

Chapter 5

Chemical Safety

Chemicals and chemical compounds are present in all workplaces. In the process and manufacturing industries, chemicals are used for a wide variety of applications: from fertilizer production for agriculture, to petrochemical and plastics production, to paints for the automotive industry, to pulp and paper mills, to textile production, to water treatment, to food production – the list will go on and on. Even in offices, we use cleaning chemicals, fragrances, adhesives, printing inks, disinfectants, etc.

While chemicals are a great help to us, their inherent hazards present themselves through improper use and storage. Not surprisingly, many of the world's catastrophic incidents are the result of chemical accidents:

- **FLIXBOROUGH, UK (1974)** - June 1, In 1974, cyclohexane vapor leaked from ruptured pipework at the Nynas (UK) site at Flixborough. This resulted in an explosion that killed 28 people and injured 36. Offsite, 53 injuries were reported. Property in the surrounding area was also severely damaged. The disaster led to the Health and Safety at Work Act, introduced the same year, when the Health and Safety Executive was also established.
- **SEVESO, ITALY (1976)** - On July 10, 1976, in a small Italian town north of Milan, a reactor at the ICMESA chemical plant overheated, resulting in

an explosion and the first, and highest known exposure, to dioxins in a residential area. A toxic cloud containing 2,4,5-Trichlorophenol - used to make pesticides and antiseptics - spread to the densely populated city of Seveso. This became the catalyst for the Seveso Directive, in 1982, which has since undergone numerous amendments. It was replaced by the Seveso II directive in 1996.

- **BOPAL, INDIA (1984)** - On December 3, 1984, methyl isocyanate gas leaked from the Union Carbide facility in Bopal, during the early hours of the morning while local residents slept. Around 2,000 people died immediately, with another 8,000 dying later. The initial investigation suggested that large volumes of water had entered the chemical tank, which caused a chemical reaction and led to the leak. The incident highlighted the problem of urbanization and having a plant located near a densely populated area.
- **TOULOUSE, FRANCE (2001)** – In September 21, 2001 there was an explosion at Atofina's Grande Paroisse fertilizer plant in Toulouse, France. Around 300 tons of Ammonium Nitrate (AN) exploded, destroying the site and wrecking buildings 3km (1 mile) away in the city center. The blast left a crater 50m (164 feet) wide and 10m deep. It was responsible for the death of 30 people, and 10,000 injuries.
- **TEXAS CITY, TEXAS, US 2005** - In March 23, 2005, a series of explosions occurred when a

hydrocarbon isomerization unit was restarted and a distillation tower flooded with hydrocarbons. As a result, 15 were killed and another 180 were injured. BP admitted to charges and accepted fines, with BP America chairman Bob Malone conceding that the company was guilty of a felony "for failing to have adequate written procedures for maintaining the ongoing mechanical integrity of process equipment at the Texas City refinery. "If our approach to process safety and risk management had been more disciplined and comprehensive, this tragedy could have been prevented," he said.

- **BEIRUT, LEBANON (2020)** – On August 11, 2020, some 2,750 tons of Ammonium Nitrate stored in a warehouse in the Port of Beirut in Lebanon exploded, flattening the surrounding structures, leaving ~250,000 people homeless. More than 200 are confirmed dead while more than 6,000 were injured, with still many declared missing. The Ammonium Nitrate was said to have remained in a warehouse since 2014, after the ship carrying it had to make an unscheduled stop in the port due to technical problems and had to be detained because of some deficiencies after inspection by port authorities.

A study was done by the **Centers for Disease Control and Prevention (CDC)** of the US in 2015 of the Top Five Chemicals Resulting in Injuries from Acute Chemical Incidents, involving 9 states. Of the 57,975 incidents that

were reported, 54,989 (95%) involved the release of only one chemical. The top five chemicals associated with injury were Carbon Monoxide (2,364), Ammonia (1,153), Chlorine (763), Hydrochloric acid (326), and Sulfuric acid (318).

Carbon Monoxide (CO) incidents were mostly in the residential setting, with the gas build-up caused by engines left running in enclosed or semi-enclosed spaces. Similar incidents also happen in workplaces where work is done in confined spaces (more about this in a later chapter). A good way to protect persons against this is by using CO detectors in spaces where it may accumulate to dangerous concentration levels. CO is a common industrial hazard resulting from the incomplete burning of natural gas and any other material containing carbon such as gasoline, kerosene, oil, propane, coal, or wood. Forges, blast furnaces and coke ovens produce CO.

Ammonia (NH₃) is a colorless gas with a very distinct odor that is familiar to many persons because it is used in smelling salts, many household and industrial cleaners, and window-cleaning products. Ammonia gas dissolved in water is called liquid ammonia or aqueous ammonia. Once exposed to open air, liquid ammonia quickly turns into a gas. Ammonia is highly corrosive and exposure to high levels of ammonia can cause irritation and serious burns on the skin and in the mouth, throat, lungs, and eyes. At high levels, ammonia can cause death.

Chlorine is a toxic gas with an irritating odor. Because it is heavier than air, it tends to accumulate at the bottom of poorly ventilated spaces. At low levels of exposure (<15

ppm), nose, eye, and throat irritation can occur. Immediate chest pain, coughing, changes in breathing rate, and vomiting might occur at 30 ppm and lung damage at 60 ppm. After a few minutes of exposure to 1,000 ppm, death can occur.

Hydrochloric acid is a clear, colorless solution of hydrogen chloride in water. It is a highly corrosive, strong mineral acid also known as muriatic acid. Used in the manufacture of fertilizers, dyes, rubber, ore refining and pickling of metal, it also has numerous smaller-scale applications, including household cleaning and commercial pool cleaning. Hydrochloric acid is corrosive to human tissue; upon exposure it can harm respiratory organs, eyes, skin, and intestines irreversibly. Persons exposed to unsafe levels of hydrochloric acid and have skin or eye irritation need to be decontaminated. To prevent injuries, persons handling hydrochloric acid should wear skin, eye, and respiratory protection.

Sulfuric acid (also called sulphine acid, battery acid, and hydrogen sulfate) is a clear, colorless, oily liquid that is very corrosive. It is used in the manufacture of fertilizers, explosives, other acids, and glue; in the purification of petroleum; in the pickling of metal; and in lead-acid batteries (used in most vehicles). Because of its corrosiveness, sulfuric acid at a high concentration can cause very serious damage (e.g., chemical and thermal burns). Sulfuric acid burns the cornea and can lead to permanent blindness if splashed onto eyes.

Other chemical hazards found in various workplaces include:

Hydrogen Sulfide - (also known as H₂S, sewer gas, swamp gas, stink damp, and sour damp) is a colorless gas known for its pungent "rotten egg" odor at low concentrations. It is extremely flammable and highly toxic. It is present in varying concentrations in sewage systems, septic tanks, oil refinery processes, oil and gas wells, volcanoes, geothermal steam sources, etc. Being heavier than air, hydrogen sulfide can collect in low-lying and enclosed spaces, such as manholes, sewers, and underground telephone vaults. Its presence makes work in confined spaces potentially very dangerous. The health effects of hydrogen sulfide depend on how much H₂S a worker breathes and for how long. However, many effects are seen even at low concentrations. Effects range from mild: like headaches or eye irritation, to very serious: unconsciousness and death.

Welding fumes – another chemical hazard commonly present in workplaces, particularly in construction and maintenance jobs. Welding fumes contain a variety of metals (e.g., Aluminum, Antimony, Arsenic, Beryllium, Cadmium, Chromium, Cobalt, Copper, Iron, Lead, Manganese, Molybdenum, Nickel, Silver, Tin, Titanium, Vanadium, Zinc), and gases (Argon, Helium, Nitrogen, Carbon Dioxide – for shielding; Nitric Oxide, Nitrogen Dioxide, Carbon Monoxide, Ozone, Phosgene, Hydrogen Fluoride, Carbon Dioxide – process by-products).

Lead - Lead enters the body primarily through inhalation and ingestion. Today, adults are mainly exposed to lead by breathing in lead-containing dust and fumes at work, or from hobbies that involve lead. In general industry, workers come in contact with lead in solder, plumbing

fixtures, rechargeable batteries (lead-acid type), lead bullets, leaded glass, brass, or bronze objects, and radiators (repair works). Workers with prolonged contact with lead in concentrations above tolerable limits may develop a variety of ailments, such as neurological effects, gastrointestinal effects, anemia, and kidney disease.

Silica - Silica dust is hazardous when very small (respirable) particles are inhaled. These respirable dust particles can penetrate deep into the lungs and cause disabling and sometimes fatal lung diseases, including **silicosis and lung cancer, as well as kidney disease**. Occupational exposure to respirable crystalline silica occurs when cutting, sawing, drilling, and crushing concrete, brick, ceramic tiles, rock, and stone products, as well as in operations that process or use large quantities of sand, such as foundries and the glass, pottery and concrete products industries.

Asbestos - the name given to a group of naturally occurring minerals that are resistant to heat and corrosion. Asbestos has been used in products, such as insulation for pipes (steam lines for example), floor tiles, building materials, and in vehicle brakes and clutches. Heavy exposures tend to occur in the construction industry and in ship repair, particularly during the removal of asbestos materials due to renovation, repairs, or demolition. Workers are also likely to be exposed during the manufacture of asbestos products (such as textiles, friction products, insulation, and other building materials) and during automotive brake and clutch repair work. Breathing asbestos fibers can cause a buildup of scar-

like tissue in the lungs called **asbestosis** and result in loss of lung function that often progresses to disability and death. Asbestos also causes **cancer of the lungs** and other diseases such as **mesothelioma of the pleura** which is a fatal malignant tumor of the membrane lining the cavity of the lung or stomach.

Major routes of entry for chemicals

How do these hazards eventually reach and affect the worker? The common routes of exposure entry are:

- Inhalation – the most common route - breathing in the contaminants, usually in operations like grinding, cutting, sawing and sanding (dust); painting and spraying (mists), processing, manufacturing and reacting (gases); welding (fumes), construction and demolition (dust and fibers)
- Ingestion – cross contamination (food and water); mucus contamination (particulates)
- Dermal/Optical (through skin and eye) – laboratory work (acids, bases, toxic substances); cleaning operations (solvents and other cleaning chemicals); improper product handling
- Injection – hydraulics (pressurized chemicals); industrial hole punching/injection processes; sharps (needles)

There are probably as many chemical and compounds as there are processes in the industry, that it would be impossible to discuss all of them here. Rather, we shall try to give practical guidelines on how we can protect

workers from the hazards they present. For this we employ Risk Assessment and Control Procedures.

Identification of Hazards

As always, the first requirement for dealing with hazards is to identify them. This means we should have a good working knowledge of the processes involved in the workplace, as well as the chemicals in use. Knowing what the chemicals are and at which point of the process they are used, we should get a fairly good idea of what hazards they present.

Rule 1070 of the Occupational Safety and Health Standards mandates that **Work Environment Measurement (WEM)** be done in all workplaces at least annually, or as frequent as necessary (depending on the type of work done and materials used). This is a good start at identifying some of the common chemical hazards in the workplace. Among other methods used in identifying existing and potential chemical hazards are:

1. Walk-through/Ocular Inspection – regular safety inspections go a long way towards identifying existing and potential chemical hazards
2. Review of the processes involved – with particular attention on how chemical hazards may be generated in the processes
3. Knowing the raw materials, by-products and finished products
4. Gathering workers' complaints – workers would not complain if there were no real reasons

5. Checking Safety Data Sheet (SDS) of chemicals used in the workplace

Safety Data Sheets (SDS) of the particular chemicals in use in the workplace will help greatly. The **SDS** is like a bio-data of the chemical – it gives us in 16 Sections all the important information we will ever need to know about the chemical.

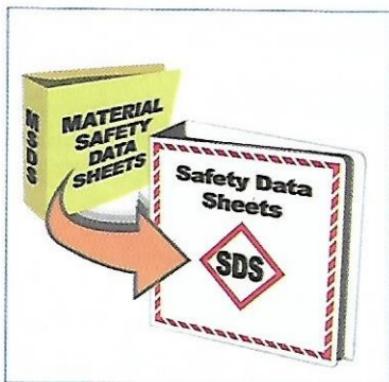
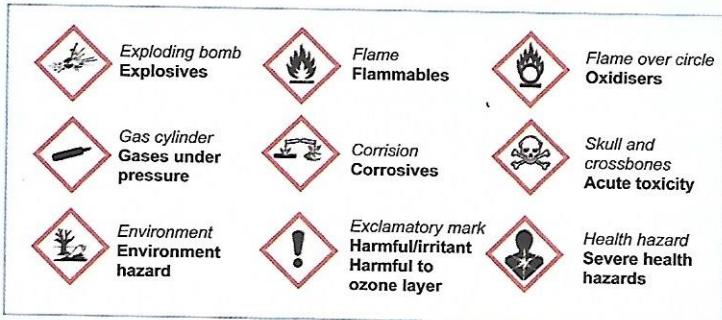


Figure 5.1

Information such as the properties of each chemical; the physical, health, and environmental health hazards; protective measures; and safety precautions for handling, storing, and transporting the chemical. Sections 1 through 8 contain general information about the chemical, identification, composition, safe handling practices, hazards, and emergency control measures (e.g., fire-fighting). This information should be helpful to those that need to get the information quickly. Sections 9 through 11 and 16 contain other technical and scientific information, such as physical and chemical properties, stability and reactivity information, toxicological information, exposure control information, and other information including the date of preparation or last revision. When the party preparing the **SDS** does not find relevant information for any required element, the **SDS** must state that no applicable information was found. The **SDS** must also contain Sections 12 through 15, to be consistent with the **UN Globally Harmonized System of**

Classification and Labeling of Chemicals (GHS).

Some typical examples of GHS labels are given below.



Once hazards are identified, an evaluation must be made of how much risk they pose to workers, and based on this assessment, which control measures should be implemented. In evaluating hazards of this type, there is a need to have a basis for determination of acceptable limits of exposure. Here, a number of standards are in use.

Evaluation of hazards

The process of evaluating hazards is really nothing more than comparing them with known and accepted standards (limits). Most common among these standards are:

- Occupational Safety and Health Standards, as printed in the Annexes, Tables 8 and 8a
- Threshold Limit Values – TLV (NIOSH)
- Permissible Exposure Limits – PEL (OSHA)
- Indicative Occupational Exposure Limit Values – IOELV (European Union - Council Directive 98/24/EC)

The TLVs (as well as OSHA's PEL) are given as:

- Time-Weighted-Average (**TLV-TWA**) – 8-hrs exposure on the basis of an 8-hours exposure for 5 workdays per week or a total of 40 hours per week
- Short-Term-Exposure-Limit (**TLV-STEL**) – A 15-minute TWA exposure that should not be exceeded at any time during a workday, even if the 8-hour TWA is within the TLV-TWA, provided further that exposures are not more than 4 episodes per day, with no less than one-hour interval in between.
- Ceiling Limit (**TLV-C**) – absolute exposure limit that should not be exceeded at any time

Toxicity

Toxicity is the degree to which a chemical substance or a particular mixture of substances can damage an organism. Toxicity can refer to the effect on a whole organism, such as an animal, bacterium, or plant, as well as the effect on a substructure of the organism, such as a cell (cytotoxicity) or an organ such as the liver (hepatotoxicity).

The toxicity of a substance may be classified according to onset of symptoms as: **Acute**, if symptoms appear relatively quickly (within a few hours or days, up to 3 months); and **Chronic**, if symptoms appear beyond three months, or years after exposure. An example of acute toxicity is that of high levels of Hydrogen Sulfide (H_2S), where the effect on the person exposed is rather immediate. Exposure to Asbestos fiber, on the other

hand takes as many as 10-20 years before effects becomes radiographically discernible.

According to how toxic substances disrupt the functions of the body, they may be classified as: **Local**, if effects are felt at the immediate site of exposure; and **Systemic**, if they affect the whole body, or some particular organ not directly in contact with them. A toxic chemical may cause local effects, systemic effects, or both. For example, if ammonia gas is inhaled, it quickly irritates the lining of the respiratory tract (nose, throat, and lungs). Almost no ammonia passes from the lungs into the blood. Since damage is caused only at the point of initial contact, ammonia is said to exert a local effect. An epoxy resin is an example of a substance with local effects on the skin. On the other hand, if liquid phenol contacts the skin, it irritates the skin at the point of contact (a local effect) and can also be absorbed through the skin, and may damage the liver and kidneys (systemic effects).

Interactions of hazardous chemical with each other, can have any of the following effects on their toxicity:

- **Additive Effect** - This action occurs when the combined effect of two or more chemicals is equal to the sum of the effect of each agent given alone.
[1+1 = 2]
Example: coal dust + silica dust = dust laden lungs
- **Synergistic** – This is the situation where the combined effect of two chemicals is much greater than the sum of the effects of each agent given alone. [1+1 > 2]

Example: Asbestos + Cigarette = much greater chance of lung cancer

- **Potentiation** - One substance that does not normally have a toxic effect is added to another chemical, it makes the second chemical much more toxic. $[0+2 > 2]$
Example: Isopropyl alcohol (no effect in the liver) + carbon tetrachloride = greatly increase the toxicity of carbon tetrachloride
- **Antagonistic** – Antagonism is the opposite of synergism. It is the situation where the combined effect of two or more compounds is less toxic than the sum of their individual effects. $[2+3 < 5]$
Example: Methanol + Ethanol = ethanol is antidote for methanol poisoning

Control Measures

There are a number of ways we can control the chemical hazards:

- At the source – right where the hazard is generated
- Along the path – along the path it must travel to reach the worker
- At the receiver – at the point of contact of hazard with the worker

As always, Engineering Controls are most preferred and should be applied first, whenever possible. If residual hazards remain present, then apply Administrative Controls and finally PPE.

At the source

Hazards are best addressed right where they are generated. Solvent-based paints can be replaced by water-based ones (substitution). Dust generated during dry sand blasting operation can be largely eliminated by using a process of wet blasting (changing the process). Fumes produced from welding works can be removed by properly designed local exhaust ventilation systems, removing the contaminant before it can spread through the workplace. One of the most common flexible isolation systems is glovebox containment, which can be used as an enclosure around small-scale powder processes, such as mixing and drying. Rigid glovebox isolation units also provide a method for isolating the worker from the process and are often used for medium-scale operations involving transfer of powders.

Along the path

General ventilation (also called dilution ventilation) is a good example of control of hazard along the path. We can use air curtains to prevent contaminants from entering through doorways. Provision of barriers, along with signage to warn workers of hazards are good administrative controls, as is worker training on safe work with the chemicals involved. Good housekeeping will help prevent the spread of contaminants (e.g., build-up of dust or contaminant on ledges, or beams). In the event of spills, proper containment equipment and procedures are important aspects of emergency response programs. Designing the workplace so as to increase distances between the source and the receiver will help keep

whatever chemical hazards that remain at minimal concentrations.

At the receiver

One of the most effective means here is by enclosing workers in control rooms (isolation of worker from hazards). Because this will not always be possible – workers will still need to go out of the control room from time to time – the next method would be to limit the duration of exposure (e.g., by rotation schedule). Training on correct procedures will also help limit workers' exposure. Lastly, the use of PPE is an important control measure applied at the receiver not only because it acts as an additional barrier to prevent the hazard from reaching the worker, but also because it gives the worker additional protection, in case other the control measures fail.

Selection of proper PPE cannot be over-emphasized. For example, nitrile gloves are excellent for Lactic acid or even Phosphoric acid (70+ %), but not recommended for use with Sulfuric acid (70+ %). Or consider that a pair of safety glasses may be suited for general industry work, but not if you work where chemicals might splash and reach your eyes (i.e., in chemical stores and laboratories). Some consideration must also be given to comfort when wearing/using **PPE** – workers will be more likely to use the PPE if they have no real comfort issues with them. Availability of emergency shower/eyewash stations in locations where there are chemical hazards will allow for faster response in case they are needed.

Chemical Spill Procedures

If the site contains any material that requires a Safety Data Sheet (SDS) or, really, any liquid that is capable of harming a person or the environment, then there ought to be procedures for spill containment and clean-up. Chemical spill procedures should be part of the Emergency Response Plans, which should be thoroughly explained to workers. This will include the formation of dedicated Hazardous Materials Response (HAZMAT) Teams. Depending on site requirements, the HAZMAT Team may be a separate entity altogether of a part of the Fire Brigade.

To be able to respond properly to chemical spills, Spill Kits must be provided in suitable locations (preferably near the area where spills are expected). This kits must contain at least the following: first aid kit, chemical handling PPE, appropriate absorbent materials - mats or socks, or berms to quickly contain the spill (consider what chemicals are in use), labels, signage, plugging device to stop the leak, and Spill Containment Instructions.



Figure 5.2

Regularly check to verify that all necessary safety equipment and spill cleanup materials are available and in good working order.

Additionally, ensure that the individuals who may need to participate in spill response activity are trained in equipment use and applicable spill cleanup procedures.

Finally, inspect all materials and equipment regularly to ensure that they will be fully functional when needed.