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CHEMICAL PROCESS SAFETY

FUNDAMENTALS WITH APPLICATIONS

THIRD EDITION

DANIEL A. CROWL • JOSEPH F. LOUVAR

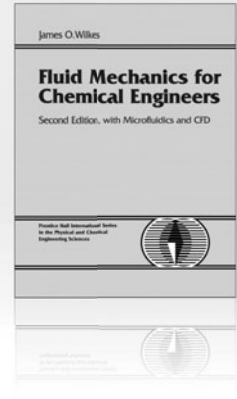
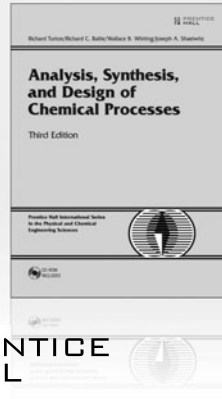
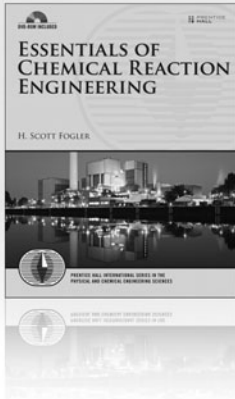


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Chemical Process Safety

Third Edition

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Daniel A. Crowl

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Preface

The third edition of *Chemical Process Safety* is designed to enhance the process of teaching and applying the fundamentals of chemical process safety. It is appropriate for an industrial reference, a senior-level undergraduate course, or a graduate course in chemical process safety. It can be used by anyone interested in improving chemical process safety, including chemical and mechanical engineers and chemists. More material is presented than can be accommodated in a three-credit course, providing instructors with the opportunity to emphasize their topics of interest.

The primary objective of this textbook is to present the important technical fundamentals of chemical process safety. The emphasis on the fundamentals will help the student and practicing scientist to *understand* the concepts and apply them accordingly. This application requires a significant quantity of fundamental knowledge and technology.

The third edition has been rewritten to include new process safety technology, new references, and updated data that have appeared since the first edition was published in 1990 and the second edition in 2002. It also includes our combined experiences of teaching process safety in both industry and academia during the past 20 years.

The third edition contains two new chapters. Chapter 8, “Chemical Reactivity,” was added due to the recommendations from the US Chemical Safety Board (CSB) as a result of the T2 Laboratories accident investigation. Chapter 13, “Safety Procedures and Designs,” was added to consolidate some material that was scattered throughout the previous editions and to present a more complete and detailed discussion. We removed the chapter on accident investigations that appeared in the first and second editions; much of the content was moved to Chapter 13.

We continue to believe that a textbook on safety is possible only with both industrial and academic inputs. The industrial input ensures that the material is industrially relevant. The academic input ensures that the material is presented on a fundamental basis to help professors and students understand the concepts. Although the authors are (now) both from universities,

one has over 30 years of relevant experience in industry (J.F.L.), and the other (D.A.C.) has accumulated significant industrial and government consulting experience since the writing of the first edition.

Since the first edition was published, many universities have developed courses or course content in chemical process safety. This new emphasis on process safety is the result of the positive influences from industry and the Accreditation Board for Engineering and Technology (ABET). Based on faculty feedback, this textbook is an excellent application of the fundamental topics that are taught in the first three years of undergraduate education.

Although professors normally have little background in chemical process safety, they have found that the concepts in this text and the accompanying problems and solutions are easy to learn and teach. Professors have also found that industrial employees are enthusiastic and willing to give specific lectures on safety to enhance their courses.

This textbook is designed for a dedicated course in chemical process safety. However, we continue to believe that chemical process safety should be part of every undergraduate and graduate course in chemistry and chemical and mechanical engineering, just as it is a part of all the industrial experiences. This text is an excellent reference for these courses. This textbook can also be used as a reference for a design course.

Some will remark that our presentation is not complete or that some details are missing. The purpose of this book, however, is not to be complete but to provide a starting point for those who wish to learn about this important area. This book, for example, has a companion text titled *Health and Environmental Risk Analysis* that extends the topics relevant to risk analysis.

We are indebted to our many friends who helped us learn the fundamentals of chemical process safety and its application. Several of these friends have passed on—including G. Boicourt, J. Wehman, and W. Howard. We especially wish to thank S. Gossel, industrial consultant; B. Powers, retired from Dow Chemical Company; D. Hendershot, retired from Rohm and Haas; R. Welker, retired from the University of Arkansas; R. Willey of Northeastern University; R. Darby, retired from Texas A&M University; and Tom Spicer of the University of Arkansas. R. Willey of Northeastern University and V. Wilding of BYU provided very useful reviews of the entire manuscript. Several reviewers provided helpful comments on Chapter 8, “Chemical Reactivity,” including S. Horsch, H. Johnstone, and C. Mashuga of Dow Chemical Company; R. Johnson of Unwin Corporation; J. Keith of Michigan Technological University; and A. Theis of Fauske and Associates.

We also acknowledge and thank all the members of the Safety and Chemical Engineering Education (SACHE) Committee of the Center for Chemical Process Safety and the Safety and Loss Prevention Committee of the American Institute of Chemical Engineers. We are honored to be members of both committees. The members of these committees are the experts in safety; their enthusiasm and knowledge have been truly educational and a key inspiration to the development of this text.

Finally, we continue to acknowledge our families, who provided patience, understanding, and encouragement throughout the writing of these three editions.

We hope that this textbook helps prevent chemical plant and university accidents and contributes to a much safer future.

Daniel A. Crowl and Joseph F. Louvar

About the Authors

Daniel A. Crowl is the Herbert H. Dow Professor for Chemical Process Safety at Michigan Technological University. Professor Crowl received his B.S. in fuel science from Pennsylvania State University and his M.S. and Ph.D. in chemical engineering from the University of Illinois.

He is coauthor of the textbook *Chemical Process Safety: Fundamentals with Applications*, First and Second Editions, published by Prentice Hall. He is also author/editor of several AIChE books on process safety and editor of the safety section in the eighth edition of *Perry's Chemical Engineer's Handbook*.

Professor Crowl has won numerous awards, including the Bill Doyle award from AIChE, the Chemical Health and Safety Award from ACS, the Walton/Miller award from the Safety and Health Division of AIChE, and the Gary Leach Award from the AIChE Board.

Professor Crowl is a Fellow of AIChE, ACS Safety and Health Division, and CCPS.

Joseph F. Louvar has a B.S., M.S., and Ph.D. in chemical engineering. He is currently a professor at Wayne State University after having retired from the BASF Corporation. While working at the BASF Corporation, he was a director of BASF's chemical engineering department; his responsibilities included the production of specialty chemicals, and he managed the implementation and maintenance of five processes that handled highly hazardous chemicals that were covered by Process Safety Management. As a professor at Wayne State University, he teaches chemical process safety, risk assessment, and process design.

Professor Louvar is the author of many safety-related publications and the coauthor of two books, *Chemical Process Safety: Fundamentals with Applications*, First and Second Editions, and *Health and Environmental Risk Analysis: Fundamentals with Applications*. Both books are published by Prentice Hall. Professor Louvar has been the chair of the Loss Prevention Committee and the Safety and Health Division. He is the CCPS staff consultant for the Undergraduate Education Committee, commonly known as the Safety and Chemical Engineering Education Committee (SACHE), and he is the coeditor of AIChE's journal for process safety, *Process Safety Progress*.

On the Cover

The picture on the front cover shows the consequences of a waste receiver vessel explosion at the Bayer Cropscience plant in Institute, West Virginia on August 28, 2008. Due to start-up difficulties, a large amount of unreacted chemical accumulated in the receiver vessel. A runaway reaction occurred resulting in the explosion. See the complete investigation report at www.csb.gov. (Photo courtesy of the US Chemical Safety and Hazard Investigation Board.)

Nomenclature

a	velocity of sound (length/time)
A	area (length ²) or Helmholtz free energy (energy/mole); or process component availability; or arrhenius reaction rate pre-exponential constant (time ⁻¹)
A_t	tank cross sectional area (length ²)
ΔA	change in Helmholtz free energy (energy/mole)
B	adiabatic reactor temperature increase (dimensionless)
C	mass concentration (mass/volume) or capacitance (Farads)
C_0	discharge coefficient (unitless), or concentration at the source (mass/volume)
C_1	concentration at a specified time (mass/volume)
C_m	concentration of dense gas (volume fraction)
C_p	heat capacity at constant pressure (energy/mass deg)
C_{ppm}	concentration in parts per million by volume
C_v	heat capacity at constant volume (energy/mass deg)
C_{vent}	deflagration vent constant (pressure ^{1/2})
C_x	concentration at location x downwind from the source (mass/volume)
$\langle C \rangle$	average or mean mass concentration (mass/volume)
d	diameter (length)
d_p	particle diameter (length)
d_f	diameter of flare stack (length)
D	diffusion coefficient (area/time)
D_c	characteristic source dimension for continuous releases of dense gases (length)
D_i	characteristic source dimension for instantaneous releases of dense gas (length)
D_0	reference diffusion coefficient (area/time)

D_m	molecular diffusivity (area/time)
D_{tid}	total integrated dose due to a passing puff of vapor (mass time/volume)
E_a	activation energy (energy/mole)
ERPG	emergency response planning guideline (see Table 5-6)
EEGL	emergency exposure guidance levels (see Section 5.5)
f	Fanning friction factor (unitless) or frequency (1/time)
$f(t)$	failure density function
f_v	mass fraction of vapor (unitless)
F	frictional fluid flow loss term (energy mass) or force or environment factor
FAR	fatal accident rate (fatalities/10 ⁸ hours)
FEV	forced expired volume (liters/sec)
FVC	forced vital capacity (liters)
g	gravitational acceleration (length/time ²)
g_c	gravitational constant (mass length/force time ²)
g_o	initial cloud buoyancy factor (length/time ²)
g_x	buoyancy factor at location x (length/time ²)
G	Gibbs free energy (energy/mole) or mass flux (mass/area time)
G_T	mass flux during relief (mass/area time)
ΔG	change in Gibbs free energy (energy/mole)
h	specific enthalpy (energy/mass)
h_L	fluid level above leak in tank (length)
h_L^0	initial fluid level above leak in tank (length)
h_s	leak height above ground level (length)
H	enthalpy (energy/mole) or height (length)
H_f	flare height (length)
H_r	effective release height in plume model (length)
ΔH	change in enthalpy (energy/mole)
ΔH_c	heat of combustion (energy/mass)
ΔH_r	release height correction given by Equation 5-65
ΔH_v	enthalpy of vaporization (energy/mass)
I	sound intensity (decibels)
ID	pipe internal diameter (length)
IDLH	immediately dangerous to life and health (see Section 5.5)
I_0	reference sound intensity (decibels)
I_s	streaming current (amps)
ISOC	in-service oxygen concentration (volume percent oxygen)
j	number of inerting purge cycles (unitless)
J	electrical work (energy)
k	non-ideal mixing factor for ventilation (unitless), or reaction rate (concentration ^{1-m} /time)
k_1, k_2	constants in probit equations
k_s	thermal conductivity of soil (energy/length time deg)
K	mass transfer coefficient (length/time)
K_b	backpressure correction for relief sizing (unitless)
K_f	excess head loss for fluid flow (dimensionless)

K_i, K_{∞}	constants in excess head loss, given by Equation 4-38
K_G	explosion constant for vapors (length pressure/time)
K_j	eddy diffusivity in x, y or z direction (area/time)
K_P	overpressure correction for relief sizing (unitless)
K_{St}	explosion constant for dusts (length pressure/time)
K_V	viscosity correction for relief sizing (unitless)
K_0	reference mass transfer coefficient (length/time)
K^*	constant eddy diffusivity (area/time)
L	length
LEL	lower explosion limit (volume %)
$LFL = LEL$	lower flammability limit (volume %)
LOC	limiting oxygen concentration (volume percent oxygen)
LOL	lower flammable limit in pure oxygen (volume %)
m	mass
m_f	mass fraction
m_0	total mass contained in reactor vessel (mass)
m_{LR}	mass of limiting reactant in Equation (8-34) (mass)
m_T	total mass of reacting mixture in Equation (8-34) (mass)
m_{TNT}	mass of TNT
m_v	mass of vapor
M	molecular weight (mass/mole)
M_0	reference molecular weight (mass/mole)
Ma	Mach number (unitless)
MOC, MSOC	Minimum oxygen concentration or maximum safe oxygen concentration. See LOC
MTBC	mean time between coincidence (time)
MTBF	mean time between failure (time)
n	number of moles or, reaction order
OSFC	out of service fuel concentration (volume percent fuel)
p	partial pressure (force/area)
p_d	number of dangerous process episodes
p_s	scaled overpressure for explosions (unitless)
P	total pressure or probability
P_b	backpressure for relief sizing (psig)
PEL	permissible exposure level (see Section 2.8)
PFD	probability of failure on demand
P_g	gauge pressure (force/area)
P_{max}	maximum pressure for relief sizing (psig)
P_s	set pressure for relief sizing (psig)
P^{sat}	saturation vapor pressure
q	heat (energy/mass) or heat intensity (energy/area time)
q_f	heat intensity of flare (energy/time area)
q_g	heat flux from ground (energy/area time)
q_s	specific energy release rate at set pressure during reactor relief (energy/mass)
Q	heat (energy) or electrical charge (coulombs)

Q_m	mass discharge rate (mass/time)
Q_m^*	instantaneous mass release (mass)
Q_v	ventilation rate (volume/time)
r	radius (length)
R	electrical resistance (ohms) or reliability
\bar{R}	Sachs scaled distance, defined by Equation 6-29 (unitless)
R_d	release duration for heavy gas releases (time)
RHI	reaction hazard index defined by Equation 14-1
r_f	vessel filling rate (time ⁻¹)
R_g	ideal gas constant (pressure volume/mole deg)
Re	Reynolds number (unitless)
S	entropy (energy/mole deg) or stress (force/area)
S_m	material strength (force/area)
SP EGL	short term public exposure guideline (see Section 5.5)
t	time
t_d	positive phase duration of a blast (time)
t_e	emptying time
t_p	time to form a puff of vapor
t_v	vessel wall thickness (length)
t_w	worker shift time
Δt_v	venting time for reactor relief
T	temperature (deg)
T_d	material decomposition temperature (deg)
T_i	time interval
TLV	threshold limit value (ppm or mg/m ³ by volume)
T_m	maximum temperature during reactor relief (deg)
T_s	saturation temperature at set pressure during reactor relief (deg)
TWA	time weighted average (ppm or mg/m ³ by volume)
TXD	toxic dispersion method (see Section 5.5)
u	velocity (length/time)
u_d	dropout velocity of a particle (length/time)
\bar{u}	average velocity (length/time)
$\langle u \rangle$	mean or average velocity (length/time)
U	internal energy (energy/mole) or overall heat transfer coefficient (energy/area deg time) or process component unavailability
UEL	upper explosion limit (volume %)
$UFL = UEL$	upper flammability limit (volume %)
UOL	upper flammable limit in pure oxygen (volume %)
v	specific volume (volume/mass)
v_f	specific volume of liquid (volume/mass)
v_g	specific volume of vapor (volume/mass)
v_{fg}	specific volume change with liquid vaporization (volume/mass)
V	total volume or electrical potential (volts)
V_c	container volume
W	width (length)

W_e	expansion work (energy)
W_s	shaft work (energy)
x	mole fraction or Cartesian coordinate (length), or reactor conversion (dimensionless), or distance from the source (length)
x_t	is the distance from the source to the transition (length),
x_v	is the virtual distance (length), and
x_{nb}	is the distance used in the neutrally buoyant model to compute the concentration downwind of the transition. (length)
X_f	distance from flare at grade (length)
y	mole fraction of vapor (unitless) or Cartesian coordinate (length)
Y	probit variable (unitless)
Y_G	gas expansion factor (unitless)
z	height above datum (length) or Cartesian coordinate (length) or compressibility (unitless)
z_e	scaled distance for explosions (length/mass ^{1/3})

Greek Letters

α	velocity correction factor (unitless) or thermal diffusivity (area/time)
β	thermal expansion coefficient (deg ⁻¹)
δ	double layer thickness (length)
ε	pipe roughness (length) or emissivity (unitless)
ε_r	relative dielectric constant (unitless)
ε_0	permittivity constant for free space (charge ² /force length ²)
η	explosion efficiency (unitless)
Φ	nonideal filling factor (unitless), or phi-factor for calorimeter thermal inertia (dimensionless)
γ	heat capacity ratio (unitless)
γ_c	conductivity (mho/cm)
Γ	dimensionless activation energy
χ	function defined by Equation 9-10
λ	frequency of dangerous episodes
λ_d	average frequency of dangerous episodes
μ	viscosity (mass/length/time) or mean value or failure rate (faults/time)
μ_v	vapor viscosity (mass/length/time)
Ψ	overall discharge coefficient used in Equation 10-15 (unitless)
ρ	density (mass/volume)
ρ_L	liquid density (mass/volume)
ρ_{ref}	reference density for specific gravity (mass/volume)
ρ_v	vapor density (mass/volume)
ρ_x	density at distance x downwind from source (mass/volume)
σ	standard deviation (unitless)
$\sigma_x, \sigma_y, \sigma_z$	dispersion coefficient (length)
τ	relaxation time, or dimensionless reaction time
τ_i	inspection period for unrevealed failures

τ_0	operation period for a process component
τ_r	period required to repair a component
τ_u	period of unavailability for unrevealed failures
ζ	zeta potential (volts)

Subscripts

a	ambient
ad	adiabatic
c	combustion
f	formation or liquid
g	vapor or gas
H	higher pressure
i	initiating event
j	purges
L	lower pressure
m	maximum
s	set pressure
o	initial or reference

Superscripts

$^{\circ}$	standard
$'$	stochastic or random variable

Introduction

In 1987, Robert M. Solow, an economist at the Massachusetts Institute of Technology, received the Nobel Prize in economics for his work in determining the sources of economic growth. Professor Solow concluded that the bulk of an economy's growth is the result of technological advances.

It is reasonable to conclude that the growth of an industry is also dependent on technological advances. This is especially true in the chemical industry, which is entering an era of more complex processes: higher pressure, more reactive chemicals, and exotic chemistry.

More complex processes require more complex safety technology. Many industrialists even believe that the development and application of safety technology is actually a constraint on the growth of the chemical industry.

As chemical process technology becomes more complex, chemical engineers will need a more detailed and fundamental understanding of safety. H. H. Fawcett said, "To know is to survive and to ignore fundamentals is to court disaster."¹ This book sets out the fundamentals of chemical process safety.

Since 1950, significant technological advances have been made in chemical process safety. Today, safety is equal in importance to production and has developed into a scientific discipline that includes many highly technical and complex theories and practices. Examples of the technology of safety include

- Hydrodynamic models representing two-phase flow through a vessel relief
- Dispersion models representing the spread of toxic vapor through a plant after a release, and

¹H. H. Fawcett and W. S. Wood, *Safety and Accident Prevention in Chemical Operations*, 2nd ed. (New York: Wiley, 1982), p. 1.

- Mathematical techniques to determine the various ways that processes can fail and the probability of failure

Recent advances in chemical plant safety emphasize the use of appropriate technological tools to provide information for making safety decisions with respect to plant design and operation.

The word “safety” used to mean the older strategy of accident prevention through the use of hard hats, safety shoes, and a variety of rules and regulations. The main emphasis was on worker safety. Much more recently, “safety” has been replaced by “loss prevention.” This term includes hazard identification, technical evaluation, and the design of new engineering features to prevent loss. The subject of this text is loss prevention, but for convenience, the words “safety” and “loss prevention” will be used synonymously throughout.

Safety, hazard, and risk are frequently used terms in chemical process safety. Their definitions are

- *Safety or loss prevention*: the prevention of accidents through the use of appropriate technologies to identify the hazards of a chemical plant and eliminate them before an accident occurs.
- *Hazard*: a chemical or physical condition that has the potential to cause damage to people, property, or the environment.
- *Risk*: a measure of human injury, environmental damage, or economic loss in terms of both the incident likelihood and the magnitude of the loss or injury.

Chemical plants contain a large variety of hazards. First, there are the usual mechanical hazards that cause worker injuries from tripping, falling, or moving equipment. Second, there are chemical hazards. These include fire and explosion hazards, reactivity hazards, and toxic hazards.

As will be shown later, chemical plants are the safest of all manufacturing facilities. However, the potential always exists for an accident of catastrophic proportions. Despite substantial safety programs by the chemical industry, headlines of the type shown in Figure 1-1 continue to appear in the newspapers.

1-1 Safety Programs

A successful safety program requires several ingredients, as shown in Figure 1-2. These ingredients are

- System
- Attitude
- Fundamentals
- Experience
- Time
- You



Figure 1-1 Headlines are indicative of the public's concern over chemical safety.

First, the program needs a system (1) to record what needs to be done to have an outstanding safety program, (2) to do what needs to be done, and (3) to record that the required tasks are done. Second, the participants must have a positive attitude. This includes the willingness to do some of the thankless work that is required for success. Third, the participants must understand and use the fundamentals of chemical process safety in the design, construction, and operation of their plants. Fourth, everyone must learn from the experience of history or be doomed to repeat it. It is especially recommended that employees (1) read and understand

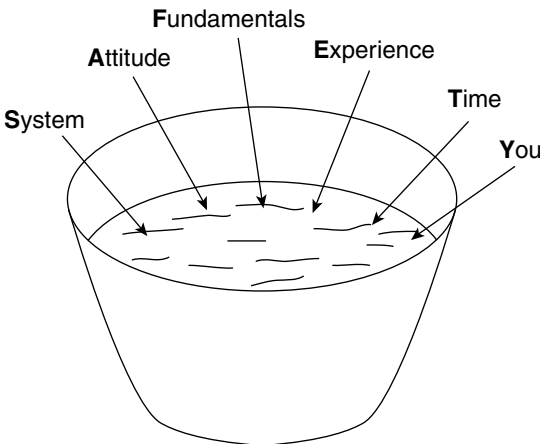


Figure 1-2 The ingredients of a successful safety program.

case histories of past accidents and (2) ask people in their own and other organizations for their experience and advice. Fifth, everyone should recognize that safety takes time. This includes time to study, time to do the work, time to record results (for history), time to share experiences, and time to train or be trained. Sixth, everyone (you) should take the responsibility to contribute to the safety program. A safety program must have the commitment from all levels within the organization. Safety must be given importance equal to production.

The most effective means of implementing a safety program is to make it everyone's responsibility in a chemical process plant. The older concept of identifying a few employees to be responsible for safety is inadequate by today's standards. All employees have the responsibility to be knowledgeable about safety and to practice safety.

It is important to recognize the distinction between a good and an outstanding safety program.

- A *good* safety program identifies and eliminates existing safety hazards.
- An *outstanding* safety program has management systems that prevent the existence of safety hazards.

A good safety program eliminates the existing hazards as they are identified, whereas an outstanding safety program prevents the existence of a hazard in the first place.

The commonly used management systems directed toward eliminating the existence of hazards include safety reviews, safety audits, hazard identification techniques, checklists, and proper application of technical knowledge.

1-2 Engineering Ethics

Most engineers are employed by private companies that provide wages and benefits for their services. The company earns profits for its shareholders, and engineers must provide a service to the company by maintaining and improving these profits. Engineers are responsible for minimizing losses and providing a safe and secure environment for the company's employees. Engineers have a responsibility to themselves, fellow workers, family, community, and the engineering profession. Part of this responsibility is described in the Engineering Ethics statement developed by the American Institute of Chemical Engineers (AIChE), shown in Table 1-1.

1-3 Accident and Loss Statistics

Accident and loss statistics are important measures of the effectiveness of safety programs. These statistics are valuable for determining whether a process is safe or whether a safety procedure is working effectively.

Many statistical methods are available to characterize accident and loss performance. These statistics must be used carefully. Like most statistics they are only averages and do not reflect the potential for single episodes involving substantial losses. Unfortunately, no single method is capable of measuring all required aspects. The three systems considered here are

Table 1-1 American Institute of Chemical Engineers Code of Professional Ethics

Fundamental principles
Engineers shall uphold and advance the integrity, honor, and dignity of the engineering profession by
1. using their knowledge and skill for the enhancement of human welfare;
2. being honest and impartial and serving with fidelity the public, their employers, and clients;
3. striving to increase the competence and prestige of the engineering profession.
Fundamental canons
1. Engineers shall hold paramount the safety, health, and welfare of the public in the performance of their professional duties.
2. Engineers shall perform services only in areas of their competence.
3. Engineers shall issue public statements only in an objective and truthful manner.
4. Engineers shall act in professional matters for each employer or client as faithful agents or trustees, and shall avoid conflicts of interest.
5. Engineers shall build their professional reputations on the merits of their services.
6. Engineers shall act in such a manner as to uphold and enhance the honor, integrity, and dignity of the engineering profession.
7. Engineers shall continue their professional development throughout their careers and shall provide opportunities for the professional development of those engineers under their supervision.

- OSHA incidence rate,
- Fatal accident rate (FAR), and
- Fatality rate, or deaths per person per year

All three methods report the number of accidents and/or fatalities for a fixed number of workers during a specified period.

OSHA stands for the Occupational Safety and Health Administration of the United States government. OSHA is responsible for ensuring that workers are provided with a safe working environment. Table 1-2 contains several OSHA definitions applicable to accident statistics.

The OSHA incidence rate is based on cases per 100 worker years. A worker year is assumed to contain 2000 hours (50 work weeks/year × 40 hours/week). The OSHA incidence rate is therefore based on 200,000 hours of worker exposure to a hazard. The OSHA incidence rate is calculated from the number of occupational injuries and illnesses and the total number of employee hours worked during the applicable period. The following equation is used:

$$\text{OSHA incidence rate (based on injuries and illness)} = \frac{\text{Number of injuries and illnesses} \times 200,000}{\text{Total hours worked by all employees during period covered.}} \quad (1-1)$$

Table 1-2 Glossary of Terms Used by OSHA and Industry to Represent Work-Related Losses^{a,b}

Term	Definition
First aid	Any one-time treatment and any follow-up visits for the purpose of observation of minor scratches, cuts, burns, splinters, and so forth that do not ordinarily require medical care. Such one-time treatment and follow-up visits for the purpose of observation are considered first aid even though provided by a physician or registered professional personnel.
Incident rate	Number of occupational injuries and/or illnesses or lost workdays per 100 full-time employees.
Lost workdays	Number of days (consecutive or not) after but not including the day of injury or illness during which the employee would have worked but could not do so, that is, during which the employee could not perform all or any part of his or her normal assignment during all or any part of the workday or shift because of the occupational injury or illness.
Medical treatment	Treatment administered by a physician or by registered professional personnel under the standing orders of a physician. Medical treatment does not include first aid treatment even though provided by a physician or registered professional personnel.
Occupational injury	Any injury such as a cut, sprain, or burn that results from a work accident or from a single instantaneous exposure in the work environment.
Occupational illness	Any abnormal condition or disorder, other than one resulting from an occupational injury, caused by exposure to environmental factors associated with employment. It includes acute and chronic illnesses or diseases that may be caused by inhalation, absorption, ingestion, or direct contact.
Recordable cases	Cases involving an occupational injury or occupational illness, including deaths.
Recordable fatality cases	Injuries that result in death, regardless of the time between the injury and death or the length of the illness.
Recordable nonfatal cases without lost workdays	Cases of occupational injury or illness that do not involve fatalities or lost workdays but do result in (1) transfer to another job or termination of employment or (2) medical treatment other than first aid or (3) diagnosis of occupational illness or (4) loss of consciousness or (5) restriction of work or motion.
Recordable lost workday cases due to restricted duty	Injuries that result in the injured person not being able to perform their regular duties but being able to perform duties consistent with their normal work.
Recordable cases with days away from work	Injuries that result in the injured person not being able to return to work on their next regular workday.
Recordable medical cases	Injuries that require treatment that must be administered by a physician or under the standing orders of a physician. The injured person is able to return to work and perform his or her regular duties. Medical injuries include cuts requiring stitches, second-degree burns (burns with blisters), broken bones, injury requiring prescription medication, and injury with loss of consciousness.

^a*Injury Facts*, 1999 ed. (Chicago: National Safety Council, 1999), p. 151.

^bOSHA regulations, 29 CFR 1904.12.

An incidence rate can also be based on lost workdays instead of injuries and illnesses. For this case

$$\text{OSHA incidence rate (based on lost workdays)} = \frac{\text{Number of lost workdays} \times 200,000}{\text{Total hours worked by all employees during period covered.}} \quad (1-2)$$

The definition of a lost workday is given in Table 1-2.

The OSHA incidence rate provides information on all types of work-related injuries and illnesses, including fatalities. This provides a better representation of worker accidents than systems based on fatalities alone. For instance, a plant might experience many small accidents with resulting injuries but no fatalities. On the other hand, fatality data cannot be extracted from the OSHA incidence rate without additional information.

The FAR is used mostly by the British chemical industry. This statistic is used here because there are some useful and interesting FAR data available in the open literature. The FAR reports the number of fatalities based on 1000 employees working their entire lifetime. The employees are assumed to work a total of 50 years. Thus the FAR is based on 10^8 working hours. The resulting equation is

$$\text{FAR} = \frac{\text{Number of fatalities} \times 10^8}{\text{Total hours worked by all employees during period covered.}} \quad (1-3)$$

The last method considered is the fatality rate or deaths per person per year. This system is independent of the number of hours actually worked and reports only the number of fatalities expected per person per year. This approach is useful for performing calculations on the general population, where the number of exposed hours is poorly defined. The applicable equation is

$$\text{Fatality rate} = \frac{\text{Number of fatalities per year}}{\text{Total number of people in applicable population.}} \quad (1-4)$$

Both the OSHA incidence rate and the FAR depend on the number of exposed hours. An employee working a ten-hour shift is at greater total risk than one working an eight-hour shift. A FAR can be converted to a fatality rate (or vice versa) if the number of exposed hours is known. The OSHA incidence rate cannot be readily converted to a FAR or fatality rate because it contains both injury and fatality information.

Table 1-3 Accident Statistics for Selected Industries

Industrial activity	OSHA incident rates (U.S.)					
	Recordable ^a	Days away from work ^a	Fatality ^{b, 2}		FAR (U.K.) ^c	
	2007	2007	2000	2005	1974–78	1987–90
Agriculture ¹	6.1	3.2	24.1	27	7.4	3.7
Chemical and allied products	3.3	1.9	2.5	2.8	2.4	1.2
Coal mining	4.7	3.2	50	26.8	14.5	7.3
Construction	5.4	2.8	10	11.1	10	5.0
Vehicle manufacturing	9.3	5.0	1.3	1.7	1.2	0.6
All manufacturing	5.6	3.0	3.3	2.4	2.3	1.2

^a*Injury Facts* (Chicago: National Safety Council, 2009), p. 62.

^bFatal occupational injuries, total hours worked, and rates of fatal occupational injuries, 2000, www.bls.gov/iif/oshwc/foi/cfoi_rates_2000.pdf.

S. Mannan, ed., *Lees' Loss Prevention in the Process Industries*, 3rd ed., Vol. 1 (London: Butterworth Heinemann), p. 2/12.

¹Crop and animal products.

²Fatalities per 100,000 employed.

Example 1-1

A process has a reported FAR of 2. If an employee works a standard 8-hr shift 300 days per year, compute the deaths per person per year.

Solution

$$\begin{aligned} \text{Deaths per person per year} &= (8 \text{ hr/day}) \times (300 \text{ days/yr}) \times (2 \text{ deaths}/10^8 \text{ hr}) \\ &= 4.8 \times 10^{-5}. \end{aligned}$$

Typical accident statistics for various industries are shown in Table 1-3. A FAR of 1.2 is reported in Table 1-3 for the chemical industry. Approximately half these deaths are due to ordinary industrial accidents (falling down stairs, being run over), the other half to chemical exposures.²

The FAR figures show that if 1000 workers begin employment in the chemical industry, 2 of the workers will die as a result of their employment throughout all of their working lifetimes. One of these deaths will be due to direct chemical exposure. However, 20 of these same

²T. A. Kletz, "Eliminating Potential Process Hazards," *Chemical Engineering* (Apr. 1, 1985).

Table 1-4 Fatality Statistics for Common Nonindustrial Activities^{a,b}

Activity	FAR (deaths/10 ⁸ hours)	Fatality rate (deaths per person per year)
Voluntary activity		
Staying at home	3	
Traveling by		
Car	57	17×10^{-5}
Bicycle	96	
Air	240	
Motorcycle	660	
Canoeing	1000	
Rock climbing	4000	4×10^{-5}
Smoking (20 cigarettes/day)		500×10^{-5}
Involuntary activity		
Struck by meteorite		6×10^{-11}
Struck by lightning (U.K.)		1×10^{-7}
Fire (U.K.)		150×10^{-7}
Run over by vehicle		600×10^{-7}

^aFrank P. Lees, *Loss Prevention in the Process Industries* (London: Butterworths, 1986), p. 178.

^bFrank P. Lees, *Loss Prevention in the Process Industries*, 2nd ed. (London: Butterworths, 1996), p. 9/96.

1000 people will die as a result of nonindustrial accidents (mostly at home or on the road) and 370 will die from disease. Of those that perish from disease, 40 will die as a direct result of smoking.³

Table 1-4 lists the FARs for various common activities. The table is divided into voluntary and involuntary risks. Based on these data, it appears that individuals are willing to take a substantially greater risk if it is voluntary. It is also evident that many common everyday activities are substantially more dangerous than working in a chemical plant.

For example, Table 1-4 indicates that canoeing is much more dangerous than traveling by motorcycle, despite general perceptions otherwise. This phenomenon is due to the number of exposed hours. Canoeing produces more fatalities per hour of activity than traveling by motorcycle. The total number of motorcycle fatalities is larger because more people travel by motorcycle than canoe.

Example 1-2

If twice as many people used motorcycles for the same average amount of time each, what will happen to (a) the OSHA incidence rate, (b) the FAR, (c) the fatality rate, and (d) the total number of fatalities?

³Kletz, "Eliminating Potential Process Hazards."

Solution

- a. The OSHA incidence rate will remain the same. The number of injuries and deaths will double, but the total number of hours exposed will double as well.
- b. The FAR will remain unchanged for the same reason as in part a.
- c. The fatality rate, or deaths per person per year, will double. The fatality rate does not depend on exposed hours.
- d. The total number of fatalities will double.

Example 1-3

If all riders used their motorcycles twice as much, what will happen to (a) the OSHA incidence rate, (b) the FAR, (c) the fatality rate, and (d) the total number of fatalities?

Solution

- a. The OSHA incidence rate will remain the same. The same reasoning applies as for Example 1-2, part a.
- b. The FAR will remain unchanged for the same reason as in part a.
- c. The fatality rate will double. Twice as many fatalities will occur within this group.
- d. The number of fatalities will double.

Example 1-4

A friend states that more rock climbers are killed traveling by automobile than are killed rock climbing. Is this statement supported by the accident statistics?

Solution

The data from Table 1-4 show that traveling by car (FAR = 57) is safer than rock climbing (FAR = 4000). Rock climbing produces many more fatalities per exposed hour than traveling by car. However, the rock climbers probably spend more time traveling by car than rock climbing. As a result, the statement might be correct but more data are required.

Recognizing that the chemical industry is safe, why is there so much concern about chemical plant safety? The concern has to do with the industry's potential for many deaths, as, for example, in the Bhopal, India, tragedy. Accident statistics do not include information on the total number of deaths from a single incident. Accident statistics can be somewhat misleading in this respect. For example, consider two separate chemical plants. Both plants have a probability of explosion and complete devastation once every 1000 years. The first plant employs a single operator. When the plant explodes, the operator is the sole fatality. The second plant employs 10 operators. When this plant explodes all 10 operators succumb. In both cases the FAR and OSHA incidence rate are the same; the second accident kills more people, but there are a correspondingly larger number of exposed hours. In both cases the risk taken by an individual operator is the same.⁴

It is human nature to perceive the accident with the greater loss of life as the greater tragedy. The potential for large loss of life gives the perception that the chemical industry is unsafe.

⁴Kletz, "Eliminating Potential Process Hazards."

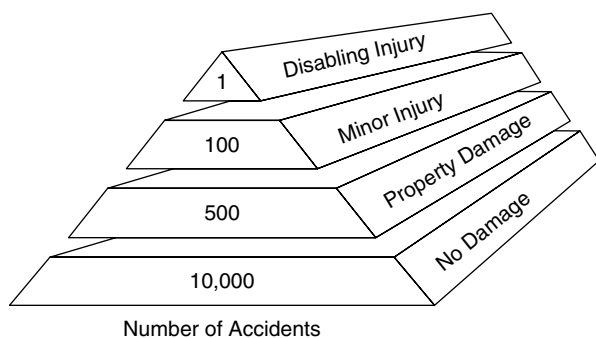


Figure 1-3 The accident pyramid.

Loss data⁵ published for losses after 1966 and in 10-year increments indicate that the total number of losses, the total dollar amount lost, and the average amount lost per incident have steadily increased. The total loss figure has doubled every 10 years despite increased efforts by the chemical process industry to improve safety. The increases are mostly due to an expansion in the number of chemical plants, an increase in chemical plant size, and an increase in the use of more complicated and dangerous chemicals.

Property damage and loss of production must also be considered in loss prevention. These losses can be substantial. Accidents of this type are much more common than fatalities. This is demonstrated in the accident pyramid shown in Figure 1-3. The numbers provided are only approximate. The exact numbers vary by industry, location, and time. “No Damage” accidents are frequently called “near misses” and provide a good opportunity for companies to determine that a problem exists and to correct it before a more serious accident occurs. It is frequently said that “the cause of an accident is visible the day before it occurs.” Inspections, safety reviews, and careful evaluation of near misses will identify hazardous conditions that can be corrected before real accidents occur.

Safety is good business and, like most business situations, has an optimal level of activity beyond which there are diminishing returns. As shown by Kletz,⁶ if initial expenditures are made on safety, plants are prevented from blowing up and experienced workers are spared. This results in increased return because of reduced loss expenditures. If safety expenditures increase, then the return increases more, but it may not be as much as before and not as much as achieved by spending money elsewhere. If safety expenditures increase further, the price of the product increases and sales diminish. Indeed, people are spared from injury (good humanity), but the cost is decreased sales. Finally, even higher safety expenditures result in uncompetitive product pricing: The company will go out of business. Each company needs to determine an appropriate level for safety expenditures. This is part of risk management.

From a technical viewpoint, excessive expenditures for safety equipment to solve single safety problems may make the system unduly complex and consequently may cause new safety

⁵*The 100 Largest Losses, 1972–2001: Large Property Damage Losses in the Hydrocarbon-Chemical Industries*, 20th ed., Marsh’s Risk Consulting Practice, Feb. 2003.

⁶Kletz, “Eliminating Potential Process Hazards.”

Table 1-5 All Accidental Deaths^a

Type of death	1998 deaths	2007 deaths
Motor-vehicle		
Public nonwork	38,900	40,955
Work	2,100	1,945
Home	200	200
Subtotal	41,200 (43.5%)	43,100 (35.4%)
Work		
Non-motor-vehicle	3,000	2,744
Motor-vehicle	2,100	1,945
Subtotal	5,100 (5.4%)	4,689 (3.9%)
Home		
Non-motor-vehicle	28,200	43,300
Motor-vehicle	200	200
Subtotal	28,400 (30.0%)	43,500 (35.7%)
Public	20,000 (21.1%)	30,500 (25%)
All classes	94,700	121,789

^a*Injury Facts*, 2009, p. 2.

problems because of this complexity. This excessive expense could have a higher safety return if assigned to a different safety problem. Engineers need to also consider other alternatives when designing safety improvements.

It is also important to recognize the causes of accidental deaths, as shown in Table 1-5. Because most, if not all, company safety programs are directed toward preventing injuries to employees, the programs should include off-the-job safety, especially training to prevent accidents with motor vehicles.

When organizations focus on the root causes of worker injuries, it is helpful to analyze the manner in which workplace fatalities occur (see Figure 1-4). Although the emphasis of this book is the prevention of chemical-related accidents, the data in Figure 1-4 show that safety programs need to include training to prevent injuries resulting from transportation, assaults, mechanical and chemical exposures, and fires and explosions.

1-4 Acceptable Risk

We cannot eliminate risk entirely. Every chemical process has a certain amount of risk associated with it. At some point in the design stage someone needs to decide if the risks are

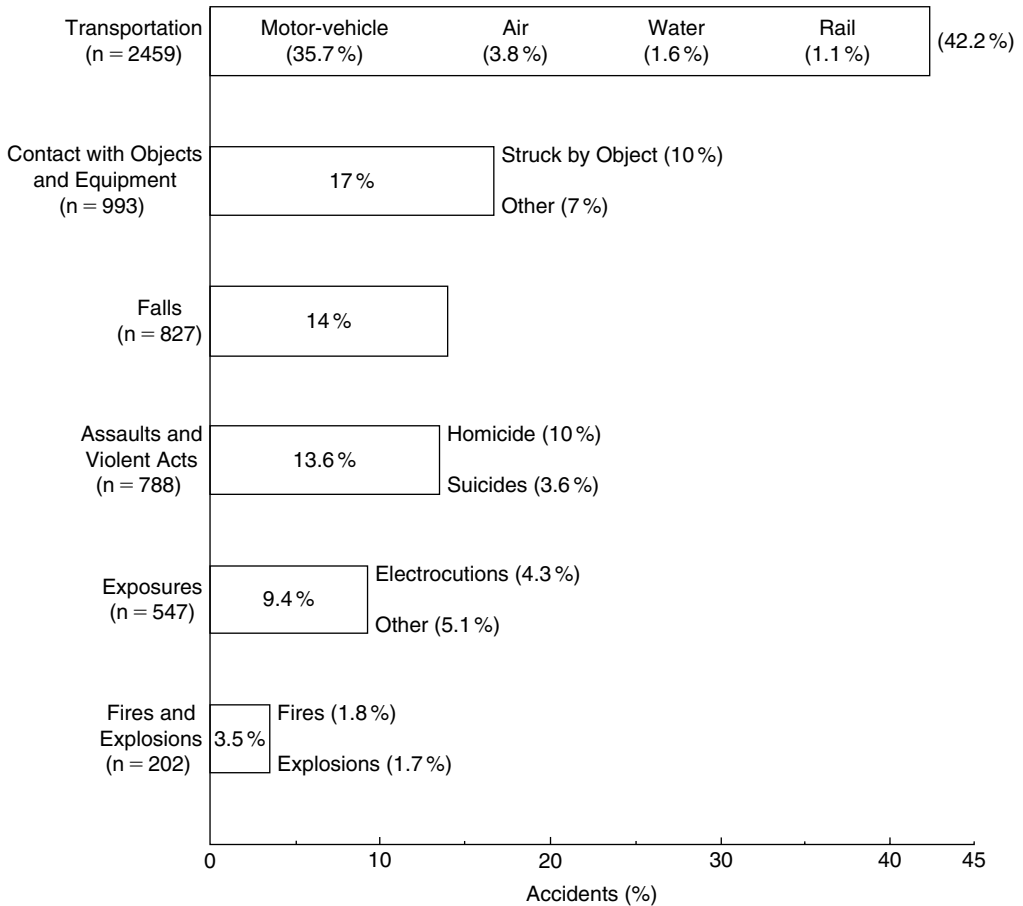


Figure 1-4 The manner in which workplace fatalities occurred in 2006. The total number of workplace fatalities was 5840; this includes the above plus 14 for bodily reaction and exertion, and 10 nonclassified. Data source: *Injury Facts*, 2009, p. 56.

“acceptable.” That is, are the risks greater than the normal day-to-day risks taken by individuals in their nonindustrial environment? Certainly it would require a substantial effort and considerable expense to design a process with a risk comparable to being struck by lightning (see Table 1-4). Is it satisfactory to design a process with a risk comparable to the risk of sitting at home? For a single chemical process in a plant composed of several processes, this risk may be too high because the risks resulting from multiple exposures are additive.⁷

⁷Modern site layouts require sufficient separation of plants within the site to minimize risks of multiple exposures.

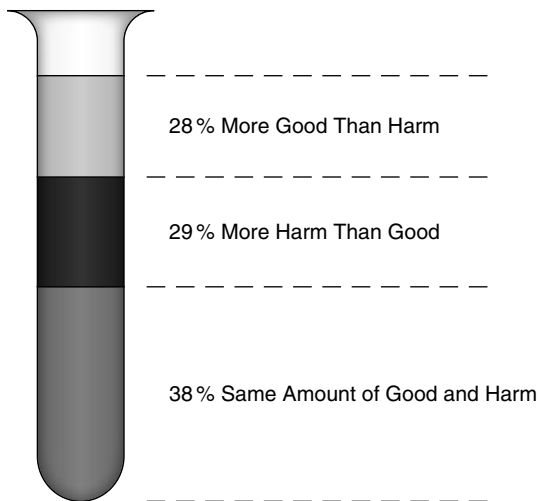


Figure 1-5 Results from a public opinion survey asking the question, “Would you say chemicals do more good than harm, more harm than good, or about the same amount of each?” Source: *The Detroit News*.

Engineers must make every effort to minimize risks within the economic constraints of the process. No engineer should ever design a process that he or she knows will result in certain human loss or injury, despite any statistics.

1-5 Public Perceptions

The general public has great difficulty with the concept of acceptable risk. The major objection is due to the involuntary nature of acceptable risk. Chemical plant designers who specify the acceptable risk are assuming that these risks are satisfactory to the civilians living near the plant. Frequently these civilians are not aware that there is any risk at all.

The results of a public opinion survey on the hazards of chemicals are shown in Figure 1-5. This survey asked the participants if they would say chemicals do more good than harm, more harm than good, or about the same amount of each. The results show an almost even three-way split, with a small margin to those who considered the good and harm to be equal.

Some naturalists suggest eliminating chemical plant hazards by “returning to nature.” One alternative, for example, is to eliminate synthetic fibers produced by chemicals and use natural fibers such as cotton. As suggested by Kletz,⁸ accident statistics demonstrate that this will result in a greater number of fatalities because the FAR for agriculture is higher.

⁸Kletz, “Eliminating Potential Process Hazards.”

Table 1-6 Three Types of Chemical Plant Accidents

Type of accident	Probability of occurrence	Potential for fatalities	Potential for economic loss
Fire	High	Low	Intermediate
Explosion	Intermediate	Intermediate	High
Toxic release	Low	High	Low

Example 1-5

List six different products produced by chemical engineers that are of significant benefit to mankind.

Solution

Penicillin, gasoline, synthetic rubber, paper, plastic, concrete.

1-6 The Nature of the Accident Process

Chemical plant accidents follow typical patterns. It is important to study these patterns in order to anticipate the types of accidents that will occur. As shown in Table 1-6, fires are the most common, followed by explosion and toxic release. With respect to fatalities, the order reverses, with toxic release having the greatest potential for fatalities.

Economic loss is consistently high for accidents involving explosions. The most damaging type of explosion is an unconfined vapor cloud explosion, where a large cloud of volatile and flammable vapor is released and dispersed throughout the plant site followed by ignition and explosion of the cloud. An analysis of the largest chemical plant accidents (based on worldwide accidents and 1998 dollars) is provided in Figure 1-6. As illustrated, vapor cloud explosions

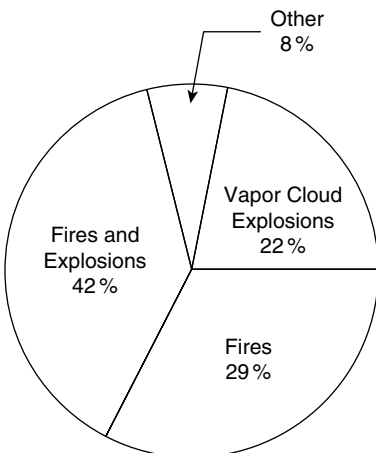


Figure 1-6 Types of loss for large hydrocarbon-chemical plant accidents. Data from *The 100 Largest Losses, 1972-2001*.

account for the largest percentage of these large losses. The “other” category of Figure 1-6 includes losses resulting from floods and windstorms.

Toxic release typically results in little damage to capital equipment. Personnel injuries, employee losses, legal compensation, and cleanup liabilities can be significant.

Figure 1-7 presents the causes of losses for these largest accidents. By far the most frequent cause is mechanical failures, such as pipe failures due to corrosion, erosion, and high pressures, and seal/gasket failures. Failures of this type are usually due to poor maintenance or the poor utilization of the principles of inherent safety (Section 1-7) and process safety management (Section 3-1). Pumps, valves, and control equipment will fail if not properly maintained. The second largest cause is operator error. For example, valves are not opened or closed in the proper sequence or reactants are not charged to a reactor in the correct order. Process upsets caused by, for example, power or cooling water failures account for 3% of the losses.

Human error is frequently used to describe a cause of losses. Almost all accidents, except those caused by natural hazards, can be attributed to human error. For instance, mechanical failures could all be due to human error as a result of improper maintenance or inspection. The term “operator error,” used in Figure 1-7, includes human errors made on-site that led directly to the loss.

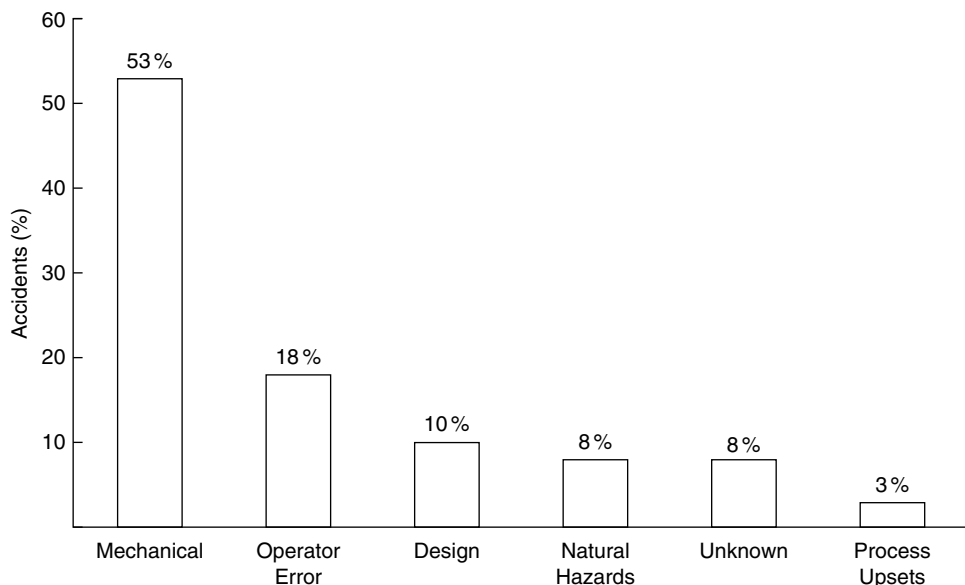


Figure 1-7 Causes of losses for largest hydrocarbon-chemical plant accidents. Data from *The 100 Largest Losses, 1972-2001*.

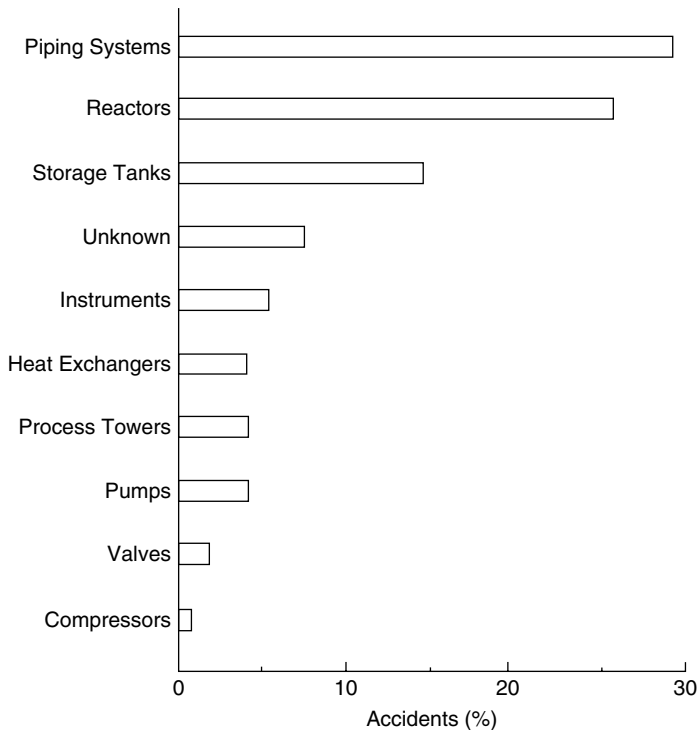


Figure 1-8 Hardware associated with the largest hydrocarbon-chemical plant accidents. Data from *The 100 Largest Losses, 1972–2001*.

Figure 1-8 presents a survey of the type of hardware associated with large accidents. Piping system failure represents the bulk of the accidents, followed by storage tanks and reactors. An interesting result of this study is that the most complicated mechanical components (pumps and compressors) are minimally responsible for large losses.

The loss distribution for the hydrocarbon and chemical industry over 5-year intervals is shown in Figure 1-9. The number and magnitude of the losses increase over each consecutive 10-year period for the past 30 years. This increase corresponds to the trend of building larger and more complex plants.

The lower losses between 1992 and 1996 are likely the temporary result of governmental regulations that were implemented in the United States during this time; that is, on February 24, 1992, OSHA published its final rule “Process Safety Management of Highly Hazardous Chemicals (PSM).” This rule became effective on May 26, 1992. As shown, however, the lower losses between 1992 and 1996 were probably a start-up benefit of PSM because in the last 5-year period (1997-01) the losses went up again.

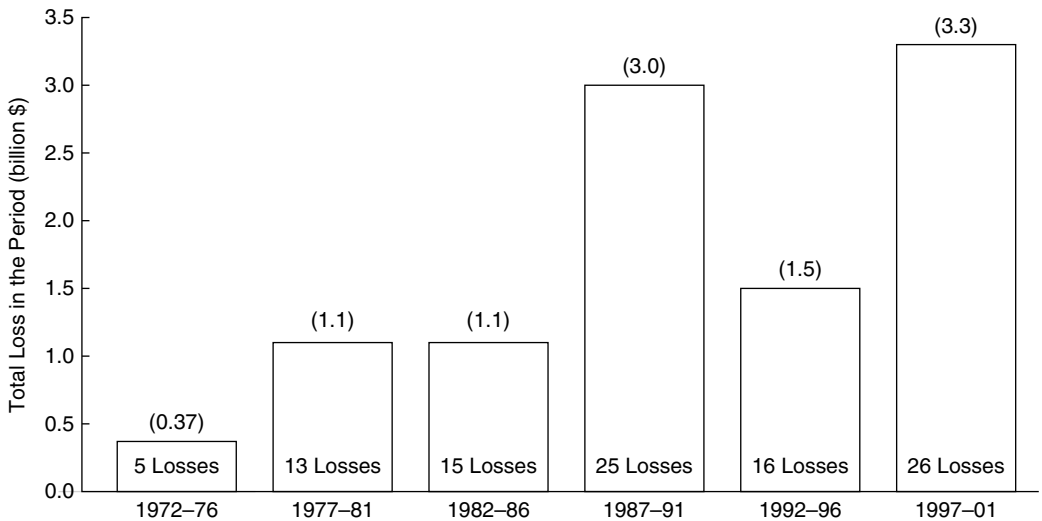


Figure 1-9 Loss distribution for the largest hydrocarbon-chemical plant accidents over a 30-year period. Data from *The 100 Largest Losses, 1972–2001*.

Accidents follow a three-step process. The following chemical plant accident illustrates these steps.

A worker walking across a high walkway in a process plant stumbles and falls toward the edge. To prevent the fall, he grabs a nearby valve stem. Unfortunately, the valve stem shears off and flammable liquid begins to spew out. A cloud of flammable vapor rapidly forms and is ignited by a nearby truck. The explosion and fire quickly spread to nearby equipment. The resulting fire lasts for six days until all flammable materials in the plant are consumed, and the plant is completely destroyed.

This disaster occurred in 1969⁹ and led to an economic loss of \$4,161,000. It demonstrates an important point: Even the simplest accident can result in a major catastrophe.

Most accidents follow a three-step sequence:

- Initiation (the event that starts the accident)
- Propagation (the event or events that maintain or expand the accident), and
- Termination (the event or events that stop the accident or diminish it in size)

In the example the worker tripped to initiate the accident. The accident was propagated by the shearing of the valve and the resulting explosion and growing fire. The event was terminated by consumption of all flammable materials.

⁹*One Hundred Largest Losses: A Thirty-Year Review of Property Losses in the Hydrocarbon-Chemical Industries* (Chicago: M & M Protection Consultants, 1986), p. 3.

Table 1-7 Defeating the Accident Process

Step	Desired effect	Procedure
Initiation	Diminish	Grounding and bonding Inerting Explosion proof electrical Guardrails and guards Maintenance procedures Hot work permits Human factors design Process design Awareness of dangerous properties of chemicals
Propagation	Diminish	Emergency material transfer Reduce inventories of flammable materials Equipment spacing and layout Nonflammable construction materials Installation of check and emergency shutoff valves
Termination	Increase	Fire-fighting equipment and procedures Relief systems Sprinkler systems Installation of check and emergency shutoff valves

Safety engineering involves eliminating the initiating step and replacing the propagation steps with termination events. Table 1-7 presents a few ways to accomplish this. In theory, accidents can be stopped by eliminating the initiating step. In practice this is not effective: It is unrealistic to expect elimination of all initiations. A much more effective approach is to work on all three areas to ensure that accidents, once initiated, do not propagate and will terminate as quickly as possible.

Example 1-6

The following accident report has been filed¹⁰.

Failure of a threaded 1½" drain connection on a rich oil line at the base of an absorber tower in a large (1.35 MCF/D) gas producing plant allowed the release of rich oil and gas at 850 psi and -40°F. The resulting vapor cloud probably ignited from the ignition system of engine-driven recompressors. The 75' high × 10' diameter absorber tower eventually collapsed across the pipe rack and on two exchanger trains. Breaking pipelines added more fuel to the fire. Severe flame impingement on an 11,000-horsepower gas turbine-driven compressor, waste heat recovery, and super-heater train resulted in its near total destruction.

Identify the initiation, propagation, and termination steps for this accident.

¹⁰*One Hundred Largest Losses*, p. 10.

Solution

Initiation:	Failure of threaded 1½" drain connection
Propagation:	Release of rich oil and gas, formation of vapor cloud, ignition of vapor cloud by re-compressors, collapse of absorber tower across pipe rack
Termination:	Consumption of combustible materials in process

As mentioned previously, the study of case histories is an especially important step in the process of accident prevention. To understand these histories, it is helpful to know the definitions of terms that are commonly used in the descriptions (see Table 1-8).

1-7 Inherent Safety

An inherently safe plant^{11,12} relies on chemistry and physics to prevent accidents rather than on control systems, interlocks, redundancy, and special operating procedures to prevent accidents. Inherently safer plants are tolerant of errors and are often the most cost effective. A process that does not require complex safety interlocks and elaborate procedures is simpler, easier to operate, and more reliable. Smaller equipment, operated at less severe temperatures and pressures, has lower capital and operating costs.

In general, the safety of a process relies on multiple layers of protection. The first layer of protection is the process design features. Subsequent layers include control systems, interlocks, safety shutdown systems, protective systems, alarms, and emergency response plans. Inherent safety is a part of all layers of protection; however, it is especially directed toward process design features. The best approach to prevent accidents is to add process design features to prevent hazardous situations. An inherently safer plant is more tolerant of operator errors and abnormal conditions.

Although a process or plant can be modified to increase inherent safety at any time in its life cycle, the potential for major improvements is the greatest at the earliest stages of process development. At these early stages process engineers and chemists have the maximum degree of freedom in the plant and process specifications, and they are free to consider basic process alternatives, such as changes to the fundamental chemistry and technology.

The following four words are recommended to describe inherent safety:

- Minimize (intensification)
- Substitute (substitution)
- Moderate (attenuation and limitation of effects)
- Simplify (simplification and error tolerance)

¹¹Center for Chemical Process Safety (CCPS), *Guidelines for Engineering Design for Process Safety* (New York: American Institute of Chemical Engineers, 1993).

¹²Center for Chemical Process Safety (CCPS), *Inherently Safer Chemical Processes: A Life Cycle Approach*, 2nd ed. (Hoboken, NJ: John Wiley & Sons, 2009).

Table 1-8 Definitions for Case Histories^a

Term	Definition
Accident	The occurrence of a sequence of events that produce unintended injury, death, or property damage. "Accident" refers to the event, not the result of the event.
Hazard	A chemical or physical condition that has the potential for causing damage to people, property, or the environment.
Incident	The loss of containment of material or energy; not all events propagate into incidents; not all incidents propagate into accidents.
Consequence	A measure of the expected effects of the results of an incident.
Likelihood	A measure of the expected probability or frequency of occurrence of an event. This may be expressed as a frequency, a probability of occurrence during some time interval, or a conditional probability.
Risk	A measure of human injury, environmental damage, or economic loss in terms of both the incident likelihood and the magnitude of the loss or injury.
Risk analysis	The development of a quantitative estimate of risk based on an engineering evaluation and mathematical techniques for combining estimates of incident consequences and frequencies.
Risk assessment	The process by which the results of a risk analysis are used to make decisions, either through a relative ranking of risk reduction strategies or through comparison with risk targets.
Scenario	A description of the events that result in an accident or incident. The description should contain information relevant to defining the root causes.

^aCenter for Chemical Process Safety (CCPS), *Guidelines for Consequence Analysis*.

The types of inherent safety techniques that are used in the chemical industry are illustrated in Table 1-9 and are described more fully in what follows.

Minimizing entails reducing the hazards by using smaller quantities of hazardous substances in the reactors, distillation columns, storage vessels, and pipelines. When possible, hazardous materials should be produced and consumed in situ. This minimizes the storage and transportation of hazardous raw materials and intermediates.

Vapor released from spills can be minimized by designing dikes so that flammable and toxic materials will not accumulate around leaking tanks. Smaller tanks also reduce the hazards of a release.

While minimization possibilities are being investigated, substitutions should also be considered as an alternative or companion concept; that is, safer materials should be used in place of hazardous ones. This can be accomplished by using alternative chemistry that allows the use of less hazardous materials or less severe processing conditions. When possible,

Table 1-9 Inherent Safety Techniques

Type	Typical techniques
Minimize (intensification)	Change from large batch reactor to a smaller continuous reactor Reduce storage inventory of raw materials Improve control to reduce inventory of hazardous intermediate chemicals Reduce process hold-up
Substitute (substitution)	Use mechanical pump seals vs. packing Use welded pipe vs. flanged Use solvents that are less toxic Use mechanical gauges vs. mercury Use chemicals with higher flash points, boiling points, and other less hazardous properties Use water as a heat transfer fluid instead of hot oil
Moderate (attenuation and limitation of effects)	Use vacuum to reduce boiling point Reduce process temperatures and pressures Refrigerate storage vessels Dissolve hazardous material in safe solvent Operate at conditions where reactor runaway is not possible Place control rooms away from operations Separate pump rooms from other rooms Acoustically insulate noisy lines and equipment Barricade control rooms and tanks
Simplify (simplification and error tolerance)	Keep piping systems neat and visually easy to follow Design control panels that are easy to comprehend Design plants for easy and safe maintenance Pick equipment that requires less maintenance Pick equipment with low failure rates Add fire- and explosion-resistant barricades Separate systems and controls into blocks that are easy to comprehend and understand Label pipes for easy “walking the line” Label vessels and controls to enhance understanding

toxic or flammable solvents should be replaced with less hazardous solvents (for example, water-based paints and adhesives and aqueous or dry flowable formulations for agricultural chemicals).

Another alternative to substitution is moderation, that is, using a hazardous material under less hazardous conditions. Less hazardous conditions or less hazardous forms of a material include (1) diluting to a lower vapor pressure to reduce the release concentration, (2) refrigerating to lower the vapor pressure, (3) handling larger particle size solids to minimize dust, and (4) processing under less severe temperature or pressure conditions.

Containment buildings are sometimes used to moderate the impact of a spill of an especially toxic material. When containment is used, special precautions are included to ensure worker protection, such as remote controls, continuous monitoring, and restricted access.

Simpler plants are friendlier than complex plants because they provide fewer opportunities for error and because they contain less equipment that can cause problems. Often, the reason for complexity in a plant is the need to add equipment and automation to control the hazards. Simplification reduces the opportunities for errors and misoperation. For example, (1) piping systems can be designed to minimize leaks or failures, (2) transfer systems can be designed to minimize the potential for leaks, (3) process steps and units can be separated to prevent the domino effect, (4) fail-safe valves can be added, (5) equipment and controls can be placed in a logical order, and (6) the status of the process can be made visible and clear at all times.

The design of an inherently safe and simple piping system includes minimizing the use of sight glasses, flexible connectors, and bellows, using welded pipes for flammable and toxic chemicals and avoiding the use of threaded pipe, using spiral wound gaskets and flexible graphite-type gaskets that are less prone to catastrophic failures, and using proper support of lines to minimize stress and subsequent failures.

1-8 Seven Significant Disasters

The study of case histories provides valuable information to chemical engineers involved with safety. This information is used to improve procedures to prevent similar accidents in the future.

The seven most cited accidents (Flixborough, England; Bhopal, India; Seveso, Italy; Pasadena, Texas; Texas City, Texas; Jacksonville, Florida; and Port Wentworth, Georgia) are presented here. All these accidents had a significant impact on public perceptions and the chemical engineering profession that added new emphasis and standards in the practice of safety. Chapter 14 presents case histories in considerably more detail.

The Flixborough accident is perhaps the most documented chemical plant disaster. The British government insisted on an extensive investigation.

Flixborough, England

The accident at Flixborough, England, occurred on a Saturday in June 1974. Although it was not reported to any great extent in the United States, it had a major impact on chemical engineering in the United Kingdom. As a result of the accident, safety achieved a much higher priority in that country.

The Flixborough Works of Nypro Limited was designed to produce 70,000 tons per year of caprolactam, a basic raw material for the production of nylon. The process uses cyclohexane, which has properties similar to gasoline. Under the process conditions in use at Flixborough (155°C and 7.9 atm), the cyclohexane volatilizes immediately when depressurized to atmospheric conditions.

The process where the accident occurred consisted of six reactors in series. In these reactors cyclohexane was oxidized to cyclohexanone and then to cyclohexanol using injected air in the presence of a catalyst. The liquid reaction mass was gravity-fed through the series of reactors. Each reactor normally contained about 20 tons of cyclohexane.

Several months before the accident occurred, reactor 5 in the series was found to be leaking. Inspection showed a vertical crack in its stainless steel structure. The decision was made to remove the reactor for repairs. An additional decision was made to continue operating by connecting reactor 4 directly to reactor 6 in the series. The loss of the reactor would reduce the yield but would enable continued production because unreacted cyclohexane is separated and recycled at a later stage.

The feed pipes connecting the reactors were 28 inches in diameter. Because only 20-inch pipe stock was available at the plant, the connections to reactor 4 and reactor 6 were made using flexible bellows-type piping, as shown in Figure 1-10. It is hypothesized that the bypass pipe section ruptured because of inadequate support and overflexing of the pipe section as a result of internal reactor pressures. Upon rupture of the bypass, an estimated 30 tons of cyclohexane volatilized and formed a large vapor cloud. The cloud was ignited by an unknown source an estimated 45 seconds after the release.

The resulting explosion leveled the entire plant facility, including the administrative offices. Twenty-eight people died, and 36 others were injured. Eighteen of these fatalities occurred in the main control room when the ceiling collapsed. Loss of life would have been substantially greater had the accident occurred on a weekday when the administrative offices were filled with employees. Damage extended to 1821 nearby houses and 167 shops and factories. Fifty-three civilians were reported injured. The resulting fire in the plant burned for over 10 days.

This accident could have been prevented by following proper safety procedures. First, the bypass line was installed without a safety review or adequate supervision by experienced engineering personnel. The bypass was sketched on the floor of the machine shop using chalk!

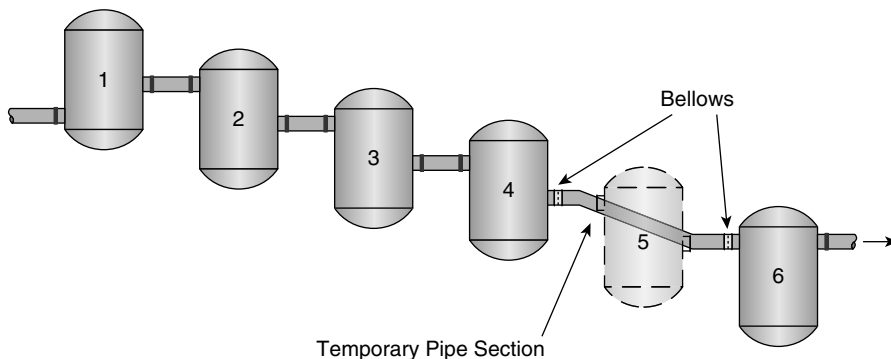


Figure 1-10 A failure of a temporary pipe section replacing reactor 5 caused the Flixborough accident.

Second, the plant site contained excessively large inventories of dangerous compounds. This included 330,000 gallons of cyclohexane, 66,000 gallons of naphtha, 11,000 gallons of toluene, 26,400 gallons of benzene, and 450 gallons of gasoline. These inventories contributed to the fires after the initial blast. Finally, the bypass modification was substandard in design. As a rule, any modifications should be of the same quality as the construction of the remainder of the plant.

Bhopal, India

The Bhopal, India, accident, on December 3, 1984, has received considerably more attention than the Flixborough accident. This is due to the more than 2000 civilian casualties that resulted.

The Bhopal plant is in the state of Madhya Pradesh in central India. The plant was partially owned by Union Carbide and partially owned locally.

The nearest civilian inhabitants were 1.5 miles away when the plant was constructed. Because the plant was the dominant source of employment in the area, a shantytown eventually grew around the immediate area.

The plant produced pesticides. An intermediate compound in this process is methyl isocyanate (MIC). MIC is an extremely dangerous compound. It is reactive, toxic, volatile, and flammable. The maximum exposure concentration of MIC for workers over an 8-hour period is 0.02 ppm (parts per million). Individuals exposed to concentrations of MIC vapors above 21 ppm experience severe irritation of the nose and throat. Death at large concentrations of vapor is due to respiratory distress.

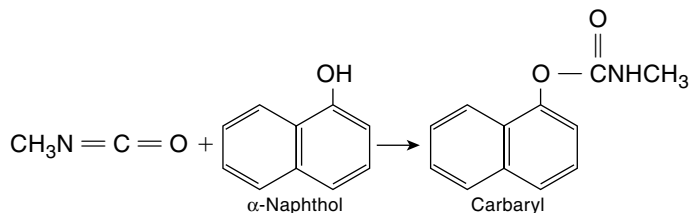
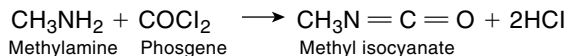
MIC demonstrates a number of dangerous physical properties. Its boiling point at atmospheric conditions is 39.1°C, and it has a vapor pressure of 348 mm Hg at 20°C. The vapor is about twice as heavy as air, ensuring that the vapors will stay close to the ground once released.

MIC reacts exothermically with water. Although the reaction rate is slow, with inadequate cooling the temperature will increase and the MIC will boil. MIC storage tanks are typically refrigerated to prevent this problem.

The unit using the MIC was not operating because of a local labor dispute. Somehow a storage tank containing a large amount of MIC became contaminated with water or some other substance. A chemical reaction heated the MIC to a temperature past its boiling point. The MIC vapors traveled through a pressure relief system and into a scrubber and flare system installed to consume the MIC in the event of a release. Unfortunately, the scrubber and flare systems were not operating, for a variety of reasons. An estimated 25 tons of toxic MIC vapor was released. The toxic cloud spread to the adjacent town, killing over 2000 civilians and injuring an estimated 20,000 more. No plant workers were injured or killed. No plant equipment was damaged.

The exact cause of the contamination of the MIC is not known. If the accident was caused by a problem with the process, a well-executed safety review could have identified the problem. The scrubber and flare system should have been fully operational to prevent the release. Inventories of dangerous chemicals, particularly intermediates, should also have been minimized.

Methyl isocyanate route



Nonmethyl isocyanate route

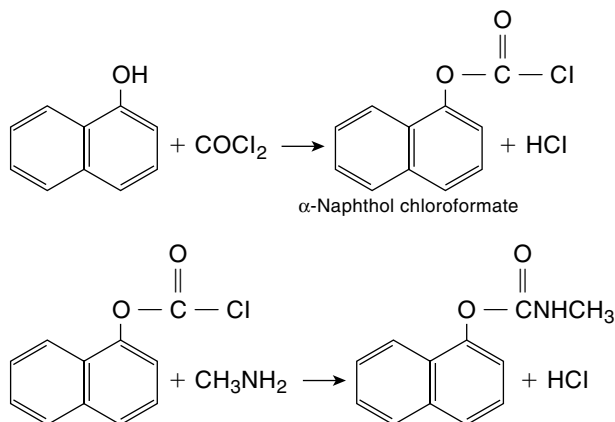


Figure 1-11 The upper reaction is the methyl isocyanate route used at Bhopal. The lower reaction suggests an alternative reaction scheme using a less hazardous intermediate. Adapted from *Chemical and Engineering News* (Feb. 11, 1985), p. 30.

The reaction scheme used at Bhopal is shown at the top of Figure 1-11 and includes the dangerous intermediate MIC. An alternative reaction scheme is shown at the bottom of the figure and involves a less dangerous chloroformate intermediate. Another solution is to redesign the process to reduce the inventory of hazardous MIC. One such design produces and consumes the MIC in a highly localized area of the process, with an inventory of MIC of less than 20 pounds.

Seveso, Italy

Seveso is a small town of approximately 17,000 inhabitants, 15 miles from Milan, Italy. The plant was owned by the Icmesa Chemical Company. The product was hexachlorophene, a bactericide, with trichlorophenol produced as an intermediate. During normal operation, a small

amount of TCDD (2,3,7,8-tetrachlorodibenzoparadioxin) is produced in the reactor as an undesirable side-product.

TCDD is perhaps the most potent toxin known to humans. Animal studies have shown TCDD to be fatal in doses as small as 10^{-9} times the body weight. Because TCDD is also insoluble in water, decontamination is difficult. Nonlethal doses of TCDD result in chloracne, an acne-like disease that can persist for several years.

On July 10, 1976, the trichlorophenol reactor went out of control, resulting in a higher than normal operating temperature and increased production of TCDD. An estimated 2 kg of TCDD was released through a relief system in a white cloud over Seveso. A subsequent heavy rain washed the TCDD into the soil. Approximately 10 square miles were contaminated.

Because of poor communications with local authorities, civilian evacuation was not started until several days later. By then, over 250 cases of chloracne were reported. Over 600 people were evacuated, and an additional 2000 people were given blood tests. The most severely contaminated area immediately adjacent to the plant was fenced, the condition it remains in today.

TCDD is so toxic and persistent that for a smaller but similar release of TCDD in Duphar, India, in 1963 the plant was finally disassembled brick by brick, encased in concrete, and dumped into the ocean. Less than 200 g of TCDD was released, and the contamination was confined to the plant. Of the 50 men assigned to clean up the release, 4 eventually died from the exposure.

The Seveso and Duphar accidents could have been avoided if proper containment systems had been used to contain the reactor releases. The proper application of fundamental engineering safety principles would have prevented the two accidents. First, by following proper procedures, the initiation steps would not have occurred. Second, by using proper hazard evaluation procedures, the hazards could have been identified and corrected before the accidents occurred.

Pasadena, Texas

A massive explosion in Pasadena, Texas, on October 23, 1989, resulted in 23 fatalities, 314 injuries, and capital losses of over \$715 million. This explosion occurred in a high-density polyethylene plant after the accidental release of 85,000 pounds of a flammable mixture containing ethylene, isobutane, hexane, and hydrogen. The release formed a large gas cloud instantaneously because the system was under high pressure and temperature. The cloud was ignited about 2 minutes after the release by an unidentified ignition source.

The damage resulting from the explosion made it impossible to reconstruct the actual accident scenario. However, evidence showed that the standard operating procedures were not appropriately followed.

The release occurred in the polyethylene product takeoff system, as illustrated in Figure 1-12. Usually the polyethylene particles (product) settle in the settling leg and are removed through the product takeoff valve. Occasionally, the product plugs the settling leg, and

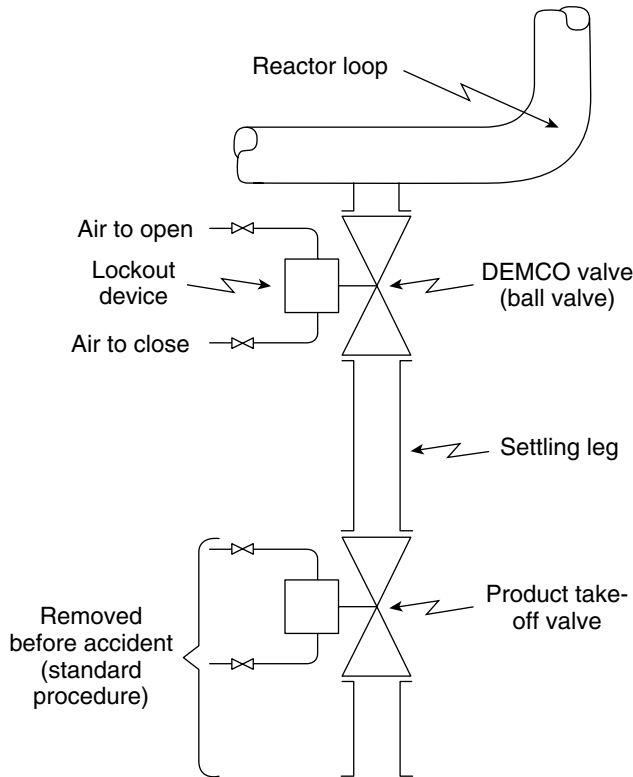


Figure 1-12 Polyethylene plant settling leg and product takeoff system.

the plug is removed by maintenance personnel. The normal—and safe—procedure includes closing the DEMCO valve, removing the air lines, and locking the valve in the closed position. Then the product takeoff valve is removed to give access to the plugged leg.

The accident investigation evidence showed that this safe procedure was not followed; specifically, the product takeoff valve was removed, the DEMCO valve was in the open position, and the lockout device was removed. This scenario was a serious violation of well-established and well-understood procedures and created the conditions that permitted the release and subsequent explosion.

The OSHA investigation¹³ found that (1) no process hazard analysis had been performed in the polyethylene plant, and as a result, many serious safety deficiencies were ignored or overlooked; (2) the single-block (DEMCO) valve on the settling leg was not designed to fail to a safe

¹³Occupational Safety and Health Administration, *The Pasadena Accident: A Report to the President* (Washington, DC: US Department of Labor, 1990).

closed position when the air failed; (3) rather than relying on a single-block valve, a double block and bleed valving arrangement or a blind flange after the single-block valve should have been used; (4) no provision was made for the development, implementation, and enforcement of effective permit systems (for example, line opening); and (5) no permanent combustible gas detection and alarm system was located in the region of the reactors.

Other factors that contributed to the severity of this disaster were also cited: (1) proximity of high-occupancy structures (control rooms) to hazardous operation, (2) inadequate separation between buildings, and (3) crowded process equipment.

Texas City, Texas

A petroleum refinery had large explosions on March 23, 2005, that killed 15 workers and injured about 180.¹⁴ The explosions were the result of a sudden release of flammable liquid and vapor from an open vent stack in the refinery's isomerization (ISOM) unit. The ISOM unit converts pentane and hexane into isopentane and isohexane (gasoline additive). The unit works by heating the pentane and hexane in the presence of a catalyst. This unit includes a splitter tower and associated process equipment, which is used to prepare the hydrocarbon feed of the isomerization reactor.

This accident was during the startup of this ISOM process unit. In this startup, hydrocarbons were pumped into the splitter tower for three hours without any liquid being removed and transferred to storage (which should have happened). As a result, the 164-foot-tall tower was overfilled. The resulting high pressure activated three pressure relief valves, and the liquid was discharged to a vented blowdown drum. The blowdown drum overfilled with hydrocarbons, producing a geyser-like release from the vented stack. The flammable hydrocarbons pooled on the ground, releasing vapors that ignited, resulting in multiple explosions and fires. Many of those killed were working in or around two contractor office trailers located near a blowdown drum.

The CSB investigation identified the following major findings: (1) the occupied trailers were sited in an unsafe location (all 15 fatalities occurred in or around two contractor trailers); (2) the ISOM unit should not have been started up because there were existing and known problems that should have been repaired before a startup (known equipment malfunctions included a level indicator and alarm, and a control valve); and (3) previously there were at least four other serious releases of flammables out of this blowdown drum vent, and even though these serious near-misses revealed the existing hazard, no effective investigations were conducted nor were appropriate design changes made (a properly designed flare system would have burned these effluents to prevent this unsafe release of the flammable liquid and combustible vapors).

¹⁴D. Holmstrom, F. Altamirano, J. Banks, G. Joseph, M. Kaszniak, C. Mackenzie, R. Shroff, H. Cohen, and S. Wallace, "CSB Investigation of the Explosions and Fire at the BP Texas City Refinery on March 23, 2005," *Process Safety Progress* (2006), 25(4): 345–349.

Jacksonville, Florida

CSB investigated an accident¹⁵ that occurred in a chemical manufacturing plant (gasoline additive) on December 19, 2007. A powerful explosion and fire killed 4 employees and injured 32, including 4 employees and 28 members of the public who were working in surrounding businesses. This plant blended and sold printing solvents and started to manufacture methylcyclopentadienyl manganese tricarbonyl (MCMT) in a 2500-gallon batch reactor in January of 2004.

The accident occurred while the plant was producing its 175th batch of MCMT. The process included two exothermic reactions, the first a necessary step in the production of MCMT, and the second an unwanted side reaction that occurs at about 390°F, which is slightly higher than the normal operating temperature. The reactor cooling failed (line blockage or valve failure), and the temperature increased, setting off both runaway reactions uncontrollably. About ten minutes after the initial cooling failure, the reactor burst and its contents exploded due to the uncontrolled high temperatures and pressures. The pressure burst the reactor and the reactor's contents exploded with a TNT equivalent to 1400 pounds of TNT. Debris from the reactor was found up to one mile away, and the explosion damaged buildings within one-quarter mile of the facility.

CSB found that (1) the cooling system was susceptible to only single-point failures due to the lack of design redundancy, (2) the reactor relief system was incapable of relieving the pressure from the runaway reactions, and (3) despite a number of previous and similar near-misses the company employees failed to recognize the hazards of the runaway reactions associated with this manufacturing process (even though the two owners of the company had undergraduate degrees in chemistry and chemical engineering).

The CSB recommendations in this accident investigation report focused on improving the education of chemical engineering students on the hazards of reactive chemicals.

Port Wentworth, Georgia

On February 7, 2008, a series of sugar dust explosions at a sugar manufacturing facility resulted in 14 fatalities and 36 injuries.¹⁶ This refinery converted raw sugarcane into granulated sugar. A system of screw and belt conveyors and bucket elevators transported granulated sugar from the refinery to storage silos, and to specialty sugar processing areas.

A recently installed steel cover panel on the belt conveyor allowed explosive concentrations of sugar dust to accumulate inside the enclosure. The first dust explosion occurred in this enclosed steel belt conveyor located below the sugar silos. An overheated bearing in the steel belt conveyor was the most likely ignition source. This primary explosion dispersed sugar dust that

¹⁵“Investigation Report—T2 Laboratories, Inc. Runaway Reaction,” U.S. Chemical Safety and Hazard Investigation Board, Report No. 2008-3-I-FL, Sept. 2009.

¹⁶“Investigation Report—Sugar Dust Explosion and Fire,” U.S. Chemical Safety and Hazard Investigation Board, Report No. 2008-05-I-GA, Sept. 2009.

had accumulated on the floors and elevator horizontal surfaces, propagating more explosions throughout the buildings. Secondary dust explosions occurred throughout the packing buildings, parts of the refinery, and the loading buildings. The pressure waves from the explosions heaved thick concrete floors and collapsed brick walls, blocking stairwell and other exit routes.

The CSB investigation identified three major causes: (1) The conveying equipment was not designed to minimize the release of sugar dust and eliminate all ignition sources in the work areas; (2) housekeeping practices were poor; and (3) the company failed to correct the ongoing and known hazardous conditions, despite the well-known and broadly published hazards associated with combustible dusts.

Prior to this Port Wentworth accident, CSB undertook a study¹⁷ in 2005 concerning the extent of the industrial dust explosion problem. They identified 200 fires and explosions due to dusts over a 25-year period that took 100 lives and caused 600 injuries. The tragic event in Port Wentworth demonstrates that dust explosions in industry continue to be a problem.

Suggested Reading

General Aspects of Chemical Process Safety

Robert M. Bethea, *Explosion and Fire at Pasadena, Texas* (New York: American Institute of Chemical Engineers, 1996).

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A. Sam West, Dennis Hendershot, John F. Murphy, and Ronald Willey, "Bhopal's Impact on the Chemical Industry," *Process Safety Progress* (Dec. 2004), 23(4): 229–230.

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Dennis C. Hendershot and John F. Murphy, "Expanding Role of the Loss Prevention Professional: Past, Present, and Future," *Process Safety Progress* (March 2007), 26(1): 18–26.

¹⁷"CSB Reports Chemical Dust Explosions Are a Serious Problem," www.csb.gov/newsroom/detail.aspx?nid=272&SID=0&pg=1&F.

Walter B. Howard, "Seveso: Cause; Prevention," *Plant/Operations Progress* (Apr. 1985), 4(2): 103–104.
J. Sambeth, "What Really Happened at Seveso," *Chemical Engineering* (May 16, 1983), pp. 44–47.

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S. Mannan, ed. *Lees' Loss Prevention in the Process Industries*, 3rd ed., vol. 3, Appendix 2, Pages 1–18. (London: Butterworth-Heinemann, 2005).

General Case Histories

T. Kletz, *Learning from Accidents*, 3rd ed. (Boston: Butterworth-Heinemann, 2001).

T. Kletz, *What Went Wrong? Case Histories of Process Plant Disasters and How They Could Have Been Avoided*, 5th ed. (Boston: Butterworth-Heinemann, 2009).

Problems

- 1-1. An employee works in a plant with a FAR of 4. If this employee works a 4-hr shift, 200 days per year, what is the expected deaths per person per year?
- 1-2. Three process units are in a plant. The units have FARs of 0.5, 0.3, and 1.0, respectively.
 - a. What is the overall FAR for the plant, assuming worker exposure to all three units simultaneously?
 - b. Assume now that the units are far enough apart that an accident in one would not affect the workers in another. If a worker spends 20% of his time in process area 1, 40% in process area 2, and 40% in process area 3, what is his overall FAR?
- 1-3. Assuming that a car travels at an average speed of 50 miles per hour, how many miles must be driven before a fatality is expected?
- 1-4. A worker is told her chances of being killed by a particular process are 1 in every 500 years. Should the worker be satisfied or alarmed? What is the FAR (assuming normal working hours) and the deaths per person per year? What should her chances be, assuming an average chemical plant?
- 1-5. A plant employs 1500 full-time workers in a process with a FAR of 5. How many industrial-related deaths are expected each year?
- 1-6. Consider Example 1-4. How many hours must be traveled by car for each hour of rock climbing to make the risk of fatality by car equal to the risk of fatality by rock climbing?

1-7. Identify the initiation, propagation, and termination steps for the following accident reports.¹⁸ Suggest ways to prevent and contain the accidents.

- a.** A contractor accidentally cut into a 10-in propane line operating at 800 psi at a natural gas liquids terminal. The large vapor cloud estimated to cover an area of 44 acres was ignited about 4–5 min later by an unknown source. Liquid products from 5 of 26 salt dome caverns fed the fire with an estimated 18,000–30,000 gal of LPGs for almost 6 hr before being blocked in and the fires extinguished. Both engine-driven fire pumps failed, one because intense radiated heat damaged its ignition wires and the other because the explosion broke a sight glass fuel gauge, spilling diesel fuel, which ignited, destroying the fire pump engine.
- b.** An alkylation unit was being started up after shutdown because of an electrical outage. When adequate circulation could not be maintained in a deisobutanizer heater circuit, it was decided to clean the strainer. Workers had depressurized the pipe and removed all but three of the flange bolts when a pressure release blew a black material from the flange, followed by butane vapors. These vapors were carried to a furnace 100 ft away, where they ignited, flashing back to the flange. The ensuing fire exposed a fractionation tower and horizontal receiver drums. These drums exploded, rupturing pipelines, which added more fuel. The explosions and heat caused loss of insulation from the 8-ft × 122-ft fractionator tower, causing it to weaken and fall across two major pipelines, breaking piping — which added more fuel to the fire. Extinguishment, achieved basically by isolating the fuel sources, took 2½ hours.

The fault was traced to a 10-in valve that had been prevented from closing the last ¾-inch by a fine powder of carbon and iron oxide. When the flange was opened, this powder blew out, allowing liquid butane to be released.

- 1-8.** The airline industry claims commercial airline transport has fewer deaths per mile than any other means of transportation. Do the accident statistics support this claim? In 1984 the airline industry posted 4 deaths per 10,000,000 passenger miles. What additional information is required to compute a FAR? a fatality rate?
- 1-9.** A university has 1200 full-time employees. In a particular year this university had 38 reportable lost-time injuries with a resulting 274 lost workdays. Compute the OSHA incidence rate based on injuries and lost workdays.
- 1-10.** Based on workplace fatalities (Figure 1-4) and assuming you are responsible for a safety program of an organization, what would you emphasize?
- 1-11.** Based on the causes of the largest losses (Figure 1-7), what would you emphasize in a safety program?
- 1-12.** After reviewing the answers to Problems 1-10 and 1-11, can inherent safety help?
- 1-13.** What conclusions can you derive from Figure 1-9?
- 1-14.** What is the worst thing that could happen to you as a chemical engineer in industry?
- 1-15.** An explosion has occurred in your plant and an employee has been killed. An investigation shows that the accident was the fault of the dead employee, who manually charged the

¹⁸*One Hundred Largest Losses.*

wrong ingredient to a reactor vessel. What is the appropriate response from the following groups?

- a. The other employees who work in the process area affected.
- b. The other employees elsewhere in the plant site.
- c. Middle management.
- d. Upper management.
- e. The president of the company.
- f. The union.

1-16. You have just begun work at a chemical plant. After several weeks on the job you determine that the plant manager runs the plant with an iron fist. He is a few years away from retirement after working his way up from the very bottom. Also, a number of unsafe practices are performed at the plant, including some that could lead to catastrophic results. You bring up these problems to your immediate supervisor, but he decides to do nothing for fear that the plant manager will be upset. After all, he says, “We’ve operated this plant for 40 years without an accident.” What would you do in this situation?

- 1-17. a.** You walk into a store and after a short while you decide to leave, preferring not to do any business there. What did you observe to make you leave? What conclusions might you reach about the attitudes of the people who manage and operate this store?
- b.** You walk into a chemical plant and after a short while you decide to leave, fearing that the plant might explode at any moment. What did you observe to make you leave? What conclusions might you reach about the attitudes of the people who manage and operate this chemical plant?

Comment on the similarities of parts a and b.

1-18. A large storage tank is filled manually by an operator. The operator first opens a valve on a supply line and carefully watches the level on a level indicator until the tank is filled (a long time later). Once the filling is complete, the operator closes the valve to stop the filling. Once a year the operator is distracted and the tank is overfilled. To prevent this, an alarm was installed on the level gauge to alert the operator to a high-level condition. With the installation of the alarm, the tank now overfills twice per year. Can you explain?

1-19. Careful numbering of process equipment is important to avoid confusion. On one unit the equipment was numbered J1001 upward. When the original allocation of numbers ran out the new equipment was numbered JA1001 upward. An operator was verbally told to prepare pump JA1001 for repairs. Unfortunately, he prepared pump J1001 instead, causing an upset in the plant. What happened?

1-20. A cover plate on a pump housing is held in place by eight bolts. A pipefitter is instructed to repair the pump. The fitter removes all eight bolts only to find the cover plate stuck on the housing. A screwdriver is used to pry off the cover. The cover flies off suddenly, and toxic liquid sprays throughout the work area. Clearly the pump unit should have been isolated, drained, and cleaned before repair. There is, however, a better procedure for removing the cover plate. What is this procedure?

- 1-21.** The liquid level in a tank 10 m in height is determined by measuring the pressure at the bottom of the tank. The level gauge was calibrated to work with a liquid having a specific gravity of 0.9. If the usual liquid is replaced with a new liquid with a specific gravity of 0.8, will the tank be overfilled or underfilled? If the actual liquid level is 8 m, what is the reading on the level gauge? Is it possible that the tank will overflow without the level gauge indicating the situation?
- 1-22.** One of the categories of inherent safety is simplification/error tolerance. What instrumentation could you add to the tank described in Problem 1-21 to eliminate problems?
- 1-23.** Pumps can be shut-in by closing the valves on the inlet and outlet sides of the pump. This can lead to pump damage and/or a rapid increase in the temperature of the liquid shut inside the pump. A particular pump contains 4 kg of water. If the pump is rated at 1 HP, what is the maximum temperature increase expected in the water in °C/hr? Assume a constant water heat capacity of 1 kcal/kg/°C. What will happen if the pump continues to operate?
- 1-24.** Water will flash into vapor almost explosively if heated under certain conditions.
- What is the ratio in volume between water vapor at 300 K and liquid water at 300 K at saturated conditions?
 - Hot oil is accidentally pumped into a storage vessel. Unfortunately, the tank contains residual water, which flashes into vapor and ruptures the tank. If the tank is 10 m in diameter and 5 m high, how many kilograms of water at 300 K are required to produce enough water vapor to pressurize the tank to 8 in of water gauge pressure, the burst pressure of the tank?
- 1-25.** Another way of measuring accident performance is by the LTIR, or lost-time injury rate. This is identical to the OSHA incidence rate based on incidents in which the employee is unable to continue their normal duties. A plant site has 1200 full-time employees working 40 hr/week and 50 weeks/yr. If the plant had 2 lost-time incidents last year, what is the LTIR?
- 1-26.** A car leaves New York City and travels the 2800-mi distance to Los Angeles at an average speed of 50 mph. An alternative travel plan is to fly on a commercial airline for 4½ hr. What are the FARs for the two methods of transportation? Which travel method is safer, based on the FAR?
- 1-27.** A column was used to strip low-volatile materials from a high-temperature heat transfer fluid. During a maintenance procedure, water was trapped between two valves. During normal operation, one valve was opened and the hot oil came in contact with the cold water. The result was almost sudden vaporization of the water, followed by considerable damage to the column. Consider liquid water at 25°C and 1 atm. How many times does the volume increase if the water is vaporized at 100°C and 1 atm?
- 1-28.** Large storage tanks are designed to withstand low pressures and vacuums. Typically they are constructed to withstand no more than 8 in of water gauge pressure and 2.5 in of water gauge vacuum. A particular tank is 30 ft in diameter.

- a. If a 200-lb person stands in the middle of the tank roof, what is the resulting pressure (in inches of water gauge) if the person's weight is distributed across the entire roof?
- b. If the roof was flooded with 8 in of water (equivalent to the maximum pressure), what is the total weight (in pounds) of the water?
- c. A large storage tank was sucked in when the vent to the outside became plugged and the operator turned on the pump to empty the tank. How did this happen?

Note: A person can easily blow to a pressure of greater than 20 in of water gauge.

- 1-29. A 50-gal drum with bulged ends is found in the storage yard of your plant. You are unable to identify the contents of the drum. Develop a procedure to handle this hazard. There are many ways to solve this problem. Please describe just one approach.
- 1-30. The plant has been down for extensive maintenance and repair. You are in charge of bringing the plant up and on-line. There is considerable pressure from the sales department to deliver product. At about 4 AM a problem develops. A slip plate or blind has accidentally been left in one of the process lines. An experienced maintenance person suggests that she can remove the slip plate without depressurizing the line. She said that she routinely performed this operation years ago. Since you are in charge, what would you do?
- 1-31. Gasoline tank trucks are load restricted in that the tank must never be between 20% and 80% full when traveling. Or it must be below 20% and above 80%. Why?
- 1-32. In 1891 the copper industry in Michigan employed 7702 workers. In that year there were 28 fatalities in the mines. Estimate the FAR for this year, assuming that the workers worked 40-hour weeks and 50 weeks per year. Compare the result to the published FAR for the chemical industry.
- 1-33. The Weather Channel reports that, on average, about 42 Americans are killed by lightning each year. The current population of the U.S. is about 300 million people. Which accident index is suitable for this information: FAR, OSHA incident rate, or deaths per person per year? Why? Calculate the value of the selected index and compare it to published values.
- 1-34. The CSB video "Preventing Harm from Sodium Hydrosulfide" presents an incident involving sodium hydrosulfide (NaSH) and hydrogen sulfide (H_2S). Go on-line and find at least two material safety data sheets (MSDS) for both of these chemicals. Tabulate the following physical properties for these chemicals at room temperature and pressure, if available: physical state density, PEL, TLV, and vapor pressure. List any other concerns that might be apparent from the MSDS. Which of these properties are of major concern in using these chemicals?

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