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

- 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 INCIDENTS CLASSIFIED BY FUEL TYPE

- Coal
- Food
- Inorganic
- Metal
- Plastic
- Wood
- Miscellaneous
US Agricultural Dust Explosions 1991 – 2005*

# Dust Explosions based on Commodity Type

- Other
- Wheat (Starch) (Gluten)
- Wheat Flour
- Rise (Bran) (Flour) (Hulls)
- Mixed Feed
- Corn Starch
- Beet Pulp
- Oats
- Barley (malted)
- Wheat
- Soybeans

# Dust Explosions based on Type of Facility

- Other
- Rice Mill
- Corn Milling, Wet
- Corn Milling, Dry
- Flour Mill
- Feed Mill
- Grain Elevator

# Fatalities based on Type of Facility

- Sugar Plant
- Feed Ingredient
- Pelleting Plant
- Grain Elevator
- Flour Mill
- Corn Processing
- Feed Mill
- Bulk Flour Storage

# Fatalities per Explosion based on Type of Facility

- Other
- Rice Mill
- Corn Milling, Wet
- Corn Milling, Dry
- Flour Mill
- Feed Mill
- Grain Elevator

*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

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

Dr. Ray A. Mentzer

Purdue University
BP Texas City, 2005; 15 fatalities

Piper Alpha, UK 1988; 167 fatalities

West, TX – 2013; 15 fatalities

Imperial Sugar, Georgia – 2008; 14 fatalities
<table>
<thead>
<tr>
<th>Why study process safety? Syllabus</th>
<th>Piper Alpha video</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chapter 1. Introduction</td>
<td></td>
</tr>
<tr>
<td>Teamwork</td>
<td></td>
</tr>
<tr>
<td>Chapter 2. Toxicology</td>
<td>Nitrogen Asphyxiation video</td>
</tr>
<tr>
<td>Chapter 3. Regulations &amp; Mgmt Systems</td>
<td>Quiz 1</td>
</tr>
<tr>
<td>Chapter 3. Industrial Hygiene</td>
<td></td>
</tr>
<tr>
<td>Chapter 4. Source Models – I, liquids</td>
<td>BP TX City video</td>
</tr>
<tr>
<td>Chapter 4. Source Models – II, gases</td>
<td>Bhopal</td>
</tr>
<tr>
<td>Exam I</td>
<td></td>
</tr>
<tr>
<td>Chapter 5. Toxic Release &amp; Dispersion Models</td>
<td>Fatal Exposure – DuPont; Project topics distr.</td>
</tr>
<tr>
<td>Chapter 6. Fires &amp; Explosions</td>
<td>Blast Waves in Danvers</td>
</tr>
<tr>
<td>Chapter 7. Designs to Prevent Fires &amp; Explosions - I</td>
<td>Static Electricity video; Quiz 2</td>
</tr>
<tr>
<td>Chapter 7. Designs to Prevent Fires &amp; Explosions – II</td>
<td>Imperial Sugar video</td>
</tr>
<tr>
<td>Chapter 8. Chemical Reactivity</td>
<td>T-2 Incident video</td>
</tr>
<tr>
<td>Exam II</td>
<td></td>
</tr>
<tr>
<td>What Does Safe Look &amp; Feel Like?</td>
<td>Deepwater Horizon video</td>
</tr>
<tr>
<td>Chapter 9. Relief Sizing</td>
<td></td>
</tr>
<tr>
<td>Chapter 10. Relief Sizing</td>
<td>Formosa Fire &amp; Explosion video</td>
</tr>
<tr>
<td>Chapter 11. Hazards Identification – I</td>
<td></td>
</tr>
<tr>
<td>Chapter 11. Hazards Identification – II</td>
<td>Quiz 3</td>
</tr>
<tr>
<td>Thanksgiving Break</td>
<td></td>
</tr>
<tr>
<td>Chapter 12. Risk Assessment</td>
<td>West explosion</td>
</tr>
<tr>
<td>Emergency Response &amp; Incident Investigation</td>
<td>Emergency Preparedness video</td>
</tr>
<tr>
<td>Exam III</td>
<td></td>
</tr>
</tbody>
</table>
1 - Safety Culture

Personnel Safety

Process Safety
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

- Lagging Indicators
  - Fatality
  - Catastrophe
  - Lost Time
- API PSI
- Other LOPC Incidents
- Near Miss - Challenges to Safety Systems
- Behaviors / Management System Execution
- Risk Control Barriers (Design and Execution)
- Personal Safety
- Process Safety
OSHA Process Safety Management Program

**14 elements**

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

Failure $\rightarrow$ Source Term $\rightarrow$ Release and Dispersion

Toxic

Immediate Ignition

Flammable

Delayed Ignition
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 \( P_g \): 
\[
t_e = \frac{1}{C_0 g} \left( \frac{A_t}{A} \right) \left[ \sqrt{2 \left( \frac{g_c P_g}{\rho} + g h_L^o \right)} - \sqrt{\frac{2 g_c P_g}{\rho}} \right]
\]

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 \( P \):
\[
t_e = \frac{1}{C_0 g} \left( \frac{A_t}{A} \right) \sqrt{2 g h_L^o}
\]

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 $\lambda = 0$ to find the $P/P_0$ for max flow:

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

**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 $P_{\text{choked}}$ 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:

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

$$
Q_{m, \text{choked}} = C_0 A P_0 \sqrt{\frac{g_c M}{R_g T_0}} \left( \frac{2}{1 + 1} \right)^{1+1}
$$
Adiabatic Choked Gas Flow, Through Pipe

External, $P < P_{choked}$

$\Delta z \sim 0; W_s = 0$ \hspace{1cm} $\Delta Q = 0$

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

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 toxics & 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)

\[ C_{ppm} = \frac{Q_m R_g T}{k Q_v PM} \times 10^6 \]

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

- Vaporization of liquid

\[ C_{ppm} = \frac{K A P_{sat}}{k Q_v P} \times 10^6 \]

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 $\sigma_i$ 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 $x$:

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

Distance downwind for $C_{\text{max}}$:

$$\sigma_z = \frac{H_r}{\sqrt{2}} \quad \text{Find } x$$
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

a. The mean concentration of SO$_2$ on the ground 500 m downwind.
b. The mean concentration on the ground 500 m downwind and 50 m crosswind.
c. The location and value of the maximum mean concentration on ground level directly downwind.

Solution

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

\[
(C)(x, 0, 0) = \frac{Q_m}{\pi \sigma_x \sigma_z} \exp \left[ -\frac{1}{2} \left( \frac{H}{\sigma_z} \right)^2 \right].
\]

(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:

\[
\sigma_y = 0.08x(1 + 0.0001x)^{-1/2}
\]

\[
= (0.08)(500 \text{ m})[1 + (0.0001)(500 \text{ m})]^{-1/2} = 39.0 \text{ m},
\]

\[
\sigma_z = 0.06x(1 + 0.0015x)^{-1/2}
\]

\[
= (0.06)(500 \text{ m})[1 + (0.0015)(500 \text{ m})]^{-1/2} = 22.7 \text{ m}.
\]

Substituting into Equation 5-51, we obtain

\[
(C)(500 \text{ m}, 0, 0) = \frac{80 \text{ g/s}}{(3.14)(39.0 \text{ m})(22.7 \text{ m})(6 \text{ m/s})} \exp \left[ -\frac{1}{2} \left( \frac{60 \text{ m}}{22.7 \text{ m}} \right)^2 \right]
\]

\[
= 1.45 \times 10^{-4} \text{ g/m}^3.
\]
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

\[ \log\left(\frac{dP}{dt}\right)_{\text{max}} = \log K_G - \frac{1}{3} \log V \]

• 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

**********
2006 CSB study from 1980 – 2005 found 281 dust fires and explosions occurred in U.S. industrial facilities with 119 fatalities and 718 injuries
**********
<table>
<thead>
<tr>
<th>Pressure (psig)</th>
<th>kPa</th>
<th>Damage</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02</td>
<td>0.14</td>
<td>Annoying noise (137 dB if of low frequency, 10–15 Hz)</td>
</tr>
<tr>
<td>0.03</td>
<td>0.21</td>
<td>Occasional breaking of large glass windows already under strain</td>
</tr>
<tr>
<td>0.04</td>
<td>0.28</td>
<td>Loud noise (143 dB), sonic boom, glass failure</td>
</tr>
<tr>
<td>0.1</td>
<td>0.69</td>
<td>Breakage of small windows under strain</td>
</tr>
<tr>
<td>0.15</td>
<td>1.03</td>
<td>Typical pressure for glass breakage</td>
</tr>
<tr>
<td>0.3</td>
<td>2.07</td>
<td>“Safe distance” (probability 0.95 of no serious damage below this value); projectile limit; some damage to house ceilings; 10% window glass broken</td>
</tr>
<tr>
<td>0.4</td>
<td>2.76</td>
<td>Limited minor structural damage</td>
</tr>
<tr>
<td>0.5–1.0</td>
<td>3.4–6.9</td>
<td>Large and small windows usually shatter; occasional damage to window frames</td>
</tr>
<tr>
<td>0.7</td>
<td>4.8</td>
<td>Minor damage to house structures</td>
</tr>
<tr>
<td>1.0</td>
<td>6.9</td>
<td>Partial demolition of houses, made uninhabitable</td>
</tr>
<tr>
<td>1–2</td>
<td>6.9–13.8</td>
<td>Corrugated asbestos shatters; corrugated steel or aluminum panels, fastenings fail, followed by buckling; wood panels (standard housing), fastenings fail, panels blow in</td>
</tr>
<tr>
<td>1.3</td>
<td>9.0</td>
<td>Steel frame of clad building slightly distorted</td>
</tr>
<tr>
<td>2</td>
<td>13.8</td>
<td>Partial collapse of walls and roofs of houses</td>
</tr>
<tr>
<td>2–3</td>
<td>13.8–20.7</td>
<td>Concrete or cinder block walls, not reinforced, shatter</td>
</tr>
<tr>
<td>2.3</td>
<td>15.8</td>
<td>Lower limit of serious structural damage</td>
</tr>
<tr>
<td>2.5</td>
<td>17.2</td>
<td>50% destruction of brickwork of houses</td>
</tr>
<tr>
<td>3</td>
<td>20.7</td>
<td>Heavy machines (3000 lb) in industrial buildings suffer little damage; steel frame buildings distort and pull away from foundations</td>
</tr>
<tr>
<td>3–4</td>
<td>20.7–27.6</td>
<td>Frameless, self-framing steel panel buildings demolished; rupture of oil storage tanks</td>
</tr>
<tr>
<td>4</td>
<td>27.6</td>
<td>Cladding of light industrial buildings ruptures</td>
</tr>
<tr>
<td>5</td>
<td>34.5</td>
<td>Wooden utility poles snap; tall hydraulic presses (40,000 lb) in buildings slightly damaged</td>
</tr>
<tr>
<td>5–7</td>
<td>34.5–48.2</td>
<td>Nearly complete destruction of houses</td>
</tr>
<tr>
<td>7</td>
<td>48.2</td>
<td>Loaded train wagons overturned</td>
</tr>
<tr>
<td>7–8</td>
<td>48.2–55.1</td>
<td>Brick panels, 8–12 in thick, not reinforced, fail by shearing or flexure</td>
</tr>
<tr>
<td>9</td>
<td>62.0</td>
<td>Loaded train boxcars completely demolished</td>
</tr>
<tr>
<td>10</td>
<td>68.9</td>
<td>Probable total destruction of buildings; heavy machine tools (7000 lb) moved and badly damaged, very heavy machine tools (12,000 lb) survive</td>
</tr>
<tr>
<td>300</td>
<td>2068</td>
<td>Limit of crater lip</td>
</tr>
</tbody>
</table>

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
To assess degree of hazard

**Dow Fire and Explosion Index**

<table>
<thead>
<tr>
<th>FIRE &amp; EXPLOSION INDEX</th>
</tr>
</thead>
<tbody>
<tr>
<td>AREA/DEPARTMENT</td>
</tr>
<tr>
<td>MANUFACTURING UNIT</td>
</tr>
<tr>
<td>LOCATION</td>
</tr>
<tr>
<td>DATE</td>
</tr>
</tbody>
</table>

**Penalty factors**

Material factor MF

**General Process Hazard Factor**

\[ F_1 = \sum \text{(Penalty Factors)} \]

**Special Process Hazards Factor**

\[ F_2 = \sum \text{(Penalty Factors)} \]

**F&EI Value**

\[ \text{F&EI Value} = MF \times F_1 \times F_2 \]
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
<table>
<thead>
<tr>
<th>Item</th>
<th>Process parameters</th>
<th>Deviations</th>
<th>Possible causes</th>
<th>Possible consequences</th>
<th>Action required</th>
<th>Assigned to</th>
</tr>
</thead>
</table>
| 1A   | Cooling cells     | Flow       | No             | 1. Control valve fails closed  
2. Plugged cooling coils | 1. Loss of cooling, possible runaway | 1. Select valve to fail open  
2. Install filter with maintenance procedures | DAC 1/63 |
|      |                   |            | 3. Cooling water service failure | 2. Install cooling water flow meter and low flow alarm | DAC 2/93 |
|      |                   |            | 4. Controller fails and closes valve | 3. Install high temperature alarm to start operator | DAC 3/93 |
|      |                   |            | 5. Air pressure falls, closing valve | 4. Check and monitor reliability of water service | DAC 4/93 |
|      |                   |            | 6. Control valve fails to open | 5. Place controller on critical instrumentation list | DAC 5/93 |
| 1B   |                   |            | High           | 1. Reactor coils, reactor conc. build, possible runaway on heating | 1. Consult operations and update procedures | JFL 1/63 |
|      |                   |            | Low            | 2. Partially plugged cooling line | 2. See 1A-1 |
|      |                   |            |                | 3. Partial water source failure | 3. See 1A-2 |
|      |                   |            |                | 4. Control valve fails to respond | 3. See 1A-3 |
| 1C   |                   |            |                | 1. Contamination of water supply | 1. Not possible here | JFL 1/63 |
| 1D   |                   |            |                | 1. Contaminates under IC | 1. Loss of cooling, possible runaway | JFL 1/63 |
| 1E   |                   |            |                | 1. Failure of water service resulting in backflow | 1. Interlock between cooling flow and reactor feed | JW 1/63 |
| 1F   |                   |            |                | 2. Backflow due to high backpressure | 1. None | JW 1/63 |
| 1G   |                   |            |                | 3. Not considered possible | 1. None | JW 1/63 |
| 1H   |                   |            |                | 4. Cooling normally started early | 1. None | JW 1/63 |
| 1I   |                   |            |                | 5. Operator error | 1. None | JW 1/63 |
| 1J   |                   |            |                | 1. Not considered possible | 1. None—controller handles | JW 1/63 |
| 1K   |                   |            |                | 1. Low water supply temperature | 1. Interlock with feed line | JW 1/63 |
| 1L   |                   |            |                | 1. High water supply temperature | 1. Interlock with feed line | JW 1/63 |
| 2A   | Silencer          | Agitation  | No             | 1. Silencer motor malfunction | 1. None | JW 1/63 |
| 2B   | Minors            | Agitation  | No             | 2. Power failure | 2. Monomer feed valve must fail closed on power loss | JW 1/63 |
|      |                   |            |                | 3. Coolant chilled the failure, resulting in high motor speed | 1. None | JW 1/63 |
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

Risk can not be justified except in extraordinary circumstances

Risk is tolerable only if:

a) Further risk reduction is impracticable or if its cost is grossly disproportionate to the improvement gained.

a) Society desires the benefit of the activity given the associated risk

Level or residual risk regarded as negligible and further measures to reduce risk not usually required. No need for detailed working to demonstrate ALARP

Precautionary Principle – a more conservative approach used in some regions / countries
### Typical 4x4 Risk Matrix

<table>
<thead>
<tr>
<th>Severity</th>
<th>Likelihood</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Frequent</td>
</tr>
<tr>
<td>Major</td>
<td>Very High</td>
</tr>
<tr>
<td>Serious</td>
<td>Very High</td>
</tr>
<tr>
<td>Minor</td>
<td>High</td>
</tr>
<tr>
<td>Incidental</td>
<td>Moderate</td>
</tr>
</tbody>
</table>

Severity & Likelihood can be defined qualitatively or semi-quantitatively in terms of degree of impact on: personnel, community, environment, facility, reputation, etc.
Quantitative Risk Assessment (QRA)
- Individual Risk Contours Around Cl\textsubscript{2} Loading Facility

**LEGEND**
- Chlorine rail tank car
- Flammable liquids rail tank car
- Rail line
- Plant fence line
- Chlorine pipe rack
- Flammables pipe rack
- Residential area: 400 people uniformly distributed (approximately 10 people per acre). Other areas vacant.
- Level 1 Risk Contour
- Level 2 Risk Contour
- Level 3 Risk Contour

Residential Area

- Level 1 Risk Contour: 1.2x10\textsuperscript{-7}/yr
- Level 2 Risk Contour: 2.4x10\textsuperscript{-5}/yr
- Level 3 Risk Contour: 5.2x10\textsuperscript{-5}/yr

Chlorine Loading facility
N.T.S.
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

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

where d & L are pipe diameter & length, \( \tau \) 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 
  - Time since onset temperature
  - Maximum 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 \( (\tau) \), adiabatic temperature rise \( (B) \), activation energy \( (\Gamma) \), and conversion \( (x) \)

- 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
  \[ G_T = 0.9 \psi \frac{\Delta H_v}{v_f g} \sqrt{\frac{g_c}{C_p T_s}} \]

- Building design to reduce structural impact of explosion; use of blowout panels
- Fire and thermal relief of process vessels
In general, flow is choked with $P_{ch} > P_{ext}$

$$(Q_m)_{ch} = C_o A P \sqrt{\frac{\gamma g_c M}{R_g T} \left(\frac{2}{\gamma + 1}\right)^{(\gamma + 1)/(\gamma - 1)}}$$

Rearranging and adding compressibility factor & backpressure correction:

$A = \frac{Q_m}{C_o \chi K_b P} \sqrt{\frac{T z}{M}}$  
$\chi = \sqrt{\frac{\gamma g_c}{R_g} \left(\frac{2}{\gamma + 1}\right)^{(\gamma + 1)/(\gamma - 1)}}$

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

Eqn 4-50  
p. 143
Two-Phase Mass Discharge

Clausius Clapyron equation:

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

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

\[ \psi = 1 \text{ for an orifice} \]

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

\[ m_o = \text{mass before release} \]

Heat terms: numerator - q generated by process & denominator: removed by discharge & heat absorbed by fluid via \( \Delta T \) associated with \( \Delta P \) (OP)
Overpressurization of Vessels due to Plugging of Relief Line
Process and Relief System Design

- Process Vessel
- Relief System
- Knockout Drum
- Scrubber
- Condenser
- Standard relief valve
- Balanced bellows
- Rupture disc
- Flare
- Incinerator
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