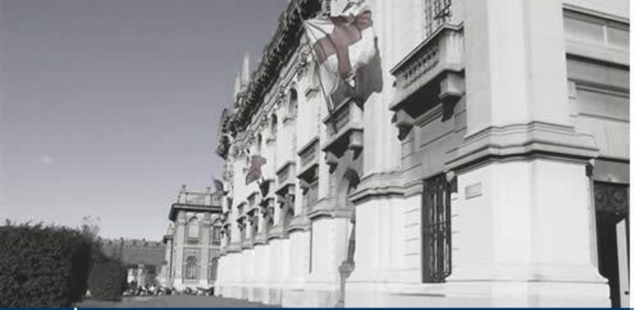


POLITECNICO DI MILANO

School of Industrial and Information Engineering

Course 096125 (095857)

Introduction to Green and Sustainable Chemistry

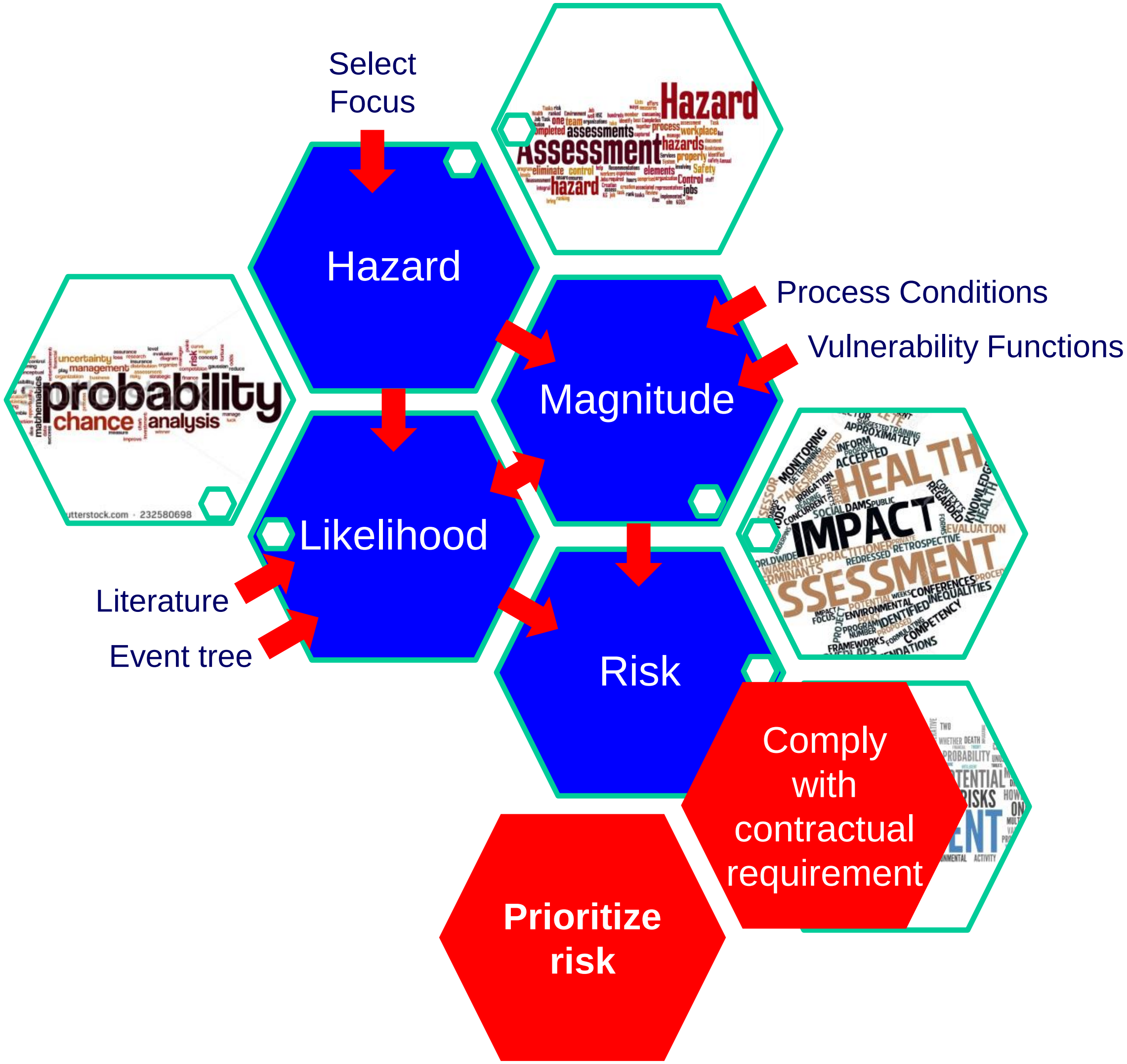




Inherent Safety and Inherently Safer Reactions.

Prof. Attilio Citterio
Dipartimento CMIC "Giulio Natta"
https://iscamapweb.chem.polimi.it/citterio/it/education/course-topics/

Risk Assessment Approach.



Risk = (Likelihood × Magnitude)

Select focus of the analysis:

- Human;
- Productivity;
- Asset damage;
- Environmental;

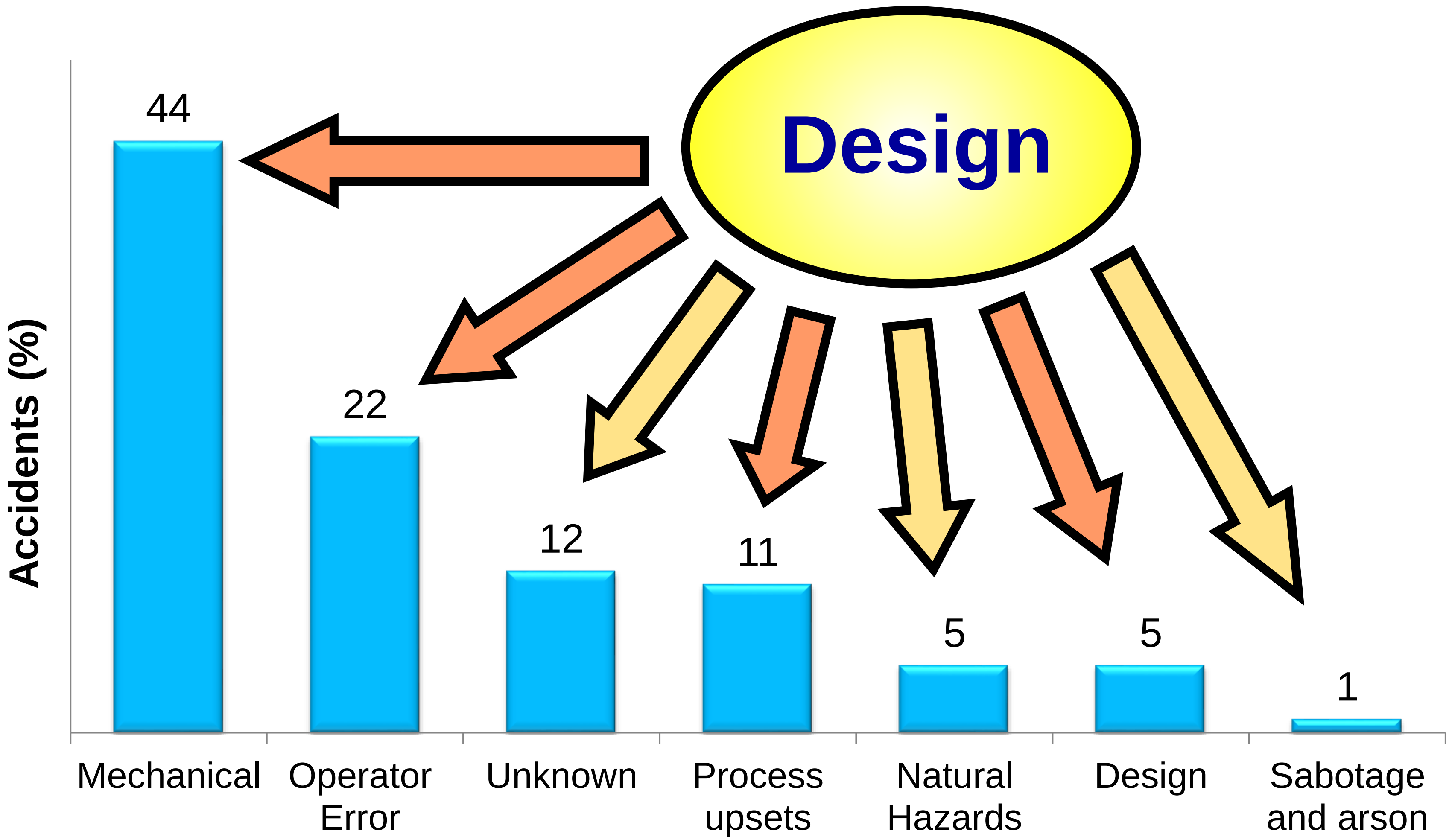
Physical effects depends upon Hazard and process conditions;

From physical effects to impact on targets;

From release frequency to outcome frequency (interaction with consequence assessment);

Risk is a function of Likelihood and Magnitude.

Causes of Losses in Large Plant Accidents.

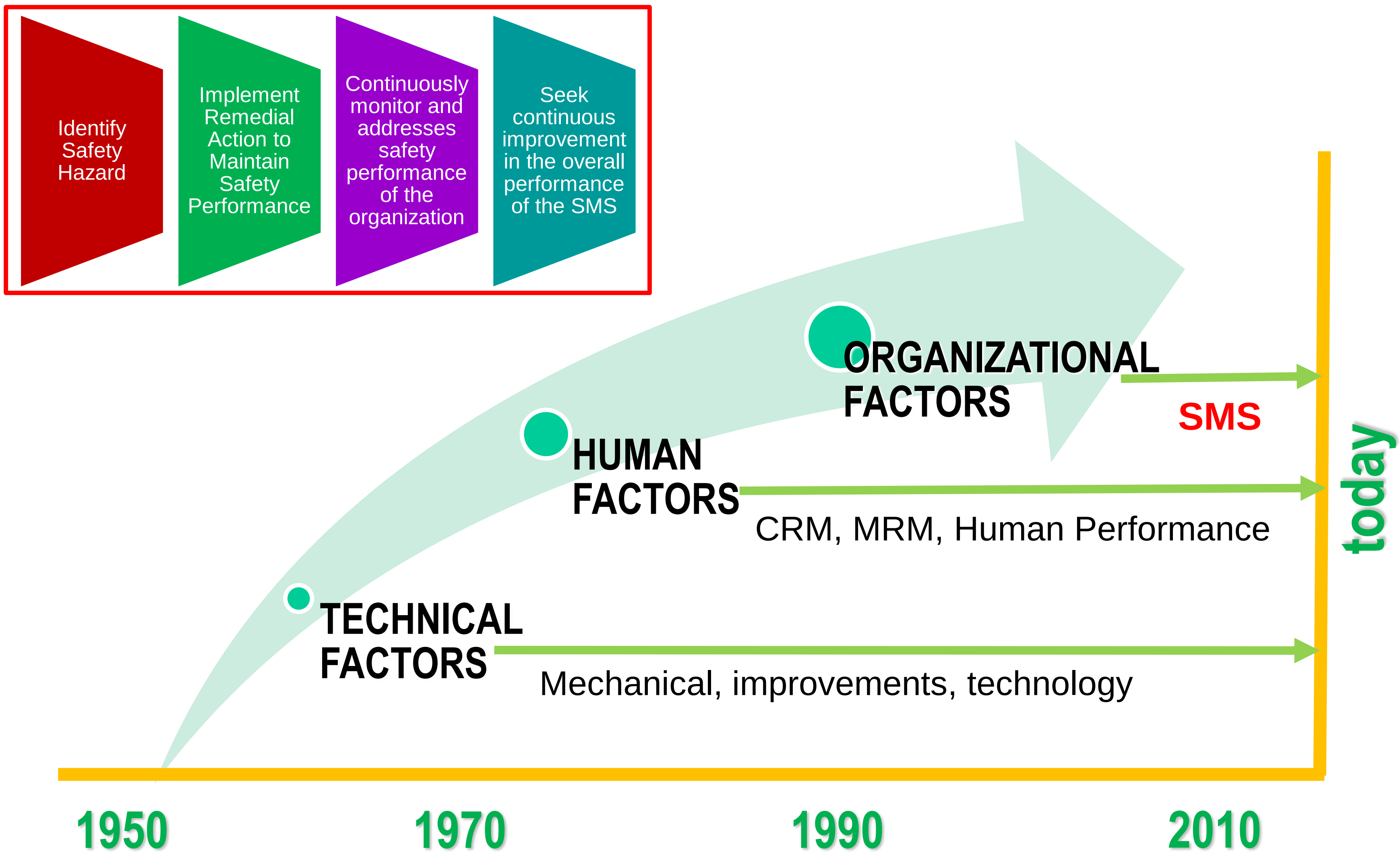


Concept of Safety.

- ❖ The elimination of accidents (and serious incidents) is unachievable
- ❖ Failures will occur, in spite of the most accomplished prevention efforts
- ❖ No human endeavour or human-made system can be free from risk and error.
- ❖ Controlled risk and error is acceptable in an inherently safe system.

Safety is the state in which the risk of harm to persons or property damage is reduced to, and maintained at or below, an **acceptable level** through a continuing process of **hazard identification** and **risk management.**

The Evolution of Safety Thinking.



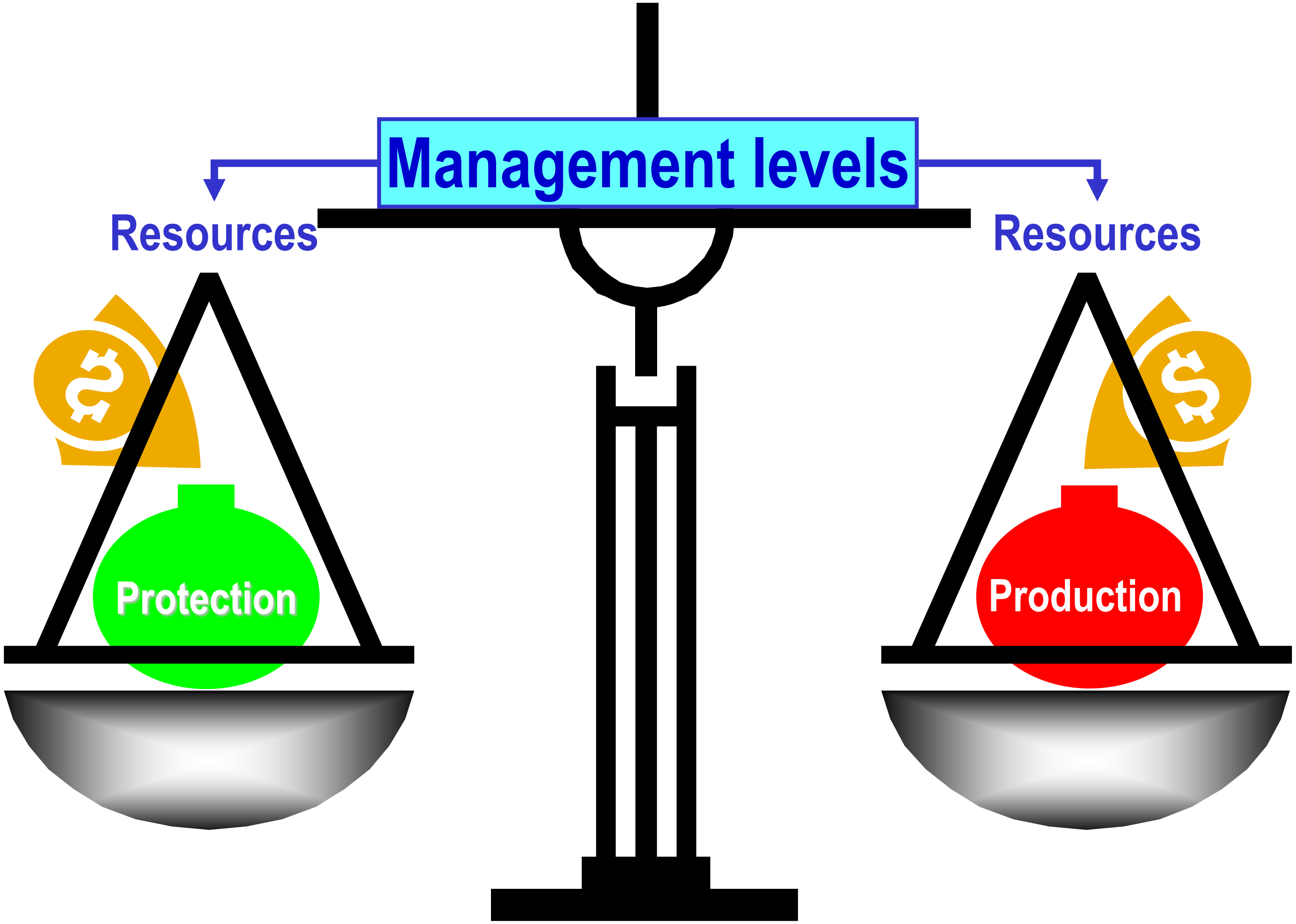
Inherent Safety (Previous and Recent Strategies).

Pre-1930's	Identify who caused the loss and punish the guilty
Pre-1970's	Find breakdown in, and fix man-machine interface (Trevor Kletz)
1970's, 80's	Develop risk assessment techniques and systematic approaches
1980's	Performances, risk based standards; regulations
2000's	'green' and 'inherent safety' design
2000's	Safety Management Systems Complete (SMS-C).

Management commitment & responsibility	Safety Risk Management	Safety Assurance	Safety promotion
• Safety accountabilities • Appointment of key safety Personnel • Coordination of emergency response planning • SMS documentation	• Hazard identification • Risk assessment & mitigation	• Safety performance monitoring & measurement • The management of change • Continuous improvement of the SMS	• Training and education • Safety communication

CJChE, vol 81, pp. 2-16 (2003); * ICAO Safety Management manual (2010)

The Management Dilemma.



Conflicts and Compromises.

The properties of a technology that makes it dangerous can be the same which makes it useful:

- Airplanes travel at 960 $km \cdot h^{-1}$
- Gasoline is flammable (substitute must be able to stock a big quantity of energy in a compact form)

the danger control is a critical problem in obtaining safely the benefits of technology.

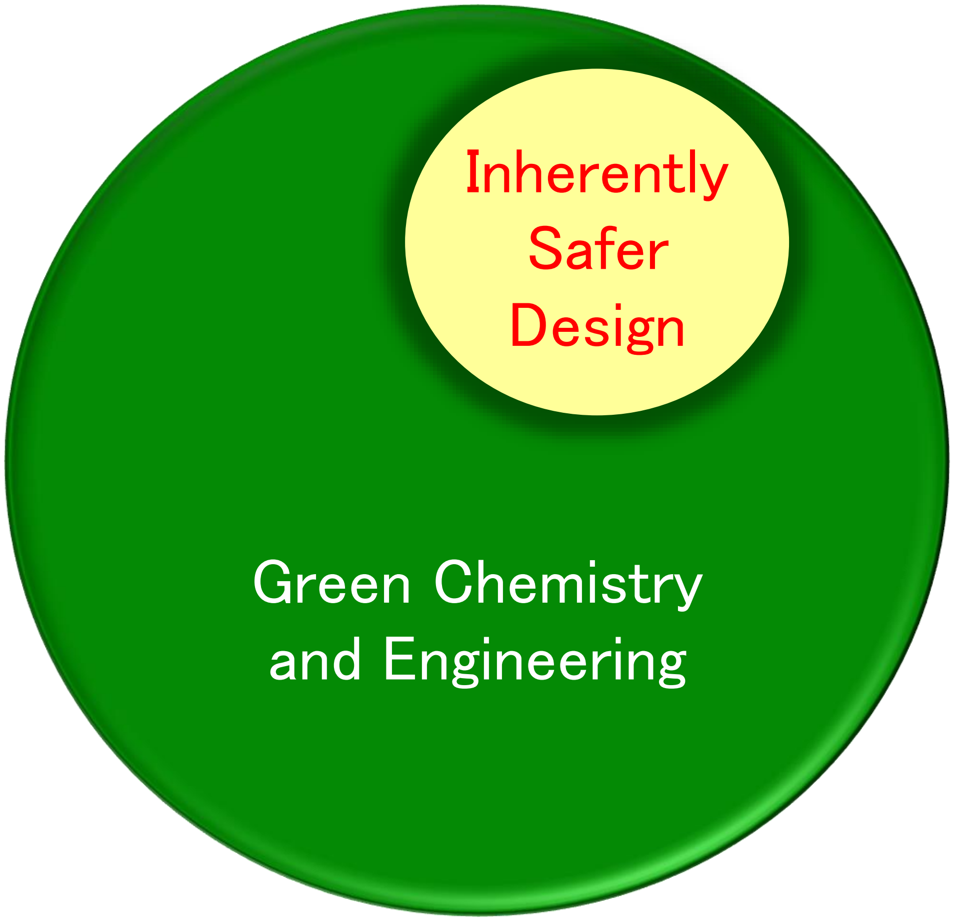
Everything presents multiple dangers:

- Travel in car
  - speed (energy), flammable fuel, toxicity of exhaust gases, hot surfaces, pressurized cooling systems, electricity ......
- Chemical process or product
  - Acute toxicity, flammability, corrosivity, chronic toxicity, various environmental impacts, reactivity ....

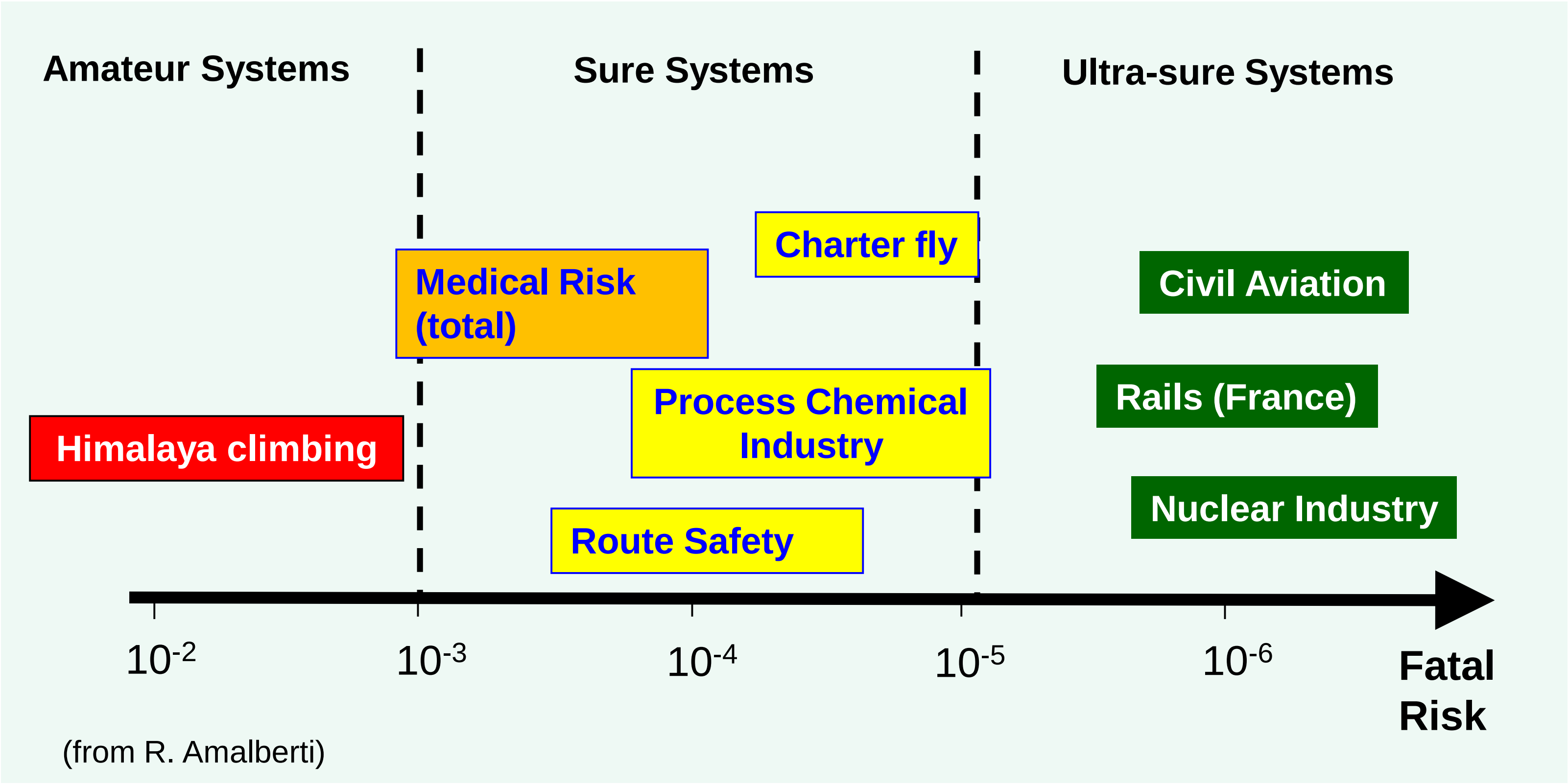
What means Inherently Safer Design?

- ***Inherent*** - "existing in something as a permanent and inseparable element..."
  - safety "built in", not "added on"
- Eliminate/minimize process hazards than control them
- Three parts:
  - Hazard Identification,
  - Hazard Evaluation and
  - Inherent Safety Evolution
- More a Philosophy and way of thinking than a specific set of tools and methods
  - Applicable at all levels of design and operation from conceptual design to plant operations
- ***"Safer"*** **, not *"Safe" !***

Inherently Safer Design, Green Chemistry, and Green Engineering.

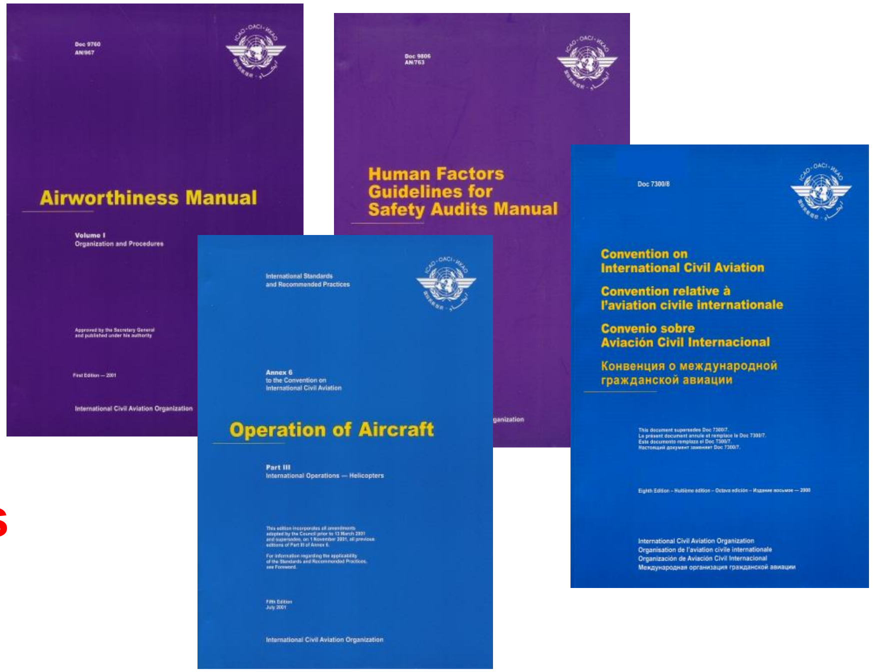


Risk Level in Same Sectors.

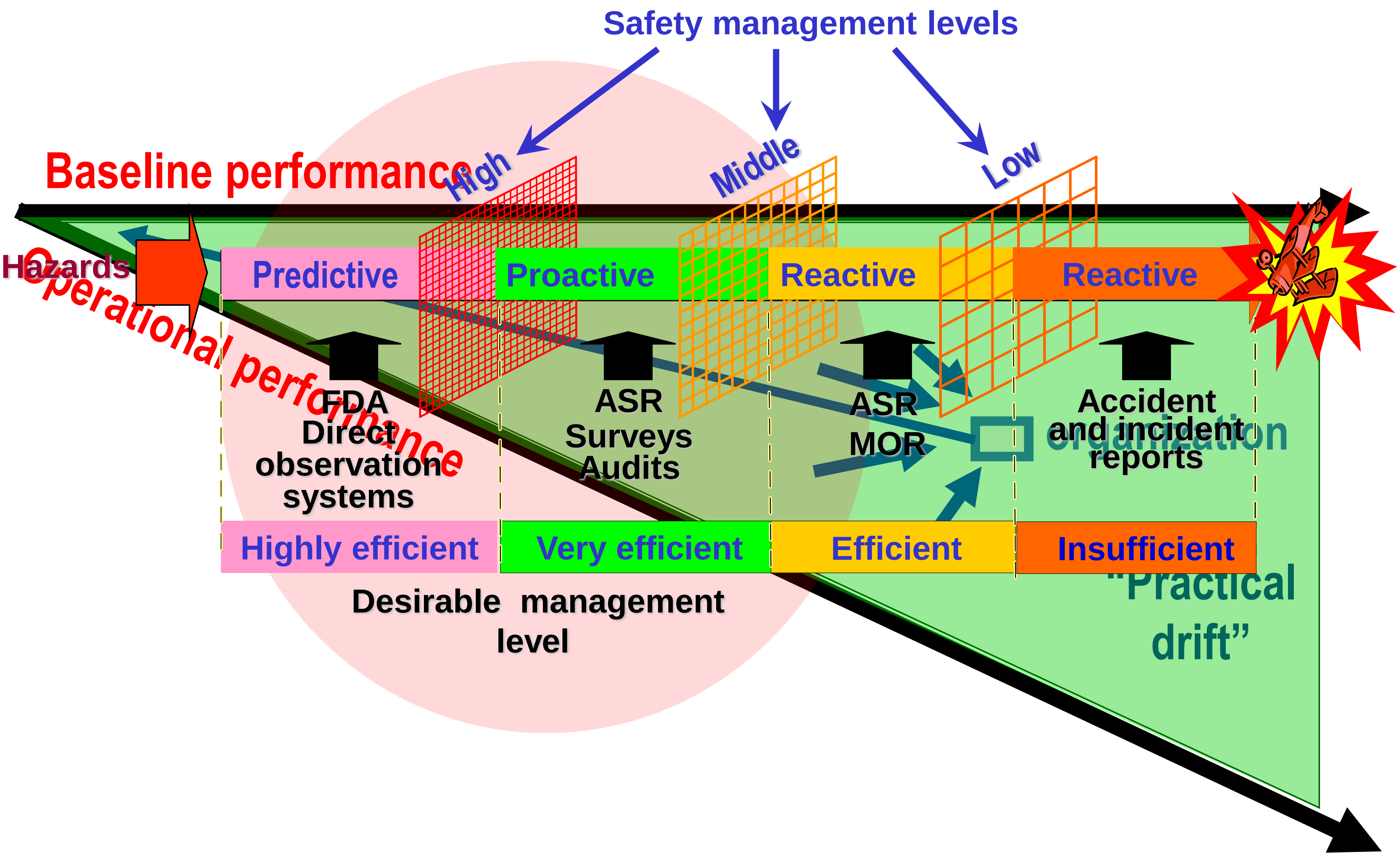


Control Systems in Aircraft Industry.

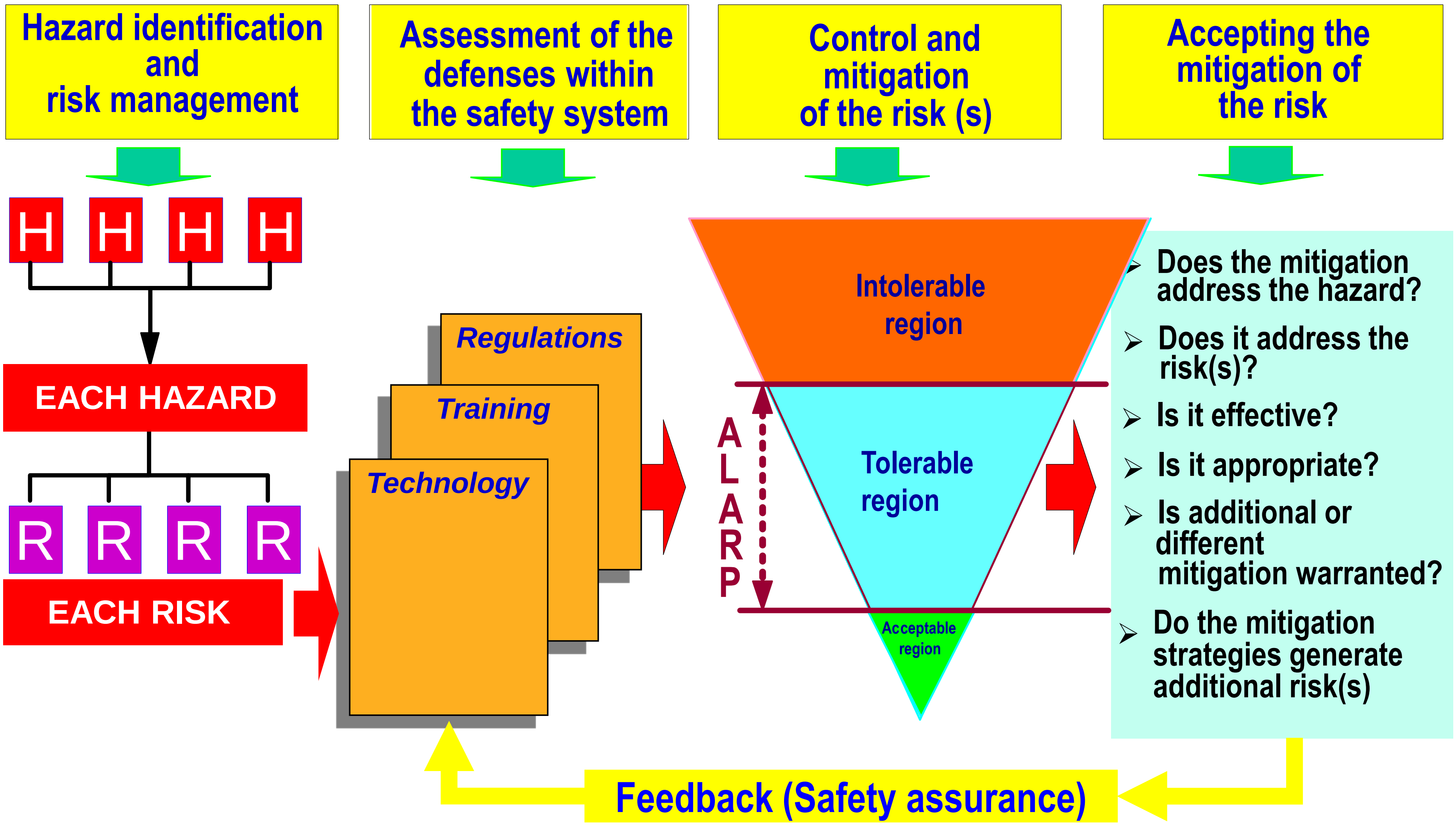
- Operation of aircraft
- Maintenance of aircraft
- Air traffic services
- Aerodromes
  - **Two audience groups**
    - ✓ States
    - ✓ Service providers
  - **Three distinct requirements**
    - ✓ Safety programme
    - ✓ SMS
    - ✓ Management accountability.



Strategies – Levels of Intervention and Tools.



Risk Mitigation at a Glance.



Hazard and Risk.

- A Hazard is defined as an <u>inherent</u> physical or chemical characteristic that has the potential for causing harm to people, the environment or property. (CCPS, 1992).
- Hazards are characteristic of the materials and chemistry.
- Hazards are characteristic of the process variables.

- Chemical process plants have an inherent risk. Managers of each site must decide what is a tolerable risk. Risk can be reduced by reducing the consequence and/or reducing the probability.

Examples

- Phosgene – toxic by inhalation; Acetone - flammable
- High pressure steam - potential energy due to pressure and high temperature

Risk of an Event = Consequence * Probability

Occupational Safety vs. Process Safety.

Occupational Health and Safety

- Workplace rules
- Worker training
- Supervision
- Individual behaviors
- Safety equipment, PPE
- Focus on individual well being

Objective: to eliminate injuries and illnesses to personnel, and to protect assets, production, and the environment.

Process Safety

- Collective commitment
- Addresses events over which the individual worker often has little or no control
- Focus on systems
- Broader impact – events that could affect groups of workers or general public

Objective: to eliminate, prevent, avoid process-related incidents.

Process Safety is the use of engineering and management competence focused on preventing catastrophic accidents, in particular explosions, fires, and toxic releases, associated with the use of chemicals and petroleum products.
Occupational Safety vs. Process Safety

Hazard for Chemicals and Related Risks.

The industrial activities and consumer products have led to the creation of > 70,000 chemicals. The rate at which new chemicals are formulated outpaces the rate at which their safety can be evaluated.

There is not always a threshold below which there is no adverse health effect. For example, carcinogens always cause a risk no matter how low the dose is. So, there is a matter of exposure level.

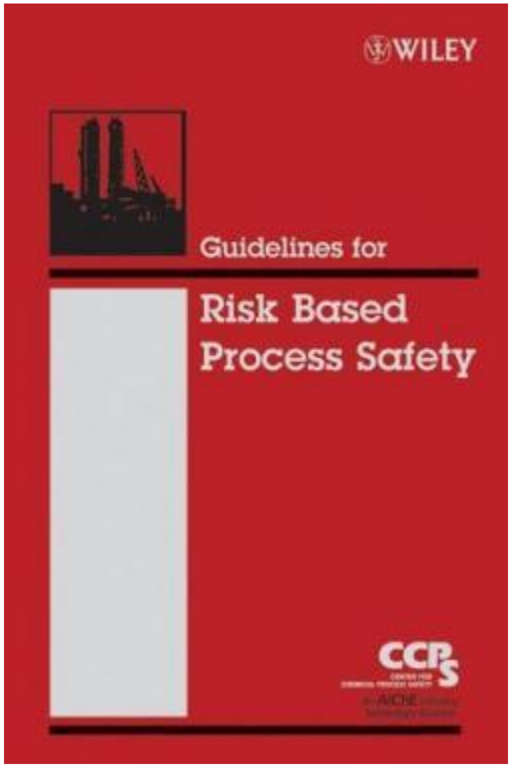
Risk = f (hazard, exposure)

How bad the substance is → hazard

How much have we taken in → exposure

Primary questions: How clean is clean?   How safe is safe?

Risk Based Process Safety.



ISBN: 978-0-470-16569-0

Commit to Process Safety
- Process Safety Culture
- Compliance with Standards
- Process Safety Competency
- Workforce Involvement
- Stakeholder Outreach

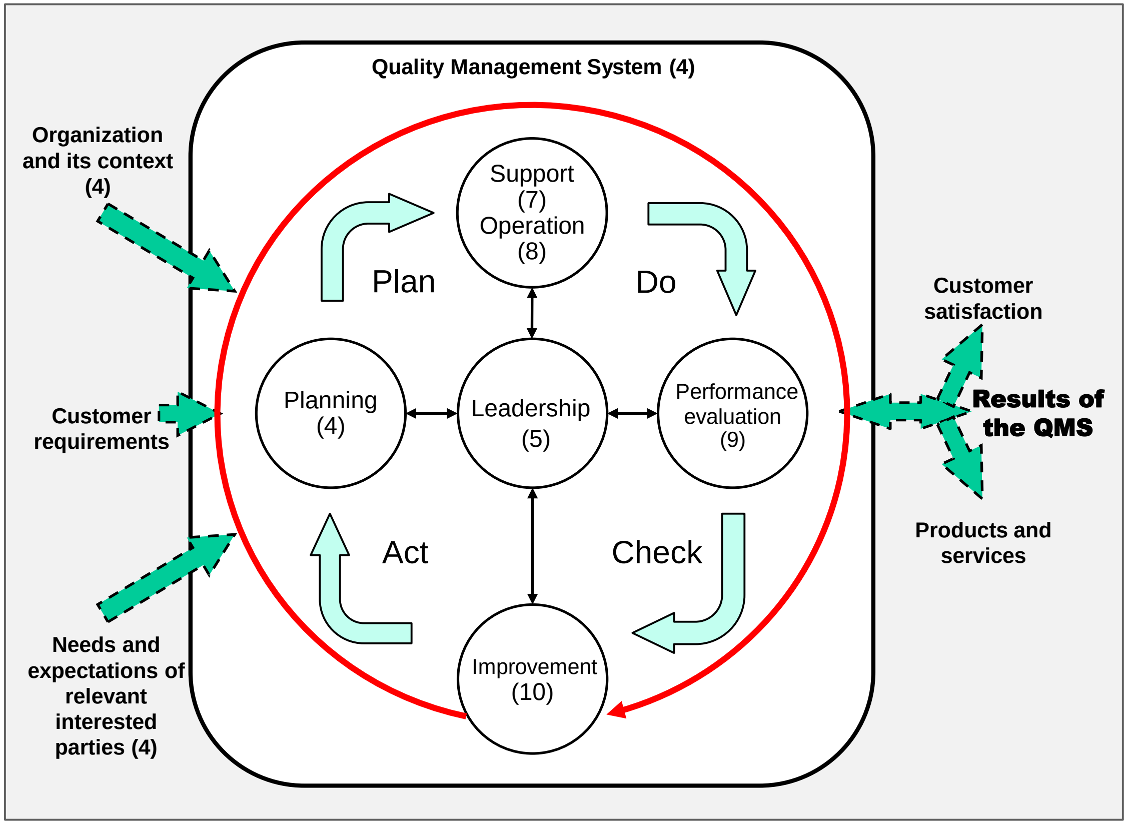
Understand Hazards and Risk
- Process Knowledge Management
- Hazard Identification and Risk Analysis

Manage Risk
- Operating Procedures
- Safe Work Practices
- Asset Integrity and Reliability
- Contractor Management
- Training and Performance Assurance
- Management of Change
- Operational Readiness
- Conduct of Operations
- Emergency Management

Learn from Experience
- Incident Investigation
- Measurement and Metrics
- Auditing
- Management Review and Continuous Improvement

ISO 9001:2015 Quality Management Systems Requirements.

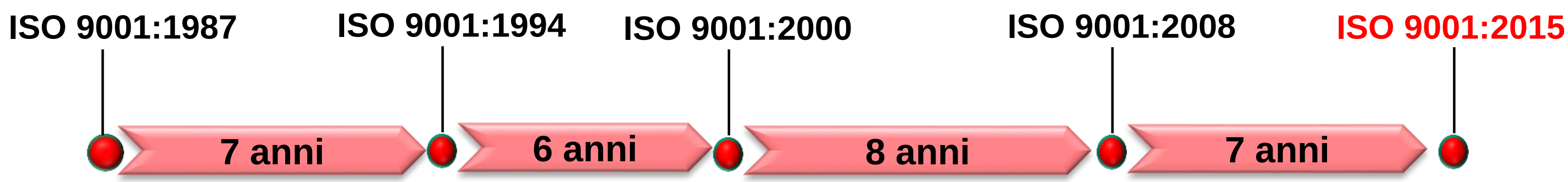
Risk-based thinking

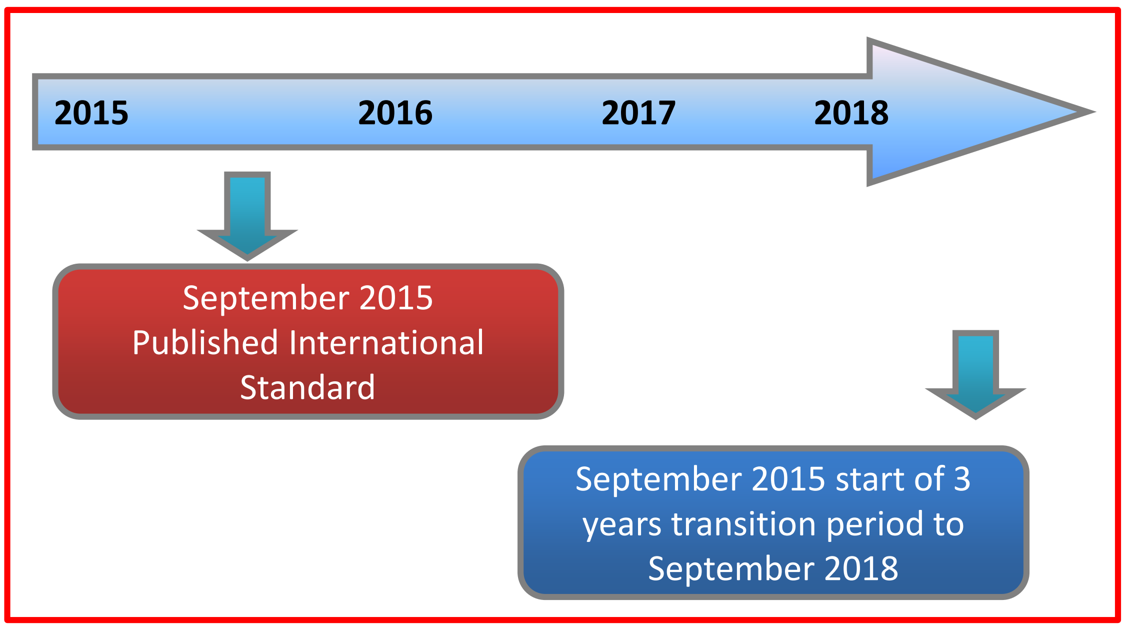


QMS Structure Re-organized.

4. Context of Organization – addresses needs and expectations of interested parties, scope of QMS
5. Leadership – addresses management commitment, policy, roles, responsibility & authority
6. Planning – includes risks, opportunities, objectives and plans to achieve them, the planning of changes
7. Support – includes resources, competence, awareness, communication, documented information
8. Operation – includes planning & control, determine market needs, interaction w/customers, planning process, control of external provisions of goods/services, production of goods, provision of services, release of goods/services, non-conforming goods/services
9. Performance Evaluation – includes monitoring, measurement, analysis & evaluation, internal audit, management review
10. Improvement – addresses non-conformity & corrective action, improvement.

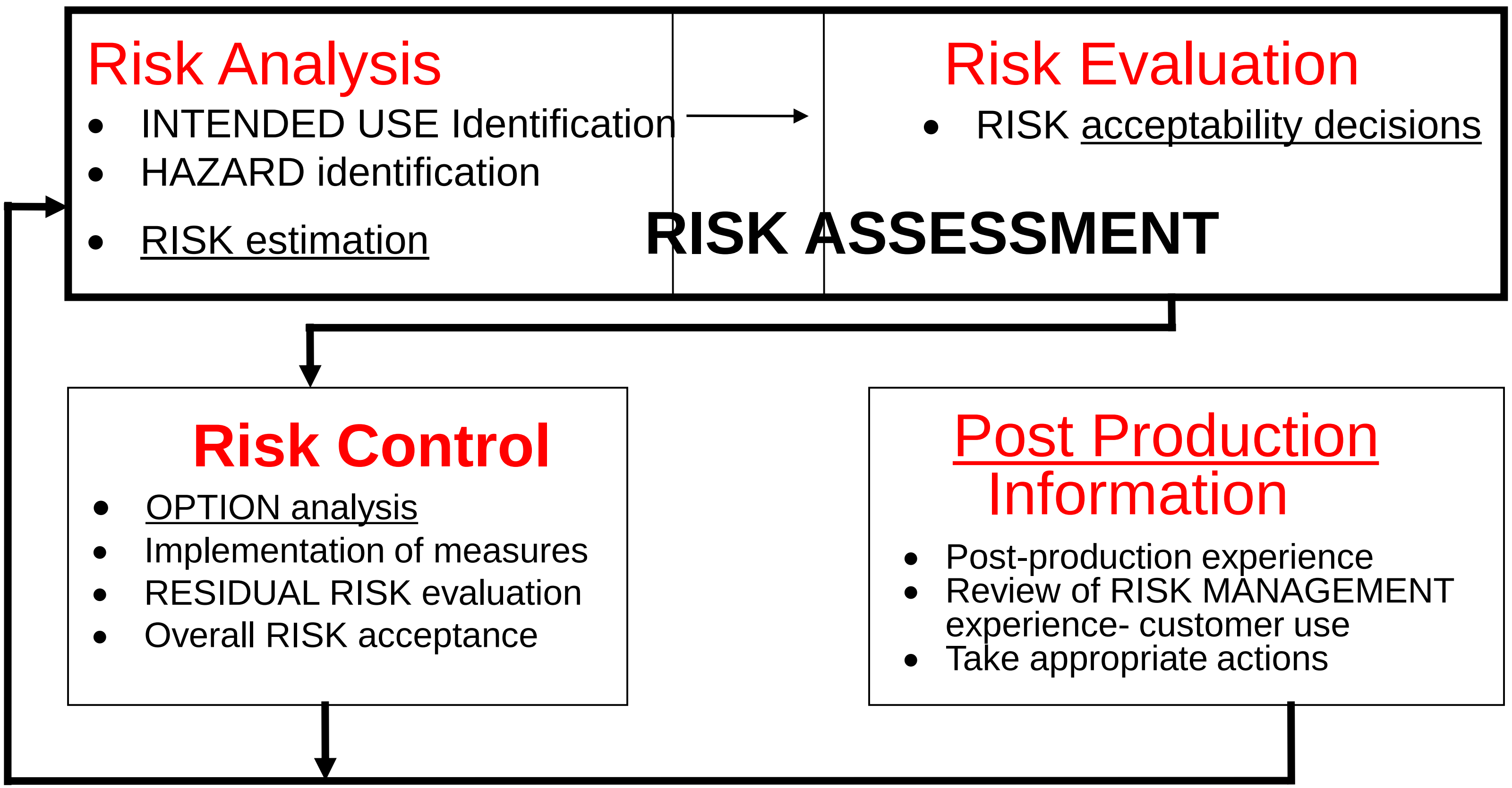
Timeline to Revision Release and Client Transition.





Certified organizations will have a transition period of three years starting from September 2015 to update their Quality Management Systems to new requirements.

Four Phases of Risk.

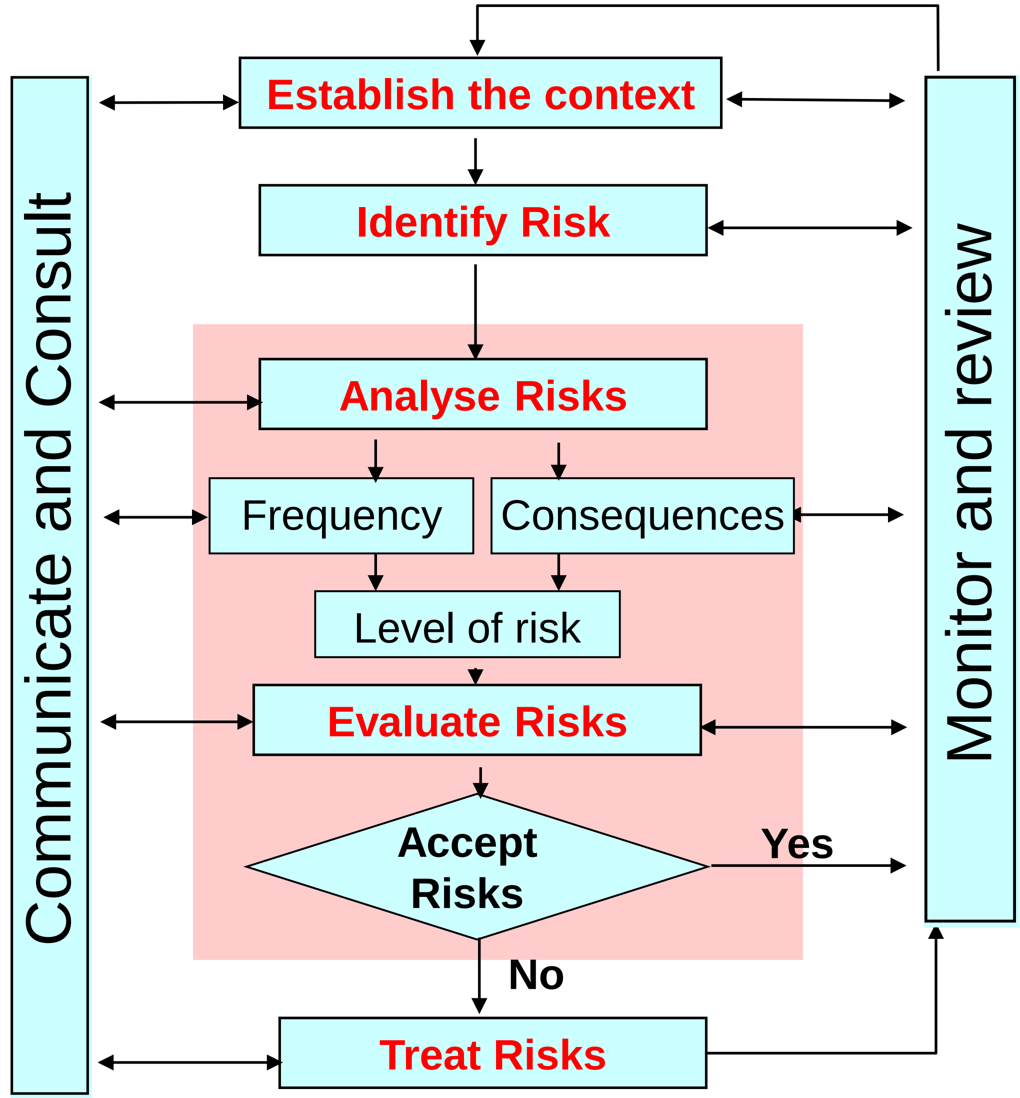


Safety Analysis.

Analyse process according to ESARR 4 and standards for risk management.

Documentation:

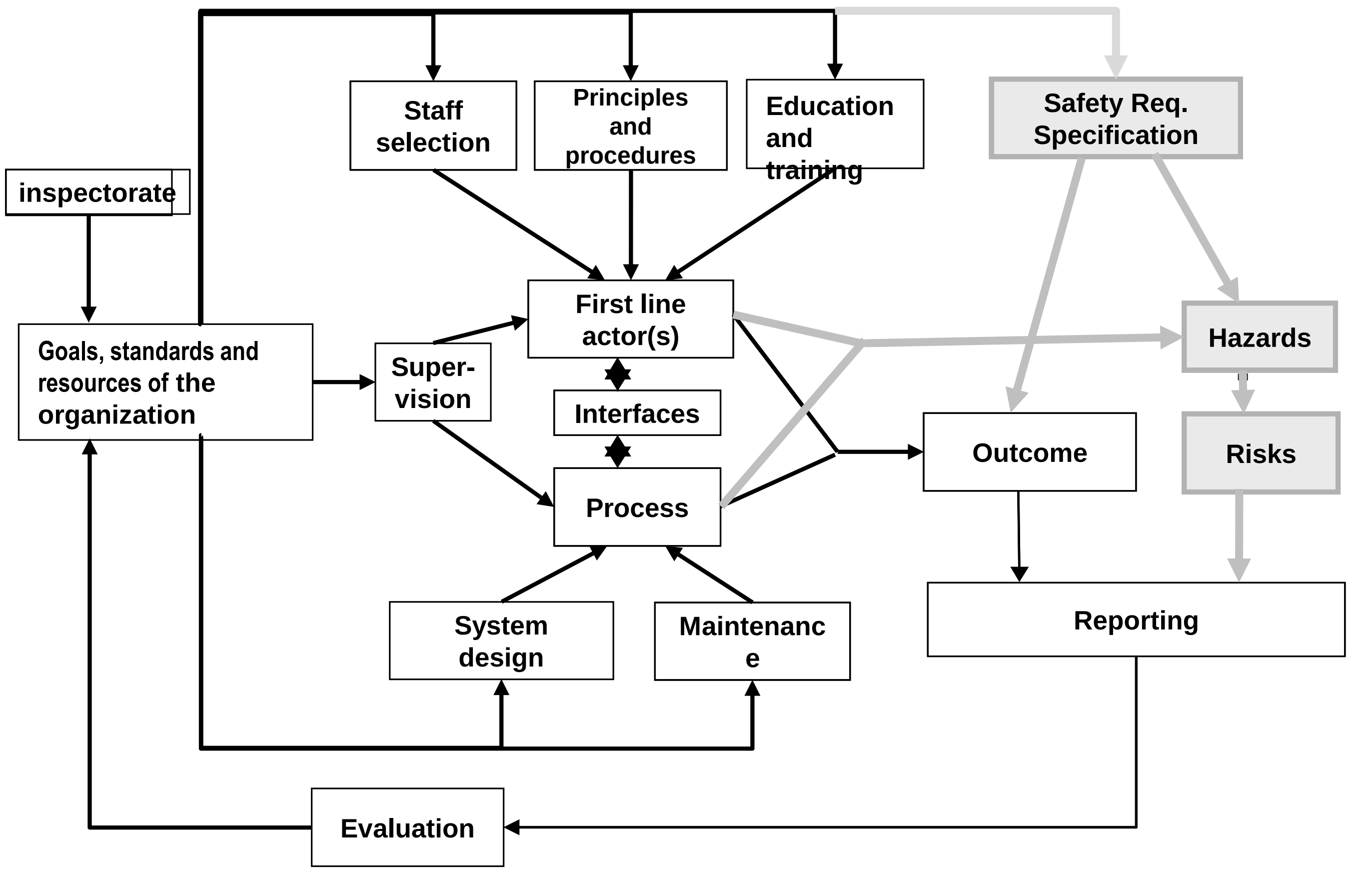
- FHA
- PSSA
- SSA
- Safety Case



Risk Evaluation Methods.

Methods (SAM):

- Hazop
- FMECA
- FTA
- ETA
- Reliability



Risk-informed MTO approach

Acronyms of Various Safety Methods.

SAM = Safety Assessment Methodologies

HAZOP = HAZard and OPerability analysis

FTA = Fault tree analysis, o analisi dell'albero dei guasti

ETA = Event Tree Analysis

FMEA = Failure Mode and Effect Analysis

FMECA = Failure Mode, Effects, and Criticality Analysis

MTO = Man-Technique-Organisation

FHA = Functional Hazard Assessment

PSSA = Preliminary System Safety Assessment

SSA = System Safety Assessment

ESARR 4 = EUROCONTROL Safety Regulatory Requirement

CPPs = Critical Control Points

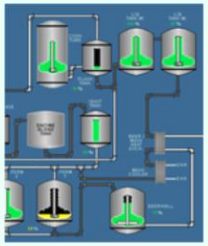
QMS = Quality Management System.

Hazard Identification.

Hazards relevant to the plant/site

- Interaction with third parties
- Natural events

HAZID MSDS → Early identification of project Hazard



Hazards relevant to the process configuration

- Process deviations

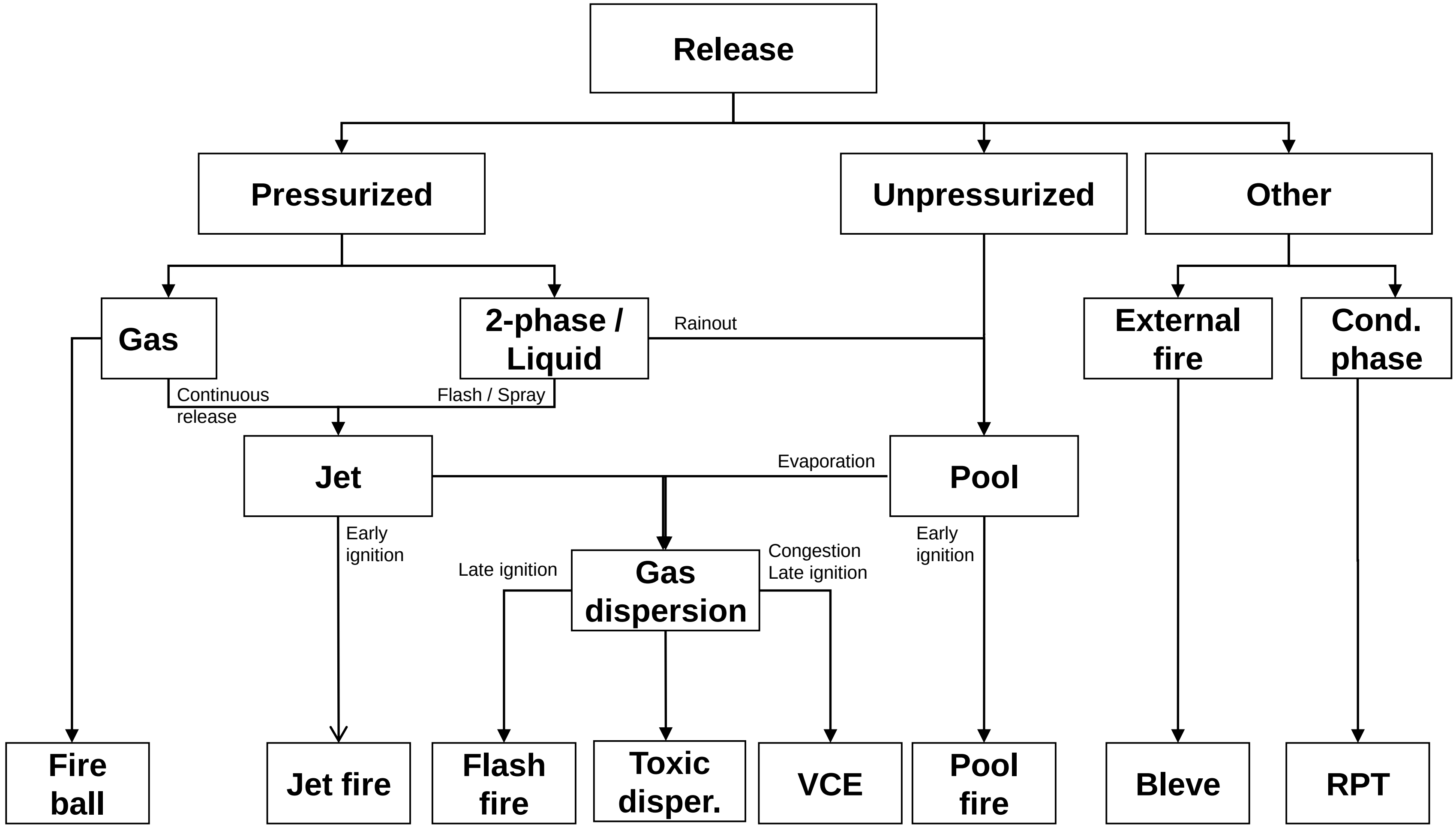
HAZOP FMECA → Guidelines and principles for HAZOP
Project improvement

Hazards relevant to the pieces of equipment

- Corrosion and Material defects,
- Fabrication errors, etc.

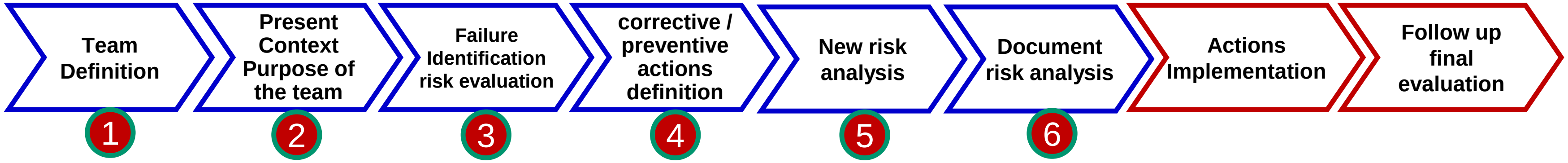
Statistical analysis → Detailed and quantitative analysis to improve project safety

Hazard Identification (2).



FMEA.

FMEA PROCESS



- List ALL possible failures
- Classification and quantification (1 to 10) of failures based on:
  - Frequency (**F**)/ probability of failure occurs
  - Severity (**S**) of the effect
  - Detection (**D**) of the failure (capacity to detect)
- Prioritization by calculating **Risk Priority Number**:

RPN = F × S × D

FMEA Metrics.

- Fishbone diagram per unit operation to structure process parameters
- A 5 level scale is used to rank the parameters to calculate the Risk Priority Number RPN = I × D × P ;
- A threshold is settled;
- Any value above the setting was studies within a DoE;
- Severity/Impact threshold can be added as additional requirement;
- Critically is dependent on risk: P×I .

	Impact	Detectability	Probability
1	negligible	very high	extremely unlikely
2	marginal	high	remote
3	moderate	moderate	occasional
4	major	low	probable
5	Critical (unknown)	Very low	frequent

Risk Acceptability.

- National/international decision – level of an acceptable loss (ethical, political and economic).

Risk Analysis Evaluation:

ALARP – as low as reasonable practical (UK, USA)

“Societal risk has to be examined when there is a possibility of a catastrophe involving a large number of casualties”.

GAMAB – Globalement Au Moins Aussi Bon = not greater than before (France)

“All new systems must offer a level of risk globally at least as good as the one offered by any equivalent existing system”.

MEM – minimum endogenous mortality

“Hazard due to a new system would not significantly augment the figure of the minimum endogenous mortality for an individual”.

Risk Acceptability (2).

Tolerable hazard rate (THR) – A hazard rate which guarantees that the resulting risk does not exceed a target individual risk.

SIL	PFD_{avr}	Risk Reduction	Availability (%)
4	10^{-4} to 10^{-5}	10,000 to 100,000	99.99 to 99.999
3	10^{-3} to 10^{-4}	1,000 to 10,000	99.9 to 99.99
2	10^{-2} to 10^{-3}	100 to 1,000	99 to 99.9
1	10^{-1} to 10^{-2}	10 to 100	90 to 99

PDF_{ave} = average probability of failure on demand

Potential Loss of Life (PLL) expected number of casualties per year.

Assessing Risk.

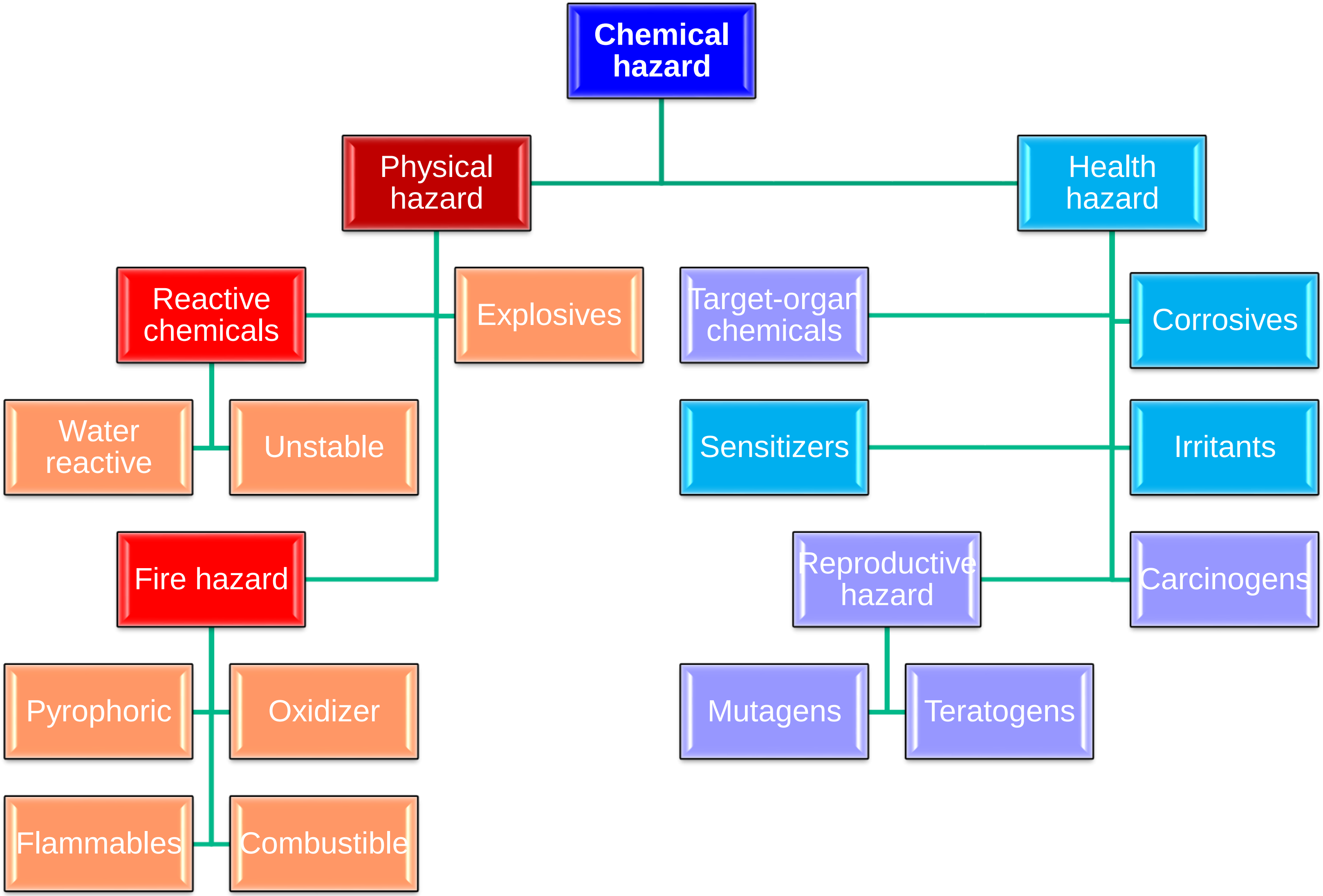
- Identify Potential Risks
  - Begin with a HAZOP
- Assess Potential Risk Likelihood
  - Equipment failure
  - Human error
- Assess Potential Risk Consequences
  - Impact of an event.

Health Hazards.

- **Category A - Biological Agents**
- **Category B - Physical Agents**
- **Category C - Chemical Agents**

(only this last section analyzed)

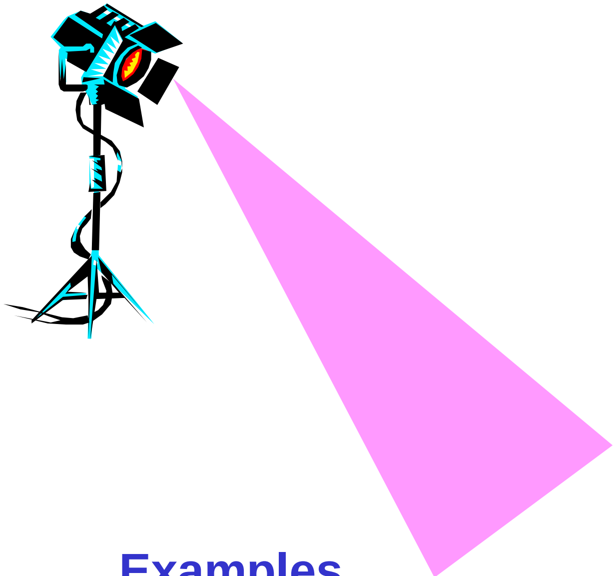
Chemical Hazard.



Chemical Health Effects.

- Irritants: Inflame skin tissue on contact.
- Corrosives: Destroy skin tissue at point of contact.
- Sensitizers: Cause allergic reactions.
- Target-Organ Chemicals: Damage specific body organs and systems.
- Reproductive Hazards: Change genetic information in egg or sperm cells and/or damage fetus after conception.
- Carcinogens: Cause cancer.

Examples of Hazard.



Acute Toxicity
Chronic Toxicity
Flammability
Instability
Extreme Conditions
Air Pollution
Water Pollution
Groundwater Contamination
Waste Disposal

Examples

Chlorine is toxic by inhalation
Sulfuric acid is extremely corrosive to the skin
Ethylene is flammable
High pressure confined steam contains pV energy
Styrene can polymerize releasing heat
Nuclear material is contains chronic toxicity
Large mass at high temperature is an energy source

Toxic, Flammable, Temperature, Pressure

Representative List of Types of Hazards.

Fires
- Flash fires
- Pool fires
- Jet fires

Explosions
- Vapor clouds
- Confined deflagrations
- Detonations
- Pressure Vessel Ruptures
  - Runaway Reactions
  - Overpressure
  - Brittle fracture
  - Polymerizations
  - Decomposition
  - Contamination reactions
  - Boiling liquid, expanding vapor

Toxicity
- Environmentally
  - Chronic
  - Acute
  - Individually toxic
  - Broadly toxic
- Pesticides
- Fungicides
- Herbicides
- Insecticides
- Fumigants

Product
- Customer injury
- Waste disposal

Representative Hazardous Molecular Groupings.

Ammonia →	*Toxicity and Fire*
Chlorinated hydrocarbons →	*Toxicity*
Cyano compounds →	*Toxicity*
Multi-bond hydrocarbons →	*Fire and Explosion*
Epoxides →	*Explosion*
Hydrides and Hydrogen →	*Explosion*
Metal acetylides →	*Explosion*
Nitrogen compounds →	*Explosion*
Oxygenated compounds of halogens →	*Explosion*
Oxygenated manganese compounds →	*Explosion*
Peroxides →	*Fire and Explosion*
Polychlorinated byphenyls →	*Environmental*
Poly-cyclic aromatic hydrocarbons →	*Environmental*

Reactive Combinations of Chemicals.

A +	B		Hazardous Event
Acids	Chlorates	→	*Spontaneous Ignition*
	Chlorites	→	*Spontaneous Ignition*
	Hypochlorites	→	*Spontaneous Ignition*
	Cyanides	→	*Toxic/Flam Gas*
	Fluorides	→	*Toxic Gas*
	Epoxides	→	*Heat/Polymerization*
Combustibles	Oxidizers	→	*Explosion*
	Anhydrous Chromic Acid	→	*Spontaneous Ignition*
	Potassium Permanganate	→	*Spontaneous Ignition*
	Sodium Peroxide	→	*Spontaneous Ignition*
Alkali	Nitro Compounds	→	*Easy to Ignite*
	Nitroso Compounds	→	*Easy to Ignite*

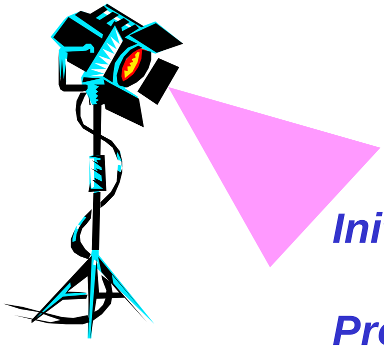
Reactive Combinations of Chemicals (2).

A +	B		Hazardous Event
Ammonium	Chlorates	→	*Explosive Salts*
Salts	Nitrates	→	*Explosive Salts*
Alkali Metals	Alcohols	→	*Flammable Gas*
	Glycols	→	*Flammable Gas*
	Amides	→	*Flammable Gas*
	Amines	→	*Flammable Gas*
	Azo Compounds	→	*Flammable Gas*
	Diazo Compounds	→	*Flammable Gas*
Inorganic Sulfide	Water	→	*Toxic/Flam Gas*
Metals	Explosives	→	*Heat/Explosion*
	Polymerizable Compounds	→	*Polymerization*

Relevant Chemical Accidents or Blasts.

PLACE	DATE	CHEMICAL	ESTIMATED AMOUNT	CASUALTIES
Oppau/Ludwigshafen	September 21, 1921	ammonium sulfate, ammonium nitrate	4,500 t exploded	ca. 550 + 50 dead, 1,500 injured
Flixborough	June 1, 1974	cyclohexane	400 ton inventory, 40 ton escaped	28 dead, 36 + 53 injured
Beek	November 7, 1975	(mainly) propylene	> 10,000 m3 inventory, 5.5 ton escaped	14 dead, 104 + 3 injured
Seveso	July 10, 1976	2,4,5-trichlorophenol, dioxin	7 ton inventory, 3 ton escaped	no direct casualties, ca. 37,000 people exposed
San Juan, Mexico City	November 19, 1984	LPG	> 10,000 m^3 inventory	5 + ca. 500 dead, 2 + 7000 injured (mainly outside the plant)
Bhopal	December 3, 1984	methyl isocyanate	41 ton released	3,800 dead, 2,720 permanently disabled
Pasadena	October 23, 1989	ethylene, isobutane, hexene, hydrogen	33 ton escaped	23 dead, 130-300 injured
Toulouse	September 21, 2001	ammonium nitrate	200-300 ton	31 dead, 2442 injured
Tianjin	12 August 2015	Sodium cyanide and ammonium nitrate	300 ton (NaCN) and 800 ton (NH_4NO_3)	114 dead, 720 injured

Accident Sequence.



Initiation	*The event that starts the accident*
Propagation	*The events that maintain/expand the accident*
Termination	*The events that stop or diminish the accident*

The goal of Loss Prevention is:

Minimize the probability that the accident begins.

Maximize the probability that the sequence terminates benignly if it does start.

Minimize the consequence if it terminates malignantly.

Inherently safer strategies can impact the accident process at any of these three stages.

Reduce Inherent Hazards and Improve Protection Layers.

→ **Hazard**

Material or energy - inherent in material or chemistry
Process variable - how chemistry works in the process

→ **Layers of Protection**

Passive
Active
Procedural

→ **Receptors**

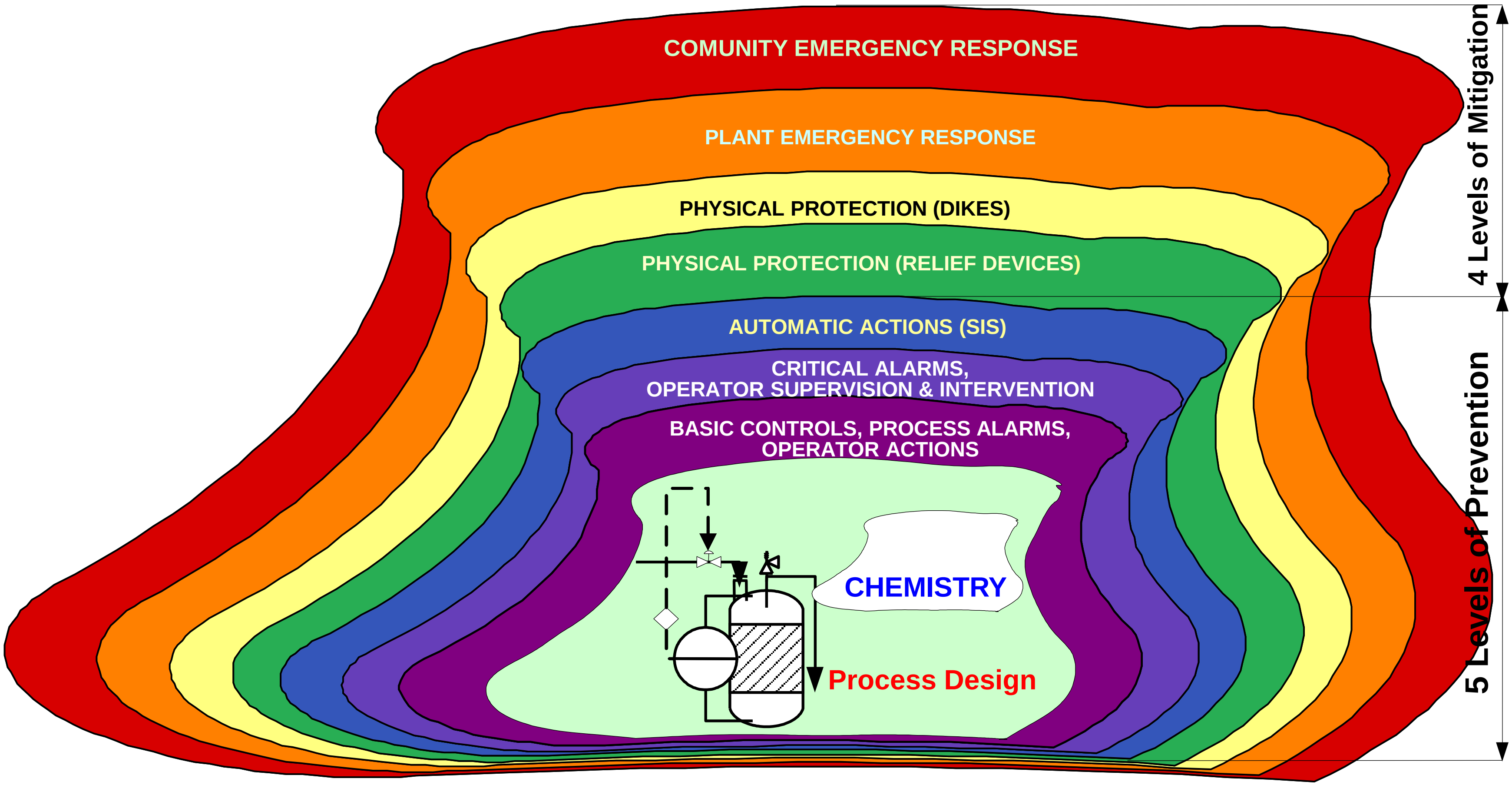
Process
Nearby process
Workers
Nearby workers
Public
Environmental

Reduce or eliminate inherent hazard

Improve inherent protection capability

Gives reduced risk

Prevention/Mitigation and Inherent Safety (*Typical Layers of Protection - Onion Model*).



Process Hazards Management.

Process Safety Information
Operating Procedures
Mechanical Integrity
Process Hazards Analysis
Safe Work Practices
Training
Management of Change
Pre-Startup Review
Emergency Response
Accident Investigation
Audit

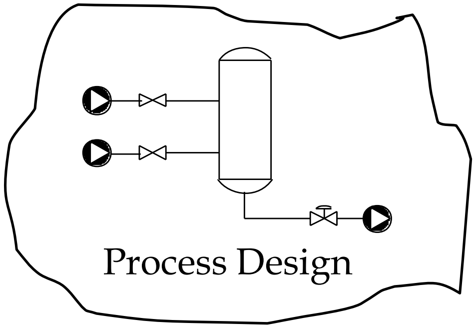
The above are the eleven aspects of the API 750 Recommended Practice. This has been adopted in a similar form by OSHA. The above requires significant investment in time, equipment and effort. The object is to reduce Risk given that a Hazard exists. These topics are covered in Plant & Environmental Safety.
We are interested in reducing the need for the above by invoking Inherently Safer Processes.

Traditional Risk Management.

Consider the following factors:

- Capital cost of safety and environmental equipment
- Capital cost of passive barriers
- Operating and maintenance cost
- Increased maintenance cost for safety instruments
- Increase maintenance for process equipment due to safety requirements
- Operator safety training costs for hazardous materials or processes
- Regulatory costs
- Insurance costs
- Potential property damage, product loss, and business interruption costs if an incident occurs
- Potential liability.

Layers of Protection.



The layers of protection are expensive to build and maintain:

Capital, Operating, Safety Training, Maintenance, Diversion

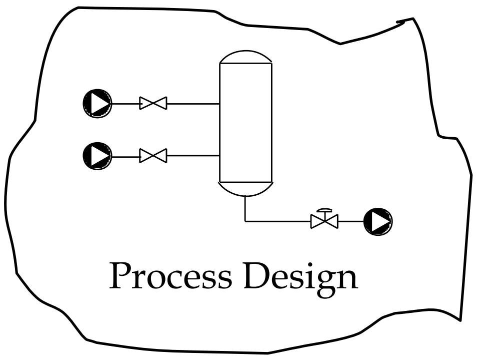
The hazard remains:

Some combination of failures of the layers of protection will result in an accident.

Accidents can occur by mechanisms that were unanticipated:

The hazard remains. Unanticipated mechanisms may not be protected against.

Inherently Safer Processes.



'A chemical manufacturing process is

INHERENTLY SAFER

if it reduces or eliminates the hazards associated with materials and operations used in the process, and this reduction or elimination is permanent and inseparable.'

Strategies for Reducing Risk.

INHERENT	Eliminating the hazard by using materials and process conditions which are nonhazardous.
PASSIVE	Minimizing the hazard by process equipment design features which reduce either the probability or consequence of the hazard without active functioning.
ACTIVE	Using controls, safety interlocks, and emergency shutdown systems to detect and correct process deviations (engineering controls).
PROCEDURAL	Using operating procedures, administrative checks, emergency response, and other management approaches to prevent incidents, or to minimize the consequences (administrative controls).

Presented in order of reliability!

Strategies for Reducing Risk in Chemical Process – Examples – Inherency.

- Eliminate or reduce the hazard by changing to a process or materials 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.

EXAMPLES

- Substituting water for a flammable solvent (latex paints compared to oil base paints).
- An atmospheric pressure reaction using nonvolatile solvents. (No potential for overpressure).

Strategies for Reducing Risk in Chemical Process - Examples – Passive.

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

EXAMPLES

- Containment dike around a hazardous material storage tank.
- A reaction capable of generating 10 *atm* pressure in case of a runaway in a vessel designed for 20 *atm*. (The reactor can contain the accident unless e.g. damage).
- Arrange an expansion room to collect gases and liquids originated from possible failures.

Strategies for Reducing Risk in Chemical Process – Examples – Active.

- Controls, safety interlocks, automatic shutdown systems.
- Multiple active elements
  - Sensors - detect hazardous conditions
  - Logic device – decide what to do
  - Control elements – implement action
- Prevent incidents, or mitigate the consequences of incidents.

EXAMPLE

- High level alarm in a tank shuts automatic feed valve.
- A reaction capable of generating 150 psig pressure in case of a runaway in a 15 psig reactor with a 5 psig interlock that stops feeds and a rupture disk to reduce pressure directing contents to effluent treatment. (What could happen?)

Caution: Also protective systems can cause accidents!

Strategies for Reducing Risk in Chemical Process – Examples – Procedural.

Using Standard operating procedures, administrative checks, emergency response, training and other management approaches to prevent incidents, or to minimize the consequences (administrative controls).

EXAMPLES

- Confined space entry procedures.
- The same reactor as in the previous example without the interlock. The operator is instructed to monitor the pressure and shut down feed. (Human error).

Example: Batch Chemical Reactor.

Hazard of concern:

Runaway reaction causing high temperature and pressure and the potential reactor rupture.

Passive

- Maximum adiabatic pressure for reaction determined to be 10 atm.
- Run reaction in a 20 atm design reactor.
- Hazard (pressure) still exists, but passively contained by the pressure vessel.

Example: Batch Chemical Reactor (2).

Active

- Maximum adiabatic pressure for 100% reaction is 8 atm, the reactor design pressure is 3 atm
- Gradually add limiting reagent with temperature control to limit the potential energy from reaction
- Use high temperature and pressure interlocks to stop feed and apply emergency cooling
- Provide emergency relief systems.

Procedural

- The maximum adiabatic pressure for 100% reaction is 8 atm, the design pressure of reactor is 3 atm
- Add gradually the limiting reagent controlling the temperature to limit the potential energy of reaction
- Train operator to observe temperature, stop feeds and apply cooling if temperature exceeds operating limit.

Example: Batch Chemical Reactor (3).

Inherent

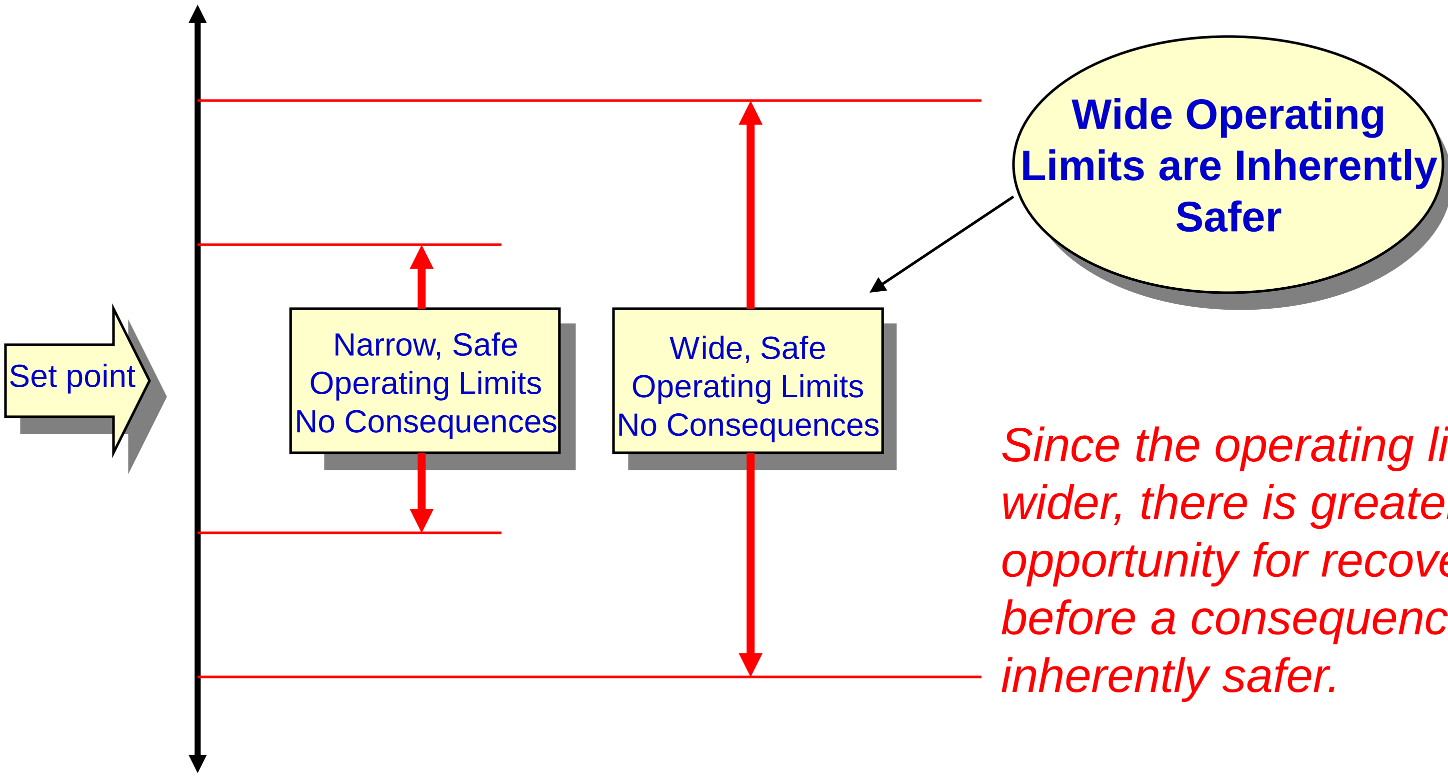
- Develop chemistry which is not exothermic, or mildly exothermic
  - Maximum adiabatic exothermic temperature < boiling point of all ingredients and onset temperature of any decomposition or other reactions.

Since Inherently Safer is the most reliable strategy, what are the potential options under inherently safer?

Inherently Safer Processes Strategies.

MINIMIZE	Use smaller quantities of hazardous materials when the use of such materials cannot be avoided. Perform a hazardous procedure as few times as possible when the procedure is unavoidable. (Intensification).
SUBSTITUTE	Replace a substance with a less hazardous material or processing route with one that does not involve hazardous material. Replace a hazardous procedure with one that is less hazardous.
MODERATE	Use less hazardous conditions, a less hazardous form of a material, or facilities which minimize the impact of a release of hazardous material or energy. Identify processing options that involve less severe processing conditions- (Attenuation or Limitation).
SIMPLIFY	Design facilities which eliminate unnecessary complexity and make operating errors less likely, and which are forgiving of errors which are made. (Error Tolerance).

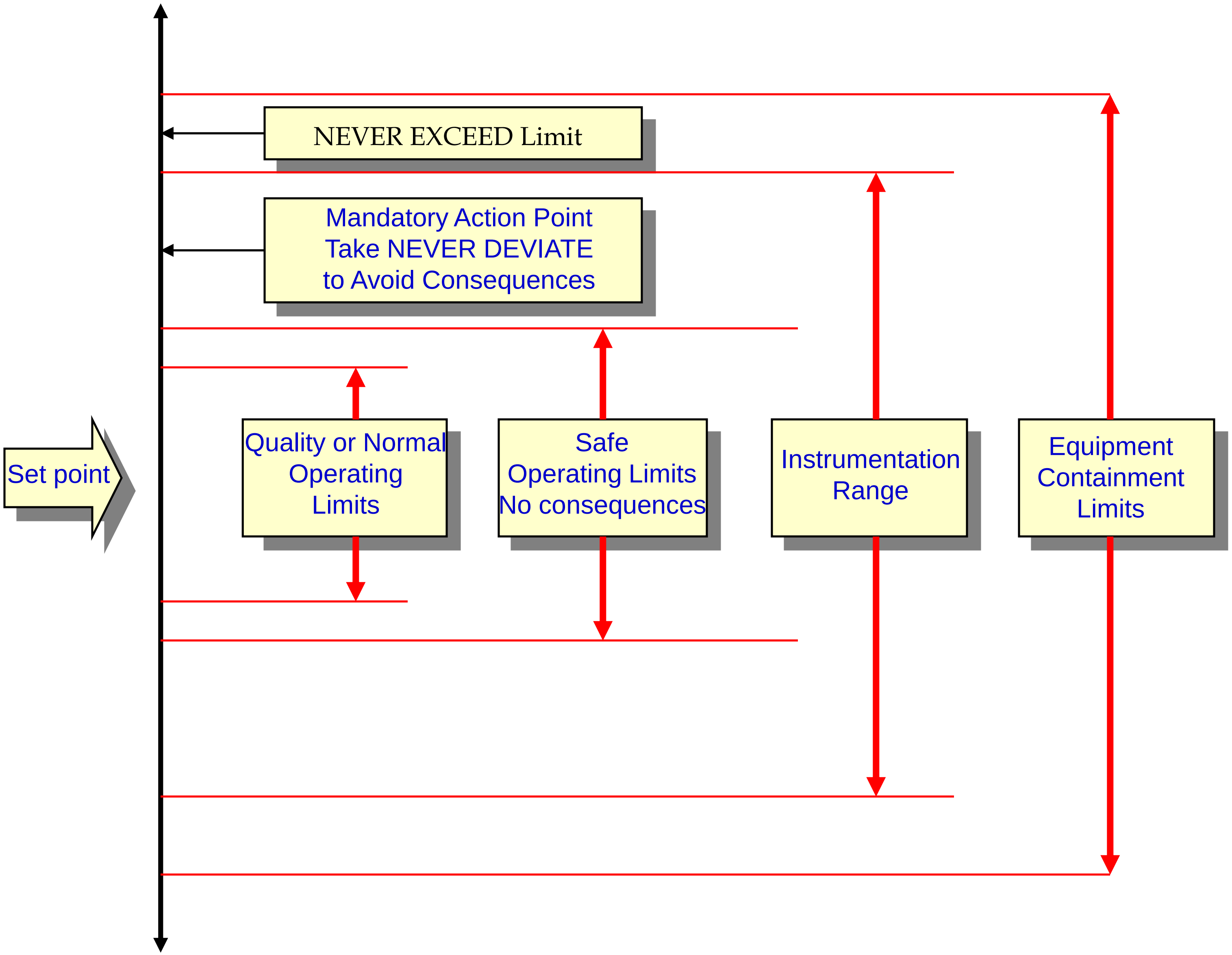
Process Design Safe Limits.



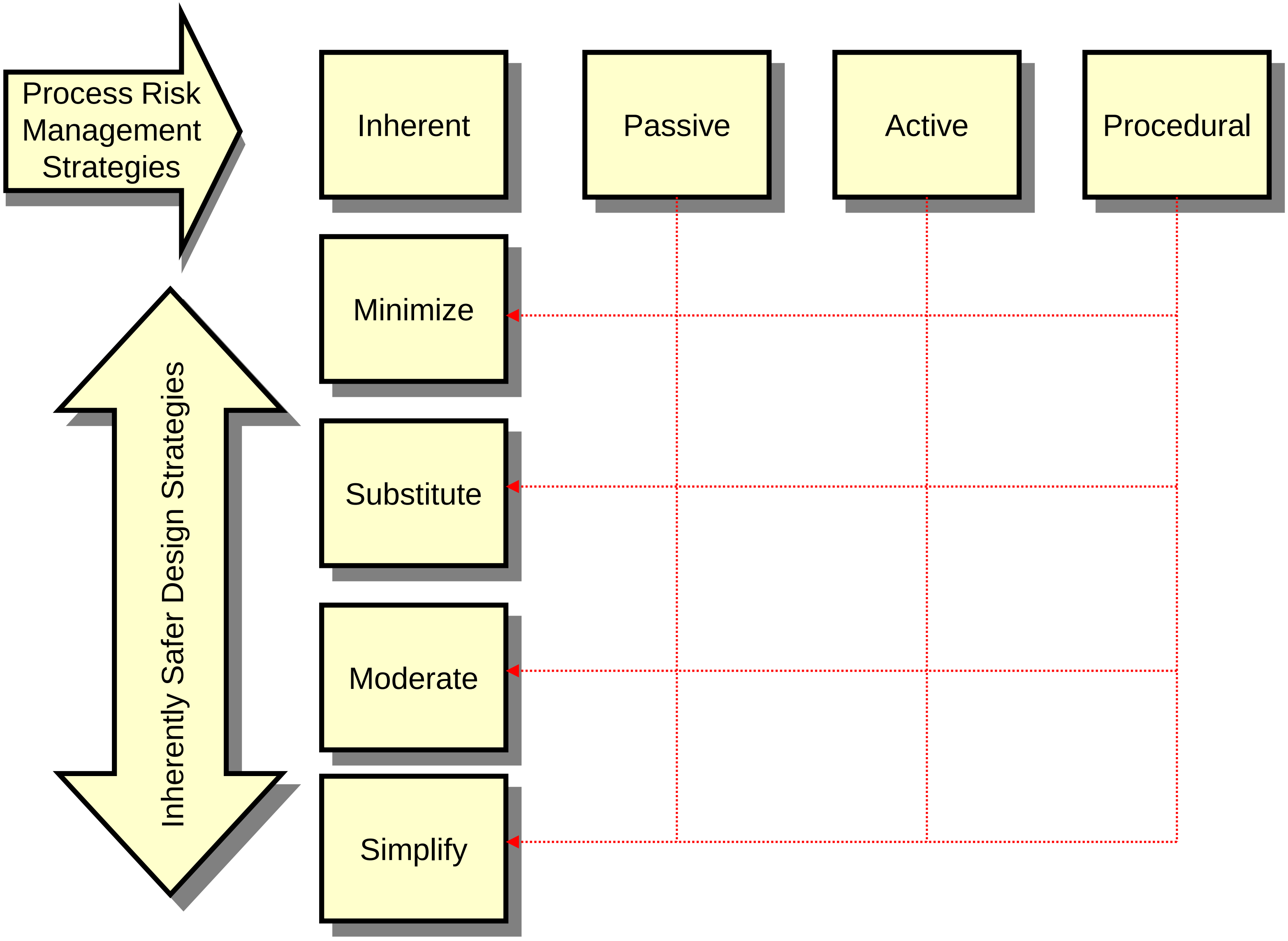
Since the operating limits are wider, there is greater opportunity for recovery before a consequence – inherently safer.

When developing a process design, we have typically worried about the robustness in the design specifications and equipment sizes. We want to incorporate safety concerns into our considerations.

Operating Ranges & Limits.



Process Risk Management Strategies.



Inherently Safety in Process Synthesis
(Conceptual Process Design).

The structure that we used during process synthesis is given below.

Remember that this isn't a procedure, it is a decision hierarchy that we follow as the design evolves. Since it is a structure, inherent safety permeates the entire design evolution.

Process Information

Process Structure

Feed, Product, Byproduct & Waste Structure

Inherent Safety Structure

Recycle Structure

Separation Structure

Heat Integration

Process Control Structure

Inherently Safer Design Questions.

Decision Point	Key Questions	Information Used
Initial Specifications	What Product? What Capacity?	Market Research R&D New Product Ideas
Process Synthesis Route	How? What Route? What Reactions, Materials?	R&D Chemists Research Known Synthesis Routes
Chemical Flowsheet	Basis Unit Operation Selection Temperatures, Pressures Solvents, Catalysts Flows, Conversions	Process Synthesis Route Laboratory/Pilot Tests Existing Process Knowledge
Process Flowsheet	Batch v. Continuous Detailed Unit Operations Control & Operation Philosophy	Process Engineering Principles
Process Conceptual Design	Equipment, Inventory, Utilities Flexibility, Overdesign, Recycles Location, Controls, Instrumentation Layout, Materials of Construction	Equipment Suppliers Data
Process Detailed Design	Equipment Specification Leak Paths, Ease of Control Simplify Hazardous Activities	Standards/Procedures Experience

Minimize.

'To minimize is to reduce the quantity of material or energy contained in a manufacturing process or plant.'

Reactor Systems

- Understand reaction kinetics
- Use continuous reactors when possible
- Produce and consume hazardous materials in-situ
- Add reactants to a batch reactor continuously.

Separation Systems

- Remove hazardous materials early in the distillation sequence
- Use column internals which minimize hold-up and connections
- Evaluate other separation systems which may be safer (τ, inventory)
- Use heat exchangers with minimal area to reduce inventory.

Minimize (2).

'To minimize is to reduce the quantity of material or energy contained in a manufacturing process or plant.'

Storage Systems

- Minimize Storage of hazardous raw materials and intermediates
- Consider 'just-in-time' supply
- Reduce pressure driving force (liquids, refrigeration, dilution) to minimize leaks
- Use large particle size, slurries, pastes to minimize dust explosion hazard.

Smaller tanks do little to reduce the hazard when :

- *Hazard is primarily from connecting and disconnecting tank trucks or tank cars serving tanks.*
- *Exposure arises from the number of vents, and number and extent of nozzles, valves and lines connecting the tank.*

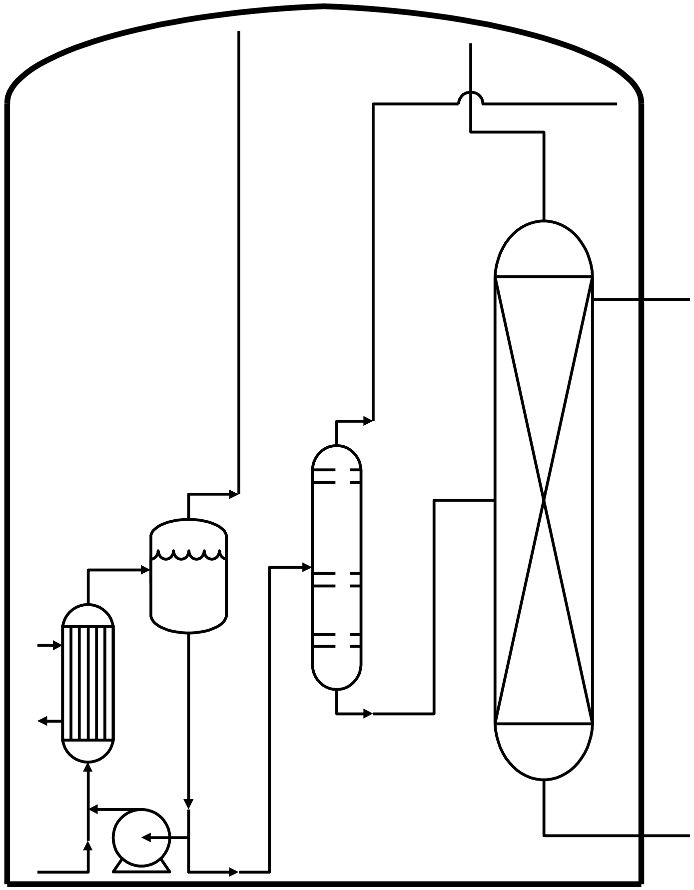
Minimize (3).

'To minimize is to reduce the quantity of material or energy contained in a manufacturing process or plant.'

Piping, etc.

- Design dike drainage so that flammable and combustible materials will not accumulate around tanks
- Minimize surface area of spills of toxic materials with high vapor pressure to minimize vapor released
- Optimize pipeline length by attention to layout
- Pipe size should be sufficient to convey required amount and no more
- Provide proper support especially for small pipe
- Transfer by gas, if possible, instead of liquid

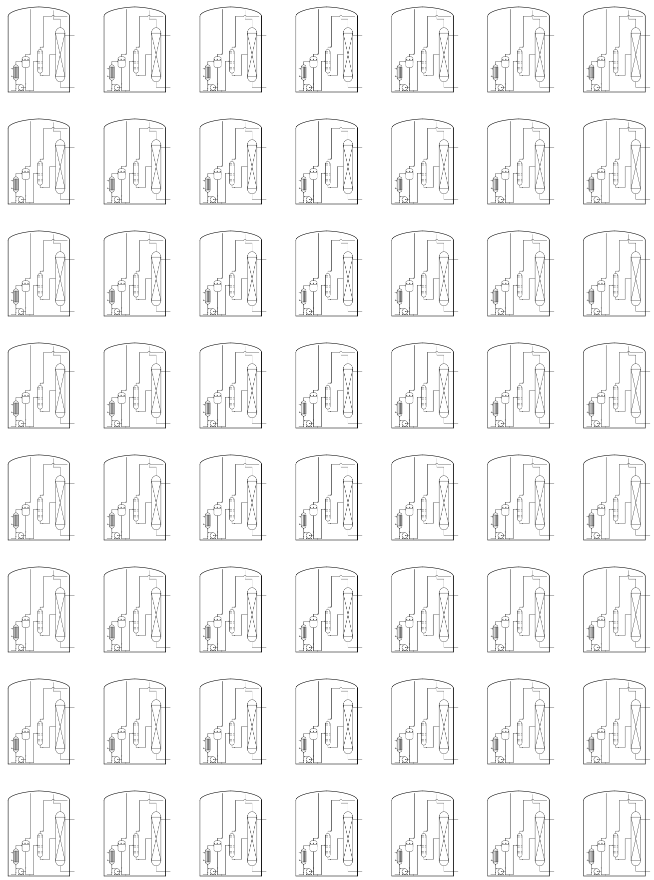
Minimize: Scale-up?



- Minimize
  - Use small quantity of energy or dangerous compounds
  - Storage of raw materials
  - Storage of intermediates
  - Piping
  - Process equipment

“Process Intensification”
(continuous processes)

Scale out.



- **Reduced consequences of accidents (explosions, fires, emission of toxic materials) and no production stop.**
- **Improved efficiency and use of other protection systems**

  ***for example*:**

  - **Secondary containment**
  - **Reactor unloading or extinction systems.**

Minimization Checklist.

- Have all in-process inventories of hazardous materials in storage tanks been eliminated?
- Are all of the proposed in-process storage tanks really needed?
- Has all processing equipment handling hazardous materials been design to minimize inventory?
- Is process equipment located to minimize length of hazardous material piping?
- Can piping sizes be reduced to minimize inventory?
- Can other types of unit operations or equipment reduce material inventories?
- Is it possible to feed hazardous materials as a gas instead of liquid, to reduce inventories?
- Is it possible to generate hazardous reactants ‘in-situ’ from less hazardous raw materials?
- Is it possible to generate hazardous reactants on site from less hazardous materials, minimizing the need to store or transport large quantities of hazardous materials?

Substitute.

'Substitution means the replacement of a hazardous material or process with an alternative which reduces or eliminates the hazard.'

Alternative Chemistry

- **Polymerize then halogenate to avoid using hazardous monomers**
- **Generate and immediately consume the hazardous substance - DuPont v. Union Carbide for carbamate insecticides**
- **Phase transfer of catalysts.**

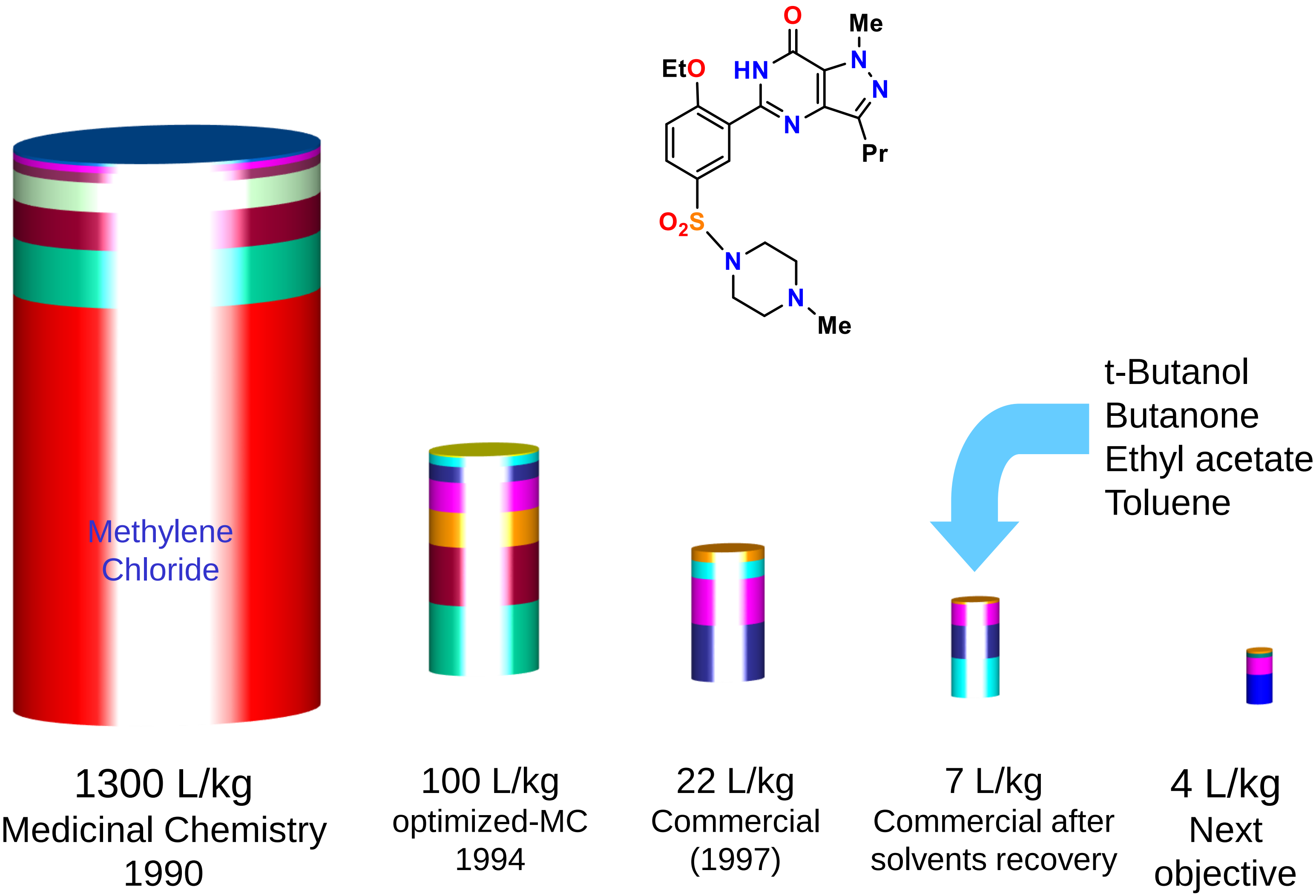
Alternative Solvents

- **Use water-based solvents v. organic-based**
- **Use aqueous or dry flowable formulations of agricultural chemicals**
- **Minimize use of chlorofluorocarbons for cleaning**
- **Use less toxic solvents in extractive distillation.**

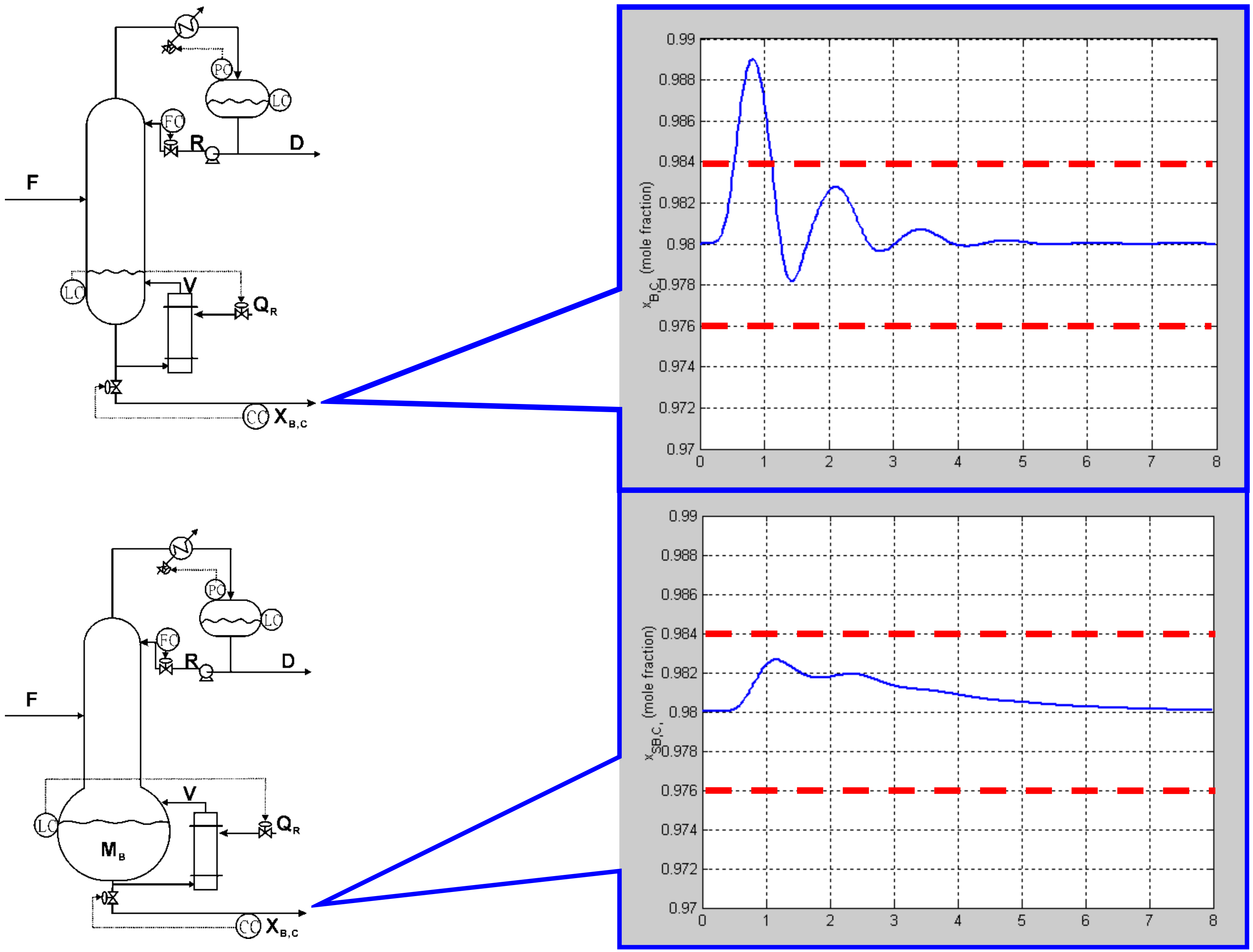
Utility Systems

- **Use water or steam for heat transfer**
- **Use high flashpoint oils or molten salts where steam or water is not feasible.**

Improvements in Manufacturing Process of Viagra™ (Pfizer).



Inherent safe design-inventory only?



Substitution Checklist.

- Is it possible to completely eliminate hazardous raw materials, process intermediates, or by-products by using an alternative process or chemistry?
- Is it possible to completely eliminate in-process solvents by changing chemistry or processing conditions?
- Is it possible to substitute more hazardous raw materials?
  - Noncombustible rather than flammable solvents
  - Less volatile raw materials
  - Less toxic raw materials
  - More stable raw materials
- Is it possible to substitute more hazardous final product solvents?
- For equipment containing materials which become unstable at elevated temperature or freeze at low temperature, is it possible to use heating and cooling which limit the maximum and minimum temperatures attainable?

Moderate.

'Moderate means using materials under less hazardous conditions.'

Dilution

- **Dilute to lower vapor pressure**
- **Dilute to reduce initial release concentration.**

Refrigeration

- **Refrigerate to reduce storage pressure**
- **Refrigerate to reduce initial flash in event of a leak**
- **Refrigerate to eliminate aerosol formation in invent of a leak (reduced driving force, reduced superheat, reduced two phase jet).**

Particle Size

- **Use large particle size to reduce employee exposure**
- **Use slurry or paste.**

Moderate (2).

Moderate means using materials under less hazardous conditions.'

Operating Conditions

- **Use conditions which reduce temperature**
- **Use conditions which reduce pressure.**

Isolation by Siting/Location

- **Design to reduce the potential of an incident at one operating site initiating an incident at another**
- **Consider opportunities to eliminate transport of hazardous materials within the plant.**

Moderate (3).

Moderate means using materials under less hazardous conditions.'

Process Deviations

- **Limit rate of material addition by pump sizing and line sizing**
- **Size charge/feed tanks to prevent overcharging reactants**
- **Design fill piping/valving to prevent direct charging from storage tanks to the reactor**
- **Select heat transfer media to limit maximum or minimum attainable reactor temperature.**

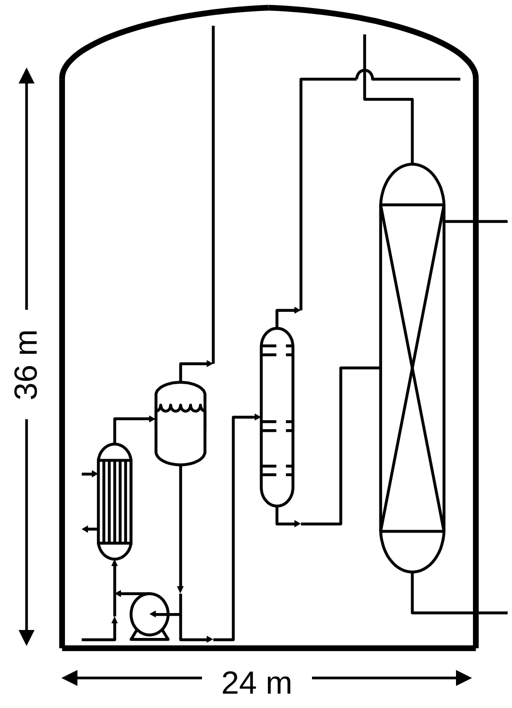
Storage Tanks

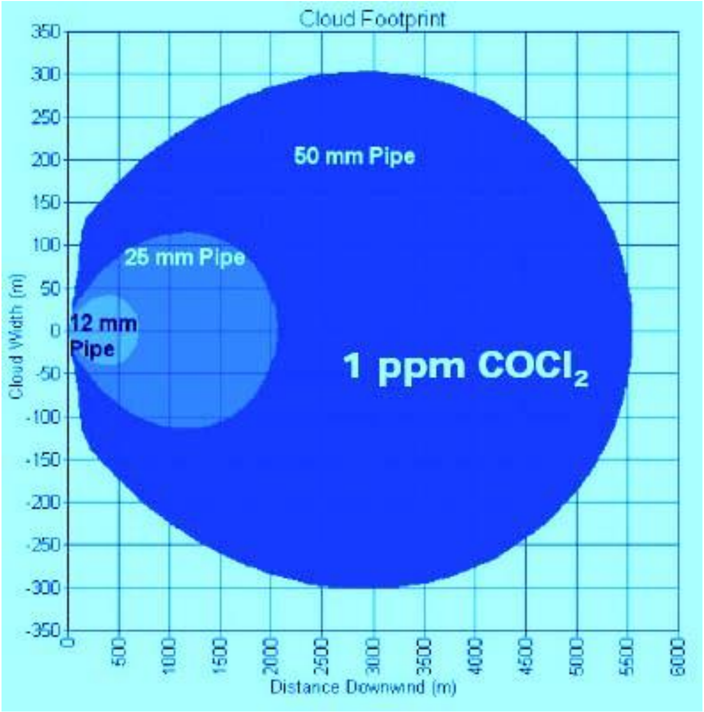
- **Dike properly to reduce consequences of a spill.**

Containment Buildings

- **Limit impact of loss of containment for toxic materials.**

Moderate - Example.

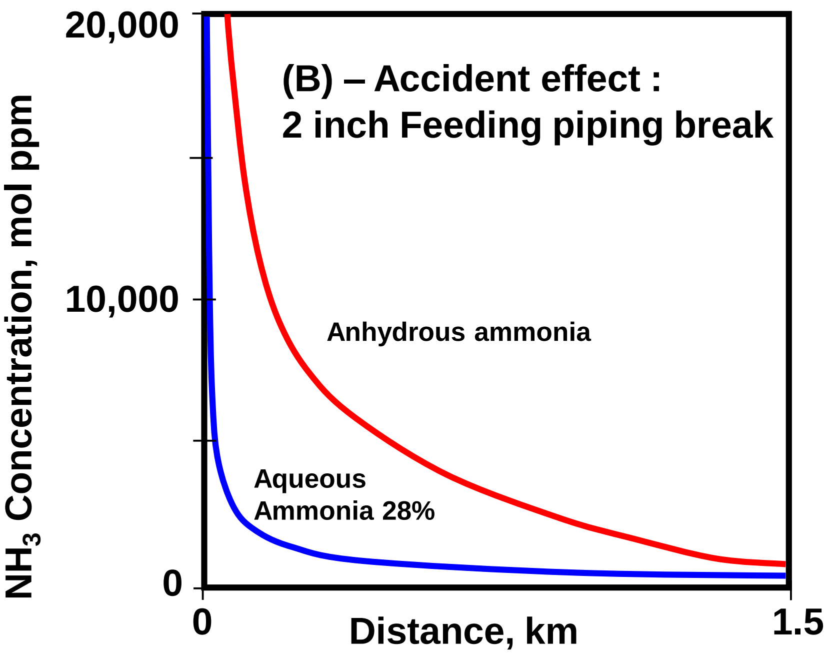




The containment building and small pipe moderates the consequence of a leak, accident or failure.

Moderate - Example: Dilution.

- Aqueous ammonia instead of anhydrous one
- Aqueous HCl instead of anhydrous HCl
- Sulfuric acid instead of oleum
- Wet benzoyl peroxide instead the anhydrous one
- Dynamite instead of liquid nitroglycerin.



Moderation Checklist.

- Can the supply pressure of raw materials be limited to less than the working pressure of the vessels they are delivered to?
- Can reaction conditions (temperature, pressure) be made less severe by using a catalyst or by using a better catalyst?
- Can the process be operated at less severe conditions? If this results in lower yield or conversion, can raw material recycle compensate for this loss?
- Is it possible to dilute hazardous raw materials to reduce the hazard potential?
- Can process units be located to reduce or eliminate adverse impacts from other adjacent hazardous installations?
- Can the plant site be chosen to minimize the need for transportation of hazardous materials and to use safer transport methods and routes?
- Can a multi-step process, where the steps are done at separate sites, be divided up differently to eliminate the need to transport hazardous materials?

Simplify.

'Simplifies means designing to eliminate unnecessary complexity, reducing the opportunities for error and misoperation.'

Equipment

- Design equipment to contain excursion within equipment (min/max)
- Consider a separate vessel for containment and treatment for relief effluent
- Design S&T HEX to contain maximum pressure.

Piping Systems

- Minimize use of sight glasses, flexible connections, bellows etc.
- Use welded pipe
- Use gaskets less prone to catastrophic failure
- Provide proper support
- Use gravity, pressure and vacuum systems for transfer
- Use seal less pumps.

Simplify (2).

'Simplifies means designing to eliminate unnecessary complexity, reducing the opportunities for error and misoperation.'

Processing Steps

- Avoid multi-step reactions in a single vessel

Fail Safe Valving

- Specify process valves to fail closed
- Specify cooling valves to fail open

  Note that in some cases, specify valves to fail in last position

Control

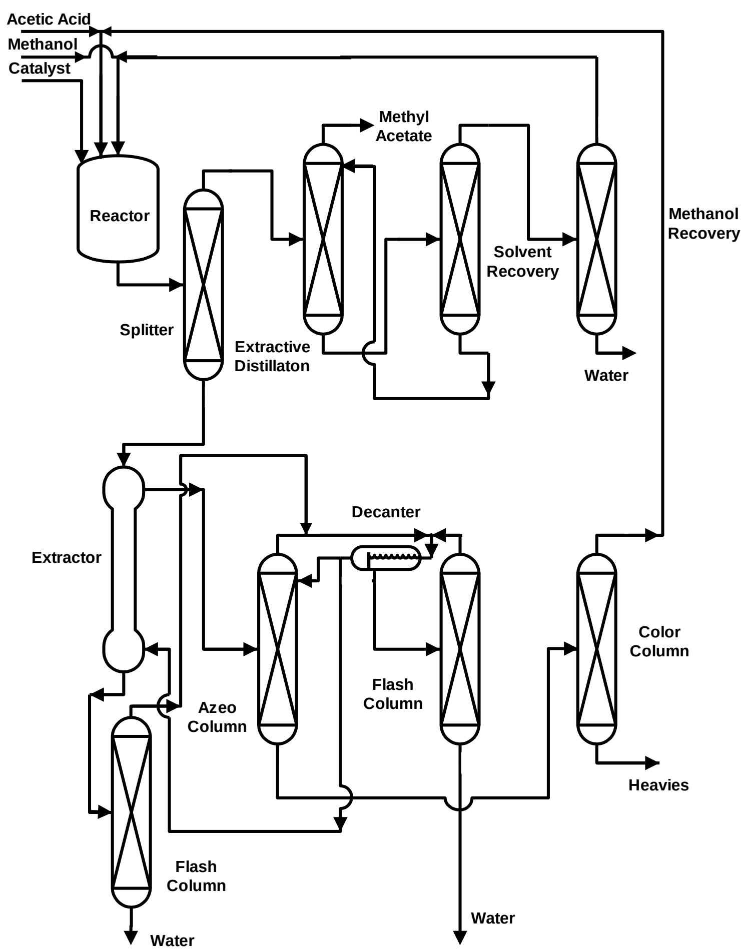
- Avoid catastrophic failure due to module failure having multiple inputs/outputs

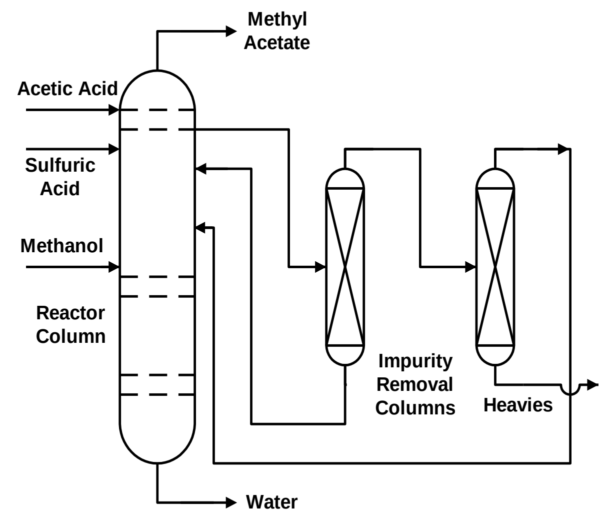
Information

- Avoid information overload on the operators
- Control the number of alarms
- Provide adequate communication.

Simplify - Eliminate Equipment.

- Reactive distillation methyl acetate process (Eastman Chemical)
- Which is simpler?





Fewer vessels, pumps, flanges, valves, piping, instruments….

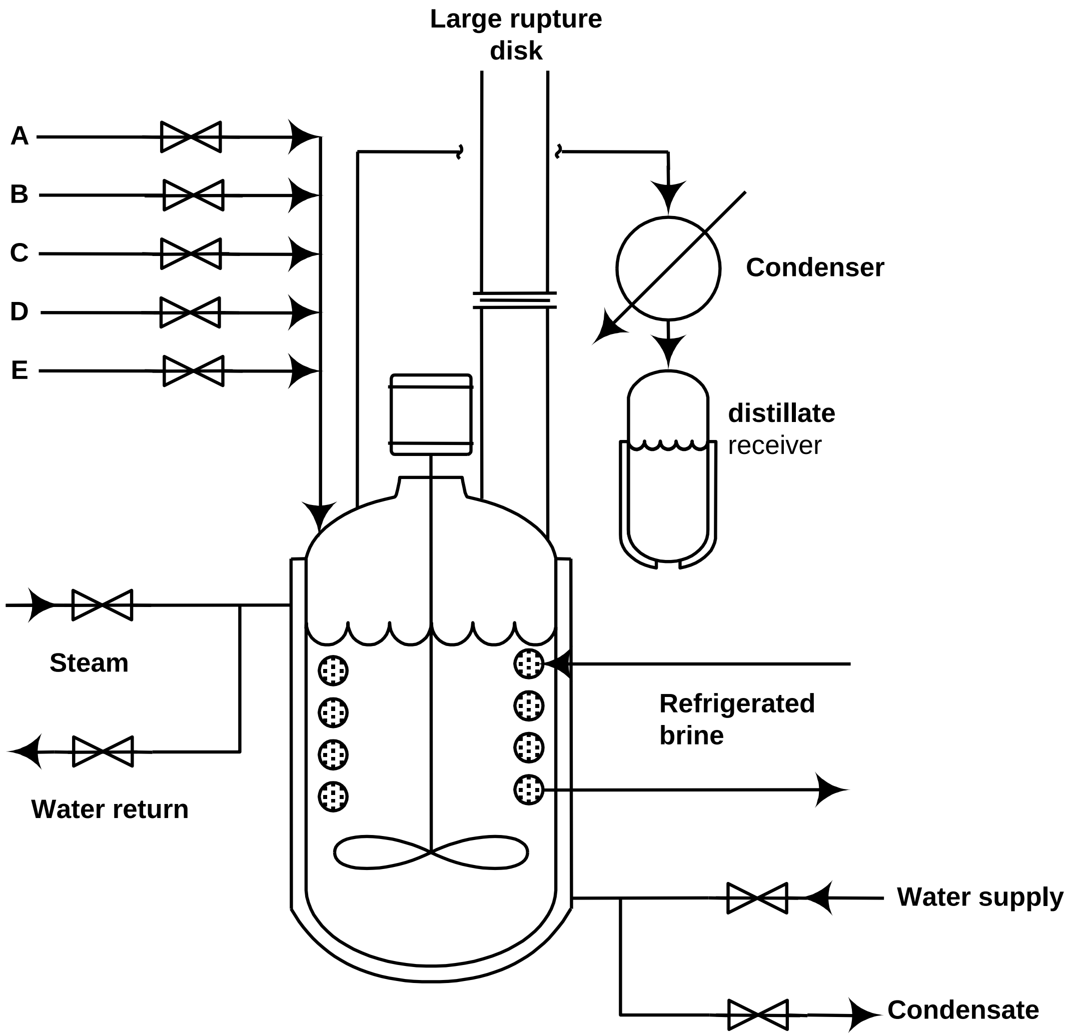
But: Reactive distillation column itself is more complex

Multiple unit operations occur within one vessel.

More complex to design

More difficult to control and operate.

Complex Batch Single Reactor.



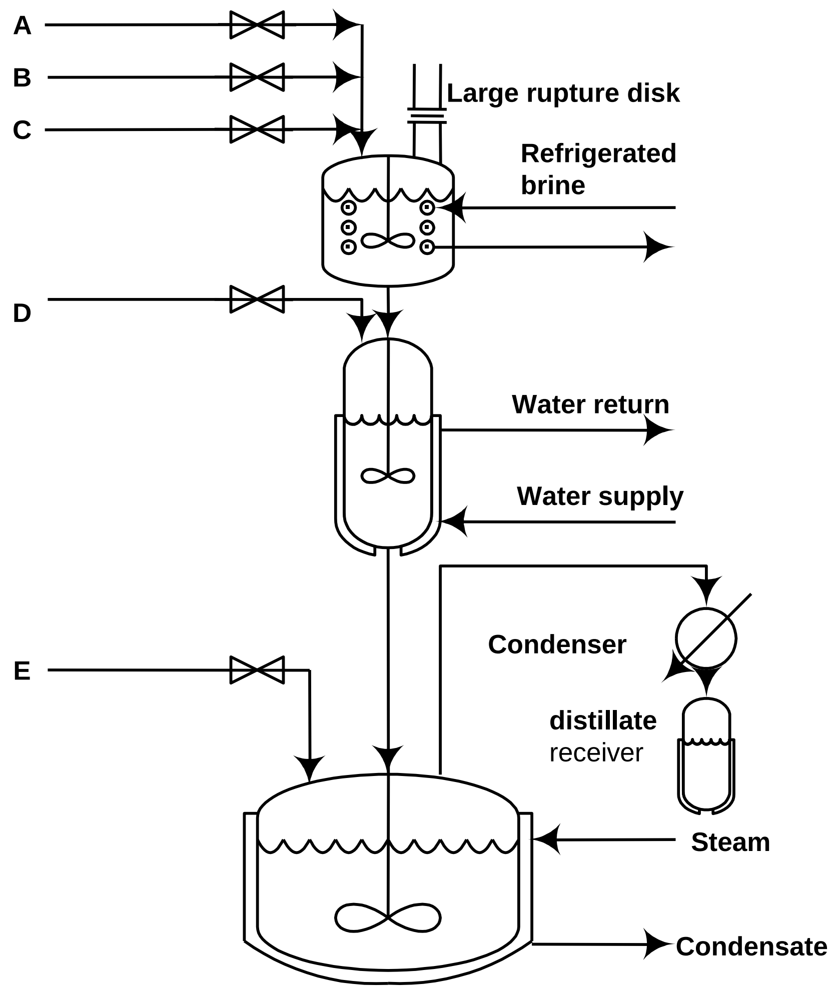
More Simple Batch Reactor Sequence for the Same Process.

This simpler system reduces the opportunity for chemical interactions and utility usage mistakes.

But there are conflicts of inherent safety.

- now there are three vessels, the overall plant is somewhat more complex.

- Need to understand the specific hazard for each situation to settle which is the best.



Simplification Checklist.

- Can equipment be designed sufficiently strong to totally contain the maximum pressure generated, even if the ‘worst credible event’ occurs?
- Is all equipment designed to totally contain the materials which might be present inside at ambient temperature or the maximum attainable process temperature?
- Can several process steps be carried out in separate processing vessels rather than a single multipurpose vessel? This reduces complexity and the number of raw materials, utilities and auxiliary equipment connected to a specific vessel, thereby reducing the potential for hazardous interactions.
- Can equipment be designed such that it is difficult or impossible to create a potential hazardous situation due to an operating error?

Best Available Techniques (BAT).

Bring together environmental issues and economic viability.

More specifically ….

Best = "(….) most effective in achieving a high general level of protection of the environment as a whole.

Available = "techniques' (…) developed on a scale which allows implementation in the relevant industrial sector, under economically and technically viable conditions, taking into account the costs and advantages, (….)*

Techniques = "(….) both the technology used and the way in the installation is designed, build, maintained, operated and decommissioned.

IPPC directive, article 2

*Consideration to be taken into account when determining Best Available Techniques are listed in the **Annex IV** of the IPPC directive.

CT and EOPA are included in BAT.

- BAT Technologies include both **Clean Technologies** AND **End of Pipe Approaches:**

Clean Technologies	End of pipe approaches
Forward looking, anticipate and prevent approach	After the event, reach and treat approach

Best Available Techniques

Since BAT also include End of Pipe Approaches, it is not always the optimal solution from an ecological, economical, and social point of view.

BAT Measures for Principal Process Units in Tannery.

	PROCESS UNIT	BAT is:
BEAMHOUSE	Curing and soaking	• To process fresh hides as far as they are available Exceptions: • When long transport time is necessary (max 8 - 12 hours for fresh, unchilled hides; 5 – 8 days if a cooling chain of 2°C is maintained) • For certain types of end-products • Sheepskins, calf skins • To reduce the amount of salt used as far as possible.
	Unhearing & liming	• To use hair-save technology, but economics can be an issue for existing plants when re-use of the saved hair is impossible • To reduce sulphide consumption by the use of enzyme preparations; not for sheepskins • To recycle spent liquors only when processing sheepskins, which are dewoolled by painting
	Splitting	• To use lime splitting Exceptions: - When the starting material is wet blue - When a firmer leather has to be produced (e.g. shoe-leather) - When a more uniform and accurate thickness is needed in the final product • To maximise the use of split

BAT Measures for Principal Process Units in Tannery (2).

	PROCESS UNIT	BAT is:
TANYARD OPERATIONS	**Deliming and bating**	● To make a partial substitution of ammonium salts with CO_2 and/or weak organic acids
	Sheepskin degreasing	● To optimise wet degreasing using surfactants, with or without organic solvents ● Closed machines with abatement for air and waste water releases when organic solvents are used to degrease skins in dry state
	Pickling	● To use partial recycling or re-use of pickle liquors ● To use a volume of floats in the range of 50 – 60 % (based on fleshed weight) for ovine skins and bovine hides in order to reduce salt consumption
	Tanning	● To increase the efficiency of the chrome tanning process through careful control of pH, float, temperature, time and drum speed, all in combination with chrome recovery through precipitation for waste water streams containing Cr_{total} > 1 g/l ● To use high-exhaustion tanning methods where chrome recovery is not possible ● To maximise exhaustion of the vegetable tanning liquor with counter-current (pit system) or recycling (drum tanning)

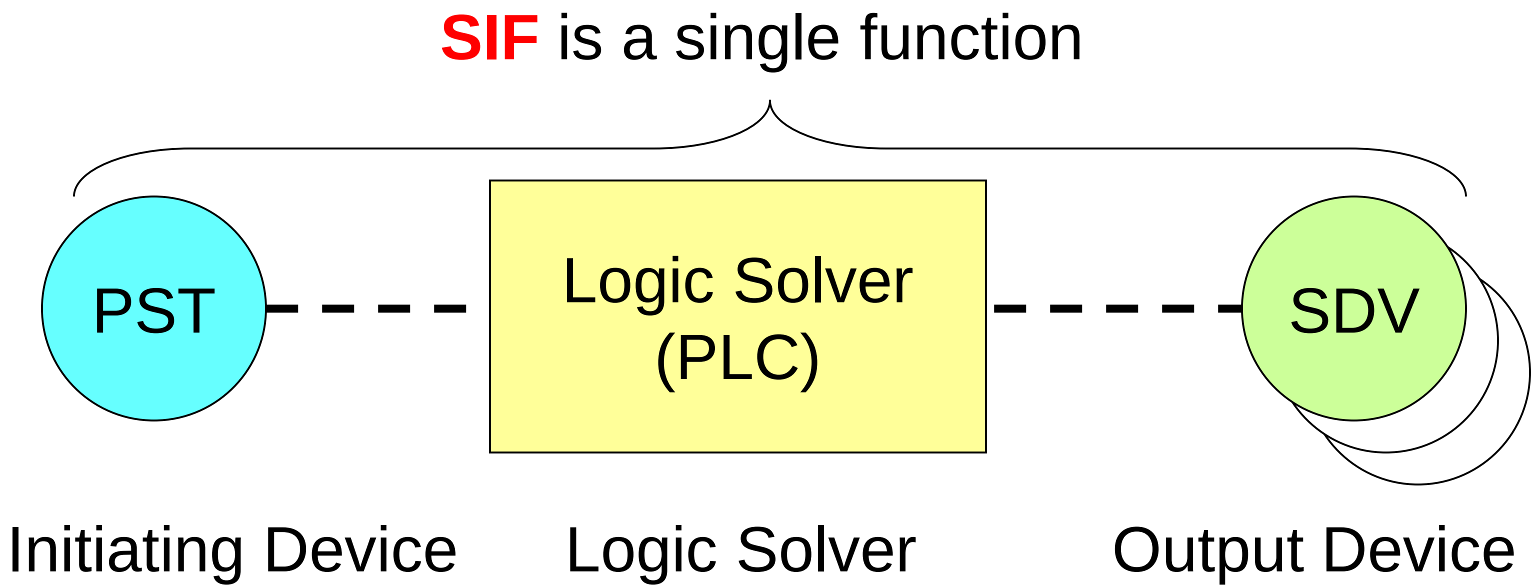
BAT Measures for Principal Process Units in Tannery (3).

	PROCESS UNIT	BAT is:
POST-TANNING OPERATIONS	**Retanning, chrome fixation and neutralization**	● To enhance exhaustion of post-tanning treatment agents and fixation of tanning agents in the leather ● To reduce the salt content of spent liquors
	Dyeing	● To enhance exhaustion of dyestuffs
	Fat liquoring	● To enhance exhaustion of fat liquor
	Drying	● To optimise mechanical dewatering prior to drying where possible
	Applying a surface coat	● To use roller coating ● To use curtain coating ● To use HVLP spray guns ● To use airless spray guns Exception for all four above-mentioned techniques: ● When very thin finishes are applied, e.g. on aniline and aniline-type leather

Performance Based Terminology.

- SIF – Safety Instrumented Function
- SIL – Safety Integrity Level
- SIS – Safety Instrumented System
- Failure Modes
  - ✓ **Fail to Safe vs. Fail to Danger**
  - ✓ **Fail Detected vs. Fail Undetected**
- Quantitative Risk Analysis Methods
  - ✓ **LOPA – Layer of Protection Analysis**
  - ✓ **Fault Tree**
  - ✓ **Markov Models**
- PFD – Probability of Failure on Demand.

Explaining the Terminology.



SIL is the strength of the SIF, how reliable does it need to be.

SIS is the entire process safety system, but mainly focuses on the logic solver

Hazard Analysis / Risk Mitigation.

- Hazard Analysis / Risk Mitigation requires knowing the chance that something will fail. Either creating a hazard or failing to protect from a hazard.
- Probability of failure on demand (PFD) is required for any type of quantitative risk analysis.
- PFD is the chance that a device will fail in an un-safe manner that places the facility at risk and is based on the failure rate and the test interval.

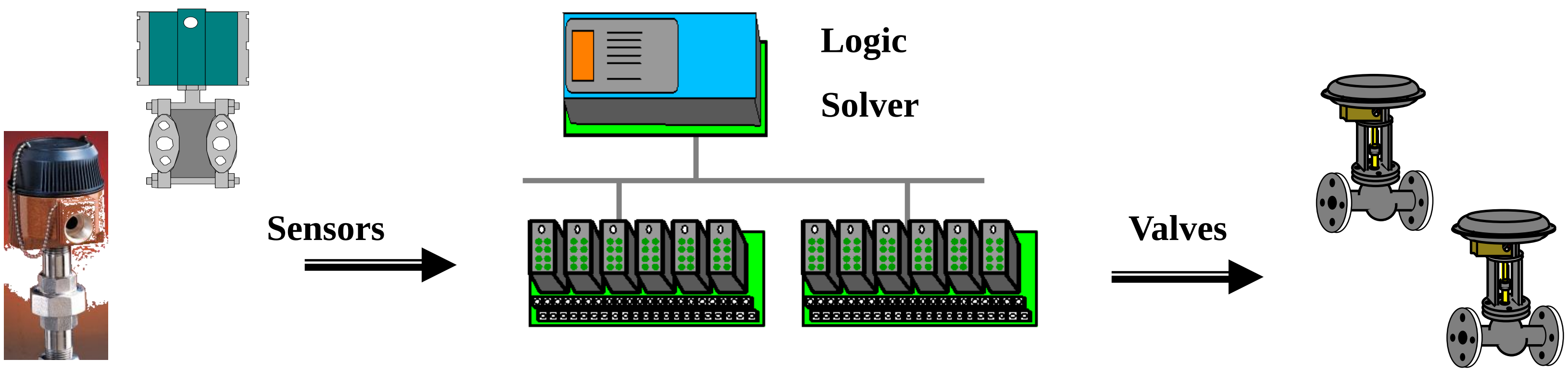
Reliability vs. Availability.

- Availability is the percent of time the device is available to operate. Percentage of time the system works satisfactorily.
- Reliability The likelihood that the system will work satisfactorily over a given period of time and in appropriate circumstances. (Low PFD) is usually achieved at the cost of availability.
- To have high reliability and high availability requires voting logic of multiple sensors, logic solvers and output devices.
- Cost of field devices can rapidly escalate the cost of the safety system.

Safety Instrumented System (SIS).

"System comprised of sensors, logic solvers, and final control elements for the purpose of taking a process to a safe state when predetermined conditions are violated." **(As defined in ANSI/ISA 84.00.01)**

ex. Transmitters, Logic Solver , & Valves



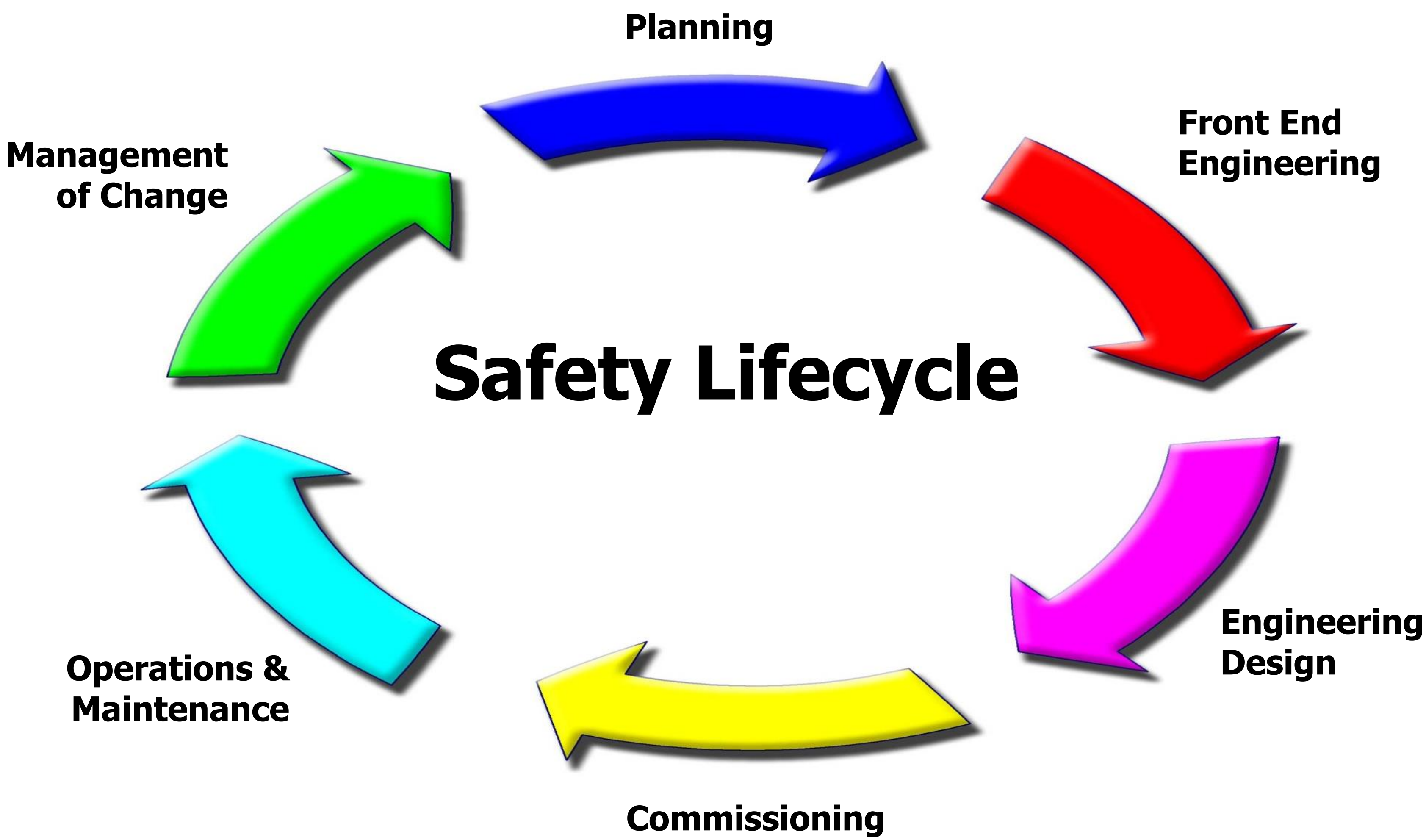
SIL Calculations.

$$PFD_{avg} \text{ Sensors} + PFD_{avg} \text{ Logic Solver} + PFD_{avg} \text{ Final Element} = PFD_{avg} \text{ SIF}$$

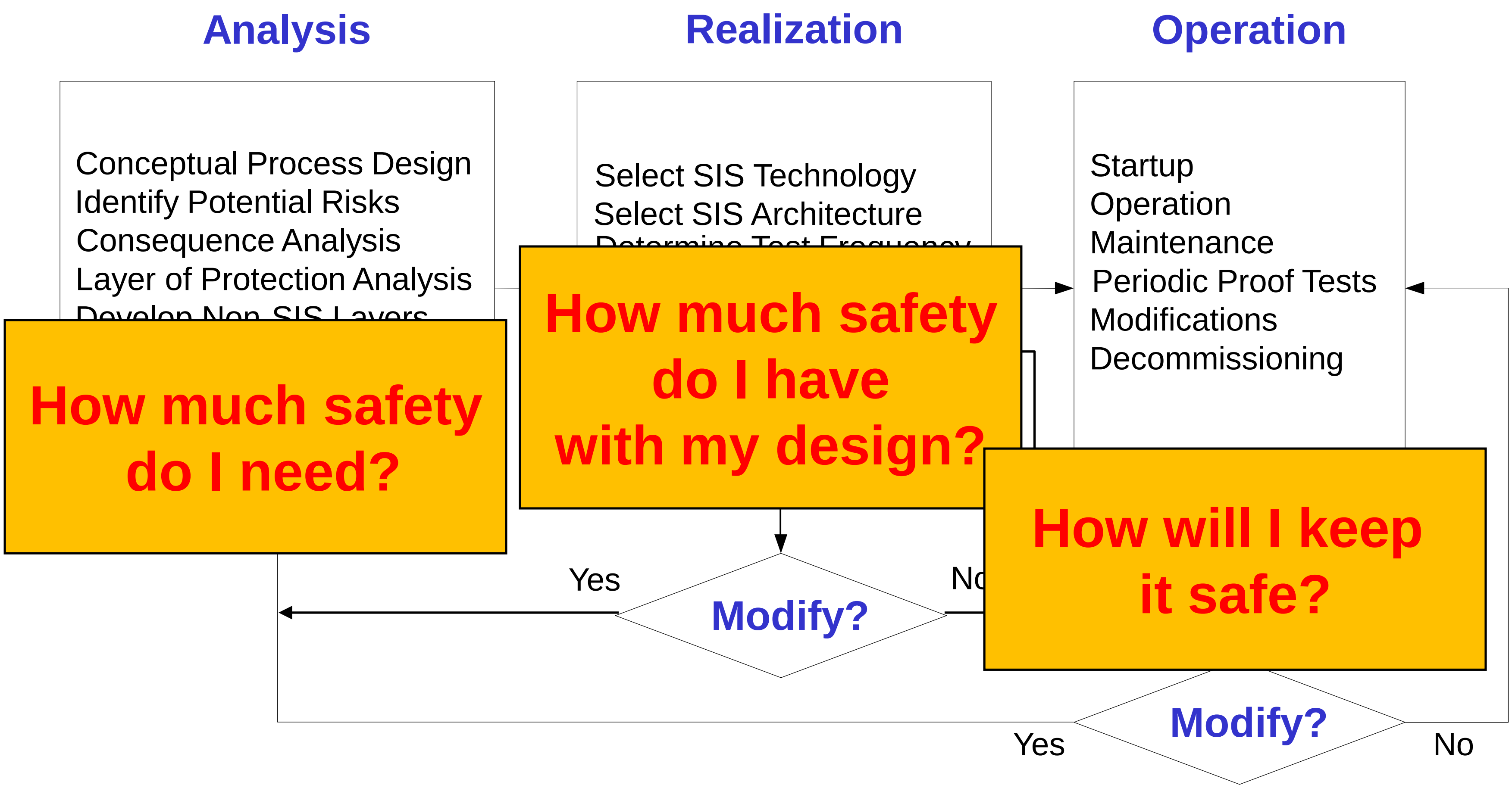
Things to be modeled include:

- Sensors: transmitters, switches, intrinsically safe barriers, interposing relays, etc.
- Logic Solver: relays, solid state devices, PLC’s, Safety PLC’s, interposing relays, etc.
- Final Elements: valves, solenoids, motor starters, interposing relays, intrinsically safe barriers, etc.

Safety Lifecycle.

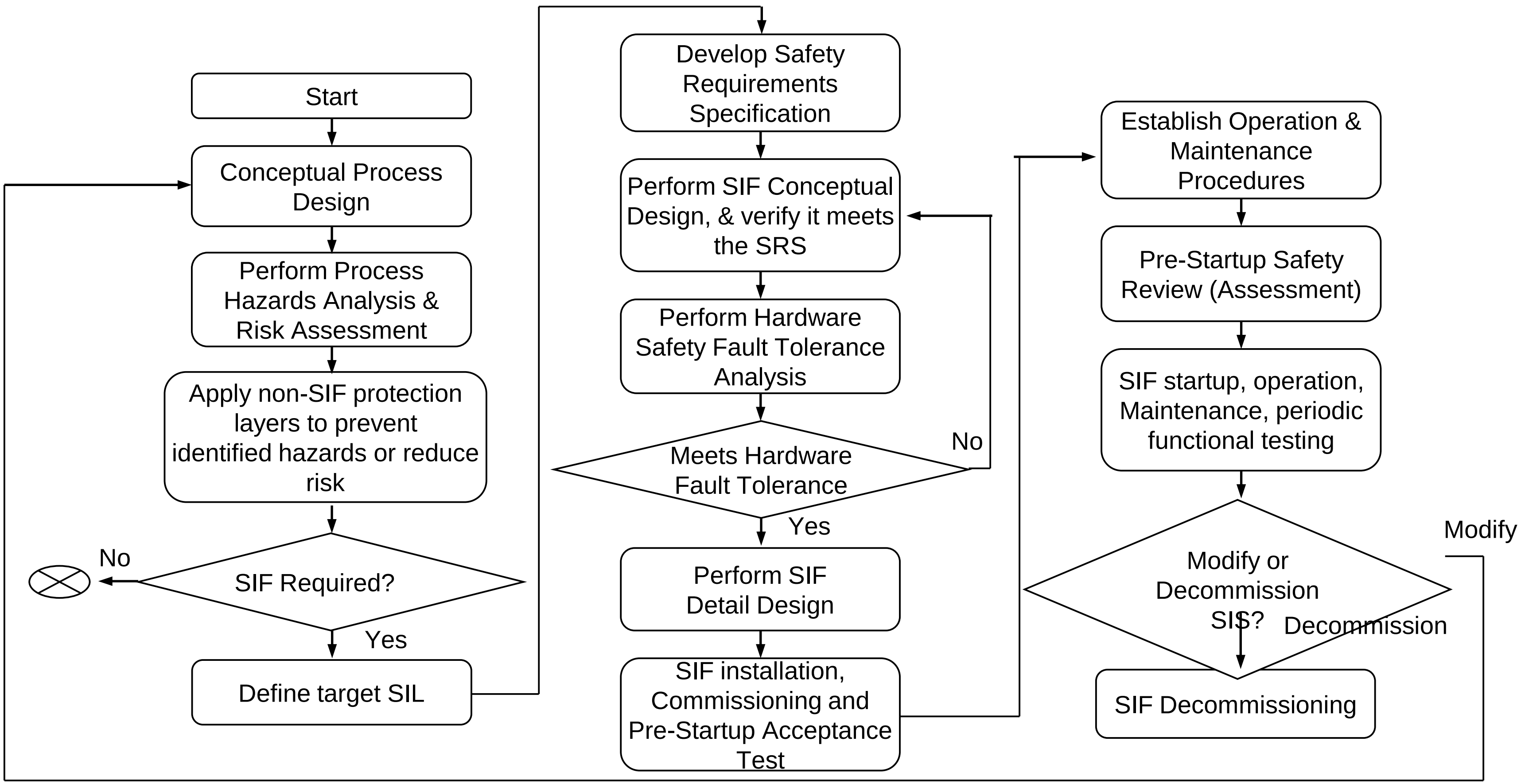


Safety Life Cycle – ISA S84.00.01-2004.



Drawing by Hal Thomas

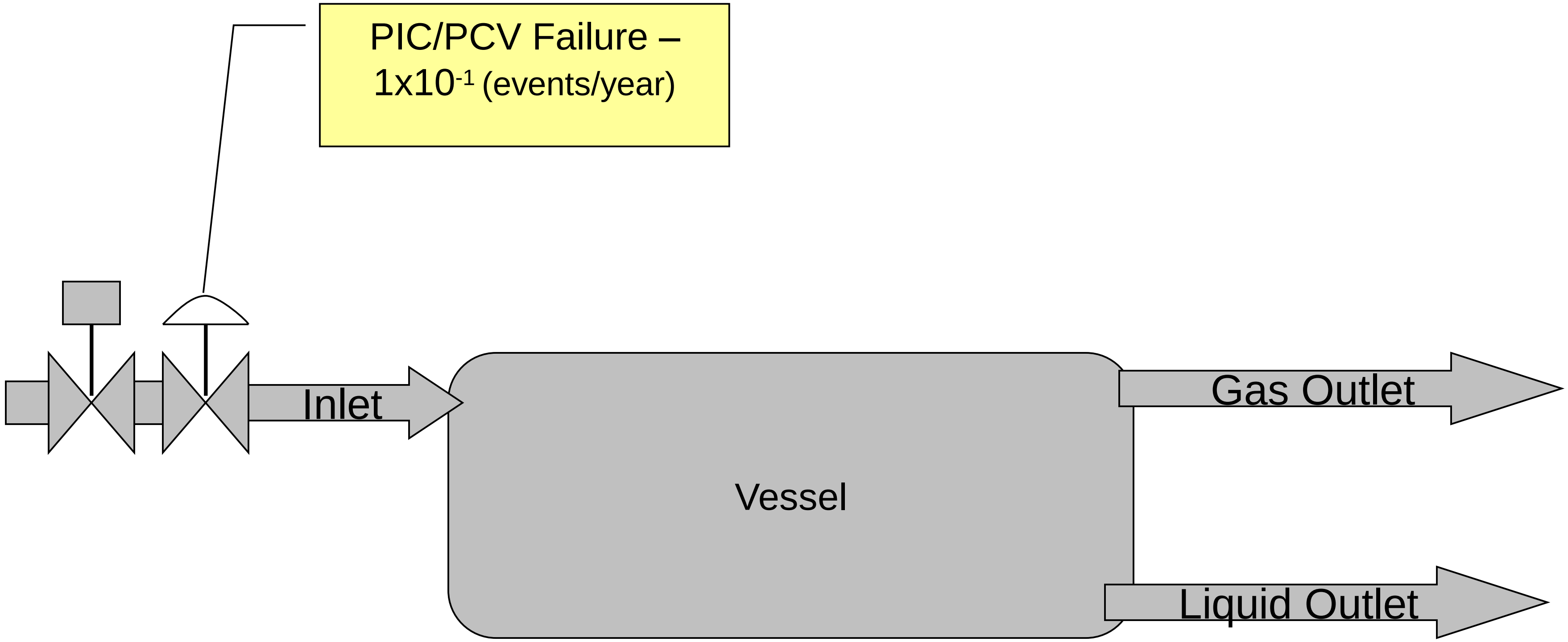
Safety Lifecycle.



Average Probability of Failure on Demand (PFD_{avg}).

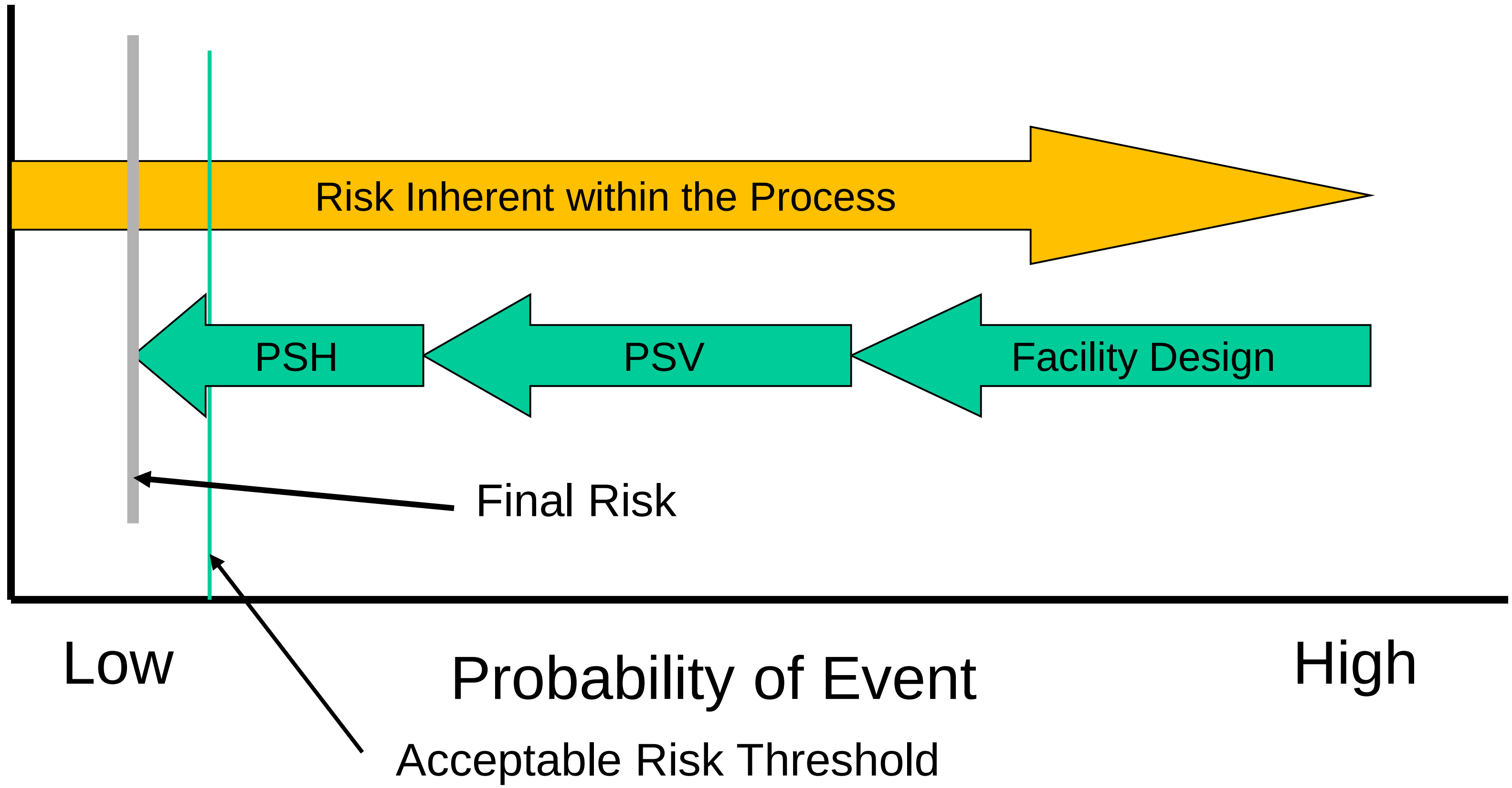
SIL 1	>0.01 to < 0.1
SIL 2	>0.001 to < 0.01
SIL 3	>0.0001 to < 0.001
SIL 4	>0.00001 to < 0.0001

Performance Based Example.



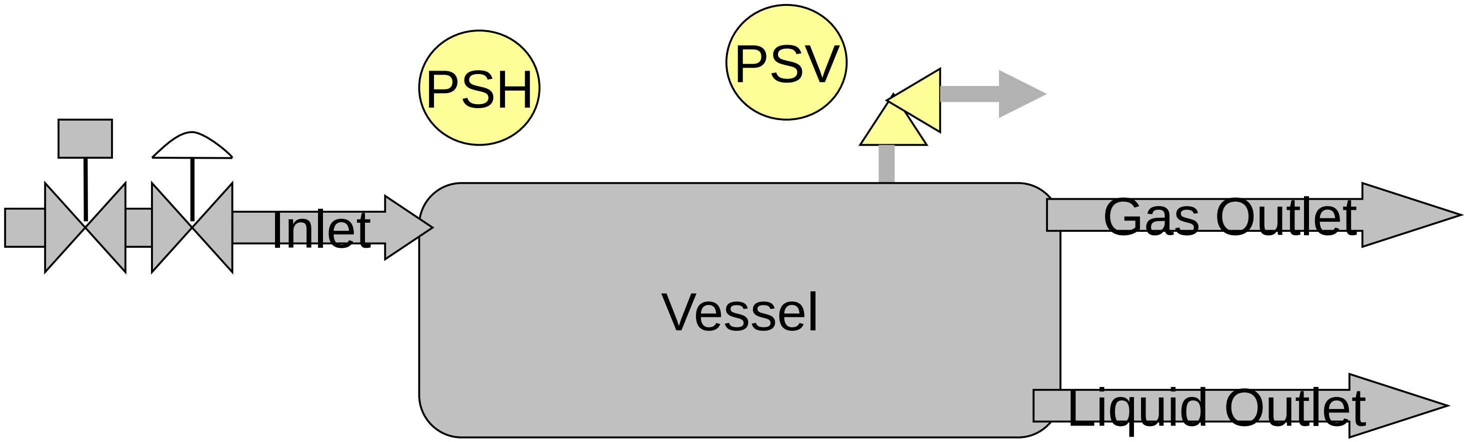
Result – The inherent risk of over pressuring the vessel is the sum of the causes which is 1.0×10^{-1} events/year or 10% chance or an event every 10 years.

Performance - Risk Based Analysis.



Multiple ways to perform analysis exist (Risk Graph, Risk Matrix, Layer of Protection, Quantitative Risk Analysis).

Performance Based Example.



Base Risk of 1.0×10^{-1} /year or 10%
Establish Risk Threshold of 1×10^{-5} /year or 0.001% chance

Add PSV (PFD 1×10^{-3}) results in a remaining risk of 1.0×10^{-4} /year or 0.01% chance.
Required PFD of the PSH is equal to risk threshold divided by remaining risk = $(1\times10^{-5}/1.0\times10^{-4}) = 1.0\times10^{-1}$
This is a SIL 1 PSH

Safety Instrumented System Standards.

IEC 61508 - "Functional Safety: Safety Related Systems"

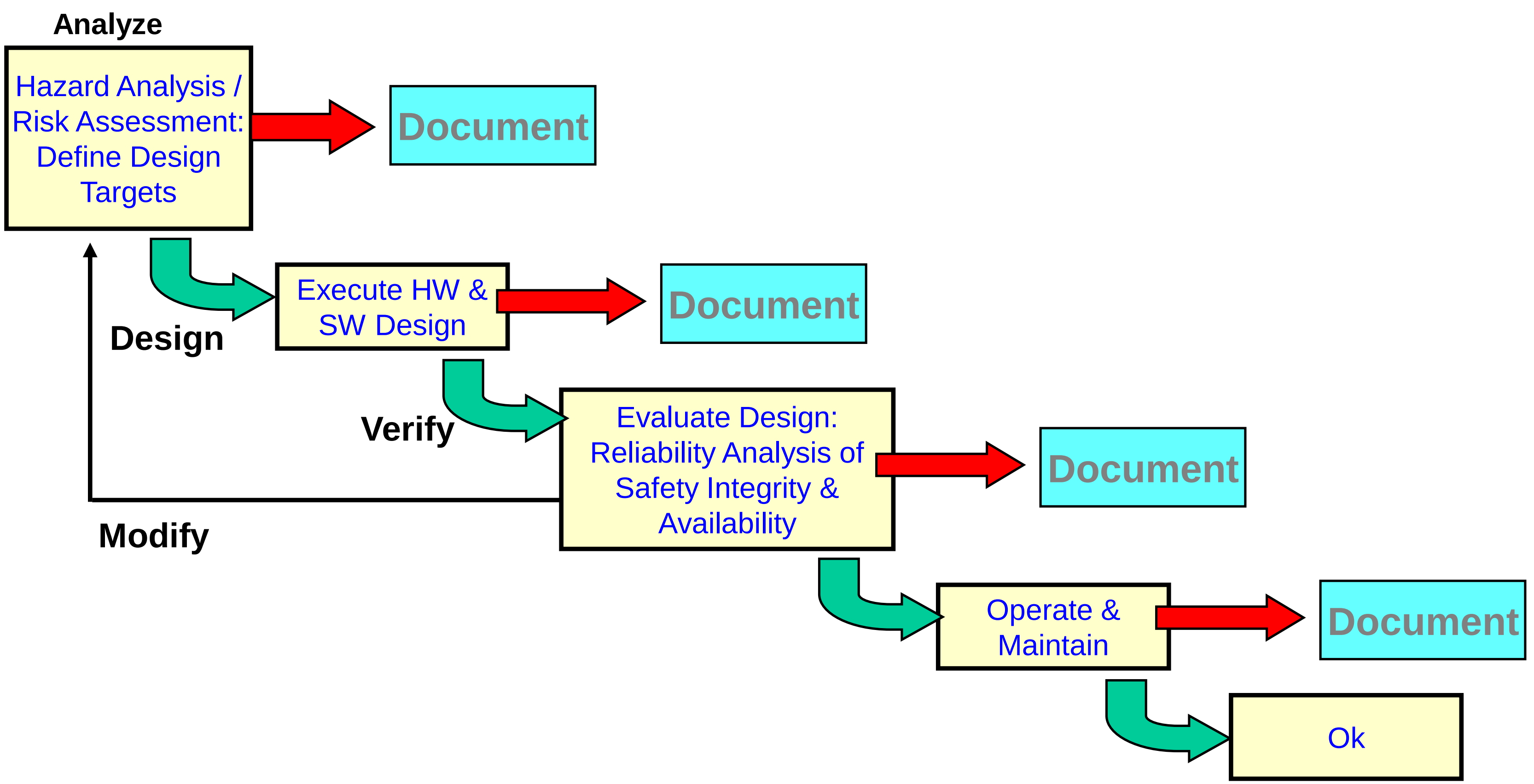
Current version released 1999

Revision released 2005

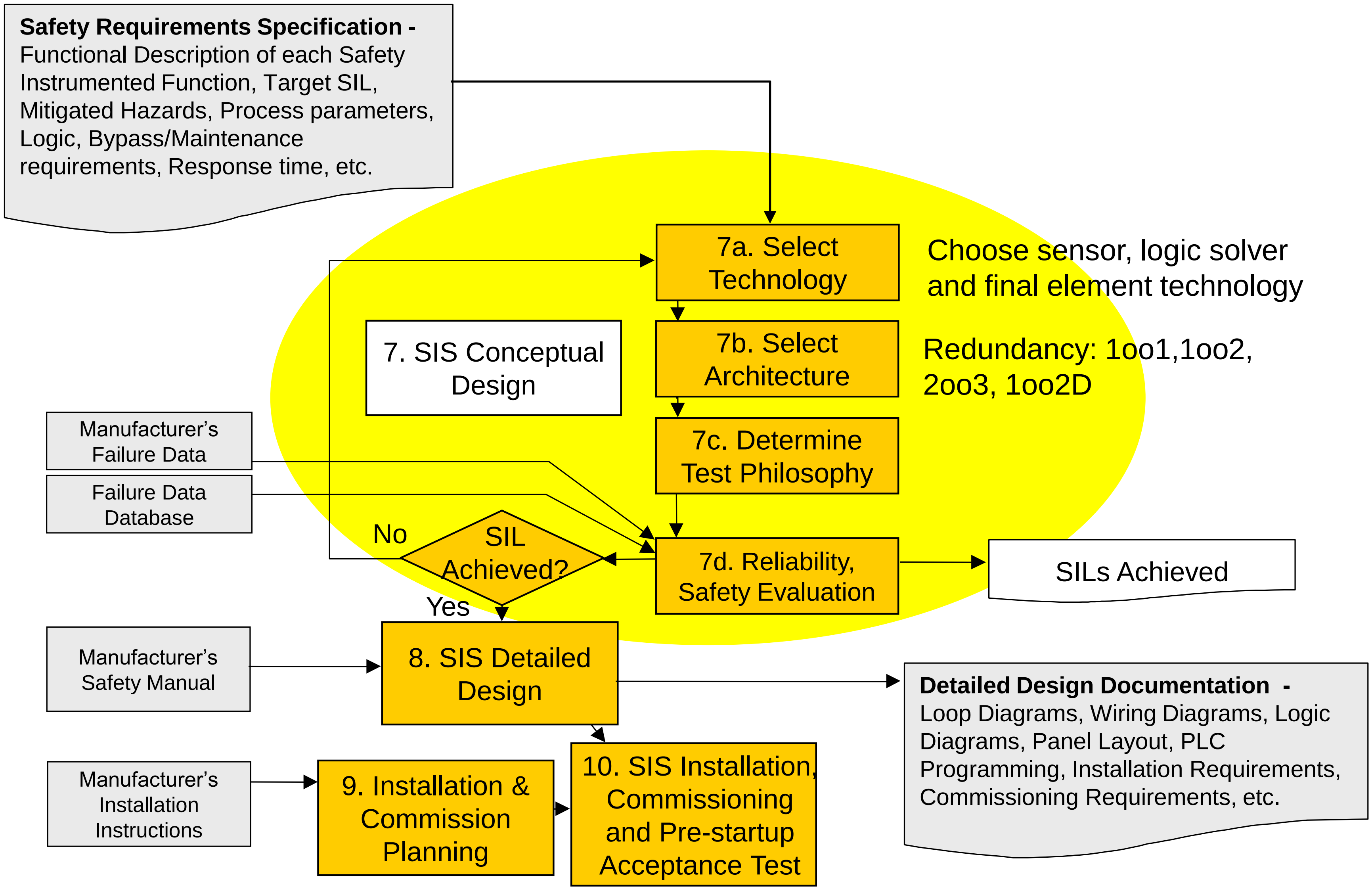
IEC 61511 - "Functional Safety: Safety Instrumented Systems for the Process Industry Sector"
Published 2003

ISA 84.01-2003 - "Functional Safety: Safety Instrumented Systems for the Process Industry Sector"
Identical to IEC 61511 with inclusion of grandfather clause
Published October 2003

IEC 61511 Safety Lifecycle Objectives.



Realization Phase - SIF Design Process.



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