



Process Hazards (Chemical)

Core Body of Knowledge for the
Generalist OHS Professional



Safety Institute
of Australia Ltd



Australian OHS Education
Accreditation Board

Copyright notice and licence terms

Copyright (2017 Safety Institute of Australia Ltd, Tullamarine, Victoria, Australia)

This work is copyright and has been published by the Safety Institute of Australia Ltd (SIA). Except as may be expressly provided by law and subject to the conditions prescribed in the Copyright Act 1968 (Commonwealth of Australia), or as expressly permitted below, no part of the work may in any form or by any means (electronic, mechanical, microcopying, digital scanning, photocopying, recording or otherwise) be reproduced, stored in a retrieval system or transmitted without prior written permission of the SIA.

You are free to reproduce the material for reasonable personal, or in-house, non-commercial use for the purposes of workplace health and safety as long as you attribute the work using the citation guidelines below and do not charge fees directly or indirectly for use of the material. You must not change any part of the work or remove any part of this copyright notice, licence terms and disclaimer below.

A further licence will be required and may be granted by the SIA for use of the materials if you wish to:

- reproduce multiple copies of the work or any part of it
- charge others directly or indirectly for access to the materials
- include all or part of the materials in advertising of a product or services, or in a product for sale
- modify the materials in any form, or
- publish the materials.

Enquiries regarding the licence or further use of the works are welcome and should be addressed to:

The Manager, OHS Body of Knowledge

Safety Institute of Australia Ltd, PO Box 2078, Gladstone Park, Victoria, Australia, 3043

info@ohsbok.org.au

Bibliography

ISBN 978 0 980843 2 7

Citation of the whole *Body of Knowledge* should be as:

Safety Institute of Australia (SIA), (2017) The Core Body of Knowledge for Generalist OHS Professionals. Tullamarine, VIC. Safety Institute of Australia.

This chapter should be cited as:

Kerin, T. (2017). Process Hazards (Chemical) In *The Core Body of Knowledge for Generalist OHS Professionals.* Tullamarine, VIC. Safety Institute of Australia.

Disclaimer

This material is supplied on the terms and understanding that the Safety Institute of Australia Ltd and their respective employees, officers and agents, the editor, or chapter authors and peer reviewers shall not be responsible or liable for any loss, damage, personal injury or death suffered by any person, howsoever caused and whether or not due to negligence, arising from the use of or reliance of any information, data or advice provided or referred to in this publication. Before relying on the material, users should carefully make their own assessment as to its accuracy, currency, completeness and relevance for their purposes, and should obtain any appropriate professional advice relevant to their particular circumstances.

Readers should refer to 1 *Preliminaries* for a full list of chapters and authors and a synopsis of the OHS Body of Knowledge. Chapter 2, *Introduction* describes the background and development process while Chapter 3, *The OHS Professional in Australia* provides a context by describing the role and professional environment.

Acknowledgements

This chapter is the result of a joint project between the Safety Institute of Australia and the Institution of Chemical Engineers.



The Safety Institute of Australia financially and materially supports the OHS Body of Knowledge as a key requirement of the profession.

Under the strategic pillar of *Capability*, the SIA has the strategic objective to

Provide an up-to-date body of knowledge for the profession on which Higher Education and continuing professional development is based.

Thus, the OHS Body of Knowledge is strategically important to the SIA and vital for the profession.



The OHS Body of Knowledge provides a framework for OHS professional education and for continuing professional development. As the body managing accreditation of OHS professional education, the Australian OHS Education Accreditation Board is the ‘custodian’ of the OHS Body of Knowledge, and has a major role in the development and review of individual chapters to ensure that the quality and evidence-base reflects current OHS research and leading edge thinking and so provides a suitable standard for OHS education and professional development.



The IChemE Safety Centre (ISC) is a not-for-profit industry-led organisation with a vision to be a global go to organisation for process safety benchmarking, sharing of best practice and education, and be a forum for developing solutions to common problems. This collaboration with the OHS Body of Knowledge fits with ISC strategic direction to maintain close connections with other like-minded organisations and set the benchmark for process safety across industry and academia.

Process Hazards (Chemical)

Trish Kerin BEng(Mech)(Hons), DipOHS, GAICD, CEng, FIChemE, Professional Process Safety Engineer, FIEAust

Director, IChemE Safety Centre, Institution of Chemical Engineers

Email: tkerin@icheme.org

After graduating with honours in mechanical engineering, Trish spent several years working in project management, operational and safety roles for the oil, gas and chemical industries. Trish has represented industry on many government committees related to process safety, and currently sits on the board of the National Offshore Petroleum Safety and Environmental Management Authority (NOPSEMA) and the Mary Kay O'Connor Process Safety Center steering committee. Trish leads the IChemE Safety Centre, a not-for-profit industry-led consortium focused on improving process safety.

**Core Body of
Knowledge for the
Generalist OHS
Professional**

Topic Specific Technical Panel

Members of the Topic Specific Technical Panel and authors were selected on the basis of their demonstrated specialist expertise. Panel members were not remunerated; they provided input and critical comment as part of their contributions to the OHS profession and to workplace health and safety.

Trish Kerin	Chair	Director, IChemE Safety Centre
Pam Pryor	OHSBOKEA liaison	Registrar, Australian OHS Education Accreditation Board
Joe Aiken	Topic specialist	Consultant, Safety Solutions
Andrew Battye	Topic specialist	Team Coordinator, Dangerous Goods & Explosives, SafeWork NSW
Daniel Grivicic	Topic specialist	Lead Engineer, Machine Safety, Electro80
Roisin Johnson	Topic specialist	Manager, Risk Engineering, WorleyParsons
Yogesh Koirala	Topic specialist	Researcher, Mary Kay O'Connor Process Safety Center, Texas
Fiona Murfitt	Generalist OHS professional	Group HSSE Manager, Viva Energy
Ivica Ninic	Topic specialist	Principal Process Safety Engineer, Origin
Alan Munn	Topic specialist	Consultant, MMI Engineering
Chad Pettitt	Generalist OHS professional	Lead Consultant, AusSafe
Zeeshan Qureshi	Topic specialist	Inspector, Major Hazards Unit, SafeWork NSW
Vanessa Russell	Generalist OHS professional	Principal Advisor HSE, Origin
Tony Smith	Generalist OHS professional	Manager, Business Risk, East Gippsland Water
Jon Temby	Generalist OHS professional	Director, Axento Safety
Andrew Woodhams	Topic specialist	Director, Safety Programs, Australian Petroleum Production & Exploration Association

Peer reviewers

Sidney Abiodun	Senior Inspector Onshore, Major Hazards Facility, WA Department of Mines and Petroleum
Paul Amyotte	Professor, Dalhousie University, Canada
Kym Bills	Executive Director, National Resource Sciences Precinct, Perth
Simon Farrar	Manager Systems Safety, WorkSafe Victoria
Jan Hayes	Associate Professor, RMIT University
Peter Hicks	Prelude Production HSSE Manager, Shell Australia
Andrew Hopkins	Emeritus Professor, Australian National University
Jennifer Lourie	Production AIPSM Lead, Shell Australia
Vince McNeilly	General Manager, McNeilly Consulting, UK
Tony Pooley	CEO, Principle Seven
Leo Ruschena	Senior Lecturer, RMIT University
David Skegg	Lecturer, Central Queensland University
Derek Viner	Associate Professor, Central Queensland University
Laurentiu Zamfirescu	Senior Inspector (Technical Process Safety), WA Department of Mines and Petroleum

Andrew Hopkins
Emeritus Professor, Australian National University

If I were an OHS professional I'd be delighted to have this material gathered together in one place like this. ...
An OHS professional who grasps this material will be far more effective as a result.

Dame Judith Hackitt DBE FREng
Chair of the UK Health and Safety Executive 2007 -2016 and Past President of IChemE

I applaud the work of the group who have produced this vital material which will enable process safety specialists and OHS professionals to work together with common understanding of each other's languages and competences. This is a vital step in moving towards a fully integrated approach to safety which focusses on all of the issues and, most importantly, breaks down the silos in thinking.

Peter Dunphy
Executive Director, SafeWork NSW
Acting Deputy Secretary, Better Regulation Division, Department of Finance, Services and Innovation

It has been a pleasure for SafeWork NSW to contribute to the Process Safety chapters of the OHS Body of Knowledge. This collaborative effort has helped benchmark the core knowledge for generalist OHS professionals who work in a process safety environment, as well as in helping make workplaces safer.

Marnie Williams
Executive Director Health & Safety, WorkSafe Victoria"

As original sponsors of the OHS Body of Knowledge project, WorkSafe Victoria is pleased to see the inclusion of the Process Safety chapters. WorkSafe Victoria supports the development of the new chapters as a part of the education of any OHS professional exposed to process safety, with the aim of achieving safer workplaces.

Patrick Murphy
Chair, Safety Institute of Australia

Low probability high consequence events have sadly been taking place throughout history. The emergence of process safety has contributed to broadening our knowledge and understanding of such events. I am pleased to see the addition of this chapter to the Body of Knowledge as it provides a common basis to closing the knowledge gap between the OHS generalist and other professionals who collectively work to prevent such events in workplaces.

Core Body of Knowledge for the Generalist OHS Professional

Process Hazards (Chemical)

Abstract

Chemical process hazards may be associated with high-consequence outcomes of fire, explosion and/or release of toxic substances. While the management of such hazards is usually the responsibility of those with specialist process safety or chemical expertise, generalist occupational health and safety (OHS) professionals should understand the basic science underpinning the characteristics of such hazards, the mechanisms by which they cause harm, potential consequences – fire, explosion and toxic effect – and common controls. As a companion chapter to *OHS Body of Knowledge Managing Process Safety*, and with reference to the Globally Harmonised System (GHS) of Classification of Labelling of Chemicals, this chapter provides information vital for understanding and applying process safety management strategies. Such knowledge will enable generalist OHS professionals to effectively engage with process safety and chemical safety experts, contribute to better hazard control and reduce the risk of catastrophic events.

Keywords

process safety, hazardous substances, chemical, fire, explosion, toxic release, GHS, barrier

Contents

1	Introduction.....	1
1.1	Process for developing the chapter content.....	2
2	Historical perspective.....	2
3	Extent of the problem.....	3
4	Underpinning science.....	3
5	Chemical process hazards	5
5.1	Hazardous substances.....	5
5.2	Sources of ignition	11
5.3	Operating temperatures	13
6	Consequences.....	13
6.1	Fires.....	14
6.2	Explosions	15
6.3	Toxic effects.....	20
7	Legislation and standards.....	22
8	Control	23
8.1	Layers of protection	23
8.2	Barriers	24
8.3	Elimination	26
8.4	Prevention.....	26
8.5	Mitigation.....	26
9	Implications for OHS practice	27
10	Summary	27
	Useful resources.....	28
	References.....	29

List of Figures

Figure 1	Fire tetrahedron	7
Figure 2	Relationships between flammability characteristics and flammability range	8
Figure 3	Dust explosion pentagon	18
Figure 4	Representation of overpressure contours and flame spread in a refinery explosion.....	20
Figure 5	3-D representation of the impact of a carbon monoxide release in a refinery	21
Figure 6	‘Onion’ representation of LOPA	23
Figure 7	Schematic LOPA diagram	24
Figure 8	Summary of hazardous substances, consequences and impacts with barriers as controls	28

List of Tables

Table 1	Sources of ignition	12
---------	---------------------------	----

1 Introduction

Discussions of risk and the mechanisms of hazardous-chemical-event causation often differentiate between low-likelihood events of high potential consequence and higher-likelihood events of lower consequence (e.g. Hale, 2001). Many high-consequence events are associated with the hydrocarbon or processing industries. A review of the 100 largest losses in the hydrocarbon industry occurring globally between 1974 and 2015 identified a total of US\$20.22 billion in insurable losses (Marsh, 2016),¹ and more than 3000 fatalities associated with these and other high-consequence events in the oil, gas and coal industries.

The management of hazards associated with potentially high-consequence events, especially those in the oil, gas, hydrocarbon and coal industries, has become the discipline of ‘process safety’.² This chapter summarises the basic science underpinning the characteristics of process hazards and the mechanisms by which these hazards cause harm, and provides an introduction to common controls. The scope of this chapter is limited to what might be considered ‘chemical’ process hazards while recognising that the range of process hazards may be very broad.³

The primary target audience for this chapter includes generalist OHS professionals (without engineering or chemical backgrounds) who are:

- Working in Major Hazard Facilities or other process environments with process safety professionals or
- Working in facilities with process hazards where process safety professionals are not available on site but may be available on a consulting basis or
- Seeking an understanding of process hazards to inform their practice more generally.

This chapter, and the *OHS Body of Knowledge* companion chapter Managing Process Safety, support achievement of the *Australian Work Health and Safety Strategy 2012-22* vision for “healthy, safe and productive working lives” (SWA, 2012, p. 3). This strategic objective is to be achieved by reducing exposure to hazards and risk with improved controls. A broad understanding of process hazards will contribute to better hazard controls as well as to reduced risk of a catastrophic event. These chapters also contribute to achievement of the strategic outcome that “Those providing work health and safety...advice have the appropriate capabilities” (SWA, 2012, p. 9).

¹ This estimate does not include uninsured losses such as regulatory fines, legal costs, personal injury costs and impact on reputation.

² See *OHS BoK* Managing Process Safety for an outline of concepts underpinning the discipline of process safety from the perspective of the generalist OHS professional. Participation of the generalist OHS professional in managing process safety requires knowledge of chemical hazards generally as well as knowledge of the nature and action of chemical hazards with potentially high consequences.

³ See *OHS BoK* Chemical Hazards.

1.1 Process for developing the chapter content

This chapter is the outcome of a joint project of the Institution of Chemical Engineers (IChemE) Safety Centre (ISC) and the Safety Institute of Australia (SIA). Chapter scope and content was determined by a technical panel of process safety professionals and generalist OHS professionals. In some cases, members of the technical panel also contributed text. A chapter draft was reviewed by a number of process safety and generalist OHS professionals with the final version being the result of professional editing to ensure consistency with other chapters of the *OHS Body of Knowledge*.

2 Historical perspective

There has been a litany of disasters through which our understanding of process hazards has evolved. Early understanding of the potential consequences of loss of control of chemical processes was demonstrated by the Du Pont company, which was founded in 1802 with a strong emphasis on accident prevention and mitigation. Company founder E. I. du Pont asserted “we must seek to understand the hazards we live with” (Klein, 2009, p. 114) and, over the next 200 years, the design and operation of Du Pont explosives factories were gradually improved as the result of consistent effort to understand cause and prevention of catastrophic explosions.

Coal dust and methane explosions were a constant risk in mining during the industrial revolution and remain so today. A 1906 coal dust explosion at the Courrières Colliery in France killed 1099 miners and was pivotal in focusing attention on dust explosions and the need to research for prevention and management (Sapko et al., 2010). More recently the US Chemical Safety Board identified “281 combustible dust incidents between 1980 and 2005 that killed 119 workers and injured 718” (Atherton & Gil, 2008, p. 143).

The second half of the twentieth century saw a number of disastrous chemical releases of 2,4,5-trichlorophenol (dioxin).⁴ In 1976, an explosion at a chemical plant in Seveso, Italy, resulted in a toxic vapour cloud that spread over a large, densely populated area, contaminating humans, animals, crops and land (Atherton & Gil, 2008). A significant policy outcome of the Seveso disaster was the European Community’s Seveso Directive that introduced a new system of industrial regulation for ‘Major Hazards’. Although this directive has been updated following other disasters, at the time it constituted paradigm change (Atherton & Gil, 2008; da Cruz & Bentez, 2013).

The 1984 release of a toxic cloud of methyl isocyanate at the Union Carbide India Limited pesticide plant in Bhopal is considered the world’s worst industrial accident (Essa, 2014).

⁴ e.g. 1949 Monsanto (USA), 1953 BASF (Germany), 1960 Dow Chemical (USA), 1963 Philips Duphar (Netherlands), 1968 Coalite & Chemical Products (UK) (Atherton & Gil, 2008).

Thousands of deaths and hundreds of thousands of injuries occurred, with an unknown number of people continuing to suffer physically and psychologically. The Bhopal event created awareness of the importance of safety by design, which has since become a key focus of process safety (Essa, 2014; da Cruz & Bentes, 2013).

From a petroleum industry perspective, the full impact of a high-consequence event was realised in 1988 following an explosion and fire on the Piper Alpha drilling platform in the North Sea. The result was the loss of 167 lives and the highest-recorded property loss associated with a hydrocarbon event (Marsh, 2016). The Piper Alpha disaster led to legislation requiring safety cases and a safety management system in high-hazard environments to ensure effective and consistent application of controls.⁵

3 Extent of the problem

As noted in section 1, the 100 largest insurable property losses occurring globally in the hydrocarbon industry between 1974 and 2015 amounted to US\$20.22 billion, an estimate that does not include uninsured losses such as regulatory fines and other legal costs, or reputational impact on business (Marsh, 2016). More than 3000 people died as a result of disasters involving process hazards during this period.⁶

Outcomes of events associated with loss of control of chemical process hazards (mainly hydrocarbons) include fire, explosion, release of toxic product and mechanical damage. Explosions (mainly vapour cloud explosions) account for nearly 63% of financial losses associated with the 100 largest losses since 1974 and fire events are responsible for 13% (Marsh, 2016).

4 Underpinning science

Knowledge of some basic science principles is required to understand process hazards, and their actions and potential consequences.⁷ A very basic summary is provided below.

⁵ The purpose of a safety case is to “communicate a clear, comprehensive and defensible argument that a system is acceptably safe to operate in a particular context” (Kelly, 2003). It is developed through a systematic process of hazard and risk identification, and describes how the risks are controlled and the safety management system in place. See *OHS BoK Managing Process Safety*.

⁶ See *OHS BoK Managing Process Safety* for further detail on the extent of the problem.

⁷ *OHS BoK Foundation Science* stipulates that generalist OHS professionals must have a broad multidisciplinary knowledge base, including a grasp of basic physical/chemical and biological/health sciences together with the principles and key concepts of psychology. Figure 1 in that chapter is a topic map of physical/chemical science concepts that underpin OHS practice, highlighting various forms of energy and providing a basis for understanding physical and chemical hazards as sources of potentially damaging energy. Aspects of the science described in that topic map, particularly those related to pressure, chemical and heat energy are important in understanding process hazards.

Matter

- Matter essentially occurs in three states – solid, liquid and gas. The gaseous forms of substances that are solids or liquids under normal temperature are vapours.
- Gases differ from solids and liquids in that a gas expands spontaneously to fill its container. A gas is highly compressible. The relationship between pressure, temperature and volume of a gas can be described mathematically by the Combined Gas Law, which is based on three key relationships:
 - The volume of a gas is inversely related to the pressure at a given temperature
 - At constant pressure, the volume of a gas is directly proportional to its temperature
 - The pressure of a gas at constant volume is proportional to the temperature.If the temperature changes then either the pressure or volume or both will change in proportion to the temperature.

$$(P_1V_1)/T_1=(P_2V_2)/T_2 \text{ (Combined Gas Law)}$$

Most importantly in process safety, as the volume decreases the pressure increases, and as the pressure for a fixed volume of gas increases, the temperature will also increase.

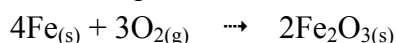
Energy

- Energy cannot be created or destroyed, but it can be transferred to another object or transformed into another form of energy.
- Heat transfer occurs from hot to cold via conduction, convection and/or radiation.
- Matter is made up of molecules, which are individual atoms held together by bonds that embody energy.

Chemical reactions

- Chemical reactions involve the breaking and/or making of molecular bonds with associated changes in energy level. Breaking molecular bonds requires an input of energy (endothermic reaction) while creating bonds releases energy (exothermic reaction).
- Chemical reactivity is the tendency of a substance to undergo chemical reaction, either by itself or with other materials and, in most cases, to release energy.
- The rate of a chemical reaction is affected by: concentration and physical state of the reactants; temperature; surface area of the reactants; presence of solvents and catalysts; and, for gases, pressure. If the heat generated by a reaction is greater than the maximum rate of cooling, a runaway reaction can occur where the reaction speed continues to accelerate until reactants are used up or the vessel containing it overpressures and loses containment, frequently with high risk of injury and equipment damage. Loss of control of the process can be indicated by the process operating outside temperature limits, which will affect pressure as well as rate of reaction.
- A catalyst speeds up the rate of reaction by lowering the amount of energy required to make the reaction happen without itself being changed by the chemical reaction.

- An initiator speeds up the rate of reaction by lowering the amount of energy required to make the reaction happen and is consumed in the chemical reaction.
- A chemical reaction important in process safety is the oxidation-reduction reaction; this is known as a REDOX reaction, as the two processes occur simultaneously. The formation of rust is an example of a REDOX reaction between iron and oxygen involving moisture; this process can be represented in the chemical equation:



While oxidation involves oxygen, the presence of oxygen gas is not a requirement for a REDOX reaction as other chemicals may act as oxidisers (section 5.1.3). REDOX reactions have the potential to damage the integrity of materials used in construction, creating process hazards.

5 Chemical process hazards

Chemical process hazards include substances with inherently hazardous properties as well as materials stored, handled or processed under conditions that make them hazardous. Chemical process hazards with inherently hazardous properties are addressed here under two headings: (1) hazardous substances and (2) sources of ignition. Materials that, depending on conditions, may become hazardous (e.g. compressed air, hot water and molten metal) are not addressed in this chapter. A third section considers the relevance of operating temperatures.

5.1 Hazardous substances

From 2017, Australian workplaces are required to be compliant with the Globally Harmonised System (GHS) of Classification and Labelling of Chemicals.⁸ Under the GHS, manufacturers and importers of hazardous chemicals are required to provide information on chemicals in a standard format via labels and safety data sheets (SDSs).⁹ The GHS defines nine categories of hazardous chemicals, five of which are considered in this chapter as hazards that may be involved in a hazardous process event:

- Flammable
- Explosive
- Oxidising
- Corrosive
- Gases under pressure.

Aspects of other GHS hazard categories are considered in a single section:

- Acute toxicity – health hazards and environmental hazards.

⁸ See *OHS BoK Chemical Hazards* for an introduction to the GHS.

⁹ See *OHS Bok Chemical Hazards* section 4.3 (Identifying chemical hazards) for information on labels and SDSs.

In addition, this chapter considers four further hazards that may be implicated in process events:

- Reactive and incompatible substances
- Steam
- Combustible dusts
- Inert gases.

Hazardous substances may demonstrate hazardous characteristics of more than one category.

5.1.1 Flammable

Under the GHS, flammable substances include solids, liquids, gases, liquefied gases, aerosols/mists and atmospheres.

Three elements – often referred to as the ‘fire triangle’ – are required for a flammable substance to ignite:

- Fuel – the flammable substance
- Oxidant – usually oxygen contained in air is sufficient for the chemical fire reaction
- Ignition source – the energy source capable of igniting the substance (see section 5.2) (e.g. Mannan, 2012).¹⁰

More recently a fourth element has been added – an uninhibited chemical chain reaction to feed heat back to the fire to maintain it – with the four elements referred to as the ‘fire tetrahedron’ (Figure 1).

¹⁰ When confined, these same elements may result in an explosion (see section 6.2).

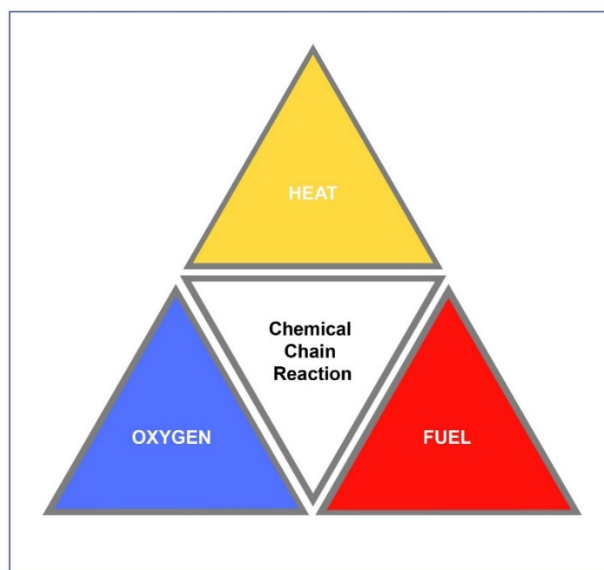


Figure 1: Fire tetrahedron

While it is often believed that removal of one component of the tetrahedron will prevent a fire, the ubiquity of sources of ignition dictates that the primary focus should be on preventing formation of flammable atmospheres (Kletz, 1996).

Flammability is described in terms of flammability limits. “A flammable gas or vapor will burn in air only over a limited range of compositions” (Smith, 2016). Below a certain concentration of gas in air, the *lower flammability/explosive limit* (LFL/LEL), the mixture will not burn; above a certain concentration, the *upper flammability/explosive limit* (UFL/UEL), the mixture will not burn as the excess air acts as an inert gas and absorbs energy. The concentration between these two values is the *flammability range* (Smith, 2016). The LEL and UEL are temperature and pressure dependent.

Autoignition temperature (AIT) is the lowest temperature at which a substance will spontaneously ignite at atmospheric pressure without an external source of ignition.

Flammability of a liquid is described in terms of *flash point* – the lowest temperature at which a mixture of air saturated with vaporised liquid can be ignited. At this temperature, the released energy will be insufficient to vaporise more liquid and sustain the flame (hence the ‘flash’). Increasing the temperature a few degrees to the *fire point* will enable the flame to be sustained. Liquids handled at temperatures below their flash point present a lower risk than those handled above flash point. Care should be taken in using the flash point as a basis for assessing the hazard as a liquid may be ignited well below its flash point if it is in the form of a fine mist, a thin film, at low pressure or contaminated with a liquid of lower flash point (Kletz, 1996).

The interaction between temperature and flammability characteristics is depicted in Figure 2, which highlights the zone where a substance is most likely to be ignited (Zabetakis as cited in Mannan, 2012).

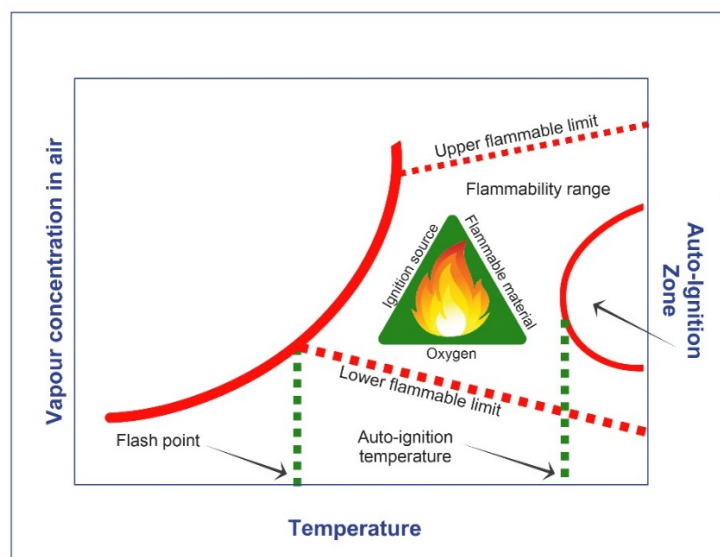


Figure 2: Relationships between flammability characteristics and flammable range

5.1.2 Explosive

“Explosive properties [of a substance] are associated with the presence of certain chemical groups in a molecule which can react to produce very rapid increases in temperature or pressure” (UN, 2011, p. 50). Explosive substances differ from explosive atmospheres, in that oxygen in the atmosphere is not needed to sustain the reaction (Eckhoff, 2016). These substances may be specifically formulated to produce this effect (e.g. trinitrotoluene or TNT) or may be formulated for other purposes (e.g. ammonium nitrate) with detonation occurring via either accidental triggering (e.g. through external influence, such as lightning or chemical degradation making the substance unstable) or deliberate action through a detonator. The GHS defines an explosive substance as:

...a solid or liquid substance (or mixture of substances) which is in itself capable by chemical reaction of producing gas at such a temperature and pressure and at such a speed as to cause damage to the surroundings. Pyrotechnic substances are included even when they do not evolve gases. (UN, 2011, p. 12)

5.1.3 Oxidising

Oxidisers are substances that produce oxygen when they react under certain conditions. This oxygen can subsequently fuel a fire or result in a REDOX reaction. Oxidising substances include:

- Solids (e.g. metal peroxides, ammonium nitrate)
- Liquids (e.g. hydrogen peroxide, nitric acid, perchloric acid)
- Gases (e.g. oxygen, fluorine, chlorine).

5.1.4 Corrosive

Corrosive substances can damage equipment and structures by undergoing a REDOX reaction with the base material of construction, resulting in structural failure. The corrosive nature of substances may be dependent on the conditions under which they are stored. Eleven common types of corrosion (Mannan, 2012, p. 594) are:

- General corrosion
- Scaling
- Exfoliation
- Galvanic corrosion
- Crevice corrosion
- Pitting
- Stress-related corrosion
 - Stress corrosion cracking
 - Corrosion fatigue
 - Stress-enhanced corrosion
- Intergranular corrosion
- Knife-line corrosion
- Erosion
- External corrosion.

Decisions in design and construction phases should consider the most appropriate methods to manage the risk of corrosion. This may be selection of a specific material, or the addition of a corrosion allowance to account for the expected corrosion.

5.1.5 Gases under pressure

The storage of gas under pressure creates stored potential energy, which is a hazard. Rapid release of the gas, such as in structural failure of a vessel or valve, releases stored potential energy, which can result in:

- A jet of gas that can apply excessive force on objects in its path
- Movement of the storage vessel in the opposite direction to the jet
- Significant cooling of the gas jet and anything in its path (which may cause freezing or embrittlement issues for other equipment)
- Erosion at the original release point resulting in catastrophic failure of the storage vessel
- Catastrophic failure of the storage vessel.

5.1.6 Reactive and incompatible substances

Some substances are reactive by nature; they tend to react and change form of their own accord. Examples of reactive substances include monomers and resins, which tend to polymerise (e.g. a monomer gas reacting and forming a solid polymer). Such reactions are frequently exothermic and the heat generated increases the rate of reaction, thereby generating more heat and so on. This type of reaction is often used in industry; for safe outcomes, however, temperatures and pressures must be strictly controlled.

Substances are considered incompatible when they react together to generate undesirable outcomes (e.g. create toxic, corrosive or reactive products or intermediates and result in temperature or pressure changes). For example, sulphuric acid and sodium hypochlorite may be stored at the same facility, but mixing of these two substances will generate chlorine gas, which may result in a toxic exposure.

5.1.7 Steam

Steam is a common feature in many workplaces and processes. Steam may provide power or heating, purge equipment as part of startup or shut down, or be an integral part of the process.

Steam is produced by heating water. At atmospheric pressure, water will vaporise into steam at 100°C with both the water and steam at the same temperature. If the escape of steam is restricted, the pressure will increase requiring higher temperatures to continue boiling the water. However, when steam is separated from water further heating will increase the steam temperature with the steam becoming ‘superheated’.

Escaping steam can cause severe burns both by direct contact with the steam and indirectly through contact with objects heated by the steam. Also, steam can cause thermal expansion of vessels and piping leading to over-stressing and potential rupture, and cooling steam can leave condensate that reacts with the process or the condensing steam may cause pressure to fall. In piping systems this can rapidly accelerate ‘slugs’ of water, resulting in water hammer due to impact on pipe fittings and pipe ends, and potentially cause pipe deformations and ruptures. Furthermore, condensing steam can draw air into a vessel creating a flammable mixture, and steam jets can produce static electricity that acts as an ignition source in a flammable atmosphere.

5.1.8 Combustible dusts

“A dust explosion can occur when particulate solid material is suspended in air and a sufficiently energetic ignition source is present” (Amyotte & Eckhoff, 2010, p. 15).

Combustible dusts include most solid organic materials (e.g. sugar, flour, grain, wood, coal),

many metals and some non-metallic inorganic materials (CCOHS, 2015). (See section 6.2.2 for an explanation of dust explosions.)

5.1.9 Inert gases

Inert gases are commonly used in workplaces and processes to provide atmospheres where a fire cannot propagate. Gases such as carbon dioxide (CO₂) can be used for firefighting in electrical systems, as the CO₂ extinguishes the fire by removing the oxygen in the air. (See section 5.1.1 for fire tetrahedron.) Nitrogen, helium and argon are other inert gases commonly used to displace air from systems, thereby removing the oxygen.

Displacing the air, while good for fire prevention, creates a hazard for humans, as oxygen is required to support life. There have been many instances where an inert gas has displaced air and people have subsequently died from asphyxiation. This is of particular concern when working in confined spaces (CCOHS, 1997).

5.1.10 Acute toxicity – health hazards and environmental hazards

Many chemicals used in process environments are toxic to human health and to the environment. Most toxic exposures in process safety are acute exposures as a result of loss of containment of chemicals that are part of the process. Such exposure may occur through:

- A process malfunction leading directly to release of the chemical
- A release resulting from a fire or explosion
- Actions to control an emergency such as the runoff of fire water contaminating local waterways.

5.2 Sources of ignition

With the exception of autoigniting (pyrophoric) substances, a source of ignition is an essential requirement for a fire or explosion. While the objective is to eliminate sources of ignition in environments containing flammable or explosive substances, this is not usually possible due to the abundance of ignition sources in industrial environments. Potential sources of ignition must be identified and strategies put in place to manage the risks so that the other elements of the fire tetrahedron (section 5.1.1) or dust explosion pentagon (section 6.2.2) do not occur concurrently. Table 1 lists a number of sources of ignition with examples and potential controls. Three of these sources are explained below the table.

Table 1: Sources of ignition

Source of ignition	Example	Potential control
Flame	Matches, lighters, flares Oxyacetylene	Elimination Work procedures addressing control of sources of ignition
Hot surfaces	Piping, pumps, boiler surfaces	Lagging/insulation Isolation
Mechanically generated sparks, friction	Welding, grinding, cutting, impact equipment	Cold cutting (air-powered hacksaw) Control of work procedures
Electrostatic discharge*	Static generation through accumulation of electrical charge suddenly discharging as a spark	Electrical earthing and bonding Settling time for pumped liquids Minimisation of liquid splashing Non-synthetic clothing
Electrical and electronic equipment	Flashlights, cameras, radio transmitters, powered tools	Use of intrinsically safe devices Work procedures
Diesel/petrol vehicles	In an enveloping flammable gas cloud a diesel engine may continue to run even though the engine is turned off	Elimination through use of bicycles/walking Control of vehicle access
Adiabatic compression*	Sudden closing of valves or presence of a liquid slug	Design to avoid compression/pressure increases
Pyrophoric substances*	Iron sulphide in oil service	Wetting of the substance and removal
Lightning	Direct strike on storage tank or indirect strike on surrounding structures creating a 'bound' charge; ignition of vents (e.g. sumps, tanks)	Bypass conductors and grounding/earthing on floating roof tanks and sub-surface shunts Lightning protection, grounding/earthing, flame arrestors
Auto-oxidation/ignition	Processes that raise the temperature of the substance	Removal of oxygen and introduction of an inert atmosphere

*Source of ignition explained below.

Electrostatic discharge / static electricity refers to the build-up of electrical charge on the surface of objects, where it can remain if the object is an insulator, or discharge to earth if a conductor. Discharge can occur through a person (static shock) or through slow-charge bleeding in a humid environment. Static charge can build up whenever any fluid (powder, liquid or gas) is transferred through a pipe or other conduit, especially when the fluid has low electrical conductivity. In a flammable environment, a discharge in the form of a spark can provide enough energy to initiate an explosion or fire.¹¹

Adiabatic compression of a flammable gas mixture (e.g. in a diesel engine) may result in the gas being heated to its autoignition point and combusting. Significant transient pressure surges caused by liquid slugs in gas pipelines or by pumping against an obstruction, such as a

¹¹ See *OHS BoK Physical Hazards: Electricity*.

suddenly closed valve, could be sufficient to result in ignition of a flammable mixture. For example:

When a valve of an oxygen cylinder is opened quickly, the oxygen will rush into the high-pressure hose or the stem of the oxygen regulator and when reaching the end of the hose or regulator...adiabatic compression may occur [resulting in ignition] (Andersen, 2016, p. 1).

Pyrophoric substances (which autoignite in the presence of air at ambient temperatures) may act as ignition sources for other flammable materials with exothermic reactions providing the ignition energy. With reactive substances, this may not require oxygen to be present. (See section 6.1.6 on pyrophoric fires.)

5.3 Operating temperatures

Operating temperatures are one of the key factors influencing the design of plant and the selection of materials for construction. Should a process operate at temperatures outside its design parameters the plant will be subject to stress, which may cause structural failure.

5.3.1 Low temperature

Most process plant is constructed of steel. At low temperatures, steel tends to suffer a loss of toughness and becomes brittle; the temperature at which steel becomes brittle is dependent on the type and quality of the steel (Mannan, 2012).

Low-temperature embrittlement has caused many process failures. The most well-known Australian example is the 1998 explosion and fire at the Esso Longford gas plant when

...a severe process upset caused an automatic shutdown of the circulation of 'lean' oil which warmed the plant. Operators did not manage to restart the circulation for some hours. This caused a 14-tonne metal heat exchanger to become extremely cold... [when the warm oil was re-introduced] the cold brittle metal fractured in catastrophic way ... (Hopkins, 2000, p. 11).

5.3.2 High temperature

At high temperatures, tensile strength decreases. Also, metals tend to 'creep' or deform under stress with creep being more severe when the metal is subjected to high temperatures for long periods. Creep and resultant deformation can result in failure of the structure or equipment.

6 Consequences

Outcomes of an event involving chemical process hazards may include fire, explosion and/or releases that have toxic effect on humans and/or the environment. These impacts may be stand-alone or combined events, e.g. anhydrous ammonia is both toxic and flammable. Also, there may be a domino effect where a combination of consequences cause secondary releases

that greatly increase the impact.¹² For example, a flammable release may result in an initial flash fire followed by a vapour cloud explosion and subsequent jet fire. It may also create toxic fumes due to incomplete combustion (i.e. smoke) or by the release and combustion of other substances during the incident.

6.1 Fires

Six types of fire that may occur in a chemical process environment are described below.

6.1.1 Pool

Pool fires occur when there is a pool of liquid on a surface that may be solid or liquid, such as petrol floating on water, is ignited. A pool fire creates a steady burn, as the fuel required to feed the fire is derived from vaporisation of the liquid pool driven by the heat of the fire.

6.1.2 Jet

Jet fires occur when a liquid or gas released under pressure is ignited. They burn with intense radiant heat and a stable flame that is not affected by atmospheric conditions. If there is both gas and liquid in the jet fire, the liquid may not fully combust and may ‘drop out’ of the flame, producing a pool fire. The high-velocity flame from a jet fire can cause significant damage if allowed to impinge on sensitive equipment such as pressure vessels or structures. A jet fire impinging on a liquified gas tank may result in a boiling liquid expanding vapour explosion (BLEVE).

6.1.3 Fireball

Fireballs occur when a quantity of flammable liquid or mist/vapour is rapidly released as a cloud and ignites. The fire occurs in a spherical shape that rises into the air and the fuel burns rapidly. The size of a fireball is determined by the mass of the fuel released. As an example, a fireball may occur after a BLEVE.

6.1.4 Flash

Flash fires occur when a flammable gas accumulates in the open air and then ignites. The flame front travels very quickly through the gas, accelerating as it goes, and may lead to other fires. Depending on the amount of oxygen present, the speed of the flame front may approach sonic velocity and create explosive overpressures given sufficient degree of confinement. Flash fires may also involve a combustible dust.

¹² For more information on the domino effect see Kadri, F. E. & Chatelet, P. L. (2013). The assessment of risk caused by fire and explosion in the chemical process industry: A domino effect-based study. *Journal of Risk Analysis & Crisis Response*, 3(2), 66-76.

6.1.5 Dust

Dust fires are of two types – dispersed dust or dust layer. Dispersed-dust ignition requires a significant ignition source similar to liquid-mist ignition. A dust layer or pile may ignite without a specific additional ignition source in two ways:

- Slow oxidation reactions and the insulating effect of the dust enable the combustible dust to self-heat and smoulder with combustion limited by the slow diffusion of oxygen through the dust. (e.g. brown coal). If smouldering dust is disturbed then the rapid addition of oxygen may increase the rate of combustion, resulting in a small fire that may act as an ignition source for a flammable gas or liquid release. As the dust resettles it may return to smouldering or go out as the rapid combustion may not be sustained.
- A pile of dust heated by contact with a hot surface and disturbed by rapid addition of oxygen can result in a fire. The dust layer acts as a thermal insulator that may allow the surface to get hotter than design parameters.

Ignition of a dust cloud may result in either a dust flash fire or a dust explosion depending on the dust reactivity and degree of confinement. (See section 6.2.2 on dust explosions.)

6.1.6 Pyrophoric

Pyrophoric fires are caused by pyrophoric substances that have an autoignition temperature below ambient conditions. This means that they may spontaneously self-ignite in air. For example, iron sulphide formed in steel crude oil pumps and pipelines, due to the presence of hydrogen sulphide in the crude oil and an absence of oxygen, can spontaneously combust on exposure to air when equipment is undergoing maintenance.

6.2 Explosions

An explosion is characterised by:

- (a) Sudden release of physically or chemically generated and stored energy.
- (b) A shock wave / blast wave of significant magnitude, rapidly moving out from the explosion source.

Depending on the conditions of the blast, debris/flying fragments may originate from containment of the source of the explosion, or materials in immediate contact with it. Cratering of the soil directly underneath the source may also lead to projectiles (Abbasi, Pasman & Abbasi, 2010, p. 2).

An explosion may be an initial incident or secondary to a fire.

Understanding of the types of explosion assists in identifying causation and predicting potential consequences. As noted by Abbasi et al. (2010), there are a number of classification schemes for explosions, most of which suffer inconsistencies and shortcomings. Sections 6.2.1 and 6.2.2 draw on Abbasi et al.'s (2010) classification of physical and chemical explosions in the chemical process industry, and section 6.2.3 briefly considers factors affecting the impact of explosions in process industries.

6.2.1 Physical explosions (Abbasi et al., 2010)

A physical explosion occurs when the accumulated energy is suddenly released in a rapid physical change such as the expansion of a compressed gas. Three types of physical explosions are identified below.

Compressed gas/vapour explosions occur when a pressurised gas-filled vessel ruptures catastrophically. Such a rupture may be as a result of overpressure due to a failure in pressure relief equipment, reduction in a vessel wall thickness from corrosion or chemical attack, reduction in vessel wall strength due to overheating or embrittlement, or other mechanical damage.

Boiling liquid expanding vapour explosions (BLEVEs) occur when a vessel containing a substance in a liquid form under pressure is superheated and then suddenly depressurised. As the heat vaporises the liquid, the pressure rises until vaporised liquid is released via the relief valve, reducing the vessel inventory and liquid level. Where the flame impinges on the wall of the vessel below the liquid level (i.e. 'wetted area'), the latent heat of vaporisation limits the temperature rise of the metal. As the liquid level drops, the heated wall is no longer cooled by the liquid and the temperature rises rapidly; the mechanical strength of the vessel decreases, resulting in a catastrophic failure. This failure releases large quantities of pressurised vapour, causing depressurisation of the vessel and rapid boil-off of more vapour, all of which is ignited, usually creating a fireball.

Rapid phase transition explosions may occur when cryogenic liquids are accidentally exposed to a hotter environment. For example, if liquefied natural gas (LNG, which is at very cold temperatures) is spilled on or in water or if firefighting water is directly used on a pool of LNG.

6.2.2 Chemical explosions (Abbasi et al., 2010)

Chemical explosions are events where generation of a large volume of gas and build-up of pressure sufficient to cause an explosion is the result of a chemical reaction. Subcategories of chemical explosions are identified; the first is based on where in the material the chemical reaction occurs, and the second is based on the level of confinement.

Where the chemical reaction occurs

Homogeneous chemical explosions. In these explosions the reaction occurs throughout the material all at once. Such explosions occur as a result of an exothermic reaction creating a sharp rise in temperature (thermal explosion) or by a chemical reaction propagated by reactive groups of molecules that, in excess, can accelerate a chemical reaction even at relatively low temperatures (radical explosion).

Deflagrations and detonations. In deflagration, an exothermic reaction produces heat which moves from hot reaction gases to unreacted material; this movement may be slow when unconfined or extremely fast, but is always subsonic. In detonation, the energy transfer is caused by compression in a shock wave of high velocity and the temperature caused by the sudden compression starts the reaction. Deflagrations and detonations may occur together; while deflagrations are often accompanied by fire, detonations are always associated with fire and are always destructive.

Degree of confinement

Substantial confinement. Where there is substantial confinement, deflagrations, detonations and homogeneous chemical explosions may result in runaway reactions and explosions.

Unconfined or partially confined. Five types of explosion may occur when the chemical reaction is unconfined or partially confined:

- **Condensed phase explosions** occur when high-energy materials (e.g. munitions, commercial-grade explosives and ammonium nitrate) catch fire, resulting in a pressure wave of energy and speed high enough to cause an explosion even in an unconfined space. The explosive material is a solid or liquid (hence ‘condensed’), and therefore differentiated from a vapour cloud explosion.
- **Vapour cloud explosions (VCEs)** commence with release into the air of a large quantity of a flammable gas that forms a vapour cloud. Should ignition occur, the flame ball will initially be slow moving then accelerate, fed by internal turbulence in the cloud due to the fire and external factors such as partial confinement created by surrounding pipework, equipment or even vegetation.
- **Aerosol/mist explosions** are similar to VCEs, but the presence of liquid droplets increases the probability of cloud flammability and violence of the explosion.
- **Gas explosions** occur in a vessel or pipe carrying a gaseous mixture of fuel and oxidiser where the ratio of the two substances is in the flammability range. The reaction may be contained within the vessel with little noticeable outcome or, due to overpressure, the vessel may fail catastrophically. Where multiple vessels are connected via pipework, an explosion in one may pressurise others causing a greater secondary explosion (pressure piling).
- **Dust explosions** occur when dust particles raised into the air as a dust cloud ignite and explode. The resulting pressure wave may disperse more dust and allow the explosion to propagate by triggering subsequent explosions that may be comparable to a flammable gas or mist explosion.

The circumstances for a dust explosion are often created when dusts such as sugar, flour, wood, paper or metals accumulate on surfaces and are then disturbed. Amyotte and Eckhoff (2010) summarise factors relating to causation, prevention and mitigation of dust explosions. The five elements required for a dust cloud to explode – often referred to as the ‘dust explosion pentagon’ (Figure 3) – are:

- *Fuel*: a material that is combustible with a particle size capable of propagating flame
- *Dispersion/mixing*: the dust must be airborne and of a density optimal for ignition
- *Confinement*: the dust is within a fixed volume, allowing the development of overpressure
- *Oxidant*: usually just the oxygen contained in air will create a dust/oxidant suspension to support a chemical fire reaction
- *Ignition source*: the energy source capable of igniting the dust (see section 5.2).

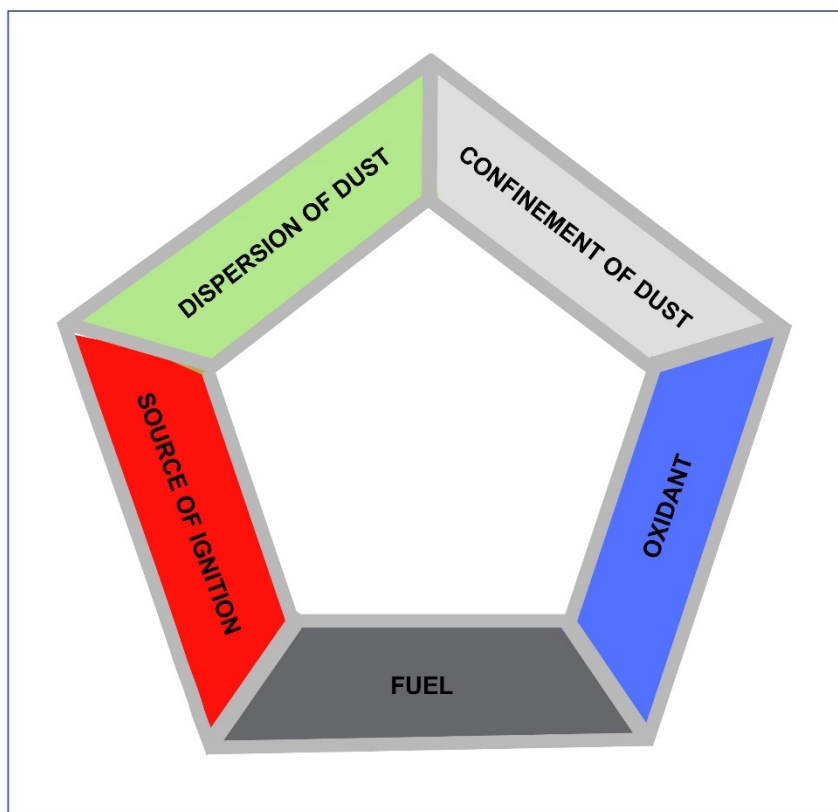


Figure 3: Dust explosion pentagon

The risk of a dust explosion is dependent on:

- Material characteristics (moisture content, particle size, shape and porosity)
- Density of the dust cloud (lower densities are a personal health / occupational hygiene risk; higher densities result in a consolidated dust layer)

- Environmental conditions (volume, turbulence)
- Ignition source (Amyotte & Eckhoff, 2010).

Dust explosions often occur as primary explosions inside process vessels and during storage or transport (Amyotte & Eckhoff, 2010).

The potential for explosion is increased where dust settles and remains on hot surfaces, such as electric motor casings, as the dust thermally insulates the surfaces allowing them to exceed their design temperature. “The required amount of layered dust which, once airborne, could sustain a secondary dust explosion is often grossly overestimated”; the risk is further increased where there is hybrid mixture of a flammable dust and a flammable gas (e.g. methane / coal dust mixture) (Amyotte & Eckhoff, 2010, p. 20).

Burning dust settling onto surfaces has a relatively high heat capacity, and can cause significant burn injuries. People attempting to escape through settled dust frequently redisperse the dust, creating more fires.

6.2.3 Impact

The impact of explosions will depend on:

- The reactivity of the substances(s)
- Whether the propagation is exothermic or deflagration/detonation
- The state of the fuel-oxidiser mix (gas, dust, aerosol/mist or condensed phase)
- Degree of confinement (Abbasi et al., 2010).

The pressure wave from an explosion is often the most damaging aspect as it can cause widespread destruction of equipment and buildings. When there is a confined overpressure, such as a tank or pipe rupture, and depending on how the equipment fails under pressure, part of the equipment such as valves or wall sections may be ejected as shrapnel. In the case of BLEVEs, shrapnel can be ejected several kilometers.

Computer programs such as PHASTTM and FLACS produce explosion-effect models that are used in consequence analysis relevant to emergency response and risk management. Such programs model the overpressure wave, and thermal and toxic effects, and have some limited ability to model shrapnel. They produce either two-dimensional plot plans that map pressure waves, or complex three-dimensional videos showing wave movement. Figure 4 is an example of a 3-D representation developed through such modelling.

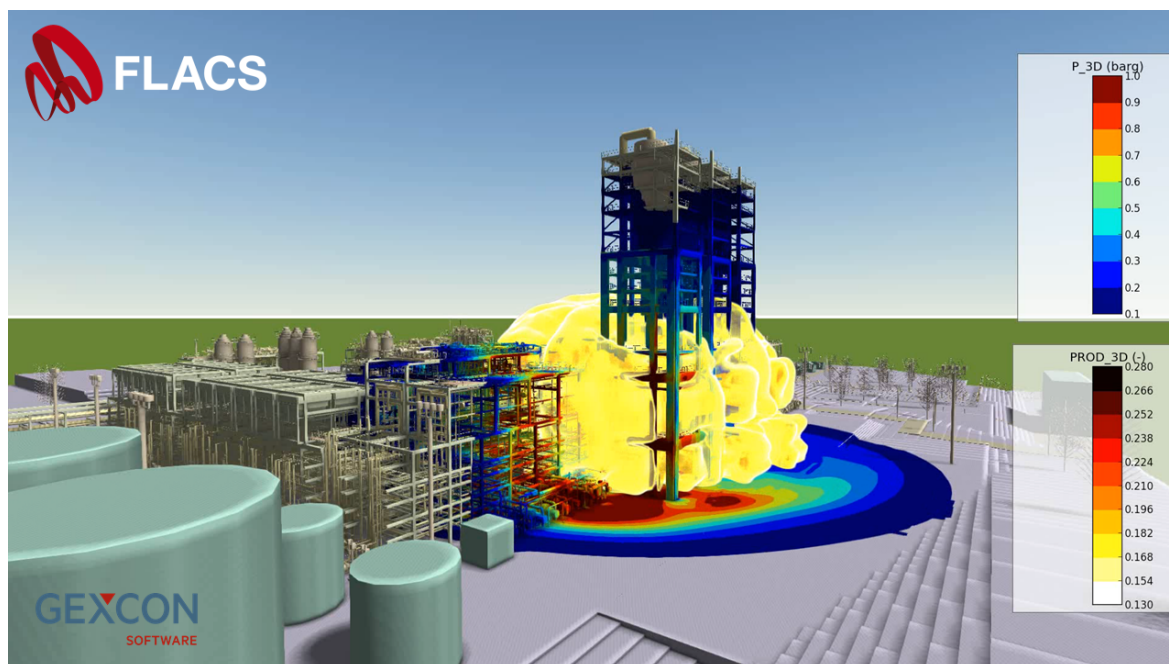


Figure 4: Representation of overpressure contours and flame spread in a refinery explosion (image courtesy of Gexcon AS)

6.3 Toxic effects

Toxic effects may result from process-related incidents either as a stand-alone loss of containment or a toxic release as an outcome of fire or explosion. These toxic effects are usually acute with chronic effects typically managed through occupational hygiene strategies.

Many toxic substances are used or generated during chemical processes. For example, ammonia is often used as a refrigerant coolant. While small leaks of ammonia pose an industrial hygiene risk through chronic exposure, a large loss of containment can pose a fatal risk from an acute exposure. Also, there are many examples of large-scale toxic releases in process incidents. The 1984 Bhopal incident resulted in estimated 2000 fatalities, 100,000 injuries and significant damage to livestock and crops as a result of acute exposure to methyl isocyanate (Atherton & Gil, 2008). Toxic issues can also arise from firefighting efforts during process incidents. In Switzerland in 1986, the fire water runoff during response to a chemical storage warehouse fire resulted in contamination of 40 km of the Rhine River, killing aquatic animals and preventing use of the river for aquaculture for many months (Atherton & Gil, 2008).

The scale of toxic effect will depend on:

- Toxicity of the chemical (usually measured in terms of LD_{50})¹³
- Concentration of the chemical
- Length of time of exposure
- Size of the gas plume (determined by flow rate and dispersion factors such as wind direction and speed).¹⁴

Modelling can be used to estimate concentrations of toxic substances at various distances from the release point (e.g. Figure 5).

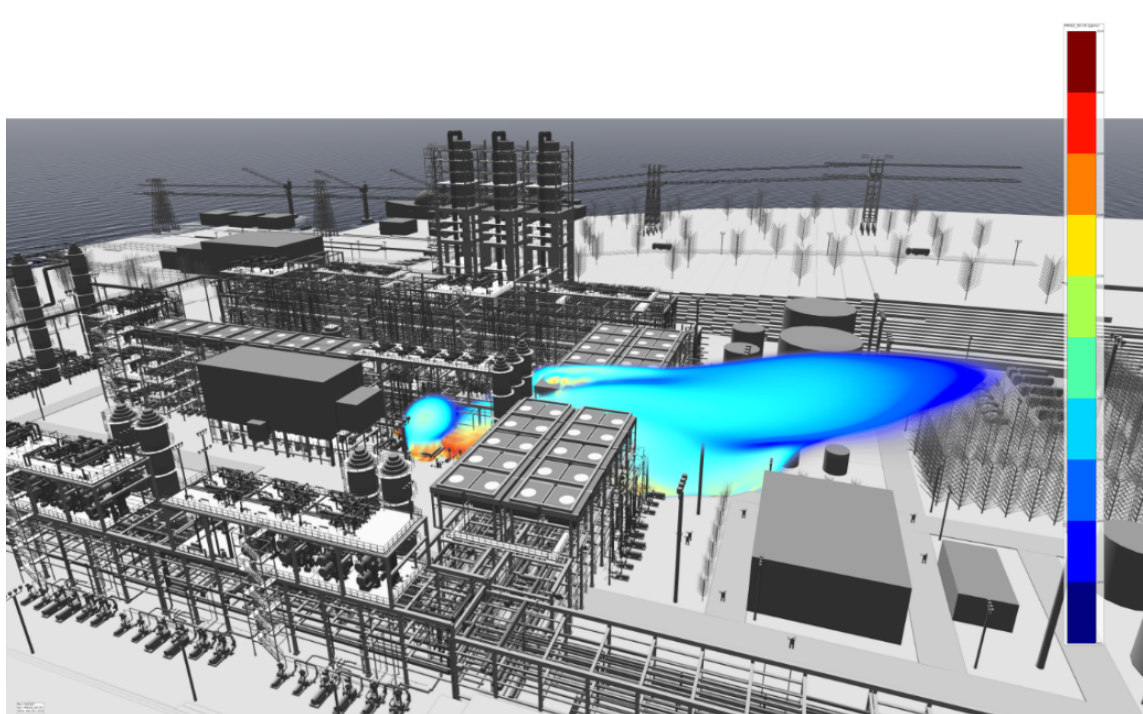


Figure 5: 3-D representation of the impact of a carbon monoxide release in a refinery (image courtesy of Gexcon AS)

The biggest issue with toxic releases is the potential offsite impact. The severity of impact of toxic substances on the community can be rated based on the Emergency Response Planning Guidelines (ERPGs) developed by the American Industrial Hygiene Association. ERPGs, which specify three tiers of airborne chemical concentration, are “tools to assess the adequacy of incident prevention and emergency response plans, including transportation

¹³ “LD stands for ‘Lethal Dose’. LD_{50} is the amount of a material, given all at once, which causes the death of 50% (one half) of a group of test animals. The LD_{50} is one way to measure the short-term poisoning potential (acute toxicity) of a material.” (CCOHS, 2013)

¹⁴ See *OHS BoK Chemical Hazards* for discussion of toxic substances, routes of exposure, dose-related impact and exposure levels.

emergency planning, community emergency response plans and incident prevention and mitigation” (AIHA, 2016). In late 2016, ERPGs had been developed for about 150 chemicals (NOAA, 2016).¹⁵

7 Legislation and standards

Process safety hazards are regulated under state and national occupational and work health safety (WHS) legislation.¹⁶

From 2017, compliance with the Globally Harmonised System (GHS) for Classification and Labelling of Chemicals is mandatory for those Australian states operating under the model WHS legislation (New South Wales, Queensland, Tasmania and South Australia) and is being adopted by Victoria. While Western Australia and the Australian Capital Territory have not mandated the GHS they do require communication of information on hazardous substances and it is prudent to comply with the GHS (SWA, 2016).

Under the model WHS legislation, manufacturers, importers and suppliers are required to determine if a chemical is hazardous and to correctly classify the chemical according to the GHS. Also, they are required to supply GHS-compliant labels and safety data sheets for hazardous chemicals. Workplace end-users of chemicals must only accept hazardous chemicals that have been classified and labelled in accordance with the GHS (SWA, 2016).

While not having the power of legislation (unless cited in regulations), there are many accepted standards – national and global – that should be considered in management of process safety. They cover not only the handling of the substances – e.g. *AS 1940 The Storage and Handling of Flammable and Combustible Liquids* (SA, 2004) and *AS/NZS 4745 Code of Practice for Handling Combustible Dusts* (SA/SNZ, 2012) – but also define how facilities shall be designed and what equipment is necessary – e.g. *AS/NZS 60079.25 Explosive Atmospheres – Intrinsically Safe Electrical Systems* (SA/SNZ, 2011) and *IEC 61511 Functional Safety – Safety Instrumented Systems for the Process Industry Sector* (IEC, 2003). This chapter does not attempt to list the many standards relevant to process safety, but rather alerts the generalist OHS professional to their existence for consultation as required.

¹⁵ For an example of the application of ERPGs in Australia, see Workplace Health and Safety Queensland (2011).

¹⁶ See *OHS BoK Managing Process Safety* for discussion of legislation and associated obligations. See also *OHS BoK Principles of OHS Law* for discussion of general obligations under OHS/WHS legislation.

8 Control

Considering the high potential consequences of a process safety event, control requires multiple layers of protection (section 8.1) with barriers (section 8.2) at each layer applied through a prioritised approach to achieve:

1. Elimination of the hazard and of sources of ignition (section 8.3)
2. Prevention of loss of control (section 8.4)
3. Mitigation including emergency management (section 8.5).¹⁷

8.1 Layers of protection

The chemical process industry has developed a method of analysing controls that are in place to prevent or mitigate hazardous events. Layer of Protection Analysis (LOPA) is a concept that combines protection layers with strategies such as safety instrumented systems (SIS) and methods to determine the safety integrity level (SIL). Standards have been developed defining the different layers. LOPA is often described as an onion, with the layers reflecting the levels of protection with inherently safer design at the core¹⁸ (Figure 6). A basic LOPA bow-tie diagram (e.g. Figure 7) shows the layers of detection and protection that would apply for a range of potential initiating events.

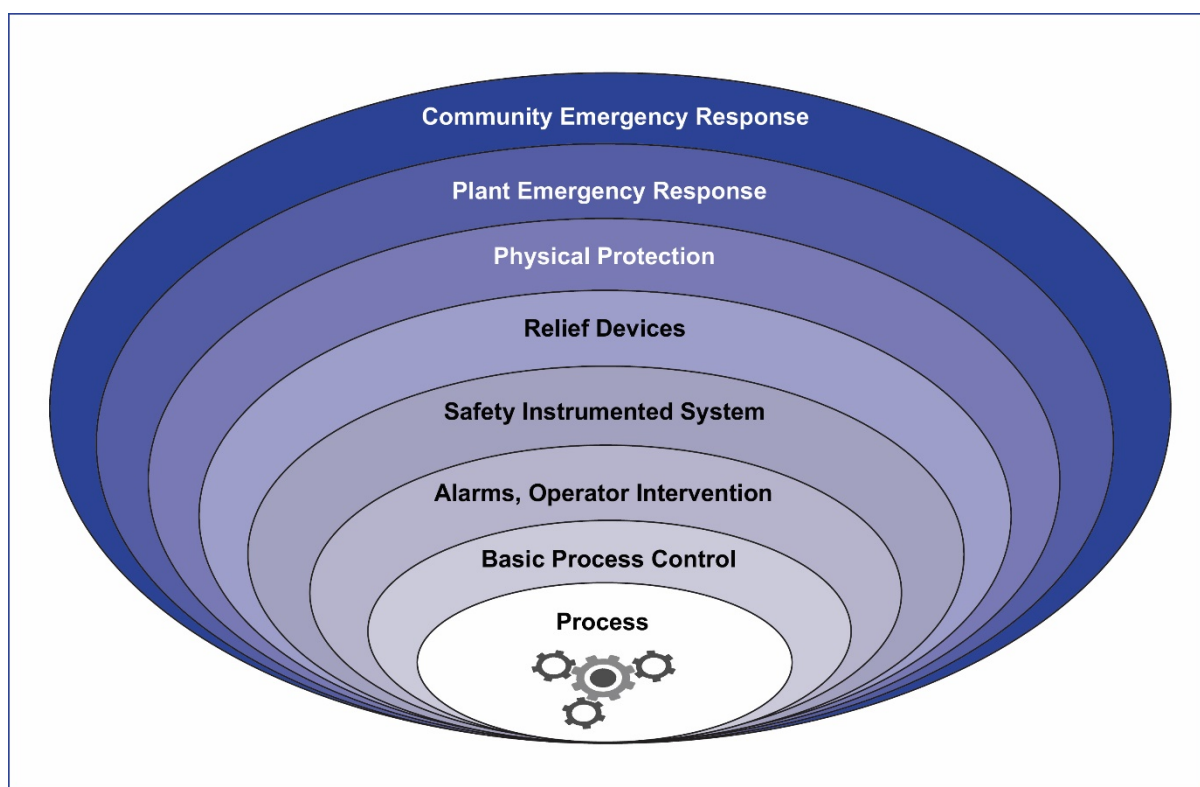


Figure 6: 'Onion' representation of LOPA

¹⁷ See *OHS BoK Control: Prevention and Intervention* for discussion of principles of risk control.

¹⁸ See *OHS BoK Managing Process Safety* for discussion of inherently safer design.

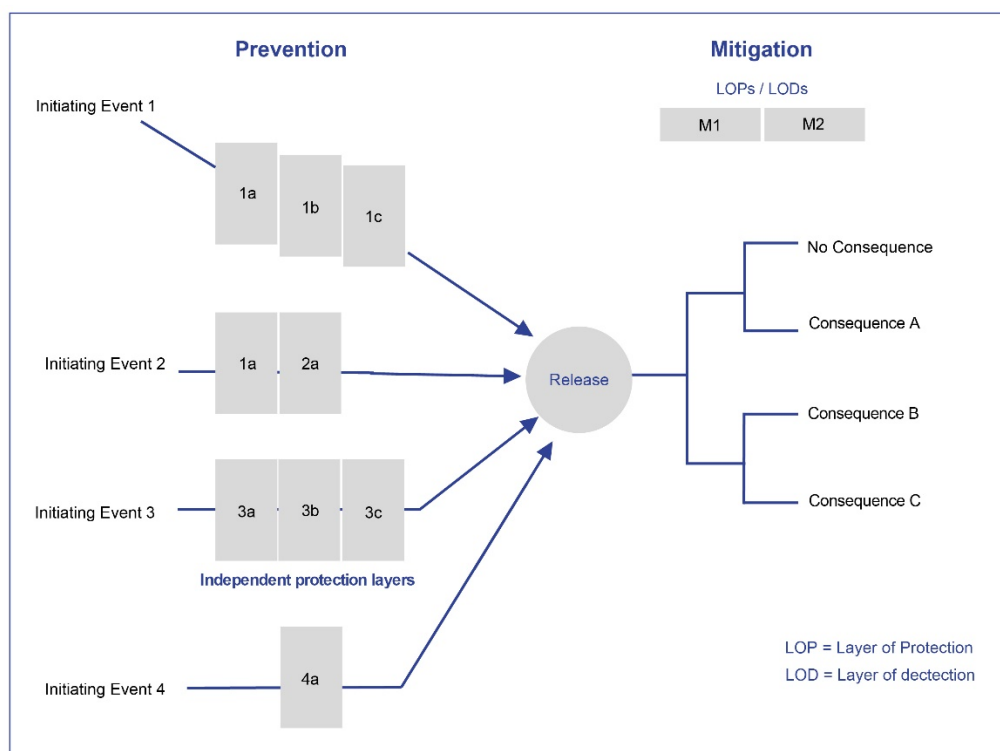


Figure 7: Schematic LOPA diagram (ICChemE, 2014)

8.2 Barriers

Whereas generalist OHS professionals refer to risk controls, in process safety the terminology frequently used is ‘barriers’. The International Association of Oil and Gas Producers (IOGP) defines a barrier as: “A risk control that seeks to prevent unintended events from occurring, or prevent escalation of events into incidents with harmful consequences” (IOGP, 2016, p. 5). The IOGP (2016) categorises barriers as either hardware or human barriers, with hardware barriers including:

- Structural integrity
- Process containment
- Ignition control
- Detection systems
- Protection systems, including deluge and firewater systems
- Shutdown systems
- Emergency response
- Life-saving equipment, including evacuation systems.

While the generalist OHS professional should be aware of this approach to barriers, this chapter classifies barriers as either passive-engineered, active-engineered or administrative;

this classification more appropriately reflects a hierarchy of control and provides a basis for a shared understanding of risk control strategies by OHS and process safety professionals.

8.2.1 Passive

Passive barriers are the most reliable and are usually developed at the design stage. They do not require action by a person or device; they perform their function just by existing, but often require maintenance to ensure they continue to meet the design performance standards. Examples include:

- Making equipment more robust (e.g. appropriate thickness of materials)
- Shielding by fire walls and doors, explosion walls
- Collapsible panels (e.g. explosion vents for buildings with combustible dusts, entire walls for gas compression buildings).

8.2.2 Active

Active barriers detect a hazardous condition and initiate an automated response. Such equipment includes:

- Alarms and trip systems
- Pressure relief valves
- Automated shutdown systems
- Automated deluge systems, e.g.
 - Active water systems
 - Water curtains for mitigating gas release
 - Hi-fog systems for liquid hydrocarbon fires
 - Chemical suppressant systems for oxidising agents, reactive metals.

Active barriers should be designed to fail to a safe state so that inadvertent failure does not trigger an incident. The design should ensure that a warning occurs when the system is not 'live' and so will not function in the event of an incident.

8.2.3 Administrative

Administrative or procedural barriers, which are the least reliable as they involve people carrying out specific tasks, may include:

- Operating procedures
- Operator-initiated process adjustments
- Operator-initiated response to alarms
- Muster and evacuation procedures.

8.3 Elimination

This chapter has shown that chemical process hazards can be associated with fires, explosions and toxic releases with consequences ranging from minor to catastrophic. Four factors are required for a fire or (non-dust) explosion – fuel (the flammable substance), air (oxygen), an ignition source, and an uninhibited chemical chain reaction to feed heat back to the fuel to maintain the fire (i.e. the fire tetrahedron, section 6.1). In the case of dust explosions, the factors are fuel (dust), air (oxygen), ignition source, and dispersion and confinement (i.e. the dust explosion pentagon, section 6.2).

If any one of these factors is missing, then the likelihood of a hazardous event is eliminated. As the fuel is often the essential part of the process, fuel elimination is not usually practical. While design and work processes should target elimination of sources of ignition, elimination of all sources of ignition is not usually feasible. Also, oxygen will always be present when there is exposure to the air. Thus, process and equipment design should focus on elimination of conditions enabling a mixture of fuel and air.¹⁹

8.4 Prevention

While most process events involve a loss of containment, such a loss is preceded by a loss of control of the process. As not all loss-of-control events lead to an actual loss of containment, strategies focused on preventing, detecting and responding to any loss of control enable intervention early in the causation timeline. Focusing on loss of control can be the key to prevention of incidents and minimisation of consequences.

8.5 Mitigation

A two-stage approach is applied to mitigation:

- Minimisation of escalation
- Post-event emergency response.

8.5.1 Minimisation of escalation

Once a loss of control has occurred, it is important to minimise the consequences. This is usually achieved by a range of active-engineered barriers (e.g. detection systems and fire suppression systems) and administrative barriers (e.g. evacuation).

¹⁹ See *OHS BoK Managing Process Safety* for discussion of inherently safer design.

8.5.2 Emergency response

A comprehensive, integrated risk-management approach to emergency planning that incorporates Prevention, Preparedness, Response and Recovery (PPRR) is advocated.²⁰

Some hazard-specific implications to be considered in emergency response associated with hazardous chemicals include:

- Foam used for firefighting can generate static electricity, which can ignite a spill
- Some foam types may be incompatible with certain chemicals (e.g. alcohol-containing fuels)
- Certain types of foam can have a major impact on pollution of water resources if the runoff is not controlled through pre-installed containment facilities such as aeration chambers and foam dams
- Some fires are simply too dangerous to try to put out and fire crews must be evacuated, e.g. an LPG BLEVE with a fireball several hundred metres in diameter; a crude oil tank after several hours of a full-surface burn where it may approach boil-over conditions with potential for a fireball hundreds of metres high.

9 Implications for OHS practice

As a companion chapter to *OHS Body of Knowledge* Managing Process Safety, this chapter provides information vital for understanding and applying process safety management strategies. Knowledge of key scientific principles underpinning the action of chemical process hazards, categories of hazardous substances and potential sources of ignition, and the various types of fire, explosion and toxic effects will enable generalist OHS professionals to effectively engage with process safety and chemical safety experts, contribute to better hazard control and reduce the risk of catastrophic events.

10 Summary

This chapter began by identifying substances involved in chemical processes as hazardous to human, environmental and property safety, and to business since the industrial revolution. While these hazards with potential high consequences of fire, explosion and/or toxic effect are usually managed by process safety and chemical safety professionals, generalist OHS professionals have a role in identifying these hazards and their potential consequences, and in supporting specialists in their management. To fulfill this role, generalist OHS professionals require an understanding of the underpinning science, the actions of the hazards, the nature of

²⁰ See *OHS BoK* Mitigation: Emergency Preparedness, which examines key concepts in emergency preparedness for organisations. See *OHS BoK* Managing Process Safety for discussion of emergency preparedness as it applies to process safety.

the consequences and common controls as described in this chapter. The substances, consequences and impacts with the barriers as controls are summarised in Figure 8.

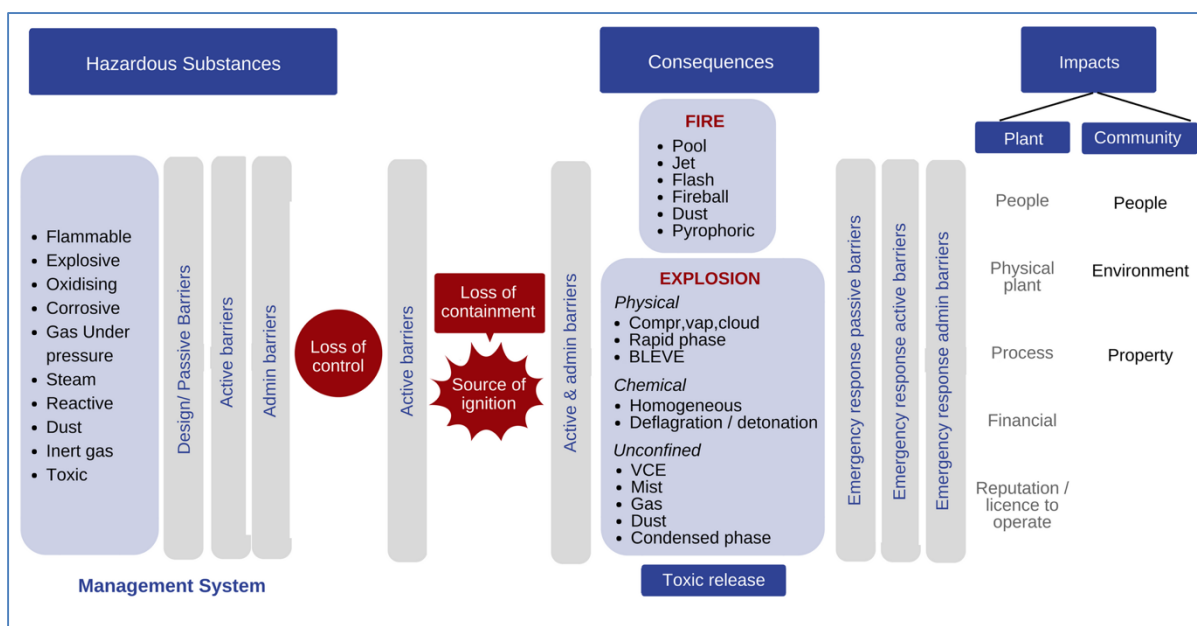


Figure 8: Summary of hazardous substances, consequences and impacts with barriers as controls

This knowledge provides a basis for the generalist OHS professional to contribute to the management of process safety. Strategies, activities and tools for managing process safety are described from the generalist OHS professional's perspective in the *OHS Body of Knowledge* companion chapter, Managing Process Safety.

Useful resources

BP Process Safety Series: <http://www.icheme.org/bp-safety>

Titles include:

- Hazards of Water
- Hazards of Air and Oxygen
- Hazards of Steam
- Hazards of Trapped Pressure and Vacuum
- Hazardous Substances in Refineries
- Hazards of Electricity and Static Electricity
- Hazards of Nitrogen and Catalyst Handling.

References

- Abbasi, T., Pasman, H. J., & Abbasi, S.A. (2010). A scheme for the classification of explosions in the chemical industry. *Journal of Hazardous Materials*, 174(1-3), 270-280.
- AIHA (American Industrial Hygiene Association). (2016). Emergency Response Planning Guidelines. Retrieved from <https://www.aiha.org/get-involved/AIHAGuidelineFoundation/EmergencyResponsePlanningGuidelines/Pages/default.aspx>
- Amyotte, P. R. & Eckhoff, R. K. (2010). Dust explosion causation, prevention and mitigation: An overview. *Journal of Chemical Health & Safety*, 17(1), 15-28.
- Andersen, L. (2016). *Understanding the Danger of Adiabatic Compression* (Technical Update). Wilhelmsen Ships Service. Retrieved from <https://www.wilhelmsen.com/globalassets/marine-products/welding/documents/technical-update---understanding-the-danger-of-adiabatic-compression.pdf>
- API (American Petroleum Institute). (2009). *Recommended Practice for Lightning Protection of Aboveground Storage Tanks for Flammable or Combustible Liquids* (API Recommended Practice 545). Retrieved from http://www.booksfiles.org/xiazai/API_545_SET_pre.pdf
- Atherton, J. & Gil, F. (2008). *Incidents that define process safety*. Hoboken, NJ: John Wiley & Sons.
- CCOHS (Canadian Center for Occupational Health and Safety). (1997). Compressed gases – hazards (OHS Answers Fact Sheets). Retrieved from <https://www.ccohs.ca/oshanswers/chemicals/compressed/compress.html>
- CCOHS (Canadian Center for Occupational Health and Safety). (2013). What is a LD₅₀ and LC₅₀? (OSH Answers Fact Sheets). Retrieved from <https://www.ccohs.ca/oshanswers/chemicals/ld50.html>
- CCOHS (Canadian Center for Occupational Health and Safety). (2015). What is a combustible dust? (OSH Answers Fact Sheets). Retrieved from https://www.ccohs.ca/oshanswers/chemicals/combustible_dust.html
- da Cruz, M. & Bentes, S. R. (2013). The Seveso directives and their application to enterprise risk management. *International Journal of Latest Trends in Finance & Economic Sciences*, 3(3), 563-571.
- Eckhoff, R. K. (2016). *Explosion hazards in the process industries* (2nd ed.). Cambridge, MA: Gulf Professional Publishing.
- Essa, I. (2014). Lessons from Bhopal (Editorial). *Loss Prevention Bulletin*, 240. Rugby, UK: Institution of Chemical Engineers.
- Hale, A. R. (2001). Conditions of occurrence of major and minor accidents. *Institution of Occupational Safety & Health Journal*, 5(1), 7-20.

- Hopkins, A. (2000). *Lessons from Longford: The ESSO gas plant explosion*. Sydney, NSW: CCH Australia.
- ICHEME (Institute of Chemical Engineers). (2014). *Layer of Protection Analysis (LOPA) training program*. Rugby, UK: IChemE.
- IEC (International Electrotechnical Commission). (2003). *IEC 61511 Functional Safety – Safety Instrumented Systems for the Process Industry Sector*. Geneva, Switzerland: International Electrotechnical Commission.
- IOGP (International Association of Oil & Gas Producers). (2016). *Standardization of Barrier Definitions: Supplement to Report 415 (Report 544)*. England: IOGP.
- Kelly, T. (2003). *A Systematic Approach to Safety Case Management*. SAE Technical Paper. Retrieved from <http://citeseerx.ist.psu.edu/viewdoc/download?doi=10.1.1.20.8520&rep=rep1&type=pdf>
- Klein, J. A. (2009). Two centuries of process safety history at DuPont. *Process Safety Progress*, 28(2), 114-122.
- Kletz, T. (1996). *Dispelling chemical engineering myths* (3rd ed.). London: Taylor & Francis.
- Mannan, S. (Ed.). (2012). *Lees' loss prevention in the process industries: Hazard identification, assessment and control* (volumes 1-3) (4th ed.). Oxford: Elsevier.
- Marsh. (2016). *The 100 largest losses 1974-2015* (24th ed.). London: Marsh & McLennan.
- NOAA (National Oceanic and Atmosphere Administration). (2016). *Emergency Preparedness and Response Guidelines (ERPGs)*. US Department of Commerce. <http://response.restoration.noaa.gov/oil-and-chemical-spills/chemical-spills/resources/emergency-response-planning-guidelines-erpgs.html>
- SA (Standards Australia). (2004). *AS 1940-2004: The Storage and Handling of Flammable and Combustible Liquids*. Sydney, NSW: Standards Australia.
- SA/SNZ (Standards Australia/Standards New Zealand). (2011). *AS/NZS 60079.25:2011 Explosive Atmospheres – Intrinsically Safe Electrical Systems*. Sydney and Wellington: Standards Australia/Standards New Zealand.
- SA/SNZ (Standards Australia/Standards New Zealand). (2012). *AS/NZS 4745:2012 Code of Practice for Handling Combustible Dusts*. Sydney and Wellington: Standards Australia/Standards New Zealand.
- Sapko, M. J., Weiss, E. S., Harris, M. L., Man, C.-K., & Harteis, S. P. (2010). A centennial of mine explosion prevention research. *2010 SME Annual Meeting and Exhibit*, Phoenix, Arizona. Retrieved from <https://www.cdc.gov/niosh/mining/UserFiles/works/pdfs/acompe.pdf>
- Smith, R. (2016). *Chemical process: Design and integration* (2nd ed.). West Sussex: John Wiley & Sons.

- SWA (Safe Work Australia). (2012). *Australian Work Health and Safety Strategy 2012-2022*. Canberra, ACT: Safe Work Australia. Retrieved from <http://www.safeworkaustralia.gov.au/sites/swa/about/publications/pages/australian-work-health-and-safety-strategy-2012-2022>
- SWA (Safe Work Australia). (2016). *Globally Harmonised System (GHS) of Classification and Labelling of Chemicals Information Sheet*. Retrieved from [http://www.safeworkaustralia.gov.au/sites/swa/about/publications/pages/globally-harmonised-system-of-classification-and-labelling-of-chemicals-\(ghs\)-information-sheet](http://www.safeworkaustralia.gov.au/sites/swa/about/publications/pages/globally-harmonised-system-of-classification-and-labelling-of-chemicals-(ghs)-information-sheet)
- UN (United Nations). (2011). *Globally Harmonized System of Classification and Labelling of Chemicals (GHS)* (4th ed.). New York and Geneva: United Nations. Retrieved from https://www.unece.org/fileadmin/DAM/trans/danger/publi/ghs/ghs_rev04/English/ST-SG-AC10-30-Rev4e.pdf