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through people, process and technology

## **BP Process Safety Series**

# **Hazardous Substances in Refineries**

**A collection of booklets  
describing hazards and  
how to manage them**



**IChem<sup>E</sup>**

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This booklet is intended as a safety supplement to operator training courses, operating manuals, and operating procedures. It is provided to help the reader better understand the 'why' of safe operating practices and procedures in our plants. Important engineering design features are included. However, technical advances and other changes made after its publication, while generally not affecting principles, could affect some suggestions made herein. The reader is encouraged to examine such advances and changes when selecting and implementing practices and procedures at his/her facility.

While the information in this booklet is intended to increase the store-house of knowledge in safe operations, it is important for the reader to recognize that this material is generic in nature, that it is not unit specific, and, accordingly, that its contents may not be subject to literal application. Instead, as noted above, it is supplemental information for use in already established training programmes; and it should not be treated as a substitute for otherwise applicable operator training courses, operating manuals or operating procedures. The advice in this booklet is a matter of opinion only and should not be construed as a representation or statement of any kind as to the effect of following such advice and no responsibility for the use of it can be assumed by BP.

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Published by  
Institution of Chemical Engineers (IChemE)  
Davis Building  
165–189 Railway Terrace  
Rugby, CV21 3HQ, UK

IChemE is a Registered Charity in England and Wales  
Offices in Rugby (UK), London (UK) and Melbourne (Australia)

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ISBN-10: 0 85295 482 4  
ISBN-13: 978 0 85295 482 9

First edition 2005

Typeset by Techset Composition Limited, Salisbury, UK  
Printed by Henry Ling, Dorchester, UK

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Note: All units in this book are in US and SI systems

# 1

# Introduction to hazardous substances

## 1.1 Introduction

### What are hazardous substances?

They are any material or item that has the potential to harm humans, animals, or the environment. They can act directly or through interaction with other factors.



Petroleum and chemical facilities, in particular, handle large amounts of highly hazardous substances. These materials are most dangerous when released uncontrollably so it is important that facility personnel recognize the threat and know what steps to take when exposure is likely.



The following are some of the most frequently encountered hazardous substances in the petroleum and chemical industries. Does your site handle these materials? Can you identify the hazards they pose?

Hydrogen sulphide (H <sub>2</sub> S)	Liquefied Natural Gas (LNG)
Nitrogen (N <sub>2</sub> )	Liquefied Petroleum Gas (LPG)
Hydrogen fluoride (HF)	Flammable liquids like gasoline
Ammonia (NH <sub>3</sub> )	Benzene (C <sub>6</sub> H <sub>6</sub> )
Chlorine (Cl <sub>2</sub> )	Ethylene oxide (C <sub>2</sub> H <sub>4</sub> O)
Tetrachloroethylene (C <sub>2</sub> Cl <sub>4</sub> )	Hydrogen cyanide (HCN)
Hydrochloric acid (HCl)	Acrylonitrile
Sulphuric acid (H <sub>2</sub> SO <sub>4</sub> )	Boron trifluoride (BF <sub>3</sub> )
Caustic	Radiation
Lead	Asbestos

This booklet focuses primarily on the hazardous substances handled in the petroleum industry.

**The data found in this booklet should not be used as replacement for your site's Material Safety Data Sheets (MSDSs).**

The information contained in this booklet is only provided to raise awareness and may require research by personnel likely to encounter various hazardous materials in the course of their work activities.

## 1.2 Classification of hazardous substances

In view of the dangers of handling hazardous materials, several international and governmental bodies have classified them according to the threats they pose. Some of these bodies are:

- International Maritime Dangerous Goods Code (IMDG);
- U.S. National Fire Protection Association (NFPA);
- U.S. Department of Transportation (DOT);
- European Union Directives on Dangerous Substances and Dangerous Preparations.

Generally, hazardous materials can be categorized as follows:

- toxic;
- radioactive;
- corrosive;
- cryogenic;
- flammable;
- reactive.
- explosive;

Some substances can be a combination of the above categories. For example, *benzene* is both flammable and toxic as demonstrated by the two incident descriptions on the next page.

**ACCIDENT** Spray of benzene leaves a loading operator dead!!!

A loading operator and a trainee were at the beginning of a benzene loading operation for a string of railcars. The loading operator had removed a top loading port cap to relieve pressure within the railcar when benzene started spraying from the opening. The spray hit the loading operator in the face and body. Although he was given emergency CPR treatment, he did not survive.

**ACCIDENT** Explosion during loading of benzene!!!

An explosion damaged this cargo tank while it was being loaded with benzene. Investigations concluded that the direct cause of the explosion was a flammable atmosphere of benzene mist (fine liquid droplets in air) that was ignited by a discharge of static electricity.



The physical form of a substance sometimes determines its potential risk. A substance that is safe in its solid form may be toxic or flammable in its vapour state, or give off hazardous fumes in its liquid form.

We are most often concerned with materials that give rise to immediate consequences, but hazardous substances also constitute materials that only display adverse consequences many years later.



Asbestos can cause asbestosis, a scarring of the lungs that leads to breathing problems and lung failure. Workers exposed to asbestos for a short time may develop lung cancer, which only becomes evident 20 to 30 years later.

## 1.2.1 Toxic

Substances that are toxic can trigger adverse health effects in the human body. The severity of these effects depends upon the toxicity of the material and amount involved. This amount is often referred to as the 'toxic dose'. Section 1.4 details the routes of entry of toxic materials into the body and definitions of toxicology concepts. It is important to know the acute effects, as well as the chronic effects of toxic substances.



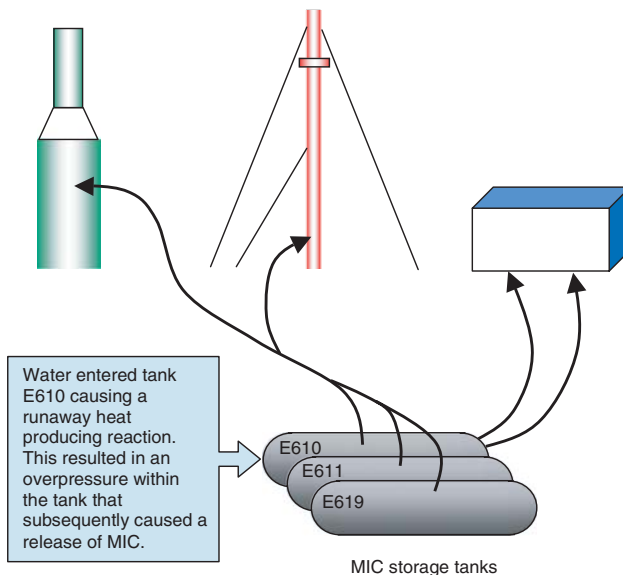
### **ACCIDENT** The Bhopal disaster!!!

A plant in Bhopal, India, produced pesticides using methyl isocyanate (MIC) as an intermediate compound. MIC is an extremely dangerous compound that severely irritates the nose and throat causing respiratory distress. On 3 December, 1984, an estimated 25 tons of MIC vapour was released. The toxic cloud spread over a shantytown nearby, killing 2,000 and injuring a further 20,000, marking it as one of the most significant disasters in the history of the chemical industry.

**Vent gas scrubber**  
The leaking gas could have been detoxified but the scrubber was turned off

**Flare**  
Designed to burn off gas but a connecting pipe had been removed for maintenance

**Refrigeration system**  
System to cool liquid MIC was shutdown to save on operating costs



E610 contained 40 tonnes of MIC, E611 contained 15 tonnes while E619 was empty.

### 1.2.2 Corrosive

Corrosive materials are substances that can cause visible damage or irreversible alterations to living tissue.

They can act directly by chemically destroying the tissues, or indirectly through inflammation. These injuries are sometimes referred to as chemical burns.

Acids and bases are common corrosive materials. Typical examples are hydrofluoric acid, hydrochloric acid, sulphuric acid, and sodium hydroxide. Corrosives such as these are sometimes referred to as 'caustics'.



The severity of damage to living tissue following contact depends largely on the type of substance, the concentration of corrosive material, and the contact area. In the case of hydrofluoric acid, the acid continues to attack the calcium in bones and is a particularly insidious chemical requiring special precautions to avoid exposure and to treat properly.

### 1.2.3 Flammable

Flammable materials are substances that can catch fire. Fires are obviously dangerous because they can cause burn injuries to the human body, widespread asset damage, and release of toxic fumes and pollutants into the atmosphere. Combustible materials also have the potential to burn, but require higher temperatures to pose a significant risk. However, even combustible materials can ignite at lower temperatures if they exist as a mist.



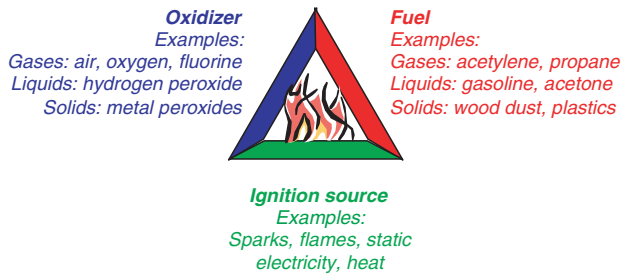
Thermal burns are a result of exposure to thermal energy radiated from fires. The intensity of the thermal radiation emitted in a fire depends on:

- type of flammable material;
- amount of flammable material;
- pressure of release;
- surrounding conditions (enclosed, open, windy conditions, etc.);
- proximity to the flames.

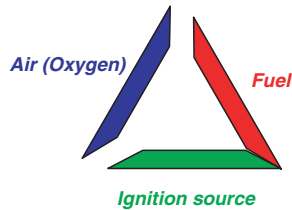


Three elements must be present before a fire can happen. They are fuel, oxygen and an ignition source. The absence of any one of these elements means that a fire will not occur. (Recent fire triangles sometimes include chemical chain reaction as an element.)

The fire triangle

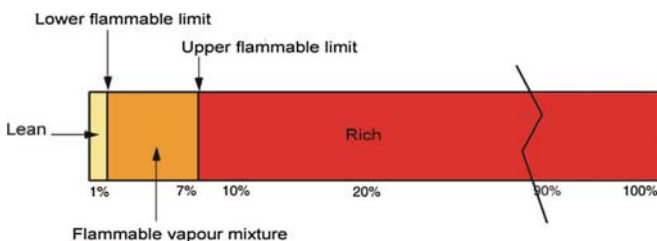


It is often best to eliminate oxygen rather than the ignition source because ignition sources, even if identifiable, are difficult to control.



For an ignition to occur the fuel and air (oxygen) mixture must be within a certain range. This range is determined by the Lower Flammability/Explosive (LFL/LEL) and Upper Flammability/Explosive Limits (UFL/UEL). Different flammable materials have different flammability limits. For example,

	LFL/LEL	UFL/UEL
Benzene	1.2%	7.8%
Methane	5%	15%
Kerosene	0.7%	5%



Flammability range of benzene

## Flammable and combustible liquids

Liquids can be divided into the following classes according to their flash points and boiling points [NFPA 11].

Classification (NFPA)	Class	Flash point	Boiling point	Preferred type of tank
Flammable liquid (a liquid having a closed cup flash point below 100°F (37.8°C) and having a vapour pressure not exceeding 40 psia (2068 mmHg) at 100°F (37.8°C) shall be known as a Class I liquid)	IA	<73°F (22.8°C)	<100°F (37.8°C)	Floating roof
	IB	<73°F (22.8°C)	>100°F (37.8°C)	
	IC	73°F ≤ X < 100°F (22.8°C ≤ X < 37.8°C)	N.A.	
Combustible liquid (a liquid having a closed cup flash point at or above 100°F (37.8°C))	II	100°F ° X < 140°F (37.8°C ≤ X < 60°C)	N.A.	Fixed roof
	IIIA	140°F ≤ X < 200 °F (60°C ≤ X < 93°C)	N.A.	
	IIIB	<200°F (93°C)	N.A.	

N.A. = Not Applicable

## European model code of safe practice

Class of liquids	Flash point	Storage condition	Preferred type of tank
I	< 21°C (<69.8°F)	-	Floating roof
II (2)	21–55°C (69.8–131°F)	Handled at a temperature above its flash point*	
III (1)	55–100°C (131–212°F)	Handled at a temperature below its flash point*	Fixed roof
Unclassified	>100°C (>212°F)	-	

\* Dependent upon ambient and process rundown temperatures to tanks.

Note: Flash point is the lowest temperature at which the liquid gives off enough vapour to form an ignitable mixture in air.

Refer to BP Process Safety Booklet *Hazards of Air and Oxygen* for more details.

### 1.2.4 Explosive

Explosive substances are compounds that can undergo rapid chemical reaction, decomposition or combustion to generate large amounts of heat and gases. Examples are nitroglycerin and trinitrotoluene.



The generated gases have a combined volume much greater than the original substance, which produces a rapidly moving pressure or shock wave. It is the shock wave that causes explosion (or 'blast') damage.

Explosive vapours in air can ignite if the mixture is within the explosive/flammability limits. On the other hand, some explosives do not need to be in an oxygen atmosphere to detonate as the oxygen is chemically bonded to the compound.

Some materials are shock sensitive and can explode by mere friction or touch (e.g. nitrogen triiodide and dry picric acid) while other explosions can be caused by mixing incompatible chemicals. This is common in laboratory accidents.

**ACCIDENT** Explosion in a fume cupboard!!!

A laboratory test was being conducted which involved cleaning of an electrode using concentrated nitric acid. At the end of the cleaning, approximately 100 ml (0.026 U.S. gal) of the waste concentrated nitric acid was poured into a Winchester bottle in a fume cupboard. The bottle was labelled as 'Waste Acid' and contained a mixture of acetic acid, acetic anhydride, perchloric acid, toluene and various other hydrocarbon materials.

Approximately 15 minutes after pouring the acid into the waste bottle, a 'hissing' sound was heard and was soon followed by a very loud 'bang'. The bottle cap was blown 10–15 ft (3–4.6 m) from the fume cupboard. The glass waste container did not break but its entire contents were discharged into the air and over the inside and outside of the fume cupboard. Fortunately, no waste material splashed onto any person. The acid waste was mopped up immediately using spillage absorption granules and the affected area was then washed with clean water.

The immediate cause of the incident was the mixing of an oxidizing mineral acid with organic materials leading to a chemical reaction and pressure build-up in the waste container. Investigations revealed a failure to carry out a hazard analysis on the concentrated nitric acid cleaning procedure and a lack of instruction on waste acid disposal. No specific training had been given to analysts on the acid disposal procedure.

The power of an explosion does not only depend on the amount and type of substance involved but also on the degree of confinement and obstacle density. Generally, areas of higher degrees of confinement and obstacle density produce more severe blasts. Refer to BP Process Safety Booklet *Hazards of Air and Oxygen* for more details on deflagration and detonation.

Large explosions are extremely dangerous because they often cause structural damage, which can result in collapse or damage to equipment and/or piping which adds to the severity of the situation and can result in further loss of life. One of the main dangers in an explosion is the severe hazard caused by flying debris (especially glass from windows) or from collapsing structures.

Many old buildings and even control rooms were not built to withstand explosions—some even contain windows looking out to the plant. A number of measures are available to help reduce explosion damage to older buildings.

### 1.2.5 Radioactive

Radioactive materials are substances that can emit energy spontaneously. The energy, referred to as radiation, is produced when changes occur within the nuclei of atoms.

Exposure to radiation can affect the body in a number of ways. Exposure to very large doses of radiation may cause death within a few days or months, while exposure to lower doses may lead to skin reddening and an increased risk of developing cancer or other adverse health effects. The adverse health consequences may not be observed for many years.



The best way to protect against exposure to radiation is to avoid these materials altogether. If this is not possible, limit the amount of time spent near the source of radiation, increase your distance from the source and make sure the appropriate forms of shielding or barrier are in place. A personal dosimeter can be worn to monitor the radiation dose absorbed.

**ACCIDENT** Radioactive material disposed as scrap!!!

A radioactive level gauge on a tank was to be replaced with a non-radioactive level measurement device. The person-in-charge instructed two craftsmen to remove the level gauge equipment entirely, thinking that the radioactive source had already been extracted. But this was not the case as he had confused this tank with another tank, where the radioactive material had indeed been removed. A normal permit-to-work was used instead of the special form for handling radioactive equipment.

As a result, the craftsmen removed the level gauge with the radioactive source still intact and placed it in a scrap container for disposal. The container was only found to contain radioactive material when the disposal company performed a routine check for radiation at their site. The radioactive source holder was isolated in a dedicated containment and was traced back to the facility.

The cause of the incident was a failure to check the status of the level gauge and crosscheck this with the responsible department for radiation protection. If the disposal company had not performed a check for radiation, the radioactive material would have been lost and left to contaminate its surroundings, or subject disposal site personnel to radiation exposure.



*Level gauge on top of tank*

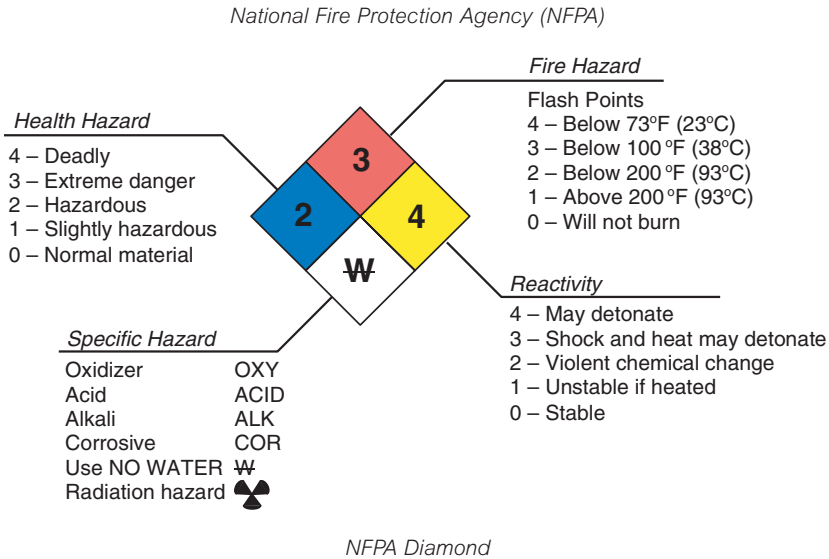


*The recovered radioactive source holder*

### 1.2.6 Signs and symbols















Systems of signs and symbols for hazardous substances have been developed by several agencies and organizations to provide quick identification and double up as warning signs for handlers. They are required to be placed in prominent locations and should be hardy enough to withstand the elements and damage.

Two examples of codes and signs for classification of hazardous materials are provided here (NFPA and IMDG).



The NFPA classification for hazardous materials will be used for illustration in this booklet.

*International Maritime Dangerous Goods (IMDG DOT) Code*

	Explosives		Dangerous when wet materials
	Flammable gas		Oxidizing agents
	Non-flammable, non-poisonous, compressed gas		Toxic materials other than gas
	Gas poisonous by inhalation		Infectious substances
	Flammable liquids		Radioactive substances
	Flammable solid		Corrosive materials
	Spontaneously combustible material		Miscellaneous dangerous substances

## 1.3 Introduction to Material Safety Data Sheets (MSDSs)

### 1.3.1 Safe handling of hazardous substances

When hazardous substances are used or handled, several issues must be considered. They include, among others:

- approval from the relevant authorities;
- adequate safe storage facilities;
- amount stored to be within safe limits;
- reliable release detection systems;
- appropriate mitigation measures and safeguards in the event of a release;
- prominent signs, labels, and warnings;
- training for safe handling and emergency response;
- safe disposal;
- substance details provided (Material Safety Data Sheets).

Before any of the steps above are taken, the following questions should be considered:

**Is this chemical really needed? Can it be replaced with a less hazardous substance?**

If the use of a hazardous material can be substituted with a safer material, the potential hazards that may arise can also be reduced. If a less hazardous material is selected, careful consideration must be given to make sure that no unforeseen problems arise from its use and that it can perform as required.

When a hazardous material cannot be substituted, make sure that risk assessments and Job Safety Analyses (JSAs) are performed to:

- identify the possible hazardous scenarios;
- determine the risks to personnel;
- determine if sufficient safeguards are in place;
- identify what further safeguards may be required.

**Follow a proper Management of Change (MOC) process when changes are made to chemicals being used.**



### 1.3.2 Material Safety Data Sheets (MSDSs)

Material Safety Data Sheets (MSDSs) contain useful information for the safe handling of hazardous materials. They are prepared to provide clear and concise information for quick reference. The information contained in MSDSs is useful for day-to-day operations but is vital during emergencies.

MSDSs of all hazardous materials must be available at strategic locations for easy access by plant personnel. They must also be provided to emergency response services to ensure that correct measures are taken in the event of an incident.

MSDSs should contain the following information as outlined by the UK Health & Safety Commission (HSC) Approved Code of Practice:

<b>a) Identification of the substance/preparation and company</b>
<b>b) Composition/information on ingredients</b>
<b>c) Hazards identification</b>
<b>d) Critical hazards to man</b> <ul style="list-style-type: none"> <li>• Symptoms and adverse health effects.</li> </ul>
<b>e) First-aid measures</b> <ul style="list-style-type: none"> <li>• Instructions for action on the spot.</li> <li>• Whether or not assistance by a doctor is needed.</li> </ul>
<b>f) Fire-fighting measures</b> <ul style="list-style-type: none"> <li>• Suitable extinguishing media.</li> <li>• Extinguishing media that must not be used.</li> <li>• Combustion products or gases.</li> <li>• Special Personal Protective Equipment (PPE) for firefighters.</li> </ul>
<b>g) Accidental release measures</b> <ul style="list-style-type: none"> <li>• Personal and environmental precautions.</li> <li>• Methods for cleaning up.</li> </ul>
<b>h) Handling and storage</b>
<b>i) Exposure controls/personal protection</b> <ul style="list-style-type: none"> <li>• Type of equipment for respiratory, hand, eye and skin protection.</li> </ul>
<b>j) Physical and chemical properties</b> <ul style="list-style-type: none"> <li>• Appearance, odour, pH, boiling point, melting point, flash point, auto ignition temperature, vapour pressure, relative density, etc.</li> </ul>
<b>k) Stability and reactivity</b> <ul style="list-style-type: none"> <li>• Conditions and materials to avoid.</li> </ul>
<b>l) Toxicological information</b> <ul style="list-style-type: none"> <li>• Immediate and delayed health effects.</li> </ul>
<b>m) Ecological information</b> <ul style="list-style-type: none"> <li>• Mobility, degradability, accumulation, ecotoxicity, other adverse effects.</li> </ul>
<b>n) Disposal considerations</b>
<b>o) Transport information</b>
<b>p) Regulatory information</b>
<b>q) Other information</b>

Ensure that you have continuous access to up-to-date MSDSs for all the products at your site, both for process and other activities such as maintenance (oils, grease, etc.), cleaning (detergent, soaps, etc.), and firefighting (foam concentrates, dry powder, etc.).

### **ACCIDENT** Confined space incident escalates due to confusion over properties of material!!!

Firefighters rushed to the scene when they were summoned to rescue a worker who had fallen unconscious in a tank which still contained some toluene. The worker entered the tank to perform cleaning operations without proper protective clothing or breathing apparatus.



During initial radio communications, there was some mispronunciation of the product name which caused confusion and delay in researching its properties, although it was confirmed as toluene within a few minutes. Thinking that they were dealing with a 'toxic material' the firefighters decided to cut a hole in the tank wall using power saws.

An explosion occurred, ignited by the cutting operation, which hurled the firefighters through the air. The saw operator was thrown against the bund wall and killed instantaneously. In all, 14 firefighters were injured in addition to the fatality. An autopsy of the fallen man within the tank indicated that he had died of asphyxiation and inhalation of toluene even before the cutting operation started.

This incident emphasizes the need for recognition of all the properties of hazardous materials before the application of appropriate procedures, especially during fire and rescue operations.

**ACCIDENT** Wrong material used causes disaster!!!

A chemical manufacturing company produced two products: *Firemaster*—a fire retardant and *Neuromaster*—an animal feed supplement. Both products were packed in their own specific bags with distinctive markings. However, the company ran out of the normal bags and used the same paper sacks for each product with the trade name correctly stencilled.

A farm service company dispatched a lorry to collect an order for the feed supplement. Unfortunately the driver was illiterate and loaded the fire retardant material instead of animal feed supplement. The farm service company, thinking that the product was an 'improved' feed supplement, added the fire retardant material into an animal feed mixture.

In the autumn of that year, cattle started dying in the fields, hens stopped laying eggs and milk yields started dropping. The cattle were slaughtered and sold which led to the chemical entering the human food chain. This resulted in complaints varying from hair loss to swollen joints and fatigue.



**Always check the order form against the label of the product when loading and delivering material.**

**The change of design of the packaging should be passed through the Management of Change (MOC) procedure.**

**Always segregate products that may have serious implications if mistaken.**

**ACCIDENT** Over 1600 poisoned by PCBs (Poly Chlorinated Biphenyls)!!!

More than 1600 people in Japan were poisoned by cooking oil (rice oil) contaminated with PCBs (Poly Chlorinated Biphenyls) in 1968. PCBs had entered the cooking oil from a heat transfer unit. The contaminating oil likely contained furans and dioxins, compounds generally more toxic than PCBs themselves. The ensuing illness became known as 'Yusho' or 'rice oil disease' and is an acute form of chloracne.

PCBs are used in electrical equipment as transformer/capacitor oil. Any electrical equipment built before 1980 with dielectric oil is likely to have PCB-containing oil!

Any equipment containing PCB oil should be clearly labelled. PCB containing equipment must be disposed of in an approved and environmentally friendly manner.

## 1.4 Toxicity and health effects

**Toxicity** is the first factor that determines the hazard level of a toxic material; it is a measure of the material's ability to cause adverse health effects to humans.

For different materials, the doses needed to produce an adverse health effect vary widely. LD<sub>50</sub> and LC<sub>50</sub> values are used as a coarse index to compare the acute toxicity of different materials.

- **Lethal Dose 50% (LD<sub>50</sub>)** is the dose that kills 50% of a group of test animals. The dose is administered, all at once, orally or applied to the skin. It is usually expressed as milligrams of material administered per kilogram of the body weight of the test animal.
- **Lethal Concentration 50% (LC<sub>50</sub>)** is the concentration (in air or in water) that kills 50% of a group of test animals exposed to that concentration for a specified time period, usually 1 or 4 hours. It is usually expressed as parts per million (ppm) of material inhaled per kilogram of the body weight of the test animal.

Toxicity data for a material is usually obtained by administering the material to mice or rats. Autopsies reveal which of the animal's organs were affected. It is roughly expected that the same effects will occur in humans who are exposed to the same material for an equivalent concentration and time.

Toxicity Classes				Spectrum of Toxic Dose (orally or applied to skin)	
Toxicity Rating	Descriptive Term	LD <sub>50</sub> (wt/kg) Single Oral Dose Rats	LC <sub>50</sub> (ppm) 4 Hour Inhalation Rats	Materials	LD <sub>50</sub> (mg/kg)
1	Extremely toxic	1 mg or less	<10	Dioxin	0.001
2	Highly toxic	1–50 mg	10–100	Nicotine	1
				Hydrogen cyanide	3.7
3	Moderately toxic	50–500 mg	100–1,000	Ethylene oxide	72
				Acrylonitrile	78
4	Slightly toxic	0.5–5 g	1,000–10,000	Ammonia	350
				Toluene	636
5	Practically non-toxic	5–15 g	10,000–100,000	Benzene	930
				Hydrogen fluoride	1,276
6	Relatively harmless	15g or more	>100,000	Sulphuric acid	2,140
				Xylene	4,300
				Tetrachloroethylene	8,850
				Ethanol	10,000

*Toxicity class and an example of spectrum of toxic dose*

**Only a very small amount of a very toxic material can cause serious adverse effects.**

**What is PPM?**

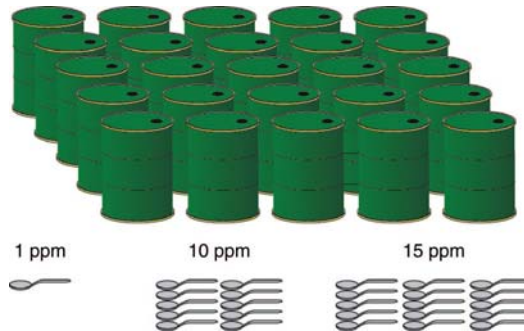
PPM stands for Parts Per Million. It is a unit of concentration that is convenient to use when the amount of substance in a solution is very small. PPM is a ratio that compares a number to 1,000,000.

$$ppm = \left( \frac{\text{Mass of component}}{\text{Mass of solution}} \right) \times 1,000,000$$

The concept of PPM is not much different from percentage. 1% is one part out of 100 equal parts while 1 ppm is one part in 1,000,000 equal parts. Therefore, one percent equals to 10,000 ppm.

**How small is 1 ppm?**

*One part per million (ppm) would be one (1) teaspoonful in approximately 25 drums*



Highly toxic materials require such tiny amounts to seriously affect humans that their limit concentrations are usually given in ppm (e.g., the Threshold Limit Value of hydrogen sulphide is 10 ppm).

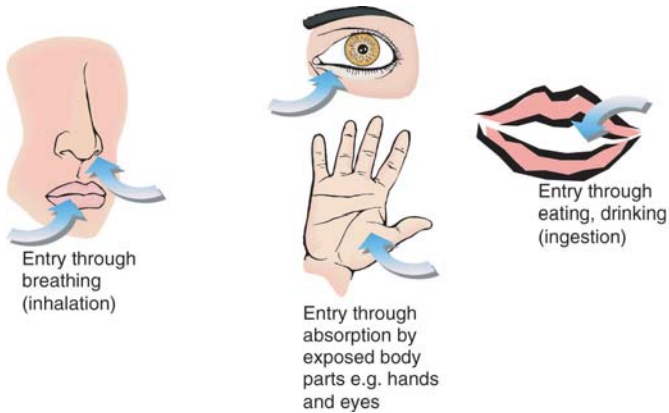
Note that hydrogen sulphide ( $H_2S$ ) is also flammable but it is the toxicity that is far more lethal.  $H_2S$  can kill long before its concentration reaches the Lower Explosive Limit (LEL). It is important to recognize that some properties of a substance are more significant than others.

### 1.4.1 Methods of entry

In order for a hazardous materials to affect a person's health, it must first contact or enter the body.

Hazardous materials can enter our body through:

- inhalation through breathing;
- absorption through skin and eyes;
- ingestion through eating and drinking.



**Hazardous materials can enter our body through inhalation, absorption and ingestion.**

#### Inhalation

Inhalation is the most common way for hazardous materials to enter the body. Through breathing of contaminated air at the workplace, the hazardous gas, vapour, mist, fume, smoke or dust enters our nose and/or mouth, and subsequently into our lungs.

The hazardous materials are then absorbed into the blood stream and transferred to other organs in our body. These materials can cause damage to specific organs (target organs).

Some hazardous gases and vapours have distinctive odours, for example, rotten egg smell of hydrogen sulphide ( $H_2S$ ), bitter almond smell of hydrogen cyanide (HCN), aromatic smell of benzene, pungent urine smell of ammonia, pungent and piercing smell of chlorine, and suffocating odour like musty hay of phosgene.

Some hazardous gases are odourless and colourless, and they can kill a person instantly without warning. Examples are carbon monoxide (CO), and inert atmospheres of nitrogen ( $N_2$ ) or carbon dioxide ( $CO_2$ ).

Never rely on your nose to detect toxic gases. Some products cannot be smelled before it is too late while others have no odour, as described previously. There are also products that inhibit the sense of smell like H<sub>2</sub>S. Always use a portable personal gas detector and alarm.

Install fixed gas detectors and an alarm system in the plant at locations where leaks of hazardous gases are expected. Wear personal gas monitors when working around hazardous materials with acute health effects.

Excessive inhalation of dust and particulates (such as silica, asbestos, etc) can also cause scarring of the lung tissues (fibrosis).

Do not smoke, weld, burn or use any naked lights/open flames in areas which may contain the vapour of *chlorinated solvents*. When heated or burned, chlorinated solvents decompose to give off high concentrations of toxic vapours, such as *phosgene* and *hydrogen chloride*.

It is best to anticipate the hazards of working with these substances. Always use adequate engineering controls, administrative controls, and wear the appropriate PPE (Personal Protective Equipment) (i.e. respiratory protection) to avoid inhalation of hazardous gas and dusts.

### **Absorption**

Some materials, when contacted, can seep through the skin and eyes into the blood stream. This process is similar to applying Vicks vapour rub (medicated ointment for cold relief) onto your body, using a medicated plaster to relieve an aching neck, or a nicotine patch to give up smoking.

Some gas or liquid materials such as hydrogen cyanide (HCN), phenol, benzene, carbon tetrachloride, carbon disulphide, and methanol can pass through unbroken skin and mucous membranes (for example, eyes and mouth), and subsequently enter the blood stream. Some materials are so corrosive they burn holes in the skin, allowing entry for infection or other materials.

Absorption into the body is faster through open wounds (such as cuts, bruises and injuries). All wounds must be treated and dressed promptly.

Use a safety shower and eyewash when you come in contact with or are accidentally splashed with hazardous materials.

Always use adequate engineering controls, administrative controls, and wear appropriate PPE to minimize exposure to hazardous materials.

Avoid skin contact with hazardous materials, solvents and any products containing solvents by wearing suitable protective clothing (coveralls, gloves, safety goggles, boots, face shield, etc.) where necessary. Report any defective equipment.

If work clothes become drenched or saturated with solvents, they will act as a reservoir to bathe the body continually with the harmful materials. Remove and change work clothes or PPE promptly when they become drenched or soaked with harmful materials.

Wash, dry, and maintain PPE in accordance with manufacturer's recommendations. If possible, leave contaminated work clothes and PPE at the workplace for cleaning, laundry and drying. Do not wear or bring them home.

Do not leave solvent-contaminated rags lying around.



### **ACCIDENT** Contractor dies when acetone cyanohydrin (ACH) penetrates clothing!!!

A contractor was working around pumps in a cyanide area. While crouching, his back accidentally nudged open a quarter turn ball valve on an adjacent pipe. Some liquid fell on him but he did not notice this.

After finishing his job, the contractor went home and developed flu-like symptoms. His wife, a nurse, recognizing that something was wrong, took him to the local hospital. The medical staff at the hospital had no knowledge that he had been exposed to ACH (Acetone Cyanohydrin) and were not trained to handle patients with exposure to cyanide. The contractor died in hospital.

### **ACCIDENT** Operator collapses after donning contaminated clothing!!!

An operator was cleaning wastewater filters when he was splashed with wastewater. The wastewater was from the ACH (Acetone Cyanohydrin) plant. He later returned to the control room. His colleagues, observing that he was looking unwell, suggested that he have a shower and get some rest. After showering, the operator put on his old boots and collapsed. He was revived after amyl nitrite and oxygen were administered.



**Never put on soiled or contaminated clothes. Many people have collapsed after wearing contaminated coats, gloves, boots, etc.**

### **Ingestion**

Hazardous materials can enter our body through eating and drinking food and beverages contaminated by unwashed hands, gloves, clothing, or are left exposed in the workplace. Nail biting and smoking can also contribute to the ingestion of hazardous materials.

Liquid materials may also enter the body through accidental consumption. For example, if a liquid is transferred to a bottle and not labelled adequately, a worker may mistake it for water or a beverage.



Do not eat or smoke in areas where there are hazardous materials.

After working with hazardous materials, wash thoroughly before eating or smoking. Launder or dispose of contaminated clothing appropriately.

### **ACCIDENT** Man ingests cyanide while taking a smoke!!!

An operator entered a plant laboratory to look for some Draeger tubes. He put his PVC gloves down on the ledge of a fume cupboard, knocking over a pile of old sample bottles. Instinctively he reached out to the bottles, getting his fingers wet in the process. Believing the dampness to be water, he put on his gloves and left the laboratory.

On his way back to the control room, he stopped for a smoke. He removed his gloves and rolled his cigarette, licking his fingers. His fingers had a funny taste and he had a few puffs before recognizing that they had been contaminated with cyanide!

He quickly went to the locker room to wash his hands. He sat down upon returning to the control room and fell unconscious. He was lucky to have recovered after being given medical treatment.

## 1.4.2 Dose and response

How toxic a material is depends on its toxicity. Its potential to cause harm to workers also depends on the *concentration* and *duration* of exposure.

**All personnel, employees and contractors alike, must be protected against any potential exposure to toxic materials.**

### Types of exposures

There are two types of human exposure to hazardous materials at the workplace—*acute* and *chronic* exposures.

#### *Acute exposure (sudden and short-term)*

A one-time exposure to a relatively large amount of a material usually during an accidental release from operations or maintenance activities (improper handling of the materials, runaway reactions, cleaning of equipment that normally contains materials, e.g. solvent vat). Exposure may last for minutes, hours or days.

#### *Chronic exposure (repeated and long-term)*

A repeated exposure over a long period of time, usually to a small quantity of fugitive emissions from flanges, valves, pumps, sampling, loading and unloading operations, etc. The exposure levels may be too small to cause any immediate ill health effects. Exposure may last for months or years.

### **Types of health effects**

Once inside our body, the toxic materials are carried and distributed to areas of the body by the *blood stream*. In this way, they can attack and harm specific target organs, such as lungs, kidneys, liver, the central nervous system CNS (brain and spinal cord), bones, and muscle tissues, which are susceptible to these materials.

The ill-health effects caused by hazardous materials may be:

- acute or chronic (immediate or delayed);
- temporary or permanent (reversible or irreversible);
- local or systemic (affecting initial contact area or target organs).

#### *Acute vs. chronic*

An *acute* effect develops immediately, or a short time, after an exposure. Acute health effects may appear minutes, hours or even days after an exposure. Examples are chlorine, methyl iso-cyanate (Bhopal incident), hydrogen sulphide, sulphur dioxide, carbon monoxide, and phosgene poisoning.

A *chronic* effect develops slowly over a long period of time and persists or recurs frequently. Chronic health effects may appear months or years after an exposure. Examples are mesothelioma, and cancer.

*Note: An acute exposure does not necessarily lead to acute effects only. They can lead to both acute and chronic effects.*

#### *Temporary vs. permanent*

Health effects may be *temporary*, such as skin irritation, coughing, nausea, dizziness, and fatigue. They may also be *permanent*, such as blindness, scars from acid burns, fibrosis, mental impairment and damage to organs. Although some effects are temporary (such as dizziness, reduction of the ability to think clearly and coordinate movements, and loss of consciousness), they may impair a victim's ability to rescue himself or herself, potentially resulting in death.

#### *Local vs. systemic*

*Local* effects occur at an area of the body that has been in initial contact with the material. Examples are skin irritation, acid burns and lung fibrosis.

*Systemic* effects occur after the material has been absorbed and distributed via the bloodstream from the entry point to other parts of the body (for example, target organs which are susceptible to the materials). *Chlorinated solvents* are a systemic poison whose target organ is primarily the liver. Most substances produce systemic effects, but some substances may cause both types of effects. An example is *tetraethyl lead* (a gasoline additive), which produces skin irritation at the contact site. It is absorbed and transported into the body causing damage to the central nervous system and other organs.

Major target organs that are susceptible to various hazardous materials are:

- lungs;
- liver;
- reproductive system;
- kidneys;
- bones and muscle tissues;
- central nervous system (CNS), which includes the brain and spinal cord.

### Asphyxia

In addition to the direct impacts from hazardous materials, the *central nervous system (CNS)* is also easily affected by the lack of oxygen supply—a condition called asphyxia. *Simple asphyxia* is caused by a lack of oxygen in the inhaled air, such as inert atmosphere of nitrogen or carbon dioxide. *Chemical asphyxia* is caused by chemicals (chlorine, phosgene, CO, H<sub>2</sub>S, HCN, CS<sub>2</sub>, EO, methyl chloride, etc.) that reduce the blood's ability to carry oxygen. For example, *carbon monoxide*, a colourless, odourless, flammable, and very toxic gas produced by incomplete combustion of carbon compounds and a by-product of many chemical processes, blocks the proper utilization of oxygen. Haemoglobin (oxygen carrier in the red blood cells) absorbs carbon monoxide 200 times more readily than it does oxygen. The CO-haemoglobin bonding is also stronger than the O<sub>2</sub>-haemoglobin bonding.



Victims of carbon monoxide poisoning often have blue lips and fingernails, a condition known as 'cyanosis'. The condition arises from deoxygenated haemoglobin. Cyanosis gets its name from the colour cyan, which is a greenish blue, not from the symptoms of cyanide poisoning. (While cyanide poisoning does interfere with the body's handling of oxygen, its mechanism of action involves cytochrome oxidase rather than haemoglobin.)

### Loss of ability to save oneself

Exposure to certain materials that attack the CNS directly or via asphyxia, may cause a slowing down of the function of the brain. Symptoms include:

Rapid respiration	Poor coordination of movements
Accelerated pulse rate	Reduced awareness of surroundings
Dizziness	Faulty judgment
Difficulty and weakening of speech	Convulsions
A gradual loss of balance	Loss of consciousness

When this happens, victims lose the ability to think clearly, react sensibly, escape from the hazards, or rescue themselves.

**Retreat from hazardous areas on the first signs of any toxic effects. Remove victims to fresh air and call for help. Do not enter the hazardous area without giving off an alert AND wearing the appropriate breathing apparatus.**

### How much is too much?

The human body can sometimes tolerate certain amounts of a toxic substance before succumbing to ill effects. How do we know what amount is too much for the many different toxic materials?

There are several references for exposure limits of toxic substances that may be inhaled. Some of the more commonly used are available from:

- American Conference of Governmental Industrial Hygienist (ACGIH);
- Occupational Safety and Health Administration (OSHA);
- UK Health & Safety Executive (HSE) EH40.

There may be legal obligations to keep below the exposure limits for some lists, depending on the source organization and country laws, while other lists are given as recommendations. Generally, the more conservative (lower exposure limits) or recently updated values are used.



### Exposure limits

Exposure limits are usually given with respect to the period of exposure, taking into account the difference between acute and chronic exposures. The exposure limits available are usually for 8-hour, 30-minute, and 15-minute exposures. Some toxic substances have exposure limits which no person should be exposed to at any time. These limits are known as *ceiling limits*.

*Time Weighted Average (TWA) Limits* are maximum concentrations that it is believed most workers may be repeatedly exposed, day after day, without adverse effects for a conventional 8-hour workday and a 40-hour workweek. *Threshold Limit Values (TLV)* set by ACGIH, *Permissible Exposure Limits (PEL)* given by OSHA, and *Occupational Exposure Limits (OEL)* specified by HSE EH40 are TWA-based concentrations. They allow excursions above the given exposure limits, provided that there is a compensating equivalent excursion below the limit during the workday.

*Short Term Exposure Limits (STEL)* are maximum concentrations that a worker can be exposed to for a period of up to 15 minutes continuously without suffering:

- intolerable irritation;
- chronic or irreversible tissue change;
- narcosis of sufficient degree to increase the likelihood of accidents, impair self-rescue, or materially reduce work efficiency.

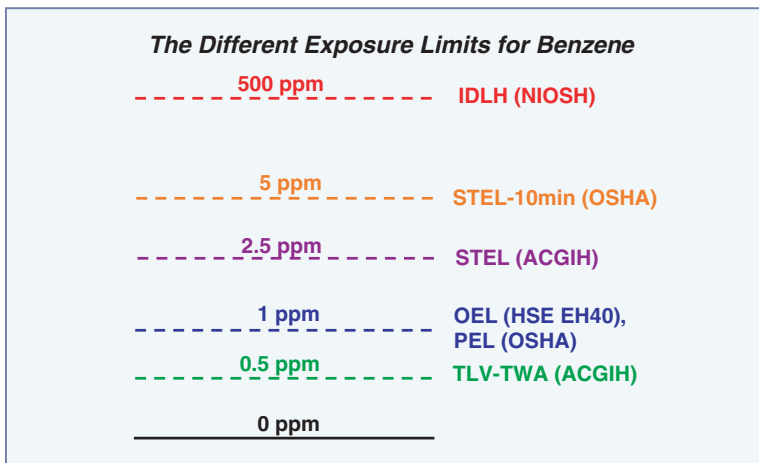
No more than four STEL periods per day are permitted, with at least 60 minutes between exposure periods. Note that the daily TWA limit must not be exceeded.

*Immediately Dangerous to Life or Health (IDLH) Concentrations* are concentrations from which a worker could escape without injury or without irreversible health effects in the event of respiratory protection equipment failure. Only 'highly reliable' respirators are to be used at concentrations above IDLH. Refer to BP Process Safety Booklet *Hazards of Nitrogen and Catalyst Handling*.



IDLHs are based on the effects that might occur as a consequence of a 30-minute exposure, although in most cases, exit from a hazardous atmosphere could occur in much less than 30 minutes. However, the 30-minute period is a safety margin and is *not* meant to imply that workers should stay in the work environment any longer than necessary following the failure of respiratory protection equipment. Every effort should be made to exit immediately!

*Note: The choice of type of exposure limit to use depends largely on the conditions and purpose of the activity (such as confined space work, rescue situations, etc.).*



### 1.4.3 Dust and particulate matter

Though not acutely toxic, dust and particulate matter can cause significant damage to our respiratory system. Air is breathed in through the nose or mouth. Large dust particles may be filtered by nasal hair, trapped in the mucous lining along the air passage, or swallowed and destroyed by macrophages (scavenger cells). Particulate matter equal to or smaller than 10 micrometer (PM-10) may pass through all the above defence mechanisms in our body and be retained in our lungs.

Wedged in the lungs, these particles (asbestos fibres, for example, are long and sharp) cause fibrous or scar tissue to form around them. This tissue is the body's normal way of repairing itself. However, too much fibrous tissue and scarring (fibrosis) can cause the lungs to lose their elasticity and become stiff, thus impairing normal lung functions and causing a permanent disability.

*Possible sources of dust and particulate matter in oil and petrochemical facilities are from:*



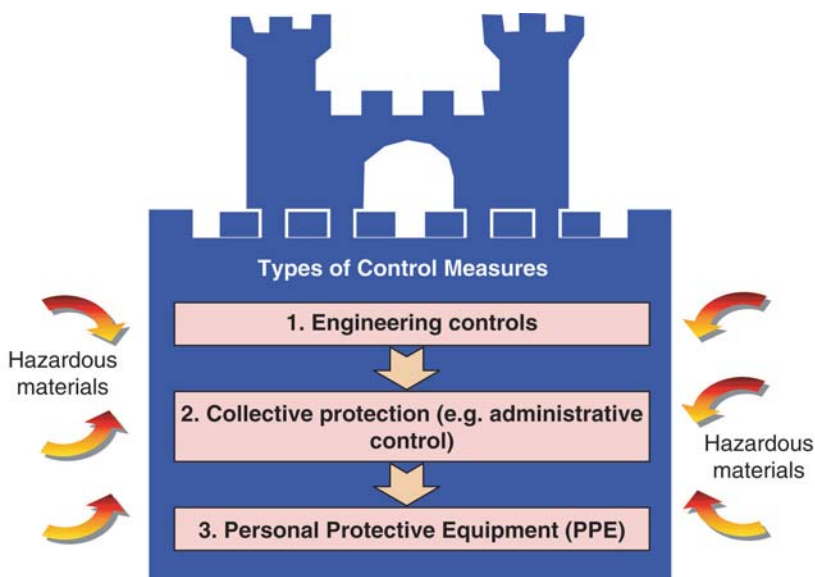
Note: Dust from inside furnaces burning oil can contain Vanadium Pentoxide ( $V_2O_5$ ), which may cause coughing, laboured breathing, and a burning sensation.

Engineering and administrative controls must be put in place to avoid respiratory problems caused by exposure to dust. Some examples are:

- substitution of solid substances with liquids;
- use of wet processes;
- enclosure of dust-producing processes under negative air pressure (slight vacuum compared to air pressure outside the enclosure);
- exhausting air containing dust through a collection system before emission to the atmosphere;
- use of vacuum cleaning instead of brooms;
- good housekeeping;
- efficient storage and transport;
- controlled disposal of dangerous waste.

## 1.5 Control of exposures

Where the use of hazardous materials cannot be eliminated or substituted, the following measures may be used to control exposure, in descending order of priority:



### 1.5.1 Engineering controls

Engineering controls are the *most effective* method because they *remove, isolate or reduce* the source of the hazard rather than lessen the damage that may result from the hazard. Control must only come after the anticipation and recognition of a hazard.

*Substitution* of a hazardous material or industrial process with a non-hazardous one is the best way to remove a hazard at the source. It totally eliminates exposure to materials that are hazardous.

Other engineering controls, such as mechanical ventilation, pneumatic dust transfer, and process enclosure, should be built into the work process. They are less dependent on the chemical user who, unfortunately, is subject to human errors (for example, forgetfulness, preoccupation, insufficient knowledge).

Some techniques used in engineering controls are:

- substitution of a hazardous material with a less or non-hazardous material;
- substitution of a hazardous process with an inherently safer process;
- process or equipment modification;

- isolation or total enclosure;
- ventilation (by general and/or local exhaust ventilation);
- reduction of process temperatures and pressures;
- reduction of storage inventory of hazardous raw materials and products;
- use of equipment that requires less maintenance;
- use of equipment with no moving part seals;
- use of secondary containment on mechanical seal/glands.

### 1.5.2 Administrative controls

Administrative controls are required either as supplemental hazard controls or to ensure that engineering controls are developed, maintained, properly functioning and effective. Administrative controls consist of managerial efforts to reduce hazards through *planning, information and training* (such as hazard communication, MSDSs), *written policies and procedures* (for example, the Chemical Hygiene Plan), *safe work practices*, and *environmental and medical surveillance* (for example, work place inspections, equipment preventive maintenance, exposure monitoring, and workers' health monitoring). They primarily address the human element of hazard controls.

Other administrative controls include:

- reduction of the number of exposed workers;
- reduction of the duration and/or frequency of exposure of workers;
- good housekeeping;
- education, training and evaluation;
- Management of Change (MOC);
- regular environmental and medical monitoring or surveillance to check that the above control methods are effective.

#### Gas testing

Gas testing is important when personnel are required to work in areas where exposure to hazardous substances is a possibility. Inadequate or improper gas testing can be a cause of fatal accidents because many people do not understand the basic working principle of flammable gas detectors.

Most portable flammable gas detectors operate by the catalytic combustion of a flammable gas on a heated filament (usually platinum), to give a reading of the %LEL (or %LFL). Accordingly, there must be approximately 21% oxygen in the sample to give an accurate reading. If the atmosphere being tested is deficient in oxygen,





for example, purged with nitrogen, it is not possible to use a standard type of flammable gas detector to detect hydrocarbon vapours.

Flammable gas detectors must be maintained, calibrated and operated in accordance with the manufacturer's recommendations in order to give accurate results.

Always use the correct instrument for measurement of oxygen, LEL and percentage of toxics. Do not use gas tube detectors (which change colour upon detection) for measurement of %LEL. Gas tube detectors are used to determine the presence of low concentrations of a known contaminant as each tube is designed for a specific contaminant.

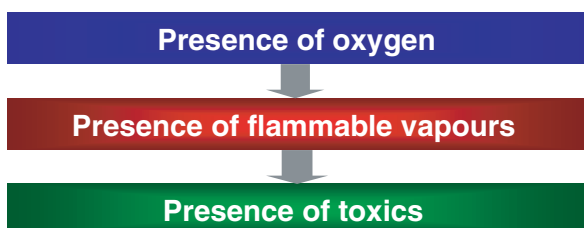
Note that some gases may cross influence detectors, a condition known as cross-sensitivity, resulting in less accurate results. For example, Draeger tubes for acetic acid testing results in the same colour change (yellow) not only for acetic acid but also for sulphur dioxide, leading to inaccurate test results in the presence of this contaminant. Refer to your manufacturer's data to ensure that the right detector is chosen to obtain accurate results.

Similarly, combustible gas detectors should not be used to measure toxic substances as they will not measure the very low concentrations of toxic substances present (in parts per million) that may pose a health risk.

Fortunately, single detectors are now manufactured to be able to detect a number of gases, for example, O<sub>2</sub>-LEL-H<sub>2</sub>S-CO. This makes gas testing more convenient, without having to carry multiple instruments. However, the background knowledge of gas testing is still fundamental in the interpretation of test results and cannot be overlooked.

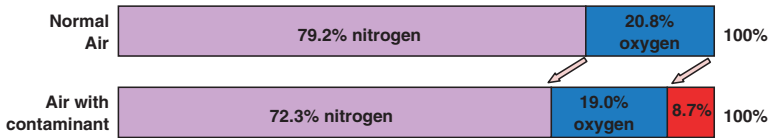
#### Notes

- a) Gas testing must be undertaken in the following order:



- b) If the gas testing equipment is calibrated on one specific flammable mixture, it may be inaccurate for measuring the LEL for another mixture, for example, if calibrated with methane/air mixture of 10% LEL it may give a reading of 29% LEL for toluene/air mixture.
- c) A low O<sub>2</sub> reading may mean the presence of a contaminant. This is because when a gaseous substance is introduced, it displaces air (nitrogen and oxygen) resulting in an oxygen level of less than 20.8%.

If the reading is 19.0% O<sub>2</sub>, then the atmosphere contains 8.7% of another contaminant (the ratio of nitrogen to oxygen in air is always 79.2 / 20.8).



If O<sub>2</sub> is above 20.8%, which is the normal O<sub>2</sub> content in air, there is a leak from an oxygen source.

- d) Make sure all areas of the work area are gas tested and visually inspected.
- e) Remember that some vapours are heavier than air and tend to settle in low places, particularly in confined spaces.

Refer to BP Process Safety Booklets *Confined Space Entry* and *Safe Tank Farm and (Un)Loading Operations* for more on gas testing practices.

### 1.5.3 Personal Protective Equipment (PPE)

Personal protective equipment (PPE) is clothing or devices worn to help isolate a person from direct exposure to a hazardous material or situation. PPE reduces or eliminates the risk of injury by *interrupting the routes of entry* (inhalation, absorption, ingestion) of hazardous material(s) into the body. Recommended personal protective equipment for a particular material is often listed in its MSDS.

The use of personal protective equipment is the least preferred method of protection from hazardous exposures as it can be unreliable and, if it fails, the person can be left completely unprotected.

Sometimes, personal protective equipment may be needed along with engineering controls. For example, a ventilation system (an engineering control) reduces the inhalation hazard of a material, while gloves and an apron (personal protective equipment) reduce skin contact.

Use of personal protective equipment may be vital, but it is nevertheless the *last and weakest* layer of protection.

**Personal protective equipment should not be a substitute for proper engineering and administrative control and should be used only where other control methods are not yet effective or are inadequate.**

Personal protective equipment can be an important means of protection when engineering controls are not practical, for example, during an emergency or other temporary conditions such as maintenance operations.

Personal protective equipment includes respiratory protective equipment, protective clothing and footwear, equipment to protect the face, eyes and hands, and equipment to prevent an accumulation of static electricity, such as anti-static footwear.

PPE against hazardous chemicals may include:

- splash-proof chemical safety goggles or face-shield (eight-inch minimum);
- chemical resistant and anti-static gloves, coveralls, aprons, boots, etc.;
- dust masks or respirators, or SCBA;
- hard hats;
- chemical suits.



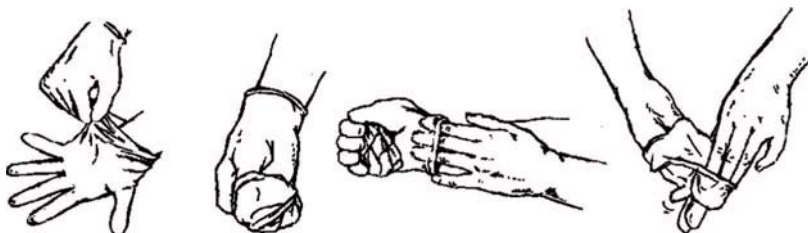
An effective personal protective equipment programme requires the following steps and resources:

- A thorough *hazard assessment*.
- The *correct equipment* such as a respirator designed to protect against dust is useless if the hazardous material is present as a gas; and many solvents can rapidly penetrate natural rubber gloves.
- A thorough *training programme* for workers who are required to use the equipment, with refresher training at regular intervals.
- Appropriate *fit tests* to ensure that equipment (particularly face masks and respirators) fits correctly.
- Special *medical surveillance* for workers who work in potentially hazardous areas.
- A regular *equipment maintenance programme* that includes regular inspection, cleaning and maintenance of equipment to ensure that it is operating correctly, and regular replacement of items such as gloves or disposable parts such as respirator filters. Respirator filters should be replaced at regular time intervals (according to manufacturer's recommendation) rather than only when they have become clogged.
- A *personal set of equipment* for each worker and a secure and clean place in which to store it.

In cases of highly toxic materials, it may be necessary to undertake specific 'chemical breakthrough testing' on PPE, as suppliers' own claims have been proven to be false for certain chemicals, especially when mixtures of materials are involved.

### How to remove gloves

The following figures show the correct way to remove used gloves to avoid contamination.



1. Grasp the outside of one glove

2. Hold the glove with your gloved hand

3. Insert your fingers on the inside of the glove

4. Turn the glove inside out over the first glove

### Appropriate coveralls for flash fire hazards

If flammable materials are handled at the workplace, the coveralls must be able to protect the operator during a flash fire. The temperatures attained by flash fires have been estimated to range from 550 to 1050°C (1022 to 1922°F). Most regular clothing fabrics burst into flames at these temperatures. *Untreated cotton, polyester, nylon and polycotton blends* are *inappropriate* clothing materials because they have low ignition temperatures, ignite easily and/or melt readily, causing more severe burns than uncovered head and hands. Therefore, coveralls must be made of inherently fire resistant materials and must be anti-static. They protect workers from exposure to intense heat and flames for short periods of time (i.e. flash fires). Statistics show that chances of survival are much higher for victims who were protected from flash fires and able to run to safety.

### Conditions for confined space entry without respiratory protection\*

- The confined space is clear of all deposits, scale and sludges likely to give off vapours when disturbed.
- The work to be done inside the confined space will not release or generate flammable or toxic vapours.
- The confined space is adequately ventilated and tested to ensure a safe atmosphere.

\*Note: Air purifying respirators may only be worn in a confined space under specified conditions defined by the safety/industrial hygiene specialist or respiratory program co-coordinator.

**Conditions for confined space entry with air supplied respiratory protection**

- Potentially harmful deposits, scale or sludges are present which cannot be removed by outside cleaning.
- All practicable measures have been taken to eliminate flammable or toxic vapours.
- Ventilation is maintained to reduce the concentration of contaminants to a minimum.
- Constant monitoring of the confined space is required to ensure harmful contaminants remain within acceptable limits.
- Authorized entrants must be withdrawn immediately if these conditions are exceeded and conditions re-evaluated by the Issuing Authority before any subsequent entry.

**A Risk Assessment is required prior to entry into a confined space for gas testing, and controlled through a Confined Space Entry Permit in accordance with the site's Safety Rules.**

**Gas tests and a visual inspection will be required to determine whether there is a safe working environment for hot work.**

A standby attendant must remain on duty outside the tank for the duration of the entry. Standby attendants should be given proper training and provided with:

- Full instructions on their duties.
- Appropriate PPE and breathing apparatus—so that they can look into the confined space.
- Strict instructions not to enter the tank under any circumstances. Their role is to raise the alarm and wait for rescuers to arrive and then communicate vital information to the rescue team.
- A copy of and training in the emergency/rescue plan.

**Standby attendants are strictly not allowed to enter the confined space under any circumstances!**

Refer to BP Process Safety Booklet *Confined Space Entry* for more information on gas testing.

**Diagram showing authorization requirements for entry  
against various levels of gas concentration**

	Oxygen	Flammable	Toxic
Entry without breathing apparatus (BA)	20.8%	<1% LEL	<10% OEL
Special risk assessment for use of BA	19.5–23.5%	Up to 20% LEL*	Up to STEL
Unsafe—no entry allowed	>23.5%, or <19.5%	>20% LEL	> STEL

\*flammable gas concentration should be below 10% LEL (this should be considered as an entry criteria, with 20% LEL used as an exit criteria where work should stop and persons be withdrawn from the confined space).

**LEL**—abbreviation for 'Lower Flammable Limit' which is the lowest concentration of a flammable gas in air capable of being ignited by a spark or flame. The term 'Lower Explosive Limit', or 'LEL' is sometimes used to describe the same effect.

**OEL**—abbreviation used for Occupational Exposure Limit value used to restrict total long-term intake by inhalation over one or more work periods to levels to which an average worker may be exposed without harmful effect. This is normally quoted as the time weighted average (TWA) concentration over an 8-hour working day. National Authorities publish their own exposure limit type data (for example, the UK Health & Safety Executive publishes Occupational Exposure Limits, and in the US TLV's (threshold limit values) are published by ACGIH).

**STEL**—abbreviation used for Short Term Exposure (usually not exceeding 15 minutes) which is applied to restrict brief exposures over the OEL which are unlikely to produce serious short or long term effects on health over the time it is reasonable to expect the excessive exposure to be identified and remedied. For substances assigned both an OEL and STEL the total number of exposures above the OEL should not exceed one hour in a 24-hour period (i.e. four per day), and should not cause the OEL measured as a time weighted average to be exceeded. Again, National Authorities publish their own exposure data as indicated above, and describe methods of determining short term exposure limits if none are quoted in the standard.

**Life Threatening Atmospheres**—no person should be allowed to enter a life threatening atmosphere with, or without, normally available respiratory protection as this does not provide adequate protection to work safely. A life threatening atmosphere can be considered to be one where:

- the oxygen content is below 19.5% or above 23.5%;
- concentrations of flammable gas or vapour are above 20% LEL;
- concentrations of toxic gases or vapours are above short term exposure values (STEL).

Where national standards are more stringent, these must be followed.

# 2

## Specific properties of some hazardous products

This chapter contains basic product properties and incident accounts of some hazardous substances commonly handled in oil installations.


The basic product properties provided are for reference only and they are by no means complete. Please refer to the detailed MSDSs provided by your manufacturers for more information relating to the chemicals at your location.

The exposure limits contained in this chapter are from the American Conference of Governmental Industrial Hygienists (ACGIH) guidelines unless otherwise stated. The definitions of terms contained in the basic product properties are provided in Chapter 3: Glossary. Please refer to Section 1.2.6 for information on how to interpret the NFPA Diamond on the top right hand side of the MSDSs.

In addition to the detailed MSDSs available at your plant, other documentation requirements of hazardous substances include:

- Product label:
  - indicates compliance with standard;
  - lists items that are part of preparation/ensemble.
- Includes certification organization mark:
  - technical data package;
  - detailed descriptions of PPE, materials, and accessories.
- technical data demonstrating compliance;
- user instructions.

## 2.1 Hydrogen sulphide

<b>HYDROGEN SULPHIDE</b>				
CAS No:	<b>7783-06-4</b>	Formula:	<b>H<sub>2</sub>S</b>	
UN No:	<b>1053</b>	Molecular mass (g/mol):	<b>34.1</b>	
<b>Physical &amp; Chemical Properties</b>				
Boiling Point:	<b>-60°C (-76°F)</b>	Specific Gravity (Water =1):	<b>1.54 (liquefied)</b>	
Vapour Pressure (kPa):	<b>1875 at 20°C (272 psi at 69 °F)</b>	Relative Vapour Density (Air = 1):	<b>1.19</b>	
Appearance and Odour:	<b>Colourless GAS. Sense of smell is inhibited above 100 ppm. Characteristic odour similar to that of rotten eggs</b>			
<b>Toxic Hazard Data</b>				
<1 ppm	<b>Detectable by smell</b>	Immediately Dangerous to Life and Health (IDLH)	ACGIH Exposure Criteria	
About 30 ppm	<b>Eye and respiratory tract irritation</b>			
About 100 ppm	<b>Loss of sense of smell</b>			
About 500 ppm	<b>Within 15 min.: dizzy, headache, nausea, abdominal pains After 30 min.: Loss of consciousness, possible death</b>	<b>100 ppm</b>	TLV (8 hours)	<b>10 ppm</b>
1,000 ppm and above	<b>Rapid loss of consciousness Death within minutes</b>		STEL (10 min)	<b>15 ppm</b>
<b>Emergency Response Data</b>				
First Aid:	<b>Remove to ventilated area; immediately remove any contaminated clothing and wash contaminated areas for 15 minutes using water. Seek medical attention immediately.</b>			
Flash Point:	<b>Not Determined</b>	Auto Ignition Temperature:	<b>260°C (500°F)</b>	
Explosive Limits (vol % in air):	<b>LEL 4.3%</b>		<b>UEL 46.0%</b>	
Extinguishing media:	<b>Stop flow of gas before attempting to extinguish fire. Use foam, dry powder or water fog. Do NOT use water jets.</b>			
Special Firefighting Procedures:	<b>Extremely flammable gas. Burning gives off sulphur dioxide and other poisonous gases. Wear full protective clothing and SCBA.</b>			
<b>Personal Protective Equipment for Leak Response</b>				
Respiratory Protection	<b>Use a positive pressure SCBA with full facepiece, or use a supplied-air respirator operated in continuous flow mode. Air purifying respirators do NOT provide protection in oxygen deficient atmospheres.</b>			
Protective Gloves	Eye Protection	Other Protective Clothing		
<b>Impervious, Thermal Protective</b>	<b>Chemical Goggles or Face Mask</b>	<b>Protective Apron (avoid skin contact)</b>		



Many incidents involving H<sub>2</sub>S have occurred at oil installations over the years. Among the issues associated with these incidents are:

- inadequate isolation;
- inadequate purging;
- plugged lines/equipment;
- violation of work permit requirements;
- difficulties in performing job wearing PPE;
- leaks from valves, pumps, compressors, etc.;
- desorption from materials such as crude, molecular sieves, etc.;
- absence of hazard assessments.

However, the most common trait in these incidents is the failure to wear proper breathing apparatus.

**Always wear the prescribed Personal Protective Equipment where H<sub>2</sub>S is concerned or suspected.  
Equipment containing H<sub>2</sub>S should be clearly identified.**

**Personnel working in potential H<sub>2</sub>S areas should carry personal H<sub>2</sub>S alarms.**

### **ACCIDENT** Inadequate purging leads to gassing fatality!!!

A propane dryer had been purged with nitrogen for seven days, and several hydrogen sulphide and hydrogen tests were done before a work permit was issued to remove valves from the skid. A slight nitrogen purge was on the equipment to prevent air from entering, and preventing possible ignition of pyrophoric material in the dryer.

On the day of the incident, an employee and a boilermaker had removed one valve without problems. While they were working on a second valve, the employee slumped to one side. The boilermaker tried to move the victim but was unsuccessful as the area where he was lying was congested with piping and valves. He then propped the unconscious man up against a bracket and went for help.

The victim's position in between piping and valves led to great difficulties in extricating him and administering medical treatment. With great effort the victim was finally lifted up and over the top of the dryer skid piping. Despite continuous cardiopulmonary resuscitation efforts en route to the hospital, the victim was pronounced dead on arrival.

Investigations determined that H<sub>2</sub>S had been trapped in a section of pipe where the second valve was located. Upon loosening the bolts, it is believed that the slight nitrogen purge pushed the H<sub>2</sub>S gas out and into the face of the victim. Inadequate purging often leaves pockets of gas or material in the system and procedures must reflect the possibility of H<sub>2</sub>S presence even after purging has been completed (for example, the wearing of the correct PPE).

**When breaking containment, follow all safety procedures associated with the system and type of material expected, and use the appropriate respiratory protection.**

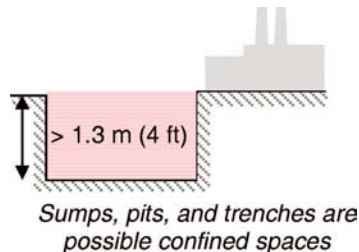
### **ACCIDENT Fatalities from a H<sub>2</sub>S incident in a confined space!!!**

Two men were carrying out a minor modification to a pipe known to contain H<sub>2</sub>S. Due to a change in the scope of work, it was necessary to excavate a two-metre (6.6 ft) deep pit to expose an additional section of pipeline.

One man entered this pit unprotected and collapsed due to H<sub>2</sub>S inhalation while working on the pipeline. Two other men in the vicinity immediately entered the pit to attempt a rescue but one of the would-be rescuers also collapsed. They had not worn the appropriate PPE. One of the three was fortunate in that he was able to crawl out and call for help. Despite attempts at resuscitation, the other men both died.

The lack of compliance to the site procedure was a key factor in this incident. A permit-to-work should have been issued stipulating the use of positive pressure breathing apparatus for work where there is a possibility of H<sub>2</sub>S release. All reasonably practicable measures should have been taken to eliminate the risk of exposure, for example, by a properly thought out program of isolation followed by drainage and purging.

A simple risk assessment would have helped those responsible to recognize that a confined space may be created by digging a two-metre (6.6 ft) pit. Coupled with the release of H<sub>2</sub>S, the atmosphere inside the confined space became lethal (hydrogen sulphide is denser than air and will collect in low-lying areas). The work should have been carried out with a Confined Space Entry Permit and with all the associated safety and protective equipment necessary to complete the work safely.



**Job Safety Assessments (JSAs) should be performed to identify all possible hazards and to determine the measures that must be taken to eliminate or contain the hazard.**

**Ensure that all rescuers are equipped with the correct Personal Protective Equipment before attempting rescue.**

**ACCIDENT** Operator gassed when breaking containment!!!

A sulphur plant operator was removing a pressure gauge from a pipeline when she was exposed to hydrogen sulphide in sufficient concentration to cause a brief loss of consciousness. She had not been wearing respiratory protection. The standby operator immediately went to her aid without donning fresh air equipment or calling for help. A telephone was located 25 ft (7.6 m) away from the scaffold (which was later confirmed to be working) while an air pack was located 15 ft (4.6 m) away (this was later found to be defective).

He attracted the attention of contractors nearby and asked them to get help. One of the contractors went to the operator's shelter but found no one there, so he continued to the central control room and informed an operator there of the emergency.

The 'call for help' number was dialled, which should have alerted the safety department staff to provide transport for the nurse. However, they were at a meeting in a trailer next to the safety building and remained uninformed of the emergency for nearly an hour after the H<sub>2</sub>S gassing. Since the safety department could not be reached, the operations shift supervisor contacted a contract nurse (standing in for the plant nurse) for help. She responded to the emergency but had to flag down a passing vehicle to get to the sulphur plant.

Meanwhile, the casualty had revived and was administered oxygen. When the nurse arrived, she carried out a medical examination but was not told that the casualty had lost consciousness during the incident (under the refinery medical protocol, loss of consciousness requires hospitalization for observation). The casualty returned to work but was later admitted to hospital for observation when she complained of back and shoulder pains, and was shivering.

**Provide emergency response training and drills for the specific chemicals that are handled to ensure that a quick, efficient, and correct response is obtained.**

**Good communication is absolutely essential in emergency situations to avoid mix-ups and delays.**



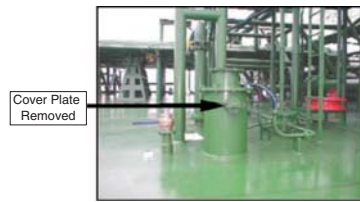
**ACCIDENT** **Fatality during sampling of sour crude in a cargo tank!!!**

Two inspectors and one crew member were conducting sampling/dipping operations on a ship's cargo tank during unloading. The cargo tank contained crude with high sulphur content (sour crude). (The cargo tank was blanketed with inert gas to ensure that a flammable atmosphere was not created in the vapour space.) The  $H_2S$  content in the vapour space was expected to be low, as is the usual case, but on this occasion the two inspectors and one crew member were exposed to a very high  $H_2S$  concentration at an opening to the cargo tank.

All three victims were transported immediately to hospital. One inspector was discharged after a week and a half while the other inspector was in a coma for two weeks. The crew member, unfortunately, did not survive.

Many crudes come out of wells with high levels of  $H_2S$ , but this level is usually reduced by a stabilization process before delivery to a vessel. However, the amount of stabilization may be temporarily reduced at times while other crudes never stabilize and can release high levels of  $H_2S$  gas.  $H_2S$  can also be encountered in naphtha, bitumens, gas oils, fuel/bunker oils, etc.

Other than the high  $H_2S$  concentration, the inert gas content could have played a part in their collapse. Humans generally succumb almost immediately when oxygen levels are extremely low, which does not allow us to save ourselves. The three victims were not required to wear personal protective equipment (PPE) nor were they provided with devices to monitor the atmosphere. Further, it was suspected that they had put their heads over the opening (a clear 'unsafe' act).



*The measurement cargo gauge on the ship*

**Provide personal monitors to allow verification of a safe atmosphere where the presence of a hazardous atmosphere is expected or suspected.**

**Establish a maintenance/calibration program for these devices and provide regular training on their use.**

In view of such high levels of  $H_2S$  being produced, closed gauging/sampling systems should be used. Otherwise, personnel conducting gauging/sampling tasks should wear the correct respiratory protection.

**Note that air-purifying respirators do NOT provide protection in oxygen deficient atmospheres.**

Sampling and dipping are potentially hazardous activities not only because the sampler/dipper may be exposed to toxic or oxygen-deficient atmospheres but also because the activity can generate sparks (through static electricity) and ignite flammable material within the tank. Refer to BP Process Safety Booklet *Hazards of Electricity and Static Electricity* for more information.

**ACCIDENT H<sub>2</sub>S release from molecular sieves kills three!!!**


The incident involved the dumping of molecular sieves, which had been used to remove water from natural gas liquids (NGL). The NGL also contained compressed H<sub>2</sub>S. The removal of the sieves was done by raking them from the drier into a chute that directed the material into a high-sided tipper truck. The dumped sieves had been wetted with a fire hose to reduce the risk of any pyrophoric material igniting and to restrict dust generation in the windy conditions.

After a while, a mound of molecular sieve material had formed at the back of the truck. A contractor decided to enter the truck to level the mound by shovelling the material to the front. A second contractor joined him in the truck but collapsed shortly after entering. The first contractor went to his assistance and was joined by a third contractor. All three fell unconscious and died. A fourth man, who climbed the vehicle ladder to see what was happening, also became unconscious. He was fortunate to have been pulled out by rescuers.

The staff and contractors did not recognize that H<sub>2</sub>S could be released from the molecular sieves. The H<sub>2</sub>S evolved, or desorbed, from the molecular sieves after coming into contact with water—its affinity for water far exceeds its affinity for H<sub>2</sub>S. Further, the levelling of the molecular sieve material would have released any trapped H<sub>2</sub>S.

It is important to recognize the presence of H<sub>2</sub>S early because without proper monitoring devices, our sense of smell will gradually dull to the point where we no longer register the smell of 'rotten eggs' (H<sub>2</sub>S). We may then start to think that the hazard of H<sub>2</sub>S is gone when it is still present or has even escalated.

## 2.2 Nitrogen

<b>NITROGEN</b>			
CAS No:	<b>7727-37-9</b>	Formula:	<b>N<sub>2</sub></b>
UN No:	<b>1066 (compressed) 1977 (refrigerated liquid)</b>	Molecular mass (g/mol):	<b>28.01</b>
<b>Physical &amp; Chemical Properties</b>			
Boiling Point:	<b>-196°C (-320°F)</b>	Specific Gravity (Water=1):	<b>0.81 (liquefied)</b>
Vapour Pressure (kPa):	<b>3394 (critical pressure) (492 psi)</b>	Relative Vapour Density (Air = 1):	<b>0.97</b>
Appearance and Odour:	<b>Colourless, odourless, tasteless GAS</b>		
<b>Health Hazard Data</b>			
Inhalation:	<b>Nitrogen is an asphyxiant gas. Initial symptoms are those of oxygen starvation—diminished mental alertness, headache, dullness, shortness of breath, and impaired muscle coordination. Continued exposures lead to faulty judgment, depression of senses, rapid fatigue, unconsciousness, convulsions, coma, and death.</b>		
Skin and Eyes:	<b>Contact with compressed gas or liquid nitrogen can cause frostbite and burns.</b>		
<b>Emergency Response Data</b>			
First Aid:	<b>Remove to ventilated area and provide respiratory assistance and administer CPR. Remove all contaminated clothing and flush with large amounts of SLIGHTLY WARM water. Seek medical attention immediately.</b>		
Extinguishing media:	<b>Nitrogen will not ignite. Use an extinguishing agent suitable to surrounding media.</b>		
Special Firefighting Procedures:	<b>Fire can produce toxic vapours and gases—wear full protective clothing and SCBA. Contact with liquid nitrogen may cause frostbite. Heat will build pressure and may rupture closed storage containers. Use water spray to keep fire-exposed containers cool.</b>		
<b>Personal Protective Equipment for Leak Response</b>			
Respiratory Protection	<b>Nitrogen is a simple asphyxiant. Do NOT use cartridge-type respirators (ineffective). Use a powered supplied-air respirator or a positive pressure SCBA with full face-piece.</b>		
Protective Gloves	Eye Protection	Other Protective Clothing	
<b>Impervious, Thermal Insulated Gloves</b>	<b>Chemical Goggles and/or Face Mask</b>	<b>Protective Boots, Gauntlets, Apron</b>	

**ACCIDENT** Operator falls into manhole as a result of nitrogen gassing!!!

An operator removed the cover from this manhole completely to take a sample of the atmosphere from the reactor. The reactor was under nitrogen purge at the time. As a result he became asphyxiated, and fell to his death through the open manhole.

He was working alone and had not been warned of the oxygen deficient atmosphere and the necessity to wear breathing apparatus prior to sampling. There was an inadequate assessment of the needs and risks associated with taking samples from the nitrogen-rich atmosphere.



Nitrogen, when misused, has a potential almost equal to that of hydrogen sulphide in producing fatal gassing incidents. Nitrogen is considered a hazardous material not because it is poisonous like hydrogen sulphide, but because the gas displaces oxygen in the atmosphere causing asphyxiation in humans. Unless oxygen is supplied quickly to the victim, death quickly follows. There have been instances where nitrogen was used in place of breathable air (e.g. yard air, instrument air), which have resulted in fatalities.

**ACCIDENT** Fatality when nitrogen is used as back-up!!!

Following a power failure at the plant, instrument air was switched over to nitrogen back-up. An instrumentation technician entered the analyzer house only to be discovered unconscious on the floor some time later. He was removed from the analyzer house but a site first-aider was not able to resuscitate him. He was taken to the local hospital and later pronounced dead.


The controls and safeguards that were required to be completed prior to switching over from instrument air to nitrogen gas had not been fully implemented, one of which should have been the locking of the analyzer house doors. The design of the analyzer house permitted a nitrogen rich atmosphere to develop by using instrument air as a purge. As a result of this administrative breakdown, the instrumentation technician was asphyxiated when he was allowed to enter the analyzer house.



*The door to the analyzer room through which the deceased entered*

Refer to BP Process Safety Booklet *Hazards of Nitrogen and Catalyst Handling* for more on nitrogen.

## 2.3 Hydrogen fluoride

<b>HYDROGEN FLUORIDE</b>			
CAS No:	<b>7664-39-3</b>	Formula:	<b>HF</b>
UN No:	<b>1052</b>	Molecular mass (g/mol):	<b>20.0</b>
			
<b>Physical &amp; Chemical Properties</b>			
Boiling Point:	<b>20°C (69°F)</b>	Specific Gravity (Water=1):	<b>0.99</b>
Vapour Pressure (kPa):	<b>122 at 20°C (17.7 psi at 69°F)</b>	Relative Vapour Density (Air = 1):	<b>0.7</b>
Appearance and Odour:	<b>Colourless GAS or fuming LIQUID Strong irritating odour</b>		
<b>Toxic Hazard Data</b>			
Inhalation:	<b>Corrosive. Vapours cause irritation to the upper respiratory tract. May cause pulmonary oedema and can be fatal if inhaled.</b>	Immediately Dangerous to Life and Health (IDLH)	ACGIH Exposure Criteria
Skin and Eyes:	<b>Contact causes swelling, blistering and burning. Burns can be bone deep.</b>	<b>30 ppm</b>	TLV (ceiling) <b>3 ppm</b>
<b>Emergency Response Data</b>			
First Aid:	<b>Remove to ventilated area, provide respiratory assistance and administer CPR. Remove all contaminated clothing and flush with large amounts of water. Seek medical attention immediately.</b>		
Extinguishing media:	<b>Carbon dioxide, alcohol foam (Do NOT use water—generates hydrofluoric acid solution and heat).</b>		
Special Firefighting Procedures:	<b>Wear full protective clothing and SCBA. Use water spray to keep fire-exposed containers cool. Poisonous gases are produced in fire. Potentially explosive reaction with certain metals. HF, in the presence of water, can produce explosive hydrogen gas. However, water spray or fog may be used to knock down and absorb HF vapours.</b>		
<b>Personal Protective Equipment for Leak Response</b>			
Respiratory Protection	<b>Use a supplied-air respirator or a positive pressure SCBA.</b>		
Protective Gloves	Eye Protection	Other Protective Clothing	
<b>Acid Resistant Neoprene or PVC</b>	<b>Chemical Goggles or Face Mask</b>	<b>Protective Apron</b>	



**ACCIDENT Inadequate isolation and purging on HF alkylation unit!!!**

A fitter was cutting a line on a purged and isolated HF alkylation unit when a mixture of sulphides and HF was released, forming a vapour cloud around the fitter from the waist up (he was dressed only in 'B' type clothing—boots, face shield, safety goggles, alky trousers, and alky jacket). The fitter quickly moved out of the mist to avoid the hazardous vapours.

Another contractor and a plant inspector were about 10 ft (3 m) downwind from the release. Seeing the cloud, the contractor pushed the inspector out of its path. However, the cloud did contact the contractor's neck. The contractor and fitter ran to the nearest safety shower but no water came out when they pulled on the lever. The contractor ran to the next nearest safety shower but this was also found not to be working.

At this point, an alky operator found the contractor and took him to the operators' change house, where they began splashing water and mild caustic on his neck. The plant inspector called for help on his radio and the Refinery Emergency Response (RER) team, along with paramedics, arrived at the scene to provide medical assistance to the fitter. Another worker was also sent to hospital after he had inhaled fumes 20–30 ft (6–9 m) downwind of the release.

**Do not isolate safety showers. They must be regularly checked and maintained to ensure that they are always operating correctly.**



Check periodically that the emergency medical kit is well stocked and contains the correct salves and solutions for HF burn injuries.

It is essential that systems, which have been purged, be verified to be clear of materials before containment is broken. More often than not, inadequate isolation and purging is the cause of HF releases.

**ACCIDENT HF burn injuries while draining down acid cooler!!!**

An alkylation unit operator went to check the drain at an acid cooler as part of the plant shutdown procedure prior to overhaul. He carefully opened the drain valve, but nothing came out. Recognizing the hazard of a blocked drain he was about to close the valve when the blockage suddenly cleared. Material came out from the drain at high velocity, hit the ground and splashed up.

The operator was wearing the correct protective clothing for the job, including visor and goggles, however the material came up under the visor resulting in HF burns. Thankfully, the goggles succeeded in preventing HF getting into his eyes. Two other operators received minor vapour burns while attempting to close the valve.

It is very important to wear the correct PPE for the material being handled, as shown in this incident. Many HF burn incidents have occurred when workers were not correctly equipped for the job.

Even so, although the operator followed the guidelines for protective clothing, he was let down by poor engineering design. This was rectified by fitting an extension piece to the drain after de-blanking to route drainings to a point remote from the operator. In many cases, drain valves are too close to the ground resulting in high potential for splash back on the operator using the drain valve.

**ACCIDENT A substantial release of HF and butane!!!**


A failure to fully isolate the acid rerun system resulted in a major leak of 94% HF and 6% Butane (a total of 3–4 tonnes). A large HF vapour cloud formed around the area. There were some problems in establishing what was the best combination of clothing and breathing equipment to use but full protective suits (Zoot suits) were finally worn because of the cloud size.

Operators tried initially to force back the cloud using steam hoses, but this proved unsuccessful and eventually hindered the emergency services as it vapourized acid and added to the size of the cloud. The build up of water spray from fixed water monitors and fire hoses gradually pushed back the HF vapour cloud and allowed firemen and operators to isolate the system.

Do not use steam to tackle HF leaks.

**Always check against your MSDS before deciding on mitigative measures.**

## 2.4 Ammonia

<b>AMMONIA</b>			
CAS No:	<b>7664-41-7</b>	Formula:	<b>NH<sub>3</sub></b>
UN No:	<b>1005</b>	Molecular mass (g/mol):	<b>17.03</b>
			
<b>Physical &amp; Chemical Properties</b>			
Boiling Point:	<b>-33°C (-28°F)</b>	Specific Gravity (Water=1):	<b>0.7 (at -33°C/-28°F)</b>
Vapour Pressure (kPa):	<b>1013 at 26°C (147 psi at 79°F)</b>	Relative Vapour Density (Air = 1):	<b>0.59</b>
Appearance and Odour:	<b>Colourless GAS Extremely pungent, intense, irritating, suffocating odour</b>		
<b>Toxic Hazard Data</b>			
Inhalation:	<b>Nose and throat irritant. Causes respiratory distress, chest pain, and pulmonary oedema.</b>	Immediately Dangerous to Life and Health (IDLH)	ACGIH Exposure Criteria
Skin and Eyes:	<b>NH<sub>3</sub> is corrosive to skin. Long exposures may result in tissue destruction.</b>	<b>300 ppm</b>	TLV (ceiling) <b>25 ppm</b> STEL (15 min) <b>35 ppm</b>
<b>Emergency Response Data</b>			
First Aid:	<b>Remove to ventilated area, provide respiratory assistance and administer CPR. Remove all contaminated clothing and flush with large amounts of water. Seek medical attention immediately.</b>		
Flash Point:	<b>N.A. (Gas)</b>	Auto Ignition Temperature:	<b>651°C (1204°F)</b>
Explosive Limits (vol % in air):	<b>LEL 15.0%</b>		<b>UEL 28.0%</b>
Extinguishing media:	<b>Reactive Gas. (Ammonia is difficult to ignite but presents an explosion hazard when exposed to flames.)</b>		
Special Firefighting Procedures:	<b>Gas is a serious health hazard—wear full protective clothing and SCBA. Emits toxic fumes of NH<sub>3</sub> and NO<sub>x</sub> when exposed to heat. Use water spray to absorb and disperse vapours.</b>		
<b>Personal Protective Equipment for Leak Response</b>			
Respiratory Protection	<b>Use an approved full face-piece with an ammonia vapour cartridge. For greater protection, use a supplied-air respirator or a positive pressure SCBA with full face-piece.</b>		
Protective Gloves	Eye Protection	Other Protective Clothing	
<b>Butyl Rubber</b>	<b>Chemical Goggles and/or Face Mask</b>	<b>Rubber Apron</b>	

**ACCIDENT Ammonia gassing incident!!!**

A contractor's supervisor inhaled ammonia vapours during maintenance work on a small diameter flange connected to an ammonia tank. Believing that the work environment was safe, he had removed his breathing apparatus presumably to see more clearly. He was taken to hospital, kept in overnight and discharged. He was readmitted the following day with a throat infection which had developed.

**All known hazards must be removed or adequately controlled and communicated before work permits are issued.**

**ACCIDENT Spillage of ammonia from overpressured road tanker!!!**

The driver of a road tanker connected up plant air to the tanker compartment in an effort to speed up unloading, instead of using a small air compressor. The compartment was overpressured and split open, flooding the area with liquid ammonia. The refinery fire fighting crew was quick to dilute the ammonia with water.

The use of water sprays in tackling aqueous solutions of ammonia was correct here, but extra care must be taken in the application of water to anhydrous ammonia or to serious spillages. The heat of reaction between water and anhydrous ammonia can lead to a more rapid vaporization of the ammonia.

**ACCIDENT Poor emergency response results in seven fatalities!!!**

Workers on top of a new tank reported hearing 'rushing water' sounds as a refrigerated ammonia tank nearby moved 25 m (82 ft) sideways, leaving its floor behind. It demolished the retaining wall as it went and released 7,000 tonnes of ammonia. The resultant ammonia pool was initially 70 cm (2.3 ft) deep and a fire quickly developed.

Twelve military firefighters responded and arrived at the scene to tackle the spillage from upwind. (The site was located in a military zone and was poorly equipped with firefighting and other emergency equipment. Very primitive oxygen supplied breathing apparatus were available, but there were no effective protective suits.) They initially applied water, which aggravated the fire. After some 20 minutes, they stopped, and the fire went out. By this time, other parts of the plant were on fire, and continued to burn for three days. This incident resulted in seven fatalities.

**The direction of water jets into a pool of refrigerated liquids often only makes matters worse, although fine water sprays can sometimes aid in dispersing vapour.**

## 2.5 Chlorine

<b>CHLORINE</b>				
CAS No:	<b>7782-50-5</b>	Formula	<b>Cl<sub>2</sub></b>	
UN No:	<b>1017</b>	Molecular mass (g/mol):	<b>70.9</b>	
<b>Physical &amp; Chemical Properties</b>				
Boiling Point:	<b>-34°C (-29°F)</b>	Specific Gravity (Water=1):	<b>1.4 at 20°C/69°F, 6.86 atm/100.8 psi</b>	
Vapour Pressure (kPa):	<b>673 at 20°C (98 psi at 69 °F)</b>	Relative Vapour Density (Air = 1):	<b>2.5</b>	
Appearance and Odour:	<b>Greenish-yellow GAS, LIQUID or RHOMBIC CRYSTALS Strong, irritating, suffocating odour</b>			
<b>Toxic Hazard Data</b>				
Inhalation:	<b>Extremely irritating to the lungs, throat, and nose. Can cause coughing, shortness of breath, pulmonary oedema, and permanent damage to the lungs.</b>	Immediately Dangerous to Life and Health (IDLH)	ACGIH Exposure Criteria	
Skin and Eyes:	<b>Contact with liquid may cause severe burns and persistent rash, and permanent eye damage.</b>	<b>10 ppm</b>	TLV (8 hours)	<b>0.5 ppm</b>
			STEL (15 min)	<b>1 ppm</b>
<b>Emergency Response Data</b>				
First Aid:	<b>Remove to ventilated area, provide respiratory assistance and administer CPR. Remove all contaminated clothing and flush with large amounts of water. Seek medical attention immediately.</b>			
Extinguishing media:	<b>Chlorine itself does not burn. Use extinguishing agent suitable to surrounding media.</b>			
Special Firefighting Procedures:	<b>Chlorine is a powerful oxidizer. Wear full protective clothing and SCBA. Use water spray to keep fire-exposed containers cool. Poisonous gases are produced in fire. Fire and explosion hazard when exposed to heat or incompatible materials.</b>			
<b>Personal Protective Equipment for Leak Response</b>				
Respiratory Protection	<b>Use a full face-piece respirator with chlorine gas cartridge for low exposures. For higher exposures, use a supplied-air respirator with full face-piece, hood or helmet in continuous flow mode, or use a positive pressure SCBA.</b>			
Protective Gloves	Eye Protection	Other Protective Clothing		
<b>Neoprene Rubber</b>	<b>Chemical Goggles or Face Mask</b>	<b>Neoprene Rubber Apron</b>		

**ACCIDENT Three dead and one injured in chlorine gas incident!!!**

A contractor employee from a septic tank cleaning company ran into the plant, requesting help. Two employees hurried to the tank outside, finding four workers lying at the bottom of the tank. They had been exposed to a high concentration of chlorine gas and were overcome while working in the confined space.

Fans were used to ventilate the tank, which ran for about four minutes before emergency services arrived. Two rescue services personnel, equipped with SCBAs, went down and began removing victims from the sludge. Two men were in cardiac arrest. All four workers were sent to hospital but two were dead on arrival. Another worker died a few days later while the remaining worker, only eighteen years old, survived but suffered severe brain damage.

Refer to BP Process Safety Booklet *Confined Space Entry* for more information on working in and rescue from confined spaces.

**ACCIDENT Crane snags overhead chlorine line!!!**


A moving pendulum crane snagged some overhead gas lines, causing several pipes, including a chlorine gas line, to rupture. Seven employees were exposed to chlorine gas in a number of situations:

- attempting to repair the damage without donning SCBA;
- removing SCBA when they thought they were in clear air;
- bringing extra SCBAs into the contaminated zone;
- continuing the job in the contaminated area;
- unaware of the chlorine gas cloud.

No chlorine monitoring equipment or alarm system was available.



## 2.6 Caustic soda

<b>CAUSTIC SODA</b>			
CAS No:	<b>1310-73-2</b>	Formula:	<b>NaOH</b>
UN No:	<b>1823 (solid)</b>	Molecular mass (g/mol):	<b>40.0</b>
			
<b>Physical &amp; Chemical Properties</b>			
Boiling Point:	<b>1390°C (2534°F)</b>	Specific Gravity (Water=1):	<b>2.1</b>
Vapour Pressure (kPa):	<b>&lt; 0.13 at 739°C (&lt; 0.019 psi at 1362 °F)</b>	Relative Vapour Density (Air = 1):	<b>1.0</b>
Appearance and Odour:	<b>Colourless to white odourless SOLID May appear as flakes, beads, or in granular form</b>		
<b>Toxic Hazard Data</b>			
Inhalation:	<b>Extremely corrosive to tissues in the respiratory system. Causes burns, pulmonary oedema, cough, and congestion.</b>	Immediately Dangerous to Life and Health (IDLH)	ACGIH Exposure Criteria
Skin and Eyes:	<b>Causes skin damage, burns, deep ulceration, permanent scarring, and permanent loss of vision.</b>	<b>10 mg/m<sup>3</sup></b>	TLV (ceiling) <b>2 mg/m<sup>3</sup></b>
<b>Emergency Response Data</b>			
First Aid:	<b>Remove to ventilated area, provide respiratory assistance and administer CPR. Remove all contaminated clothing and flush with large amounts of water. Seek medical attention immediately.</b>		
Extinguishing media:	<b>Use agents suitable to surrounding fire. Avoid water—reacts to generate extreme heat and may ignite surrounding combustible materials. If water must be used, make sure it is as cold as possible. For large fires use fog or foam.</b>		
Special Firefighting Procedures:	<b>Poisonous gases are produced in fire. Wear appropriate respiratory protection where NaOH may be present. NaOH may melt and flow when heated in fire.</b>		
<b>Personal Protective Equipment for Leak Response</b>			
Respiratory Protection	<b>NaOH is extremely destructive to any tissue it contacts. At any concentration use a positive pressure SCBA with full face-piece, or a continuous flow supplied-air respirator.</b>		
Protective Gloves	Eye Protection	Other Protective Clothing	
<b>Impervious Material</b>	<b>Chemical/Dust Goggles with Side Shields</b>	<b>Acid-type Protective Clothing</b>	

**ACCIDENT Caustic soda splash accident!!!**

An assistant operator on the hydrocarbon treatment unit plant was splashed on the face with caustic while working at the Merox catalyst mixing pot. He suffered some irritation to his eyes and face which forced him to remain off work for two days.

Although an emergency shower was located outside within 50 ft (15 m) of the Merox pot, the injured man attempted to use a drinking fountain inside the control room to wash off the caustic. Only prompt action by another operator, who took him to the shower in the changing room, saved him from more serious burns. The operator's eyesight was saved from permanent damage by the safety goggles he was wearing at the time.

The following factors contributed to the incident:

- The caustic line was steam traced causing the caustic to heat up, expand and blow out when released into the mixing pot.
- A check valve, originally installed in the caustic line, had been removed because of plugging problems.

However, none of the above factors would have mattered if the operator had followed the instructions in the manual. The manual stated that *water*, instead of caustic soda, is to be used for mixing the Merox catalyst!

**ACCIDENT Violent reaction sends caustic solution splashing out of barrel!!!**

A contract-drilling employee was mixing caustic soda (sodium hydroxide) in the caustic mixing barrel in the mud area of the drilling rig. He had mixed one fifty-pound (22 kg) sack into the mixing barrel. As he began to mix a second sack into the same solution, a violent reaction occurred. The mixture was forced out of the barrel into his face, coating his upper body with concentrated caustic solution. It resulted in severe burns and impaired vision. The recommended practice of mixing only one sack of caustic per batch was ignored and proper PPE had not been worn.

**Always read and understand the material's handling instructions before commencing work. Ensure that proper training has been provided to personnel so that work is performed in as safe a manner as possible.**

Considerable heat is generated when caustic soda is mixed with water. Therefore, when making solutions, follow these steps carefully:

- Always wear *all* the prescribed PPE.
- *Never* add water to the caustic.
- *Always* add the caustic to water, with slow and constant stirring. Check that the caustic is completely dissolved before adding more.



## 2.7 Acids

<b>ACIDS</b>	
<b>Hazard Data</b>	
<p>Acids are considered hazardous because they are corrosive and can react with other substances evolving large amounts of heat.</p> <p>Their hazard ratings are largely dependent upon their concentrations. Highly concentrated acid solutions are more hazardous because they can react more violently with other chemicals such as alkalis and bases, and attack materials such as metals and living tissue more aggressively. The attack on living tissue results in burn-like injuries where the tissue is destroyed.</p>	
<b>Emergency Response Data</b>	
First Aid (General):	Inhalation: Remove the person from the exposure. Provide respiratory assistance and CPR. Seek medical attention immediately. Skin and Eyes: Remove all contaminated clothing and flush with large amounts of water. Seek medical attention immediately.
Leak Response:	Check your site's MSDS of the particular acid for specific instructions. Water sprays may be used with caution to disperse vapours. The acid may react with water to generate extreme heat and ignite surrounding combustible materials. Use suitable means for safe clean-up and disposal of spills.
<b>Personal Protective Equipment for Leak Response</b>	
<p>The correct PPE must be worn when handling acids according to their type and concentrations. Generally, personal protective clothing must be impervious to acid attacks while respiratory protection is sometimes necessary if acidic vapours are formed. Refer to specific MSDSs for the acidic materials handled at your site.</p>	

**ACCIDENT Leak on truck unloading hydrochloric acid!!!**

A truck was unloading hydrochloric acid using compressed air when a leak occurred at the bottom of the tank car. The air pressure had created cracks in the protective internal lining and the acid found its way to the metal shell and quickly attacked it. The leak was plugged by the local fire brigade using special protective equipment under water curtains.

It is not recommended to use compressed air to unload road trucks. It is preferable to use a closed piping system and a pump.

**ACCIDENT Corrosive hydrochloric acid solution causes valve failure!!!**

A sample point valve located on a preflash tower overhead line came apart releasing about 400 lb (181 kg) of  $C_4-C_6$  hydrocarbons to the atmosphere. Fortunately, an operator who was in the immediate vicinity heard the noise of the release and isolated the sample point within five minutes. There was no injury nor did it result in a reportable environmental incident. However, it could have been much worse had the release gone undetected, or had the valve come apart while being operated.

The preflash tower overhead stream is primarily  $C_4-C_6$  with small amounts of anhydrous HCl. The system is normally very dry (less than 1 ppm water) so the anhydrous HCl is not corrosive but when the valve packing started to leak, the anhydrous HCl came into contact with moisture from the atmosphere and formed corrosive hydrochloric acid. The packing bolt threads corroded away and allowed the valve internals to blow out.



*Condition of the sample point valve*

**ACCIDENT** Basic chemical reaction causes fire and explosion!!!

A HF alkylation unit had been modified by replacing the liquid caustic neutralizer with a tower containing solid potassium hydroxide (KOH). On the day of the incident, the HF stripper tower was not operating satisfactorily. Although the unit operators were aware of this, they did not know the implications and the corrective actions to be taken. (The operating manuals had not been updated to reflect this change.)

A plant upset sent a slug of hydrofluoric acid (HF) into the potassium hydroxide tower (KOH) which resulted in an exothermic reaction, causing an explosion and fire. The force of the blast threw the side of the cooling tower some 300 ft (91 m) away.

This incident illustrates the dangers of uncontrolled mixing of acids and bases (or alkalis) which are capable of producing sufficient heat of reaction to rupture equipment.

**Always follow the Management of Change (MOC) procedure when modifications are made. Never start up a modified plant without the proper manuals and training in place.**

## 2.8 LPG (Liquefied Petroleum Gas)

<b>LPG (LIQUEFIED PETROLEUM GAS)</b>			
CAS No:	<b>68476-86-8</b>	Formula:	<b>Hydrocarbons C<sub>3</sub>-C<sub>4</sub></b>
UN No:	<b>1075</b>	Molecular mass (g/mol):	<b>44-58</b>
<b>Physical &amp; Chemical Properties</b>			
Boiling Point:	<b>-42°C (-43.8°F) (Propane) -0.5°C (31.1°F) (Butane)</b>	Specific Gravity (Water=1):	<b>0.50-0.58 at 15°C (59°F)</b>
Vapour Pressure (kPag):	<b>1300 at 38°C (100°F) (Propane) 360 at 38°C (100°F) (Butane)</b>	Relative Vapour Density (Air = 1):	<b>1.5 (Propane) 2.0 (Butane)</b>
Appearance and Odour:	<b>Colourless LIQUID (GAS at ambient pressure) Sulphurous/distinctive odour when odourized</b>		
<b>Toxic Hazard Data</b>			
Inhalation:	<b>May cause drowsiness and unconsciousness due to displacement of breathable air.</b>	Immediately Dangerous to Life and Health (IDLH)	EH40 Exposure Criteria
Skin and Eyes:	<b>Contact with liquid can cause frostbite and burns.</b>	<b>2100 ppm (Propane)</b>	TLV (8 hours) <b>1000 ppm</b>
			STEL (15 min) <b>1250 ppm</b>
<b>Emergency Response Data</b>			
Flash Point:	<b>&lt;-50°C (-58°F)</b>	Auto Ignition Temperature:	<b>287°C (549°F) (C<sub>4</sub>)</b>
Explosive Limits (vol % in air):	<b>LEL 2.2% (Propane) 1.9% (Butane)</b>	<b>UEL 9.5% (Propane) 8.5% (Butane)</b>	
Extinguishing media:	<b>Stop flow of gas/liquid to stop fire. If this is not possible, letting fire burn itself out may be the only alternative.</b>		
Special Firefighting Procedures:	<b>LPG is extremely flammable and explosive. Poisonous gases are evolved from fire. Wear a SCBA with full face-piece. Ensure ALL sources of escaping gas are controlled. Monitor area long after fire is extinguished. Use water spray to cool fire-exposed containers. Containers may explode in flame. Keep fire personnel well away (see BLEVE explanation on the next page).</b>		
<b>Personal Protective Equipment for Leak Response</b>			
Respiratory Protection	<b>LPG can be an asphyxiant by displacing oxygen. It is best to avoid entering a LPG vapour cloud entirely.</b>		
Protective Gloves	Eye Protection	Other Protective Clothing	
<b>Insulated Neoprene or Polyurethane</b>	<b>Goggles and/or Face Mask</b>	<b>Cold-insulating Apron</b>	

A **BLEVE** (Boiling Liquid Expanding Vapour Explosion) is a sudden release of a large mass of pressurized superheated liquid to the atmosphere. The best-known BLEVE incidents involve LPG. The primary cause is usually an external flame impinging on the shell of an LPG vessel. The fire heats the LPG inside the tank, causing it to boil and vaporize (*boiling liquid*), and increase the pressure within the tank. When the set point is exceeded, the relief valve will lift to relieve the pressure. However, as boiling continues, the temperature of the tank wall increases, while the strength of the tank steel wall decreases. At some point, the weakened steel can no longer resist the pressure-induced forces inside the tank causing the wall of the tank to rupture. Losing its containment, the boiling LPG rapidly flashes into the surrounding atmosphere (*expanding vapour*), and is ignited by the external flame to give rise to a huge fireball (*explosion*). The fireball releases heat at a rate much lower than that of a vapour cloud explosion (VCE), but generally for a longer period of time (around 20 seconds). Also, tank fragments are propelled at high velocities in many different directions. Both the fireball and shooting fragments are fatal to people and property in the immediate vicinity.

It should be noted that a BLEVE can occur due to any mechanism that results in the sudden failure of containment allowing a superheated liquid to flash, typically increasing its volume over 200 times. Also, when an external flame is impinging on the shell of the vessel above liquid level, the weakening process of steel is quickened because there is no internal cooling by the liquid. (Most vapours are poor heat conductors compared to liquids.) A jet fire above the liquid level may lead to a BLEVE within 5–10 minutes, while a pool fire usually takes 15–30 minutes to cause a BLEVE.

It is also noted that a pressure relief valve does not protect against this mode of failure. Sometimes, the mechanical integrity of steel may be compromised even before the internal pressure exceeds the set point of the relief valve. Further, when the relief valve opens to vent the tank, the content escaping from the relief valve will burn as a jet fire, usually ignited by the external flame. This jet fire may in turn impinge on other LPG vessels or other equipment. Therefore it is important to route the discharge from relief valves to remote and safe locations, far from plant, equipment or personnel (preferably to flare systems).

A BLEVE is a highly dangerous phenomenon. A number of such incidents have occurred including San Carlos, Spain (11 July 1978); Crescent City, Illinois (21 June 1970) and Mexico City, Mexico (19 November 1984).

Refer to BP Process Safety Booklet *Safe Handling of Light Ends* for more details and incidents.

**ACCIDENT BLEVEs at Pemex, Mexico City!!!**

The PEMEX LPG terminal in Mexico received supplies from three gas refineries every day via underground pipelines. The LPG pressure storage consisted of four spheres of 1,600 m<sup>3</sup> (10,060 bbls) and two spheres of 2,400 m<sup>3</sup> (15,000 bbls) capacity, plus 48 horizontal cylindrical storage tanks of various capacities. All storage was contained within 1 m (3.3 ft) high concrete walled enclosures.

On 18 November, 1984 the terminal was being filled from a refinery 400 km away. The next morning a drop in pressure was noticed by the control room and a pipeline pumping station, but the operators were unable to determine that the cause was the rupturing of an 8" (20 cm) pipe connecting one of the spheres to a series of cylinders. It is believed that the initiating release came from overfilling one or more pressure storage tanks and/or overpressure of a storage tank or interconnecting pipeline.


The release of LPG continued for between 5 and 10 minutes, resulting in a 2 m (6.6 ft) high cloud covering an area of 200 m by 150 m (656 ft × 492 ft). Ignition is thought to have occurred when the cloud came into contact with a ground flare at the bottling plant. A flash fire resulted with the flame front accelerating as it approached the source of the leak. A series of BLEVEs ensued for approximately an hour and a half as vessels exploded, further spreading burning LPG. The resulting fires and explosions destroyed the terminal, killing approximately 500 residents in the neighbouring areas, and were powerful enough to register on a seismograph at the University of Mexico 20 km away.



*Scenes from the accident site*

Some similar products like butadiene have similar fire characteristics but are also carcinogenic and are prone to exothermic decomposition. Refer to BP Process Booklet *Safe Handling of Light Ends* for more details.

## 2.9 Gasoline

<b>GASOLINE</b>			
CAS No:	<b>86290-81-5</b>	Formula:	<b>Hydrocarbons C<sub>4</sub>-C<sub>12</sub></b>
UN No:	<b>1203</b>	Molecular mass (g/mol):	<b>72 (approx)</b>
<b>Physical &amp; Chemical Properties</b>			
Boiling Point:	<b>30–215°C (86–419°F)</b>	Specific Gravity (Water=1):	<b>0.72–0.78</b>
Vapour Pressure (kPa):	<b>35–90 (5–13 psia) at 20°C (69°C)</b>	Relative Vapour Density (Air = 1):	<b>3–4</b>
Appearance and Odour:	<b>Clear LIQUID with pungent characteristic gasoline odour. Dye is added to differentiate the grades of gasoline.</b>		
<b>Toxic Hazard Data</b>			
Inhalation:	<b>May cause drowsiness, confusion, cough, and headache.</b>	ACGIH Exposure Criteria	
Skin and Eyes:	<b>Contact with liquid may result in redness, dry skin, and pain.</b>	TLV (8 hours)	<b>300 ppm</b>
		STEL (15 min)	<b>500 ppm</b>
<b>Emergency Response Data</b>			
Flash Point:	<b>&lt;–20°C (–4°F)</b>	Auto Ignition Temperature:	<b>250°C (482°F)</b>
Explosive Limits (vol % in air):	<b>LEL 0.6%</b>	<b>UEL 8.0%</b>	
Extinguishing media:	<b>Foam, dry chemicals, carbon dioxide, water fog/spray, or inert gas (nitrogen).</b>		
Special Firefighting Procedures:	<b>Water fog and spray are effective in cooling containers and adjacent structures. However, water can cause frothing and/or may not extinguish the fire. Water can be used to cool the external walls of vessels to prevent excessive pressure, auto ignition or explosion. DO NOT use a solid stream of water directly on the fire as the water may spread the fire to a larger area.</b>		
<b>Personal Protective Equipment for Leak Response</b>			
Respiratory Protection	<b>SCBA or NIOSH-approved organic vapour respirator if adequate protection is provided, used in accordance with OSHA requirements (29 CFR 1910.134).</b>		
Protective Gloves	Eye Protection	Other Protective Clothing	
<b>Disposable PVC, neoprene, nitrile, vinyl, or PVC/NBR gloves. DO NOT use this material as a skin cleaner.</b>	<b>Safety glasses with side shields, chemical goggles. Suitable eye wash water should be readily available.</b>	<b>Long-sleeved fire- resistant garments (e.g., Nomex). Apron, boots and facial protection if splashing is likely.</b>	

## Static electricity discharge at self-service gas stations



Fire incidents have occurred at self-service gas stations where customers ignited a fire around the fill spout while refuelling their vehicles. These incidents may be related to static electricity build-up and discharge, most frequently in cool or cold, dry conditions. One of many possible causes of static electricity build-up is re-entering a vehicle during refuelling. This can

cause a build-up of static electricity similar to the shuffling of feet on a carpet when the air in the room is dry. A brief flash fire could occur at the filling point if a customer returns from their vehicle's interior to remove the fuelling nozzle without discharging any static build-up. This could happen because the spark resulting from a static discharge would, under the right conditions, ignite gasoline vapours around the fill spout.

A simple precaution to help avoid this potential problem is to stay near the vehicle's fuelling point. *Customers should not get back into their vehicle during refuelling*—even when using the nozzle's automatic hold-open latch. However, if they must re-enter their vehicle, they should discharge any static electricity build-up by touching the outside metal portion of their vehicle, away from the filling point, before attempting to remove the nozzle.

*If a flash fire occurs during refuelling*, the customer should leave the nozzle in the vehicle fill pipe and back away from the vehicle. The attendant should be notified at once and the emergency shut-off activated.


Remember:

- *Always* turn your vehicle engine off while refuelling.
- *Never* smoke, light matches or use lighters while refuelling.
- Avoid getting back into your vehicle during refuelling.
- To avoid gasoline spills, do not overfill or top off your vehicle fuel tank.
- *Never* jam or force the hold-open latch open by using some other object such as the gas cap.

Refer to BP Process Safety Booklets *Hazards of Electricity and Static Electricity* and *Safe Tank Farm and (Un)Loading Operations* for more details on the hazards of static electricity.



## 2.10 Kerosene

KEROSENE			
CAS No:	<b>8008-20-6</b>	Formula	<b>Hydrocarbons C<sub>9</sub>-C<sub>16</sub></b>
UN No:	<b>1223</b>	Molecular mass (g/mol):	<b>Varies</b>
			
<b>Physical &amp; Chemical Properties</b>			
Boiling Point:	<b>153–258 °C (313–496 °F)</b>	Specific Gravity (Water=1):	<b>0.804 (at 15°C / 59°F)</b>
Vapour Pressure (kPa):	<b>N.A.</b>	Relative Vapour Density (Air = 1):	<b>4.5</b>
Appearance and Odour:	<b>Colourless to light brown LIQUID with characteristic kerosene odour</b>		
<b>Toxic Hazard Data</b>			
Inhalation:	<b>Possible irritation to upper respiratory tract, headache, nausea, dizziness, and unconsciousness.</b>		
Skin and Eyes:	<b>Possible irritation to skin and eyes. The liquid defats skin.</b>		
<b>Emergency Response Data</b>			
Flash Point:	<b>&gt;38°C (100°F)</b>	Auto Ignition Temperature:	<b>220°C (428°F)</b>
Explosive Limits (vol % in air):	<b>LEL 0.7%</b>	<b>UEL 5.0%</b>	
Special Properties:	<b>Kerosene is a static accumulator</b>		
Extinguishing media:	<b>Powder, carbon dioxide, foam. Do NOT use water jets.</b>		
Special Firefighting Procedures:	<b>Water fog and spray are effective in cooling containers and adjacent structures. Toxic fumes may be evolved on burning or exposure to heat.</b>		
<b>Personal Protective Equipment for Leak Response</b>			
Respiratory Protection	<b>Use an MSHA/NIOSH-approved air-purifying organic vapour respirator, a powered air-purifying respirator, or a self- contained breathing apparatus (SCBA) with full face-piece operated in positive pressure mode.</b>		
Protective Gloves	Eye Protection	Other Protective Clothing	
<b>Disposable PVC, neoprene, nitrile, vinyl, or PVC/NBR gloves. DO NOT use this material as a skin cleaner.</b>	<b>Safety glasses with side shields, chemical goggles. Suitable eye wash water should be readily available.</b>	<b>Long-sleeved fire- resistant garments (e.g., Nomex). Apron, boots and facial protection if splashing or spraying conditions exist.</b>	

Kerosene has a flashpoint (38°C/100°F) that is higher than typical ambient temperatures. It does not let off flammable vapours when no external heat is provided. So gas testing alone cannot verify that no flammable atmosphere will be formed. Any container that has carried a high flash point flammable or combustible material needs to be certified safe by both visual inspection and gas testing.

**ACCIDENT Exploding drum!!!**

A tank-cleaning contractor removed an empty drum from a refinery's scrap yard with the intention of making oil containment pans out of it. The drum had been used previously in a laboratory to store kerosene slops. It was labelled 'Kerosene' and 'Flammable' but the contractor could not read or speak English.

The contractor took the drum to the workshop and washed it out with water before putting a grinding wheel to it to commence cutting. The drum had not been cleaned out fully. Kerosene still remained after the drum was washed only with water. As a result, the residual kerosene ignited and the drum exploded when the contractor cut into it. Fortunately, no one was injured.

**ACCIDENT Laboratory technician on fire!!!**

An experienced senior laboratory technician was conducting an analysis on an Atomic Absorption Spectrometer (AAS) when the waste container on the equipment, which held kerosene, exploded. The technician was drenched in kerosene, which caught fire and caused full thickness burns to 80% of his body. He died in hospital four days later.

The contract for the repair, servicing, and training of this equipment had been awarded to a company that was not approved by the original equipment manufacturer. During a previous repair of the apparatus, the drain tube to the



*This waste collection vessel blew up, drenching the laboratory technician in kerosene.*

waste collection vessel was installed incorrectly. An ineffective liquid seal and wrongly positioned check valve led to a flashback and an explosion in the waste collection vessel. Although explosions had occurred previously, the laboratory personnel regarded this as 'normal'. No inquiries were made into the matter. Further, the procedures for operating this apparatus were inadequate, as was the knowledge level of the laboratory staff.

## 2.11 Gas oil/diesel

<b>GAS OIL / DIESEL</b>			
CAS No:	<b>68334-30-5</b>	Formula:	<b>Hydrocarbons C<sub>10</sub>-C<sub>28</sub></b>
UN No:	<b>1202</b>	Molecular mass (g/mol):	<b>Varies</b>
<b>Physical &amp; Chemical Properties</b>			
Boiling Point:	<b>160–385 °C (320–725 °F)</b>	Specific Gravity (Water=1):	<b>0.82–0.88 at 15°C (60°F)</b>
Vapour Pressure (kPa):	<b>&lt;0.3 at 20°C (69°F)</b>	Relative Vapour Density (Air = 1):	<b>4</b>
Appearance and Odour:	<b>Clear, light brown LIQUID with characteristic diesel-like odour</b>		
<b>Toxic Hazard Data</b>			
Inhalation:	<b>Possible irritation to nose and throat.</b>		
Skin and Eyes:	<b>Prolonged/repeated exposure may lead to dermatitis. May cause transient eye redness if contact occurs.</b>		
<b>Emergency Response Data</b>			
Flash Point:	<b>&gt;60°C (140°F)</b>	Auto Ignition Temperature:	<b>&gt;254°C (489°F)</b>
Explosive Limits (vol % in air):	<b>LEL 0.6% UEL 6.5%</b>		
Special Properties:	<b>Diesel is a static accumulator</b>		
Extinguishing media:	<b>Dry chemicals, carbon dioxide, foam, water fog/spray, or inert gas (nitrogen).</b>		
Special Firefighting Procedures:	<b>Water fog and spray are effective in cooling containers and adjacent structures. However, water can cause frothing and/or may not extinguish the fire. DO NOT use a solid stream of water directly on the fire as the water may spread the fire to a larger area.</b>		
<b>Personal Protective Equipment for Leak Response</b>			
Respiratory Protection	<b>Respiratory protection is normally not required unless the product is heated or misted. Use a SCBA or NIOSH-approved organic vapour respirator with a dust/mist prefilter.</b>		
Protective Gloves	Eye Protection	Other Protective Clothing	
<b>Disposable PVC, neoprene, nitrile, vinyl, or PVC/NBR gloves. DO NOT use this material as a skin cleaner.</b>	<b>Safety glasses with side shields, chemical goggles. Suitable eye wash water should be readily available.</b>	<b>Long-sleeved fire-resistant garments (e.g., Nomex). Apron, boots and facial protection if splashing/spraying.</b>	

*Gas oil* is a petroleum middle distillate that is also called *diesel* fuel, heating oil, furnace oil, stove oil, and other names in various parts of the world. It has a boiling range that is generally considered to start at 160°C and end at about 385°C.

Although the flash point of diesel (60°C/140°F) is higher than normal room temperature/handling temperature, it is possible to form a flammable cloud when it is heated or misted. Fine mists are generated during splash filling, agitation or jet mixing. These mists create flammable atmospheres, even below the flash point. Refer to BP Process Safety Booklets *Hazards of Electricity and Static Electricity* and *Safe Tank Farm and (Un)Loading Operations* for more information.

**ACCIDENT** Shipping engineer receives fatal burns while witnessing diesel engine test!!!

A shipping engineer was badly burned and later died following an explosion while witnessing a diesel engine test. He was supervising work on a series of VLCCs (Very Large Crude Carriers) being built for his company at the contractor's shipbuilding site. The engine being tested exploded after a camshaft drive bearing overheated and melted down. The engineer was apparently standing next to the pressure relief valve. Yards, engine makers, owners, and classification societies are all taking steps to ensure that oil mist detection devices are installed in engines during test-bed checks. It is understood that the flame arrestor functioned properly but the hot gas that was emitted re-ignited. Others in the vicinity suffered minor burns.

**ACCIDENT** Diesel driven generator fire on offshore production platform!!!

A fire occurred on a production platform as operators were filling a diesel tank for a generator. An operator noticed that it was taking too long to fill the diesel tank and began to check for a problem. By this time, the tank had already been overfilled and diesel had begun to fill the vent pipe that extended approximately 40 feet (12 m) above the diesel tank. When he removed the level gauge (which was giving a wrong indication of  $\frac{3}{4}$  full) to determine the exact fuel level, the head pressure of the diesel in the vent pipe along with the pressure from the diesel supply system caused the diesel to spray out of the tank and into the generator enclosure. The diesel oil contacted the generator exhaust which ignited the fuel. The fuel tank and filling system was not equipped with an automatic level switch to sound an alarm and shut off the fuel pump on overfilling.

**Avoid refuelling diesel driven engine, including generators and fire pumps, while the engine is operating.**

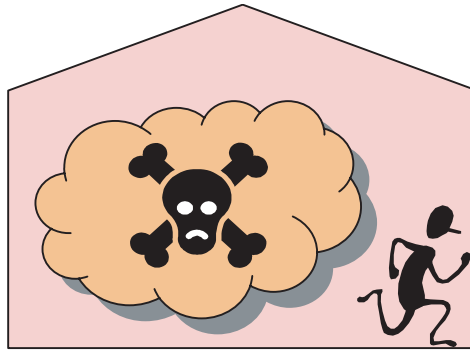
## 2.12 Benzene

<b>BENZENE</b>			
CAS No: <b>71-43-2</b>		Formula: <b>C<sub>6</sub>H<sub>6</sub></b>	
UN No: <b>1114</b>		Molecular mass (g/mol): <b>78.1</b>	
Physical & Chemical Properties			
Boiling Point:	<b>80°C (176°F)</b>	Specific Gravity (Water=1):	<b>0.88</b>
Vapour Pressure (kPa):	<b>10 at 20°C (1.45 psi at 69°F)</b>	Relative Vapour Density (Air = 1):	<b>2.7</b>
Appearance and Odour:	<b>Colourless to light yellow liquid of highly refractive nature. Characteristic aromatic odour. Odour threshold = 12 ppm.</b>		
Toxic Hazard Data			
Inhalation:	<b>May cause headache, vomiting, dizziness, suffocation, severe irritation or burns of the respiratory system, pulmonary oedema, or lung inflammation.</b>	Immediately Dangerous to Life and Health (IDLH)	ACGIH Exposure Criteria
Skin and Eyes:	<b>Irritation with possible redness and pain. Benzene absorbs into skin and may cause dermatitis and temporary corneal damage.</b>	<b>500 ppm human carcinogen</b>	TLV (8 hours) <b>0.5 ppm</b> STEL (15 min) <b>2.5 ppm</b>
Emergency Response Data			
Flash Point:	<b>-11°C (12°F) closed cup</b>	Auto Ignition Temperature:	<b>498°C (928°F)</b>
Explosive Limits (vol % in air):		<b>LEL 1.2%</b>	<b>UEL 8.0%</b>
Special Properties:	<b>Benzene is a known carcinogen. Monitor exposure of personnel. Use closed circuits for sampling/dipping.</b>		
Extinguishing media:	<b>Use alcohol foam, dry chemical, or carbon dioxide (water may be ineffective).</b>		
Special Firefighting Procedures:	<b>Wear SCBA. Poisonous gases are produced in fire. Moderate explosion hazard when exposed to heat or flame. Containers may explode in fire. The vapour is heavier than air and may travel for some distance before igniting, causing a flash fire back to the source. Water sprays may be used to control vapours.</b>		
Personal Protective Equipment for Leak Response			
Respiratory Protection	<b>Use an approved powered air-purifying respirator or use a positive pressure SCBA.</b>		
Protective Gloves	Eye Protection	Other Protective Clothing	
<b>Polyvinyl Alcohol Gloves</b>	<b>Chemical Goggles or Face Mask</b>	<b>Protective Apron if splashing is likely</b>	

Benzene, toluene, and xylene (BTX) are aromatic hydrocarbons, so named for their characteristic strong, sweet odour. They are produced commercially and have many industrial uses, most notably as a solvent for numerous materials and as a gasoline fuel additive (to increase octane number). Although they are very useful chemicals, they are also extremely hazardous.

**ACCIDENT Contractor fatality due to benzene exposure!!!**

Contractors were attempting to unplug a blockage in a pump suction line in the bottom of a mix tank used in their patented process to convert hazardous waste material into cement kiln fuel. After a number of hours of moderately successful effort from outside the tank, one of the contractors decided to enter the tank, contrary to instructions from his supervisor, in an attempt to expedite the work. He entered the tank through a small, obstructed opening. He was wearing an air purifying respirator (canister mask) and protective clothing but quickly became disoriented and lost consciousness. The man was removed from the tank more than half an hour later by his supervisor and rescue team. He was given medical attention at site and sent to the hospital by helicopter. However, he was pronounced dead after arrival. An autopsy concluded the cause of death to be due to benzene exposure.



*Do not enter a confined space without proper engineering control and adequate personal protective equipment*

Refer to Section 1.2, page 3 for details of two other benzene accidents.

## 2.13 Crude oil

<b>CRUDE OIL</b>			
CAS No:	<b>8002-05-9</b>	Formula	<b>Complex hydrocarbon mixture (C<sub>3+</sub>)</b>
UN No:	<b>1267</b>	Molecular mass (g/mol):	<b>Varies</b>
<b>Physical &amp; Chemical Properties</b>			
Boiling Point (Initial):	<b>-10–0 °C (14–32 °F)</b>	Specific Gravity (Water=1):	<b>0.75–1.0 at 15°C (60°F)</b>
Vapour Pressure (kPa):	<b>40–100 at 20°C (69°F)</b>	Relative Vapour Density (Air = 1):	<b>Varies</b>
Appearance and Odour:	<b>Dark brown liquid with pungent odour</b>		
<b>Toxic Hazard Data</b>			
Inhalation:	<b>Irritation to respiratory tract, headache, nausea, and dizziness at high concentrations. May be toxic when H<sub>2</sub>S is present in the vapour.</b>		
Skin and Eyes:	<b>Prolonged/repeated exposure may lead to dermatitis and possibly irreversible skin disorders, including cancer.</b>		
<b>Emergency Response Data</b>			
Flash Point:	<b>Typically around -50°C (-58°F)</b>	Auto Ignition Temperature:	<b>Varies</b>
Explosive Limits (vol % in air):	<b>LEL 0.6%</b>	<b>UEL 8.0%</b>	
Special Properties:	<b>Some crudes can contain significant amounts of benzene, which is a known carcinogen. Risk assessments and/or consultations with industrial hygienists are recommended to determine if protective measures are adequate.</b>		
Extinguishing media:	<b>Foam, dry powder or water fog. Do not use water jets.</b>		
Special Firefighting Procedures:	<b>Any spillage should be regarded as a potential fire risk. Toxic fumes may be evolved from fires.</b>		
<b>Personal Protective Equipment for Leak Response</b>			
Respiratory Protection	<b>Wear suitable approved respiratory equipment if exposure to vapour, mist, or fumes is anticipated.</b>		
Protective Gloves	Eye Protection	Other Protective Clothing	
<b>Impervious Gloves</b>	<b>Wear Face Visor or Goggles</b>	<b>Impervious Coveralls</b>	

Crude oil is unprocessed oil pumped out of the ground, and possibly stabilized to remove gases and light ends ( $C_3$ ,  $C_4$ ). It is also known as petroleum. It contains mainly hydrocarbons, and small quantities of many other different substances.

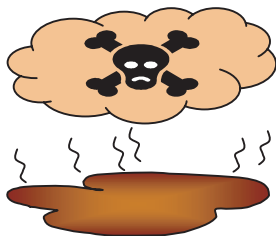
- 'Sour' crude oil contains high levels of *hydrogen sulphide* ( $H_2S$ ), which is toxic, corrosive, and flammable.
- Crude oil also contains *light ends*, which can evaporate easily to form a flammable and toxic atmosphere.
- The *sludge* from crude oil is also a source of hazards. Many fire incidents have occurred during sludge cleaning, removal and demolition of crude oil tanks. (Sludge from crude oil can also contain a range of heavy metals.)

### **ACCIDENT** Fatalities during cleaning operations of crude oil rail car!!!

Rail cars that had been used for carrying crude oil were delivered to a specialist cleaning contractor for the removal of sludge deposits. Two contractors entered into the rail car to clean out the residual sludge manually. When it was noticed that the sludge discharge chute was not fitting correctly at its point of contact with the disposal skip, one of the two contractors positioned around the skip decided to solve the problem by grinding off a section of the chute. The resulting sparks from the grinding operation ignited the flammable mixture in the chute causing a flashback into the top rail car. The flash fire killed the two men inside the rail car.

It was discovered that the specialist contractor had:


- failed to carry out gas checks inside the rail car to establish that safe conditions existed, before allowing personnel to enter;
- failed to prevent a source of ignition (i.e. sparks from grinding operation) being present in the near vicinity of the cleaning operations;
- failed to provide satisfactory firefighting facilities throughout the duration of the cleaning operations.



*Crude oil sludge can give off flammable and toxic atmosphere*



## 2.14 Asphalt/bitumen (hot products)

<b>ASPHALT / BITUMEN (HOT PRODUCTS)</b>			
CAS No:	<b>8052-42-4</b>	Formula	<b>Complex Hydrocarbon Substance</b>
UN No:	<b>3257</b>	Molecular mass (g/mol):	<b>Varies</b>
			
<b>Physical &amp; Chemical Properties</b>			
Boiling Point:	<b>&gt;450°C (842°F)</b>	Specific Gravity (Water=1):	<b>&gt;1.0</b>
Vapour Pressure (kPa):	<b>N.A.</b>	Relative Vapour Density (Air = 1):	<b>&gt;1</b>
Appearance and Odour:	<b>Black viscous liquid with tar-like odour (solid at ambient temperatures)</b>		
<b>Toxic Hazard Data</b>			
Inhalation:	<b>Unlikely at ambient temperature. Prolonged periods of inhalation may result in cancer due to the presence of polycyclic aromatic hydrocarbons.</b>		
Skin and Eyes:	<b>Burns if hot material contacts skin. Prolonged/repeated contact with condensate from vapour, mists, or fumes may cause dermatitis.</b>		
<b>Emergency Response Data</b>			
Flash Point:	<b>&gt;250°C (482°F)</b>	Auto Ignition Temperature:	<b>400°C (752°F)</b>
Explosive Limits (vol % in air):	<b>LEL 0.7%</b>		<b>UEL 6.0%</b>
Extinguishing media:	<b>Foam, CO<sub>2</sub>, powder, dry chemical, or water fog.</b>		
Special Firefighting Procedures:	<b>Molten material can form flaming droplets if ignited. Water or foam can cause frothing. Use of water on product above 100°C (212°F) can cause product to expand with explosive force. Withdraw immediately from the area if there is a rising sound from a venting safety device or discoloration of vessels or pipes. Do not allow hot liquid product to runoff to sewers.</b>		
<b>Personal Protective Equipment for Leak Response</b>			
Respiratory Protection	<b>Use air-supplied respirators when H<sub>2</sub>S concentrations are expected to exceed applicable workplace exposure levels.</b>		
Protective Gloves	Eye Protection	Other Protective Clothing	
<b>When handling product at elevated temperatures, use long-cuffed leather or heat-resistant gloves.</b>	<b>Use a full-face shield and chemical safety goggles.</b>	<b>Use insulated, heat-resistant clothing such as a chemical resistant apron or slicker suit.</b>	

Asphalt/bitumen needs to be stored at temperatures well above 100°C/212°F (typically around 160°C/320°F). As such, many incidents have occurred involving sprays of hot asphalt/bitumen onto workers resulting in serious burn injuries. It needs to be noted also that prolonged or repeated contact with condensate from asphalt/bitumen vapour, mists, or fumes may result in dermatitis (a disease in which the skin is red and painful and can be debilitating).

**ACCIDENT Asphalt/bitumen blower vessel explosion and failure!!!**

An asphalt/bitumen blower vessel (an oxidizer) suddenly failed at the bottom seam due to an internal explosion, spraying hot asphalt on three workers in the vicinity and fatally injuring them.

The continuous oxidation process blows air through hot asphalt to achieve improved melt point and stability characteristics. The reaction is exothermic. Water and steam are added in an attempt to control liquid temperature between 475–510°F (246–266°C) and inert the vapour space. The vapour effluent from the reaction vessel is directed to an incinerator to control emissions. Normal operating temperature for the incinerator is 1,100°F (593°C).

At the time of the incident, the oxidizer was operating at 535°F (279°C). At elevated liquid temperatures, production of low boiling reaction products accelerates rapidly due to thermal cracking. The incinerator was operating at 1,750°F (954°C) and tripped out on high temperature alarm. Repeated attempts by operators to relight the incinerator failed and they concluded that there was too much steam in the vapour coming off the oxidizer to the incinerator. The vapour stream was actually hydrocarbon rich. It was decided to shut off all but one of the sources of steam and water going into the oxidizer. These moves allowed the vapour space to go into the flammable range. Operators lit the incinerator, causing a flash back to the oxidizer. The

**There must always be sufficient diluent steam or other inerting medium within a bitumen/asphalt blowing tank/oxidizer to maintain the upper space outside the flammable limits and the system should be designed to relieve internal explosions in a safe manner.**

**ACCIDENT Hazards of hot liquids!!!**

The photographs below are graphic reminders of what happens when hot oil (in this case asphalt) is added to trailers that had been cleaned with water. Serious injuries and fatalities have resulted from incidents such as these. When excess water is not removed from a closed system, introducing a hot oil can cause the water to turn to steam where it will expand to 1600 times its original volume causing significant overpressure, vessel rupture, and violent foaming/spraying of hot oil. Further, hot asphalt begins to foam when the material comes into contact with water.

**Situations to be aware of**

This type of event has happened many times, often involving heat transfer fluids, mineral oils, or other 'heavy organic' materials (like asphalt). The event begins when a *hot material* is added to a vessel or piping which contains materials with a boiling point below the temperature of the hot material. In general, the larger the difference between the temperature of the hot material and the boiling point of the lower boiling material, the more significant the damage. As heat is transferred from the hotter material, vaporization of the lower boiling material occurs and the pressure that results can cause serious damage! Refer to BP Process Safety Booklet *Hazards of Water*.

**How you can avoid similar problems**

- During *any* material transfer, if the liquid being transferred is hotter than 100°C (212°F), take steps to make certain that there is no water in the downstream equipment.
- Water removal is often difficult in complex piping systems—low point drains *must* be opened, piping must be properly designed and carefully examined for 'traps' and flanges may need to be opened in *many* locations.
- Shipping containers are frequently cleaned with water, so any shipping container must be assumed to contain water unless steps have been taken to remove it.
- Proceed slowly when starting up processes following shutdowns, especially with very hot fluids. This will help avoid a steam explosion.
- Avoid draining hot materials (>100°C/212°F) to drains, sewers, or sumps.

## 2.15 Asbestos

<b>ASBESTOS</b>			
CAS No:	<b>1332-21-4</b>	Formula	<b>Mg<sub>3</sub>Si<sub>2</sub>H<sub>4</sub>O<sub>6</sub> (white)</b>
UN No:	<b>2590 (white)</b>	Molecular mass (g/mol):	<b>554 (white)</b>
<b>Physical &amp; Chemical Properties</b>			
Decomposition Point:	<b>Decomposes completely at 1000°C (1832 °F)</b>	Specific Gravity (H <sub>2</sub> O=1):	<b>2.2–2.6 (white)</b>
Appearance and Odour:	<b>White, grey, green or yellowish fibrous SOLID</b>		
<b>Toxic Hazard Data</b>			
Inhalation:	<b>May cause coughing. Long-term or repeated exposure may result in pulmonary fibrosis and mesothelioma. Asbestos is a known carcinogen.</b>	ACGIH Exposure Criteria TLV (8 hours) <b>0.1 fibres/cc</b>	
<b>Emergency Response Data</b>			
First Aid:	<b>Remove to fresh air. Remove all contaminated clothing and rinse with large amounts of water. Seek medical attention.</b>		
Extinguishing media:	<b>Asbestos is not combustible. In case of fire in the surroundings, all extinguishing agents are allowed.</b>		
Special Firefighting Procedures:	<b>Care should be taken to contain asbestos materials that may have been disturbed in a fire. Avoid breathing asbestos fibres by wearing full protective clothing and SCBA.</b>		
<b>Personal Protective Equipment for Leak Response</b>			
Respiratory Protection	<b>Asbestos is a human carcinogen. At any exposure level, use an approved combination respirator which includes a Type-C supplied air respirator with full face-piece operated in positive demand mode, and either emergency High Efficiency Particulate Air (HEPA) back-up filter, or auxiliary SCBA with full face-piece operated in positive pressure mode.</b>		
Protective Gloves	Eye Protection	Other Protective Clothing	
<b>Impervious Rubber</b>	<b>Dust Goggles and Face Mask</b>	<b>Full Body Protective Suit (disposable) with Boots and Head Protection</b>	



## What is asbestos?

Asbestos is a name given to a number of naturally occurring fibrous silicate minerals with white asbestos (chrysotile) being the most common type. The material is commonly used for thermal insulation, acoustic insulation, fireproofing, and in other building materials.

## Why is asbestos a hazard?

Asbestos is made up of microscopic bundles of fibre. They can become airborne when distributed and may cause significant health problems when inhaled into the lungs. The effects of asbestos exposure often go unnoticed for 15–40 years. Some of these health problems include:

- *Asbestosis*—Scarring of the lungs when the body tries to remove the fibres from the lungs. Scarring may become so severe that the lungs cannot function. (Asbestosis is a result of severe acute exposure conditions that have existed in the past, such as in mining and ship construction, but is seldom seen anymore.)
- *Mesothelioma*—Cancer of the outer lining of the lung and chest cavity and/or the lining of the abdominal wall.
- *Lung Cancer*—The risk of cancer from asbestos is higher among smokers.

Asbestos-containing materials generally do not pose a health risk as long as they are intact. They may become hazardous and pose an increased risk when they are damaged, disturbed, or deteriorate over time thus releasing asbestos fibres into the air.

Some examples of asbestos-containing materials are given below.

- insulation/refractory;
- concrete pipes/panels;
- packing materials (for wall/floor penetrations);
- floor tiles;
- false ceiling panels;
- fire blankets/curtains/doors.



Each facility should ensure that all remaining asbestos-containing materials have been identified, labelled with a 'danger sign', and listed in a register.

Always wear the respiratory protective equipment that is provided when dealing with asbestos.

Never misuse them, for example, do not loosen the straps, cut parts of the face seal, or make gaps in the seal to make it more comfortable. If you have not been given PPE and you think you might need it, or you are worried that you do not have the right PPE for the job, speak to your employer or safety representative. Do not take risks with your health and life.

**ACCIDENT Stolen vacuum cleaner was full of asbestos**

Asbestos insulation was being removed from two small process towers in a refinery. During the weekend, thieves stole miscellaneous tools, including an industrial vacuum cleaner whose bag was full of asbestos. Equipment containing hazardous substances must be secure with clear warning signs.

## 2.16 Others

Besides the materials already discussed, there are many other chemicals or products that are used frequently in the oil and chemical industries. Some hazardous fuel additives and chemicals used during maintenance activities are discussed here.

### Fuel additives

Uneven fuel combustion and knocking in car engines caused researchers to look for an appropriate additive that would improve fuel quality directly. This research led to the discovery and use of *Tetraethyl Lead (TEL)* as an efficient, low concentration gasoline additive that eliminated the knocking and boosted octane. TEL is toxic and can act on the brain and central nervous system to cause convulsions, dizziness, headaches, and psychosis. Further, this additive contributes to the presence of lead particles in combustion products from car exhaust. Lead was later found to be toxic to human beings. It accumulates in the bone marrow, kidneys, and nerve tissue—including the brain. Children are more susceptible to lead poisoning because lead is absorbed and accumulated in their nervous system as their bodies grow and develop rapidly. Besides car exhausts, other sources of lead exposure include paints, water pipes, and lead-acid batteries that contain lead.

Since 1979, *MTBE* (methyl tertiary-butyl ether) has been used in place of lead as a fuel additive in motor gasoline. MTBE is a synthetic compound that is manufactured by the chemical reaction of methanol and isobutylene. At room temperature, MTBE is a volatile, flammable and colourless liquid that dissolves easily in water. Therefore, MTBE can seep into groundwater from leaking fuel tanks faster, farther and more easily. A growing number of studies have detected MTBE in ground water throughout the US; in some instances these contaminated waters are sources of drinking water. Low levels of MTBE can make drinking water supplies undrinkable due to its offensive taste and odour. Furthermore, MTBE is a suspected carcinogen. *ETBE* (ethyl tertiary-butyl ether) is closely related to MTBE and has similar characteristics. It has a lower vapour pressure which makes it more attractive to use in warm climates as compared to MTBE.

Therefore, the handling of these products must be restricted and accomplished using strict procedures and adequate precautions.

## Maintenance in confined spaces

Maintenance activities in confined spaces may involve the use of various materials that are hazardous. Below are some examples and incidents involving resin, paint, refractory material, inspection and cleaning products.

**MSDSs must be checked for all jobs and is a critical element of the risk assessment for Confined Space Entry authorization.**

Refer to BP Process Safety Booklet *Confined Space Entry* for more on maintenance activities in confined spaces.

## Paint

### **ACCIDENT** Explosion in floating roof tank pontoon!!!

An explosion occurred inside a pontoon space of a floating roof tank which was under construction at a refinery. A worker dropped a live welding cable with its attached electrode holder onto the pontoon roof, and the subsequent electric arc melted a hole in the metal top of one section of pontoon. Solvent vapours from the paint (the inside bulkheads of the pontoons had been painted on the previous day) ignited in the confined space and the explosion distorted the pontoon and a large area of the roof plates.

**Confined spaces which have been painted with solvent based paints need to be treated with great care until the paint has 'cured' and the space well ventilated and gas-free checked before adjacent use of ignition sources is allowed. The toxic hazard of paint solvent has to be considered also.**



*Spray painting*

## Cleaning products

### **ACCIDENT** Incident during chemical cleaning!!!

After chemical cleaning, a boiler was opened for maintenance work. The removal of pinoches (buffer pads made partly of wood in the boiler drums) was difficult, so drilling was required. This resulted in trapped deposits and chemicals being released from the pinoches. A chemical reaction between deposits and the acidizing solution (hydrochloric acid and ammonium bifluoride was used in chemical cleaning) produced an atmosphere (vapour and aerosol phases) containing fluoride compounds, which caused skin contamination and eye irritation to eight workers, five of whom were seriously affected.



*Pinoches*

**Buffer pad, demister, packing, or plugs are capable of retaining chemicals or deposits. They should be removed before chemical cleaning with hazardous materials.**

## Resin

### **ACCIDENT** Incident involving resin!!!

A procedure to change out absorbent resin on an ethyl benzene plant caused some leaks in the small bore piping of the system and the release of residual benzene. The MSDS for the resin indicated that it was stable for storage and usage up to a temperature of 190°C (374°F), but it was later learned from the supplier that the resin would react with water or decompose to generate sulphur dioxide SO<sub>2</sub>, which formed sulphurous acid (H<sub>2</sub>SO<sub>3</sub>) in the presence of steam at a lower temperature of 120°C (248°F) especially when the resin was not completely deactivated. The sulphurous acid caused corrosion in parts of the system.

**All catalyst/resin suppliers should be consulted on their products to ensure that compatibility with the full range of plant processes, including shutdowns and start-ups, is properly identified and reflected adequately in all procedures. To base this evaluation on MSDS information alone is not sufficient.**



## Inspection products

### **ACCIDENT** Gassing incident during inspection!!!

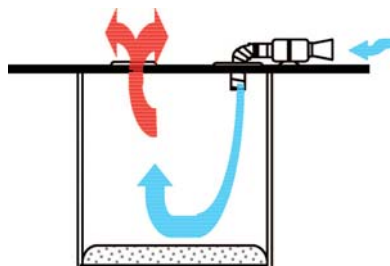
An inspector entered a tall reactor to inspect welds by a stain detection test. The test involved the use of liquid trichloroethylene solvent to wipe off excess red dye. As the solvent had run out, the inspector asked the supervisor outside the reactor to obtain more. The supervisor returned after ten minutes. Looking through the manhole, he saw the inspector unconscious on the second scaffolding platform inside the reactor. The inspector was rescued and revived.

A number of factors that led to the incident were discovered:

- The weld to be checked was exceptionally long (more than 8 m) and the quantity of solvent used was enough to make the inspector unwell in a confined space.
- It was only possible to reach the first scaffolding platform in the reactor by means of a cradle operated from outside. Consequently, the presence of a supervisor outside was essential to help those inside to exit.
- The inspector committed an error of judgment in asking the supervisor to go and fetch some trichloroethylene, since during that time, he deprived himself of supervision and of the possibility of leaving the vessel.
- There were several clear breaches of the Confined Space Entry Golden Rule.



**The use of harmful solvents should be kept to a minimum or substituted by other less toxic and non-flammable materials.**



**Ensure that forced ventilation is used for confined spaces where natural ventilation is inadequate.**

## Refractory materials

### **ACCIDENT** Refractory explosion!!!

Some refractory repair work was necessary in a refinery. The material INSLAG previously used was out of production, and a similar material INSLAG 'AF' (signifying an asbestos free grade) was sourced and used.

The new material was being used in the confined space of the regenerator offgas pressure reduction chamber, and an explosion occurred when some hot work was also carried out on the equipment. Fortunately, no one was injured.

When water was added to the material during a test in the laboratory, hydrogen gas was released. There was no indication on the MSDS that any flammable gas would be given off during mixing. The manufacturer later confirmed this effect, but claimed that the material is used in the iron/steel production industry, where normally large equipment is involved with good ventilation. The supplier promised to update the MSDS to include the potential hazard of hydrogen release and the need for good ventilation.

## Poly aromatic hydrocarbons

Certain refinery processes (catalytic cracking and lube oil aromatic extraction processes) concentrate high boiling point aromatic compounds, such as PAHs. PAHs are generally carcinogenic and care should be taken when handling heavy oil compounds.

## Knowledge and training saves lives

**Remember that knowing the properties and hazards of the hazardous substance you handle and how to respond to an emergency can make a difference.**

### **ACCIDENT** Emergency training saves the life of a car driver!!!

A hydrocarbon truck was travelling at around 40 mph (64 kmph) along a road in a rural area when a car emerged suddenly from a side road. The truck hit the right side of the car and the car engine caught fire. The driver was trapped inside the car with the windows and doors jammed shut. The truck driver responded immediately with his fire extinguisher and managed to put out the fire in the engine compartment. As the fire spread to inside the car, he broke the windows with the extinguisher and put out the fire with water obtained from a local farmer, and waited with the trapped driver until emergency services arrived. The car driver suffered two broken legs and a punctured lung from the accident but the emergency response training given to this contractor hydrocarbon truck driver had clearly saved the driver's life.



*Fire and First Aid exercise for BP truck drivers*

### Lessons learned

- Training in handling of emergencies must be provided to all employees and contractors to ensure familiarity with emergency procedures and plans.
- Real life scenarios in training make a huge difference to the effectiveness of training and can literally save lives.
- Engaging other stakeholders, such as contractors, in safety is both a worthwhile and necessary aspect of the business.
- Defensive driver training is essential in preventing accidents on the road. All drivers must have a mind set that every single accident is preventable and they can help to prevent them from happening.

# Glossary

Term	Definition	MSDS Relevance
ACGIH	American Conference of Governmental Industrial Hygienists	
Auto Ignition Temperature	A fixed temperature above which adequate energy is available in the environment to provide an ignition source.	The material should not be exposed to temperatures at and above this value.
Boiling Point	The temperature at which a liquid changes to a gas (vapour). More specifically it is the temperature at which the vapour pressure of a liquid is equal to the applied pressure (usually atmospheric pressure).	The boiling point is an important consideration for storage to avoid vaporization of a liquid.
CAS No	Chemical Abstracts Service Registry Number	It uniquely identifies a chemical to avoid confusion
Ceiling Values	This exposure limit should at no time be exceeded.	Relevant to TLV, representing a maximum exposure level.
CNS	Central Nervous System	
CO	Carbon Monoxide	
CO <sub>2</sub>	Carbon Dioxide	
CS <sub>2</sub>	Carbon Disulphide	
EO	Ethylene Oxide	
Flash Point	The lowest temperature at which enough vapour is given off to form an ignitable mixture with air. (The two most commonly used methods to determine the flash point are the open-cup and closed-cup methods.)	When the temperature of a material is at or above its flash point, always avoid heat, open flame, sparks or other sources of ignition.
H <sub>2</sub> S	Hydrogen Sulphide	
HCN	Hydrogen Cyanide	
HEPA Filter	High Efficiency Particulate Air Filter	
IDLH	Immediately Dangerous to Life and Health	This is the maximum amount or concentration of a chemical that a worker is able to escape from without suffering permanent health damage or that may impair his/her escape. This limit can be utilized to assist in making decisions regarding respirator use.
LC <sub>50</sub>	Lethal Concentration 50%	The concentration (in air or in water) that kills 50% of the group of test animals exposed for a specific period of time.
LD <sub>50</sub>	Lethal Dose 50%	The dose when administered orally or applied to the skin kills 50% of the group of test animals.
LEL	Lower Explosive Limit—the minimum concentration of flammable vapour in air necessary for combustion.	A mixture of substance and air below this limit lacks sufficient fuel (substance) to burn.
LNG	Liquefied Natural Gas	
LPG	Liquefied Petroleum Gas	

Term	Definition	MSDS Relevance
NIOSH	National Institute for Occupational Health and Safety	
O <sub>2</sub>	Oxygen	
OEL	Occupational Exposure Limit	This is the maximum amount or concentration of a chemical that a worker may be exposed to as given by UK's Health & Safety Executive EH40 for use with the Control of Substances Hazardous to Health (COSHH) regulations.
OSHA	Occupational Safety and Health Administration	
PEL	Permissible Exposure Limit	Similar to OEL but provided by OSHA
PPE	Personal Protective Equipment	
Relative Vapour Density	The ratio of the density of a gaseous substance to the density of air.	It helps indicate if the gaseous material will sink in air to low lying areas, or remain buoyant.
SCBA	Self-Contained Breathing Apparatus	
Specific Gravity	The ratio of the density of a substance to the density of water	It can help determine volume or mass, and indicate if the material will sink or float in water or other liquid (assuming that it does not dissolve)
STEL	Short-Term Exposure Limit	This is the maximum concentration to which workers can be exposed for a period of 15 minutes continuously without suffering from irritation, permanent tissue damage or narcotic effects.
TLV (8 hours)	Threshold Limit Values (Guidelines prepared by ACGIH)	This reflects the level of exposure that the typical worker can experience without an unreasonable risk of disease or injury over a typical workday (8-hour period).
TWA Limits	Time-Weighted Average Limits	Maximum concentrations that allow excursions above the given limit, provided that there is a compensating equivalent excursion below the limit during the workday.
UEL	Upper Explosive Limit—the maximum concentration of flammable vapour in air necessary for combustion.	Knowing this value can help prevent a flammable/explosive mixture from forming. A mixture of substance and air above this limit is too rich in fuel (deficient in oxygen) to burn.
UN No	United Nations Number	It is used worldwide in international commerce and transportation to identify hazardous chemicals
Vapour Pressure	The pressure exerted by its vapour when the liquid and vapour are in dynamic equilibrium.	The vapour pressure is an indication of the volatility of a liquid.

# 4

## Some points to remember



1. Is this chemical really needed? Can it be replaced with a less hazardous substance?

2. Follow a proper Management of Change (MOC) process when changes are made to *chemicals* being used.



3. Always follow the Management of Change (MOC) procedure when *plant modifications* are made. Never start-up a modified plant without the proper manuals and training in place.



4. Ensure that you have permanent access to up-to-date MSDSs for all the products at your site, both for process and other activities such as maintenance (oils, grease, etc.), cleaning (detergent, soaps, etc.), and firefighting (foam concentrates, dry powder, etc.).

5. Always check the order form against the label of the product when loading and delivering material.

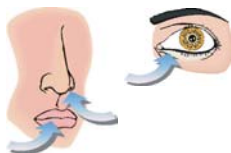
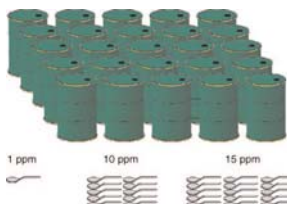


6. Any change of design of the packaging should be passed through the Management of Change (MOC) procedure.



7. Always segregate products that may have serious implications if mistaken.

8. Only a very small amount of a very toxic material can cause serious adverse effects.



9. Hazardous materials can enter our body through inhalation, absorption and ingestion.

10. Never put on soiled or contaminated clothes. Many people have collapsed after wearing contaminated coats, gloves, boots, etc.



11. All personnel, employees and contractors alike, must be protected against any potential exposure to toxic materials.



12. Retreat from hazardous areas on the first signs of any toxic effects.

13. Personal protective equipment should not be a substitute for proper engineering and administrative control and should be used only where other control methods are not yet effective or are inadequate.



14. A risk assessment is required prior to entry into a confined space for gas testing, and controlled through a Confined Space Entry Permit in accordance with the site's safety rules.

15. Gas tests and a visual inspection will be required to determine whether there is a safe working environment for hot work.

16. Standby attendants are strictly not allowed to enter the confined space under any circumstances!



17. Always wear the prescribed Personal Protective Equipment where H<sub>2</sub>S is concerned or suspected.
18. Equipment containing H<sub>2</sub>S should be clearly identified.
19. Personnel working in potential H<sub>2</sub>S areas should carry personal H<sub>2</sub>S alarms.



20. When breaking containment, follow all safety procedures associated with the system and type of material expected, and use the appropriate respiratory protection.



21. Job Safety Assessments (JSAs) should be performed to identify all possible hazards and to determine the measures that must be taken to eliminate or contain the hazard.

22. Ensure that all rescuers are equipped with the correct Personal Protective Equipment before attempting rescue.



23. Provide emergency response training and drills for the specific chemicals that are handled to ensure that a quick, efficient, and correct response is obtained.
24. Good communication is absolutely essential in emergency situations to avoid mix-ups and delays.

25. Note that air-purifying respirators do *not* provide protection in oxygen deficient atmospheres.







- 26. Provide personal monitors to allow verification of a safe atmosphere where the presence of a hazardous atmosphere is expected or suspected.
- 27. Establish a maintenance/calibration program for these devices and provide regular training on their use.

- 28. Do not isolate safety showers. They must be regularly checked and maintained to ensure that they are always operating correctly.



- 29. Always check against your MSDS before deciding on mitigative measures.

- 30. All known hazards must be removed or adequately controlled and communicated before work permits are issued.



- 31. The direction of water jets into a pool of refrigerated liquids often only makes matters worse, although fine water sprays can sometimes aid in dispersing vapour.

- 32. Always read and understand the material's handling instructions before commencing work. Ensure that proper training has been provided to personnel so that work is performed in as safe a manner as possible.



- 33. Always follow the Management of Change (MOC) procedure when modifications are made. Never start up a modified plant without the proper manuals and training in place.

34. All equipment handling hazardous substances must be constructed to meet all specifications, including proper selection of materials of construction.



35. MSDSs must be checked for all jobs and is a critical element of the risk assessment for Confined Space Entry authorization.

36. All catalyst/resin suppliers should be consulted on their products to ensure that compatibility with the full range of plant processes, including shutdowns and start-ups, is properly identified and reflected adequately in all procedures. To base this evaluation on MSDS information alone is not sufficient.



37. Confined spaces which have been painted with solvent based paints need to be treated with great care until the paint has 'cured'. The space must be well ventilated and gas free checked before adjacent use of ignition sources is allowed. The toxic hazard of paint solvent should also be considered.

38. Buffer pad, demister, packing, or plugs are capable of retaining chemicals or deposits. They should be removed before chemical cleaning with hazardous materials.



*Pinoches*



39. The use of harmful solvents should be kept to a minimum or substituted by other less toxic and non-flammable materials.

40. Ensure that forced ventilation is used for confined spaces where natural ventilation is inadequate.



41. Knowing the properties and hazards of the hazardous product you handle and how to respond to an emergency can make a difference.

# Test yourself!

## General

1. Hazardous materials affect health, safety, property, and the environment.  
**True**  **False**
2. The physical form of a substance never determines its potential risk. A hazardous substance in solid form is always as dangerous as in liquid form.  
**True**  **False**
3. Corrosive materials can act 'directly' by chemically destroying tissue, or 'indirectly' through inflammation.  
**True**  **False**
4. Fuel, oxygen, and an ignition source must be present before a fire can occur.  
**True**  **False**
5. The handling of radioactive material must be controlled to avoid exposure.  
**True**  **False**
6. Your chemical supplier is not obliged to submit the MSDS of the chemicals he sells to you.  
**True**  **False**

## Toxicity and health effects

7. Toxicity data for a hazardous substance is usually obtained by administering the substance to test animals and adjusting the data for humans.  
**True**  **False**
8. Hazardous materials can enter the body through inhalation, absorption, and ingestion.  
**True**  **False**
9. It is acceptable practice to put on contaminated clothing after a shower.  
**True**  **False**
10. Dust is not a major health concern because all dust particles are trapped before they reach the lungs.  
**True**  **False**

**Control measures**

11. Engineering controls tend to be more effective than administrative controls and Personal Protective Equipment (PPE) because they are less dependent on the chemical user who is subject to forgetfulness, preoccupation, insufficient knowledge, etc.
- True  False
12. Substitution of a hazardous chemical with a non-hazardous chemical is the most effective control measure because it removes the source of the hazard rather than lessening the damage that may result from the hazard.
- True  False
13. Personal Protective Equipment (PPE) is considered the last layer of protection from hazardous exposures.
- True  False
14. Personal Protective Equipment (PPE) can be used as a substitute for a proper dust control system, such as catalyst changeover by vacuum truck.
- True  False
15. The proper sequence for gas testing in confined spaces is the following: Toxics, Flammables, Oxygen.
- True  False
16. Combustible gas meters/explosimeters should be used to detect toxic gases because they can measure all types of gases.
- True  False
17. Any oxygen concentration above 20.8% in a confined space (where flammable and toxic gas readings are acceptable) means it is safe to enter without the use of breathing apparatus.
- True  False

**Specific properties of some hazardous products**

18. Hydrogen sulphide has a distinctive smell of rotten eggs that can be detected by the nose at any concentration and for any duration.
- True  False
19. When breaking confinement, it is not necessary to wear any respiratory protection because purging and washing will have eliminated all potential hazards.
- True  False
20. Personal monitors need to be provided for verification of a safe atmosphere where the presence of a hazardous atmosphere is expected, suspected, or likely.
- True  False

21. Hydrogen sulphide has the potential to poison and kill a person well before its flammable concentration is reached.  
**True**  **False**
22. Nitrogen makes up the bulk of the air we breathe (78%). It is a safe gas.  
**True**  **False**
23. The direction of water jets into a pool of refrigerated liquid often only makes matters worse as it supplies heat that evaporates the refrigerated liquid, generating a larger vapour cloud.  
**True**  **False**
24. MSDSs need to be available to rescue services so that the correct response measures can be taken.  
**True**  **False**
25. Acids are hazardous because they are corrosive and can react with other substances, such as caustic soda (or even water), to evolve large amounts of heat.  
**True**  **False**
26. Gas testing for LPG is done close to the ground because LPG vapours are lighter than air.  
**True**  **False**
27. Benzene is a carcinogen. Closed circuits are required for any sampling/dipping activities.  
**True**  **False**
28. Confined spaces that have recently been painted need to be well ventilated and gas tested before ignition sources are introduced to adjacent spaces/areas.  
**True**  **False**
29. A substance may be allowed to reach its auto ignition temperature as long as all known sources of ignition are eliminated.  
**True**  **False**
30. It is safe to have a source of ignition above the surface of a liquid which is at a temperature above its flash point.  
**True**  **False**



ANSWERS  
 11/2F/3T/4T/5T/6F/7T/8T/9F/10F  
 11T/12T/13T/14F/15F/16F/17F  
 18F/19F/20T/21T/22F/23T/24T  
 25T/26F/27T/28T/29F/30F

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Handbook of Emergency Chemical Management, 1994, David R. Quigley.

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Risk Management for Hazardous Chemicals, Jeffery W. Vincoli, 1996 CRC Press, Inc.

**Refer to your MSDS and to local regulations/legislations.**