3.4 Chemical Leakages

3.4.1 Chemical Accidents

Chemical accidents are the result of an uncontrolled release of a substance that is poisonous or harmful to property or the environment. The risks depend on the characteristics of the substance in question, the quantities being handled and the processes used, as well as the vulnerability of the surroundings and the emergency measures taken to minimize the consequences of the accident

3.4.2 How Dangerous are Chemicals?

Chemical substances are either elements or compounds. There are between 100 and 200 different kinds of atoms and elements are made up of just one of those kinds. Compounds are made up of a variety of elements such as methane (carbon and hydrogen), water (hydrogen and oxygen) and salt (sodium and chlorine). Preparations are made up of mixtures of chemical substances, for example paint which consists of a pigment, a resin and a solvent.

A substance can be dangerous in many ways. It can be toxic, reactive, explosive, inflammable, radioactive or corrosive. Two important aspects are toxicity and reactivity

Toxicity

Most substances that can give rise to serious injuries to people and animals are marked with T or a skull and crossbones.

There are several ways that a toxic substance can be taken in:

- inhalation of contaminated air
- absorbtion through the skin
- ingestion via the mouth

Some substances lead to a general poisoning of the whole body Other substances only affect certain organs. Corrosive and irritating gases such as chlorine, sulphur dioxide and ammonia can seriously damage the lungs. The level at which a substance is toxic varies greatly depending on its effects. Dioxin, or 2 3.7.8-tetrachlorodibenzoparadioxin (TCDD), is an extremely toxic substance with a variety of harmful effects. Trials on guinea pigs have shown it to be fatal in a dose as low as a millionth of a gram per kilogram bodyweight.

Chemical releases in the environment can poison animals directly, but they can also have an indirect effect, for example in rivers or lakes when the biological breaking-down of a chemical uses up the oxygen in the water. The consequent severe oxygen shortage kills many kinds of plants and fish. Substances that are difficult to break down can find their way into the food chain, accumulating at the upper end and causing great damage to the whole eco-system

Reactivity

Damage can occur when a reactive chemical reacts with another chemical in an uncontrolled way. Mistakes with raw materials or temperature and pressure can cause a reactor vessel to rupture and lead to the unintentional production of highly toxic substances. When a fire takes place it can convert a relatively harmless chemical into something dangerous which is then spread in the surroundings as the result of the fire itself or of the efforts to put the fire out.

Table 3.4.1, page 72, shows various types of hazardous chemicals and their harmful properties

Containers and packaging for hazardous chemicals must have markings showing them to be dangerous when in transport, for sale or being used in industry. There should also be written information about hazards and precautions. This should give information on risk classification, composition and characteristics. In addition, potential injuries should be listed, together with details on combustibility and the risk of explosions, as well as advice on preventive measures and emergency routines. Special arrangements to convey such information, e.g. translation into other languages, may be necessary when chemicals are transported (by rail, highway or air) into other countries. For example, dangerous chemicals have been released during fires at airport warehouses.

In places where hazardous substances are handled there should be an up-to-date list covering the particular chemicals in question. This list, together with the written information about hazards and precautions, is an important reservoir of information when identifying risk sources. Information is also required on the properties of these chemicals when evaluating the probabilities and consequences of accidents in a risk analysis.

Under the heading **composition**, the written information about hazards and precautions should give details on what toxic substances are present and in what proportions. The physical properties of a substance are of significance for how it disperses in the environment. The following information on the product should therefore be given under the heading **physical/chemical properties:**

• form (solid,powder,granular liquid-viscosity,colour etc) • boiling point • melting point • density • gas density relative to air	**properties affecting dispersal**
• flash point • ignition temperature • flammability range	**flammability**
• pressure at 20oC • speed of evaporation relative to ether • solubility in organic solvent	**dispersal and flammability**
• solubility in water at 20oC • pH when cincentrated and in normal dilution	**corrosive and environmental effects**

Under **biological properties** the following information is given:

- fatal dose for a mouse, rat or rabbit, toxic effects on plants and animals
- mutagenic and carcinogenic effects, allergic reactions

▶ **toxicity**

- how the substance breaks down
- chemical/biological need of oxygen
- risk of bioaccumulation

▶ **environmental effects**

In some cases certain points are omitted. When something is not relevant for a particular product, this should be stated. A lack of information is then clearly due to insufficient knowledge or a mistake on the part of the manufacturer or importer.

Chemical information sheets have been produced for a great number of elements and compounds They contain much the same information on physical, chemical and toxic properties as should appear in the written information about hazards and precautions.

Radioactive substances are an especially dangerous group. Certain radioactive substances such as plutonium are so poisonous that their toxicity can constitute a greater danger than their radioactivity.

Information on various substances, their properties and risks can be found in international "Dangerous Goods folders".

3.4.3 Hazards

Dangerous goods are a hazard at all times. However the risk they constitute depends on how likely it is that they will leak and what consequences that would have. The most dangerous class is gases condensed under pressure, such as LPG, chlorine, sulphur dioxide and ammonia. Large quantities of these gases are handled and an accident could have catastrophic consequences.

About 200 substances are given in the EC "Seveso directive". A limit is set for each substance If that safe limit is exceeded, then the establishment must be described carefully. Details must be given on its location, surroundings, layout and equipment as well as on the risks present, methods of operation and systems of maintenance. The size of the workforce and its safety training must also be stated, together with a catastrophe plan and methods for informing those who live nearby.

Risks are involved when processing chemicals. In some cases the form or composition of a dangerous chemical can be altered to make a process safer.

It is through increased knowledge of risks and suitable methods of handling hazardous substances that the dangers can be kept at an tolerable level. In spite of all the risks, there have been relatively few very serious accidents; and with proper rescue efforts the damage caused by an accident can be minimized

The Risks of Handling Chemicals

An important factor is the quantity of the chemical being handled. Table 3.4.2 gives examples of the safe limits for a variety of chemicals, as given in the EC "Seveso

Directive". If these values are exceeded, then the operator has to supply information on risks and counter-measures. Of course accidents can still happen when a chemical is being handled in a quantity well below the safe limit.

Technical factors such as the pressure and temperature of a process also affect the hazard.

Gases condensed by cooling are less of a risk than gases condensed by pressure. Substances that are normally liquid can, when processed at a high pressure and temperature, leak out and evaporate in large quantities.

The level of risk also increases if two chemicals that react strongly are being processed or if there are many steps in the process. Loading and unloading material is a hazardous operation. The equipment also affects the risk associated with any given process.

To handle dangerous substances in a safe way, there must be administrative measures to maximize safety; such as operational routines and regular maintenance, waste disposal, training and risk analysis of the system and the installation as a whole.

A hazard analysis for a locality can rarely include a detailed inspection of equipment and methods in the chemicals industry Competence and resources for this should exist within the company operating the installation From the local authority perspective it is most important to find out:

- which dangerous substances are being handled in a quantity that could cause a serious accident

- what damage could be done and how widespread it could be

- if the technical conditions increase the hazard (pressure, temperature, process type, common storage)

- if there is an understanding about hazards and the need for safe equipment, safe methods, training, catastrophe plans, etc., at the company in question

- if the hazards demand a response from the local authorities

The greatest hazards would appear to exist in large-scale chemical plants. However knowledge about hazards and the need for the correct response to them has meant that so far there have been few very serious accidents in these plants.

The effects of the surroundings on risk

The probability of an accident occurring is affected to some extent by the conditions around the chemical plant in question.

Hazards and risks associated with the road transport of chemicals depend on traffic intensity, speed limits and road conditions. So-called "external factors", such as land slides, flooding, extreme weather or power cuts, can lead to uncontrolled releases of dangerous substances from a chemical plant.

Factors such as temperature, extreme precipitation and winds can affect the amount of a chemical that is released and its dispersal, which has a bearing on the consequences.

Another factor which influences the consequences of an accident is the distance to buildings containing workers, as well as the distance to houses, hospitals, schools etc As far as the environment is concerned water supplies, lakes, rivers, agricultural land and nature reserves are especially sensitive to chemical leakages.

Sabotage could lead to the large scale leakage of dangerous chemicals from tanks at a time when safety systems have been put out of action. This means that the theoretical "worst case" could occur - something for which the rescue service plans are not usually geared up. The handling of chemicals in new places could put a large number of people at risk. Damaged buildings and temporary accomodation offer less protection against gases than a normal, relatively air- tight building does The emergency services will be hard pressed, leading to difficulties in limiting damage and taking care of the injured.

3.4.4 Examples of Accidents Caused by Leakages of Chemicals.

In the accidents described below chemical leakages led to damage as the result of poisoning. About 40 such accidents occurring in the years 1914-1979 are given in F.R. Lees' book "Loss Prevention in the Process Industries", Vol 2. Many of these took place when dangerous goods were under transport In addition about 130 accidents caused by fires or explosions are described in the book.

Accidents involving petroleum products may have serious consequences for life, property and the environment.

Here are some examples showing different types of accidents:

Year	Location	Event	Deaths	Injured
1959	California, USA	Explosion of LPG and fire	23	
1968	Pernis,the Netherlands	Explosion and oil slops	2	25
1976	Seveso, Italy	Leakage of dioxin	0	193
1977	Umm Said Quatar	Fire (1 sq mile) and explosion	7	many
1979	Bantry Bay, Eire	Explosion on oiltanker at terminal	50	
1984	San Juanico Mexico	Explosions and fire LPG	600	7 000
1984	Bhopal, India	Leakage of methyl isocyanate	>2,500	>10,000

Chlorine was both the first poison gas used in war and the first pressure-condensed gas to be handled on a large scale. At first, equipment, materials, knowhow and routines for liquid chlorine were not safe enough in relation to the dangers it posed. Until the 1950's, accidents with chlorine dominate the statistics. Since then the number of accidents with chlorine has decreased. At the same time other hazardous substances have been handled in ever increasing quantities, leading to new risks and, unfortunately, new accidents.

According to OECD statistics the probability of being killed in an accident involving dangerous substances which causes at least five fatalities is much the same as that of being struck by lightning. In addition, the frequency of accidents is diminishing slowly.

Oil fires and explosions are now the main cause of serious accidents. A number of accidents involving oil tankers, storage tanks and pipelines have resulted in the release of large quantities of oil into the environment. Accidents of this type, together with growing use of and transportation of petroleum products throughout the world, have created an awareness of the risks associated with oil. For a long time to come, oil will still be the dominant fuel and a necessity of our industrial society.

Movement of petroleum products from oil fields to the consumer requires various types of transport, including tankers, pipelines, trains and trucks. Numbers of spills at the point of transfer from one type to another is high.

No two oil spills are exactly alike. The behaviour of oil on water or land is dependent on the type of product Pre-emergency planning at local level is the most effective tool to deal with any oil spill. The risk of fire and explosion is a major concern for all concerned with handling, storage, transport or clean-up operations.

Transport

Freight transport is an essential activity upon which many industries are dependent. Geographic and demographic condititons can make transport very important. According to OECD about 10 per cent of all tonnage transported consists of hazardous substances. Increasing quantities of dangerous goods are transported by road, with more and more diversified risks to road users, the general public and the environment. However, accidents with dangerous goods can also occur on the railways, at sea or in the air - that is to say, more or less anywhere at any time.

Transport of dangerous goods is to a large extent border-crossing traffic. This is of international concern and calls for co- operation, internationally agreed rules and sharing of information and experience.

Accidents with the transport of dangerous goods have received much publicity recently There has been increased public concern since the 1978 road accident at Los Alfaques in Spain, when 200 people lost their lives because of a BLEVE (Boiling Liquid Expanding Vapour Explosion) of propylene.

It is therefore important to define precisely what is meant by a dangerous goods accident. A vehicle carrying dangerous goods may be involved in an accident without the load influencing what happens A distinction should be made between this kind of accident and one where the dangerous goods affect the course of events. A part (however small) of the load must escape for the event to be considered a dangerous goods accident.

The probability of being killed in an accident involving dangerous goods is very small. The consequences of an accident with dangerous goods can be very serious, so it is important that the probability of such events remains low.

The risks can vary from substance to substance and also for a given substance under different conditions. Accidents can take several different forms. (N.B. Accidents with dangerous goods often occur when they are being loaded or unloaded.)

Here are some selected major road accidents involving hazardous goods and materials:

Year	Place	Substance	Deaths	Injured
1970	Ohio, USA	LPG	6	
1973	France, Saint Amand des Eaux	Propane	9	45
1976	Houston, USA	Ammonia	6	178
1987	Herborn, Germany	Petrol	4	

Transport accident, Paris area.
Photo : François Cepas, D.S.C.R.

Table 3.4.1 **Hazardous Chemicals**
- types, characteristic properties, examples
(Source Riskhantering 3. Kemikontorets forlag AB)

Type	Criteria	Examples
Explosives	Classed as an explosive	ethyleneglycoldinitrate picric acid trinitrotoluene
Inflammable gas, compressed or condensed	gases that can burn in air at or below + 21oC	acetylene ethylene oxide LPG
Very inflammable liquid	liquids with flame point at or below + 21oC	acetone petrol carbon disulphide
Inflammable solid	solids than can easily be ignited and will then continue to burn*	red phosphorous
Self-igniting substance	substances that at normal temperatures ignite in air without an external source of energy*	raney-nickel trichlorosilane white phosphorous
Substance giving off inflammable gases on contact with water	substances that give off dangerous quantities of inflammable gases (1 litre of gas per kg per hour) on contact with water or damp air*	calcium carbide calcium sodium
Oxidizing agent or reactive substance	substances that react exothermically when in contact with other substances (for example by giving off oxygen) and therefore constitute a fire risk	sodium nitrate hydrogen peroxide
Poisonous gas, compressed or condensed	Gases with LC50<2000mg/m3 for rats exposed for 4 hours	formaldehyde hydrogen sulphide chlorine sulphur dioxide
Poisonous liquid or solid	substances with LD50<400 mg/kg dermal for rats or rabbits, or LD50<200 mg/kg oral for rats	calcium cyanide carbon disulphide tolvene diisocyanate

Corrosive liquid or solid	substances that cause ulceration of the skin on up to 4 hour's contact	phenol hydroftoric acid sodium hydroxide nitric acid

Large quantities of gases with a low toxicity such as freons, carbon dioxide and nitrogen can also constitute a serious health risk in closed spaces

* See Official Journal of European Communities No L 257/15, 1983

Table
3.4.2 Examples of chemicals and safe limits

From the EC council Directive 24th June 1982 (Revised 19th March 1987) on the major accident hazards of certain industrial activities (the so-called "Seveso Directive")

Substance	**Max. total quantity being handled (in tons)**
Inflammable gases	200
Inflammable liquids, class 1	50 000
Acrylonitrile	200
Ammonia (anhydrous)	500
Chlorine	25
Sulphur dioxide	250
Sulphur trioxide	75
Sodium nitrate (as fertilizer)	5 000
Sodium chlorate	250
Acid (liquid)	2 000

Releases amounting to a small percentage of the above limits can cause serious accidents. The consequences depend on the substance's properties and such factors as the speed of the release, conditions for dispersal and the vulnerability of the surroundings.