

Purdue Chemical Engineering

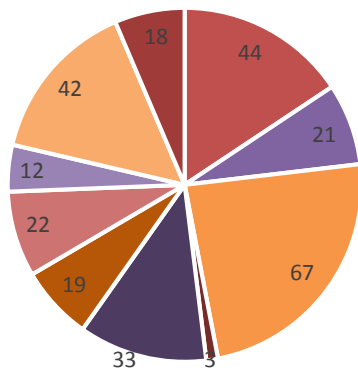
Undergraduate Process Safety Research

November 10, 2016

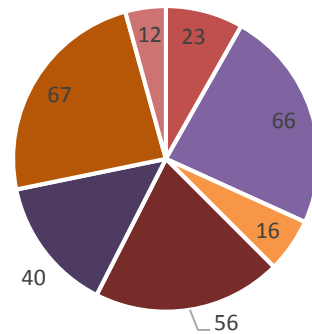
US DUST EXPLOSION INCIDENTS 1980 – 2005 STUDIED BY CSB

- 281 fires & explosions & 119 fatalities -

OF INCIDENTS CLASSIFIED BY INDUSTRY

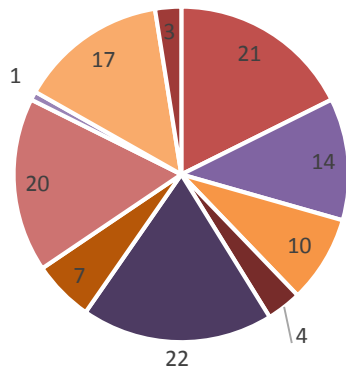


OF INCIDENTS CLASSIFIED BY FUEL TYPE

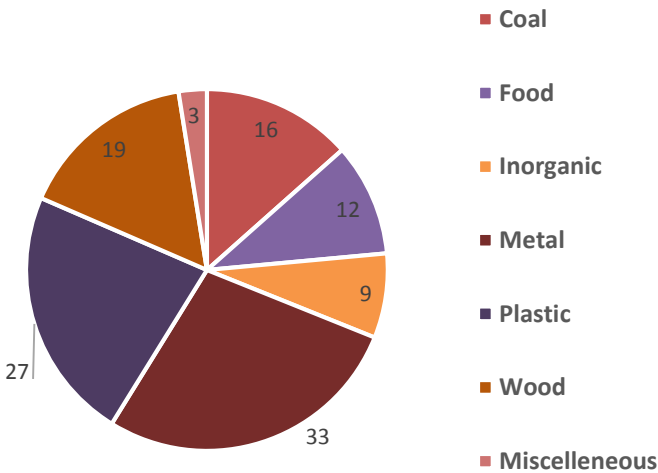


- Primary Metal Industries / Fabricated Metal Products
- Electrical Devices/Services
- Food Products
- Packaging & Storage
- Chemical Manufacturing
- Equipment Manufacturing
- Rubber & Plastic Products
- Furniture & Fixtures
- Lumber & Wood Products
- Other

OF FATALITIES CLASSIFIED BY INDUSTRY



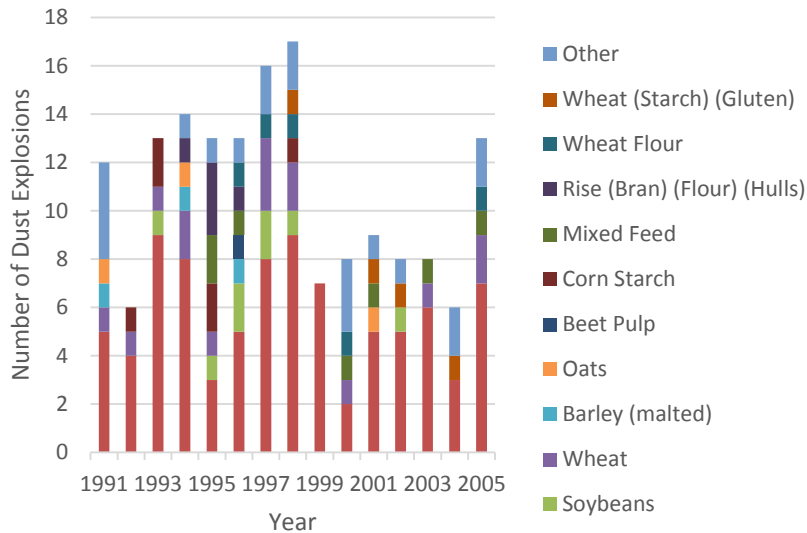
OF FATALITIES CLASSIFIED BY FUEL TYPE



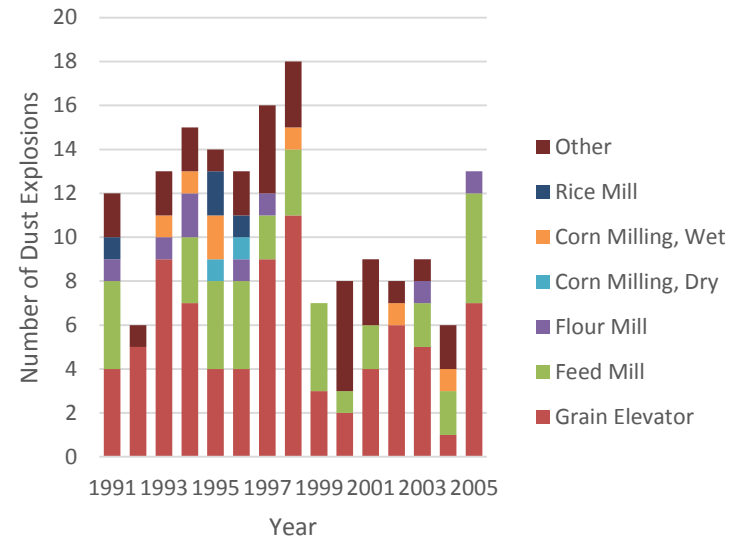
- Coal
- Food
- Inorganic
- Metal
- Plastic
- Wood
- Miscellaneous

US Agricultural Dust Explosions 1991 – 2005*

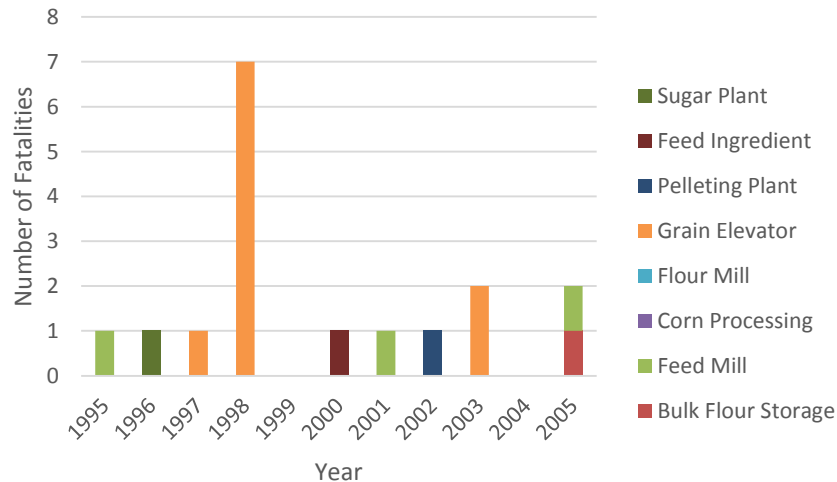
Dust Explosions based on Commodity Type



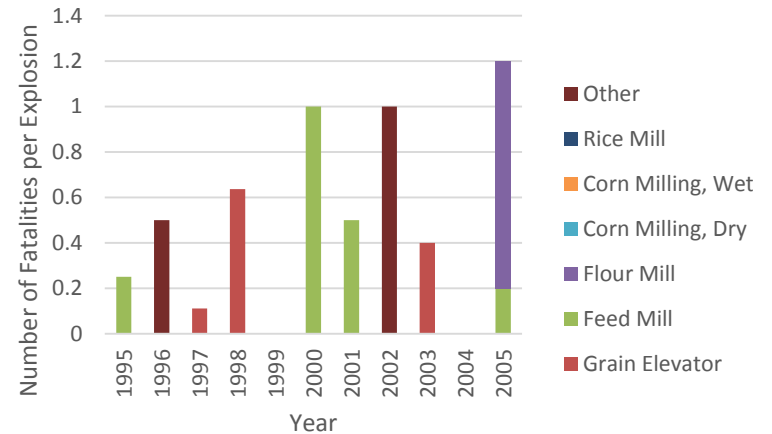
Dust Explosions based on Type of Facility



Fatalities based on Type of Facility



Fatalities per Explosion based on Type of Facility

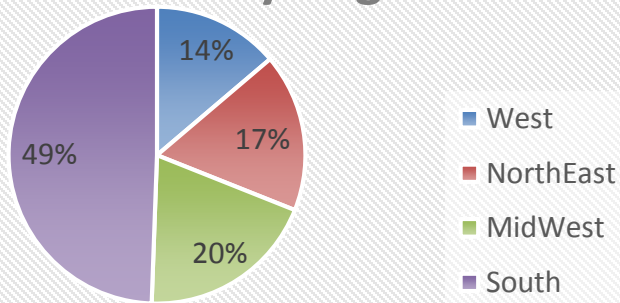


*Robert W. Schoeff, Kansas State University, in cooperation with FGIS-USDA, March 20, 2006

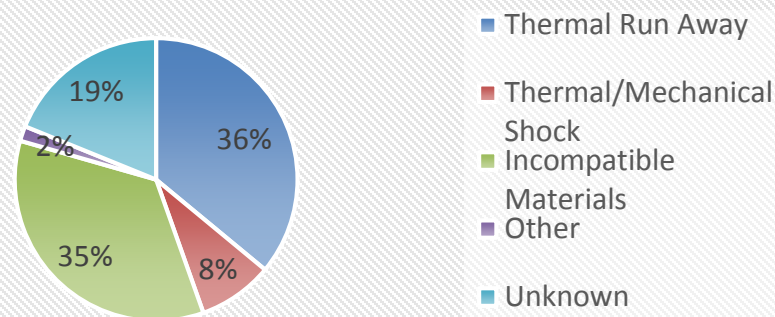
Reactive Chemical Incidents

CSB study of 167 US reactive chemical incidents from 1980 – 2001 with 108 fatalities

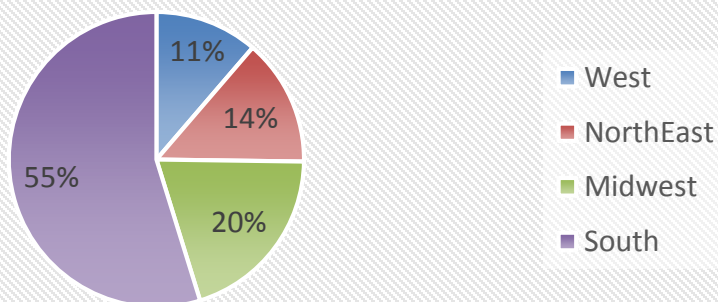
Incidents by Region



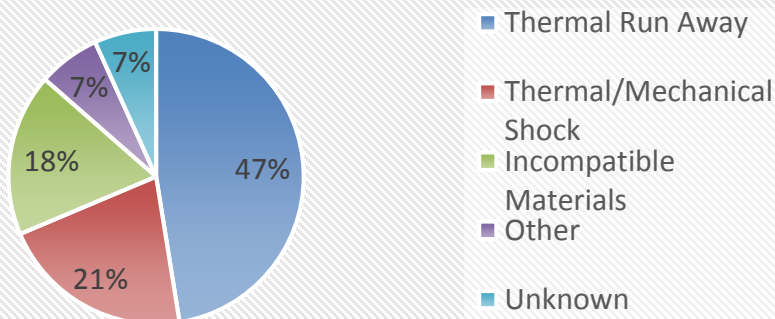
Incidents by Accident Type



Deaths by Region



Deaths by Accident Type



Source: Chemical Safety Board, Improving Reactive Hazard Management, Reactive Incident Data Table, 1980 to 2001

Nanotechnology Safety

- The emergence of nanotechnology with focus on the production of nanomaterials without full understanding of their safety and health effects.
- **Concerns with nanotechnology:**
 - **Toxicity** of small particles that are able to pass through skin and blood,
 - **Small particles** can deposit in the lungs,
 - **Large surface area** contributes to more reactivity, and
 - **Adverse effects on the environment from** nanoparticle waste.
- **Process Safety**
 - Nano silver particles released into waste water from sock manufacturing companies. May have adverse effects on waste-water treatment, due to Nano silver interaction with microbiological bacteria.
- **Personnel Safety**
 - August 2009; 2 fatalities, 5 injuries. Several women obtained serious lung injuries in a print plant in Beijing due to fumes of polystyrene boards. Lack of knowledge of hazards of materials and to follow workplace safety.
 - August 22nd, 2016: 2 fatalities; Loss of control of airplane due to fire caused by flammable materials including Lithium Ion batteries carried on board. Lack of knowledge of how to handle such situations; now implementing fire control devices.

Chemical Process Safety @ Purdue

– CHE 420; Required senior level course

November 10, 2016

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Purdue University



Piper Alpha, UK 1988; 167 fatalities



BP Texas City, 2005; 15 fatalities



West, TX – 2013; 15 fatalities



Imperial Sugar, Georgia – 2008; 14 fatalities

CHE 420 Schedule

Why study process safety? Syllabus	Piper Alpha video
Chapter 1. Introduction	
Teamwork	
Chapter 2. Toxicology	Nitrogen Asphyxiation video
Chapter 3. Regulations & Mgmt Systems	Quiz 1
Chapter 3. Industrial Hygiene	
Chapter 4. Source Models – I, liquids	BP TX City video
Chapter 4. Source Models – II, gases	Bhopal
Exam I	
Chapter 5. Toxic Release & Dispersion Models	Fatal Exposure – DuPont; Project topics distr.
Chapter 6. Fires & Explosions	Blast Waves in Danvers
Chapter 7. Designs to Prevent Fires & Explosions - I	Static Electricity video; Quiz 2
Chapter 7. Designs to Prevent Fires & Explosions – II	Imperial Sugar video
Chapter 8. Chemical Reactivity	T-2 Incident video
Exam II	
What Does Safe Look & Feel Like?	Deepwater Horizon video
Chapter 9. Relief Sizing	
Chapter 10. Relief Sizing	Formosa Fire & Explosion video
Chapter 11. Hazards Identification – I	
Chapter 11. Hazards Identification – II	Quiz 3
Thanksgiving Break	
Chapter 12. Risk Assessment	West explosion
Emergency Response & Incident Investigation	Emergency Preparedness video
Exam III	



I - Safety Culture

**Personnel
Safety**

**Process
Safety**

Process Incident Definition

A process incident is the sudden unintended release of or exposure to a hazardous substance, which results in or might reasonably have resulted in, deaths, injuries, significant property or environmental damage, evacuation or sheltering in place.

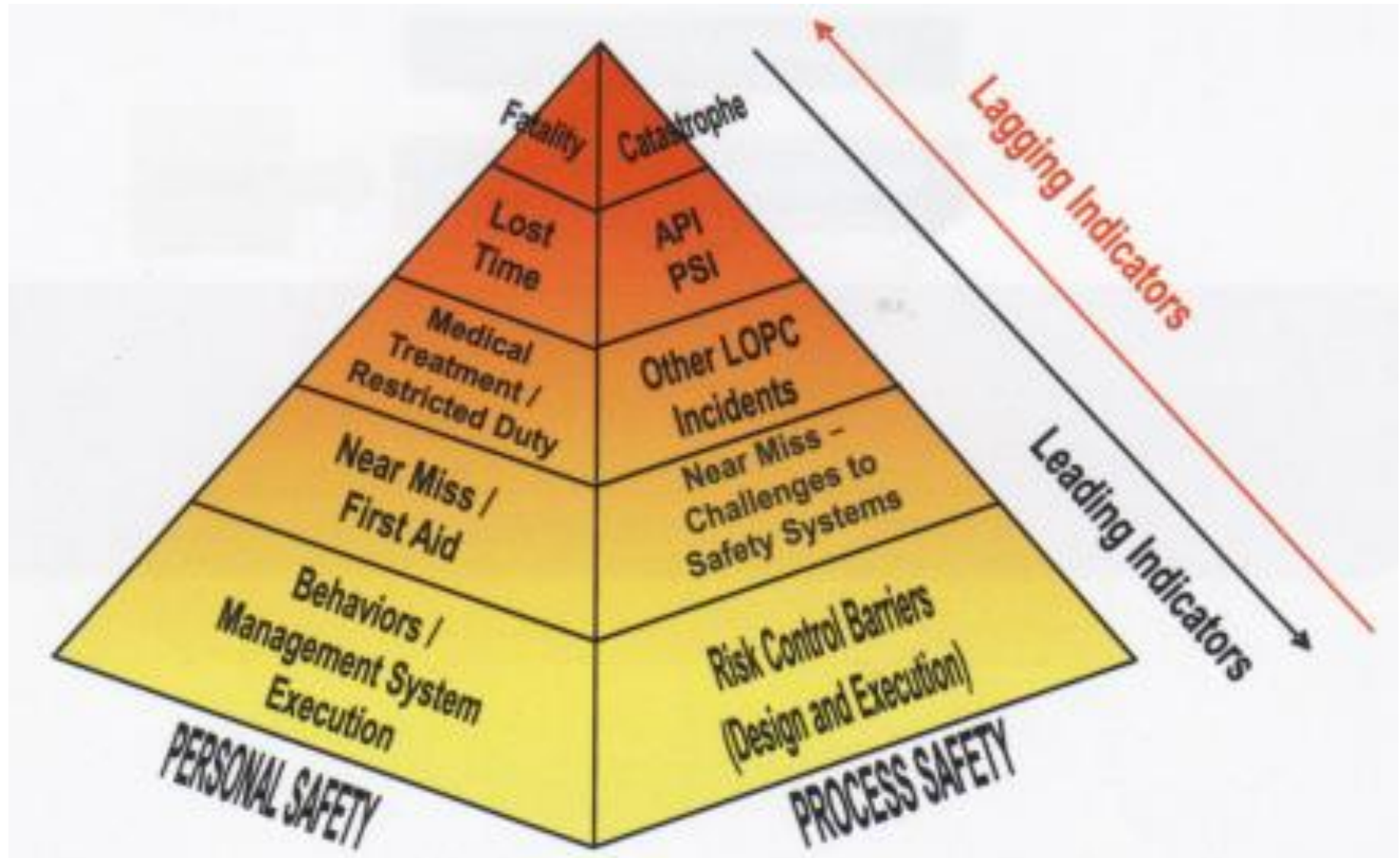


VS.



T-2 Laboratories, FL – '09; 4 fatalities

Process Safety Metrics



OSHA Process Safety Management Program

****14 elements****

- Employee Participation
- Process Safety Information
- Process Hazards Analysis
- Operating Procedures
- Training
- Contractors
- Pre-startup Safety Review
- Mechanical Integrity
- Hot Work Permits
- Management of Change
- Incident Investigation
- Emergency Planning & Response
- Compliance Audit
- Trade Secrets

Industrial Compliance with PSM, RMP, ...

- How does industry comply with the various federal, state & local regulations?
- Are regulations the minimum standard ... and should companies consider implementing PSM type requirements at other sites, beyond PSM required sites?
- What about international sites? Should those facilities be held to a different (only local?) standard? What about PSM type requirements?
 - Should international employees be exposed to different levels of risk than domestic employees with same company?

Industrial Compliance with OSHA PSM

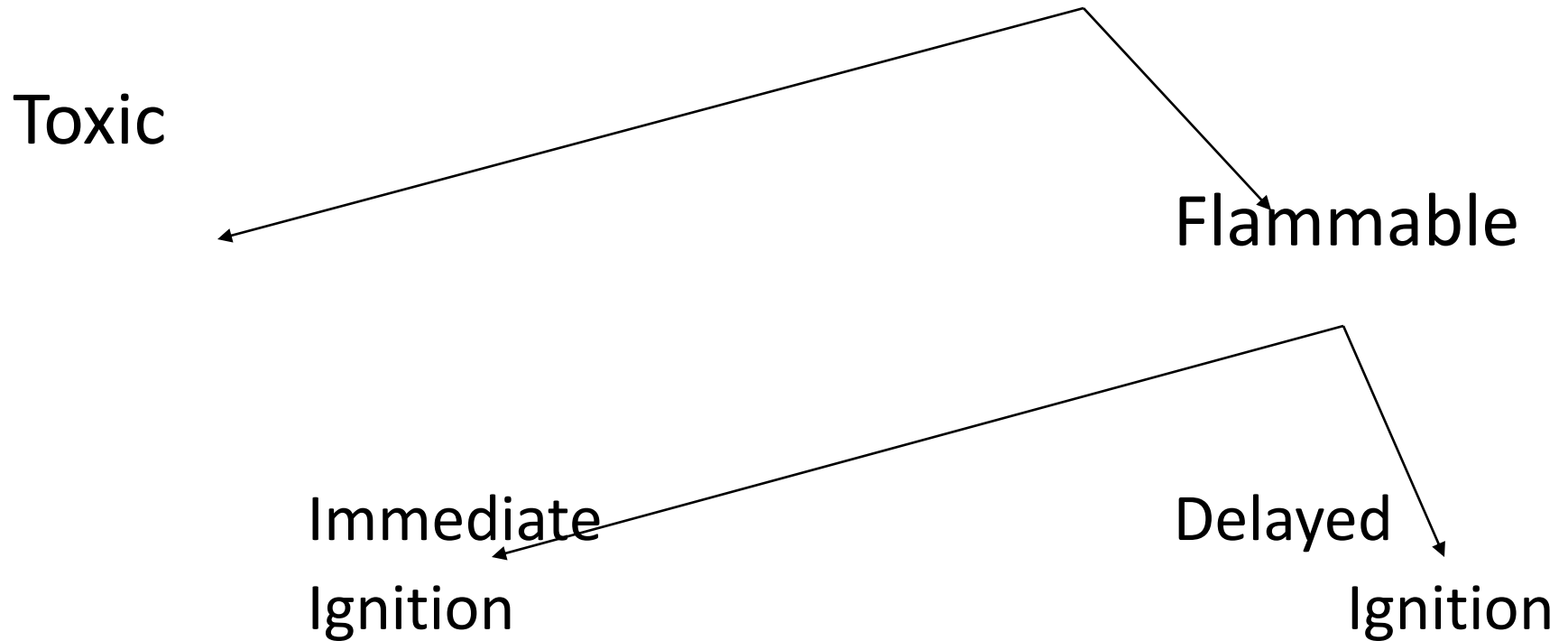
- ExxonMobil's "Operations Integrity Mgmt System" (OIMS) for all global operations
 - Many other companies have similar systems

OIMS 11 Elements

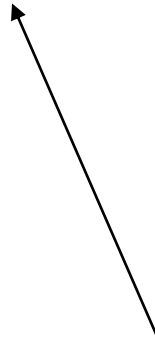


Anatomy of a Release

Failure → Source Term → Release and Dispersion



RISK = CONSEQUENCE X FREQUENCY



Much of course addresses toxics & flammables

Source Term Modeling – lbs / hr

- How does one determine the volume of a liquid or gas release for Emergency Response Planning?
- What's the Source or Volume term for various scenarios examined?
- 'Tank problems' - time to drain tank through hole or broken pipe, volume lost in time required to respond to mishap, maximum spill rate, etc?
- What's special about 'choke' flow conditions for gases in terms of upstream / downstream pressures & fluid velocity?

Tank Liquid Discharge: Leak Time, $Q_m(t)$

Time to leak at P_g : $t_e = \frac{1}{C_o g} \left(\frac{A_t}{A} \right) \left[\sqrt{2 \left(\frac{g_c P_g}{\rho} + g h_L^o \right)} - \sqrt{\frac{2 g_c P_g}{\rho}} \right]$

Where 'A' is the area of the hole & the subscript 't' means tank. The time to empty tank at $P_g \sim 0$, for tank at atmospheric P:

$$t_e = \frac{1}{C_o g} \left(\frac{A_t}{A} \right) \sqrt{2 g h_L^o}$$

Substitute $h_L(t)$ into original Q_m to obtain $Q_m(t)$, mass discharge rate at any time:

$$Q_m = \rho \bar{u} A = \rho A C_o \sqrt{2 \left(\frac{g_c P_g}{\rho} + g h_L^o \right)} - \frac{\rho g C_o^2 A^2}{A_t} t$$

Initial height of liquid, h_L^o

Gas Release – 'Choked' Pressure

For safety assessments: **Need maximum flow rate**

Differentiate Q_m expression wrt P/P_0 & set = 0 to find the P/P_0 for max flow:

$$\frac{P_{choked}}{P_0} = \left(\frac{2}{g + 1} \right)^{\frac{g}{g-1}} \quad \left(P_{ext} < P_{choked} \right), \text{function of } g$$

Choked pressure: Is the maximum downstream pressure resulting in the maximum flow through a hole or pipe. Sonic velocity (**u**) occurs at throat regardless of further decrease below P_{choked} in downstream pressure.

Maximum flow at choked conditions, obtained by inserting the choked pressure ratio into the mass flow rate expression, is independent of downstream conditions and is given by:

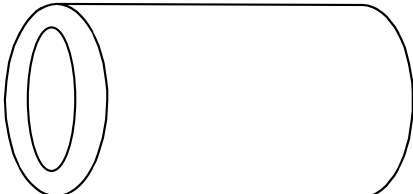
$$Q_m = r \bar{u} A = C_0 A P_0 \sqrt{\frac{2g_c M}{R_g T_0} \frac{g}{g-1} \left[\left(\frac{P}{P_0} \right)^{\frac{2}{g}} - \left(\frac{P}{P_0} \right)^{\frac{(g+1)}{g}} \right]}$$

$$Q_{m, choked} = C_0 A P_0 \sqrt{\frac{g g_c M}{R_g T_0} \left(\frac{2}{g + 1} \right)^{\frac{(g+1)}{(g-1)}}}$$

Adiabatic Choked Gas Flow, Through Pipe

External, $P < P_{choked}$

$$\Delta z \sim 0; W_s = 0 \quad \Delta Q = 0$$

$$P_1, T_1, u_1, Ma_1 \rightarrow \text{Pipe} \rightarrow P_{choked}, T_2, a_s, Ma_2 = 1$$


Mach is the ratio of the gas velocity to the velocity of sound in the gas

<Simplified procedure per pages 150 – 153 of text>

Mass flux

$$G = \frac{\dot{m}}{A} = Y_g \sqrt{\frac{2g_c \rho_1 (P_1 - P_2)}{\sum K_{f_i}}}$$

(choked or not choked; ideal gas)

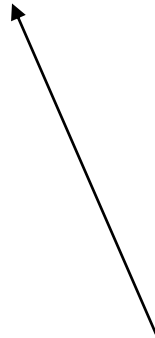
G is mass flux, K frictional term, alpha ratio of heat capacities, Y gas unit-less gas expansion factor

Gas expansion factor, Y_g

$$Y_g = Ma_1 \sqrt{\frac{\gamma \sum K_{f_i}}{2} \left(\frac{P_1}{P_1 - P_2} \right)}$$

(choked only)

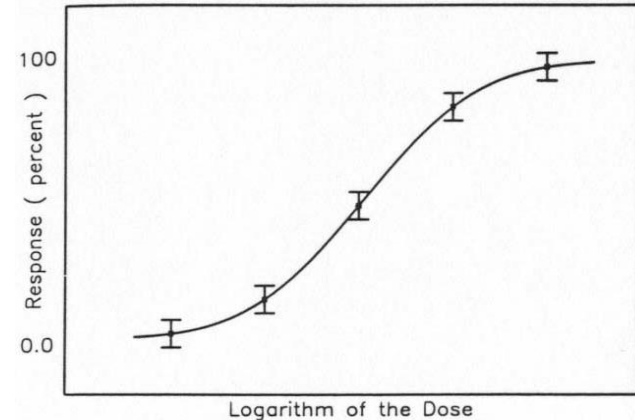
RISK = CONSEQUENCE X FREQUENCY



Much of course addressing toxic & flammables

Toxicity

- Use of Material Safety Data Sheets (MSDS) or new SDS per GHS
- Various published chemical limits: TLV, PELs, IDLH
- Use of probits to approximate dose – response curve for acute exposures
 - Can predict toxic impacts, as well as impact of explosions and fires in terms of damage, injuries and deaths
- Y is the probit variable to estimate probability or % of individuals affected



$$\text{Probability, \%} = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{Y-5} \exp\left(-\frac{u^2}{2}\right) du$$

- Correlations available for probits in terms of concentration, time, overpressure, impact energy, etc

Example Probit Estimation

- A blast produces a peak overpressure of 6 psig.
 - What fraction of structures will be damaged by exposure to this overpressure?
 - What fraction of people exposed will die as a result of lung hemorrhage?
 - What fraction will have eardrums ruptured?
 - What are some conclusions about the effects of this blast?

Chronic Workplace Exposures

- Single & multiple volatile toxicants $TWA = \frac{1}{8} \int_0^{t_w} C(t)$
- Dust & noise handled much the same way
- Toxic vapors in enclosure, with ventilation (e.g., standing near opening to storage tank)

$$C_{ppm} = \frac{Q_m R_g T}{k Q_v P M} 10^6$$

where Q_m is the source term, Q_v the ventilation rate & k mixing factor

- Vaporization of liquid

$$C_{ppm} = \frac{K A P^{\text{sat}}}{k Q_v P} \times 10^6$$

where K the mass transfer coefficient & A the area of opening

Vapor Releases & Air Dispersion Modeling

- How to estimate the downwind concentration of a chemical continuously released?
- Suppose the release is elevated, such as from a stack?
- How do the calculations change if the release is instantaneous vs. continuous ... such as for an upset?
- What are the important variables involved in dispersion modeling? What does one need to know / assume?
- What are the criteria for the airborne concentration of toxics & how do they differ from PELs, TLVs, etc?

The Plume Model

Source: Crowl and Louvar, 2002

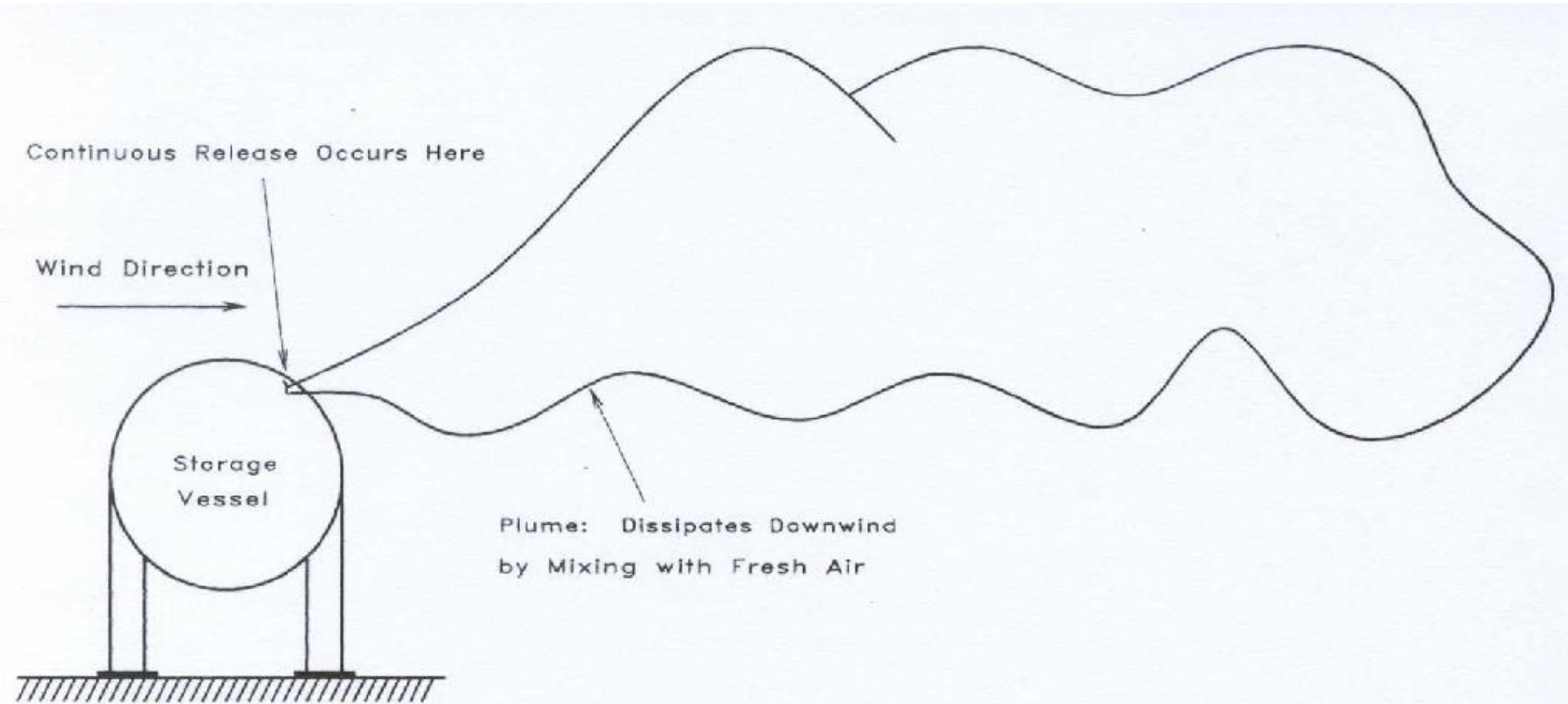


Figure 5-1 Characteristic plume formed by a continuous release of material.

Neutrally Buoyant Dispersion Models (Gaussian Models)

For a release of a gas, assuming no reaction or molecular diffusion and mixing by turbulence, the material concentration and air velocity are related by:

$$\frac{\partial C}{\partial t} + \frac{\partial}{\partial x_j} (u_j C) = 0$$

where u_j is the velocity of the air and the subscript j indicates summation over x , y & z .

After various simplifying assumptions and introducing the eddy diffusivity, K , one arrives at the fundamental equation for dispersion modeling:

$$\frac{\partial \langle C \rangle}{\partial t} + \langle u_j \rangle \frac{\partial \langle C \rangle}{\partial x_j} = \frac{\partial}{\partial x_j} \left(K_j \frac{\partial \langle C \rangle}{\partial x_j} \right)$$

Gas Dispersion: Plume, Source at H_r , u Constant

Ground concentration, $z=0$:

$$\langle C(x, y, 0) \rangle = \frac{Q_m}{\pi \sigma_y \sigma_z u} \exp \left[-\frac{1}{2} \left(\frac{y}{\sigma_y} \right)^2 - \frac{1}{2} \left(\frac{H_r}{\sigma_z} \right)^2 \right]$$

where σ_i are Pasquill Gifford dispersion coefficients dependent on distance, atmospheric stability, plume vs. puff and rural vs. urban setting

Centerline:
$$\langle C(x, 0, 0) \rangle = \frac{Q_m}{\pi \sigma_y \sigma_z u} \exp \left[-\frac{1}{2} \left(\frac{H_r}{\sigma_z} \right)^2 \right]$$

Max ground C along x :
$$\langle C(x, 0, 0) \rangle_{\max} = \frac{2Q_m}{e\pi u H_r^2} \left(\frac{\sigma_z}{\sigma_y} \right)$$

Distance downwind for C_{\max} :
$$\sigma_z = \frac{H_r}{\sqrt{2}} \longrightarrow \text{Find } x$$

Dispersion Modeling

- Key Variables / Factors
 - Quantity of release
 - Wind speed
 - Atmospheric stability – stable, neutral, unstable
 - Ground conditions – rural vs. urban .. buildings, open water, trees, ...
 - Height of release above ground
 - Momentum and buoyancy of the initial release
- Toxic Effect Criteria
 - Various criteria for short term exposures at higher than TLV-TWA values available from many sources: ERPG, TLV-STEL, TLV-C, IDLH, ..., EEGl, Toxic Endpoints

Example 5-1

On an overcast day a stack with an effective height of 60 m is releasing sulfur dioxide at the rate of 80 g/s. The wind speed is 6 m/s. The stack is located in a rural area. Determine

- The mean concentration of SO_2 on the ground 500 m downwind.
- The mean concentration on the ground 500 m downwind and 50 m crosswind.
- The location and value of the maximum mean concentration on ground level directly downwind.

Solution

- This is a continuous release. The ground concentration directly downwind is given by Equation 5-51:

$$(C)(x, 0, 0) = \frac{Q_m}{\pi \sigma_y \sigma_z u} \exp \left[-\frac{1}{2} \left(\frac{H_r}{\sigma_z} \right)^2 \right]. \quad (5-51)$$

From Table 5-1 the stability class is D.

The dispersion coefficients are obtained from either Figure 5-11 or Table 5-2. Using Table 5-2:

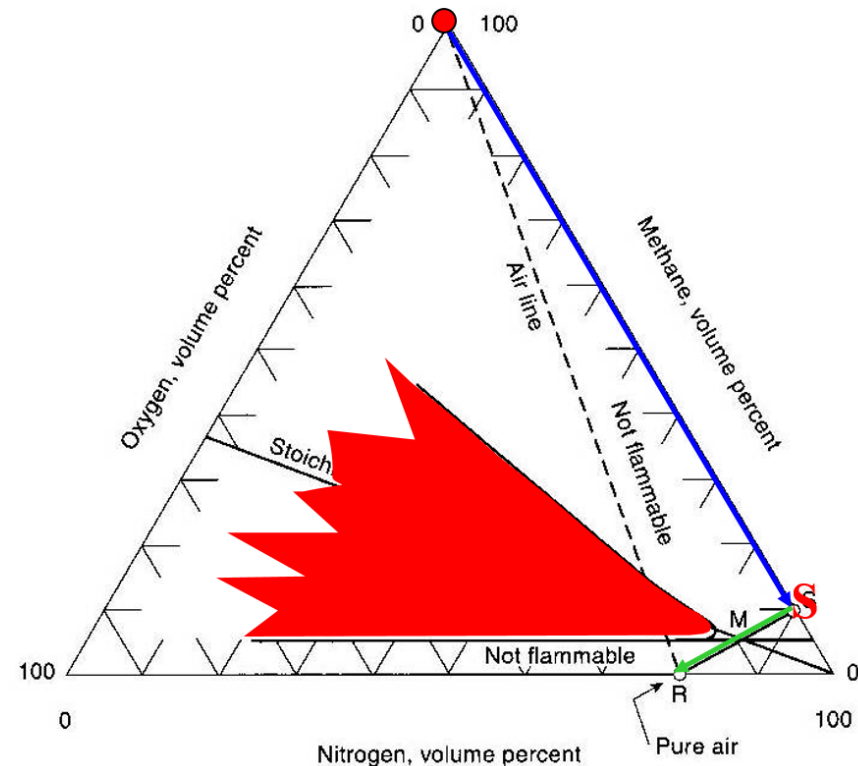
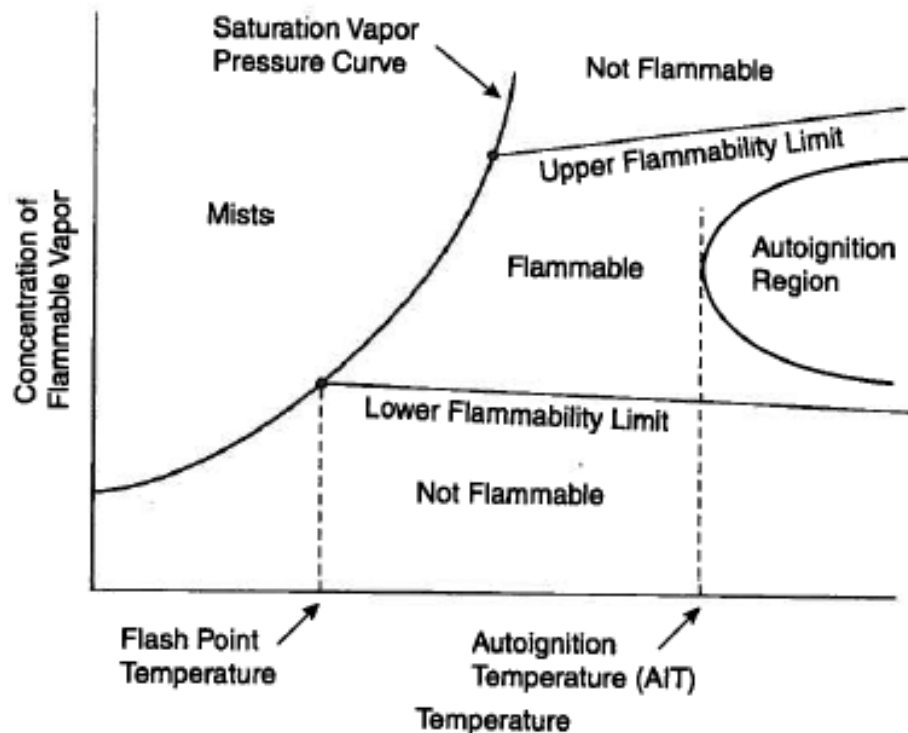
$$\begin{aligned} \sigma_y &= 0.08x(1 + 0.0001x)^{-1/2} \\ &= (0.08)(500 \text{ m})[1 + (0.0001)(500 \text{ m})]^{-1/2} = 39.0 \text{ m}, \\ \sigma_z &= 0.06x(1 + 0.0015x)^{-1/2} \\ &= (0.06)(500 \text{ m})[1 + (0.0015)(500 \text{ m})]^{-1/2} = 22.7 \text{ m}. \end{aligned}$$

Substituting into Equation 5-51, we obtain

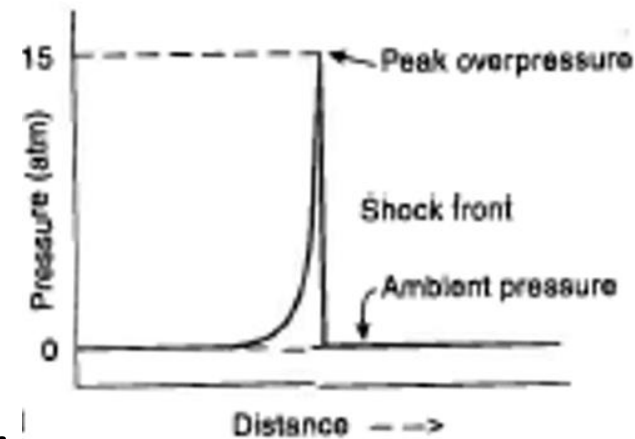
$$\begin{aligned} (C)(500 \text{ m}, 0, 0) &= \frac{80 \text{ g/s}}{(3.14)(39.0 \text{ m})(22.7 \text{ m})(6 \text{ m/s})} \exp \left[-\frac{1}{2} \left(\frac{60 \text{ m}}{22.7 \text{ m}} \right)^2 \right] \\ &= 1.45 \times 10^{-4} \text{ g/m}^3. \end{aligned}$$

Fires / Combustion

- Fire triangle: need for fuel, oxygen & ignition source
- Upper & lower flammability limits (UFL & LFL), limiting oxygen concentration (LOC) & minimum ignition energy (MIE)
- Flammability diagrams; taking vessel in / out of service



Explosions



- Deflagration vs. detonation

- Correlate in terms of deflagration index

$$\log\left(\frac{dP}{dt}\right)_{\max} = \log K_G - (1/3)\log V$$

- TNT equivalency method correlating mass of explosive, overpressure & distance

- Relation of overpressure to damage

- Vapor cloud explosions & BLEVE's (Boiling Liquid Expanding Vapor Explosion)



Buncefield, '05, UK - DDT

Metal dust explosion in Kunshan, Jiangsu, China – August 2, 2014

- 75 killed; 185 injured (44 died instantly & 31 in hospitals)
- Zhongong Metal Products Co., Ltd - General Motors parts supplier
- Combustible dust: Metal dust (Aluminum)
- Potential Ignition Sources: Spark from electrical equipment or heat released from reaction between metal and water



Screenshot from Tengxun News

2006 CSB study from 1980 – 2005 found 281 dust fires and explosions occurred in U.S. industrial facilities with 119 fatalities and 718 injuries

Damage Estimates of Common Structures – C&L, p 289

Table 6-9 Damage Estimates for Common Structures Based on Overpressure (these values are approximations)^a

Pressure		Damage
psig	kPa	
0.02	0.14	Annoying noise (137 dB if of low frequency, 10–15 Hz)
0.03	0.21	Occasional breaking of large glass windows already under strain
0.04	0.28	Loud noise (143 dB), sonic boom, glass failure
0.1	0.69	Breakage of small windows under strain
0.15	1.03	Typical pressure for glass breakage
0.3	2.07	“Safe distance” (probability 0.95 of no serious damage below this value); projectile limit; some damage to house ceilings; 10% window glass broken
0.4	2.76	Limited minor structural damage
0.5–1.0	3.4–6.9	Large and small windows usually shatter; occasional damage to window frames
0.7	4.8	Minor damage to house structures
1.0	6.9	Partial demolition of houses, made uninhabitable
1–2	6.9–13.8	Corrugated asbestos shatters; corrugated steel or aluminum panels, fastenings fail, followed by buckling; wood panels (standard housing), fastenings fail, panels blow in
1.3	9.0	Steel frame of clad building slightly distorted
2	13.8	Partial collapse of walls and roofs of houses
2–3	13.8–20.7	Concrete or cinder block walls, not reinforced, shatter
2.3	15.8	Lower limit of serious structural damage
2.5	17.2	50% destruction of brickwork of houses
3	20.7	Heavy machines (3000 lb) in industrial buildings suffer little damage; steel frame buildings distort and pull away from foundations
3–4	20.7–27.6	Frameless, self-framing steel panel buildings demolished; rupture of oil storage tanks
4	27.6	Cladding of light industrial buildings ruptures
5	34.5	Wooden utility poles snap; tall hydraulic presses (40,000 lb) in buildings slightly damaged
5–7	34.5–48.2	Nearly complete destruction of houses
7	48.2	Loaded train wagons overturned
7–8	48.2–55.1	Brick panels, 8–12 in thick, not reinforced, fail by shearing or flexure
9	62.0	Loaded train boxcars completely demolished
10	68.9	Probable total destruction of buildings; heavy machine tools (7000 lb) moved and badly damaged, very heavy machine tools (12,000 lb) survive
300	2068	Limit of crater lip

^aV. J. Clancey, “Diagnostic Features of Explosion Damage,” paper presented at the Sixth International Meeting of Forensic Sciences (Edinburgh 1972)

Hazard Identification

What systematic processes are available to identify the hazards associated with a facility or sub-unit / process?

- What-If; Checklist; What-If/Checklist
- FMEA – Failure Mode & Effects Analysis
- FTA – Fault Tree Analysis
- Hazard Surveys**
- HAZOP** – Hazards & Operability study

Dow Fire and Explosion Index

To assess degree of hazard

Material factor MF



General Process Hazard Factor



$$F_1 = \sum(\text{Penalty Factors})$$

Special Process Hazards Factor



$$F_2 = \sum(\text{Penalty Factors})$$

FIRE & EXPLOSION INDEX

AREA / COUNTRY		DIVISION		LOCATION		DATE	
SITE		MANUFACTURING UNIT		PROCESS UNIT			
PREPARED BY:		APPROVED BY: (Superintendent)		BUILDING			
REVIEWED BY: (Management)		REVIEWED BY: (Technology Center)		REVIEWED BY: (Safety & Loss Prevention)			
MATERIALS IN PROCESS UNIT							
STATE OF OPERATION				BASIC MATERIAL(S) FOR MATERIAL FACTOR			
DESIGN <input type="checkbox"/> START UP <input type="checkbox"/> NORMAL OPERATION <input type="checkbox"/> SHUTDOWN <input type="checkbox"/>							
MATERIAL FACTOR (See Table 1 or Appendix A or B) Note requirements when unit temperature over 140 °F (60 °C)							
1. General Process Hazards						Penalty Factor Range	Penalty Factor Used(1)
Base Factor						1.00	1.00
A. Exothermic Chemical Reactions						0.30 to 1.25	
B. Endothermic Processes						0.20 to 0.40	
C. Material Handling and Transfer						0.25 to 1.05	
D. Enclosed or Indoor Process Units						0.25 to 0.90	
E. Access						0.20 to 0.35	
F. Drainage and Spill Control gal or cu.m.						0.25 to 0.50	
General Process Hazards Factor (F ₁)							
2. Special Process Hazards						1.00	1.00
Base Factor						1.00	1.00
A. Toxic Material(s)						0.20 to 0.80	
B. Sub-Atmospheric Pressure (< 500 mm Hg)						0.50	
C. Operation In or Near Flammable Range <input type="checkbox"/> Inerted <input type="checkbox"/> Not Inerted							
1. Tank Farms Storage Flammable Liquids						0.50	
2. Process Upset or Purge Failure						0.30	
3. Always in Flammable Range						0.80	
D. Dust Explosion (See Table 3)						0.25 to 2.00	
E. Pressure (See Figure 2)							
Operating Pressure psig or kPa gauge							
Relief Setting psig or kPa gauge							
F. Low Temperature						0.20 to 0.30	
G. Quantity of Flammable/Unstable Material:							
Quantity lb or kg							
H _C = BTU/lb or kcal/kg							
1. Liquids or Gases in Process (See Figure 3)							
2. Liquids or Gases in Storage (See Figure 4)							
3. Combustible Solids in Storage, Dust in Process (See Figure 5)							
H. Corrosion and Erosion						0.10 to 0.75	
I. Leakage - Joints and Packing						0.10 to 1.50	
J. Use of Fired Equipment (See Figure 6)							
K. Hot Oil Heat Exchange System (See Table 5)						0.15 to 1.15	
L. Rotating Equipment						0.50	
Special Process Hazards Factor (F ₂)							
Process Unit Hazards Factor (F ₁ x F ₂) = F ₃							
Fire and Explosion Index (F ₃ x MF = F&EI)							

Penalty factors

Penalty factors

$$\text{F\&EI Value} = \text{MF} * \text{F}_1 * \text{F}_2$$

Creating a HAZOP

- Exhaustively examines the potential consequences of process upsets or failure to follow procedures
- Systematically identifies engineering and administrative safeguards and the consequences of safeguard failures
- Uses multi-disciplinary team approach
- Guide word based –e.g., no, more, less ... T, P, flow ..
- Structured and systematic
- Requires detailed information – PFD, P&IDs, equipment specs, material & energy balances, etc

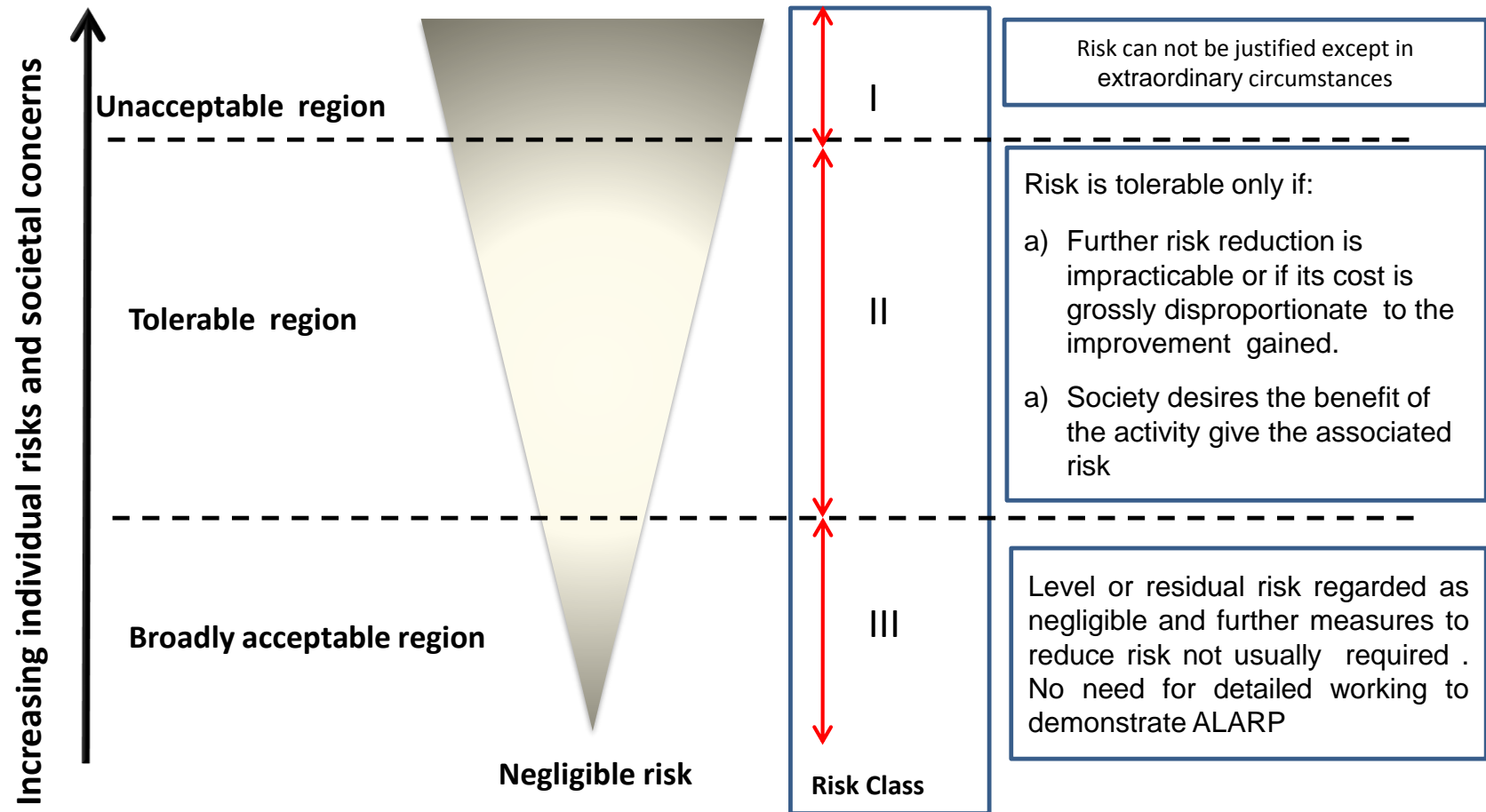
HAZOP

Hazards and Operability Review									
Project name: Example 10-2					Date: 1/1/93		Page 1 of 2		Completed:
Process: Reactor of Example 10-2								No action:	
Section: Reactor shown in Example 10-2					Reference drawing: Figure 10-3			Reply date:	
Item	Study node	Process parameters	Deviations (guide words)	Possible causes	Possible consequences	Action required	Assigned to:		
1A	Cooling coils	Flow	No	1. Control valve fails closed 2. Plugged cooling coils	1. Loss of cooling, possible runaway 2.	1. Select valve to fail open 2. Install filter with maintenance procedure Install cooling water flow meter and low flow alarm Install high temperature alarm to alert operator	DAC	1/93	
				3. Cooling water service failure	3.	3. Check and monitor reliability of water service	DAC	2/93	
				4. Controller fails and closes valve	4.	4. Place controller on critical instrumentation list	DAC	1/93	
1B			High	5. Air pressure fails, closing valve 1. Control valve fails open	5. 1. Reactor cools, reactant conc. builds, possible runaway on heating	5. See 1A.1 1. Instruct operators and update procedures	JFL	1/93	
1C			Low	2. Controller fails and opens valve 1. Partially plugged cooling line	2. 1. Diminished cooling, possible runaway	2. See 1A.4 1. See 1A.2			
				2. Partial water source failure 3. Control valve fails to respond	2. 3.	2. See 1A.2 3. Place valve on critical instrumentation list	JFL	1/93	
1D 1E 1F			As well as, part of, reverse	1. Contamination of water supply 1. Covered under 1C 1. Failure of water source resulting in backflow	1. Not possible here 1. Loss of cooling, possible runaway	1. None 1. See 1A.2			X X
1G 1H 1I			Other than, sooner than, later than	2. Backflow due to high backpressure 1. Not considered possible 1. Cooling normally started early 1. Operator error	2. 1. None 1. Temperature rise, possible runaway	2. Install check valve 1. Interlock between cooling flow and reactor feed	JFL JW	2/93 1/93	X X
1J 1K 1L		Temp.	Where else Low High	1. Not considered possible 1. Low water supply temperature 1. High water supply temperature	1. None—controller handles 1. Cooling system capacity limited, temp. increases	1. None 1. Install high flow alarm and/or cooling water high temp. alarm	JW	1/93	X X
2A	Stirrer	Agitation	No	1. Stirrer motor malfunction	1. No mixing, possible accumulation of unreacted materials	1. Interlock with feed line	JW	1/93	
				2. Power failure	2. Monomer feed continues, possible accumulation of unreacted materials	2. Monomer feed valve must fail closed on power loss	JW	2/93	
2B			More	1. Stirrer motor controller fails, resulting in high motor speed	1. None				X

Risk Assessments

- Once one has identified the hazards associated with a facility, how does one assess the frequency and consequence of various scenarios?
- Risk Assessment Methods:
 - Event Trees & Fault Trees – probabilistic risk assessment
 - **Risk Matrix Approach**
 - LOPA – Layer of Protection Analysis
 - **Quantitative Risk Assessment**

ALARP (As Low As Reasonably Practicable) Principle



Precautionary Principle – a more conservative approach used in some regions / countries

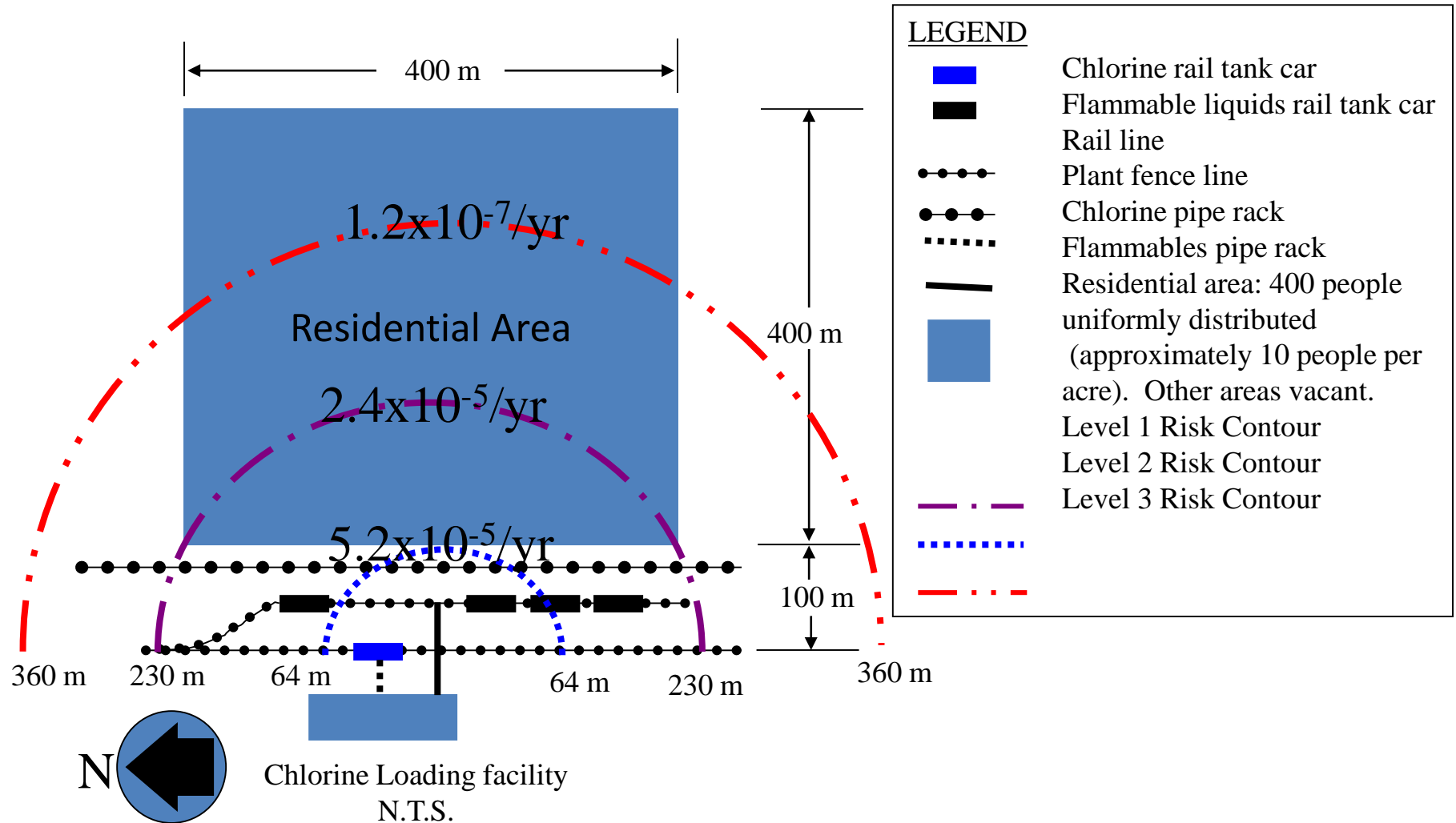
Typical 4x4 Risk Matrix

		Likelihood			
		Frequent	Possible	Rare	Remote
Severity	Major	Very High	Very High	High	Moderate
	Serious	Very High	High	Moderate	Low
	Minor	High	Moderate	Low	Low
	Incidental	Moderate	Low	Low	Low

Severity & Likelihood can be defined qualitatively or semi-quantitative in terms of degree of impact on: personnel, community, environment, facility, reputation, etc.

Quantitative Risk Assessment (QRA)

- Individual Risk Contours Around Cl₂ Loading Facility



Designs to Reduce Hazards & Risk

- Use of inerts (such as N₂ & CO₂) to reduce concentration of oxygen in combustible mixture below LOC
- Approaches using the flammability diagram
- Ventilation
- Static electricity
 - Streaming current developed by flow of liquid or solid

$$I_s = \left[\frac{10 \times 10^{-6} \text{ amp}}{(m/s)^2 (m)^2} \right] (ud)^2 \left[1 - \exp\left(-\frac{L}{u\tau}\right) \right]$$

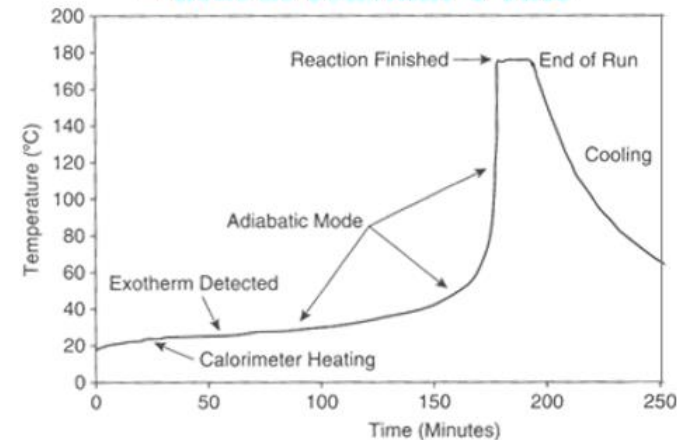
where d & L are pipe diameter & length, τ the relaxation coefficient

- Bonding, grounding & use of explosion proof equipment

Reactive Chemical Hazards

- CSB investigated 167 reactive chemical incidents from 1980 – 2001
 - 48 of these incidents resulted in 108 fatalities
- Identification of reactive chemical hazards
- Use of calorimetry to determine
 - Current conversion
 - Current self-heating rate $\frac{dx}{d\tau} = (1 - x)^n \cdot \exp\left(\frac{\Gamma B x}{1 + B x}\right)$
in terms of reaction order (n), dimensionless time (τ), adiabatic temperature rise (B), activation energy (Γ), and conversion (x)
 - Time since onset temperature
 - Maximum self-heating rate
- Controlling reactive hazards in terms of inherent safety, passive, active and procedural steps

Thermal Scan mode – heat at constant T rate

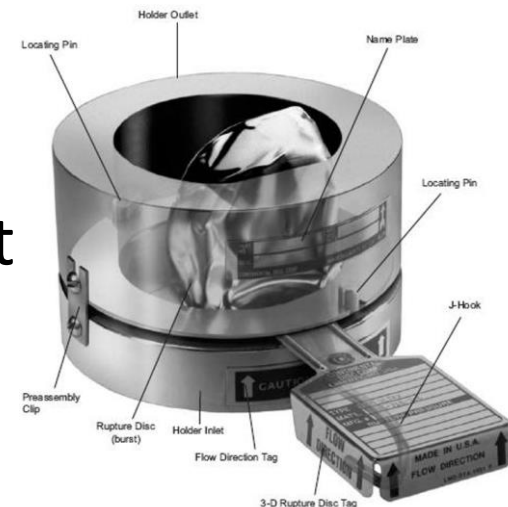
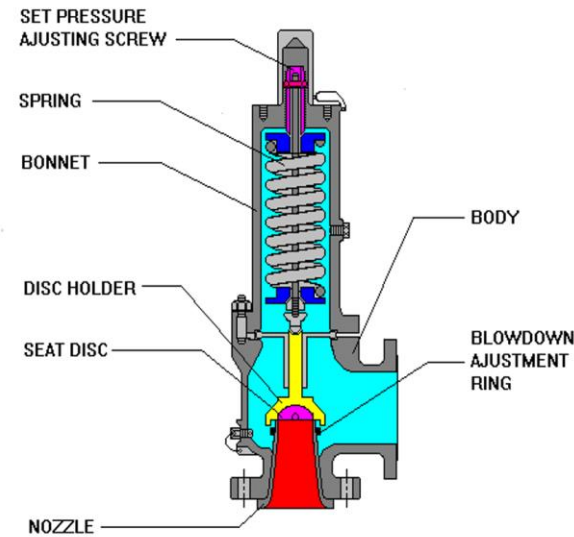


Relief System Design

- Are relief devices needed?
- Location & type of relief devices?
- Develop credible worst case relief scenarios
- Selection and sizing of relief devices: conventional spring operated or bellows, or rupture discs
- Sizing of relief valves for two phase flow, such as runaway reactions

$$G_T = 0.9 \psi \frac{\Delta H_v}{v_{fg}} \sqrt{\frac{g_c}{C_p T_s}}$$

- Building design to reduce structural impact of explosion; use of blowout panels
- Fire and thermal relief of process vessels



1b - Spring Relief Valves for Gases

In general, flow is choked with $P_{ch} > P_{ext}$

$$(Q_m)_{ch} = C_o A P \sqrt{\frac{\gamma g_c M}{R_g T} \left(\frac{2}{\gamma + 1} \right)^{(\gamma + 1)/(\gamma - 1)}} \quad \text{Eqn 4-50 p. 143}$$

Rearranging and adding compressibility factor & backpressure correction:

$$A = \frac{Q_m}{C_o \chi K_b P} \sqrt{\frac{T z}{M}}$$

z , compressibility factor
 P , max absolute discharge pressure
 K_b , backpressure correction

$$\chi = \sqrt{\frac{\gamma g_c}{R_g} \left(\frac{2}{\gamma + 1} \right)^{(\gamma + 1)/(\gamma - 1)}}$$

Two-Phase Mass Discharge

Clausius Clapyron equation:

$$\frac{dP}{dT} = \frac{\Delta H_v}{T v_{fg}}$$

$$G_T = 0.9 \psi \frac{\Delta P}{\Delta T} \sqrt{\frac{g_c T_s}{C_p}}$$

$\psi = 1$ for an orifice

$$A = m_o q / G_T \left(\sqrt{\frac{V}{m_o} \frac{\Delta H_v}{v_{fg}}} + \sqrt{C_v \Delta T} \right)^2$$

m_o = mass before release

With CC equation:

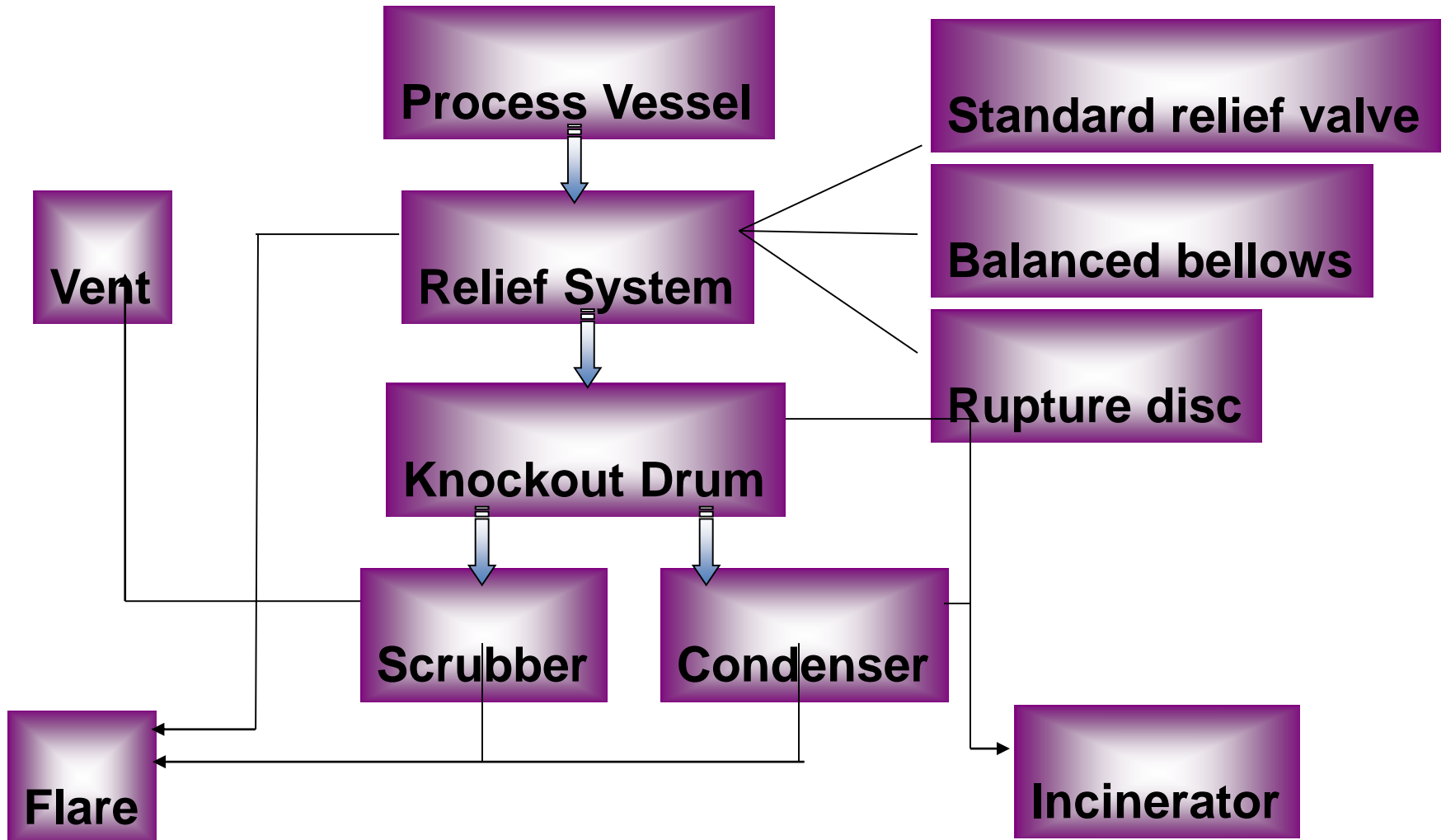
$$A = m_o q / G_T \left(\sqrt{\frac{V}{m_o} T_s \frac{dP}{dT}} + \sqrt{C_v \Delta T} \right)^2$$

Heat terms: numerator - q generated by process & denominator: removed by discharge & heat absorbed by fluid via ΔT associated with ΔP (OP)

Overpressurization of Vessels due to Plugging of Relief Line



Process and Relief System Design



Conclusion

- Scope of chemical process safety not recognized by many
- A challenging quantitative / technical discipline
- Applicable to many industries: oil & gas, chemicals, pharmaceuticals, agriculture, ...
- Growing need & demand for engineers with these skills