An Overview of Inherently Safer Design

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Inherently safer design focus

- Safety – immediate impacts of single events
  - People
  - Environment
  - Property and business – “Loss Prevention”
- Fires, explosions, immediate toxic impacts
- These events will also have long term health and environmental impacts

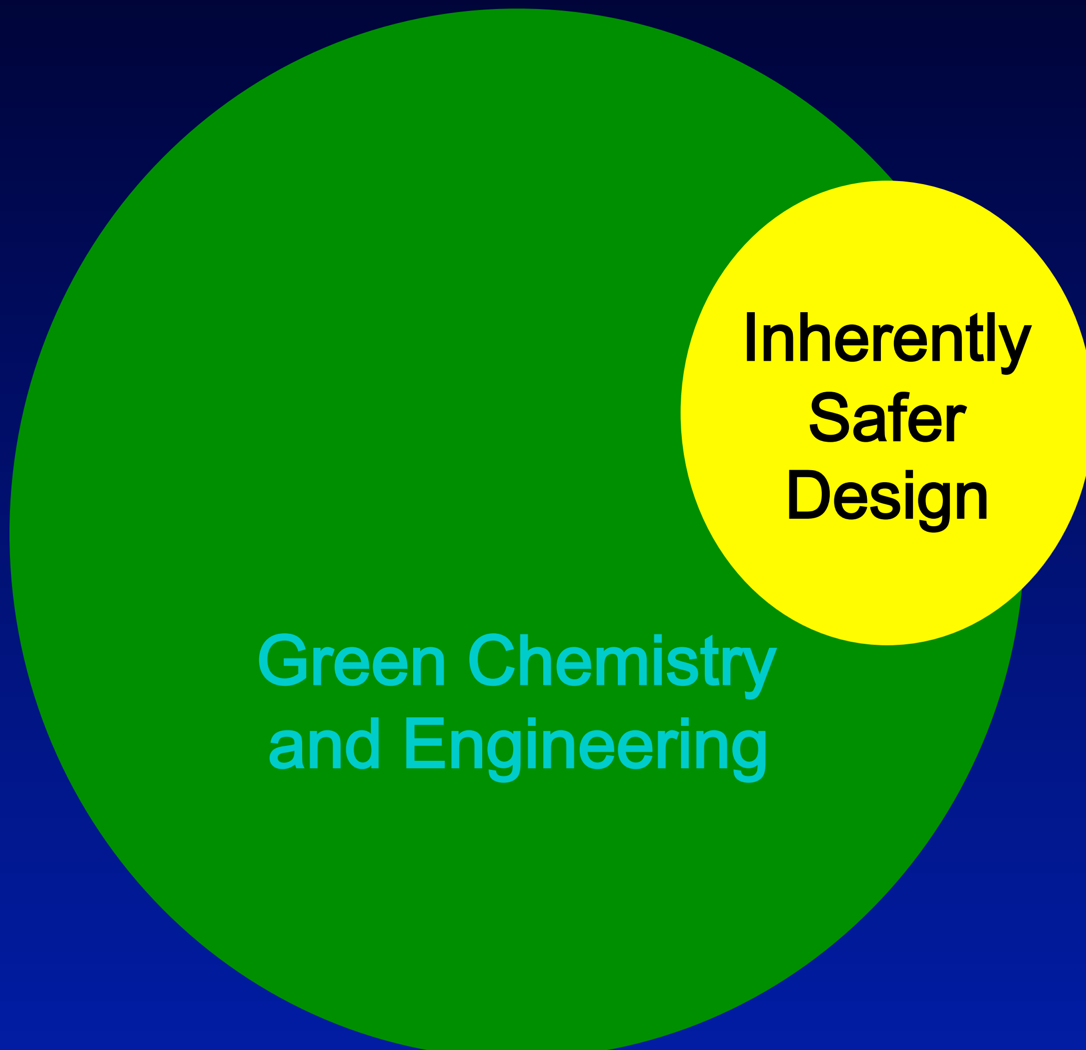
History of inherently safer design concept

- **Technologists have always tried to eliminate hazards**
  - **Some examples:**
    - **In-situ manufacture of nitroglycerine in 1860s railroad construction**
    - **Alfred Nobel – dynamite in place of pure nitroglycerine for mining, construction**
- **Trevor Kletz, ICI, UK (1977)**
  - **Response to 1974 Flixborough, UK explosion (35 years ago last June 1)**
  - **Named the concept**
  - **Developed a set of design principles for the chemical industry**

What is inherently safer design?

- Inherent - "existing in something as a permanent and inseparable element..."
  - safety "built in", not "added on"
- Eliminate or minimize hazards rather than control hazards
- Potential benefit – simpler, cheaper, safer plants
- More a philosophy and way of thinking than a specific set of tools and methods

ISD and Green Chemistry/Engineering



Hazard

- An inherent physical or chemical characteristic that has the potential for causing harm to people, the environment, or property (CCPS, 1992).
- Hazards are intrinsic to a material, or its conditions of use.
- Examples
  - Chlorine - toxic by inhalation
  - Gasoline - flammable
  - High pressure steam - potential energy due to pressure, high temperature

Chemical Process Safety Strategies

Inherent

- Eliminate or reduce the hazard by changing the process or materials to use materials or conditions which are non-hazardous or less hazardous
- Integral to the product, process, or plant - cannot be easily defeated or changed without fundamentally altering the process or plant design
- EXAMPLE
  - Substituting water for a flammable solvent (latex paints compared to oil base paints)

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Passive

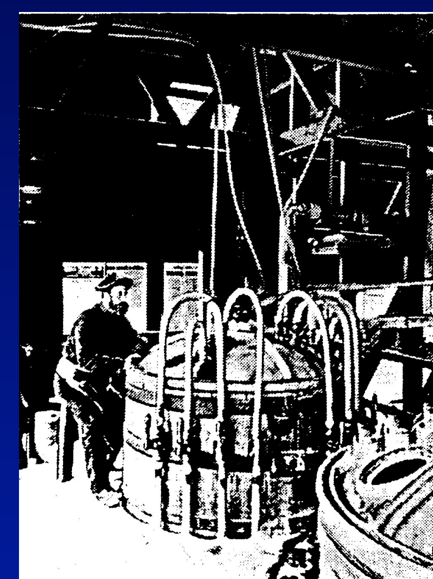
- Minimize hazard using process or equipment design features which reduce frequency or consequence without the active functioning of any device
- EXAMPLE
  - Conducting a chemical reaction capable of generating a maximum of 5 bar pressure in a reactor designed for 10 bar

Active

- Controls, safety instrumented systems (SIS)
- Multiple active elements
  - Sensor - detect hazardous condition
  - Logic device – receive signal from sensor, decide what to do, send signal to control element
  - Control element - implement action
- Prevent incidents, or mitigate the consequences of incidents
- EXAMPLES
  - High level alarm in a tank shuts the feed valve
  - Fire protection – sprinkler system

Procedural

- **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**



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Which strategy should we use?

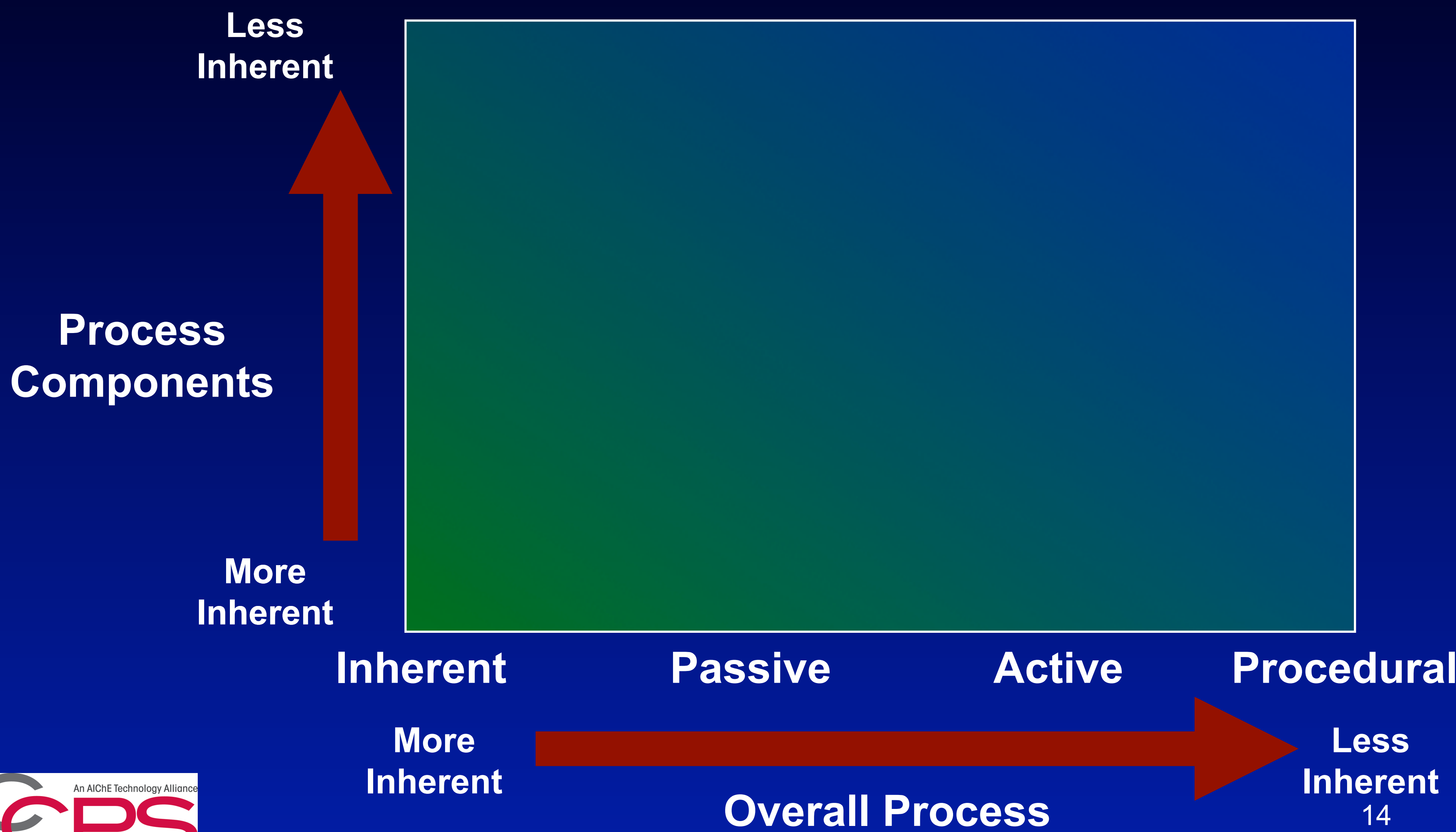
- Generally, in order of robustness and reliability:
  - Inherent
  - Passive
  - Active
  - Procedural
- But you will need all of them – especially when considering the multiple hazards in any chemical process or product
- Inherent strategies often involve changes to basic process chemistry and unit operations – best considered as early in process development as possible.
- But – it is never too late for inherently safer design!

IST and Safe Design/Operation

Inherent | Passive | Active | Procedural

No clear boundary between IST and overall safe design and operation

Actually more like this



Inherently safer design strategies

- **Substitute**
- **Minimize**
- **Moderate**
- **Simplify**

Substitute

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

Reaction Chemistry - Acrylic Esters

- **Reppe Process**

$$CH \equiv CH + CO + ROH \xrightarrow[HCl]{Ni(CO)_4} CH_2 = CHCO_2R$$

- **Acetylene - flammable, reactive**
- **Carbon monoxide - toxic, flammable**
- **Nickel carbonyl - toxic, environmental hazard (heavy metals), carcinogenic**
- **Anhydrous HCl - toxic, corrosive**
- **Product - a monomer with reactivity (polymerization) hazards**

Alternate chemistry

- **Propylene Oxidation Process**

$$CH_2{=}CHCH_3 + \frac{3}{2}O_2 \xrightarrow{Catalyst} CH_2{=}CHCO_2H + H_2O$$

$$CH_2{=}CHCO_2H + ROH \xrightarrow{H^+} CH_2{=}CHCO_2R + H_2O$$

- **Inherently safe?**
- **No, but inherently *safer*. Hazards are primarily flammability, corrosivity from sulfuric acid catalyst for the esterification step, small amounts of acrolein as a transient intermediate in the oxidation step, reactivity hazard for the monomer product.**

By-products and side reactions

- Organic intermediate production
  - Intended reaction - hydrolysis done in ethylene dichloride solvent

    Organic raw material + sodium hydroxide --->

    product + sodium salt
- Reaction done in ethylene dichloride solvent

Hazardous side reaction

- Sodium hydroxide + ethylene dichloride solvent:

$$C_2H_4Cl_2 + NaOH \rightarrow C_2H_3Cl + NaCl + H_2O$$

- The product of this reaction is vinyl chloride (health hazard)
- A different solvent (perchloroethylene) was used

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Other examples

- Alternate routes to carbamate insecticides which do not use methyl isocyanate (the material released at Bhopal)
- Ammoxidation process for acrylonitrile avoids hydrogen cyanide and acetylene

Substitute less hazardous materials

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

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Minimize – A batch nitration process

$$\text{Organic substrate (X-H)} + HNO_3 \xrightarrow[\text{Solvent}]{H_2SO_4}$$

$$\text{Nitrated Product (X-}NO_2\text{)} + H_2O$$

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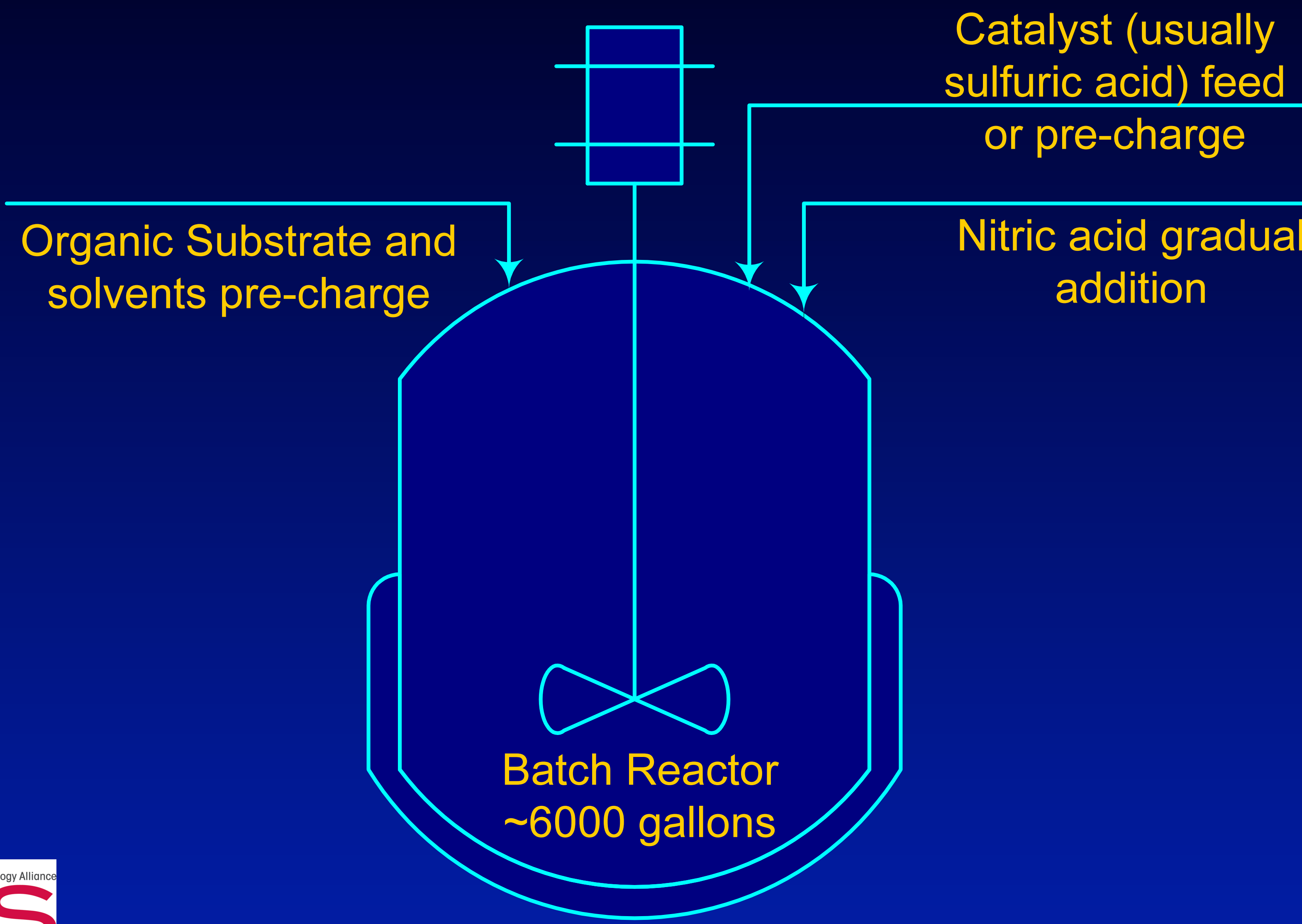
Minimize – A batch nitration process



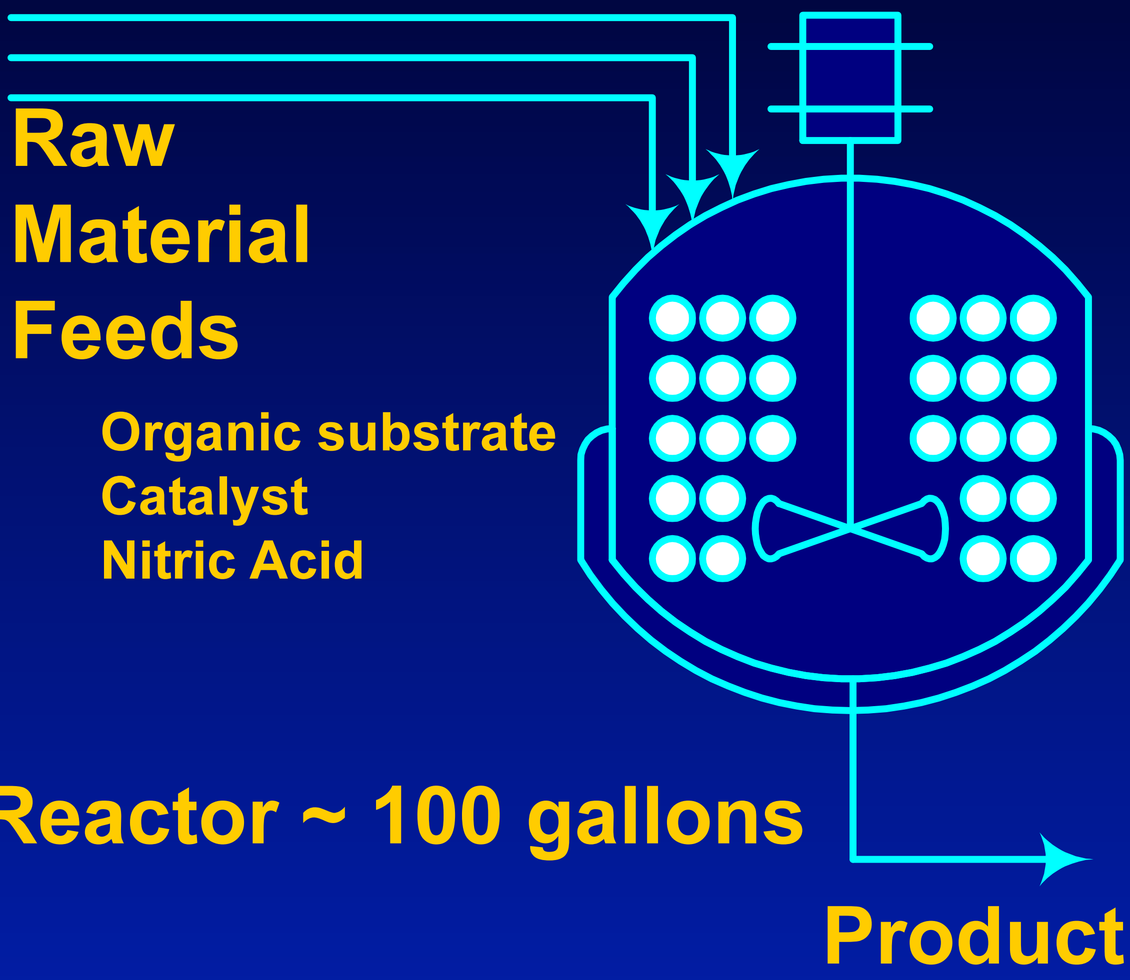
What controls the reaction?

- 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

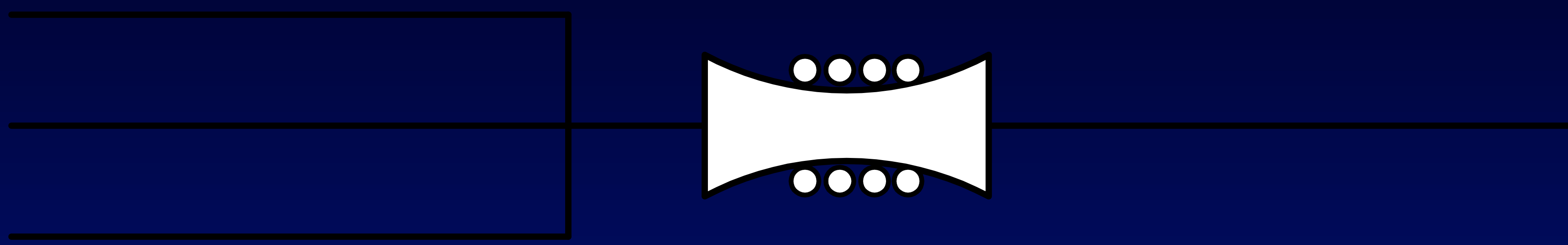
To minimize reactor size

- 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

Continuous Stirred Tank Reactor Nitration Process



Will a pipe reactor work?



Raw Material Feeds

- **Organic substrate**
- **Catalyst**
- **Nitric Acid**

Cooled continuous mixer/reactor

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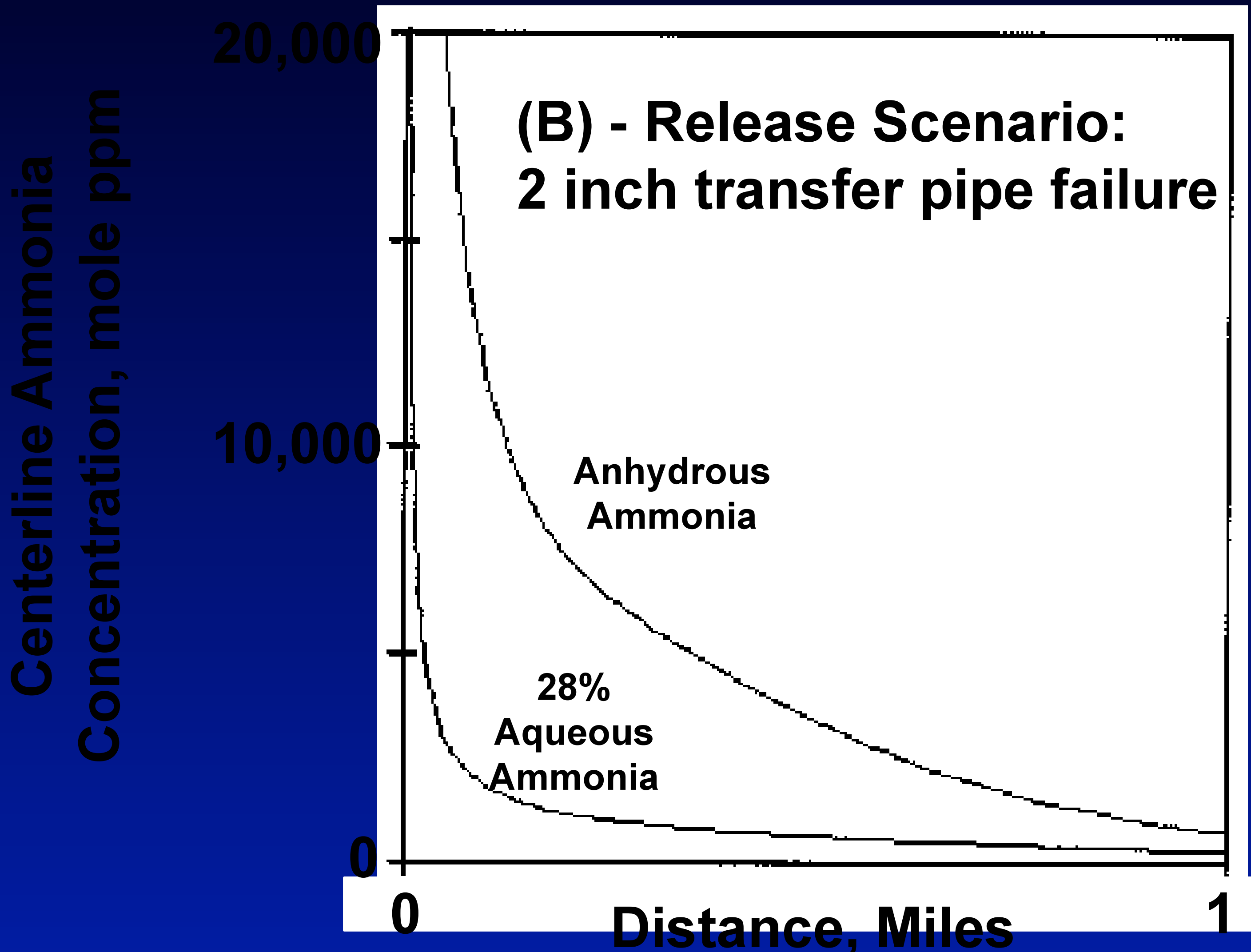
Moderate

- For example, DILUTION
  - Aqueous ammonia instead of anhydrous
  - Aqueous HCl in place of anhydrous HCl
  - Sulfuric acid in place of oleum
  - Wet benzoyl peroxide in place of dry
  - Dynamite instead of nitroglycerine

Effect of dilution



Storage and Transfer Examples

- **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?**

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**

Simplify

- **Eliminate unnecessary complexity to reduce risk of human error**
  - ***QUESTION ALL COMPLEXITY!*** **Is it really necessary?**

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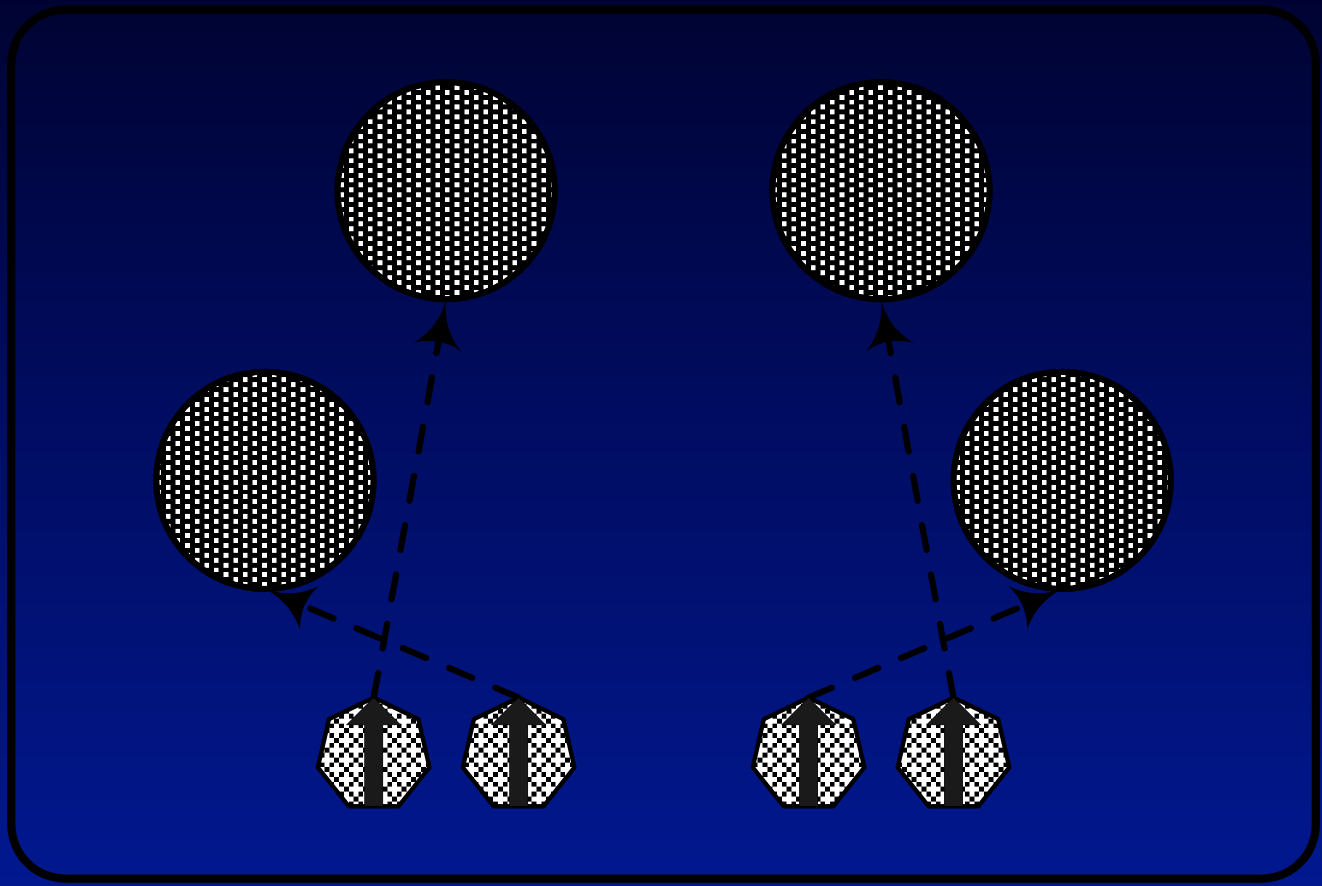
Controls on a stove



From Don Norman, "Turn Signals are the Facial Expressions of Automobiles"

Surely nobody would do this!

401 Reactor | 402 Reactor | 403 Reactor | 404 Reactor

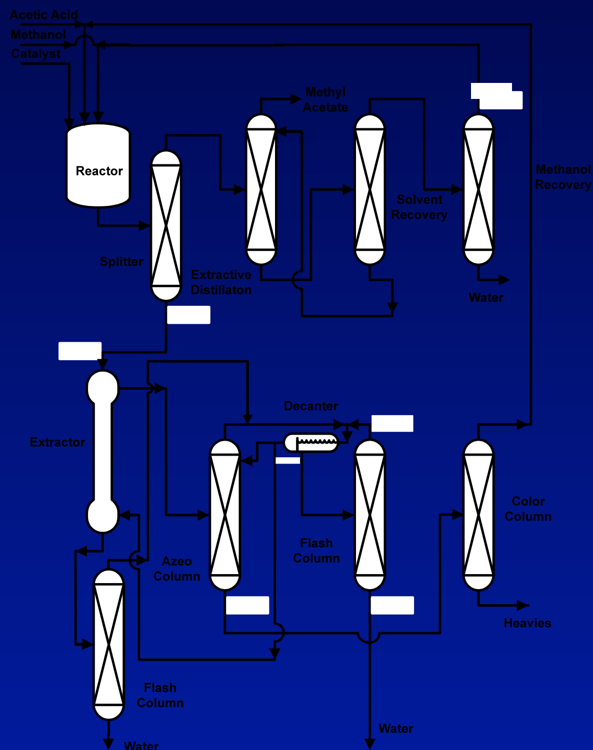
Unit 421 | Unit 413 | Unit 401 | Unit 402

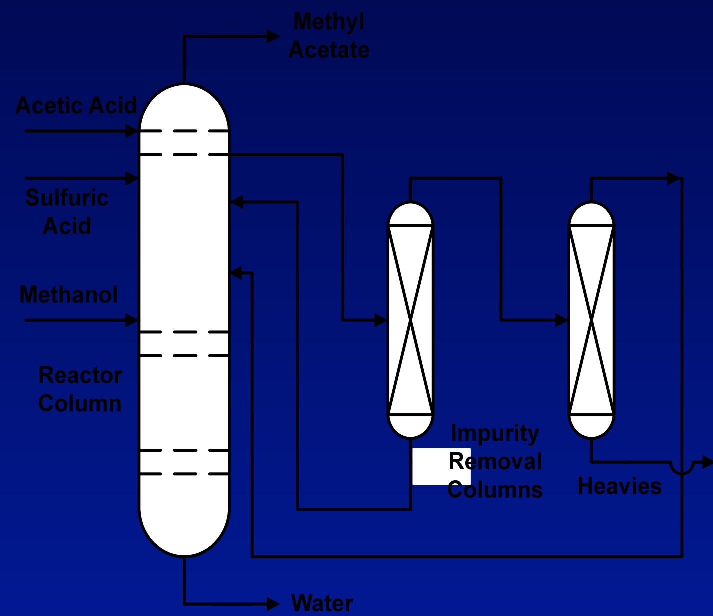
Unit 415 | Unit 416 | Unit 403 | Unit 404

405 Reactor | 406 Reactor | 407 Reactor | 408 Reactor

Eliminate Equipment

- **Reactive distillation methyl acetate process**





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?**

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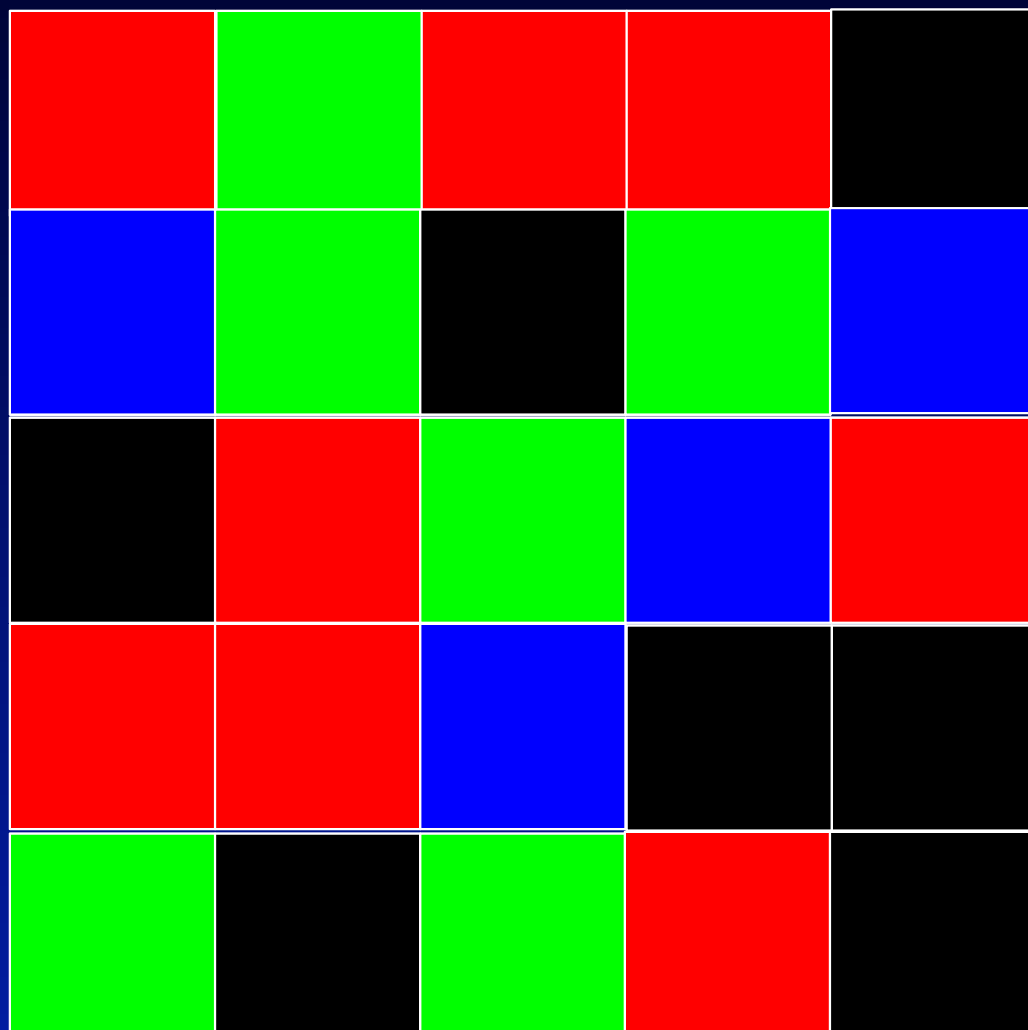
How Many Red Squares?



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

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

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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
  - So, if we don’t, is it an “operating error” or a “design error”?

Design Error or Operator Error?

Display Appearance	Selection Error Probability
Dissimilar to adjacent displays	**Negligible**
Similar displays, but with clearly-drawn “process mimic” lines	**0.0005**
Similar displays in functional groups in a panel	**0.001**
Similar displays in an array identified by label only	**0.003**

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Inherent safety at various levels of process design

- **Overall technology**
  - **What technology for drinking water treatment (disinfection) - chlorine, ozone, UV, others?**
- **Implementation of the selected technology**
  - **How is water chlorination to be implemented (chlorine gas, sodium hypochlorite, other ways of chlorinating water)**

Inherent safety at various levels of process design

- **Detailed design for selected technology**
  - **Water treatment - size of equipment, operating conditions, general layout of plant, single large system or multiple smaller systems, etc.**
- **Detailed equipment design**
  - **Water treatment - selection of specific pieces of equipment, location of equipment and piping, location of valves, controls, etc.**
- **Operation**
  - **User friendly operating procedures, maintenance procedures, etc.**

Some problems

- The properties of a technology which make it ***hazardous*** may be the same as the properties which make it ***useful***
  - Airplanes travel at 600 mph
  - Gasoline is flammable
  - Chlorine is toxic
- ***Control*** of the hazard is the critical issue in safely getting the benefits of the technology

Multiple hazards

- Everything has multiple hazards
  - Automobile travel
    - velocity (energy), flammable fuel, exhaust gas toxicity, hot surfaces, pressurized cooling system, electricity......
  - Chemical process or product
    - acute toxicity, flammability, corrosiveness, chronic toxicity, various environmental impacts, reactivity.......

Any change affects everything!

“When we try to pick out anything by itself, we find it hitched to everything else in the universe.”

- John Muir, 1911

in *My First Summer in the Sierra*

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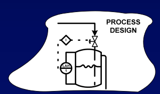
What does inherently safer mean?

- Inherently safer is in the context of one or more of the multiple hazards
- There may be conflicts
  - Example - CFC refrigerants
    - Low acute toxicity, not flammable
    - Environmental damage, long term health impacts
    - Are they inherently safer than alternatives such as propane (flammable) or ammonia (flammable and toxic)?
    - "Green" refrigerators available in Europe – use ~ 100 grams hydrocarbon, but required a significant re-design to minimize flammable material inventory.

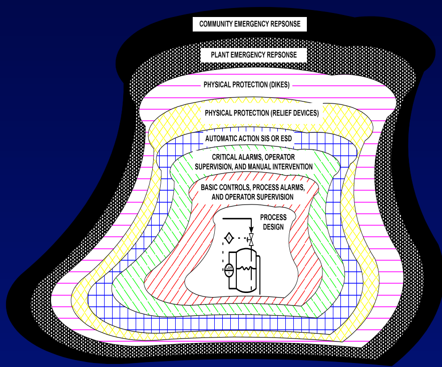
Managing multiple hazards

Toxicity



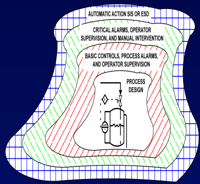
Hazard 1 - Inherent

Explosion



Hazard 2 – Passive, Active, Procedures

Fire



Hazard 3 – Passive, Active, Procedures

…

…..

Hazard n – ????

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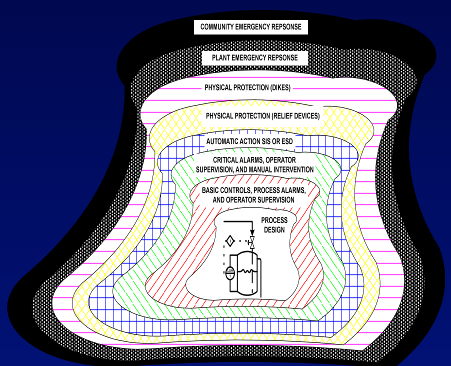
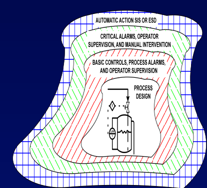
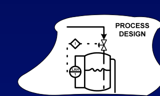
What if you change the process?

Toxicity | **Explosion** | **Fire** | **…..**







Hazard 1 – Passive, Active, Procedures

Hazard 2 – Passive, Active, Procedures

Hazard 3 - Inherent

…

Hazard n – ????

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Different Concerns

- **Different populations may perceive the inherent safety of different technology options differently**
  - **Chlorine handling - 1 ton cylinders vs. a 90 ton rail car**
    - **Neighbor several kilometers away would consider the one ton cylinder inherently safer**
    - **Operators who have to connect and disconnect cylinders 90 times instead of a rail car once would consider the rail car inherently safer**
  - **Who is right?**

Reducing risk or transferring risk?

- Reduce size of hazardous material storage tank at a plant
- Requires changing shipping mode from 150,000 Kg rail cars to 15,000 Kg trucks (smaller tank won't hold a rail car load)
- 10 X as many shipments, on road (more hazardous?) rather than on railroad
- Reduced site risk, possibly overall increased risk to society
- Supplier may have to maintain larger inventory at his plant

Holistic view of inherent safety

- **Consider the full process and product life cycle**
  - **raw materials**
  - **manufacturing process**
  - **transportation**
  - **storage**
  - **end use**
  - **safety consequences of changing technology (demolition and construction)**

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Holistic view of inherent safety

- ***CONSIDER ALL HAZARDS!***
  - **HAZARD IDENTIFICATION – You can't manage a hazard which you have not identified!**
  - **Informed decisions about conflicting goals**
  - **May be different choices for different situations**
    - **One floor houses eliminate risk of falling down stairs**
    - **So, why are many houses on a beach near the ocean built on stilts?**
      - **concern about a different hazard**
- **Think inherent safety at all levels of design and operation**

Some myths about inherently safer design - #1

- Inherently safer design will eliminate all hazards
  - It is unlikely that any process or material will ever be completely non-hazardous, and there are plenty of examples of “no good deed goes unpunished” where a change intended to improve safety resulted in a new hazard or increased the risk of a different existing hazard

Some myths about inherently safer design - #2

- **Because an inherently safer design represents “the best” approach to managing a particular hazard, you must always implement that design**
  - **This is not true because there may be other hazards and risks to be considered, and also because the societal benefits of a technology may justify the robust application of passive, active, and procedural risk management strategies. The objective is SAFETY, not necessarily INHERENT SAFETY.**

Some myths about inherently safer design - #3

- **Inherently safer design is only applicable at early stages of process research and development and plant design**
  - **IS applies at any stage in a plant life cycle. While the greatest benefits accrue from selection of inherently safer basic technology, there are many examples of significant improvements in inherently safer operation of existing plants.**

Some myths about inherently safer design - #4

- **Plant operating personnel have little to contribute to implementing inherently safer design.**
  - **There are many examples of inherently safer design improvements in plants which have been suggested by operating personnel. Who is in a better position to identify issues with complex systems setting up operators for making errors than the people who use those systems every day?**

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Some myths about inherently safer design - #5

- **There is a "best technology" which is always inherently safer for the manufacture of a particular product.**
  - **"Best" technology for inherent safety may be highly dependent on local factors such as plant location and environment, proximity of population, practicality of other (passive, active, procedural) safety strategies at a particular location. Example – ranch houses eliminate the risk of injury from falling down the steps, but, if you live in a flood plain, perhaps a second floor is a good idea!**

Implementing ISD

- Two strategies
  - Separate ISD reviews at various stages of life cycle
  - Incorporate ISD into existing process hazard analysis studies at various stages in the life cycle
- Both are used successfully
- Primary tools are checklists of ISD options for consideration by designers, operators, PHA teams

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Questions designers should ask when they have identified a hazard in a PHA study

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? (layers of protection – passive, active, procedural)**

Regulations

- Regulatory requirements – ISD Consideration
  - New Jersey Toxic Catastrophe Prevention Act (TCPA)
  - Contra Costa County CA Industrial Safety Ordinance
- Legislation introduced in every session of Congress since 2001
- November 2009 – House of Representatives passed the Chemical & Water Security Act of 2009 (H.R. 2868), now under consideration by the Senate
- Several US Senate and House of Representatives committee hearings in recent years, most recently:
  - House of Representatives - April 2009
  - Senate – February 2010

http://www.senate.gov/fplayers/I2009/urlPlayer.cfm?fn=govtaff030310&st=1125&dur=9270

- US EPA Risk Management Plan (RMP) regulations encourage ISD – eliminate or reduce inventory below threshold to avoid being covered

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Public Attention

- Frequent media coverage, including 60 Minutes, Bill Moyers Journal, Philadelphia Inquirer, others.
- Increased attention as an approach to improved chemical security following September 2001 terrorist attacks
- Recent focus on methyl isocyanate (MIC), the material released at Bhopal in the wake of a 2008 explosion in Institute, WV at the only US plant with a large inventory of MIC (explosion did not involve MIC, but was near the MIC storage area)
  - Bayer Crop Sciences has announced a plan to significantly reduce the inventory of MIC in response to public concern.

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AIChE/CCPS Activities

- Definition of IST to be prepared by CCPS under contract to the US Department of Homeland Security
- Initial workshops in February 2010 in Baltimore and Houston
- Draft definition presented in IST sessions and panel discussions at the Global Congress on Process Safety at the AIChE Spring Meeting in San Antonio on March 22
- Final report to be issued in May

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New York Times Editorial May 17, 2009

Chemical plants, where large amounts of highly toxic chemicals are routinely stored, are the nation's greatest terrorism vulnerability. Since the Sept. 11 attacks, environmental groups and others have been pushing for a federal law that imposes tough safety regulations on the plants. One of their highest priorities has been a mandate that plants replace particularly dangerous chemicals, like chlorine, with safer alternatives when practical.

So far, Congress has failed to come through. In 2006, it sided with the chemical industry and passed an extremely weak law. That faulty law sunsets this fall, which gives Congress a new chance to make things right.

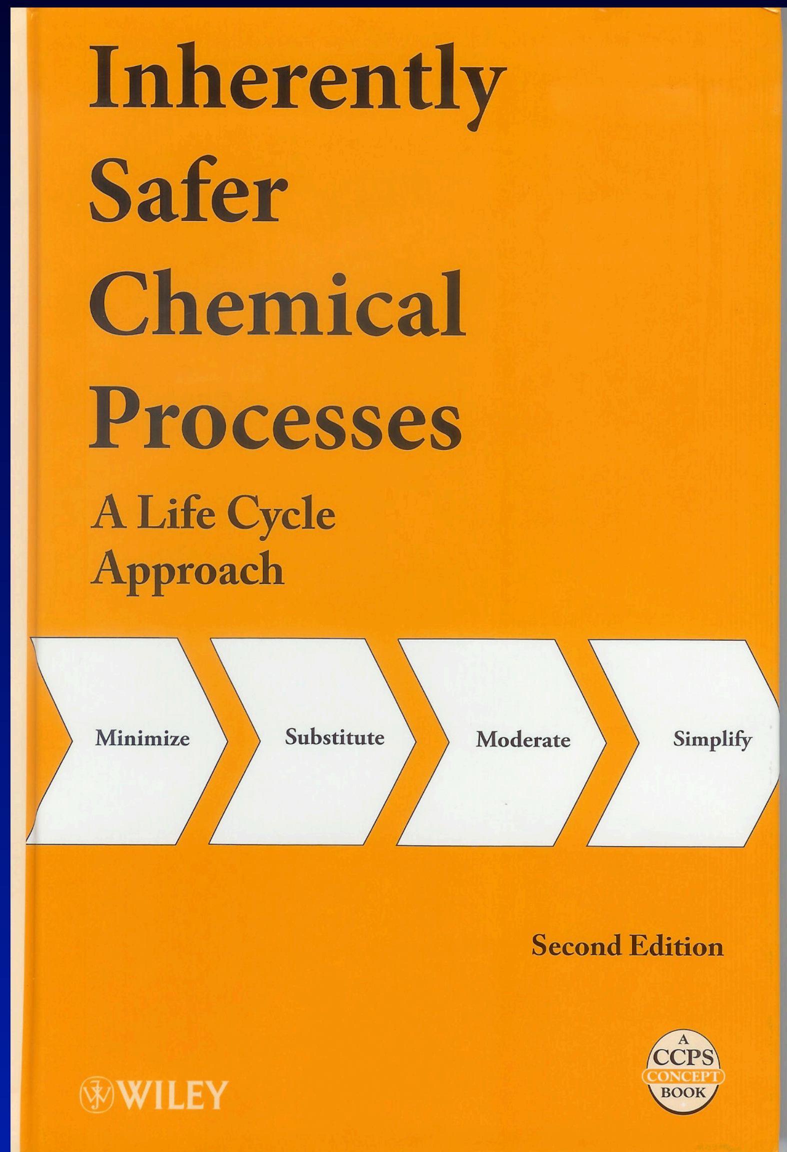
The next law should impose strong, mandatory safety rules. It should contain a safer-chemicals requirement, protection for whistleblowers, and a provision allowing citizens to sue for violations. It should make clear that the federal rules do not pre-empt state laws, so states can do more to protect their residents if they want.

For More Information

- **Center for Chemical Process Safety (CCPS). *Inherently Safer Chemical Processes - A Life Cycle Approach*, 2nd Edition. John Wiley & Sons, Hoboken, NJ, 2009.**
- **Kletz, T. A., *Process Plants - A Handbook for Inherently Safer Design*, Taylor and Francis, London, 1998.**
- **CCPS overview document:**

  http://www.aiche.org/ccps/webknowledge/inherentlysafer.aspx

Thank You



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