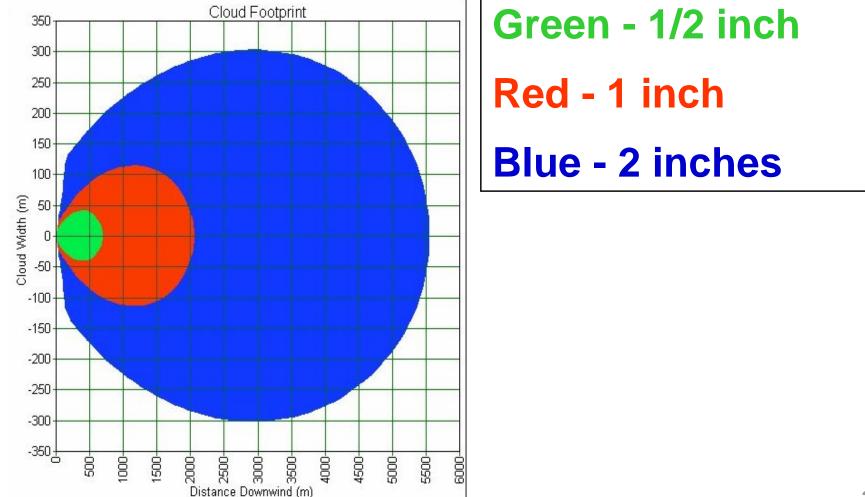


Chlorine Transfer Line Size





Toxic cloud for 3 sizes of phosgene pipe



Technology Intermediate Storage

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- Question the need for all storage of hazardous materials
- If intermediate storage is needed, reduce to minimum
- Plant "buffer" storage
 - Can some other, less hazardous material be stored to provide the buffer?

Chilworth Technology Substitute

- Substitute a less hazardous reaction chemistry
- Replace a hazardous material with a less hazardous alternative



On demand chlorine generation

- In-situ generation of chlorine gas from salt water - ElectroChlor[®] process
- Initial installation at Severn Trent Water's Frankley Water Treatment Works in the UK
- 2000 Institution of Chemical Engineers (IChemE) award for Excellence in Safety and Environment

Chilworth Technology Substitute materials

- Water based coatings and paints in place of solvent based alternatives
 - Reduce fire hazard
 - Less toxic
 - Less odor
 - More environmentally friendly
 - Reduce hazards for end user and also for the manufacturer

Technology Substitute materials

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- Organic solvents with a higher flash point and/or lower toxicity
 - Paints and coatings
 - Dyes
 - Agricultural product formulations
 - Dibasic ethers and organic esters as paint removers

Chilworth Technology Substitute materials

- Aqueous formulations (emulsions or suspendable concentrates) for agricultural chemicals
- Dry flowable formulations for agricultural products
- Aqueous formulations for cleaning printed circuit boards and other electronic applications in place of organic solvents

Chilworth Technology Moderate

- Dilution
- Refrigeration
- Less severe processing conditions
- Physical characteristics
- Containment
 - Better described as "passive" rather than "inherent"



Technology

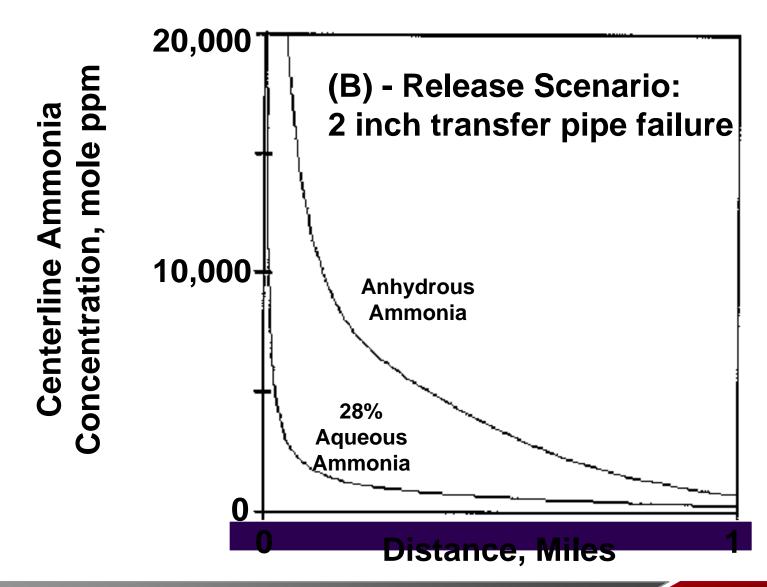
How does dilution moderate hazards?

- Dilute the hazardous agent with a less hazardous or non-hazardous material
- Reduce evaporation rate from a spill
- For some materials, reduce pressure of storage vessels
 - aqueous ammonia vs. anhydrous
 - aqueous HCI vs. anhydrous



- Aqueous ammonia instead of anhydrous
- Aqueous HCI in place of anhydrous HCI
- Sulfuric acid in place of oleum
- Wet benzoyl peroxide in place of dry
- Dynamite instead of nitroglycerine

Chilworth Technology Effect of dilution



Chilworth Technology Refrigeration

- Particularly useful for liquefied gases
- Lower storage pressure
 - Lower or no driving force for leak from vapor space of a storage tank
 - Reduced driving force for a liquid leak

Technology Refrigeration - liquefied gases

- Reduced flashing in case of a leak
 - Material is at or only slightly above its atmospheric boiling point
 - Released material does not boil forms pool which will then evaporate more slowly
 - Opportunities to reduce evaporation rate by containment, dike design

Technology Refrigeration - liquefied gases

- Reduced or no liquid aerosol formation
 - Quantity of material in downwind cloud is much larger than what would be calculated from a flash evaporation calculation
 - Some or all of the liquid is in the form of small droplets which are suspended in the air, blow downwind with the cloud, and subsequently evaporate

Technology Impact of refrigeration

Monomethylamine	Distance to
Storage	ERPG-3 (500 ppm)
Temperature	Concentration,
(°C)	km
10	1.9
3	1.1
-6	0.6

Some refrigeration examples

- Some materials for which refrigerated storage has been reported to be beneficial include
 - chlorine
 - butadiene
 - ethylene oxide
 - propylene oxide
 - vinyl chloride
 - methylamines



Technology Change physical characteristics

- Pellets or granules instead of dusty powders
- Immobilized reactive agents (bonded to a solid substrate or surface)

Technology Plant siting - limit potential impacts

- Separation of hazards from potentially impacted people, environment, property
- Separation of hazardous units to limit "knock on" effects
- Site selection avoid transport and storage of hazardous materials



Technology Site Layout Considerations

- Safety
 - Separation of high hazard operations from
 - each other
 - ignition sources
 - large concentrations of people
 - emergency response facilities
 - evacuation points, "safe havens"
 - critical utilities



Technology Site Layout Considerations

- Minimize need for "day tanks", other "unnecessary" inventory of hazardous material
- Minimize length and size of hazardous material pipes
- Avoid routing pipes through "high hazard" areas
 - over, under roads; lifting operations



- Eliminate unnecessary complexity to reduce risk of human error
 - <u>QUESTION ALL COMPLEXITY!</u> Is it really necessary?





Technology

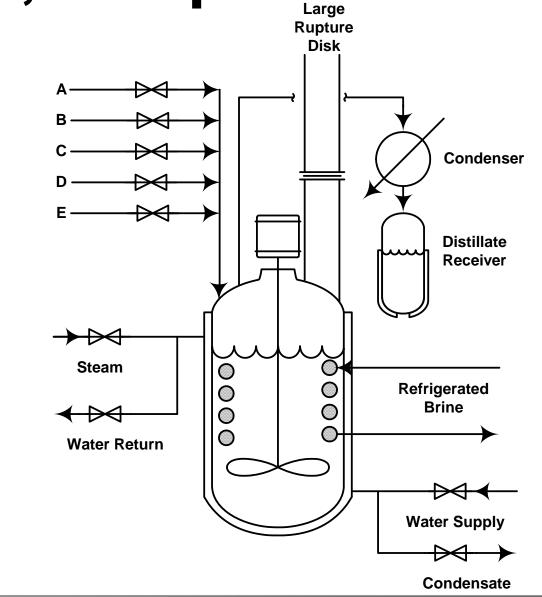
Separate process steps

- Multi-step batch process
 - One vessel that can "do anything"
 - Must represent a compromise among many competing design criteria
 - Multiple vessels, each optimized for a particular operation



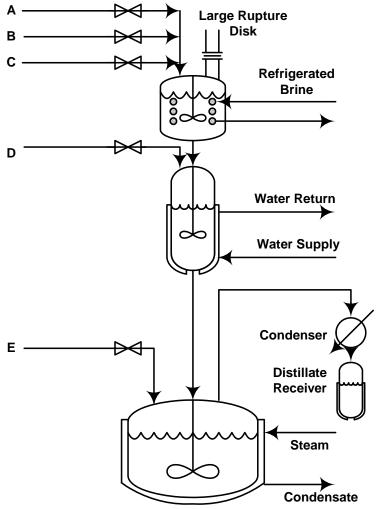
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Single, complex batch reactor





A sequence of simpler batch reactors for the same process



Other simplification examples

- Gravity flow eliminate pumps
- Reactor geometry to make overheating difficult or impossible
 - Examples in nuclear power
 - Maleic acid manufacture by partial oxidation of benzene - catalyst geometry provides temperature self-regulation



Simplify - Human Factors Considerations

"User friendly plant design"



Technology

Presenting information to the operator

- Does the way we display information for the operator affect
 - how quickly he can react to the information?
 - how likely he is to observe information?
 - how likely he is to do the right thing?



Technology How Many Red Squares?



Now, How Many Red Squares?

BLACK	RED	BLACK	BLUE	GREEN
RED	RED	BLUE	GREEN	BLUE
BLACK	BLUE	GREEN	RED	BLUE
BLACK	RED	GREEN	RED	BLACK
BLACK	YELLOW	GREEN	RED	RED

Technology How about now?

BLUE	RED	BLACK	GREEN	RED
BLACK	RED	GREEN	BLUE	GREEN
GREEN	BLUE	RED	BLACK	BLUE
GREEN	GREEN	BLACK	BLUE	RED
BLACK	RED	GREEN	RED	GREEN



Technology Is "none" a correct answer?

BLACK	RED	BLACK	BLUE	GREEN
RED	RED	BLUE	GREEN	BLUE
BLACK	BLUE	GREEN	RED	BLUE
BLACK	RED	GREEN	RED	BLACK
BLACK	YELLOW	GREEN	RED	RED



Technology

How we present information matters!

- Much of this has been quantified
- People are not going to change
- Significant error rates even with highly trained, motivated people - astronauts, test pilots
- We know how to do it better



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Design Error or Operator Error?

Display Appearance

Dissimilar to adjacent displays

Similar displays, but with clearlydrawn "process mimic" lines

Similar displays in functional groups in 0.001 a panel

Similar displays in an array identified 0.003 by label only

Selection Error Probability

Negligible

0.0005



Questions designers should ask when they have identified a hazard

Ask, in this order:

- 1. Can I eliminate this hazard?
- 2. If not, can I reduce the magnitude of the hazard?
- 3. Do the alternatives identified in questions 1 and 2 increase the magnitude of any other hazards, or create new hazards?

(If so, consider all hazards in selecting the best alternative.)

- 4. At this point, what technical and management systems are required to manage the hazards which inevitably will remain?
 - How can I make those systems inherently more robust and reliable?



CCPS "Guidelines for Design Solutions for Process Equipment Failures" (1998)

- Excellent series of specific checklists for common unit operations
- Also offer examples of design approach to addressing the hazards
 - Inherent/passive
 - Active
 - Procedural



Technology Unit operations covered

- Vessels
- Reactors
- Mass transfer equipment
 - absorption, extraction, distillation, etc.
- Heat transfer equipment
- Dryers

- Fluid transfer equipment
 - pumps, blowers, compressors
- Solid fluid separators
- Solids handling and processing equipment
- Fired Equipment
- Piping and piping components



Technology Checklist example - reactor

- Deviation Overpressure
- Failure Scenario Loss of cooling resulting in runaway reaction



Potential Design Solutions - Inherent/Passive

- Design vessel to accommodate maximum expected pressure
- Use large inventory of naturally circulating, boiling coolant to accommodate exotherm



Potential Design Solutions -Active

- Low coolant flow or pressure, or high reactor temperature to activate secondary cooling medium via separate supply
- Automatic isolation of reactor feed on detection of loss of cooling
- Emergency pressure relief device





Potential Design Solutions -Procedural

- Manual activation of secondary cooling system
- Manual activation of bottom discharge valve to drop batch into dump tank with reaction poison, shortstop, quench



Implement IS Philosophy in All PHA Activities

- Process Hazard Analysis
- Management of Change
- Incident Investigation
- ...
- An example of using inherently safer design thinking in <u>Incident Investigation</u>



Thank you.

Questions and comments.