

**Process Safety Management
of Highly Hazardous &
Explosive Chemicals**



NC OSHA PSM Training
Process Safety Information (PSI)

**Process Safety Information
(PSI)**

“The compilation of written process safety information is to enable the employer and the employees involved in operating the process to identify and understand the hazards posed by those processes involving highly hazardous chemicals” - OSHA

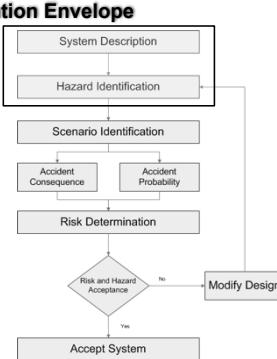
Process Safety Information (PSI) – Defines Safe Operation Envelope

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

- 1. Properties of materials
- 2. Process technology
- 3. Equipment design

How Can We Know Without the Necessary PSI?

HIRA Logic Diagram Source: CCPS Boot Camp Training



Process Safety Information



Process Safety Information Required for a PHA

- Materials of Construction
- Process Chemistry
- Reactive Chemistry Information – Kinetic Data
- Design Energy & Mass Balances
- Correct P&ID's
- Mechanical Integrity
- Relief Calculations
- Electrical Classifications
- Operating Procedures: Walked Down & Correct
- Codes & Specifications
- Vendor Drawings
- MOC Packages
- Incident/Accident Reports
- Special/Unique Design Specifications
- Maintenance Procedures
- Testing & Inspection Reports
- Ventilation Systems
- Safety Systems (SIL's)
- Emergency Procedures

Process Safety Information (PSI)

Includes the Following:

- Chemical Hazards Information
- Process Technology Information
- Equipment Information

Kept for the lifetime of the process

Updated whenever changes other than "replacement in kind" are made (or whenever necessary even if replacement in kind)

PSI applicable to various employees' jobs must be shared with those employees (operators, maintenance, contractors)

PSI – Chemical Toxicity Hazards

- What Chemicals and Hazards are in the Process?
- What Do We Need to Ask For?

Process Safety Information (PSI) – Chemical Hazards Information

Includes information specific to process materials (desired and undesired)

- Toxicity data
- Permissible exposure limits
- Physical data
- Reactivity data
- Corrosivity data
- Thermal and chemical stability
- Chemical incompatibility

An SDS is acceptable in meeting this requirement to the extent that the necessary information is available on the MSDS

However, it is likely the SDS must be supplemented with process chemistry information including runaway reaction and overpressure hazards if applicable

Physical Properties and Hazards

Chemical Hazards Information
Physical Data

Physical Data

- Appearance
- Physical state
- Molecular weight
- Vapor pressure
- Viscosity
- Freezing point
- Particle size distribution
- Melting point
- Solubility in water
- Odor and odor threshold
- Specific gravity
- Surface tension
- Cryogens
- dielectric constant
- Vapor density versus air
- pH
- Flammability and Combustibility
 - Boiling point,
 - Flash point,
 - LFL
 - UFL
 - Minimum Oxygen Concentration



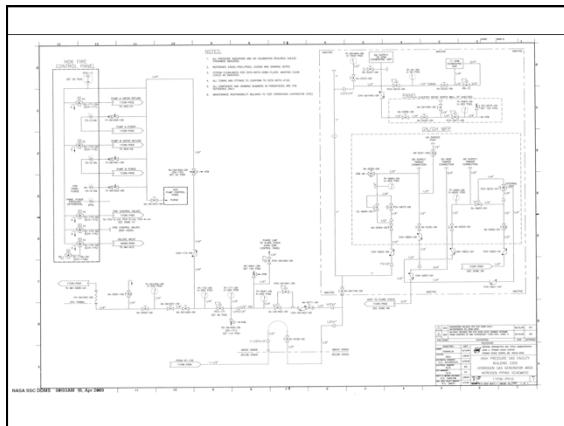
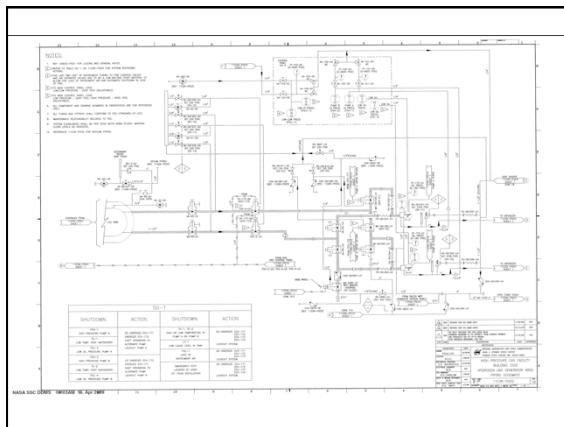
So, How Do We Understand P&ID's

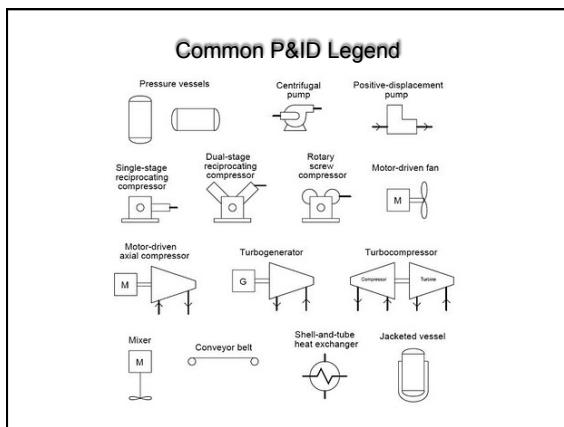
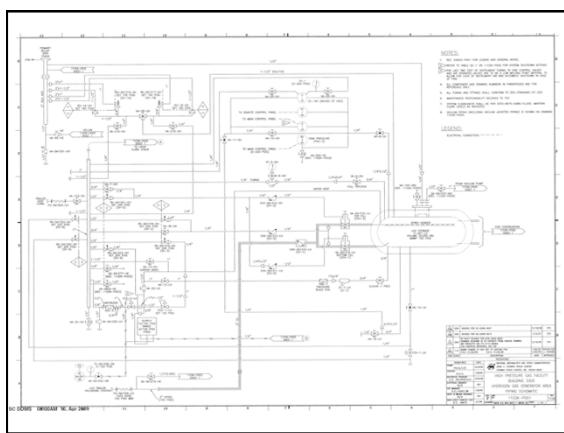
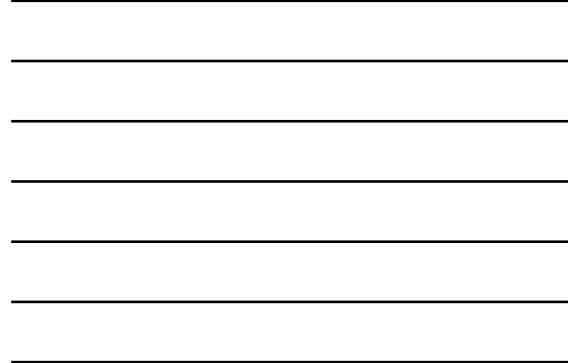
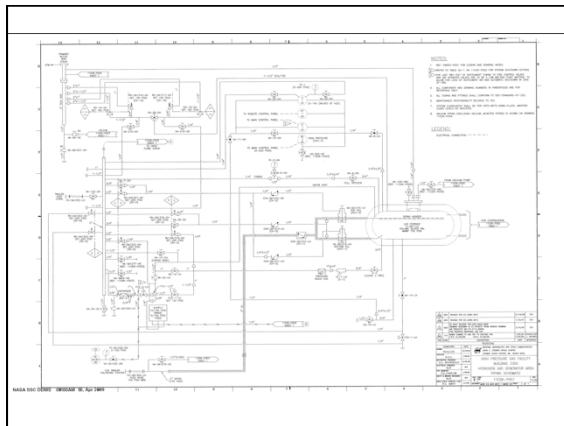
Learn the Symbols and Callouts

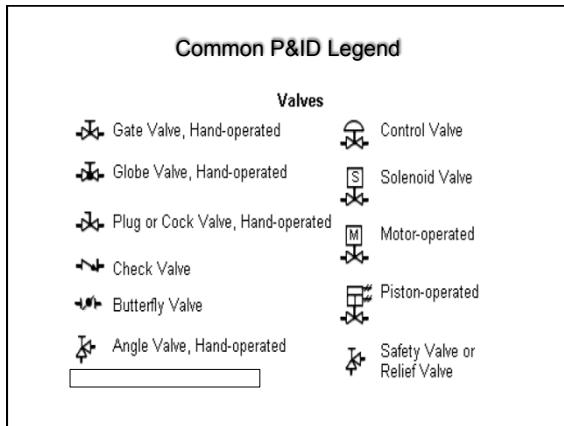
Learn the Asset Numbering Method

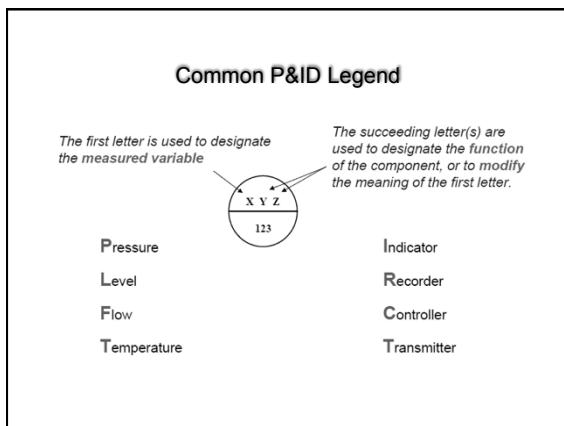
P&ID's

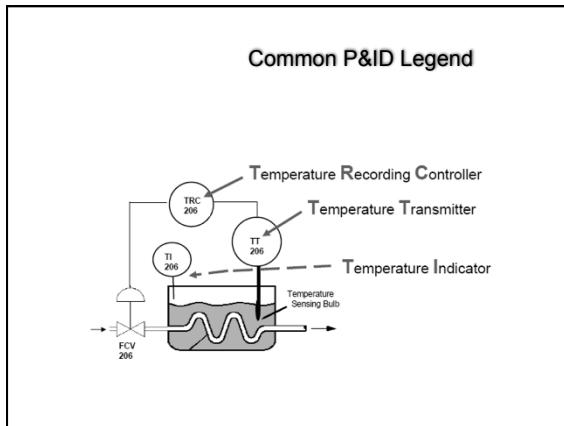
- PHA Team Members Must Understand P&ID's
- P&ID Methodology and Call outs should be standardized
- P&ID's must be walked down, red marked and Correct

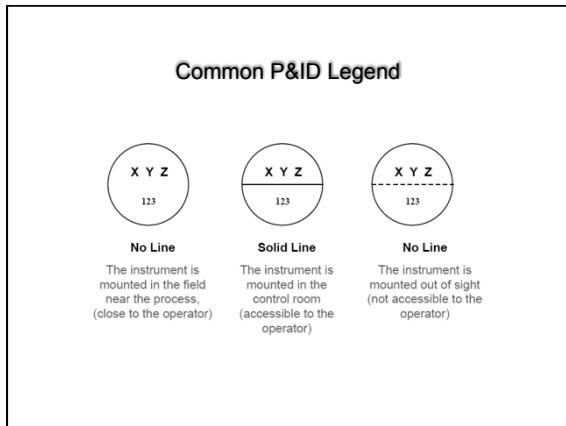


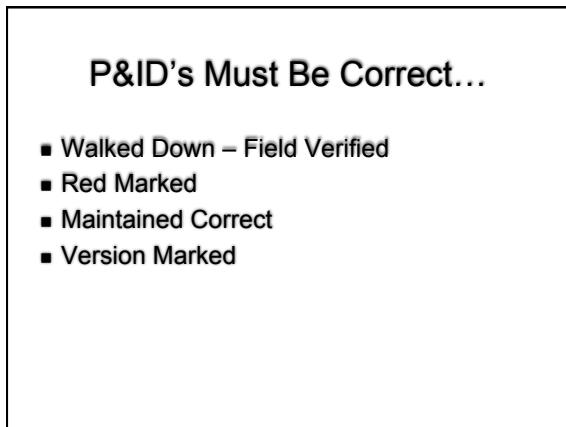


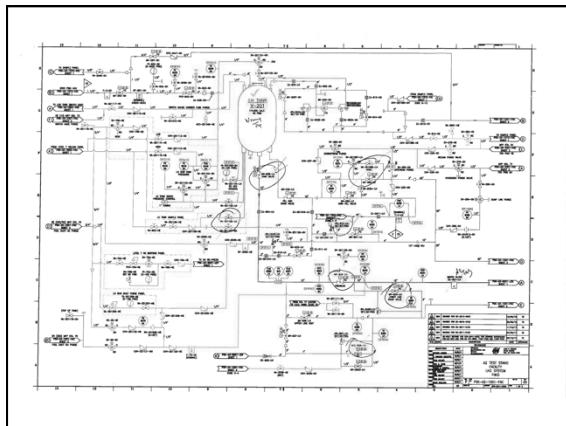






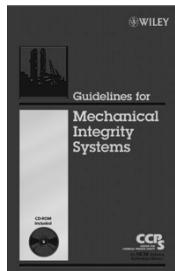






Code Tables and the CCPS

- The CCPS Book Contains Many Tables that are Useful
- Let's Review Some of these Tables...



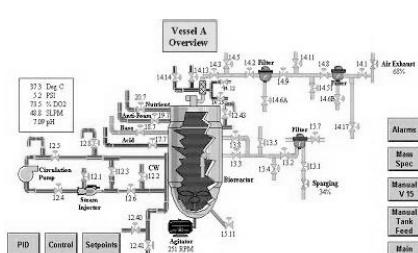
Mechanical Integrity & CCPS

TABLE 9-1 RAGAGEPs for Pressure Vessels			
Issuing Organization	Document Number	Title	Application
API	API 510	Pressure Vessel Inspection Code: Maintenance Inspection, Rating, Repair, and Alteration	Covers the maintenance, inspection, repair, alteration, and rerating procedures for pressure vessels.
API	Recommended Practice (RP) 572	Inspection of Pressure Vessels	Covers the inspection of pressure vessels.
API	ANSI/API 660 or International Organization for Standardization (ISO) 16812	Shell-and-Tube Heat Exchangers for General Refinery Services	Defines the minimum requirements for the mechanical design, material selection, fabrication, inspection, testing, and preparation for shipment of shell-and-tube heat exchangers.
ASME	ASME Code, Section VIII	ASME Boiler and Pressure Vessel Code (BPVC), Unified Pressure Vessel	Provides requirements applicable to the design, fabrication, inspection, testing, and certification of pressure vessels operating at either internal or external pressures exceeding 15 psig.
NBBPVI	National Board (NB)-23	National Board Inspection Code	Provides rules and guidelines for in-service inspection of boilers, pressure vessels, piping, and pressure relief valves (PRVs). Also provides rules for the repair, alteration, and rerating of pressure-retaining items and for the repair of PRVs.

MI Process & CCPS What We Must Consider

a. ITEMS:											
	Boilers	Pressure Vessels	Piping	Valves	Aboveground Storage Tanks	Safety/Safety Related Valves	Pumps	Instrumentation and Control	Pipelines (49 CFR 192-199)		
b. DESIGN OR CONSTRUCTION CODES:	ASME I ASME IV	ASME VIII DP - 1 & 2	ASME B31.1 ASME B31.3	ASME B31.24 API 600 API 609	API 12B API 650 API 620	ASME I ASME IV ASME B31.1 API 2000	API 610 API 214-475	VARIOUS ISA STANDARDS AND PRISI	BS14 BS18 API 1104		
c. INSPECTION, REPAIR, ALTERATION, RERATING, OR FITNESS FOR SERVICE CODES:	NBIC	NBIC API 570 API 579	API 570 API 579	API 598 API RP598	API 653 API 579	NBIC	API RP583 MFG STDS	ISAMFG STANDARDS	ASME B31G		
d. "SUPPORT" OR "REFERENCED" CODES OR PUBLICATIONS:	ASME I-ASCD ASME V ASME VI & VI ASME VIII API RP 573 SNT-TC-1A	ASME V-ASCD ASME V ASME IX ASME B31.3 ASME B31.5 SNT-TC-1A	ASME I-ASCD ASME V ASME IX ASME B31.3 ASME B31.5 SNT-TC-1A	API RP 574 API 2207 ASME B31.3 ASME B31.5 ASME V ASME IX SNT-TC-1A	API 651 API 2016 API 2207 ASME B31.3 ASME V ASME IX SNT-TC-1A	ASME PTC-25 API 627 ASME B31.3 ASME V ASME IX SNT-TC-1A	MPG STANDARDS INSTRUMENTERS HANDBOOK MFG STANDARDS	INSTRUMENTERS HANDBOOK MFG STANDARDS	ASME V ASME IX		

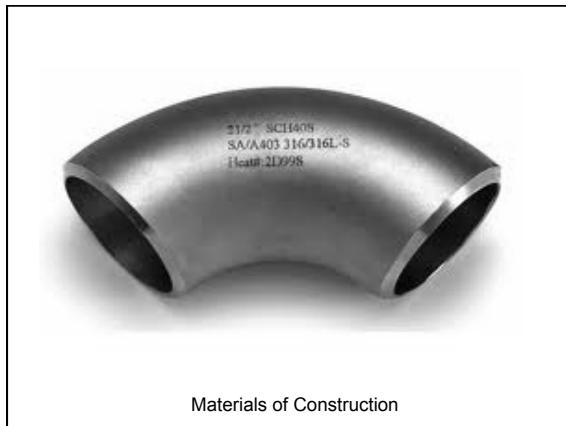
Process Chemistry



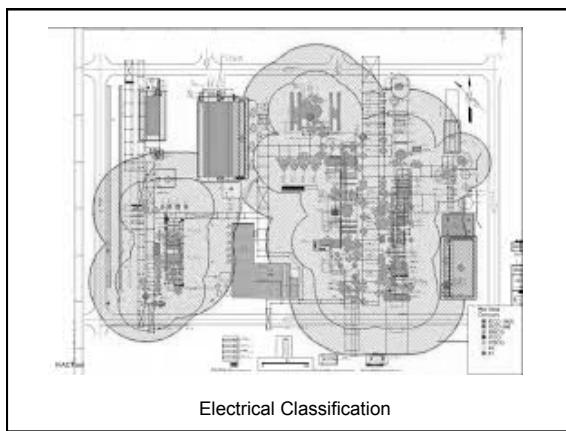
Process Chemistry



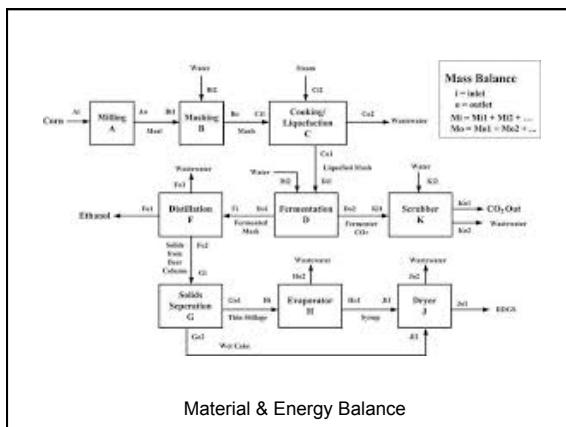
Process Chemistry - Reactions



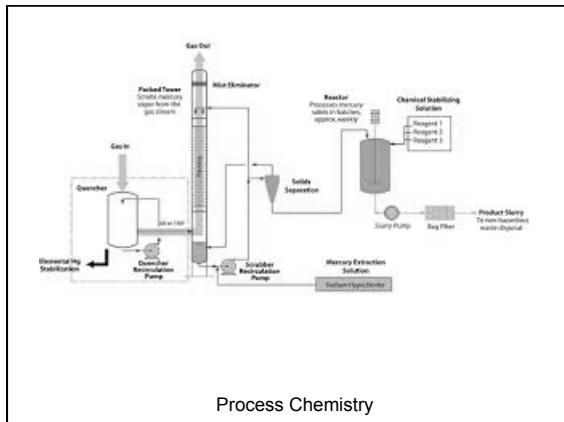
Materials of Construction



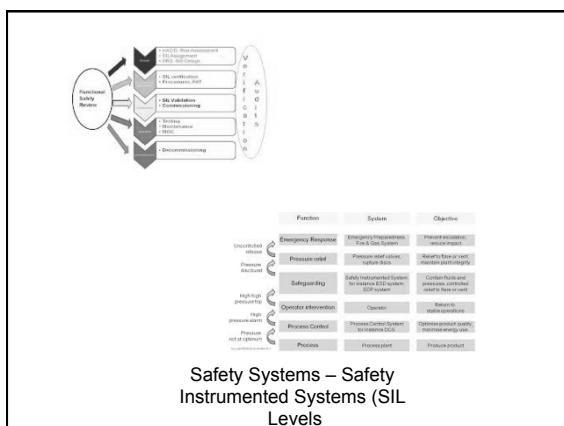
Electrical Classification



Material & Energy Balance

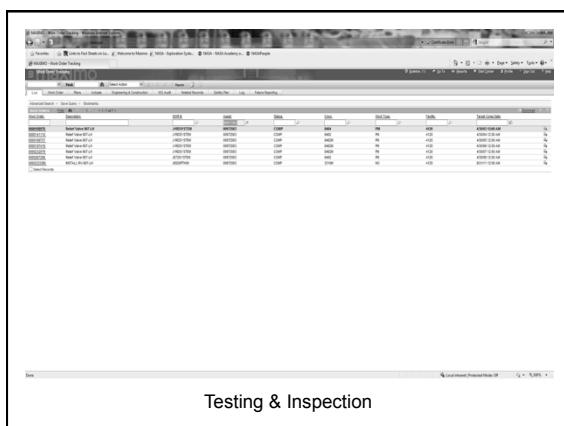
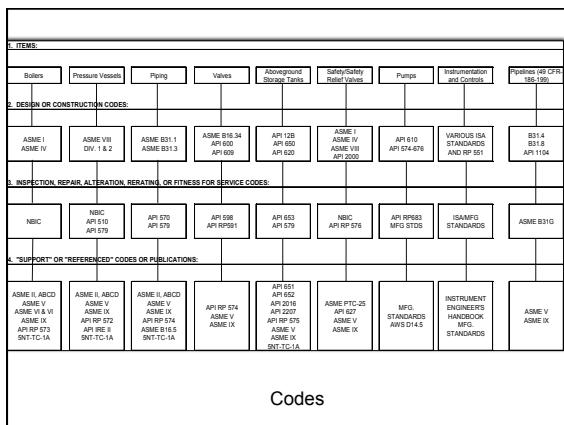


Process Chemistry



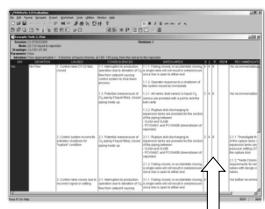


Mechanical Integrity



What Do We Do With the PHAs Developed?

- Using the Risk Column, Begin:
 - Reviewing Mitigation Design
 - Warning/Alarms to Warn of Deviations
 - Ventilation Systems



Let's Discuss Mitigation Methods...

Mitigation Methods

Examples of Mitigation

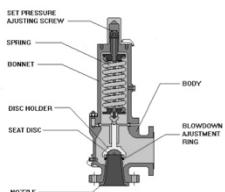
Passive or Active

- Relief Valves
- Piping Designs
- Detection Sensors
- Monitoring Cameras
- Containment Systems or Dikes



Mitigation Methods

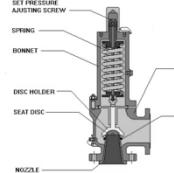
Pressure Relief Valves (PRVs)



- Relief Valve (RV)
- Pressure Safety Valve (PSV)
- Safety Valve (SV)
- Pop-Off Valve
- Blow-Off Valve

Mitigation Methods

Pressure Relief Valves (PRVs)

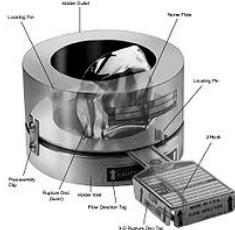


- PRVs protect equipment from failing by releasing the minimum quantity of its contents
- PRVs release to preferred places (e.g., incinerators, scrubbers, remote locations, catch tanks, atmosphere)
- PRVs reclose when the pressure is lowered below the set point
- Pressure relief devices must be designed

Mitigation Methods

Rupture Disks

- Operate Similar to relief valves
- Do not reseat
- One-time use
- Must discharge to a safe location



Mitigation Methods

Pressure / Vacuum Vents

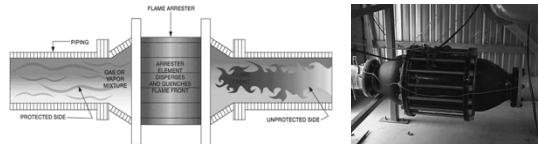
- Installed on low pressure tanks & storage vessels
- Used when loading a tank or drawing liquid from tank
 - breather vent
 - conservation vent



Mitigation Methods

Flame Arrestors

■ Protect Systems from Flame Fronts



A flame arrester functions by forcing a flame front through channels too narrow to permit the continuance of a flame

Mitigation Methods

Flares

- **Flare stacks or gas flares** are vent pipes used in for burning off flammable gas released by pressure relief systems during planned or unplanned over-pressuring of the system



If Relief is Used, They Must Be Properly Designed.

Relief Calculations Should be Reviewed for Completeness

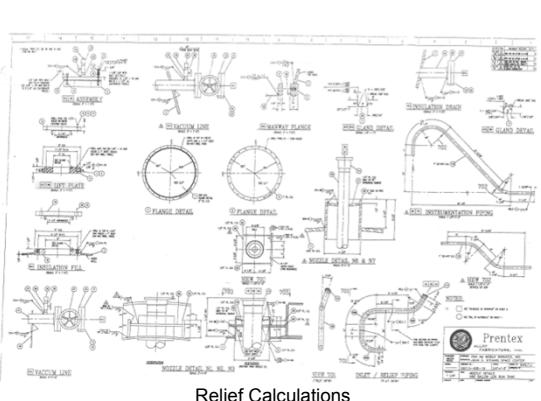
Relief Devices Design RAGAGEPs

API 520 – Sizing, Selection, and Installation of Pressure-relieving Devices in Refineries

API 521 – Pressure-relieving and Depressuring Systems

API 2000 – Venting Atmospheric and Low-pressure Storage Tanks

API RP 576 – Inspection of Pressure Relieving Devices



8.7 PRESSURE RELIEF VALVE

Relief valve must function at a pressure between 2 and 16 psig. The minimum I.D. of the nozzle is 3.5 inch.

At 2 psig $F = \frac{1}{2}(4 \text{ in.})^2 (2 \text{ psig}) = 25.13 \text{ lbs.}$

At 16 psig $F = \frac{1}{2}(4 \text{ in.})^2 (16 \text{ psig}) = 201.06 \text{ lbs.}$

Using 4 springs $\text{Rating force per spring} = \frac{201.06}{4} = 50.27 \frac{\text{lbs}}{\text{spring}}$

For $\frac{1}{2} \text{ in. travel minimum spring rate} = \frac{50.27}{0.5} = 100.53 \frac{\text{lbs}}{\text{in}}$

For a spring rate of 7 lbs/in, preload length = $l = \frac{100.53}{7} = 0.0088 \text{ in.}$

Assume $\frac{1}{2} \text{ in. preload}$

From the LEE SPRINGS CO. catalog, use part #KHC-750A-4, $K = 100 \frac{\text{lbs}}{\text{in}}$

OPERATING PRESSURE OF VALVE

Appropriate weight of Cover = $\frac{1}{2}(4 \text{ in.})^2(44.48) = 18.94 \text{ lbs.}$

Amount of preload = $4(100(0.15)) = 60 \text{ lb}$

Total resulting force = $16(8.0) + 60 = 88.80 \text{ lb}$

minimum pressure to open the valve = $P = \frac{88.80}{2(47)} = 5.33 \text{ psig}$

2.0 psig < $P < 5.33 \text{ psig}$ L-1.12 pg. 206a, 206b

USE 1:

Free length = 1.75 in.; Spring rate = $100 \frac{\text{lbs}}{\text{in}}$

Solid height = 0.81 in.; Rod diameter = $\frac{3}{8} \text{ in}$

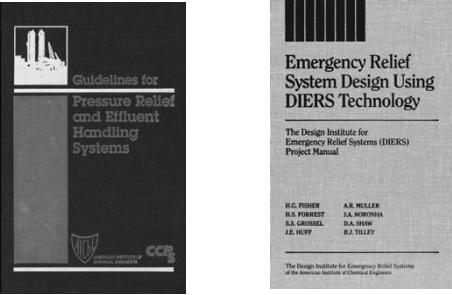
Hold Diameter = $\frac{3}{8} \text{ in.}$; Free spring length = $\frac{15}{16} \text{ in.}$

Rod Length = 3.69 in.; Compression at installation = $\frac{3}{8} \text{ in.}$

Compressed spring length = $1\frac{1}{2} - \frac{3}{8} = 1\frac{1}{8} \text{ in.}$

Relief Calculations

Relief Systems – CCPS Guidelines



Guidelines for Pressure Relief and Effluent Handling Systems

Emergency Relief System Design Using DIERs Technology

The Design Institute for Emergency Relief Systems (DIERs) Project Manual

H. G. FISHER A. B. MULLER
H. S. FOREST J. A. NORNOMA
S. S. GROSSEL D. B. SHAW
J. E. HUFF R. J. TALLEY

The Design Institute for Emergency Relief Systems
of the American Institute of Chemical Engineers

Mitigation Methods

Early Detection of Release



IR Camera

Additional Safety Systems

- Bonding and grounding
- Secondary containment systems
- Gas detection systems
- Flame /Detonation arrestors
- Suppression systems
- (Mechanical isolation systems) Fast-acting valves
- Inerting systems
- Purging systems
- Fire protection equipment
- Structural fireproofing
- Fire walls and fire stops
- Explosion or blast panels or explosion suppression systems
- Scrubber systems



Inherently Safe Design

- causes and/or reducing the consequences of potential process upsets.
- Inherently Safe Process Design is a technique applied during the conceptual phase of process design.
- Inherently Safe Process Design targets the **HAZARD** rather than reducing the **RISK** after the fact.
- This technique is based on making inherently safer design choices at a point in the process development where the engineer has the most influence on the final design.

Inherently Safe Process Design

- **Definitions**

- Inherently safe process design can be grouped into 5 categories

Category	Example
1 Intensification	Continuous reactor vs. batch reactor
2 Substitution	Change of feedstock
3 Attenuation	Alternate technology
4 Limitation of effects	Minimization of storage volume
5 Simplification	Gravity flow vs. pumping

- Each of these inherently safer design choices is applied in the conceptual phase of development.

Inherently Safe Process Design

- **Traditional Process**

- Sample Risk Assessment using What If? Methodology

What If...?	Initiating Cause	Consequence
1. There is higher pressure in the Entrainer Vessel?	1.1 External fire in the process area.	1.1 Potential increased temperature and pressure leading to possible vessel leak or rupture. Potential release of flammable material to the atmosphere. Potential personnel injury due to exposure.
	1.2 Pressure regulator for inert gas pad fails open.	1.2 Potential for vessel pressure to increase up to the inert gas supply pressure. Potential vessel leak or rupture leading to release of flammable material to the atmosphere. Potential personnel injury due to exposure.
2. There is higher level in the Entrainer Vessel?	2.1 Vessel level transmitter fails and indicates lower than actual volume.	2.1 Potential to overfill vessel with cyclohexane. Potential to release flammable liquid reaching the vent gas incinerator. Potential to overwhelm incinerator leading to possible explosion. Potential personnel injury due to exposure.

- Consider what types of safeguards would be required to mitigate the Process Risk due to these scenarios.

Inherently Safe Process Design

- When considering the potential upset scenarios for the process, the benefits of the inherently safer process become clear.

Upset Scenario	Traditional Process	Inherently Safer Process
External Fire	Large volume of flammable liquid circulating in process.	Flammable volume limited to recovered solvent only.
Overfill	Cyclohexane entrainer more volatile than 1-propanol.	Minimal liquid hold up in Pervaporation Unit.
Overpressure	Larger liquid hold-up leads to higher severity in the event of a release.	Volume limited to solvent distillation hold-up.

Inherently Safe Process Design

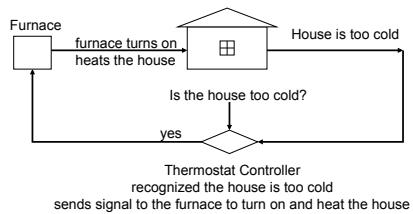
- Based on this risk comparison, it is clear that multiple independent protection layers would be required to mitigate the operating risk of the traditional process.
- This risk can be reduced by designing an inherently safer, i.e., less hazardous process.
- Although a complete economic analysis would be required, this example has illustrated that the need for independent protection layers is reduced in the inherently safer process design.

Process Control – A Few Basics



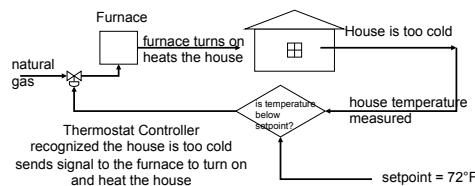
What is Basic Process Control?

- Process control loop: control component monitors desired output results and changes input variables to obtain the result.
- Example: thermostat controller

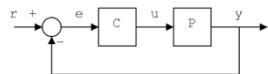


Basic Control

Controlled variable: temperature (desired output)
 Input variable: temperature (measured by thermometer in thermostat)
 Setpoint: user-defined desired setting (temperature)
 Manipulated variable: natural gas valve to furnace (subject to control)



Feedback Control Theory

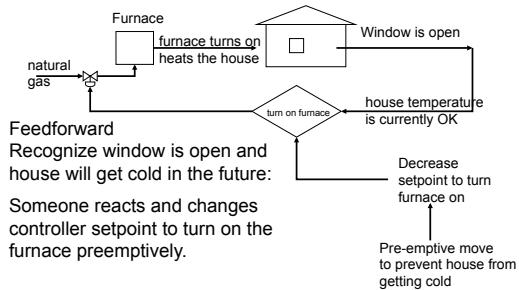


- Output of the system $y(t)$ is fed back to the reference value $r(t)$ through measurement of a sensor
- Controller C takes the difference between the reference and the output and determines the error e
- Controller C changes the inputs u to Process under control P by the amount of error e

Limitations of Feedback Control

- Feedback control is not predictive
- Requires management or operators to change set points to optimize system
 - Changes can bring instability into system
 - Optimization of many input and output variables almost impossible
 - Most processes are non-linear and change according to the state of the process
- Control loops are local

Feedforward Control

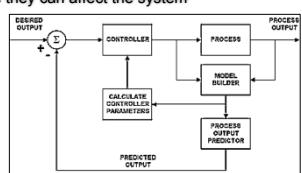


Feedforward Control

- Feedforward control avoids slowness of feedback control
- Disturbances are measured and accounted for before they have time to affect the system
 - In the house example, a feedforward system measured the fact that the window is opened
 - As a result, automatically turn on the heater before the house can get too cold
- Difficulty with feedforward control: effects of disturbances must be perfectly predicted
 - There must not be any surprise effects of disturbances

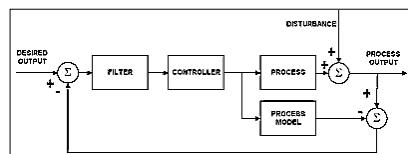
Combined Feedforward/Feedback

- Combinations of feedback and feedforward control are used
 - Benefits of feedback control: controlling unknown disturbances and not having to know exactly how a system will respond
 - Benefits of feedforward control: responding to disturbances before they can affect the system



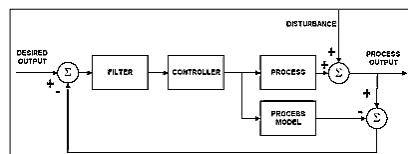
Multivariable Control

- Most complex processes have many variables that have to be regulated
- To control multiple variables, multiple control loops must be used
 - Example is a reactor with at least three control loops: temperature, pressure and level (flow rate)
 - Multiple control loops often interact causing process instability
- Multivariable controllers account for loop interaction
- Models can be developed to provide feedforward control strategies applied to all control loops simultaneously



Internal Model-Based Control

- Process models have some uncertainty
 - Sensitive multivariate controller will also be sensitive to uncertainties and can cause instability
- Filter attenuates unknowns in the feedback loop
 - Difference between process and model outputs
 - Moderates excessive control
- This strategy is powerful and framework of model-based control



Important Data Issues

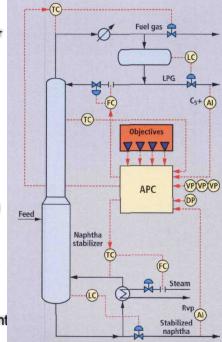
- Inputs to advanced control systems require accurate, clean and consistent process data
 - “garbage in garbage out”
- Many key product qualities cannot be measured on-line but require laboratory analyses
 - Inferential estimation techniques use available process measures, combined with delayed lab results, to infer product qualities on-line
- Available sensors may have to be filtered to attenuate noise
 - Time-lags may be introduced
 - Algorithms using SPC concepts have proven very useful to validate and condition process measurement
- With many variables to manipulate, control strategy and design is critical to limit control loop interaction

Advanced Process Control

- State-of-the-art in Modern Control Engineering
- Appropriate for Process Systems and Applications
- APC: *systematic approach to choosing relevant techniques and their integration into a management and control system to enhance operation and profitability*

Distillation Tower Example

- Simple distillation column with APC
 - Column objective is to remove pentanes and lighter components from bottom naphtha product
- APC input:
 - Column top tray temperature
 - Top and bottom product component laboratory analyses
 - Column pressures
 - Unit optimization objectives
- APC controlled process variables
 - Temperature of column overhead by manipulating fuel gas control valve
 - Overhead reflux flow rate
 - Bottom reboiler outlet temperature by manipulating steam (heat) input control valve
- Note that product flow rates not controlled
 - Overhead product controlled by overhead drum level
 - Bottoms product controlled by level in the tower bottom
- APC anticipates changes in stabilized naphtha product due to input variables and adjusts relevant process variables to compensate



Distributed Control System & PLC's



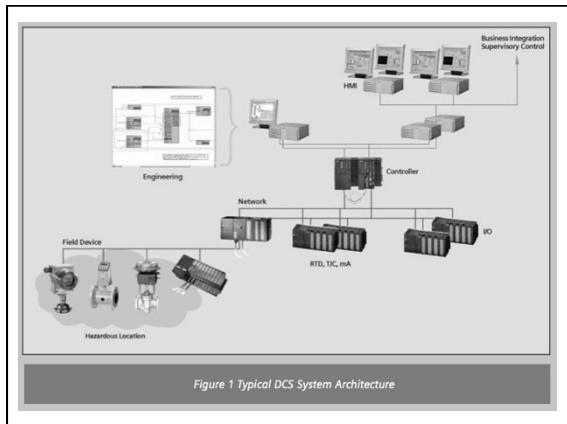


Figure 1 Typical DCS System Architecture

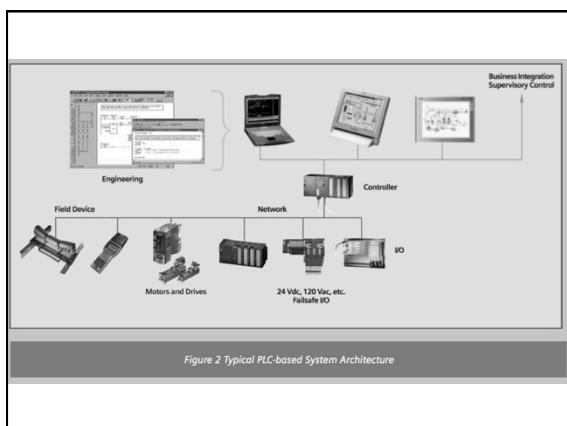
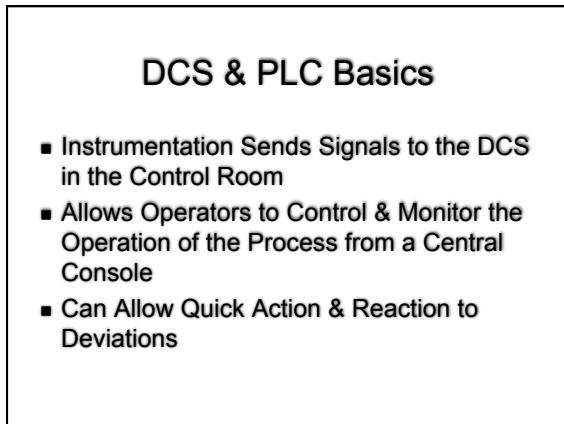
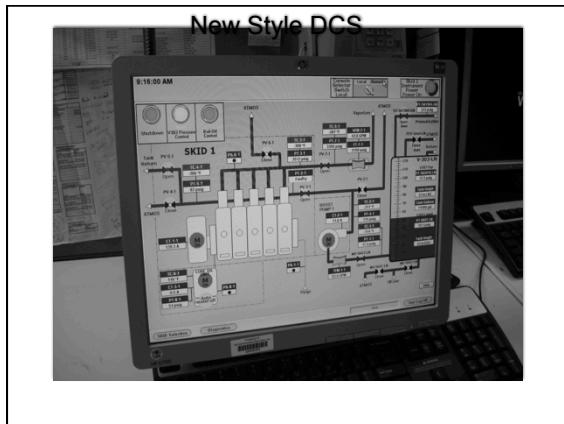


Figure 2 Typical PLC-based System Architecture





DCS & PLC Basics

- Must Have Reliable Instrumentation
- Instrumentation must be inspected, calibrated and tested
- Set points must signal and allow the operators to maintain the system within the operating envelope
- Software must be robust and ensure that significant deviations are visible to the operators

Instrumentation Reliability

- Critical Instrumentation: Might Consider
 - Safety Instrumented Systems (SIS)
 - SIL Levels 1,2,3
 - Expensive
 - Married To Them

Some Questions You Should Ask?

- What Kind of DCS Do They Use?
- What Calibration and Testing is Performed on their instrumentation?
- Do They Have SIL Level Devices? If so, Inspection and Testing Records.
- Details of Operator DCS Training and Re-Training
- Configuration of Deviation Alarms – How Are Operators Notified of a Deviation?

Interviews to Consider

- Operators – Multiple
- Maintenance – Multiple
- Instrumentation – Multiple
- Emergency and Security Personnel?

Additional Considerations Facility Siting



Facility Siting Methods to Consider

- Guidelines for Facility Siting, CCPS 2003
- Guidelines for Evaluating Process Plant Buildings for External
- Explosions, Fires and Toxic Releases, CCPS 2012
- Management of Hazards Associated with the Location of Process Plant Portable Buildings, API 753 2007
- Management of Hazards Associated with the Location of Process Plant Permanent Buildings, API 752 2009

Facility Siting Items to Consider

Plant Siting

- Locating chemical containing units with consideration of prevailing wind direction as far as possible from the general community outside the site boundaries.
- Protecting on-site buildings occupied by a large number of people through a combination of engineering controls, administrative procedures and/or distance, together within a site to minimize the spread of phosgene-containing areas.

Facility Siting Items to Consider

Plant Siting

- Locating phosgene containing units away from other processes which have potential for explosion or fire, or events which may impact or damage equipment containing phosgene.
- Incorporating additional safety and loss prevention precautions if phosgene must be transported across plant boundaries either by pipeline or in pressurized containers.

Facility Siting Items to Consider

Plant Layout

- Providing that all sections of the plant are easily accessible for maintenance and emergency response purposes.
- Locating phosgene generating or processing sections in plant areas with low traffic density whenever possible and minimizing phosgene containing pipelines.
- Having additional engineering controls for prevention and mitigation of leaks from the equipment where plant sections have special process conditions, or where because of the surrounding situation, other controls may be needed.

Facility Siting Items to Consider

Plant Layout

- Selecting the location of the control building in relation to the phosgene containing sections and with consideration of the prevailing wind direction.
- Ensuring that temporary facilities (such as trailers) used during construction, maintenance contractors or office space for plant support personnel are located with consideration to the hazards of phosgene. Emergency procedures should include the occupants of these temporary facilities.

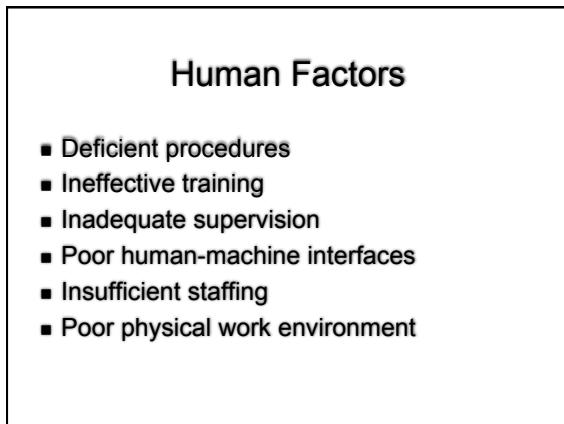
Facility Siting Design Final Review

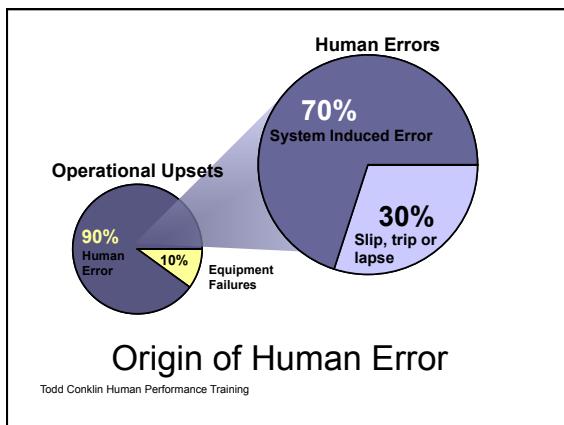
Resources to Use:

- Center For Chemical Process Safety Dow FEI and CEI Guidelines;
- Center For Chemical Process Safety Book on Guidelines for Safe Storage and Handling of Highly Toxic Hazardous Materials; and
- US EPA Risk Management Planning, Section 112 regulations and application guidelines.

BP Texas City







Human Failure Rate

1 in Every 100 Times

Human Factors-Realities

- We Can Engineer the Safest System We Can...
- Then...We Add Humans

Guaranteed, Sometimes...We Will Mess It Up

What's Next

- Now that We Have Process Safety Information...
- What About Mechanical Integrity?

Process Safety Management of Highly Hazardous & Explosive Chemicals



29CFR1910.119

Clearly Understanding the Standard

